The synthesis, characterization and polymerization behavior of ansa cyclopentadienyl fluorenyl complexes; the X-ray structures of the complexes [(C$_{13}$H$_8$)SiR$_2$(C$_5$H$_4$)]ZrCl$_2$ (R = Me or Ph)

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Abstract

The preparation and characterization of the ansa metallocene complexes [(C$_{13}$H$_8$)ER$_2$(C$_5$H$_4$)]ZrCl$_2$, [(2,7-^{t}Bu$_2$C$_{13}$H$_6$)-SiR$_2$(C$_5$H$_4$)]ZrCl$_2$ and [(2,7-^{t}Bu$_2$C$_{13}$H$_6$)SiR$_2$(C$_{13}$H$_8$)]ZrCl$_2$ (E = Si or Ge; R = Me or Ph) are reported. The crystal structures of [(C$_{13}$H$_8$)SiR$_2$(C$_5$H$_4$)]ZrCl$_2$ (R = Me, or Ph) have been determined and are discussed. The complexes are compared in respect to their polymerization behavior of propylene.

Keywords: Catalysis; Metallocene complexes; Silicon; Syndiotactic polypropylene; Zirconium; Germanium

1. Introduction

In the past few years, ansa metallocene dichloride complexes have been established as excellent catalyst precursors for the polymerization of α-olefins [1–21]. Depending on the symmetry of the metallocene complex, α-olefins, such as propylene, can be polymerized in a stereospecific manner [22,23]. It has been shown that C$_s$ symmetry of the metallocene dichloride complex is a necessary but not sufficient condition for the production of syndiotactic polypropylene. Examples are the complexes [(C$_{13}$H$_8$)CMe$_2$(C$_5$H$_4$)]MCl$_2$ (M = Zr or Hf) [2].

Recently it was demonstrated that phenyl instead of methyl substituents in the methylene bridge of an ansa metallocene complex with a cyclopentadienyl and a fluorenyl ligand have a strong influence on the activity and stereoselectivity in the propylene polymerization reaction [21].

In this paper, we describe the influence of a heteroatom in the bridge of cyclopentadienyl fluorenyl complexes on the polymerization behavior. Further we investigated the effects of substituents in the bridge and in the fluorenyl ligand.
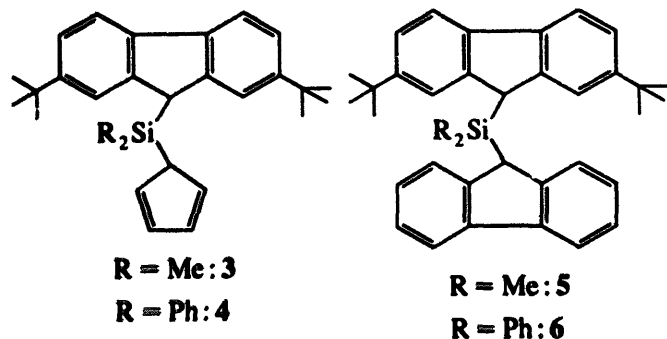
2. Results and discussion

2.1. Synthesis of the ligand precursors

The reaction schemes show the synthesis of the organosilicon (1–6) and organogermanium (7) compounds used for the preparation of the corresponding metallocene complexes:

R = Me : 1
R = Ph : 2
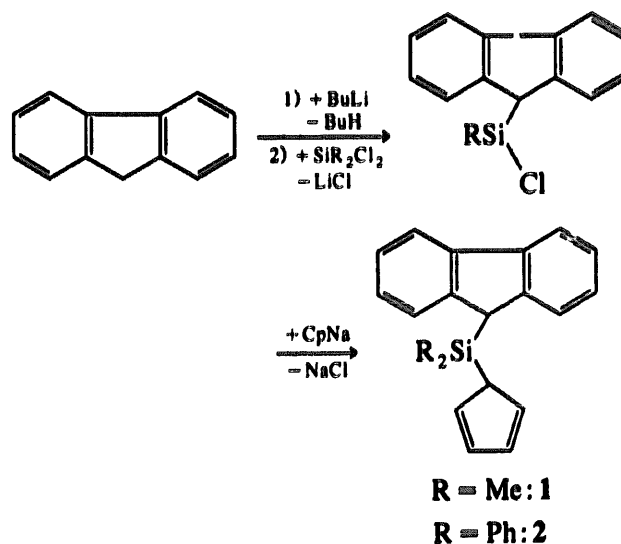
In this manner also 3–6 have been prepared:

R = Me : 3
R = Ph : 4

R = Me : 5
R = Ph : 6

The reaction of fluorenyl lithium with dimethyldichlorosilane or diphenyldichlorosilane results in the formation of the monosubstituted compounds. In order to reduce the tenfold excess of R_2SiCl_2 in the reaction described in the patent literature [24], pentane instead of ether was used as a solvent. An interesting feature of the diphenyl compound is the low stability observed in the presence of tetrahydrofuran (THF). The combination of $(C_{13}H_9)Ph_2SiCl$ and THF results in the formation of fluorene, difluorenyldiphenylsilane and an insoluble residue, which was not identified.

Reaction of the compounds $(C_{13}H_9)R_2SiCl$ with cyclopentadienyl sodium produces the products 1 and 2. While in the case of R = Me, THF could be used as solvent. The synthesis with R = Ph failed in THF because of the aforementioned instability of $(C_{13}H_9)Ph_2$ SiCl. In this case, the reaction was carried out in a mixture of ether and hexamethyl phosphoric acid triamide (hmpt) or tetramethyl ethylene diamine (tmeda). Note that the schemes show only one of the three possible isomers in respect of the cyclopentadienyl.

An analogous reaction can also be used for the preparation of $(2,7\text{-}^tBu_2C_{13}H_7)SiR_2(C_5H_5)$ (3, 4) if $2,7\text{-}^tBu_2C_{13}H_8$ is used instead of fluorene. Because of the lower reactivity of the substituted fluorene, the first

step of the reaction was carried out in ether. The second step, the reaction with cyclopentadienyl sodium, was again carried out in a mixture of ether and hmpt. Compounds containing a substituted and an unsubstituted fluorenyl group (5, 6) could be prepared in the same way if fluorenyl lithium instead of cyclopentadienyl sodium is used in the second step.

Compound 7 was prepared starting with $GeCl_4$ by substitution of the chlorine atoms with fluorenyl, cyclopentadienyl and phenyl groups. Other lithium and Grignard reagents can be used in the place of phenyl lithium to introduce other substituents in the bridge.

2.2. Characterization of 1–6

Compounds 1–6 were characterized by their ^1H, ^{13}C NMR and their mass spectra. The data are collected in Tables 1–4. Note that, for 1 and 4, two isomers (A and B) could be detected while, for 2 and 3 only one isomer (A) has been observed:

A

B
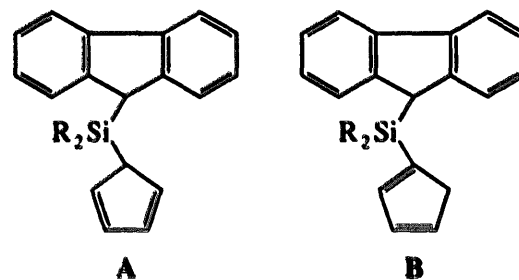
The NMR spectra of 7 gave only broad signals. The compound was characterized by mass spectroscopy.

2.3. Synthesis of the metal complexes

The reaction of 1–7 with two equivalents of butyllithium results in the formation of the corresponding dianions. The dianions, when reacted with zirconium
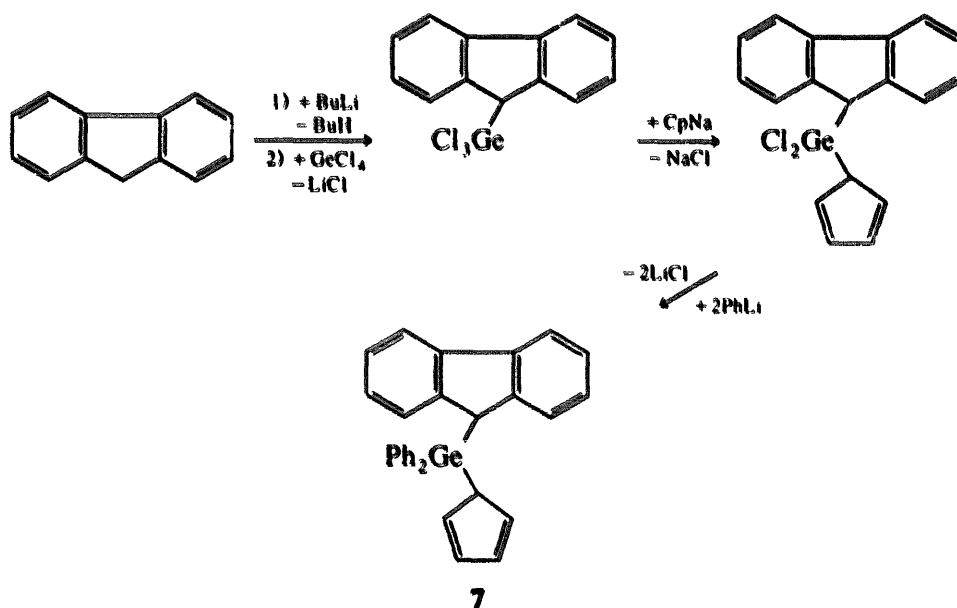

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Table 1
^{1}H NMR data, MS and melting points of 1–4

Compound	^{1}H NMR [a]					MS (M$^+$)	Melting point (°C)
	δ(CH(Ar)) [b] (ppm)	δ(C(9)H) (ppm)	δ(CH(Cp)) (ppm)	δ(Si–CH$_3$) (ppm)	δ(C(CH$_3$)$_3$) (ppm)		
1A, 1B [c]	7.95 (d,2) (J(H,H) = 7.2 Hz), 7.85–7.88 (m), 7.58–7.63 (m), 7.30–7.46 (m)	4.33 (s), 4.02 (s)	6.71, 6.62 6.23, 3.28, 2.81	−0.14 (s) −0.15 (s)	—	288	—
2	7.66 (d,2) (J(H,H) = 7.5 Hz), 7.23–7.33 (m,6), 7.12–7.19 (m,10)	4.55 (s,1)	6.48, 6.39 3.99	—	—	412	151
3	7.78 (d,2) (J(H,H) = 8.0 Hz), 7.59 (m,2) 7.41–7.46 (m,2)	3.93 (s,1), 3.14	6.55, 6.12	−0.13 (s,6)	1.42 (s,18)	400	104
4A, 4B [c]	7.55–7.69 (m), 7.19–7.41 (m), 6.95 (s)	4.50 (s), 4.16 (s)	6.71, 6.56 6.50, 6.42, 6.33, 3.78, 2.39	—	1.20 (s), 1.14 (s)	524	143

[a] In CDCl$_3$, at 25°C, δ relative to CHCl$_3$ (δ = 7.24 ppm).
[b] The values for the phenyl and fluorenyl groups of 2 and 4 are summarized.
[c] For 1 and 4, two isomers (referring to Cp) are detected.

tetrachloride, give the corresponding metal complexes 1a–7a, for instance

1) + 2BuLi, − 2BuH
2) + ZrCl$_4$, − 2LiCl
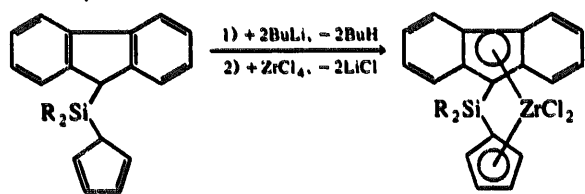
R = Me : 1a
R = Ph : 2a

The synthesis of the lithium compound and the corresponding metal complex were carried out in a single reaction vessel (one-pot synthesis) with ether as a solvent. As solids, all metallocene complexes except 7a are stable against air and moisture for several days. The germanium containing complex 7a decomposes almost immediately when exposed to air. In contrast, the complexes are very unstable in solution. Even at low temperatures, traces of moisture cause decomposition within a few minutes.

2.4. Characterization of 1a–4a

The ^{1}H NMR spectra of 1a–4a show similar patterns for the four protons of the cyclopentadienyl ring. The two pseudotriplets lay in the range 5.6–6.5 ppm with

Table 2
^{13}C and ^{29}Si NMR data of 1–4

Compound	^{13}C NMR [a]						^{29}Si NMR, δ(^{29}Si) [d] (ppm)
	δ(C$_q$(Ar)) [b] (ppm)	δ(CH(Ar)) [b] (ppm)	δ(C$_g$) (ppm)	δ(C(Cp)) (ppm)	δ(Si–CH$_3$) (ppm)	δ(C(CH$_3$)$_3$) (ppm)	
1A, 1B [c]	145.1, 145.0, 140.8, 140.5	126.2, 125.8, 125.6, 125.2, 124.2, 124.1, 120.1, 119.8	45.7	143.7, 138.5, 132.8, 130.9, 48.8	−3.8 −5.8	—	−5.7
2	144.6, 144.0, 141.1, 140.9, 132.7	129.6, 127.7, 127.0, 126.0, 125.7, 125.2, 124.8, 119.8	41.2	132.7, 130.8, 46.6	—	—	−5.8
3	149.0, 145.0, 138.0	122.7, 121.2, 119.3	43.0	132.9, 130.6, 48.7	−5.4	34.8 (C$_q$) 31.7 (CH$_3$)	−6.0
4A, 4B [c]	148.7, 148.5, 143.8, 138.5, 138.4, 132.4, 131.9	136.1, 129.5, 129.5, 127.8, 127.7, 122.8, 122.7, 122.2, 122.0, 119.0, 118.9	41.7 41.0	144.5, 139.8, 135.3, 135.1, 133.1, 127.1, 46.1, 45.9	—	34.7 (C$_q$) 34.6 (C$_q$) 31.4 (C$_q$)	−7.4 −15.9

[a] In CDCl$_3$, at 25°C, δ relative to CDCl$_3$ (δ = 77 ppm).
[b] The values for the phenyl and fluorenyl groups of 2 and 4 are summarized.
[c] For 1 and 4, two isomers are detected.
[d] In CDCl$_3$, at 25°C, δ relative to tetramethylsilane (external) (TMS$_{ext}$) (δ = 0 ppm).

[1]H, ^{1}H coupling constants of 2.2–2.4 Hz. The protons of the fluorenyl ligand in **1a** show four signals (d, t, d, t), while for **3a** only three signals (d, d, s) are detected. The spectra of **2a** and **4a** are more complicated because of the additional phenyl substituents which show signals in the same region as the fluorenyl ligands.

The summarized ^{1}H and ^{13}C NMR data are given in Tables 5 and 6.

Table 3
^{1}H NMR data, MS and melting points of 5 and 6

Compound	^{1}H NMR [a]				MS (M[+])	Melting point (°C)
	δ (CH(Ar)) (ppm)	δ(C(9)H) (ppm)	δ(Si–CH₃) (ppm)	δ(C(CH₃)₃) (ppm)		
5	7.87 (d,2), (J(H,H) = 7.5 Hz), 7.76 (d,2), (J(H,H) = 8.1 Hz), 7.54 (t,2), (J(H,H) = 0.9 Hz), 7.34–7.41 (m,4), 7.24–7.30 (m,4)	4.13 (s,1) 4.05 (s,1)	−0.44 (s,6)	1.35 (s,18)	500	184
6 [b]	7.84–7.87 (m,2), 7.77 (s,2), 7.62–7.66 (m,2), 7.44 (d,2), (J(H,H) = 8.1 Hz), 7.29–7.34 (m,6), 7.16–7.22 (m,2), 6.94 (t,4), (J(H,H) = 7.7 Hz), 6.77 (dd,4), (J(H,H) = 7.8; 1.0 Hz)	5.07 (s,1) 4.97 (s,1)		1.28 (s,18)	624	195

[a] In CDCl₃, at 25°C, δ ppm relative CHCl₃ (δ = 7.24 ppm).
[b] The values for the phenyl and fluorenyl groups are summarized.

Table 4
^{13}C and ^{29}Si NMR data of 5 and 6.

Compound	^{13}C NMR [b]					^{29}Si NMR [b], δ([29]Si) (ppm)
	δ(C₄(Ar)) (ppm)	δ(CH(Ar)) (ppm)	δ(C₉) (ppm)	δ(Si–CH₃) (ppm)	δ(C(CH₃)₃) (ppm)	
5	149.0, 145.2, 145.0, 140.7, 138.2	126.2, 125.5, 124.3, 122.7, 121.3, 120.1, 119.3	40.1, 40.3	−5.9	31.7 (C₉), 34.8 (CH₃)	7.5
6 [c]	148.7, 143.9, 143.4, 141.3, 138.6	135.1, 129.0, 126.3, 126.1, 125.6, 124.6, 122.4, 121.8, 119.8, 118.9	38.1, 38.0		31.5 (C₉) 34.7 (CH₃)	−2.8

[a] In CDCl₃, at 25°C, δ relative to CDCl₃ (δ = 77 ppm).
[b] In CDCl₃, at 25°C, δ relative to TMS_ext (δ = 0 ppm).
[c] The values for the phenyl and fluorenyl groups are summarized.

Table 5
^{1}H NMR data of 1a–4a

Complex	^{1}H NMR [a]			
	δ(CH(Ar) [b]) (ppm)	δ(CH(Cp)) (ppm)	δ(Si–CH₃) (ppm)	δ(C(CH₃)₃) (ppm)
1a	8.10 (d,2), (J(H,H) = 8.0 Hz), 7.63 (t,2), (J(H,H) = 7.7 Hz), 7.56 (d,2), (J(H,H) = 8.8 Hz), 7.29 (t,2), (J(H,H) = 7.7 Hz)	6.56 (t,2), (J(H,H) = 2.2 Hz), 5.74 (t,2), (J(H,H) = 2.2 Hz)	1.13 (s,6)	—
2a	8.10–8.14 (m,6), 7.53–7.65 (m,8), 7.00–7.06 (m,2), 6.83 (d,2), (J(H,H) = 8.6 Hz)	6.72 (t,2), (J(H,H) = 2.4 Hz), 5.96 (t,2), (J(H,H) = 2.4 Hz)	—	—
3a	7.95 (d,2), (J(H,H) = 8.8 Hz), 7.69 (d,2), (J(H,H) = 8.8 Hz), 7.36 (s,2)	6.54 (t,2), (J(H,H) = 2.1 Hz), 5.62 (t,2), (J(H,H) = 2.1 Hz)	1.12 (s,6)	1.28 (s,18)
4a	8.14–8.17 (m,4), 7.95 (d,2), (J(H,H) = 8.8 Hz), 7.54–7.65 (m,8), 6.60 (s,2)	6.67 (t,2), (J(H,H) = 2.4 Hz), 5.80 (t,2), (J(H,H) = 2.4 Hz)	—	0.92 (s,18)

[a] In CD₂Cl₂, at −40°C, δ relative to CDHCl₂ (δ = 5.32 ppm).
[b] For 2a and 4a the values for the fluorenyl and phenyl groups are summarized.

2.5. Crystal structures of 1a and 2a

The molecular structures of **1a** and **2a** are shown in Figs. 1 and 2. Selected bond lengths and internal angles are given in Tables 7 and 8.

The increasing distances from the metal to C(9)–C(13) are consistent with those reported by Razavi and Ferarra [25] for $[(C_{13}H_8)CMe_2(C_5H_4)]ZrCl_2$. There are literature reports of η^3 and η^5-bonded fluorenyl ligands [2,25] in these types of complex. We postulate an η^5-bonded fluorenyl ligand. The assumption of an η^3-bonded species would result in a 14e⁻ complex, which is not consistent with the high stability of the complex against oxygen and moisture. It is suggested that the variations in the distances are due to a repulsive interaction between the chlorine ligands and the six-membered rings of the fluorenyl.

While the deviations of the Zr–C distances within the fluorenyl ligand are in the range of up to 30 pm, they are much smaller for the Cp ligand. The resulting higher bond strength may explain the high stability of
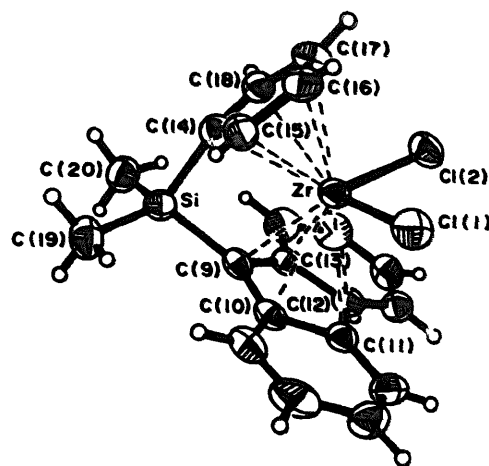

Fig. 1. X-ray structure of 1a.

bis(cyclopentadienyl) complexes and the low stability of fluorenyl complexes against coordinating reagents.

The angles cent(Cp)–Zr–cent(Flu) have values of 127.9° for **1a** and 129.3° for **2a**. The increase of about

Table 6
¹³C NMR data of 1a–4a

Complex	¹³C NMR [a]			
	$\delta(C_q(Ar)$ [b]) (ppm)	$\delta(CH(Ar))$ [b] (ppm)	$\delta(Si-CH_3)$ (ppm)	$\delta(C(CH_3)_3)$ (ppm)
1a	127.6, 126.3, 104.3	128.7, 126.6, 125.0, 124.9, 124.1, 110.9	−1.2	
2a	132.7, 129.5, 128.0, 99.8	134.5, 131.1, 129.0, 128.8, 127.1, 125.2, 125.0, 124.8, 112.3		
3a	151.2, 127.4, 126.0, 102.6	126.0, 124.5, 124.1, 118.7, 109.6	−1.2	34.9 (C_q), 30.3 (CH_3)
4a	150.8, 131.8, 127.2, 126.3, 98.0	134.2, 130.9, 128.8, 126.2, 124.7, 123.9, 119.8, 110.8		34.5 (C_q), 29.7 (CH_3)

[a] In CD_2Cl_2, at −40°C, δ relative to CD_2Cl_2 (δ = 53.8 ppm).
[b] The values for the cyclopentadienyl, fluorenyl and phenyl groups are summarized.

Table 7
Selected bond lengths (Å) and bond angles (°) of 1a

Bond lengths					
Zr–C(9)	242.6	Zr–C(10)	255.1	Zr–C(11)	273.2
Zr–C(12)	274.5	Zr–C(13)	255.4	Zr–C(14)	247.8
Zr–C(15)	247.1	Zr–C(16)	252.7	Zr–C(17)	252.6
Zr–C(18)	245.7	Zr–Cl(1)	242.5	Zr–Cl(2)	242.3
Si–C(9)	187.4	Si–C(14)	187.4	Si–C(19)	185.4
Si–C(20)	179.9	C(9)–C(10)	145.1	C(9)–C(13)	145.3
C(10)–C(11)	144.5	C(11)–C(12)	144.2	C(12)–C(13)	144.1
C(14)–C(15)	142.1	C(14)–C(18)	142.5	C(15)–C(16)	141.3
C(16)–C(17)	138.6	C(17)–C(18)	141.3		

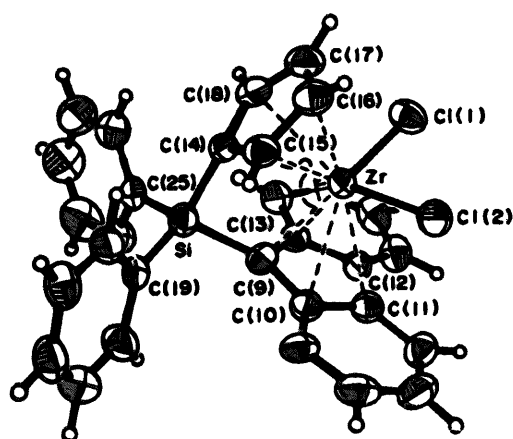| Bond angles					
Cl(1)–Zr–Cl(2)	96.6	C(9)–Si–C(14)	93.4	C(19)–Si–C(20)	111.4
Cent(Cp)–Zr–Cent(Flu)	127.9				

Fig. 2. X-ray structure of 2a.

10° in comparison with the complex with an isopropylidene bridge (cent(Cp)–Zr–cent(Flu), 118.6°) [25] corresponds to the longer Si–C bond length.

2.6. Polymerization behavior of 1a–7a

Table 9 shows the results of the propylene polymerization when 1a–7a are activated with methylalumoxane (MAO).

Compounds 1a–7a show a strong decrease in stereoregularity for propylene polymerization compared with the [(C₁₃H₈)CMe₂(C₅H₄)]ZrCl₂ complex [2]. Com-

plexes 1a and 2a show only a small difference (2%) in their syndiotactic block lengths; differences in their activity and molecular weight are more distinct. Complex 1a produces a polymer having a higher molecular weight than the polymer obtained with 2a, while 2a shows a higher activity. The syndiotacticity of the polymer decreases to values of about 65% when two tert-butyl groups are introduced into the fluorenyl ligand (3a and 4a) and reaches a minimum of about 32% for 5a.

There is no obvious explanation for this behavior. Apparently a whole series of parameters determine the kinetics of the polymerization process.

2.7. The influence of the bridge in ansa metallocene complexes on the polymerization reaction of propylene (a mechanistic consideration)

The function of MAO as cocatalyst in the polymerization of α-olefins with organometallic compounds has been investigated by several groups [26,27]. Other ionizing agents are also able to activate metallocene dimethyl complexes [28–31] to give catalysts for the polymerization of olefins.

The comparison of the syndiotacticities for the polypropylene produced with 1a, 2a and 7a and those reported by other groups for the analogous carbon-bridged complexes [2,15,21,25] shows that the tacticities decrease in the order C > Si > Ge. Additional bulky

Table 8
Selected bond lengths (Å) and bond angles (°) of 2a

Bond lengths

Zr–C(9)	241.0	Zr–C(10)	255.9	Zr–C(11)	274.4
Zr–C(12)	274.5	Zr–C(13)	254.1	Zr–C(14)	248.2
Zr–C(15)	245.5	Zr–C(16)	253.9	Zr–C(17)	254.4
Zr–C(18)	246.6	Zr–Cl(1)	240.8	Zr–Cl(2)	242.5
Si–C(9)	187.2	Si–C(14)	184.0	Si–C(19)	185.9
Si–C(25)	186.3	C(9)–C(10)	144.5	C(9)–C(13)	144.5
C(10)–C(11)	143.3	C(11)–C(12)	143.5	C(12)–C(13)	142.9
C(14)–C(15)	144.8	C(14)–C(18)	143.0	C(15)–C(16)	139.9
C(16)–C(17)	138.0	C(17)–C(18)	141.1		

Bond angles

Cl(1)–Zr–Cl(2)	96.9	C(9)–Si–C(14)	95.5	C(19)–Si–C(25)	111.9
Cent(Cp)–Hz–Cent(Flu)	129.3				

Table 9
Polymerization results with 1a–7a

Compound	Productivity (×10⁶ g polypropylene (mol Zr)⁻¹ h⁻¹)	M_w (×10³)	M_w/M_n	rr (%)	Syndiotactic block
1a	25.4	95.2	2.34	76.18	9.01
2a	117.4	46.0	1.92	74.45	8.86
3a	166.4	96.1	2.00	64.95	5.56
4a	96.4	113.6	1.97	66.50	5.87
5a	30.2	132.0	2.20	32.46	2.33
7a [a]	8.28	287.6	2.32	65.46	6.05

[a] No hydrogen added to the reactor.

tert-butyl substituents on the fluorenyl ligand (3a and 4a) cause a further negative effect on the syndiotacticity of the polypropylene.

The influence of structural features of ansa metallocenes on their polymerization behavior has been investigated [32–34] widely. Interactions between β-hydrides of the growing polymer chain and the metal are reported to have a strong influence on the stereospecifity of the catalyst by proper positioning of the polymer chain in the ligand framework [35,36]. Cavallo et al. [37] employed theoretical calculations to explain the influence of structural features of metallocenes on the polymerization behavior. They showed that the steric interaction between the ligand framework and the growing polymer chain is responsible for the extent of tacticity in polypropylene by influencing the coordination of the incoming propylene molecules.

The latter explanation corresponds to the polymerization results mentioned in this paper. The decrease in syndiotacticity of the polymer in the order C > Si > Ge results from the increase of the angles cent(Cp)–Zr–cent(Flu) causing a widening of the ligand framework. This means a lower steric interaction between ligand and growing polymer chain and subsequently a lower influence of the chain on monomer coordination, which could result in a reduction in stereospecificity.

Structural features of the catalyst do not correlate with the differences in productivity and molecular weight. Although there are only small deviations in the molecular structures between 1a and 2a the differences in productivity and molecular weight are larger. While 1a shows higher molecular weights for the produced polypropylene, 2a shows 4.6-fold higher productivity. This could be because electronic effects in the catalyst molecule cause a lower metal–carbon bond strength. This could result in an increase in the propagation rate (increase in activity) and also an increase in the rate of the β-hydride chain termination reaction (decrease in molecular weight). Vice versa, the higher molecular weight of the polymer obtained from 1a could result from a stronger metal–carbon bond in the active species, causing a slower insertion of the monomer (lower activity) and a reduced termination rate of the growing chain at the metal atom (higher molecular weight). If the termination rate is reduced more than the propagation rate, one would observe decreased activity and increased molecular weight. This was observed in the polymerization experiments.

3. Experimental devices

All operations were carried out with Schlenk techniques under argon. Pentane, hexane, ether and THF were dried and distilled over Na–K alloy. Methylene chloride was dried over P_2O_5 and CaH_2.

Fluorene (purity, 90–95%; Fluka) was dissolved in pentane and the solution was filtered through silica gel (Merck silica gel 60). All other reagents were used without further purification.

NMR spectra were performed on a Bruker AC300 using anhydrous $CDCl_3$ and CD_2Cl_2 as solvents.

Gas chromatography (GC)–mass spectroscopy analyses were obtained from a Varian 3700 GC connected with a Varian MAT 312 MS.

2,7-di-tert-butylfluorene was prepared following literature procedures [38,39].

3.1. Preparation of $(C_{13}H_9)SiR_2Cl$ and $(2,7-{}^tBu_2-C_{13}H_7)SiR_2Cl$ (R = Me or Ph)

3.1.1. $(C_{13}H_9)SiMe_2Cl$

20 g (0.12 mol) of fluorene were dissolved in 150 ml of ether and 76 ml butyllithium (1.6 m in hexane) were added dropwise at room temperature. The resulting orange solution was stirred for an additional 2 hs. and then the solvent was removed under reduced pressure. The solid fluorenyl lithium was added in portions to a solution of 23.3 g (0.18 mol) of Me_2SiCl_2 in 700 ml of pentane at room temperature. The reaction mixture was stirred for 1 h and then filtered over dry Na_2SO_4 to remove solid LiCl. The residue was washed with an additional 150 ml of pentane, and the combined solutions were reduced to a volume of about 200 ml. The bright-yellow solution was crystallized at −30°C, yielding a white solid characterized with ^1H, ^{13}C NMR and GC–MS as $C_{13}H_9SiMe_2Cl$ (yield, 90%).

3.1.2. $(C_{13}H_9)SiPh_2Cl$

The procedure is analogous to that given in Section 3.1.1. However, for the purification process ether has been used instead of pentane (yield, 90%).

3.1.3. $(2,7-{}^tBu_2C_{13}H_7)SiMe_2Cl$

5 g (0.018 mol) of $2,7-{}^tBu_2C_{13}H_8$ were dissolved in 100 ml of ether and 11.2 ml of butyllithium were added dropwise. The solution was stirred until gas evolution was finished and then the solvent was removed at reduced pressure. The solid lithium compound was added in portions to a solution of 2.8 g of Me_2SiCl_2 in 200 ml of ether and the reaction mixture was stirred for 1 h at room temperature. The mixture was filtered over Na_2SO_4 and the residue washed with 100 ml of ether. The solution was reduced to a volume of 100 ml and crystallized at −30°C to yield colorless crystals of $(2,7-{}^tBu_2C_{13}H_7)SiMe_2Cl$ which were characterized by ^1H, ^{13}C NMR and GC–MS (yield, 85%).

3.1.4. $(2,7-{}^tBu_2C_{13}H_7)SiPh_2Cl$

The procedure is analogous to that given in Section 3.1.3. The reaction yields an orange oil characterized by ^1H, ^{13}C NMR and GC–MS (yield, 85%).

3.2. Preparation of the ligand precursors 1–7

3.2.1. $(C_{13}H_9)SiMe_2(C_5H_5)$ (1)

5 g of $(C_{13}H_9)SiMe_2Cl$ (0.02 mol) were dissolved in 100 ml of ether containing 10 ml of hmpt. Then 3.4 g (0.04 mol) of cyclopentadienyl sodium were added to the solution. The reaction mixture was stirred for 4 h and then it was hydrolyzed with a saturated solution of NH_4Cl in water. The organic layer was separated, washed several times with water and then dried over Na_2SO_4. Evaporation of the solvent yields an orange oil which could not be crystallized and which was used without further purification. The product was identified by ^1H, ^{13}C NMR and GC–MS (yield, 87%).

3.2.2. $(C_{13}H_9)SiPh_2(C_5H_5)$ (2)

The procedure is analogous to that given in Section 3.2.1. Crystallization of the crude product in pentane at $-30°C$ gives a white solid (yield, 82%).

3.2.3. $(2,7-{}^tBu_2C_{13}H_7)SiMe_2(C_5H_5)$ (3) and $(2,7-{}^tBu_2C_{13}H_7)SiPh_2(C_5H_5)$ (4)

The procedure is analogous to that given in Section 3.2.1. Crystallization of the products in pentane at $-30°C$ gives white solids (yield, 88% for 3 and 82% for 4).

3.2.4. $(C_{13}H_9)SiMe_2(2,7-{}^tBu_2C_{13}H_7)$ (5)

3.4 g (0.02 mol) of fluorene were dissolved in 100 ml of ether. Then 13 ml of butyllithium were added to the solution. After the gas evolution was finished, the solvent was evaporated and the solid fluorenyl lithium was added at room temperature to a solution of $(2,7-{}^tBu_2C_{13}H_7)SiMe_2Cl$ in 100 ml of ether and 10 ml of tmeda. The reaction mixture was stirred for 4 h and then it was hydrolyzed with a saturated solution of NH_4Cl in water. The organic layer was washed several times with water and then dried over Na_2SO_4. After evaporation of the solvent the residue was dissolved in pentane and crystallized at $-30°C$. The obtained white powder was analyzed by ^1H, ^{13}C NMR and GC–MS (yield, 85%).

3.2.5. $(C_{13}H_9)SiPh_2(2,7-{}^tBu_2C_{13}H_7)$ (6)

The procedure is analogous to that given in Section 3.2.4 (yield, 81%).

3.2.6. $(C_{13}H_9)GePh_2(C_5H_5)$ (7)

To a solution of 10 g (0.06 mol) of fluorene in 150 ml of ether 38 ml of butyllithium were added dropwise. After the gas evolution the solvent was evaporated and the solid fluorenyl lithium was added in portions to a solution of 13 g (0.06 mol) of $GeCl_4$ in 400 ml of pentane at room temperature. After a reaction period of 2 h the solvent was evaporated and the residue was extracted with CH_2Cl_2. The mixture was filtered over

Na_2SO_4 to remove precipitated LiCl and then the solution was reduced to a volume of 30 ml and crystallized at $-30°C$ to yield colorless needles. The compound was analyzed by ^1H, ^{13}C NMR and GC–MS as $(C_{13}H_9)GeCl_3$ (yield, 85%).

5 g (0.015 mol) of $(C_{13}H_9)GeCl_3$ were suspended in 100 ml of ether, and then 1.4 g (0.016 mol) cyclopentadienyl sodium were added to the solution. The mixture was stirred for 12 h at room temperature and then the solvent was evaporated. The residue was extracted with CH_2Cl_2 and the suspension was filtered over Na_2SO_4. After evaporation of the solvent the residue was washed with pentane to yield a white powder analyzed by GC–MS as $(C_{13}H_9)GeCl_2(C_5H_5)$, which was used without further purification (yield, 90%).

To a suspension of 2 g (0.005 mol) of crude $(C_{13}H_9)GeCl_2(C_5H_5)$ in 150 ml of ether 1.3 g (0.016 mol) of solid phenyl lithium were added. After a reaction period of 12 h the solvent was evaporated and the residue was extracted with CH_2Cl_2. After filtration over Na_2SO_4, the solvent was evaporated, and the residue was washed with pentane to yield a bright-yellow powder characterized by its mass spectra (yield, 85%). The product was used without further purification.

3.3. Preparation of 1a–7a

For the preparation of the complexes the following general procedure has been used.

4 mmol of the ligand precursor (1–7) was dissolved in 250 ml of ether and reacted with 8 mmol of butyllithium. After the gas evolution 1 g (4 mmol) of $ZrCl_4$ was added and the reaction mixture was stirred for 1 h. After the evaporation of the solvent the residue was washed with pentane and extracted with CH_2Cl_2. The suspension was filtered over Na_2SO_4 to remove precipitated LiCl. The solution was reduced and recrystallized at $30°C$ to yield orange to red colored powders (yields, 85–90%). Compounds 1a and 2a were crystallized in CH_2Cl_2 with a layer of hexane at $-30°C$.

3.4. Propylene polymerization with 1a–7a

The polymerizations were performed in a 1 gal Autoclave Engineers reactor in liquid propylene at 70°C. Complexes were reacted with 10% MAO (Schering AG). The aluminium:zirconium ratio was 1000:1. The catalyst solution was stirred for 15 min at room temperature and charged into a 1 gal reactor. The hydrogen was added from a 300 cm³ cylinder (15 inf cm⁻² preassure drop), and 2.5 l of propylene were added to the reactor. After heating the reactor contents to 70°C, it was stirred for 1 h. The polymerization was terminated by venting surplus propylene. The polymer was recovered, dried, weighed and analysed.

Acknowledgments

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