Synthesis and characterization of methyl-phenyl-substituted cyclopentadienyl zirconium complexes

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Abstract

The trisubstituted methyl-phenyl-silyl-cyclopentadienes [Me-Ph-C5H3(SiMe2X)] (X = Me, Cl, NH-t-Bu) and [(Me-Ph-C5H3)2SiMe2] and the lithium salts Li2[Me-Ph-C5H2(SiMe2Nt-Bu)] and Li2[(Me-Ph-C5H2)2SiMe2] have been isolated by conventional methods and characterized by NMR spectroscopy. Desilylation of [Me-Ph-C5H3(SiMe3)] with ZrCl4(SMe2)2 gave the monocyclopentadienyl complex [Zr(g5-1-Ph-3-Me-C5H3)Cl3]. The ansa-metallocene [Zr{(g5-2-Me-4-Ph-C5H3)SiMe2(g5-2-Ph-4-Me-C5H2)}Cl2] was obtained from the mixture of isomers formed by transmetallation of Li2[(Me-Ph-C5H2)2SiMe2] to ZrCl4 and characterized as the meso-diastereomer by X-ray diffraction methods. Similar transmetallation of Li2[Me-Ph-C5H2(SiMe2Nt-Bu)] gave the silyl-amido complex [Zr{(g5-2-Me-4-Ph-C5H2(SiMe2-g5-Nt-Bu)}Cl2] that was further alkylated to give [Zr{(g5-2-Me-4-Ph-C5H2(SiMe2-g5-Nt-Bu)}R2] (R = Me, CH2Ph) and used as a catalyst precursor, activated with MAO, for ethene and propene polymerization. All of the new compounds were characterized by elemental analysis and NMR spectroscopy.

Keywords: Cyclopentadienyl; Zirconium; Metallocenes; Silyl-amido; Polymerization

1. Introduction

Group 4 transition metal cyclopentadienyl-type complexes have received special and intense research interest through their applications as olefin polymerization catalysts. The electronic and steric effects of different substituents in the cyclopentadienyl ring give rise to significant changes in the reactivity and cationic activity of their metal complexes in ethene and propene polymerization [1]. The control of the polyolefin stereochemistry and the stereoselectivity in propene polymerization induced by C2-symmetric ansa-metallocenes are well established [2]. Similarly, styrene polymerisation has driven much of the chemistry of the mono-cyclopentadienyl and -indenyl group 4 metal compounds with many studies reporting [3] the effect of different substituents on the activity, tacticity and molecular weight of the resulting polystyrene. The CGC-catalysts based on η5-cyclopentadienyl-silyl-η-amido group 4 metal compounds [4,5] are receiving increasing interest, initially reported with a tetramethyl substituted ring containing a silyl-η-t-butylamido group [6,7] and more recently extended to studying aspects of stereospecific copolymerization [8] and the effect of different substituents at the amido-N [9] and the bridging group [10]. Although some stereochemical mechanistic studies on different transition metal complexes with the 1-phenyl-3-methyl-cyclopentadienyl ligand had been reported previously [11,12], this ligand was used [13] to prepare the first group 4 ansa-metallocenes with tetrathylethylene and dimethylsilylethyl bridges. Similar disubstituted tetrahydroindenyl compounds have been reported [14] more
recently. However, few studies have been focused on the regioselectivity of reactions made to introduce a third substituent on any of the three possible positions of the 1-Ph-3-Me-cyclopentadiene or on the electronic and steric effects of the methyl and phenyl substituents and their relative location on the reactivity of the resulting metal complexes. In line with our interest in studying the steric and electronic effects of bulky ligands on the reactivity of their metallocone and cyclopentadienylsilyle-η-amido group 4 metal complexes, we have reported [15] the use of the disubstituted Me-Pcyclopentadienyl ligand to prepare non-bridged and tetramethyldisiloxane-bridged group 4 metal complexes. We report herein the results observed when different silyl groups [SiMe₃, SiMe₂Cl, SiMe₂(NHᵗ-Bu) and SiMe₂(Me-Ph-C₅H₃)] are introduced into the 1-Ph-3-MeC₅H₄ ring and the structural consequences when the corresponding cyclopentadienyl, ansa-dicyclopentadienyl and ansa-cyclopentadienyl-silyl-η-amido zirconium complexes.

2. Results and discussion

2.1. Mono- and di-cyclopentadienyl complexes

The lithium salt of the disubstituted 1-phenyl-3-methyl-cyclopentadiene Li[1-Ph-3-Me-C₅H₃] (1) has been prepared and reacted in situ [13] with dichlorodimethylsilane to prepare the dimethylsilyl-bis(2-methyl-4-phenyl-cyclopentadiene), which was further deprotonated and used for the subsequent formation of the corresponding dimethylsilyl-bridged metallocones. With the aim of isolating the CG-type silyl-η-amido complexes of this disubstituted methyl-phenyl-cyclopentadienyl ligand, it was convenient to isolate all of the intermediate cyclopentadienes and their lithium salts involved in that procedure (see Scheme 1).

The lithium salt 1 was obtained in high yield by deprotonation of [1-Ph-3-Me-C₅H₃] with Liₙ-N-Bu as a white solid, which was characterized by elemental analysis and ¹H NMR spectroscopy (see Section 4). Reaction of 1 with 1.1 equiv (10% excess) of chlorotrimethylsilane and dichlorodimethylsilane in THF gave the trisubstituted silyl derivatives [Me-Ph-C₅H₃(SiMe₃)] (2) and [Me-Ph-C₅H₃(SiMe₂Cl)] (3), respectively. Further reaction of 3 with 2 equiv of t-BuNH₂ in THF gave the aminosilylcyclopentadiene [Me-Ph-C₅H₃(SiMe₂NHᵗ-Bu)] (4), whereas reaction of 3 with 1 equiv of the lithium salt 1 in diethyl ether gave the dimethylsilyl-di(cyclopentadiene) [(Me-Ph-C₅H₃)₂SiMe₂] (5) in 80% yield. Compounds 2-4 were isolated as yellow liquids and were characterized by ¹H NMR spectroscopy and elemental analysis (2 and 4). The ¹H NMR spectra show that compounds 2 and 4 contain a mixture of two isomers whereas 3 is one unique isomer. In agreement with the data discussed below for their metal complexes, the ¹H NMR spectra are consistent with 2 and 4 being mixtures in 3:1 and 5:1 molar ratios, respectively, of the two isomers (a) and (b) represented in Scheme 2, in which the silyl substituent is always bound to C(sp³) and located in an α position with respect to Me (a) and Ph (b), whereas the third possible isomer with the silyl group between both Me and Ph groups was absent. In contrast, the more electrophilic –SiMe₂Cl selectively gave the isomer 3(a) as the unique reaction product.

On the basis of these data, formation of three isomers would be expected for the dicyclopentadiene 5 resulting from the different combinations of these two isomeric configurations. However, compound 5 appeared as a mixture of isomers which could not be identified in the ¹H NMR spectrum, which shows very broad signals.

![Scheme 1](image-url)

![Scheme 2](image-url)
The dilithium salt Li₂[Me-Ph-C₅H₅(SiMe₂Nr-Bu)] (6) was isolated as a white solid in almost quantitative yield by deprotonation of 4 with 2 equiv of Li₂-Bu in diethyl ether and was characterized by elemental analysis. Analogous deprotonation of the dicyclopentadiene 5 with 2 equiv of Li₂-Bu in the smallest amount of diethyl ether gave the dilithium salt Li₂[(Me-Ph-C₅H₅)₂SiMe₂] (7), which was isolated in low yield as a colourless solid and characterized by NMR spectroscopy. The ¹H NMR spectrum of 7 in C₆D₆/C₅D₅N showed two singlets for SiMe₂ groups, two singlets for Me phenyl groups and the expected four doublets for the ring-H protons. The ¹H NMR spectrum of 7 in CD₂Cl₂ showed one singlet for the SiMe₂ groups, two singlets for the ring-Me protons, two sets of signals for non-equivalent enantiotopic faces of both (2-Me-4-Ph-C₅H₅) and (2-Ph-4-Me-C₅H₅) rings of the starting dimethylsilyl-(cyclopentadienyl) ligand in 7b moved us to try to isolate its corresponding zirconium complexes. As shown in Eq. (1) the reaction of 7a or (c) + 7b with 1 equiv of ZrCl₄·2THF in toluene gave, after cooling the concentrated solution to −30 ºC, a yellow crystalline solid which was characterized as the dichloro-ansa-zirconocenes [Zr{(η⁵-Me-Ph-C₅H₅)₂SiMe₂}Cl₂] (9) by elemental analysis. The ¹H NMR spectra of 9 demonstrated the presence of the two diastereomers [Zr{(η⁵-Me-Ph-C₅H₅)₂SiMe₂}Cl₂] (rac-9a and meso-9a) and reported previously [13] together with a third isomer 9b in a molar ratio of ca. 2:2:1, respectively. Formation of these three isomers demonstrated that the isomer 7c shown in Scheme 3 was not present in the dilithium salt which must therefore contain a mixture of two isomers 7a, as the major and 7b, as the minor components.

Recrystallization of this mixture of isomers from toluene gave a yellow solid containing meso-9a and 9b with traces of the more soluble rac-9a, which after separation from the mother liquor and removal of the solvent, gave a mixture of two isomers. The ¹H and ¹³C NMR spectra of this mixture (see Section 4) are consistent with the ¹H NMR spectra reported [13] for the meso-9a and rac-9a diastereoisomers. Repeated recrystallization of the first yellow solid fraction from toluene allowed isolating the less soluble 9b as a yellow crystalline solid, although it was always contaminated by variable very small amounts of meso-9a of intermediate solubility. Crystals of 9b appropriate for X-ray diffraction studies were obtained by cooling its concentrated toluene solutions at −30 ºC.

The enantiotopic faces of both (2-Me-4-Ph-Cp) and (2-Ph-4-Me-Cp) rings of the starting dimethylsilyl-(cyclopentadienyl) ligand in 7b have the potential to have the enantiomeric pairs of the asymmetric diastereomers 9b and 9c represented in Scheme 5.

However, formation of diastereoisomer 9c was never observed, probably due to a high degree of facial selectivity. The ¹H NMR spectrum of the resulting yellow crystalline solid confirmed the presence of only one set of signals corresponding to one unique diastereomer, 9b. It shows two singlets for SiMe₂ groups, two singlets for ring-Me protons, two sets of signals for non-equivalent phenyl groups and the expected four doublets for the

\[
\text{Li}_2[(\text{Me-Ph-C}_5\text{H}_5)_2\text{SiMe}_2] + \text{ZrCl}_4(\text{THF})_2 \\
\text{Toluene} \xrightarrow{-2\text{LiCl}} \text{Zr}((\text{Me-Ph-C}_5\text{H}_5)_2\text{SiMe}_2)_2\text{Cl}_2
\]

(1)

It has been reported [13] that THF solutions of the dilithium salt 7 prepared and used in situ reacted with ZrCl₄·2THF to give a mixture of diastereomers (rac:meso, 1:1 from the crystallized solid and further extraction from the mother liquor). The presence of 7b in the mixture of isomers contained in the dilithium salt 7 moved us to try to isolate its corresponding zirconium complexes. As shown in Eq. (1) the reaction of 7a or (c) + 7b with 1 equiv of ZrCl₄·2THF in toluene gave, after cooling the concentrated solution to −30 ºC, a yellow crystalline solid which was characterized as the dichloro-ansa-zirconocenes [Zr{(η⁵-Me-Ph-C₅H₅)₂SiMe₂}Cl₂] (9) by elemental analysis. The ¹H NMR spectra of 9 demonstrated the presence of the two diastereomers [Zr{(η⁵-Me-Ph-C₅H₅)₂SiMe₂}Cl₂] (rac-9a and meso-9a) and reported previously [13] together with a third isomer 9b in a molar ratio of ca. 2:2:1, respectively. Formation of these three isomers demonstrated that the isomer 7c shown in Scheme 3 was not present in the dilithium salt which must therefore contain a mixture of two isomers 7a, as the major and 7b, as the minor components.

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proton AB spin system of two non-equivalent cyclopentadienyl rings. Its $^{13}$C NMR spectrum is also consistent with the asymmetric character of this *ansa*-zirconocene. A definitive structural assignment to the *meso*-zirconocene, the *meso*-13, the distances from zirconium to the internal ring carbons (C$_{ipso}$ and C$_{176}$) of the *π*-coordinated cyclopentadienyl ligands are slightly shorter [2.460(18)–2.493(17) and 2.4945(15)–2.5391(15) Å] than those [2.5639(16)–2.6006(15) and 2.5711(15)–2.5889(14) Å] to the external carbons (C$_{ipso}$). The largest distances corresponding to the methyl- and phenyl-substituted carbons [2.4938(17) and 2.5391(15) Å for C$_{ipso}$ and 2.6006(15) and 2.5889(14) Å for C$_{ipso}$]. As also observed for *meso*-9a [13], the silyl-bridge is bent away from the vicinal methyl group ($\alpha_2$–$\alpha_1 = 6.43^\circ$; $\beta_1$–$\beta_2 = 3.55^\circ$) and this in plane bending is much larger for the vicinal bulkier phenyl ring ($\alpha_2$–$\alpha_1 = 12.57^\circ$; $\beta_1$–$\beta_2 = 2.10^\circ$). Nevertheless, the cyclopentadienyl rings are almost eclipsed with a symmetrical disposition of the Cl–Ti–Cl and Me–Si–Me systems. The phenyl and cyclopentadienyl rings are not coplanar and show twist angles of 5.01° (C1 to C5 and C31–C36), and 36.45° (C6 to C10 and C71–C76), respectively. This large difference may be attributed to packing effects in the crystal. The bite angle of the two cyclopentadienyl rings amounts to 119.11°.

### 2.2. Cyclopentadienylsilyl-η-amido complexes

As shown in Scheme 6, reaction of the dilithium salt 6 with ZrCl$_4$·2THF in toluene at room temperature gave the cyclopentadienylsilyl-η-amido zirconium complex [Zr{($\eta^5$-2-Me-Ph-C$_5$H$_2$)(SiMe$_2$-η-$\eta^5$-N$_3$Bu)}Cl$_2$] (10) which was isolated in high yield as a yellow crystalline solid and characterized by elemental analysis and NMR spectroscopy. The $^1$H and $^{13}$C NMR spectra show the presence of one unique isomer exhibiting two resonances ($^1$H and $^{13}$C) for the bridging SiMe$_2$ group, one singlet ($^1$H) and two signals ($^{13}$C) due to the $t$-Bu substituent and two doublets ($^1$H) and five signals

| Bond distances (Å) and angles (°) for complex *meso*-9b (1R,1’S)-enantiomer |
|-----------------------------|-----------------------------|-----------------------------|
| Zr–Cl1                     | 2.4213(5)                  | C11–Zr–Cl2                  | 97.86(2)                  |
| Zr–Cl2                     | 2.4300(4)                  | C1–Si–C6                    | 94.43(7)                  |
| Zr–C1                     | 2.4602(18)                 | C11–Si–C12                  | 108.65(9)                 |
| Zr–C2                     | 2.4707(17)                 | Cl1–Zr–Cl2                  | 121.74(11)                |
| Zr–C3                     | 2.6006(15)                 | Cl1–Si–C6                   | 128.17(12)                |
| Zr–C4                     | 2.5639(16) (α1)            | Si–C1–C2                    | 124.29(15)                |
| Zr–C5                     | 2.4938(17) (α2)            | Si–C1–C5                    | 129.24(15)                |
| Zr–C6                     | 2.4945(15) (β1)            | C1–C5–C51                   | 127.84(16)                |
| Zr–C7                     | 2.5391(15) (β2)            | C4–C5–C51                   | 124.29(15)                |
| Zr–C8                     | 2.5711(15) (α1’)           | C11–C6–C10                  | 118.57(11)                |
| Zr–C9                     | 2.5889(14) (α2’)           | Si–C6–C10                   | 131.14(11)                |
| Zr–C10                    | 2.4800(15) (β1’)           | C6–C7–C7                    | 126.84(15)                |
| Si–C1                     | 1.8705(16) (β2’)           | C8–C7–C71                   | 124.74(14)                |
| Si–C6                     | 1.8887(17)                 |                                |                            |
| Si–C11                    | 1.8502(19)                 |                                |                            |
| Si–C12                    | 1.8512(2)                  |                                |                            |

Fig. 1. Ellipsoid plot of compound *meso*-9b (1S,1’R) enantiomer. Hydrogen atoms have been omitted for clarity.
(13C) corresponding to the cyclopentadienyl ring of an asymmetric molecule. However, this behaviour does not allow a definitive assignment of the relative position of the silyl group with respect to the other two Me and Ph substituents, which must certainly be located at the same 1-3-positions observed for either of the two isomers of the precursor silylamine cyclopentadiene 4.

A definitive structural assignment was made by NOE spectroscopy in CDCl₃. As shown in Scheme 7(a), selective excitation (PFG WFG NOESY1D pulse sequence) of one of the Si–Me signals at δ 0.56 enhanced the resonances at δ 1.41 for the t-Bu group and at δ 6.54 for one of the ring protons whereas excitation of the other Si–Me signal at δ 0.65 enhanced the signals at δ 1.41 due to the t-Bu group and at δ 2.32 due to the ring methyl group. Additional behaviour that guarantees this structural assignment is based on the following spectroscopic feature: the 1H NMR spectrum of complex 10 shows the ring-methyl signal coupled with its α-H, appearing as a doublet with 3J_H-Me = 0.4 Hz (see Scheme 7(b))) whereas two doublets are observed for this H with 3J_H-Me = 0.4 Hz and 4J_H-H = 2.4 Hz by coupling with its β-H. Therefore, the substituents occupying the two ring-α positions with respect to the bridging silyl group have to be H and Me, in agreement with the structure represented in Scheme 6.

Treatment of complex 10 with 2 equiv of alkylating agents (MgMeCl and Mg(CH₂Ph)Cl) in diethyl ether at room temperature afforded the dialkyl complexes [Zr{η⁵-2-Me-4-Ph-C₅H₅(SiMe₂-η-Nt-Bu)}Me₂] (11) and [Zr{η⁵-2-Me-4-Ph-C₅H₅(SiMe₂-η-Nt-Bu)}(CH₂Ph)₂] (12) which were isolated in high yield as a colourless oily product and a yellow microcrystalline solid, respectively. Complex 12 was characterized by elemental analysis [16] and both were characterized by NMR spectroscopy. Complexes 11 and 12 are very soluble in all the usual organic solvents and can be stored for long periods under an inert atmosphere, although they are extremely air-sensitive compounds. The 1H and 13C NMR spectra of both complexes are consistent with the behaviour expected for asymmetric molecules; complex 11 shows two singlets (1H) and two signals (13C) due to the non-equivalent Zr-methyls whereas four doublets (1H) corresponding to diastereotopic methylene protons and two methylene signals (13C) are observed for the two non-equivalent Zr-benzyl groups. One of the Zr-methylene doublets (11) and two of the Zr-methylene doublets (12) are substantially shifted highfield [δ ≈0.12 (11), δ 1.18, δ 1.44 (12)] as expected for protons located under the anisotropic effect of the phenyl ring bound to the Cβ of the cyclopentadienyl ligand.

2.3. Olefin polymerisation

Complex 10 was used as a precursor to generate the “CGC” catalyst by activation with a large excess methylalumoxane (MAO) (Al/Zr molar ratio 1500/1) in toluene. This catalytic system polymerizes ethene at 1 atm to give linear polyethylene with similar activities between 20 and 70 °C. The catalytic activity was reasonably high, the maximum being observed after 30 min (2.5 × 10⁵ gPE/mol Zr·h·atm at 20 °C) decreasing slightly for longer periods (1.5 × 10⁵ gPE/mol Zr·h·atm at 20 °C after 60 min). The molecular weight (Mw) of the resulting polyethylene was rather low being between 11.2 × 10⁵ (15 min) and 9.7 × 10⁵ g/mol (30 min) with polydispersities between 2.2 and 1.9, typical of single site catalysts, and melting points at 137.1 and 137.9 °C, respectively.

Complex 10 was also an active catalyst for propene polymerization. The activity was 3.56 × 10⁵ g PP/mol Zr·h·bar when the polymerization was carried out at 70 °C using 1.0 × 10⁻⁵ mol/l of catalyst with a molar ratio MAO/Zr of 1500 at 5.0 bar propene in heptane. Under these conditions a fraction (28%) of the resulting PP was insoluble in heptane and was characterized by its 13C NMR spectrum ([MMMM] pentade at δ 21.8) as 68% isotactic-PP whereas the soluble fraction (72%) was essentially atactic-PP (14% isotacticity).
3. Conclusions

Substitution at the ring-4 position of the 1-Ph-3-Me-cyclopentadiene is highly selective for –SiMe 2Cl and more favourable than at ring-5 position for –SiMe 3, –SiMe 2(NHt-Bu) and bridging –SiMe 2– in dicyclopentadiene derivatives. However, the ring-2 position is never influenced by electronic or steric effects. As a consequence one unique [2-Me-4-Ph-C 5H 3(SiMe 2-X)] isomer is obtained for X = Cl, whereas mixtures of [2-Me-4-Ph-C 5H 3(SiMe 2-X)] and [2-Ph-4-Me-C 5H 3(SiMe 2-X)] are formed for X = Me and NHt-Bu in molar ratios 3:1 and 5:1, respectively. The monocyclopentadiene was dried and stored over molecular sieves. NH 2 was previously dried and freshly distilled under argon. Other solvents were pre-dried and used as received except for NH 2 which was previously distilled. LiCH 2Ph (12), 2THF [17] were isolated by reported methods.

4. Experimental

4.1. General methods

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or a M. Braun dry box. Solvents used were previously dried and freshly distilled under argon. Deuterated solvents from Scharlau were degassed, dried and stored over molecular sieves. NH 2-Bu, Me 2SiClMe, MgCl 2Bz, LiN-Bu, LiMe, ZrCl 4, Me 2SiCl 2, Me 2SiCl 2 and Me 2S were obtained from commercial sources and used as received except for NH 2-Bu which was previously distilled. [1-Ph-3-Me-C 5H 3] 2 and ZrCl 4·2THF [17] were isolated by reported methods.

1H and 13C NMR spectra were recorded on Varian Unity VXR-300 or Varian Unity 500 Plus instruments. Chemical shifts, δ in ppm, are measured relative to residual 1H and 13C resonances for C 6D 6 and CHCl 3-d 3 used as solvents and coupling constants are in hertz. Analyses were carried out with a Perkin-Elmer 240-C analyzer.

4.2. Synthesis of Li[1-Ph-3-Me-C 5H 3] (1)

A solution of 1-phenyl-3-methyl-cyclopentadiene (2.29 g, 19.0 mmol) in hexane (70 ml) was treated with 1.6 M hexane solution of n-butyllithium (20 ml, 32.0 mmol) at –78 °C. After the addition was complete the mixture was allowed to warm gradually to room temperature and then stirred for an additional 5 h. The mixture was filtered and the residue washed with pentane (2 × 50 ml) and dried under vacuum for several hours to give compound 1 as a white solid (2.25 g, 13.80 mmol, 94%). 1H NMR (300 MHz, THF-d 8, 25 °C): 2.26 (s, 3H, CH 3), 5.79 (t, 1H, J = 3.2, C 3H 3), 6.16 (t, 1H, J = 2.0, C 5H 3), 6.24 (t, 1H, J = 3.2, C 5H 3), 6.77 (t, 1H, J = 7.1, H 5 (C 5H 3)), 7.09 (t, 2H, J = 8.0, H 5 (C 5H 3)), 7.53 (d, 2H, J = 7.2, H 8 (C 5H 3)). 13C NMR (300 MHz, pyridine-d 5/benzene-d 6, 25 °C): 2.34 (s, 3H, CH 3), 5.81 (t, 1H, J = 3.2, C 5H 3), 6.24 (t, 1H, J = 2.0, C 5H 3), 6.35 (t, 1H, J = 3.2, C 5H 3), 6.99 (t, 1H, J = 7.1, H 5 (C 5H 3)), 7.18 (t, 2H, J = 8.0, H 5 (C 5H 3)), 7.50 (d, 2H, J = 7.2, H 8 (C 5H 3)). Anal. Calcd. for C 17H 11Li: C, 88.88; H, 6.84%. Found: C, 88.54; H, 6.89%.

4.3. Synthesis of [Me-Ph-C 5H 3(SiMe 3)] (2)

SiMe 2Cl (3.68 ml, 27.0 mmol) was added to a solution of the lithium salt 1 (4.30 g, 26.0 mmol) in THF (50 ml) cooled at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred until the reaction was extended for an additional 12 h to give a yellow solution. The solvent was removed under vacuum and the residue was extracted into hexane (50 ml). After filtration the solvent was completely removed from the resulting solution to give a yellow liquid identified as the cyclopentadiene 2 (5.02 g, 22.00 mmol, 83%). 1H NMR (300 MHz, CDCl 3, 25 °C): 0.19 a/b (s, 9H, SiCp 3), 2.07 a/b (s, 3H, CH 3), 3.27 a/b (s, 1H, H(C 5H 3)), 6.58 a/b (m, 2H, H(C 5H 3)), 7.14 a/b (m, 1H, H(C 5H 3)), 7.24 a/b (m, 2H, H(C 5H 3)), 7.37 a/b (m, 2H, H(C 5H 3)). Data for the major a and minor b isomers. Anal. Calcd. For C 17H 20Si: C, 78.88; H, 8.89%.

4.4. Synthesis of [2-Me-4-Ph-C 5H 3(SiMe 2Cl)] (3)

A solution of Me 2SiCl 2 (1.87 ml, 15.40 mmol) in THF (30 ml) was added to a solution of the lithium salt 1 (2.30 g, 14.18 mmol) in THF (30 ml) cooled to –78 °C. The mixture was heated to room temperature and the mixture was allowed to warm to room temperature and then stirred for 12 h. The THF was removed under vacuum and the residue was extracted into hexane (50 ml) and filtered. Removal of the solvent under vacuum gave a yellow viscous liquid (2.70 g, 10.85, mmol, 78%). 1H NMR (300 MHz, CDCl 3, 25 °C): 0.65 (s, 6H, Si-CH 3), 2.21 (m, 3H, Cp-CH 3), 3.56 (m, 1H, H(C 5H 3)), 6.70 (m, 1H, H(C 5H 3)), C 5H 3),
6.78 (m, 1H, H(Csp^2) C5H3), 7.33 (m, 4H, C6H5), 7.51 (m, 1H, C6H5).

4.5. Synthesis of [Me-Ph-C5H3(SiMe2Nt-Bu)] (4)

NH2-t-Bu (3.30 ml, 28.40 mmol) was added to a solution of 3 (3.59 g, 14.4 mmol) in THF (70 ml) with 0.5 M LiCl (1.65 ml, 0.83 mmol). The resulting suspension was stirred for 12 h. After filtration of the suspension, the solvent was removed under vacuum to give 4 as a yellow oil (2.86 g, 1.00 mmol, 37%). 1H NMR (300 MHz, CDCl3, 25°C): 0.80 (s, 6H, Si–CH3), 2.27 (s, 6H, Cp–CH3). 6.67 (m, 2H, H(Csp^2) C5H3), 6.94 (m, 2H, H(Csp^2) C5H3), 6.91 (t, 2H, HnC6H5), 7.19 (t, 4H, HnC6H5), 7.72 (d, 4H, HnC6H5).

4.6. Synthesis of [(Me-Ph-C5H3)2SiMe2] (5)

A solution of 3 (3.43 g, 13.05 mmol) in diethyl ether (10 ml) was slowly added to a stirred suspension of 1 (2.30 g, 13.05 mmol) in the same solvent (30 ml). The mixture was stirred overnight and then the solvent was removed under vacuum and the residue was extracted into hexane (50 ml) and the solution filtered. The solvent was removed from the filtrate under vacuum to give an orange viscous liquid (4.15 g, 10.46 mmol, 80%). 1H NMR (300 MHz, CDCl3, 25°C): 0.00–0.20 (SiC–H), 2.00–2.20 (Cp–CH3), 3.05–3.40 H (Csp^3), 5.98–6.73 H(Csp^2) C5H3, 7.10–7.60 H (Csp^2)Ph.

4.7. Synthesis of Li2[(Me-Ph-C5H3)(SiMe2Nt-Bu)] (6)

A 1.6 M solution of Lin-Bu in hexane (11.65 ml, 18.64 mmol) was added dropwise at −78 °C to a solution of 4 (2.66 g, 9.30 mmol) in diethyl ether (70 ml). The reaction mixture was slowly warmed to room temperature and stirred for 4 h. After filtration of the solvent the residue was washed with hexane (2×25 ml) and dried under vacuum to give 6 as a white solid (2.45 g, 2.21 mmol, 93%). Anal. Calc. for C18H32NSiLi2: C, 72.70; H, 8.47; N, 4.71. Found: C, 72.03; H, 8.34; N, 5.03%.

4.8. Synthesis of Li2[(Me-Ph-C5H3)2SiMe2] (7)

A 1.6 M solution of Lin-Bu (6.40 ml, 10.24 mmol) was added to a stirred solution of 5 (1.84 g, 4.99 mmol) in diethyl ether (30 ml) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 3 h to give a white solid. After filtration, the white solid was washed with hexane (2×20 ml), dried under vacuum and characterized as the dilithium salt 7 (0.53 g, 1.84 mmol, 37%). 7a: 1H NMR (300 MHz, pyridine-d5/benzene-d6, 25°C): 0.72 (s, 6H, Si–CH3), 2.45 (s, 3H, Cp–CH3). 6.45, 6.77 (m, 1H, H(Csp^2) C5H3), 6.88, 6.96 (m, 1H, H(Csp^2) C5H3), 7.01 (t, 2H, HnC6H5), 7.19 (t, 4H, HnC6H5), 7.72 (d, 4H, HnC6H5).

4.9. Synthesis of [Zr(η^5-1-Ph-3-Me-C5H3)Cl3] (8) and [Zr(η^5-1-Ph-3-Me-C5H3)Cl3·DME] (8·DME)

SM2 (1.84 ml, 20.70 mmol) was added at 0 °C to a suspension of ZrCl4 (2.50 g, 10.70 mmol) in dichloromethane (80 ml). After stirring for 20 min, the solution was treated with the silylcyclopentadiene 2 (2.86 g, 12.5 mmol) and the mixture was stirred for an additional 12 h. The resulting suspension was filtered and the solution was concentrated to 30 ml to give 8 as a dark red solid by cooling at −30 °C (1.62 g, 4.60 mmol, 43%). 1H NMR (300 MHz, CDCl3, 25°C): 2.41 (s, 3H, CH3), 6.45 (t, 1H, J = 2.0, C5H3), 6.59 (t, 1H, J = 2.0, C5H3), 6.79 (t, 1H, J = 2.0, C5H3), 7.31 (t, 1H, J = 7.4, HnC6H5), 7.38 (t, 2H, J = 7.4, HnC6H5), 7.58 (t, 2H, J = 7.3, HnC6H5). 13C NMR (300 MHz, CDCl3, 25°C): 26.6 (CH3), 111.1 (C5H3), 121.6 (C5H3), 123.9 (C5H3), 126.1 (C5H3), 127.2 (C5H3), 128.7 (CmC6H5), 134.9 (Cipso-Me-C6H5), 136.8 (Cipso-Ph-C6H5). Anal. Calc. for C12H11Cl3Zr: C, 40.84; H, 3.11. Found: C, 40.01; H, 3.09%.

The same procedure was followed to synthesize 8·DME by addition of DME (8.77 ml, 20.40 mmol) to give 8·DME as a dark red solid (2.80 g, 6.32 mmol, 59%). 1H NMR (300 MHz, CDCl3, 25°C): 2.50 (s, 3H, CH3), 3.00–4.20 (DME), 6.45 (t, 1H, J = 2.0, C5H3), 6.60 (t, 1H, J = 2.0, C5H3), 6.89 (t, 1H, J = 2.0, C5H3), 7.28 (t, 1H, J = 7.4, HnC6H5), 7.36 (t, 2H, J = 7.4, HnC6H5), 7.49 (t, 2H, J = 7.3, HnC6H5).

4.10. Synthesis of [Zr{(η^5-Me-Ph-C5H3)2SiMe2}Cl2] (9)

Toluene (20 ml) was added at room temperature to a mixture of ZrCl4·2THF (0.65 g, 1.72 mmol) and the dilithium salt (7a+7b) (0.50 g, 1.72 mmol) and the yellow suspension was stirred for 12 h. After filtration of the LiCl, the solution was concentrated to 15 ml. The ansa-zirconocenes 9 were isolated by cooling the toluene solution to −30 °C as a yellow microcrystalline solid, which contained a mixture of three diastereomers [meso-9a, rac-9a and (1R,1'S)(1S,1'R)-meso-9b] (0.57 g, 1.08 mmol, 64%). Recrystallization from toluene gave a solid fraction containing meso-9a, meso-9b and traces...
of rac-9a. Fractional recrystallization of this solid from toluene/hexane gave meso-9b with traces of meso-9a as a crystalline yellow solid which was studied by X-ray diffraction methods. meso-9a: 1H NMR (300 MHz, CDCl3, 25 °C): 0.78 (s, 3H, Si–CH3), 0.99 (s, 3H, Si–CH3), 2.31 (s, 6H, Cp–CH3), 5.81 (d, 2H, J = 2.4, C2H2), 6.78 (d, 2H, J = 2.4, C2H2), 7.18 (t, 2H, J = 2.2, H2C=C6H4), 7.28 (t, 4H, J = 7.1, H2C=C6H4), 7.36 (m, 4H, J = 7.1, H2C=C6H4). 13C NMR (300 MHz, CDCl3, 25 °C): 1.6 (Si–CH3), 2.7 (Si–CH3), 17.7 (Cp–CH3), 106.0 (CipSO–Si–C6H3), 121.9 (C6H3), 122.9 (C6H3), 126.8 (C6H3), 128.0 (CpC6H3), 128.3 (CipSO–C6H3), 132.0 (CipSO–Me–C6H3), 133.4 (CipSO–Ph–C2H2), 160.4 (CipSO–C5H5). meso-9b: 1H NMR (300 MHz, CDCl3, 25 °C): 0.93 (s, 6H, Si–CH3), 2.24 (s, 6H, Cp–CH3), 5.89 (d, 2H, J = 2.2, C2H2), 7.01 (d, 2H, J = 2.4, C2H2), 7.24 (m, 2H, H2C=C6H4), 7.41 (m, 4H, H2C=C6H4), 7.50 (m, 4H, H2C=C6H4). 13C NMR (300 MHz, CDCl3, 25 °C): 1.8 (Si–CH3), 17.7 (Cp–CH3), 103.4 (CipSO–Si–C6H3), 120.3 (C6H3), 122.9 (C6H3), 126.8 (C6H3), 128.0 (C6H3), 128.3 (CipSO–C6H3), 133.0 (CipSO–Me–C6H3), 133.7 (CipSO–Ph–C2H2), 157.2 (CipSO–C5H5). rac-9a: 1H NMR (300 MHz, CDCl3, 25 °C): 0.66 (s, 3H, Si–CH3), 0.78 (s, 3H, Si–CH3), 1.49 (s, 3H, Si–CH3), 2.23 (s, 3H, Cp–CH3), 5.36 (d, 1H, J = 2.3, C2H2), 5.65 (d, 1H, J = 2.3, C2H2), 6.62 (d, 1H, J = 2.3, C2H2), 6.83 (d, 1H, J = 2.3, C2H2), 7.25 (m, 2H, H2C=C6H4), 7.29 (m, 4H, H2C=C6H4), 7.67 (m, 4H, H2C=C6H4). 13C NMR (300 MHz, CDCl3, 25 °C): 0.6 (Si–CH3), 1.4 (Si–CH3), 16.7 (Cp–CH3), 18.3 (Cp–CH3), 107.4 (CipSO–Si–C6H3), 109.5 (CipSO–Si–C6H3), 120.8 (C6H3), 122.0 (C2H2), 122.9 (C2H2), 123.7 (C2H2), 126.3, 127.0, 128.5, 128.9, 129.3 (C6H3), 133.4 (CipSO–Me–C6H3), 134.0 (CipSO–Me–C6H3), 134.9 (CipSO–Ph–C2H2), 135.0 (CipSO–Ph–C2H2), 142.5 (CipSO–C5H5). Anal. Calc. for C18H18SiCl2Zr: C, 59.07; H, 4.91. Found: C, 59.03; H, 4.89%. 

11. 4.12. Synthesis of [Zr{η5-2-Me-4-Ph-C5H3(/SiMe2-η-Nt-Bu)}Me2] (I1)

A 3 M solution of MgClMe in THF (0.44 ml, 1.32 mmol) was added to a solution of 10 (0.24 g, 0.60 mmol) in diethyl ether (20 ml) cooled at −78 °C. The reaction mixture was slowly warmed to room temperature and then stirred for 12 h. The volatiles were removed under reduced pressure and the residue was extracted into hexane (25 ml). After filtration, the solvent was removed under vacuum to give 11 as a colourless oil (0.18 g, 0.45 mmol, 68%). 1H NMR (300 MHz, C6D6, 25 °C): −0.12 (s, 3H, Zr–CH3), 0.19 (s, 3H, Zr–CH3), 0.40 (s, 3H, Si–CH3), 0.43 (s, 3H, Si–CH3), 1.38 (s, 9H, Nt-Bu), 2.05 (s, 3H, Cp–CH3), 6.38 (d, 1H, J = 2.4, C2H2), 6.67 (d, 1H, J = 2.4, C2H2), 7.06 (m, 1H, H2C=C6H4), 7.18 (m, 2H, H2C=C6H4), 7.43 (m, 2H, H2C=C6H4). 13C NMR (300 MHz, C6D6, 25 °C): 2.5 (Si–CH3), 4.2 (Si–CH3), 25.1 (Cp–CH3), 32.6 (Zr–CH3), 34.3 (Zr–CH3), 34.2 (CMe3), 55.3 (CMe3), 102.7 (CipSO–Si–C6H3), 115.5 (CipSO–C6H3), 115.8 (CipSO–C6H3), 125.7 (CipSO–C6H3), 127.3 (CpC6H3), 128.9 (CpC6H3), 131.2 (CipSO–Me–C6H3), 134.7 (CipSO–PH–C2H2) 134.9 (CipSO–C5H5). Anal. Calc. for C28H32NSiCl2Zr: C, 59.38; H, 7.72 N, 3.46. Found: C, 58.33; H, 7.01; N, 3.78%. 

4.13. Synthesis of [Zr{η5-2-Me-4-Ph-C5H3(/SiMe2-η-Nt-Bu)}(CH2Ph)2] (12)

A 2 M solution of MgClBz in THF (1.30 ml, 2.60 mmol) was added to a solution of 10 (0.65 g, 1.18 mmol) in diethyl ether (20 ml) cooled at −78 °C. The reaction mixture was slowly warmed to room temperature and then stirred for 12 h. The volatiles were removed under reduced pressure and the residue was extracted into hexane (20 ml). After filtration, the solvent was removed under vacuum to give 12 as an analytically pure yellow microcrystalline solid (0.41 g, 0.74 mmol, 73%). 1H NMR (300 MHz, C6D6, 25 °C): 0.32 (s, 3H, Si–CH3), 0.44 (s, 3H, Si–CH3), 1.18 (d, 1H, J = 10.0, CH2Ph), 1.21 (s, 9H, Nt-Bu), 1.44 (d, 1H, J = 10.0, CH2Ph), 2.00 (d, 1H, J = 11.0, CH2Ph), 2.10 (s, 3H, Cp–CH3), 2.32 (d, 1H, J = 11.0, CH2Ph), 6.12 (d, 1H, J = 2.0, C2H2), 6.28 (d, 1H, J = 2.0, C2H2), 6.61, 6.87, 6.99, 7.06, 7.15, 7.21 (m, 15H, C6H3). 13C NMR (300 MHz, C6D6, 25 °C): 1.3 (Si–CH3), 1.8 (Si–CH3), 22.9 (Cp–CH3), 33.5 (CMe3), 56.4 (Zr–CH2Ph), 57.0 (CMe3), 59.7 (Zr–CH2Ph), 104.8 (CipSO–Si–C6H3), 116.1 (C2H2), 118.5 (C2H2), 126.1,
126.6, 127.2, 127.4, 128.3, 128.5, 128.7, 130.4, 131.0 (C\(_6\)H\(_5\)), 133.9 (C\(_{ipso}\)-Me-C\(_6\)H\(_5\)), 134.2 (C\(_{ipso}\)-Ph-C\(_6\)H\(_5\)), 141.9 (C\(_{ipso}\)C\(_6\)H\(_5\)), 142.5 (C\(_{ipso}\)C\(_6\)H\(_5\)), 148.6 (C\(_{ipso}\)C\(_6\)H\(_5\)).

4.14. X-ray structure determination of compound 
\[\text{[Zr} \{\eta^2-\text{2-Me-4-Ph-C}_6\text{H}_5\} \text{SiMe}_2(\eta^2-\text{2-Ph-4-Me-}
\text{C}_6\text{H}_5)\}\text{Cl}_2 \} \text{ (meso-9b)}\]

Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in Table 2. Crystals of complex 9b suitable for an X-ray single crystal structure determination were obtained by cooling its concentrated toluene solution at \(-30^\circ\text{C}\). Preliminary examination and data collection were carried out on a kappa-CCD device (Nonius MACH3) at the window of a rotating anode (NOMIUS FR591; 50 kV; 60 mA; 3.0 kW) and graphite monochromated Mo K\(\alpha\) radiation (\(\lambda = 0.71073\) Å) [18]. The unit cell parameters were obtained by full-matrix least-squares refinement of 4070 reflections. Data collection was performed at 123 K (20 s per film exposure time; 7 film sets; 449 films; phi and omega scans; 2\(^o\) scan-width). A total number of 23441 reflections were integrated. Raw data were corrected for Lorentz and polarization effects. If necessary, corrections for absorption and decay effects were applied during the scaling procedure [19]. After merging, sums of 4148 independent reflections remained, and were used for all calculations. The structure was solved by a combination of direct methods [20] and difference-Fourier syntheses [21]. All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were found in the final Fourier maps and refined with isotropic displacement. Full-matrix least-squares refinements were carried out by minimizing \(\sum w(F_o^2 - F_c^2)^2\) with SHELXL-97 weighting scheme and stopped at maximum shift/err \(< 0.001\). The centro-symmetric space group P1 implies both enantiomers (1.5\(S\)R) 9b and (1.5\(S\)S) 9b. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography. All other calculations (including ORTEP graphics) were done with the program PLATON [22].

4.15. Polymerization procedures

Polymerization of ethene was carried out with magnetic stirring in 100 ml glass reactors previously evacuated and purged under argon. The reactors were charged with freshly distilled toluene (40.0 ml) and then saturated with ethene (dried through P\(_2\)O\(_5\) and AlEt\(_3\)) and treated at 25 °C with a 10% toluene solution of MAO (Witco). The reactor was heated to the required temperature and the polymerization was initiated by injection of a 0.17 \(\times\) 10\(^{-3}\) M toluene solution (1.0 ml) of the Zr catalyst under ethene (1 atm). The reaction was stopped after the required time by addition of methanol/HCl 10/1 (5 ml) and the resulting PE was recovered by filtration and dried at 50 °C for 24 h.

Polymerization of propene was carried out in a 600 ml glass reactor with mechanical stirring under 5 bar propene at 70 °C following the same procedure described above for ethylene.

5. Supplementary data

Crystallographic data for the structures reported have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC No. 244773 (9b). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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[16] Acceptable analytical data could not be obtained for the oily compound H.


