



Synthesis, crystal structure and catalytic activity of some new chiral *ansa*-metallocenes of yttrium, lanthanum, samarium, lutetium and of zirconium¹

Herbert Schumann^{a,*}, Kerstin Zietzke^a, Roman Weimann^a, Jörg Demtschuk^a,
Walter Kaminsky^b, Anne-Meike Schauwienold^b

^a Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany

^b Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstraße 45, D-20146 Hamburg, Germany

Received 17 February 1998

Abstract

Chiral silicon bridged yttrio- and lanthanidocene chlorides $[\text{MeRSi}(\text{C}_5\text{H}_4)(\text{C}_5\text{Me}_4)\text{LnCl}]_2$ (R = Et (**a**), Ph (**b**); Ln = Y (**4a**, **b**), La (**5a**, **b**), Sm (**6a**, **b**), Lu (**7a**, **b**)) and zirconocene dichlorides $[\text{MeRSi}(\text{C}_5\text{H}_4)(\text{C}_5\text{Me}_4)\text{ZrCl}_2]$ (R = Et (**8a**), Ph (**8b**)) were synthesized. Compounds **4–7** react with sodium acetate yielding the corresponding monomeric acetates $[\text{MeRSi}(\text{C}_5\text{H}_4)(\text{C}_5\text{Me}_4)\text{LnO}_2\text{CMe}]$ (R = Et (**a**), Ph (**b**); Ln = Y (**9a**, **b**), La (**10a**, **b**), Sm (**11a**, **b**), Lu (**12a**, **b**)). All compounds were characterized by elemental analysis, ¹H and ¹³C{¹H}-NMR spectroscopy, and by mass spectrometry. Single crystal X-ray structure determinations show a dimer for **6a** and a monomer for **8a**. The zirconocenes **8a**, **b** are active catalysts for the polymerization of ethylene and propylene in the presence of methylalumoxane (MAO). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: *ansa*-Metallocenes; Bridged cyclopentadienyl compounds; Organolanthanide compounds; Polymerizations; Zirconocenes

1. Introduction

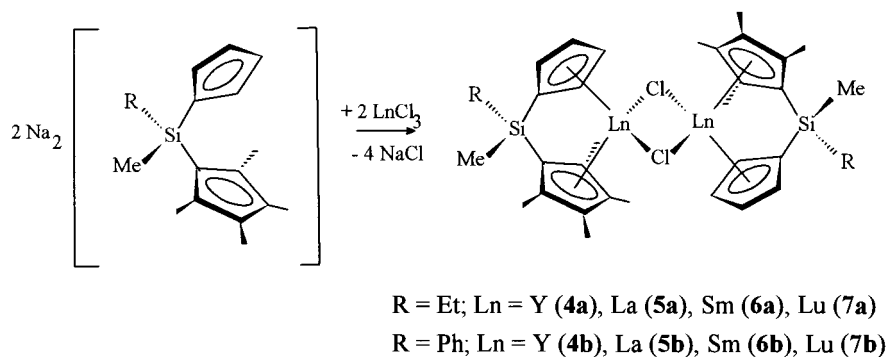
Organometallic complexes containing two cyclopentadienyl or two tetramethylcyclopentadienyl ligands bridged by Me₂Si or Et₂Si units are known of several transition metals including zirconium [2,3] and of some lanthanide metals [4–11]. Also asymmetric complexes of zirconium [12,13] and of some lanthanides [4,7] containing one unsubstituted cyclopentadienyl and one tetramethylcyclopentadienyl ligand bridged by the Me₂Si group were already reported. Several symmetrically and asymmetrically substituted dimethylsilylene

bridged zirconocenes [14] and lanthanidocenes [15] were tested as catalysts for olefin polymerization. The first *ansa*-cyclopentadienyl compound with two different substituents at the bridging silicon atom, $[\text{Me}(\text{H})\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2]$, was prepared by Köpf et al. in 1983 [16]. Chirality can be generated in such *ansa*-silylene complexes if also the two cyclopentadienyl moieties differ from each other. Whereas chiral *ansa*-metallocenes bridged by CRR' units were already synthesized [17], corresponding silylene bridged compounds were unknown up to now.

In this context we were interested in synthesizing and characterizing chiral *ansa*-lanthanidocenes and zirconocenes with silicon as the chiral center surrounded by two differently substituted cyclopentadienyl ligands and two different alkyl or aryl groups. Furthermore, we wanted to study the influence of the chiral silicon bridge on the catalytic properties of these compounds.

* Corresponding author. Tel.: +49 30 31423984; fax: +49 30 31422168; e-mail: Schumann@chem.zrz.tu-berlin.de

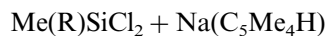
¹ Part 125 of the series Organometallic Compounds of the Lanthanides. For Part 124 see Ref. [1]. Dedicated to Professor Dr Peter Jutzki on the occasion of his 60th birthday with gratitude.



Scheme 1.

2. Synthesis and properties

The way of preparing the ligands CpCp*SiRR' differs somewhat from the method given in the literature [7]. Dichloroethylmethylsilane or dichloromethylphenylsilane reacted with equimolar amounts of sodium tetramethylcyclopentadienide in THF giving the monotetramethylcyclopentadienyl substituted silanes **1a** or **1b** as pale yellow liquids. Treatment of **1a** or **1b** with sodium cyclopentadienide produced orange or dark yellow colored, oily cyclopentadienyl(ethyl)(methyl) (tetramethylcyclopentadienyl)silane (**2a**) or cyclopentadienyl(methyl)(phenyl)(tetramethylcyclopentadienyl)silane (**2b**), respectively. The compounds **2a** and **2b** were reacted without further purification with sodium amide yielding the corresponding disodium salts **3a** and **3b**. Like the intermediate products **1a, b** and **2a, b**, the disodium salts are sensitive towards air and moisture. In contrast to **1a, b** and **2a, b** which are soluble in common organic solvents, **3a, b** are only soluble in THF.



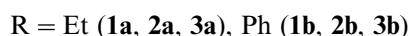
1a, b



2a, b



3a, b



The trichlorides of yttrium, lanthanum, samarium and lutetium react with **3a** and **3b** in THF with formation of the dimeric lanthanidocene chlorides **4a, b** to **7a, b** (Scheme 1).

Like dicyclopentadienyl lanthanide chlorides in general, **4a, b** to **7a, b** are very sensitive towards air and moisture. Compounds **4b–7b** containing the phenyl substituted silicon bridge are moderately soluble in saturated and unsaturated hydrocarbons like hexane, benzene or toluene whereas the complexes **4a–7a** with the ethyl group at the silicon bridge are only slightly soluble in toluene and benzene. All compounds are soluble in donor solvents like diethylether or tetrahydrofuran.

The ¹H-NMR spectra of **7a, 5b, 6b** and **7b** in d₅-pyridine and an X-ray structural analysis of poor quality crystals of **7a** [18] indicate that monomeric, THF containing complexes of the type MeRSi(C₅H₄)(C₅Me₄)-LnCl(THF) are the primary products which on vacuum drying lose their THF with formation of dimers. In accordance with this fact, no evidence is found for coordinated THF performing elemental analysis of the dried complexes. **4a, b** to **7a, b** have two possibilities to dimerize, either with two equal or with two different cyclopentadienyl ligands at the same site of the lanthanide atoms. For each of these isomers two racemic homochiral and one meso heterochiral isomer can exist. The ¹H- and ¹³C{¹H}-NMR solution spectra of **5a, b** and **6a, b** which show two signals with an intensity ratio of 2:1 for the CH₃ group attached to each bridging silicon atom indicate the presence of two isomers with different rings on the same site of the lanthanide atoms. In the mass spectra of **4a, b** to **7a, b** the peak for the ion of the dimeric molecules is the peak of highest mass.

The single crystal X-ray structure determination of crystals of **6a** obtained by recrystallization from ether-THF shows the dinuclear complex with two molecules of THF completing the coordination sphere around the samarium atoms (Fig. 1). These solvent molecules are removed by vacuum drying of the complex. The vacuum dried, solvent-free dinuclear lanthanidocene chlorides are less soluble in hydrocarbons and diethyl ether than the complexes crystallized from THF.

Zirconiumtetrachloride reacts with **3a** and **3b** to give the zirconocene dichlorides **8a** and **8b** (Scheme 2).

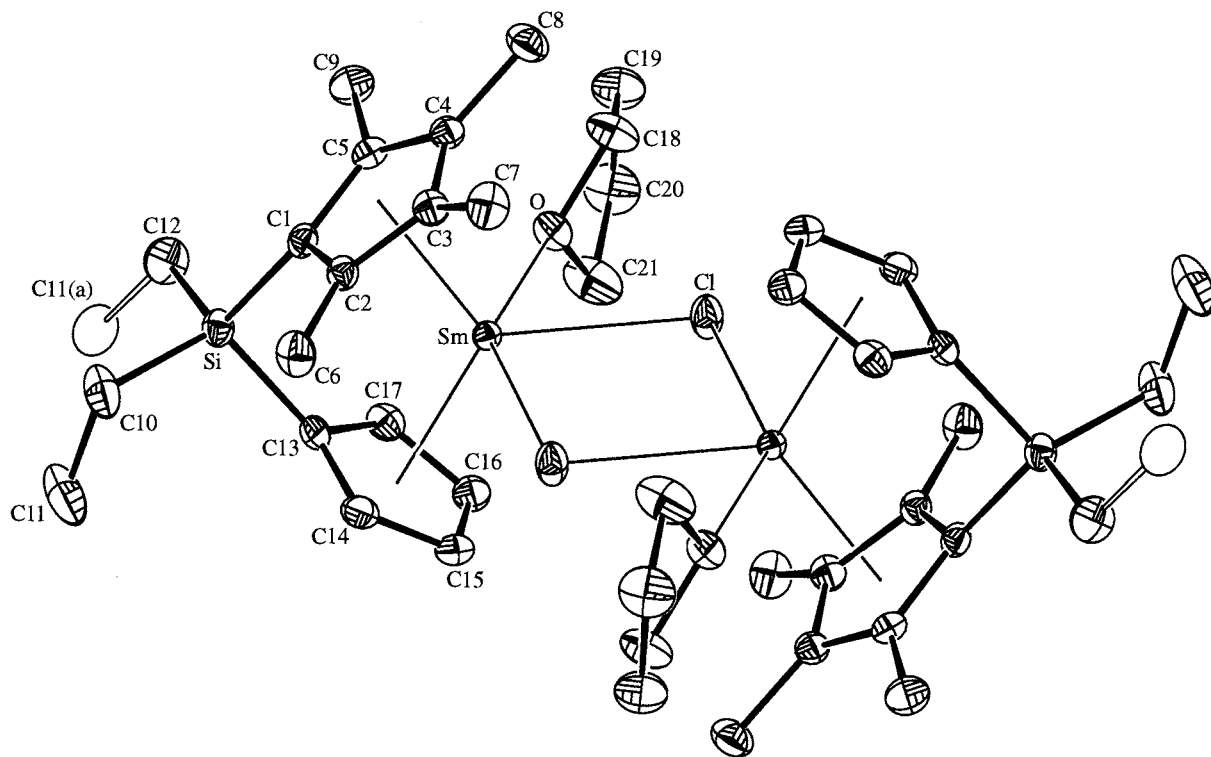


Fig. 1. ORTEP plot [19] of **6a**. Selected bond distances [Å] and angles [°] (estimated standard deviations in parentheses; Cp and Cp* define the centroids of the ring atoms C(1)–C(5) and C(13)–C(17), respectively): Sm–Cl 2.7793(14), Sm–Cl' 2.8169(9), Sm–O 2.614(2), Sm–Cp* 2.446(2), Sm–Cp 2.458(2), Si–C(10) 1.891(4), Si–C(12) 1.875(4), Si–C(1) 1.867(3), Si–C(13) 1.861(3); Cl–Sm–O 71.71(6), O–Sm–Cp* 102.31(7), Cp*–Sm–Cl 122.79(4), Cp–Sm–Cl' 95.75(3), Cp*–Sm–Cp 118.60(5), C(1)–Si–C(13) 100.29(13), C(10)–Si–C(12) 107.0(2).

Both zirconocenes are air and moisture sensitive. Compound **8b** is better soluble in saturated and unsaturated hydrocarbons and in donor solvents than **8a**. NMR and mass spectra show the expected patterns. The molecular structure of **8a** could be proved by single crystal X-ray structure determination (Fig. 2).

The new lanthanidocene chlorides react with sodium acetate forming the corresponding lanthanidocene acetates with 80–90% yield (Scheme 3).

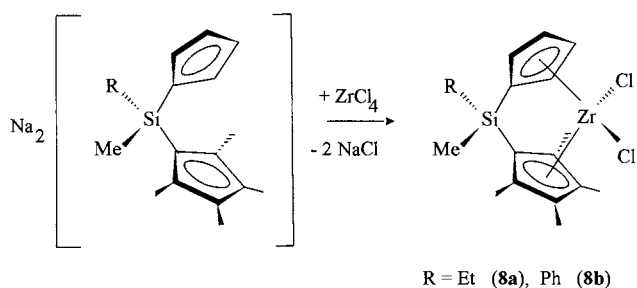
Compared to the corresponding chlorides, the acetates are more stable against air and moisture, better soluble in unpolar solvents like hexane, benzene or toluene and much better in polar solvents like THF or diethyl ether. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra (d_5 -pyridine, 20 and -40°C) show patterns which are

characteristic of monomeric complexes containing only one stereocenter, thus giving rise for the formation of only one pair of enantiomers. In the case of **11a, b** and **12b**, the monomeric structure was confirmed by cryoscopic molecular weight determinations in benzene. The mass spectra show the parent ion and the fragmentation pattern expected for the monomeric compounds, but also fragments which must be assigned to the dimeric molecular ion. Therefore, a dimeric structure of the complexes in the solid state can not be excluded.

3. Molecular structures of **6a** and **8a**

The molecular structures of **6a** and **8a** were determined by single crystal X-ray diffraction. The crystal data and refinement parameters are given in Table 1.

Fig. 1 shows an ORTEP plot [19] of **6a** with the atomic numbering scheme. Compound **6a** crystallizes as a dimer with one tetrahydrofuran molecule coordinated to each samarium resulting in nine coordinate Sm^{3+} centers. Tetrahydrofuran solvated structures were also found in some other bicyclopentadienylsamarium chlorides such as $[(\text{C}_5\text{H}_4\text{Me})_2\text{Sm}(\text{THF})\text{Cl}]_2$ [20]. The coordination pattern around the samarium centers of **6a** is of the $(\text{C}_5\text{R}_5)_2\text{MX}$ 'bent-sandwich' type and is roughly similar to that of other crystallographically character-



Scheme 2.

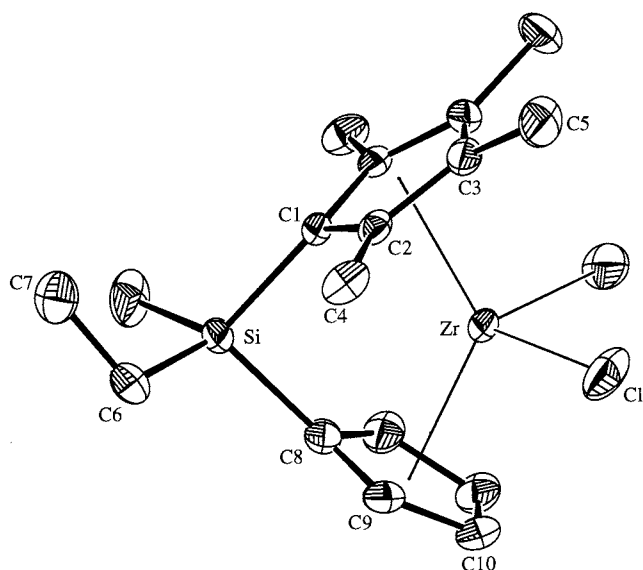


Fig. 2. ORTEP plot [19] of **8a**. Selected bond distances [Å] and angles [°] (estimated standard deviations in parentheses; Cp and Cp* define the centroids of the ring atoms C(1), C(2), C(3), C(3'), C(2') and C(8), C(9), C(10), C(10'), C(9'), respectively): Zr–Cl 2.4336(8), Zr–Cp* 2.218(2), Zr–Cp 2.219(2), Si–C(6) 1.856(3), Si–C(1) 1.875(3), Si–C(8) 1.876(3); Cl–Zr–Cl' 101.17(5), Cp*–Zr–Cl' 106.32(3), Cp–Zr–Cl 106.77(6), Cp*–Zr–Cp 126.70(4), C(1)–Si–C(8) 93.82(14), C(6)–Si–C(6') 107.0(2).

ized lanthanidocenes with Cl and THF ligation. The principal structural change that arises when the cyclopentadienyl rings are linked by a dialkylsilyl group, is a decrease of the ring centroid–M–ring centroid angle compared to samarocenes with unbridged cyclopentadienyl rings. The angle of 118.60(5)° in **6a** is in the same range as in $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{SmCl}(\text{THF})_2]$ (115.4 and 115.8°) [21], but smaller than in $(\text{C}_5\text{Me}_5)_2\text{SmCl}(\text{THF})$ (133(1)°) [22], $[(\text{C}_5\text{H}_4\text{Me})_2\text{Sm}(\text{THF})(\mu\text{-Cl})_2]$ (126.4°) [20] and in the Me_2Ge -bridged samarocene $\text{Me}_2\text{Ge}(\text{C}_5\text{Me}_4)_2\text{Sm}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (124.5°) [23]. This effect also could be observed for **8a**. Structure refinement of **6a** shows the terminal carbon atom of the ethyl substituent to be disordered racemically (50:50%) between the positions C(11) and C(11'). The bond lengths Sm–Cl and Sm–Cl' are not equivalent (2.7793(14) and 2.8169(9) Å), a situation which was also found for the Sm–Cl distances in $[(\text{C}_5\text{H}_4\text{Me})_2\text{Sm}(\text{THF})\text{Cl}]_2$ (2.759 and 2.819 Å) [20]. Bridging Sm–Cl distances are usually longer than terminal Sm–Cl distances as e.g. in $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})\text{Cl}]$ (2.709 Å) [22]. The bond length Sm–O (2.614(2) Å) is slightly longer than that in $[(\text{C}_5\text{H}_4\text{Me})_2\text{Sm}(\text{THF})\text{Cl}]_2$ (2.563 Å) [20] and very similar to that in $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2]$ (2.63 Å) [24]. The distance Si–C(10) (1.881(4) Å) is only slightly longer than the distance Si–C(12) (1.875(4) Å). They correspond to the bond lengths found in $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_3\text{R}^*)(\text{C}_5\text{Me}_4)\text{SmCH}(\text{SiMe}_3)_2]$ (1.848 and 1.861 Å) or in $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_3\text{R}^*)(\text{C}_5\text{Me}_4)\text{SmN}(\text{SiMe}_3)_2]$

(1.85 and 1.87 Å) with $\text{R}^* = \text{neomenthyl}$ [25]. All other bond lengths and angles are comparable to those found in samarocene chloride complexes like $[(\text{C}_5\text{H}_4\text{Me})_2\text{Sm}(\text{THF})\text{Cl}]_2$ [20], $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})\text{Cl}$ [22], and $(\text{C}_5\text{H}_5)_2\text{Sm}(\text{Cl})(\text{THF})_2(\mu\text{-Cl})_2\text{Sm}(\text{Cl})_2(\text{THF})_3$ [26].

Solution of the X-ray diffraction data of **8a** generated the structure shown in Fig. 2. The crystal consists of monomeric molecules in a racemic 1:1 mixture with regard to the ethyl and methyl group at the bridging silicon atom. The angle ring centroid–Zr–ring centroid of 126.70(4)° and the angle C(1)–Si–C(8) of 93.88(14)° are similar to those in $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$ (125.40°/93.2°) [2], $\text{Me}_2\text{Si}(1\text{-C}_5\text{H}_2\text{-3-'Bu-5-Me})_2\text{ZrCl}_2$ (126.7°/94.3°) [14]b and *rac*- $\text{Me}_2\text{Si}(1\text{-C}_5\text{H}_2\text{-2-Me-4-Ph})_2\text{ZrCl}_2$ (126.0°/93.3°) [14]e. The angle Cl–Zr–Cl' (101.17(5)°) is larger than that in comparable compounds like $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$ (97.98°) [2], $\text{Me}_2\text{Si}(1\text{-C}_5\text{H}_2\text{-3-'Bu-5-Me})_2\text{ZrCl}_2$ (97.6°) [14]a or *rac*- $\text{Me}_2\text{Si}(1\text{-C}_5\text{H}_2\text{-2-Me-4-Ph})_2\text{ZrCl}_2$ (98.8°) [14]e. All other bond distances and angles are similar to those found in $\text{Me}_2\text{Si}(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$ [2], $\text{Me}_2\text{Si}(1\text{-C}_5\text{H}_2\text{-3-'Bu-5-Me})_2\text{ZrCl}_2$ [14]a and *rac*- $\text{Me}_2\text{Si}(1\text{-C}_5\text{H}_2\text{-2-Me-4-Ph})_2\text{ZrCl}_2$ [14]e.

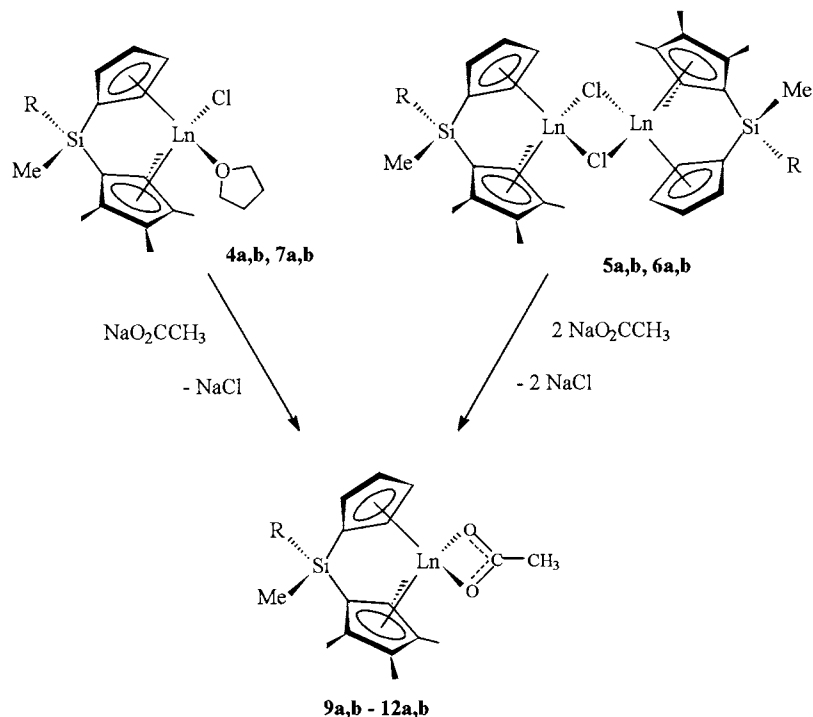
In accordance with the larger ionic radius of samarium compared to zirconium, the bond distances M–(C₅H₄) and M–(C₅Me₄) decrease in the order **6a** (2.458(2), 2.446(2) Å) to **8a** (2.219(2), 2.218(2) Å) just as do the angles C(1)–Si–C(13) and C(1)–Si–C(8) (**6a** (100.29(13)°, **8a** (93.82(14)°), whereas the angles ring centroid–M–ring centroid increase in the same order (**6a** 118.60(5)°, **8a** 126.70(4)°).

4. Catalytic activity of **8a**, **8b** and $[(\text{C}_5\text{H}_5)(\text{C}_5\text{Me}_5)\text{ZrCl}_2]$ (**13**)

The polymerization of ethylene and propylene was conducted at 30°C in the presence of **8a**/MAO, **8b**/MAO and the unbridged system $[(\text{C}_5\text{H}_5)(\text{C}_5\text{Me}_5)\text{ZrCl}_2]$ (**13**)/MAO. The results of the experiments are given in Table 2.

Besides the electronic and steric influence of the silylene bridge itself, the linkage of the two cyclopentadienyl ligands changes structure and energy of the metal orbitals [27] and the angle between the ring planes, the last fact influencing the space available for reactions at the metal center. Different reactivities in ethylene and propylene polymerizations should be the consequence.

The results of the polymerization experiments using the zirconocene complexes **8a** and **13** as catalysts demonstrate that, compared to the unbridged complex **13**, the silyl-bridged complex **8a** shows a notable decrease in ethylene polymerization activity, but a strong increase in propylene polymerization activity. A similar trend is observed for the molecular weights of the polymers obtained, though that of polyethylene is much



R = Et, n = 1, Ln = Y (**9a**), Lu (**12a**); n = 2, Ln = La (**10a**), Sm (**11a**)

R = Ph, n = 1, Ln = Y (**9b**), Lu (**12b**); n = 2, Ln = La (**10b**), Sm (**11b**)

Scheme 3.

more susceptible to changes in the ligand structure of the catalyst compared to the results in propylene polymerization where the increase in molecular weight is rather small. Exchange of ethyl for phenyl as one of the two substituents bound to the silylene bridge leads to a decrease in polymerization activity for both monomers. Interestingly, a strong increase in the molecular weight of the polyethylene produced is observed whereas virtually no influence is detected in propylene polymerization.

No significant differences were observed in pentad distribution between the simple and the bridged zirconocenes and also an exchange of the substituents bound to the bridging silicon atom had no influence on the microstructure of the polymer. All examined metallocenes produce atactic polypropylene (mm = 19%, mr = 50%, rr = 31%). Only a very slight preference for syndiotactic enchainment could be detected that can be attributed to the different size of the C_5H_5 and the C_5Me_5 ligands. Polymer ^{13}C -NMR also revealed that for these metallocenes β -hydrogen elimination is the single chain termination mechanism. Vinyl or isopropyl chain ends representing β -methyl elimination which was found to be the main termination pathway in the highly

crowded $\text{Cp}_2^*\text{ZrCl}_2/\text{MAO}$ system [28] were not detected.

5. Experimental details

5.1. General comments

All reactions were carried out in an atmosphere of dry, oxygen free nitrogen using Schlenk techniques. Solvents were dried over sodium/benzophenone and distilled prior to use. The NMR spectra were recorded on a Bruker ARX 200 or a Bruker ARX 400 spectrometer (^1H : d_5 -pyridine, 20°C; $^{13}\text{C}\{^1\text{H}\}$: d_5 -pyridine, 20°C; δ in ppm relative to the remaining proton content of the solvent; unless otherwise specified). CH analyses were performed on a Perkin-Elmer 240 C elemental analyser. Mass spectra were determined on a Varian MAT 311 A spectrometer using electron impact. Kryptoscopic molecular weight measurements were carried out in benzene. The ligand precursors $\text{Na}[\text{C}_5\text{Me}_4\text{H}]$ [29] and $\text{Na}[\text{C}_5\text{H}_5]$ [30] as well as the anhydrous LnCl_3 [31] were prepared by published procedures. Dichloro(ethyl)methyl- and dichloro(methyl)phenylsilane (ABCR) were distilled prior to use.

5.2. Syntheses of the ligands

5.2.1. Chloro(ethyl)(methyl)(2,3,4,5-tetramethylcyclopentadienyl)silane (**1a**)

A solution of 4.00 g (29.82 mmol) Na[C₅Me₄H] in 80 ml of THF was cooled to –78°C. 4.26 g (4.04 ml = 29.82 mmol) of dichloro(ethyl)(methyl)silane were added over a period of 30 min. The reaction mixture was warmed very slowly to room temperature (over 6 h) and stirred for another 12 h. The solvent was removed under reduced pressure, and 80 ml of Et₂O were

added into the reaction flask. The resulting mixture was stirred for 10 min, filtered and the filtrate evaporated until a yellow liquid remained. Fractional distillation yielded a pale yellow liquid. Yield 5.22 g (76%) of **1a**. B.p.: 61–63°C/0.1 mbar. ¹H-NMR (400 MHz, C₆D₆): 0.11 (s, 3H, SiMe), 0.51 (m, 1H, SiCH₂CH₃), 0.59 (m, 1H, SiCH₂CH₃), 0.92 (t, 3H, J(HH) = 4 Hz), SiCH₂CH₃), 1.71 (s, 6H, C₅Me₄), 1.93 (s, 6H, C₅Me₄), 2.95 (s, 1H, SiC₅H). ¹³C{¹H}-NMR (100.64 MHz, C₆D₆): –1.64, 7.06, 8.59, 10.73, 15.34, 55.58, 131.46, 131.60, 137.83.

Table 1
Crystal data and structure refinement for **6a** and **8a**

	6a	8a
Empirical formula	C ₃₄ H ₃₈ Cl ₂ Si ₂ Sm ₂ (C ₄ H ₈ O) ₂	C ₁₇ H ₂₄ Cl ₂ SiZr
Formula weight (g mol ⁻¹)	1018.69	418.57
Temperature (K)	240(2)	162(2)
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>Pnma</i> (No. 62)
Unit cell dimensions		
<i>a</i> (Å)	11.225(5)	13.417(2)
<i>b</i> (Å)	11.6278(2)	9.938(2)
<i>c</i> (Å)	9.116(2)	13.486(4)
α (°)	93.865(14)	
β (°)	113.57(2)	
γ (°)	77.98(2)	
Volume (m ³)	1066.4(6) × 10 ⁻³⁰	1798.3(6) × 10 ⁻³⁰
<i>Z</i>	2	4
Density (calculated, mg m ⁻³)	1.602	1.546
Absorption coefficient (mm ⁻¹)	2.820	0.916
<i>F</i> (000)	512	840
Crystal size (mm)	0.30 × 0.36 × 0.50	0.20 × 0.23 × 0.33
Aperture (mm)	2.4	2.3
Scan angle (°)	(0.86 + 0.35tan θ)	(0.68 + 0.35tan θ)
Range of data collection	4° < 2 θ < 55°	2° < 2 θ < 55°
Index ranges	0 ≤ <i>h</i> ≤ 14, –15 ≤ <i>k</i> ≤ 15, –11 ≤ <i>l</i> ≤ 11	0 ≤ <i>h</i> ≤ 17, 0 ≤ <i>k</i> ≤ 12, –17 ≤ <i>l</i> ≤ 17
Reflections collected	5213	4202
Independent reflections	4852 (<i>R</i> _(int) = 0.0163)	2137 (<i>R</i> _(int) = 0.0203)
Refinement method	Full-matrix least- squares on <i>F</i> ²	Full-matrix least- squares on <i>F</i> ²
Data/restraints/parameters	4829/0/235	2106/0/106
Goodness-of-fit on <i>F</i> ² ^c	1.060	1.086
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ ^a = 0.0284, <i>wR</i> ₂ ^b = 0.0786	<i>R</i> ₁ ^a = 0.0331, <i>wR</i> ₂ ^b = 0.0852
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0295, <i>wR</i> ₂ = 0.0856	<i>R</i> ₁ = 0.0439, <i>wR</i> ₂ = 0.1108
Largest difference peak and hole (e Å ⁻³)	Max. 1.280, min. –1.044	Max. 0.653, min. –0.440

^a *R*₁ = $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$.

^b *wR*₂ = $[\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$.

^c GOOF = $[\Sigma w(|F_o| - |F_c|)^2 / (n - p)]^{1/2}$.

5.2.2. [(Cyclopentadienyl)(ethyl)(methyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]disodium (**3a**)

Na[C₅H₅] (2.01 g, 22.80 mmol) was dissolved in 10 ml of THF and was added to a solution of 5.19 g (22.80 mmol) of **1a** in 30 ml of THF at –78°C. The reaction mixture was then allowed to warm up to ambient temperature. After stirring for 12 h, the THF was removed in vacuo, and the orange residue was extracted with hexane. The hexane was evaporated under reduced pressure to yield 4.83 g (82%) of (cyclopentadienyl)(ethyl)(methyl)(tetramethylcyclopentadienyl)silane (**2a**) as an orange oil, which was used without further purification.

NaNH₂ (1.47 g, 37.39 mmol) was suspended in 60 ml of THF, and 4.83 g (18.70 mmol) of **2a** dissolved in 10 ml of THF were slowly added. The suspension was stirred for 12 h, filtered, and the solvent was removed in vacuo. The resulting pale brown residue was washed several times with hexane to obtain a cream-colored solid, which was dried in vacuo at 0.1 mbar. Yield 6.44 g (92%) of the adduct of **3a** with 1 THF. Anal. Found: C, 66.73; H, 8.11. C₂₁H₃₂Na₂OSi·(374.66 g mol⁻¹) (**3a**). Calc.: C, 67.34; H, 8.61%. ¹H-NMR (400 MHz): 0.92 (s, 3H, SiMe), 1.17 (m, 2H, SiCH₂CH₃), 1.41 (m, 3H, SiCH₂CH₃), 1.61 (m, 4H, THF), 2.25 (s, 6H, C₅Me₄), 2.64 (s, 6H, C₅Me₄), 3.66 (m, 4H, THF), 6.65 (m, 2H, C₅H₄), 6.81 (m, 2H, C₅H₄). ¹³C{¹H}-NMR (100.64 MHz): 0.36, 9.21, 10.75, 12.28, 15.12, 25.43, 67.46, 103.43, 107.33, 109.25, 111.41, 114.36, 116.51.

5.2.3. Chloro(methyl)(phenyl)(2,3,4,5-tetramethylcyclopentadienyl)silane (**1b**)

The procedure described above for the synthesis of **1a** was carried out with 4.45 g (30.87 mmol) of Na[C₅Me₄H] and 5.89 g (5.03 ml = 30.87 mmol) of dichloromethyl-(phenyl)silane in 70 ml of THF. Workup as described above and fractional distillation of the resulting yellow oil yielded a pale yellow liquid. Yield 4.65 g (55%) of **1b**. B.p.: 94–96°C/0.1 mbar. ¹H-NMR (C₆D₆, 200 MHz): 0.50 (s, 3H, SiMe), 1.67 (s, 3H, C₅Me₄), 1.68 (s, 3H, C₅Me₄), 1.72 (s, 3H, C₅Me₄),

Table 2

Polymerization results obtained with $[(C_5H_5)(C_5Me_5)ZrCl_2]$ (**13**) and $[RR'Si(C_5H_4)(C_5Me_4)ZrCl_2]$ (R = Me; R' = Et (**8a**), Ph (**8b**))^a

Metalloocene	Monomer	Activity ^b	M_n (g mol ⁻¹)	M_w/M_n	T_m (°C)
13	Ethylene	22500	2135000	n.d. ^c	136
8a	Ethylene	6700	439000	n.d. ^c	134
8b	Ethylene	3600	1029000	n.d. ^c	137
13	Propylene	600	13900	2.0	a ^d
8a	Propylene	2800	16100	2.1	a ^d
8b	Propylene	1150	17500	1.9	a ^d

^a At 30°C, 2 bar monomer pressure, 200 ml toluene, [MAO] = 2 g l⁻¹, [Zr] = 1×10^{-6} mol l⁻¹ (ethylene) and 5×10^{-6} mol l⁻¹ (propylene), $t_{pol} = 60$ min.

^b In kg Pol (mol Zr·h)⁻¹.

^c n.d., not determined.

^d a, amorphous.

2.06 (s, 3H, C₅Me₄), 3.42 (s, 1H, SiC₅H), 7.43 (m, 3H, C₆H₅), 7.64 (m, 2H, C₆H₅). ¹³C{¹H}-NMR (CDCl₃, 50.32 MHz): -2.58, 11.11, 11.13, 14.15, 14.38, 55.95, 127.49, 128.31, 130.13, 133.62, 133.65, 134.63, 138.24, 148.98.

5.2.4. [(Cyclopentadienyl)(methyl)(phenyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]disodium (**3b**)

Compound **1b** (4.60 g, 16.62 mmol) was dissolved in 60 ml of THF, and the solution was cooled to -78°C. Then, 1.46 g (16.62 mmol) of Na[C₅H₅] dissolved in 10 ml of THF were added slowly. The reaction mixture was allowed to warm up to room temperature very slowly over a period of 6 h and was stirred for 12 h at ambient temperature. The THF was evaporated in vacuo and the remaining residue was extracted with hexane. The solvent was removed under reduced pressure to yield 3.78 (74%) of (cyclopentadienyl)(methyl)(phenyl)(tetramethylcyclopentadienyl)silane (**2b**) as a dark yellow oil, which was used without further purification.

To a suspension of 0.95 g (24.68 mmol) of NaNH₂ in 80 ml of THF were slowly added 3.78 g (12.34 mmol) of **2b** dissolved in 10 ml of THF. The reaction mixture was stirred for 12 h, filtered and the THF was evaporated under reduced pressure. The resulting pale brown residue was washed several times with hexane to give a cream-coloured solid, which was dried in vacuo at 0.1 mbar. Yield 3.59 g (83%) of **3b**. Anal. Found: C, 70.99; H, 6.50. C₂₁H₂₄Na₂Si (350.56 g mol⁻¹) (**3b**). Calc.: C, 71.97; H, 6.90%. ¹H-NMR (200 MHz): 1.06 (s, 3H, SiMe), 2.23 (s, 6H, C₅Me₄), 2.36 (s, 6H, C₅Me₄), 6.73 (m, 2H, C₅H₄), 6.99 (m, 2H, C₅H₄), 7.24 (m, 3H, C₆H₅), 8.44 (m, 1H, C₆H₅), 8.47 (m, 1H, C₆H₅). ¹³C{¹H}-NMR (50.32 MHz): 3.69, 12.19, 15.74, 102.28, 107.74, 110.75, 111.87, 113.98, 115.10, 126.76, 135.73, 148.71.

5.3. Syntheses of metallocene chlorides with ethyl, methyl substitution at the bridging silicon atom

5.3.1. [Bis(μ-chloro)(cyclopentadienyl)(ethyl)(methyl)-(2,3,4,5-tetramethylcyclopentadienyl)silyl]ditytrium (**4a**)

A 100 ml Schlenk flask was charged with 1.17 g (2.83 mmol) of YCl₃(THF)₃ and 1.06 g (2.83 mmol) of **3a**. An 80 ml volume of THF was added and the reaction mixture was stirred for 12 h at room temperature, followed by refluxing with stirring for 12 h and additional stirring for 12 h at ambient temperature. The THF was removed in vacuo. The resulting yellow solid was first washed with 60 ml of Et₂O and the product was then separated by soxhlet extraction with 80 ml of Et₂O. The pale yellow extract was concentrated to 25 ml and cooled to -30°C. The resulting colourless microcrystalline product was isolated by decantation and subsequent vacuum drying at 0.1 mbar. Yield 0.39 g (36%) of **4a**. Anal. Found: C, 53.57; H, 6.40. C₃₄H₄₈Cl₂Si₂Y₂ (761.73 g mol⁻¹) (**4a**). Calc.: C, 53.62; H, 6.35%. ¹H-NMR (400 MHz): 0.88 (s, 3H, SiMe), 1.33 (m, 5H, SiEt), 1.69 (br s, 3H, C₅Me₄), 2.12 (s, 3H, C₅Me₄), 2.14 (s, 3H, C₅Me₄), 6.20 (m, 1H, C₅H₄), 6.21 (m, 1H, C₅H₄), 6.70 (m, 2H, C₅H₄). ¹³C{¹H}-NMR (100,64 MHz): -2.98, 7.07, 7.59, 10.86, 13.55, 13.82, 103.05, 113.05, 113.55, 114.20, 118.05, 118.46, 121.69, 122.59, 125.39. MS (220°C, ³⁵Cl, ²⁸Si, *m/z* (%)): 760 (35) [(MeEtSi(C₅Me₄)(C₅H₄)YCl)₂=D]⁺, 731 (81) [D-Et]⁺, 716 (18) [D-Et-Me]⁺, 380 (23) [MeEtSi(C₅Me₄)(C₅H₄)YCl]⁺, 351 (44) [MeSi(C₅Me₄)(C₅H₄)YCl]⁺, 345 (100) [MeEtSi(C₅Me₄)(C₅H₄)Y]⁺, 336 (40) [Si(C₅Me₄)(C₅H₄)YCl]⁺, 316 (40) [MeSi(C₅Me₄)(C₅H₄)Y]⁺ and other fragments.

5.3.2. [Bis(μ-chloro)(cyclopentadienyl)(ethyl)(methyl)-(2,3,4,5-tetramethylcyclopentadienyl)silyl]dilanthanum (**5a**)

The preceding described synthesis for **4a** was carried out with 1.84 g (5.79 mmol) of LaCl₃(THF) and 2.17 g

(5.79 mmol) of **3a** in 70 ml of THF to yield a pale yellow solid. Yield 0.44 g (18%) of **5a**. Anal. Found: C, 48.39; H, 5.85. $C_{34}H_{48}Cl_2La_2Si_2$ (861.73 g mol⁻¹) (**5a**). Calc.: C, 47.39; H, 5.61%. ¹H-NMR (400 MHz): 0.70 (s, 2H, SiMe), 0.73 (s, 1H, SiMe), 1.29 (m, 5H, SiEt), 1.99–2.17 (m, 12H, C₅Me₄), 6.18 (m, 1H, C₅H₄), 6.22 (m, 1H, C₅H₄), 6.59 (m, 2H, C₅H₄). ¹³C{¹H}-NMR (100,64 MHz): -3.97, -2.85, 7.41, 7.80, 11.06–13.74, 112.08, 113.23, 115.38, 116.06, 117.67, 120.88, 121.08, 121.61, 121.67, 121.98. MS (329°C, ³⁵Cl, ²⁸Si, ¹³⁹La, *m/z* (%)): 860 (21) [(MeEtSi(C₅Me₄)(C₅H₄)LaCl)₂=D]⁺, 725 (15) [D-(C₅H₄)SiMeEt]⁺, 513 (37) [D-2(C₅Me₄)SiMeEt]⁺, 430 (26) [MeEtSi(C₅Me₄)(C₅H₄)LaCl]⁺, 395 (100) [MeEtSi(C₅Me₄)(C₅H₄)La]⁺, 366 (18) [MeSi(C₅Me₄)(C₅H₄)La]⁺ and other fragments.

5.3.3. [Bis(μ-chloro)(cyclopentadienyl)(ethyl)(methyl)-(2,3,4,5-tetramethylcyclopentadienyl)silyl]disamarium (**6a**)

Compound **6a** was prepared analogously to **4a** from 0.97 g (3.78 mmol) of SmCl₃ and 1.42 g (3.78 mmol) of **3a** in 60 ml of THF as an orange microcrystalline solid, which was recrystallized from Et₂O/THF (10:1) at -30°C to obtain single crystals for X-ray structure determination. Yield 0.89 g (53%) of **6a**. Anal. Found: C, 46.52; H, 5.52. $C_{34}H_{48}Cl_2Si_2Sm_2$ (884.75 g mol⁻¹) (**6a**). Calc.: C, 46.11; H, 5.46%. ¹H-NMR (400 MHz): -0.35 (s, 2H, SiMe), -0.26 (s, 1H, SiMe), 0.73 (m, 3H, SiCH₂CH₃), 1.13 (m, 1.25H, SiCH₂CH₃), 1.52 (m, 0.75H, SiCH₂CH₃), 1.83–2.11 (m, 12H, C₅Me₄), 5.57 (s, 0.66H, C₅H₄), 5.69 (s, 0.33H, C₅H₄), 9.05 (m, 1H, C₅H₄), 9.72 (s, 0.66H, C₅H₄), 9.81 (s, 0.33H, C₅H₄), 12.78 (s, 0.66H, C₅H₄), 12.95 (s, 0.33H, C₅H₄). ¹³C{¹H}-NMR (100,64 MHz): -0.39, -0.30, 5.01, 7.29, 8.22, 10.47, 11.55, 11.70, 14.50, 14.69, 18.79–18.91, 95.39, 103.11, 105.10, 107.28, 108.01, 111.37, 115.66, 117.09, 117.95, 118.55, 118.98, 119.43, 126.70, 131.01, 134.27. MS (220°C, ³⁵Cl, ²⁸Si, ¹⁵²Sm, *m/z* (%)): 886 (42) [(MeEtSi(C₅Me₄)(C₅H₄)SmCl)=D]⁺, 857 (22) [D-Et]⁺, 443 (23) [MeEtSi(C₅Me₄)(C₅H₄)SmCl]⁺, 408 (100) [MeEtSi(C₅Me₄)(C₅H₄)Sm]⁺, 399 (17) [Si(C₅Me₄)(C₅H₄)SmCl]⁺, 379 (15) [MeSi(C₅Me₄)(C₅H₄)Sm]⁺ and other fragments.

5.3.4. [Bis(μ-chloro)(cyclopentadienyl)(ethyl)(methyl)-(2,3,4,5-tetramethylcyclopentadienyl)silyl]dylutetium (**7a**)

The procedure described above for the synthesis of **4a** was followed with 1.13 g (4.01 mmol) of LuCl₃ and 1.50 g (4.01 mmol) of **3a** in 70 ml of THF to yield a colorless microcrystalline solid, which was recrystallized from Et₂O/THF (10:1) to obtain single crystals for X-ray structure determination. Yield 0.47 g (25%) of **7a**. Anal. Found: C, 43.65; H, 4.84. $C_{34}H_{48}Cl_2Lu_2Si_2$ (933.87 g mol⁻¹) (**7a**). Calc.: C, 43.73; H, 5.18%. ¹H-NMR (400 MHz): 0.86 (s, 3H, SiMe), 1.28–1.45 (m, 5H, SiEt), 1.60 (m, THF), 1.62 (br s, 6H, C₅Me₄), 2.11

(s, 3H, C₅Me₄), 2.13 (s, 3H, C₅Me₄), 3.64 (m, THF), 6.17 (m, 1H, C₅H₄), 6.21 (m, 1H, C₅H₄), 6.25 (m, 2H, C₅H₄). ¹³C{¹H}-NMR (100,64 MHz): -3.07, 7.05, 7.84, 10.74, 11.00, 13.61, 13.89, 25.42, 67.44, 102.94, 111.70, 112.34, 113.33, 118.15, 118.57, 124.90, 124.94, 130.55. MS (220°C, ³⁵Cl, ²⁸Si, *m/z* (%)): 932 (37) [(MeEtSi(C₅Me₄)(C₅H₄)LuCl)₂=D]⁺, 903 (100) [D-Et]⁺, 466 (17) [MeEtSi-(C₅Me₄)(C₅H₄)LuCl]⁺, 437 (23) [MeSi(C₅Me₄)(C₅H₄)LuCl]⁺, 431 (39) [MeEtSi(C₅Me₄)-(C₅H₄)Lu]⁺, 401 (23) [MeEtSi(C₅Me₄)Lu-Cl]⁺ and other fragments.

5.3.5. [(Cyclopentadienyl)(ethyl)(methyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]zirconiumdichloride (**8a**)

1.92 g (8.24 mmol) of ZrCl₄ were carefully dissolved in 40 ml of THF and 3.08 g (8.24 mmol) of **3a** were added. The suspension was stirred for 48 h at ambient temperature. The solvent was removed in vacuo, and the yellow residue was extracted twice with 40 ml of Et₂O. The yellow extracts were concentrated to 25 ml and cooled to -30°C. The resulting pale yellow crystals were isolated by decantation and subsequent vacuum drying. Single crystals for X-ray structure determination were obtained by recrystallizing the product from Et₂O/THF (10:1) at 0°C. Yield 1.64 g (48%) of **8a**. M.p. (sealed): 195°C. Anal. Found: C, 48.68; H, 5.70. $C_{17}H_{24}Cl_2SiZr$ (418.64 g mol⁻¹) (**8a**). Calc.: C, 48.78; H, 5.78%. ¹H-NMR (400 MHz): 0.74 (s, 3H, SiMe), 1.18 (m, 5H, SiEt), 1.90 (s, 3H, C₅Me₄), 1.92 (s, 3H, C₅Me₄), 2.05 (s, 6H, C₅Me₄), 5.85 (m, 1H, C₅H₄), 5.90 (m, 1H, C₅H₄), 7.09 (m, 2H, C₅H₄). ¹³C{¹H}-NMR (100,64 MHz): -4.13, 6.29, 6.49, 11.92, 11.95, 14.40, 14.65, 98.20, 107.04, 112.62, 113.34, 125.42, 126.27, 126.38, 127.01, 135.37, 135.41. MS (120°C, ³⁵Cl, ⁹⁰Zr, ²⁸Si, *m/z* (%)): 416 (55) [MeEtSi(C₅Me₄)(C₅H₄)ZrCl₂]⁺, 381 (100) [MeEtSi(C₅Me₄)(C₅H₄)ZrCl]⁺, 352 (58) [MeEtSi(C₅Me₄)ZrCl₂]⁺, 346 (6) [MeEtSi(C₅Me₄)(C₅H₄)Zr]⁺, 331 (3) [EtSi(C₅Me₄)(C₅H₄)Zr]⁺, 317 (12) [MeSi(C₅Me₄)(C₅H₄)Zr]⁺, 302 (5) [Si(C₅Me₄)(C₅H₄)Zr]⁺, 296 (5) [MeEtSi(C₅H₄)ZrCl₂]⁺, 282 (4) [MeEtSi(C₅Me₄)Zr]⁺, 274 (5) [(C₅Me₄)(C₅H₄)Zr]⁺, 226 (6) [MeEtSi(C₅H₄)Zr]⁺ and other fragments.

5.4. Syntheses of metallocene chlorides with methyl, phenyl substitution at the bridging silicon atom

5.4.1. [Bis(μ-chloro)(cyclopentadienyl)(methyl)(phenyl)-(2,3,4,5-tetramethylcyclopentadienyl)silyl]ditytrium (**4b**)

A 100 ml Schlenk flask was charged with 1.44 g (3.51 mmol) of YCl₃(THF)₃ and 1.23 g (3.51 mmol) of **3b**. A 60 ml volume of THF were added, and after stirring this mixture for 12 h at room temperature it was heated to reflux for 12 h followed by stirring at ambient temperature for additional 12 h. The THF was evaporated in vacuo, and the resulting yellow solid was

washed with 30 ml of Et₂O and the residue was extracted three times with Et₂O. The extracts were evaporated to dryness in vacuo and the product was isolated by soxhlet extraction with 80 ml of hexane. The pale yellow solution was evaporated to about 25 ml and cooled to –30°C to give a cream-coloured solid, which was dried in vacuo at 0.1 mbar. Yield 0.69 g (46%) of **4b**. Anal. Found: C, 58.13; H, 5.95. C₄₂H₄₈Cl₂Si₂Y₂ (857.82 g mol⁻¹) (**4b**). Calc.: C, 58.81; H, 5.64%. ¹H-NMR (400 MHz): 0.73 (s, 3H, SiMe), 1.71 (s, 3H, C₅Me₄), 1.73 (s, 3H, C₅Me₄), 1.75 (s, 3H, C₅Me₄), 1.75 (s, 3H, C₅Me₄), 6.65 (m, 1H, C₅H₄), 6.73 (m, 1H, C₅H₄), 6.98 (m, 2H, C₅H₄), 7.34 (m, 1H, C₆H₅), 7.39 (m, 1H, C₆H₅), 7.61 (m, 1H, C₆H₅), 7.72 (m, 1H, C₆H₅), 7.79 (m, 1H, C₆H₅). ¹³C{¹H}-NMR (50.32 MHz): –7.78, 10.88, 11.00, 13.53, 13.99, 95.97, 98.69, 113.30, 115.58, 117.45, 118.61, 120.55, 127.18, 128.26, 131.41, 132.77, 134.42, 135.88, 144.83. MS (240°C, ³⁵Cl, ²⁸Si, *m/z* (%)): 856 (1.5) [(MePhSi(C₅Me₄)(C₅H₄)YCl)₂=D]⁺, 736 (6) [D–SiMePh]⁺, 616 (28) [D–SiMePh(C₅Me₄)]⁺, 428 (11) [MePhSi(C₅Me₄)(C₅H₄)YCl]⁺, 393 (5) [MePhSi(C₅Me₄)(C₅H₄)Y]⁺, 337 (100) [Si(C₅Me₄)(C₅H₄)YCl]⁺, 303 (29) [Si(C₅Me₄)(C₅H₄)Y]⁺ and other fragments.

5.4.2. [Bis(μ-chloro)(cyclopentadienyl)(methyl)(phenyl)-(2,3,4,5-tetramethylcyclopentadienyl)silyl]dilanthanum (**5b**)

This compound was prepared from 1.27 g (4.00 mmol) of LaCl₃(THF) and 1.40 g (4.00 mmol) of **3b** in 80 ml THF by the method described for **4b** to give a pale yellow solid. Yield 0.31 g (16%) of **5b**. Anal. Found: C, 51.72; H, 4.45. C₄₂H₄₈Cl₂La₂Si₂ (957.82 g mol⁻¹) (**5b**). Calc.: C, 52.67; H, 5.05%. ¹H-NMR (200 MHz): 0.76 (s, 2H, SiMe), 1.01 (s, 1H, SiMe), 1.59 (m, 8H, THF), 2.14–2.75 (m, 12H, C₅Me₄), 3.64 (m, 8H, THF), 6.07 (m, 1H, C₅H₄), 6.42 (m, 1H, C₅H₄), 6.73 (m, 1H, C₅H₄), 6.92 (m, 1H, C₅H₄), 7.44 (m, 3H, C₆H₅), 8.01 (m, 1H, C₆H₅), 8.25 (m, 1H, C₆H₅). ¹³C{¹H}-NMR (50.32 MHz): 0.59, 1.36, 10.94, 11.37, 13.71, 15.57, 25.36, 64.31, 98.14, 109.88, 114.95, 116.06, 118.07, 121.48, 122.94, 124.19, 124.91, 128.03, 129.69, 134.94, 140.99, 142.35. MS (240°C, ³⁵Cl, ²⁸Si, *m/z* (%)): 956 (1.5) [(MePhSi(C₅Me₄)(C₅H₄)LaCl)₂=D]⁺, 836 (6) [D–SiMePh]⁺, 716 (28) [D–SiMePh(C₅Me₄)]⁺, 478 (11) [MePhSi(C₅Me₄)(C₅H₄)LaCl]⁺, 443 (5) [MePhSi(C₅Me₄)(C₅H₄)La]⁺, 387 (100) [Si(C₅Me₄)(C₅H₄)LaCl]⁺, 353 (29) [Si(C₅Me₄)(C₅H₄)La]⁺ and other fragments.

5.4.3. [Bis(μ-chloro)(cyclopentadienyl)(methyl)(phenyl)-(2,3,4,5-tetramethylcyclopentadienyl)silyl]disamarium (**6b**)

This compound was prepared by using the method described for **4b** from 1.30 g (5.04 mmol) of SmCl₃ and 1.77 g (5.04 mmol) of **3b** in 50 ml THF to yield an orange microcrystalline solid. Yield 0.59 g (24%) of **6b**. Anal. Found: C, 51.52; H, 4.96. C₄₂H₄₈Cl₂Si₂Sm₂

(980.84 g mol⁻¹) (**6b**). Calc.: C, 51.42; H, 4.93%. ¹H-NMR (200 MHz): 0.38 (s, 2H, SiMe), 0.58 (s, 1H, SiMe), 1.65 (m, 8H, THF), 1.96–2.20 (m, 12H, C₅Me₄), 3.68 (m, 8H, THF), 6.43 (m, 1H, C₅H₄), 6.91 (m, 1H, C₅H₄), 7.53 (m, 2H, C₅H₄), 7.64 (m, 3H, C₆H₅), 8.05 (m, 1H, C₆H₅), 8.58 (m, 1H, C₆H₅). ¹³C{¹H}-NMR (50.32 MHz): 1.93, 11.16, 17.99, 18.14, 19.20, 19.81, 94.06, 99.54, 107.96, 108.13, 115.49, 118.26, 120.06, 121.55, 127.40, 128.03, 129.25, 134.03, 134.24, 142.82. MS (280°C, ³⁵Cl, ²⁸Si, ¹⁵²Sm, *m/z* (%)): 982 (26) [(MePhSi(C₅Me₄)(C₅H₄)SmCl)₂=D]⁺, 862 (8) [D–SiMePh]⁺, 742 (1) [D–SiMePh(C₅Me₄)]⁺, 707 (5) [D–SiMePh(C₅Me₄)–Cl]⁺, 643 (15) [MePhSi(C₅Me₄)(C₅H₄)Sm₂Cl]⁺, 491 (15) [MePhSi(C₅Me₄)(C₅H₄)SmCl]⁺, 456 (15) [MePhSi(C₅Me₄)(C₅H₄)Sm]⁺, 399 (1) [Si(C₅Me₄)(C₅H₄)SmCl]⁺, 304 (10) [MePhSi(C₅Me₄)(C₅H₄)]⁺, 107 (100) [MeSi(C₅H₄)]⁺ and other fragments.

5.4.4. [Bis(μ-chloro)(cyclopentadienyl)(methyl)(phenyl)-(2,3,4,5-tetramethylcyclopentadienyl)silyl]dilutetium (**7b**)

Compound **7b** was synthesized in a similar manner to **4b** from 1.01 g (3.59 mmol) of LuCl₃ and 1.26 g (3.59 mmol) of **3b** in 70 ml THF to obtain a colorless solid. Yield 0.41 g (22%) of **7b**. Anal. Found: C, 48.12; H, 4.25. C₄₂H₄₈Cl₂Lu₂Si₂ (1029.96 g mol⁻¹) (**7b**). Calc.: C, 48.99; H, 4.70%. ¹H-NMR (200 MHz): 1.00 (s, 3H, SiMe), 1.11 (t, 3H, Et₂O), 1.59 (m, 4H, THF), 1.62 (s, 3H, C₅Me₄), 1.96 (s, 3H, C₅Me₄), 2.13 (s, 3H, C₅Me₄), 2.21 (s, 3H, C₅Me₄), 3.33 (q, 4H, Et₂O), 3.63 (m, 4H, THF), 6.23 (m, 1H, C₅H₄), 6.39 (m, 1H, C₅H₄), 6.45 (m, 1H, C₅H₄), 6.80 (m, 1H, C₅H₄), 7.40 (m, 3H, C₆H₅), 7.53 (m, 1H, C₆H₅), 8.18 (m, 1H, C₆H₅). ¹³C{¹H}-NMR (50.32 MHz): 0.35, 10.81, 11.58, 14.19, 15.05, 25.35, 67.39, 101.60, 109.27, 111.20, 112.10, 112.32, 112.76, 117.74, 118.01, 118.48, 119.46, 128.26, 129.39, 134.33, 139.26. MS (210°C, ³⁵Cl, ²⁸Si, *m/z* (%)): 1028 (38) [(MePhSi(C₅Me₄)(C₅H₄)LuCl)₂=D]⁺, 908 (17) [D–SiMePh]⁺, 788 (35) [D–SiMePh–(C₅Me₄)]⁺, 514 (84) [MePhSi(C₅Me₄)(C₅H₄)LuCl]⁺, 479 (74) [MePhSi(C₅Me₄)(C₅H₄)Lu]⁺, 422 (71) [Si(C₅Me₄)(C₅H₄)LuCl]⁺, 387 (10) [Si(C₅Me₄)(C₅H₄)Lu]⁺, 395 (22) [MePhSi(C₅H₄)LuCl]⁺, 335 (38) [PhSi(C₅H₄)Lu]⁺, 185 (100) [MePhSi(C₅H₄)]⁺ and other fragments.

5.4.5. [(Cyclopentadienyl)(methyl)(phenyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]zirconiumdichloride (**8b**)

ZrCl₄ (2.06 g, 8.85 mmol) was dissolved carefully in 70 ml of THF, and 3.10 g (8.85 mmol) of **3b** were added. The suspension was stirred for 96 h at room temperature, the solvent was removed under reduced pressure and the remaining pale brown residue first was washed with 20 ml of Et₂O and then extracted two times with 40 ml of Et₂O. The yellow extracts were

reduced in vacuo to 25 ml, and the solvent was cooled to -78°C to give a pale yellow solid, which was separated by decanting and subsequent drying of the solid in vacuo. The remaining product was recrystallized from $\text{Et}_2\text{O}/\text{THF}$ (10:1) to obtain a pale yellow microcrystalline solid, which was dried in vacuo at 0.1 mbar. Yield 1.49 g (36%) of **8b**. M.p.(sealed): 163°C . Anal. Found: C, 54.17; H, 5.47. $\text{C}_{21}\text{H}_{24}\text{Cl}_2\text{SiZr}$ (466.78 g mol^{-1}) (**8b**). Calc.: C, 54.05; H, 5.18%. $^1\text{H-NMR}$ (200 MHz): 0.91 (s, 3H, SiMe), 1.45 (s, 3H; C_5Me_4), 1.98 (s, 3H, C_5Me_4), 2.01 (s, 3H, C_5Me_4), 2.09 (s, 3H, C_5Me_4), 5.85 (m, 2H, C_5H_4), 6.14 (m, 2H, C_5H_4), 7.14 (m, 1H, C_6H_5), 7.20 (m, 1H, C_6H_5), 7.96 (m, 3H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ -NMR (50.32 MHz): -0.35 , 12.04, 12.49, 15.09, 15.30, 97.60, 105.65, 112.97, 115.00, 125.27, 125.50, 128.19, 129.13, 129.22, 130.88, 134.29, 134.81, 137.33, 142.21. MS (25°C , ^{35}Cl , ^{90}Zr , ^{28}Si , m/z (%)): 464 (49) $[\text{MePhSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{ZrCl}_2]^+$, 429 (100) $[\text{MePhSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{ZrCl}]^+$, 414 (17) $[\text{PhSi}(\text{C}_5\text{Me}_4)\text{-ZrCl}]^+$, 400 (4) $[\text{MePhSi}(\text{C}_5\text{Me}_4)\text{ZrCl}_2]^+$, 394 (7) $[\text{MePhSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{Zr}]^+$, 379 (6) $[\text{PhSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{-Zr}]^+$, 344 (2) $[\text{MePhSi}(\text{C}_5\text{H}_4)\text{ZrCl}_2]^+$, 330 (3) $[\text{MePhSi}(\text{C}_5\text{Me}_4)\text{Zr}]^+$, 317 (2) $[\text{MeSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{-Zr}]^+$, 302 (2) $[\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{Zr}]^+$ and other fragments.

5.5. Syntheses of organolanthanide acetates with ethyl, methyl substitution at the bridging silicon atom

5.5.1. [(Cyclopentadienyl)(ethyl)(methyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]yttriumacetate (**9a**)

A 50 ml Schlenk flask was charged with 0.30 g (0.39 mmol) of **4a** and 0.07 g (0.79 mmol) of sodium acetate. 35 ml of THF were added and the reaction mixture was stirred for 48 h at room temperature. The THF was removed in vacuo, and the product was separated by soxhlet extraction with Et_2O . The extract was reduced in vacuo to 25 ml and cooled to -30°C to give a colourless microcrystalline solid. The product was isolated by decantation and dried in vacuo at 0.1 mbar. Yield 0.25 g (78%) of **9a**. Anal. Found: C, 56.42; H, 6.94. $\text{C}_{19}\text{H}_{27}\text{O}_2\text{SiY}$ (404.43 g mol^{-1}) (**9a**). Calc.: C, 56.43; H, 6.73%. $^1\text{H-NMR}$ (200 MHz): 0.90 (s, 3H, SiMe), 1.33 (m, 3H, SiCH_2CH_3), 1.57 (m, 2H, SCH_2CH_3), 1.85 (s, 6H, C_5Me_4), 2.11 (s, 3H, O_2CCH_3), 2.37, 2.38 (s, 6H, C_5Me_4), 6.30 (br m, 4H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ -NMR (50.32 MHz): -2.45 , 7.41, 8.07, 10.51, 13.99, 14.32, 23.94, 103.29, 104.02, 107.08, 112.78, 113.19, 119.66, 121.51, 122.04, 122.62, 180.61. MS (305°C , ^{28}Si , m/z (%)): 808 (33) $[(\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{YO}_2\text{CCH}_3)_2=\text{D}]^+$, 779 (1) $[\text{D}-\text{Et}]^+$, 736 (1) $[\text{D}-\text{SiMeEt}]^+$, 404 (100) $[\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{YO}_2\text{CCH}_3]^+$, 375 (13) $[\text{MeSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{YO}_2\text{CCH}_3]^+$, 345 (8) $[\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{Y}]^+$, 339 (19) $[\text{MeEtSi}(\text{C}_5\text{Me}_4)\text{YO}_2\text{CCH}_3]^+$, 316 (9) $[\text{MeSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{-}$

$\text{Y}]^+$, 258 (4) $[\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)]^+$ and other fragments.

5.5.2. [(Cyclopentadienyl)(ethyl)(methyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]lanthanumacetate (**10a**)

Compound **10a** was prepared from 0.69 g (0.80 mmol) of **5a** und 0.13 g (1.60 mmol) of sodium acetate in 35 ml THF by the same method described for **9a** to give a cream-coloured solid. Yield 0.64 g (88%) of **10a**. Anal. Found: C, 49.54; H, 5.15. $\text{C}_{19}\text{H}_{27}\text{LaO}_2\text{Si}$ (454.43 g mol^{-1}) (**10a**). Calc.: C, 50.22; H, 5.99%. $^1\text{H-NMR}$ (200 MHz): 0.94 (s, 3H, SiMe), 1.35 (m, 5H, SEt), 2.01 (br s, 9H, C_5Me_4), 2.57 (s, 3H, C_5Me_4), 2.61 (s, 3H, C_5Me_4), 6.38 (m, 2H, C_5H_4), 6.59 (m, 2H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ -NMR (50.32 MHz): -1.82 , 7.74, 8.83, 11.38, 14.25, 14.56, 15.18, 25.01, 65.43, 102.37, 108.22, 114.31, 114.57, 115.05, 121.12, 121.33, 121.53, 122.18, 131.33, 182.17. MS (280°C , ^{28}Si , m/z (%)): 908 (32) $[(\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{LaO}_2\text{CCH}_3)_2=\text{D}]^+$, 836 (2) $[\text{D}-\text{SiMeEt}]^+$, 454 (36) $[\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{LaO}_2\text{-CCH}_3]^+$, 425 (100) $[\text{MeSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{LaO}_2\text{CCH}_3]^+$, 395 (53) $[\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{La}]^+$, 258 (27) $[\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)]^+$ and other fragments.

5.5.3. [(Cyclopentadienyl)(ethyl)(methyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]samariumacetate (**11a**)

The procedure described above for the synthesis of **9a** was repeated with 0.36 g (0.41 mmol) of **6a** and 0.07 g (0.82 mmol) of sodium acetate in 35 ml of THF to yield an intensive yellow microcrystalline solid. Yield 0.31 g (81%) of **11a**. Anal. Found: C, 47.99; H, 5.81. $\text{C}_{19}\text{H}_{27}\text{O}_2\text{SiSm}$ (465.94 g mol^{-1}) (**11a**). Calc.: C, 48.90; H, 5.84%. Molecular mass (kryoscopic): 502 g mol^{-1} . $^1\text{H-NMR}$ (200 MHz): 0.39–0.58 (m, 8H, SiMe, SiEt), 0.90, 0.94, 1.01, 1.62 (s, 12H, C_5Me_4), 3.13 (br s, 3H, O_2CCH_3), 7.05 (s, 1H, C_5H_4), 9.72 (s br, 2H, C_5H_4), 12.29 (s, 1H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.64 MHz): -0.78 , 7.03, 9.97, 15.04, 15.42, 17.50, 17.60, 21.86, 93.77, 104.49, 105.30, 107.85, 108.44, 110.94, 111.59, 114.86, 115.79, 116.56, 183.47. MS (220°C , ^{28}Si , ^{152}Sm , m/z (%)): 934 (24) $[(\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{SmO}_2\text{-CCH}_3)_2=\text{D}]^+$, 890 (2) $[\text{D}-\text{Me}-\text{Et}]^+$, 862 (2) $[\text{D}-\text{SiMeEt}]^+$, 678 (6) $[\text{D}-(\text{C}_5\text{H}_4)(\text{C}_5\text{Me}_4)\text{SiMeEt}]^+$, 467 (100) $[\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{-SmO}_2\text{CCH}_3]^+$, 408 (96) $[\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{Sm}]^+$, 379 (18) $[\text{MeSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\text{-Sm}]^+$, 258 (23) $[\text{MeEtSi}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)]^+$ and other fragments.

5.5.4. [(Cyclopentadienyl)(ethyl)(methyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]lutetiumacetate (**12a**)

Compound **12a** was prepared analogously to **9a** from 0.51 g (0.55 mmol) of **7a** and 0.09 g (1.10 mmol) of sodium acetate in 40 ml of THF to give a colourless microcrystalline solid. Yield 0.47 g (88%) **12a**. Anal. Found: C, 45.47; H, 5.28. $\text{C}_{19}\text{H}_{27}\text{LuO}_2\text{Si}$ (490.50 g

mol⁻¹) (**12a**). Calc.: C, 46.53; H, 5.55%. ¹H-NMR (200 MHz): 0.88 (s, 3H, SiMe), 1.38 (m, 5H, SiEt), 1.86 (s, 6H, C₅Me₄), 2.09 (s, 3H, C₅Me₄), 2.11 (s, 3H, C₅Me₄), 2.38 (s, 3H, O₂CCH₃), 6.21 (m, 2H, C₅H₄), 6.31 (m, 2H, C₅H₄). ¹³C{¹H}-NMR (50.32 MHz): -2.50, 7.27, 8.14, 10.59, 14.07, 14.96, 24.49, 103.36, 104.00, 107.07, 112.13, 113.39, 113.82, 114.08, 118.14, 119.49, 120.84, 183.63. MS (260°C, ²⁸Si, *m/z* (%)): 980 (36) [(MeEtSi(C₅Me₄)(C₅H₄)LuO₂CCH₃)₂=D]⁺, 490 (100) [MeEtSi(C₅Me₄)(C₅H₄)LuO₂C-CH₃]⁺, 461 (16) [MeSi(C₅Me₄)(C₅H₄)LuO₂CCH₃]⁺, 431 (5) [MeEtSi(C₅Me₄)(C₅H₄)-Lu]⁺, 418 (11) [(C₅Me₄)(C₅H₄)LuO₂CCH₃]⁺ and other fragments.

5.6. Syntheses of organolanthanide acetates with methyl, phenyl substitution at the bridging silicon atom

5.6.1. [(Cyclopentadienyl)(methyl)(phenyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]yttriumacetate (**9b**)

Compound **9b** was synthesized in a similar manner as described for **9a** from 0.56 g (0.65 mmol) of **4b** and 0.11 g (1.30 mmol) of sodium acetate in 40 ml of THF to obtain a colourless solid. Yield 0.54 g (92%) of **9b**. Anal. Found: C, 60.69; H, 5.85. C₂₃H₂₇O₂SiY (452.48 g mol⁻¹) (**9b**). Calc.: C, 61.06; H, 6.01%. ¹H-NMR (400 MHz): 0.26 (s, 3H, SiMe), 1.69 (s, 3H, C₅Me₄), 1.71 (s, 3H, C₅Me₄), 1.74 (s, 3H, C₅Me₄), 1.77 (s, 3H, C₅Me₄), 2.03 (s, 3H, O₂CCH₃), 6.78 (m, 1H, C₅H₄), 7.40 (m, 5H, C₆H₅), 7.88 (m, 2H, C₅H₄), 7.95 (m, 1H, C₅H₄). ¹³C{¹H}-NMR (50.32 MHz): 5.29, 10.80, 10.90, 14.15, 14.98, 26.53, 106.59, 120.19, 122.07, 125.20, 127.77, 128.35, 129.45, 132.86, 133.81, 136.26, 143.54, 179.51. MS (288°C, ²⁸Si, *m/z* (%)): 904 (1) [(MePhSi(C₅Me₄)(C₅H₄)YO₂CCH₃)₂=D]⁺, 812 (6) [D-Me-Ph]⁺, 784 (2) [D-SiMePh]⁺, 692 (2) [D-Me-Ph-(C₅Me₄)]⁺, 664 (8) [D-SiMePh(C₅Me₄)]⁺, 452 (16) [MePhSi(C₅Me₄)(C₅H₄)YO₂CCH₃]⁺, 393 (48) [MePhSi(C₅Me₄)(C₅H₄)Y]⁺, 375 (44) [MeSi(C₅Me₄)(C₅H₄)-YO₂CCH₃]⁺, 315 (100) [MeSi(C₅Me₄)(C₅H₄)Y-H]⁺, 303 (28) [Si(C₅Me₄)(C₅H₄)Y]⁺, 255 (29) [MeSi-(C₅H₄)-YO₂CCH₃]⁺ and other fragments.

5.6.2. [(Cyclopentadienyl)(methyl)(phenyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]lanthanumacetate (**10b**)

Compound **10b** was prepared by using the same method as described for **9a** from 0.46 g (0.48 mmol) of **5b** and 0.08 g (0.96 mmol) of sodium acetate in 40 ml of THF to give a cream-coloured solid. Yield 0.45 g (94%) of **10b**. Anal. Found: C, 55.47; H, 5.34. C₂₃H₂₇LaO₂Si (502.48 g mol⁻¹) (**10b**). Calc.: C, 54.98; H, 5.42%. ¹H-NMR (200 MHz): 0.32 (s, 3H, SiMe), 1.70–1.85 (m, 12H, C₅Me₄), 1.92 (br s, 3H, O₂CCH₃), 6.43 (m, 1H, C₅H₄), 6.58 (m, 1H, C₅H₄), 6.65 (m, 1H, C₅H₄), 6.73 (m, 1H, C₅H₄), 7.36 (m, 1H, C₆H₅), 7.40 (m, 2H, C₆H₅), 7.64 (m, 2H, C₆H₅). ¹³C{¹H}-NMR (50.32 MHz): 1.53, 10.91, 14.06, 15.15, 25.43, 99.97, 105.21, 107.62, 112.50,

113.88, 116.04, 127.03, 127.68, 133.87, 143.87, 182.32. MS (240°C, ²⁸Si, *m/z* (%)): 1004 (2) [(MePhSi(C₅Me₄)(C₅H₄)LaO₂CCH₃)₂=D]⁺, 820 (6) [D-MePhSi(C₅H₄)]⁺, 764 (5) [D-SiMePh(C₅Me₄)]⁺, 502 (17) [MePhSi(C₅Me₄)(C₅H₄)-LaO₂CCH₃]⁺, 443 (41) [MePhSi(C₅Me₄)(C₅H₄)La]⁺, 351 (2) [Si(C₅Me₄)(C₅H₄)La]⁺, 185 (100) [MePhSi(C₅H₅)]⁺ and other fragments.

5.6.3. [(Cyclopentadienyl)(methyl)(phenyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]samariumacetate (**11b**)

The procedure described for **9a** was performed with 0.37 g (0.38 mmol) of **6b** and 0.07 g (0.76 mmol) of sodium acetate in 40 ml of THF to obtain an intensive yellow microcrystalline solid. Yield 0.31 g (79%) of **11b**. Anal. Found: C, 52.97; H, 4.95. C₂₃H₂₇O₂SiSm (513.99 g mol⁻¹) (**11b**). Calc.: C, 53.76; H, 5.30%. Molecular mass (kryoscopic): 589 g mol⁻¹. ¹H-NMR (200 MHz): 0.51 (s, 3H, SiMe), 0.92 (br s, 6H, C₅Me₄), 1.56 (s br, 3H, O₂CCH₃), 2.35 (s br, 6H, C₅Me₄), 6.78 (m, 1H, C₅H₄), 7.51 (m, 3H, C₅H₄), 7.82 (m, 1H, C₆H₅), 7.90 (m, 1H, C₆H₅), 8.43 (m, 3H, C₆H₅). ¹³C{¹H}-NMR (50.32 MHz): 2.53, 14.00, 14.05, 17.81, 19.12, 21.38, 92.98, 102.40, 107.40, 110.20, 114.19, 116.23, 128.04, 128.91, 134.20, 143.63, 181.92. MS (288°C, ²⁸Si, ¹⁵²Sm, *m/z* (%)): 1030 (59) [(MePhSi(C₅Me₄)(C₅H₄)SmO₂CCH₃)₂=D]⁺, 910 (19) [D-SiMePh]⁺, 846 (39) [D-MePhSi(C₅H₄)]⁺, 790 (19) [D-SiMePh(C₅Me₄)]⁺, 726 (11) [D-MePhSi(C₅Me₄)(C₅H₄)]⁺, 515 (76) [MePhSi(C₅Me₄)(C₅H₄)SmO₂CCH₃]⁺, 456 (100) [MePhSi(C₅Me₄)(C₅H₄)Sm]⁺, 438 (13) [MeSi(C₅Me₄)(C₅H₄)SmO₂-CCH₃]⁺, 379 (14) [Si(C₅Me₄)(C₅H₄)Sm]⁺ and other fragments.

5.6.4. [(Cyclopentadienyl)(methyl)(phenyl)(2,3,4,5-tetramethylcyclopentadienyl)silyl]lutetiumacetate (**12b**)

The preceding synthesis for **9a** was carried out with 0.35 g (0.34 mmol) of **7b** and 0.06 g (0.68 mmol) of sodium acetate in 40 ml of THF to yield a colourless microcrystalline solid. Yield 0.34 g (92%) of **12b**. Anal. Found: C, 50.71; H, 5.25. C₂₃H₂₇LuO₂Si (538.55 g mol⁻¹) (**12b**). Calc.: C, 51.30; H, 5.05%. Molecular mass (kryoscopic): 554 g mol⁻¹. ¹H-NMR (200 MHz): 0.40 (s, 3H, SiMe), 1.68 (s, 3H, C₅Me₄), 1.72 (m, 4H, THF), 1.82 (s, 6H, C₅Me₄), 1.96 (s, 3H, C₅H₄), 2.21 (s, 3H, O₂CCH₃), 3.65 (m, 4H, THF), 6.79 (m, 2H, C₅H₄), 6.88 (m, 2H, C₅H₄), 7.29 (m, 3H, C₆H₅), 7.87 (m, 2H, C₆H₅). ¹³C{¹H}-NMR (50.32 MHz): -6.30, 11.11, 14.44, 14.61, 24.47, 25.42, 67.45, 104.07, 105.27, 107.65, 108.62, 113.54, 113.90, 121.08, 126.98, 127.53, 133.24, 134.49, 143.03, 184.99. MS (200°C, ²⁸Si, *m/z* (%)): 1076 (3) [(MePhSi(C₅Me₄)(C₅H₄)LuO₂CCH₃)₂=D]⁺, 956 (2) [D-SiMePh]⁺, 892 (3) [D-Me-Ph-C₅H₄]⁺, 836 (5) [D-SiMePh(C₅Me₄)]⁺, 538 (10) [MePhSi(C₅Me₄)(C₅H₄)LuO₂CCH₃]⁺, 479 (33) [MePhSi(C₅Me₄)(C₅H₄)-Lu]⁺, 387 (12) [Si(C₅Me₄)(C₅H₄)Lu]⁺, 185 (100) [MePhSi(C₅H₅)]⁺ and other fragments.

5.7. X-ray crystallographic analyses

An Enraf Nonius CAD-4 automatic diffractometer (ω - 2θ scan, $\lambda = 0.71096 \text{ \AA}$, variable scan time 45 s) fitted with a liquid nitrogen low-temperature device was used for the intensity measurements. The unit cell parameters were obtained from the angles of 25 reflections in the range of $18.6^\circ < 2\theta < 28.0^\circ$ for **6a** and $18.8^\circ < 2\theta < 29.8^\circ$ for **8a**. Reflections were scanned with variable scan time, depending on intensities, with 2/3 of the time used for scanning the peak and 1/6 measuring each the left and the right background. The intensities of three check reflections monitored every 2 h showed only statistical fluctuations during the data collection. The orientation of the crystal was checked every 200 intensity measurements by scanning three strong reflections well distributed in reciprocal space. A new orientation matrix would have automatically been calculated from a list of 25 recentered reflections, if the angular change was larger than 0.1%. The raw data were corrected for Lorentz, polarisation and absorption effects [32]. The positions of the heavy atoms were determined from a Patterson synthesis (SHELXS-86) [33]. Structure solution and refinement was carried out with the SHELXS-86 [33] and SHELXL-93 [34] software respectively. The non-hydrogen atoms were refined with anisotropic temperature factors. The C–H hydrogen atoms were calculated in idealized positions ($C-H = 0.96 \text{ \AA}$, $U_{iso} = 0.08 \text{ \AA}^2$). Scattering factors were taken from references [35–37]. The non-hydrogen atoms of the solvent molecules were refined with isotropic temperature factors. Data reduction was performed using PC-software [32]. All other calculations were performed with SHELXL-93 [34]. Molecular plots were obtained with the program ZORTEP [19]. **6a**: During the refinement of the structure the terminal atom of the ethyl substituent was found to be disordered racemically between the positions C(11) and C(11'). **8a**: The normalized structure amplitudes indicated the space group $Pbn2_1$ (No. 33, non standard orientation). After structure refinement the absolute structure could not be determined. The ethyl and methyl substituents at the silicon atom are racemically distributed (50:50). Therefore the structure was transferred to the centrosymmetric space group $Pnma$ (No. 62) and refined with a disordered atom C(7). Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository numbers CSD-407288 (**6a**) and CSD-407287 (**8a**).

5.8. Catalysis tests

All procedures were carried out under argon using Schlenk techniques. MAO was purchased from Witco,

propylene from Gerling, Holz and Co. and ethylene from Linde. The gases were purified by passage through columns with Cu catalyst (BASF R3-11) and a molecular sieve of 10 \AA . Toluene was refluxed over Na/K for several days prior to use. Polymerizations were performed in a 1l type I Büchi autoclave with an additional internal cooling loop. For a typical experiment the reactor was evacuated at 95°C for 1 h, flushed several times with argon and filled with 200 ml of toluene and 400 mg of MAO. Propylene or ethylene pressure of 2 bar was applied and the polymerization started by injection of the metallocene. Monomer consumption was monitored with a Peteric 3002 pressflow controller and a Büchi bds 488 data system. The polymerization was terminated by injection of 5 ml ethanol and venting off the monomer. Polyethylenes were stirred with ethanol/HCl overnight and filtered, washed with NaHCO_3 and water. The polypropylene solutions were stirred with aqueous HCl followed by phase separation, neutralization, washing and removal of toluene on a rotatory evaporator. The polymer yields were determined after drying for 48 h at 60°C in vacuo.

5.9. Polymer analyses

$^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded at 373 K on a Bruker MSL 300 spectrometer at 75 MHz. Samples were prepared in 10 mm tubes as 10 wt. % solutions of the polymer in perchlorobutadiene/tetrachloroethane- d_2 . DSC-analyses were carried out on a Perkin-Elmer DSC 4 with a heating rate of $20^\circ\text{C min}^{-1}$. The results of the second scan are reported. Gel permeation chromatography was performed on a Waters 150-C instrument (135°C /trichlorobenzene) equipped with a PL 360 evaporation light scattering detector. Viscosimetry was carried out in decahydronaphthalene at 135°C using a Ubbelohde capillary 0a and a Lauda viscosboy. Mark-Houwink constants were taken from literature [38].

Acknowledgements

This work was financially supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (Graduiertenkolleg 'Synthetische, mechanistische und reaktionstechnische Aspekte von Metallkatalysatoren') and the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie (BMBF 03D 0023 D3).

References

- [1] G.A. Molander, E.D. Dowdy, H. Schumann, *J. Org. Chem.* 63 (1998) 3386.
- [2] C.S. Bajgur, W.R. Tikkanen, J.L. Petersen, *Inorg. Chem.* 24 (1985) 2539.

- [3] P. Jutzi, R. Dickbreder, Chem. Ber. 119 (1986) 1750.
- [4] G. Jeske, L.E. Schock, P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8103.
- [5] N. Höck, W. Oroschin, G. Poalucci, R.D. Fischer, Angew. Chem. 98 (1986) 748.
- [6] C.M. Fendrick, L.D. Schertz, V.M. Day, T.J. Marks, Organometallics 7 (1988) 1828.
- [7] D. Stern, M. Sabat, T.J. Marks, J. Am. Chem. Soc. 112 (1990) 9558.
- [8] W.E. Piers, P.J. Shapiro, E.E. Bunel, J.E. Bercaw, Synlett 2 (1990) 74.
- [9] T. Akhnoukh, J. Müller, K. Qiao, X.-F. Li, R.D. Fischer, J. Organomet. Chem. 408 (1991) 47.
- [10] K. Qiao, R.D. Fischer, G. Paolucci, J. Organomet. Chem. 456 (1993) 185.
- [11] E.B. Coughlin, L.M. Henling, J.E. Bercaw, Inorg. Chim. Acta 242 (1996) 205.
- [12] S. Miya, T. Yoshimura, T. Mise, H. Yamazaki (Chisso Corp.; Institute of Physical and Chemical Research), EP 316,155 (1989), JP 282,538 (1987).
- [13] S. Miya, T. Mise, A. Kageyama, H. Yamazaki (Chisso Corp. Rikagaku Kenkyusho), JP 05,202,124 [93,202,124] (1993).
- [14] For some examples see: (a) J.A. Ewen, Stud. Surf. Sci. Cat. 25 (1986) 271. (b) H. Wiesenfeldt, A. Reinmuth, E. Barsties, K. Evertz, H.-H. Brintzinger, J. Organomet. Chem. 369 (1989) 359. (c) T. Mise, S. Miya, H. Yamazaki, Chem. Lett. (1989) 1853. (d) W. Röhl, H.-H. Brintzinger, B. Rieger, R. Zolk, Angew. Chem. 102 (1990) 339. (e) P. Burger, K. Hortmann, J. Diebold, H.-H. Brintzinger, J. Organomet. Chem. 417 (1991) 9. (f) K. Hortmann, H.-H. Brintzinger, New J. Chem. 16 (1992) 51.
- [15] For some examples see: (a) R.E. Marsh, W.P. Schaefer, E.B. Coughlin, J.E. Bercaw, Acta Cryst. C48 (1992) 1773. (b) E.B. Coughlin, J.E. Bercaw, J. Am. Chem. Soc. 114 (1992) 7606. (c) H. Schumann, M. Glanz, H. Hemling, Chem. Ber. 127 (1994) 2363.
- [16] H. Köpf, N. Klouras, Z. Naturforsch. 38B (1983) 321.
- [17] See for example: (a) G.H. Llinas, R.O. Day, M.D. Rausch, J.C.W. Chien, Organometallics 12 (1993) 1283. (b) G. Erker, C. Psiorz, C. Krüger, M. Nolte, Chem. Ber. 127 (1994) 1551.
- [18] The data could be refined only to $R_1 = 0.1246$. K. Zietzke, Diss., TU Berlin, 1997.
- [19] L. Zsolnai, H. Pritzkow, ZORTEP, Ortep Program for PC, Universität Heidelberg, Deutschland, 1994.
- [20] W.J. Evans, R.A. Keyer, J.W. Ziller, J. Organomet. Chem. 450 (1993) 115.
- [21] C. Sun, G. Wei, Z. Jin, W. Chen, Polyhedron 13 (1994) 1483.
- [22] W.J. Evans, J.W. Grate, K.R. Levan, I. Bloom, T.T. Petersen, R.I. Dvedens, H. Zhang, J.L. Atwood, Inorg. Chem. 25 (1986) 3614.
- [23] H. Schumann, L. Esser, J. Löbel, A. Diedrich, D. van der Helm, X. Ji, Organometallics 10 (1991) 2585.
- [24] W.J. Evans, I. Bloom, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 103 (1981) 6507.
- [25] M.A. Giardello, V.P. Conticello, L. Brard, M.R. Gagné, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10212.
- [26] G. Depaoli, P. Zanonato, G. Valle, Inorg. Chim. Acta 170 (1990) 109.
- [27] J.W. Lauher, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729.
- [28] L. Resconi, F. Piemontesi, G. Franciscano, L. Abis, T. Fiorani, J. Am. Chem. Soc. 114 (1992) 1025.
- [29] H. Schumann, M. Glanz, H. Hemling, J. Organomet. Chem. 445 (1993) 1.
- [30] J.J. Eisch, R.B. King, Organometallic Syntheses, New York, 1965, p. 64.
- [31] W.A. Herrmann, G. Brauer, Synthetic Methods of Organometallic and Inorganic Chemistry, vol. 6, Thieme Verlag, Stuttgart, New York, 1997.
- [32] Kretschmar, CAD-4/PC-Version, 1994.
- [33] G.M. Sheldrick, SHELXL 86, Program for Crystal Structure Determination, Universität Göttingen, Deutschland, 1986.
- [34] G.M. Sheldrick, SHELXS 93, Program for Crystal Structure Determination, Universität Göttingen, Deutschland, 1993.
- [35] D.T. Cromer, J.B. Mann, Acta Crystallogr. A24 (1968) 321.
- [36] D.T. Cromer, D. Liberman, J. Chem. Phys. 53 (1970) 1891.
- [37] R.F. Stewart, E.R. Davidson, W.T. Simpson, J. Chem. Phys. 42 (1965) 3175.
- [38] T.G. Scholte, N.L.J. Meijerink, H.M. Schoffeleers, A.M.G. Brands, J. Appl. Pol. Sci. 29 (1984) 3763.