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Isospecific Propylene Polymerization with a Novel 2-Substituted Bis(indenyl) *ansa*-Zirconocene

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The preparation and crystal structure of the first group 4 *ansa*-metallocene with an oxygen atom directly bonded to the 2-position of an η^5-indenyl moiety, *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]zirconium dichloride (**3**), is reported. In combination with methylaluminoxane (MAO), complex **3** polymerizes propylene to highly isotactic crystalline polypropylene (T_m = 148 °C; M_w = 19 000; M_w/M_n = 2.4). Under similar conditions, the propylene polymerization activity of **3**/MAO exceeds that of the conventional *ansa*-metallocene catalyst system (dimethylsilyl)bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride (**4**)/MAO by a factor of 2 (5300 vs 2300 kg of PP/mol of Zr/h; T_p = 20 °C; $P(C_3H_6)$ = 2.0 bar; [Al]:[Zr] = 3 000:1). Complex **3** crystallizes in the unusual indenyl-backward conformation. The molecular structure is consistent with the expected C_2 symmetry.

Introduction

Chiral *ansa*-metallocenes exhibiting C_2 symmetry, e.g. *rac*-[ethylenebis(indenyl)]zirconium dichloride, have received considerable interest in isospecific polymerization of propylene.[1] Extensive structure−performance studies have shown that higher rigidity of the metallocene framework in combination with favorable electronic characteristics drastically improves the catalyst performance. Especially methyl substitution in the 2-position of the indenyl ligand together with appropriate aromatic substituents result in activities, stereospecifities, and polymer molecular weights comparable with those obtained with heterogeneous Ziegler−Natta catalyst systems.[2]

Halogen and alkoxy substitution in the six-membered rings of the indenes reduces catalyst activity and polymer molecular weight.[3] The effect of alkoxy or siloxy substitution in the 2-position has not been studied previously.

In this paper we report the preparation and crystal structure of a new stereorigid propylene polymerization catalyst precursor, *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]zirconium dichloride (**3**). Complex **3** is the first group 4 *ansa*-metallocene with an oxygen atom directly bonded to the 2-position of an η^5-indenyl moiety.

Results and Discussion

The reaction of 2-indanone with *tert*-butyldimethylchlorosilane and imidazole in dimethylformamide gave 2-(*tert*-butyldimethylsiloxy)indene (**1**) in 90% yield. Compound **1** was converted into bis(2-(*tert*-butyldimethylsiloxy)indenyl)ethane (**2**) in 60% yield via standard procedures.[4] Treatment of **2** with BuLi in THF and addition of this solution to $ZrCl_4$ in THF at −80 °C gave an approximately 14:1 mixture of *rac*- and *meso*-**3**, as confirmed by ^{1}H NMR analysis.[5] Crystallization from dichloromethane gave the pure racemic diastereomer in 21% isolated yield (Scheme 1). Single crystals for X-ray diffraction were obtained from a concentrated toluene solution at ambient temperature.

The molecular structure of **3** is displayed in Figure 1. The crystallographic data and parameters for **3** are presented in Table 1 with selected bond distances and angles in Table 2. The bond lengths and angles are comparable to those of related ethylene-bridged bis(indenyl) zirconocenes.[2d,6] A notable feature of the structure is the shortening of the C(2)−O bond [1.362(5) Å] indicating a partial double-bond character. The racemic stereoisomer shown in Figure 1 has an *S*,*S* configuration of the bridgehead carbon atoms and a λ conformation of the C(1),C(10),C(10′),C(1′) chain in the metallacycle. The C_2 symmetry axis bisects the Cl−Zr−Cl angle and the C(10)−C(10′) bond. Both coordination sites are equally shielded by the substituents of the indenyl moieties, as required for equivalent enantiofacial coordination of prochiral substrates. Complex **3**

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(1) For a recent review, see: Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(2) (a) Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1347. (b) Spaleck, W.; Küber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954. (c) Spaleck, W.; Antberg, M.; Aulbach, B.; Bachmann, B.; Dolle, V.; Haftka, S.; Küber, F.; Rohrmann, J.; Winter, A. In *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, Heidelberg, 1995; p 83. (d) Kaminsky, W.; Rabe, O.; Schauwienold, A.-M.; Schupfner, G. U.; Hanss, J.; Kopf, J. *J. Organomet. Chem.* **1995**, *497*, 181.

(3) (a) Lee, I. K.; Gauthier, W. J.; Ball, J. M.; Iyengar, B.; Collins, S. *Organometallics* **1992**, *11*, 2115. (b) Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990**, *9*, 3098.

(4) See for example: Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501.

(5) A similar ratio of the diastereomers was observed when the reaction was carried out at ambient temperature. Alternatively, the bis(lithium) salt of **2** was prepared in diethyl ether and isolated as an off-white powder. Complex **3** was prepared by mixing the bis(lithium) salt with $ZrCl_4$ followed by addition of precooled dichloromethane at −80 °C.

(6) (a) Piemontesi, F.; Camurati, I.; Resconi, L.; Balboni, D.; Sironi, A.; Moret, M.; Zeigler, R.; Piccolrovazzi, N. *Organometallics* **1995**, *14*, 1256. (b) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem. Macromol. Symp.* **1991**, *48/49*, 253.

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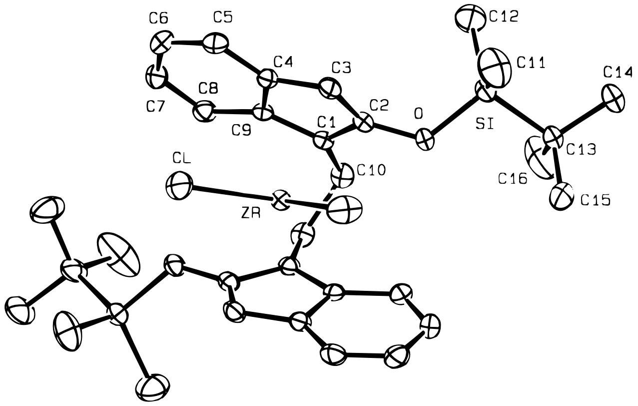
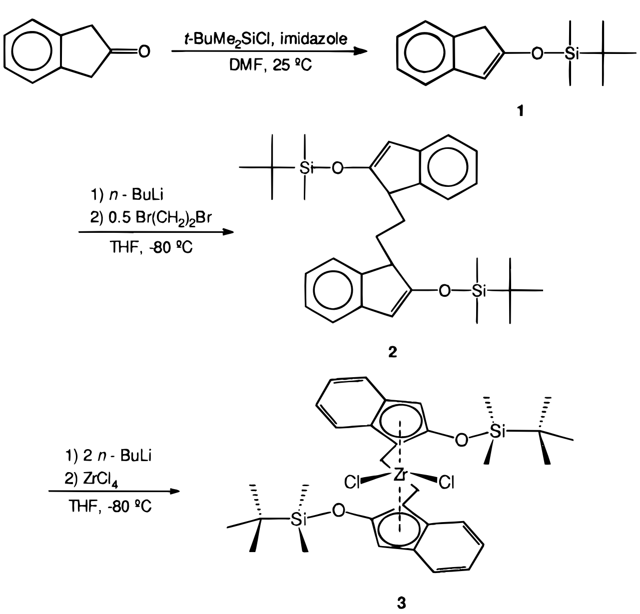


Figure 1. Molecular structure of **3** showing 30% thermal ellipsoids.

Scheme 1



crystallizes in the unusual indenyl-backward conformation that has been previously observed for the *O*-acetyl-*R*-mandelic acid derivative of *rac*-[ethylenebis(tetrahydroindenyl)]titanium dichloride.[7] This unfavorable conformation is apparently caused by crystal packing effects.

Complex **3** was empolyed as a catalyst precursor for homopolymerizations of propylene and ethylene. In combination with methylaluminoxane (MAO), **3** polymerizes propylene to highly isotactic crystalline polypropylene. Under similar conditions, the propylene polymerization activity of **3**/MAO exceeds that of the conventional *ansa*-metallocene catalyst system (dimethylsilyl)bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride (**4**)/MAO by a factor of 2 (5300 vs 2300 kg of PP/mol of Zr/h; $T_p = 20$ °C; $P(C_3H_6) = 2.0$ bar; [Al]:[Zr] = 3000:1). The polypropylene produced with **3**/MAO has a similar melting point (148 vs 146 °C) and crystallinity (45 vs 43%) compared with the polypropylene sample produced with **4**/MAO. The molecular weight is, however, lower (M_w = 19 100 vs 53 200; M_w/M_n = 2.4). Ethylene polymerization activity of **3**/MAO is slightly higher compared with the **4**/MAO catalyst system (6900 vs 6400 kg of PE/mol of Zr/h; $T_p = 80$ °C; $P(C_2H_4) = 1.6$ bar; [Al]:[Zr] = 3000:1).

Table 1. Crystal Data and Structure Refinement for 3

empirical formula	$C_{16}H_{22}ClOSiZr_{0.5}$
fw	679.00
temp	293(2) K
wavelength	0.710 69 Å
cryst system	monoclinic
space group	*C*2/*c*
unit cell dimens	$a = 14.847(3)$ Å $b = 15.642(4)$ Å $c = 14.710(2)$ Å $\alpha = 90°$ $\beta = 99.559(14)°$ $\gamma = 90°$
V	3368.9(12) Å^3
Z	8
d(calcd)	1.339 Mg/m^3
abs coeff	0.583 mm^{-1}
F(000)	1416
cryst size	0.34 × 0.32 × 0.24 mm
θ range for data collcn	1.91−25.00°
index ranges	$0 \le h \le 17, 0 \le k \le 18, -17 \le l \le 17$
reflcns collcd	2974
independent reflcns	2974 [*R*(int) = 0.042]
absn corr	ψ-scan
max and min transm	1.00 and 0.91
refinement method	full-matrix least-squares on F^2
data/restraints/params	2962/0/210
goodness-of-fit on F^2	1.07
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0418$, $wR2 = 0.0917$
R indices (all data)	$R1 = 0.0815$, $wR2 = 0.1990$
largest diff peak and hole	1.141 and −0.388 e·Å^{-3}

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 3[a,b]

Bond Distances			
Zr−Cl	2.4118(13)	C(2)−C(3)	1.401(6)
Zr−C(1)	2.486(4)	C(3)−C(4)	1.427(6)
Zr−C(9)	2.526(4)	C(4)−C(5)	1.416(6)
Zr−C(2)	2.569(4)	C(4)−C(9)	1.434(6)
Zr−C(3)	2.587(4)	C(5)−C(6)	1.361(7)
Zr−C(4)	2.625(4)	C(6)−C(7)	1.404(7)
Si−O	1.673(3)	C(7)−C(8)	1.358(7)
Si−C(12)	1.828(6)	C(8)−C(9)	1.425(6)
Si−C(11)	1.860(6)	C(10)−C(10)*	1.523(9)
Si−C(13)	1.864(5)	C(13)−C(15)	1.511(8)
O−C(2)	1.362(5)	C(13)−C(14)	1.533(6)
C(1)−C(2)	1.420(6)	C(13)−C(16)	1.556(8)
C(1)−C(9)	1.440(6)	Zr−Cen	2.254
C(1)−C(10)	1.505(6)		
Bond Angles			
Cl−Zr−Cl′	99.28(9)	C(5)−C(4)−C(9)	119.9(4)
O−Si−C(13)	104.2(2)	C(3)−C(4)−C(9)	107.4(4)
C(2)−O−Si	126.0(3)	C(6)−C(5)−C(4)	118.7(5)
C(2)−C(1)−C(9)	106.2(4)	C(5)−C(6)−C(7)	121.3(5)
C(2)−C(1)−C(10)	126.1(4)	C(8)−C(7)−C(6)	122.3(5)
C(9)−C(1)−C(10)	127.3(4)	C(7)−C(8)−C(9)	118.4(5)
O−C(2)−C(3)	127.3(4)	C(8)−C(9)−C(4)	119.3(4)
O−C(2)−C(1)	122.5(4)	C(8)−C(9)−C(1)	132.5(4)
C(3)−C(2)−C(1)	110.1(4)	C(4)−C(9)−C(1)	108.2(4)
C(2)−C(3)−C(4)	107.7(4)	C(1)−C(10)−C(10)*	111.3(3)
C(5)−C(4)−C(3)	132.6(4)	Cen−Zr−Cen*	125.90

[a] Symmetry transformations used to generate equivalent atoms: *, $-x, y, -z + 1/2$. [b] Cen refers to the centroids of the C_5 ring and * denotes an atom or centroid related by the crystallographic 2-fold axis.

The polypropylene sample produced with **3**/MAO was analyzed by ^{13}C NMR spectroscopy. The stereochemical triad composition of the polymer, expressed as the fraction of isotactic mm = 94.7, heterotactic mr = 3.1,

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and syndiotactic rr = 0.7% triads, is typical for polypropylene prepared over *ansa*-metallocene catalysts.[8] The configurational microstructure suggests that the propagation step is mainly enantiomorphic site controlled. Strong signals corresponding to an isobutylene end group can be observed, indicating that the major chain-transfer mechanism is transfer to Al. Vinylidene and *n*-propyl end groups in a 1:1 ratio can be detected, which is consistent with 1,2-addition/β-H elimination. The presence of signals at δ 15−18, 30.4, and 35.8 ppm indicates that propylene insertion proceeds also by 2,1-addition, thus showing that insertion is not totally regiospecific. Traces of 1,3-misinsertions are, however, not detected. Apparently for this catalytic system, transfer to Al and β-H elimination are the main reasons for the rather low molecular weight of the produced polypropylene.

In summary, we have demonstrated that also very large 2-substituents in the indenyl moieties of chiral *ansa*-metallocene catalyst precursors may induce high polymerization activity and high stereospecifity. The role of the heteroatom requires, however, further investigation. The dynamic behavior and detailed olefin polymerization behavior of **3** and its hydrogenated congener will be discussed elsewhere. We are currently preparing other siloxyindenes and their transition metal complexes.

Experimental Section

General Considerations. All operations were carried out in an argon or nitrogen atmosphere using standard Schlenk, vacuum, or glovebox techniques. Solvents were dried and distilled under argon prior to use. 2-Indanone (Aldrich) and *tert*-butyldimethylchlorosilane (ABCR GmbH & Co.) were used without further purification. Racemic (dimethylsilyl)bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride was prepared as described previously.[2d,9] Methylaluminoxane (MAO 29.3% w/w toluene solution, Al total 13.1% w/w, Al as TMA 3.50% w/w) was supplied by Witco and used as received. High-purity ethylene and propylene (99.5%) were obtained from Neste Oy, Finland.

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solution using a JEOL GX 400 or JEOL ALPHA 500 NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Direct inlet electron ionization mass spectra (EIMS) were obtained at 70 eV on a Varian VG-7070E mass spectrometer.

2-(*tert*-Butyldimethylsiloxy)indene (1). A solution of *tert*-butyldimethylchlorosilane (248.69 g, 1.65 mol) and imidazole (112.33 g, 1.65 mol) in DMF (900 mL) was reacted with 2-indanone (198.24 g, 1.50 mol) and then stirred overnight at room temperature. The reaction mixture was treated with water (800 mL) and extracted with diethyl ether (3 × 400 mL). The combined organic phases were washed with water (2 × 400 mL) and dried over sodium sulfate. The solvents were removed under reduced pressure to leave an orange oil. Distillation under reduced pressure afforded 331.2 g (89.6%) of pure **1** as a yellow oil (bp 105−107 °C/0.1 mmHg). ^{1}H NMR ($CDCl_3$, δ): 7.19−7.07 (m, 3H); 6.97 (td, $^{3}J = 7.3$ Hz, $^{4}J = 1.4$ Hz, 1H); 5.72 (dd, $^{4}J = 1.9$ Hz, 1.1 Hz, 1H); 3.24 (dd, $^{4}J = 1.7$ Hz, 1.1 Hz, 2H); 0.96 (s, 9H); 0.23 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 162.44; 145.14; 136.53; 126.44; 123.01; 122.39; 118.92; 106.58; 39.46; 25.59; 18.14; −4.68.

Bis(2-(*tert*-butyldimethylsiloxy)indenyl)ethane (2). To a solution of **1** (36.96 g, 150.0 mmol) in THF (150 mL) at 0 °C was added dropwise *n*-BuLi (60.0 mL of a 2.5 M solution in hexane, 150.0 mmol), and the reaction mixture was stirred overnight at room temperature. The resulting solution was then cooled to −80 °C and treated dropwise with a solution of dibromoethane (14.09 g, 75.0 mmol) in THF (50 mL). After completed addition the reaction mixture was stirred overnight at room temperature and washed with saturated ammonium chloride solution (300 mL). Solvents from the organic phase were evaporated, and the product was dissolved in Et_2O (300 mL), washed with water (2 × 200 mL), and dried over sodium sulfate. Repeated crystallizations at −15 °C afforded 22.54 g (57.9%) of **2** as an off-white solid. Mp: 108−110 °C. The first crystalline fraction consisted of diastereomerically pure material that was used for spectral characterization.[10] EIMS (calcd/found): *m/e* 518.3036/518.3028. ^{1}H NMR ($CDCl_3$, δ): 7.17−7.05 (m, 6H); 6.97 (td, $^{3}J = 7.4$ Hz, $^{4}J = 1.2$ Hz, 2H); 5.63 (s, 2H); 3.21 (m, 2H); 1.76−1.75 (m, 4H); 0.94 (s, 18H); 0.22 (s, 6H); 0.20 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 165.18; 144.35; 140.68; 126.53; 122.71; 122.35; 118.74; 104.87; 49.04; 25.67; 25.30; 18.14; −4.77.

***rac*-[Ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]zirconium Dichloride (3).** To an ice-cooled solution of **2** (5.37 g, 10.3 mmol) in THF (50 mL) was added dropwise *n*-BuLi (8.3 mL of a 2.5 M solution in hexane, 20.7 mmol), and the reaction mixture was stirred overnight at room temperature. The resultant off-yellow suspension was then added via cannula to a suspension of $ZrCl_4$ (2.41 g, 10.3 mmol) in THF (20 mL) at −80 °C. The reaction mixture was gradually warmed to room temperature and stirred overnight. Evaporation of the solvents left a yellow solid that was extracted with CH_2Cl_2 (150 mL) and filtrated through Celite to remove lithium chloride. Concentration and cooling to −30 °C gave 1.47 g (21.0%) of **3** as a yellow microcrystalline solid. Single crystals for X-ray diffraction were obtained from a concentrated toluene solution at ambient temperature. In the EIMS mass spectrum of **3**, parent ions of composition $C_{32}H_{44}Si_2O_2ZrCl_2^{+}$ were observed in the appropriate isotope ratios at *m/e* = 676−684. ^{1}H NMR (CD_2Cl_2, δ): 7.64 (dq, $J = 8.6$ Hz, 1.9 Hz, 0.9 Hz, 2H); 7.31−7.27 (m, 4H); 7.07−7.03 (m, 2H); 5.93 (d, $J = 0.8$ Hz, 2H); 4.01−3.90 (m, AA′, 2H); 3.58−3.47 (m, BB′, 2H); 1.00 (s, 18H); 0.20 (s, 6H); 0.19 (s, 6H). ^{13}C NMR (CD_2Cl_2, δ): 150.12; 126.17; 125.14; 124.86; 124.79; 123.35; 116.99; 108.54; 98.61; 26.30; 25.80; 18.61; −3.94; −4.27.

Polymerization Procedure. Sampling of the catalyst and activator were carried out under nitrogen in an MBROWN glovebox containing <2 ppm oxygen and <5 ppm water. The polymerizations were performed in a 0.5-L Büchi glass autoclave in 200 mL of toluene. In a typical run half of the MAO/toluene solution was added to the reactor and stirred for 5 min in order to reduce any impurities in the reactor. In a parallel procedure 1.1×10^{-2} mmol of the metallocene was dissolved in the remaining half of the MAO/toluene solution quantity and preactivated at 25 °C for 5 min. The catalyst/activator mixture was charged into the reactor, and the polymerization was started by introducing the monomer. The polymerization was interrupted after 20 or 60 min by addition of methanol. The polymer was analyzed after being washed with methanol/HCl.

X-ray Structure Determination. The data set was collected on a Rigaku AFC5S diffractometer using Mo Kα radiation ($\lambda = 0.710\,69$ Å) at 293 K. The intensities were corrected for Lorentz and polarization effects. The experimental absorption correction was carried out (ψ-scan). Also the decay of the crystal (12%) was taken into account. The

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[9] Luttikhedde, H. J. G.; Leino, R. P.; Näsman, J. H.; Ahlgrén, M.; Pakkanen, T. *Acta Crystallogr.* **1995**, *C51*, 1488.

[10] Reaction of **1**−Li with 0.5 equiv of dimethyldichlorosilane gives the dimethylsilyl-bridged analogue of **2**. The crystalline product consists exclusively of the racemic diastereomer in 45% yield. Reliable identification of the different isomers of **2** by NMR spectroscopy is more difficult because of the highly symmetric structure of both diastereomers.

structure was solved by direct methods and refined by least-squares techniques to the $R1$ value of 0.0418, the $wR2$ value of 0.0917 [$(I > 2\sigma(I))$], and GOF = 1.057 for all 2174 independent reflections. Heavy atoms were refined with anisotropic and hydrogen atoms with isotropic displacement parameters except methyl hydrogen atoms, which were included in calculated positions with fixed displacement parameters (1.2 × that of the host atom). All refinements were performed using SHELXL93 software.[11] Figures were plotted on ORTEPII.[12]

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Supporting Information Available: Listings of atomic coordinates, bond distances and angles, and thermal parameters and ORTEP diagrams (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

OM9600957

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