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Synthesis and Reactivity of Alkenyl-Substituted Zirconocene Complexes and Their Application as Olefin Polymerisation Catalysts

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The zirconocene complexes $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}Cl_2]$ (**4**) and $[Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}_2Cl_2]$ (**5**) were synthesised from the reaction of the lithium derivative $[Li\{C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}]$ (**1**) with $[Zr(\eta^5\text{-}C_5H_5)Cl_3]$ or $ZrCl_4$, respectively. The *ansa*-zirconocene complex $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH{=}CH_2\})\}Cl_2]$ (**6**) was obtained from the reaction of the lithium precursor $[Li_2\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH{=}CH_2\})\}]$ (**3**) with zirconium tetrachloride. Catalytic hydrogenation of **4**–**6** gave the zirconocene complexes $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_3)\}Cl_2]$ (**7**), $[Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_3)\}_2Cl_2]$ (**8**) and $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_3\})\}Cl_2]$ (**9**), respectively. Hydroboration of **4**–**6** with 9-BBN (9-borabicyclo[3.3.1]nonane) yielded $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2BC_8H_{14})\}Cl_2]$ (**10**), $[Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2BC_8H_{14})\}_2Cl_2]$ (**11**) and $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_2BC_8H_{14}\})\}Cl_2]$ (**12**), respectively, and the catalytic hydrosilylation of **4**–**6** with $SiHMe_2Cl$ gave $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2SiMe_2Cl)\}Cl_2]$ (**13**), $[Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2SiMe_2Cl)\}_2Cl_2]$ (**14**) and $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_2SiMe_2Cl\})\}Cl_2]$ (**15**), respectively. The dinuclear complex $[Cl_2Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2(CH_2)_4SiMe_2OSiMe_2(CH_2)_4Me_2C\}\eta^5\text{-}C_5H_3)(\eta^5\text{-}C_5Me_4)SiMe_2\}ZrCl_2]$ (**16**) was obtained upon controlled hydrolysis of **15**. The zirconocene compounds were tested as catalysts in the polymerisation of ethylene and propylene. Isotactic polypropylene with [mmmm] pentads of the order of 75 % were obtained with the *ansa*-zirconocene catalysts, whereas the unbridged metallocene catalysts produced atactic polypropylene. The molecular structures of **4** and **5** were determined by single-crystal X-ray diffraction studies.

Introduction

Metallocene dichloride complexes of group 4 metals have received a large amount of attention in the past few decades because they are excellent catalysts for the polymerisation of α-olefins[1] and for other processes in organic synthesis such as carbometallation, hydrometallation, carbonylation, acylation, isomerisation, hydrogenation, hydroamination, dehydrosilylation and hydrosilylation.[2]

The current goal in the field of olefin polymerisation with metallocene catalysts is moving towards supported catalysts that allow homogeneous single-site selectivity in a heterogeneous medium.[3] A variety of routes have been developed for supporting metallocene complexes on silica, including the direct reaction of silica with a metallocene complex followed by activation with a co-catalyst, such as MAO, reaction of MAO-modified silica with a metallocene complex, or similar approaches where other co-catalysts are supported on silica.[4] Recently, considerable attention has been focused on the anchoring of metallocene complexes on silica through either metallocene synthesis on the support or reaction of a suitably functionalised metallocene complex with silica.[4,5] One of the most common routes for the immobilisation of metallocene complexes is the reactivity of the C=C double bond of an alkenyl substituent on the cyclopentadienido ring or at the *ansa*-bridge atom.[6]

In contrast to their late transition metal analogues,[7] the use and transformation of functional groups at the cyclopentadienido rings of early transition metal compounds has been rather limited.[8] The reactivity of such alkenyl-functionalised metallocene complexes has been mainly studied in olefin metathesis reactions[9,10] and hydrometallation.[10]

As a continuation of our work on the synthesis and catalytic reactivity of group 4 metallocene complexes,[11] we report here the synthesis of new alkenyl-substituted zirconocene and *ansa*-zirconocene complexes and their reactivity in hydrogenation, hydroboration and hydrosilylation processes. We also describe the catalytic behaviour of the zirconocene complexes in the polymerisation of ethylene and propylene.

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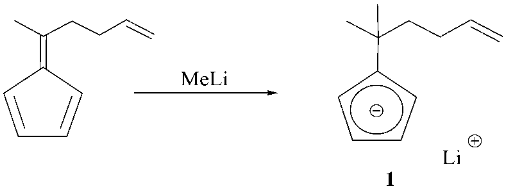
Results and Discussion

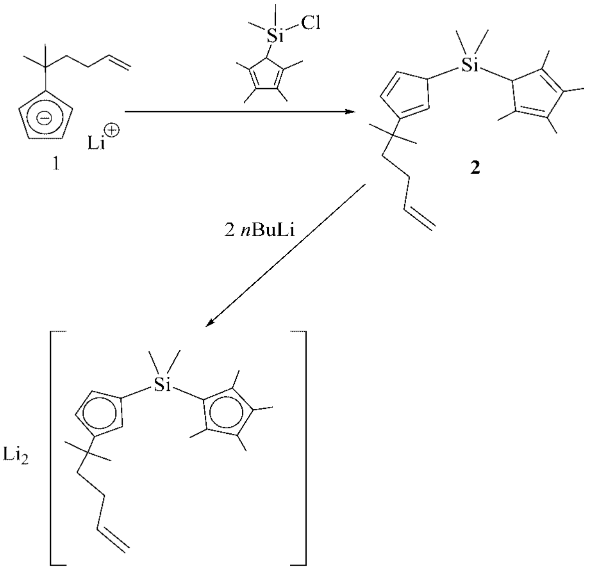
Methyllithium reacts with 6-(4-buten-1-yl)-6-methylfulvene by nucleophilic addition at the exocyclic double bond to give the cyclopentadienidolithium compound [Li{$C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)$}] (**1**) [Equation (1)].



1 (1)

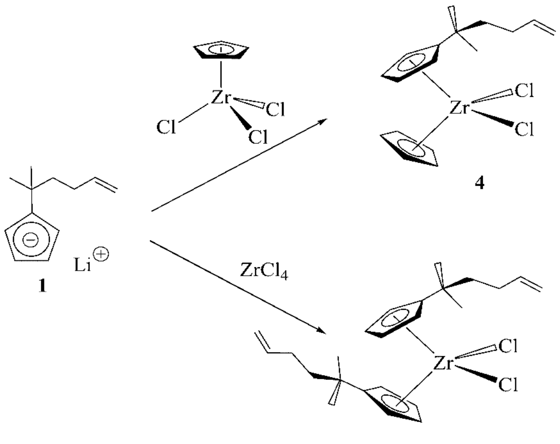
Complex **1** was characterised by ^{1}H and ^{13}C NMR spectroscopy (see Experimental Section). Two multiplets at δ = 5.46 and 5.48 ppm in the ^{1}H NMR spectrum of **1** can be assigned to the cyclopentadienido ring protons, with a singlet due to the two methyl groups substituting the carbon atom bonded to the cyclopentadienido ring at δ = 1.19 ppm. The alkenyl fragment exhibits four sets of signals, two corresponding to the CH_2 protons (two multiplets at δ = 1.50 and 1.91 ppm), one corresponding to the proton at C-γ (a multiplet at δ = 5.73 ppm) and two for the terminal olefinic protons (multiplets at δ = 4.74 and 4.87 ppm). The $^{13}C\{^1H\}$ NMR spectrum of **1** shows the expected signals (one signal at δ = 46.5 ppm for the carbon atom bonded to the cyclopentadienido ring, one signal at δ = 35.4 ppm for the two methyl groups, four signals at δ = 31.0, 31.1, 112.8 and 128.8 ppm for the alkenyl fragment, and three signals at δ = 100.9, 101.8, and 141.6 ppm for the cyclopentadienido moiety).

The asymmetrically substituted *ansa* ligand precursor $Me_2Si(C_5HMe_4)\{C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}$ (**2**) was prepared by treating **1** with $Me_2Si(C_5HMe_4)Cl$ according to previously reported synthetic protocols [Equation (2)].[11a,11b,11f] Compound **2** was isolated as a mixture of the double bond positional isomers, with one isomer being predominant as confirmed by ^{1}H NMR spectroscopy. This compound was also characterised by electron impact mass spectrometry (see Experimental Section). The dilithium derivative, [$Li_2\{Me_2Si(C_5Me_4)(C_5H_3\{CMe_2CH_2CH_2CH{=}CH_2\})\}$] (**3**) was obtained in the traditional manner by treating **2** with *n*-butyllithium. It was isolated as a highly moisture- and oxygen-sensitive white solid and characterised by elemental analysis (carbon and hydrogen; see Experimental Section).



3 (2)

Treatment of **1** with either [$Zr(\eta^5\text{-}C_5H_5)Cl_3$] or $ZrCl_4$ yielded the corresponding zirconocene(IV) dichloride complexes [$Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}Cl_2$] (**4**) and [$Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}_2Cl_2$] (**5**), respectively [Equation (3)], which were isolated as crystalline solids and characterised spectroscopically. The ^{1}H NMR spectrum of **4** shows one singlet for the unsubstituted cyclopentadienido ring protons at δ = 6.48 ppm, two multiplets at δ = 6.36 and 6.45 ppm for the substituted cyclopentadienido ring protons, and a singlet at δ = 1.39 ppm corresponding to the two methyl groups. The alkenyl fragment exhibits four sets of signals, two corresponding to the CH_2 protons (two multiplets at δ = 1.56 and 1.75 ppm), one for the proton at C-γ (a multiplet at δ = 5.71 ppm) and two corresponding to the terminal olefinic protons (multiplets at δ = 4.89 and 4.96 ppm). A similar spectral pattern was also observed for the alkenyl fragment in the ^{1}H NMR spectrum of **5** along with a singlet at δ = 1.41 ppm (assigned to the two methyl groups) and two multiplets at δ = 6.32 and 6.41 ppm for the cyclopentadienido protons. The $^{13}C\{^1H\}$ NMR spectrum of **4** shows one signal at δ = 115.9 ppm assigned to the unsubstituted C_5 ring and three signals at δ = 112.2, 113.0 and 143.3 ppm for the substituted C_5 ring. The carbon atom bonded to the cyclopentadienido ring appears in the spectrum as one signal at δ = 46.1 ppm, and the carbon atoms of the two methyl groups are observed as one signal at δ = 36.4 ppm. The four signals at δ = 27.2, 29.0, 114.1 and 138.5 ppm were assigned to the alk-



5 (3)

enyl moiety. The expected signals were observed in the $^{13}C\{^{1}H\}$ NMR spectrum of **5** (see Experimental Section).

The molecular structures of **4** and **5** were determined by single-crystal X-ray diffraction studies. The molecular structures and atomic numbering schemes are shown in Figures 1 and 2, respectively, and selected bond lengths and angles for **4** and **5** are given in Table 1.

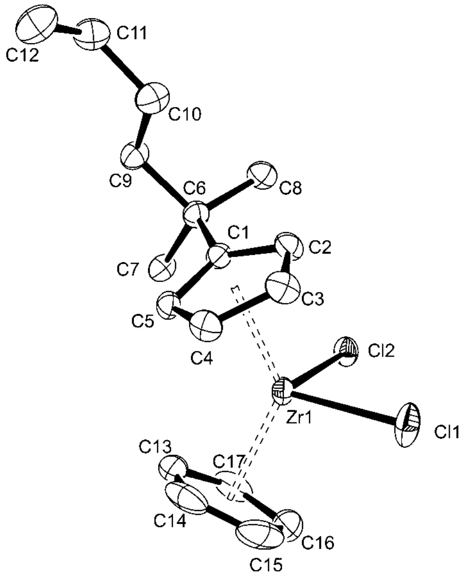


Figure 1. Molecular structure and atom-labelling scheme for $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}Cl_2]$ (**4**), with thermal ellipsoids at 50% probability.

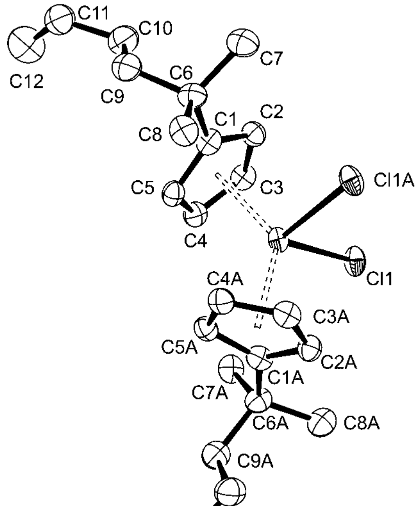


Figure 2. Molecular structure and atom-labelling scheme for $[Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}_2Cl_2]$ (**5**), with thermal ellipsoids at 50% probability.

Complex **4** crystallises in the triclinic space group $P\bar{1}$ with four molecules in the unit cell and two in the asymmetric unit that are structurally almost identical. Complex **5**, on the other hand, crystallises in the centrosymmetric monoclinic space group *C2/c* with four molecules in the unit cell and only half of the molecule in the asymmetric unit; the other half is generated by symmetry operations. The molecular structures of **4** and **5** reveal that the zirconium atoms have a distorted tetrahedral geometry with both C_5 rings bound to the metal atom in an η^5 mode. The centroids of the cyclopentadienido rings form an angle with the zirconium atom of 129.98° and 130.10° for **4** and 129.22° for **5**, which are typical for zirconocene dichloride complexes. The Zr–Cl distances (approx. 2.45 Å) and Cl–Zr–Cl angle (approx. 95°) for **4** and **5** are in the expected range.[1e] The bond lengths in the butenyl moiety are also normal [C(9)–C(10) 1.541(5) and 1.531(5) Å for **4** and 1.532(5) Å for **5**; C(10)–C(11) 1.496(6) and 1.491(6) Å for **4** and 1.494(5) Å for **5**; C(11)–C(12) 1.294(7) and 1.304(7) Å for **4** and 1.288(6) Å for **5**]. The C(11)–C(12) distances are typical for terminal C–C double bonds[10c,10e] and the C(10)–C(11)–C(12) angle [125.7(4) and 125.4(4)° for **4** and 126.1(4)° for **5**] confirms the sp^2 hybridisation of C(12) in both cases. Selected structural data for **4** and **5** are compared with those of similar zirconocene complexes in Table 2.

Table 1. Selected bond lengths [Å] and angles [°] for **4** and **5**.

	4	4a	5
Zr(1)–Cent(1)	2.211	2.216	2.211
Zr(1)–Cent(2)	2.200	2.197	
Zr(1)–Cl(1)	2.451(1)	2.450(1)	2.4533(8)
Zr(1)–Cl(2)	2.447(1)	2.458(1)	
C(9)–C(10)	1.541(5)	1.531(5)	1.532(5)
C(10)–C(11)	1.496(6)	1.491(6)	1.494(5)
C(11)–C(12)	1.294(7)	1.304(7)	1.288(6)
Cent(1)–Zr(1)–Cent(2)[a]	129.98	130.10	129.22
Cl(1)–Zr(1)–Cent(1)	106.91	108.59	107.20
Cl(1)–Zr(1)–Cent(2)	105.47	105.31	
Cl(2)–Zr(1)–Cent(1)	106.36	106.14	
Cl(2)–Zr(1)–Cent(2)	106.36	106.30	
Cl(1)–Zr(1)–Cl(2)	94.58(3)	94.83(3)	
Cl(1)–Zr(1)–Cl(1A)			94.92(9)
C(9)–C(10)–C(11)	112.0(3)	111.8(3)	112.0(3)
C(10)–C(11)–C(12)	125.7(4)	125.4(4)	126.1(4)

[a] Cent(1) and Cent(2) are the centroids of C(1)–C(5) and C(13)–C(17) for **4** and C(1)–C(5) and C(1A)–C(5A) for **5**, respectively.

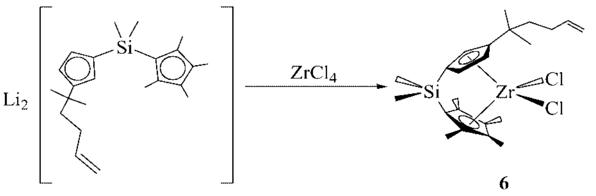
Treatment of the dilithium derivative **3** with $ZrCl_4$ gave the corresponding *ansa*-metallocene dichloride complex $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH{=}CH_2\})\}Cl_2]$ (**6**) [Equation (4)], which was isolated as a crystalline solid and characterised spectroscopically. The ^1H NMR spectrum for **6** shows three multiplets for the protons of the alkenyl-substituted C_5 ring (between δ = 5.5 and 7.0 ppm), four singlets for the methyl groups of the tetramethyl-substituted C_5 ring (between δ = 1.9 and 2.1 ppm), and two singlets corresponding to the methyl groups of the $SiMe_2$ bridging unit (δ = 0.83 and 0.87 ppm).

The signals for the alkenyl fragment have similar chemical shifts and identical spectral patterns to those observed in the zirconocene complexes **4** and **5**. However, the methyl groups substituting the carbon atom bonded to the cyclopentadienido ring are diastereotopic in **6** due to the planar

Table 2. Selected structural data of some zirconocene complexes.

Complex	Zr–Cl [Å]	Cp–Zr–Cp[a] [°]	Cl–Zr–Cl [°]	C=C [Å]	C–C=C [°]	Ref.
$[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}Cl_2]$ (**4**)	2.451(1) 2.447(1)	130.0 130.1	94.6(1)	1.298(6)	125.7(4)	this work
$[Zr(\eta^5\text{-}C_5H_4\{CMe_2CH_2CH_2CH{=}CH_2\})_2Cl_2]$ (**5**)	2.453(1)	129.2	94.9(1)	1.288(6)	126.1(4)	this work
$[Zr(\eta^5\text{-}C_5H_4\{CCH_3({=}CH_2)\})_2Cl_2]$	2.446(1)	129.8	96.2(1)	1.34(2)	123.3(11)	[9g]
$[Zr(\eta^5\text{-}C_5H_3tBu\{CCH_3({=}CH_2)\})_2Cl_2]$	2.433(1) 2.442(1)	130.5	96.1(1)	1.345(4) 1.374(5)	120.5(3) 119.9(3)	[9g]
$[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CH_2CH{=}CH_2\})\}Cl_2]$	2.429(1) 2.429(1)	126.0	98.7(1)	1.304(4)	125.9(3)	[9c]
$[Zr\{Me(CH_2CH{=}CH_2)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$	2.444(2) 2.431(2)	125.4	98.1(1)	1.26(5)	124(5)	[11c]
$[Zr\{Me(CH_2CH{=}CH_2)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$	2.428(2) 2.429(2)	126.7	100.9(1)	1.320(10)	123.0(10)	[11c]
$[Zr\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	2.425(3) 2.413(3)	128.5	97.5(1)	1.330(10)	124.8(9)	[11e]

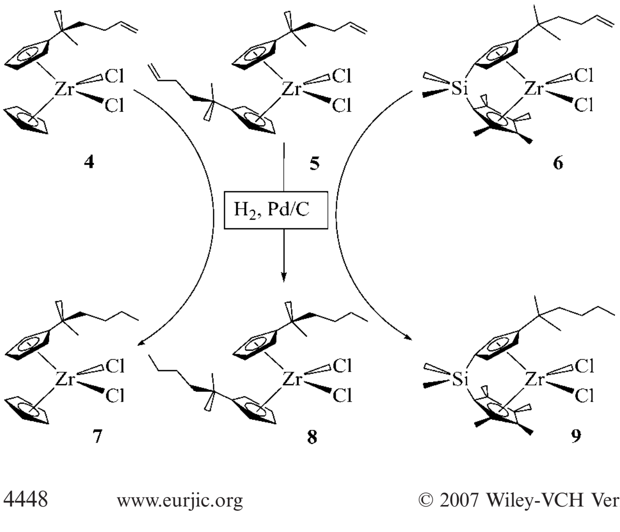
[a] Cp refers to the C_5H_5, C_5H_4 or C_5Me_4 moiety.



3 **6** (4)

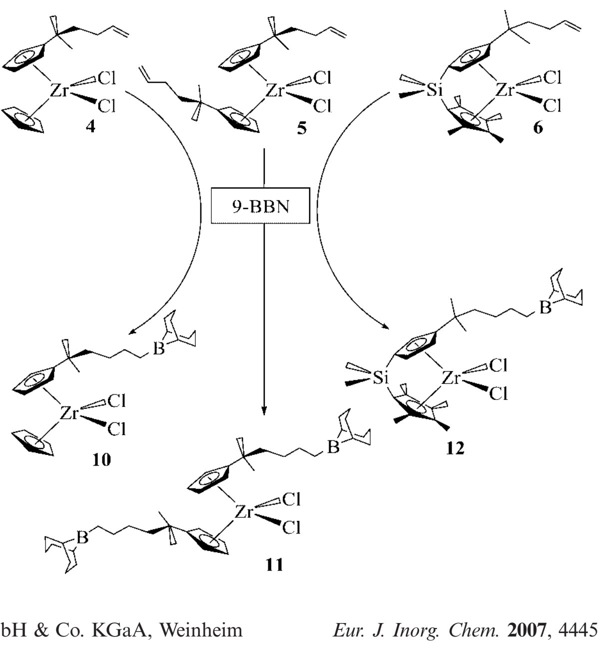
chirality present in the molecule and thus appear as two singlets (δ = 1.42 and 1.51 ppm) in the ^1H NMR spectrum.

We next attempted to hydrogenate the C=C double bond of the alkenyl fragment in complexes **4**–**6**. These complexes react with H_2 in a Pd/C-catalysed hydrogenation to give the saturated metallocene compounds $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_3)\}Cl_2]$ (**7**), $[Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_3)\}_2Cl_2]$ (**8**) and $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_3\})\}Cl_2]$ (**9**), respectively, as the only products [Equation (5)]. The ^1H NMR spectra of these complexes show four multiplets about $\delta \approx$ 0.8, 0.9, 1.2 and 1.4 ppm due to the newly formed alkyl moiety, with four signals in the alkyl carbon region between δ = 23 and 28 ppm in the $^{13}C\{^1H\}$ NMR spectra.



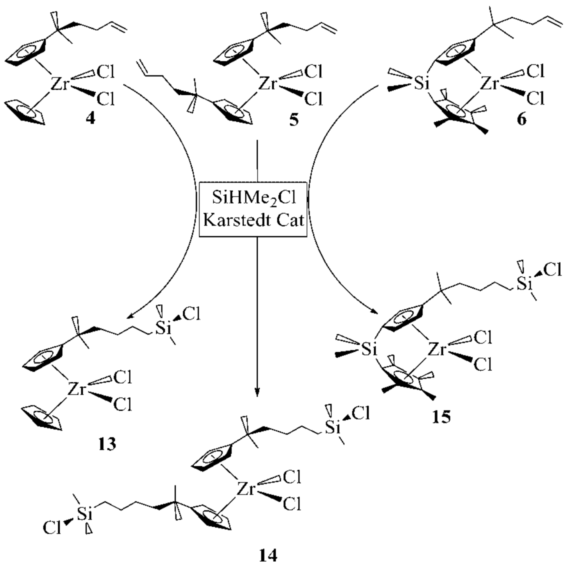
(5)

The alkenyl substituent in complexes **4**–**6** should also be suitable for the introduction of borane groups by hydroboration. Since previous studies have shown that a further functionalisation of the alkenyl side-chain and the isolation of the respective product is rather difficult,[10a–10d,11c,12] highly selective 9-borabicyclo[3.3.1]nonane (9-BBN) was chosen as the hydroboration agent. Reaction of complexes **4**–**6** with 9-BBN gave the product resulting from anti-Markovnikoff addition, namely $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2BC_8H_{14})\}Cl_2]$ (**10**), $[Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2BC_8H_{14})\}_2Cl_2]$ (**11**) and $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_2BC_8H_{14}\})\}Cl_2]$ (**12**), respectively [Equation (6)]. Complexes **10**–**12** were characterised by standard spectroscopic techniques. The ^1H NMR spectra of **10**–**12** show four multiplets between δ = 1.2 and 1.9 ppm for the boranyl moiety, corresponding to the four distinct proton environments (see Experimental Section). In these cases a change in the signals previously attributed to the alkenyl moiety in **4**–**6** to four multiplets at $\delta \approx$ 0.9, 1.0, 1.2 and 1.4 ppm was observed.



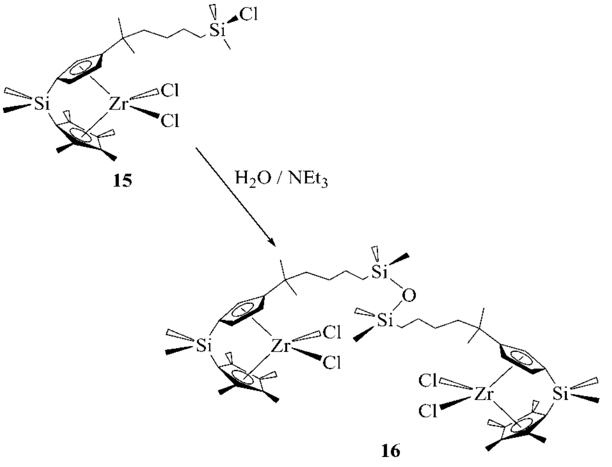
(6)

Catalytic hydrosilylation reactions are an excellent method for constructing different structures containing metallocene complexes.[6,11d,11e,13] With this in mind, we carried out the hydrosilylation reaction of **4**–**6** with an excess of chlorodimethylsilane in the presence of Karstedt's catalyst to give the β-hydrosilylation products $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2SiMe_2Cl)\}Cl_2]$ (**13**), $[Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2SiMe_2Cl)\}_2Cl_2]$ (**14**) and $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_2\text{-}SiMe_2Cl\})\}Cl_2]$ (**15**), respectively [Equation (7)]. Complexes **13**–**15** were characterised by ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR and IR spectroscopy and also by mass spectrometry. Completion of the hydrosilylation reaction was monitored by ^1H NMR spectroscopy, where the spectra recorded showed the absence of the olefinic proton signals of the alkenyl moiety and the appearance of four multiplets corresponding to the $–CH_2CH_2CH_2CH_2Si–$ fragment in the region $\delta = 0.7–1.6$ ppm. Additional signals due to the methyl groups attached to the silicon atom are present at $\delta \approx 0.4$ ppm. The $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectroscopic data confirmed the proposed structures (see Experimental Section), with a resonance being observed in the $^{29}Si\{^1H\}$ NMR spectra at $\delta \approx 30$ ppm due to the silicon atom of the new silyl fragment. Mass spectrometric analysis showed the molecular ion peak in all the cases (see Experimental Section).



(7)

The dinuclear, Si–O–Si-bridged complex $[Cl_2Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2(CH_2)_4SiMe_2OSiMe_2(CH_2)_4\text{-}Me_2C\}\eta^5\text{-}C_5H_3)(\eta^5\text{-}C_5Me_4)SiMe_2\}ZrCl_2]$ (**16**) was obtained upon addition of a stoichiometric amount of H_2O to a toluene solution of complex **15** [Equation (8)]. Selective hydrolysis of the Si–Cl bond and formation of an Si–O–Si bridge was confirmed by multinuclear NMR and IR spectroscopy. Complex **15** contains an element of planar chirality, therefore coupling of two such units should lead to the formation of two diastereoisomers (*rac* and *meso*). However, only one set of signals was observed in the NMR spectra of **16**. This is most probably due to the fact that the two chiral metallocene subunits are sufficiently separated in space that the signals corresponding to the respective *rac* and *meso* isomers coincide.



(8)

The signal for the methyl groups attached to the siloxane silicon atoms in the ^1H NMR spectrum of **16** is displaced from $\delta = 0.39$ (in **15**) to 0.00 ppm. The $^{29}Si\{^1H\}$ NMR spectrum shows a new signal at $\delta = 7.1$ ppm due to the silicon atoms of the Si–O–Si fragment as well as the signal corresponding to the silicon atoms of the *ansa* bridge ($\delta = –14.2$ ppm). This chemical shift is in agreement with those reported in other studies.[14] It should be noted that similar reactions for early transition metals have been reported recently.[15]

We also examined the polymerisation of ethylene using the zirconocene derivatives described in this paper as catalyst. The polymerisation experiments were conducted with an MAO/metal catalyst ratio of 1000:1 at 20 °C and an olefin pressure of 2 bar during 15 min. Polymerisation 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 and polymer molecular weights and molecular weight distributions are given in Table 3.

The symmetrical metallocene systems **5**, **8**, **11** and **14** show lower catalytic activities than the asymmetric or *ansa* complexes. Indeed, **11** is not catalytically active in the polymerisation of ethylene. The asymmetric metallocene catalysts, on the other hand, are active to different degrees, with **13** proving to be the most active catalyst of the series tested, **10** one of the least and **4** giving a value comparable to that of the reference catalyst $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$. The catalytic activity of the *ansa*-metallocene complexes **6**, **9** and **12** is relatively high, although lower activities were observed for **15** and the dinuclear complex **16**.

In order to explain the zero activity of **11** in polymerisation we prepared the dimethyl/borane derivatives, $[ZrCp'_2Me][MeB(C_6F_5)_3]$, of **10**–**12** on an NMR scale. According to Horton and co-workers, the chemical shift difference between the *meta*- and *para*-fluorine atoms in the ^{19}F NMR spectra provides information about the possible in-

Table 3. Ethylene polymerisation results for **4**–**16** and $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$.[a]

Catalyst	Activity[b]	M_w	M_w/M_n
$[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$	11650	169000	2.3
4	9717	881000	9.6
5	3070	978000	5.7
6	8170	62000	3.8
7	6925	742000	8.8
8	1435	576000	6.5
9	10231	42000	4.0
10	3400	938000	8.6
11	0	–	–
12	9100	62000	5.9
13	15867	168000	10.6
14	4067	157000	3.3
15	4867	224000	4.0
16	2800	664000	7.5

[a] At 20 °C, 2 bar monomer pressure, 200 mL of toluene, $[Al] = 3 \times 10^{-2}$ M, $[Zr] = 3 \times 10^{-5}$ M, t = 15 min. [b] In kg polymer $(\text{mol Zr h bar})^{-1}$.

teraction between the anion and the metal centre.[16] A difference of less than 3 ppm indicates the absence of anion coordination to the metal centre, whilst a value between 3 and 6 ppm suggests coordination. We observed that the dimethyl/borane derivatives of **10** and **12** gave values of about 2.1 ppm, thus indicating that anion coordination does not take place and permitting the formation of a vacant site at the metal centre which allows polymerisation. This value is 3.3 ppm for the derivative of the inactive catalyst **11**, and using the above argument one can reason that the anion is coordinated to the metal centre, therefore a vacant site cannot be readily formed at the metal atom for polymerisation.

With the exception of **15** and **16**, the *ansa*-metallocene catalysts gave polyethylene with lower molecular weights (approx. 60000) than that produced with the other catalysts employed in this study. High molecular weight polyethylene was produced with catalysts **4**, **5**, **7** and **10**. The unbridged metallocene complexes **4**, **5**, **7**, **8**, **10** and **13** produced broad polymer molecular weight distributions with polydispersity values between 6 and 10. This phenomenon has previously been explained by considering the rotation of the C_5 ring to be slower than the propagation of the polymer chain, which creates different rotamers of the catalyst that act as distinct active centres.[8g,17] One can thus envisage the formation of multi-site catalysts generated by the rotation of the substituted cyclopentadienido ligands. The *ansa*-metallocene catalysts **6**, **9**, **12** and **15** generally gave lower polydispersity values than their analogous unbridged complexes.

The polymerisation of propylene using the zirconocene derivatives **5**, **6**, **8**, **9**, **11**, **12**, **14**, **15** and **16** as catalyst was also examined. The polymerisation experiments were conducted with an MAO/metal catalyst ratio of 3000:1 at 0 °C and an olefin pressure of 2.5 bar during 60 min. Polymerisation 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, molecular weight distributions and isotacticities are given in Table 4.

Table 4. Propylene polymerisation results for **5**, **6**, **8**, **9**, **11**, **12**, **14**, **15**, **16** and $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$.[a]

Catalyst	Activity[b]	M_w	M_w/M_n	[mmmm] [%]
$[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$	48	2000	1.8	4.0
5	76	2300	2.0	12.1
6	123	18100	3.0	75.2
8	156	2200	1.9	12.3
9	192	13700	3.1	79.0
11	0	–	–	–
12	85	13100	2.4	77.1
14	94	2500	1.8	12.0
15	109	2800	1.9	78.6
16	85	2000	1.8	75.9

[a] At 0 °C, 2.5 bar monomer pressure, 200 mL of toluene, $[Al] = 2.25 \times 10^{-1}$ M, $[Zr] = 7.5 \times 10^{-5}$ M, t = 60 min. [b] In kg polymer $(\text{mol Zr h bar})^{-1}$.

All the catalysts tested gave higher activities than the reference catalyst $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$, although no polymerisation was observed with **11**. The *ansa*-metallocene catalysts **6**, **9** and **12** produced polypropylene with molecular weights significantly higher than that produced with the other catalysts. The polydispersity values observed were between 1.8 and 3.1 and are typical for single-site catalysts. It appears that rotation of the C_5 ring is restricted in the low-temperature polymerisation of propylene, thus preventing the formation of multiple active sites like those proposed in the polymerisation of ethylene.

The isotacticity of the polymers was measured by $^{13}C\{^1H\}$ NMR spectroscopy using the pentad method. The [mmmm] pentad values for the *ansa*-metallocene catalysts **6**, **9**, **12**, **15** and **16** were of the order of 75% and are comparable with those reported previously for similar C_1-symmetric complexes.[11b,11f,18] The stereoselectivity exhibited in the polymerisation can be explained by either a Cossee–Arlman site control[11f] or a back-skip mechanism.[11f,18b,19]

The unbridged metallocene catalysts **5**, **8** and **14** produced atactic polypropylene with [mmmm] pentads of 12%. We have previously observed that rotation of the cyclopentadienido ring in similar metallocene systems can be restricted by the introduction of bulky substituents and this translates into the formation of stereoselective active sites and polypropylene with low to medium isotacticity.[11g] However, this is not the case for **5**, **8** and **14**, where one can envisage that the alkenyl or alkyl chain substituents are flexible enough to position themselves so as not to restrict rotation of the cyclopentadienido rings.

Conclusions

We have reported the synthesis and catalytic activity of new alkenyl-substituted zirconocene complexes along with their structural characterisation. The reactivity of these complexes in hydrogenation, hydroboration and hydrosilylation processes has been studied and opens up not only the possibility of ligand design and modification but also the potential of supporting the catalysts on distinct substrates.

We have also studied the catalytic activity of the zirconocene and *ansa*-zirconocene complexes in the polymerisation of ethylene and propylene. The polymerisation of propylene using the C_1-symmetric *ansa*-metallocene complexes as catalysts gave polymers with relatively high isotacticity.

Experimental Section

General Remarks: All reactions were performed using standard Schlenk tube techniques under dry nitrogen. Solvents were distilled from the appropriate drying agents and degassed before use. $C_5H_2Me_4$, $ZrCl_4$, $HSiMe_2Cl$, $SiMe_3Cl$, *n*BuLi (1.6 M in hexane), MeLi (1.6 M in Et_2O), MAO (10 wt.-% in toluene), 9-BBN (0.5 M in thf) and $CH_3COCH_2CH_2CH{=}CH_2$ were purchased from Aldrich and the Karstedt catalyst from ABCR. All commercial reagents were used directly. 6-(4-Buten-1-yl)-6-methylfulvene was prepared according to the methodology described by Little and coworkers.[20] IR spectra were recorded with a Thermo Nicolet Avatar 330 FT-IR spectrophotometer. ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded with a Varian Mercury FT-400 spectrometer. Microanalyses were carried out with a Perkin–Elmer 2400 or LECO CHNS-932 microanalyzer. Mass spectrometric analyses were performed with a Hewlett–Packard 5988A instrument (*m*/*z* = 50–1000). Polymer molecular weights and distributions were determined by GPC (Waters 150C Plus or Alliance GPC-2000) in 1,2,4-trichlorobenzene at 150 °C. Polymer isotacticity was calculated from the $^{13}C\{^1H\}$ NMR spectra of polymer samples dissolved in 1,2,4-trichlorobenzene/C_6D_6 (1:1).

Preparation of [Li{$C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)$}] (1): MeLi (12.8 mL, 20.51 mmol) was added dropwise to a solution of 6-(4-buten-1-yl)-6-methylfulvene (3.00 g, 20.51 mmol) in Et_2O (75 mL) at –78 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. The solvent was then removed in vacuo to give a white solid, which was washed with hexane (2 × 50 mL) and dried under vacuum to yield the title complex as a free flowing white solid. Yield: 2.48 g (72%). ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 1.19 (s, 6 H, CMe_2), 1.50 and 1.91 (2 m, each 2 H, CH_2CH_2), 4.74 (*cis*) and 4.85 (*trans*) (2 dd, $^3J_{cis}$ = 10.0, $^3J_{trans}$ = 16.8 Hz, each 1 H, CH_2-$CH{=}CH_2$), 5.73 (m, 1 H, CH_2-$CH{=}CH_2$), 5.46 and 5.48 (2 m, each 2 H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_8$]THF, 25 °C): δ = 31.0 and 31.1 (CH_2CH_2), 35.4 (CMe_2), 46.5 (Cp*C*), 100.9, 101.8 and 141.6 (C_5H_4), 112.8 (CH_2-$CH{=}CH_2$), 128.8 ($CH_2CH{=}CH_2$) ppm. $C_{12}H_{17}Li$ (168.2): calcd. C 85.69, H 10.19; found C 85.33, H 10.17.

Preparation of $Me_2Si(C_5HMe_4)\{C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}$ (2): $Me_2Si(C_5HMe_4)Cl$ (2.55 g, 11.89 mmol) in thf (50 mL) was added to a solution of **1** (2.00 g, 11.89 mmol) in thf (50 mL) at –78 °C. The reaction mixture was warmed to room temperature and stirred for 6 h. The solvent was then removed in vacuo and hexane (150 mL) was added to the resulting dark orange oil. The mixture was filtered and the solvent removed from the filtrate under reduced pressure to yield the title compound as a dark yellow oil. Yield: 3.96 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C; for the predominant isomer): δ = –0.11 (s, 6 H, $SiMe_2$), 1.19 (s, 6 H, CMe_2), 1.59 and 1.83 (2 m, each 2 H, CH_2CH_2), 1.88 and 2.01 (2 s, each 6 H, C_5Me_4), 2.96 and 3.23 (2 m, each 1 H, 2 × HC_5), 4.90 (*cis*) and 4.97 (*trans*) (2 dd, $^3J_{cis}$ = 10.2, $^3J_{trans}$ = 16.9 Hz, each 1 H, $CH_2CH{=}CH_2$), 5.81 (m, 1 H, $CH_2CH{=}CH_2$), 5.92, 6.33 and 6.57 (3 m, each 1 H, C_5H_3) ppm. EI MS: *m*/*z* (%) = 340 (28) [M$^+$], 285 (46) [M$^+$ – $CH_2CH_2CH{=}CH_2$], 243 (100) [M$^+$ – $CMe_2CH_2CH_2CH{=}CH_2$]. $C_{23}H_{36}Si$ (340.6): calcd. C 81.10, H 10.65; found C 81.00, H 10.61.

Preparation of [$Li_2\{Me_2Si(C_5Me_4)(C_5H_3\{CMe_2CH_2CH_2CH{=}CH_2\})\}$] (3): *n*BuLi (11.0 mL, 17.62 mmol) was added dropwise to a solution of **4** (3.00 g, 8.81 mmol) in Et_2O (100 mL) at –78 °C. The mixture was warmed to 25 °C and stirred for 15 h. The solvent was then removed in vacuo to give a white solid, which was washed with hexane (2 × 50 mL) and dried under vacuum to yield the title complex as a white solid (2.54 g, 82%). $C_{23}H_{34}Li_2Si$ (352.5): calcd. C 78.37, H 9.72; found C 77.97, H 9.75.

Preparation of [$Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}Cl_2$] (4): A solution of **1** (1.00 g, 5.94 mmol) in thf (50 mL) was added dropwise during 15 min to a solution of [$Zr(\eta^5\text{-}C_5H_5)Cl_3$] (1.56 g, 5.94 mmol) in thf (50 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. The solvent was then 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 yield crystals of the title complex. Yield: 1.43 g (62%). IR (ZnSe): $\tilde{\nu}$ = 3100 (ν_{CH}), 1640 ($\nu_{C=C}$) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.39 (s, 6 H, CMe_2), 1.56 and 1.75 (2 m, CH_2CH_2), 4.89 (*cis*) and 4.96 (*trans*) (2 dd, $^3J_{cis}$ = 10.6, $^3J_{trans}$ = 17.2 Hz, each 1 H, $CH_2CH{=}CH_2$), 5.71 (m, 1 H, $CH_2CH{=}CH_2$), 6.36 and 6.45 (2 m, each 2 H, C_5H_4), 6.48 (s, 5 H, C_5H_5) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 27.2 and 29.0 (CH_2CH_2), 36.4 (CMe_2), 46.1 (Cp*C*), 112.2, 113.0 and 143.3 (C_5H_4), 115.9 (C_5H_5), 114.1 (CH_2-$CH{=}CH_2$), 138.5 (CH_2-$CH{=}CH_2$) ppm. EI MS: *m*/*z* (%) = 386 (20) [M$^+$], 331 (36) [M$^+$ – $CH_2CH_2CH{=}CH_2$], 225 (100) [M$^+$ – $C_5H_4(CMe_2CH_2CH_2$-$CH{=}CH_2)$]. $C_{17}H_{22}Cl_2Zr$ (388.5): calcd. C 52.56, H 5.71; found C 52.51, H 5.69.

Preparation of [$Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}_2Cl_2$] (5): The synthesis of **5** was carried out in an identical manner to **4** from **1** (1.00 g, 5.94 mmol) and $ZrCl_4$ (0.69 g, 2.97 mmol). Yield: 0.83 g (58%). IR (ZnSe): $\tilde{\nu}$ = 3103 (ν_{CH}), 1637 ($\nu_{C=C}$) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.41 (s, 12 H, 2 × CMe_2), 1.56 (4 H) and 1.77 (4 H) (2 m, each 4 H, 2 × CH_2CH_2), 4.88 (*cis*) and 4.95 (*trans*) (2 dd, $^3J_{cis}$ = 10.2, $^3J_{trans}$ = 16.9 Hz, each 2 H, 2 × $CH_2CH{=}CH_2$), 5.71 (m, 2 H, 2 × $CH_2CH{=}CH_2$), 6.32 and 6.41 (2 m, each 4 H, 2 × C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 27.1 and 29.0 (CH_2CH_2), 36.5 (CMe_2), 46.2 (Cp*C*), 112.2, 116.2 and 142.8 (C_5H_4), 114.0 ($CH_2CH{=}CH_2$), 138.7 ($CH_2CH{=}CH_2$) ppm. EI MS: *m*/*z* (%) = 484 (1) [M$^+$], 321 (100) [M$^+$ – $C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)$], 266 (34) [M$^+$ – $C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)$ – $CH_2CH_2CH{=}CH_2$], 231 (41) [M$^+$ – $C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)$ – $CH_2CH_2CH{=}CH_2$ – Cl]. $C_{24}H_{34}Cl_2Zr$ (484.7): calcd. C 59.48, H 7.07; found C 59.39, H 7.02.

Preparation of [$Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2\text{-}CH{=}CH_2\})\}Cl_2$] (6): The synthesis of **6** was carried out in an identical manner to **4** from **5** (1.50 g, 4.25 mmol) and $ZrCl_4$ (0.99 g, 4.25 mmol). Yield: 1.00 g (47%). IR (ZnSe): $\tilde{\nu}$ = 3099 (ν_{CH}), 1632 ($\nu_{C=C}$) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.83 and 0.87 (2 s, each 3 H, $SiMe_2$), 1.42 and 1.51 (2 s, each 3 H, CMe_2), 1.56 and 1.69 (2 m, each 2 H, CH_2CH_2), 1.92, 2.01, 2.03 and 2.06 (4 s, each 3 H, C_5Me_4), 4.88 (*cis*) and 4.95 (*trans*) (2 dd, $^3J_{cis}$ = 10.3, $^3J_{trans}$ = 16.9 Hz, each 1 H, $CH_2CH{=}CH_2$), 5.73 (m, 1 H, $CH_2CH{=}CH_2$), 5.57, 5.71 and 6.85 (3 m, each 1 H, C_5H_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = –0.4 and 0.4 ($SiMe_2$), 12.3, 12.5, 15.3 and 15.4 (C_5Me_4), 27.4 and 29.0 (CH_2CH_2), 36.5 (CMe_2), 46.2 (Cp*C*), 97.5 and 104.2 (C^1-Cp), 113.9 ($CH_2CH{=}CH_2$), 138.9 ($CH_2CH{=}CH_2$), 111.2, 123.9, 135.0 and 149.9 (C_5H_3), 113.5, 126.6, 127.2 and 136.2 (C_5Me_4) ppm. $^{29}Si\{^1H\}$

NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = –22.0 (*Si*Me$_2$) ppm. EI MS: *m*/*z* (%) = 498 (11) [M^+], 443 (38) [M^+ – $CH_2CH_2CH{=}CH_2$], 407 (100) [M^+ – $CH_2CH_2CH{=}CH_2$ – Cl]. $C_{23}H_{34}Cl_2SiZr$ (500.7): calcd. C 55.17, H 6.84; found C 54.93, H 6.79.

Preparation of $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_3)\}Cl_2]$ (7): Compound **4** (0.15 g, 0.39 mmol) was dissolved in CH_2Cl_2 (50 mL) and the Pd/C (10% palladium) catalyst was added (8 mg). Hydrogen was passed through the solution at 1 bar with stirring for 2 h. The resulting suspension was filtered and the solvent removed from the filtrate under reduced pressure to give the title complex as a crystalline solid. Yield: 0.14 g (97%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.91 (m, 3 H, $CH_2CH_2CH_2CH_3$), 0.98, 1.19 and 1.44 (3 m, each 2 H, $CH_2CH_2CH_2CH_3$), 1.39 (s, 6 H, C*Me*$_2$), 6.35 and 6.44 (2 m, each 2 H, C_5H_4), 6.47 (s, 5 H, C_5H_5) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.0, 23.1, 26.6 and 27.1 ($CH_2CH_2CH_2CH_3$), 36.3 (C*Me*$_2$), 46.7 (Cp*C*), 113.3, 115.5 and 144.1 (C_5H_4), 115.9 (C_5H_5) ppm. EI MS: *m*/*z* (%) = 388 (14) [M^+], 331 (55) [M^+ – $CH_2CH_2CH_2CH_3$], 225 (100) [M^+ – $C_5H_4(CMe_2CH_2CH_2CH_2CH_3)$]. $C_{17}H_{24}Cl_2Zr$ (390.5): calcd. C 52.29, H 6.19; found C 52.01, H 6.23.

Preparation of $[Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_3)\}_2Cl_2]$ (8): The synthesis of **8** from **5** (0.15 g, 0.31 mmol) was carried out in an identical manner to **7**. Yield: 0.14 g (92%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.82 (m, 6 H, 2 × $CH_2CH_2CH_2CH_3$), 0.96, 1.18 and 1.43 (3 m, each 4 H, 2 × $CH_2CH_2CH_2CH_3$), 1.36 (s, 12 H, 2 × C*Me*$_2$), 6.32 and 6.40 (2 m, each 4 H, 2 × C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.0, 23.2, 26.6 and 27.0 ($CH_2CH_2CH_2CH_3$), 36.4 (C*Me*$_2$), 46.8 (Cp*C*), 112.4, 116.1 and 143.5 (C_5H_4) ppm. EI MS: *m*/*z* (%) = 486 (4) [M^+], 429 (72) [M^+ – $CH_2CH_2CH_2CH_3$], 387 (100) [M^+ – $C_5H_4(CMe_2CH_2CH_2CH_2CH_3)$]. $C_{24}H_{38}Cl_2Zr$ (488.7): calcd. C 58.99, H 7.84; found C 58.66, H 7.86.

Preparation of $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_3\})\}Cl_2]$ (9): The synthesis of **9** from **6** (0.15 g, 0.30 mmol) was carried out in an identical manner to **7**. Yield: 0.12 g (81%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.81 and 0.85 (3 H) (2 s, each 3 H, Si*Me*$_2$), 0.83 (m, 3 H, $CH_2CH_2CH_2CH_3$), 0.95, 1.17 and 1.42 (3 m, each 2 H, $CH_2CH_2CH_2CH_3$), 1.37 and 1.46 (2 s, each 3 H, C*Me*$_2$), 1.90, 1.99, 2.01 and 2.04 (4 s, each 3 H, C_5Me_4), 5.55, 5.67 and 6.84 (3 m, each 1 H, C_5H_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = –0.5 and 0.2 (Si*Me*$_2$), 12.1, 12.3, 14.1 and 15.1 (C_5Me_4), 23.2, 24.5 26.6 and 27.2 ($CH_2CH_2CH_2CH_3$), 36.4 (C*Me*$_2$), 46.9 (Cp*C*), 97.5 and 104.1 (C^1-Cp), 111.3, 123.9, 127.3 and 150.9 (C_5H_3), 113.6, 126.7, 135.1 and 136.4 (C_5Me$_4$) ppm. $^{29}Si\{^1H\}$ NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = –14.2 (*Si*Me$_2$) ppm. EI MS: *m*/*z* (%) = 502 (11) [M^+], 443 (38) [M^+ – $CH_2CH_2CH_2CH_3$], 407 (100) [M^+ – $CH_2CH_2CH_2CH_3$ – Cl]. $C_{23}H_{36}Cl_2SiZr$ (502.8): calcd. C 54.95, H 7.22; found C 54.93, H 7.27.

Preparation of $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2\text{-}BC_8H_{14})\}Cl_2]$ (10): Complex **4** (0.15 g, 0.39 mmol) was dissolved in thf (50 mL), and 9-BBN (0.5 M in thf; 0.78 mL, 0.39 mmol) was added dropwise at room temperature during 5 min. The solution was then stirred for 15 h. The solvent was removed under reduced pressure to give the title compound as a crystalline solid (0.20 g, 100%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.96, 1.02, 1.19 and 1.44 (4 m, each 2 H, $CH_2CH_2CH_2CH_2B$), 1.35 and 1.84 (2 m, each 2 H, γ-H of 9-BBN), 1.63 and 1.84 (2 m, each 4 H, β- and δ-H of 9-BBN), 1.80 (m, 2 H, α-H of 9-BBN), 1.35 (s, 6 H, C*Me*$_2$), 6.34 and 6.45 (2 m, each 2 H, C_5H_4), 6.48 (s, 5 H, C_5H_5) ppm. $^{11}B\{^1H\}$ NMR (85.6 MHz, $CDCl_3$, 25 °C): δ = 86 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 24.9, 25.6, 27.6and 28.9 ($CH_2CH_2CH_2CH_2B$), 23.2, 27.0, 27.1 and 33.1 (9-BBN), 36.4 (C*Me*$_2$), 47.2 (Cp*C*), 113.3, 115.6 and 144.0 (C_5H_4), 115.9 (C_5H_5) ppm. EI MS: *m*/*z* (%) = 508 (2) [M^+], 331 (74) [M^+ – $CH_2CH_2CH_2CH_2BC_8H_{14}$], 255 (100) [$M^+$ – $CH_2CH_2CH_2CH_2$-BC_8H_{14} – Cl]. $C_{25}H_{37}BCl_2Zr$ (510.5): calcd. C 58.82, H 7.31; found C 58.47, H 7.30.

Preparation of $[Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2BC_8H_{14})\}_2Cl_2]$ (11): The synthesis of **11** from **5** (0.15 g, 0.31 mmol) and 9-BBN (0.5 M in thf; 1.24 mL, 0.62 mmol) was carried out in an identical manner to **10**. Yield: 0.21 g (100%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.97, 1.01, 1.21 and 1.46 (4 m, each 4 H, 2 × $CH_2CH_2CH_2CH_2B$), 1.32 and 1.83 (2 m, each 4 H, 2 × γ-H of 9-BBN), 1.64 and 1.88 (m, each 8 H, 2 × β- and δ-H of 9-BBN), 1.81 (m, 4 H, 2 × α-H of 9-BBN), 1.38 (s, 12 H, 2 × C*Me*$_2$), 6.31 and 6.40 (2 m, each 4 H, 2 × C_5H_4) ppm. $^{11}B\{^1H\}$ NMR (85.6 MHz, $CDCl_3$, 25 °C): δ = 86 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 25.1, 25.7, 27.7 and 31.0 ($CH_2CH_2CH_2CH_2B$), 23.3, 27.1, 27.2 and 33.2 (9-BBN), 36.6 (C*Me*$_2$), 47.4 (Cp*C*), 112.3, 116.1 and 143.2 (C_5H_4) ppm. EI MS: *m*/*z* (%) = 726 (7) [M^+], 549 (21) [M^+ – $CH_2CH_2CH_2CH_2BC_8H_{14}$], 373 (100) [$M^+$ – 2 $CH_2CH_2CH_2CH_2BC_8H_{14}$]. $C_{40}H_{64}B_2Cl_2Zr$ (728.7): calcd. C 65.93, H 8.85; found C 65.50, H 8.81.

Preparation of $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2\text{-}CH_2BC_8H_{14}\})\}Cl_2]$ (12): The synthesis of **12** from **6** (0.15 g, 0.30 mmol) and 9-BBN (0.5 M in thf; 0.60 mL, 0.30 mmol) was carried out in an identical manner to **10**. Yield: 0.18 g (100%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.83 and 0.86 (2 s, each 3 H, Si*Me*$_2$), 0.97, 1.17, 1.21 and 1.45 (4 m, each 2 H, $CH_2CH_2CH_2CH_2B$), 1.33 and 1.83 (2 m, each 2 H, γ-H of 9-BBN), 1.65 and 1.85 (2 m, each 4 H, β and δ-H of 9-BBN), 1.78 (m, 2 H, α-H of 9-BBN), 1.39 and 1.49 (2 s, each 3 H, C*Me*$_2$), 1.91, 2.00, 2.03 and 2.05 (4 s, each 3 H,C_5Me_4), 5.55, 5.66 and 6.83 (3 m, each 1 H,C_5H_3) ppm. $^{11}B\{^1H\}$ NMR (85.6 MHz, $CDCl_3$, 25 °C): δ = 86 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = –0.4 and 0.4 (Si*Me*$_2$), 12.2, 12.4, 14.3 and 15.2 (C_5Me_4), 19.1, 24.4, 25.1 and 27.7 ($CH_2CH_2CH_2CH_2B$), 23.3, 27.5, 33.2 and 33.3 (9-BBN), 36.6 (C*Me*$_2$), 47.6 (Cp*C*), 97.8 and 104.0 (C^1-Cp), 111.3, 123.8, 127.1 and 150.7 (C_5H_3), 113.5, 126.4, 135.0 and 136.1 (C_5Me$_4$) ppm. $^{29}Si\{^1H\}$ NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = –14.2 (*Si*Me$_2$) ppm. EI MS: *m*/*z* (%) = 620 (9) [M^+], 443 (27) [M^+ – $CH_2CH_2CH_2CH_2BC_8H_{14}$], 409 (100) [$M^+$ – $CH_2CH_2CH_2$-$CH_2BC_8H_{14}$ – Cl], 374 (66) [M^+ – $CH_2CH_2CH_2CH_2BC_8H_{14}$ – 2 Cl]. $C_{31}H_{49}BCl_2SiZr$ (622.8): calcd. C 59.79, H 7.93; found C 59.67, H 7.88.

Preparation of $[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2\text{-}SiMe_2Cl)\}Cl_2]$ (13): Two drops of the Karstedt catalyst [divinyltetramethylsiloxaneplatinum(0) in xylene (3–3.5%)] were added to a solution of **4** (0.15 g, 0.39 mmol) in toluene (25 mL) and the mixture was stirred at room temperature for 10 min. An excess of $SiHMe_2Cl$ (0.15 g, 1.56 mmol) was then added to this solution dropwise and the reaction mixture stirred for 6 h. The mixture was filtered, and volatiles were removed from the filtrate under reduced pressure to give the title product as a light brown solid. Yield: 0.18 g (99%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.39 (s, 6 H, Si*Me*$_2$Cl), 0.76, 1.05, 1.32 and 1.47 (4 m, each 2 H, $CH_2CH_2CH_2CH_2Si$), 1.36 (s, 6 H, C*Me*$_2$), 6.35 and 6.43 (2 m, each 2 H, C_5H_4), 6.48 (s, 5 H, C_5H_5) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 1.8 (Si*Me*$_2$Cl), 19.1, 23.6, 27.2 and 27.9 ($CH_2CH_2CH_2CH_2$-Si), 36.4 (C*Me*$_2$), 46.7 (Cp*C*), 113.1, 115.5 and 143.7 (C_5H_4), 115.8 (C_5H_5) ppm. $^{29}Si\{^1H\}$ NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = 31.7 (*Si*Me$_2$Cl) ppm. EI MS: *m*/*z* (%) = 480 (100) [M^+], 331 (41) [M^+ – $CH_2CH_2CH_2CH_2SiMe_2Cl$], 255 (23) [M^+ – $CH_2CH_2CH_2CH_2SiMe_2Cl$ – Cl]. $C_{19}H_{29}Cl_3SiZr$ (483.1): calcd. C 47.24, H 6.05; found C 47.47, H 6.07.

Preparation of $[\mathrm{Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH_2CH_2SiMe_2Cl)\}_2Cl_2}]$ (14): The synthesis of **14** from **5** (0.15 g, 0.31 mmol) and $\mathrm{SiHMe_2Cl}$ (0.15 g, 1.56 mmol) was carried out in an identical manner to **13**. Yield: 0.21 g (98%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 0.37 (s, 12 H, $2\times \mathrm{Si}Me_2\mathrm{Cl}$), 0.74, 1.04, 1.33 and 1.44 (4 m, each 4 H, $2\times \mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{Si}$), 1.36 (s, 12 H, $2\times \mathrm{C}Me_2$), 6.32 and 6.40 (2 m, each 4 H, $2\times \mathrm{C_5}H_4$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 1.8 ($\mathrm{Si}Me_2\mathrm{Cl}$), 19.3, 23.6, 27.1 and 27.8 ($C\mathrm{H_2}C\mathrm{H_2}C\mathrm{H_2}C\mathrm{H_2Si}$), 36.5 ($C\mathrm{Me_2}$), 46.3 (Cp$C$), 112.2, 116.1 and 143.1 ($C_5\mathrm{H_4}$) ppm. ^{29}Si{^{1}H} NMR (79.5 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 31.8 ($Si\mathrm{Me_2Cl}$) ppm. EI MS: m/z (%) = 670 (97) [M$^+$], 635 (100) [M$^+$ – Cl], 521 (44) [M$^+$ – $\mathrm{CH_2CH_2CH_2CH_2SiMe_2Cl}$]. $\mathrm{C_{28}H_{48}Cl_4Si_2Zr}$ (673.9): calcd. C 49.90, H 7.18; found C 50.12, H 7.21.

Preparation of $[\mathrm{Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_2SiMe_2Cl\})\}Cl_2}]$ (15): The synthesis of **15** from **6** (0.15 g, 0.30 mmol) and $\mathrm{SiHMe_2Cl}$ (0.15 g, 1.56 mmol) was carried out in an identical manner to **13**. Yield: 0.18 g (100%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 0.39 (s, 6 H, $\mathrm{Si}Me_2\mathrm{Cl}$), 0.83 and 0.87 (2 s, each 3 H, $\mathrm{Si}Me_2$ *ansa* bridge), 0.79, 0.99, 1.28 and 1.45 (4 m, each 2 H, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{Si}$), 1.39 and 1.49 (2 s, each 3 H, $\mathrm{C}Me_2$), 1.92, 2.01, 2.03 and 2.05 (4 s, each 3 H, $\mathrm{C_5}Me_4$), 5.56, 5.68 and 6.84 (3 m, each 1 H, $\mathrm{C_5}H_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = –0.4 and 0.3 ($\mathrm{Si}Me_2$ *ansa* bridge) 1.8 ($\mathrm{Si}Me_2\mathrm{Cl}$), 12.2, 12.5, 15.2 and 19.1 ($\mathrm{C_5}Me_4$), 23.4, 23.6, 24.7 and 27.9 ($C\mathrm{H_2}C\mathrm{H_2}C\mathrm{H_2}C\mathrm{H_2Si}$), 36.5 ($C\mathrm{Me_2}$), 46.8 (Cp$C$), 97.5 and 104.2 ($C^1$-Cp), 111.2, 123.9, 127.2 and 150.5 ($C_5\mathrm{H_3}$), 113.5, 126.4, 135.1 and 136.2 ($C_5\mathrm{Me_4}$) ppm. ^{29}Si{^{1}H} NMR (79.5 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = –14.2 ($Si\mathrm{Me_2}$ *ansa* bridge), 31.8 ($\mathrm{Si}Me_2\mathrm{Cl}$) ppm. EI MS: m/z (%) = 595 (63) [M$^+$], 557 (21) [M$^+$ – Cl], 443 (100) [M$^+$ – $\mathrm{CH_2CH_2CH_2CH_2SiMe_2Cl}$], 409 (72) [M$^+$ – $\mathrm{CH_2CH_2CH_2CH_2SiMe_2Cl}$ – Cl]. $\mathrm{C_{25}H_{41}BCl_3Si_2Zr}$ (595.4): calcd. C 50.44, H 6.94; found C 50.67, H 6.88.

Preparation of $[\mathrm{Cl_2Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2(CH_2)_4SiMe_2OSiMe_2(CH_2)_4Me_2C\}\eta^5\text{-}C_5H_3)(\eta^5\text{-}C_5Me_4)SiMe_2\}ZrCl_2}]$ (16): Degassed distilled water (4.5 µL, 0.25 mmol) was added to a mixture of **15** (0.30 g, 0.50 mmol) and $\mathrm{NEt_3}$ (70.2 µL, 0.50 mmol) in toluene (15 mL). After stirring at room temperature for 2 h, the solution was filtered, and the volatiles were removed under vacuum to give **16** as a brown solid. Yield: 0.14 g (51%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 0.00 (s, 12 H, $2\times \mathrm{Si}Me_2\mathrm{O}$), 0.84 (6 H), 0.87 (6 H) (2 s, each 6 H, $2\times \mathrm{Si}Me_2$ *ansa* bridge), 0.45, 0.97, 1.19 and 1.44 (4 m, each 4 H, $2\times \mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{Si}$), 1.40 and 1.49 (2 s, each 6 H, $2\times \mathrm{C}Me_2$), 1.93, 2.01, 2.03 and 2.06 (4 s, each 6 H, $2\times \mathrm{C_5}Me_4$), 5.56, 5.67 and 6.84 (3 m, each 2 H, $2\times \mathrm{C_5}H_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = –0.4 and 0.4 ($\mathrm{Si}Me_2$ *ansa* bridge), 0.6 ($\mathrm{Si}Me_2\mathrm{O}$), 12.2, 12.5, 15.2 and 18.6 ($\mathrm{C_5}Me_4$), 21.6, 24.0, 27.4 and 28.3 ($C\mathrm{H_2}C\mathrm{H_2}C\mathrm{H_2}C\mathrm{H_2Si}$), 36.5 ($C\mathrm{Me_2}$), 47.2 (Cp$C$), 97.5 and 104.1 ($C^1$-Cp), 111.2, 123.9, 127.1 and 150.7 ($C_5\mathrm{H_3}$), 113.5, 126.4, 135.0 and 136.1 ($C_5\mathrm{Me_4}$) ppm. ^{29}Si{^{1}H} NMR (79.5 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = –14.2 ($Si\mathrm{Me_2}$ *ansa* bridge), 7.2 ($\mathrm{Si}Me_2\mathrm{O}$) ppm. EI MS: m/z (%) 631 (22) [M$^+$ – $\mathrm{Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_2\})\}Cl_2}$], 557 (8) [M$^+$ – $\mathrm{Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_2SiMe_2O\})\}Cl_2}$], 443 (50) [M$^+$ – $\mathrm{Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_2SiMe_2OSiMe_2CH_2CH_2CH_2CH_2\})\}Cl_2}$], 409 (100) [M$^+$ – $\mathrm{Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CMe_2CH_2CH_2CH_2CH_2SiMe_2OSiMe_2CH_2CH_2CH_2CH_2\})\}Cl_2}$ – Cl]. $\mathrm{C_{50}H_{82}Cl_4OSi_4Zr_2}$ (1135.8): calcd. C 52.87, H 7.28; found C 52.69, H 7.29.

Polymerisation 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 $\mathrm{N_2}$ pressure inside the autoclave was reduced under vacuum, an ethylene pressure of 2 bar was applied and maintained and stirring of the mixture commenced (1000 rpm). Stirring was halted after exactly 15 min 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, washed with ethanol and dried under vacuum at 90 °C for 16 h.

Polymerisation of Propylene: The zirconocene catalyst (15 µmol), MAO (10% in toluene) (45000 µmol) and toluene (200 mL) were mixed together for 15 min in a 1 L glass autoclave. The $\mathrm{N_2}$ pressure inside the autoclave was reduced under vacuum, a propylene pressure of 2.5 bar was then applied and maintained and stirring of the mixture commenced (1000 rpm). Stirring was halted after exactly 60 min and the propylene pressure released. Excess MAO was then destroyed by cautiously adding a mixture of methanol/HCl (90:10). The 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.

X-ray Structure Determination of $[\mathrm{Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}Cl_2}]$ (4) and $[\mathrm{Zr\{\eta^5\text{-}C_5H_4(CMe_2CH_2CH_2CH{=}CH_2)\}_2Cl_2}]$ (5): Data for **4** and **5** were collected with a Siemens SMART CCD diffractometer [λ(Cu-K_α) = 1.54178 Å] in the ω- and ϕ-scans modes. Semiempirical absorption corrections were carried out with SADABS.[21] The structures were solved by direct methods.[22] Structure refinement was carried out with SHELXL-97,[23] which is included in the software package WINGX.[24] All non-hydrogen atoms were refined anisotropically, and the H atoms of the cyclopentadienido rings and the hydrogen atoms of the terminal double bonds were located by difference maps and refined isotropically. Weights were optimised in the final cycles. Crystallographic data are given in Table 5. CCDC-642241 (**4**) and -642240 (**5**) contain the supplementary crystallographic data for this paper.

Table 5. Crystal and structure refinement data for **4** and **5**.[a]

	4	5
Empirical formula	$\mathrm{C_{17}H_{22}Cl_2Zr}$	$\mathrm{C_{24}H_{34}Cl_2Zr}$
Formula mass	388.47	484.63
T [K]	100(2)	100(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a [Å]	12.4708(2)	26.5942(5)
b [Å]	12.7217(2)	6.62880(10)
c [Å]	13.0835(2)	13.9555(2)
α [°]	116.2580(10)	90
β [°]	99.5690(10)	106.3420(10)
γ [°]	105.5060(10)	90
V [Å^3]	1693.75(5)	2360.79(7)
Z	4	4
$D_{\text{calcd.}}$ [g cm^{-3}]	1.523	1.364
μ [mm^{-1}]	8.106	5.923
F(000)	792	1008
Crystal size [mm]	$0.12\times0.09\times0.04$	$0.07\times0.06\times0.03$
θ range [°]	3.90–67.11	3.46–71.18
hkl range	$-14 \le h \le 14$, $-15 \le k \le 14$, $-15 \le l \le 15$	$-31 \le h \le 32$, $-8 \le k \le 8$, $-16 \le l \le 17$
Data/parameters	5693/461	2183/125
Goodness-of-fit on F^2	1.006	1.011
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0351, wR_2 = 0.0842	R_1 = 0.0345, wR_2 = 0.0831
R indices (all data)	R_1 = 0.0466, wR_2 = 0.0913	R_1 = 0.0461, wR_2 = 0.0892
Largest diff. peak/hole [e Å^{-3}]	1.335/–0.444	0.779/–0.366

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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