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ansa-Metallocene derivatives

XVII *. Racemic and *meso* diastereomers of group IV metallocene derivatives with symmetrically substituted, dimethylsilanediyl-bridged ligand frameworks. Crystal structure of *R*,*S*-$Me_2Si(3\text{-t-Bu-5-}MeC_5H_2)_2ZrCl_2$

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Abstract

The formation of racemic and *meso* diastereomers of the disubstituted *ansa*-zirconocenes $(CH_3)_2Si(1\text{-}C_5H_3\text{-}3\text{-}R)_2ZrCl_2$ (R = t-butyl, trimethylsilyl, α,α-dimethylbenzyl and 1-phenylcyclohexyl) from dimethylsilanediyl-bridged, symmetrically substituted bis-cyclopentadienyl dianion derivatives and $ZrCl_4 \cdot 2THF$ has been studied under a variety of conditions. Rac/*meso* ratios close to 1 were obtained in all cases. Similar product ratios were observed for analogous titanium and hafnium complexes with R = trimethylsilyl. A significant increase in the rac/*meso* product ratio was observed when an additional substituent was present next to the dimethylsilyl bridge as in $(CH_3)_2Si(1\text{-}C_5H_2\text{-}3\text{-}R\text{-}5\text{-}CH_3)_2ZrCl_2$ (R = $CH(CH_3)_2$, $C(CH_3)_3$). It is suggested that intermediates with one η^1-bound ring ligand control the stereochemical course of the *ansa*-metallocene formation. The crystal structure of *R*,*S*-$(CH_3)_2Si(1\text{-}C_5H_2\text{-}3\text{-}C(CH_3)_3\text{-}5\text{-}CH_3)_2ZrCl_2$ is reported.

Introduction

In a previous study, aimed at the preparation of symmetrically substituted chiral *ansa*-metallocene derivatives of the group IV transition metals (other than the bis-indenyl and bis-tetrahydroindenyl complexes studied previously [2–4]), we en-

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* For part XVI see ref. 1

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countered the difficulty that reactions of group IV transition metal halides with the appropriately substituted bridged bis-cyclopentadienyl dianion invariably gave, together with the desired racemate, substantial amounts of the achiral *meso* isomer [1] *. We report here on the influence of various ring substituents, metal derivatives and other reaction parameters on the racemic/*meso* diastereomer ratio of the symmetrically substituted dimethylsilanediyl-bridged metallocene products.

Results

1. Synthesis by metal-exchange reactions

The necessary dimethylsilanediylbis(alkylcyclopentadienyl) ligands were obtained without difficulty from a reaction of the appropriately substituted cyclopentadienyl derivatives with dimethyldichlorosilane. With a few exceptions (see Experimental), these substances were obtained as oily liquids and had to be used without further purification. Deprotonation was most conveniently achieved by stirring with solid KH in THF suspension **.

The resulting dianions were allowed to react with $ZrCl_4 \cdot 2THF$ in THF, typically for 2–4 days at room temperature. Subsequent removal of solvent and extraction of the residue with pentane gave crude product mixtures with complex ^1H NMR spectra, from which the expected *ansa*-zirconocene products could be isolated by fractional crystallization in yields of 15–20%. A partial or (in some cases) a complete separation of the racemic and *meso* isomers was achieved by further recrystallization from pentane; this and the appearance of one and of two $Si(CH_3)_2$ ^1H NMR resonances, respectively, for their rac and *meso* isomers allowed the assignment of the ^1H NMR signals given in Table 1 to these diastereomers. Inspection of the ^1H NMR spectra of the crude product mixtures revealed that for all the complexes studied, even when the ligand carried the bulky 1-phenylcyclohexyl substituent, the rac/*meso* diastereomer product ratio was 1/1 within the error limits. The same rac/*meso* ratio was observed when the reaction was carried out for ca. 24 h in refluxing THF or in the presence of two equivalents of tetramethylethylenediamine.

Distinctly higher rac/*meso* ratios of about 2/1 and 6/1 were obtained by an analogous route for the bis-disubstituted *ansa*-zirconocene complexes **5**-$ZrCl_2$, $(CH_3)_2Si(1\text{-}C_5H_2\text{-}3\text{-}C(CH_3)_3\text{-}5\text{-}CH_3)_2ZrCl_2$ and **6**-$ZrCl_2$, $(CH_3)_2Si(1\text{-}C_5H_2\text{-}3\text{-}CH(CH_3)_2\text{-}5\text{-}CH_3)_2ZrCl_2$ ***. In these cases, the pure rac isomers (which are substantially less soluble in pentane than the corresponding *meso* isomers) were obtained crystalline.

Crystallization from pentane also yielded the rac before the *meso* isomer for the bis(t-butyl)-substituted compound **1**-$ZrCl_2$, but this was not the case with other *ansa*-zirconocenes: For **2**-$ZrCl_2$ and **3**-$ZrCl_2$ the *meso* isomer crystallized first from

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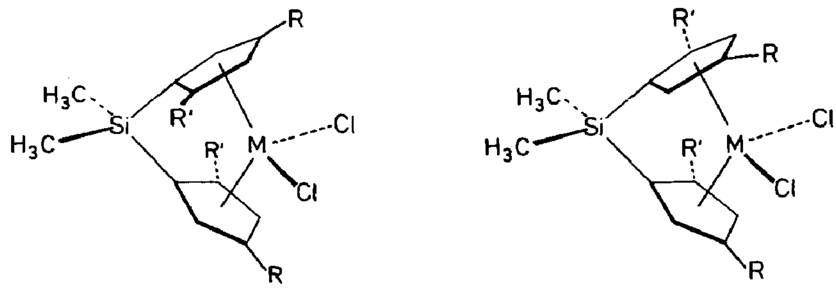
* Formation of the *meso* isomers has also been reported in the case of the two related compounds, $(CH_3)_2Si(1\text{-}C_5H_3\text{-}2\text{-}CH_3)_2TiCl_2$ and $(CH_3)_2Si(1\text{-}C_5H_3\text{-}3\text{-}C(CH_3)_3)_2ScCl$ [5,6].

** The 2- and 3-substituted isomers of the silanediylbis(alkylcyclopentadienyl) derivatives probably undergo interconversion by a rapid silyl migration (see ref. 7 and references therein); deprotonation, however, apparently leads predominantly to the less hindered 3-alkyl isomer.

*** We have not relabelled the ring positions in these disubstituted ring ligands, according to the IUPAC rules, since this would complicate comparison with the monosubstituted analogues.



rac meso

Scheme 1. Racemic and *meso* isomers of $(CH_3)_2Si$-bridged metallocenes **1–6**

	1	**2**	**3**	**4**	**5**	**6**
$R^1 =$	$C(CH_3)_3$	$Si(CH_3)_3$	$C(CH_3)_2C_6H_5$	$C(CH_2)_5C_6H_5$	$C(CH_3)_3$	$CH(CH_3)_2$
$R^2 =$	H	H	H	H	CH_3	CH_3
rac/*meso*	1/1	1/1	1/1	1/1	2/1	6/1

the pentane solution; solubility differences for the isomers of **4**-$ZrCl_2$ were not sufficient for isolation of either one in pure form.

In addition to the dipotassium salt, we prepared magnesium and tin derivatives in the case of the bis(t-butyl)- and the bis(trimethylsilyl)-substituted ligands by treating either the neutral ligand with two equivalents of isopropylmagnesium chloride or its dipotassium salt with two equivalents of tributyltin chloride. Reaction of the metal derivatives thus obtained with $ZrCl_4$ in refluxing toluene likewise gave only 1/1 mixtures of the rac and *meso* isomers of $(CH_3)_2Si(1\text{-}C_5H_3\text{-}3\text{-}C(CH_3)_3)_2ZrCl_2$ and its trimethylsilyl analogue.

Finally, analogous reactions of $(CH_3)_2Si(1\text{-}C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2K_2$ were carried out with $TiCl_3 \cdot 3THF$ and with $HfCl_4$ in THF. The latter gave results essentially identical with those observed for the zirconium analogues, i.e. a rac/*meso* ratio of about 1/1 in the crude product mixture, which was obtained in about 10% yield. For the titanium complex **2**-$TiCl_2$, as well as for the similarly prepared complex **1**-$TiCl_2$, the *meso* isomer dominates, with a rac/*meso* ratio of ca. 1/2. Complete separation of the rac and *meso* isomers formed proved unattainable in both cases. ^1H NMR data for **1**-$TiCl_2$, **2**-$TiCl_2$ and **2**-$HfCl_2$ are also given in Tab. 1.

The chemical shift patterns, with two resonances at 5.5–6.0 ppm and one resonance at 6.7–7.1 ppm, observed for the cyclopentadienyl protons of both diastereomers of these complexes (Tab. 1) are practically identical with those from the analogously 3-alkyl-substituted tetramethylethanediyl-bridged metallocene dichlorides, the structures of some of which were determined by X-ray crystallography [1]; this supports the β-alkylcyclopentadienyl geometry assigned to complexes **1–4**. The appearance of only one resonance, at ca. 5.5 and 6.4 ppm, respectively, for each of the complexes **5**-$ZrCl_2$ and **6**-$ZrCl_2$, in which a methyl group replaces one of the α-protons (see section 2), further confirms that these resonances at 5.5–6.0 ppm are due to two α-protons in complexes **1–4**, i.e. that one of the β-positions is occupied by the alkyl substituent. In accord with our previous observations [1], a substantially larger chemical shift difference between the two α-proton signals distinguishes the *meso* from the racemic isomer of each of the complexes **1–4**.

Table 1

^{1}H NMR data for the dimethylsilanediyl-bridged metallocenes **1**-TiCl$_2$, **1**-ZrCl$_2$, **2**-TiCl$_2$, **2**-ZrCl$_2$, **2**-HfCl$_2$, **3**-ZrCl$_2$, **4**-ZrCl$_2$, **5**-ZrCl$_2$ and **6**-ZrCl$_2$ in C$_6$D$_6$ solution at room temperature, δ in ppm at 250 MHz (s = singlet, d = doublet, t = pseudotriplet with J(H,H) ≈ 3 Hz, sp = septet, m = multiplet)

1-TiCl$_2$ (R = C(CH$_3$)$_3$)		**1**-ZrCl$_2$ (R = C(CH$_3$)$_3$)		**2**-TiCl$_2$ (R = Si(CH$_3$)$_3$)		**2**-ZrCl$_2$ (R = Si(CH$_3$)$_3$)		**2**-HfCl$_2$ (R = Si(CH$_3$)$_3$)		Assignment
rac	*meso*	rac	*meso*	rac	*meso*	rac	*meso*	rac	*meso*	
0.18 (s,6)	0.03 (s,3)	0.19 (s,6)	0.08 (s,3)	0.14 (s,6)	−0.01 (s,3)	0.21 (s,6)	0.10 (s,3)	0.23 (s,6)	0.12 (s,3)	1-Si(CH_3)$_2$
	0.29 (s,3)		0.29 (s,3)		0.25 (s,3)		0.30 (s,3)		0.31 (s,3)	1-Si(CH_3)$_2$
				0.43 (s,18)	0.52 (s,18)	0.40 (s,18)	0.45 (s,18)	0.39 (s,18)	0.44 (s,18)	3-Si(CH_3)$_3$
1.43 (s,18)	1.51 (s,18)	1.39 (s,18)	1.45 (s,18)							3-C(CH_3)$_3$
5.74 (m,4)	5.66 (t,2)	5.67 (m,4)	5.54 (t,2)	5.87 (t,2)	5.61 (t,2)	5.80 (t,2)	5.63 (t,2)	5.74 (t,2)	5.58 (t,2)	α-C$_5H_3$
	5.83 (t,2)		5.87 (t,2)	5.96 (t,2)	6.08 (t,2)	5.91 (t,2)	6.09 (t,2)	5.84 (t,2)	6.02 (t,2)	α-C$_5H_3$
6.87 (t,2)	7.04 (t,2)	6.72 (t,2)	6.84 (t,2)	7.26 (t,2)	7.31 (t,2)	6.98 (t,2)	7.09 (t,2)	6.99 (t,2)	7.01 (t,2)	β-C$_5H_3$

3-ZrCl$_2$ (R = C(CH$_3$)$_2$C$_6$H$_5$)		**4**-ZrCl$_2$ (R = C(CH$_2$)$_5$C$_6$H$_5$)		Assignment	**5**-ZrCl$_2$ (R = C(CH$_3$)$_3$, CH$_3$)		**6**-ZrCl$_2$ (R = CH(CH$_3$)$_2$, CH$_3$)		Assignment
rac	*meso*	rac	*meso*		rac	*meso*	rac	*meso*	
0.12 (s,6)	0.11 (s,3)	0.03 (s,6)	0.03 (s,3)	1-Si(CH_3)$_2$	0.35 (s,6)	0.32 (s,3)	0.30 (s,6)	0.20 (s,3)	1-Si(CH_3)$_2$
	0.23 (s,3)		0.13 (s,3)	1-Si(CH_3)$_2$		0.40 (s,3)		0.43 (s,3)	1-Si(CH_3)$_2$
		1.20	1.20	3-C(CH_2)$_5$C$_6$H$_5$			1.13 (d ^{a},6)	1.07 (d ^{a},6)	3-CH(CH_3)$_2$
		to (m,12)	to (m,12)						
		1.70	1.70				1.32 (d ^{a},6)	1.25 (d ^{a},6)	3-CH(CH_3)$_2$
1.90 (s,6)	1.95 (s,6)			3-C(CH_3)$_2$C$_6$H$_5$	1.45 (s,18)	1.41 (s,18)			3-C(CH_3)$_3$
2.10 (s,6)	2.13 (s,6)			3-C(CH_3)$_2$C$_6$H$_5$	1.95 (s,6)	2.10 (s,6)	1.88 (s,6)	2.06 (s,6)	5-CH_3
		2.60	2.60	3-C(CH_2)$_5$C$_6$H$_5$					
		to (m,8)	to (m,8)				3.12 (sp ^{a},2)	3.24 (sp ^{a},2)	3-CH(CH$_3$)$_2$
		3.10	3.10						
5.64 (t,2)	5.39 (t,2)	5.57 (t,2)	5.32 (t,2)	α-C$_5H_3$	5.48 (d,2)	5.64 (d,2)	5.20 (d ^{b},2)	5.13 (d ^{b},2)	α-C$_5H_2$
5.83 (t,2)	6.14 (t,2)	5.68 (t,2)	5.98 (t,2)	α-C$_5H_3$					
6.73 (t,2)	6.73 (t,2)	6.72 (t,2)	6.76 (t,2)	β-C$_5H_3$	6.54 (d,2)	6.32 (d,2)	6.52 (d ^{b},2)	6.31 (d ^{b},2)	β-C$_5H_2$
6.80	6.80	6.90	6.90	3-C(CH$_x$)$_y$C$_6H_5$					
to (m,10)	to (m,10)	to (m,10)	to (m,10)						
7.46	7.46	7.50	7.50						

[a] J(H,H) 6.8 Hz. [b] J(H,H) 2.4 Hz.

2. *Structure of* $R,S\text{-}(CH_3)_2Si(1\text{-}C_5H_2\text{-}3\text{-}C(CH_3)_3\text{-}5\text{-}CH_3)_2ZrCl_2$

Cube-shaped crystals of this racemic complex were obtained by recrystallizing the crude rac/*meso* (2/1) mixture from pentane. Space group, cell parameters and X-ray diffraction intensities were determined at 220 K on a Syntex-P3 four-circle diffractometer (Mo-K_α, λ 71.069 pm, graphite monochromator, ω-scan, with $\Delta\omega$ 1°; $2.4 \le \dot{\omega} \le 20°$ min^{-1}; $3 \le 2\theta \le 53°$). The crystals were orthorhombic, space group *Pbcn* with *a* 1818.6 (0.5), *b* 986.4 (0.2), *c* 1349.9 (0.4) pm; 4 crystallographically equivalent molecules (2 enantiomer pairs) per unit cell; V 2422×10^6 pm^3; d_{calcd} 1.34 g/cm^3. For resolution and refinement of the structure, 1848 independent reflections with $I > 2\sigma(I)$ were used, without absorption corrections (μ 7.2 cm^{-1}). The position of the Zr atom was located by the Patterson method, those of all other atoms by difference Fourier synthesis (programme SHELXTL, G.H. Sheldrick 1984). Refinement with a partial anisotropic model converged at $R_1 = 0.0379$ and $R_2 = 0.0389$ * (minimal and maximal electron densities: -0.37 and $+0.33$ e Å^{-3}). H atom positions were taken from the difference Fourier map but not refined.

The molecular structure of complex 5-Zr, represented in Fig. 1, shows the expected axial symmetry, the molecular symmetry axis coinciding with a crystallographic C_2 axis, and confirms the β-position of the t-butyl group relative to the bridgehead atom. A number of distortions point to a substantial repulsive interaction between each of the t-butyl groups and the adjacent Cl ligand: The $ZrCl_2$ plane intersects the centroid–Zr–centroid plane at an angle of 94° (instead of the normal 90°) and is twisted relative to the $Si(CH_3)_2$ plane by 9°, while the $C\text{–}C(CH_3)_3$ bond is bent out of the mean plane of the C_5 ring by 10° (the CH_3 substituent being coplanar with it within ca. 1°).

A similar out-of-plane bending of the $C\text{–}C(CH_3)_3$ bond by 10° had been observed in the related chiral *ansa*-zirconocene derivative $(CH_3)_4C_2(1\text{-}C_5H_3\text{-}3\text{-}C(CH_3)_3)_2ZrCl_2$ [1]. Other structural parameters of 5-$ZrCl_2$ (e.g. the

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters for complex 5-$ZrCl_2$

	x	*y*	*z*	*U* [a]
Zr(1)	0	6974(1)	7500	33(1)
Cl(1)	815(1)	5357(1)	8283(1)	79(1)
Si(1)	0	10347(1)	7500	46(1)
C(1)	367(2)	9053(3)	6609(2)	36(1)
C(2)	1030(2)	8329(3)	6807(2)	38(1)
C(3)	1070(2)	7172(3)	6198(2)	36(1)
C(4)	405(2)	7125(3)	5667(2)	33(1)
C(5)	−30(2)	8261(3)	5902(2)	34(1)
C(6)	743(3)	11429(4)	7995(3)	73(2)
C(31)	1736(2)	6271(4)	5998(3)	47(1)
C(32)	2320(2)	6421(5)	6801(4)	75(2)
C(33)	1501(2)	4784(4)	5899(3)	57(1)
C(34)	2053(2)	6739(4)	5002(3)	62(1)
C(51)	−760(2)	8564(4)	5438(3)	47(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor (Å$^2 \times 10^3$).

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* $R_1 = (\Sigma\,||F_o| - |F_c||)/\Sigma|F_o|$ and $R_2 = [\Sigma\omega(|F_o| - |F_c|)^2]^{1/2}/[\Sigma\omega|F_o|^2]^{1/2}$.

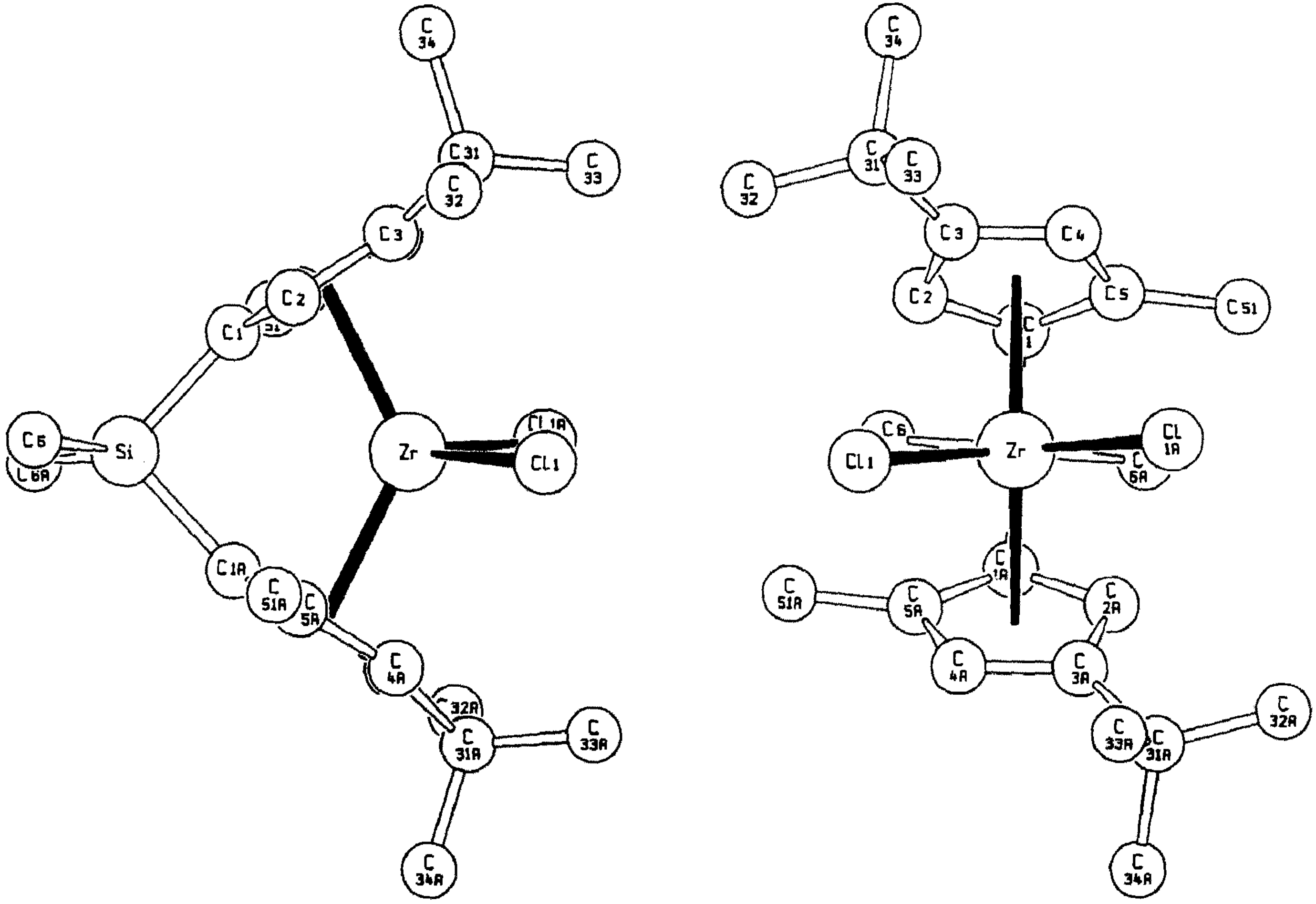

Fig. 1. Structure of R,S-$(CH_3)_2Si(1\text{-}C_5H_2\text{-}3\text{-}C(CH_3)_3\text{-}5\text{-}CH_3)_2ZrCl_2(5\text{-}ZrCl_2)$; projections normal to the centroid-Zr-centroid plane (left) and parallel to the molecular symmetry axis (right).

Table 3

Bond lengths (in pm) and bond and dihedral angles (in degrees) for complex 5-$ZrCl_2$

Zr–Cl(1)	242.0(1)	Cl(1)–Zr–Cl(1A)	97.6(1)
Zr–C(1)	247.0(3)	CR(1)–Zr–CR(1A) [a]	126.7
Zr–C(2)	248.4(3)	C(1)–Si–C(1A)	94.3(1)
Zr–C(3)	262.9(3)	C(6)–Si–C(6A)	109.4(1)
Zr–C(4)	258.6(3)	PL(1)–PL(1A) [a]	62.6
Zr–C(5)	250.4(3)		
Si–C(1)	187.6(3)	TiCl(1)Cl(1A)–TiCR(1)CR(1A) [a]	94.3
Si–C(6)	184.7(5)	Si–C(1)–PL(1) [a]	15.8 (*endo*)
Zr–CR(1) [a]	223.1	C(31)–C(3)–PL(1) [a]	10.1 (*exo*)

[a] CR = centroid, PL = mean plane of η^5-C_5ring.

centroid–Zr–centroid angle of 127° and the somewhat widened Cl–Zr–Cl angle of 98°) are also rather similar to those (125 and 100°, respectively) for the tetramethylethanediyl-bridged analogue [1]. Structural similarities were noted previously for the unsubstituted, ethanediyl- and dimethylsilanediyl-bridged complexes $C_2H_4(C_5H_4)_2TiCl_2$ [8] and $(CH_3)_2Si(C_5H_4)_2TiCl_2$ [9]. As in $(CH_3)_2Si(C_5H_4)_2ZrCl_2$ [9], the dimethylsilanediyl bridge of 5-$ZrCl_2$ is rather severely distorted: A C(1)–Si–C(1A) angle of only 94° and a bending of the Si–C(1) bond out of the mean plane of the cyclopentadienyl ring by ca. 16° are required to accommodate the four-membered Zr–C(1)–SiC(1A) chelate ring of this dimethylsilanediyl-bridged metallocene *.

Discussion

The formation of practically equal amounts of racemic and *meso* diastereomers for all metallocenes with dimethylsilanediyl-bridged, mono-substituted ring ligands described above, irrespective of the preparative method used, is a major obstacle to their expedient synthesis. We consider here possible causes.

It seems most unlikely that this lack of preference for one of the isomers is of thermodynamic origin. The steric interactions between ring substituents and chloride ligands, revealed e.g. by the distorted molecular structure of 5-$ZrCl_2$, are unlikely to give rise to equal free energies for the racemic and *meso* diastereomers. The unbiased formation of these two must, therefore, be kinetically controlled.

The rac or *meso* configuration of the metallocene product is determined by the *re*- or *si*-enantiofacial attachment of the second ring ligand to the transition metal, i.e. to a $ZrCl_3$ group η^5-coordinated to one cyclopentadienyl ring (cf. Scheme 2). If the four-centre mechanism usually assumed for alkyl-transfer reactions (cf. ref. 10) also operates for cyclopentadienyl transfer, the entering transition metal would be attached to the same side of the cyclopentadienyl ring as the leaving main group metal. For the latter, however, *re*- and *si*-coordination to the cyclopentadienyl ring must have close-to-even probabilities. Main group metals for which exchange between opposite faces of a cyclopentadienyl ring is slow, as might be the case for a

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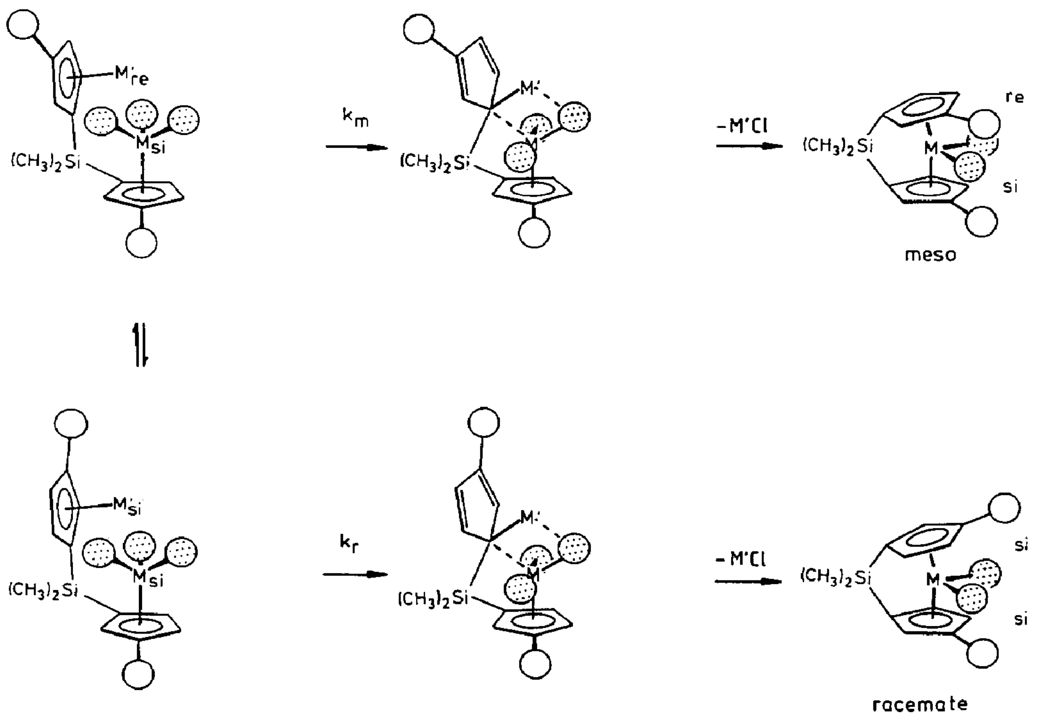
* Structural data for this compound are available on request from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, upon quotation of deposit number CSD 53635, the authors and the Journal reference for this article.



Scheme 2. Stereochemical control of *ansa*-metallocene chelate formation.

trialkyl tin group, could thus transfer their indiscriminate occupation of these faces to the entering transition metal.

For more ionically bound main group metals, however, metal exchange between the faces of the carbanionic ligands should be much faster than transfer of the latter to the transition metal. The rates of formation of rac and *meso* diastereomers are then controlled by the energies of the alternative ligand-transfer transition states, which involve an incipient σ-bond between the cyclopentadienyl carbanion and the Lewis-acidic cyclopentadienyl zirconium trichloride *. Since the geometries of these transitions states, especially the degree of interaction with the leaving halide and main group metal ions, cannot be estimated in sufficient detail, we propose to consider, as a substitute for these transition state geometries, those of the closely related yet better defined intermediates in which the second ring is η^1-coordinated to the transition metal.

In intermediates of this kind, the metal could be bound either to the bridgehead atom C(1) or to one of the α-C atoms C(2) or C(5) (cf. Scheme 3). Which of these three geometries is lowest in energy and, hence, the favoured reaction intermediate, is not discernible at present. Nevertheless, the relative energies of the pre-rac and the pre-meso epimers in each of these three epimer pairs, which are critical for the stereochemical course of the chelate formation reaction, can be reasonably estimated from Scheme 3.

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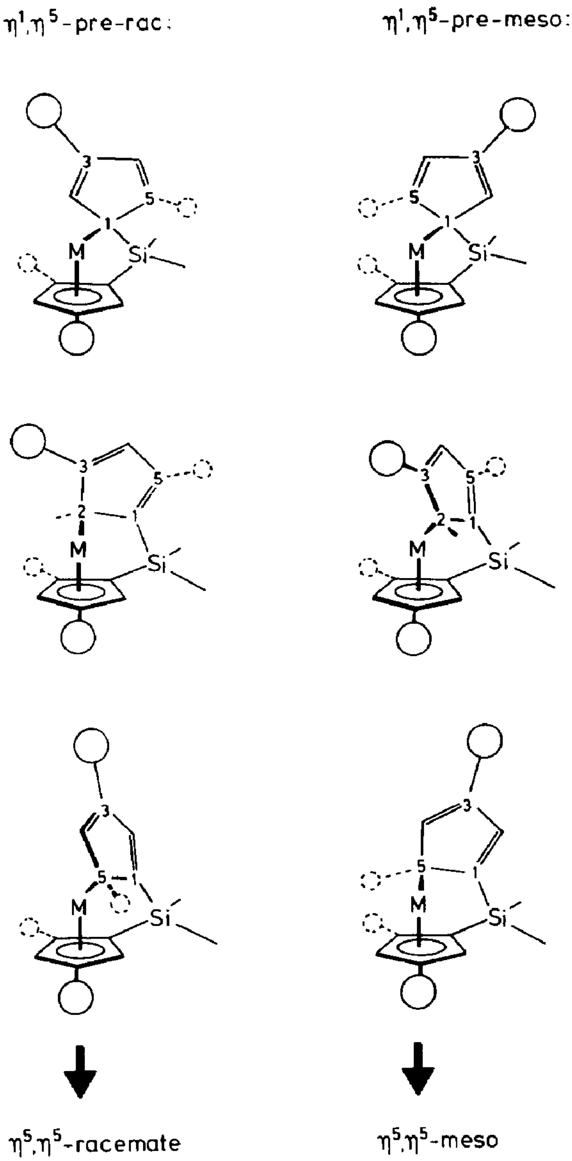
* The lower Lewis acidities of cyclopentadienyltitanium trichloride intermediates, especially their lower degrees of solvation (cf. ref. 11), might correlate with their consistently increased tendency to give the *meso* isomer of the *ansa*-metallocene product.



Scheme 3. η^1-Coordinated intermediates in *ansa*-metallocene formation.

If there is only a single substituent, in the β-position, on both rings, the two members of each of the three pairs of epimers should differ little in free energy as their β-substituents are quite remote from each other. Irrespective of the relative importance of the C(1)-, C(2)- or C(5)-bonded species, it would thus be expected that the rac and *meso* isomers would be formed in practically equal amounts, as was observed. When the cyclopentadienyl rings carry a second substituent at their α-positions, however, a different situation can be foreseen from this scheme: Both in the C(1)- and the C(5)-bonded intermediates, the steric repulsions between the two 5-alkyl substituents will be substantially stronger in the pre-*meso* than in the pre-rac intermediates. A distinct preference for the racemate is now to be expected, and is indeed observed for the bis-disubstituted *ansa*-zirconocenes 5-$ZrCl_2$ and 6-$ZrCl_2$ *. The observation of a substantially higher rac/*meso* ratio in the isopropyl substituted complex 6-$ZrCl_2$ than in the t-butyl analogue 5-$ZrCl_2$ is in line with our previous observation [1] that tertiary carbon substituents in 3-position of the C_5-ring introduce more steric strain for the rac than for the *meso* product. This unfavourable thermodynamic effect of the 3-t-butyl substituent appears to counteract part of the kinetic bias in favour of the racemate that is exerted by the 5-methyl substituent.

Experimental

All solvents used were thoroughly dried. All manipulations, unless otherwise stated, were carried out under nitrogen. The zirconium and hafnium complexes obtained were somewhat sensitive to air even as solids and were stored under N_2. The lithium salt of t-butylcyclopentadiene and of α,α-dimethylbenzylcyclopentadiene were obtained by reaction of 6,6-dimethylfulvene with methyllithium and phenyllithium in diethyl ether solution, respectively (cf. ref. 12); reaction of phenyllithium with cyclohexyliden – cyclopentadiene (6,6-pentamethylenefulvene) gave the lithium salt of 1-phenylcyclohexylcyclopentadiene. Trimethylsilylcyclopentadiene was prepared as previously described [13,14] and converted into its lithium salt by reaction with a slight excess of n-butyllithium in hexane.

1. Synthesis of dimethyl[bis(alkyl-cyclopentadienyl)]silanes

As an example the synthesis of dimethylbis(t-butylcyclopentadienyl)silane is reported in detail.

To a solution of 24.4 g (190 mmol) of t-butylcyclopentadienyllithium in 100 ml THF and 60 ml pentane, 9.5 ml (73 mmol) of dichlorodimethylsilane were added at room temperature during 1 h. After 3 h stirring, the solvent was removed in vacuo and replaced by 150 ml pentane. The solution was filtered, shaken with 20 ml of saturated aqueous NH_4Cl, dried ($MgSO_4$), evaporated to a volume of ca. 80 ml, and placed in a cold chest at $-80\,^\circ$C. After several days the product had crystallized in the form of yellow platelets, and the supernatant solution was removed at $-80\,^\circ$C. The crystals were allowed to warm to room temperature and the resulting yellow oil was kept under dynamic vacuum for 8 h to remove any volatile contaminants. The product (19.8 g; 90% yield), which showed a main GLC peak of about 90% integrated intensity, was used without further purification.

Essentially analogous procedures were employed for dimethylbis(1-phenylcyclohexylcyclopentadienyl)silane (crystalline at $-80\,^\circ$C, oil at room temperature), the bis(trimethylsilyl)- and bis(α,α-dimethylbenzyl)-substituted dimethylsilanes (oils even at $-80\,^\circ$C, obtained by removal of solvent in vacuo at room temperature). These compounds all gave broad resonances in their ^{1}H NMR spectra in $CDCl_3$ solution at room temperature, as expected from their degenerate silyl migrations [7]. Dimethyl bis(3-butyl-5-methylcyclopentadienyl)silane is crystalline even at room temperature; its sharp ^{1}H NMR signals (6.27 (s, 2H), 5.92 (s, 2H), 3.13 (s, 2H), 2.08 (d, 6H), 1.16 (s, 18H) and -0.28 ppm (s, 6H)) indicate that one isomer predominates in $CDCl_3$ solution at room temperature. Similar observations apply to

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* The predominant formation of the rac isomer for bis(indenyl) *ansa*-metallocene derivatives [2] could likewise be due to the mutual repulsion of the two C(7)H groups flanking the ethanediyl bridge in the corresponding η^5,η^1-coordinated intermediate.

the bis(3-isopropyl-5-methyl) analogue with ^1H NMR signals at 6.18 (s, 2H), 5.89 (s, 2H), 3.12 (s, 2H), 2.63 (septet, 6.7 Hz, 2H), 2.07 (s, 6H), 1.12 (d, 6.7 Hz, 6H), 1.14 (d, 6.0 Hz, 6H) and −0.27 ppm (s, 6H).

2. *Synthesis of dimethylsilanediylbis(alkylcyclopentadienyl)zirconium dichlorides*

The synthesis of dimethylsilanediylbis(t-butylcyclopentadienyl)zirconium dichloride is described as an example.

To a suspension of 6.3 g (156 mmol) of KH in 75 ml THF at −30 °C were added 12.4 g (41 mmol) dimethylbis(t-butylcyclopentadienyl)silane. After 24 h stirring at room temperature, the excess of KH was allowed to settle and the supernatant solution was transferred through a steel canula to a solution of 9.0 g (38.5 mmol) $ZrCl_4$ in 40 ml THF; the mixture was stirred at room temperature for 2 days, and the solvent then removed in vacuo. The solid residue was taken up in 250 ml pentane, and the solution was filtered and evaporated in vacuo to a volume of ca. 100 ml. This solution contained, in addition to a small amount of bis(t-butylcyclopentadienyl)zirconium dichloride, the racemic and *meso* isomers of the product in a 1/1 ratio, as indicated by the ^1H NMR spectrum in C_6D_6 of the residue obtained by evaporation of a small sample of the solution. Upon cooling to −30 °C, a small amount of bis(t-butylcyclopentadienyl)zirconium dichloride was deposited.

Evaporation to 30 ml and cooling to −30 °C gave 2.4 g of a yellow precipitate, which consisted of a 6/1 mixture of rac and *meso* isomers of **1**-$ZrCl_2$. Further evaporation of the mother liquor to 10 ml and cooling to −30 °C afforded another crop of 1.0 g of **1**-$ZrCl_2$ containing predominantly the *meso* isomer (rac/*meso* 1/6), the total isolated yield of **1**-$ZrCl_2$ thus was 19%. Recrystallisation of the first product fraction from pentane yielded 1.3 g of pure racemic **1**-$ZrCl_2$.

The product was characterized by ^1H NMR spectra as given in Tab. 1, by mass spectra with parent ion at *m/e* 458 and from elemental analysis: Found: C, 52.04; H, 6.56; Si, 6.11; Cl, 15.27. $C_{20}H_{30}Cl_2SiZr$ calcd.: C, 52.14; H, 6.51; Si, 6.10; Cl, 15.52%.

Essentially identical syntheses were employed using the other dimethylbis(alkylcyclopentadienyl)silanes described above. Dimethylsilanediylbis(α,α-dimethylbenzylcyclopentadienyl)zirconium dichloride (**3**-$ZrCl_2$) was obtained in 14% total yield. The *meso* isomer crystallized first from a pentane solution at 0 °C; pure racemate was obtained by repeated crystallization at −80 °C. Dimethylsilanediylbis(1-phenylcyclohexylcyclopentadienyl)zirconium dichloride (**4**-$ZrCl_2$) was obtained in 16% total yield; the rac isomer was only slightly less soluble than the *meso* form; repeated recrystallization from diethyl ether/pentane gave a mixture containing rac and *meso* isomers in a ratio of 9/1.

Dimethylsilanediylbis(3-t-butyl-5-methylcyclopentadienyl)zirconium dichloride, **5**-$ZrCl_2$, and its bis(3-isopropyl-5-methyl) analogue **6**-$ZrCl_2$ were isolated in total yields of ca. 15%. In both cases the racemate was substantially less soluble than its *meso* isomer; a first crystallization from pentane gave products with a rac/*meso* ratio of about 10/1 from which pure racemate was obtained by further recrystallization. Both the racemic and the *meso* isomers (the latter being predominant in the recrystallization mother liquors) of **3**-$ZrCl_2$, **4**-$ZrCl_2$, **5**-$ZrCl_2$, and **6**-$ZrCl_2$ were characterized by the ^1H NMR spectra given in Tab. 1.

3. *Dimethylsilanediylbis(trimethylsilylcyclopentadienyl)metal dichlorides*

The dipotassium salt, which was prepared with an excess of KH from $(CH_3)_2Si(C_5H_4Si(CH_3)_3)_2$ in THF solution, was treated with an equivalent of solid

$TiCl_3 \cdot 3THF$, of $ZrCl_4$ or of $HfCl_4$ for 2 days at room temperature, to give the following results.

Very small amounts of **2**-$TiCl_2$ (predominantly of the *meso* form) (sufficient however, for recording of the ^1H NMR spectra, see Table 1) were obtained, after oxidation of the crude product with 6 *M* HCl in the presence of air, by repeated crystallization from pentane. This was accompanied, however, by considerable loss of the highly soluble product.

For **2**-$ZrCl_2$ three fractions with rac/*meso* ratios of 3/10, 4/5 and 8/2, giving a total yield of ca. 9%, were obtained by recrystallization from pentane. Characterization by ^1H NMR, as given in Tab. 1, by mass spectra with parent ion at *m/e* 490–499 of appropriate isotope distribution and from elemental analysis: Found: C, 43.61; H, 6.00; Si, 17.05 and Cl, 14.18. $C_{18}H_{30}Cl_2Si_3Zr$ calcd.: C, 43.86; H, 6.09; Si, 17.06 and Cl, 14.41%.

A rac/*meso* mixture of **2**-$HfCl_2$ was analogously obtained in 9% yield and was characterized by the ^1H NMR data given in Tab. 1, by the mass spectrum, which had the parent ion at *m/e* 576–584 with the expected isotope distribution, and from elemental analysis. Found: C, 37.04; H, 5.19; Si, 14.25 and Cl, 12.14. $C_{18}H_{30}Cl_2Si_3Hf$ calcd.: C, 37.25; H, 5.17; Si, 14.53 and Cl, 12.24%.

There is a distinct gradation of solubilities in this series of complexes, **2**-$TiCl_2$ having the highest and **2**-$HfCl_2$ the lowest solubility in pentane. Solutions of **2**-$TiCl_2$ are stable towards air while pentane or benzene solutions of **2**-$ZrCl_2$ and **2**-$HfCl_2$ decompose upon exposure to air for several hours or several minutes, respectively.

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References

1 S. Gutmann, P. Burger, U. Hund, J. Hofmann and H.H. Brintzinger, J. Organomet. Chem., 369 (1989) 343.
2 F.R.W.P. Wild, L. Zsolnai, G. Huttner and H.H. Brintzinger, J. Organomet. Chem., 232 (1982) 233; F.R.W.P. Wild, M. Wasiucionek, G. Huttner and H.H. Brintzinger, ibid., 288 (1985) 63.
3 J.A. Ewen and L. Haspeslagh, J. Am. Chem. Soc., 109 (1987) 6544; J.A. Ewen, L. Haspeslagh, M.J. Elder, J.L. Atwood, H. Zhang and H.N. Cheng, in W. Kaminsky and H. Sinn (Eds.), Transition Metals and Organometallics as Catalysts for Olefin Polymerization, Berlin, 1987, p. 281.
4 S. Collins, B.A. Kuntz, N.J. Taylor and D.G. Ward, J. Organomet. Chem., 342 (1988) 21.
5 N. Klouras and H. Köpf, Monatsh. Chem., 112 (1981) 887; H. Köpf and H. Klouras, Z. Naturforsch. 38B (1983) 321.
6 E. Bunel, B.J. Burger and J.E. Bercaw, J. Am. Chem. Soc., 110 (1988) 976.
7 P. Jutzi, H. Saleske, D. Bühl and H. Grohe, J. Organomet. Chem., 252 (1983) 29.
8 J.A. Smith, J. von Seyerl, G. Huttner and H.H. Brintzinger, J. Organomet. Chem., 173 (1979) 175.
9 C.S. Bajgur, W.R. Tikkanen and J.L. Petersen, Inorg. Chem., 24 (1985) 2539; C.S. Bajgur, S.B. Jones and J.L. Petersen, Organometallics, 4 (1985) 1929.
10 A. Yamamoto, Organotransition Metal Chemistry, New York, 1986, p. 110.
11 N.J. Wells, J.C. Huffman and K.G. Caulton, J. Organomet. Chem., 213 (1981) C17.
12 M.E. Sullivan and W.F. Little, J. Organomet. Chem., 8 (1967) 277.
13 C.S. Kraihansel and M.L. Losee, J. Am. Chem. Soc., 90 (1968) 471.
14 E.M. Schulman, A.E. Merbach, M. Turin, P. Wedinger and W.J. Le Noble, J. Am. Chem. Soc., 105 (1983) 3988.