ansa-Metallocene Derivatives. 27. Chiral Zirconocene Complexes with Two Dimethylsilylene Bridges[1]

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Doubly bridged zirconocene derivatives with C_2 symmetrically disposed substituents, $((CH_3)_2Si)_2$(3,4-dimethyl-1,2-cyclopentadienediyl)$_2ZrCl_2$ (4A) and $((CH_3)_2Si)_2$(4,5,6,7-tetrahydro-1,2-indenediyl)$_2ZrCl_2$ (4B) were synthesized by reactions of the corresponding ligand dilithium salts with $ZrCl_4$ in toluene; the racemic isomers were obtained by fractionated crystallization of the diastereomeric product mixtures. X-ray diffraction studies give space group $P\bar{1}$ with a = 9.596 (5) Å b = 13.160(7) Å, c = 16.645 (9) Å, α = 96.60 (4)°, β = 90.33 (4)°, γ = 98.66 (4)°, and Z = 4 (two crystallographically independent molecules) for 4A and space group $P2_1/n$ with a = 9.994 (4) Å, b = 15.040(6) Å, c = 15.078(8) Å, β = 95.09(4)°, and Z = 4 for 4B. Both complexes show the expected C_2-axial symmetry. In combination with methylalumoxane, 4A and 4B are slowly converted to catalysts for the polymerization of propene, which yield polymers with low and medium isotacticities, respectively. Control experiments indicate that conversion of these complexes to active catalysts involves degradation of their strained ligand frameworks; intact 4A and 4B do not appear to give rise to catalytic activity.

Introduction

Studies on the structures of *ansa*-metallocene complexes and on their properties as catalysts for α-olefin polymerization[2] have led to the question whether these properties might be affected by a facile "consymmetric" rotation of the metallocene ligand framework around the metal–C_5 ring centroid axes.[3] We were therefore interested in the synthesis of chiral *ansa*-metallocenes with two interannular bridging units, since an increased stereorigidity is to be expected for complexes of this kind.

Multiply bridged but otherwise unsubstituted cyclopentadienyl compounds[4-6] and some of the their metal complexes[6c,7] have been investigated in recent years from different perspectives. Bercaw and Bulls have prepared a zirconocene complex with two Me_2Si bridges, $((CH_3)_2Si)_2$(4-*tert*-butyl-1,2-cyclopentadienediyl)$_2ZrCl_2$, from *tert*-butylcyclopentadiene by repeated deprotonation and reaction with $(CH_3)_2SiCl_2$ and subsequent complexation of the ligand dianion with $ZrCl_4$.[8] In accord with expectations, an achiral, C_{2v}-symmetric structure was found for this complex, since its *tert*-butyl substituents are placed in the mirror plane which bisects the $ZrCl_2$ angle.[8] Here, we report syntheses and crystal structures of doubly Me_2Si bridged zirconocene complexes which are chiral by virtue of carrying two C_2 symmetrically disposed, vicinal substituents at each C_5 ring.

Results and Discussion

The anions of 1,2-dimethylcyclopentadiene (**1A**) and of 4,5,6,7-tetrahydroindene (**1B**), which were obtained (with some modifications; see Experimental Section) by previously published procedures,[9-11] were converted—via the singly bridged intermediates **2A** and **2B** and subsequent introduction of a second Me_2Si bridge—to the doubly Me_2Si bridged ligand compounds **3A** and **3B** (Scheme I). Compounds **3A** and **3B** were obtained, in ca. 50% and 90% theoretical yield, as crystalline and oily materials, respectively. ^1H NMR spectra of these compounds (see Experimental Section) indicated that the racemic isomers *rac*-**3A** and *rac*-**3B** are the predominant products.[12] If one assumes that the single Me_2Si bridge in **2A** and **2B** is preferably placed in a position β to both ring substituents, reaction with a second Me_2SiCl_2 unit would primarily generate the meso isomers of **3A** and **3B**. Silatropic shifts, which have been shown, by work in the groups of Jutzi[5]

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[12] For ligand **3A**, the racemic isomer was obtained immediately from the workup procedure described; for ligand **3B**, conversion to the predominant final product rac-**3B** occurred in the course of 1–2 days at room temperature.

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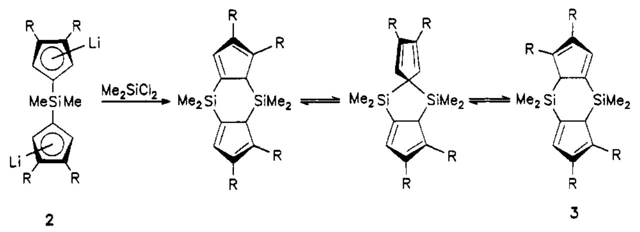
Scheme I



A: R,R = $-CH_3$, $-CH_3$

B: R,R = $-CH_2-CH_2-CH_2-CH_2-$

and Köhler,[6] to proceed relatively rapidly in related silyl-substituted cyclopentadienyl derivatives, are then likely to convert the primary products *meso*-**3A** and *meso*-**3B** to their racemic isomers by way of an ipso-bridged spiro intermediate (cf. Scheme I).

Reaction of the dilithium salts of **3A** and **3B** with $ZrCl_4$ in toluene at room temperature (see Experimental Section) afforded the zirconocene complexes **4A** and **4B**, in roughly 15 and 25% total yield, respectively. ^1H NMR spectra of the crude reaction products indicated the presence of two metallocene complexes, presumably the respective racemic and meso isomers, in ratios of 3:1 (**4A**) and 3:2 (**4B**). From these product mixtures, the racemic complexes were obtained by diffusion-induced, fractional crystallization. After three to four crystallizations, pure *rac*-**4A** and *rac*-**4B** were obtained in crystalline form. Crystal structures (Figure 1, Table I) and ^1H NMR spectra determined for these compounds (Table II) are largely in accord with expectation.

Noteworthy is an unusually large dihedral angle of 72–73° between the mean planes of the eclipsed C_5 rings in each complex. These ring inclination angles exceed those observed in related complexes with a single dimethylsilylene bridge[13] by 10–12°. This strong ring inclination is connected with Zr–C distances which differ by more than 20 pm and, hence, with a deviation of each Zr–centroid line from the normal on the respective C_5-ring mean plane by ca. 8°. The bending of Si–C bonds out of the mean plane of the adjacent C_5 ring, 18.4–19.9°, is not much greater, however, than in singly Me_2Si bridged zirconocenes (17.4–18.4°).[13]

Due to the particular eclipsed C_5-ring conformation in these complexes, one substituent at each ring is placed close to the meridional plane which bisects the Cl–Zr–Cl angle.[14] The second substituent is oriented in such a way that both molecules, although not situated on a crystallographic C_2 axis, conform quite closely to the expected C_2 symmetry.

We have further investigated the catalytic properties of **4A** and **4B** in methylalumoxane-activated propene polymerization. When **4A** or **4B** (ca. 1.6×10^{-5} M in toluene solution) is combined with methylalumoxane (MAO) in an Al:Zr ratio of 1200:1 catalytic propene polymerization is observed, which is, however, peculiar in several regards: The isotacticities of the resulting polymers (38 and 80% mmmm, respectively) are much lower than those obtained with comparably substituted, singly bridged zirconocenes.[2b,d] The polymer obtained with **4A** is, in fact, an oily wax rather than a solid.

Even more unusual is the time course of these polymerizations: Normally, *ansa*-zirconocene/MAO systems reach a maximum of productivity immediately after mixing the zirconocene and MAO components; activities then decline over the course of several hours.[15] Quite in contrast to this, the activity of the present catalyst systems is almost nil in the first 10–30 min; it then increases substantially over the course of several hours. This prolonged lag phase indicates that the complexes are slowly transformed into some secondary products, which then act as the catalyst proper or are rapidly converted to it. After prolonged reaction times (>16 h), activities decline again.

In order to assess the stability of these complexes under catalysis conditions, we have incubated 5–10-mg samples of **4A** and **4B** and of the singly bridged complex $Me_2Si(2\text{-}Me\text{-}4\text{-}^tBu\text{-}1\text{-}C_5H_2)_2ZrCl_2$[13] with 5 mL of a 10% solution of MAO in toluene (Al:Zr $\approx$ 300) for ca. 8 h at 50 °C. The solutions were then slowly hydrolyzed at −78 °C with HCl/CH_3OH and their evaporation residues extracted with $CDCl_3$.

For the singly bridged $Me_2Si(2\text{-}Me\text{-}4\text{-}^tBu\text{-}1\text{-}C_5H_2)_2ZrCl_2$ the ^1H NMR spectrum of the recovered product showed practically exclusively the signals of intact, regenerated starting material with only traces of signals due to other products. For **4A** and **4B**, however, the original complex accounts for only about half of the total ^1H NMR intensity of the recovered material, while additional broad signals, mainly between 1.2 and 1.6 ppm, represent comparable contributions to the total ^1H NMR intensity. While we have not been able to further characterize these additional materials, it is evident that substantial portions of **4A** and **4B** suffer degradation of their ligand frameworks when exposed to methylalumoxane.

The strong distortions in the Zr–C_5 ring bonding apparent in the structures of **4A** and **4B** appear to make these complexes more susceptible to degradation by MAO than their singly bridged analogs. If the degradation products were to retain one of their two Me_2Si bridges, or one of their two η^5-C_5-ring ligands, the still-chiral ligand geometry of these secondary products could give rise to the observed isotacticities of the resulting polymers.

It is not immediately apparent why the intact ligand structures of complexes **4A** and **4B** should not be compatible with their effective activation for olefin polymerization catalysis. We note here that we have recently observed a similarly unexpected, total inactivity with respect to MAO-activated propene polymerization for chiral, biphenyl-bridged zirconocenes.[1] Possible factors responsible for the lack of catalytic activity in these and other related cases[2c] are to be the subject of a separate analysis.

Experimental Section

1,2-Dimethylcyclopentadiene. The procedure reported by Schmitt[9] was modified in that dimethylcyclopentenone (**8**) was reduced with diisobutylaluminum hydride instead of $LiAlH_4$; dehydration of dimethylcyclopentenol (**9**) was furthermore induced by treatment with I_2 in diethyl ether, as proposed by Doll.[10] In this manner, 1,2-dimethylcyclopentadiene (**1A**) was obtained from crotonic acid isopropyl ester in an overall yield of about 30% (Scheme II).

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(14) Similar eclipsed conformations of bridged C_5 rings and similar orientations of ring substituents were recently observed in biphenyl-bridged titanocene and zirconocene complexes.[1]

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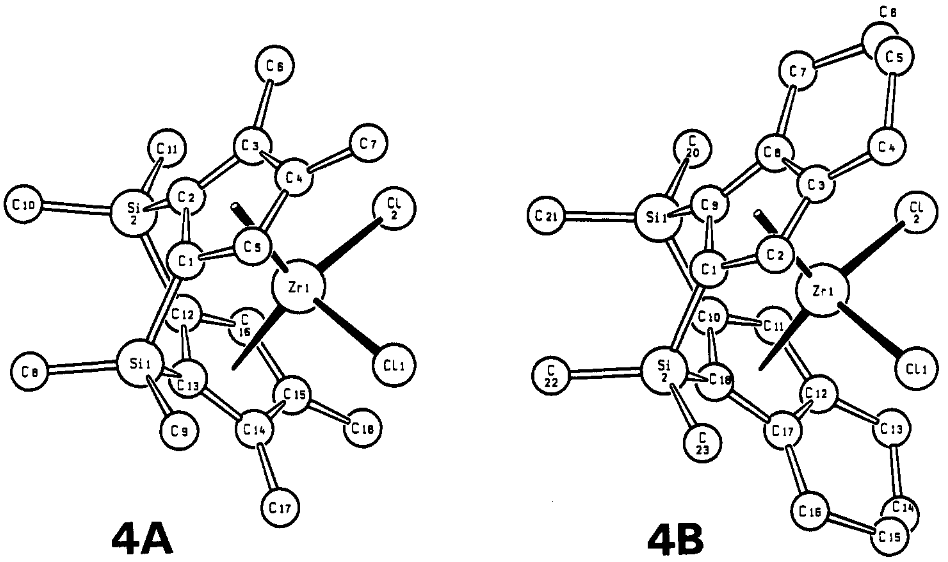


Figure 1. Structures of the bis(dimethylsilylene)-bridged complexes 4A (left) and 4B (right) as analyzed by X-ray diffraction.

Table I. Selected Distances (pm) and Angles (deg) for the Bis(dimethylsilylene)-Bridged Complexes 4A and 4B

4A[a]		4B	
Zr(1)–Cl(1)	243.8(3)	Zr(1)–Cl(1)	243.5(2)
Zr(1)–Cl(2)	244.0(3)	Zr(1)–Cl(2)	243.1(2)
Zr(1)–C(1)	243.3(10)	Zr(1)–C(1)	242.6(5)
Zr(1)–C(2)	243.3(9)	Zr(1)–C(9)	242.0(4)
Zr(1)–C(3)	259.3(9)	Zr(1)–C(8)	259.1(4)
Zr(1)–C(4)	264.0(9)	Zr(1)–C(3)	265.6(5)
Zr(1)–C(5)	253.6(9)	Zr(1)–C(2)	255.3(5)
Zr(1)–C(12)	241.6(9)	Zr(1)–C(10)	241.5(5)
Zr(1)–C(13)	241.8(8)	Zr(1)–C(18)	241.2(5)
Zr(1)–C(14)	260.0(8)	Zr(1)–C(17)	259.7(5)
Zr(1)–C(15)	264.7(8)	Zr(1)–C(12)	266.5(5)
Zr(1)–C(16)	253.7(9)	Zr(1)–C(11)	256.2(5)
Cl(1)–Zr(1)–Cl(2)	98.7(1)	Cl(1)–Zr(1)–Cl(2)	99.7(1)
CR(1)–Zr(1)–CR(2)[b]	121.8	CR(1)–Zr(1)–CR(2)[b]	122.5
PL(1)–PL(2)[c]	72.1	PL(1)–PL(2)[c]	72.9
C(1)–Si(1)–C(13)	92.9(4)	C(9)–Si(1)–C(10)	92.1(2)
C(2)–Si(2)–C(12)	92.4(4)	C(1)–Si(2)–C(18)	93.1(2)
C(8)–Si(1)–C(9)	106.5(5)	C(20)–Si(1)–C(21)	107.8(2)
C(10)–Si(2)–C(11)	108.7(6)	C(22)–Si(2)–C(23)	109.1(2)

[a] Corresponding distances and angles for the second molecule of **4A** agree with those given here, generally within standard deviations. [b] CR(1) and CR(2) denote the centroids of lower and higher numbered C_5 rings, respectively. [c] PL(1) and PL(2) denote the mean planes of lower and higher numbered C_5 rings, respectively.

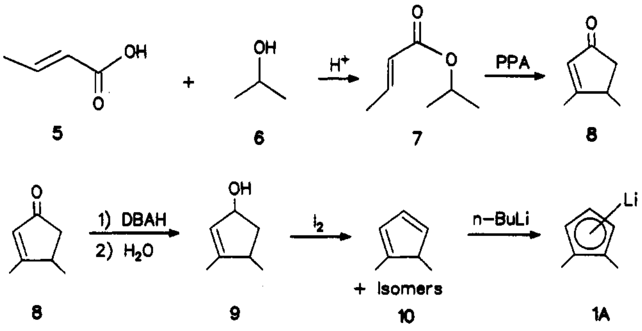
Table II. ^{1}H NMR Data for the Bis(dimethylsilylene)-Bridged Metallocenes *rac*-4A, *meso*-4A, *rac*-4B, and *meso*-4B in $CDCl_3$ and C_6D_6 Solution at Room Temperature[a]

rac-**4A** (C_6D_6)	*rac*-**4A** ($CDCl_3$)	*meso*-**4A** ($CDCl_3$)	assignt
0.32 (s, 6)	0.51 (s, 6)	0.48 (s, 3)	Si(C*H*$_3$)
0.55 (s, 6)	0.84 (s, 6)	0.55 (s, 3)	Si(C*H*$_3$)
		0.85 (s, 6)	Si(C*H*$_3$)
2.03 (s, 6)	2.08 (s, 6)	2.10 (s, 12)	C_5(C*H*$_3$)
2.04 (s, 6)	2.11 (s, 6)		C_5(C*H*$_3$)
6.46 (s, 2)	6.51 (s, 2)	6.48 (s, 2)	C_5*H*

rac-**4B** (C_6D_6)	*rac*-**4B** ($CDCl_3$)	*meso*-**4B** ($CDCl_3$)	assignt
0.32 (s, 6)	0.47 (s, 6)	0.46 (s, 3)	Si(C*H*$_3$)
0.60 (s, 6)	0.84 (s, 6)	0.47 (s, 3)	Si(C*H*$_3$)
		0.83 (s, 3)	Si(C*H*$_3$)
		0.84 (s, 3)	Si(C*H*$_3$)
1.29–2.96 (m, 16)	1.45–2.85 (m, 16)	1.25–2.90 (m, 16)	C_5(C_4*H*$_8$)
6.52 (s, 2)	6.57 (s, 2)	6.49 (s, 2)	C_5*H*

[a] Conditions and legend: internal standard TMS; δ in ppm at 250 MHz; s = singlet, m = multiplet.

Scheme II



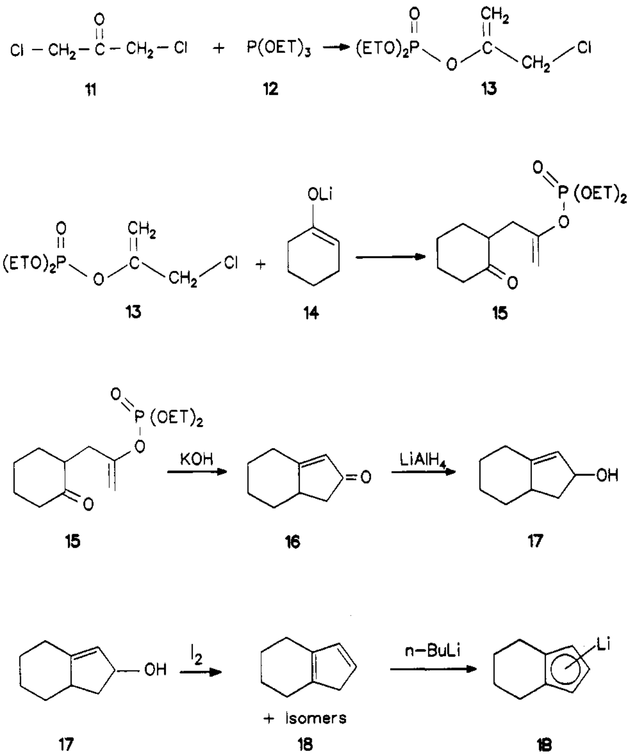
4,5,6,7-Tetrahydroindene. The hexahydroinden-2-one (**16**) was prepared as described by Welch et al.[11] (cf. Scheme III). As we found it impossible to free this compound from side products of the preceding condensation step by distillation, the distilled raw product was converted, without any intervening purification steps, to hexahydro(2*H*)indenol (**17**), by reduction with $LiAlH_4$ in refluxing diethyl ether; **17** was dehydrated to tetrahydroindene (**18**) by treatment with iodine in diethyl ether at room temperature (2 h). A solution of **18** in dry pentane was rapidly filtered through a short silica column. Treatment with *n*-butyllithium under exclusion of air at 0 °C precipitated the lithium salt of 4,5,6,7-tetrahydroindene (**1B**; 6% theoretical yield, based on **14**). A small sample of pure **18** was obtained by hydrolysis of the dilithium salt: MS (EI) *m/z* 120 (M^+); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.67–1.71 (4H, m), 2.26–2.32 (4H, m), 2.84 (2H, d, 1.4 Hz), 6.22 (1H, d, 5.4 Hz), 6.32 (1H, d, 5.4 Hz).

All subsequent reactions were carried out under an inert-gas atmosphere, with solvents thoroughly dried, to exclude all traces of moisture or air.

Ligand 3A. A solution of 7.4 g (78 mmol) of 1,2-dimethylcyclopentadiene in 100 mL of THF was treated at −50 °C with 44 mL of a 1.6 M solution of *n*-butyllithium in hexane. After the resulting suspension was warmed to room temperature, 4.4 g (34 mmol) of dimethyldichlorosilane was added at once and the reaction mixture stirred overnight. After addition of 100 mL of diethyl ether, the organic phase was washed twice with 50 mL of saturated aqueous NH_4Cl solution and once with water, dried over $MgSO_4$, and evaporated to dryness.

The brown oil thus obtained was dissolved in 100 mL of pentane and treated with 42.5 mL of a 1.6 M solution of *n*-butyllithium in hexane for 2 h at room temperature. The resulting suspension was evaporated to half its volume; the dilithium salt of **2A** was collected by filtration, washed with 10 mL of pentane, and dried in vacuo: yield 8.7 g (34 mmol, 86% of theory).

Scheme III



A solution of the total amount of this dilithium salt in 60 mL of THF was treated with 4.2 g (32.5 mmol) of dimethyldichlorosilane at 20 °C and stirred for 45 min. The resulting suspension was evaporated to a volume of 10 mL, treated with 80 mL of pentane, and filtered over a short column of Kieselguhr, and the solid residue was washed twice with 20-mL portions of pentane. When the combined filtrate and washings were evaporated to 20 mL and cooled to −80 °C overnight, **3A** precipitated in the form of colorless needles which were collected by filtration and dried in vacuo: yield 4.8 g (16 mmol, 49% of theory); MS (EI) *m/z* 300 (M^+), 285 ($M^+ - CH_3$), 150 ($M/2^+$); ^1H NMR (250 MHz, $CDCl_3$, −50 °C) δ −0.52 (6H, s), 0.48 (6H, s), 1.92 (6H, s), 2.00 (6H, s), 3.25 (2H, s), 6.76 (2H, s), as expected for *rac*-**3A**.

Ligand 3B. A procedure analogous to the preceding one, starting with 7.2 g (57 mmol) of the lithium salt of 4,5,6,7-tetrahydroindene, led to 8.0 g (26 mmol, 94% of theory) of the dilithium salt of **2B**. Treatment of this compound with $(CH_3)_2SiCl_2$, as described above, gave 8.4 g of **3B** as a yellow oil (24 mmol, 92% theoretical yield), which had to be freed of pentane by evaporation in vacuo: MS (EI) *m/z* 352 (M^+); ^1H NMR (250 MHz, $CDCl_3$, 20 °C) δ −0.45 (6H, s), 0.48 (6H, s), 1.60–1.76 (8H, m), 2.39–2.55 (8H, m), 3.19 (2H, d, 1.1 Hz), 6.75 (2H, d, 1.1 Hz), as expected for *rac*-**3B**.

The dilithium salt of this compound was obtained by treatment of 8.4 g of **3B**, dissolved in 50 mL of pentane, with 30 mL of a 1.6 M solution of *n*-butyllithium in hexane at 0 °C. Filtering, washing with two 10-mL portions of pentane, and drying in vacuo gave 6.9 g (19 mmol, 79% of theory) of the dilithium slat.

Complex 4A. A solution of 4.8 g (16 mmol) of **3A** in 80 mL of pentane was treated at −20 °C with 12.8 mL of a 1.6 M solution of *n*-butyllithium in hexane, warmed to room temperature, and stirred overnight. The dilithium salt of **3A** was collected, as a viscous oil, by evaporation of the reaction mixture to dryness. After addition of 60 mL of toluene and 4 g (17.2 mmol) of $ZrCl_4$, the brown suspension was stirred for 6 h and evaporated to dryness and the solid residue extracted with three 100-mL portions of pentane. When the combined pentane solutions were evaporated to about 10 mL, a yellow solid deposited, which was collected by filtration, washed with a small volume of pentane, and dried in vacuo: yield 0.98 g (2.13 mmol, 13.5% of theory). The ^1H NMR spectrum indicated the presence of a 3.5:1 mixture of *rac*-**4A** and some other isomer, presumably its meso diastereomer. The racemic isomer was purified by diffusion-induced recrystallization from toluene/pentane. When this procedure was repeated three more times, 91 mg of pure, crystalline racemate was obtained: MS (EI) *m/z* 460 (M^+), 445 ($M^+ - CH_3$), 300 ($M^+ - ZrCl_2$), 285 ($M^+ - ZrCl_2 - CH_3$); ^1H NMR, see Table II. Anal. Calcd for $C_{18}H_{16}Cl_2Si_2Zr$: C, 46.93; H, 5.69. Found: C, 46.58; H, 5.60.

Table III. Crystallographic and Experimental Data for Complexes 4A and 4B[a]

	4A	4B
formula	$C_{18}H_{26}Cl_2Si_2Zr$	$C_{22}H_{30}Cl_2Si_2Zr$
fw	460.7	512.8
cryst color; form	yellow; near-cubic prism	yellow; near-cubic prism
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (pm)	959.6(5)	999.4(4)
b (pm)	1316.0(7)	1504.0(6)
c (pm)	1664.5(9)	1507.8(8)
α (deg)	96.60(4)	
β (deg)	90.33(4)	95.09(4)
γ (deg)	98.66(4)	
V (10^6 pm^3)	2064(2)	2257(2)
d_{calcd} (g/cm^3)	1.48	1.51
Z	4	4
cryst dimens (mm)	0.2 × 0.2 × 0.2	0.3 × 0.3 × 0.3
abs coeff (μ) (cm^{-1})	8.97	8.28
T (K)	296	243
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0011F^2$	$w^{-1} = \sigma^2(F) + 0.0009F^2$
scan mode	Wyckoff	Wyckoff
scan range (deg)	0.8	0.8
2θ range (deg)	4.0–52.0	4.0–54.0
scan speed (deg/min)	2.3–29.3	2.0–29.3
no. of data collected	8546	5452
no. of indep data	8034	4874
no. of unique data	5099	4060
observn criterion	$F > 3.0\sigma(F)$	$F > 4.0\sigma(F)$
no. of params	412	244
R_F[b]	0.082	0.052
R_{wF}[c]	0.093	0.074
residual density (10^{-6} e/pm^3)	0.96	0.83

[a] Conditions: Syntex/Siemens-P3 four-circle diffractometer, Mo Kα radiation (71.073 pm), graphite monochromator. [b] $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_c\delta|$. [c] $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{1/2}$.

Complex 4B. An analogous procedure was employed, starting from 6.9 g (19 mmol) of the dilithium salt of **3B**; this yielded 2.6 g (5.1 mmol, 27% of theory) of a 3:2 mixture of *rac*-**4B**, presumably with the isomer *meso*-**4B**. Repeated diffusion-induced recrystallization gave 0.6 g of pure, crystalline *rac*-**4B**: MS (EI) *m/z* 512 (M^+), 474 ($M^+ - HCl$); ^1H NMR, see Table II. Anal. Calcd for $C_{22}H_{30}Cl_2Si_2Zr$: C, 51.50; H, 5.90. Found: C, 51.04; H, 5.56.

^1H NMR data assignable to the second, probably meso-configurated complex isomers, observed in the primarily obtained product mixture, are also listed in Table II.

Crystal and Molecular Structures of Complexes 4A and 4B. Crystals of **4A** and **4B** were obtained by diffusion-induced crystallization from toluene/pentane solutions at 4 °C and sealed in thin-walled capillaries. Crystals of **4B** suitable for an X-ray structure determination were thus obtained. For most of the crystals of **4A** studied, however, twinning was indicated by their reflection profiles. After an extensive search, crystals of reasonable quality, although with a still somewhat broadened reflection profile, were finally identified. The crystals were cut into near-cubic shape to minimize absorption anisotropies. Crystallographic and experimental data for both complexes are summarized in Table III. For solution and refinement, the data were used without absorption corrections.

The structures were solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. The hydrogen atoms were calculated in idealized positions and included in the refinement (riding model). Structural parameters obtained for **4A** and **4B** are represented in Tables IV and V.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (pm^2 × 10^{-1}) for Complex 4A

	x	*y*	*z*	*U*(eq)[a]
Zr(1)	9694(1)	2952(1)	6420(1)	41(1)
Si(1)	11853(3)	2164(2)	7585(2)	46(1)
Si(2)	12742(3)	2832(2)	5666(2)	52(1)
Cl(1)	7719(3)	2818(2)	7337(2)	58(1)
Cl(2)	8555(3)	3583(2)	5302(2)	68(1)
C(1)	10923(10)	1512(6)	6627(5)	41(3)
C(2)	11233(10)	1784(7)	5810(5)	42(3)
C(3)	9986(11)	1434(7)	5326(5)	51(4)
C(4)	8911(10)	1007(7)	5808(6)	46(3)
C(5)	9513(10)	1049(6)	6597(6)	46(3)
C(6)	9807(12)	1445(9)	4418(6)	67(4)
C(7)	7424(12)	552(9)	5538(7)	74(5)
C(8)	13650(11)	1901(8)	7791(7)	71(5)
C(9)	10796(12)	1811(8)	8453(6)	63(4)
C(10)	14482(13)	2409(10)	5732(7)	83(5)
C(11)	12630(15)	3438(10)	4718(6)	90(6)
C(12)	12137(10)	3748(6)	6501(5)	44(3)
C(13)	11736(9)	3489(7)	7311(5)	41(3)
C(14)	10870(9)	4236(7)	7623(5)	43(3)
C(15)	10666(11)	4880(7)	7024(6)	50(4)
C(16)	11446(11)	4587(7)	6355(6)	52(4)
C(17)	10296(11)	4360(8)	8464(6)	58(4)
C(18)	9811(12)	5754(7)	7093(7)	71(5)
Zr(2)	4335(1)	2505(1)	1524(1)	44(1)
Si(3)	7266(3)	2720(2)	595(2)	50(1)
Si(4)	6746(3)	1510(2)	2340(2)	50(1)
Cl(3)	3013(3)	3359(2)	617(2)	73(1)
Cl(4)	2509(3)	2076(3)	2490(2)	76(1)
C(21)	5886(10)	1565(7)	686(5)	48(3)
C(22)	5623(10)	1030(6)	1408(5)	45(3)
C(23)	4197(10)	507(7)	1328(6)	49(4)
C(24)	3561(11)	737(7)	612(6)	53(4)
C(25)	4619(11)	1345(7)	222(6)	52(4)
C(26)	3452(12)	−237(8)	1862(7)	71(5)
C(27)	2064(11)	364(8)	309(7)	72(5)
C(28)	9143(12)	2539(8)	567(7)	72(5)
C(29)	6856(12)	3308(9)	−329(6)	72(5)
C(30)	8563(11)	1171(8)	2284(7)	65(4)
C(31)	5968(12)	1122(9)	3297(6)	71(5)
C(32)	6545(9)	2893(7)	2278(5)	44(3)
C(33)	6709(9)	3426(6)	1566(5)	42(3)
C(34)	5932(10)	4278(6)	1671(6)	45(3)
C(35)	5251(11)	4263(8)	2428(6)	54(4)
C(36)	5651(10)	3442(7)	2796(6)	52(4)
C(37)	5882(9)	5114(6)	1144(5)	78(5)
C(38)	4320	5017	2771	83(5)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Propene Polymerization Studies. Polymerizations were carried out under Ar in solutions of methylalumoxane (0.45 g, 7.6 mmol of $(CH_3AlO)_n$, Schering AG, mean molecular weight 900) in 400 mL of dry toluene containing 6.25 × 10^{-6} mol (ca. 3 mg) of **4A** and **4B**, respectively, under 2 bar of propene. Relative rates of propene uptake were estimated by determining the rate at which the propene pressure dropped upon intermittent shutoff of the propene supply and by following the increase in total volume of the reaction solution. By both criteria, we observe catalytic activities which are close to nil during the initial 10–30 min but increase steadily over reaction periods of 2–8 h.

Table V. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (pm^2 × 10^{-1}) for Complex 4B

	x	*y*	*z*	*U*(eq)[a]
Zr(1)	−910.5(4)	−1656.6(3)	−2982.2(2)	28(1)
Cl(1)	1507(1)	−1455(1)	−2982(1)	45(1)
Cl(2)	−1476(1)	−1961(1)	−4554(1)	42(1)
Si(1)	−3871(1)	−1770(1)	−2324(1)	35(1)
C(20)	−4935(5)	−2104(4)	−3342(3)	49(2)
C(21)	−4980(5)	−1679(4)	−1397(4)	51(2)
Si(2)	−1014(1)	−1401(1)	−889(1)	39(1)
C(22)	−2086(6)	−1397(4)	76(3)	55(2)
C(23)	764(5)	−1150(4)	−470(3)	53(2)
C(1)	−1561(4)	−641(3)	−1846(3)	34(1)
C(2)	−672(4)	−104(3)	−2303(3)	36(1)
C(3)	−1247(4)	87(3)	−3175(3)	31(1)
C(4)	−670(5)	647(3)	−3866(3)	40(1)
C(5)	−1761(5)	948(4)	−4574(3)	52(2)
C(6)	−2727(6)	241(4)	−4868(3)	53(2)
C(7)	−3464(4)	−168(3)	−4108(3)	38(1)
C(8)	−2516(4)	−315(3)	−3274(3)	30(1)
C(9)	−2747(4)	−797(3)	−2480(3)	30(1)
C(10)	−2410(4)	−2558(3)	−2188(3)	34(1)
C(11)	−2103(4)	−3155(3)	−2865(3)	36(1)
C(12)	−739(5)	−3409(3)	−2732(3)	36(1)
C(13)	19(5)	−4051(3)	−3280(3)	46(2)
C(14)	1209(6)	−4405(5)	−2731(5)	72(2)
C(15)	1988(6)	−3744(5)	−2209(5)	77(3)
C(16)	1218(5)	−3197(4)	−1564(4)	47(2)
C(17)	−167(4)	−2987(3)	−1956(3)	38(1)
C(18)	−1172(4)	−2424(3)	−1603(3)	34(1)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

^{13}C NMR spectra of the polymers obtained were measured at 120 °C in solutions containing 120–150 mg of polymer in 0.4 mL of $C_2D_2Cl_4$, on a Bruker AC-250 FT spectrometer, and analyzed by known methods.[16]

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Supplementary Material Available: Tables of crystal data and data collection and refinement details, bond distances and angles, anisotropic thermal parameters, H atom coordinates, and dihedral angles and deviations from planarity of the cyclopentadienyl rings for **4A** and **4B** (19 pages). Ordering information is given on any current masthead page.

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