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Synthesis of chiral unbridged zirconocene complexes: Applications in the polymerization of ethylene and propylene

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Abstract

The lithium derivatives of the chiral substituent bearing cyclopentadienyl ligands, Li{C_5H_4(CHRR′)} (R = Pr^i, R′ = Me (**1**); R = Pr^i, R′ = Ph (**2**); R = Bu^t, R′ = Me (**3**); R = Bu^t, R′ = Ph (**4**)), were prepared via the reaction of alkyllithium compounds with the corresponding fulvene reagent. The mixed cyclopentadienyl zirconocene complexes [Zr(η^5-C_5H_5)(η^5-C_5H_4{CHRR′})Cl_2] (R = Pr^i, R′ = Me (**5**); R = Pr^i, R′ = Ph (**6**); R = Bu^t, R′ = Me (**7**); R = Bu^t, R′ = Ph (**8**)) were prepared via the reaction of the lithium precursors **1**–**4** with [Zr(η^5-C_5H_5)Cl_3]. The symmetrical zirconocene complexes, [Zr(η^5-C_5H_4{CHRR′})$_2Cl_2$] (R = Pr^i, R′ = Me (**9**); R = Pr^i, R′ = Ph (**10**); R = Bu^t, R′ = Me (**11**); R = Bu^t, R′ = Ph (**12**)), were synthesized from the reaction of two molar equivalents of **1**–**4** with $ZrCl_4$. When the mono(cyclopentadienyl) complexes [Zr(η^5-C_5H_4{CHRR′})Cl_3] (R = Pr^i, R′ = Me (**17**); R = Pr^i, R′ = Ph (**18**); R = Bu^t, R′ = Me (**19**); R = Bu^t, R′ = Ph (**20**)) were reacted with Li(C_9H_7) the zirconocene derivatives, [Zr(η^5-C_9H_7)(η^5-C_5H_4{CHRR′})Cl_2] (R = Pr^i, R′ = Me (**21**); R = Pr^i, R′ = Ph (**22**); R = Bu^t, R′ = Me (**23**); R = Bu^t, R′ = Ph (**24**)), were obtained. The molecular structure of **11** has been determined by single-crystal X-ray diffraction studies. **5**–**12** and **21**–**24** have been tested as catalysts in the polymerization of ethylene and propylene. Isotactic polypropylene with [mmmm] pentads between 20 and 40% were obtained and their tacticity can be related directly to the structure of the catalyst.

Keywords: Metallocenes; Zirconium; Polymerization; Polyethylene; Polypropylene

1. Introduction

Since the discovery of metallocene/MAO catalytic systems in the polymerization of olefins by Sinn and Kaminsky [1], there has been a rapid development in this field at both academic and industrial level [2].

It is well established that the structural make up of the metallocene complex directly influences the catalytic activity and selectivity in olefin polymerization [2c] and this is made evident by the large number of metallocene complexes with different substituents on the cyclopentadienyl ring that have been reported [3].

Kaminsky and Steiger made the first report of an isospecific unbridged zirconocene polypropylene catalyst [4]. Subsequently Erker et al. have synthesized unbridged zirconocene complexes containing bulky substituents and observed them to be isoselective in the polymerization of propylene at low temperatures [5]. Waymouth et al. have studied similar metallocene systems containing substituted indenyl ligands and reported that the conformational dynamics of the catalysts give conversion between stereoselective and non-stereoselective conformations leading to atactic/isotactic block polymers in the polymerization of propylene [6]. Mixed indenyl–cyclopentadienyl unbridged zirconocene systems have received less attention than their symmetrical counterparts. Alt et al. have synthesized different zirconocene complexes with indenyl and substituted cyclopentadienyl ligands and observed high catalytic activity in the polymerization of ethylene [3c,7]. Recently Huang and coworkers reported the synthesis of a series of similar compounds [8].

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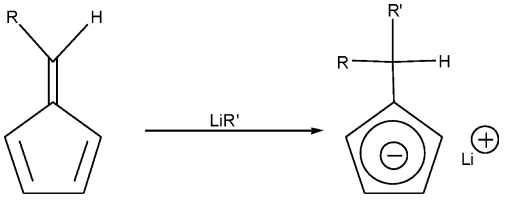
As part of our ongoing studies in the design of olefin polymerization catalysts [9] we present in this paper a series of unbridged bis(cyclopentadienyl) and indenyl–cyclopentadienyl zirconium complexes with chiral substituents, and their catalytic behaviour in the polymerization of ethylene and propylene.

2. Results and discussion

2.1. Synthesis and characterization of cyclopentadienyl precursors

The alkyllithium reagents, LiR′ (R′ = Me, Ph), react with 6-(*iso*-propyl)- or 6-(*tert*-butyl)-fulvene via nucleophilic addition at the exocyclic double bond to give the lithium cyclopentadienyl compounds, Li{C_5H_4(CHRR′)} (R = Pr^i, R′ = Me (**1**); R = Pr^i, R′ = Ph (**2**); R = Bu^t, R′ = Me (**3**); R = Bu^t, R′ = Ph (**4**)) (Eq. (1)) [10].

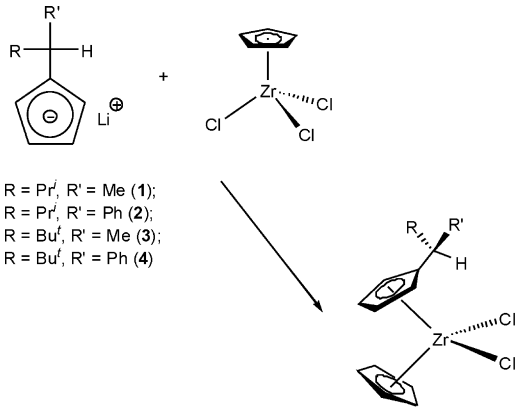


R = Pr^i, R' = Me (**1**);
R = Pr^i, R' = Ph (**2**);
R = Bu^t, R' = Me (**3**);
R = Bu^t, R' = Ph (**4**) (1)

1–4 were characterized by ^{1}H and ^{13}C NMR spectroscopy (see Section 4). Two multiplets were observed between 5.5 and 5.7 ppm in the ^{1}H NMR spectra of **1–4** and assigned to the cyclopentadienyl ring protons. In **1** and **2**, two doublets and a multiplet were observed for the two diastereotopic methyl groups and proton of the *iso*-propyl fragment, respectively. For **1**, a multiplet at 2.67 ppm and a doublet at 1.33 ppm, were observed, corresponding to the proton and methyl group bonded to the stereocentre carbon atom of the cyclopentadienyl substituent, respectively. For **2**, the proton bonded to the stereocentre carbon atom gave a doublet signal at 3.30 ppm. Three multiplets (between 7.0 and 7.3 ppm) were recorded for the phenyl moiety. The *tert*-butyl signal in **3** and **4** was observed in the ^{1}H NMR spectra as a singlet at 0.9 ppm. For **3**, a quartet, at 2.53 ppm, and a doublet, at 1.28 ppm, were observed corresponding to the proton and methyl group bonded to the stereocentre carbon atom of the cyclopentadienyl substituent, respectively. For **4**, the proton bonded to the stereocentre carbon atom gave a singlet signal at 3.58 ppm and three multiplets (between 7.0 and 7.4 ppm) which were assigned to the phenyl moiety. The ^{13}C{^{1}H} NMR spectra for **1–4** showed the expected signals (stereocentre carbon atom, one signal at ca. 42.0 ppm for **1** and 46.3 ppm for **3** and 57.6 ppm for **2** and 60.9 ppm for **4**; methyl, one signal at ca. 19 ppm; *iso*-propyl, three signals at ca. 20, 21 and 36 ppm; *tert*-butyl, two signals at ca. 29 and 35 ppm; phenyl, four signals at ca. 125, 128, 129 and 150 ppm; cyclopentadienyl, three signals at ca. 101, 103, and 124 ppm).

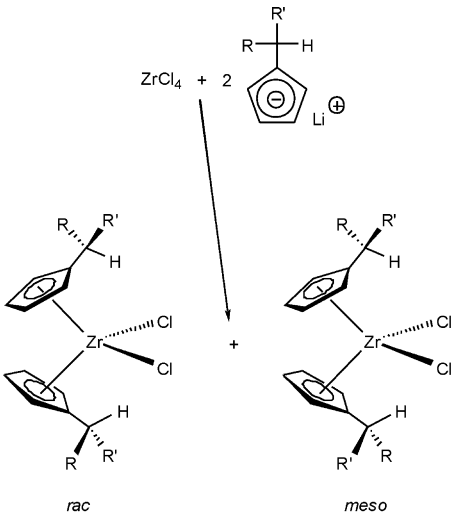
2.2. Synthesis and characterization of zirconocene complexes

The reaction of **1–4** with [Zr(η^5-C_5H_5)Cl_3] yielded the zirconocene compounds [Zr(η^5-C_5H_5)(η^5-C_5H_4{CHRR′})Cl_2] (R = Pr^i, R′ = Me (**5**); R = Pr^i, R′ = Ph (**6**); R = Bu^t, R′ = Me (**7**); R = Bu^t, R′ = Ph (**8**)) (Eq. (2)) which were isolated as white crystalline solids and characterized spectroscopically. The pair of α, and likewise the pair of β protons, of the cyclopentadienyl unit of **5–8** are diastereotopic due to the presence of the chiral substituent and thus four multiplets, between 5.9 and 7.0 ppm, were observed in the ^{1}H NMR spectra. In addition, one singlet at ca. 6.0 ppm was assigned to the unsubstituted cyclopentadienyl ring. The signals for the corresponding cyclopentadienyl substituent were observed with similar chemical shifts and identical spectral patterns as those recorded in the spectra of **1–4**. The ^{13}C{^{1}H} NMR spectra of **5–8** showed in all cases five signals between 100 and 145 ppm for the substituted C_5 ring and one signal at ca. 115 ppm corresponding to the unsubstituted cyclopentadienyl ligand. The signals for the different cyclopentadienyl substituents are similar to those described for the compounds **1–4**.



R = Pr^i, R' = Me (**5**);
R = Pr^i, R' = Ph (**6**);
R = Bu^t, R' = Me (**7**);
R = Bu^t, R' = Ph (**8**) (2)

The metallocene complexes, [Zr(η^5-C_5H_4{CHRR′})$_2Cl_2$] (R = Pr^i, R′ = Me (**9**); R = Pr^i, R′ = Ph (**10**); R = Bu^t, R′ = Me (**11**); R = Bu^t, R′ = Ph (**12**)), were prepared by the reaction of two molar equivalents of **1–4** with $ZrCl_4$ (Eq. (3)). **9–12** were isolated as white crystalline solids and characterized spectroscopically. The existence of two stereocentres in the molecules leads to formation of the *rac*- and *meso*-isomers. NMR spectroscopy confirmed the presence of the two diastereomers in the final product in a 1:1 ratio. Our attempts to separate them by fractional recrystallization proved to be unsuccessful. The ^{1}H NMR spectra of **9–12** are similar in nature to those recorded for the parent lithium derivatives **1–4**. However, **9–12** differ in the fact that the ring protons are more sensitive to the chiral environment of the alkyl substituent giving four multiplets for each isomer in the ^{1}H NMR spectra compared with two signals observed in **1–4**.



R = Pr^i, R' = Me (**9**);
R = Pr^i, R' = Ph (**10**);
R = Bu^t, R' = Me (**11**);
R = Bu^t, R' = Ph (**12**) (3)

Although we were unable to satisfactorily separate the *meso*- and *rac*-isomers of **9**–**12** we were, however, able to isolate, by crystallization from toluene, a small amount of crystals of **11**, which proved to be, by single-crystal X-ray diffraction analysis, the *meso*-isomer. The molecular structure of **11** and atomic numbering scheme are shown in Fig. 1. Selected bond lengths and angles are given in Table 1.

The molecular structure of **11** revealed that both C_5 rings are bound to the metal in an η^5 mode. The usual bent metallocene confirmation was observed with the geometry around the metal atom being pseudo-tetrahedral as defined by the two chlorine atoms and the two cyclopentadienyl moieties. The centroids of the cyclopentadienyl rings form an angle with the zirconium atom of 128.9° which is typical for zirconocene dichloride complexes.

The cyclopentadienyl substituents are positioned, with respect to each other, in such a way as to give a near C_2 symmetrical arrangement. In addition, the *tert*-butyl groups are orientated away (outwards) from, and the methyl groups towards (inwards), the zirconium atom. This type of arrangement has previously been reported by Erker et al. in a similar metallocene complex and was attributed to steric factors [5a]. The stereocentre carbon atoms (C(6) and C(17)) of the alkyl substituent are located only 0.12(1)° and 0.15(1)° out of the plane defined by the cyclopentadienyl unit. The structure corresponds to that of the *meso*-isomer with the stereocentre carbon atoms (C(6) and C(17)) bonded to the two different cyclopentadienyl rings having alternate absolute configurations. Selected structural data of **11** can be compared with similar zirconocene complexes using Table 2.

The reaction of **1**–**4** with [Zr(η^5-C_9H_7)Cl_3] was carried out in order to obtain the mixed cyclopentadienyl–indenyl zirconocene complexes. However this synthetic route led to an inseparable mixture of products containing, as well as the desired product, the bis(cyclopentadienyl) and bis(indenyl) zirconium derivatives.

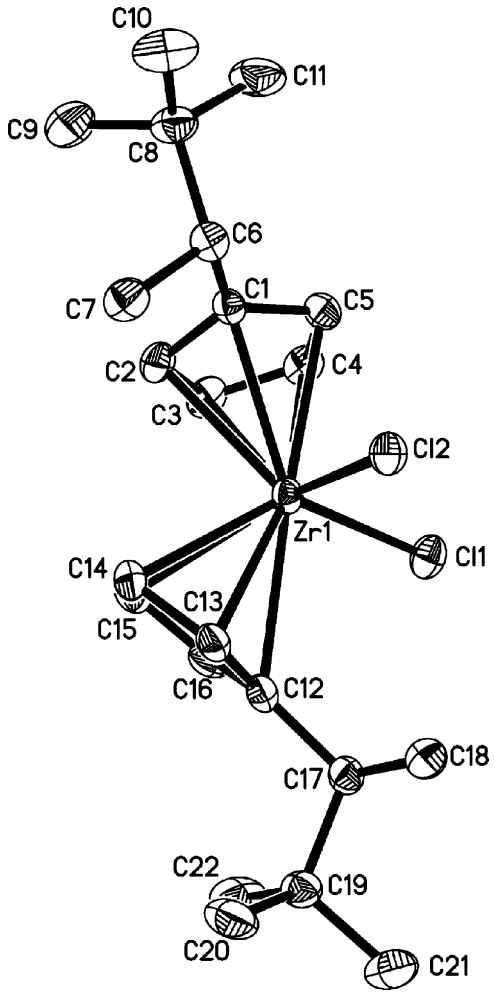


Fig. 1. Molecular structure and atom-labeling scheme for *meso*-[Zr(η^5-C_5H_4{CHBu^{t}Me}$)_2Cl_2$] (**11**), with thermal ellipsoids at 20% probability.

Therefore the synthetic strategy to obtain the mixed ring compound was changed to that of the reaction of the mono(cyclopentadienyl) zirconium trichloride with indenyllithium.

In order to prepare [Zr(η^5-C_5H_4{CHRR′})Cl_3], the trimethylsilyl cyclopentadienyl precursors C_5H_4(CHRR′)($SiMe_3$) (R = Pr^i, R′ = Me (**13**); R = Pr^i, R′ = Ph (**14**); R = Bu^t, R′ = Me (**15**); R = Bu^t, R′ = Ph (**16**)) were synthesized by the reaction of one equivalent of the corresponding lithium derivative **1**–**4** and one equivalent of $SiMe_3Cl$ (Eq. (4)). **13**–**16** were isolated as isomeric mixtures. The predominant isomer was characterized by ^{1}H NMR spectroscopy.

R = Pr^i, R' = Me (**1**);
R = Pr^i, R' = Ph (**2**);
R = Bu^t, R' = Me (**3**);
R = Bu^t, R' = Ph (**4**)

R = Pr^i, R' = Me (**13**);
R = Pr^i, R' = Ph (**14**);
R = Bu^t, R' = Me (**15**);
R = Bu^t, R' = Ph (**16**) (4)

Table 1
Selected bond lengths (Å) and angles (°) for **11**

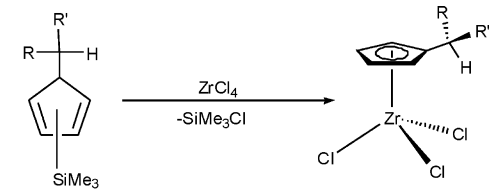
Zr(1)–Cent(1)	2.212
Zr(1)–Cent(2)	2.209
av Zr(1)–C[C(1)–C(5)][a]	2.513(6)
av Zr(1)–C[C(12)–C(16)][a]	2.510(6)
Zr(1)–Cl(1)	2.445(2)
Zr(1)–Cl(2)	2.449(1)
C(1)–C(6)	1.508(7)
C(12)–C(17)	1.503(7)
C(6)–C(7)	1.538(8)
C(6)–C(8)	1.560(8)
C(17)–C(18)	1.544(8)
C(17)–C(19)	1.561(8)
Cent(1)–Zr(1)–Cent(2)	128.9
Cl(1)–Zr(1)–Cent(1)	107.0
Cl(1)–Zr(1)–Cent(2)	105.1
Cl(2)–Zr(1)–Cent(1)	105.6
Cl(2)–Zr(1)–Cent(2)	108.5
Cl(1)–Zr(1)–Cl(2)	97.37(6)
C(1)–C(6)–C(7)	110.6(5)
C(1)–C(6)–C(8)	112.0(5)
C(7)–C(6)–C(8)	112.2(5)
C(12)–C(17)–C(18)	110.5(5)
C(12)–C(17)–C(19)	112.7(5)
C(18)–C(17)–C(19)	112.7(5)
C(6)–C(1)–Cent(1)	175.8
C(17)–C(12)–Cent(2)	174.9

Cent(1) and Cent(2) are the centroids of C(1)–C(5) and C(12)–C(16), respectively.

[a] Average bond distance between Zr(1) and the carbon atoms of the C_5 ring of the corresponding cyclopentadienyl moiety.

The mono(cyclopentadienyl) trichloride complexes, [Zr(η^5-C_5H_4{CHRR′})Cl_3] (R = Pr^i, R′ = Me (**17**); R = Pr^i, R′ = Ph (**18**); R = Bu^t, R′ = Me (**19**); R = Bu^t, R′ = Ph (**20**)) were then prepared by the reaction of **13**–**16** with $ZrCl_4$ in toluene and the subsequent elimination of $SiMe_3Cl$ (Eq. (5)). **17**–**20** have been characterized by ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectra of **17**–**20** four multiplets between 6.0 and 7.0 ppm were observed and assigned to the cyclopentadienyl protons. In **17** and **18**, two doublets for the two diastereotopic methyl groups and a multiplet for the proton of the *iso*-propyl fragment, were observed. For **17**, a multiplet at 3.23 ppm and a doublet at 1.32 ppm, were observed, corresponding, respectively, to the proton and methyl group bonded to the stereocentre carbon atom of the cyclopentadienyl substituent. For **18**, the proton bonded to the stereocentre carbon atom gave a doublet signal at 4.55 ppm and three multiplets (between 7.0 and 7.3 ppm) were recorded for the phenyl moiety. The *tert*-butyl signal in **19** and **20** was observed in the ^{1}H NMR spectra as a singlet at ca. 0.9 ppm. For **19**, a quartet at 2.96 ppm and a doublet at 1.30 ppm, were observed and assigned, respectively, to the proton and methyl group bonded to the stereocentre carbon atom of cyclopentadienyl substituent. For **20**, the proton bonded to the stereocentre carbon atom gave a singlet signal at 4.08 ppm and the phenyl moiety three multiplets (between 7.0 and 7.3 ppm).

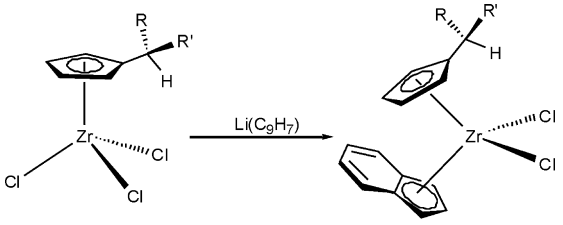
The ^{13}C{^{1}H} NMR spectra for **17**–**20** showed one signal at ca. 45 ppm for the stereocentre carbon atom; one signal for the methyl group at ca. 14 ppm in **17** and **19**; for the *iso*-propyl group three signals at ca. 18, 20 and 34 ppm in **17** and **18**; two signals at ca. 28 and 34 ppm for the *tert*-butyl in **19** and **20**; for the phenyl group in **18** and **20**, four signals between 125 and 135 ppm; five signals between 115 and 145 ppm for the cyclopentadienyl ring carbon atoms.



R = Pr^i, R' = Me (**13**); R = Pr^i, R' = Ph (**14**); R = Bu^t, R' = Me (**15**); R = Bu^t, R' = Ph (**16**)

R = Pr^i, R' = Me (**17**); R = Pr^i, R' = Ph (**18**); R = Bu^t, R' = Me (**19**); R = Bu^t, R' = Ph (**20**) (5)

The cyclopentadienyl–indenyl mixed ring metallocene complexes, [Zr(η^5-C_9H_7)(η^5-C_5H_4(CHRR′))Cl_2] (R = Pr^i, R′ = Me (**21**); R = Pr^i, R′ = Ph (**22**); R = Bu^t, R′ = Me (**23**); R = Bu^t, R′ = Ph (**24**)), were prepared by the reaction of Li(C_9H_7) with **17**–**20**, respectively (Eq. (6)). **21**–**24** were isolated as crystalline solids and characterized spectroscopically. The ^{1}H NMR spectra of **21**–**24** are similar to those observed for **17**–**20**, with in addition four multiplets, between 5.0 and 8.0 ppm, being observed and assigned to the indenyl ligand protons. The ^{13}C{^{1}H} NMR spectra of **21**–**24** gave five signals between ca. 100–130 ppm corresponding to the indenyl ligand carbon atoms.



R = Pr^i, R' = Me (**17**); R = Pr^i, R' = Ph (**18**); R = Bu^t, R' = Me (**19**); R = Bu^t, R' = Ph (**20**)

R = Pr^i, R' = Me (**21**); R = Pr^i, R' = Ph (**22**); R = Bu^t, R' = Me (**23**); R = Bu^t, R' = Ph (**24**) (6)

2.3. Polymerization of ethylene

The polymerization of ethylene using the zirconocene derivatives, **5**–**12** and **21**–**24**, as catalyst (in the case of **9**–**12** the 1:1 *rac*/*meso* isomer mixture) with a MAO–metal catalyst ratio of 1000:1, has been carried out. The polymerization experiments were conducted at 20 °C and at an olefin pressure of 2 bar during 30 min. The polymerization was also carried out with the reference compound [Zr(η^5-C_5H_5)$_2Cl_2$], under the same experimental conditions. The catalytic activities and polymer molecular weight and distribution values are given in Table 3.

The catalytic activities recorded for all the complexes, with the exception of **9** and **11**, are lower than that of the reference compound [Zr(η^5-C_5H_5)$_2Cl_2$]. In all cases, markedly lower activities were observed for the phenyl substituted compounds (**6**, **8**, **10**, **12**, **22** and **24**) in comparison with the methyl

Table 2
Selected structural data of some zirconocene complexes[a]

Complex	Zr–Cp (Å)[b]	Zr–Cl (Å)	Cp–Zr–Cp (°)	Cl–Zr–Cl(°)	Reference
[Zr(η^5-C_5H_5)$_2$Cl$_2$][c]	2.20(1) 2.20(1) 2.21(1) 2.20(1)	2.44 2.45 2.45 2.45	129.5(1) 129.1(1)	97.0(1) 97.1(1)	[11]
[Zr(η^5-$C_5H_4Pr^i$)$_2$Cl$_2$]	2.207	2.448(3)		96(1)	[12]
[Zr(η^5-$C_5H_4Bu^t$)$_2$Cl$_2$]	2.217	2.457(1)	128.6	94.2(6)	[13]
[Zr(η^5-C_5H_4Ph)$_2$Cl$_2$]	2.22(1)	2.45	129.3(2)	95.2(1)	[14]
meso-[Zr(η^5-C_5H_4{CHBu^{t}Me})$_2$Cl$_2$]	2.212 2.209	2.445(2) 2.449(1)	128.9	97.37(6)	This work
rac-[Zr(η^5-C_5H_4{CHPhMe})$_2$Cl$_2$]		2.462(2) 2.456(2)		96.6(1)	[5a]
[Zr(η^5-C_5H_4{CH_2Ph})$_2$Cl$_2$]	2.16	2.461(6)	126	94.4(1)	[15]
[Zr(η^5-C_5H_4{$CH_2CH_2PPh_2$})$_2$Cl$_2$]	2.205	2.4448(6)	130.9	99.69(3)	[16]
rac-[Zr(η^5-C_5H_4{$CHMePPh_2$})$_2$Cl$_2$]		2.441(1)	130.6	98.85(6)	[17]
rac-[Zr(η^5-C_5H_4{CH*n*BuNMe$_2$})$_2$Cl$_2$]		2.4529(5)	131.7	97.70(3)	[18]
[Zr(η^5-C_5H_4{C(=CH_2)C_6H_3Me-2})$_2$Cl$_2$]		2.442(1) 2.440(1)		96.5(1)	[19]
[Zr(η^5-C_5H_4{CMe_2CHMe_2})$_2$Cl$_2$]	2.223	2.4546(6)	129.4	93.95(3)	[20]
[Zr(η^5-C_5H_4{C(C_5H_{10})Me})$_2$Cl$_2$]	2.224(1)	2.457(1)		93.5(1)	[21]
rac-[Zr(η^5-C_5H_4{CH(Me)CH_2OMe})$_2$Cl$_2$][d]	2.196 2.180 2.200 2.214 2.190 2.198	2.448(7) 2.470(5) 2.440(7) 2.473(6) 2.459(4) 2.464(8)	133.7 131.5 130.1	94.2(2) 95.1(2) 94.2(2)	[22]
[Zr(η^5-C_5H_4{methylestratrienyl})$_2$Cl$_2$]	2.2		128.7	95.2	[23]
[Zr(η^5-C_5H_4{C(=CH_2)C_6H_{11}})$_2$Cl$_2$]	2.215(1)	2.437(1)	130.1	98.0(1)	[5b]
[Zr(η^5-C_5H_4{C(CH_2)$_5CH_2CH_2CHMe_2$})$_2$Cl$_2$]	2.224(1)	2.460(1)	130.1(1)	93.7(1)	[24]
[Zr(η^5-C_5H_4{$SiMe_3$})$_2$Cl$_2$]	2.21	2.49	129.1	94	[25]
[Zr(η^5-C_5H_4{$SiPh_2$Me})$_2$Cl$_2$]	2.210(2) 2.224(2)	2.4253(9) 2.4337(8)	130.2(2)	95.90(3)	[26]
[Zr(η^5-C_5H_4{$SiMe_2CH_2C_6F_5$})$_2$Cl$_2$]	2.209(1) 2.216(1)	2.4571(6) 2.4379(6)	127.94(4)	99.48(2)	[27]
[Zr(η^5-C_5H_4{$SiMe_2CH_2CH_2C_6F_{13}$})$_2$Cl$_2$]	2.199(1)	2.4524(7)	129.61(5)	96.50(3)	[27]
[Zr(η^5-C_5H_4{$SiMe_2$N($SiMe_3$)$_2$})$_2$Cl$_2$][c]	2.2 2.2			105.7 99.5	[28]

[a] Blank spaces in this table indicate that this data were not reported; ESD values are given when reported.
[b] Cp refers to the C_5H_4R moiety.
[c] There are two independent molecules in the asymmetric cell.
[d] There are three independent molecules in the asymmetric cell.

substituted analogues (**5**, **7**, **9**, **11**, **21** and **23**). This observation can be explained by the more than likely intramolecular coordination of the phenyl moiety to the zirconium active centre during the polymerization [29].

The activities for the *iso*-propyl substituted compounds (**5**, **6**, **9** and **10**), were higher than their *tert*-butyl analogues (**7**, **8**, **11** and **12**). In the case of the indenyl derivatives, **21**–**24**, this trend was reversed. A correlation in the catalytic activities between the different metallocene systems (cp–cp′ = **5**–**8**, cp'_2 = **9**–**12**, and ind–cp′ = **21**–**24**) is not easy. The catalysts with the methyl substituent (**5** and **7**) gave higher activities (approximately triple) for the cp'_2 system compared with those for both the cp–cp′ and ind–cp′ metallocene systems. For the phenyl substituted catalysts little difference was observed in the activities between the different metallocene systems.

The polymer molecular weights are, in all the cases, higher than for the reference complex and are between 300,000 and 600,000, except for **7** and **23** which give values of approximately 1,200,000.

The complexes **5**–**12** and **21**–**24** produced broad polymer molecular weight distributions with polydispersity values between 4 and 9. This phenomenon has previously been explained considering the rotation of the C_5 ring to be slower than the propagation of the polymer chain creating different

Table 3
Ethylene polymerization results for **5–12**, **21–24** and [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$][a]

Catalyst	Activity[b]	M_w	M_w/M_n
[Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$]	23,300	169,000	2.3
[Zr(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4${CHPr^{i}Me})Cl$_2$] (**5**)	16,747	331,000	5.0
[Zr(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4${CHPr^{i}Ph})Cl$_2$] (**6**)	8,707	421,000	4.2
[Zr(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4${CHBu^{t}Me})Cl$_2$] (**7**)	13,233	1,212,000	7.5
[Zr(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4${CHBu^{t}Ph})Cl$_2$] (**8**)	4,820	3,83,000	4.2
[Zr(η^5-C$_5$H$_4${CHPr^{i}Me})$_2$Cl$_2$] (**9**)	40,747	4,87,000	7.9
[Zr(η^5-C$_5$H$_4${CHPr^{i}Ph})$_2$Cl$_2$] (**10**)	7,333	5,42,000	8.1
[Zr(η^5-C$_5$H$_4${CHBu^{t}Me})$_2$Cl$_2$] (**11**)	34,960	4,22,000	7.1
[Zr(η^5-C$_5$H$_4${CHBu^{t}Ph})$_2$Cl$_2$] (**12**)	3,347	609,000	8.8
[Zr(η^5-C$_9$H$_7$)(η^5-C$_5$H$_4${CHPr^{i}Me})Cl$_2$] (**21**)	12,033	3,71,000	4.1
[Zr(η^5-C$_9$H$_7$)(η^5-C$_5$H$_4${CHPr^{i}Ph})Cl$_2$] (**22**)	4,033	494,000	4.1
[Zr(η^5-C$_9$H$_7$)(η^5-C$_5$H$_4${CHBu^{t}Me})Cl$_2$] (**23**)	13,347	1,149,000	6.8
[Zr(η^5-C$_9$H$_7$)(η^5-C$_5$H$_4${CHBu^{t}Ph})Cl$_2$] (**24**)	8,607	458,000	4.2

[a] At 20 °C, 2 bar monomer pressure, 200 mL toluene, [Al] = 3 × 10^{-2} mol L^{-1}, [Zr] = 3 × 10^{-5} mol L^{-1}, t_{Pol} = 30 min.
[b] In kg Pol (mol Zr h)$^{-1}$.

rotamers of the catalyst which act as distinct active centres [8,30].

2.4. Polymerization of propylene

The polymerization of propylene using the zirconocene derivatives, **9–12** and **21–24**, as catalyst (in the case of **9–12** as the 1:1 *rac/meso* isomer mixture) with a MAO cocatalyst–metal catalyst ratio of 3000:1 has been carried out. The polymerization experiments were conducted at 0 °C and at an olefin pressure of 2.5 bar during 60 min. The polymerization was also carried out with the reference compound [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$] under the same experimental conditions. The catalytic activities, polymer molecular weight and distribution values and tacticity are given in Table 4. Pentad distribution percentages are shown in Table 5.

The catalytic activities of the complexes **9–12** are higher than that recorded for the reference compound. Lower activities were observed for the phenyl substituted compounds (**10**, **12**, **22** and **24**) in comparison with their methyl substituted analogues (**9**, **11**, **21** and **23**). The cp'_2 system (**9–12**) catalysts gave higher activities (approximately double) compared with the ind–cp′ metallocene system catalysts (**21–24**).

The polymer molecular weights are in all the cases much higher than that obtained for the reference complex and are in the order of 50,000. Catalyst **23** produced polypropylene with the highest molecular weight, approximately 100,000.

The polydispersities of the polypropylenes obtained with the metallocene catalysts are also of a high nature and again can be explained by different rotamers of the same complex acting as active centres in the polymerization [8,30].

The isotacticity of the polymers was measured by the pentad method using ^{13}C NMR spectroscopy. The [mmmm] pentad measured for the polypropylene obtained with the catalysts **9–12** and **21–24** were between 20 and 40% and are comparable with those previously reported for similar unbridged metallocene complexes [5a,b].

Considering **9–12** as conformationally dynamic systems in which the two extremes are described when the cyclopentadienyl substituents are eclipsed or orientated in opposite directions, then the two possible rotamers should produce either non-selective (atactic) or isoselective coordination of the monomer (Fig. 2a). The greater steric imposition of the substituents will make the *syn* conformation less stable than the *anti* conformations and thus make the catalyst more isoselective. Indeed the phenyl containing complexes **10** and

Table 4
Propylene polymerization results for **9–12**, **21–24** and [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$][a]

Catalyst	Activity[b]	M_w	M_w/M_n	[mmmm] (%)
[Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$]	121	2,000	1.8	4.0
[Zr(η^5-C$_5$H$_4${CHPr^{i}Me})$_2$Cl$_2$] (**9**)	211	49,000	7.4	20.4
[Zr(η^5-C$_5$H$_4${CHPr^{i}Ph})$_2$Cl$_2$] (**10**)	162	45,000	10.1	36.5
[Zr(η^5-C$_5$H$_4${CHBu^{t}Me})$_2$Cl$_2$] (**11**)	264	55,000	7.0	20.6
[Zr(η^5-C$_5$H$_4${CHBu^{t}Ph})$_2$Cl$_2$] (**12**)	132	51,000	9.2	37.4
[Zr(η^5-C$_9$H$_7$)(η^5-C$_5$H$_4${CHPr^{i}Me})Cl$_2$] (**21**)	111	66,000	7.3	19.3
[Zr(η^5-C$_9$H$_7$)(η^5-C$_5$H$_4${CHPr^{i}Ph})Cl$_2$] (**22**)	67	52,000	12.9	40.7
[Zr(η^5-C$_9$H$_7$)(η^5-C$_5$H$_4${CHBu^{t}Me})Cl$_2$] (**23**)	102	102,000	4.9	16.7
[Zr(η^5-C$_9$H$_7$)(η^5-C$_5$H$_4${CHBu^{t}Ph})Cl$_2$] (**24**)	97	26,000	9.1	28.1

[a] At 0 °C, 2.5 bar monomer pressure, 200 mL toluene, [Al] = 9 × 10^{-2} mol L^{-1}, [Zr] = 3 × 10^{-5} mol L^{-1}, t_{Pol} = 60 min.
[b] In kg Pol (mol Zr h)$^{-1}$.

Table 5
Pentad distribution, calculated from $^{13}C\{^1H\}$ NMR spectroscopy, for polypropylene synthesized from **9**–**12** and **21**–**24**

Catalyst	[mmmm] (%)	[mmmr] (%)	[rmmr] (%)	[mmrr] (%)	[mmrm] + [rmrr] (%)	[mrmr] (%)	[rrrr] (%)	[mrrr] (%)	[mrrm] (%)
[Zr(η^5-C_5H_4{CHPr^{i}Me})$_2$Cl$_2$] (**9**)	20.4	16.5	5.8	10.7	18.3	12.2	4.0	5.6	6.5
[Zr(η^5-C_5H_4{CHPr^{i}Ph})$_2$Cl$_2$] (**10**)	36.5	15.8	3.7	11.4	14.1	7.4	2.3	3.4	5.4
[Zr(η^5-C_5H_4{CHBu^{t}Me})$_2$Cl$_2$] (**11**)	20.6	16.8	5.5	11.1	20.2	10.4	3.6	4.7	7.1
[Zr(η^5-C_5H_4{CHBu^{t}Ph})$_2$Cl$_2$] (**12**)	37.4	15.5	3.9	11.3	13.8	7.3	2.5	3.3	5.0
[Zr(η^5-C_9H_7)(η^5-C_5H_4{CHPr^{i}Me})Cl$_2$] (**21**)	19.3	17.1	5.3	10.4	20.7	12.0	3.2	6.1	5.9
[Zr(η^5-C_9H_7)(η^5-C_5H_4{CHPr^{i}Ph})Cl$_2$] (**22**)	40.7	15.4	3.5	10.1	13.2	7.9	1.2	2.9	5.1
[Zr(η^5-C_9H_7)(η^5-C_5H_4{CHBu^{t}Me})Cl$_2$] (**23**)	16.7	15.8	5.5	14.2	18.4	10.7	3.9	8.1	6.7
[Zr(η^5-C_9H_7)(η^5-C_5H_4{CHBu^{t}Ph})Cl$_2$] (**24**)	28.1	17.5	4.3	9.2	18.3	9.4	2.8	4.7	5.7

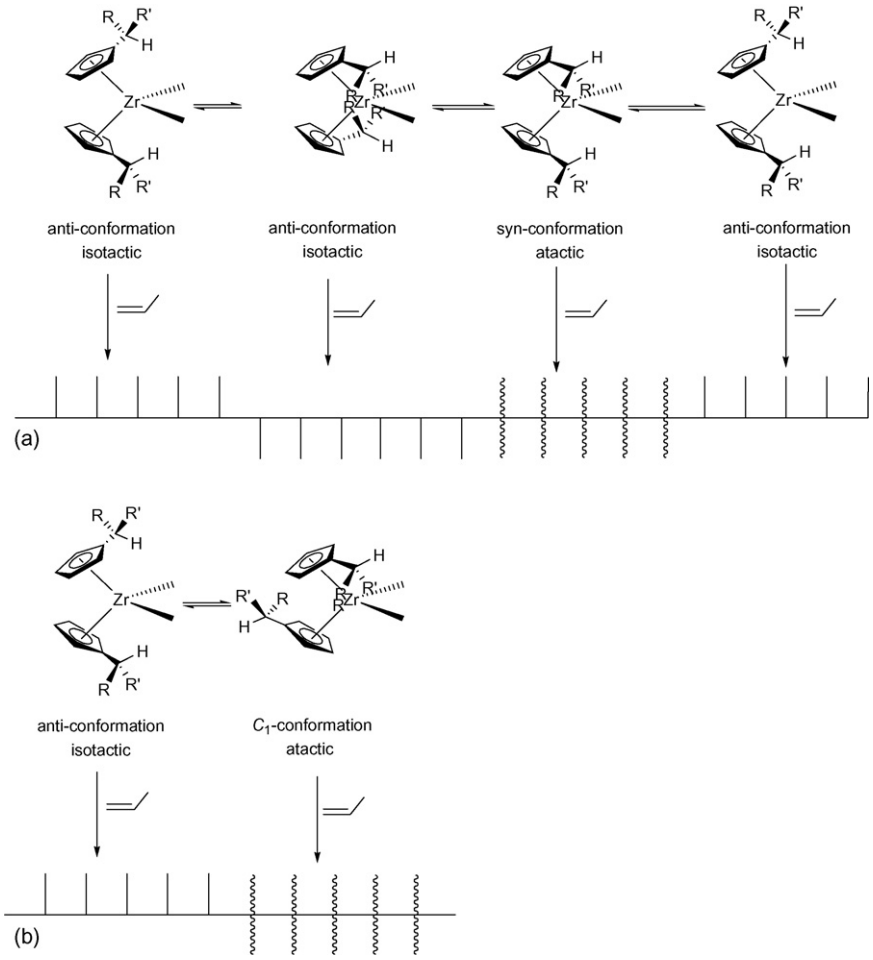


Fig. 2. Possible conformational dynamics in **9**–**12**.

12 give higher [mmmm] values than the methyl substituted analogues **9** and **11**. Analogous behaviour was also observed for the indenyl–cyclopentadienyl complexes **21**–**24**. Interconversion between the stereoselective *anti* and the non-stereoselective *syn* conformations has previously been proposed, by Waymouth et al., as a means of generating blocks of atactic and isotactic stereosequences in a single polymer chain [5]. However, Busico et al. have recently put in doubt this reasoning. They propose that the isoselective centre does not invert its configuration and the non-stereoselective centre is not the *syn* conformation but instead a C_1 symmetric species (Fig. 2b) [31].

3. Conclusions

New zirconocene complexes incorporating chiral alkyl substituents in different metallocene systems have been prepared and structurally characterized. The complexes are active as catalysts in the polymerization of ethylene and propylene. Catalytic activities in the polymerization were shown to be directly related to the metallocene system and the substituents present in the zirconocene catalyst. The stereoselective polymerization of propylene gave polymers with low to moderate isotacticity which again can be directly related to the cyclopentadienyl substituent. Conformational dynamics in the unbridged metallocene

complexes allows the interconversion between stereoselective and non-stereoselective rotamers thus forming stereoblocks of isotactic and atactic polypropylene. The rate of this conversion and the stability of the respective rotamers depend directly on the steric impositions of the alkyl substituent, which translates in higher tacticities being obtained for the bulkier substituents.

The work presented in this paper should allow the rational election of substituents in unbridged zirconocene complexes to permit, in the polymerization of olefins, an increase in catalytic activity and/or modulate stereoselectivity.

4. Experimental

4.1. General procedures

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

$LiBu^n$ (1.6 M in hexane), LiMe (1.6 M in Et_2O), MAO, indene, $SiMe_3Cl$, and $ZrCl_4$, were purchased from Aldrich and used directly. LiPh (2.0 M in $Bu^n{}_2O$) was purchased from Acros Organics and used without further purification. 6-*iso*-Propyl-fulvene [32], 6-*tert*-butyl-fulvene [32], $Li(C_9H_7)$ [33] and $[Zr(\eta^5\text{-}C_5H_5)Cl_3]$ [34] were prepared as previously reported.

^1H and $^{13}C\{^1H\}$ NMR spectra 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 samples dissolved in 1,2,4-trichlorobenzene and C_6D_6 (1:1).

4.2. Preparation of compounds

4.2.1. $Li\{C_5H_4(CHPr^iMe)\}$ (1)

LiMe (1.6 M in Et_2O) (13.0 mL, 20.80 mmol) was added dropwise to a solution of 6-*iso*-propyl-fulvene (2.50 g, 20.80 mmol) in Et_2O (50 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. Solvent was removed in vacuo to give a white solid which was washed with hexane (2× 50 mL) and dried under vacuum to yield a free flowing white solid of the title complex (2.78 g, 94%). ^1H NMR (400 MHz, d_8-THF): δ 1.00 (3H), 1.01 (3H) (d, $CHMe_2$), 1.33 (d, 3H, *Me*), 1.90 (m, 1H, $CHMe_2$), 2.67 (m, 1H, $CHPr^iMe$), 5.74 (2H), 5.78 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, d_8-THF): δ 19.9 (C*Me*), 20.7, 21.5, 36.3 (Pr^i), 42.0 (Cp*C*), 101.7, 102.4, 124.8 (C_5H_4). Anal. Calc. for $C_{10}H_{15}Li$: C, 84.48; H, 10.63. Found C, 84.01; H, 10.60%.

4.2.2. $Li\{C_5H_4(CHPr^iPh)\}$ (2)

The synthesis of **2** was carried out in an identical manner to **1**. LiPh (2.0 M in $Bu^n{}_2O$) (10.4 mL, 20.80 mmol) and 6-*iso*-propyl-fulvene (2.50 g, 20.80 mmol). Yield 3.86 g, 91%. ^1H NMR (400 MHz, d_8-THF): δ 0.73 (3H), 0.88 (3H) (d, $CHMe_2$) 2.23 (m, 1H, $CHMe_2$), 3.30 (d, 1H, $CHPr^iPh$), 5.55 (2H), 5.61 (2H) (m, C_5H_4), 6.98 (1H), 7.15 (2H), 7.33 (2H) (m, *Ph*). $^{13}C\{^1H\}$ NMR (100 MHz, d_8-THF): δ 22.8, 22.9, 35.7 (Pr^i), 57.6 (Cp*C*), 102.1, 102.9, 123.9 (C_5H_4), 125.0, 128.3, 128.8, 150.9 (*Ph*). Anal. Calc. for $C_{15}H_{17}Li$: C, 88.21; H, 8.39. Found C, 88.10; H, 8.33%.

4.2.3. $Li\{C_5H_4(CHBu^tMe)\}$ (3)

The synthesis of **3** was carried out in an identical manner to **1**. LiMe (1.6 M in Et_2O) (11.6 mL, 18.63 mmol) and 6-*tert*-butyl-fulvene (2.50 g, 18.63 mmol). Yield 2.79 g, 96%. ^1H NMR (400 MHz, d_8-THF): δ 0.94 (s, 9H, Bu^t), 1.28 (d, 3H, *Me*), 2.53 (q, 1H, $CHBu^tMe$), 5.59 (2H), 5.60 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, d_8-THF): δ 18.6 (*Me*), 28.9, 34.8 (Bu^t), 46.3 (Cp*C*), 101.1, 103.6, 123.4 (C_5H_4). Anal. Calc. for $C_{11}H_{17}Li$: C, 84.59; H, 10.97. Found C, 84.32; H, 10.96%.

4.2.4. $Li\{C_5H_4(CHBu^tPh)\}$ (4)

The synthesis of **4** was carried out in an identical manner to **1**. LiPh (2.0 M in $Bu^n{}_2O$) (9.3 mL, 18.63 mmol) and 6-*tert*-butyl-fulvene (2.50 g, 18.63 mmol). Yield 3.62 g, 90%. ^1H NMR (400 MHz, d_8-THF): δ 0.87 (s, 9H, Bu^t), 3.58 (s, 1H, $CHBu^tPh$), 5.53 (2H), 5.69 (2H) (m, C_5H_4), 6.98 (1H), 7.10 (2H), 7.43 (2H) (m, *Ph*). $^{13}C\{^1H\}$ NMR (100 MHz, d_8-THF): δ 29.8, 36.1 (Bu^t), 60.9 (Cp*C*), 101.9, 105.1, 121.0 (C_5H_4), 125.1, 127.6, 130.8, 148.6 (*Ph*). Anal. Calc. for $C_{16}H_{19}Li$: C, 88.05; H, 8.77. Found C, 87.88; H, 8.67%.

4.2.5. $[Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4\{CHPr^iMe\})Cl_2]$ (5)

$Li\{C_5H_4(CHPr^iMe)\}$ (**1**) (1.00 g, 7.03 mmol) in THF (50 mL) was added dropwise during 15 min to a solution of $[Zr(\eta^5\text{-}C_5H_5)Cl_3]$ (1.89 g, 7.03 mmol) in THF (50 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Solvent was removed in vacuo and hexane (125 mL) added to the resulting solid. The mixture was filtered and the filtrate concentrated (20 mL) and cooled to −30 °C to give crystals of the title complex. Yield 0.82 g, 32%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.75 (3H), 0.87 (3H) (d, $CHMe_2$), 1.15 (d, 3H, *Me*), 1.86 (m, 1H, $CHMe_2$), 2.96 (m, 1H, $CHPr^iMe$), 6.13 (1H), 6.20 (1H), 6.35 (1H), 6.50 (1H) (m, C_5H_4), 5.87 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.0 (*Me*), 18.3, 20.0, 34.5 (Pr^i), 39.7 (Cp*C*), 107.7, 115.1, 115.7, 117.3, 140.1 (C_5H_4), 115.5 (C_5H_5). MS electron impact (*m/e* (% relative intensity)): 360 (2) [M^+], 317 (19) [$M^+ - Pr^i$], 283 (100) [$M^+ - Pr^i$–Cl], 225 (55) [$M^+ - C_5H_4CHPr^iMe$]. Anal. Calc. for $C_{15}H_{20}Cl_2Zr$: C, 49.71; H, 5.56. Found C, 49.33; H, 5.51%.

4.2.6. $[Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4\{CHPr^iPh\})Cl_2]$ (6)

The synthesis of **6** was carried out in an identical manner to **5**. $Li\{C_5H_4(CHPr^iPh)\}$ (**2**) (1.00 g, 4.89 mmol), and $[Zr(\eta^5\text{-}C_5H_5)Cl_3]$ (1.27 g, 4.89 mmol). Yield 0.77 g, 37%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.81 (3H), 0.95 (3H) (d, $CHMe_2$), 2.19 (m, 1H, $CHMe_2$), 3.75 (d, 1H, $CHPr^iPh$), 6.01 (1H), 6.20 (1H), 6.56 (1H), 6.78 (1H) (m, C_5H_4), 6.00 (s, 5H, C_5H_5), 7.32

(2H), 7.35 (2H), 7.42 (1H) (m, *Ph*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.3, 22.4, 35.0 (*Pr^i*), 54.1 (Cp*C*), 106.5, 112.5, 120.0, 124.0, 141.7 (*C*$_5$H$_4$), 116.1 (*C*$_5$H$_5$), 127.2, 128.5, 130.1, 135.8 (*Ph*). MS electron impact (*m/e* (% relative intensity)): 422 (1) [M^+], 380 (39) [$M^+ - Pr^i$], 357 (70) [$M^+ - C_5H_5$], 344 (52) [$M^+ - Pr^i$–Cl], 225 (100) [$M^+ - C_5H_4CHPr^iPh$]. Anal. Calc. for $C_{20}H_{22}Cl_2Zr$: C, 56.59; H, 5.22. Found C, 56.55; H, 5.20%.

4.2.7. [Zr(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4${CHBu^{t}Me})Cl$_2$] (**7**)

The synthesis of **7** was carried out in an identical manner to **5**. Li{C_5H_4(CHBu^{t}Me)} (**3**) (1.00 g, 6.40 mmol), and [Zr(η^5-C_5H_5)Cl_3] (1.68 g, 6.40 mmol). Yield 0.83 g, 35%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (s, 9H, *Bu^t*), 1.18 (d, 3H, *Me*), 2.74 (q, 1H, C*H*Bu^{t}Me), 6.10 (1H), 6.15 (1H), 6.40 (1H), 6.55 (1H) (m, C_5H_4), 6.48 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 15.0 (*Me*), 27.9, 34.2 (*Bu^t*), 44.5 (Cp*C*), 106.4, 114.8, 116.4, 118.3, 138.9 (*C*$_5$H$_4$), 115.6 (*C*$_5$H$_5$). MS electron impact (*m/e* (% relative intensity)): 374 (3) [M^+], 317 (16) [$M^+ - Bu^t$], 282 (100) [$M^+ - Bu^t$–Cl], 225 (32) [$M^+ - C_5H_4CHBu^tMe$]. Anal. Calc. for $C_{16}H_{22}Cl_2Zr$: C, 51.04; H, 5.89. Found C, 50.92; H, 5.87%.

4.2.8. [Zr(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4${CHBu^{t}Ph})Cl$_2$] (**8**)

The synthesis of **8** was carried out in an identical manner to **5**. Li{C_5H_4(CHBu^{t}Ph)} (**4**) (1.00 g, 4.58 mmol), and [Zr(η^5-C_5H_5)Cl_3] (1.20 g, 4.58 mmol). Yield 0.66 g, 33%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 9H, *Bu^t*), 3.88 (s, 1H, C*H*Bu^{t}Ph), 5.87 (s, 5H, C_5H_5), 6.02 (1H), 6.52 (1H), 6.55 (1H), 6.87 (1H) (m, C_5H_4), 7.32 (2H), 7.37 (1H), 7.41 (2H) (m, *Ph*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 29.2, 36.2 (*Bu^t*), 58.0 (Cp*C*), 105.4, 112.4, 120.1, 120.2, 141.0 (*C*$_5$H$_4$), 115.9 (*C*$_5$H$_5$), 126.1, 126.9, 128.1, 132.9 (*Ph*). MS electron impact (*m/e* (% relative intensity)): 436 (3) [M^+], 379 (12) [$M^+ - Bu^t$], 371 (31) [$M^+ - C_5H_5$], 344 (49) [$M^+ - Bu^t$–Cl], 225 (100) [$M^+ - C_5H_4CHBu^tPh$]. Anal. Calc. for $C_{21}H_{24}Cl_2Zr$: C, 57.51; H, 5.52. Found C, 57.09; H, 5.49%.

4.2.9. [Zr(η^5-C$_5$H$_4${CHPr^{i}Me})$_2$Cl$_2$] (**9**)

The preparation of **9** was carried out in an identical manner to **5**. $ZrCl_4$ (0.81 g, 3.51 mmol) and Li{C_5H_4(CHPr^{i}Me)} (**1**) (1.00 g, 7.02 mmol). Yield 1.05 g, 69%. ^{1}H NMR (400 MHz, $CDCl_3$; two isomers): δ 0.73 (6H), 0.75 (6H), 0.87 (6H), 0.89 (6H) (d, CH*Me$_2$*), 1.15 (6H), 1.17 (6H) (d, C*Me*), 1.87 (2H), 1.88 (2H) (m, C*H*Me$_2$), 2.96 (2H), 2.97 (2H) (m, C*H*Pr^{i}Me), 6.09 (4H), 6.14 (4H), 6.32 (2H), 6.36 (2H), 6.45 (2H), 6.50 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; two isomers): δ 13.8, 13.9 (C*Me*), 18.2, 18.3, 20.0, 20.1, 34.5, 34.6 (*Pr^i*), 39.6, 39.7 (Cp*C*), 107.1, 107.8, 114.5, 114.7, 115.5, 115.8, 116.4, 116.5, 139.5, 139.9 (*C*$_5$H$_4$). MS electron impact (*m/e* (% relative intensity)): 432 (4) [M^+], 394 (40) [$M^+ - Cl$], 351 (100) [$M^+ - Cl$, $-Pr^i$]. Anal. Calc. for $C_{20}H_{30}Cl_2Zr$: C, 55.53; H, 6.99. Found C, 55.10; H, 7.06%.

4.2.10. [Zr(η^5-C$_5$H$_4${CHPr^{i}Ph})$_2$Cl$_2$] (**10**)

The preparation of **10** was carried out in an identical manner to **5**. $ZrCl_4$ (0.57 g, 2.45 mmol) and Li{C_5H_4(CHPr^{i}Ph)} (**2**) (1.00 g, 4.90 mmol). Yield 0.91 g, 67%. ^{1}H NMR (400 MHz, $CDCl_3$; two isomers): δ 0.75 (6H), 0.77 (6H), 0.89 (6H), 0.91 (6H) (d, CH*Me$_2$*), 2.14 (2H), 2.29 (2H) (m, C*H*Me$_2$), 3.73 (2H), 3.88 (2H) (m, C*H*Pr^{i}Ph), 4.64 (2H), 5.59 (2H), 5.88 (4H), 6.26 (2H), 6.28 (2H), 6.32 (2H), 6.37 (2H) (m, C_5H_4), 7.15 (4H), 7.29 (8H), 7.33 (8H) (m, *Ph*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; two isomers): δ 19.7, 20.9, 22.0, 22.1, 33.2, 34.6 (*Pr^i*), 52.7, 53.5 (Cp*C*), 106.3, 108.8, 111.9, 115.7, 116.6, 117.9, 119.2, 123.1, 135.9, 136.1 (*C*$_5$H$_4$), 126.4, 126.6, 127.7, 127.9, 129.8, 129.9, 140.9, 141.3 (Ph). MS electron impact (*m/e* (% relative intensity)): 556 (2) [M^+], 519 (4) [$M^+ - Cl$], 357 (100) [$M^+ - C_5H_4CHPr^iPh$]. Anal. Calc. for $C_{30}H_{34}Cl_2Zr$: C, 64.72; H, 6.16. Found C, 64.99; H, 6.17%.

4.2.11. [Zr(η^5-C$_5$H$_4${CHBu^{t}Me})$_2$Cl$_2$] (**11**)

The preparation of **11** was carried out in an identical manner to **5**. $ZrCl_4$ (0.75 g, 3.20 mmol) and Li{C_5H_4(CHBu^{t}Me)} (**3**) (1.00 g, 6.40 mmol). Yield 1.06 g, 72%. ^{1}H NMR (400 MHz, $CDCl_3$; two isomers): δ 0.84 (18H), 0.85 (18H) (s, *Bu^t*), 1.19 (6H), 1.21 (6H) (d, C*Me*), 2.73 (2H), 2.76 (2H) (q, C*H*Bu^{t}Me), 6.00 (4H), 6.02 (4H), 6.37 (2H), 6.45 (4H), 6.54 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; two isomers): δ 14.9, 15.0 (C*Me*), 27.8, 27.9, 34.2, 34.3 (*Bu^t*), 44.4, 44.5 (Cp*C*), 105.4, 106.7, 115.6, 115.9, 116.1, 116.2, 117.4, 118.3, 137.7, 139.0 (*C*$_5$H$_4$). MS electron impact (*m/e* (% relative intensity)): 460 (2) [M^+], 401 (14) [$M^+ - Bu^t$], 365 (89) [$M^+ - Bu^t$, −Cl]. Anal. Calc. for $C_{22}H_{34}Cl_2Zr$: C, 57.36; H, 7.44. Found C, 57.55; H, 7.38%.

4.2.12. [Zr(η^5-C$_5$H$_4${CHBu^{t}Ph})$_2$Cl$_2$] (**12**)

The preparation of **12** was carried out in an identical manner to **5**. $ZrCl_4$ (0.53 g, 2.29 mmol) and Li{C_5H_4(CHBu^{t}Ph)} (**4**) (1.00 g, 4.58 mmol). Yield 0.95 g, 71%. ^{1}H NMR (400 MHz, $CDCl_3$; two isomers): δ 0.86 (18H), 0.87 (18H) (s, *Bu^t*), 3.77 (2H), 3.81 (2H) (s, C*H*Bu^{t}Ph), 3.98 (2H), 5.21 (2H), 5.89 (2H), 6.11 (2H), 6.19 (2H), 6.28 (2H), 6.30 (2H), 6.36 (2H) (m, C_5H_4), 7.21 (4H), 7.23 (8H), 7.29 (8H) (m, *Ph*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; two isomers): δ 29.3, 29.4, 36.4, 36.5 (*Bu^t*), 58.1, 58.2 (Cp*C*), 105.8, 105.9, 108.4, 108.5, 111.8, 111.9, 118.0, 118.9, 132.5, 134.0 (*C*$_5$H$_4$), 119.2, 120.1, 126.5, 126.9, 127.1, 128.1, 141.3, 141.6 (*Ph*). MS electron impact (*m/e* (% relative intensity)): 582 (1) [M^+], 527 (7) [$M^+ - Bu^t$], 371 (60) [$M^+ - C_5H_4CHBu^tPh$]. Anal. Calc. for $C_{32}H_{38}Cl_2Zr$: C, 65.72; H, 6.55. Found C, 65.24; H, 6.50%.

4.2.13. C$_5$H$_4$(CHPr^{i}Me)(SiMe$_3$) (**13**)

$SiMe_3Cl$ (2.28 g, 14.06 mmol) in THF (10 L) was added to a solution of Li{C_5H_4(CHPr^{i}Me)} (**1**) (2.00 g, 14.06 mmol) in THF (50 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. Solvent was removed in vacuo and hexane (150 mL) was added to the resulting dark yellow oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as dark yellow oil. Yield 2.66 g, 91%. ^{1}H NMR (400 MHz, $CDCl_3$; for the predominant isomer): δ 0.04 (s, 9H, Si*Me$_3$*), 0.93 (d, 6H, CH*Me$_2$*), 1.17 (d, 3H, *Me*), 1.81 (m, 1H,

C*H*Me$_2$), 2.46 (m, 1H, C*H*Pr^{i}Me), 3.27 (1H), 6.10 (1H), 6.47 (1H), 6.54 (1H) (m, C$_5$*H*$_4$). MS electron impact (*m/e* (% relative intensity)): 208 (24) [M^+], 137 (100) [$M^+ - $CHPr^{i}Me], 135 (44) [$M^+ - $SiMe$_3$]. Anal. Calc. for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found C, 74.65; H, 11.88%.

4.2.14. $C_5H_4(CHPr^iPh)(SiMe_3)$ (**14**)

The synthesis of **14** was carried out in an identical manner to **13**. SiMe$_3$Cl (1.06 g, 9.79 mmol) and Li{C$_5$H$_4$(CHPr^{i}Ph)} (**2**) (2.00 g, 9.79 mmol). Yield 2.51 g, 95%. ^{1}H NMR (400 MHz, CDCl$_3$; for the predominant isomer): δ −0.08 (s, 9H, Si*Me*$_3$), 1.05 (d, 6H, CH*Me*$_2$), 2.38 (m, 1H, C*H*Me$_2$), 3.40 (m, 1H, C*H*Pr^{i}Ph), 3.26 (1H), 6.24 (1H), 6.45 (1H), 6.57 (1H) (m, C$_5$*H*$_4$), 7.18 (1H), 7.26 (2H), 7.30 (2H) (m, *Ph*). MS electron impact (*m/e* (% relative intensity)): 270 (12%) [M^+], 197 (69) [$M^+ - $SiMe$_3$], 137 (100) [$M^+ - $CHPr^{i}Ph]. Anal. Calc. for $C_{18}H_{26}Si$: C, 79.93; H, 9.69. Found C, 79.34; H, 9.58%.

4.2.15. $C_5H_4(CHBu^tMe)(SiMe_3)$ (**15**)

The synthesis of **15** was carried out in an identical manner to **13**. SiMe$_3$Cl (1.39 g, 12.80 mmol) and Li{C$_5$H$_4$(CHBu^{t}Me)} (**3**) (2.00 g, 12.80 mmol). Yield 2.67 g, 94%. ^{1}H NMR (400 MHz, CDCl$_3$; for the predominant isomer): δ 0.02 (s, 9H, Si*Me*$_3$), 0.91 (s, 9H, *Bu*^{t}), 1.15 (d, 3H, Me), 2.47 (m, 1H, C*H*Bu^{t}Me), 3.23 (1H), 6.07 (1H), 6.40 (1H), 6.50 (1H) (m, C$_5$*H*$_4$). MS electron impact (*m/e* (% relative intensity)): 222 (38) [M^+], 149 (42) [$M^+ - $SiMe$_3$], 137 (100) [$M^+ - $CHBu^{t}Me]. Anal. Calc. for $C_{14}H_{26}Si$: C, 75.59; H, 11.78. Found C, 75.19; H, 11.78%.

4.2.16. $C_5H_4(CHBu^tPh)(SiMe_3)$ (**16**)

The synthesis of **16** was carried out in an identical manner to **13**. SiMe$_3$Cl (1.00 g, 9.16 mmol) and Li{C$_5$H$_4$(CHBu^{t}Ph)} (**4**) (2.00 g, 9.16 mmol). Yield 2.55 g, 98%. ^{1}H NMR (400 MHz, CDCl$_3$; for the predominant isomer): δ 0.01 (s, 9H, Si*Me*$_3$), 1.03 (s, 9H, *Bu*^{t}), 3.67 (m, 1H, C*H*Bu^{t}Ph), 3.23 (1H), 6.32 (1H), 6.42 (1H), 6.69 (1H) (m, C$_5$*H*$_4$), 7.18 (1H), 7.25 (2H), 7.32 (2H) (m, *Ph*). MS electron impact (*m/e* (% relative intensity)): 284 (78) [M^+], 211 (37) [$M^+ - $SiMe$_3$], 137 (1 0 0) [$M^+ - $CHBu^{t}Ph]. Anal. Calc. for $C_{19}H_{28}Si$: C, 80.21; H, 9.92. Found C, 79.99; H, 9.78%.

4.2.17. [Zr(η^5-C$_5$H$_4${CHPr^{i}Me})Cl$_3$] (**17**)

A solution of C$_5$H$_4$(CHPr^{i}Me)(SiMe$_3$) (**13**) (1.50 g, 7.20 mmol) in toluene (25 mL) was added dropwise to a suspension of ZrCl$_4$ (1.67 g, 7.20 mmol) in toluene (15 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 6 h and subsequently heated to 80 °C and the reaction continued for an additional hour. Solvent was removed in vacuo to give a red solid which was washed with hexane (2× 50 mL), dried under vacuum and recrystallized in toluene. Yield 1.03 g, 43%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.72 (3H), 0.90 (3H) (d, CH*Me*$_2$), 1.32 (d, 3H, *Me*), 1.96 (m, 1H, C*H*Me$_2$), 3.23 (m, 1H, C*H*Pr^{i}Me), 6.11 (1H), 6.34 (1H), 6.37 (1H), 6.47 (1H) (m, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 13.3 (*Me*), 18.4, 20.7, 35.2 (*Pr*^{i}), 40.2 (Cp*C*), 116.9, 117.4, 117.9, 121.4, 142.3 (*C*$_5$H$_4$). Anal. Calc. for $C_{10}H_{15}Cl_3Zr$: C, 36.09; H, 4.54. Found C, 35.92; H, 4.49%.

4.2.18. [Zr(η^5-C$_5$H$_4${CHPr^{i}Ph})Cl$_3$] (**18**)

The synthesis of **18** was carried out in an identical manner to **17**. C$_5$H$_4$(CHPr^{i}Ph)(SiMe$_3$) (**14**) (1.50 g, 5.54 mmol) and ZrCl$_4$ (1.29 g, 5.54 mmol). Yield 1.07 g, 49%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.80 (3H), 0.91 (3H) (d, CH*Me*$_2$), 2.79 (m, 1H, C*H*Me$_2$), 4.55 (d, 1H, C*H*Pr^{i}Ph), 5.93 (1H), 6.37 (1H), 6.51 (1H), 6.62 (1H) (m, C$_5$*H*$_4$), 7.05 (2H), 7.14 (2H), 7.25 (1H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 13.6, 18.4, 20.8 (*Pr*^{i}), 40.6 (Cp*C*), 116.5, 117.3, 117.7, 121.0, 140.2 (*C*$_5$H$_4$), 126.2, 127.4, 128.3, 133.4 (*Ph*). Anal. Calc. for $C_{15}H_{17}Cl_3Zr$: C, 45.62; H, 4.34. Found C, 45.29; H, 4.27%.

4.2.19. [Zr(η^5-C$_5$H$_4${CHBu^{t}Me})Cl$_3$] (**19**)

The synthesis of **19** was carried out in an identical manner to **17**. C$_5$H$_4$(CHBu^{t}Me)(SiMe$_3$) (**15**) (1.50 g, 6.74 mmol) and ZrCl$_4$ (1.57 g, 6.74 mmol). Yield 0.98 g, 42%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.85 (s, 9H, *Bu*^{t}), 1.30 (d, 3H, *Me*), 2.96 (q, 1H, C*H*Bu^{t}Me), 5.95 (1H), 6.27 (1H), 6.36 (1H), 6.56 (1H) (m, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 14.0 (*Me*), 28.1, 34.3 (*Bu*^{t}), 44.7 (Cp*C*), 116.3, 116.8, 117.3, 122.8, 141.1 (*C*$_5$H$_4$). Anal. Calc. for $C_{11}H_{17}Cl_3Zr$: C, 38.09; H, 4.94. Found C, 37.72; H, 4.88%.

4.2.20. [Zr(η^5-C$_5$H$_4${CHBu^{t}Ph})Cl$_3$] (**20**)

The synthesis of **20** was carried out in an identical manner to **17**. C$_5$H$_4$(CHBu^{t}Ph)(SiMe$_3$) (**16**) (1.50 g, 5.27 mmol) and ZrCl$_4$ (1.22 g, 5.27 mmol). Yield 0.84 g, 39%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.00 (s, 9H, *Bu*^{t}), 4.08 (s, 1H, C*H*Bu^{t}Ph), 5.99 (1H), 6.29 (1H), 6.33 (1H), 6.54 (1H) (m, C$_5$*H*$_4$), 7.09 (2H), 7.17 (1H), 7.28 (2H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 27.6, 33.7 (*Bu*^{t}), 42.9 (Cp*C*), 115.4, 116.9, 117.2, 123.1, 143.4 (*C*$_5$H$_4$), 125.9, 127.1, 128.2, 134.0 (*Ph*). Anal. Calc. for $C_{16}H_{19}Cl_3Zr$: C, 47.00; H, 4.68. Found C, 46.75; H, 4.65%.

4.2.21. [Zr(η^5-C$_9$H$_7$)(η^5-C$_5$H$_4${CHPr^{i}Me})Cl$_2$] (**21**)

The synthesis of **21** was carried out in an identical manner to **5**. Li(C$_9$H$_7$) (0.18 g, 1.50 mmol) and [Zr(η^5-C$_5$H$_4${CHPr^{i}Me})Cl$_3$] (**17**) (0.50 g, 1.50 mmol). Yield 0.23 g, 38%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.70 (3H), 0.83 (3H) (d, CH*Me*$_2$), 1.07 (d, 3H, *Me*), 1.79 (m, 1H, C*H*Me$_2$), 2.89 (m, 1H, C*H*Pr^{i}Me), 5.46 (1H), 5.96 (1H), 6.02 (1H), 6.28 (1H) (m, C$_5$*H*$_4$), 6.53 (2H), 6.94 (1H), 7.30 (2H), 7.69 (2H) (m, C$_9$*H*$_7$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 13.9 (*Me*), 18.3, 20.0, 34.4 (*Pr*^{i}), 39.9 (Cp*C*), 102.3, 109.8, 115.5, 123.9, 140.5 (*C*$_5$H$_4$), 103.0, 117.6, 125.3, 126.0, 126.4 (*C*$_9$H$_7$). MS electron impact (*m/e* (% relative intensity)): 410 (2) [M^+], 295 (100) [$M^+ - C_9H_7$], 275 (43) [$M^+ - C_5H_4$CHPr^{i}Me], 252 (29) [$M^+ - C_9H_7$–Pr^i]. Anal. Calc. for $C_{19}H_{22}Cl_2Zr$: C, 55.32; H, 5.38. Found C, 54.93; H, 5.30%.

4.2.22. [Zr(η^5-C$_9$H$_7$)(η^5-C$_5$H$_4${CHPr^{i}Ph})Cl$_2$] (**22**)

The synthesis of **22** was carried out in an identical manner to **5**. Li(C$_9$H$_7$) (0.15 g, 1.27 mmol) and [Zr(η^5-

$C_5H_4\{CHPr^iPh\})Cl_3]$ (**18**) (0.50 g, 1.27 mmol). Yield 0.17 g, 29%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.79 (3H), 0.92 (3H) (d, $CHMe_2$), 2.18 (m, 1H, $CHMe_2$), 3.76 (d, 1H, $CHPr^iPh$), 5.19 (1H), 5.51 (1H), 6.06 (1H), 6.36 (1H) (m, C_5H_4), 6.38 (2H), 6.43 (1H), 7.37 (2H), 7.53 (2H) (m, C_9H_7), 7.21 (2H), 7.27 (2H), 7.38 (1H) (m, *Ph*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.8, 22.5, 34.7 (Pr^i), 53.7 (Cp*C*), 102.6, 109.3, 114.9, 123.2, 141.0 (C_5H_4), 102.8, 116.9, 124.9, 126.1, 126.5 (C_9H_7), 127.4, 128.7, 130.4, 136.2 (*Ph*). MS electron impact (*m/e* (% relative intensity)): 472 (4) [M^+], 429 (39) [$M^+ - Pr^i$], 357 (100) [$M^+ - C_9H_7$], 275 (43) [$M^+ - C_5H_4CHPr^iPh$]. Anal. Calc. for $C_{24}H_{24}Cl_2Zr$: C, 60.74; H, 5.10. Found C, 60.21; H, 5.00%.

4.2.23. $[Zr(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_4\{CHBu^tMe\})Cl_2]$ (**23**)

The synthesis of **23** was carried out in an identical manner to **5**. $Li(C_9H_7)$ (0.18 g, 1.44 mmol) and $[Zr(\eta^5\text{-}C_5H_4\{CHBu^tMe\})Cl_3]$ (**19**) (0.50 g, 1.44 mmol). Yield 0.27 g, 44%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81 (s, 9H, Bu^t), 1.13 (d, 3H, *Me*), 2.69 (q, 1H, $CHBu^tMe$), 5.29 (1H), 5.95 (1H), 6.12 (1H), 6.18 (1H) (m, C_5H_4), 6.53 (2H), 6.94 (1H), 7.30 (2H), 7.70 (2H) (m, C_9H_7). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.9 (*Me*), 27.8, 34.1 (Bu^t), 44.4 (Cp*C*), 102.5, 108.6, 115.7, 116.9, 139.6 (C_5H_4), 103.8, 118.2, 123.3, 125.3, 126.0 (C_9H_7). MS electron impact (*m/e* (% relative intensity)): 424 (6) [M^+], 409 (5) [$M^+ - Me$], 367 (18) [$M^+ - Bu^t$], 309 (15) [$M^+ - C_9H_7$], 275 (100) [$M^+ - C_5H_4CHBu^tMe$], 252 (28) [$M^+ - C_9H_7 - Bu^t$]. Anal. Calc. for $C_{20}H_{24}Cl_2Zr$: C, 56.32; H, 5.67. Found C, 55.99; H, 5.52%.

4.2.24. $[Zr(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5H_4\{CHBu^tPh\})Cl_2]$ (**24**)

The synthesis of **24** was carried out in an identical manner to **5**. $Li(C_9H_7)$ (0.15 g, 1.22 mmol) and $[Zr(\eta^5\text{-}C_5H_4\{CHBu^tPh\})Cl_3]$ (**20**) (0.50 g, 1.22 mmol). Yield 0.18 g, 31%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 9H, Bu^t), 3.89 (s, 1H, $CHBu^tPh$), 5.03 (1H), 5.22 (1H), 5.88 (1H), 6.43 (1H) (m, C_5H_4), 6.35 (2H), 6.59 (1H), 7.24 (2H), 7.52 (2H) (m, C_9H_7), 7.30 (1H), 7.39 (2H), 7.50 (2H) (m, *Ph*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 29.1, 36.2 (Bu^t), 57.9 (Cp*C*), 100.6, 105.5, 113.2, 123.3, 141.3 (C_5H_4), 107.7, 120.0, 125.5, 125.9, 126.9 (C_9H_7), 125.2, 125.6, 127.5, 132.7 (*Ph*). MS electron impact (*m/e* (% relative intensity)): 486 (1) [M^+], 371 (100) [$M^+ - C_9H_7$], 275 (74) [$M^+ - C_5H_4CHBu^tPh$]. Anal. Calc. for $C_{25}H_{26}Cl_2Zr$: C, 61.45; H, 5.36. Found C, 61.22; H, 5.19%.

4.3. Polymerization reactions

4.3.1. Polymerization of ethylene

The zirconocene catalyst (6 μmol), MAO (10% in toluene) (6000 μmol) and toluene (200 mL) were mixed together for 15 min in a 1 L glass autoclave. The N_2 pressure inside the autoclave was reduced by applying vacuum. Ethylene pressure of 2 bar was then applied and maintained to the autoclave and stirring of the mixture commenced (1000 rpm). After exactly 30 min, stirring was halted and the ethylene pressure released. Excess MAO was then destroyed by cautiously adding a mixture of methanol/HCl (90:10). The polymer was isolated by filtration and washed with ethanol and dried under vacuum at 90 °C for 16 h.

4.3.2. Polymerization of propylene

The zirconocene catalyst (15 μmol), MAO (10% in toluene) (45,000 μmol) and toluene (200 mL) were mixed together for 15 min in a 1 L glass autoclave. The N_2 pressure inside the autoclave was reduced by applying vacuum. Propylene pressure of 2.5 bar was then applied and maintained to the autoclave and stirring of the mixture commenced (1000 rpm). After exactly 60 min, stirring was halted and the propylene pressure released. Excess MAO was then destroyed by cautiously adding a mixture of methanol/HCl (90:10). Solvent was then removed under reduced pressure and a mixture of acetone/methanol (50:50) (200 mL) added. The mixture was stirred for 16 h and then filtered to isolate the polymer which was washed with ethanol and dried under vacuum at 25 °C for 16 h.

4.4. X-ray data collection

4.4.1. $[Zr(\eta^5\text{-}C_5H_4\{CHBu^tMe\})_2Cl_2]$ (**11**)

Data were collected on a Bruker X8 APPEX II CCD-based diffractometer, equipped with a graphite monochromated Mo Kα radiation source (λ = 0.71073 Å). The crystal data, data collection, structural solution, and refinement parameters are summarized in Table 6. Data were integrated using SAINT [35] and an absorption correction was performed with the program SADABS [36]. The structure was solved by direct methods using SHELXTL [37], and refined by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with

Table 6
Crystal data and structure refinement for **11**

Formula	$C_{22}H_{34}Cl_2Zr$
fw	460.61
T (K)	200(2)
Cryst. syst.	Monoclinic
Space group	$P2(1)/n$
a (Å)	6.756(1)
b (Å)	15.178(3)
c (Å)	22.432(4)
β (°)	94.806(4)
V (Å^3)	2292.1(8)
Z	4
Dc (g cm^{-3})	1.335
μ (mm^{-1})	0.716
F(0 0 0)	960
Cryst. dimens. (mm)	0.20 × 0.09 × 0.05
θ range (°)	1.62–22.62
$h\,k\,l$ ranges	$-7 \le h \le 7$, $-16 \le k \le 15$, $-24 \le l \le 24$
Number of reflections measured	11,610
Number of reflections observed	2102
Goodness-of-fit on F^2	1.014
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0426$, $wR2 = 0.1041$
R indices (all data)	$R1 = 0.0708$, $wR2 = 0.1330$
Largest diff. peak and hole (einstein Å^{-3})	0.341 and −0.339

$$R_1 = \frac{\sum ||Fo| - |Fc||}{\sum |Fo|}; \qquad wR_2 = \left[\sum \frac{[w(Fo^2 - Fc^2)^2]}{\sum [w(Fo^2)^2]}\right]^{0.5}.$$

anisotropic thermal parameters. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

5. Supplementary material

Crystallographic data for the structural analysis of **11** have been deposited with the Cambridge Crystallographic Data Centre, CCDC-615356. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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