

ansa-Metallocene derivatives XXXIII. ¹ 2-Dimethylamino-substituted bis-indenyl zirconium dichloride complexes with and without a dimethylsilyl bridge: syntheses, crystal structures and properties in propene polymerization catalysis ²

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Abstract

Bis(2-N,N-dimethylamino-indenyl) zirconium dichloride, $(2-(\text{CH}_3)_2\text{N}-\text{C}_9\text{H}_6)_2\text{ZrCl}_2$, and dimethylsilyl-bridged bis(2-N,N-dimethylamino-indenyl) zirconium dichloride, $(\text{CH}_3)_2\text{Si}(2-(\text{CH}_3)_2\text{N}-\text{C}_9\text{H}_5)_2\text{ZrCl}_2$, were prepared by reaction of the corresponding ligand lithium salts with ZrCl_4 in toluene. Diffractometric structure determinations reveal C_2 -symmetric complex geometries for both complexes. An increased electron density at the Zr center of the dimethylamino-substituted complexes is indicated by reduction potentials which are 0.3–0.4 V more negative than those of their unsubstituted analogs. When activated with methyl aluminoxane in toluene solution, $(\text{CH}_3)_2\text{Si}(2-(\text{CH}_3)_2\text{N}-\text{C}_9\text{H}_5)_2\text{ZrCl}_2$ catalyzes the polymerization of propene to polymers with a microstructure comparable with that of polymers produced with other Me_2Si -bridged bis(indenyl)ZrCl₂ complexes, but with a substantially increased fraction of i-propyl end groups derived from alkyl exchange between Zr-polymer and Al–Me species.

Keywords: Zirconium; ansa-Zirconocenes; 2N,N-dimethylamino-indenyl ligand

1. Introduction

The properties of chiral ansa-zirconocene complexes as catalysts for the stereoselective polymerization of α -olefins depend critically on the substitution patterns of their C_5 -ring ligands. Studies on numerous zirconocene complexes with alkyl- and aryl-substituted bis(cyclopentadienyl) and bis(indenyl) ligands have revealed interesting steric effects on the activity of these catalysts and on the stereo- and regioregularity and the molecular mass of their polyolefin products [2]. Zirconocene catalysts with functionally substituted ligands, i.e. with substantially changed electronic properties, have remained quite rare so far however [3,4]. Here we report syntheses, crystal structures and catalytic properties of bridged and unbridged bis(indenyl) zirconium

complexes with dimethylamino-substituted indenyl ligands.

2. Results and discussion

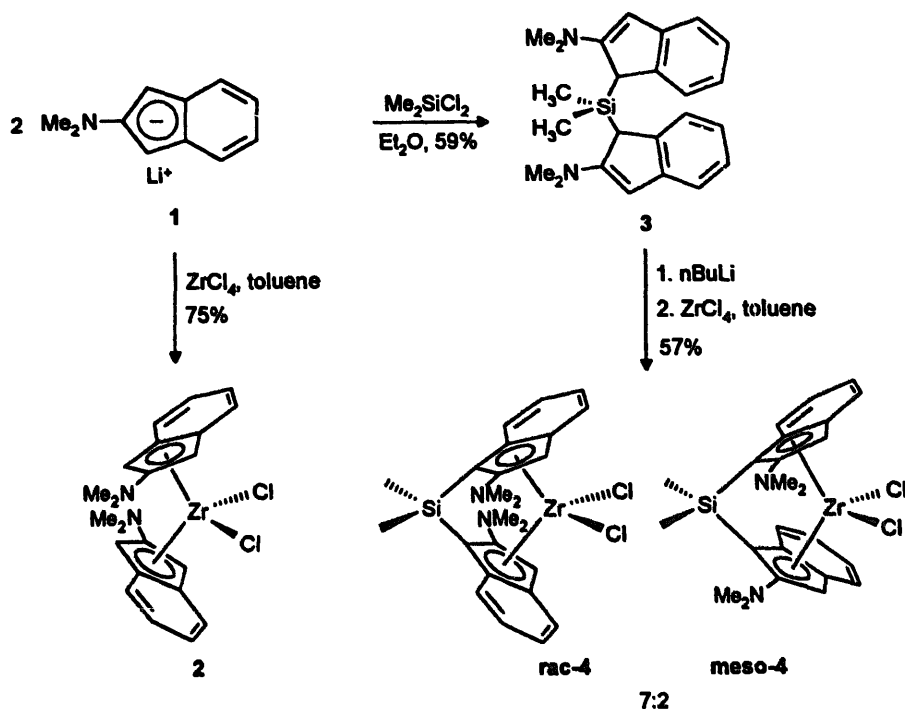
Following a report by Edlund [5] with slight modifications, 2-N,N-dimethylamino indene was obtained from 2-indanone and dimethylamine as a white solid in ca. 85% yield. Reaction with n-butyl lithium in diethyl ether gave the lithium salt **1** as a colorless precipitate in near-quantitative yield. By reacting ZrCl_4 with two equivalents of **1** in toluene at room temperature, the unbridged, amino-substituted zirconocene complex **2**, $(2-\text{Me}_2\text{N-ind})_2\text{ZrCl}_2$, was obtained in ca. 75% theoretical yield in the form of yellow crystals (Scheme 1).

Reaction of dimethyldichlorosilane with two equivalents of the 2-dimethylamino-indenyl lithium salt **1** in diethyl ether gave the Me_2Si -bridged ligand system **3**, as a mixture of the racemic and meso forms, in ca. 60%

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¹ See Ref. [1].

² In memoriam Professor Hidemasa Takaya.



theoretical yield. Renewed aromatization with *n*-butyl lithium and reaction with $ZrCl_4$ in a small volume of toluene afforded the amino-substituted ansa-zirconocene complex **4**, $Me_2Si(2-Me_2N-ind)_2ZrCl_2$, as a 7:2 mixture of the racemic and meso isomers in ca. 60% theoretical yield. Pure racemate, *rac*-**4**, which is less soluble in toluene than the meso isomer, was obtained in ca. 30% yield after extraction of the meso compound with toluene in the form of yellow platelets.

Diffraction crystal structure determinations of complexes **2** and *rac*-**4** (see Experimental) reveal the

molecular structures represented in Fig. 1, with bond distances and angles as listed in Table 1. Both structures have a crystallographically imposed C_2 -axial symmetry; Zr–C and Zr–Cl distances as well as centroid–Zr–centroid and Cl–Zr–Cl angles are comparable with those observed for unbridged [6] and Me_2Si -bridged bis(indenyl) zirconium complexes [7] respectively.

In the unbridged complex **2**, the dimethylamino group is essentially planar. A short N(1)–C(2) distance of 135 pm indicates that the nitrogen lone pair is largely delocalized into the aromatic ring system, as observed be-

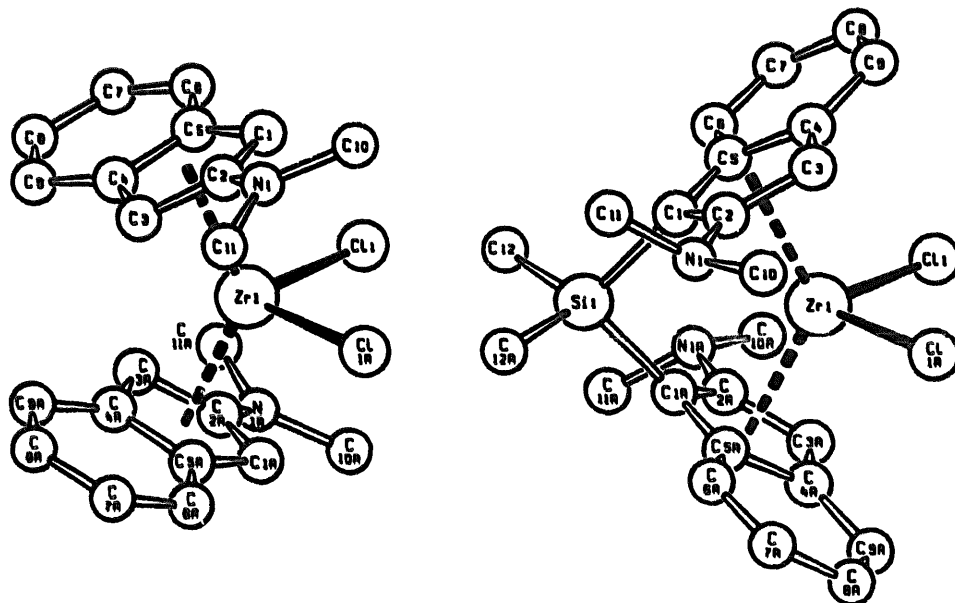


Fig. 1. Molecular structures of complexes **2** (left) and *rac*-**4** (right).

Table 1
Selected distances (ppm) and angles (deg) for complexes **2** and **rac-4**

	2	rac-4
Zr(1)–C(1)	245.5(2)	242.2(4)
Zr(1)–C(1)	246.7(6)	245.2(12)
Zr(1)–C(2)	262.0(6)	257.4(11)
Zr(1)–C(3)	251.5(5)	258.7(11)
Zr(1)–C(4)	254.3(5)	260.5(11)
Zr(1)–C(5)	254.5(5)	247.7(11)
N(1)–C(2)	135.4(7)	139.7(15)
N(1)–C(10)	144.3(7)	147.8(17)
N(1)–C(11)	143.6(6)	145.5(17)
Si(1)–C(1)		190.5(12)
Si(1)–C(12)		185.7(14)
Cl(1)–Zr(1)–C(1)	95.1(1)	94.9(2)
Cl(1)–Si(1)–C(1A)		95.0(7)
CR(1)–Zr(1)–CR(2) ^a	133.1	129.1
CP(1)–CP(2) ^b	49.8	59.2

^a CR(1), CR(2) centroids of C atoms numbered 1–5 and 6–10 respectively.

^b CP(1), CP(2) mean planes of corresponding C₅ rings.

fore in (Me₂N–C₅H₄)₂TiCl₂ [4a]. In **rac-4**, however, the dimethylamino groups deviate considerably from coplanarity. This is undoubtedly due to steric interaction with the Me₂Si bridge, as indicated by a C(11)–C(12A) distance of only 333 pm. The increased N(1)–C(2) distance of 140 pm approaches that of typical pyramidal amino groups [8].

Cyclovoltammograms of the dimethylamino-substituted complexes **2** and **rac-4** (see Experimental) differ from those of their unsubstituted analogs, (ind)₂ZrCl₂ and Me₂Si(ind)₂ZrCl₂, by the presence of an additional, irreversible oxidation peak at $E_{1/2}$ = ca. 0 V, which indicates that the amino-substituted indenyl ligands of these complexes are unstable against oxidation. The reduction peaks of complexes **2** ($E_{1/2}$ = –2.42 V) and **rac-4** ($E_{1/2}$ = –2.48 V) occur at more negative potentials than those of their unsubstituted analogs (ind)₂ZrCl₂ ($E_{1/2}$ = –2.15 V) and Me₂Si(ind)₂ZrCl₂ ($E_{1/2}$ = –2.05 V). This shift of the Zr(IV)–Zr(III) reduction to more negative potentials by 0.28 and 0.43 V respectively indicates that the dimethylamino substituents of **2** and **rac-4** increase the electron density noticeably at the Zr centers of these complexes.

When solutions containing 3.33 mg (6.25 μmol) **rac-4** in 350 ml toluene were preactivated for 30 min with excess methylaluminoxane (MAO) (Al:Zr 1200:1) and then exposed to propene at a pressure of 2 bar, formation of polypropene started after an induction period of 2–3 h. The rate of propene uptake was observed to increase further for several hours; after 15–20 h a steady rate is reached, with activities (ca. 400 kg PP [mol Zr]^{–1} h^{–1}) somewhat below those observed with unsubstituted Me₂Si-bridged bis(indenyl) zirconium catalysts [9].

Such an induction period is unusual for homogeneous, metallocene-based polymerization catalysts,

which normally reach their maximal activity after a few minutes, practically as the reaction solution becomes saturated with propene. Other modes of activation were tested to clarify the origins of the induction period. Prolonged preactivation of **rac-4** with MAO for 2–3 h did not lead to shortened induction periods; addition of excess trimethyl aluminum (0.189 g, 2.63 mmol) to the catalyst solution, however, appears to increase the induction period to ca. 4 h. Apparently, the reaction which generates the catalytically active species is inhibited, presumably by the presence of the basic dimethylamino groups in **rac-4**.

The polymers obtained with the catalyst **rac-4**/MAO at 50°C are comparable in their stereoregularity (85% mmmm, m.p. 132°C) and molar mass (M_N = 30920) with polypropene obtained with Me₂Si(ind)₂ZrCl₂/MAO [9,10]. Since congeners of this catalyst with methyl or ethyl substituents in 2-position of the indenyl ligand produce polypropene with much higher molar masses [7b,11a] we would have expected longer-chain polymers to also be produced by **rac-4**/MAO.

A remarkable distinction of unsubstituted or alkyl-substituted catalysts such as Me₂Si(ind)₂ZrCl₂/MAO or Me₂Si(2-Me-ind)₂ZrCl₂/MAO concerns the end groups of polymers obtained with **rac-4**/MAO: in addition to the normal n-propyl and 2-propenyl end groups, isopropyl end groups are apparent from conspicuous ¹³C-NMR signals at 23.7, 25.7 and 47.4 ppm [12]. In general, these isopropyl signals exceed those of the n-propyl groups by a factor of 2–4 in intensity [13].

This observation indicates that the dominant chain termination process is an exchange of methyl groups and polymer chains between Al centers of the MAO cocatalyst and Zr centers of the **rac-4**/MAO catalyst. Similar Zr to Al chain transfer reactions have been observed with sterically congested zirconocene catalysts, such as Me₂Si(2-Me-4-^tBu-C₅H₂)ZrCl₂ or (C₅Me₅)₂ZrCl₂ [12,14]. Steric congestion might also be responsible for the preferred alkyl chain exchange in the catalyst system **rac-4**/MAO. Alternatively, the increased electron density at its Zr center might decrease the rates of olefin insertion as well as of β-H transfer to such a degree that alkyl exchange with the methyl aluminum cocatalyst becomes the dominant mode of chain termination.

3. Experimental section

3.1. General information

Moisture- and air-sensitive compounds were handled under an argon atmosphere using Schlenk techniques. Toluene and diethyl ether were distilled from sodium benzophenone ketyl, pentane from CaH₂. NMR spectra

were recorded on a Bruker WM 250 MHz spectrometer with TMS as internal standard.

3.2. 2-*N,N*-dimethylaminoindene

A solution of 10.56 g (0.08 mol) 2-indanone in 300 ml methanol was cooled to -30°C . 12 ml *N,N*-dimethylamine was added in one portion. The solution immediately turned yellow and after a few minutes a white product started to precipitate. After stirring for another 2 h, the aminoindene was collected by filtration and dried in vacuo (10.81 g (0.068 mol), 85%).

3.3. Bis(2-*N,N*-dimethylaminoindenyl)zirconium dichloride (2)

To 10 g (0.063 mol) 2-*N,N*-dimethylaminoindene, dissolved in 200 ml diethyl ether, was added 39 ml of 1.6 M solution of *n*-butyl lithium in hexane at -10°C . The precipitated lithium salt **1** was collected on a frit and dried in vacuo to give 9.98 g (0.06 mol) of 2-(CH_3)₂*N*-indenyl lithium **1** as a colorless powder (96%). 5 g (0.03 mol) of 2-(CH_3)₂*N*-indenyl lithium **1** was mixed with 3.53 g (0.015 mol) zirconium tetrachloride. On addition of 150 ml toluene the reaction mixture turned yellow and some heat was evolved. After stirring for 16 h, the toluene was removed in vacuo. The remaining yellow solid was suspended in 150 ml methylene chloride and freed from insoluble products by filtration. The filtrate was concentrated to 100 ml and cooled to -80°C . Isolation of the yellow crystals by filtration gave 5.06 g (11 mmol, 75% theoretical yield) of the bis(aminoindenyl)zirconium dichloride **2**. ¹H-NMR (CDCl_3 , 250 MHz): δ 2.59 (s, 12H, $\text{N}(\text{CH}_3)_2$), 4.55 (s, 4H, $\text{CH}(1,3\text{-ind})$), 7.05–7.16, 7.53–7.61 (2m, 8H, $\text{CH}(4,5,6,7\text{-ind})$). MS (EI) (70 eV, 240°C): m/z 478 (M^+ , 30%), 320 ($\text{M}^+ - \text{C}_9\text{H}_6\text{N}(\text{CH}_3)_2$, 85%). Anal. Found: C, 54.57; H, 5.19; N, 5.45. $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{N}_2\text{Zr}$ (478.58) Calc.: C, 55.21; H, 5.06; N, 5.85%.

3.4. Dimethylsilanediybis(2-*N,N*-dimethylaminoindene) (3)

To a suspension of 28 g (0.17 mol) of 2-*N,N*-dimethylaminoindenyl lithium in 500 ml diethyl ether was slowly added a solution of 11 ml dimethyldichlorosilane in 10 ml ether. The reaction mixture was refluxed for 2.5 h. After cooling to room temperature, the resulting precipitate of lithium chloride was removed by filtration. The filtrate was concentrated in vacuo until the product began to crystallize and then cooled to -80°C for two days. Isolation by filtration gave 19.77 g (50 mmol) (59%) of bis(2-*N,N*-dimethylaminoindenyl)dimethylsilane **3** as white crystals. ¹H-NMR of *rac*-**3** (CDCl_3 , 250 MHz): δ -0.38 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 2.66 (s, 12H, $\text{N}(\text{CH}_3)_2$), 4.02 (s, 2H, $\text{CH}(1\text{-ind})$), 5.64 (s,

2H, $\text{CH}(3\text{-ind})$), 6.92–7.43 (m, 8H, $\text{CH}(4,5,6,7\text{-ind})$); *meso*-**3**: -0.56 (s, 3H, $\text{Si}(\text{CH}_3)_2$), -0.2 (s, 3H, $\text{Si}(\text{CH}_3)_2$), 2.8 (s, 12H, $\text{N}(\text{CH}_3)_2$), 3.95 (s, 2H, $\text{CH}(1\text{-ind})$), 5.71 (s, 2H, $\text{CH}(3\text{-ind})$), 6.92–7.43 (m, 8H, $\text{CH}(4,5,6,7\text{-ind})$).

3.5. Dimethylsilanediybis(2-*N,N*-dimethylaminoindenyl)zirconium dichloride (4)

6.0 g (16 mmol) bis(2-*N,N*-dimethylaminoindenyl)dimethylsilane **3** was dissolved in 100 ml ether, cooled to -30°C and 10 ml of a 1.6 M solution of *n*-BuLi in hexane was quickly added. The cooling bath was removed and the resulting suspension stirred for 2 h at room temperature. 20 ml pentane was added to precipitate all of the ligand dilithium salt. After stirring for 2 h the lithium salt was collected by filtration and dried. 6.03 g (15.5 mmol) of the dilithium compound was isolated, subsequently mixed with 3.7 g (15.9 mmol) zirconium tetrachloride and suspended in 50 ml of toluene. Immediate reaction gave an orange–brown suspension which was stirred for 24 h. The supernatant liquor was then separated by means of a cannula. This solution contained the *meso*:*rac* diastereoisomers in a 3:2 ratio. The remaining solid was extracted with a 30 ml Soxhlett apparatus with toluene for 30 min. The first extract, which still contained some *meso* compound, was added to the mother liquor. Further extraction with fresh toluene for 6 h gave, after removal of the solvent, 2.65 g pure *rac*-**4** (32% theoretical yield). From the mother liquor, the solvent was removed to yield 2.1 g (3.9 mmol) of the ansa-zirconocene **4** (25%, *meso*:*rac* 1:1) (total yield 57%). ¹H-NMR of *rac*-**4** (CDCl_3 , 250 MHz): δ 1.29 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 2.6 (s, 12H, $\text{N}(\text{CH}_3)_2$), 6.4 (s, 2H, $\text{CH}(3\text{-ind})$), 6.6–7.6 (m, 8H, $\text{CH}(4,5,6,7\text{-ind})$); *meso*-**4**: 1.32, 1.36 (2s, 6H, $\text{Si}(\text{CH}_3)_2$), 2.8 (s, 12H, $\text{N}(\text{CH}_3)_2$), 6.4 (s, 2H, $\text{CH}(3\text{-ind})$), 6.6–7.6 (m, 8H, $\text{CH}(4,5,6,7\text{-ind})$). MS (EI) (70 eV, 220°C): m/z 534 (M^+ , 22%), 376 ($\text{M}^+ - \text{C}_9\text{H}_6\text{N}(\text{CH}_3)_2$, 15%). Complex **4** is quite sensitive to air, even as a solid; owing to this air-sensitivity we have not been able to obtain a satisfactory elemental analysis. The ¹H-NMR spectrum of *rac*-**4** showed that this compound does not contain any side products, in particular no *meso* isomer.

3.6. Crystal structure determinations

Crystals of complexes **2** and *rac*-**4** were obtained by slow crystallization from CH_2Cl_2 solutions. Space groups, unit cell dimensions and diffraction intensities were determined on a Syntex/Siemens-P3 four-circle diffractometer. Table 2 summarizes the experimental data for the crystallographic structure determination, Tables 3 and 4 give the atomic position parameters. Additional data are recorded as supplementary material and can be obtained from Fachinformationszentrum

Table 2
Crystallographic and experimental data for complexes **2** and **rac-4**

	2	rac-4
Formula	C ₂₂ H ₂₄ N ₂ ZrCl ₂	C ₂₄ H ₂₈ N ₂ SiZrCl ₂
Formula weight	478.6	534.7
Color, habit	yellow plates	yellow plates
Crystal size (mm ³)	0.3 × 0.3 × 0.1	0.1 × 0.2 × 0.2
Space group ^a	C2/c	C2/c
a (Å)	18.403(4)	16.843(8)
b (Å)	8.207(2)	12.064(11)
c (Å)	14.382(3)	11.715(8)
β (deg)	112.580(10)	92.04(8)
Volume (Å ³)	2005.8(7)	2394(4)
Density (calc.) (g cm ⁻³)	1.585	1.484
Absorption coefficient μ (mm ⁻¹)	0.817	0.739
Temperature (K)	243	248
Weighting scheme	σ ² (F) + 0.0001F ²	σ ² (F) + 0.0006F ²
2θ range (deg)	4.0 to 54.0	4.0 to 40.0
Scan speed (deg min ⁻¹) ^b	2.30–29.30	2.30–14.65
Scan range (deg)	0.70	0.70
Reflections collected	4885	2531
Independent reflections	2197	1113
Observed reflections (F > 4σ(F))	1504	846
Solution (SHELXTL PLUS)	Patterson	Patterson; in Cc
Number of parameters refined	103	137
R _F ^c	4.53	6.08
R _{wF} ^d	4.29	6.59
Goodness-of-fit	1.39	1.56
Residual density 10 ⁻⁶ e Å ⁻³	+0.56 -0.45	+0.72 -1.37

Conditions: Syntex/Siemens-P3 four-circle diffractometer, Mo Kα radiation, 71.073 pm, graphite monochromator.

^a Monoclinic, Z = 4; ^b Wyckoff scan; ^c R_F = Σ||F_o| - |F_c||/Σ|F_cδ|;

^d R_{wF} = [Σw(|F_o| - |F_c||)²/ΣF_o²]^{1/2}.

Karlsruhe, D-76344 Eggenstein-Leopoldshafen 2, upon quotation of the depository number CSD-59262, the names of the authors and the journal reference for this article.

3.7. Electrochemical studies

Cyclovoltammetric measurements were conducted in a cell suitable for air- and moisture-sensitive solutions [15], in THF solutions containing 0.1 mol l⁻¹ of tetrabutyl ammonium hexafluorophosphate as conducting electrolyte and 10⁻³ mol l⁻¹ of the zirconocene complex studied. Potentials were measured at a platinum electrode against an Ag/AgNO₃(sat.) reference electrode at 25°C, with full compensation of the internal

Table 3
Atomic coordinates (×10⁴) and equivalent isotropic displacement coefficients (pm² × 10⁻¹) for complex **2**

Atom	x	y	z	U _{eq}
Zr(1)	0	7457(1)	7500	17(1)
Cl(1)	1059(1)	9477(2)	8159(1)	33(1)
N(1)	-1469(2)	7682(6)	8562(3)	26(1)
C(1)	-644(3)	5528(6)	8256(3)	24(2)
C(2)	-766(3)	7013(6)	8684(3)	24(2)
C(3)	-17(3)	7713(6)	9234(3)	22(2)
C(4)	571(3)	6506(6)	9322(3)	23(2)
C(5)	183(3)	5121(6)	8733(3)	24(2)
C(6)	625(3)	3698(6)	8737(4)	30(1)
C(7)	1417(3)	3717(7)	9282(4)	32(1)
C(8)	1803(3)	5089(7)	9824(4)	35(2)
C(9)	1396(3)	6476(7)	9849(4)	31(2)
C(10)	-1480(3)	9270(6)	8988(4)	32(1)
C(11)	-2182(3)	7021(6)	7830(4)	35(1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

resistance (IR) of the electrolyte solution. All potentials are referenced against the standard potential of the ferrocene/ferrocenium couple (E_{1/2} = -0.12 vs. Ag/AgNO₃).

3.8. Propene polymerizations and polymer analysis

Polymerizations were performed in a thermostated, well-stirred 1 l Büchi reactor. All catalyst components were handled and stored under purified argon. Polymerization grade propene (BASF AG) was used without further purification. Toluene was purified by distillation from sodium and then distilled from TiCl₄/Al(ⁱBu)₃ prior to use. The autoclave was washed with 500 ml of a solution of 5 ml Al(ⁱBu)₃ in 1 l of toluene for 1 h,

Table 4
Atomic coordinates (×10⁴) and equivalent isotropic displacement coefficients (pm² × 10⁻¹) for complex **rac-4**

Atom	x	y	z	U _{eq}
Zr(1)	0	2930(1)	2500	24(1)
Cl(1)	992(2)	4287(2)	2011(3)	42(1)
N(1)	-1761(6)	1488(8)	1778(9)	39(4)
Si(1)	0	198(4)	2500	34(2)
C(1)	-311(7)	1264(10)	1371(10)	29(5)
C(2)	-1057(6)	1854(9)	1307(10)	23(4)
C(3)	-948(7)	2848(10)	716(10)	27(5)
C(4)	187(7)	2830(9)	285(9)	27(5)
C(5)	222(6)	1872(9)	728(10)	23(4)
C(6)	1026(7)	1708(10)	415(10)	33(5)
C(7)	1365(8)	2417(12)	-309(12)	46(5)
C(8)	966(9)	3327(11)	-785(12)	45(6)
C(9)	198(8)	3548(10)	-480(11)	36(5)
C(10)	-2070(8)	480(11)	1199(13)	62(7)
C(11)	-2399(8)	2293(11)	1873(12)	57(6)
C(12)	789(8)	-714(10)	1951(12)	55(6)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

dried in vacuo for 2 h and then filled with 300 ml of toluene. A catalyst solution consisting of 5 ml of a 10 wt.% solution of MAO and 6.25 μmol *rac*-4 in 50 ml of toluene was transferred to the autoclave by means of a cannula and preincubated for 30 min at 50°C. At this temperature, propene was then added and kept at a constant pressure of 2 bar by means of an electronically controlled magnetic valve. The final zirconocene concentration was 15.625 $\mu\text{mol l}^{-1}$, with a ratio Al/Zr of 1200.

The reaction was stopped by venting excess propene and precipitating the polymer in 1 l of methanol containing 10 ml of conc. HCl. The precipitated polymer was collected by filtration, washed with methanol until neutral and dried at ambient temperature.

NMR spectra were recorded from solutions of 110–120 mg of polymer in 0.4 ml $\text{C}_2\text{D}_2\text{Cl}_4$ at 395 K on a Bruker AC-250 FT spectrometer. ^{13}C -NMR spectra were recorded at 63 MHz with a 45° pulse angle, 2.0 s acquisition time and 20 000–30 000 scans.

Melting points were determined by DSC. Polymer molar masses and molar mass distributions were determined by GPC against polystyrene standards.

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