Synthesis, Molecular Structure, and Racemate−Meso Interconversion for *rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2MCl_2$ (M = Ti and Zr)

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Received June 18, 1998

Doubly [SiMe$_2$]-bridged group IV metallocenes, *rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2MCl_2$ (M = Ti, Zr), have been synthesized, and a crystal structure of *rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2TiCl_2$ has been determined by X-ray diffraction methods. Racemate−meso interchange occurs in benzene solution just above room temperature, affording an approximately 1:1 mixture of *rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2TiCl_2$ and *meso*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2TiCl_2$. Measurements of the kinetics of the approach to equilibrium reveal $\Delta H^\ddagger = 18(1)$ kcal·mol^{-1} and $\Delta S^\ddagger = -7(2)$ eu. The corresponding zirconium compound is configurationally stable.

Introduction

Ziegler−Natta catalysts based on group IV metallocenes and promoters such as methylaluminoxane (MAO) are industrially attractive for α-olefin polymerization, since they combine the attributes of high activity and stereoselectivity with a single type of catalytic site that produces a uniform polymer microstructure and molecular weight distribution.[1] The ligand geometry strongly influences the microstructure of polymers produced by these types of catalysts: stereorigid chiral, C_2-symmetric singly bridged *ansa*-metallocenes produce isotactic polypropylenes,[2] while achiral catalysts have been employed to produce syndiotactic[3] and atactic[4] polypropylenes. Waymouth and co-workers have reported that unbridged metallocene catalysts may yield elastomeric atactic−isotactic stereoblock polypropylene, presumably due to their ability to isomerize between chiral (*rac*-like) and achiral (*meso*-like) coordination geometries during chain growth.[5]

Doubly bridged group IV metallocene catalysts represent a new class of stereorigid metallocene catalysts for stereospecific α-olefin polymerization.[6] Our group reported doubly [SiMe$_2$]-linked, C_s-symmetric $(Me_2Si)_2\{\eta^5\text{-}C_5H_2\text{-}4\text{-}CHMe_2\}\{\eta^5\text{-}C_5H\text{-}3,5\text{-}(CHMe_2)_2\}ZrCl_2$ and MAO produce highly syndiotactic polypropylene (*rrrr*% > 98.9).[7] The corresponding titanium catalyst system $(Me_2Si)_2\{\eta^5\text{-}C_5H_2\text{-}4\text{-}CHMe_2\}\{\eta^5\text{-}C_5H\text{-}3,5\text{-}(CHMe_2)_2\}TiCl_2$/MAO produces essentially atactic polypropylene.[8]

In this article we report the preparation and crystal structure of doubly [SiMe$_2$]-linked *rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2MCl_2$ (M = Zr, Ti). For the titanium complex we have discovered a very unusual racemate-to-meso interconversion, the first example, so far as we are aware, of a process that requires the metal to switch

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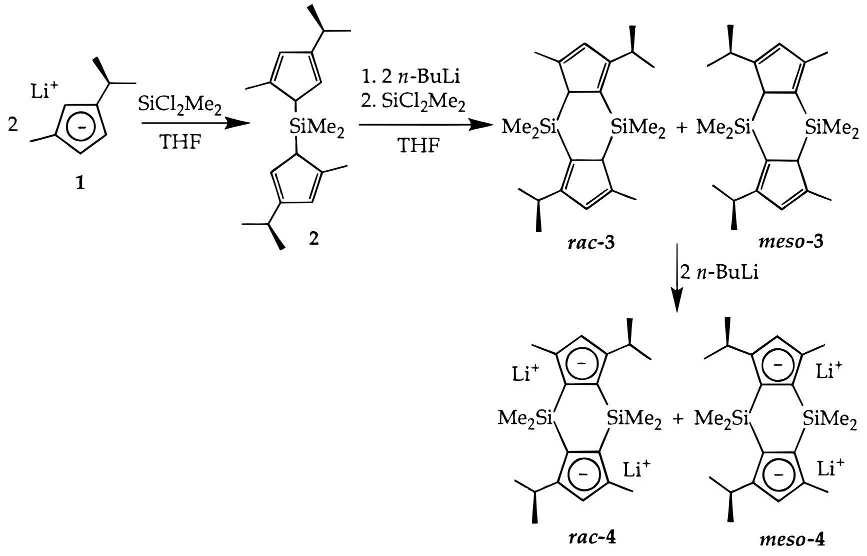
10.1021/om980505m CCC: $15.00
Publication on Web 11/11/1998

Scheme 1



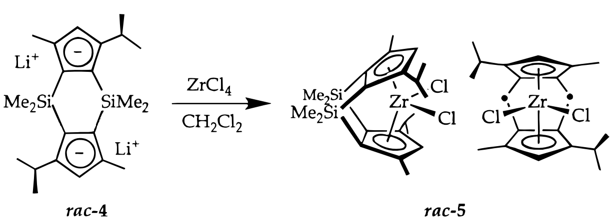
coordination between the different faces of one of the cyclopentadienyl ligands of a doubly linked *ansa*-metallocene.

Results and Discussion

Preparation of *rac*-$(Me_2Si)_2\{\eta^5$-C_5H-3-$(CHMe_2)$-5-$Me\}_2MCl_2$ (M = Zr, Ti) and X-ray Crystal Structure of *rac*-$(Me_2Si)_2\{\eta^5$-C_5H-3-$(CHMe_2)$-5-$Me\}_2TiCl_2$. The dilithio salts of the doubly [$SiMe_2$]-linked ligand used in this study are prepared as shown in Scheme 1.

Thus, singly [$SiMe_2$]-bridged bis(2-methyl-4-isopropylcyclopentadiene) (**2**) is prepared by the reaction of dimethyldichlorosilane with 2 equiv of lithium 1-isopropyl-3-methylcyclopentadienide (**1**). Conversion to the dilithio salt by reaction with 2 equiv of *n*-butyllithium in tetrahydrofuran and treatment with a second equivalent of dimethyldichlorosilane at −78 °C yields the doubly [$SiMe_2$]-bridged bis(3-isopropyl-5-methylcyclopentadienes) (**3**), which are obtained after vacuum distillation as mixture of isomers (racemate:meso = ca. 1:1). Deprotonation of the mixture of ***rac*-** and ***meso*-3** by 2 equiv of *n*-butyllithium in tetrahydrofuran leads to THF-insoluble ***rac*- 4**; ***meso*-4** remains in the filtrate.

Reaction of the dilithium salt ***rac*-4** with $ZrCl_4$ in dichloromethane affords the zirconocene dichloride ***rac*-5** in approximately 57% yield (eq 1).

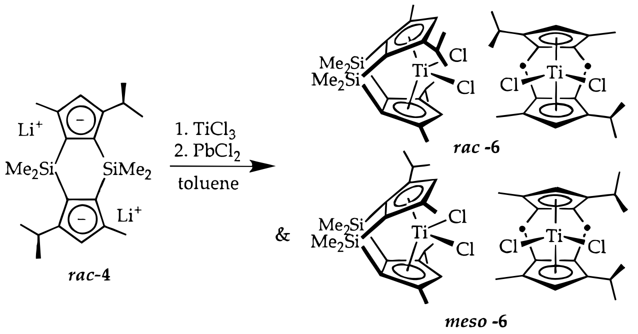


(1)

The ^1H NMR spectrum is in accord with the C_2 symmetry of the compound; in particular, there are no signals that may be attributed to the meso isomer (vide infra), even after a week at room temperature, after heating at 80 °C for 24 h, or after exposure to 6 h of California sunlight.

The racemic ligand framework was introduced onto titanium in a two-step, one-pot procedure. Dilithio ***rac*-4** and $TiCl_3(THF)_3$ were stirred overnight in toluene at room temperature, then treated with 1 equiv of $PbCl_2$ to oxidize the titanium(III) intermediate. Surprisingly, the orange powder that was obtained after workup proved to be a roughly 1:1 mixture of ***rac*-6** and ***meso*-6**, despite the fact that pure ***rac*-4** was used (Scheme 2).

Scheme 2



The molecular weight of this mixture, determined by ebulliometry, indicated that both components are monomeric, thus discounting the possibility that some type of dimeric "flyover"[9] titanocene dichloride is the meso component.

The racemic component ***rac*-6** was isolated by recrystallization from toluene as bright red single crystals suitable for X-ray crystal analysis, which confirmed the monomeric nature of ***rac*-6**. ORTEP drawings with 50% probability displacement ellipsoids showing the atom-numbering scheme are shown in Figure 1. The double [$SiMe_2$]-linked bis(cyclopentadienyl) ligand constrains the bent metallocene geometry such that, while the ring-centroid−Ti−ring centroid angle θ of 128° is only moderately less than unlinked or singly linked metallocenes (Table 3), the dihedral angle ϕ between cyclopentadienyl planes (70°) is considerably greater. Moreover, the titanium−ring carbon distances in the back of the wedge are considerably shorter than those to the front ring carbons, as reflected by the relatively large

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Table 1. Crystal and Intensity Collection Data for *rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2TiCl_2$, *rac*-6

formula	$C_{22}H_{34}Cl_2Si_2Ti$
fw	473.47
cryst color	orange-red dichroic
habit	block
cryst size	0.44 × 0.46 × 0.48 mm
$p_{calc} =$	$1.352\ g\ cm^{-3}$
cryst syst	monoclinic
space group	*C*2/c (No. 15)
a	19.756(6) Å
b	12.555(2) Å
c	9.767(2) Å
β	106.28(3)°
V	$2325.4(9)\ Å^3$
Z	4
lattice params	25 reflections, $22° \leq \theta \leq 25°$
μ	$7.07\ cm^{-1}$ ($\mu r_{max} = 0.28$)
transmission coeff (ψ-scan)	0.98−1.03
CAD-4 diffractometer, graphite monochromator	
ω scan	
Mo Kα, λ	0.7107 Å
2θ range	2−60°
h,k,l ranges	$-27 \leq h \leq 0, -17 \leq k \leq 17, -13 \leq l \leq 13$
T	85 K
F_{000}	1000
no. of reflns measured	7777
no. of ind reflns	3393
GOF_{merge}	1.22 for 3257 multiples
R_{merge}	0.014 for 2961 duplicates
final $R(F_o)$	0.025 for 3088 reflns with $F_o^2 > 3\sigma(F_o^2)$
final $R(F_o)$	0.027 for 3320 reflns with $F_o^2 > 0$
final weighted $R(F_o^2)$	0.067 for 3393 reflns
final goodness of fit	2.18 for 191 params and 3393 reflns
$(\Delta/\sigma)_{max}$ in final least squares cycle	0.02
$\Delta\rho_{max}$, $\Delta\rho_{min}$	$0.47\ e\ Å^{-3}$, $-0.29\ e\ Å^{-3}$ in final difference map

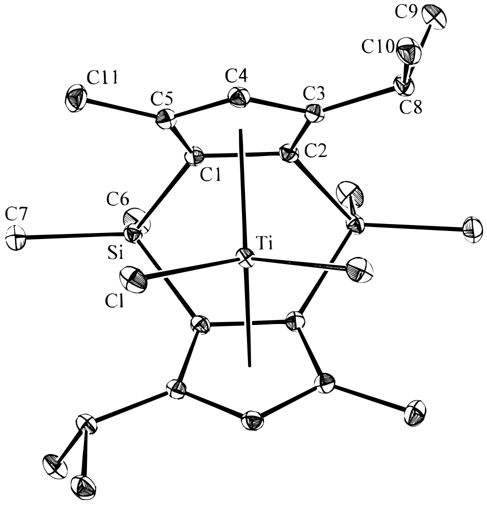


Figure 1. Molecular structure of ***rac*-6** with selected atoms labeled (50% probability ellipsoids; hydrogens omitted for clarity).

value of ω, the angle between the ring centroid−Ti vector and the normal to the cyclopentadienyl ring plane. Comparing the values of θ, ϕ, and ω to other titanocene dichlorides reveals that the two dimethylsilylene bridges and four alkyl substituents on the two cyclopentadienyl rings for ***rac*-6** combine to produce the widest angle of ring canting (ϕ) and the highest degree of titanium atom encroachment into the wedge.

The isopropyl and methyl substituents on the cyclopentadienyl rings are bent upward out of the plane of the cyclopentadienyl ring and away from titanium by 7.4° and 5.5°, respectively. The bridging $[SiMe_2]$ groups similarly are out of the cyclopentadienyl planes on the opposite side by 19.1−18.0°.

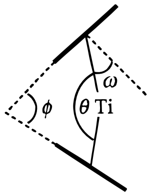
Table 2. Selected Distances and Angles for *rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2TiCl_2$, *rac*-6[a]

distance (Å)		angle (deg)	
Ti−Cl	2.3168(3)	Cp−Ti−Cp^i	128.1
Ti−Cp	2.120	Cp−Ti−Cl	106.9
Ti−Cl	2.314(1)	Cp−Ti−Cl^i	106.4
Ti−C2	2.301(1)	Cp−Ti−Cl^i	98.28(1)
Ti−C3	2.513(1)	C1−Si−$C2^i$	90.79(5)
Ti−C4	2.569(1)		
Ti−C5	2.510(1)		
Si−C1	1.882(1)		
Si−$C2^i$	1.872(1)		

[a] Symmetry code (i): x, y, $1/2 - z$.

Racemate−Meso Isomerization for *rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2TiCl_2$ (*rac*-6). The observation of both ***rac*-6** and ***meso*-6** upon treatment of pure ***rac*-4** with titanium chloride suggested to us the possibility that racemate−meso interconversion is facile. Indeed, a benzene solution of pure ***rac*-6**, which was prepared from several single crystals obtained by recrystallization from toluene, equilibrates to a nearly 1:1 racemate:meso mixture within hours, even at room temperature in the dark (Figure 2). The kinetics can readily be monitored by ^1H NMR in benzene-d_6 solution. This interconversion process obeys a first-order, two-site equilibrium rate expression. The forward first-order rate constants k_1 and final equilibrium constants K and their variations with temperature are summarized in Table 4. A linear van't Hoff dependence of the equilibrium constant with $1/T$ reveals a very small value for $\Delta H° = 0.1\ kcal\cdot mol^{-1}$, indicating that the racemic and meso isomers have similar stabilities. An Eyring plot yields $\Delta H^{\ddagger} = 18 \pm 1\ kcal\cdot mol^{-1}$ and $\Delta S^{\ddagger} = -7 \pm 2$ eu for the approach to equilibrium from the pure racemate.

Table 3. Comparative Structural Data for Titanocene Dichloride Compounds



compound	θ (deg)	ϕ (deg)	ω (deg)	ref
$(\eta^5\text{-}C_5H_5)_2TiCl_2$	130.7, 130.7	51.7, 51.3	2.1	17a
$(\eta^5\text{-}C_5Me_5)_2TiCl_2$	137.5	44.6	2.3, 0.4	17b
$\{CH_2(\eta^5\text{-}C_5H_4)_2\}TiCl_2$	121.6	65.7, 62.9	2.1	17c
$\{CMe_2(\eta^5\text{-}C_5H_4)_2\}TiCl_2$	121.5	66.9	2.5, 2.5	17d
$\{C_2H_4(\eta^5\text{-}C_5H_4)_2\}TiCl_2$	128.2	53.2	0.9	17c
$\{C_3H_6(\eta^5\text{-}C_5H_4)_2\}TiCl_2$	133	46.4	0.4, 1.3	17e
$\{SiMe_2(\eta^5\text{-}C_5H_4)_2\}TiCl_2$	128.7	56.2	2.1	17f
$\{(C_2H_4)_2(\eta^5\text{-}C_5H_3)_2\}TiCl_2$	124.5	57.8	1.5, 1.2	17g
$\{(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}TiCl_2$	126.0	64.4	5.1, 5.2	17h
rac-**6**	128.1	69.7	8.9	this work

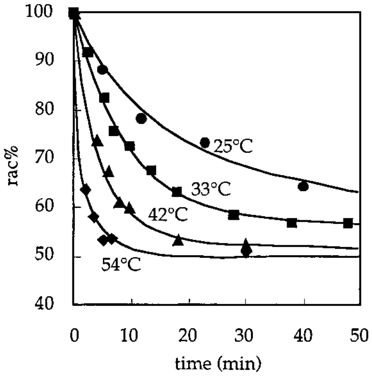


Figure 2. Equilibriation of pure ***rac*-6** with ***meso*-6** in benzene-d_6 at various temperatures.

Table 4. First-Order Rate Constants and Equilibrium Constants for the Approach to Equilibrium for *rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2TiCl_2$ (6)

T (°C)	k_1 (s^{-1})	K_{eq}
25	2.7×10^{-4}	0.85
33	5.3×10^{-4}	0.88
42	1.7×10^{-3}	0.91
54	3.9×10^{-3}	0.96

Photoinduced racemate–meso interconversion of group IV *ansa*-metallocene dichlorides has been reported.[10] The mechanism of isomerization has been investigated by several groups,[11] and there is general agreement that, at least for the titanocene complexes, photolysis leads to homolytic cleavage of a Ti–(η^5-cyclopentadienyl) bond and recombination of the cyclopentadienyl radical with the Ti(III) center. For *ansa*-metallocene derivatives, rotation of the cyclopentadienyl radical about the linking atom–Cp bond and recombination to the opposite face results in racemate–meso interconversion. Related interconversions of chiral, C_1-symmetric organolanthanide compounds have been reported by Marks and co-workers.[12] More recently, our group has found that facile racemate–meso interconversions for *ansa*-scandocene and *ansa*-yttrocene dichlorometalates and allyl derivatives are promoted by various salts, especially in tetrahydrofuran solution, even at room temperature; the isomerizations are not accelerated by light.[13] These processes are believed to involve metal–cyclopentadienyl heterolysis, rotation, and recombination.

The observations that ***rac*-6** undergoes equilibration with ***meso*-6** rapidly in hydrocarbon solvent in the dark at ambient temperature was thus unexpected. Dissociation of a cyclopentadienyl ligand, either homolytically or heterolytically, does not offer a plausible pathway for flipping to the opposite face for doubly linked *ansa*-metallocenes. We thus invoke an intermediate that arises from a reversible (simultaneous) 1,5-silatropic shift accompanied by an η^5- to Ti–C(sp^2) σ-bonded cyclopentadienyl rearrangement as shown in Scheme 3. Given the measured rates and equilibria (vida supra), we can estimate the isomerization reaction energy profile shown.

We are not aware of precedents for either the proposed intermediate or the unusual isomerization process that requires a change in cyclopentadienyl face for a doubly linked metallocene derivative.

Experimental Section

General Considerations. All operations were performed under argon using Schlenk techniques. Tetrahydrofuran, toluene, and petroleum ether, used in organometallic reactions were all dried over sodium benzophenone ketyl. Dichloromethane was dried over calcium hydride. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM500 (500.13 MHz) spectrometer. 1-Isopropyl-3-methylcyclopentadiene was prepared by modified literature methods.[14]

Preparation of New Compounds. $(Me_2Si)(C_5H_3\text{-}2\text{-}Me\text{-}4\text{-}CHMe_2)_2$ (2). To a solution of Me_2SiCl_2 (10.6 g, 82 mmol)

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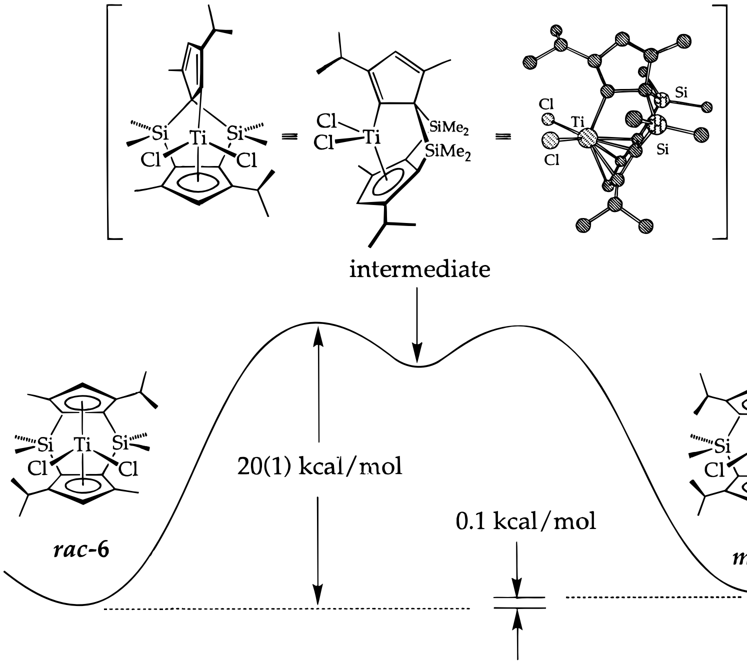
Scheme 3



in THF (200 mL) was added dropwise a solution of lithium 1-isopropyl-3-methylcyclopentadienide in THF (164 mmol, 300 mL) at 0 °C, followed by stirring for 15 min. The mixture was then gradually allowed to warm to room temperature. Water and hexane were added to the reaction mixture. The organic phase was dried over sodium sulfate and concentrated in vacuo. Short-path distillation gave 21.5 g (87% yield) of $(Me_2Si)(C_5H_3\text{-}2\text{-}Me\text{-}4\text{-}CHMe_2)_2$ (**2**), bp 115−117 °C (0.02 Torr).

$(Me_2Si)_2(C_5H_2\text{-}3\text{-}Me\text{-}5\text{-}CHMe_2)_2$ (3). A solution of 1.6 M *n*-butyllithium (67.8 mmol, 42.4 mL) in hexane was added dropwise to a solution of $(Me_2Si)(C_5H_3\text{-}2\text{-}Me\text{-}4\text{-}CHMe_2)_2$ (**2**) (10.2 g, 33.9 mmol) in THF (250 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and then gradually allowed to warm to room temperature, during which time a white precipitate formed. Stirring was continued for 4 h. To this suspension, Me_2SiCl_2 (4.4 g, 33.9 mmol) was vacuum transferred at −78 °C, and the reaction temperature was allowed to rise to room temperature. After the reaction mixture was stirred overnight, water was added, the water layer was extracted with hexane, and the organic phase was dried over sodium sulfate. Removal of solvent by evaporation followed by vacuum distillation gave 11.2 g (93% yield) of a pale yellow oil of **3**, bp 137 °C (0.02 Torr).

***rac*-$(Me_2Si)_2\{C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2Li_2(THF)_2$ (*rac*-4).** To a medium-size frit assembly equipped with a 250 mL flask were loaded 4.42 g (12.4 mmol) of $(Me_2Si)_2(C_5H_2\text{-}3\text{-}Me\text{-}5\text{-}CHMe_2)_2$ (**3**) and 80 mL of THF. A 1.6 M solution of *n*-butyllithium in hexane (24.8 mmol, 15.5 mL) was then added dropwise to the solution at room temperature, and the reaction mixture was stirred for 2 h, during which time a white precipitate formed. This solid was filtered off, washed with cold THF, and dried under vacuum, yielding 2.56 g (31.5%) of analytically pure ***rac*-4**. From the filtrate, 3.06 g of *meso*-**4** was recovered (37.1%). *rac*-**4**: ^1H NMR (in THF-d_8): δ 5.83 (s, 2H, CpH); 3.58 (THF); 3.11 (h, 2H,-C*H*Me$_2$); 2.26 (s, 6H, −Cp*Me*); 1.73 (THF); 1.19 (d, 12H, −CH*Me*$_2$); 0.31 (s, 12H, Si*Me*$_2$) ppm.

rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2ZrCl_2$ (*rac*-5).** *rac*-$(Me_2Si)_2\{C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2Li_2(THF)_2$ (rac*-4**) (2.5 g, 4.9 mmol) and $ZrCl_4$ (1.1 g, 4.7 mmol) were placed in a medium-size frit assembly equipped with a 250 mL flask. Dichloromethane (70 mL) was vacuum transferred to the flask at −78 °C, and the temperature was allowed to rise to room temperature. After dichloromethane was removed under vacuum, toluene (50 mL) was vacuum transferred onto the residue. The resultant yellow-brown suspension was filtered, and a clear toluene filtrate was obtained, which was concentrated, and sufficient petroleum ether was vacuum transferred into it to induce a white precipitate to form. The product (1.51 g; 60% yield) was filtered off, washed with cold petroleum ether, and then dried. The product was recrystallized from toluene. Anal. Calcd for $C_{22}H_{34}Cl_2Si_2Zr$: C, 51.13; H, 6.63. Found: C, 51.37; H, 6.76. ^1H NMR (benzene-d_6): δ 6.16 (s, 2H, Cp*H*); δ 2.85 (h, 2H, −C*H*Me$_2$); δ 2.21 (s, 6H, −Cp*Me*); δ 1.35 (d, 6H, −CH*Me*$_2$); δ 0.96 (d, 6H, −CH*Me*$_2$); δ 0.56 (s, 6H, Si*Me*$_2$); δ 0.46 (s, 6H, Si*Me*$_2$). ^{13}C NMR (benzene-d_6): δ 163.30, 150.94, 119.23, 111.21, 108.84 (Cp), δ 29.51, 28.75 (CHMe$_2$), δ 21.12 (Me), δ 17.55 (CHMe$_2$), δ 5.50, 1.62 (SiMe$_2$) ppm.

rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2TiCl_2$ (*rac*-6).** In the glovebox 2.7 g (5.27 mmol) of *rac*-$(Me_2Si)_2\{C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2Li_2(THF)_2$ (rac*-4**) and 1.95 g (5.27 mmol) of $TiCl_3(THF)_3$ were combined in a medium swivel frit assembly. Then 75 mL of toluene was added by vacuum transfer at −78 °C, and the light green reaction mixture was allowed to warm to room temperature. After the mixture stirred overnight the color had changed to black. Subsequently, 1.46 g (5.27 mmol) of $PbCl_2$ was added to the toluene solution, and the reaction mixture was stirred overnight at room temperature. The reddish brown solution was filtered, and the solvent of the filtrate was concentrated in vacuo to ca. 2 mL. After addition of petroleum ether, 1.4 g of orange powder was obtained as a mixture of racemate and meso titanocene dichlorides **6** (55% yield). The product was recrystallized from toluene, and the *rac*-isomer was separated as bright red crystals. ***rac*-6**: Anal. Calcd for $C_{22}H_{34}Cl_2Si_2Ti$: C, 55.81; H, 7.24. Found: C, 55.99; H, 7.16. ^1H NMR (benzene-d_6): δ 6.46 (s, 2H, Cp*H*); δ 2.75 (h, 2H, −C*H*Me$_2$); v2.22 (s, 6H, −Cp*Me*); δ 1.40 (d, 6H, −CH*Me*$_2$); δ 0.93 (d, 6H, −CH*Me*$_2$); δ 0.52 (s, 6H, Si*Me*$_2$); v0.35 (s, 6H, Si*Me*$_2$) ppm. ***meso*-6**: ^1H NMR (benzene-d_6): δ 6.44 (s, 2H, Cp*H*); δ 2.84 (h, 2H, −C*H*Me$_2$); δ 2.17 (s, 6H, −Cp*Me*); δ 1.41 (d, 6H, −CH*Me*$_2$); δ 0.97 (d, 6H, −CH*Me*$_2$); δ 0.60 (s, 3H, Si*Me*$_2$); δ 0.49 (s, 3H, Si*Me*$_2$); δ 0.43 (s, 3H, Si*Me*$_2$); δ 0.23 (s, 3H, Si*Me*$_2$) ppm.

Isomerization of *rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2TiCl_2$ (*rac*-6). A 5 mm J. Young NMR tube was charged in the glovebox with from 0.5 to about 2.0 mg of *rac*-$(Me_2Si)_2\{\eta^5\text{-}C_5H\text{-}3\text{-}(CHMe_2)\text{-}5\text{-}Me\}_2TiCl_2$ (*rac*-**6**) from a batch of single crystals. On the vacuum line, benzene-d_6 was condensed in vacuo into the tube at −78 °C. The sample was immediately inserted into the thermostated probe of a Bruker AM500, and an initial spectrum was recorded. The sample was then allowed to approach equilibrium, and after 24 h a final spectrum was recorded. The data were fit by linear least-squares analysis to the rate expression for the approach to equilibrium:

$$\ln[(X_e - X_0)/(X_e - X)] = (k + k')$$

The plot of $\ln[(X_e - X_0)/(X_e - X)]$, where X and X_e are the mole fractions of ***rac*-6** at time t and at equilibrium, respectively, versus time, afforded $k + k'$ from the slope.

X-ray Structure Determination for *rac*-6. A fragment cut from a red-orange dichroic columnar crystal under Paratone was centered on an Enraf-Nonius CAD-4 diffractometer under a stream of cold nitrogen gas. A hemisphere of data was collected. Table 1 summarizes the crystallographic data. No decay correction was needed. Individual backgrounds were replaced with a background function of 2θ derived from the backgrounds of reflections with $I < 3\sigma(I)$. Lorentz and polarization factors were applied to each, and the multiples were merged in point group $2/m$ with CRYM[15] programs.

The structure was solved with SHELXS-86.[16] The titanium atom is on a crystallographic 2-fold axis parallel to the b axis, which relates the two halves of the molecule by $-x$, y, $1/2-z$. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically. Refinement was full-matrix least-squares using CRYM programs. Weights were calculated as $1/\sigma^2(F_o^2)$; variances $(\sigma^2(F_o^2))$ were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another term, $(90.014I)^2$. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation.

Acknowledgment. The work has been supported by the USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER13431), Exxon Chemicals America, and Japan Polyolefins Co., Ltd. S.M. is grateful for a fellowship by Japan Polyolefins Co., Ltd. The authors wish to thank Dr. Dario Veghini for useful discussions.

Supporting Information Available: Details of the X-ray structure determination for *rac*-$(Me_2Sn)2\{\eta^5$-C_5H-3-$(CHMe_2)$-5-$Me\}_2TiCl_2$: ORTEP drawings, unit cell packing, crystal and intensity collection data, final heavy atom parameters, selected distances and angles, anisotropic displacement parameters, final refined hydrogen parameters, and complete distances and angles (21 pages). Ordering information is given on any current masthead page.

OM980505M

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