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(1,3-Propanediyl)silylene-bis(1-indenyl)dichlorozirconium. Synthesis and polymerization catalysis

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Abstract

Reaction of indenyllithium with 1,1-dichlorosilacyclobutane gave a mixture of diastereomeric isomers of 1,1-bis(1-indenyl)-1-silacyclobutane (**1**), and the product was in turn converted into diastereomeric (1,3-propanediyl)silylene-bis(1-indenyl)dichlorozirconium complexes (**2**) in a 5:2 racemic:meso ratio. Complex **2** was activated with either methyl aluminoxane (MAO) or $Ph_3CB(C_6F_5)_4$ to perform ethylene and propylene polymerizations over a very broad range of temperature of polymerization ($-55°C \le T_p \le 85°C$). Variations of the polymerization activity (A) and molecular weight (MW) with T_p were investigated as well as the isotactic yield (IY) in the case of propylene polymerizations. Comparisons of those results with other closely related *ansa*-zirconocene precursors were also made.

Keywords: Zirconocene; Homogeneous polymerization; α-olefin; Isospecific polymerization

1. Introduction

Isotactic polypropylene (*i*-PP) is manufactured by $TiCl_3$ catalysts at 60–70°C temperature of polymerization with or without support. The stereoselectivity is a manifestation of the chiral nature of the Ti center [1]. There are also catalytic sites present which produce amorphous products (*a*-PP). VCl_4 or $V(acac)_3$ activated with $AlEt_2Cl$ polymerizes propylene syndioselectively at low T_p [2].

Bis(η^5-cyclopentadienyl)dichlorotitanium (Cp_2TiCl_2) and AlR_2Cl polymerized ethylene with low activity (A ~ 10^4 g of PE/((mol of Ti)·$[C_2H_4]$·h)) but did not polymerize propylene [3]. Kaminsky and coworkers discovered that MAO is an excellent cocatalyst for Cp_2ZrCl_2; this system catalyzes polymerization of ethylene with an activity as high as 10^9 g of PE/((mol of Ti)·$[C_2H_4]$·h) [4]. At low T_p, Cp_2TiPh_2/MAO can produce PP with an appreciable meso structure content which was attributed to chain-end stereochemical control of enantiofacial selection [5]. Only atactic PP is produced above ambient temperature by metallocene catalyst precursors with a C_{2v} symmetry.

Wild and coworkers synthesized racemic ethylene-bis(1-η^5-indenyl)dichlorozirconium [6]. The $Et(Ind)_2ZrCl_2$/MAO catalyst system exhibits enantiomorphic-site stereochemical control of propylene insertion [5,7]. We found that this stereoselectivity of propylene polymerization is markedly lowered with an increase of T_p, as manifested by a decrease in [*mmmm*] homosteric pentad sequence distribution determined by ^{13}C NMR and T_m measured by DSC [8].

Improvements with regard to the high catalytic activity and stereoselectivity are diligently pursued both for industrial utility and scientific interests. It is generally accepted that these objectives can be achieved through "fine tuning" of the metallocene structure. To that end, we have synthesized *ansa*-bis(indenyl)zirconocene complexes with different bridging moieties and compared their polymerization behaviors. As one might expect, very different polymerization results were obtained for zirconocenes with the following bridging groups: $-CH_2-CH_2-$ [8b,9], $-CH(CH_3)-$ [10], $Me_2Si<$ [9], $(menthoxy)_2Si<$ [11], (tetraphenyl-1,3-butadiene-1,4-diyl)Ge < [12] and (1,4-butanediyl)Si < [13]. In

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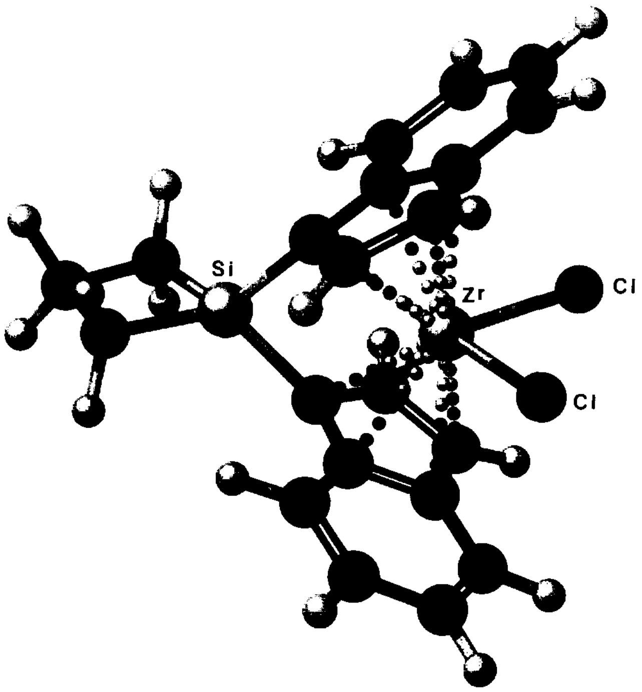


rac-**2** (MM2-derived model structure).

this paper we report on a related study, the synthesis of (1,3-propanediyl)silylene-bis(1-indenyl)dichlorozirconium (**2**) and its catalysis of ethylene and propylene polymerization.

2. Results and discussion

2.1. *Synthesis of the catalyst precursor 2*

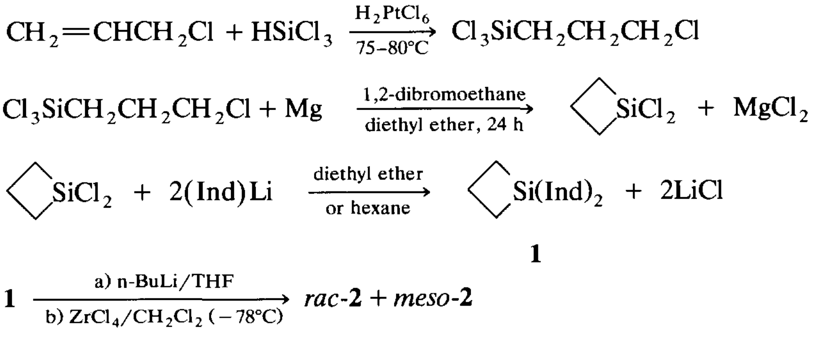
The synthesis of **2** is outlined in Scheme 1. 3-Chloropropyltrichlorosilane [14] and 1,1-dichloro-1-silacyclobutane [15] were prepared by literature procedures. The reaction between 1,1-dichloro-1-silacyclobutane and indenyllithium to form 1,1-bis(1-indenyl)-1-silacyclobutane (**1**) could be carried out either in diethyl ether or in *n*-hexane, although the yield of **1** in the former medium (57%) was higher than in the latter (43%).

A mixture of diastereomeric isomers (racemic and meso) of **1** was observed by ^{1}H NMR because of the different configurations of two chiral centers at the 1-position of the indenyl rings. The ^{1}H NMR spectrum of this product contains three sets of peaks forming an ABX spin system for each isomer in a 1 : 1 : 1 intensity ratio; isomer a: δ 6.92 (dd, $J_{AB} = 5.34$ Hz, $J_{AX} = 1.92$ Hz, 2H), 6.60 (dd, $J_{BA} = 5.34$ Hz, $J_{BX} = 1.98$ Hz, 2H), 3.57 (br.s, 2H); isomer b: δ 6.97 (dd, $J_{A'B'} = 5.34$ Hz, $J_{A'X'} = 1.92$ Hz, 2H), 6.22 (dd, $J_{B'A'} = 5.34$ Hz, $J_{B'X'} = 1.98$ Hz, 2H), 3.60 (br.s, 2H). These peaks can be assigned to the H-3, H-2 and H-1 protons for each isomer, respectively, on the indenyl rings. We have previously discussed the characterization of such isomers and studied the diastereomerization behavior by dynamic NMR methods for a similar system [16].

Metalation of **1** by *n*-butyllithium in THF and subsequent reaction with $ZrCl_4$ failed to give the *ansa*-metallocene **2** using various solvents such as THF or toluene and under diverse reaction conditions. However, a reaction conducted in methylene chloride at low temperature afforded a 49% yield of a mixture of *rac*-**2** and *meso*-**2** diastereomers in a 5 : 2 ratio according to ^{1}H NMR; racemic: δ 6.96 (d, 2H, 3-Ind H), 5.81 (d, 2H, 2-Ind H); meso: δ 6.90 (m, 2H, 3-Ind H), 6.15 (m, 2H, 2-Ind H). Attempts to separate these diastereomers were unsuccessful, and the mixture was therefore used for the polymerizations directly.

2.2. *Ethylene polymerizations catalyzed with 2*

The **2**/MAO system catalyzed extremely rapid ethylene polymerizations at high T_p (Table 1); 1.84 g of PE was produced at 85°C in just 12 min (run 1) for an activity of 1.23×10^9 g of PE/((mol of Zr) $\cdot$ [C_2H_4] $\cdot$ h). At 45°C (run 3), only 2 min of polymerization time afforded 0.62 g of PE with an activity of 1.27×10^9. The PE formed at this T_p has a T_m of 140.3°C, indicating a highly linear chain structure and consistent with the measured high $\overline{M}_w$ (2.61×10^5). The melting temperature of the PE is generally insensitive to T_p, however, the $\overline{M}_w$ increased with decreasing the T_p and the **A** decreased considerably with a decrease of T_p.



Scheme 1.

Table 1
Ethylene polymerizations catalyzed with **2**/MAO [a]

Run no.	T_p (°C)	[Zr] (μM)	[Al] (mM)	Time (min)	Yield (g)	A [b] $\times 10^{-6}$	T_m (°C)	M_w [c] $\times 10^{-4}$
I-1	85	1	100	12	1.84	1230	134.4	5.12
I-2	70	1	100	8	1.48	1080	138.1	7.55
I-3	45	1	100	2	0.62	1270	140.3	26.1
I-4	25	2	100	3	0.48	270	136.6	35.2
I-5	0	2.5	120	6	0.30	55.7	138.7	40.7
I-6	−20	2.5	120	10	0.12	11.8	135.5	54.2
I-7	−55	5	130	15	0.07	1.80	137.4	48.2

[a] Conditions: toluene 50 mL; $P(C_2H_4) = 15$ psig, except in run 7, where 50 mL of ethylene was metered in. [b] A in units of grammes of PE/((mol of Zr)·$[C_2H_4]$·h). [c] M_w by viscosity.

Ethylene was also polymerized by the zirconocenium cation ($\mathbf{2}^+$) formed in situ by the reaction of the dichloride precursor **2**, triisobutylaluminium (TIBA), and triphenylcarbenium tetrakis(pentafluorophenyl)borate $[Ph_3CB(C_6F_5)_4]$ [9]. In this method, TIBA acts also as a scavenger in the polymerization system. The polymerization results are summarized in Table 2.

The most rapid polymerization was observed at $T_p = 0$°C. At this temperature, 0.66 g of PE (run 5) was produced in 27 s and stirring stopped immediately. An approximate activity for this agitation limited polymerization is ca. 1.63×10^9 g of PE/((mol Zr)·$[C_2H_4]$·h). Polymerizations performed using an apparatus capable of much more vigorous stirring should produce even higher activity. Unlike the **2**/MAO system, the activity of the $\mathbf{2}^+$ catalytic system was reduced at both higher and lower T_p than 0°C.

The variations of activity for ethylene polymerization with T_p^{-1} are plotted in Fig. 1. In the low T_p region, $\mathbf{2}^+$ catalyzes polymerization of ethylene about ten times faster than the 2/MAO system, but the latter exceeds the former at high T_p. The two distinct temperature-dependent regions for polymerization catalyzed by $\mathbf{2}^+$ have also been observed for other systems, and were discussed previously [9]. It is noteworthy that the polymerization temperature resulting in the maximum activity varies with the characteristics of catalyst structures, and is probably a result of the relative stability of the intermediate zirconocenium/olefin π-complexes.

Fig. 2 illustrates the variations of PE molecular weight with T_p^{-1}. In the low T_p region, both catalytic systems exhibited only a small change of $\overline{M}_W$ with T_p, with an activation energy (ΔE) of approximately 0.44 kcal mol^{-1}. Above 5°C, the $\overline{M}_W$ of PE produced by $\mathbf{2}^+$ decreases with T_p at an overall ΔE of approximately −2.6 kcal mol^{-1}, and the **2**/MAO system has a ΔE of approximately 6.9 kcal mol^{-1} of $\overline{M}_W$ dependence on T_p. The bigger dependence on T_p for the **2**/MAO system in the high temperature region could be attributed to dissociation of the coordinated counter-ion (MAO or MAO$^-$) in multi-complexation equilibria between cationic species and MAO, and in turn enhanced β-hydride transfers to metal and coordinated monomer.

2.3. Propylene polymerizations catalyzed with $\mathbf{2}^+$

The results of propylene polymerization catalyzed by $\mathbf{2}^+$ are presented in Table 3. The polymerization activity (A) exhibits only slight dependence on T_p in the low T_p region, but drops rapidly at $T_p > 50$°C (Fig. 3).

A mixture of *rac*-**2**/*meso*-**2** (5 : 2) was directly used for the polymerization. Because the meso isomer generally produces atactic PP and exhibits a lower activity for the propylene polymerization [17], these complica-

Table 2
Ethylene polymerizations catalyzed with $\mathbf{2}^+$ [a]

Run no.	T_p (°C)	[Zr] (μM)	[TIBA] (mM)	Time (min)	Yield (g)	A [b] $\times 10^{-7}$	T_m (°C)	M_w [c] $\times 10^{-5}$
II-1	85	2.5	0.3	3	0.08	8.53	137.9	1.32
II-2	70	2.5	0.3	3.5	0.41	27.4	137.3	1.86
II-3	45	2.5	0.4	3	0.75	41.0	136.7	2.38
II-4	25	2.5	0.8	2	0.74	49.9	136.8	2.61
II-5	0	2.5	1.2	27 s	0.66	163	137.1	3.88
II-6	−20	5	1.4	6	0.71	5.81	136.2	4.59
II-7	−55	5	1.5	9	0.47	2.13	139.4	5.41

[a] Conditions: toluene 50 mL; $P(C_2H_4) = 15$ psig, except in run 7, where 50 mL of ethylene was metered in. [b] A in units of grammes of PE/((mol of Zr)·$[C_2H_4]$·h). [c] M_w by viscosity.

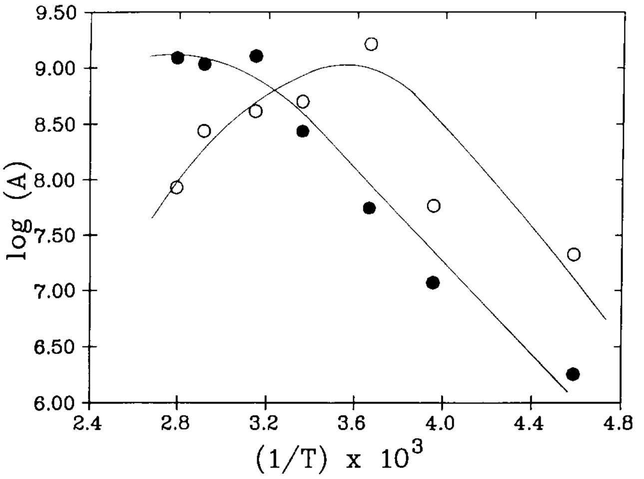


Fig. 1. Variation of activity of ethylene polymerization with T_p^{-1} catalyzed with: (●) **2**/MAO; (○) **2**$^+$.

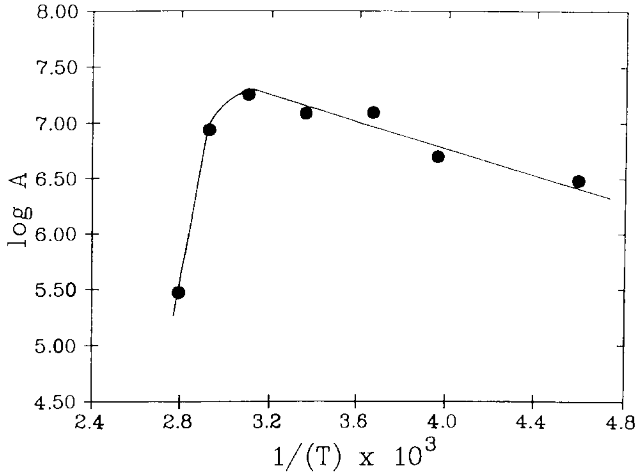


Fig. 3. Variation of activity of propylene polymerization with T_p^{-1} catalyzed with **2**$^+$.

tions need to be taken into consideration in the analysis of propylene polymerizations by **2**$^+$. A similar or even higher ethylene polymerization activity, but a lower propylene polymerization activity based on the total amount of the catalyst **2** employed, was observed as compared with *rac*-$(CH_3)_2Si(Ind)_2ZrCl_2$ [9b,9c]. Furthermore, the *meso*-**2** present in the mixture produces *a*-PP and lowers IY (weight percentage of PP insoluble in refluxing *n*-heptane, Table 3) as compared with the five-membered ring silylene-bridged analogue [13]. However, the ^{13}C NMR study of the polymer obtained indicated that the isotacticity ([*mm*]% = 73) of the polymerization is close to the mole fraction of the *rac*-complex **2** (71%) present in the catalyst mixture used. The observed relative intensities of the methyl pentads of polypropylene prepared with **2**$^+$ at T_p of 25°C are: [*mmmm*] = 0.64, [*mmmr*] = 0.07, [*rmmr*] = 0.02, [*mmrr*] = 0.06, [*mrmm* + *rmrr*] = 0.09, [*mrmr*] = 0.05, [*rrrr*] = 0.01, [*mrrr*] = 0.03 and [*mrrm*] = 0.03. These results are consistent with Ewen's earlier work with mixtures of diastereomeric, titanium-based catalysts [5].

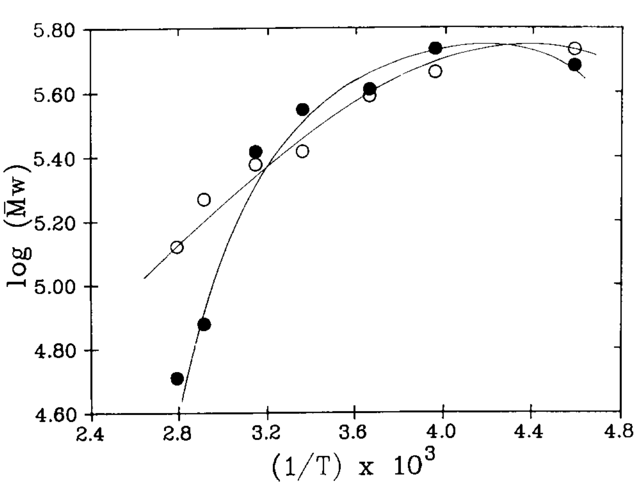


Fig. 2. Variation of $\overline{M}_w$ of PE with T_p^{-1} obtained by: (●) **2**/MAO; (○) **2**$^+$.

In conclusion, the synthesis of the title complex has been achieved, and its ethylene, as well as propylene, polymerization catalysis has been studied thoroughly. Taking into consideration the function of the meso isomer in the mixture, the two precursors, complex **2** and its five-membered ring analogue, behave similarly in ethylene and propylene polymerization, indicating that they have essentially identical constraint geometry.

3. Experimental details

All reactions with organometallic reagents were carried out under an atmosphere of dry argon using standard Schlenk tube or glove box techniques. Solvents were dried over Na/K alloy or CaH_2 (CH_2Cl_2) and distilled under argon prior to use. Routine ^1H NMR spectra were recorded on a Bruker AC 200 spectrometer at ambient temperature; chemical shifts are referenced with respect to TMS. The program used to perform the molecular mechanics calculation was Allinger's MM2 [18]. All calculations were carried out using the CAChe Modeling software system (version 3.5, 1993). Elemental analyses were performed by the Microanalytical Laboratory at the University of Massachusetts, Amherst. Melting points are uncorrected.

3-Chloropropyltrichlorosilane [14] and 1,1-dichlorosilacyclobutane [15] were prepared according to the literature. A literature procedure was also used to synthesize triphenylcarbenium tetrakis(pentafluorophenyl)borate $[Ph_3CB(C_6F_5)_4]$ [9a,19].

Methyl aluminoxane (MAO) was obtained from

Akzo Chemicals. Ethylene and propylene were purchased from Mariam Graves and purified by passing through two Matheson Gas Purifiers (Model 6406). Unless otherwise indicated, all chemicals were obtained from Aldrich.

3.1. 1,1-Bis(1-indenyl)-1-silacyclobutane (1)

A 1000 ml Schlenk flask was charged with 55.0 ml (0.47 mol) of indene and 500 ml of dry *n*-hexane. The solution was cooled to 0°C and 250 ml of *n*-BuLi (1.6 M in hexane, 0.40 mol) was added dropwise through a dropping funnel over a 2-h period. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for an additional 24 h. The resulting thick precipitate was filtered through a filter frit under argon, then washed with two portions of dry hexane. The solid was dried further in vacuo overnight to afford 46.4 g (95.0%) of indenyllithium as a white powder.

A 250 ml round-bottom flask was equipped with a reflux condenser, magnetic stirring bar and dropping funnel. Indenyllithium (5.50 g, 45.0 mmol) was added to the flask followed by 150 ml of diethyl ether. Stirring was begun and 1,1-dichloro-1-silacyclobutane (3.00 g, 21.2 mmol) in 50 ml of diethyl ether was added dropwise. After the addition was complete, the reaction mixture was heated at reflux with stirring for 12 h. The solvent was removed in vacuo and 200 ml of hexane was added. The resulting thick precipitate was filtered through a Celite plug, then washed with two portions of hexane. The solvent of the filtrate was removed to produce a sticky orange oil. The crude product was purified by passing it through a silica gel column (1:1 CH_2Cl_2 and hexane as an elution solvent) to afford 3.60 g (57.0%) of the title compound **1** as an orange oil.

^1H NMR (C_6D_6): δ 7.50–7.21 (m, 8H for each isomer, two isomers, H4-H7 (Ind)), 6.97 (dd, $J_{A'B'} = 5.34$ Hz, $J_{A'X'} = 1.92$ Hz, 2H, H-3 (Ind), isomer b), 6.92 (dd, $J_{AB} = 5.34$ Hz, $J_{AX} = 1.92$ Hz, 2H, H-3 (Ind), isomer a), 6.60 (dd, $J_{BA} = 5.34$ Hz, $J_{BX} = 1.98$ Hz, 2H, H-2 (Ind), isomer a), 6.22 (dd, $J_{B'A'} = 5.34$ Hz, $J_{B'X'} = 1.98$ Hz, 2H, H-2 (Ind), isomer b), 3.60 (br.s, 2H, H-1, isomer b), 3.57 (br.s, 2H, H-1, isomer a), 1.69–1.60 (m, 2H for each isomer, two isomers, β-(CH_2)), 1.09–0.91 (m, 4H, 2α-(CH_2), for one isomer), 0.72–0.57 (m, 4H, 2α-(CH_2), for another isomer).

3.2. (1,3-Propanediyl)silylene-bis(1-indenyl)dichlorozirconium (2)

n-Butyllithium (6.25 ml, 1.6 M in hexane, 10.0 mmol) was added dropwise to **1** (1.50 g, 4.99 mmol) in 50 ml of THF at room temperature. After 2 h of stirring, the solvent of the deep-red solution was removed in vacuo. The resulting pink powder, after washing with hexane and drying, was cooled to −78°C and 200 ml of CH_2Cl_2 was added. A suspension of $ZrCl_4$ (1.16 g, 4.99 mmol) in 100 ml of CH_2Cl_2 was added dropwise. After the addition was complete, the reaction mixture was allowed to warm to room temperature, and was stirred for an additional 12 h. The reaction mixture was filtered through a Celite plug to produce a clear orange solution. The solvent was removed in vacuo and the residue was washed with two portions of dry hexane. The dried solid was recrystallized from toluene: hexane affording 1.90 g of impure product as an orange powder. A small amount of unidentified polymer was removed by passing the product through a Bio-beads column (S-X 8, 200–400 mesh) using toluene as an eluent. Fractional recrystallization from toluene: hexane produced 1.13 g (49.1% yield) of the title compound **2**. It decomposes slowly above 175°C. Further purification failed to remove the undesired meso form from the mixture of diastereomers, and an NMR spectrum indicated the mixture of racemic and meso was in a ratio of 5 to 2.

^1H NMR (C_6D_6): δ 7.43–7.15 (m, 8H for each isomer, aromatic H), 6.96 (d, 2H, 3-Ind H, racemic), 6.90 (m, 2H, 3-Ind H, meso), 6.15 (m, 2H, 2-Ind H, meso), 5.81 (d, 2H, 2-Ind H, racemic), 1.40 (m, 2H for each isomer, β-(CH_2)), 1.28 (t, 4H, α-(CH_2), meso), 0.93 (t, 4H, α-(CH_2), racemic). Anal. Found: C, 54.83; H, 3.78. $C_{21}H_{18}Cl_2SiZr$ calc.: C, 54.76; H, 3.94%.

Table 3
Propylene polymerizations catalyzed with 2^+ [a]

Run no.	T_p (°C)	[Zr] (μM)	[TIBA] (mM)	Time (min)	Yield (g)	A [b] $\times 10^{-5}$	T_m (°C)	M_w [c] $\times 10^{-4}$	IY [d] (%)
III-1	85	10	0.7	10	0.03	2.95	98.2	0.32	0
III-2	70	25	0.8	30	0.39	86.9	119.7	1.12	0
III-3	50	10	1.0	11	0.42	178	136.2	4.43	0
III-4	25	10	1.0	15	0.76	121	154.1	7.48	39.8
III-5	0	10	1.5	11	0.85	124	153.8	12.3	67.6
III-6	−20	10	2.0	10	0.27	49.9	157.1	20.3	65.4
III-7	−55	25	3.3	5	0.39	30.5	163.1	29.4	69.6

[a] Conditions: toluene = 50 mL; $P(C_3H_6) = 10$ psig, except in run 7, where 50 mL of propylene was metered in. [b] A in units of grammes of PP/((mol Zr)·$[C_3H_6]$·h). [c] M_w by viscosity. [d] Weight percentage of PP insoluble in refluxing *n*-heptane.

3.3. Polymerization and polymer characterization

Polymerizations were carried out in a 250 ml crown-capped glass pressure reactor with a magnetic stirring bar. The system was first evacuated, flushed with argon, and injected 50 ml of toluene. The system was evacuated again and saturated with the appropriate monomer for ca. 20 min.

The order of addition of reagents and detailed procedures for polymerizations have been described previously [8b,9,20]. The polymerization mixture was quenched with acidic methanol (1% HCl), filtered, washed with methanol and dried at 70°C to a constant weight.

The values of activity (A) were calculated using the measured solubility of propylene and ethylene [21]. Intrinsic viscosities of polyethylene and polypropylene were measured in decalin at 135°C using an Ubbelohde viscometer. Melting temperatures as well as melting enthalpies were measured by a differential scanning calorimetry (Perkin-Elmer DSC 4). The stereospecificity in propylene polymerization was measured by the percent yield of insoluble (isotactic) polypropylene (IY) in refluxing *n*-heptane and its isotacticity was also judged by T_m, crystallinity, etc. Stereo- and regio-regularities of the polymers obtained were determined by ^{13}C NMR spectroscopy on a Bruker AMX-500 spectrometer (125.77 MHz) in $C_2D_2Cl_4$ at 110°C and analyzed by known methods [5,8b,22].

Acknowledgment

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