

Inorganica Chimica Acta 280 (1998) 226-232

Inorganica Chimica Acta

$$\label{eq:si2} \begin{split} & \text{Preparation of doubly-silylene-bridged zirconocene alkyl complexes,} \\ & (\text{Me}_2\text{Si})_2\{\eta^5\text{-}\text{C}_5\text{H}_2\text{-}4\text{-}\text{CHMe}_2\}\{\eta^5\text{-}\text{C}_5\text{H}\text{-}3,5\text{-}(\text{CHMe}_2)_2\}\text{ZrR}_2\ (R=CH_3, CH_2\text{Ph}) \text{ and investigations of their activity in 1-pentene polymerization.} \\ & \text{Molecular structure of } (\text{Me}_2\text{Si})_2\{\eta^5\text{-}\text{C}_5\text{H}_2\text{-}4\text{-}\text{CHMe}_2\}\{\eta^5\text{-}\text{C}_5\text{H}\text{-}3,5\text{-}(\text{CHMe}_2)_2\}\text{Zr}(CH_2\text{Ph})_2 \end{split}$$

Dario Veghini, Michael W. Day, John E. Bercaw*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, CA 91125. USA

Received 7 October 1997; accepted 28 November 1997

Dedicated to Mark Vol'pin, an inspirational scientist and a remarkable human being

Abstract

The syntheses of the doubly-[SiMe₂]-bridged zirconocene complexes, $(Me_2Si)_2\{\eta^5-C_5H_2-4-CHMe_2\}\{\eta^5-C_5H_2-4,CHMe_2\}_2R_2$ (R=Cl (2); R=CH₂Ph (3); R=CH₃ (4)) are described. The structure of $(Me_2Si)_2\{\eta^5-C_5H_2-4-CHMe_2\}\{\eta^5-C_5H_3-5-(CHMe_2)_2\}_2$ (CH₂Ph)₂ (3) has been examined by single crystal X-ray diffraction methods. It crystallizes in the triclinic space group *P*-1, with a=9.900(2), b=11.818(2), c=15.320(3) Å, $\alpha=105.02(3)$, $\beta=92.56(3)$, $\gamma=105.23(3)^\circ$ and Z=2. Compounds 3 and 4 are active stereospecific pre-catalysts for the [Ph₃C][B(C₆F₅)₄] co-catalyzed polymerization of 1-pentene. Polymerization reactions at low temperature in liquid monomer produced poly(1-pentene) with syndiotactic microstructure and narrow molecular weight distribution. By contrast, in 1-pentene/toluene solutions a broad molecular weight distribution is observed. Under all conditions examined 2/MAO systems produced high molecular weight, highly syndiotactic poly-1-pentene with narrow molecular weight distributions. $\[mathbf{0}\]$ 1998 Elsevier Science S.A.

Keywords: Crystal structures; Zirconocene complexes; Silylene-bridged complexes; Alkyl complexes; Ziegler-Natta polymerization

1. Introduction

Currently many efforts have been devoted attempting to find alternative co-catalysts to methylalumoxane (MAO) [1] for Group 4 homogeneous α -olefin polymerization systems [2]. Among the most successful examples are compounds of the type [Cp'₂ZrR][RB(Ar^F)₃] (Cp' = substituted cyclopentadienyl; R=alkyl, benzyl; Ar^F = fluorinated arylboranes) [3,4], which can be prepared in situ by the reaction of fluorinated borane and borate reagents with metallocene Group 4-alkyls; only rarely are these zirconocenium alkyls stable enough to be isolated [2c,5]. Catalysts that are activated using fluorinated borane or borate activators normally show comparable stereospecificity and often higher productivity for propene polymerizations, as compared to the analogous MAO-activated systems. We recently reported that doubly-[SiMe₂]-bridged [6] zirconocene complexes, when activated by MAO, are highly active and stereospecific catalysts for the polymerization of propene.



Among a series of derivatives, 2/MAO showed the highest syndiospecificity in neat propene (>99% [r] at 0°C). In thic contribution we report an alternative synthetic approach to compound 2, the synthesis of the dimethyl complex, the synthesis and the molecular structure of the dibenzyl complex, along with some preliminary results concerning 1-pentene

^{*} Corresponding author. Tel.: +1-626-395 6577; fax: +1-626-585 0147; e-mail: bercaw@caltech.edu

227

polymerizations when these dialkyl derivatives are activated by $[Ph_3C] [B(C_6F_5)_4]$. A comparison is drawn with the analogous 2/MAO system.

2. Experimental

2.1. General considerations

All compounds were manipulated using high vacuum line, using Schlenk techniques or in a dry box under a nitrogen atmosphere. Argon and nitrogen gases were purified by passage over columns of MNO on vermiculite and activated molecular sieves [7]. All solvents were stored under vacuum over sodium benzophenone ketyl (hexamethyldisiloxane, THF, Et₂O) or titanocene (toluene, petroleum ether) and freshly distilled immediately prior to use. ¹H and ¹³C NMR spectra were recorded on a Bruker AM 500 spectrometer at 500.13 and 125.77 MHz, respectively. ¹H and ¹³C{¹H} NMR chemical shifts are relative to SiMe4 using the residual ¹H or ¹³C chemical shift of the solvent as a second standard. Elemental analyses were carried out at the Caltech Elemental Analysis Facility by Fenton Harvey. B(C₆F₅)₃ [8], [Ph₃C]- $[B(C_6F_5)_4]$ [9], K[CH₂Ph] [10] and (Me₂Si)₂- $\{C_5H_3-4-CHMe_2\}\{C_5H_2-3,5-(CHMe_2)_2\}$ [6] were prepared as previously reported.

2.2. $Li_2[(Me_2Si)_2\{C_5H_2-4-CHMe_2\}\{C_5H-3,5-(CHMe_2)_2\}_2 \cdot 2Et_2O(1)$

A 250 ml round bottom flask was loaded with 3.8 g (10.3 mmol) $(Me_2Si)_{2}\{C_{5}H_{3}-4-CHMe_{2}\}\{C_{5}H_{2}-3,5-(CHMe_{2})_{2}\},\$ a large swivel frit was attached, and 150 ml Et2O were vacuum transferred. At 25°C a solution of n-BuLi (13.7 ml, 1.6 M in hexanes) was added to this solution over 20 min with vigorous stirring. After 20 h the solvent was almost completely removed, 100 ml petroleum ether were vacuum transferred, and the resulting white precipitate filtered off. Yield: 3.8 g (70% based on bis(diethylether) product). 'H NMR (THF-d₈): δ 0.22 (s broad, 12H, SiMe₂), 1.08 (t, $J(HH) = 15 Hz, 12H, O(CH_2Me)_2), 1.20, 1.21$ (pseudo tripiet, J(HH) = 6 Hz, 18H, CHMe₂), 2.86 (m, 1H, CHMe₂), 3.09 (m, 2H, CHMe₂), 3.35 (q, J(HH) = 15 Hz, 8H, $O(CH_2Me)_2$, 5.88 (s, 1H, Cp), 6.02 (2, 2H, Cp). ¹³C{¹H} NMR (THF-d₈): δ 5.45 (s broad, SiMe₂); 15.84 $(O(CH_2CH_3)_2); 26.51, 27.56, 29.83, 30.49 (CH(CH_3)_2);$ 66.48 (O(CH₂CH₃)₂); 101.66, 111.07, 114.21, 120.09, 134.11, 138.88 (Cp).

2.3. $(Me_2Si)_2\{\eta^5 - C_3H_2 - 4 - CHMe_2\}\{\eta^5 - C_3H - 3, 5 - (CHMe_2)_2\}ZrCl_2(2)$

In a glove box a 250 ml round bottom flask was loaded with 3 g (5.66 mmol) of complex 1 and 1.32 g (5.66 mmol) ZrCl₄, assembled to a swivel frit and 100 ml toluene vacuum transferred onto the solids. The reaction mixture was initially stirred for 2 h at -78° C and for additional 10 h at 25°C. The resulting suspension was then filtered, the filtrate concentrated to few ml, 100 ml petroleum ether vacuum transferred, and the white precipitate carefully filtered off. Yield: 1.3 g (43%).

2.4. $(Me_2Si)_2\{\eta^5-C_5H_2-4-CHMe_2\}\{\eta^5-C_5H-3,5-(CHMe_2)_2\}Zr(CH_2Ph)_2(3)$

In a glove box a 100 ml round bottom flask was loaded with 200 mg (0.37 mmol) of complex 2 and 99 mg (0.76 mmol) K[CH2Ph], a small swivel frit was attached, and 30 ml Et₂O were vacuum transferred onto the solids at -78°C. The reaction mixture was protected from light and stirred at - 78°C for 3 h and at 25°C for 14 h. After that time solvent was removed in vacuo from the resulting red suspension, 10 ml petroleum ether vacuum transferred onto the residue, and the red mixture was filtered. Removal of the solvent from the filtrate yielded 150 mg (63%) of unpure 3. The product can be washed with cold (SiMe₃)₂O yielding yellow 3 in lower yield, but in purer form ('H NMR), although an equivalent (SiMe₃)₂O could not be removed from the product, even after prolonged exposure to a dynamic vacuum. 'H NMR (benzene-d₆): δ 0.36 (s, 6H, SiMe₂), 0.60 (s, 6H, SiMe₂), $0.99 (d, J(HH) = 9 Hz, 12H, CHMe_2), 1.04 (d, J(HH) = 7$ Hz, 6H, CHMe₂), 1.68 (d, J(HH) = 11 Hz, 2H, CH₂Ph), 1.88 (m, 1H, CHMe₂), 2.41 (d, J(HH) = 12 Hz, 2H, CH₂Ph), 2.63 (m, 2H, CHMe₂), 6.46 (s, 2H, Cp), 6.47 (s, 1H, Cp), 6.88 (t, J(HH) = 12 Hz, 2H, para-Ph), 7.03 (d, J(HH) = 8 Hz, 4H, Ph), 7.13–7.16 (m, 4H, Ph). ¹³C{¹H} NMR (benzene- d_6): $\delta = 1.50, 3.38$ (SiMe₂); 21.02, 24.38, 26.19, 28.74, 29.20 (CH(CH₃)₂); 61.19 (CH₂Ph); 106.16, 111.77, 112.25, 141.67, 151.95, 155.30 (Cp); 121.68, 126.52, 129.33, 129.69 (Ph). Anal. Calc. for C37H50Si2Zr: C, 69.24; H, 7.75. Found: C, 68.19, 67.32; H, 8.18, 8.45%. Although the elemental analysis of 3 is poorly reproducible and not consistent with the calculated values, the NMR analyses are consistent with the proposed structure and the X-ray diffraction results. The high solubility of 3 in all solvents renders its purification difficult.

2.5. (Me₂Si)₂{η⁵-C₅H₂-4-CHMe₂}{η⁵-C₅H-3,5-(CHMe₂)₂}Zr(CH₃)₂ (4)

In a glove box a 250 ml round bottom flask was loaded with 500 mg (0.94 mmol) of complex 2 and 42 mg (1.88 mmol) LiCH₃, a medium swivel frit was attached, and 100 ml Et₂O were vacuum transferred onto the solids at -78° C. The reaction mixture was then protected from light and stirred at -78° C for 3 h, then allowed to warm to 25°C overnight. The solvent was then removed in vacuo, and the residue extracted with 50 ml toluene and filtered. Removal of the solvent from the filtrate yielded 4 in 75% yield (365 mg). ¹H NMR (benzene-d_o): $\delta - 0.12$ (s, 6H, ZrMe₂), 0.33 (s, 6H, SiMe₂), 0.57 (s, 6H, SiMe₂), 1.08 (d, J(HH) = 7 Hz, 6H, CHMe₂), 1.33 (d, J(HH) = 7 Hz, 6H, CHMe₂), 1.35 (d, $J(HH) = 7 \text{ Hz}, 6H, CHMe_2), 2.73 (m, 1H, CHMe_2), 3.03$ $(m, 2H, CHMe_2), 6.52 (s, 2H, Cp), 6.55 (s, 1H, Cp).$ $¹³C{¹H} NMR (benzene-d_6): <math>\delta = 1.43, 3.57 (SiMe_2); 21.00,$ $24.04 (CH(CH_3)_2); 27.50 (Zr-CH_3); 28.35, 28.83, 29.10,$ $(CH(CH_3)_2); 105.74, 110.96, 111.76, 137.63, 146.50,$ 153.83 (Cp). Anal. Calc. for C₂₅H₄₇Si₂Zr: C, 61.32; H, 8.57.Found: C, 61.17, 60.56, 60.56; H, 9.63, 8.37, 9.00%.

2.6. X-ray structure analysis of $(Me_2Si)_2\{\eta^5-C_5H_2-4-CHMe_3\}\{\eta^5-C_5H-3,5-(CHMe_2)_2\}Zr(CH_2Ph)_2(3)$

A concentrated solution of complex 3 in 5:1 hexamethyldisiloxane:petroleum ether was cooled at - 30°C. After 2 weeks a few small crystals of irregular shape formed. One of them, found to be suitable for an X-ray structure analysis, was covered with paratone oil, mounted on a glass fiber and centered on an Enraf-Nonius CAD4 diffractometer at 160 K. The unit cell parameters were determined and refined from a set of 25 equivalent reflections $(10.5 < \theta < 12.3^{\circ})$. Three standard reflections were measured every 60 min and no decay in intensity was observed. Omega scans were used for measurement. The phases were obtained by direct methods and the atoms were located by standard Fourier techniques using SHELXS-86 [11]. Although the crystal was twinned, it was possible to solve the structure using reflections from the major domain. The structure was refined with SHELXL-93 [12]. The positions of all hydrogen atoms were calculated and refined with restrained angles, free distances and unrestrained isotopic placement parameters. No disordered atoms were observed. Crystal data are given in Table 1.

2.7. Polymerization of 1-pentene

2.7.1. Neat 1-pentene

A 50 ml round bottom flask was loaded with 2 (7 mg, 13.1 μ mol)/MAO (300 mg) or 3 or 4 (7 mg, ~11 μ mol)/ [Ph₃C][B(C₆F₅)₄] (11 mg, 11 μ mol) in a glovebox. A needle valve was attached, the apparatus was transferred to a high vacuum line, and 15 ml of 1-pentene were transferred by syringe at -20° C (pre-cooled). The polymerization reactions were carried out at -10° C and quenched after 30 min by adding 10 ml methanol to the solution. The polymers so obtained were thoroughly washed with additional methanol and MeOH/HCl and dried under dynamic vacuum overnight.

2.7.2. 6.6 M 1-pentene

A solution of 2:1 1-pentene:toluene was prepared and cooled at -15° C. This solution was added via syringe to a pre-cooled (-10° C) 50 ml round bottom flask connected via a needle valve to the high vacuum line and containing **3** or **4** ($\sim 11 \, \mu$ mol)/[Ph₃C][B(C₆F₅)₄] (11 mg, 11 μ mol). With 2/MAO, 5 ml toluene was added first and 10 ml 1pentene afterwards, both via syringe and pre-cooled at -10° C. The work up of the polymers is analogous to those obtained in neat pentene. Several of the runs were repeated (1, 4, 6 and 7) in order to establish the reproducibility of the

Table 1

Crystallographic data and processing parameters for the X-ray diffraction studies of $(Me_2Si)_2(\eta^5-C_3H_2-4-CHMe_2)\{\eta^5-C_3H-3,5-(CHMe_2)_2\}-2r(CH_2Ph)_2$ (3)

	0 11 6 7
Empirical formula	C ₁₇ H ₅₀ Sl ₂ Zr 442.17
Control where	042.17
Crystal shape	no faces, twinned
Weinsteineth (Å) (Me Ka)	0.33 × 0.22 × 0.11
Wavelength (A) (Mo Kα)	0./10/3
- (Å)	0.000(3)
$a(\mathbf{A})$	9.900(2)
	11.010(2)
C(A)	15.520(5)
<i>a</i> () <i>a</i> (°)	02 56(3)
ρ() »(°)	105 23/3)
Y(1) Volume (Å ³)	103.23(3)
7	2
Cructal system	z triclinic
Space group	P-1
Density (calc.) $(a \text{ cm}^{-1})$	1 286
Absorption coefficient (mm ⁻¹)	0.428
F(000)	680
T(K)	160
A Range data collection (°)	1 39-24 97
Index ranges	$-11 \le b \le 11 - 14 \le k \le 13$
e	-18 <18</td
Reflections collected	12331
Independent reflections	5821
R (merge)	0.03
GOF (merge)	1.02
Absorption correction	φ scan
Max., min. transmission	1.17, 0.83
Refinement method	full matrix least-squares on F^2
Data/restraints/parameters	5820/0/407
Goodness-of-fit on F^2	3.041
Final R indices $(I > 2\sigma(I))$	
R1 *	0.0732
wR2 ^b	0.1526
R indices (all data)	
<i>R</i> 1	0.1011
wR2	0.1608
Max. shift/error	0.075
Avg. shift/error	0.002
Largest difference peak, hole (e Å ')	2.303, -1.270

"R1 is R-factor on F.

" wR2 is the weighted R-factor on F^2 .

activities. Run 7 consistently gave no polymer; run 4 yielded about 3 g of polymer each time; runs 1 and 4 produced polymer amounts that varied by as much as a factor of three.

3. Results and discussion

3.1. Synthesis of precatalysts 3 and 4

Our laboratory recently reported a synthetic route to complex 2 involving the reaction of the diprotonated ligand $(Me_2Si)_2\{C_5H_3-4-CHMe_2\}\{C_5H_2-3,5-(CHMe_2)_2\}$ with $Zr(NMe_2)_4$, following the procedure developed by Jordan and co-workers [13]. An alternative approach was employed





Fig. 1. Drawing of $(Me_{2}Si)_{2}\{\eta^{5}\text{-}C_{5}H_{2}\text{-}4\text{-}CHMe_{2}\}\{\eta^{5}\text{-}C_{5}H\text{-}3,5\text{-}(CHMe_{2})_{2}\}Zr(CH_{2}Ph)_{2}$ (3).

in this case: $(Me_2Si)_2\{C_3H_3-4-CHMe_2\}\{C_3H_2-3,5-(CH-Me_2)_2\}$ was deprotonated with 2 equiv. of n-BuLi, and the resulting dilithio salt Li₂[(Me₂Si)₂{C₅H₃-4-CHMe₂}{C₅H₃-3,5-(CHMe₂)₂]] (1) was treated with ZrCl₄ (Scheme 1). The 'H and ¹³C{¹H} NMR analyses for complex 1 are consistent with a structure having a mirror plane bisecting the two silicon groups and passing through the three-positions of the cyclopentadienyl groups. A broad signal at high field was assigned to the silicon bound methyl groups [14]. This signal splits into two at temperatures below - 20°C in the ¹H NMR spectra, suggesting a fluxional behaviour for 1¹.

Table 2 Selected bond distances (\hat{A}) and angles

selected bond	distances (A)	and angles () IO	(Me_SI)_{7-C_5H_2-4-
CHMe ₂ }{ŋ ⁵ -Ca	H-3.5-(CHMe);)Zr(CH ₂ Ph) ₂ (3)	

Zr-X(IA)	2.2350(9)	Pin(1a) "-Zr-Pin(1B) "	104.92(21)
Zr-X(1B) ^J	2.2702(9)	X(1A)-Zr-X(1B)	121.67(3)
Zr-Pin(IA)	2.217(3)	X(1A)-Zr-C(300)	109.2(2)
Zr-Pin(1B)	2.238(3)	X(1A)-Zr-C(400)	111.7(2)
Zr-C(300)	2.267(6)	C(300)-Zr-X(1B)	111.4(2)
Zr-C(400)	2.293(6)	C(300)-Zr-X(1B)	111.4(2)
Zr-C(1)	2.441(6)	X(1B)-Zr-C(400)	103.4(2)
Zr-C(2)	2.562(6)	C(300)-Zr-C(400)	96.5(2)
Zr-C(3)	2.686(6)		
Zr-C(4)	2.566(6)		
Zr-C(5)	2.441(6)		
Zr-C(6)	2.419(6)		
Zr-C(7)	2.631(6)		
Zr-C(8)	2.713(6)		
Zr-C(9)	2.662(6)		
Zr-C(10)	2.426(6)		
C(300)-C(301)	1.468(9)		
C(400)C(401)	1.513(8)		

"X(1A) is the centroid of C1, C2, C3, C4 and C5.

^b Pln(1A) is the plane of C1, C2, C3, C4 and C5.

⁶ Pln(1B) is the plane of C6, C7, C8, C9 and C10.

^d X(1B) is the centroid of C6, C7, C8, C9 and C10.

The alkylation reaction of complex 2 with KCH₂Ph proceeds in moderate yield giving complex 3. Its extreme solubility in aliphatic solvents makes its purification difficult, but recrystallization of 3 in $(SiMe_3)_2O$ at $-30^{\circ}C$ does yield yellow crystalline material, which was employed for the spectroscopic analyses and for the X-ray crystal structure determination. The ¹H NMR spectrum of 3 suggests an overall C_s symmetry. As expected, the methylene hydrogens are diastereotopic, displaying two doublets separated by 0.8 ppm. Their ³J(HH) of 11 Hz does not suggest an α -agostic ground state interaction [16]. The preparation of complex 4 follows the procedure generally used for the doubly bridged analogs previously prepared by Royo and co-workers [17a]. As expected, in the ¹H NMR the methyl groups attached to zirconium display a diagnostic singlet at high field ($\delta - 0.12$).

3.2. Crystal structure of complex 3

An ORTEP drawing of complex 3 is shown in Fig. 1, while selected bond angles and distances and atomic coordinates are given in Tables 2 and 3, respectively. The coordination geometry of the zirconium center is similar to previously reported structures [17]. The metal atom is η^5 -linked to both cyclopentadienyl rings forming a pseudo-symmetrical environment with the two bridging silicon atoms sharing a plane with the metal center and the methylene carbons atoms. The difference of the Zr-(cyclopentadienyl centroids) and Zr-PlnA/B² angles of 17° (121 versus 105°) indicates a slightly

¹ A crystal structure of Li₂{ (Me₂Si)₂{C₄H, 4-(+)-menthyl}{C₃H₂-3,5-(CHMe₂)₂} {(THF)₃, closely related to 1, shows a planar arrangement of the cyclopentadienide substituents and of the six-membered ring containing the two silcon atoms and connecting the two cyclopentadienides. The lith-

iums are η^{5} -coordinated to two opposite faces of the cyclopentadienide moieties [15]. This structure is analog to the previously reported Li₂[(C₅H₁(µ-SiMe₂)₂C₅H₁] · 2(TMEDA) [14].

² PIA is the plane of C1, C2, C3, C4, C5; PIB is the plane of C6, C7, C8, C9, C10.

Table 3 Atomic coordinates ($\times 10^{3}$) and equivalent isotropic displacement parameters ($\hat{A}^{2} \times 10^{3}$) for (Me₂Si)₂{ η^{5} -C₃H₂-4-CHMe₂}{ η^{5} -C₃H-3,5-(CHMe₂)₂Zr(CH₂Ph)₂ (3)

Atom	x	ÿ	5	U _{eq} "
Zr	703(1)	2128(1)	2565(1)	17(1)
Si(1)	-2196(2)	2009(2)	3410(1)	19(1)
Si(2)	1068(2)	3036(2)	4732(1)	20(1)
C(1)	-761(6)	3359(6)	3327(4)	17(1)
C(2)	- 567(7)	3750(6)	2533(4)	19(2)
C(3)	848(7)	4430(6)	2568(4)	18(2)
C(31)	1441(7)	5154(6)	1904(5)	25(2)
C(32)	370(8)	5804(7)	1675(6)	36(2)
C(33)	2850(2)	6047(7)	2288(6)	36(2)
C(4)	1564(7)	4425(6)	3379(4)	18(2)
C(5)	603(7)	3786(6)	3875(4)	18(1)
C(6)	-959(6)	1027(6)	3379(4)	15(1)
C(7)	-907(6)	4(6)	2642(4)	16(1)
C(71)	-2124(7)	-874(6)	1974(5)	20(2)
C(72)	- 1660(7)	- 1833(6)	1272(5)	27(2)
C(73)	- 3243(7)	- 1514(6)	2492(5)	31(2)
C(8)	447(6)	- 148(6)	2730(4)	16(1)
C(9)	1239(6)	689(6)	3534(4)	16(1)
C(91)	2603(7)	627(6)	3945(5)	22(2)
C(92)	3201(7)	-320(6)	3342(5)	30(2)
C(93)	2423(8)	385(7)	4868(5)	32(2)
C(10)	402(6)	1453(6)	3929(4)	15(1)
C(101)	- 3159(8)	2304(7)	4424(5)	30(2)
C(102)	- 3471(7)	1513(6)	2393(5)	28(2)
C(201)	264(8)	3238(6)	5810(5)	29(2)
C(202)	3003(7)	3630(6)	5044(5)	29(2)
C(300)	-48(7)	1453(7)	1052(4)	21(2)
C(301)	-1267(7)	1417(6)	452(5)	24(2)
C(302)	-2319(8)	317(7)	43(5)	28(2)
C(303)	- 3510(8)	284(7)	-477(5)	33(2)
C(304)	- 3696(9)	1347(8)	-620(5)	37(2)
C(305)	-2657(8)	2433(8)	- 244(6)	39(2)
C(306)	-1480(8)	2469(7)	262(5)	31(2)
C(400)	3042(6)	2299(6)	2437(5)	19(2)
C(401)	4037(7)	3247(5)	2088(5)	18(2)
C(402)	3915(7)	3180(6)	1170(5)	24(2)
C(403)	4878(8)	4022(6)	846(5)	31(2)
C(404)	5952(8)	4910(6)	1414(6)	33(2)
C(405)	6072(8)	4983(6)	2323(6)	32(2)
C(406)	5118(7)	4164(6)	2658(5)	25(2)

" U_{eq} is defined as one third of the trace of the orthogonalized U_{q} tensor.

asymmetrical coordination to the metal bridgehead carbons (Zr-C1/5 = 2.44 and Zr-C6/10 = 2.42 Å) versus the external ring carbons (Zr-C3 = 2.69, Zr-C8 = 2.71 Å). This asymmetry is common to other doubly bridged complexes, but significantly larger than in the unsubstituted ana¹og $(Me_2Si)_2(\eta^5-C_5H_3)_2ZrCl_2$ (5°) [17a]. The benzyl substituents are η^1 bound to the metal center with Zr-CH₂Ph distances (2.27 and 2.29 Å) and C400-Zr-C300 angle (96.5°) within normal ranges. The closer phenyl ring does not appear to be engaged in a significant interaction with the metal center (Zr-C306 = 4.22, Zr-C301 = 3.48 and Zr-C302 = 4.45 Å, respectively). The Zr-C400-C401 and Zr-C300-C40, angles (126 and 137°), and the position of the phenyl groups of the two benzyl substituents differ significantly, likely

adopting the sterically less hindered arrangement in the metallocene wedge with the phenyl rings occupying the region closer to the smaller cyclopentadienyl ligand and away from the bulkier one.

3.3. Polymerization reactions

Results of the polymerization reactions are reported in Table 4. Although activities were found to be rather irreproducible, the catalyst systems 2/MAO and 3/[Ph₃C]- $[B(C_6F_5)_4]$ polymerize 1-pentene with high stereocontrol. The ¹³C{¹H} NMR analysis [18] of the polymers produced showed exclusively the [rrrr] pentad at 37.5 ppm. The pentad analysis of the polymers produced by $4/[Ph_3C][B(C_6F_5)_4]$ surprisingly indicated a slight decrease in syndiospecificity for the reaction in neat monomer (run 4), which becomes even more significant for the reaction in 6.6 M 1-pentene in toluene (run 5). The decrease in stereocontrol cannot be quantified because of the overlap of most of the pentads in the ¹³C{¹H} NMR spectrum of poly-1-pentene [18]. The ¹³C NMR spectra of the polymer obtained in runs 4-6 are given in Fig. 2. Considering the very high activity of the system, we believe that insufficient reaction temperature control with a resultant exotherm is responsible. A comparison of the molecular weight for the polymers produced in run 4 and 6 is in agreement with this explanation: in both systems the species responsible for chain propagation and termination are supposedly the same. Thus the lower molecular weight shown in run 4 could be caused by a higher reaction temperature.

The narrow molecular weight distribution shown in runs 2, 4 and 6 suggests that a single species is operating in these cases. With the exception of the MAO co-catalyzed system, the polymerization reactions carried out at reduced pentene concentration either do not produce polymer (run 7) or have more than one active Zr based species (PDI \gg 2 and multimodal distribution by GPC analysis). Moreover, we observed no activity for the system $3/[Ph_3C][B(C_0F_5)_4]$, and replacement of $[Ph_3C][B(C_0F_5)_4]$ by the co-catalyst $B(C_0F_5)_3$ resulted in the production of poly(1-pentene) with very broad molecular weight distribution.

The polymerization behavior of 2/MAO with 1-pentene as a substrate closely correspond to our observations in the analogous propene polymerization reactions, where polymers having high stereospecificity, high molecular weight and nar-



Run	Catalyst	[l-pentene] (M)	poly-1-pentene obtained (g)	<i>M</i> _* (×10 ⁻¹) ⁻¹	$M_{\rm w}/M_{\rm o}$
1	2/MAO	neat	0.13	45	2.6
2	2/MAO	6.6	0.81	73	1.9
4	$4/[CPh_3][B(C_1F_5)_4]$	neat	3.3 '	69	2.6
5	$4/[CPh_3][B(C_6F_5)_4]$	6.6	3.3 °	16	12.6 ^b
6	$3/[CPh_1][B(C,F_s)_1]$	neat	0.68	103	2.1
7	$3/[CPh_3][B(C,F_5)_3]$	6.6	traces		
8	$3/B(C_sF_s)$	3	0.22	1.3	54.5 h

Table 4		
Results of	1-pentene	polymerizations

" Vs. polystyrene standards.

b GPC shows a bimodal molecular weight distribution.

" Reaction mixture became entirely solid and stirring ceased.

row molecular weight distribution are often produced. The behavior of the fluorinated borane and borate activated systems appear to be more complex, showing a significant dependence on the reacting metallocene (3 or 4) that is likely related to differing rates of initiation versus propagation (compare runs 5 and 8 with 7) and/or the number of active sites. The broad molecular distributions observed in some cases are not easily rationalized at this point. It should be noted that the interaction of 3 or 4 with [CPh₃][B(C₆F₅)₄] at low temperature in various solvents invariably led to decomposition of the starting material (¹H NMR) and to the production of unidentifiable species.

4. Supplementary material

Complete listing of fractional coordinates, displacement parameters, distances and angles, and structure factors for 3, have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 100307.

Acknowledgements

This work has been supported by the USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-88ER13431) and by Exxon Chemicals America. D.V. thanks the Swiss National Science Foundation (Stipendium für angehende Forscher) and the Jubiläum Stiftung-Ciba-Geigy for postdoctoral fellowships. Dr Timothy Herzog and Mr Shigenobu Miyake (Japan Polyolefins) are gratefully acknowledged for helpful discussions and for preparing some of the starting material for the ligand syntheses. Dr Terry Burkhardt (Exxon Chemicals America) is gratefully acknowledged for his interest and for molecular weight measurements.

References

 (a) A. Andresen, H.G. Crodes, J. Herwig, W. Kaminsky, A. Merck, R. Mottweiler, J. Pein, H. Sinn, H.J. Vollmer, Angew. Chem., Int. Ed. Engl. 15 (1976) 630; (b) H. Sinn, W. Kaminsky, H.J. Vollmer, R. Woldt, Angew. Chem., Int. Ed. Engl. 19 (1980) 396.

- [2] Reviews: (a) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. Engl. 34 (1995) 1143; (b) A. Horton, TRIP 2(5) (1994) 158; (c) M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255; (d) G. Fink, R. Mülhaupt, H.H. Brintzinger (eds.), Ziegler Catalysis, Recent Scientific Innovation and Technological Improvements, Springer, Berlin, 1995; (e) R. Mülhaupt, B. Rieger, Chimia 50 (1955) 10; (f) W. Kaminsky, Macromol. Chem. Phys. 197 (1996) 3907; (g) P.C. Möhring, N.J. Coville, J. Organomet, Chem. 479 (1994) 1.
- [3] (a) G.G. Hlatky, H.W. Turner, R.R. Eckman, J. Am. Chem. Soc. 111 (1989) 2728; (b) H.W. Turner, European Patent Application No. 277 004 (1988); (c) J.C.W. Chien, W.-M. Tsai, M.D. Rausch, J. Am. Chem. Soc. 113 (1991) 3570; (d) X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 113 (1991) 3623; (e) J. Am. Chem. Soc. 116 (1994) 10 015; (f) P.A. Deck, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 6128; (g) A. Razavi, U. Thewalt, J. Organomet, Chem. 432 (1991) 1325; (i) T.J. Marks, Acc. Chem. Res. 25 (1992) 57.
- [4] (a) M. Bochmann, S. Lancaster, Organometallics 12 (1993) 633;
 (b) Makromol. Chem., Rapid Commun. 14 (1993) 807; (c) M. Bochmann, S. Lancaster, M.B. Hursthouse, K.M.A. Malik, Organometallics 13 (1994) 2235.
- [5] For some recent examples see: (a) Y.X. Chen, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 119 (1997) 2582; (b) L. Lia, X.M. Yang, C.L. Stern, T.J. Marks, Organometallics, 16 (1997) 842; (c) Y.X. Chen, C.L. Stern, S.T. Yang, T.J. Marks, J. Am. Chem. Soc. 18 (1996) 12 451; (d) L. Lia, X. Yang, A. Ishihara, T.J. Marks, Organometallics, 14 (1995) 3135.
- [6] (a) T.A. Herzog, D.L. Zubris, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 11 988; (b) L.M. Henling, T.A. Herzog, J.E. Bercaw, Acta Crystallogr., Sect. C 52 (1996) in press.
- [7] B.J. Burger, J.E. Bercaw, in A.L. Wayda, M.Y. Darensbourg (eds.), Experimental Organometallic Chemistry, ACS Symposium Series, Vol. 357, American Chemical Society, Washington, DC, 1987, Ch. 4.
- [8] A.G. Mossey, A.J. Park, J. Organomet. Chem. 5 (1966) 218.
- [9] J.C.W. Chien, W.-M. Tsai, M. Rausch, J. Am. Chem. Soc. 113 (1991) 8570.
- [10] M. Schlosser, J. Organomet. Chem. 8 (1967) 9.
- [11] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
- [12] G.M. Sheldrick, SHELXL-93, program for structural refinement, University of Göttingen, Göttingen, Germany, 1993.
- [13] (a) G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4045; (b) J.N. Christopher, G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4038; (c) G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4030; (d) J. Am. Chem. Soc. 118 (1996) 8024; (c) G.M. Diamond, S. Rodewald, R.F. Jordan, Organometallics 14 (1995) 5.

- [14] J. Hiermeier, F.H. Köhler, G. Müller, Organometallics 10 (1991) 1787.
- [15] D. Veghini, L.M. Henling, T.J. Burkhardt, J.E. Bercaw, to be submitted.
- [16] (a) A.K. Hughes, A. Meetsma, J.H. Teuben, Organometallics 12 (1993) 1936, and Refs. therein: for an example of a Nb(V) complex see: (b) M. Etienne, R. Mathieu, B. Donnadieu, J. Am. Chem. Soc. 119 (1997) 3218.
- [17] For closely related doubly-bridged Zr complexes see: (a) A. Cano, T. Cuenca, P. Gomez-Sal, B. Royo, P. Royo, Organometallics 13 (1994) 1688; (b) W. Mengele, J. Dieblod, C. Troll, W. Röll, H.H. Brintzinger, Organometallics 12 (1993) 1932; (c) A.R. Bulls, Ph.D. Thesis, California Institute of Technology, Pasadena, 1990; (d) P. Royo, New J. Chem. 21 (1997) 791.
- [18] T. Asakura, M. Demura, Y. Nishiyama, Macromolecules 24 (1991) 2334.