

Isomeric zirconocenophane dichlorides involving two disiloxane-bridged indenyl ligands

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Abstract

The title complex **2** = $[\{O(\text{Me}_2\text{SiC}_9\text{H}_6)_2\}\text{ZrCl}_2]$ (SiC_9H_6 = 2-silylated indenyl group) has been prepared in a way slightly different from that published recently by Rausch and coworkers (*J. Organomet. Chem.*, 501 (1995) 375). In contrast to the earlier report, the ^1H NMR spectra of **2** in C_6D_6 and CD_2Cl_2 reflect clearly the presence of both *rac*-**2** and *meso*-**2** (ca. 4:1). From toluene, **2** crystallizes as a racemic mixture; *rac*-**2**: monoclinic; space group $P2_1/c$, $a = 1278.2(4)$, $b = 1196.2(4)$, $c = 1567.8(6)$ pm; $\beta = 100.8(3)^\circ$; $R_1 = 0.0314$ ($wR_2 = 0.0771$). The high-resolution ^1H NMR spectrum of *rac*-**2** does not match with the crystal structure: most probably, rapid (on the NMR time scale) racemization takes place down to at least -80°C .

Keywords: Zirconocene; Indenyl; Siloxane; Metallocenes; Crystal structure; NMR

1. Introduction

As part of the numerous attempts to develop novel *ansa*-metallocene-based complexes of early transition metals as potentially efficient catalysts for olefin polymerization, world-wide interest has, inter alia, been focused on complexes with tetramethyldisiloxanediyl-tethered cyclopentadienyl ligands. Thus, considerable attention has been paid to complexes of the general type **1**: $[\{O(\text{Me}_2\text{SiC}_5\text{H}_4)_2\}\text{MX}_n]_m$ (X = halide) with $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ($n = 2, m = 1$) [1–5]¹ and Pr and Yb ($n = 1, m \geq 2$) [6]¹ respectively. During this study, two completely independent syntheses and X-ray studies of the Zr-complex with $\text{X} = \text{Cl}$ (**1a**) were undertaken [2,3]. Quite recently, the first examples of slightly more sophisticated derivatives of complex type **1** carrying still another substituent (i.e. in addition to the Si atom) on the five-membered ring were reported [5,7]. While our group was just involved in the structural characterization of the new disiloxane-bridged bis(indenyl) complex $[\{O(\text{Me}_2\text{SiC}_9\text{H}_6)_2\}\text{ZrCl}_2]$ **2**, the synthesis and some catalytical properties of this compound were described by Rausch and coworkers [7]¹. This prompts us to also publish our present results concerning complex **2**, based

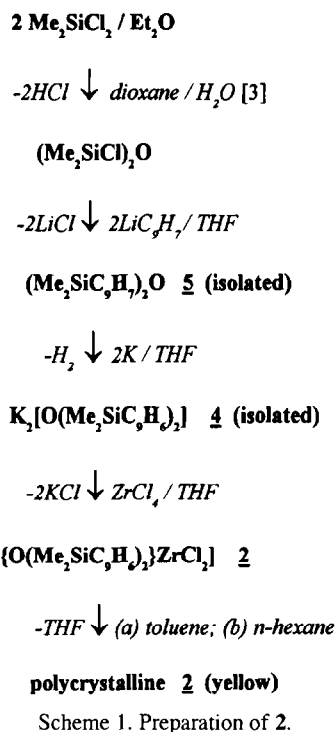
mainly on a slightly different preparative approach, more informative high-resolution ^1H NMR spectra and the successful single-crystal X-ray study of **2**.

2. Synthesis and general properties of 1,1,3,3-tetramethyldisiloxanediyl-bis(indenyl)zirconium(IV)dichloride, **2**

$[\{O(\text{Me}_2\text{SiC}_9\text{H}_6)_2\}\text{ZrCl}_2]$ **2** was prepared according to Scheme 1. While Rausch and coworkers [7] had arrived at their title compound **2** by reacting ZrCl_4/THF with the in situ prepared dilithium salt $\text{Li}_2\text{-}[\text{O}(\text{Me}_2\text{SiC}_9\text{H}_6)_2]$ **3**, the corresponding dipotassium salt **4** was isolated, characterized and applied instead of **3** in our laboratory. The unmetalated precursor **5** = $(\text{Me}_2\text{SiC}_9\text{H}_7)_2\text{O}$ of **3** and **4** was obtained by hydrolysis of $\text{Me}_2\text{SiCl}(\text{C}_9\text{H}_7)$ (**6** [7,8]) and by reaction of $(\text{Me}_2\text{SiCl})_2\text{O}$ [2,6] with LiC_9H_7 (1:2) respectively. Subsequent metalation of **5** was carried out either with $^n\text{BuLi}$ [7] or with elemental potassium. The ^1H NMR spectra of **5** and **6** reported by Rausch and coworkers [7] display a pair of apparently diastereotopic methyl groups, confirming that the indene molecule is exclusively silylated in its dissymmetric 1-position. More surprisingly, the ^1H NMR spectrum of **4** dissolved in $\text{THF-}d_8$ shows likewise two almost equally intense

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¹ See note added in proof.



methyl proton resonances, while the related salts $\text{K}_2[\text{O}(\text{Me}_2\text{SiC}_5\text{H}_3\text{R})_2]$ with $\text{R} = \text{H}$ and ${}^t\text{C}_4\text{H}_9$, give rise to just one methyl resonance [5]. In all cases, the relative intensities integrated over all indenyl and silyl proton resonances respectively match with the theoretically expected ratios.

The lemon-yellow product **2** is air stable, readily soluble even in toluene and benzene (less satisfactorily in n-hexane) and decomposes without melting above ca. 250°C (increasing darkening). Making use of the apparently different solubility of *rac*-**2** and *meso*-**2** in n-hexane, either a 4:1 mixture of the two expected stereoisomers or exclusively the more abundant isomer (most probably *rac*-**2**) could be obtained (see Experimental Section).

Needle-shaped crystals of *rac*-**2** were grown from a saturated toluene solution after addition of some n-hexane and cooling to ca. +4°C. The mass spectrum of **2** displays above ca. 120°C the signals of all expected isotopomers of the molecular ion M^+ :

| | | | | | | | | | |
|----------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| <i>m/e</i> | 520 | 521 | 522 | 523 | 524 | 525 | 526 | 527 | 528 |
| (observed as well as calculated) | | | | | | | | | |
| relative intensity (observed) | 87 | 53 | 100 | 50 | 70 | 30 | 40 | 15 | 13 |
| relative intensity (calculated) | 85 | 48 | 100 | 45 | 70 | 25 | 33 | 10 | 10 |

Only three to four other fragments containing one Zr atom (with $I_{\text{rel}} > 5\%$) occur, along with about five

Table 1

Summary of crystal data and details of data collection and refinement for **2**

| | |
|---|--|
| Formula | $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{OSi}_2\text{Zr}$ |
| <i>M</i> (g mol ⁻¹) | 522.71 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| <i>a</i> (pm) | 1278.2(4) |
| <i>b</i> (pm) | 1196.2(4) |
| <i>c</i> (pm) | 1567.8(6) |
| β (°) | 100.8(3) |
| <i>V</i> (10 ⁶ pm ³) | 2354.8(14) |
| <i>Z</i> | 4 |
| <i>D_c</i> (g cm ⁻³) | 1.474 |
| <i>F</i> (000) | 1064 |
| Temperature (K) | 293 |
| Diffractometer | Syntex P2 ₁ |
| Radiation λ (pm) | 71.073 |
| μ (Mo K α) (nm ⁻¹) | 0.711 |
| Scan technique | $2\theta - \theta$ scan |
| 2θ range (°) | $4.7 < 2\theta < 50.1$ |
| Number of reflections (total) | 6437 |
| Number of reflections in refinement | 4172 |
| Number of refined parameters | 281 |
| Goodness of fit | 1.107 |
| Final <i>R</i> indices [$\{ F_o > 2\sigma(F_o)\}$] | $R_1 = 0.0314, wR_2 = 0.0771$ |
| <i>R</i> indices (all data) | $R_1 = 0.0397, wR_2 = 0.0821$ |
| Weighting scheme | $[\sigma^2(F_o)^2 + (0.0482P)^2]^{-1}$ |
| | $P = (F_o^2 + 2F_c^2)/3$ |

comparatively intense metal-deficient ligand fragments (see Experimental Section).

3. Crystal structure of **2**

The crystallographic X-ray analysis of a needle-shaped crystal grown from a concentrated solution of **2**

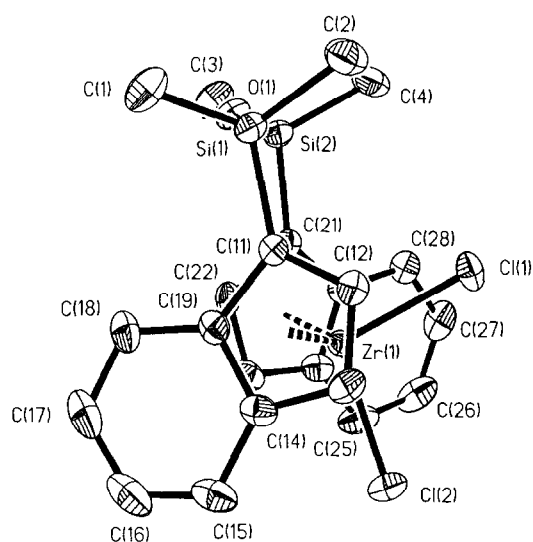


Fig. 1. ORTEP plot of the molecular structure of the (R,R)-enantiomer of **2**: the ZrCl_2 fragment almost coincides with the plane of the paper.

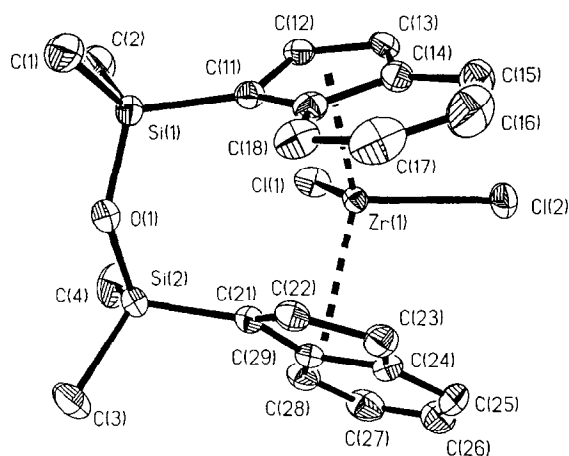


Fig. 2. ORTEP plot of the molecular structure of the (R,R)-enantiomer of **2**: the ZrCl_2 fragment is oriented almost perpendicular to the plane of the paper.

in toluene (temperature $+4^\circ\text{C}$; crystallization period ca. 5 weeks) confirms the presence of the racemic mixture *rac-2* only. Actually, *rac-2* is a priori expected to be sterically favoured [5]. Data of particular relevance for the X-ray study are given in Table 1. Figs. 1 and 2 present two alternative views of the molecular structure of the (R,R)-enantiomer of *rac-2*, and Table 2 some selected distances and bond angles respectively. As expected, the structure is very similar to that of the complex $[\{\text{C}_2\text{H}_4(\text{Me}_2\text{SiC}_9\text{H}_6)_2\}\text{ZrCl}_2]$ (**7** [9]) and, in view of the disposition of the ring-bridging $(\text{Me}_2\text{Si})_2\text{O}$ fragment, to that of the complex $\{\text{O}(\text{Me}_2\text{SiC}_5\text{H}_3\text{-}^t\text{Bu})_2\}\text{ZrCl}_2$ **8** [5]. In these compounds, the line connecting the Zr atom with the gravity centre of its two Cl atoms is no longer a C_2 axis. Consequently, the molecule possesses four crystallographically (and structurally) non-equivalent methyl groups and cyclopentadienyl CH fragments respectively, along with eight different CH fragments of the two benzo groups. Interestingly,

pseudo- C_2 symmetry is, however, reflected by the ^1H NMR spectra of **2**, **7** [9] and **8** (vide infra).

As in the structure of **8**, the Zr–C bond distances of **2** vary noticeably too. Thus, the four C-atoms shared by the five- and six-membered rings of the two indenyl units are more distant from the Zr atom (265.9 to 258.9 pm) than the six C-atoms C11–C13 and C21–C23 (251.9 to 248.5 pm), so that the coordination of the two five-membered rings might be considered as partially allyl-like. Actually, the C–C bonds connecting the allyl-like C_3 -units with the C_6 -units are on average the longest (144.1 pm), while two C–C bonds within each benzo group (C15–C16, C17–C18, C25–C26 and C27–C28) turn out to be the shortest (average 136.1 pm). The angle between the planes of the two five-membered rings ('opening angle'), which might be of particular relevance for catalytic activity [3,9], amounts to $52.1(17)^\circ$, which is even lower than that of **7** (54° [9]) and **8** ($52.6(3)^\circ$ [10]) respectively.

4. ^1H NMR spectroscopy

Rausch and coworkers [7] have reported that the 200 MHz ^1H NMR spectrum of **2** dissolved in CDCl_3 indicates the presence of one singular species only, which should, for obvious conformational reasons, correspond to the racemic mixture *rac-2* [7]. We have found that the 400 MHz ^1H NMR spectra of **2** disclose, both in C_6D_6 and CD_2Cl_2 solution, two very similar, apparently individual spectra of relative intensities 4:1 attributable to the two principally expected stereoisomers *rac-2* and *meso-2*. Correspondingly, we have observed earlier two individual NMR spectra in the case of complex **8** (relative intensities ca. 25:1 [5]), and Herrmann et al. [9] have reported that complex **7** like-

Table 2
Selected interatomic distances (bonding and non-bonding, pm) and bond angles ($^\circ$) in **2**

| Interatomic distances | | | |
|-----------------------|-----------|----------------------------|-----------|
| Zr(1)–Cl(1) | 242.2(9) | Zr(1)–Cl(2) | 244.1(10) |
| Zr(1)–C(11) | 251.5(3) | Zr(1)–C(21) | 251.9(3) |
| Zr(1)–C(13) | 249.8(3) | Zr(1)–C(23) | 250.9(3) |
| Zr(1)–C(14) | 258.9(3) | Zr(1)–C(24) | 265.3(3) |
| Zr(1)–C(19) | 261.9(3) | Zr(1)–C(29) | 265.9(3) |
| C(11)–C(12) | 142.7(4) | C(21)–C(22) | 142.9(4) |
| C(11)–C(19) | 145.7(4) | C(21)–C(29) | 145.3(4) |
| C(15)–C(16) | 134.9(6) | C(25)–C(26) | 136.0(6) |
| C(17)–C(18) | 137.3(5) | C(27)–C(28) | 136.4(4) |
| Si(1)–O(1) | 164.7(2) | Si(2)–O(1) | 165.0(2) |
| Si(1)–C(11) | 187.3(3) | Si(2)–C(21) | 186.8(3) |
| Cl(1) \cdots O(1) | 462.6(18) | Cl(2) \cdots O(1) | 643.8(2) |
| Zr(1) \cdots O(1) | 401.0(15) | | |
| Bond angles | | | |
| Cl(1)–Zr(1)–Cl(2) | 98.9(4) | Cent(1)–Zr(1)–Cent(2) | 130.9(3) |
| Cent(1)–C(11)–Si(1) | 5.3(15) | Cent(2)–C(21)–Si(2) | 6.0(15) |
| Si(1)–O(1)–Si(2) | 137.9(13) | plane(1) \cdots plane(2) | 52.1(17) |

Table 3
Survey of ^1H NMR data of **2** observed in two different solvents (room temperature)

| Compound | δ (ppm) of $\text{O}(\text{Me}_2\text{SiC}_9\text{H}_6)_2$ ligands | | |
|--|---|---|---|
| | C_5H_2 | C_6H_4 | $\text{Si}(\text{CH}_3)_2$ |
| [[$\text{O}(\text{Me}_2\text{SiC}_9\text{H}_6)_2$] ZrCl_2] Solvent C_6D_6 (400 MHz) | 6.02 (d, 2H, $J_{\text{HH}} = 3.6$ Hz) | 7.01 (t, 2H, $J_{\text{HH}} = 7.6$ Hz) | 0.44 (s, 6H) |
| | 6.64 (d, 2H, $J_{\text{HH}} = 3.6$ Hz) | 7.07 (t, 2H, $J_{\text{HH}} = 7.6$ Hz) | 0.63 (s, 6H) |
| | | 7.66 (d, 2H, $J_{\text{HH}} = 8.8$ Hz) | |
| | | 7.76 (d, 2H, $J_{\text{HH}} = 8.8$ Hz) | |
| | less abundant component (see text) | 6.39 (dd, 2H, $J_{\text{HH}} = 3.6$ Hz) 6.59 (d, 2H, $J_{\text{HH}} = 3.6$ Hz) | 6.98–7.09 (m, 4H) ^a 7.58 (dd, 2H, $J_{\text{HH}} = 8.8$ Hz) 7.73 (d, 2H, $J_{\text{HH}} = 8.8$ Hz) |
| [[$\text{O}(\text{Me}_2\text{SiC}_9\text{H}_6)_2$] ZrCl_2] Solvent $\text{CD}_2\text{Cl}_2/\text{TMS}$ (400 MHz) | 6.04 (d, 2H, $J_{\text{HH}} = 4.0$ Hz) | 7.26 (t, 2H, $J_{\text{HH}} = 7.2$ Hz) | 0.43 (s, 6H) |
| | 6.70 (d, 2H, $J_{\text{HH}} = 3.6$ Hz) | 7.37 (t, 2H, $J_{\text{HH}} = 7.2$ Hz) | 0.64 (s, 6H) |
| | | 7.62 (d, 2H, $J_{\text{HH}} = 8.8$ Hz) | |
| | | 7.85 (d, 2H, $J_{\text{HH}} = 8.8$ Hz) | |
| | less abundant component (see text) | 6.57 (d, 2H, $J_{\text{HH}} = 4.0$ Hz) 7.09 (d, 2H, $J_{\text{HH}} = 4.0$ Hz) | 7.17 (t, 2H, $J_{\text{HH}} = 7.2$ Hz) 7.24 (t, 2H, $J_{\text{HH}} = 7.2$ Hz) 7.51 (d, 2H, $J_{\text{HH}} = 8.4$ Hz) ^b |

^a Part of the two expected triplets is buried under resonances of the more abundant isomer.

^b The doublet at higher field is buried under resonances of the more abundant isomer.

wise results primarily as a mixture of the racemic and the meso form [9]. The ^1H NMR data of **2** are listed in Table 3. To illustrate the overall quality of the room temperature NMR spectra of **2** some multiplet components which disclose clearly higher-order features, two sections of the spectra recorded in CD_2Cl_2 and C_6D_6 solution, are shown in Fig. 3. A 200 MHz ^1H COSY

spectrum has, moreover, confirmed that the resonances of the two presumably “individual” spectra actually belong to different molecules.

Each of the two spectra of different relative intensity displays two CH_3 singlets, two C_5H_2 doublets [11] and two pairs of C_6H_4 doublets and triplets respectively. This feature is primarily expected for the meso-form in

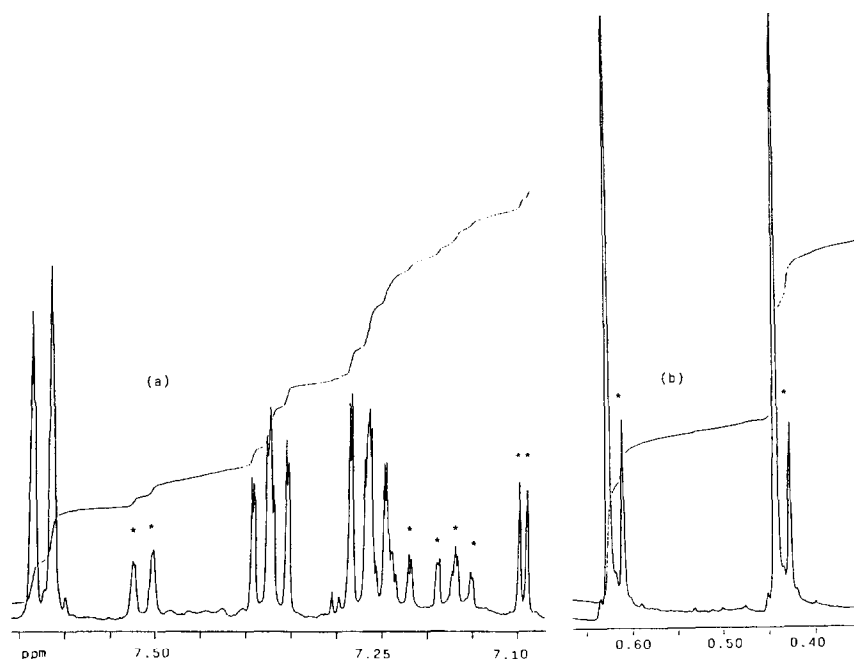


Fig. 3. Selected sections of the appropriately expanded 400 MHz ^1H NMR spectra of **2**: (a) C_9H_6 region, solvent $\text{CD}_2\text{Cl}_2/\text{TMS}$; (b) $\text{Si}(\text{CH}_3)_2$ region, solvent C_6D_6 (resonances of the less abundant species (meso-form) are marked with an asterisk).

which the two $(\text{Me}_2\text{Si})_2\text{O}$ -interlinked indenyl ligands would adopt an eclipsed configuration, making them spectroscopically equal. However, the components of the racemic form should, in the absence of any configurational mobility, display twice as many first-order proton resonances as the meso-form (vide supra). The obvious deviation of the more intense spectrum from this expectation can be considered as strong evidence of rapid (at least on the NMR timescale) configurational fluxionality. The appearance of separate spectra of *rac*-**2** and *meso*-**2** rules out, however, any mechanism involving these two isomers directly; hence, rapid intramolecular racemization is more likely. One possible pathway has been proposed by Curtis et al. [1], and a concomitant interconversion of two (indistinguishable) meso-conformers is likewise imaginable. According to a low-temperature ^1H NMR study of **2** (360 MHz, solvent toluene- d_8), the most significant section of the spectrum of *rac*-**2** between 0 and 2 ppm (range of methyl protons) did not display any change still at -80°C . This observation agrees with findings by Collins et al. [12] who did not observe, down to -115°C , spectra of virtually rigid molecules of the complex type $[\{\text{C}_2\text{H}_4(\text{C}_5\text{H}_2\text{RR}')_2\}\text{TiCl}_2]$. Virtual C_2 -symmetry is likewise displayed by the spectra of racemic **8** [5] and **7** [9], in contrast to the reported molecular structures while, for example, the spectra of both racemic and meso-configured $[\{\text{C}_2\text{H}_4(\text{C}_9\text{H}_7)_2\}\text{ZrCl}_2]$ were most recently shown to contain more complicated sections (e.g. those due to their methylene proton resonances [13]). In the latter case, variable-temperature NMR studies actually suggest facile conformational rearrangement components.

The 200 MHz $^1\text{HNMR}$ (survey) spectrum of a sample of the species assumed to be *rac*-**2** only (in CD_2Cl_2) clearly resembles the spectrum of the more abundant isomer presented above, although the 200 MHz spectrum is richer in higher-order features than the 400 MHz spectrum. One significant change is the conversion of the (at 400 MHz) well-discernible triplets of protons of the benzo group into six almost equally spaced pseudo-multiplets.

The 200 MHz NMR spectrum of the dipotassium salt $\text{K}_2[\text{O}(\text{Me}_2\text{SiC}_9\text{H}_6)_2]$ (**4**) dissolved in THF- d_6 is notably richer in surprisingly sharp lines than the spectra of *rac*-**2** and *meso*-**2** respectively. As expected for the formula of **4**, the integral over all resonances in the range of methyl protons (-0.2 to 0.9 ppm) equals that over all resonances from the C_9H_6 ring protons (5.6 to 7.8 ppm). However, *two* almost equally intense, sharp methyl singlets at 0.09 and 0.43 ppm accompanied by about four weaker high-field satellites occur. This interesting feature does not rule out the possibility that, even in THF solution, the potassium ions might be anchored comparatively tightly to distinct ring carbon atoms so that even in the anion of **4** the two CH_3 groups would

also be prochiral. Alternatively, two non-equivalent $[\text{O}(\text{Me}_2\text{SiC}_9\text{H}_6)_2]^{2-}$ anions might be present in solution. Attempts to obtain single crystals of **4** in view of a promising X-ray study are underway.

5. Experimental section

5.1. General

All operations were carried out under pure nitrogen, making use of familiar Schlenk techniques adopting throughout carefully conditioned solvents and starting materials. IR spectra were recorded on the Perkin-Elmer model 1720 (Fourier transform technique; KBr pellets), and ^1H NMR spectra either on the Bruker instruments WH 400 (400.13 MHz) and AM 360 (360 MHz) or on a Varian Gemini 200 spectrometer (200 MHz). Mass spectrometric (MS) studies were carried out on a VG 70 SE instrument (EI; 70 eV) equipped with an OPUS 200 data processing unit.

5.2. Preparation of $(\text{Me}_2\text{SiCl})_2\text{O}$, LiC_9H_7 and $(\text{Me}_2\text{SiC}_9\text{H}_7)_2\text{O}$ (**5**)

The synthesis of $(\text{Me}_2\text{SiCl})_2\text{O}$ is described in Ref. [3]. 250 ml of commercial, black indene (Merck) had to be fractionated over a 30 cm Vigreux column at a bath temperature of 70°C to arrive, at a pressure of 11.97 hPa (43°C), at about 220 ml of colourless, pure indene. Subsequently, 250 ml of a 1.6 molar solution of $^n\text{BuLi}$ in *n*-hexane (Merck) was added dropwise within ca. 80 min to a solution of 38.72 g (333.33 mmol) of indene in 200 ml of THF cooled down to -70°C . The red suspension was stirred for 1 h at lower temperatures and thereafter at room temperature (12 h). 33.39 g (273.46 mmol, 82%) of finely powdered, white LiC_9H_7 was obtained after solvent evaporation, extensive washing with *n*-hexane (several portions of ca. 100 ml), filtration and drying in vacuo. 12.71 g (104.12 mmol) of LiC_9H_7 dissolved in 200 ml of THF was added dropwise at room temperature within ca. 60 min to a solution of 10.58 g (52.06 mmol) of $(\text{Me}_2\text{SiCl})_2\text{O}$ in 250 ml of THF (colour change from golden yellow to bright red). After stirring for 3 h in a water bath (45°C), and for another 48 h at room temperature, the solvent was evaporated. The dark red, syrup-like residue was dissolved in 300 ml of *n*-hexane. After filtration (D-4 frit) and solvent evaporation 17.77 g (49.0 mmol) of greenish-brown, viscous **5** was obtained in a yield of 94%.

5.3. Preparation of $\text{K}_2[\text{O}(\text{Me}_2\text{SiC}_9\text{H}_6)_2]$ (**4**)

A solution of 17.77 g (49.0 mmol), of viscous, green-brown **5** in 100 ml of THF cooled down to 0°C (ice bath) was added dropwise within 30 min to a

suspension of 5.0 g (127.9 mmol) of freshly prepared, granulated potassium in 200 ml of THF. Hydrogen evolution is observed mainly during the first 1.5 h of subsequent stirring over an oil bath (temperature 50°C). After ca. 20 h of stirring in total, the initially greenish-brown suspension had changed to a carmine-red solution. After filtration at elevated temperature and solvent evaporation, a virtually inhomogeneous, greenish-grey wax remained, which was stirred for 1 h in 200 ml of n-hexane. The supernatant orange-red solution was replaced, and the remaining green solid dried in vacuo. Finally, 20.28 g (46.20 mmol) of a bright greyish-green product was obtained (yield 94.2% referred to **5** and 88.7% referred to (Me₂SiCl)₂O).

5.4. Preparation of [$\{O(Me_2SiC_9H_6)_2\}ZrCl_2$] (**2**)

A dark violet-brown solution of 2.78 g (6.34 mmol) of **4** in 100 ml of THF was added dropwise to a warm (ca. 50°C), faintly pink coloured solution of 2.39 g (6.34 mmol) of ZrCl₄(THF)₂ in ca. 80 ml of THF. The resulting orange juice-like suspension was stirred for 3 days in an oil bath (temperature 50°C). After solvent evaporation and uptake of the residue with n-hexane, the bright yellow suspension was filtered over a D-4

frit. The solid residue was redissolved in toluene. After slow addition of small portions of n-hexane to this orange-yellow solution (final toluene/hexane ratio 3:1) and cooling to 4°C, the major part of the dissolved product was obtained as a microcrystalline, analytically pure yellow solid. Yield 1.13 g (2.16 mmol, 34.1%). Anal. Found: C, 50.59; H, 4.71. C₂₂H₂₄Cl₂OSi₂Zr Calc.: C, 50.55; H, 4.63%. ¹H NMR: see Table 2; MS: *m/z* 522 (M⁺; 65%); 507 (M⁺-Me, 20%); 487 (M⁺-Cl, 25%); 485 (M⁺-4Me, 25%); 469 (uncertain assignment, 12%); 313 (O(SiC₉H₆)₂CH⁺; 25%); 247 (O(SiMe₂)₂C₉H₆⁺; 25%); 231 (O(SiMe₂)₂C₉H₆CH₂⁺; 10%); 172 (SiMe₂C₉H₆⁺; 100%); 158 (SiMeHC₉H₆⁺; 25%). IR (KBr): [ν/cm^{-1}] 3089 w, 3067 w, 2955 w (ν -CH); 1340 (ν -CC); 1254 s (δ -CH); 1056 s, 1045 s, 1036 s, 1010 s (ν -SiO); 830, 791, 748, 715, 702.

A sample of the pure isomer *rac-2* was obtained by dissolving the major part of the crude material (isolated from the THF solution) in n-hexane. After evaporation of all n-hexane from the clear solution, short drying and uptake with comparatively little toluene, pure *rac-2* started to crystallize from this solution at a temperature of ca. +4°C.

¹H NMR (200 MHz, CD₂Cl₂): δ 0.43 (s, 6H, CH₃), δ 0.64 (s, 6H, CH₃), δ 6.04 (dd, 2H, C₅H₂), δ 6.71 (d,

Table 4

Atom coordinates ($\times 10^4$) and isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **2** with estimated standard deviations in parentheses

| Atom | x | y | z | <i>U</i> _{eq} |
|-------|---------|----------|---------|------------------------|
| Zr(1) | 3117(1) | 1177(1) | 2418(1) | 29(1) |
| Cl(1) | 4780(1) | 174(1) | 2512(1) | 50(1) |
| Cl(2) | 3689(1) | 2570(1) | 3548(1) | 54(1) |
| C(1) | 1362(3) | 313(4) | -905(2) | 66(1) |
| C(2) | 3585(3) | -561(3) | -213(3) | 65(1) |
| C(3) | 913(3) | -2661(3) | 1560(3) | 69(1) |
| C(4) | 3300(3) | -2519(4) | 1615(3) | 72(1) |
| Si(1) | 2337(1) | -40(1) | 87(1) | 39(1) |
| O(1) | 1780(2) | -1010(2) | 599(1) | 45(1) |
| C(11) | 2638(2) | 1230(2) | 789(2) | 34(1) |
| C(12) | 3663(2) | 1735(2) | 1025(2) | 37(1) |
| C(13) | 3605(2) | 2720(2) | 1493(2) | 42(1) |
| C(14) | 2504(3) | 2937(2) | 1499(2) | 43(1) |
| C(15) | 1977(3) | 3844(3) | 1832(2) | 62(1) |
| C(16) | 902(4) | 3866(4) | 1670(3) | 79(1) |
| C(17) | 296(3) | 3013(4) | 1190(2) | 72(1) |
| C(18) | 767(2) | 2103(3) | 882(2) | 52(1) |
| C(19) | 1904(2) | 2040(2) | 1045(2) | 39(1) |
| Si(2) | 2057(1) | -1706(1) | 1523(1) | 40(1) |
| C(21) | 2121(2) | -642(2) | 2403(2) | 35(1) |
| C(22) | 1367(2) | 247(2) | 2360(2) | 39(1) |
| C(23) | 1546(2) | 863(3) | 3138(2) | 47(1) |
| C(24) | 2356(2) | 308(2) | 3735(2) | 45(1) |
| C(25) | 2817(3) | 517(3) | 4618(2) | 64(1) |
| C(26) | 3579(4) | -195(3) | 5027(2) | 71(1) |
| C(27) | 3924(3) | -1114(3) | 4596(2) | 64(1) |
| C(28) | 3518(2) | -1337(3) | 3745(2) | 48(1) |
| C(29) | 2710(2) | -628(2) | 3290(2) | 37(1) |

2H, C₅H₂), { δ 7.23 (ψ -d), 7.27 (ψ -t), 7.30 (ψ -d), 7.34 (ψ -d), 7.38 (ψ -t), 7.42 (ψ -d): 4H in total, C₆H₄}, { δ 7.61(ψ -t), 7.65 (ψ -t), 7.83 (ψ -d), 7.87 (ψ -d): 4H in total, C₆H₄}.

5.5. X-ray crystallography of 2

Owing to the excellent quality of the single crystal selected, the determination of the crystal structure of **2** turned out to be straightforward and devoid of any obstacles. A three-dimensional Patterson synthesis was adopted to determine the position of the Zr atom. Subsequent difference Fourier and LSQ calculations led to the positions of the C, O and Si atoms. All non-H atoms were refined anisotropically. Refinements of the H atoms were based on a fixed C–H distance of 96 pm and one common temperature factor. Atomic coordinates and isotropic temperature factors are collected in Table 4. Interatomic distances and bond angles (Table 2) were determined using programs specified in Ref. [14]. Crystal data and some details of data collection and refinement are given in Table 1 [15].

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Note added in proof

Most recently, the catalytic properties of the title compound **2** have been studied by two different groups: (a) B. Liang, Y. Li and G. Xie, *Macromol. Rapid Commun.*, **17** (1996) 193; (b) W. Kaminsky and coworkers (Hamburg), personal communication. The X-ray structures of two ytrocen derivatives with an (Me₂Si)₂O bridge have likewise been mentioned briefly: H. Yasuda and E. Ihara, *Macromol. Chem. Phys.*, **196** (1995) 2417.