Ansa bis(fluorenyl) complexes as homogeneous catalysts for propylene polymerization

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Preparation and characterization of new ansa-metallocene complexes containing two substituted fluorenyl ligands connected by an R_2E bridge (R = Me, Ph; E = Si, Sn) are reported. The complexes, activated with methylaluminoxane (MAO), polymerize propylene. The degree of stereospecifity of the propylene polymerization depends on the size of the hetero atom in the bridge and the position of the substituents.

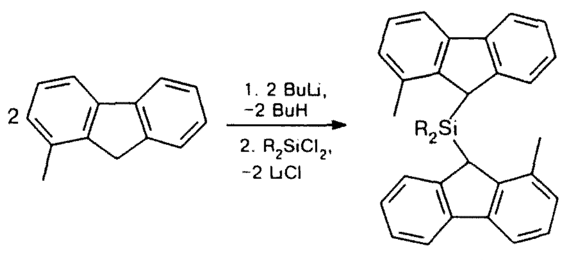
Key words: ansa bis(fluorenyl) complexes, silicon, tin; polymerization, polypropylene.

The isospecific polymerization of propylene using bridged metallocene complexes containing cyclopentadienyl and indenyl ligands has been widely investigated.[1—10] Examples of such compounds are $[(C_9H_6)_2C_2H_4]ZrCl_2$ and $[(C_9H_{10})_2C_2H_4]ZrCl_2$ synthesized by Brintzinger *et al.*[3,4] The investigations indicate that C_2 symmetry in the corresponding metallocene dichloride precursor is necessary for isospecific polymerization.[11,12] Recently it was shown that even an unbridged metallocene, namely $(1\text{-}CH_3C_{13}H_8)ZrCl_2$, is able to polymerize propylene to give isotactic polypropylene.[13,14] Although the influence of a bridge and the substituents in η^5-bonded ligands have been widely investigated,[5—7] no ansa metallocene complex containing two fluorenyl ligands has been reported for the isospecific polymerization of propylene. In this paper we describe the preparation and the characterization of new ansa bis(fluorenyl) complexes with Si and Sn heteroatoms in the bridge.[15]

Results and Discussion

Synthesis and characterization of the ligand precursors. The synthesis of the heteroatom bridged bis(fluorenyl) compounds proceeds according to the Scheme 1.

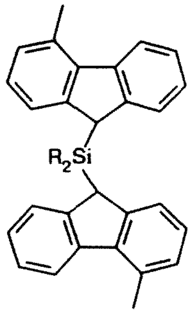
Scheme 1



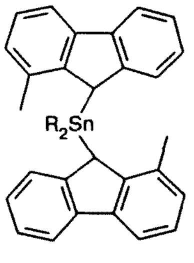
R = Me (**1**), Ph (**2**)

1, 2

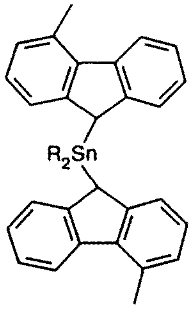
Compounds **3—8** could be prepared in the same way:



3, 4



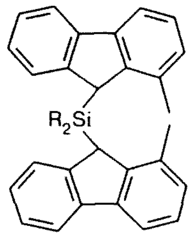
5, 6



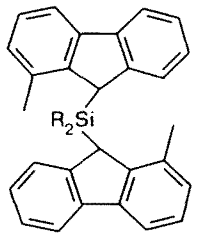
7, 8

R = Me (**3, 5, 7**), Ph (**4, 6, 8**)

All compounds were characterized by NMR spectroscopy and mass spectra (Tables 1—4). The NMR spectra exhibit the presence of *meso*- and *rac*-isomers for all compounds. Depending on the reaction conditions, the ratios of isomers for the silicon compounds vary over a wide range (50—100% racemic). The corresponding tin compounds yield a 1 : 1 mixture of *meso*- and *rac*-isomers.



meso



rac

R = Me, Ph

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Table 1. Melting points of complexes **1**—**4**, ^{1}H NMR data, and MS

Compound	M.p./°C	δ ^{1}H ($J_{H,H}$)^a				MS, [M]$^+$
		C<u>H</u>(Ar)	C(9)H (s)	Si—CH$_3$ (s)	CH$_3$ (s)	
1a,b	155	7.85—7.87 (m); 7.83 (d, J = 7.6 Hz); 7.66—7.70 (m); 7.35—7.40 (m); 7.16—7.33 (m); 7.13 (d, J = 7.4 Hz); 7.03 (d, J = 6.8 Hz)	4.39, 4.06	−0.24, −0.78, −0.89	2.32, 2.13	540
2a,b ^{b}	161	7.90 (d, J = 5.5 Hz); 7.64 (d, J = 5.3 Hz); 7.25—7.34 (m)	4.96	—	2.22	540
3a,b	151	8.02 (d, J = 7.6 Hz); 7.50—7.52 (m); 7.35—7.38 (m); 7.23—7.29 (m); 7.12—7.21 (m)	4.25	−0.41, −0.42, −0.43	2.78	416
4a,b ^{b}	159	8.10 (d, J = 8.6 Hz); 7.76—7.85 (m); 7.22—7.58 (m); 7.00 (т, J = 7.5 Hz); 6.76—6.79 (m)	5.18, 4.66	—	2.87, 2.64	416

[a] In CDCl$_3$, at 25 °C, δ in relation to CHCl$_3$ (7.24 ppm).

[b] For **2** and **4** the values for the fluorenyl and phenyl groups are summarized.

Table 2. ^{13}C and ^{29}Si NMR data for complexes **1**—**4**

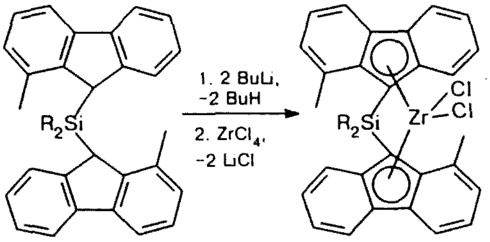
Compound	δ ^{13}C ^{a}					δ ^{29}Si ^{b}
	<u>C</u>$_q$(Ar)	<u>C</u>H(Ar)	C(9)	Si—CH$_3$	CH$_3$	
1a,b	145.9, 145.9, 145.0, 144.6, 141.0, 140.7, 140.5, 140.5, 133.0, 132.8	127.8, 127.8, 125.9, 125.8, 125.7, 125.6, 125.6, 125.4, 124.3, 123.9, 120.3, 120.0, 117.6, 117.5	40.6, 40.2	−3.9, −3.2, −1.4	20.3, 19.7	−1.8, −9.4
2a,b ^{c}	143.2, 142.8, 141.4, 140.6, 134.4, 133.9, 133.5	134.6, 134.4, 130.2, 129.7, 127.9, 127.7, 127.6, 125.9, 125.7, 125.7, 124.7, 120.0, 117.4	41.9	—	19.7	−10.0
3a,b	145.4, 145.4, 141.8, 138.8, 133.2	127.9, 125.8, 125.4, 124.1, 123.3, 121.7	40.4	−6.4	21.4	7.6
4a,b ^{c}	144.2, 144.1, 143.7, 143.6, 142.2, 142.1, 139.4, 139.2, 133.9, 133.9, 133.1	135.1, 134.6, 130.2, 128.9, 128.8, 128.1, 127.8, 127.7, 126.2, 125.8, 125.6, 125.4, 125.3, 124.7, 124.5, 123.2, 123.1, 122.4, 122.2	41.5, 38.3	—	21.3, 21.1	10.4, 9.4

[a] In CDCl$_3$, at 25 °C, δ in relation to CDCl$_3$ (77 ppm).

[b] In CDCl$_3$, at 25 °C, δ in relation to SiMe$_4$ (ext.). For **2** and **4** the values for the fluorenyl and phenyl groups are summarized.

***Synthesis and characterization of the metallocene dichloride complexes* 9—16.** Compounds **1** and **2** give the corresponding metal complexes **9** and **10** when reacted with 2 equiv. of butyl lithium and then with 1 equiv. of ZrCl$_4$ (Scheme 2).

Scheme 2



1, 2 **9, 10**

R = Me (**1**, **9**), Ph (**2**, **10**)

Analogous reactions have been used for the preparations of complexes **11**—**16** from compounds **3**—**8** (see below, only the *rac*-isomers are shown).

The stabilities of the complexes against oxygen and moisture are much higher for the silicon than for the tin bridged complexes. While complexes **9**—**12** are stable

Table 3. Melting points of complexes **5—8**, ^{1}H NMR data, and MS

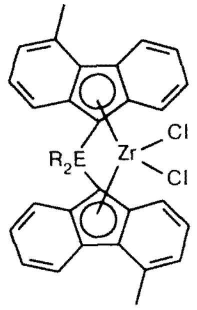
Compound	M.p./°C	δ ^{1}H ($J_{H,H}$)[a]				MS, $[M]^+$
		CH(Ar)	C(9)H (s)	Sn—CH_3 (s)	CH_3 (s)	
5a,b	156 (decomp.)	7.88—7.91 (m); 7.73—7.79 (m); 7.25—7.35 (m); 7.02—7.23 (m)	4.19, 4.18	−0.42, −0.22, −0.68	2.18, 2.05	508
6a,b [b]	182	7.73—7.85 (m); 6.79—7.41 (m); 6.41—6.62 (m); 5.96—6.18 (m)	4.69, 4.52	—	1.97, 1.76	632
7a,b	150 (decomp.)	8.02 (d, J = 5.7 Hz); 7.23—7.33 (m); 7.14—7.18 (m); 7.00—7.08 (m)	4.21	−0.27, −0.26, −0.28	2.76	508
8a,b [b]	179	7.94 (d, J = 7.7 Hz); 7.20—7.28 (m); 7.06—7.17 (m); 6.65—6.67 (m)	4.83	—	2.70	632

[a] In $CDCl_3$, at 25 °C, δ in relation to $CHCl_3$ (7.24 ppm).
[b] For **6** and **8** the values for the fluorenyl and phenyl groups are summarized.

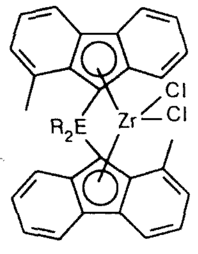
Table 4. ^{13}C and ^{119}Sn NMR data for complexes **5—8**

Compound	δ ^{13}C[a]					δ ^{119}Sn[b]
	C_q(Ar)	CH(Ar)	C(9)	Sn—CH_3	CH_3	
5a,b	146.1, 146.0, 145.0, 144.9, 139.0, 138.8, 120.3, 120.2, 117.8, 117.8	138.4, 131.4, 131.4, 127.2, 125.9, 125.9, 125.0, 124.5, 124.5, 123.3, 123.1	40.6, 40.5	−6.3, −6.8, −7.6	19.3, 19.0	40.4, 39.7
6a,b [c]	145.5, 145.2, 144.2, 144.0, 139.9, 139.6, 139.5, 139.1, 138.9, 138.8, 138.2, 132.6, 132.4	136.6, 136.4, 136.3, 136.2, 129.1, 128.6, 128.5, 128.3, 128.1, 127.7, 127.5, 127.4, 126.0, 125.9, 125.5, 125.4, 124.9, 124.9, 124.2, 123.8, 120.3, 120.2, 117.9	41.6, 41.4	—	19.6, 19.5	−99.7, −104.4
7a,b	146.3, 146.2, 139.7, 136.9	133.3, 126.7, 125.8, 125.4, 124.4, 123.3, 122.8, 120.5	40.1	−9.9	21.4	34.1, 34.0
8a,b [c]	145.1, 145.1, 140.4, 137.6, 133.3	136.9, 128.9, 127.9, 127.1, 125.8, 125.3, 124.8, 123.5, 123.3, 123.1	40.8	—	21.3	−98.7, −103.9

[a] In $CDCl_3$, at 25 °C, δ in relation to $CDCl_3$ (77 ppm).
[b] In $CDCl_3$, at 25 °C, δ in relation to Me_4Sn (ext.). For **6** and **8** the values for the fluorenyl and phenyl groups are summarized.



11, 12, 15, 16



13, 14

E = Si, R = Me (**11**), Ph (**12**)
E = Sn, R = Me (**13**, **15**), Ph (**14**, **16**)

against oxygen for several days, complexes **13—16** decompose within ~24 h.

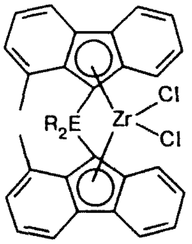
Low solubility in common solvents is a general feature of the bis(fluorenyl) complexes. This makes it difficult to obtain NMR spectra of metallocene dichloride complexes before decomposition occurs. To overcome this difficulty, the bis(fluorenyl) complexes were reacted with 2 equiv. of MeLi to obtain the corresponding metallocene dimethyl complexes **10′—16′** in 50—90% yield. The reaction of **2** with MeLi leads to the decomposition of the complex.

The NMR spectra of the dimethyl complexes **10′—16′** (Tables 5—9) show mixtures of the corresponding *meso*- and *rac*-isomers. The isomers could not be separated.

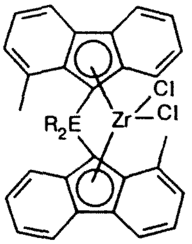
Table 5. ^{1}H NMR data for complexes **10′—12′**

Compound	δ ^{1}H ($J_{H,H}$)[a]			
	C$\underline{H}$(Ar) (m)	Si—CH$_3$ (s)	CH$_3$ (s)	Zr—CH$_3$ (s)
10′ [b]	7.94—8.00, 7.67—7.81, 6.87—7.36	—	2.28, 1.85	−1.98, −1.95
11′	7.92—7.97, 7.55—7.72, 7.40—7.50, 7.13—7.18, 6.77—6.89	1.49, 1.42, 1.35	2.55, 2.54, 2.52	−2.63, −2.66, −2.69
12′ [b]	8.26—8.32, 8.09—8.13, 7.48—7.52, 7.35—7.40, 7.19—7.28, 6.98—7.00, 6.56—6.82	—	2.69, 2.45	−2.56, −2.59, −2.62

[a] In CDCl$_3$, at 25 °C, δ in relation to CHCl$_3$ (7.24 ppm).
[b] For **10′** and **12′** the values for the fluorenyl and phenyl groups are summarized.



meso



rac

E = Si, Sn; R = Me, Ph

Polymerization results. After the activation of complexes **9**, **11**, **13**, and **16** with MAO, the resulting catalysts were used for the polymerization of propylene. Results of the polymerization in the presence of complexes **9**, **11**, **13**, and **16** are collected in Table 9.

The productivity and the stereospecificity of these catalysts are lower than those for the bis(indenyl) complexes and the syndiospecific cyclopentadienyl fluorenyl complexes.[5] This is believed to be due to the decomposition of the complex when it reacts with MAO, or due to the instability of the complexes under the polymerization conditions. The polymerization results collected in Table 9 were obtained with metallocenes that were stored in a glove box at room temperature for several weeks. Propylene polymerization conducted at 60 °C with freshly prepared **13** produced polypropylene with 78.5% *mm* triad content.

Mechanistic aspects. It has been shown by other workers[11,12] that metallocene dichloride complexes with C_2 symmetry can produce isotactic polymer. Metallocene C_2 symmetry, although necessary, is not sufficient to result in the isospecific polymerization of propylene. A more detailed description of the polymerization mechanism[16] allowed one to conclude that the agostic interactions between hydrides of the polymer chain and the metal as well as steric interactions between the monomer and the ligand framework are responsible for the right coordination of the monomer by placing it in a free sector of the ligand structure. On the other hand, calculations[17] show that steric interactions between the ligand framework, the growing polymer chain and the monomer rather than only between the ligand and the monomer determine the orientation of the next propylene molecule as it inserts into the chain.

The polymerization results are shadowed by the instability of these complexes after the reaction with MAO to form a polymerization active site. The fact that the stereoselectivity of 4-methylfluorenyl complexes is higher than that of 1-methylfluorenyl complexes can be explained by the increased interaction of the ligand framework with the monomer and the growing chain.

Table 6. ^{13}C NMR data for complexes **10′—12′**[a]

Compound	δ ^{13}C[a]				
	$\underline{C}_q$(Ar)	$\underline{C}$H(Ar)	Si—CH$_3$	CH$_3$	Zr—CH$_3$
10′ [b]	134.4, 128.5, 125.0, 124.3, 118.7, 118.6, 117.4	126.1, 126.0, 125.9, 125.8, 124.6, 124.5, 123.9, 123.8, 123.6, 123.0, 122.0, 121.5, 121.2, 121.0	—	19.4, 18.9	42.9, 41.3, 39.4
11′	137.0, 131.9, 131.4, 124.8, 123.1	126.8, 126.5, 125.8, 125.5, 125.4, 124.1, 124.1, 123.1, 122.8	3.8, 3.7	22.2, 22.0, 21.4	41.1, 40.4
12′ [b]	137.1, 136.9, 136.8, 131.6, 131.2, 125.7, 125.6, 123.8, 123.7	134.9, 134.9, 130.1, 128.6, 128.5, 126.8, 126.7, 126.6, 126.3, 126.3, 125.7, 125.7, 124.4, 124.3, 124.3, 124.1, 123.4, 123.3	—	22.2, 21.1	42.3, 41.6, 40.9

[a] In CDCl$_3$, at 25 °C, δ in relation to CDCl$_3$ (77 ppm).
[b] For **10′** and **12′** the values for the fluorenyl and phenyl groups are summarized.

Table 7. ^{1}H NMR data for complexes **13'**—**16'**

Compound	δ ^{1}H ($J_{H,H}$)^a			
	C**H**(Ar) (m)	Sn—CH$_3$ (s)	CH$_3$ (s)	Zr—CH$_3$ (s)
13'	7.97—8.00, 7.75—7.81, 7.54—7.65, 7.22—7.37, 7.07—7.12, 6.87—6.90	0.87	1.85	−1.94
14' ^{b}	7.93—8.02, 7.69—7.85, 6.89—7.38	—	1.87	−1.91
15'	7.89—8.05, 7.71—7.73, 7.52—7.56, 6.96—7.44	0.84	2.73, 2.71, 2.70	−2.12, −2.21, −2.28
16' ^{b}	8.06 (J = 8.5 Hz); 7.49—7.62, 7.33—7.40, 6.99—7.26	—	2.74, 2.68	−2.12, −2.21, −2.28

^{a} In CDCl$_3$, at 25 °C, δ in relation to CHCl$_3$ (7.24 ppm).
^{b} For **14'** and **16'** the values for the fluorenyl and phenyl groups are summarized.

Experimental

All operations were carried out with Schlenk techniques under argon. Pentane, hexane, ether, and THF were dried and distilled over Na/K alloy. For methylene chloride P_2O_5 and CaH_2 were used as drying agents. NMR spectra were obtained on a Bruker AC300 spectrometer using anhydrous CDCl$_3$ as the solvent. MAO (30 wt. % in toluene, 13 wt. %. Al total, $\bar{M}_w$ = 900) was obtained from Witco.

Preparation of the ligand precursors 1—8 (general procedure). $(1\text{-MeC}_{13}H_8)_2SiMe_2$ (1). 3 g (16.7 mmol) of 1-methylfluorene were dissolved in 100 mL of ether and reacted with 10.4 mL (1.6 M solution in hexane) of butyllithium. After the gas evolution was finished the solution was added dropwise to a solution of 1.1 g (8.5 mmol) of Me_2SiCl_2 in 150 mL of ether. The mixture was stirred for an additional hour and then it was hydrolyzed with a saturated solution of NH$_4$Cl in water. The organic layer was washed several times with water and then dried over Na$_2$SO$_4$. After evaporation of the solvent, the orange oil was dissolved in pentane and crystallized at −30 °C. The white powder obtained was analyzed by its ^{1}H, ^{13}C NMR and mass spectra

Table 8. ^{13}C NMR data for complexes **13'**—**16'**

Compound	δ ^{13}C ^{a}				
	C$_q$(Ar)	**C**H(Ar)	Sn—CH$_3$	CH$_3$	Zr—CH$_3$
13'	134.4, 128.5, 124.3, 118.7, 118.6	125.9, 125.8, 124.5, 123.9, 123.8, 121.5, 121.0	35.8, 34.1	22.3, 18.9	41.4
14' ^{b}	134.4, 133.4, 128.7, 128.5, 125.3, 124.3, 118.7, 118.5, 118.1	126.0, 126.0, 125.8, 125.8, 124.6, 124.5, 123.9, 123.8, 123.5, 123.0, 121.9, 121.5, 121.2, 120.9	—	19.3, 18.9	41.4
15'	137.0, 137.0, 133.2, 133.0, 127.0, 126.9, 126.7, 126.6, 120.0, 119.9, 118.9, 118.7	129.0, 126.7, 126.6, 126.4, 126.0, 124.9, 123.7, 123.4, 123.2, 123.1, 122.5, 122.4, 122.3, 120.6	37.1	22.2, 22.1	42.4, 41.3, 40.5
16' ^{b}	137.2, 137.0, 128.7, 128.4, 126.5, 120.0	137.9, 137.5, 137.0, 136.8, 129.1, 129.0, 128.6, 128.4, 128.2, 128.2, 126.7, 126.6, 126.4, 126.0, 123.7, 123.4, 123.2, 123.1, 122.5, 122.3, 120.9, 120.6	—	22.2, 22.1	42.4, 41.3, 40.5

^{a} In CDCl$_3$, at 25 °C, δ in relation to CDCl$_3$ (77 ppm).
^{b} For **14'** and **16'** the values for the fluorenyl and phenyl groups are summarized.

Table 9. Results of the polymerization in the presence of complexes **9**, **11**, **13**, and **16**

Complex	T/°C	p_{H_2} /atm	Productivity*	$\bar{M}_w$ /10^3 g mol^{-1}	$\bar{M}_w/\bar{M}_n$	Triads mm (%)	T_m/°C
9	70	0	3.36	20	2.28	21.8	—
9	50	0	2.02	50	2.04	28.3	—
9	60	1.70	1.15	27	2.70	27.6	—
11	70	0	0.23	47	8.47	59.0	130
11	50	0	0.31	51	5.08	63.7	132
11	40	0	0.33	149	11.20	70.8	135
13	70	1.02	2.48	4.95	2.75	29.87	—
16	70	1.02	0.22	60.45	5.67	35.49	—

* Polypropylene yield (×10^{-6} g on 1 mol Zr per hour).

as a mixture of *rac*-(1-MeC$_{13}$H$_8$)$_2$SiMe$_2$ and *meso*-(1-MeC$_{13}$H$_8$)$_2$SiMe$_2$ (yield 75—80%).

(1-MeC$_{13}$H$_8$)$_2$SiPh$_2$ (2) was obtained by analogy to **1** (yield 75—80%).

(4-MeC$_{13}$H$_8$)$_2$SiMe$_2$ (3) and (4-MeC$_{13}$H$_8$)$_2$SiPh$_2$ (4) were synthesized by analogy to **1** (yields 75—80%).

(1-MeC$_{13}$H$_8$)$_2$SnMe$_2$ (5). 3 g (16.7 mmol) of 1-methylfluorene were dissolved in 100 mL of ether (or THF) and reacted with 10.4 mL (1.6 *M* solution in hexane) of butyllithium. After the gas evolution was finished 1.8 g (8.3 mmol) of Me$_2$SnCl$_2$ were added and the mixture was stirred for 4 h at room temperature. After evaporation of the solvent the residue was extracted with CH$_2$Cl$_2$ and then filtered over Na$_2$SO$_4$ to remove the precipitated LiCl. After removal of the solvent the residue was washed several times with pentane and then dried to yield a white powder, characterized as *rac*-(1-MeC$_{13}$H$_8$)$_2$SnMe$_2$ and *meso*-(1-MeC$_{13}$H$_8$)$_2$SnMe$_2$ (yield 90%). The compound was used without further purification.

(1-MeC$_{13}$H$_8$)$_2$SnPh$_2$ (6), (4-MeC$_{13}$H$_8$)$_2$SnMe$_2$ (7), and (4-MeC$_{13}$H$_8$)$_2$SnPh$_2$ (8) were obtained by analogy to **5** (yields 90—95%).

Preparation of the metallocene dichloride complexes 9—16 (general procedure). For the preparation of these complexes, the following general procedure was used: 4 mmol of the corresponding ligand precursor **1—8** were dissolved in 250 mL of ether and reacted with 8 mmol of butyllithium. After the gas evolution stopped, 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$_2$Cl$_2$. The suspension was filtered over Na$_2$SO$_4$ to the precipitated LiCl. The volume of the solution was reduced and the solution crystallized at −30 °C to yield orange to red colored powders (yields 85—90%).

Because of the low solubility of the tin bridged complexes **13—16**, instead of extraction with CH$_2$Cl$_2$, the crude product was extracted with ether in a Soxhlet apparatus to remove starting material and LiCl.

Preparation of the metallocene dimethyl complexes 10′—16′. For the preparation of the dimethyl complexes **10′—16′** the following general procedure was used: 2 mmol of the metallocene dichloride complex were suspended in 50 mL of toluene and reacted with 4 mmol of methyllithium. The mixture was stirred for 1 to 2 h and then filtered over Na$_2$SO$_4$. After the removal of the solvent the residue was crystallized in hexane at −30 °C to yield yellow to orange colored powders (yields 50—90%).

Polymerizations. The polymerizations were performed in a one-gallon Autoclave Engineers reactor in liquid propylene. Complexes were reacted with 10% MAO (Witco). The aluminum to zirconium ratio was 1000 : 1. The catalyst solution was stirred for 15 min at room temperature and charged into the one gallon reactor. Hydrogen was added from a 300 mL-cylinder (0—1.7 atm pressure drop), and propylene (2.5 L) was added to the reactor. After heating to the appropriate temperature (40—70 °C), the reactor contents were stirred for 1 h. The polymerization was terminated by venting surplus propylene. The polymer was recovered, dried, weighed and analyzed.

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