ELSEVIER

Journal of Organometallic Chemistry 625 (2001) 154–159

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Synthesis, characterization and polymerization properties of isopropylidene(η^5-3-neomenthylcyclopentadienyl)(η^5-fluorenyl)-zirconium dichloride

Ronald L. Halterman [a,*1], Darryl R. Fahey [b,*2], Vladimir P. Marin [a], David W. Dockter [b], Masood A. Khan [a]

[a] *Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Norman, OK 73019, USA*
[b] *Research and Development, Phillips Petroleum Company, Bartlesville, OK 74004, USA*

Received 27 December 1999; received in revised form 4 October 2000

In memory of Marina V. Marin, 1976–1999

Abstract

The reaction of neomenthylcyclopentadiene with acetone solution led to 6,6-dimethyl-3-neomenthylfulvene (**6**). The bridged 3-neomenthylcyclopentadienyl-2-fluorenylpropane (**7**) has been isolated after reaction of **6** with fluorenyllithium salt. The reaction of $ZrCl_4$ with the dilithium salt of **7** in diethyl ether yields the complex isopropylidene(η^5-3-neomenthylCp)-(η^5-9-fluorenyl)$ZrCl_2$ (**4**) as a 60:40 mixture of diastereomers. The complex was fully characterized by single-crystal X-ray diffraction and NMR methods. Complex **4** is an active catalyst for the homogeneous polymerization of propylene when activated by methylaluminoxane (MAO). The polypropylene polymer produced with **4** has lower molecular weight and a lower degree of syndiotactic or hemiisotactic stereoregularity, but a higher degree of isotactic character (*mm* triad of 63%) than the polymer produced with the syndiospecific catalyst isopropylidene(Cp)(Flu)$ZrCl_2$ (**1a**) under these conditions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zirconocene dichloride; Metallocene catalyzed polymerization; Polypropylene; Neomenthylcyclopentadienyl; Chiral metallocene; Fulvene; Fluorenyl; Cyclopentadienyl

1. Introduction

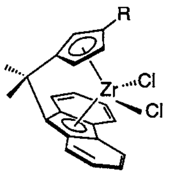
The propene polymerization behavior of isopropylidene-bridged (3-R cylopentadienyl)(9-fluorenyl)$ZrCl_2$ complexes has attracted considerable attention for the last several years [1–7]. The variation of the three-substituent has been shown to have a pronounced effect on the tacticity of the resulting polypropylene [2]; the parent R = H (**1a**) complex gives syndiotactic polypropylene, substituents of intermediate size (R = methyl **1b**, ethyl **1c**) give rise to varying degrees of hemiisotacticity [4,5], while the larger isopropyl substituted metallocene 1d gives somewhat more isotactic polypropylene(*mmmm* pentad of 44%) [5] and the *tert*-butyl substituted metallocene **1e** gives the highest degree of isotacticity in this series (*mmmm* pentad up to 87%) [6]. Marks has studied the effect of introducing a 3-menthyl substituent in related silyl bridged bis(cyclopentadienyl)zirconium (**2**) and silyl bridged (cylopentadienyl)(octahydro-9-fluorenyl)zirconium (**3**) complexes [8,9]. In order to more directly compare any possible remote effect of chiral substituents on the tacticity of propene polymerization, we have prepared the isopropylidene bridged (3-neomenthyl)(9-fluorenyl)zirconium dichloride complex **4**. In this report, we detail the synthesis, characterization and catalytic polymerization behavior of a diastereomeric mixture of zirconocene dichloride **4**.

---

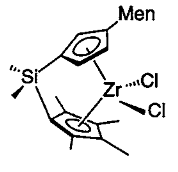
[1] *Corresponding author. Fax: + 1-405-3256111; e-mail: rhalterman@ou.edu

[2] *Corresponding author. E-mail: drfahey@ppco.com

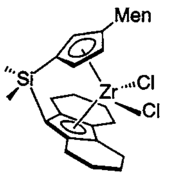
PII: S0022-328X(00)00786-5



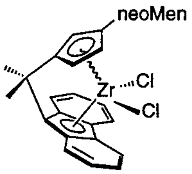
1a R = H, **1b** R = Me, **1c** R = Et, **1d** R = *iso*-Pr, **1e** R = *tert*-Bu



2



3



4

2. Results and discussion

2.1. Synthesis of the of 3-neomenthylcyclopentadienyl-2-fluorenylpropane ligand (7)

The synthesis of 3-neomenthylcyclopentadienyl-2-fluorenylpropane and zirconocene complex **4** is outlined in Scheme 1. Neomenthylcyclopentadiene (**5**) was prepared from (−)-menthol according to literature methods [10]. Condensation of the monosubstituted cyclopentadiene **5** with acetone by the Stone and Little method for the preparation of fulvenes [11] yielded the single regioisomeric 6,6-dimethyl-3-neomenthylfulvene (**6**) in high yield. As precedented with other substituted fulvenes [2–5], fluorenyllithium added to fulvene **6** to give 2-(3-neomenthylcyclopentadienyl)-2-(9-fluroenyl)-propane (**7**) as a mixture of three double bond isomers.

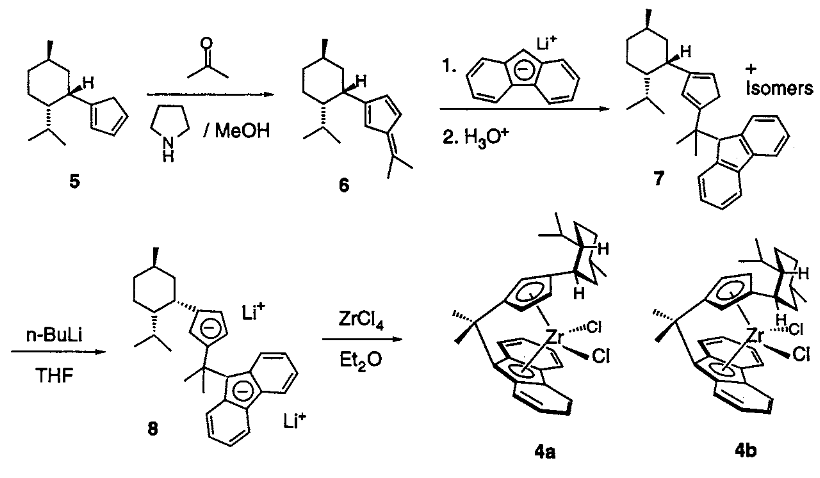
2.2. Synthesis and characterization of the zirconocene complex 4

Double deprotonation of **7** with two equivalents of *n*-butyllithium in THF solution gave the corresponding dianion **8**. After removal of the solvent, dianion **8** was reacted with one equivalent of $ZrCl_4$ in hexane or diethyl ether to yield the red complex **4** as a 60:40 mixture of diastereomers. Complex **4** is soluble in toluene and stable under vacuum or pure argon but is unstable in chlorinated solvents. Zirconocene **4** was isolated after crystallization from toluene in 66% yield. Slow evaporation of a toluene solution of **4** produced crystals suitable for X-ray diffraction. The NMR spectra of several individual crystals all exhibited a 60:40 diastereomeric ratio. The solid state structure is discussed below. In the ^{1}H-NMR spectrum of **4**, the major cyclopentadienyl vinyl hydrogen signals appeared slightly upfield from the minor peaks, and the major neomenthyl methyl groups slightly downfield from the corresponding minor signals. Given the small (< 0.1 ppm) differences) no firm conclusions regarding the exact NMR spectral assignments of **4a** and **4b** could be made.

The analogous titanocene complex appeared to be formed in the same 60:40 ratio of diastereomers upon treatment of the dianion **8** with $TiCl_3$–3THF in THF followed by oxidation with $PbCl_2$ [12]. The crude ^{1}H-NMR spectrum exhibited multiplets at δ 5.98 and 6.02 in ratio of 60:40. This complex was not isolated or further characterized.

3. Molecular structure of 4

The molecular structure of **4** was determined by single crystal X-ray diffraction. Suitable crystals were obtained from toluene. The crystallographic and data refinement parameters are listed in Table 1, the molecu-



Scheme 1.

Table 1
Crystal data and structure refinement for **4**

Empirical formula	$C_{31}H_{36}Cl_2Zr$
Formula weight	570.72
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	13.0334(11)
b (Å)	12.5874(8)
c (Å)	17.5336(9)
α (°)	90
β (°)	106.837(4)
γ (°)	90
V (Å^3)	2753.2(3)
Z	4
D_{calc} (mg m^{-3})	1.377
Absorption coefficient (mm^{-1})	0.611
F(000)	1184
Crystal size (mm)	$0.62 \times 0.60 \times 0.52$
Theta range for data collection (°)	2.02–24.98
Limiting indices	$-15 \leq h \leq 15$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$
Reflections collected	16 050
Independent reflections	9570 [$R_{int} = 0.0416$]
Absorption correction	Semi-empirical from psi-scans
Max/min transmission	0.4698 and 0.3893
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9565/1/613
Goodness-of-fit on F^2	1.019
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0414$, $wR_2 = 0.0956$
R indices (all data)	$R_1 = 0.0566$, $wR_2 = 0.1051$
Absolute structure parameter	0.00(5)
Largest difference peak and hole (e A^{-3})	0.456 and −0.307

lar structures are shown in Fig. 1. The asymmetric unit of complex **4** contains two independent diastereomers in a $P2_1$ space group. Since all other crystals from the recrystallization of **4** contained a 60:40 mixture of diastereomers, we assume that the crystal used in the X-ray determination was also a 60:40 mixture of diastereomers. Attempts to refine the model based on partially disordered occupancy of the major isomer in place of the minor or partial vacancies of the minor isomer did not lead to any conclusive assignment of the major diastereomer and the model used was a 50:50 mixture of diastereomers. The bond lengths and bond angles involving Zr, Cp, and Flu moieties are in good agreement with the reported values for $Me_2C(CpR)$-(Flu) $ZrCl_2$ (R = H, Me, t-Bu) and $Ph_2C(Cp)(Flu)ZrCl_2$ [2,4,5]. The progressive increase of the Zr–C distances from the bridge head carbon are more pronounced for the Flu ligand in **4**, the range being (2.403–2.725 Å); however, for the Cp ligand the range of 2.416–2.591 Å is less pronounced than the t-Bu complex [6], 2.427–2.618 Å. The Zr–Flu distances of 2.725(5) and 2.710(5) for **4** are significantly longer than for distances of reported complexes, but the Zr–Cp distances are still close to other complexes.

4. Catalytic activity

Complex **4** (as a 60:40 mixture of diastereomers) is an active catalyst for the homogeneous polymerization of propylene when activated by methylaluminoxane (MAO). Table 2 compares the polymerization productivity of **4** with isopropylidene-(1-cyclopentadienyl)(9-

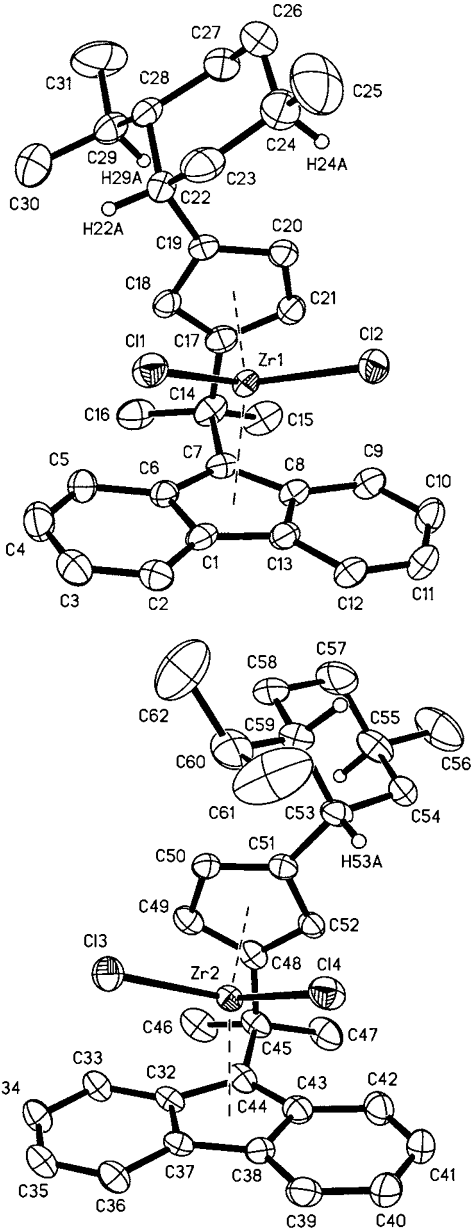


Fig. 1. Selected bond lengths and angles for **4a** and **4b**; Zr–Cl 2.412(1), 2.425(1), 2.413(1), 2.421(1), ZR–Cp(centr) 2.171(4), 2.185(4), Zr–Flu(centr) 2.277(4), 2.272(4), Zr–C(Cp) 2.41–2.56, Zr–C(Fl) 2.40–2.73, Cp–Zr–Flu 118.2(2), 117.9(2), Cl–Zr–Cl 99.10(5), 98.88(5).

Table 2
Propene polymerization results for **4**: MAO = 1:10 000 in toluene

Catalyst	Polymerization conditions			Productivity (g PP/g Zr h)
	Temperature (°C)		[Zr] M × 10^{-6}	
[1-(3-MenthylCp)-C(Me)$_2$(9-Flu)]ZrCl$_2$ (**4**)	40	Homopolymer	1.4	54 000
	60	Homopolymer	1.4	175 000
	70	Homopolymer	1.4	197 000
	80	Homopolymer	1.4	81 000
	80	+8 mmol l^{-1} H$_2$	1.4	121 000

Table 3
Analysis of polypropylene polymers produced with **4**/MAO

Catalyst	GPC (kg mol^{-1})				NMR		
	T (°C)	M_n	M_w	M_w/M_n	% [mm]	% [mr]	% [rr]
[1-(3-MenthylCp)-C(Me)$_2$(9-Flu)]ZrCl$_2$ (**4**)	40	15.1	32.0	2.1	62.5	19.7	17.8
	60	12.2	22.1	1.8	60.0	20.7	19.3
	70	10.4	28.9	2.8	60.2	21.2	18.6
	80	5.8	43.1	7.5	63.3	19.3	17.4
	80	9.2	19.1	2.1	62.2	20.2	17.6

fluorenyl)zirconium dichloride (**1a**) and Table 3 compares the molecular weight and tacticity of the polymers produced by these systems with MAO at identical conditions. The polymer produced with **4** shows a much lower molecular weight and a lower degree of stereoregularity than the polymer produced with the syndiospecific system **1a** under these conditions. Additionally, the stereoselectivity of complex **4** is quite insensitive to an increase in polymerization temperature. The molecular weight of the polymers produced decreases with increasing polymerization temperature.

The influence of cyclopentadienyl ring substituents on the stereoselectivity of isopropylidene bridged fluorenyl systems has been described earlier [3,5] To summarize this earlier work, the stereoselectivity of the isopropylidene bridged Cp–Fluorenyl system changes from syndiotactic, to hemiisotactic and then to isotactic as the substituent on the three position of the Cp ring is changed from hydrogen to methyl, ethyl, isopropyl and finally a *tert*-butyl group. The mechanistic explanation given is that the bulkier groups hinder chain migratory insertion so that insertion at only one of the diastereotopic sites is favored [5]. This current work introduces a menthyl group at the three position of the Cp ring. While the menthyl group is clearly a bulkier substituent, the tacticity is clearly not more isotactic. The key to understanding this apparent contradiction is an examination of the α-carbon of the substituent. In the case of *t*-butyl the α-carbon has more substituents than the α-carbon of the menthyl group. Thus, the menthyl can adopt a confirmation where it is less sterically demanding than the *t*-butyl group as its bulk is directed away from the growing polymer chain. The stereoselectivity of polypropylene produced using a neomenthyl group in **4** (*mm* triad of 62%) appears to be most comparable to the use of the isopropyl group in **1d** (*mmmm* pentad of 44%). No further influence of the chiral auxiliary in this diastereomeric mixture could be identified. No bimodal behavior was observed, suggesting that the two diastereomers reacted similarly.

5. Experimental

5.1. General procedures

All experiments were carried out under purified nitrogen in a Vacuum Atmospheres drybox or with standard Schlenk line techniques. Hydrocarbon solvents, diethyl ether, tetrahydrofuran, benzene-d_6 were distilled from sodium/benzophenone ketyl. Deuterated solvents were obtained from Cambridge Isotope Labs. Methyllithium, butyllithium and fluorene were obtained from Aldrich and used as received. ZrCl$_4$ was obtained from CERAC Inc. and used as received. Neomenthylcyclopentadiene was prepared according to literature procedure [10]. NMR spectra were recorded on a Varian XL-400 spectrometer, in Teflon-valved tubes, at ambient probe temperature (295 K). ^{1}H- and ^{13}C-NMR chemical shifts are referenced to the residual ^{1}H and ^{13}C solvent peaks. Elemental analyses were performed by Atlantic Microlab, Inc.

5.2. 6,6-dimethyl-3-neomenthylfulvene (***6***)

Neomenthylcyclopentadiene (prepared from (−)-menthol according to Ref. [10]) (2.80 g, 13.7 mmol) was added dropwise to stirring solution of acetone (0.87 g, 15.0 mmol) and pyrrolidine (1.67 ml, 20 mmol) in methanol (30 ml) at room temperature (r.t.). After stirring overnight, the mixture was partitioned between water and diethyl ether. The ether portion was dried over $MgSO_4$ and concentrated by rotary evaporation to yield **6** as a colorless liquid (3.02 g, 95% yield). This material was used directly in the next reaction. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.38 (s, 2H, $H_{4,5}$, 6.16 (s, 1H, H_2), 2.98 (br s, 1H, neomenthyl), 2.06 (s, 6H, CH_3 in fulvene), 1.8–0.7 (m, 18H, neomenthyl).

5.3. 3-Neomenthylcyclopentadienyl-2-fluorenylpropane (*7*)

To a stirring Et_2O (30 ml) solution of FluLi, prepared from fluorene (2.49 g, 15 mmol) and *n*-BuLi (2.5 M in hexane, 15.0 mmol), was added 6,6-dimethyl-3-neomenthylfulvene (**6**) (3.02 g, 13.0 mmol) in 25 ml of Et_2O) dropwise at r.t. under nitrogen. After stirring overnight, water was added and the mixture was extracted with Et_2O (3 ×). The combined organic portion was dried over $MgSO_4$, concentrated and purified by column chromatography (SiO_2, petroleum ether) to yield **7** as white crystals (5.15 g, 96% yield). NMR analysis showed the compound to be a mixture of three double bond isomers. M.p. 68°C. Anal. Calc. for $C_{31}H_{38}$: C, 90.67; H, 9.33. Found: C, 90.60; H, 9.33%. ^{1}H-NMR (400 MHz, $CDCl_3$): isomer (**7a**) (57.5%) δ: 7.8–7.1 (m, 8H, $C_{13}H_8$), 6.11 (s) and 5.99 (s, 2H,C*H*, from Cp), 4.08 (s, 1H, H_9 from Flu), 3.14 (br s, 2H, CH_2 from Cp, overlap with CH_2 (Cp) from isomer **7c**), 3.10–2.95 (m, 1H, CH from menthyl), 1.90–0.8 (m, 9H, CH from menthyl), 1.10–1.03 (6H, CH_3 bridged), 0.96–0.85 (m, 9H, CH_3 from menthyl). Isomer (**7b**) (26.0%) δ: 7.8–7.1 (m, 8H, $C_{13}H_8$), 6.62 (s) and 5.69 (s, 2H, C*H*, from Cp), 4.15 (s, 1H, H_9 from Flu), 3.91 (s, 2H, CH_2 from Cp), 3.10–2.95 (m, 1H, CH from menthyl), 1.90–0.8 (m, 9H, CH from menthyl), 1.10–1.03 (6H, CH_3 bridged), 0.96–0.85 (m, 9H, CH_3 from menthyl). Isomer (**7c**) (16.5%) δ: 7.8–7.1 (m, 8H, $C_{13}H_8$), 6.25 (s) and 6.01 (s, 2H,C*H*, from Cp), 4.10 (s, 1H, H_9 from Flu), 3.14 (br s, 2H, CH_2 from Cp, overlap with CH_2 (Cp) from isomer **7a**), 3.10–2.95 (m, 1H, CH from menthyl), 1.90–0.8 (m, 9H, CH from menthyl), 1.10–1.03 (6H, CH_3 bridged), 0.96–0.85 (m, 9H, CH_3 from menthyl). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.8, 155.8, 152.8, 148.9, 146.2, 146.1, 143.8, 142.7, 132.3, 132.1, 130.0, 129.9, 127.5, 126.5, 122.6, 122.5, 120.6, 120.5 120.1, 119.9, 59.2, 59.0, 56.7, 56.6, 48.9, 48.4, 45.8, 45.6, 43.4, 42.3, 41.1, 41.0, 40.9, 40.1, 39.4, 39.2, 38.6, 38.5, 37.7, 36.5, 31.1, 30.9, 27.9, 27.6, 27.2, 27.1, 26.2, 23.6, 22.1 (br). MS (EI, 12ev): *m/z*: 410 (17.8%), 245 (100%), 166 (14.1%), 137 (8.4%), 123 (7.5%), 107 (8.7%).

5.4. Preparation of [η^5-(3-neomenthylcyclopentadienyl)-η^5-(9-fluorenyl) propane]zirconium dichloride (***4***)

n-Butyllithium (1.6 M in hexane, 1.8 ml) was added dropwise to stirring solution of 3-neomenthylcyclopentadienyl-2-fluorenylpropane (**7**) (0.54 g, 1.32 mmol) in 15 ml of THF and 10 ml of hexane at −78°C. After the addition was complete, the mixture was warmed to r.t. and stirring continued for 15 h. The solvent was removed under vacuum and solid was washed with hexane. $ZrCl_4$ (0.31 g, 1.33 mmol) was added to reaction mixture. The reaction mixture was cooled to −78°C and then diethyl ether (30 ml) was added. The reaction mixture was stirred at −78°C for 15 min and then allowed to warm to r.t. The stirred continued for 20 h. The solvent was removed under vacuum. Toluene (15 ml) was added to solid and solution was filtered. The solvent was removed under vacuum to a small volume. The product formed as red crystals which were collected and dried under vacuum. Yield: 0.50 g (66%) of **4** as a mixture of isomers (40:60). We have not assigned the structure of the major isomer; the labels **4x** and **4y** are arbitrary. T_{decomp} 165–170°C. Anal. Calc. for $C_{31}H_{36}Cl_2Zr$: C, 65.24; H, 6.36. Found: C, 65.20; H, 6.35%. ^{1}H-NMR (400 MHz, C_6D_6): isomer **4x** (40% by ^{1}H-NMR): δ 7.84, 7.48, 7.29 and 7.00 (m, 8H, $C_{13}H_8$), 6.31 (t, 1H, H_2 in Cp, $J = 2.8$ Hz), 5.56 (t, 1H, $H_{4,5}$ in Cp, $J = 2.8$ Hz), 5.48 m, 1H, $H_{4,5}$ overlap with $H_{2,3}$ from **4y**), 1.88 (s) and 1.85 (s, 6H, C*H*$_3$ bridged), 2.0–0.8 (m, 9H, C*H* and C*H*$_2$ from menthyl), 0.91(d), 0.77 (d) and 0.71 (d, 9H, C*H*$_3$ from menthyl, $J = 6.4$ Hz). Isomer **4y** (60% by ^{1}H-NMR): δ 7.84, 7.48, 7.29 and 7.00 (m, 8H, $C_{13}H_8$), 6.26 (t, 1H, H_5 in Cp, $J = 2.8$ Hz), 5.52 (t, 1H, $H_{2,3}$ in Cp, $J = 2.8$ Hz), 5.48 m, 1H, $H_{2,3}$ overlap with $H_{4,5}$ from **4x**), 1.85 (s, 6H, C*H*$_3$ bridged), 2.0–0.8 (m, 9H, C*H* and C*H*$_2$ from menthyl), 1.02 (d), 0.86 (d) and 0.81 (d, 9H, C*H*$_3$ from menthyl, $J = 6.4$ Hz). ^{13}C-NMR (100 MHz, C_6D_6) for mixture of isomers: δ 129.5, 129.4, 129.3, 129.2, 125.7, 125.6, 125.5, 125.4, 124.2, 124.0, 123.9, 123.8, 123.2, 120.2, 119.0, 104.7, 103.3, 103.0, 51.3, 49.8, 40.7, 37.7, 36.8, 30.2, 29.9, 29.2, 29.1, 29.0, 28.9, 28.3, 26.2, 25.1, 23.3, 23.2, 23.0, 22.4, 21.3. MS (EI, 12ev): *m/z* 574 (28.2%), 573 (21.3%), 572 (61.3%), 571 (49.6%), 570 (98.1%), 569 (63.5), 568 (100%), 445 (27.3%), 443 (35.8%), 441 (70.7%), 439 (51.7%), 245 (75.3%), 220 (21.8%), 178 (12.4%), 165 (16.4%), 92 (12.0%).

5.5. Molecular structure determination

The data were collected at room temperature on a Siemens P4 diffractometer [13], using Mo–K$_\alpha$ (λ = 0.71073 Å) radiation. The data were corrected for

Lorentz and polarization effects; and an empirical absorption correction based on psi- scans [14] were applied. The structure was solved by the heavy atom method using SHELXTL system [15], and refined by full-matrix least-squares on F^2 using all reflections. Hydrogen atoms were included in the refinement with idealized parameters. Final $R_1 = 0.041$ is based on 7880 'observed reflections' $[I > 2\sigma(I)]$, and the $wR = 0.105$ is based on all reflections (9565 unique data). Details of the crystal data and refinement are given in Table 1.

5.6. Polymerization studies

Polymerization experiments were carried out in a 1-gallon stainless-steel autoclave reactor. The catalyst solution was prepared by the addition of enough 10% MAO in toluene (Albemarle) to the metallocene to give a 10 000:1 molar excess of aluminum. The catalyst solution was charged to the reactor followed by 2.5 l of propylene monomer, and the solution quickly brought to the desired reactor temperature. The reactor temperature was then maintained at constant temperature for 1 h. Stirring with a 3-blade propeller stirrer was maintained at 1200 rpm.

Acknowledgements

We thank the Oklahoma Center for the Advancement of Science and Technology in cooperation with Phillips Petroleum Company (AR7-11) for support of this work.

References

[1] J.A. Ewen, L.R. Jones, A. Razavi, J. Am. Chem. Soc. 110 (1988) 6255.

[2] A. Razavi, J. Ferrara, J. Organomet. Chem. 435 (1992) 292.

[3] (a) J.A. Ewen, M.J. Elder, R.L. Jones, L. Haspeslagh, J.L. Atwood, S.G. Bott, K. Robinson, Makromol. Chem. Macromol. Symp. 48 (1991) 253. (b) J.A. Ewen, M.J. Elder, C.J. Harlan, R.L. Jones, J.L. Atwood, S.G. Bott, K. Robinson, ACS Polym. Prepr. 32 (1991) 469. (c) M. Farina, G. Di Silvestro, P. Sozzani, Macromolecules 26 (1993) 946.

[4] A. Razavi, J.L. Atwood, J. Organomet. Chem. 497 (1995) 105.

[5] (a) Y. van der Leek, K. Angermund, M. Reffke, R. Kleinschmidt, R. Goretzki, G. Fink, Chem. Eur. J. 3 (1997) 585. (b) R. Kleinschmidt, M. Reffke, G. Fink Macromol. Rapid Commun. 20 (1999) 284.

[6] A. Razavi, J.L. Atwood, J. Organomet. Chem. 520 (1996) 115.

[7] H. Alt, M. Jung, J. Organomet. Chem. 568 (1998) 87.

[8] M. Giardello, M. Eisen, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 12114.

[9] Y. Obora, C.L. Stern, T.J. Marks, P.N. Nickias, Organometallics 16 (1997) 2503.

[10] E. Cesarotti, H.B. Kagan, R. Goddard, C. Kruger, J. Organomet. Chem. 162 (1978) 297.

[11] K.J. Stone, R.D. Little, J. Org. Chem. 49 (1984) 1849.

[12] R.L. Halterman, T.M. Ramsey, N.A. Pailes, M.A. Khan, J. Organomet. Chem. 497 (1995) 43.

[13] Siemens, XSCANS: X-ray single crystal analysis system, Version 2.1, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994.

[14] A.T.C. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr. A24 (1968) 351.

[15] Siemens, SHELXTL: Release 5.03, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994.