Substituted Silastannatetrahydro-*s*-indacenes as Cyclopentadienyl Transfer Agents in the Synthesis of Silanediyl-Bridged Zirconocene Complexes[1]

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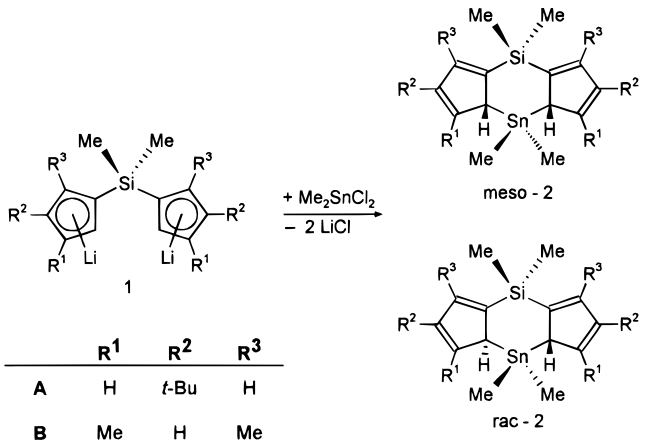
The substituted silastannatetrahydro-*s*-indacenes *meso*-$Me_2Si(t\text{-}BuC_5H_3)_2SnMe_2$, *meso*-$Me_2Si(Me_2C_5H_2)_2SnMe_2$, and *meso*-$Me_2Si(Me\text{-}i\text{-}PrC_5H_2)_2SnMe_2$, prepared from the corresponding silanediyl-bridged dicyclopentadienide dilithium salts by reaction with Me_2SnCl_2, were structurally characterized by X-ray diffraction and by ^{1}H-NMR in solution. These cyclic stannanediyl compounds react with $ZrCl_4$ to give selectively the *meso* diastereomers of the *ansa*-zirconocene complexes $Me_2Si(3\text{-}t\text{-}BuC_5H_3)_2ZrCl_2$, $Me_2Si(2,4\text{-}Me_2C_5H_2)_2ZrCl_2$, and $Me_2Si(2\text{-}Me\text{-}4\text{-}i\text{-}PrC_5H_2)_2ZrCl_2$, respectively. Reaction of $Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{-}BuC_5H_2^-\ Li^+)_2$ with Me_2SnCl_2 gives, instead of $Me_2Si(Me\text{-}t\text{-}BuC_5H_2)_2SnMe_2$, the distannyl derivative $Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{-}BuC_5H_2\text{-}1\text{-}SnMe_2Cl)_2$. This compound reacts with $ZrCl_4$ to give a 1:1 mixture of the *rac* and *meso* isomers of $Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{-}BuC_5H_2)_2ZrCl_2$. Ring-opened, racemic distannyl compounds are formed also from *meso*-$Me_2Si(t\text{-}BuC_5H_3)_2SnMe_2$, *meso*-$Me_2Si(Me_2C_5H_2)_2SnMe_2$, and *meso*-$Me_2Si(Me\text{-}i\text{-}PrC_5H_2)_2SnMe_2$ with excess Me_2SnCl_2. Competition between Me_2SnCl_2 and Zr centers for reaction with stannylcyclopentadiene units appears to limit the overall stereoselectivity of the *ansa*-zirconocene complex formation.

Introduction

While transition metal cyclopentadienyl complexes are mostly prepared by reaction of an alkali metal salt of the appropriate cyclopentadienide anion with a transition metal halide,[2] silyl- or stannylcyclopentadiene derivatives can also be used as cyclopentadienyl transfer agents.[3,4] Advantages of this synthetic route are the high solubility of the starting materials, a generally smooth transmetalation reaction, and the formation of easily removable silyl or stannyl halide side products. Another advantage of cyclopentadienyl transfer reactions of this type might be their stereoselectivity: The reaction of $TiCl_4$ with (trimethylsilyl)isodicyclopentadiene, for example, was found by Paquette and co-workers to occur under inversion of configuration, i.e., *via* back-side attack of the Ti electrophile at the Me_3-Si-substituted carbon center.[5,6]

Nifant'ev and co-workers[7−9] have observed related cyclopentadienyl transfer reactions with the silastannatetrahydro-*s*-indacene $Me_2Si(C_5H_4)_2SnMe_2$, i.e., with a cyclic Me_2Sn derivative of a dicyclopentadienylsilane. These authors have studied the fluxionality of this compound in solution as well as its reactions with group IV transition metal halides to form bimetallic, Me_2Si-bridged cyclopentadienyl complexes.

Scheme 1



	R^1	R^2	R^3
A	H	*t*-Bu	H
B	Me	H	Me
C	*t*-Bu	H	Me
D	*i*-Pr	H	Me

In view of the rather low yields and stereoselectivities of many *ansa*-metallocene syntheses, we thought it worthwhile to explore the synthetic potential of a reaction sequence in which the dilithium salt of a silyl-bridged dicyclopentadienyl ligand is first reacted with Me_2SnCl_2 to give a substituted silastannatetrahydro-*s*-indacene, i.e., a cyclic stannyl derivative, the Me_2Sn group of which is subsequently exchanged for a $ZrCl_2$ group by reaction with $ZrCl_4$ and reextrusion of Me_2-$SnCl_2$.

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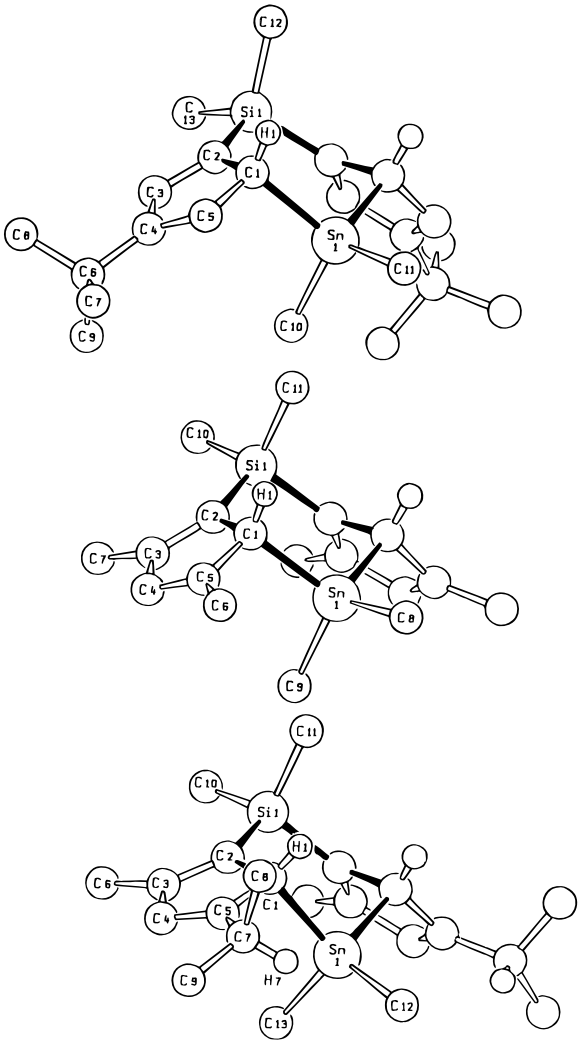

Figure 1. Crystal structures of compounds **2A** (top), **2B** (middle), and **2C** (bottom); H atoms partly omitted for clarity.

Results

1. Formation and Structures of Substituted Silastannatetrahydroindacenes. The cyclic Si- and Sn-bridged dicyclopentadienyl compounds **2A**, **2B**, and **2C** were prepared by reaction of the dilithium salts of the appropriate Me_2Si-bridged dianions with Me_2SnCl_2 (Scheme 1). Reaction of $Me_2Si(3\text{-}t\text{-}BuC_5H_5^-\ Li^+)_2$, **1A**, with 1 equiv of Me_2SnCl_2 in diethyl ether at 20−34 °C yields a product mixture that contains, as judged by its ^{1}H-NMR spectrum, the *meso* and *rac* isomers of the di-*tert*-butyl-substituted tetramethylsilastannatetrahydroindacene derivative **2A** in a ratio of 2:1. The *meso* isomer was isolated by crystallization from diethyl ether in ca. 25% yield in the form of slightly yellow crystals. The solubility of *rac*-**2A** appears to be much higher than that of the *meso* isomer. Due to its tendency to remain in the mother liquor, we have not been able to isolate *rac*-**2A**.

The crystal structure of *meso*-**2A** (Figure 1, Table 1) shows the molecule to be C_s-symmetric with the central ring in a chair conformation and the Me_2Si and Me_2Sn groups positioned in the C_s plane. The Me_2Si group is connected to sp^2-hybridized C atoms and the Me_2Sn group to sp^3-hybridized C atoms. That electropositive heteroatoms are preferentially bound to the sp^3 center of a cyclopentadiene ring has also been observed in other cases;[10,11] increased delocalization of the negative charge arising at this center into the C_5-ring appears to be the reason. The *tert*-butyl groups occupy the position at each C_5-ring that is farthest away from the bridging Me_2Si and Me_2Sn units.

Table 1. Selected Bond Lengths (pm) and Angles (deg) for Compounds 2A−C

	Compound **2A**		
Sn(1)−C(1)	221.4(4)	C(1)−C(2)	148.9(5)
Sn(1)−C(10)	210.8(6)	C(1)−C(5)	146.5(5)
Sn(1)−C(11)	215.2(7)	C(2)−C(3)	134.8(5)
Si(1)−C(2)	186.7(4)	C(3)−C(4)	144.7(5)
Si(1)−C(12)	185.0(7)	C(4)−C(5)	134.9(5)
Si(1)−C(13)	186.8(7)		
Sn(1)−C(1)−C(2)	101.5(2)	C(1)−Sn(1)−C(11)	111.0(1)
Sn(1)−C(1)−C(5)	106.2(2)	C(2)−Si(1)−C(2A)	105.2(2)
Si(1)−C(2)−C(1)	125.1(2)	C(2)−Si(1)−C(12)	111.0(2)
Si(1)−C(2)−C(3)	127.3(3)	C(2)−Si(1)−C(13)	110.5(2)
C(1)−Sn(1)−C(1A)	102.6(2)	C(10)−Sn(1)−C(11)	113.7(3)
C(1)−Sn(1)−C(10)	109.0(1)	C(12)−Si(1)−C(13)	108.7(4)
	Compound **2B**		
Sn(1)−C(1)	220.6(4)	C(1)−C(2)	149.2(5)
Sn(1)−C(8)	214.9(7)	C(1)−C(5)	149.4(5)
Sn(1)−C(9)	213.2(7)	C(2)−C(3)	137.2(6)
Si(1)−C(2)	186.7(4)	C(3)−C(4)	143.8(6)
Si(1)−C(10)	186.7(8)	C(4)−C(5)	134.8(6)
Si(1)−C(11)	187.7(8)		
Sn(1)−C(1)−C(2)	103.3(2)	C(1)−Sn(1)−C(9)	116.0(3)
Sn(1)−C(1)−C(5)	106.3(2)	C(2)−Si(1)−C(2A)	105.9(2)
Si(1)−C(2)−C(1)	119.5(3)	C(2)−Si(1)−C(10)	113.7(2)
Si(1)−C(2)−C(3)	132.4(3)	C(2)−Si(1)−C(11)	107.5(2)
C(1)−Sn(1)−C(1A)	103.7(2)	C(8)−Sn(1)−C(9)	116.0(3)
C(1)−Sn(1)−C(8)	109.9(1)	C(10)−Si(1)−C(11)	108.2(3)
	Compound **2C**		
Sn(1)−C(1)	219.7(2)	C(1)−C(2)	150.2(3)
Sn(1)−C(12)	214.1(4)	C(1)−C(5)	147.7(4)
Sn(1)−C(13)	213.5(4)	C(2)−C(3)	137.5(4)
Si(1)−C(2)	186.3(3)	C(3)−C(4)	144.3(3)
Si(1)−C(10)	186.0(4)	C(4)−C(5)	135.2(4)
Si(1)−C(11)	187.4(4)	C(5)−C(7)	150.8(4)
Sn(1)−C(1)−C(2)	100.2(2)	C(1)−C(5)−C(7)	123.5(2)
Sn(1)−C(1)−C(5)	107.8(2)	C(2)−Si(1)−C(2A)	106.2(2)
Si(1)−C(2)−C(1)	120.6(2)	C(2)−Si(1)−C(10)	113.8(1)
Si(1)−C(2)−C(3)	133.1(2)	C(2)−Si(1)−C(11)	107.9(1)
C(1)−Sn(1)−C(1A)	109.0(1)	C(2)−C(3)−C(6)	128.4(2)
C(1)−Sn(1)−C(12)	112.6(1)	C(12)−Sn(1)−C(13)	113.4(2)
C(1)−Sn(1)−C(13)	109.0(1)	C(10)−Si(1)−C(11)	107.1(2)

The ^{1}H-NMR spectrum of *meso*-**2A** (Table 2) is in complete accord with this structure. The Sn-bound CH_3 groups are distinguished by satellite signals due to a coupling to the $^{117/119}$Sn centers ($^2J_{H,Sn}$ = 55 and 51 Hz for the axial and equatorial groups, respectively). The equatorial and axial $SnCH_3$ groups are identified by their relative nuclear Overhauser effects with the H atoms in position 1; the axial CH_3 group shows an unusual high-field shift to −1.2 ppm, presumably due to its position inside the anisotropy cones of the cyclopentadienyl rings. The ^{1}H-NMR spectrum of *meso*-**2A** is unchanged upon heating to +120 °C or cooling to −90 °C; this indicates that only the solid-state structure depicted in Figure 1 is present in $CDCl_3$ or CD_2Cl_2 solutions. There is thus no indication of any fluxionality comparable to that of the unsubstituted congener $Me_2Si(C_5H_4)_2SnMe_2$, for which we observe, in accord with Nifant'ev and co-workers,[7] a fast interchange of the Me_2-

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Table 2. ^{1}H and ^{13}C NMR Data for Compounds 2A−C

compd **2A**			compd **2B**			compd **2C**		
^{1}H[a]	^{13}C[b]	C atom	^{1}H[e]	^{13}C[f]	C atom	^{1}H[e]	^{13}C[f]	C atom
4.27 (100)[c]	57.4[d]	C1, C1A	4.04 (80)[c]	60.4[d]	C1, C1A	4.23 (92)[c]	60.5[d]	C1, C1A
	147.3	C2, C2A		135.9	C2, C2A		133.5	C2, C2A
6.72 (18)[c]	132.2	C3, C3A		145.4	C3, C3A		143.4	C3, C3A
	152.7	C4, C4A	5.94	128.4	C4, C4A	6.00 (18)	124.8	C4, C4A
6.30	125.4	C5, C5A		144.4	C5, C5A		157.2	C5, C5A
	32.0	C6, C6A	2.08	15.5	C6, C6A	2.14[g]	15.5	C6, C6A
1.13	31.1	C7−C9, C7A−C9A	2.13[g]	15.7	C7, C7A	2.58	29.2	C7, C7A
−1.21 (55)[c]	−19.0	C10	0.60 (42)[c]	−0.8	C8	1.15 (7)[h]	22.5	C8
0.60 (51)[c]	−3.7	C11	−1.05 (43)[c]	−18.9	C9	1.11 (7)[h]	24.8	C9
0.30	0.0	C12	0.68	1.2	C10	0.65	−0.9	C10
0.50	−5.6	C13	0.33	−5.7	C11	0.35	1.0	C11
						0.54 (48)[c]	−4.9	C12
						−1.02 (53)[c]	−18.0	C13

[a] ^{1}H: $CDCl_2$, 250 MHz, 298 K; δ in ppm; all signals are singlets. [b] ^{13}C: $CDCl_3$, 250 MHz, 298 K; bb-decoupled; δ in ppm. [c] These signals have an additional ^2J(H−Sn) coupling; all values in parentheses are in Hz. [d] J(C−Sn) coupling; compound **2A**, 187.5 Hz; compound **2B**, 480 Hz; compound **2C**, 464 Hz. [e] ^{1}H: $CDCl_3$, 600 MHz, 298 K. [f] ^{13}C: $CDCl_3$, 150 MHz, 298 K; bb-decoupled; δ in ppm. [g] Additional doublet ^5J(H−Sn) coupling; compound **2B**, 18.6 Hz, compound **2C**, 18.9 Hz. [h] Doublet, ^3J(H−H) coupling; all values in parentheses are in Hz.

Sn bridge between C(1) and C(3) by ^{13}C-NMR spectroscopy. Accordingly, the ^{1}H−$^{117/119}$Sn coupling for the hydrogen atom attached to C(1), $^2J_{H,Sn}$ = 100 Hz, is found to be about twice as large for *meso*-**2A** as that in $Me_2Si(C_5H_4)_2SnMe_2$ (ca. 50 Hz), where the $SnMe_2$ group fluctuates between two of the C_5-ring carbon atoms. Apparently, the bulky *tert*-butyl substituents prevent an attachment of the Me_2Sn group to C(3). *meso*-**2A** appears to be stable also with respect to its configuration: Even after remaining in solution for periods up to 3 days, there is no indication of the appearance of its racemic isomer.

The dilithium salt of the bis-dimethyl-substituted dianion **1B**, $Me_2Si(2,4\text{-}Me_2C_5H_2^-\ Li^+)_2$, likewise reacts with Me_2SnCl_2 in diethyl ether at room temperature to yield a mixture containing the *rac* and *meso* isomers of the corresponding silastannatetrahydroindacene **2B**, now in a ratio of 1:1. From this mixture, the *meso* isomer is obtained in 40% yield as almost colorless crystals.

The crystal structure of compound *meso*-**2B** (Figure 1, Table 1) is similar to that of *meso*-**2A**. The placement of the two CH_3 substituents minimizes their interaction with the Me_2Si and Me_2Sn units. Steric strain is apparent, however: The Si atom and its equatorial CH_3 group are shifted away from the C1, C2, C1A, C2A plane—within the C_s plane—by 15−20 pm relative to their positions in *meso*-**2A**, apparently due to repulsion between the equatorial CH_3 group and the adjacent CH_3 groups of the disubstituted C_5-rings; the distance between these groups in *meso*-**2B** is only 348 pm.

The ^{1}H-NMR spectrum of *meso*-**2B** in CD_2Cl_2 solution (see the Experimental Section) agrees, again, with the molecular structure in Figure 1 and shows no signs of fluxionality. Apparently, the Me_2Sn group has no detectable tendency to migrate to the methyl-substituted (or any other) ring-atom. *meso*-**2B** remains unchanged in these solutions, as observed for *meso*-**2A**; its racemic isomer, in particular, remains undetectable.

In a manner analogous to that employed for **2A** and **2B**, the indacene derivative **2C** with methyl- and isopropyl-substituted C_5 rings, $Me_2Si(Me\text{-}i\text{-}PrC_5H_2)_2SnMe_2$, is obtained by reaction of the dilithio compound **1C**, $Me_2Si(2\text{-}Me\text{-}4\text{-}i\text{-}PrC_5H_2^-\ Li^+)_2$, with Me_2SnCl_2 in diethyl ether at room temperature, with a yield of ca. 40% and a *rac*/*meso* ratio of ca. 1:1. The *meso* isomer of **2C** is isolated, after recrystallization from diethyl ether, in the form of large rhombohedra.

The crystal structure of *meso*-**2C** (Figure 1, Table 1) is similar to that of *meso*-**2B** with regard to the positioning of the Me_2Si group, but differs from it by a displacement of the Me_2Sn bridge, which is shifted, within the C_s plane, away from the C1, C2, C1A, C2A plane of the central $Si(C_2)_2Sn$ ring. The cause of this displacement appears to be an increased steric repulsion by the isopropyl groups of **2C**. Apparently, the latter responds to this repulsion by adopting an arrangement in which one of their methyl groups (C9,C9A) is in an unfavorable position in the plane of the adjacent cyclopentadienyl ring, such that only atom H7 is exposed toward the Me_2Sn bridge. These data indicate that a substantial flexibility of the $Si(C_2)_2Sn$ chair can accommodate steric demands by suitable displacements of its Me_2Si and Me_2Sn units.

The ^{1}H-NMR spectrum of *meso*-**2C** (Table 2) is in complete agreement with the crystal structure. As with *meso*-**2A** and *meso*-**2B**, no tendency for rearrangement to the racemic isomer is observed for compound *meso*-2C.

In an attempt to also prepare the methyl-*tert*-butyl-disubstituted analog of **2B**, the dilithium salt **1D**, $Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{-}BuC_5H_2^-\ Li^+)_2$, was reacted with 1 equiv of Me_2SnCl_2 in diethyl ether, toluene, or THF solution. From the resulting product mixture **2D** could not be isolated; only minor traces of this compound are detectable by ^{1}H-NMR in the reaction mixture. Instead, the distannyl derivative **3D** was obtained, as the only isolable product, in ca. 10−20% yield in the form of colorless orthorhombic crystals.

The crystal structure of **3D** (Figure 2, Table 3) reveals that one $SnMe_2Cl$ unit is bound to each C_5-ring at the same C-atom as the Me_2Si bridge, and that the molecule is close to an overall C_2 symmetry. This compound thus represents a racemate. The ^{1}H-NMR spectrum of **3D** in $CDCl_3$ solution (see the Experimental Section) is entirely in accord with its solid-state structure, without evidence for any fluxionality.

Since the formation of **3D** consumes only one half of the dilithium salt **1D** if equivalent amounts of **1D** and Me_2SnCl_2 are used, we have also conducted reactions of **1D** with 2 equiv of Me_2SnCl_2. From the products of

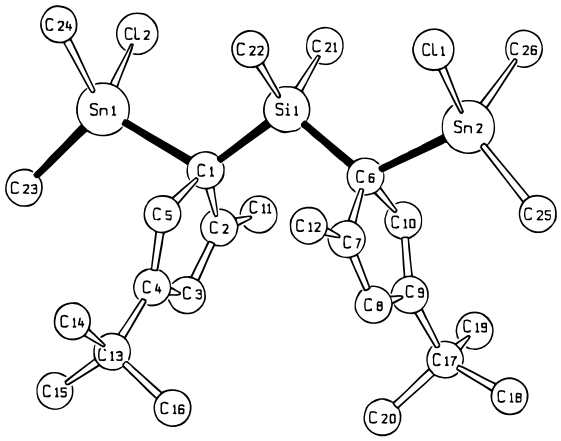


Figure 2. Crystal structure of compound **3D**.

Table 3. Selected Bond Lengths (pm) and Angles (deg) for Compound 3D

Sn(1)−C(1)	219.1(7)	C(6)−C(10)	148.6(12)
Sn(2)−C(6)	215.6(7)	C(1)−C(5)	149.4(11)
Sn(1)−Cl(2)	238.9(3)	C(6)−C(7)	149.2(12)
Sn(2)−Cl(1)	238.5(4)	C(2)−C(3)	137.2(11)
Si(1)−C(1)	188.6(7)	C(9)−C(10)	133.7(12)
Si(1)−C(6)	189.2(7)	C(3)−C(4)	142.5(12)
Si(1)−C(22)	184.2(10)	C(8)−C(9)	145.6(15)
Si(1)−C(21)	186.4(10)	C(4)−C(5)	134.5(10)
C(1)−C(2)	147.3(10)	C(7)−C(8)	130.6(13)

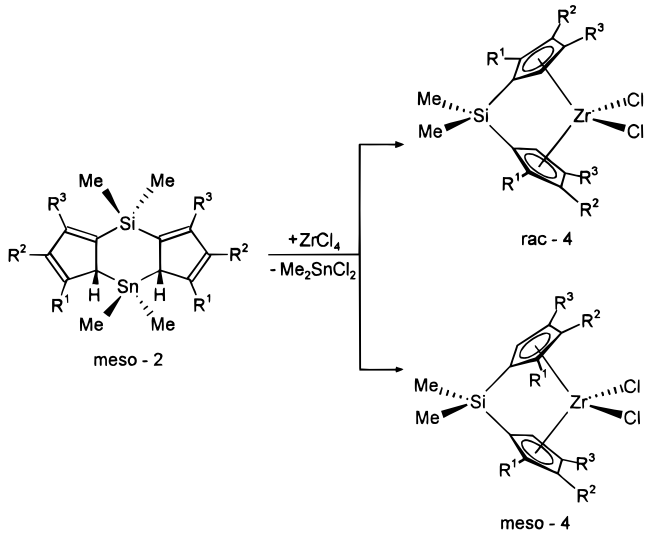
Sn(1)−C(1)−Si(1)	116.4(3)	C(5)−C(1)−Sn(1)	93.2(5)
Sn(2)−C(6)−Si(1)	117.8(4)	C(7)−C(6)−Sn(2)	103.7(4)
C(1)−Si(1)−C(6)	107.2(3)	C(10)−C(6)−Sn(2)	96.2(5)
C(2)−C(1)−Sn(1)	103.6(4)		

this reaction, **3D** is isolated in 36% yield. It appears likely, therefore, that any silastannatetrahydroindacene **2D**, which might be formed from **1D** and Me_2SnCl_2, is sterically strained even more than **2B**, such that it is attacked faster than the dilithium salt **1C** by additional Me_2SnCl_2.

This notion has led us to determine whether compounds **2A**−**C** are also cleaved by excess Me_2SnCl_2. If one of these silastanatetrahydroindacenes is treated with excess (ca. 3 equiv) Me_2SnCl_2, we do indeed observe the formation of additional species with ^{1}H-NMR spectra assignable to distannylated reaction products. Judged by their ^{1}H-NMR spectra (see the Experimental Section), the cleavage products **3A**−**C** arise only in their racemic forms. This indicates that the reactions of the *meso* forms of **2A**−**C** with excess Me_2SnCl_2 occur under inversion at the bridgehead carbon center, i.e., by backside attack of the Me_2SnCl_2 electrophile at the Sn-substituted carbon center. Even in the presence of the excess of Me_2SnCl_2 used for their generation, compounds *rac*-**3A**−**C** do not undergo any detectable conversion to their *meso* isomers.[12]

The results described above raise the question of which factors might control the relative yields for the *meso* and *rac* isomers of compounds **2A**−**C**. While the chair structures of the *meso* isomers depicted in Figure 1 would appear more stable than the twist geometry required for the racemic isomers, the configurational resistance at least of the *meso* isomer makes it unlikely that the *meso:rac* product ratio is under thermodynamic control. Even if the product ratio is kinetically controlled, however, a product-like transition state might favor the *meso* isomer.

Scheme 2



2. Cyclopentadienyl Transfer Reactions of Compounds *meso*-2A−C with $ZrCl_4$. Reaction of the *tert*-butyl-substituted, cyclic stannanediyl compound *meso*-**2A** with $ZrCl_4$ in diethyl ether or toluene solution leads, within a few minutes, to the formation of the *meso* isomer of the *tert*-butyl-substituted *ansa*-zirconocene, *meso*-**4A**, in high yields (Scheme 2). Me_2SnCl_2 can be removed and almost completely recovered from the product mixture by sublimation. In the ^{1}H-NMR spectrum of the remaining product mixture we can detect no trace of the racemic isomer *rac*-**4A**. This result is in stark contrast to the reaction of the dilithium salt **1A** with $ZrCl_4$, which gives rise to the *rac* and *meso* isomers of **4A** in practically equal amounts.[13−15]

Analogous reactions of the dimethyl-substituted silastannatetrahydroindacene *meso*-**2B** with $ZrCl_4$ in diethyl ether or toluene likewise afford the *ansa*-zirconocene **4B**,[13] in close to quantitative yields. In this case, however, the *meso*-diastereomer of **4B** contains ca. 10% of *rac*-**4B**. No significant change in this product distribution results from a choice of different solvents or reaction temperatures in the range of −90 to +100 °C. Reaction of the methylisopropyl-substituted indacene *meso*-**2C** with $ZrCl_4$ in toluene likewise yields the *meso* isomer of zirconocene **4C** together with ca. 10% *rac*-**4C**. It appears to be important that no excess of $ZrCl_4$ is present in these reaction systems; otherwise, the *meso:rac* ratio deteriorates to ca. 1:1.

^{1}H-NMR experiments show that the indacene *meso*-**2B** reacts with $ZrCl_4$ practically instantaneously; after 10−15 min, we observe a major portion (ca. 80%) of the zirconocene **4C** (already with a *meso:rac* ratio of ca. 9:1), together with minor amounts (ca. 10% each) of two other species, the ring-opened distannyl species *rac*-**3B** described above and its *meso* isomer.[12] These intermediates are then slowly (in the course of several hours) converted to the zirconocene product. Analogous observations pertain to the reaction between *meso*-**2C** and

(12) Isomer *meso*-**3B** is formed, together with comparable amounts of *rac*-**3B**, when the dilithio compound **1B** is reacted with a 3-fold excess of Me_2SnCl_2: ^{1}H-NMR (δ in ppm, 250 MHz, $CDCl_3$) 6.08, 5.58 (s, 2H, C_5-*H*), 2.08, 1.95 (s, 6H, C_5-CH_3), 0.67 (s, 6H, SiCH_3), 0.55, 0.12 (s, 6H, SnCH_3).

(13) Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 359−370.
(14) Reinmuth, A. Dissertation, University of Konstanz, 1992.
(15) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1989**, 1853−1856.

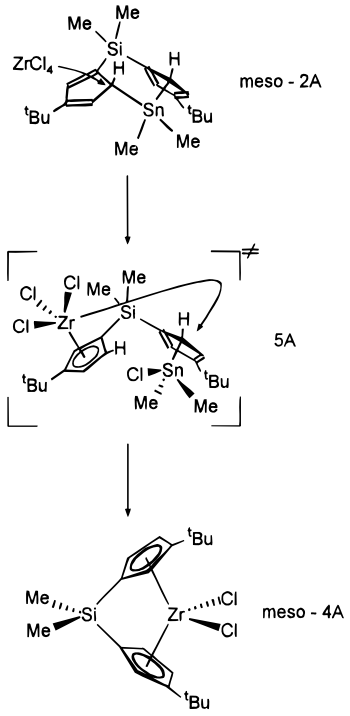
$ZrCl_4$, while no intermediates are observed in the reaction of *meso*-**2A** with $ZrCl_4$. Apparently, the Me_2SnCl_2 freed in the cyclopentadienyl transfer reaction competes with residual $ZrCl_4$ for unreacted **2B,C**, which is thus converted to the ring-opened distannyl species **3B,C**. In accord with this notion, we observe increased proportions of these distannyl species when less than stoichiometric amounts of $ZrCl_4$ are used in these reactions or when these reactions are conducted in the presence of a 3-fold excess of Me_2SnCl_2. While the distannyl species **3B,C** appear to react with $ZrCl_4$ completely to the *ansa*-zirconocenes **4A,B**, we cannot ascertain the stereochemistry of this reaction step from our data.

Reaction of $ZrCl_4$ with the distannyl compound **3D**, however, gives the methyl, *tert*-butyl-disubstituted *ansa*-zirconocene **4D**[13] with a *meso:rac* ratio of close to 1:1. While the almost quantitative yield of this reaction (as determined by experiments on the NMR scale) is substantially higher than that of the reaction between the dilithium salt **1D** and $ZrCl_4$ (ca. 20−30%), the cyclopentadienyl transfer from tin to zirconium is less stereoselective in this case than that from lithium to zirconium, which proceeds with a *meso:rac* ratio of ca. 1:2.[13−16]

The greatly varying stereoselectivities with which cyclopentadienyl units are transferred from tin to zirconium in the series **4A**−**D** must be related to differences in the individual reaction sequences. For the *tert*-butyl-substituted system, the stereospecific formation of *meso*-**4A** from *meso*-**2A** implies that both C_5-rings are transferred from Sn to Zr in the same stereochemical manner. While two consecutive reactions with retention of configuration would be conceivable, the results of Paquette and co-workers[5] with (trimethylsilyl)isodicyclopentadiene/$TiCl_4$ lead us to assume that both cyclopentadienyl transfer steps occur with inversion, i.e., by back-side attack of the Zr electrophile at the Sn-substituted C atom (Scheme 3). In any case, the stereospecificity of the overall reaction requires that the product of the first cyclopentadienyl transfer, **5A**, is configurationally stable at both C_5-ring units, i.e., that the stereospecific transfer of the second C_5-ring to the Zr center occurs faster than any configurational changes at either one of the reaction centers.

The question then arises, why the same should not be true for the corresponding intermediate **5D**, which arises from reaction of the methyl, *tert*-butyl-disubstituted distannyl compound **3D** with $ZrCl_4$: If this intermediate would be configurationally stable and would transfer the second C_5-ring unit to the Zr center in the same stereochemical sense as the first one, formation of only the racemic isomer of complex **4C** would be expected. Apparently, one or the other of these two premises breaks down in this case. While it is conceivable that the assumption of a stereochemically uniform Sn → Zr cyclopentadienyl transfer is no longer valid in this case, we wish to retain this hypothesis until proof of the contrary. Instead, we propose that the loss of stereoselectivity of the overall complex formation reaction results from a competition between Me_2SnCl_2 and Zr centers for reaction with stannylcyclopentadiene units: A rather low rate of the overall reaction indicates that the Me_2SnCl-bound C_5-ring of **5D** is attacked, due

Scheme 3



to its steric burdening, by the sterically likewise encumbered Zr center more slowly than by the Me_2SnCl_2 electrophile freed in the first cyclopentadienyl transfer step. If this latter reaction is sufficiently fast, complete racemization of the Me_2SnCl-bound C_5-ring unit will indeed precede its transfer to the Zr center.

Such a competition between Me_2SnCl_2 and Zr centers for reaction with stannyl-bound C_5-ring units could also explain the incomplete stereoselectivity of the reaction of the disubstituted silastannatetrahydroindacenes **2B** and **2C** with $ZrCl_4$: In these cases, the Me_2SnCl_2 freed in the second cyclopentadienyl transfer step apparently converts some unreacted **2B,C** to the ring-opened product **3B**,**C** which gives rise to the formation of *rac*-**4B**,**C**. Alternatively, Me_2SnCl_2 might compete also with the Zr center of intermediate **5B,C** for reaction with the Me_2SnCl-bound C_5-ring unit. The steric burden of the C_5-rings is less pronounced here than in the methyl *tert*-butyl-substituted reaction system, such that only a small fraction of **5B,C** would be expected to "leak" to the racemic complexes *rac*-**4B,C** *via* a competing reaction with Me_2SnCl_2. In accord with this notion, we observe an increased fraction of the *rac*-isomer of zirconocene complex **4B** (*meso:rac* ≈ 2:1), when a reaction of **2B** with $ZrCl_4$ is conducted, under otherwise identical conditions, in the presence of a 3-fold excess of Me_2SnCl_2.

In the monosubstituted reaction system, finally, neither reaction of **2A** nor that of intermediate **5A** with the Me_2SnCl_2 freed by metathesis with $ZrCl_4$ appears to compete noticeably with the formation of the zirconocene *meso*-**4A**. Even here, however, an analogous reaction in the presence of a 3-fold excess of Me_2SnCl_2 leads to formation of the *rac*-isomer in a ratio *meso:rac* ≈ 2.5:1, in accord with the notion that competition between Me_2SnCl_2 and Zr centers for reaction with stannylcyclopentadienyl units limits the overall stereoselectivity of the zirconocene complex formation.

(16) Chacon, S. T.; Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *497*, 171−180.

Conclusions

Metallatropic rearrangements, which are fast for silastannatetrahydro-*s*-indacenes with unsubstituted C_5-rings, are found to be suppressed in ring-substituted compounds such as *meso*-**2A**−**C**. These cyclic Me_2Sn derivatives of Me_2Si-bridged dicyclopentadienyl ligand molecules have a defined geometry; they react with $ZrCl_4$ in a stereoselective manner to give predominantly the *meso* isomers of the *ansa*-zirconocene complexes **4A**−**C**, respectively.

These results indicate that appropriately substituted silastannatetrahydro-*s*-indacenes could be used as an efficient source for chiral *ansa*-zirconocene complexes if the stannanediyl group could be introduced in a stereoselective manner, so as to give preponderantly the racemic tetrahydroindacene isomer, e.g., by replacement of the two CH_3 groups of the Me_2Sn bridge by a chiral, C_2-symmetric ligand unit.

Experimental Section

General Procedures. All manipulations were performed on an argon/vacuum manifold or in a glovebox under a purified nitrogen atmosphere. Solvents were dried and distilled from sodium benzophenone. $Me_2Si(3\text{-}t\text{-}BuC_5H_3^-\ Li^+)_2$ (**1A**), $Me_2Si(2,4\text{-}Me_2C_5H_2^-\ Li^+)_2$ (**2A**), and $Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{-}BuC_5H_2^-\ Li^+)_2$ (**3A**) were prepared according to previous reports.[13−18] NMR spectra were recorded on Bruker AC 250, Bruker DRX 600, and Jeol FX 90Q spectrometers in rubber-stoppered NMR tubes. ^{1}H-NMR chemical shifts are reported relative to $\delta(Me_4Si) = 0$ ppm and were determined by comparison with residual ^{1}H solvent peaks.

1. *meso*-2,6-Di-*tert*-butyl-4,4,8,8-tetramethyl-4-stanna-8-silatetrahydro-*s*-indacene (*meso*-2A). $Me_2Si(3\text{-}t\text{-}BuC_5H_3^-\ Li^+)_2$ (**1A**, 10.9 g, 34.9 mmol) was suspended in 200 mL of Et_2O. A solution of 7.65 g (34.9 mmol) of Me_2SnCl_2 in 100 mL of Et_2O was added slowly at room temperature. After being stirred for an additional 3 h, the light yellow suspension was filtered and the yellow filtrate evaporated until crystallization occurred. A total of 3.9 g of compound **2A** (25% theoretical yield) was isolated as slightly yellow crystals (mp 115 °C). For ^{1}H- and ^{13}C-NMR data see Table 2. Anal. Calcd for $C_{22}H_{36}SiSn$: C, 59.09; H, 8.11. Found: C, 58.82; H, 8.03.

2. *meso*-1,3,4,4,5,7,8,8-Octamethyl-4-stanna-8-silatetrahydro-*s*-indacene (*meso*-2B). To $Me_2Si(2,4\text{-}Me_2C_5H_2^-\ Li^+)_2$ (**1B**, 15.15 g, 59.18 mmol), suspended in 200 mL of Et_2O, was slowly added 12.95 g of Me_2SnCl_2 (59 mmol) dissolved in 200 mL of Et_2O at room temperature. After the mixture was stirred overnight, the solvent was replaced with pentane and a precipitate of LiCl removed by filtration. Evaporation and addition of 50 mL of Et_2O resulted in formation of almost colorless crystals after several days. Several crystallizations yielded 9.25 g (40% theoretical yield) of compound *meso*-**2B**. For ^{1}H- and ^{13}C-NMR data see Table 2. Elemental analysis: C, 55.31; H, 7.21. Anal. Calcd for $C_{18}H_{28}SiSn$: C, 55.28; H, 7.22.

3. *meso*-1,4,4′,7,8,8′-Hexamethyl-3,5-isopropyl-4-stanna-8-silatetrahydro-*s*-indacene (*meso*-2C). $Me_2Si(2\text{-methyl-}4\text{-isopropyl-}C_5H_2^-\ Li^+)_2$ (**1C**, 2 g, 6.4 mmol) was suspended in 100 mL of Et_2O. A solution of 1.4 g of Me_2SnCl_2 (6.4 mmol) in 100 mL of Et_2O was added at room temperature during 1 h. After being stirred overnight, the suspension was filtrated to remove LiCl and washed twice with 20 mL of pentane. The filtrate was evaporated to dryness in vacuo, and 15 mL of Et_2O was added. When the resulting solution was kept at −80 °C for 1 night and then stored for 1 week at room temperature, large slightly yellow crystals were formed. Several crystallizations yielded 1.14 g (40% theoretical yield) of *meso*-**2C**. As with **2A** and **2B**, the racemic isomer *rac*-**2C**, which was formed in nearly equivalent amounts, could not be isolated. For ^{1}H- and ^{13}C-NMR data see Table 2. Anal. $C_{22}H_{36}SiSn$: Calcd for C, 59.09; H, 8.11. Found: C, 58.90; H, 8.09.

Table 4. Selected ^{1}H-NMR[a] Signals for Distannyl Cleavage Products *rac*-(3A−3C), Obtained from Compounds *meso*-(2A−2C) with Excess of Me_2SnCl_2

rac-3A		*rac*-3B		*rac*-3C		
ppm	m	ppm	m	ppm	m	assignment
6.65	m	5.95	s	6.13	s	C_5-ring
6.10	m	5.68	s	5.63	s	C_5-ring
6.05	m					C_5-ring
0.45	s	0.58	s	0.63	s	CH_3Si
0.38	s	0.50	s	0.54	s	CH_3Sn
0.25	s	0.15	s	0.06	s	CH_3Sn

[a] ^{1}H-NMR: $CDCl_3$, 250 MHz, 298 K.

4. [*rac*-1,1′-Bis[1-(chlorodimethylstannyl)-2-methyl-4-tert-butylcyclopentadienyl]]dimethylsilane (*rac*-3D). $Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{-}BuC_5H_2^-\ Li^+)_2$ (**1D**, 2.6 g, 7.6 mmol) was suspended in 60 mL of Et_2O. A solution of 3.6 g of Me_2SnCl_2 (16.4 mmol) in 100 mL of Et_2O was added at room temperature during 1 h. After the solution was stirred overnight, the solvent was evaporated *in vacuo*, and 100 mL of pentane was added. The resulting precipitate was removed by filtration and the filtrate concentrated to 10 mL. This led to formation of a white precipitate, which was collected by filtration and dried *in vacuo* to yield 1.1 g (36% theoretical yield) of compound *rac*-**1D**, which was further purified by recrystallization from Et_2O. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 6.23 (s, 2H, *H*-C_5), 5.69 (s, 2H, *H*-C_5), 2.13 (s, 6H, C*H*$_3$-C_5), 1.10 (s, 18H, C(C*H*$_3$)$_3$), 0.67 (s, 6H, SiC*H*$_3$), 0.57 (s, 6H, SnC*H*$_3$, $J_{^1H,^{119}Sn} = 56.4$ Hz), 0.06 (s, 6H, SnC*H*$_3$, $J_{^1H,^{119}Sn} = 55.6$ Hz). ^{13}C-NMR, broad-band decoupled ($CDCl_3$, 250 MHz): δ 156.1 (*C*^{5}), 143.7 (*C*$_5$), 128.9 (*C*$_5$), 117.0 (*C*$_5$), 63.8 (*C*$_5$, sp^3; $J_{^{13}C,^{119}Sn} = 550$ Hz), 32.3 (*C*(CH$_3$)$_3$), 30.5 (C(*C*H$_3$)$_3$), 17.1 (*C*H$_3$-C_5), 2.2 (Si*C*H$_3$), 0.05 (Sn*C*H$_3$), −4.8 (Sn*C*H$_3$). Anal. Calcd for $C_{26}H_{46}SiSn$: C, 44.34; H, 6.67. Found: C, 44.88; H, 6.89.

5. *meso*-$Me_2Si(3\text{-}t\text{-}BuC_5H_3)_2ZrCl_2$ (4A). $ZrCl_4$ (1.3 g, 5.6 mmol) was suspended in 100 mL of toluene. To this mixture was added a solution of 2.5 g (5.58 mmol) of compound **2A** dropwise over a period of 45 min, during which time the mixture turned yellow. The resulting solution was stirred for 1 h and evaporated to dryness *in vacuo*, and 200 mL of pentane was added; some yellow residue was removed by filtration. The filtrate was evaporated again and the yellow residue heated for 10 h at 100 °C in a sublimation apparatus in a dynamic vacuum to remove Me_2SnCl_2. The residue consisted of pure *meso*-**3A** (1.8 g, 70% theoretical yield). ^{1}H-NMR ($CDCl_3$, 250 MHz, cf. ref 12): δ 6.85 (m, 2H), 6.01 (m, 2H), 5.87 (m, 2H), 1.35 (s, 18H), 0.73 (s, 3H), 0.6 (s, 3H).

6. *meso*- and *rac*-$Me_2Si(2,4\text{-}Me_2C_5H_2)_2ZrCl_2$ (4B). Compound **2B** (0.5 g, 1.28 mmol) was dissolved in 7 mL of toluene and added to a suspension of 0.3 g (1.28 mmol) of $ZrCl_4$ in toluene over a period of 10 min, during which time the mixture turned yellow. After the mixture was stirred for 2 h, the solvent was substituted by pentane, and any residues were removed by filtration. Evaporation to dryness and removal of Me_2SnCl_2 by sublimation, as described above, gives 0.46 g (90% theoretical yield) of ^{1}H-NMR-spectrally pure zirconocene **4B** with a *rac:meso* ratio of 1:10. ^{1}H-NMR ($CDCl_3$, 250 MHz, cf. ref 13): *meso*-**4B** δ 6.22 (nd, 2H), 5.25 (nd, 2H), 2.21 (s, 6H), 2.18 (s, 6H), 0.90 (s, 3H), 0.63 (s, 3H); *rac*-**4B** δ 6.42 (s, 2H), 5.25 (s, 2H), 2.27 (s, 6H), 2.03 (s, 6H), 0.75 (s, 6H).

7. *meso*- and *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}i\text{-}PrC_5H_2)_2ZrCl_2$ (4C). Fifty mg of compound *meso*-**2C** (0.11 mmol), dissolved in 25 mL of toluene, were added during 1 h to a suspension of 26 mg of $ZrCl_4$ (0.11 mmol) in 25 mL of toluene. The mixture was stirred overnight. After removal of the solvent in vacuo,

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(18) Klouras, N.; Köpf, H. *Monatsh. Chem.* **1981**, *112*, 887−897.

Table 5. Crystallographic Data[a] for Compounds 2A−C and 3D

	compd **2A**[b]	compd **2B**[b]	compd **2C**[c]	compd **3D**[b]
formula	$C_{22}H_{32}SiSn$	$C_{18}H_{28}SiSn$	$C_{22}H_{36}SiSn$	$C_{26}H_{46}Cl_2SiSn$
formula wt	443.3	391.2	447.3	695.0
cryst dimens (mm)	0.3 × 0.3 × 0.3	0.2 × 0.2 × 0.5	0.2 × 0.2 × 0.3	0.3 × 0.3 × 0.2
cryst color; form	colorless rhombohedron	yellow needle	colorless rhombohedron	yellow rhombohedron
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
space grp	*Pnma*	*Pnma*	$P2_1/m$	$P2_1/c$
a (pm)	1082.3(4)	1771.9(10)	678.6(1)	1178.4(4)
b (pm)	1810.1(8)	1381.9(8)	1404.2(3)	2021.4(7)
c (pm)	1200.1(7)	764.7(5)	1188.5(2)	1419.6(5)
β (deg)			93.93(3)	108.02(3)
vol (10^6 pm^3)	2351(2)	1873(2)	1129.8(3)	3216(2)
density$_{calcd}$ (g/cm^3)	1.252	1.388	1.315	1.436
Z	4	4	2	4
absorptn coeff. μ (mm^{-1})	1.141	1.423	1.187	1.1775
T (K)	233	235	153	253
wting scheme	$w^{-1} = \sigma^2(F) + 0.0005F^2$	unit weights	$w^{-1} = \sigma^2(F) + 0.0004F^2$	$w^{-1} = \sigma^2(F) + 0.0006F^2$
scan mode	Wyckoff	Wyckoff	$\omega/2\theta$	Wyckoff
scan range (deg)	0.70	0.70	1.40	0.80
2θ range (deg)	4.0−54.0	4.0−54.0	4.0−50.0	4.0−54.0
scan speed (deg/min)	variable; 2.30−29.30	variable; 2.30−29.30	variable; 2.00−8.00	variable; 2.30−29.30
no. of data collected	2925	2356	1965	7482
no. of independt data	2647	2122	1953	6932
no. of obsd data	2202	1756	1832	4837
observation criterion	$F > 6.0\sigma(F)$	$F > 4.0\sigma(F)$	$F > 4.0\sigma(F)$	$F > 4.0\sigma(F)$
no. of paramrs refined	120	100	118	280
R_F[d]	3.16	3.12	2.48	6.75
R_{wF}[e]	5.25	3.39	3.66	8.71
residual electron density max, min $\Delta\varrho$ (10^{-6} e/pm^3)	+0.51, −0.39	+0.67, −0.59	+0.54, −0.54	+3.75, −1.11

[a] All crystals are obtained by crystallization in diethyl ether at room temperature. [b] Measurement conditions: Syntex/Siemens-P3 four circle diffractometer, Mo Kα radiation (71.073 pm), graphite monochromator. [c] Measurement conditions: Enraf NOnius CAD 4, Mo Ka radiation (71.073 pm), graphite monochromator. Numerical absorption correction (DIFFABS). [d] $R_F = \sum||F_o| - |F_c||/\sum|F_c\delta|$. [e] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$.

Me_2SnCl_2 was removed by sublimation at 90 °C. The residue was extracted with 50 mL of pentane and the filtrate evaporated to dryness. The solid residue was found to be pure zirconocene **4C** with a *rac:meso* ratio of 1:10 by ^{1}H-NMR. ^{1}H NMR (C_6D_6, 250 MHz, cf. ref 12): δ 0.20 (s, 3H), 0.43 (s, 3H), 1.07 (d, 6H), 1.25 (d, 6H), 2.06 (s, 6H), 3.24 (septet, 2H), 5.13 (d, 2H), 6.31 (d, 2H).

8. *meso*- and *rac*-Me_2Si(2-Me-4-*t*-Bu$C_5H_2)_2ZrCl_2$ (4D). *rac*-1,1′-Bis[1-(chlorodimethylstannyl)-2-methyl-4-*tert*-butylcyclopentadienyl]dimethylsilane (**3D**, 50 mg, 0.0725 mmol) and 16.8 mg of $ZrCl_4$ (0.0725 mmol) were mixed with 0.4 mL of C_6D_6 in an NMR tube, which was then sealed and kept at room temperature. After 72 h, ^{1}H-NMR spectra showed the complete dissappearance of **3D** and the presence of a 1:1 mixture of the *rac* and *meso* isomers of compound **4C**.[12]

9. Reactions of meso-2A−C with Excess Me_2SnCl_2. Each of these compounds (0.05 mmol) was dissolved in 0.4 mL of $CDCl_3$ and then treated, in an NMR tube under N_2 atmosphere at room temperature, with 44 mg (0.2 mmol) of Me_2SnCl_2. After periods of 15 min and 4 h, ^{1}H-NMR spectra of the reaction mixtures were recorded. These showed, in addition to the reactant signals, the signals listed in Table 4, which are assigned to the racemic ring-opened species *rac*-**3A−C**, respectively.

10. Reactions of *meso*-2A and -2B with $ZrCl_4$ and Excess Me_2SnCl_2. A 0.06 mmol portion of *meso*-**2A** or *meso*-**2B**, 0.06 mmol of $ZrCl_4$, and 0.18 mmol of Me_2SnCl_2 were dissolved in 0.4 mL of C_6D_6 in an NMR tube under N_2 at room temperature. ^{1}H-NMR spectra recorded after 15 min, 2 h, and 20 h show, in addition to the signals of the *meso*-zirconocenes **4A** and **4B**, respectively, the signals of the corresponding racemic isomers in rac:meso ratios of 1:2.5 and 1:2, respectively.

11. Crystal Structure Determinations. Crystals of compounds *meso*-**2A**, *meso*-**2B**, *meso*-**2C**, and *rac*-**3D** were obtained as described above. Space group determinations, data collection and solution and refinement of the crystal structures were conducted as summarized in Table 5, using direct methods (*meso*-**2A**) and the Patterson method (*meso*-**2B**, *meso*-**2C**, and *rac*-**3D**), contained in the program package SHELXTL PLUS. The crystallographic data thus obtained are available upon request from Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen, D-76344, under quotation of deposit number CSD-59335, the journal reference, and the authors of this paper.

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Supporting Information Available: Tables of crystal data collection parameters, atom coordinates and *U* values, bond distances and angles, isotropic parameters and thermal ellipsoid plots for compounds *meso*-**2A−C** and *rac*-**3D** (37 pages). Ordering information is given on any current masthead page.

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