SYNTHESIS OF BULKY ZIRCONOCENE DICHLORIDE COMPOUNDS AND THEIR APPLICATIONS IN OLEFIN POLYMERIZATION

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Dedicated to our friend Dr Karel Mach on the happy occasion of his 70th birthday.

The bulky substituted cyclopentadienyllithium derivatives, $LiC_5H_4(CHMeR)$ (R = C_6H_5 (**1**), 1-naphthyl (**2**), 9-anthryl (**3**)), were synthesized from the reaction of 6-phenylfulvene, 6-(1-naphthyl)fulvene or 6-(9-anthryl)fulvene with LiMe. The *ansa*-bis(cyclopentadiene) ligands $Me_2Si(C_5HMe_4)\{C_5H_4(CHMeR)\}$ (R = C_6H_5 (**4**), 1-naphthyl (**5**), 9-anthryl (**6**)), and their lithium derivatives $Li_2(Me_2Si(C_5Me_4)\{C_5H_3(CHMeR)\})$ (R = C_6H_5 (**7**), 1-naphthyl (**8**), 9-anthryl (**9**)) have been prepared. The zirconocene complexes, $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4\text{-}(CHMeR)\}Cl_2]$ (R = C_6H_5 (**10**), 1-naphthyl (**11**), 9-anthryl (**12**)) and $[Zr\{\eta^5\text{-}C_5H_4(CHMeR)\}_2Cl_2]$ (R = C_6H_5 (**13**), 1-naphthyl (**14**), 9-anthryl (**15**)), were synthesized by the reaction of lithium derivatives **1**–**3** and $[Zr(\eta^5\text{-}C_5H_5)Cl_3]$ or $ZrCl_4$, respectively. The reaction of the lithium *ansa*-derivatives **7**–**9** and zirconium tetrachloride yielded the *ansa*-zirconocene complexes, $[Zr(Me_2Si(\eta^5\text{-}C_5Me_4)\{\eta^5\text{-}C_5H_3(CHMeR)\})Cl_2]$ (R = C_6H_5 (**16**), 1-naphthyl (**17**), 9-anthryl (**18**)). The zirconocene complexes have been tested in the polymerization of ethene and propene. The polymerization of propene with the *ansa*-zirconocene catalysts **16**–**18** gave polypropylene with 70% *mmmm* pentads and the symmetric zirconocene catalysts **13**–**15** 30–60% *mmmm* pentads.

Keywords: Metallocenes; Zirconocenes; Zirconium; Polymerization; Polyethylene; Polypropylene; Lewis acids.

Group 4 metallocene complexes are well known as excellent catalysts in olefin polymerization[1]. They provide superior activity and selectivity compared with other catalytic systems[2]. Crucial in the development of metallocene-based catalysts has been the direct relationship found between

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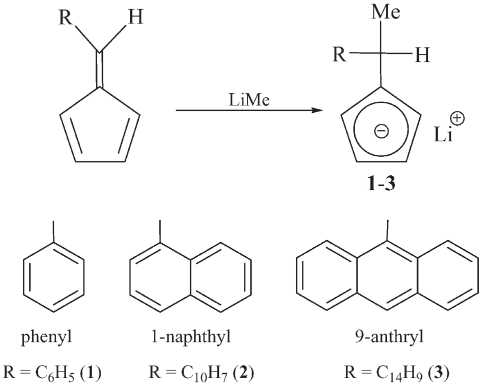
complex structure and catalytic behavior[3]. Therefore one can see the clear importance of molecular architecture of the metallocene complex in obtaining polyolefins with the desired physical properties[4]. As a continuation of our work in the field of zirconocene catalysts[5], we present here the synthesis, characterization and catalytic behavior of novel metallocene and *ansa*-metallocene complexes.

RESULTS AND DISCUSSION

*Synthesis of Cyclopentadienyllithium Derivatives **1–3***

The lithium compounds, $LiC_5H_4(CHMeR)$ (R = C_6H_5 (**1**), 1-naphthyl (**2**), 9-anthryl (**3**)), were prepared by the nucleophilic addition of methyllithium onto the exocyclic double bond of the corresponding substituted fulvene (Scheme 1).

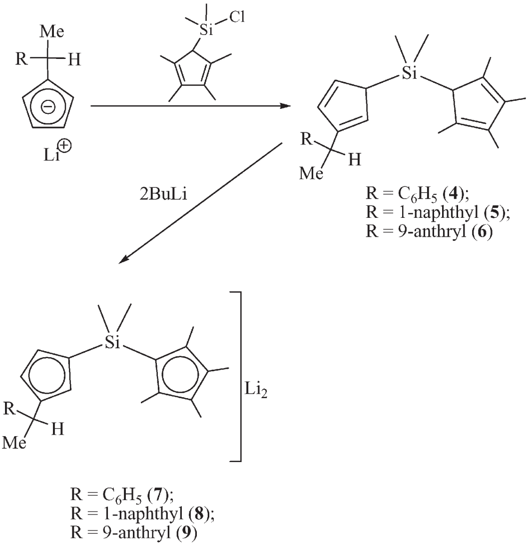


SCHEME 1

Compounds **1–3** were characterized by ^1H and ^{13}C NMR spectroscopy (see Experimental). Two multiplets at ca. 5.5 ppm were observed in the ^1H NMR spectra for the cyclopentadienyl protons. The doublet at ca. 1.7 ppm was assigned to the methyl group. The proton bonded to the chiral carbon atom gave a quadruplet at 4.00, 4.89 and 5.71 ppm for **1**, **2** and **3**, respectively. For **1**, three multiplets (6.98, 7.12 and 7.23 ppm) were observed corresponding to the phenyl protons. The 1-naphthyl group in **2** exhibited signals between 7.3 and 8.3 ppm. Multiplets were recorded between 7.2 and 8.5 ppm for the 9-anthryl moiety in **3**. ^{13}C NMR spectra of **1–3** showed the expected signals for the cyclopentadienyl moiety (ca. 102, 103 and 125 ppm). The chiral carbon atom gave a signal at ca. 35 ppm and the methyl group at ca. 25 ppm. Additional signals were observed corresponding to the aromatic group present.

Synthesis of Bis(cyclopentadienyl) Derivatives ***4*–*9***

The reaction of **1**–**3** with $Me_2SiCl(C_5HMe_4)$ (Scheme 2), following the previously reported synthetic protocols[5a], yielded the bis(cyclopentadiene) compounds, $Me_2Si(C_5HMe_4)\{C_5H_4(CHMeR)\}$ (R = C_6H_5 (**4**), 1-naphthyl (**5**), 9-anthryl (**6**)), as mixtures of the double bond position isomers, with one isomer being predominant. Compounds **4**–**6** were characterized by ^1H NMR spectroscopy and electron impact mass spectrometry (see Experimental). The dilithium derivatives, $Li_2(Me_2Si(C_5Me_4)\{C_5H_3(CHMeR)\})$ (R = C_6H_5 (**7**), 1-naphthyl (**8**), 9-anthryl (**9**)), were obtained in the usual manner by the reaction of **4-6** with butyllithium (Scheme 2).

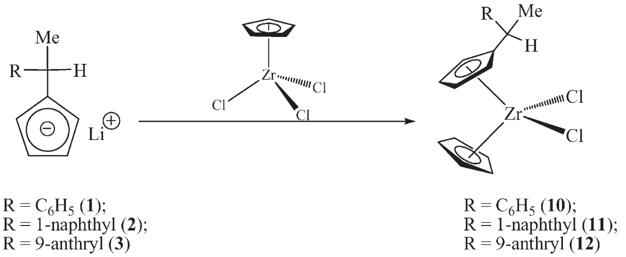


SCHEME 2

Synthesis of Mixed-Ring Zirconocene Complexes ***10*–*12***

The zirconocene complexes, $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CHMeR)\}Cl_2]$ (R = C_6H_5 (**10**), 1-naphthyl (**11**), 9-anthryl (**12**)), were prepared by the reaction of **1**–**3** with $[Zr(\eta\text{-}C_5H_5)Cl_3]$ (Scheme 3). Complexes **10**–**12** were isolated as white crystalline solids and characterized spectroscopically.

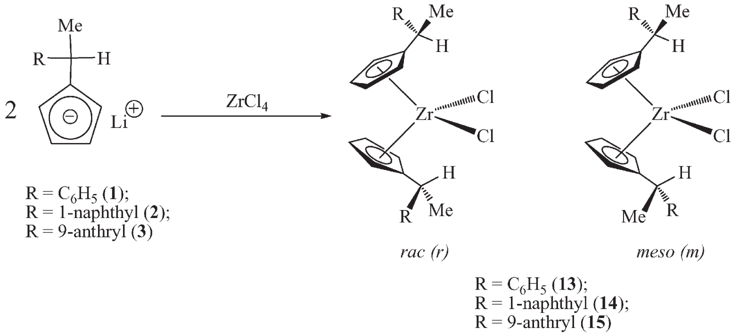
The substituted cyclopentadienyl moiety exhibited four multiplets (5.6–6.9 ppm) in the ^1H NMR spectra of **10**–**12** because of their diastereotopic nature of the α and β pairs of protons due to the presence of a chiral substituent. A singlet at ca. 6.4 ppm was observed for the unsubstituted cyclopentadienyl ligand. A quadruplet (at 4.31, 5.20 and 5.95 ppm for **10**, **11** and **12**, respectively) and doublet (at ca. 1.8 ppm) were recorded and assigned, respectively, to the proton and methyl group bonded to the chiral carbon atom. The aromatic systems gave the expected signals (see Experimental). The $^{13}C\{^1H\}$NMR spectra gave five signals for the substituted cyclopentadienyl ligand (110–145 ppm) and one signal (ca. 115 ppm) for the unsubstituted cyclopentadienyl group. Signals were observed for the methyl and chiral carbon at ca. 21 and 37 ppm, respectively. The aromatic systems, phenyl, 1-naphthyl and 9-anthryl, gave four, ten and fourteen signals, respectively.



SCHEME 3

*Synthesis of Zirconocene Complexes **13**–**15***

The reaction of two molar equivalents of **1**–**3** with $ZrCl_4$ yielded the zirconocene complexes, $[Zr\{\eta^5\text{-}C_5H_4(CHMeR)\}_2Cl_2]$ (R = C_6H_5 (**13**)[6], 1-naphthyl (**14**), 9-anthryl (**15**)) (Scheme 4). Complexes **13**–**15** were isolated as white crystalline solids and characterized. NMR spectroscopy re-

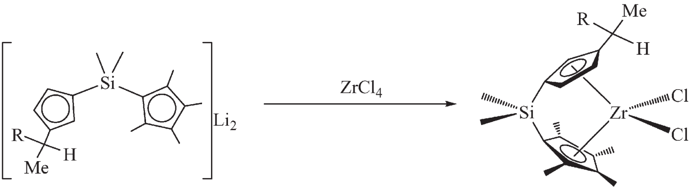


SCHEME 4

vealed the presence of the expected *rac* and *meso* isomers due to the presence of two chiral centres. In the case of **15**, the separation of one of the isomers from the mixture was achieved. The NMR spectra of complexes **13**–**15** were similar to those observed for **9**–**12**. For **13** and **14**, the signals corresponding to the two isomers in the 1:1 ratio were observed.

*Synthesis of ansa-Zirconocene Complexes **16**–**18***

The *ansa*-metallocene complexes, $[Zr(Me_2Si(\eta^5\text{-}C_5Me_4)\{\eta^5\text{-}C_5H_3(CHMeR)\})Cl_2]$ (R = C_6H_5 (**16**), 1-naphthyl (**17**), 9-anthryl (**18**)), were prepared by the reaction of **7**–**9** and $ZrCl_4$ (Scheme 5).



R = C_6H_5 (**7**);
R = 1-naphthyl (**8**);
R = 9-anthryl (**9**)

R = C_6H_5 (**16**);
R = 1-naphthyl (**17**);
R = 9-anthryl (**18**)

SCHEME 5

In addition to the chiral centre in the bulky substituent, planar chirality exists in the monosubstituted cyclopentadienyl ring. Thus for **16**–**18**, two diastereoisomers are possible (Fig. 1). In the case of **16** and **17** we were unable to separate these isomers. However, for **18**, only one of the possible isomers was found to be present in the isolated product. The ^1H NMR spectra of **16**–**18** showed, for the *ansa*-metallocene system, three multiplets for the protons of the monosubstituted C_5 ring (5.2–7.1 ppm), four singlets for the methyl groups of the C_5 ring (1.8–2.2 ppm), and two singlets corresponding to the methyl groups of the $SiMe_2$ bridging unit (at ca. 0.0 ppm). Additional signals were recorded for the chiral substituents, which were similar to those in **9**–**15**. In the NMR spectra of **16** and **17**, the signals corresponding to the two isomers in the 1:1 ratio were observed.

Polymerization of Ethene

The polymerizations of ethene using the zirconocene derivatives **10**–**18** as catalyst (in the case of **13**, **14**, **16** and **17** 1:1 isomeric mixtures) with a methylaluminoxane-metal catalyst in the ratio 1000:1, have been carried

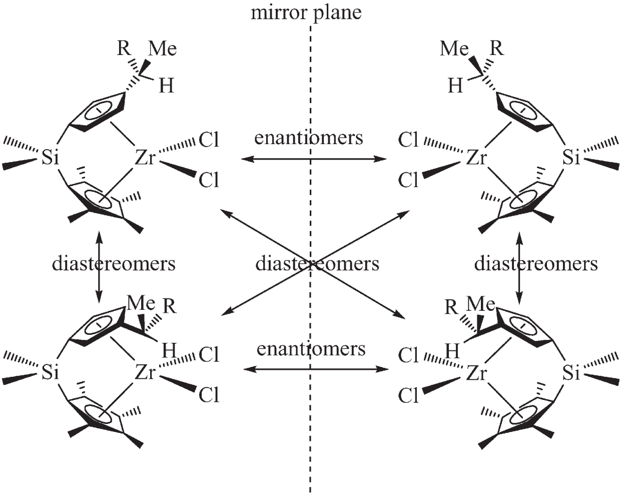


FIG. 1
Stereoisomers of complexes **16**–**18**

out. The polymerizations were conducted at 20 °C and at an ethene pressure of 2 bar during 30 min. The polymerization was also carried out with the reference compound [Zr(η^5-C_5H_5)$_2$$Cl_2$], under the same experimental conditions. The catalytic activities and polymer molecular weight and distribution are given in Table I.

The activities of all the catalysts tested proved to be lower than that recorded for the reference catalyst [Zr(η^5-C_5H_5)$_2$$Cl_2$]. This maybe due to the possible intramolecular coordination of the aromatic moiety to the zirconium centre during the polymerization[7]. Catalyst **10** showed the highest catalytic activity, far greater than the other zirconocene complexes tested and comparable with that observed for the reference catalyst. The catalytic activity decreased in dependence of the aromatic substituent present: phenyl > anthryl > naphthyl. Activities of different metallocene systems with the same aromatic substituent were similar (with the exception of **10**). Some of the catalysts produced high molecular weights of polyethylene (of the order 10^6), such as **11** and homoleptic metallocene catalysts **13**–**15**. Catalysts **10**–**18** produced polymers with broad molecular weight distributions, with polydispersity values between 4 and 7. This phenomenon has been explained previously considering the C_5 ring rotation to be slower than the propagation of the polymer chain, creating different rotamers of the catalyst which act as distinct active centres[8].

TABLE I
Ethene polymerization catalyzed with **10–18** and $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$[a]

Catalyst	Activity[b]	$M_w \times 10^{-3}$	M_w/M_n
$[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$	23300	169	2.3
$[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CHMeC_6H_5)\}Cl_2]$ (**10**)	21200	253	5.8
$[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CHMeC_{10}H_7)\}Cl_2]$ (**11**)	2567	846	5.1
$[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CHMeC_{14}H_9)\}Cl_2]$ (**12**)	3673	384	4.4
$[Zr\{\eta^5\text{-}C_5H_4(CHMeC_6H_5)\}_2Cl_2]$ (**13**)	6100	1054	4.8
$[Zr\{\eta^5\text{-}C_5H_4(CHMeC_{10}H_7)\}_2Cl_2]$ (**14**)	3760	987	4.1
$[Zr\{\eta^5\text{-}C_5H_4(CHMeC_{14}H_9)\}_2Cl_2]$ (**15**)	2000	716	4.0
$[Zr(Me_2Si(\eta^5\text{-}C_5Me_4)\{\eta^5\text{-}C_5H_3(CHMeC_6H_5)\})Cl_2]$ (**16**)	5613	197	7.1
$[Zr(Me_2Si(\eta^5\text{-}C_5Me_4)\{\eta^5\text{-}C_5H_3(CHMeC_{10}H_7)\})Cl_2]$ (**17**)	1933	79	4.4
$[Zr(Me_2Si(\eta^5\text{-}C_5Me_4)\{\eta^5\text{-}C_5H_3(CHMeC_{14}H_9)\})Cl_2]$ (**18**)	3067	524	7.5

[a] At 20 °C, ethene pressure 2 bar, 200 ml toluene, $[Al] = 3 \times 10^{-2}$ mol l^{-1}, $[Zr] = 3 \times 10^{-5}$ mol l^{-1}, t = 15 min. [b] kg(PE)/mol Zr h

Polymerization of Propene

The polymerizations of propene using zirconocene derivatives **13–18** as catalysts (in the case of **13**, **14**, **16** and **17** the 1:1 mixtures of isomers) with the methylaluminoxane cocatalyst-metal catalyst ratio 3000:1 have been carried out. The polymerizations were conducted at 0 °C for 60 min and at a propene pressure of 2.5 bar. The polymerization was also carried out with the reference compound $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ under the same experimental conditions. The catalytic activities, polymer molecular weights, polydispersity and isotacticity are given in Table II. Pentad distributions for **13–15** are shown in Table III.

The catalytic activities of the catalysts tested were lower than that recorded for the reference complex. However, complexes **16** and **17** gave activities similar to the reference compound. The anthryl-substituted catalysts, **15** and **18**, gave low activities in comparison with the other catalysts. Polypropylene molecular weights were higher for the metallocene systems compared with the *ansa*-metallocene catalysts. The polydispersity values of the polypropylenes obtained with the catalysts are also high and again this can be explained by different rotamers of the same complex acting as active centres in the polymerization[8].

The isotacticity of the polymers was measured by the pentad method using ^{13}C NMR spectroscopy. The *mmmm* pentad contents in polypropylene prepared with the *ansa*-metallocene catalysts **16**–**18** are of the order of 70% and are comparable with those reported previously for similar C_1 symmetric complexes[5b,9].

Using the Cossee–Arlman site control mechanism, the stereoselectivity of the C_1 catalysts **16**–**18** can be explained. Four possible diastereomeric intermediates (two at each binding site) are possible in the polymerization of propene. The binding sites **A** and **B** are isoselective with the polymer chain being located in the less sterically hindered positions, intermediates **A1** and **B1** (Fig. 2). Therefore, in a way similar to that predicted and observed for C_2 *ansa*-metallocene catalysts[10], the polymerization should yield isotactic polypropylene.

A back-skip mechanism may also be used to interpret the stereoselectivity of complexes **16**–**18** in the polymerization of propylene. It has previously been put forward that the presence of a bulky cyclopentadienyl substituent in the β-position (with respect to the carbon atom of the C_5 ring linked to the *ansa* bridge) does not allow the polymer chain to be located in the more sterically congested position[11]. In the absence of monomer molecule, as most likely occurs at the end of each insertion step, the steric pressure imposed by the ligand may force the growing chain to skip back to the less crowded position. Insertion, therefore, occurs with the same relative posi-

TABLE II
Propene polymerization catalyzed with complexes **13**–**18** and $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]^a$

Catalyst	Activity^b	$M_w \times 10^{-3}$	M_w/M_n	mmmm %
$[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$	121	2	1.8	4.0
$[Zr\{\eta^5\text{-}C_5H_4(CHMeC_6H_5)\}_2Cl_2]$ (**13**)	73	26	9.2	46.8
$[Zr\{\eta^5\text{-}C_5H_4(CHMeC_{10}H_7)\}_2Cl_2]$ (**14**)	89	33	9.9	33.0
$[Zr\{\eta^5\text{-}C_5H_4(CHMeC_{14}H_9)\}_2Cl_2]$ (**15**)	32	41	9.4	61.8
$[Zr(Me_2Si(\eta^5\text{-}C_5Me_4)\{\eta^5\text{-}C_5H_3(CHMeC_6H_5)\})Cl_2]$ (**16**)	115	13	4.0	71.5
$[Zr(Me_2Si(\eta^5\text{-}C_5Me_4)\{\eta^5\text{-}C_5H_3(CHMeC_{10}H_7)\})Cl_2]$ (**17**)	113	17	6.1	70.5
$[Zr(Me_2Si(\eta^5\text{-}C_5Me_4)\{\eta^5\text{-}C_5H_3(CHMeC_{14}H_9)\})Cl_2]$ (**18**)	30	13	3.2	71.7

[a] At 0 °C, propene pressure 2.5 bar, 200 ml toluene, $[Al] = 9 \times 10^{-2}$ mol l^{-1}, $[Zr] = 3 \times 10^{-5}$ mol l^{-1}, $t = 60$ min. [b] kg(PP)/mol Zr h

TABLE III
Pentad distribution, calculated from $^{13}C\{^1H\}$ NMR spectroscopy, for polypropylene synthesized in the presence of **13**–**15**

Catalyst	mmmm %	mmmr %	rmmr %	mmrr %	mmrm + rmrr %	mrmr %	rrrr %	mrrr %	mrrm %
$[Zr\{\eta^5\text{-}C_5H_4(CHMeC_6H_5)\}_2Cl_2]$ (**13**)	46.8	12.0	3.8	6.9	8.1	11.9	1.5	3.1	5.9
$[Zr\{\eta^5\text{-}C_5H_4(CHMeC_{10}H_7)\}_2Cl_2]$ (**14**)	33.0	15.0	4.4	11.3	13.0	12.0	1.7	3.7	5.3
$[Zr\{\eta^5\text{-}C_5H_4(CHMeC_{14}H_9)\}_2Cl_2]$ (**15**)	61.8	3.5	10.8	2.8	8.7	8.0	0.9	1.4	2.1

tion of the monomer and the polymer chain and leads to isotactic polypropylene (Fig. 3). Examples of the back-skip mechanism in polymerization of propene have been reported[5b,9b,12].

The non-*ansa* catalysts **13** and **14** give markedly lower *mmmm* pentad values compared with the *ansa*-metallocene complexes **16**–**18**. However, the polypropylene produced using **15** gives an *mmmm* pentad value which competes in isotacticity with that of its *ansa*-counterparts.

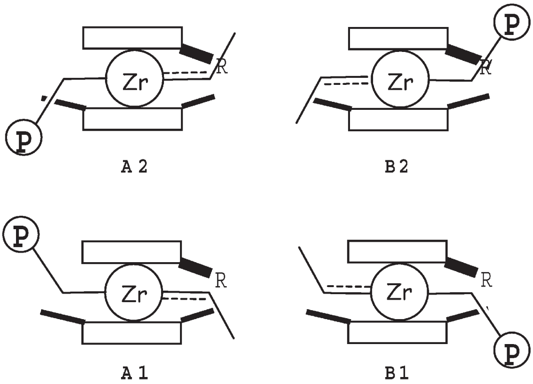


FIG. 2
Diastereomeric intermediates

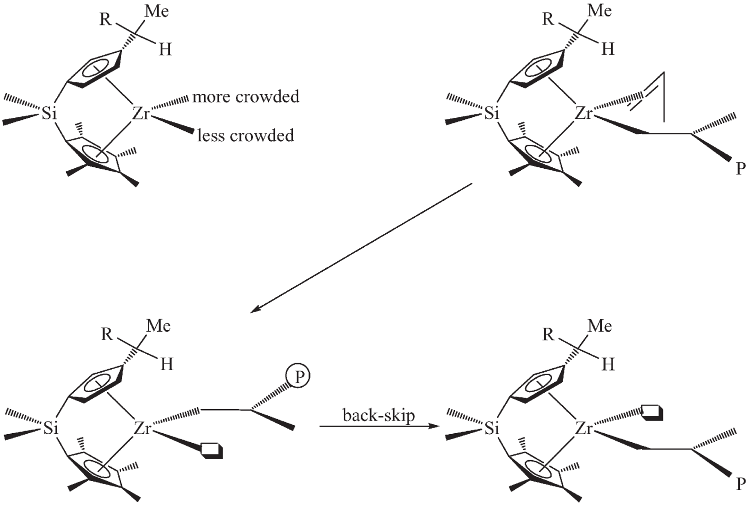


FIG. 3
Back-skip mechanism

Considering **13**–**15** as conformationally dynamic systems, for which two extremes are described with the cyclopentadienyl substituents eclipsed or in opposite direction, then the two possible rotamers will produce either nonselective (atactic) or isoselective coordination of the monomer (Fig. 4). The greater steric demand of the substituent will make the *syn* conformation less stable than the *anti* conformation and make the catalyst more isoselective. Indeed, the anthryl complex gives the highest *mmmm* pentad value. Interconversion between the stereoselective *anti* and the non-stereoselective *syn* conformations has previously been proposed as a means of generating blocks of atactic and isotactic stereosequences in a single polymer chain[13].

Analysis of the pentad distribution shows that the stereodefects are derived predominantly from *mmmr*, *mmrr*, *mmrm* and *mrmr* pentads. The presence of a relatively high concentration of *mmrm* stereodefects is consistent with the microstructure containing a significant fraction of isotactic sequences of opposite configurations separated by isolated *r* diads. These results imply that isomerization takes place between the two enantiomeric *anti* conformations, which are oppositely isoselective. The notable quantity of the *mrmr* pentad observed indicates atactic sequences in the polymer chain which most probably originate from the achiral *syn* rotamer.

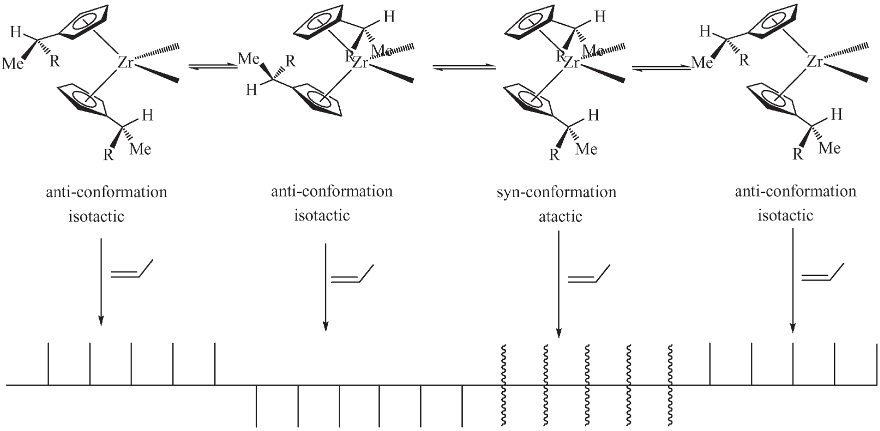


FIG. 4
Stereoselectivity for different conformations in complexes **13**–**15**

Conclusion

The synthesis and characterization of new zirconocene and *ansa*-zirconocene complexes incorporating bulky substituents is reported. The complexes proved to be active as catalysts in the polymerization of ethene and propene. The stereoselective polymerization of propene gave in the case of the C_1 symmetric *ansa*-metallocene systems isotacticity of 70%. The unbridged zirconocene complex gave tacticities between 30–60% depending on the aromatic substituent. This present study should open up the possibility of modeling the properties of polypropylene by rational design of the zirconocene catalyst.

EXPERIMENTAL

All reactions were performed using standard Schlenk tube techniques in atmosphere of dry nitrogen. Solvents were distilled from the appropriate drying agents and degassed before use.

$Me_2SiCl(C_5HMe_4)$, BuLi (1.6 M in hexane), MeLi (1.6 M in Et_2O), MAO, and $ZrCl_4$, were purchased from Aldrich and used directly. 6-Phenylfulvene, 6-(1-naphthyl)fulvene or 6-(9-anthryl)fulvene were prepared adapting the previously reported synthetic route[14]. The synthesis of $[Zr(\eta^5\text{-}C_5H_5)Cl_3]$ was carried out using the literature method[15].

^1H and $^{13}C\{^1H\}$ NMR spectra (δ, ppm; *J*, Hz) were recorded on a Varian Mercury FT-400 spectrometer and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin–Elmer 2400 or Leco CHNS-932 microanalyzer. Mass spectroscopic analyses were preformed on a Hewlett–Packard 5988A (*m/z* 50–1000) instrument. Polymer molecular weights and distributions were determined by GPC (Waters 150C Plus) in 1,2,4-trichlorobenzene at 145 °C. Polymer isotacticity was calculated from ^{13}C NMR spectra of polymer solution in 1,2,4-trichlorobenzene/C_6D_6 (1:1).

$LiC_5H_4(CHMeC_6H_5)$ (**1**). MeLi (1.6 M in Et_2O) (10.1 ml, 16.21 mmol) was added dropwise to a solution of 6-phenylfulvene (2.50 g, 16.21 mmol) in Et_2O (50 ml) at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. The solvent was removed in vacuo. A white solid which was washed with hexane (2 × 50 ml) and dried under vacuum to yield a free-flowing powder. Yield 1.85 g (65%). ^1H NMR (400 MHz, THF-d_8): 1.52 (d, 3 H, *J*(H,Me) = 7.6, CH**Me**), 4.00 (q, 1 H, C**H**Me), 5.55 (2 H), 5.57 (2 H) (m, C_5H_4), 6.98 (1 H), 7.12 (2 H), 7.23 (2 H) (m, C_6H_5). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): 25.4 (CH**Me**), 41.3 (CpC), 101.8, 102.2, 125.1 (C_5H_4), 122.0, 128.1, 128.8, 134.7 (C_6H_5). For $C_{13}H_{13}Li$ (176.2) calculated: 88.62% C, 7.44% H; found: 88.31% C, 7.39% H.

$LiC_5H_4(CHMeC_{10}H_7)$ (**2**). The synthesis of **2** was carried out in the same way as **1**: MeLi (1.6 M in Et_2O) (7.6 ml, 12.22 mmol) and 6-(1-naphthyl)fulvene (2.50 g, 12.22 mmol). Yield 1.49 g (54%). ^1H NMR (400 MHz, THF-d_8): 1.67 (d, 3 H, *J*(H,Me) = 7.2, CH**Me**), 4.89 (q, 1 H, C**H**Me), 5.56 (2 H), 5.58 (2 H) (m, C_5H_4), 7.33 (3 H), 7.45 (1 H), 7.55 (1 H), 7.75 (1 H), 8.34 (1 H) (m, $C_{10}H_7$). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): 25.2 (CH**Me**), 36.0 (CpC), 101.9, 102.1, 124.7 (C_5H_4), 124.6, 124.7, 124.8, 124.9, 125.5, 125.8, 128.8, 132.6, 134.7, 147.5 ($C_{10}H_7$). For $C_{17}H_{15}Li$ (226.3) calculated: 90.25% C, 6.68% H; found: 90.17% C, 6.59% H.

$LiC_5H_4(CHMeC_{14}H_9)$ (**3**). The synthesis of **3** was carried out in the same way as **1**: MeLi (1.6 M in Et_2O) (6.1 ml, 9.82 mmol) and 6-(9-anthryl)fulvene (2.50 g, 9.82 mmol). Yield

1.35 g (50%). ^{1}H NMR (400 MHz, THF-d_8): 1.91 (d, 3 H, J(H,Me) = 7.2, CH**Me**), 5.53 (2 H), 5.57 (2 H) (m, C_5H_4), 5.71 (q, 1 H, C**H**Me), 7.26 (4 H), 7.89 (2 H), 8.22 (1 H), 8.52 (2 H) (m, $C_{14}H_9$). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): 25.4 (CH**Me**), 34.3 (CpC), 102.3, 102.4, 124.7 (C_5H_4), 124.9, 125.4, 125.7, 129.6, 130.4, 132.5, 143.8 ($C_{14}H_9$). For $C_{21}H_{17}Li$ (276.3) calculated: 91.29% C, 6.20% H; found: 91.00% C, 6.18% H.

$Me_2Si(C_5HMe_4)\{C_5H_4(CHMeC_6H_5)\}$ (**4**). $Me_2SiCl(C_5HMe_4)$ (1.22 g, 5.68 mmol) in THF (50 ml) was added to a solution of $LiC_5H_4(CHMeC_6H_5)$ (**1**) (1.00 g, 5.68 mmol) in THF (50 ml) at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. The solvent was removed in vacuo and hexane (150 ml) was added to the resulting dark orange oil. The mixture was filtered and the solvent removed under reduced pressure to give an orange oil. Yield 1.92 g (97%). ^{1}H NMR (400 MHz, $CDCl_3$; for the predominant isomer): 0.16 (s, 6 H, $SiMe_2$), 1.59 (d, 3 H, J(H,Me) = 6.8, CH**Me**) 1.90 (6 H), 2.03 (6 H) (s, C_5Me_4), 2.97 (1 H), 3.29 (1 H) (m, HC_5), 3.94 (m, 1 H, C**H**Me), 6.01 (1 H), 6.35 (1 H), 6.44 (1 H) (m, C_5H_3), 7.22 (1 H), 7.28 (2 H), 7.31 (2 H) (m, C_6H_5). MS-EI, m/z (rel.%): 348 (15) [M^+], 243 (41) [$M^+ - Me - C_6H_5$], 179 (55) [$M^+ - C_5H_4CHMeC_6H_5$], 105 (100) [$M^+ - Me_2Si(C_5HMe_4)(C_5H_3)$]. For $C_{24}H_{32}Si$ (348.6) calculated: 82.69% C, 9.25% H; found: 82.67% C, 9.25% H.

$Me_2Si(C_5HMe_4)\{C_5H_4(CHMeC_{10}H_7)\}$ (**5**). The synthesis of **5** was carried out in the same way as **4**: $Me_2SiCl(C_5HMe_4)$ (0.95 g, 4.42 mmol) and $LiC_5H_4(CHMeC_{10}H_7)$ (**2**) (1.00 g, 4.42 mmol). Yield 1.73 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$; for the predominant isomer): –0.15 (s, 6 H, $SiMe_2$), 1.68 (d, 3 H, J(H,Me) = 8.0, CH**Me**), 1.84 (6 H), 1.98 (6 H) (s, C_5Me_4), 2.90 (1 H), 3.03 (1 H) (m, HC_5), 4.72 (m, 1 H, C**H**Me), 6.30 (1 H), 6.33 (1 H), 6.42 (1 H) (m, C_5H_3), 7.44 (4 H), 7.73 (1 H), 7.86 (1 H), 8.15 (1 H) (m, $C_{10}H_7$). MS-EI, m/z (rel.%): 398 (12) [M^+], 243 (39) [$M^+ - Me - C_{10}H_7$], 219 (31) [$M^+ - Me_2Si(C_5HMe_4)$], 179 (34) [$M^+ - C_5H_4CHMeC_{10}H_7$], 155 (100) [$M^+ - Me_2Si(C_5HMe_4)(C_5H_3)$]. For $C_{28}H_{34}Si$ (398.7) calculated: 84.36% C, 8.60% H; found: 84.67% C, 8.62% H.

$Me_2Si(C_5HMe_4)\{C_5H_4(CHMeC_{14}H_9)\}$ (**6**). The synthesis of **6** was carried out in the same way as **4**: $Me_2SiCl(C_5HMe_4)$ (0.78 g, 3.62 mmol) and $LiC_5H_4(CHMeC_{14}H_9)$ (**3**) (1.00 g, 3.62 mmol). Yield 1.54 g (95%). ^{1}H NMR (400 MHz, $CDCl_3$; for the predominant isomer): 0.00 (s, 6 H, $SiMe_2$), 1.93 (d, 3 H, J(H,Me) = 6.8, CH**Me**), 1.84 (6 H), 1.98 (6 H) (s, C_5Me_4), 2.90 (1 H), 3.10 (1 H) (m, HC_5), 5.40 (m, 1 H, C**H**Me), 6.14 (1 H), 6.22 (1 H), 6.32 (1 H) (m, C_5H_3), 7.43 (4 H), 8.01 (2 H), 8.39 (3 H) (m, $C_{14}H_9$). MS-EI, m/z (rel.%): 448 (20) [M^+], 269 (21) [$M^+ - Me_2Si(C_5HMe_4)$], 243 (35) [$M^+ - Me - C_{14}H_9$], 205 (100) [$M^+ - Me_2Si(C_5HMe_4)(C_5H_3)$]. For $C_{32}H_{36}Si$ (448.7) calculated: 85.65% C, 8.09% H; found: 85.67% C, 8.05% H.

$Li_2(Me_2Si(C_5Me_4)\{C_5H_3(CHMeC_6H_5)\})$ (**7**). BuLi (1.6 M in hexane) (5.4 ml, 8.62 mmol) was added dropwise to a solution of **4** (1.50 g, 4.31 mmol) in Et_2O (100 ml) at –78 °C. The mixture was allowed to warm to 25 °C and stirred for 15 h. The solvent was removed in vacuo. A white solid which was washed with hexane (2 × 50 ml) and dried in vacuum. Yield 1.39 g (90%). For $C_{24}H_{30}Li_2Si$ (360.5) calculated: 79.97% C, 8.39% H; found: 79.67% C, 8.35% H.

$Li_2(Me_2Si(C_5Me_4)\{C_5H_3(CHMeC_{10}H_7)\})$ (**8**). The synthesis of **8** was carried out in the same way as **7**: BuLi (1.6 M in hexane) (4.7 ml, 7.52 mmol) and **5** (1.50 g, 3.76 mmol). Yield 1.37 g (89%). For $C_{28}H_{32}Li_2Si$ (410.5) calculated: 81.92% C, 7.86% H; found: 81.77% C, 7.85% H.

$Li_2(Me_2Si(C_5Me_4)\{C_5H_3(CHMeC_{14}H_9)\})$ (**9**). The synthesis of **9** was carried out in the same way as **7**: BuLi (1.6 M in hexane) (4.2 ml, 6.68 mmol) and **6** (1.50 g, 3.34 mmol). Yield 1.34 g (87%). For $C_{32}H_{34}Li_2Si$ (460.6) calculated: 83.45% C, 7.44% H; found: 82.97% C, 7.39% H.

$[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CHMeC_6H_5)\}Cl_2]$ (**10**). $LiC_5H_4(CHMeC_6H_5)$ (**1**) (1.00 g, 5.58 mmol) in THF (50 ml) was added dropwise during 15 min to a solution of $[Zr(\eta^5\text{-}C_5H_5)Cl_3]$ (1.47 g, 5.58 mmol) in THF (50 ml) at 0 °C. The reaction mixture was allowed to warm to room tem-

perature and stirred for 2 h. The solvent was removed in vacuo and hexane (125 ml) was added to the resulting solid. The mixture was filtered, the filtrate concentrated (20 ml) and cooled to –30 °C to give crystals of the title complex. Yield 0.85 g (38%). ^{1}H NMR (400 MHz, $CDCl_3$): 1.60 (d, 3 H, *J*(H,Me) = 6.8, CH**Me**), 4.31 (q, 1 H, C**H**Me), 5.95 (1 H), 6.29 (1 H), 6.42 (1 H), 6.57 (1 H) (m, C_5H_4), 6.38 (s, 5 H, C_5H_5), 7.19 (2 H), 7.35 (2 H), 7.42 (1 H) (m, C_6H_5). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 21.0 (CH**Me**), 40.0 (CpC), 112.8, 113.5, 115.1, 116.0, 145.9 (C_5H_4), 115.0 (C_5H_5), 126.0, 127.4, 127.6, 128.7 (C_6H_5). MS-EI, *m/z* (rel.%): 396 (4) [M$^+$], 319 (18) [M$^+$ – C_6H_5], 291 (90) [M$^+$ – $CHMeC_6H_5$], 255 (52) [M$^+$ – $CHMeC_6H_5$ – Cl]. For $C_{18}H_{18}Cl_2Zr$ (396.5) calculated: 54.53% C, 4.58% H; found: 54.71% C, 4.62% H.

[Zr(η^5-C_5H_5){η^5-$C_5H_4(CHMeC_{10}H_7)$}Cl_2] (**11**). The synthesis of **11** was carried out in the same way as **10**: $LiC_5H_4(CHMeC_{10}H_7)$ (**2**) (1.20 g, 5.30 mmol) and [Zr(η^5-C_5H_5)Cl_3] (1.39 g, 5.30 mmol). Yield 0.99 g (42%). ^{1}H NMR (400 MHz, $CDCl_3$): 1.74 (d, 3 H, *J*(H,Me) = 6.8, CH**Me**), 5.20 (q, 1 H, C**H**Me), 5.90 (1 H), 6.37 (2 H), 6.73 (1 H) (m, C_5H_4), 6.47 (s, 5 H, C_5H_5), 7.04 (1 H), 7.38 (1 H), 7.52 (2 H), 7.73 (1 H), 7.88 (1 H), 8.30 (1 H) (m, $C_{10}H_7$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 22.0 (CH**Me**), 37.0 (CpC), 111.2, 113.6, 116.1, 119.0, 144.3 (C_5H_4), 116.0 (C_5H_5), 125.5, 126.1, 126.4, 127.1, 128.2, 129.0, 130.3, 132.2, 134.0 136.1 ($C_{10}H_7$). MS-EI, *m/z* (rel.%): 446 (12) [M$^+$], 319 (18) [M$^+$ – $C_{10}H_7$], 291 (90) [M$^+$ – $CHMeC_{10}H_7$], 283 (51) [M$^+$ – $C_{10}H_7$ – Cl]. For $C_{22}H_{20}Cl_2Zr$ (446.5) calculated: 59.18% C, 4.51% H; found: 58.88% C, 4.53% H.

[Zr(η^5-C_5H_5){η^5-$C_5H_4(CHMeC_{14}H_9)$}Cl_2] (**12**). The synthesis of **12** was carried out in the same way as **10**: $LiC_5H_4(CHMeC_{14}H_9)$ (**3**) (1.00 g, 3.61 mmol) and [Zr(η^5-C_5H_5)Cl_3] (0.95 g, 3.61 mmol). Yield 0.56 g (31%). ^{1}H NMR (400 MHz, $CDCl_3$): 1.99 (d, 3 H, *J*(H,Me) = 7.2, CH**Me**), 5.93 (q, 1 H, C**H**Me), 5.61 (1 H), 6.10 (1 H), 6.57 (1 H), 6.90 (1 H) (m, C_5H_4), 6.41 (s, 5 H, C_5H_5), 7.20 (1 H), 7.27 (1 H), 7.37 (1 H), 7.51 (1 H), 7.59 (1 H), 7.76 (1 H), 8.04 (2 H), 8.56 (1 H) (m, $C_{14}H_9$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 20.0 (CH**Me**), 34.0 (CpC), 110.3, 114.2, 116.0, 117.4, 141.0 (C_5H_4), 115.6 (C_5H_5), 124.1, 124.4, 125.4, 126.0, 126.1, 127.0, 127.5, 128.1, 129.0 129.4, 130.6, 131.8, 132.0, 137.2 ($C_{14}H_9$). MS-EI, *m/z* (rel.%): 496 (7) [M$^+$], 319 (12) [M$^+$ – $C_{14}H_9$], 283 (29) [M$^+$ – $C_{14}H_9$ – Cl], 248 (50) [M$^+$ – $C_{14}H_9$ – 2 × Cl]. For $C_{26}H_{22}Cl_2Zr$ (496.6) calculated: 62.89% C, 4.47% H; found: 62.61% C, 4.41% H.

[Zr{η^5-$C_5H_4(CHMeC_6H_5)$}$_2Cl_2$] (**13**). The synthesis of **13** was carried out in the same way as **10**: $LiC_5H_4(CHMeC_6H_5)$ (**1**) (1.50 g, 8.48 mmol) and $ZrCl_4$ (0.98 g, 4.20 mmol). Yield 0.89 g (42%). ^{1}H NMR (400 MHz, $CDCl_3$; two isomers): 1.59 (d, 12 H, *J*(H,Me) = 6.8, CH**Me**), 4.32 (q, 4 H, C**H**Me), 5.87 (4 H), 6.10 (2 H), 6.15 (2 H), 6.20 (2 H), 6.25 (2 H), 6.54 (4 H) (m, C_5H_4), 7.16 (8 H), 7.29 (8 H), 7.30 (4 H) (m, C_6H_5). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; two isomers): 20.0, 21.0 (CH**Me**), 39.9, 40.0 (CpC), 111.0, 112.0, 112.2, 112.5, 112.6, 114.0, 114.5, 115.0, 146.0, 146.2 (C_5H_4), 126.0, 126.4, 127.0, 127.1, 127.5, 127.9, 139.0, 139.5 (C_6H_5). MS-EI, *m/z* (rel.%): 500 (9) [M$^+$], 423 (17) [M$^+$ – C_6H_5], 388 (100) [M$^+$ – C_6H_5 – Cl], 331 (14) [M$^+$ – $C_5H_4CHMeC_6H_5$]. For $C_{26}H_{26}Cl_2Zr$ (500.6) calculated: 62.38% C, 5.23% H; found: 62.08% C, 5.18% H.

[Zr{η^5-$C_5H_4(CHMeC_{10}H_7)$}$_2Cl_2$] (**14**). The synthesis of **14** was carried out in the same way as **10**: $LiC_5H_4(CHMeC_{10}H_7)$ (**2**) (1.50 g, 6.63 mmol) and $ZrCl_4$ (0.77 g, 3.32 mmol). Yield 0.66 g (33%). ^{1}H NMR (400 MHz, $CDCl_3$; two isomers): 1.76 (6 H), 1.77 (6 H) (d, *J*(H,Me) = 7.2 and 7.2, CH**Me**), 5.25 (q, 4 H, C**H**Me), 5.90 (4 H), 6.32 (8 H), 6.72 (4 H) (m, C_5H_4), 7.04 (4 H), 7.36 (4 H), 7.51 (8 H), 7.71 (4 H), 7.87 (4 H), 8.26 (4 H) (m, $C_{10}H_7$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; two isomers): 21.0, 22.0 (CH**Me**), 31.0, 35.0 (CpC), 109.2, 109.8, 109.9, 110.0, 114.0, 114.5, 115.0, 115.8, 144.0, 144.5 (C_5H_4), 117.0, 117.4, 123.0, 123.2, 125.0, 125.4, 126.0, 126.1, 126.4, 126.9, 128.0, 128.2, 130.0, 130.3, 133.0, 133.7, 139.0, 139.4,

142.0, 142.6 ($C_{10}H_7$). MS-EI, *m/z* (rel.%): 600 (21) [M^+], 381 (70) [$M^+ - C_5H_4CHMeC_{10}H_7$], 341 (100) [$M^+ - C_5H_4CHMeC_{10}H_7 - Cl$]. For $C_{34}H_{30}Cl_2Zr$ (600.7) calculated: 67.98% C, 5.03% H; found: 67.84% C, 4.96% H.

$[Zr\{\eta^5\text{-}C_5H_4(CHMeC_{14}H_9)\}_2Cl_2]$ (**15**). The synthesis of **15** was carried out in the same way as **10**: $LiC_5H_4(CHMeC_{14}H_9)$ (**3**) (1.50 g, 5.43 mmol) and $ZrCl_4$ (0.63 g, 2.71 mmol). Yield 0.74 g (39%). ^{1}H NMR (400 MHz, $CDCl_3$): 2.00 (d, 6 H, *J*(H,Me) = 7.2, CH**Me**), 5.95 (q, 4 H, C**H**Me), 5.61 (2 H), 5.99 (2 H), 6.46 (2 H), 6.90 (2 H) (m, C_5H_4), 7.27 (4 H), 7.39 (4 H), 7.73 (2 H), 8.03 (4 H), 8.40 (2 H), 8.51 (2 H) (m, $C_{14}H_9$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 20.0 (CH**Me**), 33.0 (CpC), 110.0, 113.8, 116.2, 116.9, 143.7 (C_5H_4), 124.5, 124.7, 124.9, 125.3, 126.2, 126.9, 128.0, 128.6, 128.7, 129.0, 129.5, 129.9, 137.5, 140.7 ($C_{14}H_9$). MS-EI, *m/z* (rel.%): 700 (31) [M^+], 523 (20) [$M^+ - C_{14}H_7$], 495 (57) [$M^+ - CHMeC_{14}H_9$], 488 (11) [$M^+ - C_{14}H_9 - Cl$], 352 (100) [$M^+ - C_{14}H_9 - 2 \times Cl$]. For $C_{42}H_{34}Cl_2Zr$ (700.9) calculated: 71.98% C, 4.89% H; found: 71.75% C, 4.86% H.

$[Zr(Me_2Si(\eta^5\text{-}C_5Me_4)\{\eta^5\text{-}C_5H_3(CHMeC_6H_5)\})Cl_2]$ (**16**). THF (50 ml) was added to a solid mixture of $ZrCl_4$ (0.64 g, 2.77 mmol) and $Li_2(Me_2Si(C_5Me_4)\{C_5H_3(CHMeC_6H_5)\})$ (**7**) (1.00 g, 2.77 mmol). The resulting solution was stirred for 15 h. Solvent was removed in vacuo and mixture of toluene (75 ml) and hexane (25 ml) added to the resulting solid. The mixture was filtered and the filtrate concentrated (10 ml) and cooled to –30 °C to yield crystals of the title complex. Yield 0.56 g (40%). ^{1}H NMR (400 MHz, $CDCl_3$; two isomers): 0.74 (3 H), 0.86 (6 H), 0.91 (3 H) (s, $SiMe_2$), 1.55 (3 H), 1.65 (3 H) (d, *J*(H,Me) = 5.2 and 6.8, CH**Me**), 1.87 (3 H), 1.95 (3 H), 1.97 (3 H), 2.00 (3 H), 2.07 (3 H), 2.09 (3 H), 2.14 (6 H) (s, C_5Me_4), 4.38 (1 H), 4.45 (1 H) (q, C**H**Me), 5.23 (1 H), 5.57 (1 H), 5.61 (1 H), 5.72 (1 H), 6.29 (1 H), 6.99 (1 H) (m, C_5H_3), 7.13 (2 H), 7.22 (4 H), 7.28 (4 H) (m, C_6H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; two isomers): 0.1 (2 C), 0.2 (2 C) ($SiMe_2$), 12.3, 12.4, 12.5, 12.6, 15.0, 15.1, 15.1, 15.2 (C_5**Me**$_4$), 21.7, 21.8 (C**Me**), 39.6, 40.4 (CpC), 96.9, 105.0, 106.3, 110.3 (Si-C^1(Cp)), 112.1, 112.9, 113.9, 114.1, 114.3, 127.3, 127.5, 127.6 (C_5H_3), 124.6, 124.7, 125.3, 125.9, 126.0, 126.1, 134.8, 135.1 (C_6H_5), 128.2, 128.3, 136.0, 138.0, 144.1, 144.2, 146.5, 146.9 (C_5Me_4). MS-EI, *m/z* (rel.%): 506 (43) [M^+], 471 (100) [$M^+ - Cl$], 436 (21) [$M^+ - 2 \times Cl$], 331 (29) [$M^+ - 2 \times Cl - CHMeC_6H_5$]. For $C_{24}H_{30}Cl_2SiZr$ (508.7) calculated: 56.67% C, 5.94% H; found: 56.57% C, 5.89% H.

$[Zr(Me_2Si(\eta^5\text{-}C_5Me_4)\{\eta^5\text{-}C_5H_3(CHMeC_{10}H_7)\})Cl_2]$ (**17**). The synthesis of **17** was carried out in the same way as **16**: $ZrCl_4$ (0.57 g, 2.44 mmol) and **8** (1.00 g, 2.44 mmol). Yield 0.52 g (38%). ^{1}H NMR (400 MHz, $CDCl_3$; two isomers): 0.69 (3 H), 0.87 (6 H), 0.95 (3 H) (s, $SiMe_2$), 1.68 (3 H), 1.75 (3 H) (d, *J*(H,Me) = 7.2 and 7.2, CH**Me**) 1.84 (3 H), 1.95 (3 H), 2.02 (3 H), 2.03 (3 H), 2.09 (3 H), 2.17 (3 H), 2.19 (6 H) (s, C_5Me_4), 5.35 (q, 2 H, C**H**Me), 5.21 (1 H), 5.63 (1 H), 5.72 (1 H), 5.79 (1 H), 6.34 (1 H), 7.12 (1 H) (m, C_5H_3), 6.91 (2 H), 7.35 (2 H), 7.51 (4 H), 7.69 (2 H), 7.87 (2 H), 8.36 (2 H) (m, $C_{10}H_7$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; two isomers): –0.4, –0.3, 0.0, 0.2 ($SiMe_2$), 12.2, 12.4, 12.4, 12.6, 14.9, 15.0, 15.1, 15.2 (C_5**Me**$_4$), 21.0, 21.1 (C**Me**), 31.7, 35.5 (CpC), 97.0, 104.5, 106.6, 110.6 (Si-C^1(Cp)), 112.0, 112.9, 130.9, 133.7, 135.2, 135.9, 143.4, 144.5 (C_5H_3), 124.7, 125.4, 125.5, 125.9, 126.0, 126.1, 126.5, 128.6, 128.7, 147.0 ($C_{10}H_7$), 114.9, 123.3, 123.9, 124.4, 126.4, 131.1, 134.5, 136.4 (C_5Me_4). MS-EI, *m/z* (rel.%): 557 (26) [M^+], 521 (100) [$M^+ - Cl$], 485 (19) [$M^+ - 2 \times Cl$], 141 (87) [$M^+ - Zr\{Me_2Si(C_5Me_4)(C_5H_4)\}Cl_2 - Me$]. For $C_{28}H_{32}Cl_2SiZr$ (558.8) calculated: 60.19% C, 5.77% H; found: 60.09% C, 5.66% H.

$[Zr(Me_2Si(\eta^5\text{-}C_5Me_4)\{\eta^5\text{-}C_5H_3(CHMeC_{14}H_9)\})Cl_2]$ (**18**). The synthesis of **18** was carried out in the same way as **16**: $ZrCl_4$ (0.51 g, 2.17 mmol) and **9** (1.00 g, 2.17 mmol). Yield 0.46 g (35%). ^{1}H NMR (400 MHz, $CDCl_3$): 0.88 (3 H), 1.00 (3 H) (s, $SiMe_2$), 1.84 (d, 3 H, *J*(H,Me) =

7.2, CH**Me**), 1.92 (3 H), 2.05 (3 H), 2.07 (3 H), 2.21 (3 H) (s, C_5Me_4), 5.51 (1 H), 5.84 (1 H), 6.15 (1 H) (m, C_5H_3), 6.18 (q, 1 H, C**H**Me), 7.25 (1 H), 7.36 (1 H), 7.48 (2 H), 7.69 (1 H), 8.00 (2 H), 8.38 (1 H), 8.60 (1 H) (m, $C_{14}H_9$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): –0.3, –0.2 ($SiMe_2$), 12.0, 12.7, 15.3, 15.7 ($C_5\mathbf{Me}_4$), 21.0 (C**Me**), 33.8 (CpC), 99.2, 111.6 (Si-C^1(Cp)), 110.5, 114.7, 126.5, 145.9 (C_5H_3), 124.9, 125.2, 125.4, 126.1, 126.7, 127.2, 127.6, 128.1, 129.6, 129.8, 130.7, 131.4, 132.8, 133.0 ($C_{14}H_9$), 124.3, 129.4, 138.4, 141.9 ($\mathbf{C}_5Me_4$). MS-EI, *m/z* (rel.%): 606 (24) [M^+], 571 (93) [M^+ – Cl], 536 (100) [M^+ – 2 × Cl], 331 (17) [M^+ – 2 × Cl – $CHMeC_{14}H_9$]. For $C_{32}H_{34}Cl_2SiZr$ (608.8) calculated: 63.13% C, 5.63% H; found: 63.03% C, 5.49% H.

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