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Bis[2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindenyl]zirconium dichloride: synthesis, torsional isomerism and olefin polymerization catalysis

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Abstract

The synthesis and characterization of an unbridged metallocene catalyst precursor bis[2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindenyl]zirconium dichloride (**3**) is reported. The solid state structure of **3** reveals two different rotamers in the asymmetric unit corresponding to a C_1 symmetric, 'central/lateral:gauche'-like conformation, and a C_2 symmetric, 'central:*syn*' conformation, respectively. The ^{1}H and ^{13}C NMR spectra of **3** are, at ambient temperature, consistent with time-averaged molecular C_{2v} symmetry. Dynamic NMR measurements show splitting of the ^{1}H resonances at 173 K indicating that a single C_2 symmetric bent-metallocene conformation is observed. Upon activation with methylaluminoxane, **3** polymerizes ethylene with an activity of 500 kg PE/mol Zr/h ($T_p = 80$°C; $P(C_2H_4) = 1.6$ bar; [Al]:[Zr] = 3000:1; $M_w = 43000$; $M_w/M_n = 2.2$; $T_m = 133$°C).

Keywords: Indenyl; Zirconium; Metallocene; Siloxy; Olefin polymerization

1. Introduction

The discovery of chiral *ansa*-metallocene-based catalyst systems has revolutionized polymer synthesis and polyolefin technology [1]. Modification of the ligand substitution pattern has a direct impact on the microstructure of the produced polymer, e.g. isotactic [2], hemiisotactic [3], syndiotactic [4] and isotactic-atactic-block [5] poly-α-olefins have been prepared by employing appropriately substituted bis(cyclopentadienyl), bis(indenyl) or related complexes.

Bent metallocenes bearing two substituted η^5-indenyl ring systems are known to exhibit torsional isomerism [5,6]. Coates and Waymouth observed both *anti* and *syn* conformations of bis(2-phenylindenyl)zirconium dichloride in the unit cell [5]. Erker and coworkers have demonstrated the existence and equilibration of at least three different solution rotamers for chiral 1-substituted bis(indenyl)zirconium dichlorides [6].

We have previously reported the preparation of several siloxy-substituted bis(indenyl) *ansa*-metallocene complexes and their application in homogeneous polymerization of α-olefins [7]. The present paper describes the synthesis and characterization of an unbridged siloxy-substituted catalyst precursor bis[2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindenyl]zirconium dichloride (**3**), its molecular structure and solution dynamics, and the activation of **3** with methylaluminoxane (MAO) for polymerization of ethylene and propylene.

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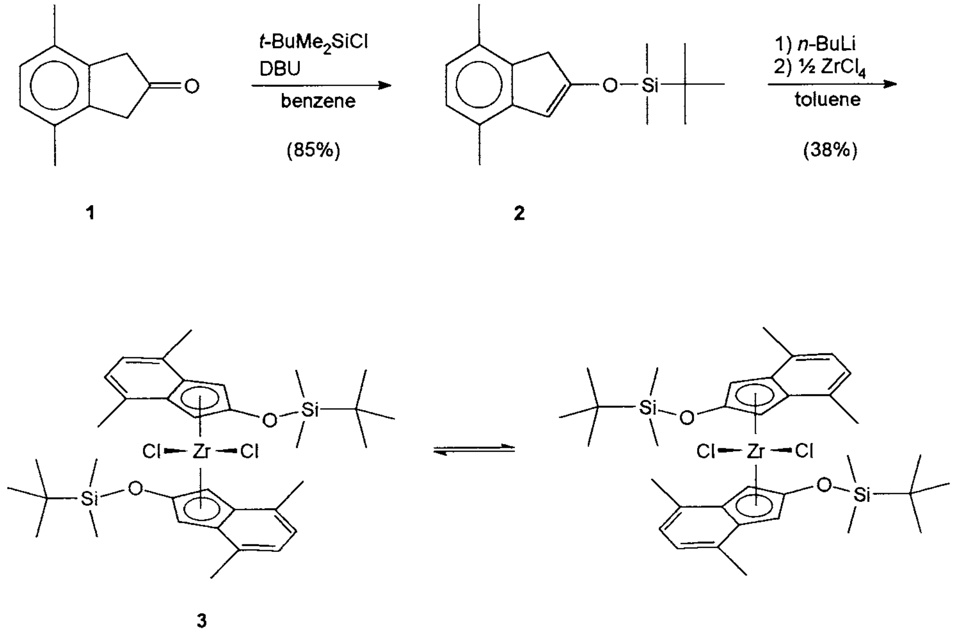

Scheme 1.

2. Results and discussion

2.1. Preparation of 3

Synthesis of **3** is illustrated in Scheme 1. 4,7-Dimethylindene was prepared according to a slighlty modified literature procedure [8] and oxidized to 4,7-dimethyl-2-indanone (**1**) as described by Horan and Schiessler for oxidation of indene [9]. Silylation of **1** with *tert*-butyldimethylchlorosilane and DBU in benzene gave 2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindene (**2**) in 85% yield. Reaction of **2**-Li with 0.5 equivalents of $ZrCl_4$ in toluene gave after work-up and crystallization from Et_2O bis[2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindenyl]zirconium dichloride (**3**) in 37% yield. Attempts to prepare the ethylene bridged analogue of **3** failed. Lithiation of **2** with BuLi and the subsequent reaction with 0.5 equivalents of dibromoethane in THF gave the desired bis(2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindenyl)ethane (**4**) in only 4.8% isolated yield. Analysis of the mother liquor by GC/MS showed an approximately 11:8:1 ratio of recovered **2**, spiro(cyclopropane-1,1′-2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindene) and 1-(bromoethyl)-2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindene, that could not be separated by vacuum distillation. A similar outcome was observed earlier for the attempted synthesis of the ethylene-bridged analogue of bis[2-(*tert*-butyldimethylsiloxy)cyclo-penta[*l*]phenanthryl]zirconium dichloride (**5**) [7]f (Fig. 1).

Formation of the cyclopropyl derivative by intramolecular bisalkylation is a major side reaction in the synthesis of ethylene bridged bis(indenyl) and bis(-cyclopentadienyl) ligand precursors [10–12]. Its nearly exclusive domination is, however, less common. E.g. Kaminsky and coworkers have reported the synthesis of bis(2,4,7-trimethylindenyl)ethane in 54% yield according to the standard procedure [13]. Analogously, bis(4,7-dimethylindenyl)ethane has been prepared in 55–65% yields [11,12]. Earlier, we prepared bis(2-(*tert*-butyldimethylsiloxy)indenyl)ethane in 58% yield [7]a. Apparently an unfavorable combination of steric and electronic properties enhances the rate of intramolecular alkylation of **2** instead of the desired intermolecular reaction.

2.2. Molecular structure and solution dynamics

X-ray structure determination of **3** revealed two rotamers in the asymmetric unit corresponding to a C_1 symmetric, ‘central/lateral:gauche’ conformation (**3g**) and a C_2 symmetric, ‘bis-central:*syn*’ conformation (**3s**),

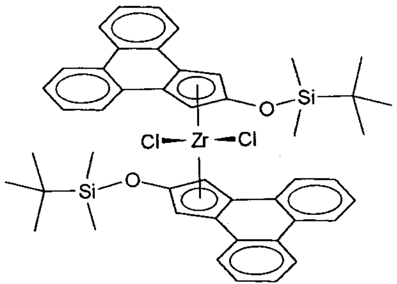

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Fig. 1. Bis[2-(*tert*-butyldimethylsiloxy)cyclopenta[*l*]phenanthryl]zirconium dichloride (**5**).

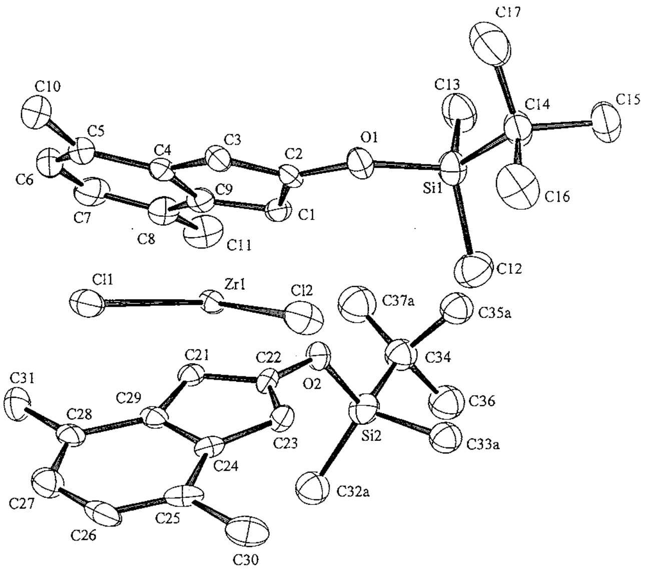

Fig. 2. Molecular structure of **3g**. Thermal ellipsoids are drawn at 20% probability. Only one conformation of the siloxane chain is shown.

Table 1
Selected interatomic distances (Å) and angles (°) for **3g**[a]

Interatomic distances			
Zr(1)–Cl(1)	2.413(3)	Zr(1)–Cl(2)	2.415(3)
Zr(1)–C(1)	2.476(9)	Zr(1)–C(21)	2.507(9)
Zr(1)–C(2)	2.611(9)	Zr(1)–C(22)	2.598(9)
Zr(1)–C(3)	2.541(9)	Zr(1)–C(23)	2.510(9)
Zr(1)–C(4)	2.575(10)	Zr(1)–C(24)	2.578(9)
Zr(1)–C(9)	2.563(10)	Zr(1)–C(29)	2.568(9)
C(2)–O(1)	1.356(11)	C(22)–O(2)	1.360(11)
Zr(1)–Cen(1)	2.252	Zr(1)–Cen(2)	2.253
Interatomic angles			
Cl(1)–Zr(1)–Cl(2)	96.93(12)	Cen(1)–Zr(1)–Cen(2)	130.260
C(2)–O(1)–Si(1)	132.6(7)	C(22)–O(2)–Si(2)	121.7(6)
Cp(1)–Cp(2)[b]	51.530		

[a] Cen(1) refers to the centroid of the C(1)–C(2)–C(3)–C(4)–C(9) ring and Cen(2) to the centroid of the C(21)–C(22)–C(23)–C(24)–C(29) ring.

[b] Angle between the cyclopentadienyl planes.

respectively [6]a,c. Rotamers **3g** and **3s** are displayed in Figs. 2 and 3 with selected bond distances and angles in Tables 1 and 2. Top views of **3g** and **3s** are presented in Figs. 4 and 5. In rotamer **3g** one siloxane chain was found in two conformations (*a* and *b*) in a 1:1 ratio. In rotamer **3s** also one siloxane chain was disordered and was found in three different conformations (*a*, *b* and *c*) in a 0.5:0.25:0.25 ratio. The presence of two rotamers in the crystal suggests that they are energetically quite similar [5]. In both rotamers the C_5 rings are nearly eclipsed instead of the staggered gauche arrangement commonly observed for other bis(indenyl) and bis(tetrahydroindenyl) zirconium dichlorides [5,6]a,c, [14] and related bis(indenyl) analogues [15]. The zirconium centers are pseudotetrahedrally coordinated with Zr–C bond lengths ranging between 2.476(9)–2.611(9) Å (**3g**) and 2.486(9)–2.579(10) Å (**3s**). The Zr–C distances to the substituted carbon atoms are slightly longer than the Zr–(CH) distances. The Zr–Cl distances [2.413(3) and 2.415(3) Å for **3g**; 2.432(3) and 2.420(3) Å for **3s**] are within the range observed previously for other

Table 2
Selected interatomic distances (Å) and angles (°) for **3s**[a]

Interatomic distances			
Zr(2)–Cl(3)	2.432(3)	Zr(2)–Cl(4)	2.420(3)
Zr(2)–C(41)	2.486(9)	Zr(2)–C(61)	2.492(9)
Zr(2)–C(42)	2.565(9)	Zr(2)–C(62)	2.553(10)
Zr(2)–C(43)	2.519(9)	Zr(2)–C(63)	2.508(9)
Zr(2)–C(44)	2.562(10)	Zr(2)–C(64)	2.573(9)
Zr(2)–C(49)	2.579(10)	Zr(2)–C(69)	2.577(10)
C(42)–O(3)	1.356(10)	C(62)–O(4)	1.371(12)
Zr(2)–Cen(3)	2.246	Zr(2)–Cen(4)	2.238
Interatomic angles			
Cl(3)–Zr(2)–Cl(4)	97.06(11)	Cen(3)–Zr(2)–Cen(4)	127.330
C(42)–O(3)–Si(3)	123.0(6)	C(62)–O(4)–Si(4a)	128.8(7)
Cp(3)–Cp(4)[b]	54.910		

[a] Cen(1) refers to the centroid of the C(41)–C(42)–C(43)–C(44)–C(49) ring and Cen(2) to the centroid of the C(61)–C(62)–C(63)–C(64)–C(69) ring.

[b] Angle between the cyclopentadienyl planes.

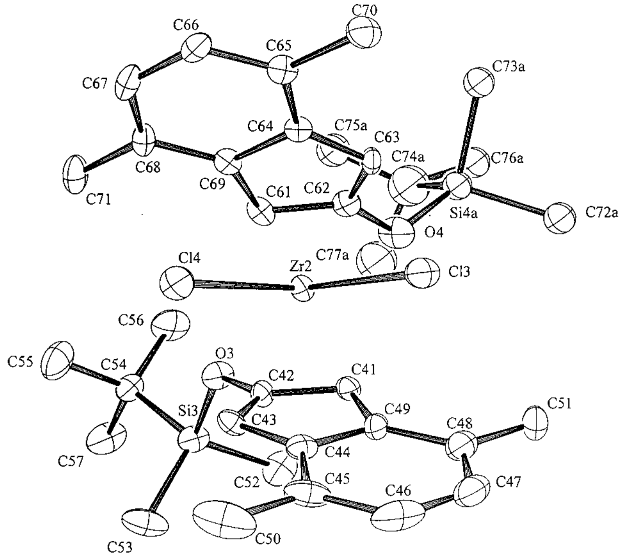

Fig. 3. Molecular structure of **3s**. Thermal ellipsoids are drawn at 20% probability. Only one conformation of the siloxane chain is shown.

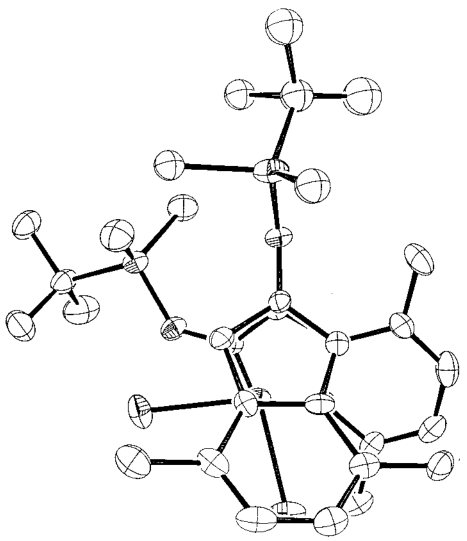

Fig. 4. A projection of the molecular geometry (top view) of **3g**. Thermal ellipsoids are drawn at 20% probability. For atomic numbering see Fig. 2.

bis(indenyl)zirconium dichlorides (2.407(1)–2.465(2) Å) [5,6]a, [14]. The ηC–O distances of **3g** [1.356(11) and 1.360(11) Å] and **3s** [1.356(10) and 1.371(12) Å] are similar to those observed in bridged bis(2-siloxyindenyl) *ansa*-zirconocenes (1.357(3)–1.366(6) Å) [7]a,c,d. In **3g** the intramolecular O(1)–Cl(2) distance is 3.141 Å, which is shorter than the sum of their relevant van der Waals radii (3.20 Å). Similar hetero-atom-chlorine close contacts have been observed previously for unbridged dimethylamino-functionalized bis(cyclopentadienyl) [16] and bis(indenyl) [14]c metallocene dichlorides.

The ^{1}H and ^{13}C NMR spectra of **3** show, at ambient temperature, time-averaged molecular C_{2v} symmetry consistent with rapid rotation of the indenyl ligands around the Centroid–Zr axis. The fast equilibration on the NMR time scale results in five singlets in the ^{1}H NMR spectrum, at 6.84, 5.83, 2.32, 1.08 and 0.34 ppm, in a 2:2:6:9:6 ratio. Dynamic behavior is observed upon lowering the temperature (Fig. 6). The ^{1}H NMR resonance of the methyl signal at 2.32 ppm becomes appreciably broadened at 218–198 K. Below coalescence ($T_c = 193$–190 K)[1] two resonances of equal intensities are observed. In a similar fashion, the methyl signal at 0.34 ppm and the methine signals at 6.84 ppm and 5.83 ppm show considerable broadening at 218–188 K and splitting to two resonances below 178 K. Finally, at 173 K a 6.3 Hz ^3J coupling is observed for the methine protons of the six-membered ring. Similar splitting is observed for most of the ^{13}C NMR signals recorded at 173 K. Splitting of the resonances indicates a single C_2 symmetric bent-metallocene conformation that is detected when the equilibration of **3** with its nonsuperimposable mirror image (Scheme 1) becomes frozen on the NMR time scale [17].

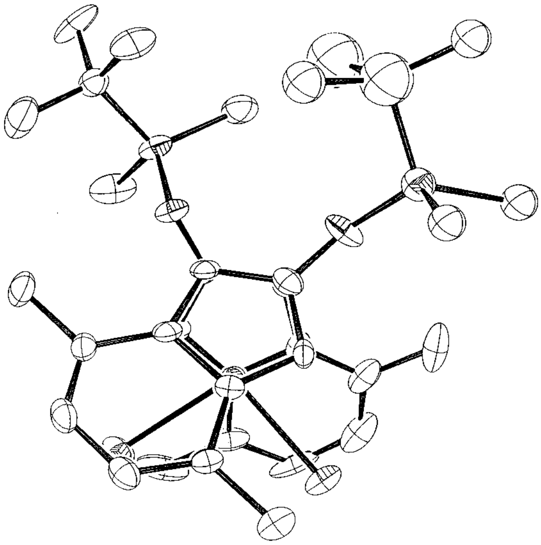

Fig. 5. A projection of the molecular geometry (top view) of **3s**. Thermal ellipsoids are drawn at 20% probability. For atomic numbering see Fig. 3.

2.3. Polymerization catalysis

Complexes **3** and **5** were activated with MAO for homogenous polymerization of ethylene and propylene. Table 3 shows a comparison of the ethylene polymerization results obtained with **3**/MAO, **5**/MAO, Cp_2ZrCl_2/MAO [18] and *rac*-Et(2-(*t*-BuMe$_2$SiO)Ind)-ZrCl$_2$/MAO [7]a under similar reaction conditions. The molecular weights of the polyethylenes produced with **3**/MAO and **5**/MAO show a similar trend as observed previously for the bridged bis(siloxyindenyl)zirconocene/MAO catalyst systems [7]b,c,e increasing slightly with decreasing aluminum concentration. The polymerization activities show here an inverse relationship and decrease with decreasing [Al]:[Zr] ratio. The low activities of **3**/MAO and **5**/MAO are somewhat unexpected. According to previous reports, the ethylene polymerization activity of Ind_2ZrCl_2/MAO is almost comparable to that of Cp_2ZrCl_2/MAO [19]. Consiglio and coworkers have reported the synthesis of (4,7-Me$_2$Ind)$_2$ZrX$_2$ (X = Cl, Bz) [15]c. The ethylene polymerization behavior of the corresponding (4,7-Me$_2$Ind)$_2$ZrX$_2$/MAO catalyst systems are similar to those of Ind_2ZrX_2/MAO [15]c. Most likely, the rapid free rotation of the indenyl ligands of **3** and **5**, combined with the bulky 2-substituent, form considerable steric hindrance to monomer coordination at the employed polymerization temperature. Both catalyst systems **3**/MAO and **5**/MAO show almost complete inactivity toward propylene. The consumption of

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[1] The coalescence temperature 190–193 K corresponds to an activation barrier of $\Delta G^{\ddagger}_{rot} \approx 9.1$–$9.3$ kcal mol^{-1}, see e.g. H. Günther, NMR Spectroscopy, 2nd Ed., Wiley, Chichester, 1995, p. 335–389.

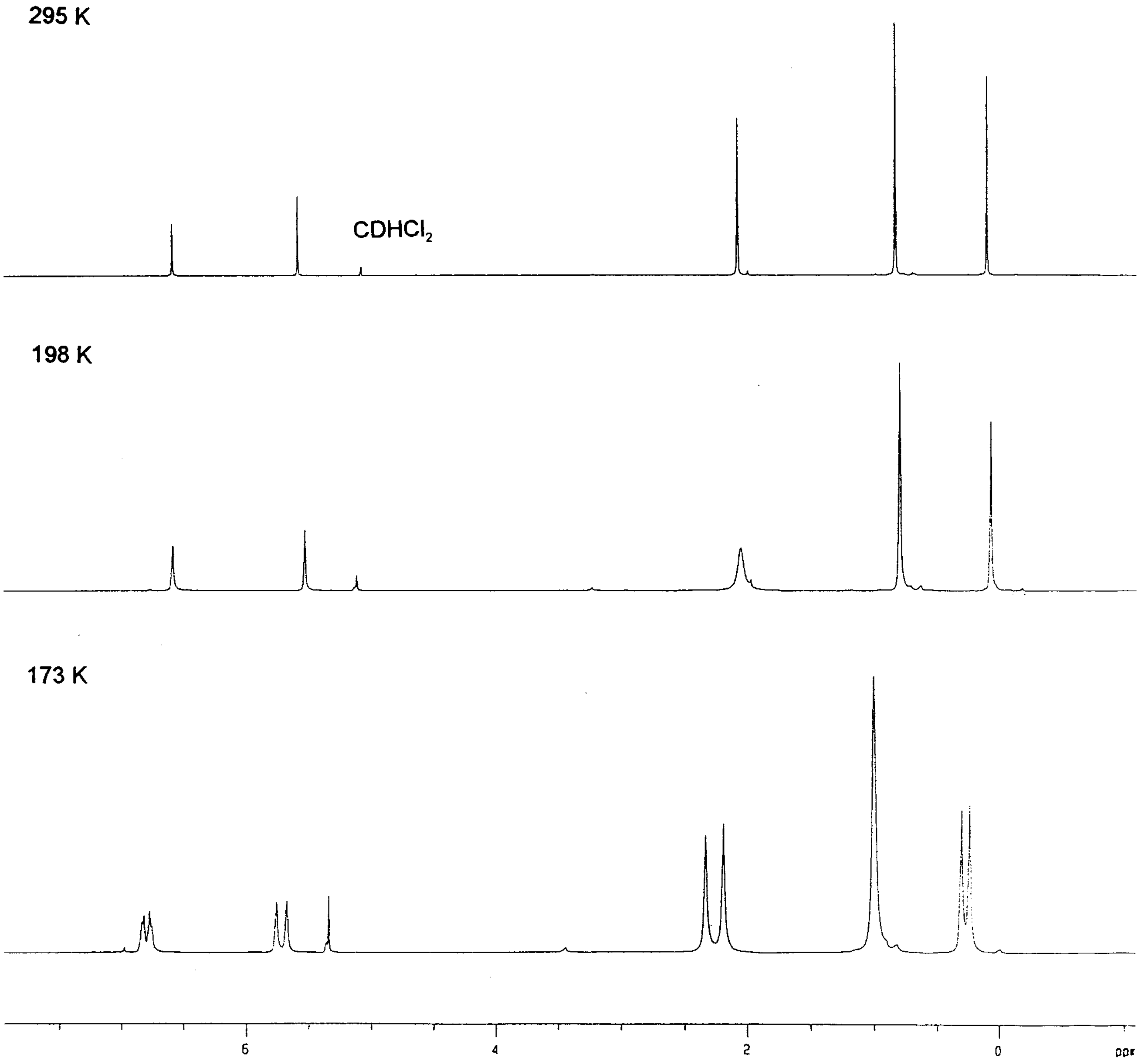

Fig. 6. Dynamic ^{1}H NMR spectrum of **3** in CD_2Cl_2 (400 MHz) at 295 K (top), 198 K (middle), 173 K (bottom).

monomer was marginal and no polypropylene could be isolated ($T_p = 20°C$; $P(C_3H_6) = 2.0$ bar; polymerization time = 60 min; [Al]:[Zr] = 500:1 and/or 3000:1).

2.4. Summary and conclusions

In summary, bis[2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindenyl]zirconium dichloride (**3**) has been prepared and its molecular structure determined. The dynamic behavior of **3** has been studied and shows that a rapid rotation of the indenyl ligands is observed at temperatures above 198 K. We conclude that the presence of an interannular bridge in 2-siloxy-substituted bis(indenyl) zirconocene/MAO catalyst systems is required to achieve high polymerization activities. In the nonstereorigid complexes increased flexibility of the molecule and blocking of the active sites by rotation of the ligands and the bulky 2-substituent appear to result in only modest or low catalytic activities.

3. Experimental section

3.1. General comments

All operations were carried out in an argon atmosphere using standard Schlenk and vacuum techniques. Solvents were dried and distilled under argon prior to

Table 3
Ethylene polymerization results obtained with Cp_2ZrCl_2/MAO, *rac*-Et(2-(*t*-$BuMe_2SiO$)Ind)$ZrCl_2$/MAO, **3**/MAO and **5**/MAO under similar conditions[a]

Metallocene	[Al]:[Zr]	Activity (kg PE/mol Zr/h)	M_w[b]	M_w/M_n	T_m (°C)
Cp_2ZrCl_2[c]	3000:1	9300	59 300	2.5	132
rac-Et(2-(*t*-$BuMe_2SiO$)Ind)$ZrCl_2$[d]	3000:1	6900	14 700	3.8	126
(2-(*t*-$BuMe_2SiO$)-Cp[*l*]Phen)$ZrCl_2$ (**5**)	3000:1	1700	32 000	2.2	131
(2-(*t*-$BuMe_2SiO$)-Cp[*l*]Phen)$ZrCl_2$ (**5**)	500:1	500	34 000	2.0	134
(2-(*t*-$BuMe_2SiO$)-4,7-Me_2Ind)$ZrCl_2$ (**3**)	3000:1	500	43 000	2.2	133
(2-(*t*-$BuMe_2SiO$)-4,7-Me_2Ind)$ZrCl_2$ (**3**)	500:1	250	54 000	2.2	131

[a] $T_p = 80$°C; $P(C_2H_4) = 1.6$ bar; Polymerization time = 20 min; [metallocene] = 11 μmol/200 ml of toluene.
[b] By GPC vs polystyrene standards.
[c] Ref. [18].
[d] Ref. [7]a.

use. Dibromoethane (Aldrich), *tert*-butyldimethylchlorosilane (ABCR) and $ZrCl_4$ (Aldrich, 99.9 + %) were used as received. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solutions using a JEOL JNM-LA400 or JEOL JNM-A500 NMR spectrometer and referenced against tetramethylsilane or the residual protons of the deuterated solvents. Direct inlet electron ionization mass spectra (EIMS) were obtained on a Varian-8000 mass spectrometer. Melting points are uncorrected. Details of the polymerization procedures and polymer analysis have been described previously [7]a,b.

Table 4
Crystal data and structure refinement for **3**

Empirical formula	$C_{34}H_{50}Cl_2O_2Si_2Zr$
Formula weight	709.040
Crystal size (mm)	0.20 × 0.15 × 0.20
Crystal system	triclinic
Space group	P1
a (Å)	16.528(3)
b (Å)	17.458(6)
c (Å)	13.670(4)
α (°)	96.36(3)
β (°)	91.817(18)
γ (°)	103.382(19)
V (Å^3)	3806.8(18)
Z	4
D_c (g cm^{-3})	1.237
F(000)	1488
Temperature (K)	293(2)
Scan type	ω-2θ
$2\theta_{max}$	45
Collected reflections	9288
Unique reflections	8874 [*R*(int) = 0.0452]
Refinement method	Full-matrix least-squares on F^2
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0677$, $wR2 = 0.1650$
Largest diff. peak and hole (e Å^{-3})	0.770 and −0.430

3.2. 4,7-dimethyl-2-indanone (*1*)

To an ice-cooled solution of H_2O_2 (23 ml, 30%) in formic acid (120 ml, 98%) was added dropwise 4,7-dimethylindene (24.0 g, 166 mmol). After completed addition the reaction mixture was stirred overnight at room temperature. The excess of formic acid was removed by distillation in vacuo. The remaining brown oil was mixed with dilute sulfuric acid (700 ml, 7% v/v). Steam distillation gave an off-white solid that was dissolved in CH_2Cl_2 (150 ml) and dried over sodium sulfate. The solvents were evaporated and the crude product was dissolved in Et_2O (150 ml). Concentration and cooling to −15°C gave 11.6 g (43.5%) of **2** as white needles. m.p. 90–92°C. EIMS (calcd/found): 160.0888/160.0878. ^1H NMR ($CDCl_3$, δ): 7.00 (s, 2H); 3.45 (s, 4H); 2.21 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 215.40; 136.56; 131.33; 128.15; 43.31; 18.99.

3.3. 2-(tert-butyldimethylsiloxy)-4,7-dimethylindene (*2*)

To a solution of *tert*-butyldimethylchlorosilane (11.8 g, 78.3 mmol) and **1** (11.4 g, 71.2 mmol) in benzene (150 ml) was added DBU (13.0 g, 85.4 mmol) and the reaction mixture was stirred for 2 h at room temperature. The mixture was diluted with Et_2O (150 ml), washed with water (2 × 150 ml), 5% HCl (150 ml), water (2 × 150 ml) and dried over sodium sulfate. Evaporation of the solvents left a red oil. Distillation under reduced pressure gave 16.6 g (85.1%) of **2** as a red oil that crystallized upon standing to form an orange solid. b.p.: 119–120°C/0.01 mbar. m.p.: 36–38°C. EIMS (calcd/found): 274.1753/274.1754. ^1H NMR ($CDCl_3$, δ): 6.94 (dq, $^3J = 7.7$ Hz, $^4J = 0.3$ Hz, 1H); 6.78 (dq, $^3J = 7.7$ Hz, $^4J = 0.3$ Hz, 1H); 5.84 (t, $^4J = 1.1$ Hz, 1H); 3.20 (m, 2H); 2.30 (s, 3H); 2.25 (s, 3H); 1.00 (s, 9H); 0.27 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 162.08; 143.39; 134.89; 129.45; 127.78; 125.49; 123.84; 105.28; 38.80; 25.65; 18.29; 18.21; −4.57.

Table 5
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3g**

Atom	x	y	z	U_{eq}
Zr(1)	2106(1)	−10268(1)	−2002(1)	49(1)
Cl(1)	1612(2)	−11642(2)	−1752(2)	81(1)
Cl(2)	3439(2)	−10045(2)	−1105(2)	89(1)
Si(1)	3221(2)	−7827(2)	−2(3)	74(1)
Si(2)	2836(3)	−8209(2)	−4406(3)	89(1)
O(1)	2647(5)	−8749(4)	3(5)	71(2)
O(2)	2406(4)	−8734(4)	−3525(5)	63(2)
C(1)	1667(6)	−9030(6)	−1477(7)	56(3)
C(2)	1980(7)	−9187(6)	−572(7)	51(3)
C(3)	1534(7)	−9916(6)	−352(7)	53(3)
C(4)	826(7)	−10170(6)	−1013(7)	56(3)
C(5)	99(8)	−10804(7)	−1044(9)	68(3)
C(6)	−508(8)	−10851(7)	−1729(11)	84(4)
C(7)	−436(8)	−10279(10)	−2414(10)	95(4)
C(8)	244(8)	−9667(7)	−2444(9)	73(3)
C(9)	888(7)	−9605(6)	−1723(8)	56(3)
C(10)	8(8)	−11370(7)	−282(9)	90(4)
C(11)	266(8)	−9025(8)	−3106(10)	107(5)
C(12)	3818(8)	−7815(8)	−1139(9)	113(5)
C(13)	2544(8)	−7122(7)	22(10)	106(5)
C(14)	3916(8)	−7667(7)	1117(9)	81(4)
C(15)	4439(8)	−6809(7)	1281(9)	105(4)
C(16)	4534(9)	−8232(8)	1021(10)	116(5)
C(17)	3410(10)	−7807(8)	2016(10)	132(6)
C(21)	1703(6)	−10148(6)	−3752(6)	53(3)
C(22)	2395(6)	−9516(6)	−3538(7)	51(3)
C(23)	3079(7)	−9830(6)	−3313(7)	56(3)
C(24)	2834(7)	−10682(6)	−3545(7)	52(3)
C(25)	3240(8)	−11316(8)	−3536(7)	68(3)
C(26)	2780(11)	−12070(7)	−3835(8)	83(4)
C(27)	1929(10)	−12263(8)	−4114(8)	80(4)
C(28)	1487(8)	−11694(6)	−4124(6)	59(3)
C(29)	1966(7)	−10857(6)	−3823(7)	55(3)
C(30)	4157(8)	−11119(8)	−3246(9)	101(4)
C(31)	587(7)	−11874(7)	−4391(8)	83(4)
C(32a)	2770(2)	−8845(15)	−5623(15)	106(9)
C(32b)	2179(18)	−8788(16)	−5570(16)	108(9)
C(33a)	3996(11)	−7909(15)	−3914(19)	85(8)
C(33b)	3959(11)	−8131(16)	−4550(2)	97(9)
C(34)	2451(9)	−7276(8)	−4299(9)	101(4)
C(35a)	2850(2)	−6835(16)	−3262(15)	98(10)
C(35b)	2350(3)	−6930(2)	−3252(18)	152(16)
C(36)	2921(10)	−6738(9)	−5097(11)	124(5)
C(37a)	1515(14)	−7290(2)	−4220(3)	148(13)
C(37b)	1578(13)	−7608(16)	−4901(19)	97(8)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.4. *Bis[2-(tert-butyldimethylsiloxy)-4,7-dimethylindenyl]zirconium dichloride (**3**)*

To a solution of **2** (6.86 g, 25.0 mmol) in Et_2O (50 ml) at 0°C was added dropwise *n*-BuLi (10.1 ml of a 2.5 M solution in hexane, 25.2 mmol), and the reaction mixture was stirred for 2 h at room temperature. The solvents were removed in vacuo to leave an off-white powder that was mixed with $ZrCl_4$ (2.91 g, 12.5 mmol) and suspended in toluene (100 ml). The resulting orange suspension was stirred for 4 h at 80°C, cooled to room temperature and filtrated through celite to remove lithium chloride. The clear orange solution was evaporated to dryness, extracted with Et_2O (100 ml) and filtrated through celite. Concentration and cooling to −30°C gave 3.29 g (37%) of **3** as a bright yellow powder. Recrystallization from the same solvent gave a

Table 6
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3s**

Atom	x	y	z	U_{eq}
Zr(2)	7487(1)	−5562(1)	−2921(1)	47(1)
Cl(3)	7925(2)	−5581(2)	−4603(2)	79(1)
Cl(4)	6991(2)	−4358(2)	−2865(2)	77(1)
Si(3)	8298(2)	−5657(2)	701(2)	74(1)
Si(4a)	7051(5)	−8527(4)	−2810(6)	79(2)
Si(4b)	6714(8)	−8443(6)	−2177(9)	59(3)
Si(4c)	7271(10)	−8373(8)	−2112(11)	81(4)
O(3)	7817(4)	−5731(4)	−423(5)	72(2)
O(4)	7270(5)	−7528(4)	−2519(6)	91(3)
C(41)	8566(6)	−5959(6)	−1916(7)	54(3)
C(42)	8223(6)	−5482(6)	−1219(6)	52(3)
C(43)	8377(6)	−4733(6)	−1478(7)	56(3)
C(44)	8908(7)	−4686(7)	−2263(7)	61(3)
C(45)	9328(8)	−4013(8)	−2767(9)	89(4)
C(46)	9876(9)	−4215(13)	−3462(10)	122(7)
C(47)	9997(10)	−4999(14)	−3671(11)	118(7)
C(48)	9587(9)	−5626(11)	−3250(9)	93(5)
C(49)	9048(7)	−5455(7)	−2520(7)	63(3)
C(50)	9199(10)	−3221(8)	−2487(11)	139(7)
C(51)	9720(8)	−6415(9)	−3543(10)	129(6)
C(52)	9012(8)	−6322(8)	657(9)	107(5)
C(53)	8891(9)	−4619(8)	1032(9)	120(5)
C(54)	7434(7)	−5943(8)	1509(8)	75(3)
C(55)	6836(9)	−5397(10)	1499(10)	134(6)
C(56)	6959(8)	−6815(9)	1215(10)	119(5)
C(57)	7802(8)	−5894(10)	2584(8)	138(7)
C(61)	6481(6)	−6508(5)	−2047(7)	55(3)
C(62)	6807(7)	−7006(6)	−2745(8)	61(3)
C(63)	6600(6)	−6871(5)	−3686(7)	50(3)
C(64)	6041(6)	−6369(6)	−3626(7)	51(3)
C(65)	5561(7)	−6087(6)	−4347(7)	57(3)
C(66)	5041(6)	−5637(6)	−4008(9)	64(3)
C(67)	4960(7)	−5437(6)	−2996(10)	72(3)
C(68)	5417(7)	−5664(6)	−2281(8)	59(3)
C(69)	5956(6)	−6152(6)	−2589(7)	50(3)
C(70)	5663(7)	−6317(7)	−5443(7)	80(4)
C(71)	5344(7)	−5444(7)	−1191(8)	88(4)
C(72a)	7878(14)	−8883(15)	−3494(19)	96(8)
C(73a)	6178(13)	−8973(14)	−3774(16)	85(7)
C(74a)	6720(2)	−8970(17)	−1665(18)	178(16)
C(75a)	5990(2)	−8641(18)	−1330(2)	113(10)
C(76a)	6769(17)	−9844(15)	−1980(19)	102(9)
C(77a)	7330(3)	−8450(2)	−840(3)	168(16)
C(72b)	5810(2)	−8880(3)	−3110(3)	82(14)
C(73b)	6400(3)	−8450(2)	−867(19)	55(11)
C(74b)	5567(15)	−8740(4)	−2140(6)	140(2)
C(72c)	8295(17)	−8490(2)	−1660(3)	54(10)
C(73c)	7920(3)	−8450(2)	−1040(2)	60(12)
C(74c)	8050(4)	−8840(4)	−2760(5)	160(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

yellow microcrystalline solid. In the EIMS mass spectrum of **3** parent ions of composition $C_{34}H_{50}O_2Si_2ZrCl_2^+$ were observed at $m/e = 706–714$ in the appropriate isotope ratios. The base peak corresponded to $C_{17}H_{25}OSiZrCl_2$ at $m/e = 433–441$. ^1H NMR (CD_2Cl_2, 295 K, δ): 6.84 (s, 4H); 5.83 (s, 4H); 2.32 (s, 12H); 1.08 (s, 18H); 0.34 (s, 12H). ^{13}C NMR (CD_2Cl_2, 295 K, δ): 155.96; 132.25; 125.52; 123.85; 94.07; 25.91; 19.34; 18.70; −4.04. ^1H NMR (CD_2Cl_2, 173 K, δ): 6.83 (d, 2H, $^3J = 6.3$ Hz); 6.76 (d, 2H, $^3J = 6.3$ Hz); 5.76 (s, 2H); 5.67 (s, 2H); 2.33 (s, 6H); 2.19 (s, 6H); 1.00 (s, 18H); 0.31 (s, 9H); 0.24 (s, 9H). ^{13}C NMR (CD_2Cl_2, 173 K, δ): 155.79; 131.54; 124.34; 123.91; 122.61; 122.51; 92.66; 91.97; 24.65; 18.84; 17.54; −4.96; −5.50.

3.5. Bis(2-(tert-butyldimethylsiloxy)-4,7-dimethylindenyl)ethane (4)

To a solution of **2** (9.96 g, 36.3 mmol) in THF (50 ml) at −50°C was added dropwise *n*-BuLi (14.7 ml of a 2.5 M solution in hexane, 36.7 mmol), and the reaction mixture was stirred for 5 h at room temperature. The resulting solution was then cooled to −80°C and treated dropwise with a solution of dibromoethane (3.41 g, 18.1 mmol) in THF (30 ml). After completed addition the reaction mixture was stirred overnight at room temperature, and washed with saturated ammonium chloride solution (150 ml) and dried over sodium sulfate. Evaporation of the solvents left a red oil that was dissolved in pentane (80 ml). Concentration and cooling to −30°C gave 0.50 g (4.8%) of **4** as a white powder. m.p.: 181–183°C. EIMS (calcd/found): 574.3662/574.3669. ^1H NMR ($CDCl_3$, δ): 6.87 (d, $^3J =$ 7.7 Hz, 2H); 6.68 (d, $^3J = 7.7$ Hz, 2H); 5.73 (d, $^4J = 1.1$ Hz, 2H); 3.15 (m, 2H); 2.27 (s, 6H); 2.21 (s, 6H); 1.79–1.70 (m, AA′, 2H); 1.44–1.35 (m, BB′, 2H); 0.88 (s, 18H); 0.20 (s, 6H); 0.15 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 163.98; 142.88; 137.78; 129.87;127.73; 125.03; 124.62; 104.23; 48.83; 25.64; 19.84; 18.66; 18.30; 18.14; −4.51; −5.03.

3.6. Crystal structure determination

Single crystals for X-ray structure determination were obtained by slowly cooling a saturated Et_2O solution of **3** to 4°C. Crystallographic data and parameters for **3** are presented in Table 4. The data set was collected on a Rigaku AFC5S diffractometer using Mo K_α radiation ($\lambda = 0.71069$ Å) at 293 K. The unit cell parameters were determined by least-squares refinements from 19 carefully centered reflections. The data obtained were corrected for Lorentz and polarization effects. Experimental absorption correction (ψ-scan) was carried out. The structure of **3** was solved by direct methods and subsequent Fourier syntheses. Least-squares refinements converged to an R value of 0.068 [$I > 2\sigma(I)$]. One siloxy group of the Zr(1) centered rotamer (**3g**) has two different orientations (a and b) where only the Si(2) atom keeps its position. In the Zr(2) centered rotamer (**3s**) one siloxy group has three conformations. All disordered atoms were refined isotropically. The rest of the heavy atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions with fixed temperature factors (1.2 × that of the host atom). The hydrogen atoms of the disordered carbons were not included. The atomic coordinates of **3g** and **3s** are collected in Tables 5 and 6. Additional data including complete listings of crystal data and structure refinement, positional and thermal parameters and intramolecular distances and angles, and ORTEP views of **3g** and **3s** are recorded as supplementary material and can be obtained from the authors upon request. All calculations were performed using the SHELX97 software [20].

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