Journal of Organometallic Chemistry 575 (1999) 232–241

Synthesis and characterisation of enantiomerically-pure zirconium complexes containing a linked amido-cyclopentadienyl ligand; X-ray structures of $[Zr\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH(Me)(Ph)\}X_2]$ ($X = NMe_2$ and Cl) and $[Zr\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH(Me)(Ph)\}Cl(\mu\text{-}Cl)]_2$

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Received 4 August 1998

Abstract

Enantiomerically-pure zirconium amido-cyclopentadienyl complexes $[Zr\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH(Me)(Ph)\}(NMe_2)_2]$ (*R*-**1** and *S*-**1**) have been prepared by the reaction of $Zr(NMe_2)_4$ with $[HC_5Me_4SiMe_2NHCH(Me)(Ph)]$ (HCp*NH). Subsequent aminolysis of *R*-**1** or *S*-**1** with Me_3SiCl gave the dimeric chloro-bridged zirconium complex $[Zr\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH(Me)(Ph)\}Cl(\mu\text{-}Cl)]_2$ (*RR*-**2** and *SS*-**2**) which upon sublimation under vacuum yielded the monomeric compound *R*- and *S*-$[Zr\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH(Me)(Ph)\}Cl_2]$ (*R*-**3** and *S*-**3**), respectively. Alternatively, the metathesis reaction of the dilithium salt $(Cp^*N)Li_2$ with $ZrCl_4(THF)_2$ afforded *RR*/*SS*-**2** in relatively low yields. Compounds **1**–**3** have been characterised in solution by NMR spectroscopy. The molecular structures of *R*-**1**, *S*-**1**, *RR*-**2** and *S*-**3** have been determined by X-ray crystallography. The Zr–N(appended amido) bond distances and Cp*(centroid)–M–N bond angles in *R*-**1**, *S*-**1**, *RR*-**2** and *S*-**3** are 2.098(2), 2.108(3), 2.052(av), 2.014(2) Å and 110.5, 100.7, 100.6(av), 101.0°, respectively. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Linked amido-cyclopentadienyl ligands; Enantiomerically-pure complexes

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1. Introduction

Group 4 transition metallocene dichloride complexes Cp_2MCl_2 together with methylaluminoxane (MAO) are active homogeneous catalyst systems but lack stereochemical control for olefin polymerisation reactions [1]. Therefore, attention has focused on the search for metallocene complexes which offer both catalytic activity and stereochemical control [2]. The catalytic activity and selectivity of the catalyst is believed to be associated with the Lewis acidity and the steric constraints at the metal centre. In principle, modification of the coordinated ligands of the complex can change its catalytic properties. Furthermore, a metal centre with an asymmetric environment could offer enantioselectivity and stereochemical control to the catalytic reactions.

Half-metallocene complexes containing linked amido-cyclopentadienyl ligands are catalysts for olefin polymerisation [3–7]. For example, $Zr[(\eta^5:\eta^1\text{-}C_5H_4SiMe_2N(Bu^t)]Cl_2$ was found to be highly active in olefin polymerisation. Since then, interest in the chemistry and catalytic activities of half-sandwich complex with pendant ligands has increased rapidly [8,11]. The less crowded metal coordination sphere and more electron-deficient (14 electrons) d^0 metal centre in $M[\eta^5:\eta^1\text{-}CpSiMe_2N(R)]Cl_2$ enhance in catalytic reactivity when

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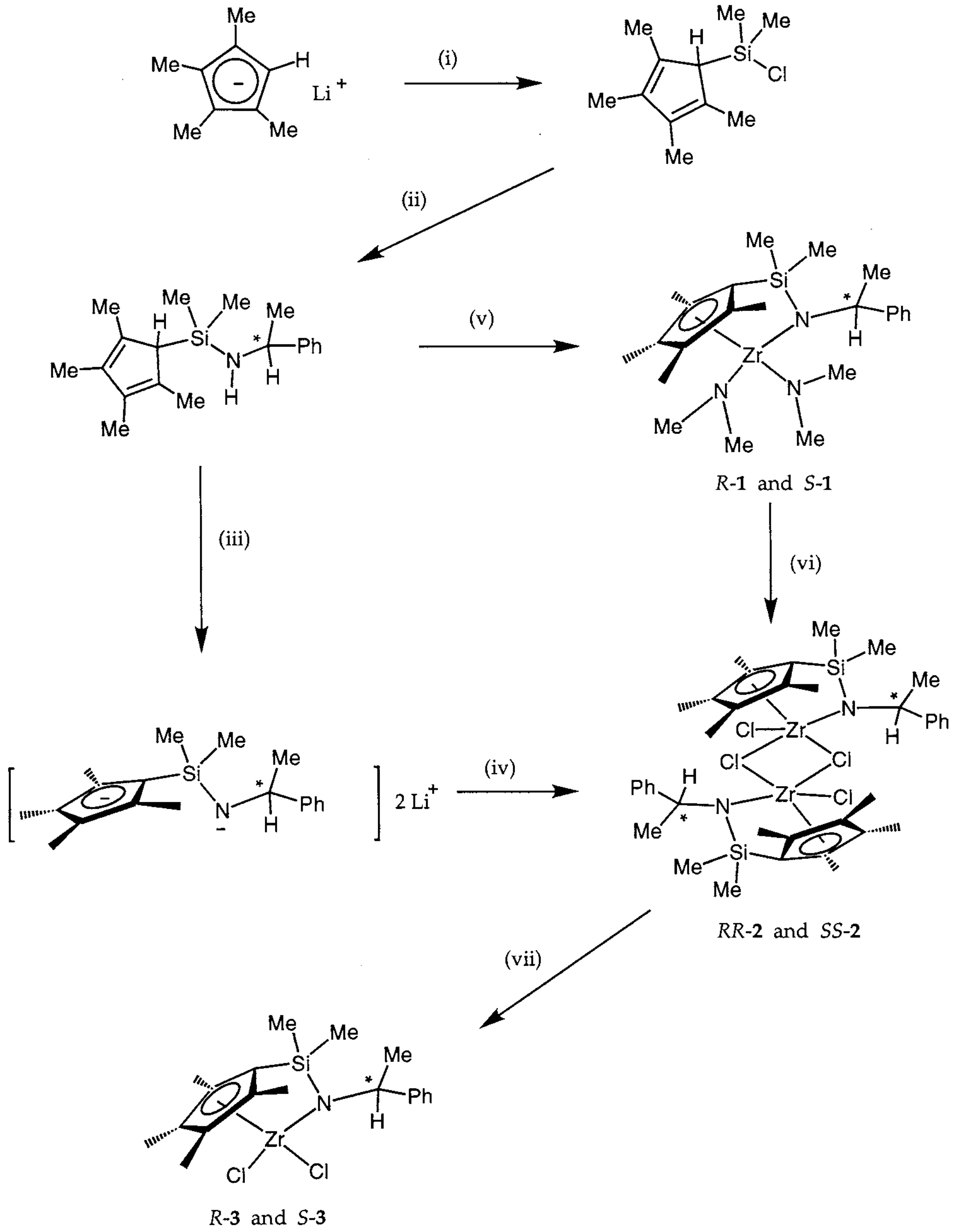
PII: S0022-328X(98)00999-1



Scheme 1. Reagents and conditions: (i) excess Me_2SiCl_2, Et_2O, 0°C; (ii) LiNHCH(Me)Ph (R or S) Et_2O, 0°C; (iii) $2LiBu^n$, hexane, 25°C; (iv) $ZrCl_4(THF)_2$, THF, −78°C to room temperature; (v) $Zr(NMe_2)_4$, toluene, 110°C; (vi) $2Me_3SiCl$, hexane, 25°C; (vii) 200°C, 0.05 mmHg.

compared with the ansa-metallocenes [9,10,12]. The high metal acidity in these complexes also promotes the approach of olefin molecules to the catalytic centre. We report here the synthesis and structural characterisation of zirconium compounds that contain an amido-cyclopentadienyl ligand $[C_5Me_4SiMe_2NCH(Me)(Ph)]^{2-}$ having an optically active group at the nitrogen. Compare with similar ligand such as $[C_5H_4SiMe_2N(Bu^t)]^{2-}$, it has a more bulky cyclopentadienyl group and a less hindered amine with an optically active group [13]. The complexes will provide a good opportunity to compare the influence of the steric crowding and substituent groups of this type of ligand at the metal centres.

2. Results and discussion

2.1. Synthesis

Tetramethylcyclopentadienyl with a pendant optically active amine $(C_5Me_4H)SiMe_2NHCH(Me)(Ph)$ in both *R* and *S* configuration were prepared separately according to the literature method [9,14]. Enantiomerically-pure zirconium amido-cyclopentadienyl complexes $[Zr\{\eta^5{:}\ \eta^1\text{-}C_5Me_4SiMe_2NCH(Me)(Ph)\}Cl_2]_2$ (*RR*-**2** and *SS*-**2**) were derived from the cyclopentadienyl-amido ligand via two different routes as shown in Scheme 1. The dilithium salt $Li_2[C_5Me_4SiMe_2NCH(Me)(Ph)]$ prepared by metallation of *R*/*S*-(C_5Me_4H)$SiMe_2$-NHCH(Me)(Ph) with two equivalents of $LiBu^n$ in hexane solution was used to react with $ZrCl_4(THF)_2$ and yielded dimeric complexes $[Zr\{\eta^5:\eta^1\text{-}C_5Me_4\text{-}SiMe_2NCH(Me)(Ph)\}Cl(\mu\text{-}Cl)]_2$ (*RR*-**2** and *SS*-**2**) in low yields (< 15%). It has been reported that the reaction of $Li_2[C_5H_4SiMe_2N(Bu^t)]$ with $TiCl_4(THF)_2$ or $TiCl_3(THF)_3$ gave less than 5% isolated yield of $Ti[C_5H_4SiMe_2N(Bu^t)]Cl_2$ have been reported. Likewise, the reaction of $Li_2[C_5H_4SiMe_2N(Bu^t)]$ with $ZrCl_4(THF)_2$ afforded a product mixture of $\{Zr[C_5H_4SiMe_2N(Bu^t)]Cl(\mu\text{-}Cl)\}_2$ and $Li(THF)_n\{[C_5H_4SiMe_2N(Bu^t)]ZrCl_3\}$ also in low yield. By adopting a similar strategy used by Teuben and coworkers for the synthesis of ansa-monocyclopentadienyl amido complexes [15], the reaction of *R*/*S*-$[C_5Me_4HSiMe_2NHCH\text{-}(Me)(Ph)]$ with $Zr(NMe_2)_4$ afforded $[Zr\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH(Me)(Ph)\}(NMe_2)_2]$ (*R*-**1** and *S*-**1**) by elimination of $HNMe_2$. Pure *R*-**1** and *S*-**1** were obtained without further purification as shown by their NMR spectra. Subsequent reactions of *R*-**1** or *S*-**1** with two equivalents of Me_3SiCl in hexane afforded the dichloride complexes $[Zr\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH(Me)(Ph)\}Cl(\mu\text{-}Cl)]_2$ (*RR*-**2** and *SS*-**2**, respectively) in good yields (> 70%). Similar aminolysis reaction of $Zr(NMe_2)_4$ with cyclopentadienyl derivatives to form zirconium cyclopentadienyl diamide complexes had been reported by several groups [13,15,16]. The preparation of *RR*-**2** and *SS*-**2** using this method was found to be more facile and gave higher yield when compared with the metathesis reactions of the dilithium salts with $ZrCl_4(THF)_2$. Furthermore, the reactions can be carried out conveniently in 'one pot' using $Zr(NMe_2)_4$ as the starting compound. Good quality crystals of the monomeric dichloride complex *R* or *S*-$[Zr\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH(Me)(Ph)\}Cl_2]$ (*R*-**3** or *S*-**3**) were obtained by sublimation of the chloro-bridged dimer *RR*-**2** and *SS*-**2** at 200 °C under vacuum (10^{-2} mmHg), respectively. The ^{1}H-NMR spectra of *R*-**3** and *S*-**3** were identical to the dimeric compounds, respectively. Waymouth and coworkers have reported the synthesis of the titanium analogue Ti[(*S*)-$C_5Me_4SiMe_2NCH(Me)(Ph)]Cl_2$ by the reaction of [(*S*)-$C_5Me_4SiMe_2NCH(Me)(Ph)]Mg_2Cl_2]$ with $TiCl_3(THF)_3$ followed by reaction with $PbCl_2$ in 15% yield.

Compounds **1**–**3** were characterised by their ^{1}H- and ^{13}C-NMR spectra, mass spectra and elemental analyses. In the ^{1}H-NMR of *RR*-**2**, the diastereotopic $SiMe_2$ bridge displayed sharp peaks at 0.07 ppm and 0.60 ppm. The four signals in the region of 2.14–2.33 ppm were assigned to the inequivalent methyl groups at the cyclopentadienyl ring. An NOE-NMR experiment of *RR*-**2** in C_6D_6 showed that the phenyl group of the amide group is pointing away from the metal centre. This is similar to the results found in the synthesis of titanium analogue $[Ti\{\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCH(Me)(Ph)\}Cl_2]$ [14]. The specific optical rotations for *R*-**1**, *S*-**1**, *RR*-**2**, and *SS*-**2** were found to be −28.0°(THF), +25.6°(THF), +7.3°(THF), and −7.1°(THF), respectively.

2.2. *X-ray structures*

The molecular structures of compounds *R*-**1**, *RR*-**2**, and *S*-**3** with the atom numbering schemes are shown in Figs. 1–3, respectively. Selected bond distances and angles are given in Tables 1–3, respectively.

The X-ray crystal structures of *R*-**1** and *S*-**1** are isostructural and consist of monomeric half-sandwich molecules of $[Zr\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH(Me)(Ph)\}(NMe_2)_2]$. The structure displays a pseudotetrahedral geometry consisting of $SiMe_2$ linked bi-functional amido-cyclopentadienyl group and the two $-NMe_2$ groups. The tetramethylcyclopentadienyl ring is bonded to the zirconium in a pentahapto fashion with the Zr–Cp*(centroid) distances of 2.236 and 2.239 Å for (*R*-**1**) and (*S*-**1**), respectively. The pendant amido group is bonded to zirconium with Zr–N(1) distances at 2.098(2) and 2.108(3) Å, respectively. The Zr–N(1) distances of (*R*-**1**) and (*S*-**1**) are similar to the distances of 2.108(4) Å in $[Zr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NBu^t)(NMe_2)_2]$ [13] although the latter has a more bulky group at N(1). The average $Zr–NMe_2$ distance of 2.068 Å in **1** is slightly longer than the $Zr–N(NMe_2)$ distance of 2.057(1) Å in $(Me_2N)_2Zr(\mu\text{-}NBu^t)_2Zr(NMe_2)_2$ and 2.062(1) Å in the parent compound $(Me_2N)_3Zr(\mu\text{-}NMe_2)_2Zr(NMe_2)_3$ [17,18]. The N(2)–Zr–N(3) (terminal amido group) angle of 104.7(1)° in *R*-**1** and 104.5(5)° in *S*-**1** is slightly larger than those angles in compounds $[Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NBu^t)(NMe_2)_2]$ [103.2(2)°] and $[Zr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NBu^t)(NMe_2)_2]$ [103.6(2)°] [13]. This is presumably due to the $[CH(Me)Ph]^-$ group at the nitrogen is less bulky than a Bu^t group. The angle sum around N(1) is 360°,

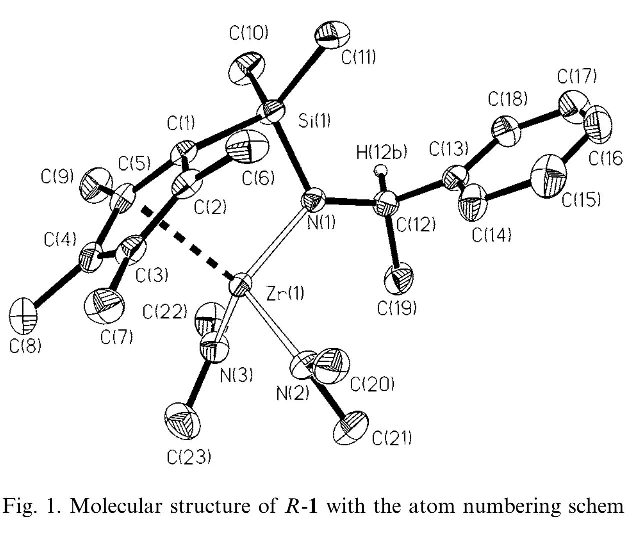


Fig. 1. Molecular structure of *R*-**1** with the atom numbering scheme.

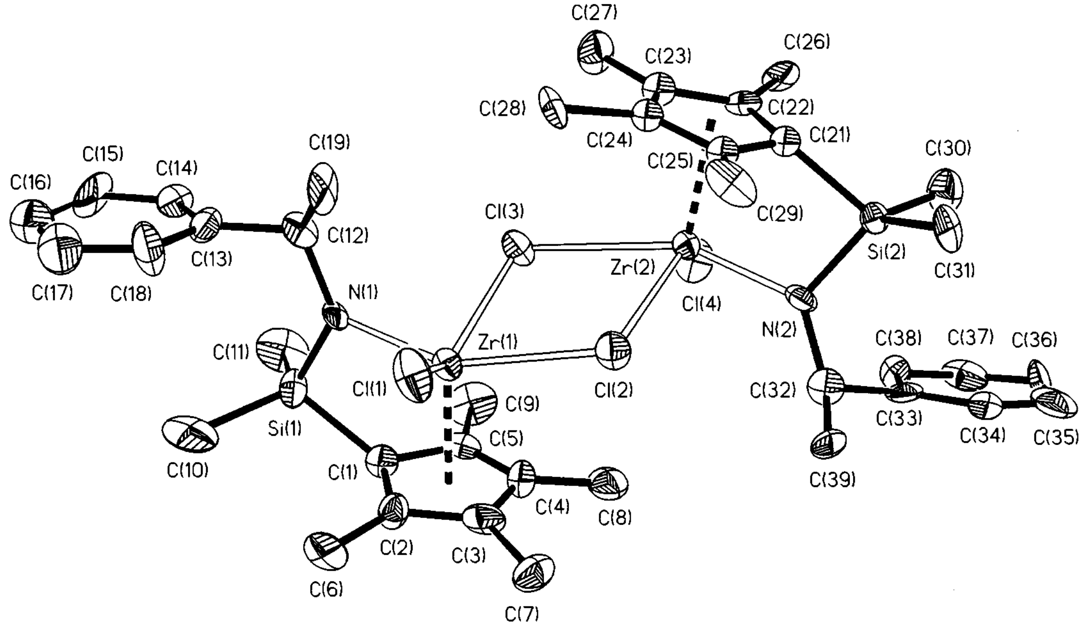


Fig. 2. Molecular structure of *RR*-**2** with the atom numbering scheme.

indicating that N(1) atom is sp^2 hybridised and adopts a trigonal planar geometry.

The crystal structure of *RR*-**2** consists of discrete chloro-bridged dimer molecules of *RR*-$[\mathrm{Zr}\{\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2NCH(Me)(Ph)}\}\mathrm{Cl}(\mu\text{-}\mathrm{Cl})]_2$. Each Zr atom of the dimer adopts a four-legged piano-stool geometry. The four bridging atoms Zr(1), Cl(2), Zr(2) and Cl(3) form a quadrilateral with Zr–Cl distances at 2.760(2), 2.541(2), 2.547(2) and 2.807(2) Å, the two longer Zr–Cl distances are opposite to each other and '*syn*' to the terminal chlorine atoms. The Zr–Zr distance of 4.282 Å is too long to be considered a bonding interaction. The bridging Zr–Cl distances are significantly longer than the terminal Zr–Cl distances of 2.432(2) and 2.435(2) Å. The Zr–Cp* groups are attached to the opposite sides of the four-membered ring and tilted at an angle of 153.5(av)°. The terminal Cl(1) and Cl(4) atoms are also attached to each side of the $(\mathrm{ZrCl})_2$ plane in '*trans*' positions. The phenyl groups of the [NCH(Me)Ph] group are oriented away from the metal centre to relieve steric interactions. Similar chloro-bridged dimeric zirconium compounds such as $[\mathrm{Zr}(\eta^5{:}\eta^1\text{-}\mathrm{C_5H_4SiMe_2NBu}^t)\mathrm{Cl}(\mu\text{-}\mathrm{Cl})]_2$ [6], $[\mathrm{Zr}(\eta^5{:}\eta^1\text{-}\mathrm{C_5H_4CH_2CH_2CH_2NMe})(\mu\text{-}\mathrm{Cl})(\mathrm{CH_2Ph})]_2$ [15], $[\mathrm{Cp^*Zr}(\mathrm{CH_2CH_2SiMe_3})\mathrm{Cl}(\mu\text{-}\mathrm{Cl})]_2$ [19], $[\mathrm{ZrCl}(\mu\text{-}\mathrm{Cl})\{\mathrm{N}(\mathrm{SiHMe_2})_2\}_2]_2$ [20], and benzamidinato complex $[\mathrm{C_6H_5C(NSiMe_3)_2ZrCl_2}(\mu\text{-}\mathrm{Cl})]_2$ have been reported [21].

The molecular structure of *S*-**3** displays similar structural features as the diamide analogue *R*-**1** and *S*-**1**. It is a monomeric compound derived from sublimation of *SS*-**2** with retention in the configuration of the cyclopentadienyl amine. The replacement of $\mathrm{NMe_2}$ groups with smaller chlorine atoms results in a decrease in Zr–Cp*(centroid) distance of 0.079 Å and Zr–N(amido) distance of 0.063 Å when compared with the diamide analogue *S*-$[\mathrm{Zr}\{\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2NCH(Me)(Ph)}\}(\mathrm{NMe_2})_2]$ (*S*-**1**). The Zr–Cl distances of 2.434(1) and 2.410(6) Å in *S*-**3** are slightly shorter than the terminal Zr–Cl distances of 2.434(1) Å and 2.437(1) Å in the chloro-bridge dimer *RR*-**2**. This is presumably due to the more congested environment in *RR*-**2**.

The Cp–M–Cp angles in ansa-metallocene complexes and the Cp–M–N angles in cyclopentadienyl-amido complexes reflect strain in the chelate ring. This less constraint favours the easy approach of the olefin monomer to the metal centre and provides spatial requirement for the propagation of polymers. The Cp*–M–N angles in *R*-**1**, *S*-**1**, *RR*-**2**, and *S*-**3** are of interests for comparison with other monocyclopentadienyl titanium and zirconium amido complexes containing ligands with different substituents. The Cp*–M–N angle of 110.5° in *R*-**1** is the largest among the monocyclopentadienyl-amido metal complexes, when compared with similar compounds such as $\mathrm{Zr}(\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2NBu}^t)(\mathrm{NMe_2})_2$ (100.2°) and $\mathrm{Ti}(\eta^5{:}\eta^1\text{-}\mathrm{C_5H_4SiMe_2NBu}^t)(\mathrm{NMe_2})_2$ (105.5°) [13]. However, the Cp*–M–N angle of 100.7° for the enantiomer *S*-**1** is smaller, and the reason is unclear. Furthermore, the Cp*–M–N angle of 100.6(av)° in the chloro-bridged dimer *RR*-**2** is similar to the angle of 101.0° in the monomer *S*-**3** and the angle of 99.6° in the dimeric compound $[\mathrm{Zr}(\eta^5{:}\eta^1\text{-}\mathrm{C_5H_4SiMe_2NBu}^t)(\mu\text{-}\mathrm{O_2CMe})(\mathrm{O_2CMe})]_2$ [21].

A comparison of selected structural data of some monocyclopentadienyl titanium and zirconium amido

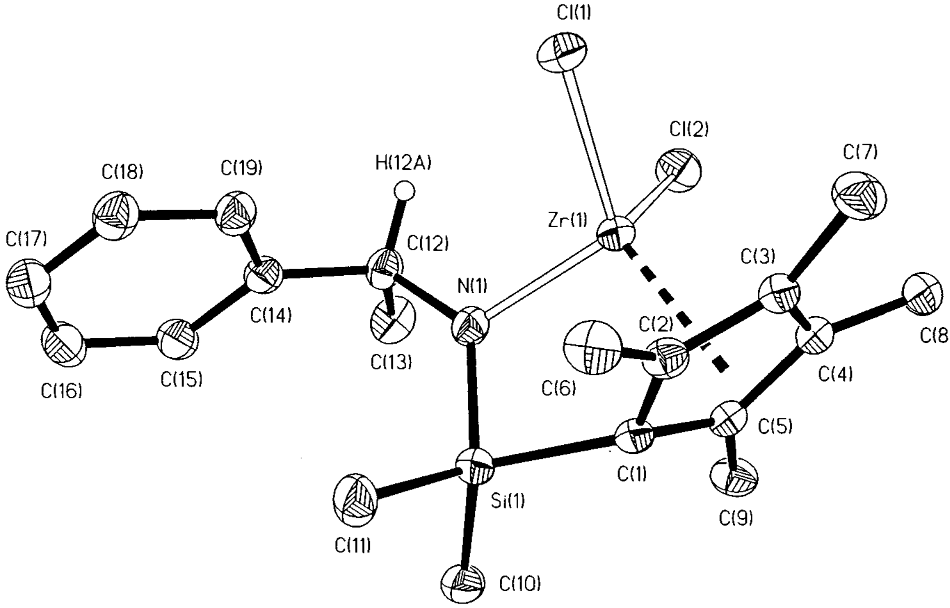


Fig. 3. Molecular structure of *S*-**3** with the atom numbering scheme.

complexes has been presented in Ref. [13]. The data provides the opportunity to study the steric effects of cyclopentadienyl-amido ligands with different substituents. It appears that for compounds with the same ligand but smaller metal sizes, there is a shortening in the M–Cp(centroid) and M–N(amido) distances due to a reduction in the ionic radius. The Cp–M–N angles of the cyclopentadienyl metal amide complexes reported in the literature are in the range of 99.6–110.5°. These angles are smaller than the Cp–M–Cp angles found in Group 4 ansa-metallocenes system, for example, in one-atom bridged $\mathrm{Zr}\{\eta^5{:}\eta^5\text{-}[(\mathrm{Cp}^*)(\mathrm{Ind})]\mathrm{SiMe_2}\}\mathrm{Cl_2}$ (118.2°) [22], *rac*-$\mathrm{Zr}[\eta^5{:}\eta^5\text{-}\{\mathrm{C_5H_2(Me)(Bu}^t)\}_2\mathrm{SiMe_2}](\mathrm{NC_4H_8})_2$ (122.5°), two atoms bridge ansa-metallocenes *rac*-$\mathrm{Zr}[\eta^5{:}\eta^5\text{-}(\mathrm{SBI})](\mathrm{NMe})_2$ (122.8°) [23] and $\mathrm{Zr}[\eta^5{:}\eta^5\text{-}(\mathrm{Flu})(\mathrm{Ind})][\mathrm{CH_2CHPh\text{-}(R)}]\mathrm{Cl_2}$(127.7°) [24], four atoms bridged compound $\mathrm{Ti}(\eta^5{:}\eta^5\text{-cyclocene})\mathrm{Cl_2}$ (131.2°) [25]. The smaller Cp–M–N angles suggest that the environment at the metal centre of these compounds are less crowded than that in ansa-metallocenes. By comparing the structural data, it was shown that an increase in steric hindrance at the cyclopentadienyl ring does not show significantly change the Cp–M–N angle. For examples, the angle of 107.6° in $\mathrm{Ti}(\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2NBu}^t)\mathrm{Cl_2}$ is comparable to the angle of 107.0° in $\mathrm{Ti}(\eta^5{:}\eta^1\text{-}\mathrm{C_5H_4SiMe_2NBu}^t)\mathrm{Cl_2}$ [13]. The increase in steric bulk at the linked amido nitrogen can increase the Cp–M–N angles, such as in $\mathrm{Zr}(\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4\text{-}SiMe_2NBu}^t)\mathrm{Cl_2}$ (102.0°) and $\mathrm{Ti}(\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2NBu}^t)\mathrm{Cl_2}$ (107.6°), when compared with *S*-**3** (101.0°).

All the compounds described above were tested for their activity in ethylene polymerisation with MAO as co-catalyst. Compound *R*-**1** shows an activity of 3.74×10^4 g PE mol^{-1} Zr h^{-1}. The other compounds (*RR*-**2** and *S*-**3**) showed very low activity in ethylene polymerisation. In contrast, the titanium analogue had shown activity of 0.38×10^4 g PP mol^{-1} Ti h^{-1} in propylene polymerisation.

3. Experimental section

All manipulations were carried out under an inert atmosphere of high purity argon or dinitrogen using standard Schlenk techniques or in a dinitrogen glovebox. Solvents were dried over and distilled from $\mathrm{CaH_2}$ (hexane, $\mathrm{CH_2Cl_2}$) and/or sodium benzophenone (ether, THF, toluene) and degassed twice prior to use. Deuterated solvents, $\mathrm{CDCl_3}$, $\mathrm{C_6D_6}$, $\mathrm{C_5D_5N}$ and $\mathrm{C_7D_8}$ used for NMR samples were dried over molecular sieves (4 Å). *R*-(+)-1-phenylethylamine and S-(−)-1-phenylethylamine were purchased from Aldrich Chemical Ltd. and used without further purification. $\mathrm{HC_5Me_4SiMe_2Cl}$ and *R*- and *S*-$\mathrm{HC_5Me_4SiMe_2NHCH(Me)(Ph)}$were prepared according to the literature method [14]. ^{1}H- and ^{13}C-NMR spectra were recorded at 250, 300 and 500 MHz using Bruker WM-250, DPX-300 and ARX-500 spectrometers, respectively. Mass spectra were recorded on a 5989-In spectrometer. Specific optical rotations were recorded on Perkin-Elmer polarimeter 341 under dinitrogen atmosphere. Microanalyses were carried out by MEDAC Ltd. in Brunel University (UK) or Shanghai Institute of Organic Chemistry (China).

Table 1
Selected bond distances (Å) and angles (°) for *R*-**1** and *S*-**1**

Bond distance (Å)	*R*-**1**	*S*-**1**	Bond angle (°)	*R*-**1**	*S*-**1**
Zr(1)–N(1)	2.098(2)	2.108(3)	N(1)–Zr(1)–N(2)	110.4(1)	110.5(1)
Zr(1)–N(2)	2.075(2)	2.079(3)	N(1)–Zr(1)–N(3)	103.5(1)	103.6(1)
Zr(1)–N(3)	2.053(2)	2.063(3)	N(2)–Zr(1)–N(3)	104.7(1)	104.5(1)
Zr(1)–C(1)	2.453(2)	2.456(3)	Zr(1)–N(1)–Si(1)	106.1(1)	105.5(1)
Zr(1)–C(2)	2.551(2)	2.556(3)	Zr(1)–N(1)–C(12)	133.7(1)	132.7(2)
Zr(1)–C(3)	2.611(2)	2.614(4)	Si(1)–N(1)–C(12)	120.2(1)	121.7(2)
Zr(1)–C(4)	2.584(2)	2.584(4)	Zr(1)–N(2)–C(20)	132.2(1)	118.4(3)
Zr(1)–C(5)	2.490(2)	2.494(3)	Zr(1)–N(2)–C(21)	119.2(2)	132.3(3)
Si(1)–N(1)	1.728(2)	1.728(3)	C(20)–N(2)–C(21)	107.6(2)	108.3(3)
N(1)–C(12)	1.486(2)	1.472(4)	Zr(1)–N(3)–C(22)	128.2(1)	127.7(3)
N(2)–C(20)	1.440(3)	1.446(6)	Zr(1)–N(3)–C(23)	118.6(2)	119.3(3)
N(2)–C(21)	1.450(3)	1.446(6)	C(22)–N(3)–C(23)	112.1(2)	112.0(5)
N(3)–C(22)	1.467(3)	1.475(7)	Cp–Zr(1)–N(1)	110.5	100.7
N(3)–C(23)	1.425(2)	1.417(7)	Cp–Zr(1)–N(2)	117.4	117.3
[a]Cp–Zr(1)	2.236	2.239	Cp–Zr(1)–N(3)	119.4	119.3

[a] Cp denotes the centroid of cyclopentadienyl ring.

3.1. Preparation of (R)-(+)-$Li_2[C_5Me_4SiMe_2NCH(Me)(Ph)]$

To a solution of *R*-(+)-$HC_5Me_4SiMe_2NHCH(Me)(Ph)$ (2.80 g, 9.36 mmol) in hexane (30 ml) was added slowly a solution of $LiBu^n$ (18.8 mmol, 11.7 ml, 1.6 M in hexane) at room temperature (r.t.) in 1 h, and a white precipitate was formed. The resulting suspension was stirred for 10 h at r.t. The crude product was collected by filtration and washed with 2 × 20 ml of hexane and dried under vacuum at r.t. to afford the title compound (2.70 g, 92.7% yield). M.p.: 175°C (decomposed). $[\alpha]_D^{25} = +22.8°$ (THF). ^1H-NMR ($C_6D_6/C_5D_5N(2/1)$, 300 MHz): δ 0.21(s, 3H, $SiCH_3$), 0.39(s, 3H, $SiCH_3$), 1.37(d, 3H, $J = 6.6$ Hz, $Ph(CH_3)CH$), 2.15(s, 6H, $CpCH_3$), 2.21(s, 6H, $CpCH_3$), 4.15(m, 1H, $Ph(Me)CH$), 7.00–7.35(m, 5H, C_6H_5). ^{13} C-NMR ($C_6D_6/C_5D_5N(2/1)$, 75 MHz): δ 3.15, 3.93, 11.61, 14.61, 28.70, 51.97, 102.00, 103.10, 108.30, 112.81, 117.56, 126.08, 126.19, 126.40, 151.50.

3.2. Preparation of (S)-(−)-$Li_2[C_5Me_4SiMe_2NCH(Me)(Ph)]$

The procedure was similar to the preparation of (*R*)-(+)-$Li_2[C_5Me_4SiMe_2NCH(Me)(Ph)]$. Treatment of a solution of *S*-(−)-$Li_2[C_5Me_4SiMe_2NCH(Me)(Ph)]$ (5.6 g, 18.7 mmol) in hexane (50 ml) with of a solution of $LiBu^n$ (37.6 mmol, 23.5 ml, 1.6 M in hexane) afforded the title compound (*S*)-(−)-$Li_2[C_5Me_4SiMe_2NCH(Me)(Ph)]$ (5.3 g, 91.4% yield). M.p.: 170°C. $[\alpha]_D^{20} = -30.90°$ (THF). ^1H-NMR ($C_6D_6/C_5D_5N(2/1)$, 300 MHz): δ 0.37(s, 3H, $SiCH_3$), 0.48(s, 3H, $SiCH_3$), 1.31(d, 3H, $J = 6.6$ Hz, $CH(CH_3)Ph$), 2.17(s, 6H, $CpCH_3$), 2.32(s, 6H, $CpCH_3$), 4.21(m, 1H, $CH(Me)Ph$), 7.00–7.50(m, 5H, C_6H_5). ^{13}C-NMR ($C_6D_6/C_5D_5N(2/1)$, 75 MHz): δ 3.96, 4.23, 11.70, 14.77, 28.52, 51.79, 101.10, 112.89, 117.72, 122.80, 124.94, 125.97, 126.44, 128.22, 151.02.

3.3. Preparation of (R)-(−)-$Zr(\eta^5{:}\eta^1-C_5Me_4SiMe_2NCH(Me)Ph)(NMe_2)_2$ (R-**1**)

To a solution of $Zr(NMe_2)_4$ (1.234 g, 4.63 mmol) in toluene (30 ml) was added a solution of *R*-(+)-$HC_5Me_4SiMe_2NHCH(Me)Ph$ (1.384 g, 4.63 mmol) in toluene (20 ml) at r.t. The reaction mixture was stirred at r.t. for 30 min. and then at 100°C for 15 h. The solvent was removed under vacuum at r.t. to afford pale yellow solid, and recrystallisation of crude product afforded a colourless crystalline title compound (2.10 g, 95.5% yield). M.p.: 92°C. $[\alpha]_D^{20} = -27.96°$ (THF). Anal. Found: C, 57.47; H, 8.10; N, 8.57; Calc. for $C_{23}H_{39}N_3SiZr$: C, 57.83; H, 8.18; N, 8.81. ^1H-NMR (C_7D_8, 250 MHz): δ 0.29(s, 3H, $SiCH_3$), 0.46(s, 3H, $SiCH_3$), 1.65(d, 3H, $J = 6.67$ Hz, $Ph(CH_3)CH$), 1.91(s, 3H, $CpCH_3$), 1.96(s, 3H, $CpCH_3$), 2.17(s, 3H, $CpCH_3$), 2.18(s, 3H, $CpCH_3$), 2.86(s, 6H, $N(CH_3)_2$), 2.94(s, 6H, $N(CH_3)_2$), 4.61(q, 1H, $J = 6.65$ Hz, $Ph(Me)CH$), 7.0–7.4 (m, 5H, C_6H_5). ^{13}C-NMR (C_6D_6, 62.5 MHz): δ 3.61, 5.35, 10.82, 10.86, 13.63, 13.74, 26.72, 43.40, 44.25, 59.00, 101.41, 123.56, 124.69, 126.38, 126.83, 127.12, 128.24, 149.84. MS (EI, 70 eV, *m*/*z*, %): 475(13.9, M^+), 430(30.2, $[M-NMe_2]^+$), 387(100.0, $[M-2NMe_2]^+$), 283(22.2, $[M-2NMe_2-CH(Me)Ph]^+$), 105(27.4, $[CH(Me)Ph]^+$).

Table 2
Selected bond distances (Å) and angles (°) for *RR*-**2**

Bond distance (Å)			
Zr(1)–N(1)	2.070(5)	C(2)–C(3)	1.387(6)
Zr(2)–N(2)	2.034(5)	C(3)–C(4)	1.441(6)
Zr(1)–Cl(1)	2.433(2)	C(4)–C(5)	1.376(6)
Zr(2)–Cl(4)	2.435(2)	C(13)–C(14)	1.391(6)
Zr(1)–Cl(2)	2.760(2)	C(13)–C(18)	1.395(6)
Zr(1)–Cl(3)	2.541(12)	C(14)–C(15)	1.376(6)
Zr(2)–Cl(2)	2.547(2)	C(15)–C(16)	1.370(6)
Zr(2)–Cl(3)	2.807(2)	C(16)–C(17)	1.364(6)
Zr(1)–C(1)	2.444(4)	C(17)–C(18)	1.375(6)
Zr(1)–C(2)	2.470(3)	C(21)–C(22)	1.438(5)
Zr(1)–C(3)	2.575(4)	C(21)–C(25)	1.440(5)
Zr(1)–C(4)	2.583(6)	C(22)–C(23)	1.381(6)
Zr(1)–C(5)	2.465(5)	C(23)–C(24)	1.444(6)
Zr(2)–C(21)	2.428(4)	C(24)–C(25)	1.378(6)
Zr(2)–C(22)	2.476(3)	C(33)–C(34)	1.396(6)
Zr(2)–C(23)	2.551(4)	C(33)–C(38)	1.410(5)
Zr(2)–C(24)	2.540(5)	C(34)–C(35)	1.372(6)
Zr(2)–C(25)	2.426(5)	C(35)–C(36)	1.366(6)
Si(1)–N(1)	1.755(5)	C(36)–C(37)	1.366(6)
Si(2)–N(2)	1.752(5)	C(37)–C(38)	1.375(6)
N(1)–C(12)	1.469(7)	Cp(1)–Zr(1)	2.199
N(2)–C(32)	1.484(8)	Cp(2)–Zr(2)	2.173
C(1)–C(2)	1.440(5)	Zr(1)···Zr(2)	4.282
C(1)–C(5)	1.446(6)		
Bond angle (°)			
N(1)–Zr(1)–Cl(1)	96.93(15)	C(12)–N(1)–Zr(1)	129.8(4)
N(1)–Zr(1)–Cl(2)	152.92(12)	Si(1)–N(1)–Zr(1)	106.0(2)
N(1)–Zr(1)–Cl(3)	88.25(14)	C(32)–N(2)–Si(2)	123.2(4)
Cl(1)–Zr(1)–Cl(2)	80.30(7)	C(32)–N(2)–Zr(2)	127.7(4)
Cl(1)–Zr(1)–Cl(3)	128.11(7)	Si(2)–N(2)–Zr(2)	108.8(2)
Cl(3)–Zr(1)–Cl(2)	73.19(6)	Cp(1)–Zr(1)–Cl(1)	113.6
N(2)–Zr(2)–Cl(2)	90.99(15)	Cp(1)–Zr(1)–Cl(2)	103.4
N(2)–Zr(2)–Cl(3)	154.78(14)	Cp(1)–Zr(1)–Cl(3)	115.3
Cl(4)–Zr(2)–Cl(2)	125.68(7)	Cp(1)–Zr(1)–N(1)	102.3
Cl(4)–Zr(2)–Cl(3)	81.02(7)	Cp(2)–Zr(2)–Cl(2)	115.2
Cl(2)–Zr(2)–Cl(3)	72.30(6)	Cp(2)–Zr(2)–Cl(3)	105.3
Zr(2)–Cl(2)–Zr(1)	107.50(6)	Cp(2)–Zr(2)–Cl(4)	117.1
Zr(1)–Cl(3)–Zr(2)	106.27(6)	Cp(2)–Zr(2)–N(2)	99.0
C(12)–N(1)–Si(1)	123.4(4)	$M_{Cp(1)}/M_{Cp(2)}$	8.3

Table 3
Selected bond distances (Å) and angles (°) for *S*-**3**

Bond distance (Å)			
Zr(1)–N(1)	2.014(2)	C(2)–C(3)	1.412(3)
Zr(1)–Cl(1)	2.409(1)	C(3)–C(4)	1.418(2)
Zr(1)–Cl(2)	2.411(1)	C(4)–C(5)	1.419(2)
Zr(1)–C(1)	2.424(2)	C(14)–C(19)	1.383(3)
Zr(1)–C(5)	2.448(2)	C(14)–C(15)	1.401(3)
Zr(1)–C(2)	2.488(2)	C(15)–C(16)	1.387(3)
Zr(1)–C(4)	2.511(2)	C(16)–C(17)	1.376(4)
Zr(1)–C(3)	2.517(2)	C(17)–C(18)	1.379(3)
Si(1)–N(1)	1.742(2)	C(18)–C(19)	1.387(3)
C(1)–C(2)	1.438(2)	[a]Cp(1)–Zr(1)	2.160
C(1)–C(5)	1.446(2)		
Bond angle (°)			
N(1)–Zr(1)–Cl(1)	108.30(4)	Si(1)–N(1)–Zr(1)	109.08(7)
N(1)–Zr(1)–Cl(2)	105.55(4)	Cp(1)–Zr(1)–Cl(1)	115.0
Cl(1)–Zr(1)–Cl(2)	107.55(2)	Cp(1)–Zr(1)–Cl(2)	118.4
C(12)–N(1)–Si(1)	132.45(12)	Cp(1)–Zr(1)–N(1)	101.0
C(12)–N(1)–Zr(1)	118.47(11)		

[a] Cp denotes the centroid of cyclopentadienyl ring.

3.4. Preparation of (S)-(+)-Zr{η^5:η^1-$C_5Me_4SiMe_2$-NCH(Me)(Ph)}(NMe_2)$_2$ (S-1)

To a solution of Zr(NMe_2)$_4$ (2.54 g, 9.5 mmol) in toluene (80 ml) was added *S*-(−)-H$C_5Me_4SiMe_2$NHCH(Me)Ph (2.40 g, 8.0 mmol) at r.t., the reaction mixture was stirred at r.t. for 30 min. and was then allowed to raise to 110°C and stand for 15 h. The solid residue was filtered, the filtrate was concentrated to 10 ml and was then allowed to keep at −30°C. The colourless crystalline product was obtained by fractional crystallisation in toluene, yielding 3.6 g (94.5%). M.p.: 93°C. $[\alpha]_D^{20} = +25.58°$ (THF). Anal. Found: C, 57.14; H, 8.16; N, 8.76; Calc. for $C_{23}H_{39}N_3SiZr$: C, 57.83; H, 8.18; N, 8.81. ^{1}H-NMR (C_6D_6, 500MHz): δ 0.28(s, 3H, SiCH_3), 0.47(s, 3H, SiCH_3), 1.66(d, 3H, $J = 6.5$ Hz, Ph(C*H*$_3$)CH), 1.94(s, 3H, CpCH_3), 1.97(s, 3H, CpCH_3), 2.17(s, 3H, CpCH_3), 2.19(s, 3H, CpCH_3), 2.86(s, 6H, N(CH_3)$_2$), 2.95(s, 6H, N(CH_3)$_2$), 4.64(q, 1H, $J = 6.5$ Hz, Ph(Me)C*H*), 7.16–7.35(m, 5H, C_6H_5). ^{13}C-NMR (C_6D_6, 125 MHz): δ 3.62, 5.35, 10.82, 10.87, 13.63, 13.74, 26.72, 43.41, 44.25, 58.99, 101.40, 123.56, 124.68, 126.37, 126.83, 127.11, 128.23, 149.83. MS(EI, 70 eV, *m*/*z*, %): 475(19.6, M^+), 431(39.1, $[M-NMe]^+$), 387(100.0, $[M-2NMe]^+$), 283(23.8, $[M-2NMe-C^*H(Me)Ph]^+$).

3.5. Preparation of (RR)-(+)-[Zr{η^5:η^1-$C_5Me_4SiMe_2$-NCH(Me)(Ph)}Cl(μ-Cl)]$_2$ (RR-2)

To a solution of (*R*)-(−)-Zr{η^5:η^1-C_5Me_4-$SiMe_2$NCH(Me)(Ph)}(NMe_2)$_2$ (*R*-**1**) (0.92 g, 1.93 mmol) in hexane (30 ml) was added slowly a solution of Me_3SiCl (3.92 mmol, 16 ml, 0.245 M in hexane) in 3 h at r.t. The white precipitate formed was stirred for 18 h and continued stirring overnight. White solid compound was separated and the filtrate was allowed to stand at −30°C to afford colourless crystals, the combined isolated yield was 0.67 g (75.6%). Anal. Found: C, 49.31; H, 6.03; N, 3.44; Calc. for $C_{19}H_{27}Cl_2NSiZr$: C, 49.67; H, 5.88; N, 3.05. M.p.: 125°C. $[\alpha]_D^{20} = +7.28°$ (THF). ^{1}H-NMR ($DCCl_3$, 300 MHz): δ 0.07(s, 3H, (SiCH_3), 0.60(s, 3H, (SiCH_3), 1.52(d, 3H, $J = 6.9$Hz, CH(C*H*$_3$)Ph), 2.14(s, 3H, CpCH_3), 2.21(s, 3H, CpCH_3), 2.28(s, 3H, CpCH_3), 2.33(s, 3H, CpCH_3), 4.09(q, 1H, $J = 6.7$Hz, C*H*(Me)Ph), 7.19–7.33(m, 5H, C_6H_5). ^{13}C-NMR ($DCCl_3$, 75 MHz): δ −0.62, 3.84, 13.26, 13.43, 16.39, 17.62, 26.95, 57.80, 126.97, 112.30, 128.72, 129.40, 129.66, 133.50, 136.00, 136.81, 145.40. MS(EI,

Table 4
Selected crystallographic and data collection parameters for compounds *R*-**1**, *S*-**1**, *RR*-**2** and *S*-**3**

	R-**1**	*S*-**1**	*RR*-**2**	*S*-**3**
Molecular formula	$C_{23}H_{39}N_3SiZr$	$C_{23}H_{39}N_3SiZr$	$C_{38}H_{54}Cl_4N_2Si_2Zr_2$	$C_{19}H_{27}Cl_2NSiZr$
Molecular weight	476.9	476.9	919.25	459.63
Colour and habit	Colourless prism	Colourless prism	Colourless prism	Colourless prism
Crystal size (mm)	0.30 × 0.36 × 0.40	0.40 × 0.42 × 0.50	0.28 × 0.16 × 0.14	0.28 × 0.28 × 0.22
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a (Å)	10.388(1)	10.380(2)	14.730(3)	10.327(2)
b (Å)	12.291(1)	12.295(2)	15.046(3)	14.190(3)
c (Å)	20.055(1)	20.043(4)	19.099(4)	14.982(3)
V (Å^3)	2560.6(13)	2557.9(13)	4232.9(15)	2195.5(8)
Z	4	4	4	4
$D_{\text{calc.}}$ (g cm^{-3})	1.237	1.238	1.442	1.391
μ (mm^{-1})	0.489	0.489	0.830	0.800
Scan type and rate (° min^{-1})	40 oscillation photos; $\phi = 0$–160°, $\Delta\phi = 4°$; 8 min per frame	60 oscillation photos; $\phi = 0$–120°, $\Delta\phi = 2°$; 8 min per frame	w, 8–32° min^{-1}	30 oscillation photos; $\phi = 0$–150°, $\Delta\phi = 5°$; 8 min per frame
2θ range (°)	3.0–55.0	3.0–55.0	4.3–51.9	4.0–51.2
Unique data (R_{int})	5178 (2.50%)	4805 (3.28%)	2805 (0.00%)	3768 (0.00%)
Observed data (n)	4862[$F > 6\sigma(F)$]	4721[$F > 6\sigma(F)$]	2356[$F > 4\sigma(F)$]	3572[$F > 4\sigma(F)$]
No. variables (ρ)	255	254	403	218
R^{a}	0.0425	0.0380	0.00817	0.0384
wR^{b}	0.0531	0.0542	0.1916	0.1142
S (goodness-of-fit)^{c}	2.10	1.75	1.071	0.91
Weighting scheme (g)^{d}	0.0002	0.0006	0.1238, 3.6959	1.000, 0.0000
Large and mean Δ/σ	0.077, 0.018	0.001, 0.000	0.016, 0.001	−0.353, 0.079
$\Delta\rho_{\max}$ (e Å^{-3})	0.57, −0.47	1.23, −1.30	0.476, −0.559	0.27, −0.29

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.

[b] $wR = [\Sigma w(F_o - F_c)/\Sigma w(F_o)]$ for *R*-**1** and *S*-**1**; $wR = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ for *RR*-**2** and *S*-**3**.

[c] $S = \{[\Sigma w(F_o - F_c)^2]/(n - p)\}^{1/2}$ for *R*-**1** and *S*-**1**; $S = \{[\Sigma w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ for *RR*-**2** and *S*-**3**.

[d] $w^{-1} = s^2(F) + g(F^2)$ for *R*-**1** and *S*-**1**; $w^{-1} = s^2(F_o^2) + (aP)^2 + (bP)$, $P = (F_o^2 + 2F_c^2)/3$ for *RR*-**2** and *S*-**3**.

70 eV, *m*/*e*, %): 459(0.58, M^+), 444(49.12, $[M-Me]^+$), 339(30.24, $[M-Me-R^*]^+$), 178(17.84, $[Cp^*Si(Me)N]^+$), 120(16.24, $[C_5Me_4]^+$).

3.6. Preparation of (SS)-(−)-[Zr{η^5:η^1-C_5Me_4-$SiMe_2NCH(Me)(Ph)$}Cl(μ-Cl)]$_2$ (SS-**2**)

The procedure was similar to the preparation of (*R*)-(+)-[Zr{η^5:η^1-$C_5Me_4SiMe_2NCH(Me)(Ph)$}Cl(μ-Cl)]$_2$ (*RR*-**2**). A solution of (*S*)-(+)-Zr{η^5:η^1-C_5Me_4-$SiMe_2$-NCH(Me)(Ph)}(NMe_2)$_2$ (*S*-**1**) (1.01 g, 2.12 mmol) in hexane (30 ml) was treated with a solution of Me_3SiCl (4.41 mmol, 18 ml, 0.245 M in hexane) and stirred overnight. The reaction mixture was concentrated to 10 ml and kept at −30°C overnight, the colourless crystalline product formed was collected and yielded 0.71 g (73.0%). M.p.: 126°C. Anal. Found: C, 49.39; H, 6.16; N, 3.61; Calc. for $C_{19}H_{27}Cl_2NSiZr$: C, 49.67; H, 5.88; N, 3.05. M.p.: 126°C. $[\alpha]_D^{20} = -7.05°$ (THF). ^{1}H-NMR ($DCCl_3$, 300 MHz): δ 0.08(s, 3H, $SiCH_3$), 0.60(s, 3H, $SiCH_3$), 1.53(d, 3H, $J = 6.9$ Hz, CH(C*H*$_3$)Ph), 2.15(s, 3H, $CpCH_3$), 2.22(s, 3H, $CpCH_3$), 2.28(s, 3H, $CpCH_3$), 2.34(s, 3H, $CpCH_3$), 4.10(q, 1H, $J = 6.6$ Hz, C*H*(Me)Ph), 7.18–7.34(m, 5H, C_6H_5). ^{13}C-NMR ($DCCl_3$, 75 MHz): δ −1.15, 3.24, 12.69, 12.83, 15.82, 17.02, 26.35, 57.17, 126.01, 126.38, 126.80, 127.33, 128.13, 128.59, 129.07, 135.70, 136.20, 144.50. MS(EI, 70 eV, *m*/*e*, %): 459(23.3, M^+), 444(91.3, $[M-Me]^+$), 422(27.0, $[M-Cl]^+$), 339(37.3, $[M-Me-R^*]^+$), 178(28.0, $[Cp^*Si(Me)N]^+$), 105(100.0, $[CH(Me)Ph]^+$).

3.7. Preparation of (RR)-(+)-[Zr{η^5:η^1-C_5Me_4-$SiMe_2NCH(Me)(Ph)$}Cl(μ-Cl)]$_2$ (RR-**2**) by metathesis reaction of $ZrCl_4(THF)_2$ and (R)-(+)-Li_2-{$C_5Me_4SiMe_2NCH(Me)(Ph)$

(*R*)-(+)-Li_2{$C_5Me_4SiMe_2NCH(Me)(Ph)$ (2.5 g, 8.04 mmol) was added to a suspension of $ZrCl_4(THF)_2$ (3.1 g, 8.22 mmol) in THF (40 ml) at −78°C. The resulting reaction mixture was stirred for 3 h and then allowed to warm to r.t. for 10 h. The solvent was removed under vacuum and CH_2Cl_2 (20 ml) was added to the residues to extracted the product and LiCl was separated by filtration. The filtrate was concentrated and hexane added to yield 0.45 g (12.2%) colourless crystals.

3.8. X-ray crystallography

Selected single crystals were sealed in Lindemann glass capillaries under dinitrogen. Details of crystal parameters, data collection, and structure refinement are summarised in Table 4. X-ray intensities were measured at 294 K on MSC/RIGAKU AFC7R four-circle diffractometer for RR-**2** on MSC/RIGAKU RAXIS IIc imaging-plate diffractometer for *R*-**1**, *S*-**1** and *S*-**3** with rotating-anode generator powered at 50 kV and 90 mA by using Mo–K_α radiation ($\lambda = 0.71073$ Å) [26–28]. Empirical absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ scan data of selected strong reflections over a range of 2θ angles for *RR*-**2** [29]. A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied by using the ABSCOR program for *R*-**1**, *S*-**1**, and *S*-**3** [30].

The crystal structures of compound *R*-**1**, *S*-**1**, *RR*-**2**, and *S*-**3** were determined by the direct method, which yielded the positions of all non-hydrogen atoms. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The computations of *R*-**1**, *S*-**1**, and *S*-**3** were performed on a IBM compatible PC with the SHELXTL-PLUS program package and *RR*-**2** with the SHELXTL-93 [31–33]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [34].

Acknowledgements

This research was supported by Hong Kong Research Grants Council Earmarked Grants CUHK 317/96P.

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