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Group 4 metallocene complexes incorporating vinyl or allyl substituted *ansa* ligands. X-Ray crystal structures of $[\text{Zr}\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\}\text{Cl}_2]$, $[\text{Zr}\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ and $[\text{Zr}\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^5\text{-C}_5\text{H}_4)\}\text{Cl}_2]$

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Abstract

The vinyl and allyl substituted *ansa*-ligand precursors, $\text{Me}(\text{R})\text{Si}(\text{C}_5\text{H}_5)_2$ ($\text{R}=\text{CH}=\text{CH}_2$ (**1**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**2**)) $\text{Me}(\text{R})\text{Si}(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_5)$ ($\text{R}=\text{CH}=\text{CH}_2$ (**5**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**6**)), and $\text{Me}(\text{R})\text{Si}(\text{C}_5\text{HMe}_4)_2$ ($\text{R}=\text{CH}=\text{CH}_2$ (**7**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**8**)), and their lithium derivatives, $\text{Li}_2\{\text{Me}(\text{R})\text{Si}(\text{C}_5\text{H}_4)_2\}$ ($\text{R}=\text{CH}=\text{CH}_2$ (**9**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**10**)), $\text{Li}_2\{\text{Me}(\text{R})\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\}$ ($\text{R}=\text{CH}=\text{CH}_2$ (**11**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**12**)), and $\text{Li}_2\{\text{Me}(\text{R})\text{Si}(\text{C}_5\text{Me}_4)_2\}$ ($\text{R}=\text{CH}=\text{CH}_2$ (**13**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**14**)), have been prepared. The Group 4 metal complexes, $[\text{M}\{\text{Me}(\text{R})\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ ($\text{R}=\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**15**), Zr (**16**), Hf (**17**); $\text{R}=\text{CH}_2\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**18**), Zr (**19**), Hf (**20**)), $[\text{M}\{\text{Me}(\text{R})\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^5\text{-C}_5\text{H}_4)\}\text{Cl}_2]$ ($\text{R}=\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**21**), Zr (**22**), Hf (**23**); $\text{R}=\text{CH}_2\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**24**), Zr (**25**), Hf (**26**)), $[\text{M}\{\text{Me}(\text{R})\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\}\text{Cl}_2]$ ($\text{R}=\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**27**), Zr (**28**), Hf (**29**); $\text{R}=\text{CH}_2\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**30**), Zr (**31**), Hf (**32**)), were synthesized from the reaction of the lithium *ansa*-derivative and the tetrachloride salts of the transition metal. The reactivity of some of the Group 4 metal complexes has been tested in hydrogenation and hydroboration processes. The molecular structures of **19**, **25** and **28** have been determined by single crystal X-ray diffraction studies.

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Keywords: *ansa*-Metallocene complexes; Titanium; Zirconium; Hafnium; Vinyl; Allyl; Hydrogenation; Hydroboration

1. Introduction

Since the discovery by Sinn and Kaminsky that zirconocene complexes in the presence of MAO were able to polymerize olefins [1] there has been a dramatic expansion in this field [2]. One of the main focuses of this research field is centred on the tailoring of metallocene complexes that can direct the catalytic reaction in producing polymers with desired physical

properties. The use of *ansa*-cyclopentadienyl ligands in these metallocene complexes has received wide attention [3] due to the increase in catalytic activity [4] and recent studies have demonstrated that the incorporation of the *ansa*-bridge may have a profound influence on the behaviour [5]. Furthermore the use of substituted *ansa*-cyclopentadienyl ligands in the stereoselective synthesis of Group 4 metal complexes and their importance in catalysis is receiving special attention [6]. Simple ligand design, as in $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_3\text{Me})_2]^{2-}$, has been shown to lead to stereoselective catalysts in α -olefin polymerization, eg. *rac*- $[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_3\text{-Me})_2\}\text{Cl}_2]$ [7].

The use of silicon in the single atom *ansa*-bridge has been widely exploited, however few examples have been

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reported with functional groups attached to the bridge-head atom [8].

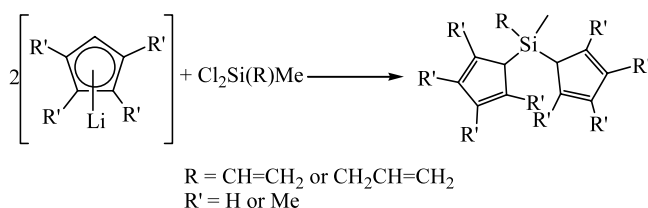
We recently developed a general synthesis of some SiMe_2 bridged asymmetric *ansa*-zirconocene complexes [9] and this series of highly active C_1 symmetric catalysts polymerize propylene with a high level of stereospecificity [9b]. Our research in this area is now focused on the elucidation of the mechanism of olefin polymerization as well as on the use of new types of metallocene complexes in stereoselective catalysis [10].

There is currently a considerable interest in the development of supported metallocene polymerization catalyst that can offer homogeneous single-site selectivity in a heterogeneous medium. The reader is referred to several studies that have recently been published [11]. In most cases in order to achieve this a functional group is introduced in the complex in order to interact with the surface of an inorganic oxide, leaving the remaining metallocene moiety untouched [8a,12].

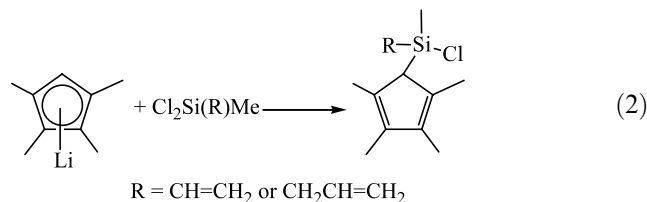
In this publication we describe the development of new *ansa* ligands that have as functional groups vinyl or allyl substituents at the silicon *ansa* bridge and their incorporation in new symmetrical and chiral *ansa*-metallocene complexes of Group 4 metals. The reactivity of these complexes towards hydrogenation and hydroboration is also included.

2. Results and discussion

The ligand systems $\text{Me}(\text{R})\text{Si}(\text{C}_5\text{H}_5)_2$ ($\text{R}=\text{CH}=\text{CH}_2$ (**1**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**2**)) and $\text{Me}(\text{R})\text{Si}(\text{C}_5\text{HMe}_4)_2$ ($\text{R}=\text{CH}=\text{CH}_2$ (**7**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**8**)) were synthesized by the reaction of two molar equivalents of cyclopentadienyllithium or tetramethylcyclopentadienyllithium with one molar equivalent of the dichlorosilane reagent, $\text{Cl}_2\text{Si}(\text{CH}=\text{CH}_2)$ or $\text{Cl}_2\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)$ (Eq. (1)). The reaction of one molar equivalent of $\text{Li}(\text{C}_5\text{HMe}_4)$ with the dichlorosilane reagent gave $\text{Me}(\text{R})\text{Si}(\text{C}_5\text{HMe}_4)\text{Cl}$ ($\text{R}=\text{CH}=\text{CH}_2$ (**3**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**4**)) (Eq. (2)) which on further reaction with $\text{Li}(\text{C}_5\text{H}_5)$ gave the mixed cyclopentadienyl *ansa* ligands $\text{Me}(\text{R})\text{Si}(\text{C}_5\text{HMe}_4)(\text{C}_5\text{H}_5)$ ($\text{R}=\text{CH}=\text{CH}_2$ (**5**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**6**)) (Eq. (3)). **1–8** were characterized by $^1\text{H-NMR}$ spectroscopy and electron impact mass spectroscopy (see Section 3).



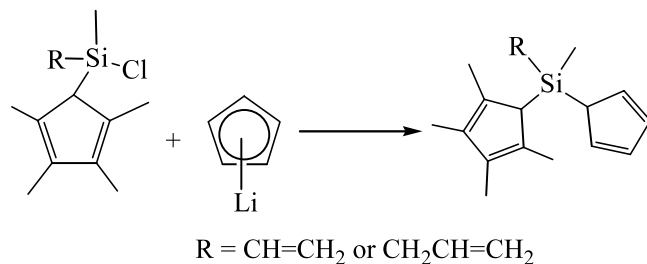
(1)



(2)

The *ansa*-ligands **1**, **2**, and **5–8** were lithiated in the normal manner with *n*-butyllithium giving the dilithium derivatives, $\text{Li}_2\{\text{Me}(\text{R})\text{Si}(\text{C}_5\text{H}_4)_2\}$ ($\text{R}=\text{CH}=\text{CH}_2$ (**9**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**10**)), $\text{Li}_2\{\text{Me}(\text{R})\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\}$ ($\text{R}=\text{CH}=\text{CH}_2$ (**11**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**12**)) and $\text{Li}_2\{\text{Me}(\text{R})\text{Si}(\text{C}_5\text{Me}_4)_2\}$ ($\text{R}=\text{CH}=\text{CH}_2$ (**13**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**14**)), in high yields.

The reaction of the di-lithium derivatives **9** to **14** with either $[\text{TiCl}_4(\text{THF})_2]$, ZrCl_4 or HfCl_4 , gave the corresponding *ansa*-metallocene dichloride complex, $[\text{M}\{\text{Me}(\text{R})\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ ($\text{R}=\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**15**), Zr (**16**) [13], Hf (**17**); $\text{R}=\text{CH}_2\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**18**), Zr (**19**) [14], Hf (**20**)), $[\text{M}\{\text{Me}(\text{R})\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^5\text{-C}_5\text{H}_4)\}\text{Cl}_2]$ ($\text{R}=\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**21**), Zr (**22**), Hf (**23**); $\text{R}=\text{CH}_2\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**24**), Zr (**25**), Hf (**26**)), $[\text{M}\{\text{Me}(\text{R})\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\}\text{Cl}_2]$ ($\text{R}=\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**27**), Zr (**28**), Hf (**29**); $\text{R}=\text{CH}_2\text{CH}=\text{CH}_2$, $\text{M}=\text{Ti}$ (**30**), Zr (**31**), Hf (**32**)), (Eq. (4)).



(3)

15–32 were isolated as crystalline solids and characterized spectroscopically. For the vinyl containing complexes an ABX system consisting of two multiplets was observed in the $^1\text{H-NMR}$ spectrum. The vinyl carbons gave in the $^{13}\text{C-NMR}$ spectra signals at ca. δ 130 (C_α) and 138 (C_β). The allyl complexes exhibited, in the $^1\text{H-NMR}$ spectra, for this group three sets of signals corresponding to the CH_2 bonded to the silicon atom (a doublet at ca. δ 1.8), the central group CH (a multiplet at ca. δ 5.6) and the olefinic protons for the terminal CH_2 (a doublet of doublets at ca. δ 4.9). Signals for the allyl carbons were observed in the $^{13}\text{C-NMR}$ spectra at ca. δ 22, 132, and 116 corresponding to the silicon bonded, central and terminal carbons, respectively. The C_s symmetric complexes **15–20** gave in the $^1\text{H-NMR}$ spectra, in addition to the vinylic or allylic signals four multiplets, in the region δ 5.4–7.1, corresponding to the

eight cyclopentadienyl protons present and in the case of **27–32** four singlets, in the region δ 1.6–2.1, corresponding to the per-methyl substituted *ansa*-ligand. The mixed cyclopentadienyl complexes gave eight signals assigned to the four protons of the unsubstituted cyclopentadienyl moiety and to the four methyl groups of tetramethylcyclopentadienyl fragment.

The molecular structures of **19**, **25**, and **28** were established by X-ray crystal studies [14]. The molecular structures and atomic numbering schemes are shown in Figs. 1–3. Selected bond lengths and angles for **19**, **25** and **28** are given in Table 1.

The structure of **28** is one of the few examples of a vinyl substituted *ansa* complex [8b,d,e]. The usual bent conformation is observed with geometry around the zirconium atom being pseudo-tetrahedral. The *ansa* ligand chelates the zirconium atom and both C₅ rings are bound to the metal in an η^5 mode. The centroids of the tetramethylcyclopentadienyl rings form an angle with the zirconium atom of 128.76° which is typical for dichloride *ansa*-zirconocene complexes. The vinyl moiety shows the distance C(2)–C(3) 1.11(1) Å typical of a carbon–carbon double bond and the angle Si(1)–C(2)–C(3) 131.8(8)° confirms the sp² hybridization of C(1). Selected structural data of **28** with similar *ansa*-zirconocene complexes can be compared using Table 2.

The structures of [Zr{Me(CH₂=CHCH₂)Si(η^5 -C₅H₄)₂}Cl₂] (**19**) and [Zr{Me(CH₂=CHCH₂)Si(η^5 -C₅Me₄)(η^5 -C₅H₄)}Cl₂] (**25**), are similar in nature to **28** namely, η^5 -bonded, chelating *ansa*-ligand with a bent metallocene confirmation and pseudo-tetrahedral geometry about the zirconium atom. The allyl moiety exhibits distances of C(2)–C(3) 1.49(3) Å, C(3)–C(4) 1.26(5) Å for **19** and C(2)–C(3) 1.49(1) Å, C(3)–C(4) 1.32(1) Å for **25**, which are typical for carbon–carbon single (C(2)–C(3)) and double bonds (C(3)–C(4)), respectively. The angles Si(1)–C(2)–C(3) 111.6(8)° **19**; 113.8(7)° **25**, and C(2)–C(3)–C(4) 124(5)° **19**; 123(1)°

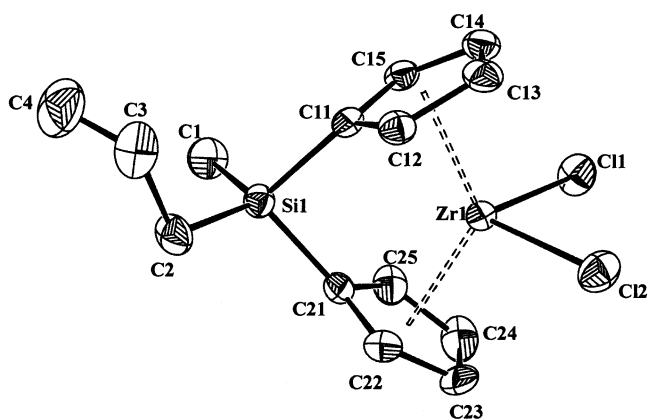


Fig. 1. Molecular structure and atom-labeling scheme for [Zr{Me(CH₂=CHCH₂)Si(η^5 -C₅H₄)₂}Cl₂] (**19**), with thermal ellipsoids at 30% probability.

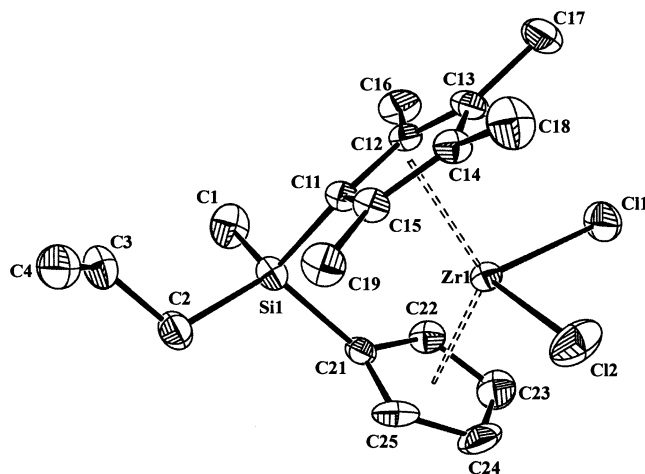


Fig. 2. Molecular structure and atom-labeling scheme for [Zr{Me(CH₂=CHCH₂)Si(η^5 -C₅Me₄)(η^5 -C₅H₄)}Cl₂] (**25**), with thermal ellipsoids at 30% probability.

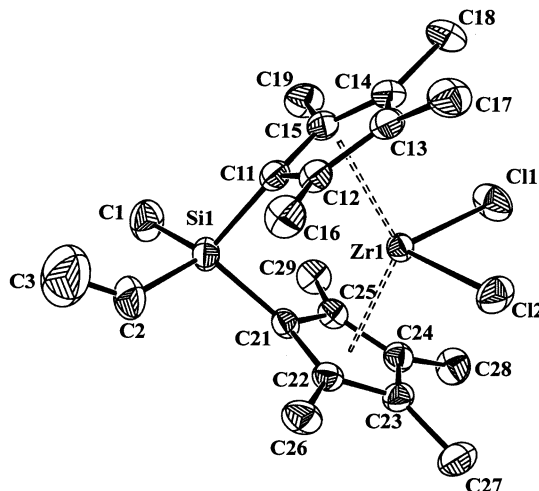


Fig. 3. Molecular structure and atom-labeling scheme for [Zr{Me(CH₂=CH)Si(η^5 -C₅Me₄)₂}Cl₂] (**28**), with thermal ellipsoids at 30% probability.

25, indicate that C(2) and C(3) are sp³ and sp² hybridized, respectively. The structures of **19** and **25** are directly comparable with their dimethylsilyl *ansa* bridged analogues [Zr{Me₂Si(η^5 -C₅H₄)₂}Cl₂] [17] and [Zr{Me₂Si(η^5 -C₅Me₄)(η^5 -C₅H₄)}Cl₂] [9a] (see Table 2).

We have tested a selection of the Group 4 complexes, namely [Ti{Me(CH₂=CH)Si(η^5 -C₅Me₄)(η^5 -C₅H₄)}Cl₂] (**21**), [Zr{Me(CH₂=CH)Si(η^5 -C₅Me₄)(η^5 -C₅H₄)}Cl₂] (**22**) and [Zr{Me(CH₂=CHCH₂)Si(η^5 -C₅H₄)₂}Cl₂] (**19**), in the hydrogenation reaction of the C=C double bond of the vinyl or allyl groups. The complexes react with H₂ in the catalytic hydrogenation (Pd/C) to give in all cases as the unique product the saturated *ansa*-metallocene complexes [Ti{Me(CH₃CH₂)Si(η^5 -C₅Me₄)(η^5 -C₅H₄)}Cl₂] (**33**), [Zr{Me(CH₃CH₂)Si(η^5 -C₅Me₄)(η^5 -C₅H₄)}Cl₂] (**34**) and [Zr{Me(CH₃CH₂CH₂)Si(η^5 -C₅H₄)₂}Cl₂] (**35**), respectively (Eq. (5)) (Schumann et al. have

Table 1
Selected bond lengths (Å) and angles (°) for **19**, **25** and **28**

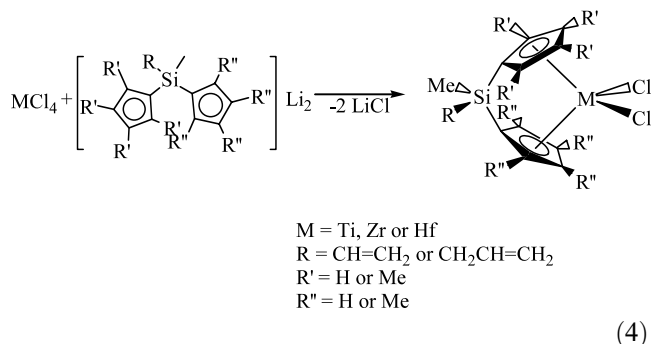
	19	25	28
Zr(1)–Cent(1)	2.211	2.220	2.217
Zr(1)–Cent(2)	2.200	2.207	2.223
av Zr(1)–C(Cent(1)) ^a	2.516	2.524	2.522
av Zr(1)–C(Cent(2)) ^a	2.505	2.523	2.527
Zr(1)–Cl(1)	2.444(2)	2.428(2)	2.417(2)
Zr(1)–Cl(2)	2.431(2)	2.429(2)	2.419(1)
Si(1)–C(1)	1.836(8)	1.86(1)	1.862(6)
Si(1)–C(2)	1.866(7)	1.868(9)	1.850(6)
C(2)–C(3)	1.49(3)	1.49(1)	1.11(1)
C(3)–C(4)	1.26(5)	1.32(1)	
Cent(1)–Zr(1)–Cent(2)	125.40	126.67	128.76
Si(1)–C(1)–Cent(1)	162.72	159.96	161.74
Si(1)–C(11)–Cent(2)	161.34	164.07	162.41
C(11)–Si(1)–C(21)	94.0(3)	95.0(3)	95.8(2)
Cl(1)–Zr(1)–Cent(1)	106.63	107.34	106.67
Cl(1)–Zr(1)–Cent(2)	107.78	105.33	106.61
Cl(2)–Zr(1)–Cent(1)	107.75	106.31	105.94
Cl(2)–Zr(1)–Cent(2)	107.81	107.58	105.78
Cl(1)–Zr(1)–Cl(2)	98.09(7)	100.9(1)	99.32(7)
C(1)–Si(1)–C(2)	112.5(4)	106.7(5)	104.2(3)
Si(1)–C(2)–C(3)	111.6(8)	113.8(7)	131.8(8)
C(2)–C(3)–C(4)	124(5)	123(1)	

Cent(1) and Cent(2) are the centroids of C(11)–C(15) and C(21)–C(25), respectively.

^a Refers to the average bond distance between Zr(1) and the carbon atoms of the C₅ ring of the corresponding cyclopentadienyl moiety.

previously reported the synthesis of **34** via the reaction of Li₂{EtMeSi(C₅Me₄)(C₅H₄)} with ZrCl₄ [15]). Thus in the case of the vinyl compounds this group was converted to ethyl as observed in the ¹H-NMR spectra by the disappearance of the ABX system and the appearance of signals corresponding to the ethyl group (see Section 3). Due to the chirality around the Si atom in **33** and **34** the CH₂ protons of the ethyl group become diastereoscopic leading to a complex multiplet being

observed in the ¹H-NMR spectrum. For the allyl group in **19** hydrogenation gave the *n*-propyl moiety which was observed in the ¹H-NMR spectrum as three multiplets at δ 1.14, 1.26 and 1.72.



Erker and coworkers have recently reported hydroboration in zirconocene complexes [18] and we have carried out in a similar manner reactions at the double bond of the vinyl or allyl group for a selection of the *ansa*-metallocene complexes, namely [Zr{Me(CH₂=CH)Si(η⁵-C₅H₄)₂}Cl₂] (**16**), [Ti{Me(CH₂=CHCH₂)Si(η⁵-C₅Me₄)(η⁵-C₅H₄)}Cl₂] (**24**) and [Zr{Me(CH₂=CHCH₂)Si(η⁵-C₅Me₄)(η⁵-C₅H₄)}Cl₂] (**25**). The reaction was carried out using 9-BBN as the hydroboration reagent and gave the products resulting from the anti-Markonikoff addition, [Zr{Me((BC₈H₁₄)CH₂CH₂)Si(η⁵-C₅H₄)₂}Cl₂] (**36**), [Ti{Me((BC₈H₁₄)CH₂CH₂-CH₂)Si(η⁵-C₅Me₄)(η⁵-C₅H₄)}Cl₂] (**37**) and [Zr{Me((BC₈H₁₄)CH₂CH₂CH₂)Si(η⁵-C₅Me₄)(η⁵-C₅H₄)}Cl₂] (**38**) (Eq. (6)). **36**–**38** were characterized by spectroscopic techniques. The ¹H-NMR spectra of **36**–**38** showed for the borane moiety four multiplets between ca. δ 1.15–1.85 corresponding to the four distinct proton environments (see Section 3). In the case of **36**, the ABX system observed for the vinyl compound **16** was replaced by

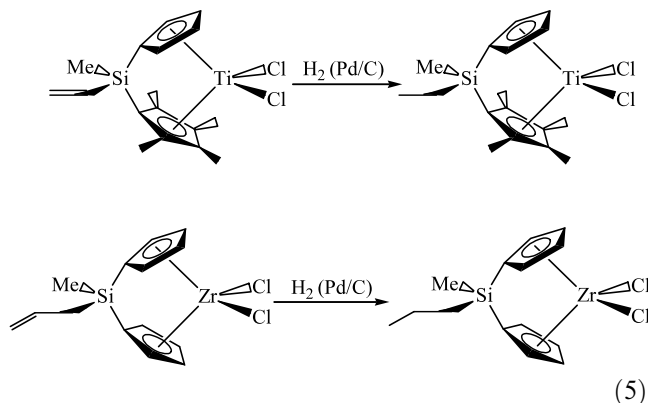
Table 2
Selected structural data of some *ansa*-zirconocene complexes

Complex	Zr–Cp ^a	Zr–Cl	Cp–Zr–Cp	Cl–Zr–Cl	C _(cp) –Si–C _(cp)	Ref.
[Zr{Me(CH ₂ =CH)Si(η ⁵ -C ₅ Me ₄) ₂ }Cl ₂] (28)	2.220	2.418	128.76	99.32(7)	95.8(2)	This work
[Zr{EtMeSi(η ⁵ -C ₅ Me ₄)(η ⁵ -C ₅ H ₄)}Cl ₂]	2.219(2) Cp 2.218(2) Cp*	2.4336(8)	126.70(4)	101.17(5)	93.82(14)	[15]
[Zr{(CH ₂ =CH) ₂ Si(η ⁵ -C ₅ H ₂ Me ₂ -2,4) ₂ }Cl ₂]	2.218	2.433	126.5	99.49(3)	94.98(9)	[8b]
[Zr{(CH ₂ =CH) ₂ Si(η ⁵ -C ₅ Me ₄) ₂ }Cl ₂]	2.235	2.4333	128.7	99.24(3)	96.3(1)	[8d]
[Zr{Me(CH ₂ =CH)Si(η ⁵ -C ₅ H ₂ Me ₂ -2,4) ₂ }Cl ₂]	2.211	2.433	126.6	99.5(1)	94.0(2)	[8e]
[Zr{Me ₂ Si(η ⁵ -C ₅ Me ₄) ₂ }Cl ₂]	2.329	2.4334(7)	128.6	92.28	95.7(1)	[16]
[Zr{Me(CH ₂ =CHCH ₂)Si(η ⁵ -C ₅ H ₄) ₂ }Cl ₂] (19)	2.205	2.437	125.40	98.09(7)	94.0(3)	This work
[Zr{Me ₂ Si(η ⁵ -C ₅ H ₄) ₂ }Cl ₂]	2.197(6)	2.452	125.4(3)	97.98(4)	93.2(2)	[17]
[Zr{Me(CH ₂ =CHCH ₂)Si(η ⁵ -C ₅ Me ₄)(η ⁵ -C ₅ H ₄)}Cl ₂] (25)	2.207 Cp 2.220 Cp*	2.428	126.67	100.9(1)	95.0(3)	This work
[Zr{Me ₂ Si(η ⁵ -C ₅ Me ₄)(η ⁵ -C ₅ H ₄)}Cl ₂]	2.198(4) Cp* 2.202(3) Cp	2.451(1)	128.10(2)	104.60(7)	95.2(2)	[9a]

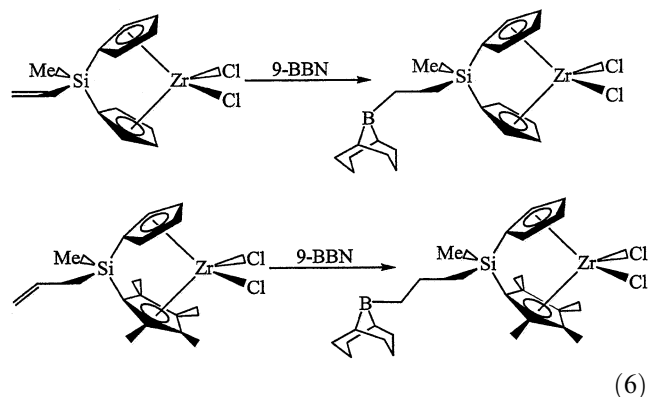
Cp* refers to the C₅Me₄ moiety.

^a Cp refers to the C₅H₄ moiety.

two multiplets at δ 1.48 and 1.52 corresponding to the $-\text{BCH}_2\text{CH}_2\text{Si}-$ fragment. For **38** and **39** the change in the signals previously attributed to the allyl group (in **24** and **25**) gave three multiplets at ca. δ 1.2, 1.4, and 1.6.



In conclusion, we describe in this paper the straightforward preparation of *ansa* ligands containing pendant vinyl or allyl groups at the silicon bridge and their incorporation into Group 4 metallocene systems. The structural characterization of these complexes is also described. The reactivity of these complexes in hydrogenation and hydroboration processes has been carried out and should open up the possibility of exploiting the unsaturation in the *ansa*-bridge in for example hydro-silylation or hydrometallation reactions.



3. Experimental

3.1. Materials and procedures

All reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. $\text{Li}(\text{C}_5\text{H}_5)$, $\text{TiCl}_4(\text{THF})_2$, ZrCl_4 , HfCl_4 , and 9-BBN were purchased from Aldrich and used directly. ^1H and ^{13}C spectra were recorded on a Varian FT-300 spectrometer and referenced to the

residual deuterated solvent. Microanalyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectroscopic analyses were performed on a Hewlett-Packard 5988A (m/z 50–1000) instrument (electron impact).

3.2. Synthesis of $\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\text{C}_5\text{H}_5)_2$ (**1**)

$\text{Me}(\text{CH}_2=\text{CH})\text{SiCl}_2$ (4.89 g, 34.70 mmol) was added to a solution of $\text{Li}(\text{C}_5\text{H}_5)$ (5.00 g, 69.40 mmol) in THF (50 ml) at -78°C . The reaction mixture was allowed to warm to room temperature and stirred for 15 h. Solvent was removed in vacuo and hexane (150 ml) was added to the resulting orange oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as a dark orange oil (6.67 g, 96%). $^1\text{H-NMR}$ (300 MHz, C_6D_6) (for the predominant isomer): δ -0.36 (s, 3H, SiMe), 2.81 (m, 2H, HC_5), 5.65 (4H), 6.80 (4H) (m, C_5H_4), 5.50 (m, 1H, $\text{CH}=\text{CH}_2$), 5.75 (m, 2H, $\text{CH}=\text{CH}_2$). MS electron impact (m/e (relative intensity)): 200 (17) [M^+], 135 (100) [$\text{M}^+ - \text{C}_5\text{H}_5$], 109 (44) [$\text{M}^+ - \text{C}_5\text{H}_5 - \text{CH}=\text{CH}_2$], 93 (35) [$\text{M}^+ - \text{C}_5\text{H}_5 - \text{CH}=\text{CH}_2 - \text{Me}$], 65 (44) [$\text{M}^+ - \text{C}_5\text{H}_5 - \text{SiMe}(\text{CH}=\text{CH}_2)$].

3.3. Synthesis of $\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\text{C}_5\text{H}_5)_2$ (**2**)

The preparation of **2** was carried out in an identical manner to **1**. $\text{Me}(\text{CH}_2=\text{CH})\text{SiCl}_2$ (5.38 g, 34.70 mmol) and $\text{Li}(\text{C}_5\text{H}_5)$ (5.00 g, 69.40 mmol). Yield 7.06 g, 95%. $^1\text{H-NMR}$ (300 MHz, C_6D_6) (for the predominant isomer): δ -0.38 (s, 3H, SiMe), 1.24 (d, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.78 (m, 2H, HC_5), 5.70 (4H), 6.74 (4H) (m, C_5H_4), 4.86 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.60 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$). MS electron impact (m/e (relative intensity)): 214 (15) [M^+], 173 (100) [$\text{M}^+ - \text{CH}_2\text{CH}=\text{CH}_2$], 149 (44) [$\text{M}^+ - \text{C}_5\text{H}_5$].

3.4. Synthesis of $\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\text{C}_5\text{HMe}_4)\text{Cl}$ (**3**)

$\text{Me}(\text{CH}_2=\text{CH})\text{SiCl}_2$ (2.20 g, 15.61 mmol) in THF (50 ml) was added to a solution of $\text{Li}(\text{C}_5\text{HMe}_4)$ (2.00 g, 15.61 mmol) in THF (50 ml) at -78°C . The reaction mixture was allowed to warm to room temperature and stirred for 15 h. Solvent was removed in vacuo and hexane (150 ml) was added to the resulting orange oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as a yellow oil (3.36 g, 95%). $^1\text{H-NMR}$ (300 MHz, C_6D_6) (for the predominant isomer): δ 0.12 (s, 3H, SiMe), 1.68 (6H), 1.87 (3H), 1.93 (3H) (s, C_5Me_4), 2.92 (m, 1H, HC_5), 5.76 (m, 2H, $\text{CH}=\text{CH}_2$), 5.85 (m, 1H, $\text{CH}=\text{CH}_2$). MS electron impact (m/e (relative intensity)): 225 (55) [M^+], 191 (28) [$\text{M}^+ - \text{Cl}$], 121 (50) [$\text{M}^+ - \text{Me}(\text{CH}_2=\text{CH})\text{SiCl}$], 105 (100) [$\text{M}^+ - \text{C}_5\text{HMe}_4$].

3.5. Synthesis of $\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\text{C}_5\text{HMe}_4)\text{Cl}$ (**4**)

The preparation of **4** was carried out in an identical manner to **3**. $\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{SiCl}_2$ (3.13 g, 15.61 mmol) and $\text{Li}(\text{C}_5\text{HMe}_4)$ (2.00 g, 15.61 mmol). Yield 4.47 g, 92%. $^1\text{H-NMR}$ (300 MHz, C_6D_6) (for the predominant isomer): δ 0.15 (s, 3H, *SiMe*), 1.46 (d, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.66 (6H), 1.84 (3H), 1.91 (3H) (s, C_5Me_4), 3.92 (m, 1H, HC_5), 4.91 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.68 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$). MS electron impact (*m/e* (relative intensity)): 240 (27) [M^+], 199 (88) [$\text{M}^+ - \text{CH}_2\text{CH}=\text{CH}_2$], 121 (77) [$\text{M}^+ - \text{Me}(\text{CH}_2=\text{CHCH}_2)\text{-SiCl}$], 119 (70) [$\text{M}^+ - \text{C}_5\text{HMe}_4$], 105 (100) [$\text{M}^+ - \text{C}_5\text{HMe}_4 - \text{Me}$].

3.6. Synthesis of $\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\text{C}_5\text{HMe}_4)(\text{C}_5\text{H}_5)$ (**5**)

$\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\text{C}_5\text{HMe}_4)\text{Cl}\}$ (**3**) (3.00 g, 13.23 mmol) in THF (50 ml) was added to a solution of $\text{Li}(\text{C}_5\text{H}_5)$ (0.95 g, 13.23 mmol) in THF (50 ml) at -78°C . The reaction mixture was allowed to warm to room temperature and stirred for 15 h. Solvent was removed in vacuo and hexane (150 ml) was added to the resulting orange oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as a dark orange oil (3.19 g, 94%). $^1\text{H-NMR}$ (300 MHz, C_6D_6) (for the predominant isomer): δ -0.15 (s, 3H, *SiMe*), 1.77 (6H), 1.80 (3H), 1.88 (3H) (s, C_5Me_4), 2.83 (1H), 3.38 (1H) (m, HC_5), 5.95 (2H), 6.77 (2H) (m, C_5H_4), 5.51 (m, 1H, $\text{CH}=\text{CH}_2$), 5.81 (m, 2H, $\text{CH}=\text{CH}_2$). MS electron impact (*m/e* (relative intensity)): 256 (46) [M^+], 191 (78) [$\text{M}^+ - \text{C}_5\text{H}_5$], 135 (100) [$\text{M}^+ - \text{C}_5\text{HMe}_4$].

3.7. Synthesis of $\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\text{C}_5\text{HMe}_4)(\text{C}_5\text{H}_5)$ (**6**)

The preparation of **6** was carried out in an identical manner to **5**. $\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\text{C}_5\text{HMe}_4)\text{Cl}\}$ (**4**) (4.00 g, 16.61 mmol) and $\text{Li}(\text{C}_5\text{H}_5)$ (1.20 g, 16.61 mmol). Yield 4.36 g, 97%. $^1\text{H-NMR}$ (300 MHz, C_6D_6) (for the predominant isomer): δ -0.15 (s, 3H, *SiMe*), 1.50 (d, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.78 (6H), 1.91 (6H) (s, C_5Me_4), 2.77 (1H), 2.86 (1H) (m, HC_5), 4.82 (2H), 6.55 (2H) (m, C_5H_4), 4.91 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.70 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$). MS electron impact (*m/e* (relative intensity)): 270 (20) [M^+], 229 (43) [$\text{M}^+ - \text{CH}_2\text{CH}=\text{CH}_2$], 205 (27) [$\text{M}^+ - \text{C}_5\text{H}_5$], 149 (100) [$\text{M}^+ - \text{C}_5\text{HMe}_4$], 121 (34) [$\text{M}^+ - \text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\text{C}_5\text{H}_5)$], 109 (46) [$\text{M}^+ - \text{C}_5\text{HMe}_4 - \text{CH}_2\text{CH}=\text{CH}_2$].

3.8. Synthesis of $\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\text{C}_5\text{HMe}_4)_2$ (**7**)

The preparation of **7** was carried out in an identical manner to **1**. $\text{Me}(\text{CH}_2=\text{CH})\text{SiCl}_2$ (2.20 g, 15.61 mmol) and $\text{Li}(\text{C}_5\text{HMe}_4)$ (4.00 g, 31.22 mmol). Yield 4.39 g, 90%. $^1\text{H-NMR}$ (300 MHz, C_6D_6) (for the predominant isomer): δ -0.10 (s, 3H, *SiMe*), 1.84 (6H), 1.98 (6H) (s, C_5Me_4), 3.19 (m, 2H, HC_5), 5.40 (m, 1H, $\text{CH}=\text{CH}_2$), 5.80 (m, 2H, $\text{CH}=\text{CH}_2$). MS electron impact (*m/e* (relative intensity)): 312 (43) [M^+], 297 (18) [$\text{M}^+ - \text{Me}$], 191 (100) [$\text{M}^+ - \text{C}_5\text{HMe}_4$].

3.9. Synthesis of $\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\text{C}_5\text{HMe}_4)_2$ (**8**)

The preparation of **8** was carried out in an identical manner to **1**. $\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{SiCl}_2$ (4.84 g, 15.61 mmol) and $\text{Li}(\text{C}_5\text{HMe}_4)$ (4.00 g, 31.22 mmol). Yield 4.48 g, 88%. $^1\text{H-NMR}$ (300 MHz, C_6D_6) (for the predominant isomer): δ -0.11 (s, 3H, *SiMe*), 1.48 (d, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.76 (6H), 1.91 (6H) (s, C_5Me_4), 2.94 (m, 2H, HC_5), 4.82 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.56 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$). MS electron impact (*m/e* (relative intensity)): 326 (16) [M^+], 285 (22) [$\text{M}^+ - \text{CH}_2\text{CH}=\text{CH}_2$], 205 (100) [$\text{M}^+ - \text{C}_5\text{HMe}_4$], 121 (26) [$\text{M}^+ - \text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\text{C}_5\text{HMe}_4)$].

3.10. Synthesis of $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\text{C}_5\text{H}_4)_2\}$ (**9**)

LiBu^n (1.6 M in hexane) (40.6 ml, 64.88 mmol) was added dropwise to a solution of **1** (6.50 g, 32.44 mmol) in Et_2O (100 ml) at -78°C . The mixture was allowed to warm to 25°C and stirred for 15 h. Solvent was removed in vacuo to give a white solid which was washed with hexane (2×50 ml) and dried under vacuum to yield a free flowing white solid of the title complex (6.06 g, 88%). Anal. Calc. for $\text{C}_{13}\text{H}_{14}\text{Li}_2\text{Si}$: C, 73.58; H, 6.65. Found C, 73.22; H, 6.53%.

The syntheses of **10–14** were carried out in an identical manner to **9**.

3.11. $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\text{C}_5\text{H}_4)_2\}$ (**10**)

From **2** (6.80 g, 31.72 mmol) and LiBu^n (1.6 M in hexane) (39.6 ml, 63.44 mmol). Yield 5.81 g, 81%. Anal. Calc. for $\text{C}_{14}\text{H}_{16}\text{Li}_2\text{Si}$: C, 74.32; H, 7.13. Found C, 74.01; H, 7.06%.

3.12. $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\}$ (**11**)

From **5** (3.00 g, 11.70 mmol) and LiBu^n (1.6 M in hexane) (14.6 ml, 23.40 mmol). Yield 2.67 g, 85%. Anal. Calc. for $\text{C}_{17}\text{H}_{22}\text{Li}_2\text{Si}$: C, 76.10; H, 8.26. Found: C, 75.78; H, 8.15%.

3.13. $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)\}$ (**12**)

From **6** (4.00 g, 14.79 mmol) and LiBu^n (1.6 M in hexane) (18.5 ml, 29.58 mmol). Yield 3.55 g, 85%. Anal. Calc. for $\text{C}_{18}\text{H}_{24}\text{Li}_2\text{Si}$: C, 76.57; H, 8.57. Found C, 76.43; H, 8.55%.

3.14. $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\text{C}_5\text{Me}_4)_2\}$ (**13**)

From **7** (4.25 g, 13.60 mmol) and LiBu^n (1.6 M in hexane) (17.0 ml, 27.20 mmol). Yield 3.49 g, 79%. Anal. Calc. for $\text{C}_{21}\text{H}_{30}\text{Li}_2\text{Si}$: C, 77.74; H, 9.32. Found C, 77.38; H, 9.23%.

3.15. $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\text{C}_5\text{Me}_4)_2\}$ (**14**)

From **8** (4.30 g, 13.17 mmol) and LiBu^n (1.6 M in hexane) (32.9 ml, 26.34 mmol). Yield 3.88 g, 87%. Anal. Calc. for $\text{C}_{17}\text{H}_{24}\text{Li}_2\text{Si}$: C, 75.53; H, 8.95. Found C, 75.26; H, 8.84%.

3.16. Synthesis of $[\text{Ti}\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ (**15**)

THF (50 ml) was added to a solid mixture of $[\text{TiCl}_4(\text{THF})_2]$ (2.00 g, 5.99 mmol) and $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}$ (**9**) (1.27 g, 5.99 mmol). The resulting solution was stirred for 15 h. Solvent was removed in vacuo and toluene added (75 ml) to the resulting solid. The mixture was filtered and the filtrate concentrated (10 ml) and cooled to -30°C to yield crystals of the title complex (0.83 g, 44%). ^1H NMR (300 MHz, C_6D_6): δ 0.16 (s, 3H, SiMe), 5.43 (2H), 5.49 (2H), 6.99 (2H), 7.05 (2H) (m, C_5H_4), 5.72 (m, 1H, $\text{CH}_2=\text{CH}$), 5.88 (m, 2H, $\text{CH}_2=\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6): δ -7.3 (SiMe), 104.5 (C^{ipso}), 117.8, 119.4, 133.8, 136.3 (C_5H_4), 129.3, 137.9 ($\text{CH}_2=\text{CH}$). Anal. Calc. for $\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{SiTi}$: C, 49.24; H, 4.45. Found C, 49.01; H, 4.39%.

The syntheses of **16–32** were carried out in an identical manner to **15**.

3.17. $[\text{Zr}\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ (**16**)

From ZrCl_4 (1.00 g, 4.29 mmol) and $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}$ (0.91 g, 4.29 mmol). Yield 0.53 g, 34%. ^1H -NMR (300 MHz, C_6D_6): δ 0.11 (s, 3H, SiMe), 5.48 (2H), 5.55 (2H), 6.70 (2H), 6.75 (2H) (m, C_5H_4), 5.79 (m, 1H, $\text{CH}_2=\text{CH}$), 5.95 (m, 2H, $\text{CH}_2=\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6): δ -6.7 (SiMe), 107.7 (C^{ipso}), 114.2, 114.9, 127.9, 129.3 (C_5H_4), 130.4, 137.6 ($\text{CH}_2=\text{CH}$). Anal. Calc. for $\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{SiZr}$: C, 43.32; H, 3.91. Found C, 43.22; H, 3.87%.

3.18. $[\text{Hf}\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ (**17**)

From HfCl_4 (1.50 g, 4.68 mmol) and $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}$ (0.99 g, 4.68 mmol). Yield 0.75 g, 36%. ^1H -NMR (300 MHz, C_6D_6): δ 0.14 (s, 3H, SiMe), 5.42 (2H), 5.50 (2H), 6.62 (2H), 6.67 (2H) (m, C_5H_4), 5.79 (m, 1H, $\text{CH}_2=\text{CH}$), 5.94 (m, 2H, $\text{CH}_2=\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6): δ -7.0 (SiMe), 105.8 (C^{ipso}), 112.0, 112.7, 126.2, 127.5 (C_5H_4), 130.0, 137.4 ($\text{CH}_2=\text{CH}$). Anal. Calc. for $\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{HfSi}$: C, 34.87; H 3.15. Found C, 34.51; H, 3.06%.

3.19. $[\text{Ti}\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ (**18**)

From $[\text{TiCl}_4(\text{THF})_2]$ (2.00 g, 5.99 mmol) and $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}$ (1.36 g, 5.99 mmol). Yield 0.83 g, 42%. ^1H -NMR (300 MHz, C_6D_6): δ 0.00 (s, 3H, SiMe), 5.42 (2H), 5.47 (2H), 6.98 (2H), 7.04 (2H) (m, C_5H_4), 1.52 (d, 2H, $\text{CH}_2-\text{CH}=\text{CH}_2$), 4.81 (*cis*), 4.85 (*trans*) (dd, 2H, $\text{CH}_2-\text{CH}=\text{CH}_2$), 5.50 (m, 1H, $\text{CH}_2-\text{CH}=\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6): δ -8.1 (SiMe), 18.6 ($\text{CH}_2-\text{CH}=\text{CH}_2$), 105.0 (C^{ipso}), 117.5, 119.5, 133.8, 136.3 (C_5H_4), 116.4 ($\text{CH}_2-\text{CH}=\text{CH}_2$), 131.1 ($\text{CH}_2-\text{CH}=\text{CH}_2$). Anal. Calc. for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{SiTi}$: C, 50.78; H, 4.87. Found C, 50.61; H, 4.84%.

3.20. $[\text{Zr}\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ (**19**)

From ZrCl_4 (1.00 g, 4.29 mmol) and $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}$ (0.97 g, 4.29 mmol). Yield 0.51 g, 32%. ^1H -NMR (300 MHz, C_6D_6): δ 0.06 (s, 3H, SiMe), 5.45 (2H), 5.49 (2H), 6.68 (2H), 6.74 (2H) (m, C_5H_4), 1.58 (d, 2H, $\text{CH}_2-\text{CH}=\text{CH}_2$), 4.82 (*cis*), 4.86 (*trans*) (dd, 2H, $\text{CH}_2-\text{CH}=\text{CH}_2$), 5.51 (m, 1H, $\text{CH}_2-\text{CH}=\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6): δ -8.0 (SiMe), 18.6 ($\text{CH}_2-\text{CH}=\text{CH}_2$), 108.0 (C^{ipso}), 113.7, 114.9, 128.5, 129.2 (C_5H_4), 116.2 ($\text{CH}_2-\text{CH}=\text{CH}_2$), 131.3 ($\text{CH}_2-\text{CH}=\text{CH}_2$). Anal. Calc. for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{SiZr}$: C, 44.90; H, 4.31. Found C, 44.76; H, 4.25%.

3.21. $[\text{Hf}\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ (**20**)

From HfCl_4 (1.50 g, 4.68 mmol) and $\text{Li}_2\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}$ (1.06 g, 4.68 mmol). Yield 0.78 g, 36%. ^1H -NMR (300 MHz, C_6D_6): δ 0.08 (s, 3H, SiMe), 5.41 (2H), 5.45 (2H), 6.62 (2H), 6.67 (2H) (m, C_5H_4), 1.61 (d, 2H, $\text{CH}_2-\text{CH}=\text{CH}_2$), 4.83 (*cis*), 4.88 (*trans*) (dd, 2H, $\text{CH}_2-\text{CH}=\text{CH}_2$), 5.58 (m, 1H, $\text{CH}_2-\text{CH}=\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6): δ -8.0 (SiMe), 18.6 ($\text{CH}_2-\text{CH}=\text{CH}_2$), 109.5 (C^{ipso}), 111.6, 112.9, 126.3, 127.7 (C_5H_4), 116.1 ($\text{CH}_2-\text{CH}=\text{CH}_2$), 131.4 ($\text{CH}_2-\text{CH}=\text{CH}_2$). Anal. Calc. for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{HfSi}$: C, 36.42; H, 3.49. Found C, 36.23; H, 3.45%.

3.22. $[Ti\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}Cl_2]$ (**21**)

From $[TiCl_4(THF)_2]$ (2.00 g, 5.99 mmol) and $Li_2\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}$ (1.61 g, 5.99 mmol). Yield 1.01 g, 45%. 1H -NMR (300 MHz, C_6D_6): δ 0.33 (s, 3H, *SiMe*), 1.52 (3H), 1.57 (3H), 2.03 (3H), 2.06 (3H) (s, C_5Me_4), 5.24 (1H), 5.29 (1H), 7.11 (1H), 7.15 (1H) (m, C_5H_4), 5.82 (m, 2H, $CH_2=CH$), 6.20 (m, 1H, $CH_2=CH$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ -2.4 (*SiMe*), 13.6, 13.9, 16.3, 16.5 (C_5Me_4), 97.3 (C^{ipso}), 115.0, 115.9, 132.1, 134.1 (C_5H_4), 102.3, 129.6, 130.8, 142.7, 144.2 (C_5Me_4), 129.0, 135.4 ($CH_2=CH$). Anal. Calc. for $C_{17}H_{22}Cl_2SiTi$: C, 54.71; H, 5.94. Found C, 54.57; H, 5.89%.

3.23. $[Zr\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}Cl_2]$ (**22**)

From $ZrCl_4$ (1.00 g, 4.29 mmol) and $Li_2\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}$ (1.15 g, 4.29 mmol). Yield 0.75 g, 42%. 1H -NMR (300 MHz, C_6D_6): δ 0.38 (s, 3H, *SiMe*), 1.63 (3H), 1.68 (3H), 1.93 (3H), 1.94 (3H) (s, C_5Me_4), 5.35 (1H), 5.40 (1H), 6.83 (1H), 6.87 (1H) (m, C_5H_4), 5.84 (m, 2H, $CH_2=CH$), 6.25 (m, 1H, $CH_2=CH$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ -1.7 (*SiMe*), 12.4, 12.7, 15.2, 15.4 (C_5Me_4), 97.4 (C^{ipso}), 112.3, 112.9, 126.3, 127.6 (C_5H_4), 105.3, 125.2, 125.8, 135.2, 136.2 (C_5Me_4), 134.8, 135.0 ($CH_2=CH$). Anal. Calc. for $C_{17}H_{22}Cl_2SiZr$: C, 49.01; H, 5.32. Found C, 48.72; H, 5.25%.

3.24. $[Hf\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}Cl_2]$ (**23**)

From $HfCl_4$ (1.50 g, 4.68 mmol) and $Li_2\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}$ (1.26 g, 4.68 mmol). Yield 0.87 g, 37%. 1H -NMR (300 MHz, C_6D_6): δ 0.39 (s, 3H, *SiMe*), 1.71 (3H), 1.77 (3H), 1.96 (3H), 1.97 (3H) (s, C_5Me_4), 5.32 (1H), 5.36 (1H), 6.76 (1H), 6.79 (1H) (m, C_5H_4), 5.85 (m, 2H, $CH_2=CH$), 6.27 (m, 1H, $CH_2=CH$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ -2.1 (*SiMe*), 11.9, 12.2, 14.6, 14.8 (C_5Me_4), 99.0 (C^{ipso}), 109.9, 110.6, 125.3, 126.9 (C_5H_4), 107.2, 122.0, 122.8, 133.3, 134.5 (C_5Me_4), 129.2, 134.9 ($CH_2=CH$). Anal. Calc. for $C_{17}H_{22}Cl_2HfSi$: C, 40.53; H, 4.40. Found C, 40.19; H, 4.33%.

3.25. $[Ti\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}Cl_2]$ (**24**)

From $[TiCl_4(THF)_2]$ (2.00 g, 5.99 mmol) and $Li_2\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}$ (1.69 g, 5.99 mmol). Yield 0.90 g, 39%. 1H -NMR (300 MHz, C_6D_6): δ 0.32 (s, 3H, *SiMe*), 1.49 (3H), 1.53 (3H), 2.03 (6H) (s, C_5Me_4), 1.80 (dd, 2H, $CH_2-CH=CH_2$), 5.19 (2H), 7.12 (2H) (m, C_5H_4), 4.90 (*cis*), 4.95

(*trans*) (dd, 2H, $CH_2-CH=CH_2$), 5.65 (m, 1H, $CH_2-CH=CH_2$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ -3.6 (*SiMe*), 13.8, 13.9, 16.4, 16.5 (C_5Me_4), 22.3 ($CH_2-CH=CH_2$), 97.5 (C^{ipso}), 115.1, 115.8, 132.7, 133.7 (C_5H_4), 103.1, 129.8, 130.8, 143.4, 143.8 (C_5Me_4), 116.4 ($CH_2-CH=CH_2$), 131.8 ($CH_2-CH=CH_2$). Anal. Calc. for $C_{18}H_{24}Cl_2SiTi$: C, 55.83; H, 6.25. Found C, 55.61; H, 6.19%.

3.26. $[Zr\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}Cl_2]$ (**25**)

From $ZrCl_4$ (1.00 g, 4.29 mmol) and $Li_2\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}$ (1.21 g, 4.29 mmol). Yield 0.83 g, 45%. 1H -NMR (300 MHz, C_6D_6): δ 0.36 (s, 3H, *SiMe*), 1.60 (3H), 1.64 (3H), 1.92 (3H), 1.93 (3H) (s, C_5Me_4), 1.84 (dd, 2H, $CH_2-CH=CH_2$), 5.28 (2H), 6.83 (2H) (m, C_5H_4), 4.91 (*cis*), 4.96 (*trans*) (dd, 2H, $CH_2-CH=CH_2$), 5.68 (m, 1H, $CH_2-CH=CH_2$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ -3.2 (*SiMe*), 12.5, 12.6, 15.2, 15.3 (C_5Me_4), 22.5 ($CH_2-CH=CH_2$), 97.8 (C^{ipso}), 112.1, 112.8, 126.6, 127.4 (C_5H_4), 106.1, 124.9, 125.9, 135.6, 135.9 (C_5Me_4), 116.3 ($CH_2-CH=CH_2$), 132.0 ($CH_2-CH=CH_2$). Anal. Calc. for $C_{18}H_{24}Cl_2SiZr$: C, 50.21; H, 5.62. Found C, 50.08; H, 5.51%.

3.27. $[Hf\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}Cl_2]$ (**26**)

From $HfCl_4$ (1.50 g, 4.68 mmol) and $Li_2\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}$ (1.32 g, 4.68 mmol). Yield 0.87 g, 36%. 1H -NMR (300 MHz, C_6D_6): δ 0.37 (s, 3H, *SiMe*), 1.68 (3H), 1.73 (3H), 1.96 (6H) (s, C_5Me_4), 1.86 (dd, 2H, $CH_2-CH=CH_2$), 5.26 (2H), 6.76 (2H) (m, C_5H_4), 4.89 (*cis*), 4.96 (*trans*) (dd, 2H, $CH_2-CH=CH_2$), 5.66 (m, 1H, $CH_2-CH=CH_2$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ -3.4 (*SiMe*), 12.2, 12.3, 14.7, 14.8 (C_5Me_4), 22.4 ($CH_2-CH=CH_2$), 99.1 (C^{ipso}), 109.6, 110.4, 125.6, 126.4 (C_5H_4), 107.9, 121.7, 122.7, 133.7, 134.0 (C_5Me_4), 116.1 ($CH_2-CH=CH_2$), 132.0 ($CH_2-CH=CH_2$). Anal. Calc. for $C_{18}H_{24}Cl_2HfSi$: C, 41.75; H, 4.67. Found C, 41.61; H, 4.63%.

3.28. $[Ti\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)_2\}Cl_2]$ (**27**)

From $[TiCl_4(THF)_2]$ (2.00 g, 5.99 mmol) and $Li_2\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)_2\}$ (1.94 g, 5.99 mmol). Yield 1.05 g, 41%. 1H -NMR (300 MHz, C_6D_6): δ 0.67 (s, 3H, *SiMe*), 1.63 (6H), 1.64 (6H), 2.06 (6H), 2.09 (6H) (s, C_5Me_4), 5.89 (m, 2H, $CH_2=CH$), 6.61 (m, 1H, $CH_2=CH$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ 2.2 (*SiMe*), 13.8, 14.0, 16.1, 16.8 (C_5Me_4), 91.4, 128.5, 129.2, 142.4, 143.4 (C_5Me_4), 134.3, 137.4 ($CH_2=CH$). Anal. Calc. for $C_{21}H_{30}Cl_2SiTi$: C, 58.75; H, 7.04. Found C, 58.57; H, 6.99%.

3.29. $[Zr\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)_2\}Cl_2]$ (**28**)

From $ZrCl_4$ (1.00 g, 4.29 mmol) and $Li_2\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)_2\}$ (1.39 g, 4.29 mmol). Yield 0.85 g, 42%. 1H -NMR (300 MHz, C_6D_6): δ 0.68 (s, 3H, *SiMe*), 1.70 (6H), 1.71 (6H), 1.99 (6H), 2.00 (6H) (s, C_5Me_4), 5.90 (m, 2H, $CH_2=CH$), 6.58 (m, 1H, $CH_2=CH$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ 3.1 (*SiMe*), 12.8, 13.0, 15.3, 16.0 (C_5Me_4), 92.7, 124.6, 125.3, 135.7, 136.4 (C_5Me_4), 134.4, 138.2 ($CH_2=CH$). Anal. Calc. for $C_{21}H_{30}Cl_2SiZr$: C, 53.56; H, 6.40. Found C, 53.09; H, 6.33%.

3.30. $[Hf\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)_2\}Cl_2]$ (**29**)

From $HfCl_4$ (1.50 g, 4.68 mmol) and $Li_2\{Me(CH_2=CH)Si(\eta^5-C_5Me_4)_2\}$ (1.52 g, 4.68 mmol). Yield 0.92 g, 35%. 1H -NMR (300 MHz, C_6D_6): δ 0.66 (s, 3H, *SiMe*), 1.80 (6H), 1.81 (6H), 1.99 (6H), 2.01 (6H) (s, C_5Me_4), 5.88 (m, 2H, $CH_2=CH$), 6.57 (m, 1H, $CH_2=CH$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ 2.8 (*SiMe*), 12.4, 12.5, 14.9, 15.6 (C_5Me_4), 94.6, 121.7, 122.5, 134.2, 135.0 (C_5Me_4), 134.3, 138.3 ($CH_2=CH$). Anal. Calc. for $C_{21}H_{30}Cl_2HfSi$: C, 45.04; H, 5.40. Found C, 44.87; H, 5.35%.

3.31. $[Ti\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)_2\}Cl_2]$ (**30**)

From $[TiCl_4(THF)_2]$ (2.00 g, 5.99 mmol) and $Li_2\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)_2\}$ (2.03 g, 5.99 mmol). Yield 1.12 g, 42%. 1H -NMR (300 MHz, C_6D_6): δ 0.68 (s, 3H, *SiMe*), 1.60 (6H), 1.62 (6H), 2.06 (12H) (s, C_5Me_4), 2.10 (d, 2H, $CH_2-CH=CH_2$), 5.00 (*cis*), 5.05 (*trans*) (dd, 2H, $CH_2-CH=CH_2$), 5.82 (m, 1H, $CH_2-CH=CH_2$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ -0.2 (*SiMe*), 14.1, 14.2, 16.4, 16.6 (C_5Me_4), 25.4 ($CH_2-CH=CH_2$), 92.2, 128.7, 129.5, 143.1, 143.2 (C_5Me_4), 116.6 ($CH_2-CH=CH_2$), 132.6 ($CH_2-CH=CH_2$). Anal. Calc. for $C_{22}H_{32}Cl_2SiTi$: C, 59.60; H, 7.28. Found C, 59.29; H, 7.23%.

3.32. $[Zr\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)_2\}Cl_2]$ (**31**)

From $ZrCl_4$ (1.00 g, 4.29 mmol) and $Li_2\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)_2\}$ (1.45 g, 4.29 mmol). Yield 0.81 g, 39%. 1H -NMR (300 MHz, C_6D_6): δ 0.69 (s, 3H, *SiMe*), 1.72 (6H), 1.74 (6H), 2.00 (12H) (s, C_5Me_4), 2.15 (d, 2H, $CH_2-CH=CH_2$), 5.00 (*cis*), 5.07 (*trans*) (dd, 2H, $CH_2-CH=CH_2$), 5.82 (m, 1H, $CH_2-CH=CH_2$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ 0.0 (*SiMe*), 12.5, 12.6, 15.0, 15.2 (C_5Me_4), 25.4 ($CH_2-CH=CH_2$), 93.0, 124.5, 125.2, 136.0, 136.0 (C_5Me_4), 116.4 ($CH_2-CH=CH_2$), 132.6 ($CH_2-CH=CH_2$). Anal. Calc. for $C_{22}H_{32}Cl_2SiZr$: C, 54.29; H, 6.63. Found C, 54.17; H, 6.61%.

3.33. $[Hf\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)_2\}Cl_2]$ (**32**)

From $HfCl_4$ (1.50 g, 4.68 mmol) and $Li_2\{Me(CH_2=CHCH_2)Si(\eta^5-C_5Me_4)_2\}$ (1.59 g, 4.68 mmol). Yield 0.86 g, 32%. 1H -NMR (300 MHz, C_6D_6): δ 0.67 (s, 3H, *SiMe*), 1.77 (6H), 1.79 (6H), 2.00 (12H) (s, C_5Me_4), 2.12 (d, 2H, $CH_2-CH=CH_2$), 4.98 (*cis*), 5.03 (*trans*) (dd, 2H, $CH_2-CH=CH_2$), 5.80 (m, 1H, $CH_2-CH=CH_2$). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ 0.1 (*SiMe*), 12.3, 12.4, 15.1, 15.3 (C_5Me_4), 25.7 ($CH_2-CH=CH_2$), 95.2, 124.3, 124.9, 135.9, 136.0 (C_5Me_4), 116.4 ($CH_2-CH=CH_2$), 132.5 ($CH_2-CH=CH_2$). Anal. Calc. for $C_{22}H_{32}Cl_2HfSi$: C, 46.04; H, 5.62. Found C, 45.71; H, 5.52%.

3.34. Synthesis of $[Ti\{Me(CH_3CH_2)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}Cl_2]$ (**33**)

21 (0.15 g, 0.40 mmol) was dissolved in CH_2Cl_2 (50 ml) and the Pd/C (10% palladium) catalyst was added (8 mg). Hydrogen was passed through the solution at 1 bar with stirring for 2 h. The resulting suspension was filtered and solvent removed from the filtrate under reduced pressure to give the title complex as a crystalline solid (0.11 g, 73%). 1H -NMR (300 MHz, C_6D_6): δ 0.28 (s, 3H, *SiMe*), 0.85 (m, 5H, Et), 1.52 (3H), 1.53 (3H), 2.03 (3H), 2.04 (3H) (s, C_5Me_4), 5.20 (1H), 5.22 (1H), 7.10 (1H), 7.12 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ -1.7 (*SiMe*), 6.4, 6.6 (*Et*), 12.4, 12.7, 15.2, 15.4 (C_5Me_4), 97.4 (C^{ipso}), 112.3, 112.9, 126.3, 127.6 (C_5H_4), 105.3, 125.2, 125.8, 135.2, 136.2 (C_5Me_4). Anal. Calc. for $C_{17}H_{24}Cl_2SiTi$: C, 54.42; H, 6.45. Found C, 54.17; H, 6.38%.

The syntheses of **34** and **35** were carried out in an identical manner to **33**.

3.35. $[Zr\{Me(CH_3CH_2)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}Cl_2]$ (**34**)

From **22** (0.15 g, 0.36 mmol). Yield 0.12 g, 80%. 1H -NMR (300 MHz, C_6D_6): δ 0.34 (s, 3H, *SiMe*), 0.89 (m, 5H, Et), 1.65 (3H), 1.66 (3H), 1.95 (3H), 1.96 (3H) (s, C_5Me_4), 5.29 (1H), 5.33 (1H), 6.84 (1H), 6.85 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ -NMR (75 MHz, C_6D_6): δ -3.2 (*SiMe*), 7.0, 7.4 (*Et*), 12.8, 12.9, 15.2, 15.5 (C_5Me_4), 98.1 (C^{ipso}), 112.4, 113.1, 126.9, 127.5 (C_5H_4), 106.8, 125.3, 126.2, 135.9, 136.0 (C_5Me_4). Anal. Calc. for $C_{17}H_{24}Cl_2SiZr$: C, 48.78; H, 5.78. Found C, 48.49; H, 5.72%.

3.36. $[Zr\{Me(CH_3CH_2CH_2)Si(\eta^5-C_5H_4)_2\}Cl_2]$ (**35**)

From **19** (0.38 g, 1.01 mmol). Yield 0.30 g, 79%. 1H -NMR (300 MHz, $CDCl_3$): δ 0.74 (s, 3H, *SiMe*), 1.14 (m, 3H, $CH_3CH_2CH_2$), 1.26 (m, 2H, $CH_3CH_2CH_2$), 1.72 (m,

2H, CH₃CH₂CH₂), 6.00 (4H), 6.98 (4H) (m, C₅H₄). ¹³C{¹H}-NMR (75 MHz, CDCl₃): δ 0.9 (SiMe), 13.5, 16.4, 18.0 (CH₃CH₂CH₂), 108.8 (C^{ipso}), 114.0, 114.9, 128.0, 129.0 (C₅H₄). Anal. Calc. for C₁₄H₁₈Cl₂SiZr: C, 44.66; H, 4.82. Found C, 44.51; H, 4.77%.

3.37. Synthesis of [Zr{Me((BC₈H₁₄)CH₂CH₂)Si(η⁵-C₅H₄)₂}Cl₂] (36)

CH₂Cl₂ (50 ml) was added to a solid mixture of **16** (0.22 g, 0.62 mmol) and 9-borabicyclo[3.3.1]nonane dimer (0.07 g, 0.31 mmol). The solution was stirred at room temperature for 15 h. Solvent was removed under reduced pressure to give the title compound as a crystalline solid (0.29 g, 100%). ¹H-NMR (300 MHz, CDCl₃): δ 0.73 (s, 3H, SiMe), 1.48 (2H), 1.52 (2H) (m, CH₂CH₂), 1.35 (2H), 1.90 (2H) (m, γ-H of 9-BBN), 1.62 (4H), 1.90 (4H) (m, β and δ-H of 9-BBN), 1.82 (m, 2H, α-H of 9-BBN), 5.98 (4H), 6.93 (2H), 6.97 (2H) (m, C₅H₄). ¹³C{¹H}-NMR (75 MHz, C₆D₆): δ 4.1 (SiMe), 23.2, 23.7 (CH₂CH₂), 23.8, 27.9, 33.8, 33.9 (9-BBN), 109.0 (C^{ipso}), 113.5, 115.4, 127.3, 129.5 (C₅H₄). ¹¹B{¹H}-NMR (64.2 MHz, C₆D₆): δ 86. Anal. Calc. for C₂₁H₂₉BCl₂SiZr: C, 52.28; H, 6.06. Found C, 52.02; H, 6.00%.

The syntheses of **37** and **38** were carried out in an identical manner to **36**.

3.38. [Ti{Me((BC₈H₁₄)CH₂CH₂CH₂)Si(η⁵-C₅Me₄)(η⁵-C₅H₄)}Cl₂] (37)

From **24** (0.27 g, 0.70 mmol) and 9-borabicyclo[3.3.1]nonane dimer (0.09 g, 0.35 mmol). Yield 0.36 g, 99%. ¹H-NMR (300 MHz, C₆D₆): δ 0.41 (s, 3H, SiMe), 1.06 (2H), 1.48 (2H), 1.62 (2H) (m, CH₂CH₂CH₂), 1.15 (2H), 1.83 (2H) (m, γ-H of 9-BBN), 1.62 (4H), 1.83 (4H) (m, β and δ-H of 9-BBN), 1.74 (m, 2H, α-H of 9-BBN), 1.65 (3H), 1.82 (3H), 2.04 (3H), 2.05 (3H) (s, C₅Me₄), 5.28 (1H), 5.31 (1H), 7.13 (1H), 7.15 (1H) (m, C₅H₄). ¹³C{¹H}-NMR (75 MHz, C₆D₆): δ -3.1 (SiMe), 13.9, 14.0, 16.4, 16.5 (C₅Me₄), 18.8, 23.2, 23.9 (CH₂CH₂CH₂), 23.8, 26.0, 28.0, 35.0 (9-BBN), 98.0 (C^{ipso}), 115.1, 116.0, 132.6, 133.9 (C₅H₄), 103.8, 129.7, 131.1, 143.3, 143.9 (C₅Me₄). ¹¹B{¹H}-NMR (64.2 MHz, C₆D₆): δ 86. Anal. Calc. for C₂₆H₃₉BCl₂SiTi: C, 61.32; H, 7.72. Found C, 61.07; H, 7.65%.

3.39. [Zr{Me((BC₈H₁₄)CH₂CH₂CH₂)Si(η⁵-C₅Me₄)(η⁵-C₅H₄)}Cl₂] (38)

From **25** (0.20 g, 0.46 mmol) and 9-borabicyclo[3.3.1]nonane dimer (0.06 g, 0.23 mmol). Yield 0.25 g, 99%. ¹H-NMR (300 MHz, C₆D₆): δ 0.51 (s, 3H, SiMe), 1.22 (2H), 1.42 (2H), 1.56 (2H) (m,

Table 3
Crystal data and structure refinement for **19**, **25** and **28**

	19	25	29
Empirical formula	C ₁₄ H ₁₆ Cl ₂ SiZr	C ₁₈ H ₂₄ Cl ₂ SiZr	C ₂₁ H ₃₀ Cl ₂ SiZr
Formula weight	374.48	430.58	472.66
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Monoclinic, <i>P</i> 2 ₁ / <i>a</i>
<i>a</i> (Å)	<i>a</i> = 7.745(1)	14.134(3)	9.969(8)
<i>b</i> (Å)	<i>b</i> = 8.474(1)	9.542(2)	23.513(7)
<i>c</i> (Å)	<i>c</i> = 12.827(1)	14.191(3)	10.006(7)
α (°)	102.88(1)		
β (°)	93.92(1)	98.05(3)	114.85(2)
γ (°)	107.60(1)		
Volume (Å ³)	773.9(1)	1895.1(7)	2128(2)
Z, Calculated density (g cm ⁻³)	2, 1.607	4, 1.509	4, 1.475
Absorption coefficient (cm ⁻¹)	11.13	9.20	8.26
<i>F</i> (0 0 0)	376	880	976
Crystal size (mm)	0.2 × 0.4 × 0.4	0.3 × 0.2 × 0.2	0.4 × 0.2 × 0.1
Theta range for data collection (°)	2.61–27.99	2.19–25.00	2.40–28.15
Limiting indices	-10 ≤ <i>h</i> ≤ 10 -11 ≤ <i>k</i> ≤ 10 0 ≤ <i>l</i> ≤ 16	-16 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 11 0 ≤ <i>l</i> ≤ 16	-13 ≤ <i>h</i> ≤ 11 0 ≤ <i>k</i> ≤ 31 0 ≤ <i>l</i> ≤ 13
Reflections collected/unique	3881/3717 [<i>R</i> _{int} = 0.0656]	3287/3172 [<i>R</i> _{int} = 0.0335]	5453/5177 [<i>R</i> _{int} = 0.0377]
Data/restraints/parameters	3717/0/182	3172/0/203	5177/0/234
Goodness-of-fit on <i>F</i> ²	0.998	1.099	1.076
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0632, <i>wR</i> ₂ = 0.1535	<i>R</i> ₁ = 0.0719, <i>wR</i> ₂ = 0.1848	<i>R</i> ₁ = 0.0483, <i>wR</i> ₂ = 0.1259
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1226, <i>wR</i> ₂ = 0.1835	<i>R</i> ₁ = 0.0844, <i>wR</i> ₂ = 0.1931	<i>R</i> ₁ = 0.0686, <i>wR</i> ₂ = 0.1558
Largest difference peak and hole (e Å ⁻³)	0.877 and -1.264	1.414 and -1.668	0.949 and -0.724

$\text{CH}_2\text{CH}_2\text{CH}_2$), 1.10 (2H), 1.86 (2H) (m, γ -H of 9-BBN), 1.69 (4H), 1.86 (4H) (m, β and δ -H of 9-BBN), 1.79 (m, 2H, α -H of 9-BBN), 1.72 (3H), 1.83 (3H), 2.00 (3H), 2.01 (3H) (s, C_5Me_4), 5.43 (1H), 5.46 (1H), 6.89 (1H), 6.92 (1H) (m, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6): δ -2.7 (SiMe), 12.6, 12.7, 15.2, 15.3 (C_5Me_4), 18.8, 19.1, 23.2 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 23.8, 31.9, 33.6, 33.7 (9-BBN), 98.1 (C^{ipso}), 112.1, 112.9, 126.5, 127.5 (C_5H_4), 106.8, 124.9, 126.2, 135.8, 136.0 (C_5Me_4). $^{11}\text{B}\{^1\text{H}\}$ -NMR (64.2 MHz, C_6D_6): δ 86. Anal. Calc. for $\text{C}_{26}\text{H}_{39}\text{BCl}_2\text{SiZr}$: C, 56.51; H, 7.11. Found C, 56.37; H, 7.09%.

3.40. X-ray structure determinations of $[\text{Zr}\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ (19**), $[\text{Zr}\{\text{Me}(\text{CH}_2=\text{CHCH}_2)\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^5\text{-C}_5\text{H}_4)\}\text{Cl}_2]$ (**25**) and $[\text{Zr}\{\text{Me}(\text{CH}_2=\text{CH})\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\}\text{Cl}_2]$ (**28**)**

The crystals were selected and mounted on a fine glass fiber with epoxy cement. The data collection were performed at 25 °C on a Nonius-Mach3 diffractometer equipped with a graphite-monochromated radiation source ($\lambda=0.71073$ Å) using a $\omega/2\theta$ scan technique to a maximum value of 56°. Unit cell dimensions were obtained by a least-squares fit of the 2θ values of 25 high-order reflections by using the Mach3 centering routines. Data were corrected in the usual fashion for Lorentz and polarization effects and a semiempirical absorption correction [19] was applied for **19** and **25**. The structures were solved by direct methods [20] and refinement on F^2 was carried out by full-matrix least-squares [21]. For **19** the C(3) and C(4) atoms are disordered over two positions with a occupation factor of 59 and 41, respectively. Anisotropic temperature parameters were considered for all non-hydrogen atoms, while the hydrogen atoms were included in calculated positions but not refined. Crystallographic data are given in Table 3.

4. Supplementary material

Crystallographic data for the structural analyses of **19**, **25** and **28** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 199453–199455. 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>).

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