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Mechanisms of Sn-to-Zr cyclopentadienyl transfer in the formation of Me_2Si-bridged zirconocenes from sila-stanna-tetrahydro-s-indacenes

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Abstract

The stereochemistry of Sn-to-Zr transmetalation was studied by reacting $ZrCl_4$ with that isomer of *meso*-BnMeSi(3-^{t}Bu–$C_5H_3)_2SnMe_2$ which has the benzyl group in axial position. Exchange of $SnMe_2$ against $ZrCl_2$ generates both isomers of the C_S-symmetric *ansa*-zirconocene *meso*-BnMeSi(3-^{t}Bu–$C_5H_3)_2ZrCl_2$, but not the C_1-symmetric, *rac*-like isomer. The major product is formed under inversion at both Sn-bound C atoms by consecutive 'back-side' attacks of the Zr electrophile, while the minor product appears to be formed, under retention at both Sn-bound C atoms, by a concerted 'front-side' attack of $ZrCl_4$.

Keywords: *ansa*-Zirconocene; Tin organyls; Transmetalation

1. Introduction

A recurring theme in the scientific work of Professor Royo and his collaborators concerns the reactivity of Me_2Si-bridged metallocene complexes [1–3]. As synthons for complexes of this type, stannylated cyclopentadienyl precursors have recently gained substantial interest. This interest concerns, in particular, the synthesis of chiral *ansa*-zirconocene complexes, since the displacement of stannyl groups from an indenyl or cyclopentadienyl unit by reaction with $ZrCl_4$ has been found to occur with high stereoselectivity [4–7]. Metal exchange reactions of this type, which occur with high yields and excellent diastereoselectivities, have been utilized for the preparation of either the racemic or the *meso* isomers of substituted *ansa*-zirconocene complexes.

With regard to the mechanisms responsible for the diastereoselectivity of these metal exchange reactions, first clues have been derived by Sivik and Paquette from studies on the stereochemical course of the reaction between $TiCl_4$ and trimethylsilyl-substituted *iso*-dicyclopentadiene, which was shown to occur under inversion of the metal-bound C atom, i.e. by, 'back-side' attack of the Ti center at the C–Si bond [8]. Metal exchange under inversion has been postulated by Nifant'ev et al. also for the stereoselective displacement of trimethyltin groups from *rac*- or *meso*-configurated Me_2Si(1-indenyl-3-$SnMe_3)_2$ by reaction with $ZrCl_4$ [4], although the stereochemistry of this reaction might also be due to exchange of both Me_3Sn groups under retention of configuration.

In order to establish which circumstances might lead to cyclopentadienyl transfer from a Sn to a Zr center under retention of configuration at the metal-bound carbon atom, we have investigated the stereochemical course of the highly diastereoselective formation of *ansa*-zirconocene complexes by transmetalation of stanna-tetrahydro-s-indacenes with $ZrCl_4$ according to Scheme 1 [6,7].

2. Results and discussion

Reaction of the *meso*-configurated Me_2Sn compound 2,6-di-*tert*-butyl-4,8-tetramethyl-8-sila-4-stanna-tetra-

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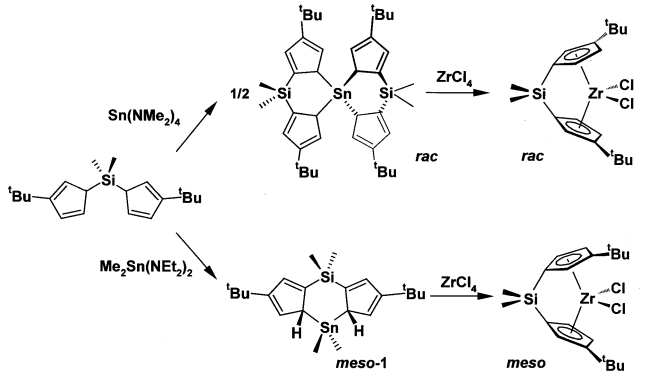
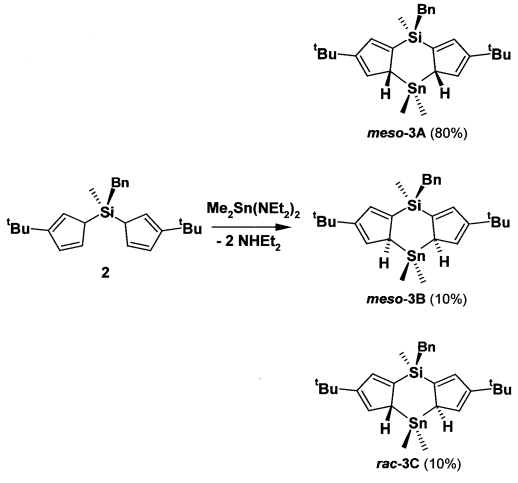


Scheme 1.

hydro-indacene, (**1**), with $ZrCl_4$ leads exclusively to the *meso*-configurated *ansa*-zirconocene dichloride (c.f. Scheme 1) [6]. This stereochemical result can arise from displacement of Me_2Sn by $ZrCl_2$ either under twofold retention or under twofold inversion, provided that the reaction modes at both Sn-bound carbon centers are identical. These two variants are not distinguishable for the reaction of compound **1** with $ZrCl_4$ but will diverge if the Si bridge carries two different substituents: in this case, twofold retention gives a product different from that resulting from twofold inversion. Interference of the changed Si substituent with the Sn–Zr exchange mechanism would be minimized by use of isotopic labelling; for practical reasons, however, we have chosen the more conveniently accessible methyl–benzyl-Si bridge as a stereochemical marker.

meso-2,6-di-*tert*-butyl-8-benzyl-4,4,8-trimethyl-8-sila-4-stanna-tetrahydroindacene (**3**) was obtained by reaction of benzyl–methyl-silanediyl-bis(3-*tert*-butyl-cyclopentadiene) (**2**) with $Me_2Sn(NEt_2)_2$ [9]. ^{1}H-NMR spectra of the product mixture indicate that the isomers **3A**, **3B** and **3C** are obtained in a ratio of 8:1:1 (Scheme 2). From this mixture, only the major isomer **3A** was



Scheme 2.

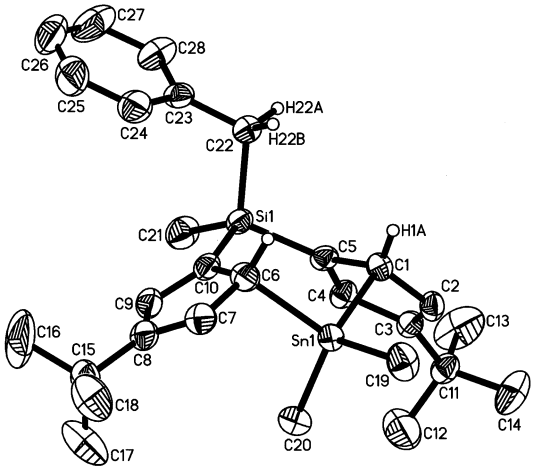


Fig. 1. Crystal structure of the benzylmethylsilyl-bridged compound **3A**. Thermal ellipsoids drawn at 50% probability, H atoms (except at C1, C6 and C22) omitted for clarity.

isolated. It was obtained, by crystallization from diethyl ether, in 48% yield and identified, by crystal structure determination, as the 8*s*-isomer with an axially positioned benzyl group (Fig. 1). As expected, the core geometry of **3A** is practically identical to that of the Me_2Si-bridged analog **1**, i.e. essentially unaffected by the benzyl substituent (Table 1). The lack of any formation

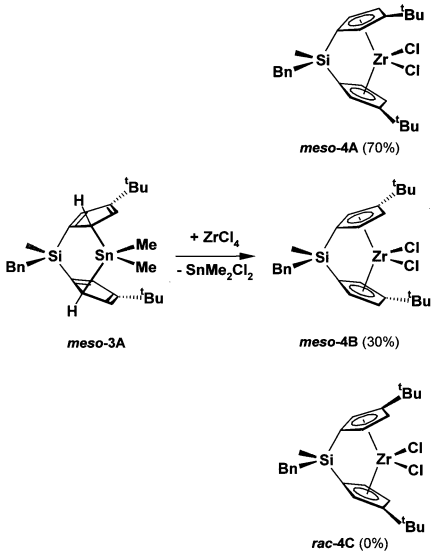
Table 1
Selected bond lengths (Å) and angles (°) of compound **3A** and, for comparison, of its dimethylsilyl-bridged analog **1** [4]

	3A	**1**
Bond lengths		
Sn(1)–C(1)	2.206(2)	2.214(4)
Sn(1)–C(6)	2.199(2)	2.214(4)
Sn(1)–C(19)	2.146(3)	2.152(7)
Sn(1)–C(20)	2.112(3)	2.108(6)
Si(1)–C(5)	1.856(2)	1.867(4)
Si(1)–C(10)	1.862(2)	1.867(4)
Si(1)–C(21)	1.845(3)	1.868(7)
Si(1)–C(22)	1.883(2)	1.850(7)
C(22)–C(23)	1.501(3)	
C(6)–C(7)	1.473(3)	1.465(5)
C(7)–C(8)	1.349(3)	1.349(5)
C(8)–C(9)	1.455(3)	1.447(5)
C(9)–C(10)	1.358(3)	1.348(5)
C(6)–C(10)	1.482(3)	1.489(5)
Bond angles		
C(2)–C(1)–Sn(1)	104.7(1)	106.2(2)
C(5)–C(1)–Sn(1)	100.6(1)	101.5(2)
C(6)–Sn(1)–C(1)	100.6(1)	102.6(2)
C(5)–Si(1)–C(10)	105.6(1)	105.2(2)
C(6)–C(10)–Si(1)	125.2(2)	125.1(2)
C(1)–C(5)–Si(1)	125.4(2)	125.1(2)
C(9)–C(10)–Si(1)	127.8(2)	127.2(3)
C(5)–Si(1)–C(22)	110.5(1)	111.0(2)
C(10)–Si(1)–C(22)	109.5(1)	111.0(2)
C(21)–Si(1)–C(22)	109.4(1)	108.7(4)
C(23)–C(22)–Si(1)	112.2(2)	

of **3B** or **3C** from $CDCl_3$ solutions of pure **3A** documents the configurational stability of this sila-stannatetrahydroindacene compound.

When a toluene solution of **3A** was reacted with a suspension of $ZrCl_4$ in toluene at room temperature, immediate appearance of the yellowish color of the *ansa*-zirconocene product and subsequent ^{1}H-NMR spectra showed that the starting material was rapidly consumed and that two new products, **4A** and **4B**, were formed in a ratio of ca. 2:1. While it was not possible to separate and isolate these complexes, complete structural assignments were possible, based on their NMR spectra. Both **4A** and **4B** give ^{1}H-NMR signals assignable to C_S-symmetric silyl-bridged zirconocenes. ROESY spectra of these products, which show distinct cross signals of the CH_3–Si and the phenyl–CH_2–Si groups with individual ring protons (Fig. 2), document that the major product **4A** has its benzyl and *tert*-butyl substituents on the same side of the molecule, while the minor isomer **4B** has the benzyl group on the side opposite to the *tert*-butyl substituents (Scheme 3). Remarkably enough, no trace of the C_1-symmetric, *rac*-like isomer **4C** can be detected by ^{1}H-NMR spectroscopy.

Preferential formation of the *meso*-configurated ansa-zirconocene isomer **4A** shows that $ZrCl_4$ attacks predominantly- presumably consecutively- at the 'backside' of both Sn-bound cyclopentadienyl units of compound **3A**, i.e. under inversion at both Sn-bound carbon atoms, as had been assumed for this type of metal exchange [4,8]. Prima facie puzzling, however, is the origin of the minor zirconocene isomer **4B**. The absence of the mixed retention–inversion product '*rac*'-**4C** implies that racemization- either of some reaction intermediate or of the final zirconocene product- cannot explain the formation of **4B**, since stepwise epimerization of a metal–cyclopentadienyl unit would always lead



Scheme 3.

primarily to the *rac*-like isomer **4C**. The Sn-to-Zr transfer of the second cyclopentadienyl unit must thus occur with the same stereochemistry as that of the first one in the formation of both **4A** and **4B**. Such a stereochemical coherence between the first and the second transmetallation step can be explained by two reaction paths.

In principle, a minor, possibly undetectable fraction of the *meso*-isomer **3B**, present in equilibrium with the dominant isomer **3A**, might give rise to the zirconocene isomer **4B** by Sn-to-Zr exchange steps under inversion at both Sn-bound C atoms. Any such equilibration between **3A** and **3B** appears unlikely, however, since the configurational stability of both isomers is documented by the observation that the 8:1 ratio of these isomers in the initial product mixture as well as the NMR spectra of pure **3A** in $CDCl_3$ solution remain unchanged for extended periods of time.

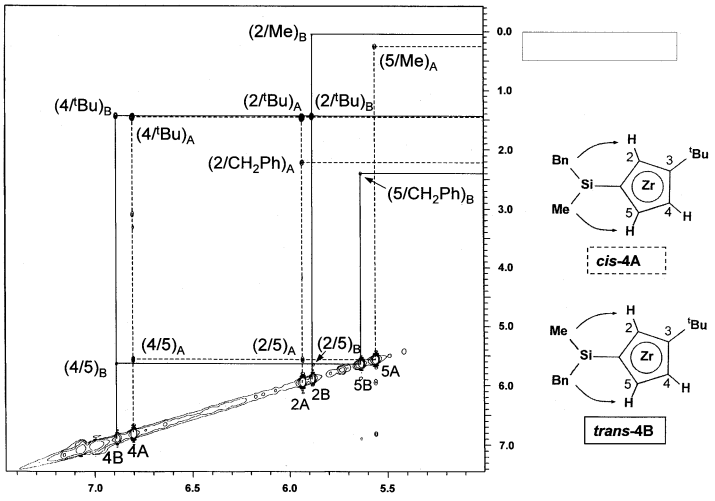


Fig. 2. ^{1}H-ROESY spectrum of the *ansa*-zirconocene product mixture containing **4A** and **4B**, in C_6D_6 solution. Broken lines correlate signals of isomer **4A**, solid lines those of isomer **4B**.

Therefore, we have to assume that the sila-stanna-tetrahydro-indacene isomer **3A** is amenable to a concerted 'front-side' attack of the electrophile $ZrCl_4$ at both Sn-bound C atoms, which leads, under retention of configuration at both of these centers, to isomer **4B** of the *ansa*-zirconocene product (Scheme 4). That this double-retention mechanism occurs with a rate comparable to that of the normally preferred inversion mechanism might be due to an accumulation of a rather high electron density at the 'front-side' of **3A** and/or to the steric shielding of its 'back-side' by the axially positioned benzyl substituent.

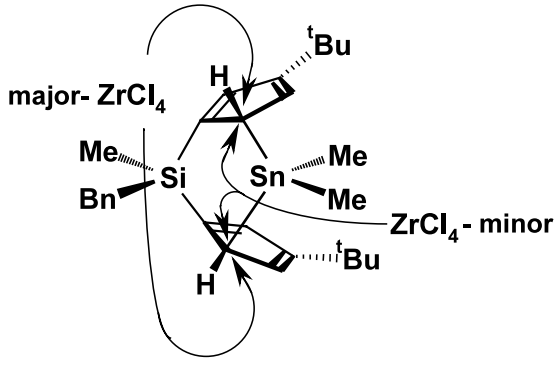
While the concerted attack of $ZrCl_4$ at the 'front-side' of the tin precursor **3A** might thus be particular to the specific sila-stanna-tetrahydro-indacene derivative studied here, our data provide first evidence that this hitherto scarcely discussed reaction mechanism has to be taken into account in designing transmetalation reactions for stereoselective syntheses. Studies on further stannylene derivatives appear necessary to delineate the conditions under which this 'front-side' reaction mode competes with the normally preferred 'back-side' attack of a metal halide at an Sn-bound C atom, which leads to an inversion of its configuration.

3. Experimental

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 and benzophenone. $Me_2Si(3\text{-}^tBu\text{–}C_5H_4)_2$ [10], $MeBnSiCl_2$ [11] and $Me_2Sn(NEt_2)_2$ [12] were prepared essentially as described in the literature. NMR spectra were obtained on a Bruker DRX 600 spectrometer.

3.1. Benzylmethylsilanediyl-bis(3-tert-butylcyclopentadiene) (2)

To a solution of 16.5 g of *tert*-butyl-cylcopentadienyl lithium (129 mmol) in 200 ml THF, pentane was added until the lithium salt just began to precipitate. Upon dropwise addition of a solution of 13.2 g of benzylmethyldichlorosilane (64 mmol) in 20 ml pentane, the solution turned yellow. After stirring overnight, the solvent was completely removed in vacuo and 50 ml of pentane was added. A colorless residue was removed by filtration, the clear filtrate treated with saturated aqueous NH_4Cl solution, neutralized with water and dried over $MgSO_4$. Removal of solvent gave the product as an oily, almost colorless residue, for which it was not possible to obtain assignable ^{1}H-NMR spectra, due to the presence of multiple isomers, and which was thus used without further purification for subsequent reactions. Crystals obtained from diethyl ether solution at −80 °C melt again when brought to room temperature (r.t.). Yield 22.9 g (63 mmol, 98% of theory).



Scheme 4.

3.2. meso-2,6-di-tert-Butyl-8s-benzyl-4,4,8-trimethyl-8-sila-4-stanna-tetrahydro-indacene (3A)

To a solution of benzylmethylsilanediyl-bis(3-*tert*-butylcyclopentadiene) (**2**, 5.8 g, 15.4 mmol) in 50 ml of diethylether a solution of 4.5 g bis(diethylamino)dimethylstannane in 25 ml of diethyl ether was slowly added via a dropping funnel. After stirring the reaction mixture for 4–5 h, the volume of the solution was reduced to 15 ml in vacuo. Storage at 0 °C gave, after a few days, colorless crystals of NMR-spectrally pure **3A**, which were collected by filtration. Yield 3.8 g (7.4 mmol, 48% of theory). ^{1}H-NMR ($CDCl_3$, 600 MHz, assignments supported by ROESY and HQMC spectra): δ 7.13 (t, $J = 17$ Hz, 2H), 7.03 (t, $J = 17$ Hz, 1H), 6.92 (d, $J = 17$ Hz, 2H), 6.68 (s, $J(^1H,Sn) = 19$ Hz, 2H), 6.28 (s, 2H), 4.14 (s, $J(^1H,Sn) = 101$ Hz, 2H), 2.40 (s, 2H), 1.16 (s, 18H), 0.52 (s, $J(^1H,Sn) = 52$ Hz, 3H), 0.41 (s, 3H), −1.21 (s, $J(^1H,Sn) = 54$ Hz, 3H). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 152.5, 145.1, 134.0, 128.6, 127.9, 125.9, 123.9, 57.0, 32.0, 31.1, 26.6, −3.9, −7.1, −19.2 ppm. These NMR spectra remained unchanged for periods of at least 3 days, indicating that compound **3A** is stable against any rearrangements.

3.3. meso-Benzylmethylsilyl-bis(3-tert-butyl-cyclopentadienyl) zirconium dichloride (4)

A solution of 500 mg of **3A** (1.0 mmol) in 20 ml of toluene was added, in the course of 20 min, to a suspension of 220 mg $ZrCl_4$ in 20 ml of toluene. The reaction mixture immediately developed the yellowish color of the *ansa*-zirconocene product. After stirring for ca. 3 h at room temperature (r.t.), the reaction mixture was filtered and the filtrate evacuated to dryness in vacuo. The solid residue was then subjected, under exclusion of light, to sublimation in vacuo at 90 °C to remove all Me_2SnCl_2. C_6D_6 solutions of the product thus obtained gave ^{1}H-NMR signals in accord with the

presence of both **4A** and **4B**, in a ratio of 2:1 (c.f. Fig. 2). ^{1}H-NMR for **4A** ($CDCl_3$, 600 MHz): δ 7.06 (pq, 2H), 6.98 (m, 3H), 6.79 (s, 2H), 5.92 (s, 2H), 5.55 (s, 2H), 2.20 (s, 2H), 1.45 (s, 18H), 0.23 (s, 3H). ^{13}C-NMR for **4A** ($CDCl_3$, 150 MHz): δ 148.8, 137.0, 129.7, 129.0, 125.5, 116.6, 113.1, 103.5, 33.7, 31.1, 20.0, −5.5 ppm. ^{1}H-NMR for **4B** ($CDCl_3$, 600 MHz): δ 7.06 (pq, 2H), 6.98 (m, 3H), 6.88 (s, 2H), 5.87 (s, 2H), 5.63 (s, 2H), 2.39 (s, 2H), 1.42 (s, 18H), 0.04 (s, 3H). ^{13}C-NMR for **4B** ($CDCl_3$, 150 MHz): δ 146.7, 136.9, 131.6, 129.0, 125.5, 119.1, 111.5, 103.0, 33.5, 31.2, 23.3, −8.9 ppm.

3.4. Crystal structure determination of compound 3A

Suitable crystals of compound **3A** were obtained from diethyl ether. Compund **3A** crystallizes as colorless prisms in the monoclinic space group $P2_1/c$ ($a = 13.666(2)$, $b = 14.769(2)$, $c = 14.024(3)$ Å, $\beta = 105.38(1)^\circ$, $V = 2729.1(8)$ Å^3, $Z = 4$, $\mu = 0.992$ mm^{-1}, $F_{000} = 1088$). X-ray diffraction analysis was carried out at 229 K on a Siemens P4 four-circle diffractometer using Mo–K_α radiation (71.073 pm) and a graphite monochromator. Crystal decay was monitored by measuring three standard reflections every 100 reflections. A total of 7404 reflections were collected in a θ-range of 2–27°, of which 5946 were independend ($R_{int} = 3.29\%$). The structure was solved using direct methods [13]. All non-hydrogen atoms were refined anisotropically by least-squares procedures based on F^2. Hydrogen atoms were located in the difference fourier map and refined isotropically except for the hydrogen atoms of the *tert*-butyl groups, which were refined on calculated positions with fixed isotropic U, using riding model techniques [13]. Final reliability factors were $R(F) = 2.94$ and $R_w(F^2) = 7.47\%$ for 5333 observed reflections with $I > 2\sigma(I)$ and $R(F) = 3.39$ and $R_w(F^2) = 7.92\%$ for all data. The Goodness-of-Fit was 1.046, the residual electron density 1.103 e$^-$ Å^{-3}, located in 1 Å distance from the Sn-atom.

4. Supporting information available

Crystallographic data and structural analysis for complex **3A** have been deposited with the Cambridge Crystallographic Data Centre no. CCDC 160359. Copies of this information may be obtained, free of charge, from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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