Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 24 (2005) 1280–1288

POLYHEDRON

www.elsevier.com/locate/poly

Bridged 1,2-azaborolyl zirconium complexes: Heterocyclic analogs of the *ansa*-zirconocene olefin polymerization catalysts

Hong Yang, Xiangdong Fang, Jeff W. Kampf, Arthur J. Ashe III *

Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, MI 48109-1055, USA

Received 10 February 2005; accepted 1 March 2005
Available online 23 March 2005

Abstract

The reaction of phenylvinylboron chloride (**11**) with allylethylamine afforded (*N*-allyl-*N*-ethylamino)vinylphenylborane (**12**) which on treatment with 5 mol% Grubbs catalyst gave 1-ethyl-2,5-dihydro-2-phenyl-1*H*-1,2-azaborole (**13**). The reaction of **13** with LDA in ether gave lithium 1-ethyl-2-phenyl-1*H*-1,2-azaborolide (**14**), which was silylated with Me_2SiCl_2 to afford **15**. Reaction of **15** with CpLi followed by LDA and then $ZrCl_4$ gave bridged compound **9**. The reaction of **15** with **14** followed by LDA and then $ZrCl_4$ gave the bridged complex **10**. The reaction of **14** with Cp^*ZrCl_3 gave **8**. The X-ray crystal structures of **8**, **9**, and **10** show that they closely resemble the corresponding zirconocene dichlorides. On activation with excess methylaluminoxane **8**, **9**, and **10** form active catalysts from the polymerization of ethylene.

Keywords: Boron heterocycles; Ziegler–Natta polymerization; Cp-surrogates; Zirconium(IV) complexes

1. Introduction

Metallocene derivatives of the group 4 metals have been extensively used as homogeneous catalysts for the Ziegler–Natta polymerization of olefins [1]. In this family dimethylsilyl-bridged *ansa*-zirconocene dihalides (**1**) have been the most studied. This small bridge pinches open the wedge between the Cp rings so that the electrophilic zirconium atom is more accessible to the olefin substrate. The bridge also prevents rotation about the metal-ring axis so that conformational mobility is restricted. Certain dimethylsilyl-bridged zirconocenes are both highly stereoselective and highly active polymerization catalysts [1–4].

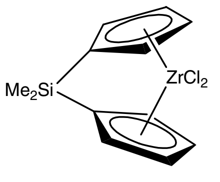
In order to expand the range of available Ziegler–Natta catalysts we have prepared new zirconium complexes in which boron-based heterocycles are used in place of Cp [5,6]. In prior work, it was found the methylaluminoxane (MAO) activated boratabenzene complex **2** [5] and 1,2-thiaborolyl complex **3** [6a] have ethylene polymerization activities which are very similar to that of Cp_2ZrCl_2 (**4**). This work was extended to the analogous dimethylsilyl-bridged complexes **5** [7] and **6** [6a] which also form active catalysts for ethylene polymerization.

Since the patent literature contains a report that 1,2-azaborolyl zirconium complex **7** is a good catalyst for olefin polymerization [8], a more detailed investigation of 1,2-azaborolyl zirconium chemistry seemed desirable. We have now developed syntheses of **8** and two dimethylsilyl-bridged 1,2-azaborolyl zirconium complexes **9** and **10** [9]. Crystal structures of **8**, **9**, and **10** demonstrate their considerable similarity to the corresponding zirconocenes. On activation with excess MAO all three complexes form active catalysts for the polymerization of ethylene.

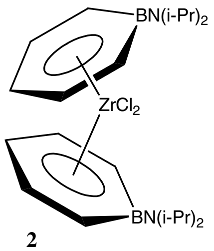
---

[*] Corresponding author. Tel.: +1 734 764 8487; fax: +1 734 647 4865.
E-mail address: ajashe@umich.edu (A.J. Ashe III).

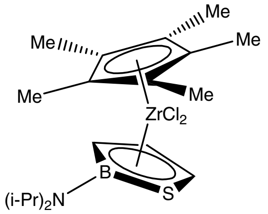
0277-5387/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2005.03.001



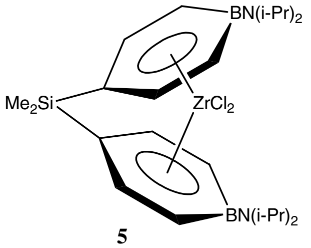
1



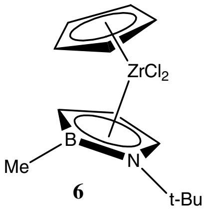
2



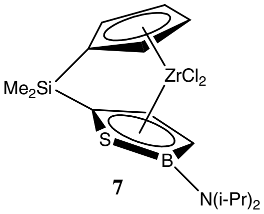
3



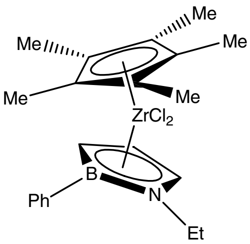
5



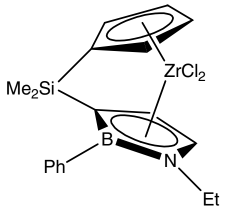
6



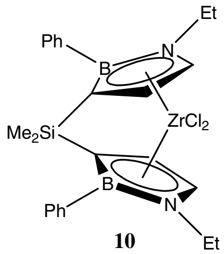
7



8



9



10

2. Experimental

2.1. General methods

^{1}H, $^{11}B\{^{1}H\}$, and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Varian INOVA-400 or 500 MHz spectrometers. The solvents used were chloroform-d_1 ($CDCl_3$), benzene-d_6 (C_6D_6), or tetrahydrofuran-d_8 (THF-d_8) as indicated. Chemical shifts (δ) are reported in parts per million (ppm). Proton and carbon chemical shifts are relative to respective solvent internal standards: 7.27 (for proton), 77.23 (for carbon) ($CDCl_3$): 7.16, 128.39 (C_6D_6): 3.58, 67.40 (THF-d_8). Boron-11 chemical shifts are relative to prospective external reference: δ 0.00 (BF_3/Et_2O 1.0 M LiCl in D_2O). The coupling constants (J) are reported in Hz. The following abbreviations are used to describe peak patterns: "s" for singlet, "d" for doublet, "t" for triplet. "q" for quartet, "m" for multiplet, and "br" for broad peak. Data are presented as follows: chemical shift (multiplicity, integrated intensity, coupling constant, and assignment). High-resolution mass spectra (HRMS) were recorded on a VG-250S spectrometer with electron-impact spectra at 70 eV. Elemental analyses were conducted on a Perkin–Elmer 240 CHN analyzer by the analytical service in the Department of Chemistry at the University of Michigan, Ann Arbor. Melting points were recorded on a Laboratory Devices MEL_TEMP melting point apparatus with an uncorrected thermometer.

Solvents were freshly distilled prior to use. THF and diethyl ether were distilled from sodium and benzophenone ketyl under N_2. Pentane and hexane were distilled from sodium. All reagents were purchased from the commercial vendors and were used as received or distilled if necessary. All reactions were conducted under an inert atmosphere of argon or in the glovebox under nitrogen unless otherwise specified.

2.2. Syntheses

2.2.1. (N-allyl-N-ethylamino)vinylphenylborane (**12**)

A solution of *N*-allyl-*N*-ethylamine (3.61 g, 42.5 mmol) in 10 mL of CH_2Cl_2 was added to a solution of phenylvinylboron chloride [10] (6.4 g, 42.7 mmol) in 20 mL of CH_2Cl_2 at −78 °C with stirring. The mixture was stirred for 1 h. Triethylamine (4.3 g, 42.6 mmol) was then added and a white precipitate formed immediately. The reaction mixture was allowed to warm to 25 °C with stirring for 3 h. The solid was removed by filtration and the solvent was removed in vacuo. Vacuum distillation of the residue gave the product as a clear colorless liquid (84%), bp 67–70 °C at 0.05 torr. The ^{1}H NMR and ^{13}C NMR spectra were consistent with it existing as two B–N rotomers with a ratio of 1:1. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.42 (d, 4 H, J = 8.0 Hz, ArH), 7.31–7.19 (m, 6H, ArH), 6.64 (dd, 1H, J = 19.0, 13.2 Hz, BCH), 6.57 (dd, 1H, J = 19.0, 13.2 Hz, BCH′), 6.02 (bt, 2H, J = 13.2 Hz, alkene), 5.80–5.50 (m, 4H, alkene), 5.12–4.91 (m, 4H, alkene), 3.68 (dt, 2H, J = 5.2, 1.7 Hz, $=CCH_2$), 3.51 (dt, 2H, J = 5.2, 1.7 Hz, $=CCH_2'$), 3.12 (q, 2H, J = 7.1 Hz, Et), 2.93 (q, 2H, J = 7.1 Hz, Et′), 0.99 (t, 3H, J = 7.1 Hz, Et), 0.81 (t, 3H, J = 7.1 Hz, Et′). ^{13}C NMR (C_6D_6, 100.6 MHz): shows two sets of signals. ^{11}B NMR (C_6D_6, 115.5 MHz): δ 39.4 HRMS (EI, *m/z*): calc. for $C_{13}H_{18}{}^{11}BN$ (M^+), 119.1532; found 119.1528. *Anal.* Calc. for $C_{13}H_{18}BN$: C, 78.42; H, 9.11; N, 7.03. Found: C, 78.28; H, 8.59; N, 6.50%.

2.2.2. *1-Ethyl-2,5-dihydro-2-phenyl-1H-1,2-azaborole (**13**)*

A solution of **12** (17.2 g, 86.4 mmol) in 20 mL of CH_2Cl_2 was added to a solution of bis (tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (Grubbs catalyst) (3.55 g, 4.31 mmol) in 40 mL of CH_2Cl_2 at 25 °C. The mixture was stirred at 25 °C for 10 h after which the color had changed from purple-red to dark brown. The solvent was removed in vacuo giving the product (12.6 g, 85%) as a clear colorless liquid, bp 60 °C at 0.05 torr. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.75 (d, 2H, J = 8.0 Hz, ArH), 7.33 (t, 2H, J = 8.0 Hz, ArH), 7.25 (t, 1H, J = 8.0 Hz, ArH), 6.93 (d, 1H, J = 8.1 Hz, vinyl), 6.60 (d, 1H, J = 8.1 Hz, vinyl), 3.51 (m, 2H, $NCH_2CH{=}$), 3.26 (q, 2H, J = 7.0 Hz, Et), 0.94 (t, 3H, J = 7.0 Hz, Et). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 148.5, 134.1, 132.3, 123.1, 128.9, 128.1, 127.6, 60.3 ($NCH_2C{=}$), 41.4 (Et), 16.7 (Et). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 39.4. HRMS (EI, *m/z*): Calc. for $C_{11}H_{14}{}^{11}BN$ (M^+), 171.1219; found, 171.1224. *Anal.* Calc. for $C_{11}H_{14}BN$: C, 77.24; H, 8.25; N, 8.19. Found: C, 77.83; H, 8.45; N, 7.68%.

2.2.3. *Lithium 1-ethyl-2-phenyl-1H-1,2-azaborolide (**14**)*

1-Ethyl-2,5-dihydro-2-phenyl-1*H*-1,2-azaborole (5.0 g, 29.2 mmol) was dissolved in 15 mL of ether at −78 °C. To this was added a solution of LDA (3.13 g, 29.2 mmol) in 15 mL of ether. The mixture was stirred at −78 °C for 2 h and at 25 °C for 10 h. After removal of the solvent the residue was washed with 3 × 20 mL of pentane. The residue was dried under vacuum to give the product as a light yellow powder (3.9 g, 77%). ^{1}H NMR (THF-d_8, 400 MHz): δ 7.51 (d, 2H, J = 8.0 Hz, ArH), 7.05 (t, 2H, J = 8.0 Hz, ArH), 6.87 (t, 1H, J = 8.0 Hz, ArH), 5.91 (m, 1H, H_4), 5.86 (m, 1H, H_5), 4.16 (m, 1H, H_3), 3.78 (q, 2H, J = 7.0 Hz, Et), 1.27 (t, 3H, J = 7.0 Hz, Et). ^{13}C NMR (THF-d_8, 100.6 MHz): δ 133.9, 127.2, 123.8, 112.8, 111.9, 86.5 (br), 43.2 (Et), 19.6 (Et). ^{11}B NMR (THF-d_8, 115.5 MHz): δ 29.4.

2.2.4. *(η-1-Ethyl-2-phenyl-1H-1,2-azaborolyl)(η-pentamethylcyclopentadienyl)zirconium(IV) dichloride (**8**)*

A solution of lithium 1-ethyl-2-phenyl-1*H*-1,2-azaborolide (0.42 g, 2.37 mmol) in 10 mL of ether was added to a suspension of pentamethylcyclopentadienylzirconium trichloride (0.78 g, 2.34 mmol) in 10 mL of ether at −78 °C. Stirring was maintained for 12 h as the mixture was slowly warmed to 25 °C. The solvent was removed in vacuo and the residue was washed with pentane and dried, affording the product (0.54 g, 56%) as a yellow powder. The product could be recrystallized from CH_2Cl_2/pentane to afford yellow crystals. ^{1}H NMR (400 MHz, C_6D_6): δ 7.79 (dd, J = 8.2, 1.4 Hz, 2H, ArH); 7.29 (t, J = 7.3 Hz, 2H, ArH); 7.19 (t, J = 7.4 Hz, 1H, ArH),; 6.24 (t, J = 2.6 Hz, 1H ring CH); 5.33 (dd, J = 4.9, 2.7 Hz, 1H, ring CH); 4.62 (dd, J = 4.9, 2.7 Hz, 1H, ring CH); 4.06 (dq, J = 14.0, 7.0 Hz, 1H, NCH); 3.86 (dq, J = 14.0, 7.0 Hz, 1H, NCH′); 1.77 (s, 15H, CpMe) 0.89 (t, J = 7.3 Hz, 3H, $NCH_2\mathit{CH_3}$). ^{13}C NMR (100.6 MHz): δ 134.5, 128.5, 127.7, 127.5, 123.5, 114.1, 44.1, 16.8, 12.1. ^{11}B NMR (115.6 MHz, C_6H_6): δ 33.7. HRMS: Calc. for $C_{21}H_{28}{}^{11}B^{35}Cl_2N^{90}Zr$, 465.0740. Found: 465.0740. *Anal.* Calc. for $C_{21}H_{28}BCl_2N^{90}Zr$: C, 53.96; H, 6.05; N, 3.00. Found: C, 52.52; H, 6.41; N, 2.79%.

2.2.5. *1-Ethyl-3-chlorodimethylsilyl-2,3-dihydro-2-phenyl-1H-1,2-azaborole (**15**)*

A solution of Me_2SiCl_2 (0.69 mL, 0.73 g, 5.65 mmol) in 15 mL of ether was added dropwise to a solution of lithium 1-ethyl-2-phenyl-1*H*-1,2-azaborolide (1.0 g, 5.65 mmol) in 25 mL of ether at −78 °C. When the addition was complete, the mixture was warmed slowly to 25 °C and stirred for 10 h. The solvent was removed under reduced pressure and the residue was extracted with pentane. The extracts were filtered through celite and the solvent was removed in vacuo leaving the product as an orange oil (1.38 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, J = 7.7, 1.8 Hz, 2H, ArH), 7.23 (m, 3H, ArH); 6.32 (dd, J = 3.8, 1.3 Hz, 1H, ViH); 5.70 (dd, J = 3.8, 2.4 Hz, 1H, ViH); 3.30 (m, 1H, NCH); 3.12 (m, 1H, NCH′); 2.64 (br s, 1H, BCH); 0.94 (t, J = 7.1 Hz, 3H, CMe), 0.14 (s, 3H, SiMe′), 0.09 (s, 3H, SiMe′). ^{13}C NMR (100.6 MHz, C_6D_6): δ 139.1, 133.5 (Ph), 128.8 (Ph), 127.9 (Ph), 122.2, 41.1 (NCH_2), 39 (br, BCH), 17.3 (CMe), 2.4 (SiMe), 0.2 (SiMe′). ^{11}B NMR (115.5 MHz, C_6D_6): δ 44.6. HRMS: Calc. for $C_{13}H_{19}{}^{11}B^{35}ClNSi$: 263.1068. Found: 263.1078. *Anal.* Calc. for $C_{13}H_{19}BClNSi$: C, 59.21; H, 7.28; N, 5.31. Found: C, 59.04; H, 7.12; N, 5.46%.

2.2.6. *1-Ethyl-3-(cyclopentadienyldimethylsilyl)-2,3-dihydro-2-phenyl-1H-1,2-azaborole (**16**)*

A solution of cyclopentadienyl lithium (0.16 g, 2.27 mmol) in 10 mL of THF was added slowly to a solution of 1-ethyl-3-chlorodimethylsilyl-2-3-dihydro-2-phenyl-1*H*-1,2-azaborole (0.60 g, 2.27 mmol) in 10 mL of THF at −50 °C. The reaction mixture was slowly warmed to 25 °C and stirred for 12 h. The solvent was removed in vacuo and the residue was extracted with pentane. Solvent was removed from the extracts leaving the desired product as a brown oil (0.58 g, 87%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.40 (dd, $J = 7.9$, 1.2 Hz, 2H, ArH); 7.16 (t, $J = 7.0$ Hz, 2H, ArH); 7.10 (t, $J = 7.0$ Hz, 1H, ArH); 6.54 (br s, 2H, Cp); 6.50 (br s, 2H, Cp), 6.28 (dd, $J = 4.0$, 1.1 Hz, 1H, ViH); 5.54 (dd, $J = 3.9$, 2.8 Hz, 1H, ViH); 3.30 (m, 1H, NCH); 3.22 (br s, 1H, Cp); 3.10 (m, 1H, N CH′), 2.45 (dd, $J = 2.6$, 1.1 Hz, 1H, BCH); 0.92 (t, $J = 7.1$ Hz, 3H, CMe); −0.13 (s, 3H, SiMe); −0.35 (s, 3H, SiMe′). ^{13}C NMR (C_6D_6, 100.6 mHz): δ 137.8, 133.5, 133.0, 130.4, 128.6; 128.0, 127.7, 113.4, 67.5, 41.1, 37.4 (br), 25.6, 17.5, −4.8, −4.9. ^{11}B NMR (115.5 Hz, C_6D_6): δ 45.0. HRMS: Calc. for $C_{18}H_{24}{}^{11}BNSi$: 293.1771. Found: 293.1774.

2.2.7. *[(η^5-cyclopentadien-1-yl)(η^5-1-ethyl-2-phenyl-1H-1,2-azaborol-3-yl)dimethylsilane]zirconium dichloride (**9**)*

A solution of lithium diisopropylamide (0.66 g, 6.20 mmol) in THF (20 mL) was added to a solution of 1-ethyl-3-[cyclopentadienyldimethylsilyl]-2,3-dihydro-2-phenyl-1*H*-1,2-azaborole (0.91 g, 3.10 mmol) in 20 mL of THF at −78 °C. The mixture was slowly warmed to 25 °C and allowed to stir for 12 h. After removal of the solvent in vacuo the residue was washed with pentane. The solid was dissolved in 20 mL of toluene and added to a suspension of $ZrCl_4$ (0.69 g, 3.00 mmol) in 10 mL of toluene at −50 °C. When the addition was complete, the mixture was allowed to warm to 25 °C with stirring for 12 h. The solvent was removed under reduced pressure and the product was extracted with ether, which was then filtered through celite. Removal of solvent left a yellow solid, which was recrystallized from CH_2Cl_2/pentane to give yellow needles. The yield was 0.80 g (59%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (m, 2H, ArH); 7.38 (d, $J = 2.5$ Hz, 1H, C_3H_2BN), 7.26 (m, 3H, ArH), 6.98 (M, 1H, Cp); 6.87 (m, 1H, Cp); 6.00 (m, 1H, Cp); 5.92 (d, $J = 2.5$ Hz, 1H, C_3H_2BN); 5.88 (m, 1H, Cp); 4.08 (dq, $J = 13.7$, 7.1 Hz, 1H, NCH); 3.75 (dq, $J = 13.7$, 7.1 Hz, NCH); 1.21 (t, $J = 7.3$ Hz, 3H, CH_3C); 0.62 (s, 3H, SiMe); 0.37 (s, 3H, SiMe′). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 140.4, 135.6, 129.5, 128.6, 127.3, 120.9, 120.6, 112.5, 110.4, 44.1, 16.8, −2.3, −3.5. ^{11}B NMR (115.6 MHz, $CDCl_3$): δ 34.6. HRMS: Calc. for $C_{18}H_{22}{}^{11}B^{35}Cl_2NSi^{90}Zr$: 451.0039. Found: 451.0016. *Anal.* Calc. for $C_{18}H_{22}B^{35}Cl_2NSi^{90}Zr$: C, 47.68; H, 4.90; N, 3.09. Found: C, 47.92; H, 5.17; N, 3.11%.

2.2.8. *Bis(1-ethyl-2,3-dihydro-2-phenyl-1H-1,2-azaborol-3-yl)dimethylsilane (**17**)*

The title compound was prepared in the same manner as (**16**) from lithium 1-ethyl-2-phenyl-1*H*-1,2-azaborolide (0.41 g, 2.31 mmol) in 15 mL of THF and 1-ethyl-3-chlorodimethylsilyl-2,3-dihydro-2-phenyl-1*H*-1,2-azaborole (0.01 g, 2.31 mmol) in 15 mL of THF. The product was obtained as a yellow oil (0.85 g, 92%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.41 (dd, $J = 8.0$, 1.5 Hz, 4H, ArH); 7.18 (t, $J = 7.3$ Hz, 4H, ArH); 7.12 (t, $J = 7.3$ Hz, 2H, ArH); 6.29 (dd, $J = 4.0$, 1.1 Hz, 2H, ViH); 5.58 (dd, $J = 3.6$, 1.1 Hz, 2H, ViH); 3.26 (m, 2H, NCH); 3.11 (m, 2H, NCH); 2.43 (dd, $J = 2.6$, 1.1 Hz, 2H, BCH); 0.89 (t, $J = 7.0$ Hz, 6H, CMe); −0.18 (s, 3H, SiMe); −0.42 (s, 3H, SiMe). ^{13}C NMR (100.6 MHz, $CDCl_3$); δ 137.4, 133.5 (Ph); 128.3 (Ph); 127.7 (Ph), 113.7, 41.2 (NCH_2), 37.2 (br, BCH), 17.9 (CMe), −4.3 (SiMe), −4.4 (SiMe). ^{11}B ($CDCl_3$, 115.5 MHz): δ 45.2. HRMS: Calc. for $C_{24}H_{32}{}^{11}B_2N_2Si$: 398.2520. Found: 398.2516.

2.2.9. *Rac-(bis(η^5-1-ethyl-2-phenyl-1H-1,2-azaborol-3-yl)dimethylsilane)zirconium dichloride (**10**)*

A solution of lithium diisopropylamide (0.46 g, 4.26 mmol) in 10 mL of THF was added to a solution of bis (1-ethyl-2,3-dihydo-2-phenyl-1*H*-1,2-azaborol-3-yl)dimethylsilane (0.85 g, 2.13 mmol) in 10 mL of THF at −78 °C. The mixture was slowly warmed to 25 °C and stirred for 8 h. The solvent was removed in vacuo and the residue was washed with 3 × 10 mL of pentane. The solid was dissolved in 10 mL of toluene and the resulting solution was added to a suspension of $ZrCl_4$ (0.49 g, 2.143 mmol) in 10 mL of toluene at −50 °C. Stirring was continued for 12 h and the mixture was warmed slowly to 25 °C. The solvent was removed in vacuo and the product was dissolved in ether which was filtered through celite. Removal of the solvent under reduced pressure gave an orange solid which was recrystallized from CH_2Cl_2 to give orange crystals of product (0.80 g, 68%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.70 (dd, $J = 8.1$, 1.5 Hz, 4H, ArH); 7.25 (t, $J = 7.6$ Hz, 4H, ArH); 7.15 (t, $J = 7.4$ Hz, 2H, ArH); 6.83 (d, $J = 2.5$ Hz, 2H, C_3H_2BN); 5.86 (d, $J = 2.5$ Hz, 2H, C_3H_2BN); 3.75 (dq, $J = 13.4$, 6.9 Hz, 2H, NCH); 3.38 (dq, $J = 13.4$, 6.9 Hz, 2H, NCH′); 0.64 (t, $J = 7.2$ Hz, 6H, CH_3), 0.32 (s, 6H, SiMe). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 135.6, 131.4, 128.5, 127.6, 119.7, 44.7, 17.2, −1.0. ^{11}B (115.6 MHz, $CDCl_3$): δ 31.8. HRMS: Calc. for $C_{24}H_{30}{}^{11}B_2{}^{35}Cl_2N_2Si^{90}Zr$: 556.0788. Found: 556.0770. *Anal.* Calc. for $C_{24}H_{30}B_2Cl_2N_2SiZr$: C, 51.62; H, 5.43; N, 5.02. Found: C, 51.32; H, 5.39; N, 5.08%.

2.3. X-ray data collection

X-ray quality crystals of **8**, **9**, and **10** were crystallized from dichloromethane at room temperature. A suitable crystal was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 158(2) K; the detector was placed at a distance of 4.959 cm from the crystal. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS [11] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL [12] (version 5.10) software package. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms located on a difference Fourier map and allowed to refine isotropically. Additional details are presented in Table 1 and are given as Supplementary materials as CIF files.

2.4. Polymerization conditions

A 2 L reactor was charged with mixed alkane solvent and 1-octene. Hydrogen was added by differential pressure expansion from a 75 mL addition tank from 2.1 MPa to near 1.9 MPa. The reaction and container were heated to 140 °C and saturated with ethylene at 3.4 MPa. In an inert atmosphere glovebox the appropriate quantities of zirconium complex and MAO (1:1000 m) were combined and this solution was transferred to a catalyst addition tank. The polymerization were initiated by injecting this catalyst solution into the reactor. The polymerization condition were maintained for 15 min with ethylene provided on demand at 3.4 MPa. The polymer solution was removed from the reactor and combined with a hindered phenol antioxidant and isopropanol. Volatile components were removed from the polymer in a vacuum oven set at 140 °C for about 20 h. The dried polymers were weighed and analyzed. Additional details are given in [13].

Table 1
Crystallographic data for complexes **8**, **9**, and **10**

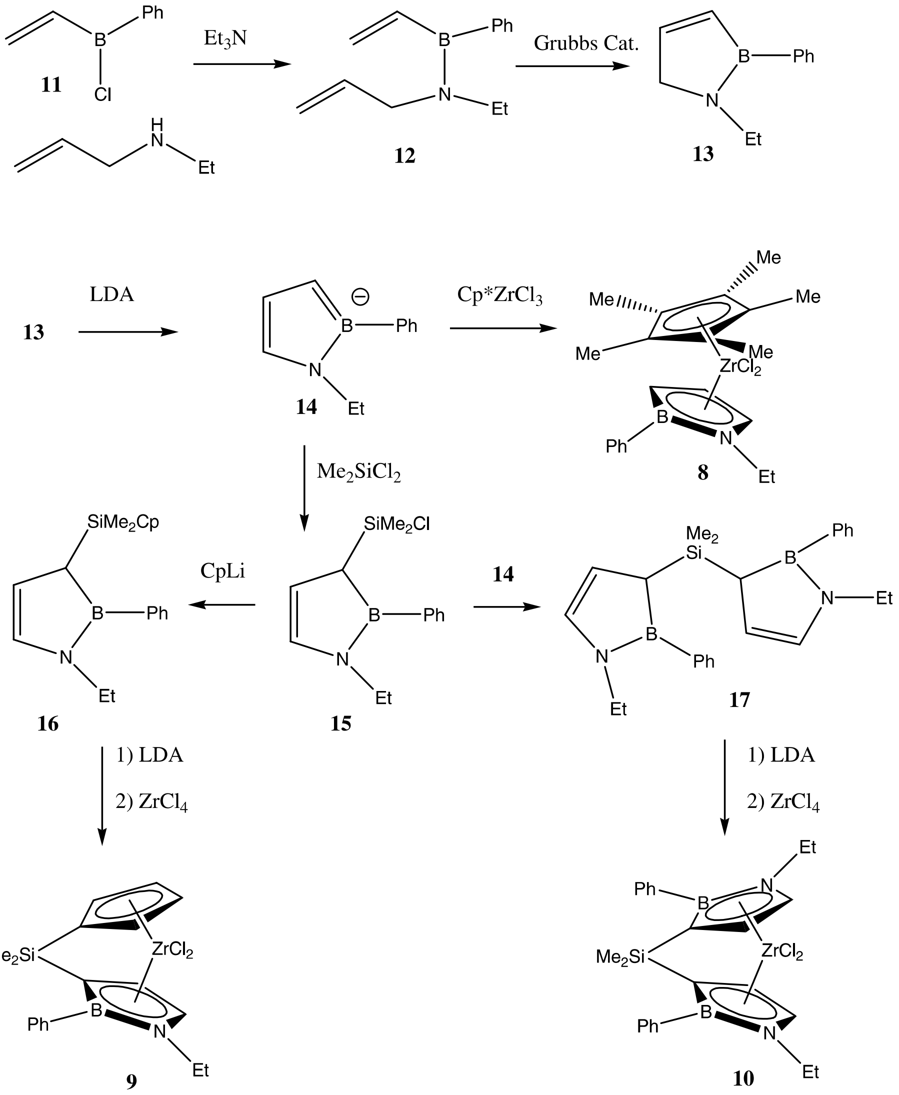
	8	**9**	**10**
Empirical formula	$C_{21}H_{28}BCl_2NZr$	$C_{18}H_{22}BCl_2NSiZr$	$C_{24}H_{30}B_2Cl_2N_2Zr(CH_2Cl_2)$
Formula weight	467.37	453.39	643.26
Temperature (K)	158(2)	158(2)	158(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	*P*2(1)/*c*	*P*2(1)/*n*	*P*1
Unit cell dimensions			
a (Å)	8.7474(11)	7.4420(6)	9.6792(13)
b (Å)	16.566(2)	12.9009(11)	12.780(2)
c (Å)	15.2556(19)	21.2678(18)	13.276(2)
α (°)			89.419(2)
β (°)	105.790(2)	93.1030(10)	79.316(2)
γ (°)			88.605(2)
Volume (Å^3)	2125.8(5)	2038.9	1446.7(4)
Z	4	4	2
$D_{\text{calc.}}$ (Mg/m^3)	1.460	1.477	1.477
Absorption coefficient (mm^{-1})	0.774	0.860	0.809
F (000)	960	920	656
Crystal size (mm)	0.22 × 0.28 × 0.42	0.10 × 0.16 × 0.44	0.28 × 0.28 × 0.38
θ range for data (%)	1.85–26.40	1.85–26.38	1.56–26.39
Collection index range	$-10 \leqslant h \leqslant 10$, $-20 \leqslant k \leqslant 20$, $-19 \leqslant l \leqslant 19$	$-9 \leqslant h \leqslant 9$, $-16 \leqslant k \leqslant 16$, $-26 \leqslant l \leqslant 26$	$-10 \leqslant h \leqslant 10$, $-15 \leqslant k \leqslant 15$, $-16 \leqslant l \leqslant 16$
Reflections collected/unique	19920/4350	20075/4184	15766/5850
Completeness to $\theta = 26.40$	99.8%	99.9	98.9
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Max. and min. transmission	0.911 and 0.821	0.942 and 0.818	0.879 and 0.786
Refinement method	full-matrix least-square on F^2	full-matrix least-square on F^2	full-matrix least-square on F^2
Data/restraints/parameters	4350/0/348	4184/0/307	5850/0/432
GOF on F^2	1.049	1.042	1.044
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0216$, $wR_2 = 0.0581$	$R_1 = 0.204$, $wR_2 = 0.0515$	$R_1 = 0.279$, $wR_2 = 0.0735$
R indices (all data)	$R_1 = 0.0241$, $wR_2 = 0.0595$	$R_1 = 0.0254$, $wR_2 = 0.0526$	$R_1 = 0.0305$, $wR_2 = 0.0753$
Largest differential peaks and hole (e Å^{-3})	0.0352 and −0.273	0.287 and −0.278	0.639 and −0.850

3. Results and discussion

3.1. Synthesis

The 1,2-azaborolyl ring system has been prepared by several routes [10,14–16]. In our hands a synthesis via a ring closing metathesis from B-vinyl-*N*-allyl-aminoboranes is particularily convenient. The B-phenyl-*N*-ethyl azaborolyl **14** was easily prepared by this route (Scheme 1) which had previously been used to prepare the corresponding B-phenyl-*N*-methyl derivative **14a** [10]. The reaction of phenylvinylboron chloride [11] with allylethylamine in pentane containing triethylamine gave a 84% yield of aminoborane **12**. The ^{1}H and ^{13}C NMR spectra of **12** are complex indicating that it exists as a 1:1 mixture of rotomers about the B–N bond. The appreciable π-bond character of this B–N bond makes the rotation about this bond slow on the NMR time scale [17]. On treatment of **12** with 5 mol% Grubbs catalyst in CH_2Cl_2 at 25 °C for 12 h, cyclization occurred to afford a 74% yield of the ring closed product **13**. The reaction of **13** with LDA in ether gave the lithium 1,2-azaborolide **14** which was isolated as a pale yellow powder in 96% yield. The ^{1}H, ^{11}B, and ^{13}C NMR chemical shift values of the ring atoms of **14** are very similar to those previously reported for corresponding N-methyl derivative **14a** [10] and other 1,2-azaborolides [14]. The reaction of **14** with Cp^*ZrCl_3 in ether gave the expected **8** as yellow crystals in 56% yield.

The dimethylsilyl-bridged mixed 1,2-azaborolyl cyclopentadienyl zirconium complex **9** was prepared by a straightforward route outlined in Scheme 1. Silylation of **14** with an excess of dichlorodimethylsilane afforded the 3-chlorodimethylsilyl isomer **15** as an orange oil in 96% yield. Compound **15** was not detectably contaminated with the possible 5-regio isomer. It seems probable



Scheme 1. Synthesis of lithium 1-ethyl-2-phenyl-1,2-azaborolide (**14**) and its conversion to zirconium complexes **8**, **9**, and **10**.

that C(3) of **14** is more nucleophilic than C(5) due to its larger negative charge density which is indicated by the higher field signal for C(3) in the ^{13}C NMR spectrum [18a]. The sequential reaction of **15** with CpLi followed by LDA and then $ZrCl_4$ gave **9** or yellow crystals in 59% yield.

The reaction of **15** with lithium azaborolide **14** afforded the dimethylsilyl derivative **17** as a yellow oil in 92% yield. As was the case from **16**, it was not detectably contaminated by regioisomers. The reaction of **17** with LDA followed by $ZrCl_4$ gave **10** as a yellow crystalline product in 68% yield. The ^{1}H and ^{13}C NMR spectra of **10** suggested that it was a single diastereomer. A subsequently obtained X-ray crystal structure showed that it is the racemic isomer.

3.2. Structure

The molecular structures of **8**, **9**, and **10** are illustrated in Figs. 1–3, respectively. Selected bond distances and angles are compared in Table 2. These compounds are the first structurally characterized monocyclic 1,2-azaborolyl zirconium complexes although we have previously reported structures for zirconium complexes of fused ring 1,2-azaborolyls [18b]. Prior crystallographic work on both early and late transition metal 1,2-azaborolyl complexes shows that the ligand usually binds in an unsymmetrical η^5-manner [15,19]. Compounds **8**, **9**, and **10** conform to this pattern. In each case the 1,2-azaborolyl ring is largely coplanar. The B–Zr distances (2.68 Å, ave) are somewhat longer than the C–Zr and N–Zr distances (2.44–2.54 Å, range). The longer boron–metal distances are consistent with the larger atomic radius of boron compared to that of carbon and nitrogen. A similar pattern is found in the structures of most metal π-coordinated complexes of boron heterocycles [20].

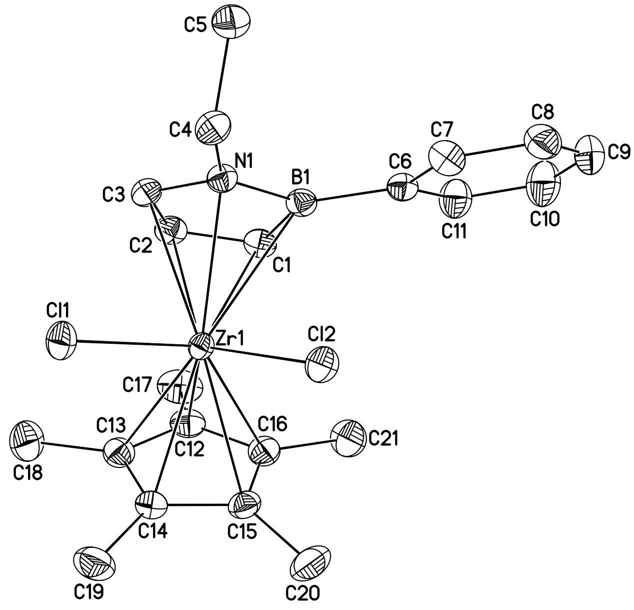


Fig. 1. Molecular structure of **8** (ORTEP). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

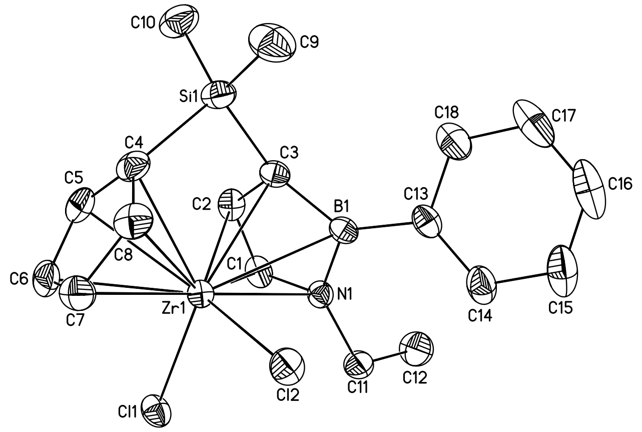


Fig. 2. Molecular structure of **9** (ORTEP). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Comparison of the structures of **8**, **9**, and **10** shows that the corresponding intraring 1,2-azaborolyl distances vary by no more than ±0.02 Å. Similarly the distance of Zr atoms to the corresponding ring atoms vary by no more than ±0.05 Å. Thus the bridges in **9** and **10** exert little perturbation on the structure found for **8**.

The structures of **8**, **9**, and **10** can also be compared with those of similar zirconocene dichlorides. The Cp planes of Cp_2ZrCl_2 intersect an angle of 52° [21]. The mean plane of the 1,2-azaborolyl ring of **8** intersects its Cp* plane at an angle of 52.5(1)°. In the dimethylsilyl bridged **1** the Cp planes intersect at 57° [22]. The corresponding Cp/1,2-azaborolyl planes of **9** intersect at 60.1(1)° and the 1,2-azaborolyl/1,2-azaborolyl planes of **10** intersect at 57.3(1)°. Thus, all three *ansa*-complexes have very similar open wedges to the Zr atoms.

3.3. Polymerization studies

On activation by a 10^3 molar excess of MAO in a hydrocarbon solvent the 1-ethyl-2-phenyl-1,2-azaborolyl zirconium complexes **8**, **9**, **10** form active catalysts for the polymerization of mixtures of ethylene and 1-octene. The results are summarized in Table 3. In all cases, the product was polyethylene with the incorporation of approximately 1% 1-octene. All three 1,2-azaborolyl complexes are significantly better catalysts than 1-diisopropylamino-1-boratabenzene zirconium complexes **2** [5a,6a] and **5** [7] and 1-diisopropylamino-1,2-thiaborolyl zirconium complex **3** [6a] under identical conditions. MAO activated **2** has previously been found to have

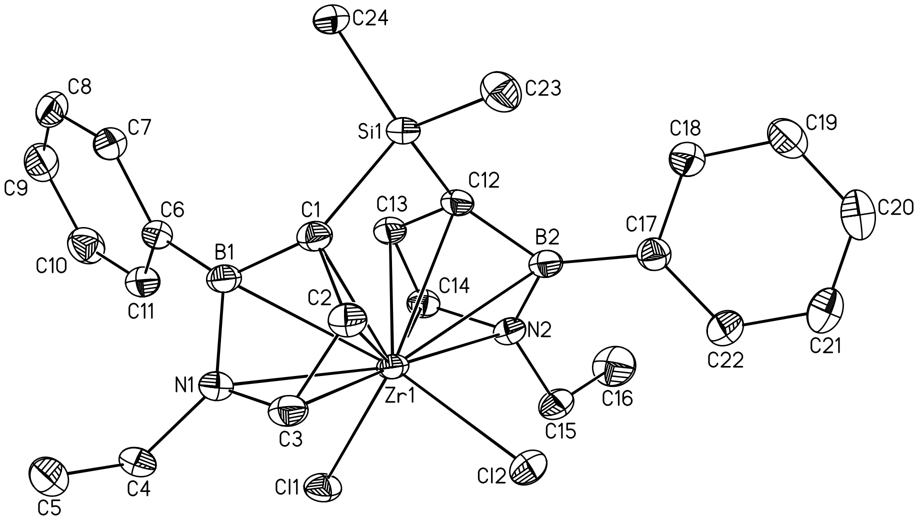


Fig. 3. Molecular structure of **10** (ORTEP). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2
Comparison of selected distances (Å) and angles (°) from **8**, **9**, and **10**

	8	9	10[a]
B–Cα[b]	1.510(2)	1.520(2)	1.537(3), 1.530(3)
Cα–Cβ[b]	1.432(2)	1.456(2)	1.438(2), 1.455(2)
Cβ–Cγ[b]	1.372(2)	1.363(2)	1.391(3), 1.384(3)
Cγ–N[b]	1.396(2)	1.393(2)	1.391(2), 1.395(2)
B–N	1.482(2)	1.485(2)	1.471(2), 1.492(2)
Zr–B	2.681(2)	2.688(2)	2.632(2), 2.679(2)
Zr–Cα[b]	2.479(2)	2.471(2)	2.478(2), 2.478(2)
Zr–Cβ[b]	2.404(2)	2.442(2)	2.459(2), 2.454(2)
Zr–Cγ[b]	2.491(2)	2.485(2)	2.504(2), 2.503(2)
Zr–N	2.531(1)	2.525(1)	2.576(2), 2.522(2)
PL (ring 1)/ PL (ring 2)	52.5(1)	60.1(1)	57.3(1)

[a] The first distance refers to ring B1C1C2C3N1. The second distance refers to ring B2C12C13C14N2.

[b] Cα, Cβ, Cγ designate the carbon atoms of the 1,2-azaboroyl rings which are 1,2 or 1,3 or 1,4 to the boron atom, respectively.

approximately the same ethylene polymerization activity as Cp_2ZrCl_2, albeit under somewhat different conditions [5a]. Thus we can safely conclude that **8**, **9**, and **10** are significantly more active than Cp_2ZrCl_2 from the polymerization of ethylene.

Table 3
Comparison of the efficiency of ethylene/1-octene polymerization of **8**, **9**, and **10** with selected other complexes

Complex	Efficiency (g polymer/mol Zr atom)	Reference
8	234×10^4	this work
9	66×10^4	this work
10	126×10^4	this work
2	20.4×10^4	[6c]
3	6.0×10^4	[6a]
5	2.4×10^4	[7]

The η^5-1,2-azaborolyl ligands of **8**, **9**, and **10** are nearly isostructural with the η^5-Cp groups of zirconocene dichlorides. Furthermore, the degree of canting of the rings of **8**, **9**, and **10** is nearly identical to that found in the corresponding zirconocenes. Therefore, it is unlikely that the greater reactivity of the 1,2-azaborolyl zirconium complexes is due to steric efforts. Fu and co-workers [15] found that the 1,2-azaborolyl ligand in Fe(II) complexes is more electron-rich than Cp. Thus, it is likely that electron density at Zr is higher for **8**, **9**, and **10** than it is for the corresponding zirconocenes. It may be that the higher catalytic activity of the 1,2-azaborolyl zirconium complexes is associated with the greater electron density and lower electrophilicity at the active metal center. It has previously been observed that electron withdrawing groups decrease the activity of zirconium-based Ziegler–Natta catalysts [23].

Contrary to our expectations the dimethylsilyl bridging in **9** and **10** led to a small decrease rather than an increase is the polymerization activity relative to **8**. It may be that the lack of conformational mobility enforced by the bridge holds that 1-ethyl and 2-phenyl substituents in positions which interfere with the propagation steps. A similar but larger drop-off in activity was observed between **2** and **5** [7].

4. Conclusion

In summary, we have developed an efficient synthetic route to Me_2Si-bridged and non-bridged (1,2-azaborolyl) zirconium(IV) dichlorides **8**, **9**, and **10**. The 1,2-azaborolyl is an electron rich surrogate for Cp and the structure of its zirconium complexes closely resemble those of the corresponding zirconocenes. On activation by excess MAO, **8**, **9**, and **10** form highly active catalysts for the polymerization of ethylene.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 262648, 262649, and 262650 for compounds **8**, **9**, and **10**, respectively. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1233 336 033; e-mail: deposit@ccdc.cam.ac.uk, or http://www.ccdc.cam.ac.uk).

Acknowledgments

This work was supported by the National Science Foundation and the Dow Chemical Company. We are grateful to the Dow Chemical Company for running the polymerization experiments. We are also grateful to the Boulder Scientific Company from a generous gift of the Grubbs catalyst.

References

[1] (a) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. Engl. 34 (1995) 1143;
(b) G. Fink, R. Mülhaupt, H.H. Brintzinger (Eds.), Ziegler Catalysts, Spinger, Berlin, Germany, 1995;
(c) J.A. Gladysz, Chem. Rev. 100 (2000) 1167.

[2] L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253.

[3] W.A. Herrmann, J. Rohrmann, E. Herdtweck, W. Spaleck, A. Winter, Angew. Chem., Int. Ed. Engl. 28 (1989) 1511.

[4] W. Spaleck, M. Antberg, J. Rohrmann, A. Winter, B. Bachmann, P. Kiprof, J. Behm, W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 31 (1992) 1347.

[5] (a) G.C. Bazan, G. Rodriguez, A.J. Ashe, III, S. Al-Ahmad, C. Müller, J. Am. Chem. Soc. 118 (1996) 2291;
(b) G.C. Bazan, G. Rodriguez, A.J. Ashe III, S. Al-Ahmad, J.W. Kampf, Organometallics 16 (1997) 2492.

[6] (a) A.J. Ashe III, X. Fang, J.W. Kampf, Organometallics 19 (2000) 4935;
(b) A.J. Ashe III, J.W. Kampf, M. Schiesher, Organometallics 19 (2000) 4681;
(c) A.J. Ashe III, X. Fang, J.W. Kampf, Organometallics 18 (1999) 1821.

[7] A.J. Ashe III, S. Al-Ahmad, X. Fang, J.W. Kampf, Organometallics 17 (1998) 3883.

[8] S. Nagy, R. Krishnamurti, B.P. Etherton, PCT Int. Appl (1996) WO96 34,021; Chem. Abstr. 126 (1997) 19432j.

[9] A.J. Ashe, III, H. Yang, F.J. Timmers PCT Int. Appl (2003) WO 2003 087114 A1 20031023; Chem. Abstr. 139 (2003) 323949.

[10] A.J. Ashe III, X. Fang, Org. Lett. 2 (2000) 2089.

[11] G.M. Sheldrick, SADABS Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 1996.

[12] G.M. Sheldrick, SHELXTL, v. 5.10 Brucker Analytical X-ray, Madison, WI, 1999.

[13] A.J. Ashe III, X. Fang, A. Hokky, J.W. Kampf, Organometallics 23 (2004) 2197.

[14] (a) G. Schmid, in: I. Shinkai (Ed.), Comprehensive Heterocyclic Chemistry II, vol. 3, Elsevier, Oxford, UK, 1996 (Chapter 3.17);
(b) G. Schmid, Comments Inorg. Chem. 4 (1985) 17.

[15] S-Y. Liu, M.M.-C. Lo, G.C. Fu, Angew. Chem., Int. Ed. 41 (2001) 174.

[16] J. Pan, J.W. Kampf, A.J. Ashe III, Organometallics 23 (2004) 5626.

[17] (a) D. Imbery, A. Jaeschke, H. Friebolin, Org. Magn. Reson. 2 (1970) 271;
(b) H. Friebolin, R. Rensch, H. Wendel, Org. Magn. Reson. 8 (1976) 287.

[18] (a) A.J. Ashe, III, X. Fang, X. Fang, J.W. Kampf, Organometallics 20 (2001) 5413;
(b) A.J. Ashe III, H. Yang, X. Fang, J.W. Kampf, Organometallics 21 (2002) 4578.

[19] (a) G. Schmid, O. Boltsch, D. Bläser, R. Boese, Z. Naturforsch. B 39 (1984) 1082;
(b) G. Schmid, D. Kampmann, W. Meyer, R. Boese, P. Paetzold, K. Delpy, Chem. Ber. 118 (1985) 2418;
(c) G. Schmid, F. Schmidt, R. Boese, Chem. Ber. 118 (1985) 1949;
(d) G. Schmid, B. Kilanowski, R. Boese, D. Bläser, Chem. Ber. 126 (1993) 899;
(e) G. Schmid, S. Haske, D. Zaika, R. Boese, D. Bläser, Chem. Ber. 127 (1994) 73.

[20] J. Chen, X. Fang, Z. Bajko, J.W. Kampf, A.J. Ashe III, Organometallics 23 (2004) 5088.

[21] (a) K. Prout, S.T. Cameron, R.A. Forder, S.R. Critchley, B. Denton, G.V. Rees, Acta Crystallogr. B 30 (1977) 2290;
(b) J.Y. Corey, X.-H. Zhu, L. Brammer, N.P. Rath, Acta Crystallogr. C 51 (1995) 565.

[22] C.S. Bajgur, W. Tikkanen, J.L. Petersen, Inorg. Chem. 24 (1985) 2539.

[23] (a) N. Piccolrovazzi, P. Pino, G. Consiglio, A. Sironi, M. Moret, Organometallics 9 (1990) 3098;
(b) I-M. Lee, W.J. Gauthier, J.M. Ball, B. Iyengar, S. Collins, Organometallics 11 (1992) 2115;
(c) M.P. Thornberry, N.T. Reynolds, P.A. Deck, F.R. Fronczek, A.L. Rheingold, L.M. Liable-Sands, Organometallics 23 (2004) 1333.