www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 604 (2000) 103–115

Synthetic and reactivity studies of mono- and dicyclopentadienyl titanium, zirconium and hafnium complexes with the chlorodimethylsilyl-cyclopentadienyl ligand. X-ray molecular structure of $Hf\{(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}Cl_2$ and $Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N^tBu)Cl$

Santiago Ciruelos, Alfredo Sebastián, Tomás Cuenca, Pilar Gómez-Sal [1], Antonio Manzanero[1], Pascual Royo *

Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, 28871 Alcalá de Henares, Spain

Received 9 February 2000; accepted 5 April 2000

Abstract

Reaction of the disilylated cyclopentadiene $C_5H_4(SiClMe_2)(SiMe_3)$ with $HfCl_4$, in heptane, gave the monocyclopentadienyl complex $Hf(\eta^5\text{-}C_5H_4SiClMe_2)Cl_3$ (**1c**). Addition of two equivalents of $C_5H_5(SiClMe_2)$ to a solution of MCl_4, in toluene under reflux and in the presence of two equivalents of NEt_3, afforded the dichloro derivatives $M(\eta^5\text{-}C_5H_4SiClMe_2)_2Cl_2$ [M = Ti (**2a**), Hf (**2c**)]. Compounds **2a** and **2c** react with a stoichiometric amount of water with selective hydrolysis of the Si–Cl bonds to give the tetramethyldisiloxane-bridged diciclopentadienyl complexes $M\{(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}Cl_2$ [M = Ti (**3a**), Hf (**3c**)]. The reaction of the trichloro metal compounds $M(\eta^5\text{-}C_5H_4SiClMe_2)Cl_3$ with $Tl(1,3\text{-}{}^tBu_2C_5H_3)$, $K(C_5Me_5)$ or $Tl(C_5H_5)$ afforded the dichloro mixed dicyclopentadienyl $MCp'(\eta^5\text{-}C_5H_4SiClMe_2)Cl_2$ derivatives [Cp′ = $1,3\text{-}{}^tBu_2C_5H_3$, M = Ti (**4a**), Zr (**4b**), Hf (**4c**); Cp′ = C_5Me_5, M = Zr (**5b**), Hf (**5c**); Cp′ = C_5H_5, M = Hf (**6c**)]. The Si–Cl bond of the mixed dicyclopentadienyl complexes $M(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\eta^5\text{-}C_5H_4SiClMe_2)Cl_2$, [M = Ti (**4a**), Zr (**4b**), Hf (**4c**)] reacts selectively with one equivalent of $LiNH^tBu$ in toluene at 50–60°C to give the amidosilyl(cyclopentadienyl) compounds $M(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\eta^5\text{-}C_5H_4SiMe_2NH^tBu)Cl_2$, [M = Ti (**7a**), Zr (**7b**), Hf (**7c**)]. The same reaction with two equivalents of the lithium amide gives the *ansa*-cyclopentadienylsilyl-amido compounds $M(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N^tBu)Cl$ [M = Ti (**8a**), Zr (**8b**), Hf (**8c**)]. The X-ray molecular structure of $Hf\{(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}Cl_2$ (**3c**) and $Zr(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N^tBu)Cl$ (**8b**) have been determined by diffraction methods. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Zirconium; Hafnium; Chlorodimethylsilyl–cyclopentadienyl; Mixed dicyclopentadienyl; Amido cyclopentadienyl

1. Introduction

Metallocene complexes of Group 4 metals have been the subject of considerable interest for many years due to their synthetic and catalytic applications [1]. Extensive studies on the applications of Group 4 dicyclopentadienyl derivatives, as homogeneous α-olefin polymerization catalysts have been reported [2]. More recently, these studies have been extended to the use of substituted cyclopentadienyl ligands which contain linking groups that can modify the steric and electronic properties of the metal centre [3]. An important class of such compounds is those formed by bidentate ligands derived from a cyclopentadienyl ring functionalized with a pendant neutral or anionic functionality. Several complexes with nitrogen [4] and oxygen [5] functionalized cyclopentadienyl ligands containing an olefin in the cyclopentadienyl substituent [6] are known and they have opened up an interesting and rapidly growing field in the organometallic chemistry of these metals.

Some of these new systems show promising possibilities for the design of well-defined organometallic compounds with selective catalytic activity. Specifically, the

---

* Corresponding author. Fax: +34-1-8854683.

[1] X-ray diffraction studies.

PII: S0022-328X(00)00213-8

so-called *ansa*-monocyclopentadienyl-amido or half sandwich metallocenes of 'constrained geometry' (CGC) are highly active systems to produce α-olefin polymers and ethylene–α-olefin copolymers with remarkable properties [7,8]. In previous papers we have reported the synthesis and reactivity of mono- and dicyclopentadienyl complexes of titanium and zirconium containing the chlorodimethylsilylcyclopentadienyl ring [9], and we have developed a new approach to the synthesis of cyclopentadienyl-amido precursors by reactions of these suitable starting materials with different lithium amides or primary amines [10]. This strategy is very efficient for titanium compounds and appears to be a good way to synthesise cyclopentadienyl-amido precursors with unsubstituted cyclopentadieny ligands.

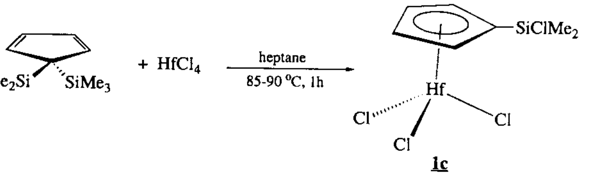
In this paper we report on the isolation of new mono- and mixed di-cyclopentadienyl Group 4 metal complexes containing chlorodimethyl-substituted rings and their reactions with lithium amides to afford novel cyclopentadienylsilyl-amido complexes.

2. Results and discussion

2.1. Mono- and di-(chlorodimethylsilyl-cyclopentadienyl) complexes

The same reaction of the disilylated cyclopentadiene $C_5H_4(SiClMe_2)(SiMe_3)$ reported previously for titanium and zirconium [9a] was carried out using $HfCl_4$ in heptane to give the monocyclopentadienyl derivative $Hf(\eta^5\text{-}C_5H_4SiClMe_2)Cl_3$ (**1c**) in 56% yield (Scheme 1). The solvent appears to be crucial because the same reaction in toluene produces a black oil from which pure samples of **1c** could be isolated in only very low yields.

Several routes have been reported [1b] to coordinate two cyclopentadienyl ligands to a transition metal centre. For Group 4 metals, the most common is the salt metathesis reaction of an alkali–metal cyclopentadienyl compound with the corresponding metal halide MCl_4 (M = Ti, Zr, Hf). However the synthesis of a stable salt of the $(C_5H_4SiClMe_2)^-$ anion has serious limitations. The salts $M'(C_5H_4SiClMe_2)$ (M′ = alkali metal or Tl) resulting from deprotonation of $C_5H_5(SiClMe_2)$ with basic reagents such as M′R or TlOEt are unstable and eliminate the alkali or thallium halide easily to give silylene intermediates [11]. A new and elegant way, introduced recently in the literature, is the reaction of homoleptic metal amides $M(NR_2)_4$ with the cyclopentadiene ligand to produce the dicyclopentadienyl diamido compounds via amine elimination. The subsequent reaction with $SiClMe_3$ yields the corresponding dichlorides [12]. The reaction of $M(NR_2)_4$ (M = Ti, Zr, Hf) with the $C_5H_5(SiClMe_2)$ ligand gave a mixture of products which could not be characterised conclusively. Exchanges between the dialkylamido groups and the $SiClMe_2$ functionality of the ring have been observed. A clean and salt free route to synthesise compounds of this type is the reaction of trimethylsilyl–cyclopentadiene reagents with MCl_4 resulting in the elimination of two equivalents of $SiClMe_3$ which can be pumped off easily [13]. We have reported that this strategy works out very well for the synthesis of dicyclopentadienyl zirconium derivatives and the dicyclopentadienyl compound $Zr(\eta^5\text{-}C_5H_4SiClMe_2)_2Cl_2$ was obtained in 74% yield [9a]. However the related dicyclopentadienyl titanium and hafnium complexes could not be synthesised in this way. The reaction with $TiCl_4$ affords the monocyclopentadienyl compound $Ti(\eta^5\text{-}C_5H_4SiClMe_2)Cl_3$ and $HfCl_4$ produces a mixture of the mono- (**1c**) and dicyclopentadienyl (**2c**) derivatives.

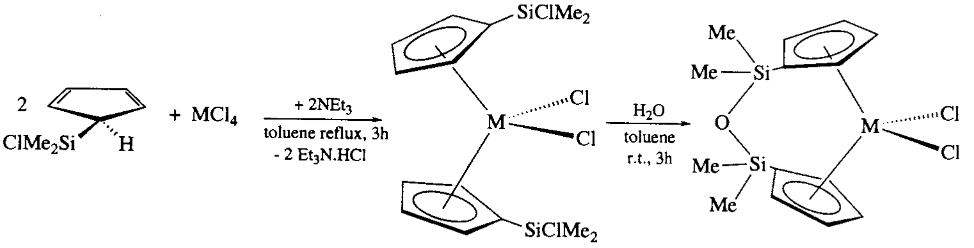


Scheme 1.

An alternative method to coordinate the cyclopentadienyl ring to the metal centre is based in the deprotonation of the precursor cyclopentadiene acidic hydrogen with NEt_3 in the presence of metal halides [1b]. When a toluene solution of $TiCl_4$ was treated with two equivalents of $C_5H_5(SiClMe_2)$ in the presence of two equivalents of NEt_3, a dark solution was obtained which after refluxing for 3 h gave the new $Ti(\eta^5\text{-}C_5H_4SiClMe_2)_2Cl_2$ (**2a**) complex in 43% yield (Scheme 2). This result contrasts with that found when the same reaction was carried out with C_5H_6, where $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ was obtained in a 3% yield only. The difference could be explained by the higher acidity of the hydrogen bound to the $SiClMe_2$-substituted sp^3 carbon atom of the ciclopentadiene $C_5H_5(SiClMe_2)$, promoted by the presence of chlorine in the $SiClMe_2$ substituent. Using this method, the known zirconium [9a] and the new hafnium $Hf(\eta^5\text{-}C_5H_4SiClMe_2)_2Cl_2$ (**2c**) complexes were also obtained in moderate yields.

Complexes **1** and **2** show the characteristic thermal stability of Group 4 mono- and dicyclopentadienyl derivatives but are moisture sensitive due to the ease of hydrolysis at the Si–Cl bond. They are insoluble in hydrocarbons and soluble in toluene and chlorinated solvents.

Compounds **2a** and **2c** react with a stoichiometric amount of water with selective hydrolysis of the Si–Cl bonds to give the corresponding tetramethyldisiloxane-bridged diciclopentadienyl complexes $M\{(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}Cl_2$ (**3a**) and (**3c**), respectively, similar to the behaviour reported previously for the analogous zirconium derivative [9a]. The



M = Ti, **2a**; Hf, **2c** M = Ti, **3a**; Hf, **3c**

Scheme 2.

preparation of **3a** was reported earlier by a reaction of the Na_2 $[(C_5H_4SiMe_2)(\mu\text{-}O)]$ salt with $TiCl_4 \cdot 2py$ [14].

The ^1H-NMR (C_6D_6 and $CDCl_3$) spectra for the new complexes **1**–**3** show the presence of one singlet for the methyl–silyl protons and two pseudotriplets corresponding to an AA′BB′ spin system for the cyclopentadienyl protons [9b,15]. Three resonances assigned to the *distal*, *proximal* and C_{ipso} carbon atoms of the cyclopentadienyl ring and one resonance for the $SiMe_2$ group are found in the ^{13}C-NMR spectra of these complexes. The chemical shift of the C_{ipso} atom being typically shifted upfield in comparison with the average shift observed for the other C_5H_4 ring carbon resonances for complexes **3a** and **3c**, and shifted downfield in comparison with those for compounds **1c**, **2a** and **2c** [9]. The value of $\Delta\delta = \delta_d - \delta_p$ (δ_d and δ_p being the chemical shifts of the *distal* and *proximal* protons of the cyclopentadienyl rings with respect to the silicon atom) and the relative chemical shifts of the bridgehead carbon (C_{ipso}) of the cyclopentadienyl rings, found in the NMR spectra for these complexes, have been used as characteristic spectroscopic parameters to define the coordination modes of the silyl-substituented cyclopentadienyl ligands [9b]. It has been observed that in chelated compounds, the C_{ipso} resonance appeared at higher fields than the *proximal* and *distal* carbon resonances of the same ring, while for bridged dinuclear derivatives or for unbridged mononuclear substituted metallocene analogues, the reverse was observed. This feature has been explained as the result of a redistribution of the π-electron density of the ring caused by the presence of the silicon atom [9b], as observed for compounds **1**–**3**, whereas the $\Delta\delta$ parameter is less useful.

Unlike the structure observed in the solid (see below), the ^1H-NMR spectra of **3a** and **3c** show (even at $-78°C$) a symmetrical AA′BB′ pattern for the cyclopentadienyl protons of both rings and one singlet for the silicon methyl protons, indicating that in solution, the cyclopentadienyl bridging siloxy groups twist to give a C_2 symmetric intermediate.

Single crystals of **3c** suitable for X-ray diffraction were obtained by slow cooling of toluene–hexane solutions. The molecular structure of compound **3c** is shown in Fig. 1 with the atom-labelling scheme. Selected bond distances and bond angles are listed in Table 1.

The molecular structure corresponds to a typical pseudotetrahedral molecule, the four ligands being the ring centroids and the chlorine atoms. The two cyclopentadienyl rings are bonded by the Si–O–Si chain and the molecule shows structural features comparable with those reported previously for the similar titanium and zirconium derivatives. A structural comparison of **3c** with the related tetramethyldisiloxane-bridged dicyclopentadienyl $M\{(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}Cl_2$ titanium [14] and zirconium [9a] complexes is shown in Table 2 and points out that the isostructural zirconium and hafnium organometallic compounds show very similar bond distances which are slightly shorter (0.01–0.02 Å) for the hafnium compound, whereas they are longer for the titanium compound with differences expected for early 3d–5d transition metals [1].

The oxygen atom is slightly out [0.049(3) Å] of the reflection plane defined by the hafnium and chlorine atoms. Both rings are located in an eclipsed disposition. The Si–O–Si bond angle of 142.3(3)°, and the Si–O bond distances [1.633(4) and 1.642(4) Å] are similar to those observed in hexamethyldisiloxane [16]. The Si–O–Si bridge is not symmetrically oriented with respect to the Cl–Hf–Cl angle causing a wedging of the ring. Because of this disposition, the minimum C–C bond distance between the rings corresponds to the proximal carbon atoms [C(25)–C(15)], being shorter than the C_{ipso}–C_{ipso} [C(11)–C(21)] distance. The angle between the Cp planes [50.5(2)°] and the Cp(centroid)–Hf–Cp(centroid) angle in **3c** (131.1°) resembles those found in hafnocene dichlorides or other hafnocene substituted compounds [17]. The carbon–carbon bond distances within the two cyclopentadienyl rings are similar, ranging from 1.385(9) to 1.432(8) Å and the same distances are also observed for the Hf–Cp(centroids) (2.183 and 2.192 Å). The Hf–C(Cp) distances, with a maximum difference of 0.082 Å, reveal η^5-coordination of both Cp rings. The Hf–Cl distances [Hf–Cl(1) 2.405(2) and Hf–Cl(2)

2.421(3) Å] and the angle between the chlorine atoms of 97.54(8)° are within the range expected for dichlorohafnocene derivatives (about 2.4 Å) [17]. However, the Hf–Cl distances, in compound **3c**, show small differences (0.016 Å) due to the different effect of the siloxi group. A similar value for this difference has also been found for the analogous zirconium compound (0.018 Å) but a significantly larger difference has been found for the titanium compound (0.042 Å). The longer bond corresponds to the chlorine atom located *trans* to the siloxy unit which bridges the two cyclopentadienyl rings. The Si–C(Cp) distance average is 1.869 Å and the Si–C(Me) bond distances are in the range 1.834 (6)–1.856 (8) Å.

2.2. Mixed dicyclopentadienyl complexes

Mixed dicyclopentadienyl transition metal complexes are known [1,18] and many titanium and zirconium derivatives with the C_5H_5 or $C_5H_4SiMe_3$ and $C_5H_4SiClMe_2$ rings have been reported [9b].

The reaction of the trichloro metal compounds $M(\eta^5\text{-}C_5H_4SiClMe_2)Cl_3$ [M = Ti, Zr, Hf (**1c**)] with one equivalent of the thallium salt $Tl(1,3\text{-}{}^tBu_2C_5H_3)$ afforded the corresponding mixed dicyclopentadienyl derivatives $M(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)(\eta^5\text{-}C_5H_4SiClMe_2)Cl_2$, [M = Ti (**4a**), Zr (**4b**), Hf (**4c**)] in high yield (60–75%). Similarly, the compounds $M(\eta^5\text{-}C_5H_4SiClMe_2)Cl_3$ [M = Zr, Hf (**1c**)] react with $K(C_5Me_5)$ or $Tl(C_5H_5)$ to give the analogous mixed dicyclopentadienyl derivatives $M(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_4SiClMe_2)Cl_2$, [M = Zr (**5b**), Hf (**5c**)] or $Hf(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SiClMe_2)Cl_2$ (**6**) [9b] (Scheme 3).

Complexes **4**–**6** are insoluble in hydrocarbons and soluble in toluene and chlorinated solvents and show the characteristic thermal stability of Group 4 dicyclopentadienyl derivatives, being moisture sensitive due to the hydrolysis of the $SiClMe_2$ unit.

The ^{1}H-NMR spectra of complexes **4**–**6** (C_6D_6 and $CDCl_3$) show the expected resonances for the chlorodimethylsilyl cyclopentadienyl ring protons as two sets of pseudotriplets due to an AA′BB′ spin system [9b,15]. In the ^{1}H-NMR spectra of complexes **4**, the di(*tert*-butyl)cyclopentadienyl ring protons appear as one singlet for the *tert*-butyl protons and one AA′B spin system [one pseudo-doublet (2H) and one pseudo-triplet (1H)] for the cyclopentadienyl ring protons. Singlets for the C_5Me_5 and C_5H_5 protons are observed in the ^{1}H-NMR spectra of compounds **5** and **6**. For all of these compounds, in the ^{13}C-NMR spectra, the resonance assigned to the C_{ipso} atom of the $C_5H_4SiClMe_2$ ligand is shifted downfield with respect to the average shift for the other C_5H_4 ring carbon resonances [9].

2.3. Reactions of the mixed dicyclopentadienyl complexes with lithium tert-butylamide

Different methods have been used in order to find a convenient preparative route for *ansa*-monocyclopenta-

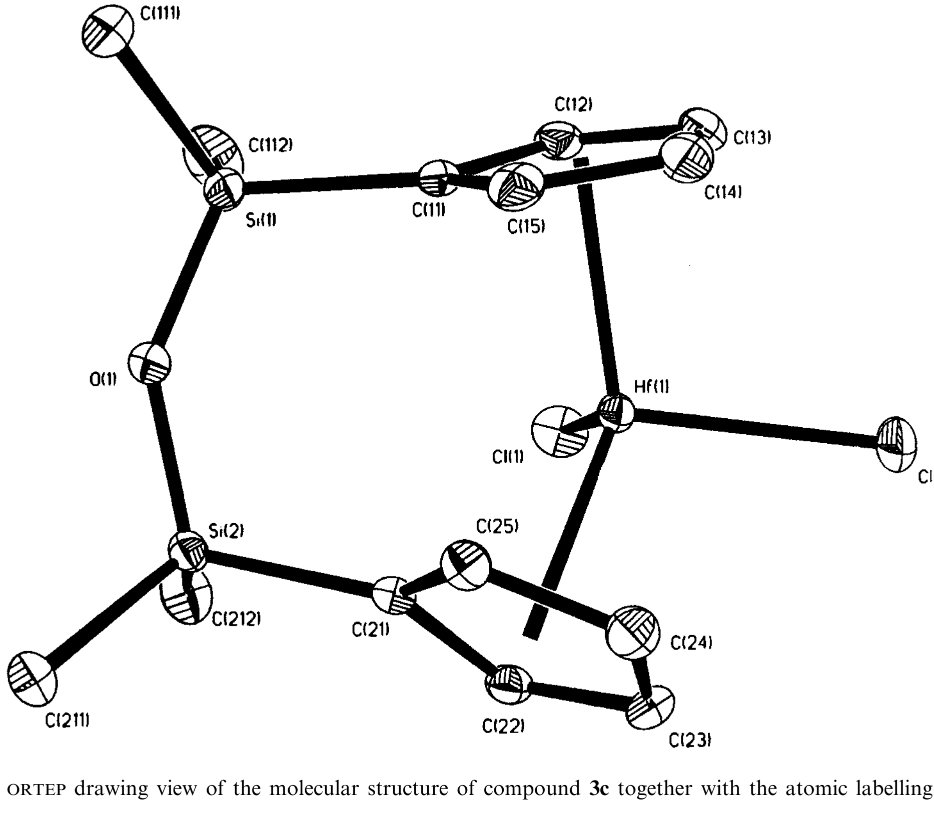


Fig. 1. ORTEP drawing view of the molecular structure of compound **3c** together with the atomic labelling scheme

Table 1
Selected bond distances (Å) and bond angles (°) for compound **3c**

Bond distances			
Hf(1)–Cl(1)	2.405(2)	Hf(1)–Cl(2)	2.421(3)
Hf(1)–Cp1	2.192	Hf(1)–Cp2	2.183
Hf(1)–C(11)	2.483(5)	Hf(1)–C(21)	2.469(5)
Hf(1)–C(12)	2.501(5)	Hf(1)–C(22)	2.500(5)
Hf(1)–C(13)	2.513(6)	Hf(1)–C(23)	2.511(5)
Hf(1)–C(14)	2.492(5)	Hf(1)–C(24)	2.488(5)
Hf(1)–C(15)	2.493(5)	Hf(1)–C(25)	2.486(5)
Si(1)–O(1)	1.633(4)	Si(2)–O(1)	1.642(4)
Si(1)–C(11)	1.877(6)	Si(2)–C(21)	1.862(5)
Si(1)–C(111)	1.856(8)	Si(2)–C(211)	1.834(6)
Si(1)–C(112)	1.843(8)	Si(2)–C(212)	1.855(8)
C(13)–C(12)	1.385(9)	C(22)–C(23)	1.388(8)
C(13)–C(14)	1.401(10)	C(24)–C(23)	1.417(8)
C(15)–C(14)	1.391(9)	C(25)–C(24)	1.396(8)
C(15)–C(11)	1.412(8)	C(21)–C(25)	1.431(7)
C(11)–C(12)	1.432(8)	C(21)–C(22)	1.425(7)
Bond angles			
Cl(1)–Hf–Cl(2)	97.54(8)	Cl(1)–Hf–Cp1	106.3
Cl(2)–Hf–Cp1	105.1	Cl(1)–Hf–Cp2	106.8
Cl(2)–Hf–Cp2	105.1	Cp1–Hf–Cp2	131.1
Si(1)–O(1)–Si(2)	142.3(3)	O(1)–Si(1)–C(112)	110.8(3)
O(1)–Si(1)–C(111)	107.5(3)	C(112)–Si(1)–C(111)	111.6(5)
O(1)–Si(1)–C(11)	110.4(2)	C(112)–Si(1)–C(11)	109.2(3)
C(111)–Si(1)–C(112)	107.4(3)	O(1)–Si(2)–C(211)	108.2(3)
O(1)–Si(2)–C(112)	111.4(3)	C(211)–Si(2)–C(212)	110.8(3)
O(1)–Si(2)–C(112)	108.1(2)	C(211)–Si(2)–C(21)	108.8(3)
C(212)–Si(2)–C(21)	109.5(3)		

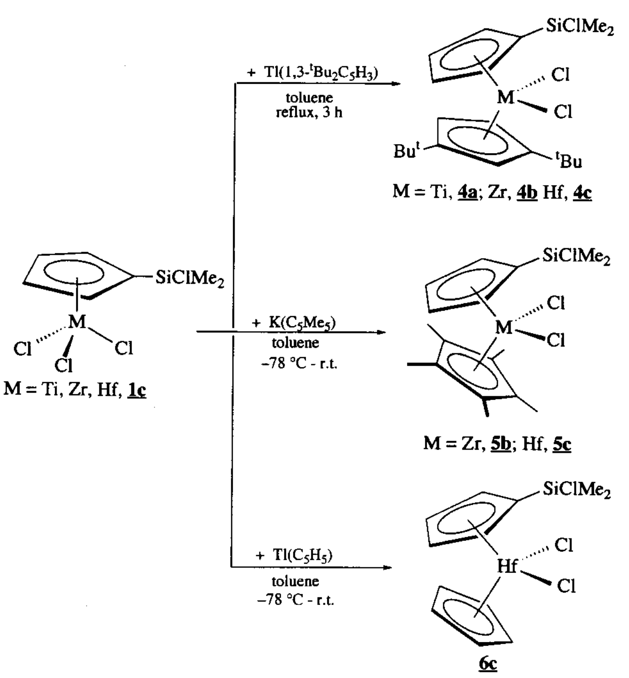
Table 2
Structural data for M{(η^5-C_5H_4)$SiMe_2OSiMe_2$(η^5-C_5H_4)}Cl_2 compounds (M = Ti, Zr, Hf)

	Ti	Zr	Hf
Bond distances (Å)			
M–Cl(1)	2.381(1)	2.4256(7)	2.405(2)
M–Cl(2)	2.339(1)	2.4443(7)	2.421(3)
Si(1)–O	1.634(3)	1.635(1)	1.633(4)
M–Cp1 [a]	2.065	2.202	2.192
M–Cp2	2.072	2.208	2.183
Si(2)–O	1.630(3)	1.627(2)	1.642(4)
Bond angles (°)			
Cl(1)–M–Cl(2)	96.22(5)	98.71(3)	97.54(8)
Cp1–M–Cp2	130.8	130.9	131.1
Si(1)–O–Si(2)	141.5(2)	143.5(1)	142.3(3)
O–Si(1)–C(1)	107.8(1)	108.24(8)	110.4
O–Si(2)–C(2)	109.8(1)	110.24(9)	108.1

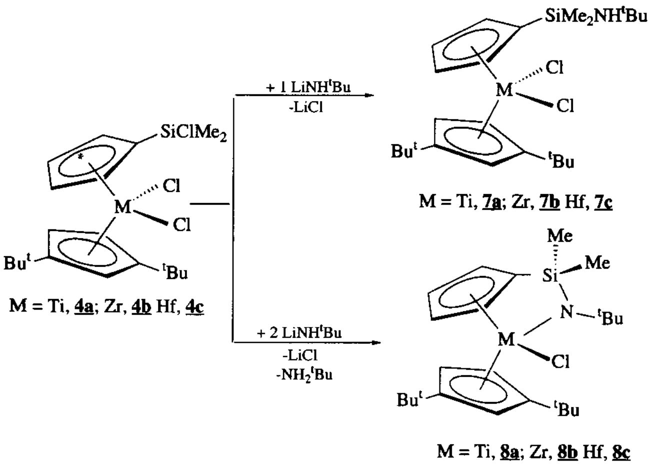
[a] Cp denotes ring centroids.

dienylsilyl-amido complexes. A possible method involves the reaction of $C_5H_4(SiClMe_2)(SiMe_3)$ with MCl_4 to give $M(C_5H_4SiClMe_2)Cl_3$ (M = Group 4 metal) which subsequently reacts with LiNHR, in the presence of NEt_3, to afford the corresponding *ansa*-monocyclopentadienyl-amido derivative [10].

When the mixed di(cyclopentadienyl) complexes M(η^5-1,3-$^t Bu_2C_5H_3$)(η^5-$C_5H_4SiClMe_2$)Cl_2, [M = Ti (**4a**), Zr (**4b**), Hf (**4c**)] were treated with one equivalent of LiNH^{t}Bu in toluene at 50–60°C, the Si–Cl bond reacted selectively to give the amidosilyl(cyclopentadienyl) compounds M(η^5-1,3-$^t Bu_2C_5H_3$)(η^5-$C_5H_4SiMe_2NH^tBu$)Cl_2, [M = Ti (**7a**), Zr (**7b**), Hf (**7c**)], obtained as red (titanium) or white (zirconium and hafnium) solids (Scheme 4). The desired *ansa*-cyclopentadienylsilyl-amido type derivatives **8** were not formed as expected from the known higher electrophilic character of the silicon atom in comparison with the transition metal centre in the dicyclopentadienyl-type derivatives. The related substituted cyclopentadienylsilyl-amido zirconium dichloride Zr(η^5-$C_5H_4SiMe_2$-NH^nBu)$_2Cl_2$ complex has been reported [19] to be



Scheme 3.



Scheme 4.

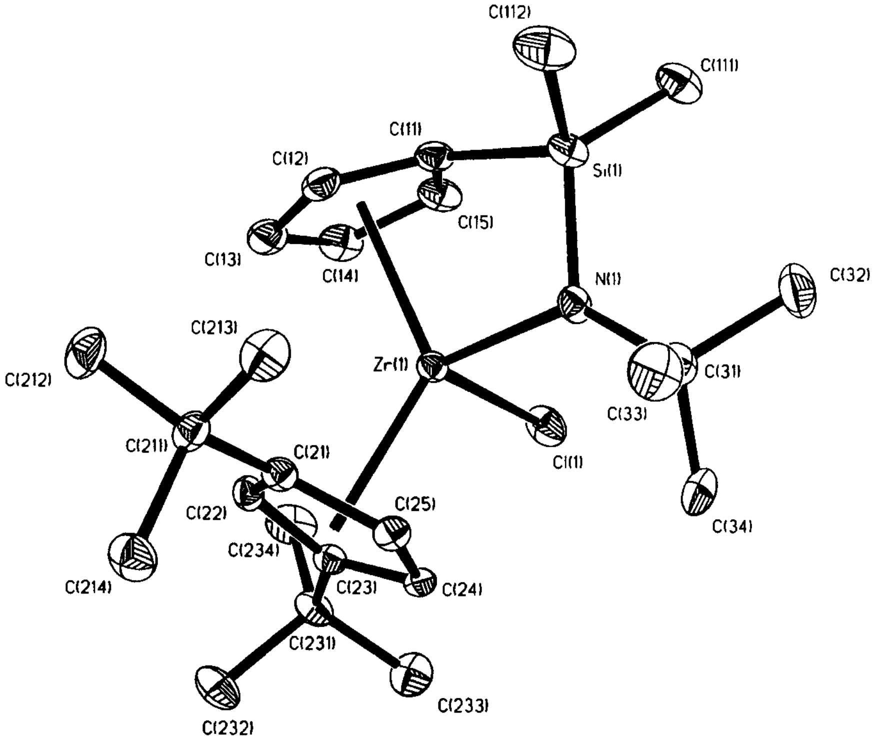


Fig. 2. ORTEP drawing view of the molecular structure of compound **8b** together with the atomic labelling scheme

formed by reacting the lithium salt Li($C_5H_4SiMe_2$-NH^nBu) with a 1/2 equivalent of $ZrCl_4$.

However, when the same reaction was carried out using a metal–lithium amide molar ratio 1/2, the *ansa*-cyclopentadienyl-amido red (titanium) and white (zirconium and hafnium) compounds M(η^5-1,3-$^tBu_2C_5H_3$)(η^5-$C_5H_4SiMe_2$-η-N^{t}Bu)Cl [M = Ti (**8a**), Zr (**8b**), Hf (**8c**)] were obtained in high yield (80–90%) with the elimination of LiCl and the amine NH_2^tBu (Scheme 4).

The new compounds **7** and **8** are soluble in chlorinated solvents (chloroform and dichloromethane) as well as in aromatic hydrocarbons (benzene and toluene) and slightly soluble in hexane and pentane. They are air- and moisture-sensitive in solution and in the solid although they can be stored unaltered for weeks if strictly anaerobic conditions are maintained.

The ^{1}H-NMR spectra (C_6D_6 and $CDCl_3$) of complexes **7** show the expected AA′BB′ spin system (two pseudotriplets) for the C_5H_4 ring protons, an AA′B spin system (two pseudotriplets) for the C_5H_3 ring protons, one singlet for the $SiMe_2$ group, and two singlets for the *tert*-butyl Cp protons which are shifted down field with respect to the resonance assigned to the ^{t}Bu–N group, the amidosilyl NH proton was not observed [19]. Compounds **8** show a chiral titanium centre and their ^{1}H-NMR spectra show an ABCD spin system (four multiplets) for the C_5H_4 ring protons, an ABC spin system (three multiplets) for the C_5H_3 ring protons, two singlets for the diastereotopic methyl–silyl groups and three singlets for the *tert*-butyl protons. Similar spectroscopic features were also observed in the $^{13}C\{^1H\}$-NMR spectra which show six different resonances assigned to the carbon atoms of the cyclopentadienyl rings, one resonance for the $SiMe_2$ group and the corresponding resonances for the *tert*-butyl groups are found for complexes **7**. A more complicated ^{13}C-NMR spectroscopic pattern was observed for complexes **8**, due to the chirality of the metal centre. The chemical shift of the cyclopentadienyl C_{ipso} atom in the C_5H_4 ring is typically shifted downfield from the average shift for the other ring carbon resonances in complexes **7** and upfield shifted in complexes **8**. These observations are diagnostic of single η^5-coordination of the cyclopentadienyl ligand in complexes **7** and chelation of the appended amido group in the silyl–amido complexes **8**.

Crystals of **8b** suitable for X-ray diffraction were obtained by slow cooling of toluene–hexane solutions. The molecular structure of **8b** is shown in Fig. 2 and selected bond distances and bond angles are given in Table 3.

The molecular structure is a typical metallocene system with the chlorine and the nitrogen atom located approximately in the bent metallocene wedge. The coordination around the zirconium can be considered tetrahedral if each cyclopentadienyl ring is taken as occupying a single coordination site. The zirconium atom in **8b** is a chiral centre and in the unit cell, only the R isomer was found.

The structural data for **8b** are comparable to those found for other dicyclopentadienyl, *ansa*-dicyclopentadienyl and mixed dicyclopentadienyl zirconium complexes [20]. The (centroid)–Zr–(centroid) angle for compound **8b** (127.9°) is within the expected range [21], although slightly smaller (10°) than that found in complexes with the same di*tert*-butylcyclopentadienyl ring or comparable bulky cyclopentadienyl ligands (bistrimethylsilylcyclopentadienyl or tri*tert*-butylcyclopentadienyl rings). This feature could be due to the presence of a constrained ligand in **8b**, which compresses the geometry to a more tetrahedral disposition.

The value of the (centroid)–Zr–N angle (100.3°) compares very well with those reported previously for related *ansa*-cyclopentadienylsilyl-amido derivatives [8a,22], being smaller than the typical (centroid)–Zr–(centroid) angles found for the *ansa*-dicyclopentadienyl complexes [9a,23].

The sum of the angles around the nitrogen atom [Si(1)–N(1)–C(31), 120.7(4)°, Zr(1)–N(1)–C(31), 135.0(4)°; Si(1)–N(1)–Zr(1), 104.2(2)°] (359.9°), is indicative of a planar triangular disposition corresponding to its sp^2 hybridisation. The Si(1)–N(1)–Zr(1) angle is 15° smaller while the Zr(1)–N(1)–C(31) angle is opened by almost the same amount with respect to the remaining Si(1)–N(1)–C(31) angle with a value of 120.7(4)°. The co-planarity of the zirconium, nitrogen, silicon and the *tert*-butyl ligand C$_{ipso}$ atoms and the smaller values observed for the Si(1)–N(1)–Zr(1) and N(1)–Si(1)–C(11) angles with respect to the theoretical values of 120 and 109°, respectively, is consistent with the behaviour known for these types of constrained geometry cyclopentadienylsilyl-amido complexes.

Table 3
Selected bond distances (Å) and bond angles (°) for compound **8b**

Bond distances			
Zr(1)–N(1)	2.124(4)	C(21)–C(22)	1.414(8)
Zr(1)–Cp1	2.226	Zr(1)–Cp2	2.272
Zr(1)–Cl(1)	2.470(2)	C(21)–C(211)	1.531(9)
Zr(1)–C(11)	2.450(6)	C(22)–C(23)	1.398(8)
Zr(1)–C(12)	2.487(7)	C(23)–C(24)	1.411(8)
Zr(1)–C(13)	2.585(7)	C(23)–C(231)	1.527(9)
Zr(1)–C(14)	2.591(6)	C(24)–C(25)	1.387(8)
Zr(1)–C(15)	2.514(6)	Si(1)–N(1)	1.747(5)
Zr(1)–C(21)	2.586(6)	Si(1)–C(112)	1.857(7)
Zr(1)–C(22)	2.595(6)	Si(1)–C(111)	1.862(6)
Zr(1)–C(23)	2.612(6)	C(211)–C(212)	1.508(9)
Zr(1)–C(24)	2.522(6)	C(211)–C(213)	1.537(8)
Zr(13)–C(25)	2.516(5)	C(211)–C(214)	1.545(8)
C(11)–C(15)	1.415(8)	C(231)–C(232)	1.523(9)
C(11)–C(12)	1.414(9)	C(231)–C(233)	1.533(9)
C(11)–Si(1)	1.852(6)	C(231)–C(234)	1.532(9)
C(12)–C(13)	1.386(9)	N(1)–C(31)	1.498(8)
C(13)–C(14)	1.39(1)	C(31)–C(33)	1.52(1)
C(14)–C(15)	1.406(9)	C(31)–C(34)	1.53(1)
C(21)–C(25)	1.403(8)	C(31)–C(32)	1.550(9)
Bond angles			
Cl(1)–Zr(1)–N(1)	96.0(1)	Cp1–Zr(1)–Cp2	127.9
Cl(1)–Zr(1)–Cp1	104.3	N(1)–Zr(1)–Cp1	100.3
Cl(1)–Zr(1)–Cp2	106.5	N(1)–Zr(1)–Cp2	116.9
N(1)–Si(1)–C(11)	95.2(2)	Si(1)–N(1)–Zr(1)	104.2(2)
Si(1)–N(1)–C(31)	120.7(4)	Zr(1)–N(1)–C(31)	135.0(4)

The Zr(1)–N(1) [2.124(4) Å] and Si(1)–N(1) [1.747(5) Å] bond distances are similar to those found for analogous interactions [24] and shorter than the estimated addition of the corresponding covalent radii, indicating the Zr–N and Si–N double-bond character with competition between the silicon and the zirconium atoms for π-bonding with the nitrogen lone pair leading to the electronic delocalisation along the Si–N–Zr system.

A slight deviation from η^5-coordination of the silyl-substituted cyclopentadienyl ligand in compound **8b** is observed, as deduced from the small differences in the Zr–C(ring) (0.141 Å) and the C–C ring distances and the distance from the silicon atom to the Cp plane (0.7986 Å).

3. Experimental

3.1. General considerations

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox model HE-63. The following solvents were purified by distillation under argon before use by employing the appropriate drying/deoxygenated agent: toluene (sodium), hexane and heptane (sodium–potassium amalgam) and diethyl ether (sodium–benzophenone). TiCl$_4$ (Fluka), HfCl$_4$ (Aldrich), TlOC$_2$H$_5$ (Panreac), NEt$_3$ (Fluka) and NH$_2^t$Bu (Aldrich) were distilled before use and stored over 4 Å molecular sieves. Ti(η^5-C$_5$H$_4$SiClMe$_2$)Cl$_3$ [9a], Zr(η^5-C$_5$H$_4$SiMe$_2$Cl)Cl$_3$ [9a], (C$_5$H$_4$)(SiClMe$_2$)(SiMe$_3$) [9a,25], C$_5$H$_5$SiClMe$_2$ [26], 1,3-^{t}Bu$_2$C$_5$H$_4$ [27], Tl(C$_5$H$_5$) [28] and K(C$_5$Me$_5$) [29] were prepared by known procedures. LiNH^{t}Bu was quantitatively prepared by reaction of NH$_2^t$Bu with Li^{n}Bu in hexane. C, H and N microanalyses were performed on a Perkin–Elmer 240B and/or Heraeus CHN–O-rapid microanalyzer. Electron impact (EI) mass spectra were recorded at 70 eV on a Hewlett–Packard 5988 spectrometer and IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer using KBr pellets; only selected MS and IR data are reported. NMR spectra, measured at 25°C, were recorded on a Varian Unity FT-300 (^{1}H-NMR at 300 MHz, ^{13}C-NMR at 75 MHz) or FT-500 (^{1}H-NMR at 500 MHz, ^{13}C-NMR at 125 MHz) spectrometer and chemical shifts are referenced to residual protons or carbons of the deuterated solvents.

3.2. Synthesis of $Tl(1,3\text{-}^tBu_2C_5H_3)$

$1,3\text{-}^tBu_2C_5H_4$ (1.85 ml, 1.56 g, 8.73 mmol) was added dropwise to a solution of $TlOC_2H_5$ (0.61 ml, 2.18 g, 8.73 mmol) in diethyl ether cooled at 0°C. The reaction mixture was stirred for 8 h at room temperature (r.t.) to give a pale yellow solid. After filtration, the solid was washed with hexane (2×10 ml), dried under vacuum and characterised as $Tl(1,3\text{-}^tBu_2C_5H_3)$ (1.0 g, 2.62 mmol, 30% yield). Anal. Calc. for $C_{13}H_{21}Tl$: C, 40.91; H, 5.55. Found: C, 41.62; H, 6.02%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 1.29 (s, 18H, ^{t}Bu), 5.80 (AA′, 2H, C_5H_3), 6.11 (B, 1H, C_5H_3). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 31.3 (C_{ipso}, ^{t}Bu), 34.4 (^{t}Bu), 101.5, 102.9 (C_5H_3), 139.1 (C_{ipso}, C_5H_3). MS (EI) *m/z*: 382 $[M]^+$ (7%); 205 $[Tl]^+$ (100%).

*3.3. Synthesis of $Hf(\eta^5\text{-}C_5H_4SiClMe_2)Cl_3$ (**1c**)*

A solution of $C_5H_4(SiClMe_2)(SiMe_3)$ (1.15 ml, 1.04 g, 4.5 mmol) in heptane was added to a suspension of $HfCl_4$ (1.30 g, 4.06 mmol) in 50 ml of the same solvent. The Schlenk was connected to a bubbler and the reaction mixture was refluxed with vigorous stirring for 1 h. The formation of a brown solution was observed when the $HfCl_4$ reacted gradually. After filtration, the hot solution was concentrated (30 ml) and cooled to −30°C to give a white solid which was recrystallised in toluene–hexane to give **1c** as a microcrystalline solid (1 g, 2.26 mmol, 56% yield). Anal. Calc. for $C_7H_{10}SiCl_4Hf$: C, 18.99; H, 2.27. Found: C, 19.36; H, 2.48%. ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C): δ 0.77 (s, 6H, $SiClMe_2$), 6.90 (AA′, 2H, C_5H_4), 7.02 (BB′, 2H, C_5H_4). (300 MHz, C_6D_6, 25°C): δ 0.43 (s, 6H, $SiClMe_2$), 5.91 (AA′, 2H, C_5H_4), 6.25 (BB′, 2H, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 2.7 ($SiClMe_2$), 123.6, 126.6 (C_2–C_5, C_5H_4), 131.5 (C_{ipso}, C_5H_4). MS (EI) *m/z*: 442 $[M]^+$ (4%); 407 $[M-Cl]^+$ (5%); 122 $[C_5H_4SiMe_2]^+$ (100%).

*3.4. Synthesis of $Ti(\eta^5\text{-}C_5H_4SiClMe_2)_2Cl_2$ (**2a**)*

$C_5H_5(SiClMe_2)$ (7.39 ml, 7.39 g, 46.57 mmol) was added to a solution containing $TiCl_4$ (2.56 ml, 4.41 g, 23.28 mmol) and NEt_3 (6.77 ml, 4.71 g, 46.57 mmol) in toluene (100 ml). The mixture was refluxed with stirring for 3 h and the formation of insoluble $Et_3N{\cdot}HCl$, was observed. After filtration, the solution was concentrated and cooled to −30°C affording a solid which was washed with cold hexane (2×15 ml) and recrystallised from toluene–hexane to give **2a** as a red microcrystalline solid (4.7 g, 10.8 mmol, 46%). Anal. Calc. for $C_{14}H_{20}Si_2Cl_4Ti$: C, 38.73; H, 4.64. Found: C, 39.05; H, 4.71%. ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C): δ 0.74 (s, 6H, $SiClMe_2$), 6.62 (AA′, 2H, C_5H_4), 6.86 (BB′, 2H, C_5H_4). (300 MHz, C_6D_6, 25°C): δ 0.74 (s, 6H, $SiClMe_2$), 5.69 (AA′, 2H, C_5H_4), 6.40 (BB′, 2H, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 2.9 ($SiClMe_2$), 120.9, 129.1 (C_5H_4), 128.1 (C_{ipso}, C_5H_4). MS (EI) *m/z*: 434 $[M]^+$ (10%); 362 $[M-2Cl]^+$ (100%); 122 $[C_5H_4SiMe_2]^+$ (66%), 107 $[C_5H_4SiMe]^+$ (31%).

*3.5. Synthesis of $Hf(\eta^5\text{-}C_5H_4SiClMe_2)_2Cl_2$ (**2c**)*

$C_5H_5(SiClMe_2)$ (0.93ml, 0.93 g, 5.9 mmol) was added to a solution containing $HfCl_4$ (0.95 g, 2.95 mmol) and NEt_3 (0.86 ml, 0.60 g, 5.9 mmol) in toluene (100 ml). The mixture was refluxed with stirring for 3 h. The insoluble $Et_3N{\cdot}HCl$ precipitate, was filtered off and the solution was concentrated and cooled to −30°C affording a light brown solid which was washed with cold hexane (2×15 ml) and recrystallised from toluene–hexane to give **2c** (1 g, 1.77 mmol, 60%). Anal. Calc. for $C_{14}H_{20}Si_2Cl_4Hf$: C, 29.77; H, 3.57. Found: C, 30.05; H, 4.00%. ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C): δ 0.72 (s, 6H, $SiClMe_2$), 6.49 (AA′, 2H, C_5H_4), 6.70 (BB′, 2H, C_5H_4). (300 MHz, C_6D_6, 25°C): δ 0.65 (s, 6H, $SiClMe_2$), 5.76 (AA′, 2H, C_5H_4), 6.29 (BB′, 2H, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 3.1 ($SiClMe_2$), 115.3, 125.6 (C_5H_4), 120.0 (C_{ipso}, C_5H_4). MS (EI) *m/z*: 564 $[M]^+$ (1%); 407 $[M-C_5H_4SiClMe_2]^+$ (100%); 122 $[C_5H_4SiMe_2]^+$ (82%), 107 $[C_5H_4SiMe]^+$ (25%).

*3.6. Synthesis of $Ti\{(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}Cl_2$ (**3a**)*

Water (50 µl, 0.05 g, 2.8 mmol) was added to a solution of $Ti(\eta^5\text{-}C_5H_4SiClMe_2)_2Cl_2$ (1.21 g, 2.8 mmol) in toluene (50 ml). The mixture was stirred for 2 h at r.t. and then concentrated and cooled to −30°C affording a red microcrystalline solid which was washed with hexane (2×15 ml), recrystallised from toluene–hexane and characterised as **3a** (0.41 g, 2.1 mmol, 77%). Anal. Calc. for $C_{14}H_{20}Si_2Cl_2OTi$: C, 44.34; H, 5.32. Found: C, 44.02; H, 5.41%. ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C): δ 0.12 (s, 6H, $SiMe_2$), 6.61 (AA′, 2H, C_5H_4), 6.93 (BB′, 2H, C_5H_4). (300 MHz, C_6D_6, 25°C): δ 0.20 (s, 6H, $SiMe_2$), 6.16 (AA′, 2H, C_5H_4), 6.50 (BB′, 2H, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 0.4 ($SiMe_2$), 119.0, 124.7 (C_5H_4), 115.6 (C_{ipso}, C_5H_4). MS (EI) *m/z*: 378 $[M]^+$ (13%); 308 $[M-2Cl]^+$ (43%); 122 $[C_5H_4SiMe_2]^+$ (100%); 107 $[C_5H_4SiMe]^+$ (46%).

*3.7. Synthesis of $Hf\{(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}Cl_2$ (**3c**)*

Water (30 µl, 0.03 g, 1.96 mmol) was added to a solution containing 1.11 g of $Hf(\eta^5\text{-}C_5H_4SiClMe_2)_2Cl_2$ (1.96 mmol) in toluene (50 ml). The mixture was stirred for 12 h and then concentrated and cooled to −30°C to give a white microcrystalline solid which was washed with hexane (2 × 15 ml), recrystallised from toluene–hexane and characterised as **3c** (1.0 g, 1.96 mmol, 100%). Anal. Calc. for $C_{14}H_{20}Si_2Cl_2OHf$: C, 32.98; H, 3.95. Found: C, 32.62; H, 3.98%. ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C): δ 0.37 (s, 6H, $SiMe_2$), 6.43 (AA′, 2H, C_5H_4), 6.76 (BB′, 2H, C_5H_4). (300 MHz, C_6D_6, 25°C): δ 0.25 (s, 6H, $SiMe_2$), 6.18 (AA′, 2H, C_5H_4), 6.35 (BB′, 2H, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 0.9 ($SiMe_2$), 119.6, 129.9 (C_5H_4), 114.5 (C_{ipso}, C_5H_4). MS (EI) *m/z*: 510 $[M]^+$ (8%); 495 $[M-2Cl+H]^+$ (75%); 122 $[C_5H_4SiMe_2]^+$ (100%); 107 $[C_5H_4SiMe]^+$ (36%).

3.8. Synthesis of Ti(η^5-1,3^{t}Bu$_2$C$_5$H$_3$)(η^5-C$_5$H$_4$SiClMe$_2$)Cl$_2$ (4a)

Tl(1,3-^{t}Bu$_2$C$_5$H$_3$) (1.40 g, 3.67 mmol) was added to a solution of Ti(η^5-C$_5$H$_4$SiClMe$_2$)Cl$_3$ (1.15 g, 3.67 mmol) in toluene (35 ml). The reaction mixture was refluxed with stirring for 12 h. After filtration, the resulting solution was concentrated (15 ml) and cooled to −30°C to give a solid which was washed with hexane (2 × 10 ml) and recrystallised from toluene–hexane. The resulting red microcrystalline solid was characterised as **4a** (1.0 g, 2.20 mmol, 60% yield). Anal. Calc. for $C_{20}H_{31}SiCl_3Ti$: C, 53.21; H, 6.74. Found: C, 52.93; H, 6.89%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.92 (s, 6H, $SiClMe_2$), 1.12 (s, 18H, ^{t}Bu), 5.57 (AA′, 2H, C_5H_3), 5.95 (AA′, 2H, C_5H_4), 6.42 (B, 1H, C_5H_3), 6.52 (BB′, 2H, C_5H_4). (300 MHz, $CDCl_3$, 25°C): δ 0.76 (s, 6H, $SiClMe_2$), 1.20 (s, 18H, ^{t}Bu), 6.36 (B, 1H, C_5H_3), 6.57 (AA′, 2H, C_5H_3), 6.62 (AA′, 2H, C_5H_4), 6.66 (BB′, 2H, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 3.3 ($SiClMe_2$), 30.9 (^{t}Bu), 35.1 (C_{ipso}, ^{t}Bu), 115.0, 115.7 (C_5H_4), 117.7 (C_{ipso}, C_5H_4), 118.3 (C_2, C_5H_3), 131.0 (C_4–C_5, C_5H_3), 151.9 (C_{ipso}, C_5H_3). MS (EI) *m/z*: 453 $[M]^+$ (2%); 275 $[M-1,3(^tBu)_2C_5H_3]^+$ (5%); 57 $[Me_3C]^+$ (100%).

3.9. Synthesis of Zr(η^5-1,3^{t}Bu$_2$C$_5$H$_3$)(η^5-C$_5$H$_4$SiClMe$_2$)Cl$_2$ (4b)

Tl(1,3-^{t}Bu$_2$C$_5$H$_3$) (1.02 g, 2.68 mmol) was added to a solution of Zr(η^5-C$_5$H$_4$SiClMe$_2$)Cl$_3$ (0.95g, 2.68 mmol) in toluene (35 ml). The reaction mixture was refluxed with stirring for 14 h. After filtration, the resulting solution was concentrated (15 ml) and cooled to −30°C to give a solid which was washed with hexane (2 × 10 ml) and recrystallised from toluene–hexane. The resulting white microcrystalline solid was characterised as **4b** (1.0 g, 2.01 mmol, 75% yield). Anal. Calc. for $C_{20}H_{31}SiCl_3Zr$: C, 47.85; H, 5.99. Found: C, 48.32; H, 6.28%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.79 (s, 6H, $SiClMe_2$), 1.15 (s, 18H, ^{t}Bu), 5.85 (AA′, 2H, C_5H_3), 6.01 (AA′, 2H, C_5H_4), 6.24 (B, 1H, C_5H_3), 6.53 (BB′, 2H, C_5H_4). (300 MHz, $CDCl_3$, 25°C): δ 0.75 (s, 6H, $SiClMe_2$), 1.26 (s, 18H, ^{t}Bu), 6.25 (AA′, 2H, C_5H_3), 6.41 (B, 1H, C_5H_3), 6.55 (AA′, 2H, C_5H_4), 6.71 (BB′, 2H, C_5H_4). ^{13}C-{^{1}H} NMR (125 MHz, $CDCl_3$, 25°C): δ 3.1 ($SiClMe_2$), 31.2 (^{t}Bu), 33.9 (C_{ipso}, ^{t}Bu), 110.8, 114.0 (C_5H_4), 114.8, 126.9 (C_5H_3), 123.2 (C_{ipso}, C_5H_4), 144.8 (C_{ipso}, C_5H_3). MS (EI) *m/z*: 496 $[M]^+$ (2%); 318 $[M-1,3(^tBu)_2C_5H_3]^+$ (100%); 122 $[C_5H_4SiClMe_2]^+$ (21%); 57 $[Me_3C]^+$ (32%).

3.10. Synthesis of Hf(η^5-1,3^{t}Bu$_2$C$_5$H$_3$)(η^5-C$_5$H$_4$SiClMe$_2$)Cl$_2$ (4c)

Tl(1,3-^{t}Bu$_2$C$_5$H$_3$) (0.93 g, 2.44 mmol) was added to a solution of Hf(η^5-C$_5$H$_4$SiClMe$_2$)Cl$_3$ (1.08 g, 2.44 mmol) in toluene (35 ml). The mixture was refluxed with stirring for 14 h and then filtered to give a solution which was concentrated (15 ml) and cooled to −30°C. The resulting solid was washed with hexane (2 × 10 ml) and recrystallised from toluene–hexane to give **4c** as a white microcrystalline solid (1.0 g, 1.71 mmol, 70% yield). Anal. Calc. for $C_{20}H_{31}SiCl_3Hf$: C, 41.11; H, 5.35. Found: C, 42.00; H, 5.27%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.66 (s, 6H, $SiClMe_2$), 1.18 (s, 18H, ^{t}Bu), 6.03 (AA′, 2H, C_5H_3), 6.20 (AA′, 2H, C_5H_4), 6.38 (B, 1H, C_5H_3), 6.53 (BB′, 2H, C_5H_4). (300 MHz, $CDCl_3$, 25°C): δ 0.75 (s, 6H, $SiClMe_2$), 1.27 (s, 18H, ^{t}Bu), 6.02 (AA′, 2H, C_5H_4), 6.12 (AA′, 2H, C_5H_3), 6.33 (B, 1H, C_5H_3), 6.47 (BB′, 2H, C_5H_4). ^{13}C-{^{1}H} NMR (125 MHz, $CDCl_3$, 25°C): δ 3.1 ($SiClMe_2$), 31.3 (^{t}Bu), 33.8 (C_{ipso}, ^{t}Bu), 110.0, 113.0 (C_5H_4), 113.2, 125.5 (C_5H_3), 120.1 (C_{ipso}, C_5H_4), 142.6 (C_{ipso}, C_5H_3). MS (EI) *m/z*: 584 $[M]^+$ (2%); 549 $[M-Cl]^+$ (10%); 407 $[M-1,3(^tBu)2C_5H_3]^+$ (100%); 122 $[C_5H_4SiClMe_2]^+$ (15%); 57 $[Me_3C]^+$ (6%).

3.11. Synthesis of Zr(η^5-C$_5$Me$_5$)(η^5-C$_5$H$_4$SiClMe$_2$)Cl$_2$ (5b)

K(C_5Me_5) (0.76 g, 4.38 mmol) was added to a solution of Zr(η^5-C$_5$H$_4$SiClMe$_2$)Cl$_3$ (1.56 g, 4.38 mmol) in toluene (50 ml) at −60°C. The mixture was warmed to r.t. and stirred for 30 m. After filtration the resulting solution was evaporated under vacuum to dryness. The purple microcrystalline solid was washed with hexane (2 × 10 ml), recrystallised from toluene–hexane and characterised as **5b** (1.0 g, 2.19 mmol, 50%). Anal. Calc. for $C_{17}H_{25}SiCl_3Zr$: C, 44.85; H, 5.53. Found: C, 43.85; H, 5.65%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.87 (s, 6H, $SiClMe_2$), 1.69 (s, 15H, C_5Me_5), 5.62 (AA′, 2H, C_5H_4), 6.46 (BB′, 2H, C_5H_4). (300 MHz, $CDCl_3$, 25°C): δ 0.76 (s, 6H, $SiClMe_2$), 2.01 (s, 15H, C_5Me_5), 6.12 (AA′, 2H, C_5H_4), 6.56 (BB′, 2H, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6, 25°C): δ 3.2 ($SiClMe_2$), 12.3 ($C_5\mathit{Me}_5$), 114.8 (C_5H_4) (one of the C_5H_4 signal collapsed with the solvent signals), 124.5 (C_5Me_5), 125.7 (C_{ipso}, C_5H_4). MS (EI) *m*/*z*: 454 $[M]^+$ (1%); 320 $[M-C_5Me_5]^+$ (21%); 135 $[C_5Me_5]^+$ (100%); 122 $[C5H_4SiMe_2]^+$ (28%).

3.12. Synthesis of *Hf(η^5-C_5Me_5)(η^5-C_5H_4SiClMe_2)Cl_2* ***(5c)***

$K(C_5Me_5)$ (0.58 g, 3.35 mmol) was added to a solution of $Hf(\eta^5\text{-}C_5H_4SiClMe_2)Cl_3$ (0.58g, 3.35 mmol) in toluene at −60°C. Following the procedure described above for **5b**, a purple microcrystalline solid characterised as **5c** was obtained (1.0 g, 1.85 mmol, 55%). Anal. Calc. for $C_{17}H_{25}SiCl_3Hf$: C, 37.65; H, 4.65. Found: C, 37.63; H, 4.61%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.85 (s, 6H, $SiClMe_2$), 1.76 (s, 15H, C_5Me_5), 5.60 (AA′, 2H, C_5H_4), 6.38 (BB′, 2H, C_5H_4). (300 MHz, $CDCl_3$, 25°C): δ 0.81 (s, 6H, $SiClMe_2$), 1.92 (s, 15H, C_5Me_5), 6.05 (AA′, 2H, C_5H_4), 6.60 (BB′, 2H, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6, 25°C): δ 3.6 ($SiClMe_2$), 15.6 ($C_5\mathit{Me}_5$), 116.7 (C_5H_4) (one of the C_5H_4 signal collapsed with the solvent signals), 124.8 (C_{ipso}, C_5H_4), 126.8 (C_5Me_5). MS (EI) *m*/*z*: 541 $[M]^+$ (5%); 407 $[M-C_5Me_5]^+$ (87%); 135 $[C_5Me_5]^+$ (36%); 122 $[C_5H_4SiMe_2]^+$ (100%).

3.13. Synthesis of *Hf(C_5H_5)(C_5H_4SiClMe_2)Cl_2* ***(6c)***

$Tl(C_5H_5)$ (0.95 g, 3.53 mmol) was added to a solution of $Hf(C_5H_4SiMe_2Cl)Cl_3$ (1.56 g, 3.53 mmol) in toluene at −78°C. The mixture was warmed to r.t. and stirred for 12 h. After filtration, the resulting solution was concentrated and cooled to −30°C to give a white solid which was washed with hexane, recrystallised from toluene–hexane and characterised as **6** (1.0 g, 2.12 mmol, 60% yield). Anal. Calc. for $C_{12}H_{15}SiCl_3Hf$: C, 30.55; H, 3.20. Found: C, 31.35; H, 3.47%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.66 (s, 6H, $SiMe_2Cl$), 5.71 (AA′, 2H, C_5H_4), 5.86 (s, 5H, C_5H_5), 6.27 (BB′, 2H, C_5H_4). (300 MHz, $CDCl_3$, 25°C): δ 0.72 (s, 6H, $SiMe_2Cl$), 6.39 (s, 5H, C_5H_5), 6.48 (AA′, 2H, C_5H_4), 6.70 (BB′, 2H, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 3.2 ($SiMe_2Cl$), 115.8, 124.2 (C_2–C_5, C5H4), 119.3 (C_{ipso}, C_5H_4) 114.9 (C_5H_5). MS (EI) *m*/*z*: 472 $[M]^+$ (2%); 437 $[M-Cl]^+$ (26%); 407 $[M-C_5H_5]^+$ (66%); 315 $[M-C_5H_4SiMe_2Cl]^+$ (14%); 122 $[C_5H_4SiMe_2]^+$ (100%).

3.14. Synthesis of *Ti(η^5-1,3^tBu_2C_5H_3)(η^5-C_5H_4SiMe_2NH^tBu)Cl_2* ***(7a)***

$LiNH^tBu$ (0.25 g, 3.14 mmol) was added to a solution of $Ti(1,3\text{-}^tBu_2C_5H_3)(\eta^5\text{-}C_5H_4SiClMe_2)Cl_2$ (1.43 g, 3.14 mmol) in toluene (50 ml). The mixture was warmed at 50–60°C with stirring for 6 h. The solution was filtered, concentrated (10 ml) and cooled at −30°C to give a red solid which was dried under reduced pressure, recrystallised from toluene–hexane and characterised as **7a** (1.0 g, 2.04 mmol, 65% yield). Anal. Calc. for $C_{24}H_{41}SiNCl_2Ti$: C, 58.77; H, 8.43; N, 2.86. Found: C, 59.67; H, 8.78; N, 2.95%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.6 (s, 6H, $SiMe_2$), 1.16 (s, 9H, ^{t}BuN), 1.18 (s, 18H, ^{t}Bu), 5.87 (AA′, 2H, C_5H_3), 6.12 (AA′, 2H, C_5H_4), 6.5 (B, 1H, C_5H_3), 6.70 (BB′, 2H, C_5H_4); the amino proton signal was not observed. (300 MHz, $CDCl_3$, 25°C): δ 0.39 (s, 6H, $SiMe_2$), 1.08 (s, 9H, ^{t}BuN), 1.24 (s, 18H, ^{t}Bu), 6.12 (AA′, 2H, C_5H_4), 6.30 (AA′, 2H, C_5H_3), 6.61 (B, 1H, C_5H_3), 6.75 (BB′, 2H, C_5H_4); the amino proton signal was not observed. ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6, 25°C): δ 2.7 ($SiMe_2$), 30.9 (^{t}Bu), 32.7 (^{t}BuN), 35.0 (C_{ipso}, ^{t}Bu), 49.6 (C_{ipso}, ^{t}BuN), 113.7, 117.5 (C_5H_4), 120.3, 131.9 (C_5H_3), 133.5 (C_{ipso}, C_5H_3), 150.4 (C_{ipso}, C_5H_4). MS (EI) *m*/*z*: 419 $[M-NH^tBu]^+$ (6%); 312 $[M-1,3(^tBu)_2C_5H_3]^+$ (9%); 256 $[M-1,3(^tBu)_2C_5H_3\text{-}^tBu]^+$ (19%); 122 $[C_5H_4SiMe_2]^+$ (25%); 57 $[Me_3C]^+$ (100%). IR (KBr): ν(N–H) = 3375 cm^{-1}.

3.15. Synthesis of *Zr(η^5-1,3^tBu_2C_5H_3)(η^5-C_5H_4SiMe_2NH^tBu)Cl_2* ***(7b)***

Following the procedure described for the synthesis of **7a**, $LiNH^tBu$ (0.22 g, 2.79 mmol) and $Zr(1,3\text{-}^tBu_2C_5H_3)(\eta^5\text{-}C_5H_4SiClMe_2)Cl_2$ (1.38 g, 2.79 mmol) were reacted to give a white microcrystalline solid characterised as **7b** (1.0 g, 1.87 mmol, 67% yield). Anal. Calc. for $C_{24}H_{41}SiNCl_2Zr$: C, 54.22; H, 7.78; N, 2.64. Found: C, 55.31; H, 7.95; N, 2.95%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.56 (s, 6H, $SiMe_2$), 1.14 (s, 9H, ^{t}BuN), 1.20 (s, 18H, ^{t}Bu), 5.9 (AA′, 2H, C_5H_3), 6.13 (AA′, 2H, C_5H_4), 6.32 (B, 1H, C_5H_3), 6.65 (BB′, 2H, C_5H_4); the amino proton signal was not observed. (300 MHz, $CDCl_3$, 25°C): δ 0.37 (s, 6H, $SiMe_2$), 1.08 (s, 9H, ^{t}BuN), 1.23 (s, 18H, ^{t}Bu), 6.17 (AA′, 2H, C_5H_3), 6.49 (AA′, 2H, C_5H_4), 6.55 (B, 1H, C_5H_3), 6.71 (BB′, 2H, C_5H_4); the amino proton signal was not observed. ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6, 25°C): δ 3.0 ($SiMe_2$), 33.4 (^{t}Bu), 35.6 (^{t}BuN), 32.6 (C_{ipso}, ^{t}Bu), 51.7 (C_{ipso}, ^{t}BuN), 110.8, 115.6 (C_5H_4), 123.6, 134.5 (C_5H_3), 135.6 (C_{ipso}, C_5H_3), 156.6 (C_{ipso}, C_5H_4). MS (EI) *m*/*z*: 462 $[M-NH^tBu]^+$ (10%); 357 $[M-1,3(^tBu)_2C_5H_3]^+$ (7%); 300 $[M-1,3(^tBu)_2C_5H_3\text{-}^tBu]^+$ (12%); 122 $[C_5H_4SiMe_2]^+$ (35%); 57 $[Me_3C]^+$ (100%). IR (KBr): ν(N–H) = 3379 cm^{-1}.

3.16. Synthesis of *Hf(η^5-1,3^tBu_2C_5H_3)(η^5-C_5H_4SiMe_2NH^tBu)Cl_2* ***(7c)***

Following the procedure described for the synthesis of **7a**, $LiNH^tBu$ (0.21 g, 2.79 mmol) and $Hf(1,3\text{-}^tBu_2C_5H_3)(\eta^5\text{-}C_5H_4SiClMe_2)Cl_2$ (1.56 g, 2.23 mmol) were reacted to give a white microcrystalline solid characterised as **7c** (1.0 g, 1.61 mmol, 58% yield). Anal.

Calc. for $C_{24}H_{41}SiNCl_2Hf$: C, 46.41; H, 6.65; N, 2.26. Found: C, 47.50; H, 6.87; N, 2.53%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.62 (s, 6H, $SiMe_2$), 1.1 (s, 9H, ^{t}BuN), 1.4 (s, 18H, ^{t}Bu), 5.83 (AA′, 2H, C_5H_3), 6.23 (AA′, 2H, C_5H_4), 6.42 (B, 1H, C_5H_3), 6.73 (BB′, 2H, C_5H_4); the amino proton signal was not observed. (300 MHz, $CDCl_3$, 25°C): δ 0.35 (s, 6H, $SiMe_2$), 1.07 (s, 9H, ^{t}BuN), 1.20 (s, 18H, ^{t}Bu), 6.41 (AA′, 2H, C_5H_3), 6.61 (AA′, 2H, C_5H_4), 6.57 (B, 1H, C_5H_3), 6.80 (BB′, 2H, C_5H_4); the amino proton signal was not observed. ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6, 25°C): δ 2.5 ($SiMe_2$), 31.6 (^{t}Bu), 37.8 (^{t}BuN), 34.3 (C_{ipso}, ^{t}Bu), 50.9 (C_{ipso}, ^{t}BuN), 112.6, 116.8 (C_5H_4), 125.3, 138.6 (C_5H_3), 138.3 (C_{ipso}, C_5H_3), 150.5 (C_{ipso}, C_5H_4). MS (EI) *m*/*z*: 549 $[M-NH^{t}Bu]^+$ (13%); 444 $[M-1,3(^{t}Bu)_2C_5H_3]^+$ (5%); 387 $[M-1,3(^{t}Bu)_2C_5H_3\text{-}^{t}Bu]^+$ (23%); 122 $[C_5H_4SiMe_2]^+$ (32%); 57 $[Me_3C]^+$ (100%). IR (KBr): $\nu(N\text{–}H) = 3379$ cm^{-1}.

3.17. Synthesis of $Ti(\eta^5\text{-}1,3^{t}Bu_2C_5H_3)(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N^{t}Bu)Cl_2$ (**8a**)

LiNH^{t}Bu (0.43 g, 5.50 mmol) was added to a solution of $Ti(1,3\text{-}^{t}Bu_2C_5H_3)(\eta^5\text{-}C_5H_4SiClMe_2)Cl_2$ (1.24 g, 2.75 mmol) in toluene (50 ml) at −78°C. The mixture was warmed to r.t. and stirred for 8 h. After filtration, the solvent was removed under vacuum to dryness to obtain a red oil. Extraction with cold hexane and cooling to −30°C gave a red microcrystalline solid characterised as **8a** (1.0 g, 2.20 mmol, 80% yield). Anal. Calc. for $C_{24}H_{40}SiNClTi$: C, 63.49; H, 8.88; N, 3.09. Found: C, 63.38; H, 8.90; N, 3.20%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.32 (s, 3H, SiMe), 0.67 (s, 3H, SiMe); 1.05 (s, 9H, ^{t}Bu), 1.27 (s, 9H, ^{t}Bu), 1.41 (s, 9H, ^{t}Bu), 5.69, 5.71, 6.19, 6.42, 6.51, 6.87, 7.19 (C_5H_3, C_5H_4). (300 MHz, $CDCl_3$, 25°C): δ 0.35 (s, 3H, SiMe), 0.59 (s, 3H, SiMe), 1.17 (s, 9H, ^{t}Bu), 1.23 (s, 9H, ^{t}Bu), 1.40 (s, 9H, ^{t}Bu), 5.76, 6.04, 6.23, 6.27, 6.84, 6.88, 6.95 (C_5H_3, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 1.7 (SiMe), 4.5 (SiMe), 31.4 (^{t}Bu), 31.5 (^{t}Bu), 34.1 (^{t}BuN), 33.6 (C_{ipso}, ^{t}Bu), 33.9 (C_{ipso}, ^{t}Bu), 66.3 (C_{ipso}, ^{t}BuN), 107.2, 112.0, 113.0, 118.4, 118.8, 121.3, 135.3 (C_5H_3, C_5H_4), 109.8, 134.4, 141.6 (C_{ipso}, C_5H_4, C_5H_3). MS (EI) *m*/*z*: 453 $[M]^+$ (3%); 276 $[M-1,3(^{t}Bu)_2C_5H_3]^+$ (100%); 261 $[M-1,3(^{t}Bu)_2C_5H_3\text{–}CH_3]^+$ (51%); 220 $[M-1,3(^{t}Bu)_2C_5H_3\text{–}CH_3\text{-}^{t}Bu]^+$ (40%).

3.18. Synthesis of $Zr(\eta^5\text{-}1,3^{t}Bu_2C_5H_3)(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N^{t}Bu)Cl_2$ (**8b**)

Following the procedure described for the synthesis of **8a**, LiNH^{t}Bu (0.37 g, 4.67 mmol) and $Zr(1,3\text{-}^{t}Bu_2C_5H_3)(\eta^5\text{-}C_5H_4SiClMe_2)Cl_2$ (1.11 g, 2.23 mmol) were reacted to give a white microcrystalline solid characterised as **8b** (1.0 g, 2.01 mmol, 90% yield). Anal. Calc. for $C_{24}H_{40}SiNClZr$: C, 57.96; H, 8.11; N, 2.82. Found: C, 57.76; H, 8.07; N, 2.82%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.38 (s, 3H, SiMe), 0.63 (s, 3H, SiMe); 1.13 (s, 9H, ^{t}Bu), 1.28 (s, 9H, ^{t}Bu), 1.32 (s, 9H, ^{t}Bu), 5.81, 5.89, 6.21, 6.28, 6.33, 6.63, 6.89 (C_5H_3, C_5H_4). (300 MHz, $CDCl_3$, 25°C): δ 0.38 (s, 3H, SiMe), 0.54 (s, 3H, SiMe), 1.21 (s, 9H, ^{t}Bu), 1.28 (s, 9H, ^{t}Bu), 1.29 (s, 9H, ^{t}Bu), 5.94, 6.08, 6.12, 6.28, 6.64, 6.71, 6.89 (C_5H_3, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 1.8 (SiMe), 4.8 (SiMe), 31.2 (^{t}Bu), 31.9 (^{t}Bu), 34.5 (^{t}BuN), 33.2 (C_{ipso}, ^{t}Bu), 33.4 (C_{ipso}, ^{t}Bu), 59.3 (C_{ipso}, ^{t}BuN), 108.9, 109.8, 114.2, 117.0, 118.2, 128.5, (C_5H_3, C_5H_4), 111.7, 135.1, 139.6 (C_{ipso}, C_5H_4, C_5H_3). MS (EI) *m*/*z*: 495 $[M]^+$ (2%); 480 $[M-CH_3]^+$ (100%); 423 $[M-{}^{t}Bu\text{-}CH_3]^+$ (19%); 302 $[M-CH_3\text{–}1,3(^{t}Bu)_2C_5H_3]^+$ (45%); 245 $[M-1,3(^{t}Bu)_2\text{-}C_5H_3\text{–}CH_3\text{-}^{t}Bu]^+$ (72%).

3.19. Synthesis of $Hf(\eta^5\text{-}1,3^{t}Bu_2C_5H_3)(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N^{t}Bu)Cl_2$ (**8c**)

Following the procedure described for the synthesis of **8a**, LiNH^{t}Bu (0.31 g, 3.93 mmol) and $Hf(1,3\text{-}^{t}Bu_2C_5H_3)(\eta^5\text{-}C_5H_4SiClMe_2)Cl_2$ (1.15 g, 1.97 mmol) were reacted to give a white microcrystalline solid characterised as **8c** (1.0 g, 1.71 mmol, 87% yield). Anal. Calc. for $C_{24}H_{40}SiNClHf$: C, 49.31; H, 6.90; N, 2.40. Found: C, 48.83; H, 6.98; N, 2.50%. ^{1}H-NMR (300 MHz, C_6D_6, 25°C): δ 0.40 (s, 3H, SiMe), 0.63 (s, 3H, SiMe); 1.16 (s, 9H, ^{t}Bu), 1.29 (s, 9H, ^{t}Bu), 1.32 (s, 9H, ^{t}Bu), 5.80, 6.14, 6.17, 6.29, 6.58, 6.78 (C_5H_3, C_5H_4). (300 MHz, $CDCl_3$, 25°C): δ 0.38 (s, 3H, SiMe), 0.55 (s, 3H, SiMe), 1.22 (s, 9H, ^{t}Bu), 1.28 (s, 9H, ^{t}Bu), 1.31 (s, 9H, ^{t}Bu), 5.86, 5.97, 6.10, 6.24, 6.53, 6.63, 6.65 (C_5H_3, C_5H_4). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 2.0 (SiMe), 4.9 (SiMe), 31.6 (^{t}Bu), 31.9 (^{t}Bu), 34.8 (^{t}BuN), 33.1 (C_{ipso}, ^{t}Bu), 33.3 (C_{ipso}, ^{t}Bu), 58.3 (C_{ipso}, ^{t}BuN), 106.7, 109.0, 110.2, 113.0, 115.5, 118.6, 127.5 (C_5H_3, C_5H_4), 110.6, 132.9, 137.9 ((C_{ipso}, C_5H_4, C_5H_3). MS (EI) *m*/*z*: 585 $[M]^+$ (2%); 570 $[M-CH_3]^+$ (100%); 513 $[M-{}^{t}Bu\text{-}CH_3]^+$ (18%); 392 $[M-CH_3\text{–}1,3(^{t}Bu)_2C_5H_3]^+$ (26%); 336 $[M-1,3(^{t}Bu)_2C_5H_3\text{–}CH_3\text{-}^{t}Bu]^+$ (65%).

3.20. Crystal structure determination of $Hf\{(\eta^5\text{-}C_5H_4)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)\}Cl_2$ (**3c**) and $Zr(C_5H_3\text{-}1,3\text{-}^{t}Bu_2)(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta\text{-}N^{t}Bu)Cl$ (**8b**)

Crystals of the two compounds were obtained by crystallisation from toluene–hexane solutions. Suitable sized crystals of **3c** and **8b** were selected, sealed in Lindemann tubes under an argon atmosphere and mounted in an Enraf–Nonius CAD 4 automatic four-

Table 4
Crystal, experimental data and structure refinement procedures for compounds **3c** and **8b**

	3c	**8b**
Formula	$C_{14},H_{20},Cl_2,O,Hf,Si_2$	C_{24},H_{40},Cl,N,Si,Zr
M_w	509.87	497.33
Crystal habit	Prismatic	Prismatic
Colour	White	White
Crystal size (mm)	$0.25 \times 0.28 \times 0.30$	$0.21 \times 0.25 \times 0.31$
Symmetry	Monoclinic, $P2_1/c$	Orthorombic, $P2_12_12_1$
Unit cell dimensions		
a (Å)	13.482(8)	8.703(3)
b (Å)	8.664(1)	15.254(4)
c (Å)	15.38(2)	19.226(7)
β (°)	97.26(3)	
V (Å^3)	1782(2)	2552(1)
Z	4	4
D_{calc} (g cm^{-3})	1.900	1.294
F(000)	984	1048
μ (cm^{-1})	62.81	5.92
Scan mode	$\omega/2\theta$, $2.67<\theta<25.05$	$\omega/2\theta$, $2.12<\theta<25.02$
Reflections measured	3328	2622
Independent reflections	3145	2569
Reflections observed	2814 [$I>2\sigma(I)$]	2052 [$I>2\sigma(I)$]
Range of hkl	$-16<h<15$, $-3<k<10$, $-3<l<18$	$0<h<10$, $-18<k<0$, $0<l<22$
Standard reflections	Three every 200 reflections	Three every 200 reflections
Refinement method	Full-matrix least-squares on F^2	
Final R indices [a]	$R_1 = 0.0281$, $wR_2 = 0.0716$	$R_1 = 0.0348$, $wR_2 = 0.0712$
Weighting scheme parameters [b]		
x	0.0448	0.0301
y	3.4441	0.9525
Largest difference peak and hole (e Å^{-3})	0.97/−0.95	0.4/−0.39
Goodness-of-fit on F^2	1.096	1.110

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[\omega((F_o^2-F_c^2)^2]/\Sigma[\omega(F_o^2)^2]\}^{1/2}$.

[b] Calc. $\omega = 1/[\sigma^2(F_o^2)+(xP)^2+yP]$ where $P=(F_o^2+2F_c^2)/3$.

circle diffractometer with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Crystallographic and experimental details for both structures are summarised in Table 4. Data were collected at r.t. Intensities were corrected for Lorentz and polarisation effects in the usual manner. No absorption or extinction corrections were made. The structures were solved by direct methods (SHELXL-90) [30] and refined by least-squares against F^2 (SHELXL-93) [31]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with a thermal parameters equivalent to that of the carbon atom to which they were attached. Calculations were carried out on an ALPHA AXP (Digital) workstation.

4. Supplementary material

The final coordinates for the non-hydrogen atoms with the equivalent isotropic thermal parameters, U_{eq}, the coordinates for the hydrogen atoms with the isotropic thermal parameters, anisotropic thermal parameters for the non hydrogen atoms, and a complete list of bond distances, angles and observed and calculated structure factors have been deposited for both structures with the Cambridge Crystallographic Data Centre as a supplementary publication, CCDC nos. 139 588 for **3c** and 139 589 for **8b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support for this research by DGICYT (Project PB97-0776) is gratefully acknowledged.

References

[1] (a) S.G. Davies, Organotransition Metal Chemistry: Applications to Organic Synthesis, Pergamon, Oxford, 1989. (b) E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II. A Review of the Literature (1982–1994), vol. 4, 1994. (c) F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, sixth ed., Wiley, New York, 1999.

[2] (a) W. Kaminsky, H. Sinn (Eds.), Transition Metals and Organometallics as Catalysts for Olefin Polymerization, Springer, New York, 1988. (b) R.F. Jordan, Adv. Organomet. Chem. 32 (1991) 3235. (c) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143. (d) M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 225.

[3] (a) J. Okuda, Comm. Inorg. Chem. 16 (1994) 185. (b) P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1. (c) P. Jutzi, U. Siemeling, J. Organomet. Chem. 500 (1995) 175 and references therein. (c) V. Varga, J. Hiller, R. Gyepes, M. Polásek, P. Sedmera, U. Thewalt, K. Mach, J. Organomet. Chem. 538 (1997) 63.

[4] (a) P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, Organometallics 9 (1990) 867. (b) P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623. (c) U. Böhme, K.H. Thiele, J. Organomet. Chem. 472 (1994) 39. (d) J. Okuda, F.J. Schattenmann, S. Wocadlo, W. Massa, Organometallics 14 (1995) 789. (e) K.E.D. Plooy, U. Moll, S. Wocadlo, W. Massa, J. Okuda, Organometallics 14 (1995) 3129. (f) R.E.v.H. Spence, W.E. Piers, Organometallics 14 (1995) 4617. (g) W.A. Herrmann, M.J.A. Morawietz, T. Priermeier, Angew. Chem. Int. Ed. Eng. 33 (1994) 1946. (h) W.A. Herrmann, M.J.A. Morawietz, T. Priermeier, K. Mashima, J. Organomet. Chem. 486 (1995) 291. (i) M.S. Blais, J.C.W. Chien, M.D. Rausch, Organometallics 17 (1998) 3775. (j) J. Okuda, T. Eberle, T.P. Spaniol, V. Piquet-Fauré, J. Organomet. Chem. 591 (1999) 127.

[5] (a) G. Erker, U. Korek, Z. Naturforsch. B Chem. Sci. 44 (1989) 1593. (b) R. Fandos, A. Meetsma, J.H. Teuben, Organometallics 10 (1991) 59. (c) R. Fandos, A. Meetsma, J.H. Teuben, Organometallics 10 (1991) 2665. (d) Y. Qiann, J. Huang, X. Chen, G. Li, W. Chen, B. Li, X. Jin, Q. Yang, Polyhedron 13. (1994) 1105. (e) G. Trouvé, D.A. Laske, A. Meetsma, J.H. Teuben, J. Organomet. Chem. 511 (1996) 255.

[6] (a) M. Ogasa, D.T. Mallin, D.W. Macomber, M.D. Rausch, R.D. Rogers, A.N. Rollins, J. Organomet. Chem. 405 (1991) 41. (b) G. Erker, S. Wilker, C. Krüger, M. Nolte, Organometallics 12 (1993) 2140. (c) Z. Wu, R.F. Jordan, J. Am. Chem. Soc. 117 (1995) 5867. (d) J. Okuda, K.E. du Plooy, P.J. Toscano, J. Organomet. Chem. 495 (1995) 195. (e) M.V. Galakhov, G. Heinz, P. Royo, J. Chem. Soc. Chem. Commun. (1998) 17.

[7] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.

[8] (a) J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rose, G.W. Kinight, S. Lai, Eur. Pat. Appl. EP-416-815-A2 (1991). (b) J.M. Canich, Eur. Pat. Appl. EP-420-436-A1 (1991). (c) J.M. Canich, G.G. Hlatky, H.W. Turner, US Pat. Appl. (1990) 542.

[9] (a) S. Ciruelos, T. Cuenca, P. Gómez-Sal, A. Manzanero, P. Royo, Organometallics 14 (1995) 177. (b) S. Ciruelos, T. Cuenca, R. Gómez, P. Gómez-Sal, A. Manzanero, P. Royo, Polyhedron 17 (1997) 1055.

[10] S. Ciruelos, T. Cuenca, R. Gómez, P. Gómez-Sal, A. Manzanero, P. Royo, Organometallics 15 (1996) 5577.

[11] T. Cuenca, P. Royo, Coord. Chem. Rev. 193–195 (1999) 447.

[12] (a) A.K. Hughes, A. Meetsma, J.H. Teuben, Organometallics 12 (1993) 1936. (b) W.A. Herrmann, M.J.A. Morawietz, J. Organomet. Chem. 482 (1994) 169.

[13] (a) G.H. Llinas, M. Mena, F. Palacios, P. Royo, R. Serrano, J. Organomet. Chem. 340 (1988) 37. (b) C.H. Winter, X.X. Zhou, D.A. Dobss, M. J. Heeg, Organometallics 10 (1991) 210.

[14] M.D. Curtis, J.J. D'Errico, D.N. Duffy, P.S. Epstein, L.G. Bell, Organometallics 2 (1983) 1808.

[15] (a) T. Cuenca, J.C. Flores, R. Gómez, P. Gómez-Sal, M Parra-Hake, P. Royo, Inorg. Chem. 32 (1993) 3608. (b) D.H. Lee, K.B Yoon, E.H. Lee, S.K. Noh, G.G. Buyn, C.S. Lee, Macromol. Rapid Commun. 16 (1995) 265. (c) J.L. Huhmann, J.Y. Corey, N.P. Rath, N.P.J. Organomet. Chem. 533 (1997) 61.

[16] C. Glidewel, D.W.H. Rankin, A.G. Robiete, G.M. Sheldrich, J. Chem. Soc. A (1970) 318.

[17] (a) C.H. Saldariaga-Molina, A. Clearfield, I. Bernal, Inorg. Chem. 13 (1974) 2880. (b) H.G. Alt, M. Jung, W. Milius, J. Organomet. Chem. 558 (1998) 111. (c) F. Amor, K.E. du Plooy, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 558 (1998) 139 and references cited therein. (d) S. Back, G. Rheinwald, L. Zsolnai, G. Huttner, H. Lang, J. Organomet. Chem. 563 (1998) 73 and references cited therein.

[18] (a) R.D. Rogers, M.M. Benning, L.K. Kurihara, K.J. Moriarty, M.D. Rausch, M.D. J. Organomet. Chem. 293 (1985) 51.(b) M. Osaga, D.T. Mallin, D.W. Macomber, M.D. Rausch, R.D. Rogers, A.N. Rollins, J. Organomet. Chem. 405 (1991) 41

[19] H.G. Alt, K. Föttinger, W. Milius, J. Organomet. Chem. 564 (1998) 109.

[20] (a) A.H. Thiele, U. Böhme, K. Peters, E.M. Peters, I. Walz, H.G. Schvering, Z. Anorg. Allg. Chem. 619 (1993) 771. (b) H. Sitzmann, P. Zhou, G. Wolmershäuser, Chem. Ver. 127 (1994) 3. (c) M.A. Schmid, H.G. Alt, W.J. Milius, J. Organomet. Chem. 514 (1996) 45. (d) R.D. Rogers, M.M. Bennig, L.K. Kurihara, K.J. Moriarty, M.D. Rauch, J. Organomet. Chem. 293 (1985) 51. (e) Y. Dusausoy, J. Protas, P. Renaut, B. Gautheron, G. Tainturier, J. Organomet. Chem. 157 (1978) 167. (f) I.A. Ronova, N.V. Alekseev, Zh. Strukt. Khim. 18 (1997) 212.

[21] (a) K. Prout, T.S. Cameron, R.A. Forder, S.R. Critchley, B. Denton, G.V. Rees, Acta Crystallogr. Sect. B 30 (1974) 2290. (b) E.L. Lyszak, J.P. O'Brien, D.A. Kort, S.K. Hendges, R.N. Redding, T.L. Busch, M.S. Hermen, K.B. Renkema, M.E. Silver, J.C. Huffman, Organometallics 12 (1993) 338.

[22] (a) D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, Organometallics 25 (1996) 1572. (b) Y. Mu, W.E. Piers, D.C. MacQuarrie, M.J. Zaworotko, Can. J. Chem. 74 (1991) 1696.

[23] M.A. Giardello, M.S. Eisen, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 12114.

[24] (a) M.F. Lappert, P.B. Power, A.R. Sanger, R.C. Srivastava, Metal and Metalloid Amines, Ellis Horwood, Chichester, West Sussex, UK, 1980. (b) R.V. Bynum, W.E. Hunter, R.D. Rogers, J.L. Atwood, Inorg. Chem. 19 (1980) 2368.

[25] (a) P.R. Jones, J.M. Rozell, B.M. Campbell, Organometallics 4 (1985) 1321. (b). M. Rozell, P.R. Jones, J. Organomet. 4 (1985) 2206.

[26] J. Hiermeier, F.H. Köhler, G. Müller, Organometallics 10 (1991) 1787.

[27] C.V. Vernier, E.W. Casserly, J. Am. Chem. Soc. 112 (1990) 2808.

[28] H. Werner, M. Otto, H.J. Kraus, J. Organomet. Chem. 328 (1986) C1.

[29] M. Mena, Doctoral Thesis, University of Alcalá, Spain, 1988.

[30] G.M. Sheldrick, Acta Crystallogr. 46 (1990) 467.

[31] G.M. Sheldrick, SHELXL 93, University of Göttingen, Germany, 1993.