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Synthesis, hydrosilylation reactivity and catalytic properties of group 4 *ansa*-metallocene complexes

Santiago Gómez-Ruiz [a], Sanjiv Prashar [a,*], Mariano Fajardo [a], Antonio Antiñolo [b], Antonio Otero [b,*], Miguel A. Maestro [c], Victoria Volkis [d], Moris S. Eisen [d], César J. Pastor [e]

[a] *Departamento de Tecnología Química y Ambiental, ESCET, Universidad Rey Juan Carlos, 28933 Móstoles, Madrid, Spain*
[b] *Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, Facultad de Químicas, Campus Universitario, 13071-Ciudad Real, Spain*
[c] *Departamento de Química Fundamental, Facultade de Ciencias, Campus da Zapateira, Universidade da Coruña, 15071 A Coruña, Spain*
[d] *Department of Chemistry and Institute of Catalysis Science and Technology, Technion-Israel Institute of Technology, Haifa 32000, Israel*
[e] *Servicio Interdepartamental de Investigación, Universidad Autónoma de Madrid, Cantoblanco 28049 Madrid, Spain*

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Abstract

The following *ansa*-ligand precursors, $Et(H)Si(C_5H_5)_2$ (**1**), $Et(H)Si(C_5HMe_4)Cl$ (**2**), $Et(H)Si(C_5HMe_4)(C_5H_5)$ (**3**), $Ph(H)Si(C_5HMe_4)Cl$ (**4**), $Ph(H)Si(C_5HMe_4)(C_5H_5)$ (**5**), $Ph(H)Si(C_5HMe_4)_2$ (**6**), $CH_2{=}CHCH_2(H)Si(C_5HMe_4)Cl$ (**7**), $CH_2{=}CHCH_2(H)Si(C_5HMe_4)(C_5H_5)$ (**8**), $CH_2{=}CHCH_2(H)Si(C_5HMe_4)_2$ (**9**), and their lithium derivatives, $Li_2\{Et(H)Si(C_5H_4)_2\}$ (**10**), $Li_2\{Et(H)Si(C_5Me_4)(C_5H_4)\}$ (**11**), $Li_2\{Ph(H)Si(C_5Me_4)(C_5H_4)\}$ (**12**), $Li_2\{Ph(H)Si(C_5Me_4)_2\}$ (**13**), $Li_2\{CH_2{=}CHCH_2(H)Si(C_5Me_4)(C_5H_4)\}$ (**14**) and $Li_2\{CH_2{=}CHCH_2(H)Si(C_5Me_4)_2\}$ (**15**) have been prepared. The group 4 metal complexes, $[M\{Et(H)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (M = Ti (**16a**), Zr (**16b**), Hf (**16c**)), $[M\{Et(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**17a**), Zr (**17b**), Hf (**17c**)), $[M\{Ph(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**18a**), Zr (**18b**), Hf (**18c**)), $[M\{Ph(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (M = Ti (**19a**), Zr (**19b**), Hf (**19c**)), $M\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**20a**), Zr (**20b**)) and $[M\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (M = Ti (**21a**), Zr (**21b**), Hf (**21c**)) were synthesized from the reaction of the lithium *ansa*-derivatives and the tetrachloride salts of the transition metal. The reactivity of the group 4 metal complexes in hydrosilylation processes has been studied. The reaction of **16b**, **17a** and **17b** with tetravinylsilane gave $[Zr\{(CH_2{=}CH)_3SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (**22b**) and $[M\{(CH_2{=}CH)_3SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**23a**), Zr (**23b**)), respectively. The reaction of **17a** and **17b** with dimethyldivinylsilane yielded the hydrosilylation products $[M\{(CH_2{=}CH)Me_2SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**24a**), Zr (**24b**)), respectively. **23b** and **24b** reacted with the silane reagent $HSiEt_3$ to form, via hydrosilylation, $[Zr\{(Et_3SiCH_2CH_2)_3SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**25b**) and $[Zr\{(Et_3SiCH_2CH_2)Me_2SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**26b**), respectively.

The previously synthesized compounds, $[M\{CH_2{=}CH(Me)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (M = Ti (**27a**), Zr (**27b**)) and $[Zr\{CH_2{=}CHCH_2(Me)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (**28b**), have also been tested in reactions of hydrosilylation with $SiHMeCl_2$ to give $[M\{Cl_2MeSiCH_2CH_2(Me)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (M = Ti (**29a**), Zr (**29b**)) and $[Zr\{Cl_2MeSiCH_2CH_2CH_2(Me)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (**30b**). All the zirconocene compounds are active to varying degrees as catalysts in the polymerization of ethylene. The molecular structures of **21b** and **21c** have been determined by single crystal X-ray diffraction studies.

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Keywords: *ansa*-Metallocene complexes; Titanium; Zirconium; Hafnium; Hydrosilylation; Polymerization

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[*] Corresponding author. Tel.: +34 914887186; fax: +34 914888143.
E-mail address: sanjiv.prashar@urjc.es (S. Prashar).

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1. Introduction

The catalytic activity of group 4 metallocene complexes in the polymerization of olefins has been the principal reason for the dramatic growth in interest towards these compounds [1]. The main focus of this research field is centred on the design of metallocene complexes towards the goal of "made to measure" catalysts that can direct the catalytic reaction in producing polymers with desired physical properties. *ansa*-Cyclopentadienyl systems are now widely recognized to afford better catalytic activity and selectivity in the polymerization of olefins than their non-*ansa* counterparts [2]. Recent studies have demonstrated that the incorporation of the *ansa*-bridge may have a profound influence on the chemical behaviour of these complexes [3].

Industry requirements for the development of supported metallocene polymerization catalysts, that can offer homogeneous single-site selectivity in a heterogeneous medium, is presently of utmost importance. Several studies on immobilized catalysts have recently been published [4]. The immobilization of the catalyst is normally achieved by the introduction of functional groups in the ligand system and their interaction with the surface of an inorganic oxide with the metallocene framework remaining, in most cases, unaltered [5].

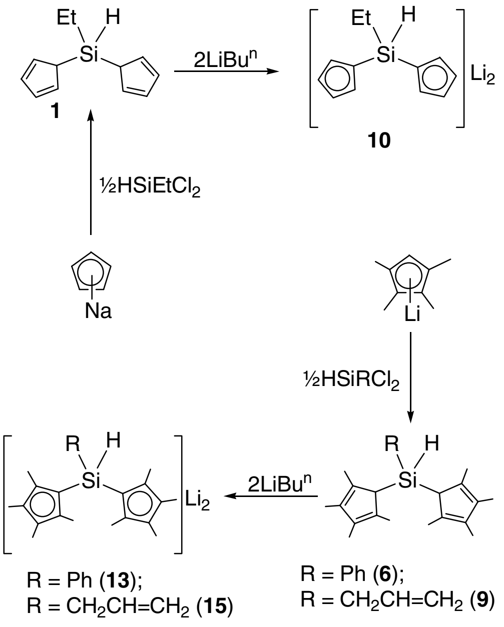
Suzuki et al. [5d] have reported the hydrosilylation of *ansa*-zirconocene complexes with vinyl substituents at the silicon *ansa* bridge to give derivatives which were subsequently supported on silica. In a similar manner O'Hare and co-worker [5e] have reported the immobilization on silica of an *ansa*-bisindenyl complex. Alt et al. [6] have also recently published their work relating to the modification by hydrosilylation of *ansa*-cyclopentadienyl ligands and their subsequent incorporation in group 4 metallocene systems. Collins and co-workers [5a] have reported the anchoring, on modified silica surfaces, of *ansa*-metallocene complexes via hydrosilylation reactions. Seyferth and Wyrwa [7] have also carried out work incorporating group 4 metallocene fragments in organosilicon dendrimers.

As part of our ongoing studies in *ansa*-metallocene complexes [8], we recently published our initial results on the modification of the *ansa*-ligand framework via hydrosilylation reactions [9]. As a continuation of this work we now report the synthesis of new group 4 *ansa*-metallocene complexes and the reactivity of the *ansa*-bridge Si–H bond in the hydrosilylation of unsaturated silane substrates. We also describe the hydrosilylation of vinyl or allyl substituents at the silicon *ansa* bridge of group 4 metallocene complexes. The catalytic activity of the *ansa*-zirconocene complexes in the polymerization of ethylene is included.

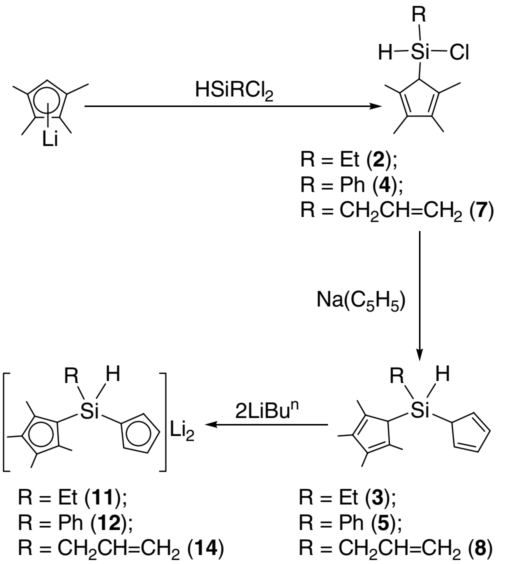
2. Results and discussion

The ligand systems, Et(H)Si$(C_5H_5)_2$ (**1**), Et(H)-Si(C_5HMe_4)Cl (**2**), Et(H)Si$(C_5HMe_4)(C_5H_5)$ (**3**), Ph(H)-Si(C_5HMe_4)Cl (**4**), Ph(H)Si$(C_5HMe_4)(C_5H_5)$ (**5**), Ph(H) Si$(C_5HMe_4)_2$ (**6**), $CH_2{=}CHCH_2$(H)Si(C_5HMe_4)-Cl (**7**), $CH_2{=}CHCH_2$(H)Si$(C_5HMe_4)(C_5H_5)$ (**8**) and $CH_2{=}CH$-CH_2(H)Si$(C_5HMe_4)_2$ (**9**) were prepared as yellow oils following previously reported synthetic protocols (Schemes 1 and 2) and isolated as mixtures of the double bond position isomers [8,9]. In the preparation of **2** and **4**, an excess of the dichlorosilane reagent was used in order to favour monosubstitution. **1**–**9** were characterized by ^{1}H NMR spectroscopy and electron impact mass spectrometry (see Section 5). The *ansa*-biscyclopentadiene compounds, **1**, **3**, **5**, **6**, **8** and **9** were lithiated in the traditional manner with *n*-butyllithium, to give the dilithium derivates, $Li_2\{Et(H)Si(C_5H_4)_2\}$ (**10**), $Li_2\{Et(H)Si(C_5Me_4)(C_5H_4)\}$ (**11**), $Li_2\{Ph(H)Si(C_5Me_4)\text{-}(C_5H_4)\}$ (**12**), $Li_2\{Ph(H)Si(C_5Me_4)_2\}$ (**13**), $Li_2\{CH_2{=}CHCH_2\text{-}(H)Si(C_5Me_4)(C_5H_4)\}$ (**14**) and $Li_2\{CH_2{=}CH\text{-}CH_2(H)Si(C_5Me_4)_2\}$ (**15**), in high yields.

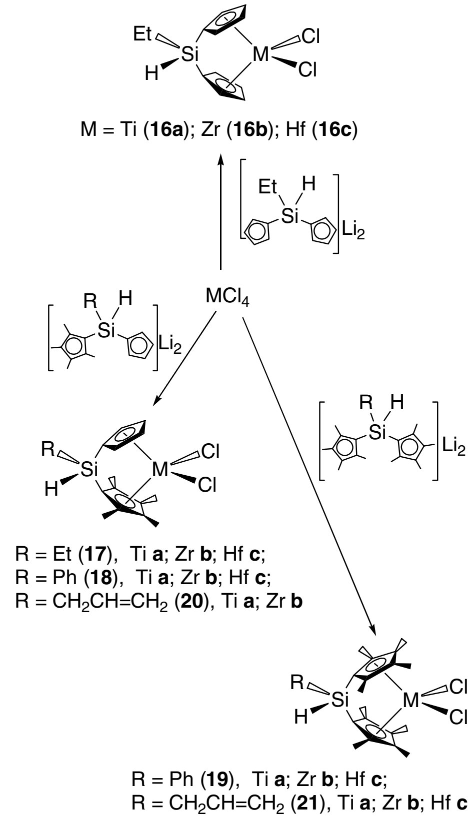
The reaction of **10**–**15** with either $[TiCl_4(THF)_2]$, $ZrCl_4$ or $HfCl_4$, yielded the corresponding *ansa*-metallocene (IV) dichloride complexes, $[M\{Et(H)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (M = Ti (**16a**), Zr (**16b**), Hf (**16c**)), $[M\{Et(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**17a**), Zr (**17b**), Hf (**17c**)), $[M\{Ph(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**18a**), Zr (**18b**), Hf (**18c**)), $[M\{Ph(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (M = Ti (**19a**), Zr (**19b**), Hf (**19c**)), $[M\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**20a**), Zr (**20b**)) and $[M\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (M = Ti (**21a**), Zr (**21b**), Hf (**21c**)) (Scheme 3).



Scheme 1.



Scheme 2.



Scheme 3.

16–**21** were isolated as crystalline solids and characterized spectroscopically.[1] The ^{1}H NMR spectra for **16** showed the expected signals, namely 4 multiplets in the region δ 6.0–7.2, corresponding to the C_5 ring protons, and two multiplets, at ca. δ 1.1 and 1.4, assigned to the ethyl group. A triplet, at ca. δ 5.1, was observed for the proton bonded directly to the silicon atom. The mixed cyclopentadienyl chiral complexes **17**, **18** and **20** gave eight signals assigned to the four protons of the unsubstituted cyclopentadienyl moiety and to the four methyl groups of the tetramethylcyclopentadienyl fragment. For **17** the α-protons of the ethyl unit are diastereoscopic and give rise to two overlapping multiplet signals (δ 1.4) with a further multiplet being observed for the β-protons (δ 1.5). The Si–H proton resonates (δ 5.2) as a pseudo-triplet due to its coupling with the two inequivalent α-protons of the ethyl group. For **18** three multiplets for the phenyl moiety (δ 7.3, 7.6 and 8.0) and a singlet (δ 5.9) assigned to the Si–H proton were observed. For **20** the α-protons of the allyl unit are again diastereoscopic and were observed as an unresolved multiplet (δ 2.5) arising from both geminal and vicinal couplings. Further multiplets were observed for the central CH (δ 6.1) and terminal olefinic protons (δ 5.2 and 5.3, *cis* and *trans*, respectively, with respect to H_β). As in the case of **17**, the Si–H signal in **20** was observed as a pseudo-triplet (δ 5.2). The C_s symmetric complexes **19** and **21** gave in the ^{1}H NMR spectra, four singlets, in the region δ 1.6–2.2, corresponding to the per-methyl substituted *ansa*-ligand. For **19**, three multiplets for the phenyl moiety (δ 7.3, 7.5 and 8.0) and a singlet for the Si–H proton (δ 6.0) were also observed. For **21**, the ^{1}H NMR spectra were completed with the assignment of four multiplets (δ 2.6, 5.2, 5.3 and 6.1) and a triplet (δ 5.3) to the allyl and Si–H protons, respectively. The $^{13}C\{^{1}H\}$ NMR spectra for **16**–**21** showed the expected signals for the different ligand systems present (see Section 5). Signals for the allyl carbons of **20** and **21** were observed in the ^{13}C NMR spectra at ca. δ 20, 132 and 117 corresponding to the silicon bonded, central and terminal carbons, respectively. The signal due to the *ansa*-bridge silicon atom in **16**–**21** was observed in the ^{29}Si NMR spectra with the nature of this signal depending on the substituents present; **16**, **17**, **20** and **21** a doublet of multiplets and **18** and **19** a doublet. The multiplicity of the signal corresponds to the coupling of the silicon atom with its hydride substituent and the α-protons of the ethyl or allyl group.

The molecular structures of **21b** and **21c** were established by single crystal X-ray diffraction studies. The molecular structures and atomic numbering schemes are shown in Figs. 1 and 2. Selected bond lengths and angles for **21b** and **21c** are given in Table 1. In the case of **21c**, there are two distinct molecules in the asymmetric unit. A disordered toluene molecule was also located in the asymmetric unit.

For **21b** and **21c**, the usual bent metallocene conformation is observed with the geometry around the metal atom being pseudo-tetrahedral. The *ansa* ligand chelates

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[1] We were unable to obtain the hafnium derivative of 20 with sufficient purity.

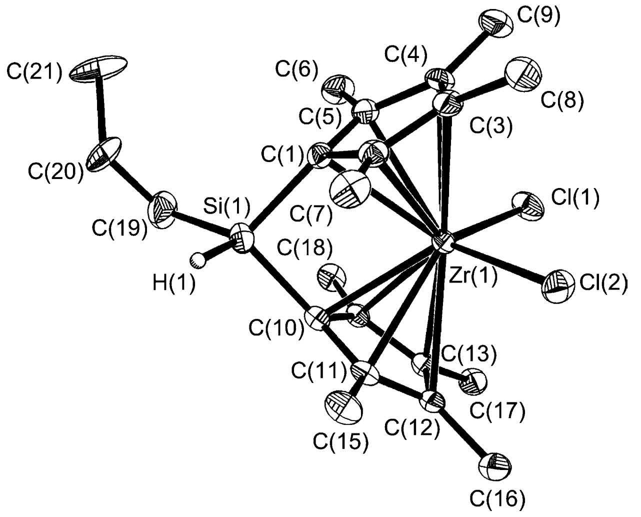


Fig. 1. Molecular structure and atom-labelling scheme for [Zr{CH_2=$CHCH_2$(H)Si(η^5-C_5Me_4)$_2$}Cl_2] (**21b**) with thermal ellipsoids at 30% probability.

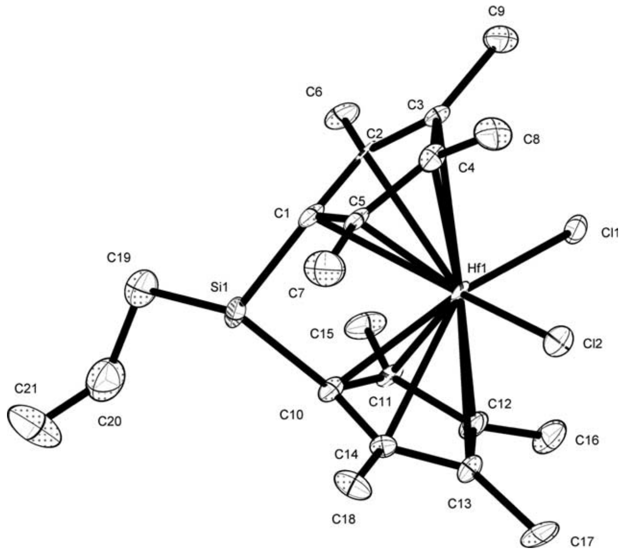


Fig. 2. Molecular structure and atom-labelling scheme for [Hf{CH_2=$CHCH_2$(H)Si(η^5-C_5Me_4)$_2$}Cl_2] (**21c**) with thermal ellipsoids at 50% probability.

the zirconium or hafnium atom and both C_5 rings are bound to the metal in an η^5 mode. The centroids of the tetramethylcyclopentadienyl rings form an angle with the metal atom of 128.5° **21b** and 129.05° and 128.65° **21c**, which is typical for dichloride group 4 *ansa*-metallocene complexes. In **21b** the hydrogen atom (H(1)) bonded to the silicon atom was located in the difference map. The carbon atoms of the allyl moiety in **21b** are disordered, therefore we make no reference to the bond distances and angles of this fragment. However, in **21c** the allyl carbon atoms were clearly resolved and exhibit bond distances of C(19)–C(20) 1.51(1) and 1.53(1) Å and C(20)–C(21) 1.33(1) and 1.26(1) Å which are typical for carbon carbon single (C(19)–C(20)) and double bonds (C(20)–C(21)), respectively. The angles Si(1)–C(19)–C(20) 108.7(5)° and 109.4(5)° and C(19)–C(20)–C(21) 124.8(9)° and 126.3(9)° indicate that C(19) and C(20) are sp^3 and sp^2 hybridized, respectively. Selected structural data of **21b** and **21c** can be compared with similar *ansa*-metallocene complexes using Table 2.

Table 1
Selected bond lengths (Å) and angles (°) for **21b** and **21c**

	21b	**21c**	
M–Cent(1)	2.229	2.219	2.202
M–Cent(2)	2.217	2.206	2.209
av M–C(Cent(1))[a]	2.531	2.522	2.513
av M–C(Cent(2))[a]	2.522	2.517	2.516
M–Cl(1)	2.425(3)	2.402(2)	2.413(2)
M–Cl(2)	2.413(3)	2.412(2)	2.416(2)
Si(1)–C(19)	1.864(8)	1.835(8)	1.879(8)
Si(1)–H(1)	1.597		
C(19)–C(20)		1.51(1)	1.53(1)
C(20)–C(21)		1.33(1)	1.26(1)
Cent(1)–M–Cent(2)	128.5	129.05	128.65
Si(1)–C(1)–Cent(1)	160.7	161.37	160.87
Si(1)–C(10)–Cent(2)	162.7	161.19	161.27
C(1)–Si(1)–C(10)	96.5(2)	96.2(3)	95.9(3)
Cl(1)–M–Cent(1)	106.5	105.70	105.99
Cl(1)–M–Cent(2)	106.3	106.50	106.02
Cl(2)–M–Cent(1)	106.7	106.22	106.58
Cl(2)–M–Cent(2)	107.0	106.23	107.78
Cl(1)–M–Cl(2)	97.54(8)	99.33(6)	97.51(6)
H(1)–Si(1)–C(1)	106.6		
H(1)–Si(1)–C(11)	106.3		
H(1)–Si(1)–C(21)	112.0		
Si(1)–C(19)–C(20)		108.7(5)	109.4(5)
C(19)–C(20)–C(21)		124.8(9)	126.3(9)

Cent(1) and Cent(2) are the centroids of C(1)–C(5) and C(10)–C(14), respectively.

[a] Refers to the average bond distance between Zr or Hf and the carbon atoms of the C_5 ring of the corresponding cyclopentadienyl moiety.

We have previously reported the modification of *ansa*-metallocene systems via hydrosilylation processes [9] and in order to gain a better understanding into the possible electronic or steric factors that may influence the outcome of these reactions we have tested **16**–**21** as hydrosilylation reagents. The hydrosilylation of Si(CH=CH_2)$_4$ by **16**–**21** in the presence of the Karstedt catalyst (divinyltetramethylsiloxane Pt(0)) was attempted. The per-methyl substituted *ansa*-complexes **19** and **21** did not react, inferring that the Si–H bond is not sufficiently reactive (even at high temperatures) to participate in the hydrosilylation reaction. This may be due to electronic effects caused by the electrodonating nature of the methyl ring substituents which translates to a less reactive Si–H bond [13]. The mixed cyclopentadienyl complexes (with four fewer methyl substituents) **17**, **18** and **20** did react with Si(CH=CH_2)$_4$ giving the product formed by the reaction of only one of the double bonds of the silane substrate. Only in the case of **17a** and **17b** were we able to isolate the final product with high purity

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

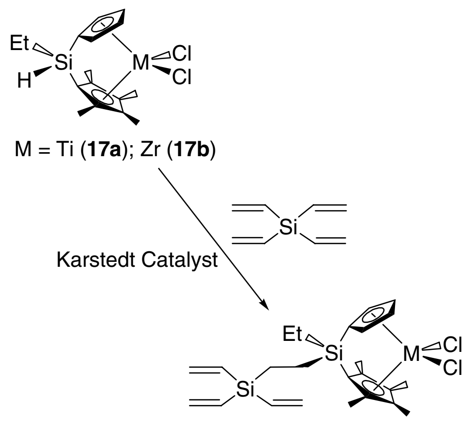
Complex	M–Cp (Å)[a]	M–Cl (Å)	Cp–M–Cp (°)	Cl–M–Cl (°)	$C_{(cp)}$–Si–$C_{(cp)}$ (°)	Reference
$[Zr\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (**21b**)	2.223	2.419	128.5	97.54(8)	96.5(2)	this work
$[Zr\{Me(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	2.230	2.427	128.5	98.85(6)	96.15(19)	[9]
$[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	2.329	2.4334(7)	128.6	92.28	95.7(1)	[10]
$[Zr\{Me(CH_2{=}CH)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	2.220	2.418	128.76	99.32(7)	95.8(2)	[8e]
$[Zr\{(CH_2{=}CH)_2Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	2.235	2.4333	128.7	99.24(3)	96.3(1)	[11]
$[Hf\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (**21c**)	2.213	2.407	129.05	99.33(6)	96.2(3)	this work
	2.206	2.415	128.65	97.51(6)	95.9(3)	
$[Hf\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	2.223	2.407(2)	129.2	98.0(1)	95.1(3)	[12]
$[Hf\{Et_2Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	2.224	2.407		98.75(8)	95.3(2)	[12]
$[Hf\{(CH_2{=}CH)_2Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$	2.217	2.405	129.2	97.98(7)	96.5(2)	[12]

	C–C (Å)	C=C (Å)	Si–C–C (°)	C–C=C (°)	Reference
$[Zr\{Me(CH_2{=}CHCH_2)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$	1.49(3)	1.26(5)	111.6(8)	124(5)	[8e]
$[Zr\{Me(CH_2{=}CHCH_2)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$	1.49(1)	1.32(1)	113.8(7)	123(1)	[8e]
$[Hf\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (**21c**)	1.51(1)	1.33(1)	108.7(5)	124.8(9)	this work
	1.53(1)	1.26(1)	109.4(5)	126.3(9)	

[a] Cp refers to the C_5Me_4 moiety.

and although the experimental conditions were directed towards the polyhydrosilylation of the silane substrate only the monohydrosilylation derivative, $[M\{(CH_2{=}CH)_3SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**23a**), Zr (**23b**)), was obtained (Scheme 4). This fact may be due to steric hindrance in the hypothetical tetra-substitution of the silane substrate by four metallocene units. However, Alt et al. [6a] have recently prepared tetranuclear complexes via the hydrosilylation of *ansa*-cyclopentadienyl ligands and their subsequent incorporation in group 4 *ansa*-metallocene systems. Our synthetic strategy differs from that used by Alt in that in our case the reactivity takes place at the group 4 *ansa*-metallocene complex and not from previous modification of the organic ligand.

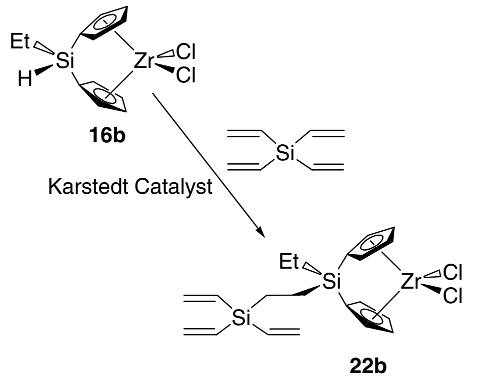
23a and **23b** were isolated as red and yellow oils, respectively, and characterized by NMR spectroscopy. The ^1H NMR spectra showed the expected signals for the cyclopentadienyl moieties namely four singlets and four multiplets. The three unreacted vinyl groups of the silane gave an ABX system in the ^1H NMR spectra and signals at ca. δ 133 (C_α) and 136 (C_β) in the $^{13}C\{^1H\}$ NMR spectra. The $–CH_2CH_2–$ fragment, resulting from the hydrosilylation of the vinyl group, gave a complex set of multiplets with geminal and vicinal couplings in the ^1H NMR spectra. Two signals were observed in the $^{29}Si\{^1H\}$ NMR spectra at ca. δ −18 and −9, corresponding to the vinyl substituted and *ansa* bridge silicon atoms, respectively. The hydrosilylation reaction can also give the alternative regioisomer, $[M\{(CH_2{=}CH)_3Si(CH_3)CH(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$, via α-addition [14]. This minor product was detected, in quantities of ca. 5–10%, by ^1H NMR spectroscopy.



Scheme 4.

The *ansa*-metallocene complex without ring substituents **16b** was also tested in this reaction. It was hoped that the complete absence of electrodonating ring substituents would aid in the polyhydrosilylation of the tetravinylsilane. However, only the monohydrosilylation product, $[Zr\{(CH_2{=}CH)_3SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (**22b**), was detected (Scheme 5). Nevertheless the Si–H bond in **16b** was shown to be more reactive than its methyl substituted counterparts **17**–**21** with the reaction of hydrosilylation being complete after 3 h at room temperature whereas for **23a** and **23b** the experimental conditions required were 100 °C and 40 h reaction time. **22b** was isolated as a yellow oil and characterized by NMR spectroscopy giving data similar to **23a** and **23b** (see Section 5).

Similar reactions have been carried out between **17a** and **17b** and dimethyldivinylsilane and gave the products $[M\{(CH_2{=}CH)Me_2SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**24a**), Zr (**24b**)), as red and yellow oils, respectively, formed by the hydrosilylation of only one of the double bonds of the silane substrate

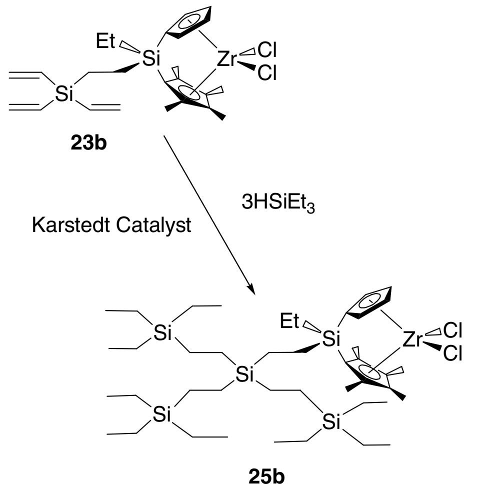


Scheme 5.

(Scheme 6). The NMR spectra of **24a** and **24b** are similar in all aspects to those previously discussed for **22** and **23** and showed in addition the presence of the minor regioisomer produced by α-addition (5–10%).

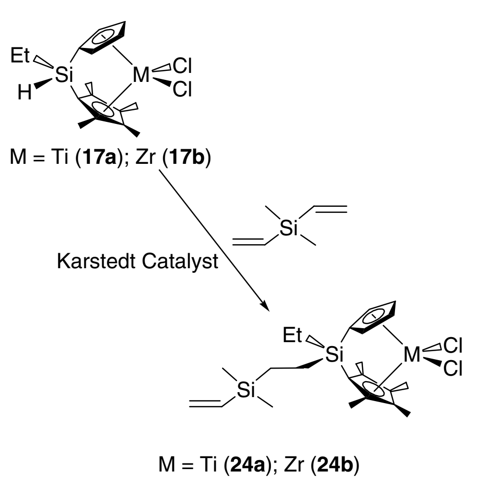
Further hydrosilylation of the vinyl groups of **22**–**24** was not possible when the hydrogen–silicon bond corresponded to the *ansa*-metallocene complexes. It appears that the reaction of one of the vinyl groups with the *ansa*-metallocene complex deactivates the remaining vinyl groups towards hydrosilylation by the Si–H of the *ansa* bridge. This may be attributed to electronic and/or steric effects. However, with triethylsilane, hydrosilylation took place at all the remaining vinyl groups of **23b** and **24b**, to give [Zr{$(Et_3SiCH_2CH_2)_3SiCH_2CH_2(Et)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)$}$Cl_2$] (**25b**) and [Zr{$(Et_3SiCH_2CH_2)Me_2SiCH_2CH_2(Et)Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)$}$Cl_2$] (**26b**) (Schemes 7 and 8).

25b and **26b** were isolated as yellow oils and characterized by NMR spectroscopy. The reaction was deemed to have gone to completion by the absence of any signals in ^{1}H and ^{13}C{^{1}H} NMR spectroscopy corresponding to the vinyl groups of the parent complexes. The ^{1}H NMR spectra showed the expected signals for the C_5H_4 and C_5Me_4 moieties. In addition two multiplets, assigned to the ethyl groups of $SiEt_3$, and a complex set of multiplets, corresponding to the two distinct $–CH_2CH_2–$ fragments, were observed. The presence of the minor α-addition regioisomers was again detected (5–10%). ^{29}Si{^{1}H} NMR spectra revealed three signals corresponding to the three distinct silicon atoms present.

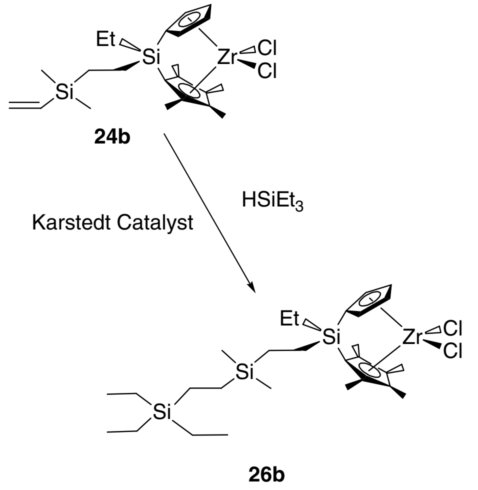


Scheme 7.

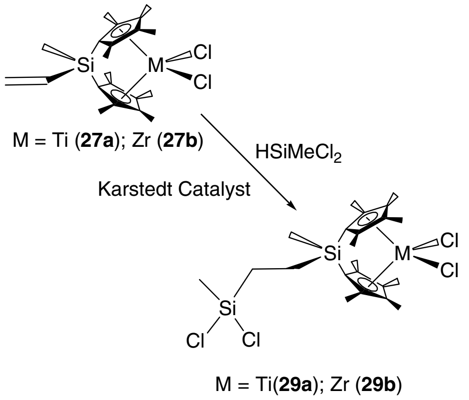
The hydrosilylation of the previously reported complexes [M{$CH_2{=}CH(Me)Si(\eta^5-C_5Me_4)_2$}$Cl_2$] (M = Ti (**27a**), Zr (**27b**)) and [Zr{$CH_2{=}CHCH_2(Me)Si(\eta^5-C_5Me_4)_2$}$Cl_2$] (**28b**) [8e], by $HSiMeCl_2$ has successfully been carried out. The reaction, in the presence of the Karstedt catalyst, gave after two hours reaction time the β-hydrosilylation products [M{$Cl_2MeSiCH_2CH_2(Me)Si(\eta^5-C_5Me_4)_2$}$Cl_2$] (M = Ti (**29a**), Zr (**29b**)) and [Zr{$Cl_2MeSiCH_2CH_2CH_2(Me)Si(\eta^5-C_5Me_4)_2$}$Cl_2$] (**30b**)



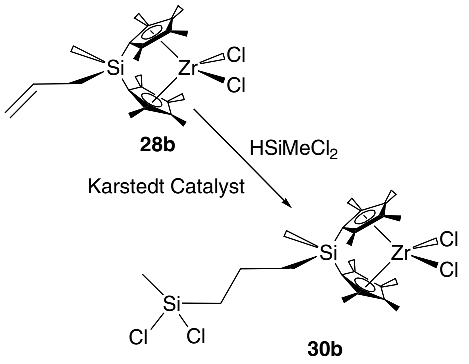
Scheme 6.



Scheme 8.



Scheme 9.



Scheme 10.

(Schemes 9 and 10). The presence of the minor α-addition regioisomer was also detected (5–10%).

29 and **30** were isolated as yellow solids and characterized by NMR spectroscopy. In the ^{1}H NMR spectra the presence of signals due to the vinyl or allyl protons of the starting products, **27** and **28**, was not observed. In the region of δ 0.5–1.8 multiplet signals were observed, two in the case of **29** (–SiCH$_2$CH$_2$Si–) and three for **30** (–SiCH$_2$CH$_2$CH$_2$Si–). For **29** and **30** a singlet at δ 0.4 was observed corresponding to the methyl protons of the dichloromethylsilyl fragment. Two signals were recorded in the ^{29}Si{^{1}H} NMR for **29** and **30** at ca. δ −10 and 32 and assigned to the *ansa* bridge and chloride bonded silicon atoms, respectively. In the ^{29}Si{^{1}H} NMR spectra of the vinyl and allyl substituted *ansa*-metallocene precursors of **29** and **30** a unique signal was observed for the *ansa* bridge silicon atom at δ −21.2, −22.7 and −15.6 for **27a**, **27b** and **28b**, respectively [15].

3. Polymerization studies

The polymerization of ethylene using the zirconium derivatives described in this paper as catalysts has been carried out. The polymerization experiments were conducted with a MAO–metal catalyst ratio of 3000:1, at 20 °C and at olefin pressure of 2 bar for 15 min. Polymerization was also carried out with the reference compound [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$], under the same experimental conditions. The catalytic activities and polymer molecular weight and distribution values are given in Table 3.

Complex **29b** proved to be the most active catalyst of the series. A slightly lower value was recorded for the reference complex [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$]. The low catalytic activities observed for **22**, **23b** and **25** may be due to steric factors as proposed previously by De Jesús and co-workers [16] for similar modified metal-

Table 3
Ethylene polymerization results for **16**–**30** and [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$][a]

Catalyst	Activity[b]	M_w	M_w/M_η
[Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$]	23750	1014670	2.1
[Zr{Et(H)Si(η^5-C$_5$H$_4$)$_2$}Cl$_2$] (**16b**)	11100	210200	3.2
[Zr{Et(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**17b**)	8760	186200	3.1
[Zr{Ph(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**18b**)	7053	185240	3.3
[Zr{(CH$_2$=CHCH$_2$)(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**20b**)	3120	133500	4.1
[Zr{Ph(H)Si(η^5-C$_5$Me$_4$)$_2$}Cl$_2$] (**19b**)	15967	194650	3.4
[Zr{(CH$_2$=CHCH$_2$)(H)Si(η^5-C$_5$Me$_4$)$_2$}Cl$_2$] (**21b**)	6373	156800	4.0
[Zr{(CH$_2$=CH)$_3$SiCH$_2$CH$_2$(Et)Si(η^5-C$_5$H$_4$)$_2$}Cl$_2$] (**22b**)	3307	139460	4.0
[Zr{(CH$_2$=CH)$_3$SiCH$_2$CH$_2$(Et)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**23b**)	5513	420000	3.1
[Zr{(CH$_2$=CH)Me$_2$Si(CH$_2$CH$_2$)(Et)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**24b**)	7213	141300	3.1
[Zr{(Et$_3$SiCH$_2$CH$_2$)$_3$SiCH$_2$CH$_2$(Et)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**25b**)	3367	717000	4.7
[Zr{(Et$_3$SiCH$_2$CH$_2$)Me$_2$SiCH$_2$CH$_2$(Et)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**26b**)	10147	669000	3.1
[Zr{CH$_2$=CH(Me)Si(η^5-C$_5$Me$_4$)$_2$}Cl$_2$] (**27b**)	15510	236000	5.4
[Zr{CH$_2$=CHCH$_2$(Me)Si(η^5-C$_5$Me$_4$)$_2$}Cl$_2$] (**28b**)	16472	136790	3.0
[Zr{Cl$_2$MeSiCH$_2$CH$_2$(Me)Si(η^5-C$_5$Me$_4$)$_2$}Cl$_2$] (**29b**)	26898	483000	4.8
[Zr{Cl$_2$MeSiCH$_2$CH$_2$CH$_2$(Me)Si(η^5-C$_5$Me$_4$)$_2$}Cl$_2$] (**30b**)	17707	558000	4.6

[a] At 20 °C, 2 bar monomer pressure, 200 mL toluene, [Al] = 9×10^{-2} mol L^{-1}, [Zr] = 3×10^{-5} mol L^{-1}, t_{Pol} = 15 min.
[b] In kg Pol (mol Zr h)$^{-1}$.

locene systems. In general, but not always, the complexes that contain a carbon carbon double bond substituent give low catalytic activities. This is most probably due to the fact that during the polymerization of ethylene, the vinyl or allyl groups of the *ansa*-ligand co-polymerize with the monomer thus immobilizing the metallocene complex on the polymer chain to give a pseudo-heterogeneous catalyst. This phenomenon with similar *ansa*-metallocene complexes has previously been reported [17].

4. Conclusions

In this paper we have reported the synthesis and catalytic activity of new *ansa*-metallocene complexes containing a Si–H bond which can be exploited in reactions of hydrosilylation to modify the ligand framework. The potential of translating this reactivity to the immobilization of *ansa*-metallocene catalysts on distinct substrates should be of great interest.

5. Experimental

All reactions were performed using standard Schlenk tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from the appropriate drying agents and degassed before use. $C_5H_2Me_4$, $[TiCl_4(THF)_2]$, $ZrCl_4$, $HfCl_4$, $HSiMeCl_2$,$Si(CH{=}CH_2)_4$, $SiMe_2(CH{=}CH_2)_2$ and $HSiEt_3$ were purchased from Aldrich, $HSiEtCl_2$ and $HSiPhCl_2$ from Fluka and $HSi(CH_2CH{=}CH_2)Cl_2$ and the Karstedt catalyst from ABCR. All the commercial reagents were used directly. $Na(C_5H_5)$ [18], **27a**, **27b** and **28b** [8e] were prepared as previously described. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrophotometer. ^1H, ^{13}C and ^{29}Si NMR spectra were recorded on a Varian Mercury FT-400 spectrometer. Microanalyses were carried out with a Perkin–Elmer 2400 or LECO CHNS-932 microanalyser. Mass spectroscopic analyses were preformed on a Hewlett–Packard 5988A (*m*/*z* 50–1000) instrument. Polymer molecular weights and distribution were determined by GPC (Waters 150C Plus or Alliance GPC-2000) in 1,2,4-trichlorobenzene at 150 °C.

5.1. Synthesis of $Et(H)Si(C_5H_5)_2$ (**1**)

$Et(H)SiCl_2$ (3.66 g, 28.38 mmol) was added to a solution of $Na(C_5H_5)$ (5.00 g, 56.76 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 (4.54 g, 85%). ^1H NMR (400 MHz, $CDCl_3$) (for the predominant isomer): δ −0.38 (2H), 0.96 (3H) (m, Si*Et*), 3.07 (m, 2H, HC_5), 3.47 (m, 1H, Si*H*), 5.52 (2H), 6.00 (2H), 6.64 (2H), 6.97 (2H) (m, C_5H_4). MS electron impact (*m*/*e* (relative intensity)): 188 (25) [M^+], 159 (19) [M^+ – Et], 123 (62) [$M^+ - C_5H_5$], 93 (100) [$M^+ - C_5H_5$, −Et].

The preparation of **2**–**9** was carried out in an identical manner to **1**.

5.2. $Et(H)Si(C_5HMe_4)Cl$ (**2**)

From $Et(H)SiCl_2$ (5.02 g, 39.00 mmol) and $Li(C_5HMe_4)$ (2.50 g, 19.50 mmol). Yield: 3.57 g, 94%. ^1H NMR (400 MHz, $CDCl_3$) (for the predominant isomer): δ −0.54 (2H), 0.94 (3H) (m, Si*Et*), 1.85 (6H), 1.99 (3H), 2.04 (3H) (s, C_5Me_4), 3.24 (m, 1H, HC_5), 4.73 (m, 1H, Si*H*). MS electron impact (*m*/*e* (relative intensity)): 214 (18) [M^+], 122 (100) [M^+ – Et(H)SiCl], 91 (52) [$M^+ - C_5HMe_4$].

5.3. $Et(H)Si(C_5HMe_4)(C_5H_5)_2$ (**3**)

From $Et(H)Si(C_5HMe_4)Cl$ (**2**) (2.00 g, 9.31 mmol) and $Na(C_5H_5)$ (0.82 g, 9.31 mmol). Yield: 2.05 g, 90%. ^1H NMR (400 MHz, $CDCl_3$) (for the predominant isomer): δ −0.48 (2H), 0.95 (3H) (m, Si*Et*), 1.88 (3H), 1.90 (3H), 1.96 (3H), 2.07 (3H) (s, C_5Me_4), 2.90 (1H), 3.01 (1H) (m, HC_5), 3.42 (m, 1H, Si*H*), 6.57 (1H), 6.59 (1H), 6.66 (1H), 6.83 (1H) (m, C_5H_4). MS electron impact (*m*/*e* (relative intensity)): 244 (18) [M^+], 215 (28) [M^+ – Et], 179 (100) [$M^+ - C_5H_5$], 123 (52) [$M^+ - C_5HMe_4$], 121 (41) [$M^+ - Et(H)SiC_5H_5$].

5.4. $Ph(H)Si(C_5HMe_4)Cl$ (**4**)

From $Ph(H)SiCl_2$ (6.92 g, 39.00 mmol) and $Li(C_5HMe_4)$ (2.50 g, 19.50 mmol). Yield: 4.66 g, 91%. ^1H NMR (400 MHz, $CDCl_3$) (for the predominant isomer): δ 1.63 (3H), 1.68 (3H), 1.96 (3H), 2.02 (3H) (s, C_5Me_4), 3.43 (m, 1H, HC_5), 5.14 (m, 1H, Si*H*), 7.30 (2H), 7.38 (2H), 7.74 (1H) (m, Si*Ph*). MS electron impact (*m*/*e* (relative intensity)): 262 (74) [M^+], 227 (26) [M^+ – Cl], 141 (23) [$M^+ - C_5HMe_4$], 122 (100) [M^+ – Ph(H)SiCl].

5.5. $Ph(H)Si(C_5HMe_4)(C_5H_5)_2$ (**5**)

From $Ph(H)Si(C_5HMe_4)Cl$ (**4**) (2.00 g, 7.61 mmol) and $Na(C_5H_5)$ (0.67 g, 7.61 mmol). Yield: 1.96 g, 88%. ^1H NMR (400 MHz, $CDCl_3$) (for the predominant isomer): δ 1.65 (3H), 1.71 (3H), 1.72 (3H), 1.91 (3H) (s, C_5Me_4), 3.06 (1H), 3.13 (1H) (m, HC_5), 3.60 (m, 1H, Si*H*), 6.63 (1H), 6.67 (1H), 6.73 (1H), 6.95 (1H) (m, $\mathrm{C_5}\mathit{H}_4$), 7.29 (2H), 7.33 (2H), 7.46 (1H) (m, Si*Ph*). MS electron impact (*m*/*e* (relative intensity)): 292 (24) [$\mathrm{M^+}$], 262 (28) [$\mathrm{M^+} - 2 \times \mathrm{Me}$], 227 (100) [$\mathrm{M^+} - \mathrm{C_5H_5}$], 171 (55) [$\mathrm{M^+} - \mathrm{C_5HMe_4}$].

5.6. *$\mathrm{Ph(H)Si(C_5HMe_4)_2}$ (**6**)*

From $\mathrm{Ph(H)SiCl_2}$ (1.73 g, 9.75 mmol) and $\mathrm{Li(C_5HMe_4)}$ (2.50 g, 19.50 mmol). Yield: 2.05 g, 90%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) (for the predominant isomer): δ 1.62 (6H), 1.68 (6H), 1.85 (6H), 1.99 (6H) (s, $\mathrm{C_5}\mathit{Me}_4$), 3.27 (m, 2H, $\mathit{H}\mathrm{C_5}$), 4.06 (m, 1H, Si*H*), 7.03 (2H), 7.17 (2H), 7.22 (1H) (m, Si*Ph*). MS electron impact (*m*/*e* (relative intensity)): 348 (9) [$\mathrm{M^+}$], 227 (100) [$\mathrm{M^+} - \mathrm{C_5HMe_4}$], 121 (14) [$\mathrm{M^+} - \mathrm{Ph(H)SiC_5HMe_4}$], 105 (17) [$\mathrm{M^+} - 2 \times \mathrm{C_5HMe_4}$].

5.7. *$\mathrm{CH_2{=}CHCH_2(H)Si(C_5HMe_4)Cl}$ (**7**)*

From $\mathrm{CH_2{=}CHCH_2(H)SiCl_2}$ (2.74 g, 19.50 mmol) and $\mathrm{Li(C_5HMe_4)}$ (2.50 g, 19.50 mmol). Yield: 3.57 g, 94%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) (for the predominant isomer): δ 1.52 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH{=}CH_2}$), 1.81 (6H), 1.82 (3H), 1.86 (3H) (s, $\mathrm{C_5}\mathit{Me}_4$), 2.74 (m, 1H, $\mathit{H}\mathrm{C_5}$), 4.77 (m, 1H, Si*H*), 4.93 (m, 2H, $\mathrm{CH_2CH{=}C}\mathit{H}_2$), 5.59 (m, 1H, $\mathrm{CH_2C}\mathit{H}\mathrm{{=}CH_2}$). MS electron impact (*m*/*e* (relative intensity)): 226 (1) [$\mathrm{M^+}$], 121 (100) [$\mathrm{M^+} - \mathrm{CH_2CH{=}\ CH_2(H)SiCl}$], 103 (46) [$\mathrm{M^+} - \mathrm{C_5HMe_4}$].

5.8. *$\mathrm{CH_2{=}CHCH_2(H)Si(C_5HMe_4)(C_5H_5)}$ (**8**)*

From $\mathrm{CH_2{=}CHCH_2(H)Si(C_5HMe_4)Cl}$ (**7**) (2.00 g, 8.81 mmol) and $\mathrm{Na(C_5H_5)}$ (0.78 g, 8.81 mmol). Yield: 1.78 g, 79%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) (for the predominant isomer): δ 1.50 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH{=}CH_2}$), 1.66 (3H), 1.74 (3H), 1.80 (3H), 1.91 (3H) (s, $\mathrm{C_5}\mathit{Me}_4$), 2.73 (1H), 3.03 (1H) (m, $\mathit{H}\mathrm{C_5}$), 4.64 (m, 1H, Si*H*), 4.94 (m, 2H, $\mathrm{CH_2CH{=}C}\mathit{H}_2$), 6.49 (m, 1H, $\mathrm{CH_2C}\mathit{H}\mathrm{{=}CH_2}$), 5.95 (2H), 6.41 (2H), (m, $\mathrm{C_5}\mathit{H}_4$). MS electron impact (*m*/*e* (relative intensity)): 256 (5) [$\mathrm{M^+}$], 215 (7) [$\mathrm{M^+} - \mathrm{CH_2CH{=}CH_2}$], 191 (19) [$\mathrm{M^+} - \mathrm{C_5H_5}$], 149 (100) [$\mathrm{M^+} - \mathrm{CH_2CH{=}CH_2}, -\mathrm{C_5H_5}, -\mathrm{H}$].

5.9. *$\mathrm{CH_2{=}CHCH_2(H)Si(C_5HMe_4)_2}$ (**9**)*

From $\mathrm{CH_2{=}CHCH_2(H)SiCl_2}$ (1.37 g, 9.75 mmol) and $\mathrm{Li(C_5HMe_4)}$ (2.50 g, 19.50 mmol). Yield: 2.86 g, 94%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) (for the predominant isomer): δ 1.48 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH{=}CH_2}$), 1.83 (12H), 1.92 (6H), 1.97 (6H) (s, $\mathrm{C_5}\mathit{Me}_4$), 2.70 (m, 2H, $\mathit{H}\mathrm{C_5}$), 3.98 (m, 1H, Si*H*), 4.88 (m, 2H, $\mathrm{CH_2CH{=}C}\mathit{H}_2$), 5.67 (m, 1H, $\mathrm{CH_2C}\mathit{H}\mathrm{{=}CH_2}$). MS electron impact (*m*/*e* (relative intensity)): 312 (21) [$\mathrm{M^+}$], 191 (85) [$\mathrm{M^+} - \mathrm{C_5HMe_4}$], 149 (100) [$\mathrm{M^+} - \mathrm{CH_2CH{=}CH_2}, -\mathrm{C_5HMe_4}$], 121 (98) [$\mathrm{M^+} - \mathrm{CH_2CH{=}CH_2(H)SiC_5HMe_4}$].

5.10. *Synthesis of $\mathrm{Li_2\{Et(H)Si(C_5H_4)_2\}}$ (**10**)*

LiBu^n (1.6 M in hexane) (13.3 mL, 21.24 mmol) was added dropwise to a solution of $\mathrm{Et(H)Si(C_5H_5)_2}$ (**1**) (2.00 g, 10.62 mmol) in hexane (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 (2.06 g, 97%). *Anal.* Calc. for $\mathrm{C_{12}H_{14}Li_2Si}$: C, 71.99; H, 7.05. Found: C, 71.58; H, 7.00%.

The preparation of **11**–**15** was carried out in an identical manner to **10**.

5.11. *$\mathrm{Li_2\{Et(H)Si(C_5Me_4)(C_5H_4)\}}$ (**11**)*

From $\mathrm{Et(H)Si(C_5HMe_4)(C_5H_5)_2}$ (**3**) (2.00 g, 8.18 mmol) and LiBu^n (1.6 M in hexane) (10.2 mL, 16.36 mmol). Yield: 1.89 g, 90%. *Anal.* Calc. for $\mathrm{C_{16}H_{22}Li_2Si}$: C, 74.98; H, 8.65. Found: C, 74.49; H, 8.60%.

5.12. *$\mathrm{Li_2\{Ph(H)Si(C_5Me_4)(C_5H_4)\}}$ (**12**)*

From $\mathrm{Ph(H)Si(C_5HMe_4)(C_5H_5)_2}$ (**5**) (2.00 g, 6.83 mmol) and LiBu^n (1.6 M in hexane) (8.6 mL, 13.66 mmol). Yield: 1.83 g, 88%. *Anal.* Calc. for $\mathrm{C_{20}H_{22}Li_2Si}$: C, 78.93; H, 7.29. Found: C, 78.66; H, 7.27%.

5.13. *$\mathrm{Li_2\{Ph(H)Si(C_5Me_4)_2\}}$ (**13**)*

From $\mathrm{Ph(H)Si(C_5HMe_4)_2}$ (**6**) (2.00 g, 5.73 mmol) and LiBu^n (1.6 M in hexane) (7.2 mL, 11.46 mmol). Yield: 1.69 g, 82%. *Anal.* Calc. for $\mathrm{C_{24}H_{30}Li_2Si}$: C, 79.97; H, 8.39. Found: C, 79.45; H, 8.31%.

5.14. *$\mathrm{Li_2\{CH_2{=}CHCH_2(H)Si(C_5Me_4)(C_5H_4)\}}$ (**14**)*

From $\mathrm{CH_2{=}CHCH_2(H)Si(C_5HMe_4)(C_5H_5)}$ (**8**) (2.00 g, 7.80 mmol) and LiBu^n (1.6 M in hexane) (9.8 mL, 15.60 mmol). Yield: 1.73 g, 83%. *Anal.* Calc. for $\mathrm{C_{17}H_{22}Li_2Si}$: C, 76.10; H, 8.26. Found: C, 75.89; H, 8.22%.

5.15. *$\mathrm{Li_2\{CH_2{=}CHCH_2(H)Si(C_5Me_4)_2\}}$ (**15**)*

From $\mathrm{CH_2{=}CHCH_2(H)Si(C_5HMe_4)_2}$ (**9**) (2.00 g, 6.40 mmol) and LiBu^n (1.6 M in hexane) (8.0 ml, 12.80 mmol). Yield: 1.70 g, 78%. *Anal.* Calc. for $\mathrm{C_{21}H_{30}Li_2Si}$: C, 77.74; H, 9.32. Found: C, 77.44; H, 9.28%.

5.16. *Synthesis of* $[Ti\{Et(H)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ *(**16a**)*

THF (50 mL) was added to a solid mixture of $[TiCl_4(THF)_2]$ (1.67 g, 4.99 mmol) and $Li_2\{Et(H)Si(\eta^5\text{-}C_5H_4)_2\}$ (**10**) (1.00 g, 4.99 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 (0.78 g, 51%). IR (ZnSe): $\nu_{Si\text{–}H}$ 2187 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.11 (3H), 1.37 (2H) (m, Si*Et*), 5.05 (t, 1H, Si*H*) ($^3J(^1H\text{–}^1H)$ 3.3 Hz), 6.02 (2H), 6.08 (2H), 7.22 (2H), 7.25 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 1.5, 7.3 (Si*Et*), 101.7 (C^{ipso}), 118.2, 120.4, 134.7, 136.2 (C_5H_4). ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −24.0 (doublet of multiplets) ($^1J(^{29}Si\text{–}^1H)$ 214.7 Hz). MS electron impact (*m/e* (relative intensity)): 304 (74) $[M^+]$, 268 (32) $[M^+ - Cl]$, 240 (37) $[M^+ - Cl, -Et]$, 176 (100) $[M^+ - Cl, -Et, -C_5H_4]$. *Anal.* Calc. for $C_{12}H_{14}Cl_2SiTi$: C, 47.24; H, 4.63. Found: C, 47.11; H, 4.59%.

The preparation of **16b**–**32** was carried out in an identical manner to **16a**.

5.17. $[Zr\{Et(H)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ *(**16b**)*

From $ZrCl_4$ (1.16 g, 4.99 mmol) and $Li_2\{Et(H)\text{-}Si(C_5H_4)_2\}$ (**10**) (1.00 g, 4.99 mmol). Yield: 0.63 g, 36%. IR (ZnSe): $\nu_{Si\text{–}H}$ 2177 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.17 (3H), 1.37 (2H) (m, Si*Et*), 5.07 (t, 1H, Si*H*) ($^3J(^1H\text{–}^1H)$ 3.3 Hz), 6.02 (2H), 6.11 (2H), 6.97 (2H), 7.00 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 1.7, 7.3 (Si*Et*), 104.6 (C^{ipso}), 113.7, 116.0, 127.8, 129.3 (C_5H_4). ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −24.2 (doublet of multiplets) ($^1J(^{29}Si\text{–}^1H)$ 213.4 Hz). MS electron impact (*m/e* (relative intensity)): 348 (70) $[M^+]$, 316 (25) $[M^+ - Et]$, 282 (39) $[M^+ - Cl, -Et]$, 253 (45) $[M^+ - Et, -C_5H_4]$. *Anal.* Calc. for $C_{12}H_{14}Cl_2SiZr$: C, 41.36; H, 4.05. Found: C, 41.05; H, 4.04%.

5.18. $[Hf\{Et(H)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ *(**16c**)*

From $HfCl_4$ (1.60 g, 4.99 mmol) and $Li_2\{Et(H)\text{-}Si(C_5H_4)_2\}$ (**10**) (1.00 g, 4.99 mmol). Yield: 0.67 g, 31%. IR (ZnSe): $\nu_{Si\text{–}H}$ 2166 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.11 (3H), 1.36 (2H) (m, Si*Et*), 5.06 (t, 1H, Si*H*) ($^3J(^1H\text{–}^1H)$ 3.3 Hz), 5.95 (2H), 6.03 (2H), 6.88 (2H), 6.90 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 1.8, 7.5 (Si*Et*), 106.1 (C^{ipso}), 111.5, 113.9, 126.4, 127.9 (C_5H_4). ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −24.9 (doublet of multiplets) ($^1J(^{29}Si\text{–}^1H)$ 215.1 Hz). MS electron impact (*m/e* (relative intensity)): 436 (26) $[M^+]$, 407 (16) $[M^+ - Et]$, 250 (65) $[M^+ - Et(H)\text{-}Si(C_5H_4)_2]$. *Anal.* Calc. for $C_{12}H_{14}Cl_2HfSi$: C, 33.08; H, 3.24. Found: C, 32.99; H, 3.19%.

5.19. $[Ti\{Et(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ *(**17a**)*

From $[TiCl_4(THF)_2]$ (1.30 g, 3.90 mmol) and $Li_2\{Et(H)Si(C_5Me_4)(C_5H_4)\}$ (**11**) (1.00 g, 3.90 mmol). Yield: 0.89 g, 63%. IR (ZnSe): $\nu_{Si\text{–}H}$ 2172 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.38 (3H), 1.48 (2H) (m, Si*Et*), 1.87 (3H), 1.90 (3H), 2.15 (3H), 2.16 (3H) (s, C_5Me_4), 5.21 (dd, 1H, Si*H*) ($^3J(^1H\text{–}^1H)$ 4.4 Hz), 5.59 (1H), 5.62 (1H), 7.17 (1H), 7.22 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 3.3, 7.8 (Si*Et*), 13.7, 15.7, 15.8 (C_5Me_4), 95.3 (C^{ipso}), 115.2, 117.0, 132.3, 134.3 (C_5H_4), 99.7, 129.8, 131.7, 144.0, 144.5 (C_5Me_4). ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −25.5 (doublet of multiplets) ($^1J(^{29}Si\text{–}^1H)$ 210.6 Hz). MS electron impact (*m/e* (relative intensity)): 360 (48) $[M^+]$, 324 (100) $[M^+ - Cl, -H]$, 288 (91) $[M^+ - 2 \times Cl, -H]$. *Anal.* Calc. for $C_{16}H_{22}Cl_2SiTi$: C, 53.20; H, 6.14. Found: C, 53.01; H, 6.09%.

5.20. $[Zr\{Et(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ *(**17b**)*

From $ZrCl_4$ (0.91 g, 3.90 mmol) and $Li_2\{Et(H)\text{-}Si(C_5Me_4)(C_5H_4)\}$ (**11**) (1.00 g, 3.90 mmol). Yield: 0.73 g, 46%. IR (ZnSe): $\nu_{Si\text{–}H}$ 2168 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.36 (3H), 1.46 (2H) (m, Si*Et*), 2.03 (3H), 2.07 (3H), 2.08 (6H) (s, C_5Me_4), 5.20 (dd, 1H, Si*H*) ($^3J(^1H\text{–}^1H)$ 4.4 Hz), 5.71 (1H), 5.78 (1H), 6.99 (1H), 7.04 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 3.6, 7.9 (Si*Et*), 12.3, 12.4, 14.4, 14.9 (C_5Me_4), 95.1 (C^{ipso}), 112.1, 113.9, 126.4, 127.8 (C_5H_4), 102.5, 124.7, 126.0, 135.7, 136.2 (C_5Me_4). ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −26.7 (doublet of multiplets) ($^1J(^{29}Si\text{–}^1H)$ 207.6 Hz). MS electron impact (*m/e* (relative intensity)): 402 (88) $[M^+]$, 366 (100) $[M^+ - Cl]$, 338 (86) $[M^+ - Cl, -Et]$. *Anal.* Calc. for $C_{16}H_{22}Cl_2SiZr$: C, 47.50; H, 5.48. Found: C, 47.33; H, 5.48%.

5.21. $[Hf\{Et(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ *(**17c**)*

From $HfCl_4$ (1.25 g, 3.90 mmol) and $Li_2\{Et(H)Si\text{-}(C_5Me_4)(C_5H_4)\}$ (**11**) (1.00 g, 3.90 mmol). Yield: 0.82 g, 43%. IR (ZnSe): $\nu_{Si\text{–}H}$ 2164 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (3H), 1.45 (2H) (m, Si*Et*), 2.03 (3H), 2.07 (3H), 2.08 (6H) (s, C_5Me_4), 5.18 (dd, 1H, Si*H*) ($^3J(^1H\text{–}^1H)$ 4.4 Hz), 5.67 (1H), 5.73 (1H), 6.91 (1H), 6.97 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 3.6, 7.8 (Si*Et*), 12.1, 12.2, 14.0, 14.5 (C_5Me_4), 97.0 (C^{ipso}), 109.5, 111.5, 125.0, 126.9 (C_5H_4), 104.6, 121.5, 123.3, 133.8, 134.3 (C_5Me_4). ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −27.3 (doublet of multiplets) ($^1J(^{29}Si\text{–}^1H)$ 207.2 Hz). MS electron impact (*m/e* (relative intensity)): 492 (85) $[M^+]$, 456 (100) $[M^+ - Cl, -H]$, 428 (19) $[M^+ - Cl, -Et]$. *Anal.* Calc. for $C_{16}H_{22}Cl_2HfSi$: C, 39.07; H, 4.51. Found: C, 39.00; H, 4.46%.

5.22. [Ti{Ph(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**18a**)

From [TiCl$_4$(THF)$_2$] (1.10 g, 3.28 mmol) and Li$_2${Ph(H)Si(C$_5$Me$_4$)(C$_5$H$_4$)} (**12**) (1.00 g, 3.28 mmol). Yield: 0.82 g, 61%. IR (ZnSe): $\nu_{\mathrm{Si–H}}$ 2167 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.49 (3H), 2.00 (3H), 2.11 (3H), 2.22 (3H) (s, C$_5$*Me*$_4$), 5.85 (s, 1H, Si*H*), 5.68 (1H), 5.81 (1H), 7.21 (2H) (m, C$_5$*H*$_4$), 7.31 (2H), 7.55 (2H), 7.95 (1H) (m, Si*Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 13.5, 13.8, 15.9, 16.8 (C$_5$*Me*$_4$), 94.5 (C^{ipso}), 115.2, 118.0, 134.7, 135.9 (*C*$_5$H$_4$), 98.4, 128.5, 129.8, 143.0, 146.0 (*C*$_5$Me$_4$), 128.8, 130.9, 131.2, 133.1 (Si*Ph*). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −32.4 (d) (^1J(^{29}Si–^{1}H) 215.4 Hz). MS electron impact (*m*/*e* (relative intensity)): 408 (26) [M$^+$], 372 (41) [M$^+$ − Cl, −H], 336 (100) [M$^+$ − 2 × Cl, −H]. *Anal.* Calc. for C$_{20}$H$_{22}$Cl$_2$SiTi: C, 58.70; H, 5.42. Found: C, 58.44; H, 5.34%.

5.23. [Zr{Ph(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**18b**)

From ZrCl$_4$ (0.77 g, 3.28 mmol) and Li$_2${Ph(H)-Si(C$_5$Me$_4$)(C$_5$H$_4$)} (**12**) (1.00 g, 3.28 mmol). Yield: 0.82 g, 55%. IR (ZnSe): $\nu_{\mathrm{Si–H}}$ 2155 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.60 (3H), 2.04 (3H), 2.12 (3H), 2.13 (3H) (s, C$_5$*Me*$_4$), 5.88 (s, 1H, Si*H*), 5.81 (1H), 5.98 (1H), 7.05 (1H), 7.13 (1H) (m, C$_5$*H*$_4$), 7.28 (2H), 7.57 (2H), 7.95 (1H) (m, Si*Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 12.3, 12.4, 14.5, 15.1 (C$_5$*Me*$_4$), 94.2 (C^{ipso}), 125.0, 128.7, 134.6, 135.1 (*C*$_5$H$_4$), 101.0, 112.2, 114.7, 128.9, 131.0 (*C*$_5$Me$_4$), 124.4, 128.6, 129.0, 134.2 (Si*Ph*). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −37.9 (d) (^1J(^{29}Si–^{1}H) 214.5 Hz). MS electron impact (*m*/*e* (relative intensity)): 452 (34) [M$^+$], 414 (57) [M$^+$ − Cl, −H], 105 (100) [M$^+$ − H, −Zr(C$_5$Me$_4$)(C$_5$H$_4$)Cl$_2$]. *Anal.* Calc. for C$_{20}$H$_{22}$Cl$_2$SiZr: C, 53.07; H, 4.90. Found: C, 52.96; H, 4.87%.

5.24. [Hf{Ph(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**18c**)

From HfCl$_4$ (1.05 g, 3.28 mmol) and Li$_2${Ph(H)-Si(C$_5$Me$_4$)(C$_5$H$_4$)} (**12**) (1.00 g, 3.28 mmol). Yield: 0.74 g, 42%. IR (ZnSe): $\nu_{\mathrm{Si–H}}$ 2172 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.66 (3H), 2.06 (3H), 2.13 (3H), 2.19 (3H) (s, C$_5$*Me*$_4$), 5.84 (s, 1H, Si*H*), 5.77 (1H), 5.93 (1H), 6.98 (1H), 7.06 (1H) (m, C$_5$*H*$_4$), 7.27 (2H), 7.55 (2H), 7.95 (1H) (m, Si*Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 12.1, 12.2, 14.2, 14.8 (C$_5$*Me*$_4$), 95.9 (C^{ipso}), 109.7, 112.5, 128.2, 130.9 (*C*$_5$H$_4$), 103.1, 121.6, 124.2, 133.3, 135.6 (*C*$_5$Me$_4$), 124.4, 128.6, 129.0, 134.2 (Si*Ph*). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −38.5 (d) (^1J(^{29}Si–^{1}H) 214.1 Hz). MS electron impact (*m*/*e* (relative intensity)): 540 (9) [M$^+$], 502 (6) [M$^+$ − Cl], 315 (5) [M$^+$ − Ph(H)Si(C$_5$Me$_4$)(C$_5$H$_4$)], 123 (100) [M$^+$ − Hf(C$_5$H$_4$Si(H)Ph)Cl$_2$]. *Anal.* Calc. for C$_{20}$H$_{22}$Cl$_2$HfSi: C, 44.49; H, 4.11. Found: C, 44.03; H, 4.08%.

5.25. [Ti{Ph(H)Si(η^5-C$_5$Me$_4$)$_2$}Cl$_2$] (**19a**)

From [TiCl$_4$(THF)$_2$] (0.92 g, 2.77 mmol) and Li$_2${Ph(H)Si(C$_5$Me$_4$)$_2$} (**13**) (1.00 g, 2.77 mmol). Yield: 0.80 g, 62%. IR (ZnSe): $\nu_{\mathrm{Si–H}}$ 2155 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.59 (6H), 1.93 (6H), 2.11 (6H), 2.18 (6H) (s, C$_5$*Me*$_4$), 6.06 (s, 1H, Si*H*), 7.26 (2H), 7.53 (2H), 7.98 (1H) (m, Si*Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 13.9, 16.1, 17.2 (C$_5$*Me*$_4$), 88.4, 125.2, 130.8, 143.2, 144.5 (*C*$_5$Me$_4$), 128.1, 128.4, 130.9, 135.0 (Si*Ph*). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −41.3 (d) (^1J(^{29}Si–^{1}H) 210.1 Hz). MS electron impact (*m*/*e* (relative intensity)): 464 (12) [M$^+$], 428 (22) [M$^+$ − Cl], 413 (25) [M$^+$ − Cl, −Me], 105 (100) [M$^+$ − Ti(C$_5$Me$_4$)$_2$Cl$_2$]. *Anal.* Calc. for C$_{24}$H$_{30}$Cl$_2$SiTi: C, 61.94; H, 6.50. Found: C, 61.55; H, 6.42%.

5.26. [Zr{Ph(H)Si(η^5-C$_5$Me$_4$)$_2$}Cl$_2$] (**19b**)

From ZrCl$_4$ (0.67 g, 2.77 mmol) and Li$_2${Ph(H)-Si(C$_5$Me$_4$)$_2$} (**13**) (1.00 g, 2.77 mmol). Yield: 0.66 g, 47%. IR (ZnSe): $\nu_{\mathrm{Si–H}}$ 2169 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.70 (6H), 2.04 (6H), 2.07 (6H), 2.13 (6H) (s, C$_5$*Me*$_4$), 6.02 (s, 1H, Si*H*), 7.26 (2H), 7.52 (2H), 7.94 (1H) (m, Si*Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 12.6, 12.7, 14.9, 16.1 (C$_5$*Me*$_4$), 89.0, 124.9, 125.2, 136.0, 136.9 (*C*$_5$Me$_4$), 128.3, 130.3, 130.7, 135.0 (Si*Ph*). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −43.0 (d) (^1J(^{29}Si–^{1}H) 208.5 Hz). MS electron impact (*m*/*e* (relative intensity)): 508 (86) [M$^+$], 471 (40) [M$^+$ − Cl], 455 (89) [M$^+$ − Cl, −Me], 105 (100) [M$^+$ − Zr(C$_5$Me$_4$)$_2$Cl$_2$]. *Anal.* Calc. for C$_{24}$H$_{30}$Cl$_2$SiZr: C, 56.66; H, 5.94. Found: C, 56.12; H, 5.91%.

5.27. [Hf{Ph(H)Si(η^5-C$_5$Me$_4$)$_2$}Cl$_2$] (**19c**)

From HfCl$_4$ (0.89 g, 2.77 mmol) and Li$_2${Ph(H)-Si(C$_5$Me$_4$)$_2$} (**13**) (1.00 g, 2.77 mmol). Yield: 0.64 g, 39%. IR (ZnSe): $\nu_{\mathrm{Si–H}}$ 2116 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.77 (6H), 2.09 (6H), 2.12 (6H), 2.16 (6H) (s, C$_5$*Me*$_4$), 5.99 (s, 1H, Si*H*), 7.18 (2H), 7.50 (2H), 7.95 (1H) (m, Si*Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 12.5, 12.6, 14.8, 16.0 (C$_5$*Me*$_4$), 91.1, 121.8, 123.4, 134.3, 135.3 (*C*$_5$Me$_4$), 128.2, 130.3, 130.5, 134.9 (Si*Ph*). ^{29}Si NMR (79.49 MHz, CDCl$_3$): δ −43.7 (d) (^1J(^{29}Si–^{1}H) 208.7 Hz). MS electron impact (*m*/*e* (relative intensity)): 596 (29) [M$^+$], 561 (3) [M$^+$ − Cl], 545 (12) [M$^+$ − Cl, −Me], 105 (100) [M$^+$ − Hf(C$_5$Me$_4$)$_2$Cl$_2$]. *Anal.* Calc. for C$_{24}$H$_{30}$Cl$_2$HfSi: C, 48.37; H, 5.07. Found: C, 48.00; H, 5.02%.

5.28. $[Ti\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**20a**)

From $[TiCl_4(THF)_2]$ (1.24 g, 3.73 mmol) and $Li_2\{CH_2{=}CHCH_2(H)Si(C_5Me_4)(C_5H_4)\}$ (**14**) (1.00 g, 3.73 mmol). Yield: 0.85 g, 61%. IR (ZnSe): $\nu_{Si–H}$ 2166, ν_{CH} 3081, $\nu_{CH{=}CH_2}$ 1625 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.90 (6H), 2.16 (6H) (s, C_5Me_4), 2.47 (m, 2H, $CH_2CH{=}CH_2$), 5.23 (dd, 1H, SiH) ($^3J(^1H–^1H)$ 4.4 Hz), 5.17 (1H) (*cis*), 5.26 (1H) (*trans*) (dd, $CH_2CH{=}CH_2$) ($^3J_{cis}(^1H–^1H)$ 10.0, $^3J_{trans}(^1H–^1H)$ 17.1 Hz), 6.06 (m, 1H, $CH_2CH{=}CH_2$), 5.63 (1H), 6.06 (1H), 7.18 (1H), 7.24 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.8, 15.8, 16.5 (C_5Me_4), 18.1 ($CH_2CH{=}CH_2$), 95.0 (C^{ipso}), 115.1, 116.9, 132.1, 134.4 (C_5H_4), 95.2, 129.5, 130.7, 143.8, 144.5 (C_5Me_4), 117.1 ($CH_2CH{=}CH_2$), 131.6 ($CH_2CH{=}CH_2$). ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −30.0 (doublet of multiplets) ($^1J(^{29}Si–^1H)$ 217.0 Hz). MS electron impact (*m/e* (relative intensity)): 372 (48) [M^+], 336 (100) [M^+ − Cl, −H], 295 (44) [M^+ − Cl, −H, −$CH_2CH{=}CH_2$], 123 (100) [$M^+ - Ti(C_5H_4Si(H)CH_2CH{=}CH_2)Cl_2$]. *Anal.* Calc. for $C_{17}H_{22}Cl_2SiTi$: C, 54.71; H, 5.94. Found: C, 54.35; H, 5.94%.

5.29. $[Zr\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**20b**)

From $ZrCl_4$ (0.87 g, 3.73 mmol) and $Li_2\{CH_2{=}CHCH_2(H)Si(C_5Me_4)(C_5H_4)\}$ (**14**) (1.00 g, 3.73 mmol). Yield: 0.79 g, 51%. IR (ZnSe): $\nu_{Si–H}$ 2170, ν_{CH} 3080, $\nu_{CH{=}CH_2}$ 1626 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00 (3H), 2.06 (3H), 2.07 (6H) (s, C_5Me_4), 2.45 (m, 2H, $CH_2CH{=}CH_2$), 5.22 (dd, 1H, SiH) ($^3J(^1H–^1H)$ 4.4 Hz), 5.14 (1H) (*cis*), 5.25 (1H) (*trans*) (dd, $CH_2CH{=}CH_2$) ($^3J_{cis}(^1H–^1H)$ 10.1, $^3J_{trans}(^1H–^1H)$ 17.1 Hz), 6.04 (m, 1H, $CH_2CH{=}CH_2$), 5.74 (1H), 5.78 (1H), 7.00 (2H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 12.3, 13.9, 14.4, 15.1 (C_5Me_4), 18.3 ($CH_2CH{=}CH_2$), 94.9 (C^{ipso}), 112.0, 113.9, 125.9, 128.0 (C_5H_4), 102.0, 124.4, 126.4, 136.0, 136.3 (C_5Me_4), 116.9 ($CH_2CH{=}CH_2$), 131.1 ($CH_2CH{=}CH_2$). ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −31.1 (doublet of multiplets) ($^1J(^{29}Si–^1H)$ 215.1 Hz). MS electron impact (*m/e* (relative intensity)): 416 (22) [M^+], 378 (23) [M^+ − Cl, −H], 337 (20) [M^+ − Cl, −H, −$CH_2CH{=}CH_2$], 303 (5) [M^+ − 2 × Cl, −H, −$CH_2CH{=}CH_2$]. *Anal.* Calc. for $C_{17}H_{22}Cl_2SiZr$: C, 49.01; H, 5.32. Found: C, 48.88; H, 5.28%.

5.30. $[Ti\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (**21a**)

From $[TiCl_4(THF)_2]$ (0.98 g, 2.93 mmol) and $Li_2\{CH_2{=}CHCH_2(H)Si(C_5Me_4)_2\}$ (**15**) (1.00 g, 2.93 mmol). Yield: 0.81 g, 64%. IR (ZnSe): $\nu_{Si–H}$ 2169, ν_{CH} 3076, $\nu_{CH{=}CH_2}$ 1627 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.83 (6H), 1.87 (6H), 2.12 (12H) (s, C_5Me_4), 2.59 (m, 2H, $CH_2CH{=}CH_2$), 5.37 (t, 1H, SiH) ($^3J(^1H–^1H)$ 5.2 Hz), 5.17 (1H) (*cis*), 5.28 (1H) (*trans*) (dd, $CH_2CH{=}CH_2$) ($^3J_{cis}(^1H–^1H)$ 9.9, $^3J_{trans}(^1H–^1H)$ 16.9 Hz), 6.10 (m, 1H, $CH_2CH{=}CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.7, 13.9, 16.0, 16.7 (C_5Me_4), 19.5 ($CH_2CH{=}CH_2$), 89.5, 129.0, 130.0, 143.4, 143.6 (C_5Me_4), 116.7 ($CH_2CH{=}CH_2$), 131.6 ($CH_2CH{=}CH_2$). ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −34.7 (doublet of multiplets) ($^1J(^{29}Si–^1H)$ 213.9 Hz). MS electron impact (*m/e* (relative intensity)): 428 (78) [M^+], 392 (100) [M^+ − Cl], 387 (44) [M^+ − $CH_2CH{=}CH_2$], 351 (22) [M^+ − Cl, −$CH_2CH{=}CH_2$]. *Anal.* Calc. for $C_{21}H_{30}Cl_2SiTi$: C, 58.75; H, 7.04. Found: C, 58.52; H, 7.01%.

5.31. $[Zr\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (**21b**)

From $ZrCl_4$ (0.68 g, 2.93 mmol) and $Li_2\{CH_2{=}CHCH_2(H)Si(C_5Me_4)_2\}$ (**15**) (1.00 g, 2.93 mmol). Yield: 0.72 g, 52%. IR (ZnSe): $\nu_{Si–H}$ 2182, ν_{CH} 3076, $\nu_{CH{=}CH_2}$ 1631 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93 (6H), 1.97 (6H), 2.07 (12H) (s, C_5Me_4), 2.55 (m, 2H, $CH_2CH{=}CH_2$), 5.34 (t, 1H, SiH) ($^3J(^1H–^1H)$ 5.2 Hz), 5.14 (1H) (*cis*), 5.25 (1H) (*trans*) (dd, $CH_2CH{=}CH_2$) ($^3J_{cis}(^1H–^1H)$ 10.0, $^3J_{trans}(^1H–^1H)$ 17.0 Hz), 6.07 (m, 1H, $CH_2CH{=}CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 12.5, 12.7, 14.8, 15.6 (C_5Me_4), 19.9 ($CH_2CH{=}CH_2$), 90.3, 124.5, 125.5, 136.0, 136.2 (C_5Me_4), 116.5 ($CH_2CH{=}CH_2$), 131.8 ($CH_2CH{=}CH_2$). ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −36.0 (doublet of multiplets) ($^1J(^{29}Si–^1H)$ 209.2 Hz). MS electron impact (*m/e* (relative intensity)): 472 (80) [M^+], 435 (44) [M^+ − Cl], 419 (100) [M^+ − Cl, −Me]. *Anal.* Calc. for $C_{21}H_{30}Cl_2SiZr$: C, 53.36; H, 6.40. Found: C, 53.31; H, 6.39%.

5.32. $[Hf\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (**21c**)

From $HfCl_4$ (0.94 g, 2.93 mmol) and $Li_2\{CH_2{=}CHCH_2(H)Si(C_5Me_4)_2\}$ (**15**) (1.00 g, 2.93 mmol). Yield: 0.71 g, 43%. IR (ZnSe): $\nu_{Si–H}$ 2165, ν_{CH} 3077, $\nu_{CH{=}CH_2}$ 1629 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (6 H), 2.04 (6H), 2.09 (6H), 2.10 (6H) (s, C_5Me_4), 2.54 (m, 2H, $CH_2CH{=}CH_2$), 5.30 (t, 1H, SiH) ($^3J(^1H–^1H)$ 5.1 Hz), 5.13 (1H) (*cis*), 5.24 (1H) (*trans*) (dd, $CH_2CH{=}CH_2$) ($^3J_{cis}(^1H–^1H)$ 10.0, $^3J_{trans}(^1H–^1H)$ 17.1 Hz), 6.06 (m, 1H, $CH_2CH{=}CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 12.4, 12.5, 14.6, 15.4 (C_5Me_4), 19.9 ($CH_2CH{=}CH_2$), 92.3, 121.6, 122.6, 134.5, 134.7 (C_5Me_4), 116.4 ($CH_2CH{=}CH_2$), 131.9 ($CH_2CH{=}CH_2$). ^{29}Si NMR (79.49 MHz, $CDCl_3$): δ −36.6 (doublet of multiplets) ($^1J(^{29}Si–^1H)$ 208.9 Hz). MS electron impact (*m/e* (relative intensity)): 560 (40) [M^+], 519 (53) [M^+ − $CH_2CH{=}CH_2$], 504 (20) [M^+ − Me, −$CH_2CH{=}CH_2$]. *Anal.* Calc. for $C_{21}H_{30}Cl_2HfSi$: C, 45.04; H, 5.40. Found: C, 45.02; H, 5.36%.

The experimental procedure described for **22**–**24** relates to the optimized synthesis of the monohydrosilylation product.

5.33. Synthesis of $[Zr\{(CH_2{=}CH)_3SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (**22b**)

Two drops of the Karstedt catalyst (divinyltetramethylsiloxane Pt(0) in xylene (3–3.5%)) were added to a solution of tetravinylsilane (0.059 g, 0.43 mmol) in toluene (5 mL) and the mixture was stirred for 5 min at room temperature. To this solution was added dropwise $[Zr\{Et(H)Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (**16b**) (0.15 g, 0.31 mmol) in toluene (10 mL) and the reaction mixture was stirred for 40 h at 100 °C and then allowed to cool to room temperature. The mixture was filtered and volatiles were removed from the filtrate under reduced pressure to give the title product as a dark yellow oil (0.19 g, 92%). IR (KBr): ν_{CH} 3046, $\nu_{CH=CH_2}$ 1599 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) (for the major isomer): δ 1.31 (3H), 1.43 (2H) (m, Si*Et*), 0.95 (2H), 1.28 (2H) (m, CH_2CH_2), 5.96 (2H), 6.00 (2H), 6.98 (4H) (m, C_5H_4), 5.86 (m, 3H, $CH_2{=}CH$), 6.19 (m, 6H, $CH_2{=}CH$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (for the major isomer): δ 1.5, 7.5 (Si*Et*), 2.9, 4.3 (CH_2CH_2), 108.3 (C^{ipso}), 114.3, 115.0, 133.2, 136.0 (C_5H_4), 133.5, 135.3 ($CH{=}CH_2$). $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) (for the major isomer): δ −18.2 ($SiCH{=}CH_2$), −10.7 (SiC_5H_4). MS electron impact (*m/e* (relative intensity)): 484 (15) $[M^+]$, 447 (7) $[M^+ - Cl]$, 310 (40) $[M^+ - Cl, -CH_2CH_2Si(CH{=}CH_2)_3]$, 109 (100) $[M^+ - Zr\{CH_2CH_2Si(Et)(C_5H_4)_2\}Cl_2]$. *Anal.* Calc. for $C_{20}H_{26}Cl_2Si_2Zr$: C, 49.56; H, 5.41. Found: C, 49.09; H, 5.36%.

The preparation of **23**–**26** was carried out in an identical manner to **22b**.

5.34. $[Ti\{(CH_2{=}CH)_3SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**23a**)

From $Si(CH{=}CH_2)_4$ (0.056 g, 0.41 mmol) and $[Ti\{Et(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**17a**) (0.15 g, 0.41 mmol). Yield: 0.20 g, 98%. IR (KBr): ν_{CH} 3050, $\nu_{CH=CH_2}$ 1592 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) (for the major isomer): δ 1.31 (3H), 1.41 (2H) (m, Si*Et*), 0.99 (2H), 1.25 (1H), 1.35 (1H) (m, CH_2CH_2), 1.84 (3H), 1.88 (3H), 2.14 (3H), 2.15 (3H) (s, C_5Me_4), 5.55 (1H), 5.58 (1H), 7.18 (2H) (m, C_5H_4), 5.84 (m, 3H, $CH_2{=}CH$), 6.18 (m, 6H, $CH_2{=}CH$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (for the major isomer): δ 4.0, 4.9 (Si*Et*), 4.3, 7.0 (CH_2CH_2), 13.6, 13.7, 16.2, 16.3 (C_5Me_4), 103.8 (C^{ipso}), 116.0, 116.3, 132.8, 133.5 (C_5H_4), 98.5, 131.1, 131.7, 144.0, 144.3 (C_5Me_4), 133.3, 135.3 ($CH{=}CH_2$). $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) (for the major isomer): δ −18.2 ($SiCH{=}CH_2$), −7.8 (SiC_5H_4). MS electron impact (*m/e* (relative intensity)): 496 (23) $[M^+]$, 460 (13) $[M^+ - Cl]$, 109 (100) $[M^+ - Ti\{CH_2CH_2Si(Et)(C_5Me_4)(C_5H_4)\}Cl_2]$. *Anal.* Calc. for $C_{24}H_{34}Cl_2Si_2Ti$: C, 57.94; H, 6.89. Found: C, 57.88; H, 6.85%.

5.35. $[Zr\{(CH_2{=}CH)_3SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**23b**)

From $Si(CH{=}CH_2)_4$ (0.051 g, 0.37 mmol) and $[Zr\{Et(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**17b**) (0.15 g, 0.37 mmol). Yield: 0.20 g, 99%. IR (KBr): ν_{CH} 3050, $\nu_{CH=CH_2}$ 1591 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) (for the major isomer): δ 1.30 (3H), 1.40 (2H) (m, Si*Et*), 0.96 (2H), 1.23 (1H), 1.33 (1H) (m, CH_2CH_2), 1.93 (3H), 1.96 (3H), 2.05 (3H), 2.06 (3H) (s, C_5Me_4), 5.66 (1H), 5.70 (1H), 7.01 (2H) (m, C_5H_4), 5.85 (m, 3H, $CH_2{=}CH$), 6.18 (m, 6H, $CH_2{=}CH$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (for the major isomer): δ 4.0, 4.6 (Si*Et*), 4.4, 6.9 (CH_2CH_2), 12.4, 15.1, 15.2 (C_5Me_4), 106.4 (C^{ipso}), 112.6, 112.9, 126.6, 127.0 (C_5H_4), 98.0, 125.8, 126.2, 135.9, 136.1 (C_5Me_4), 133.6, 135.2 ($CH{=}CH_2$). $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) (for the major isomer): δ −18.2 ($SiCH{=}CH_2$), −8.7 (SiC_5H_4). MS electron impact (*m/e* (relative intensity)): 538 (25) $[M^+]$, 503 (8) $[M^+ - Cl]$, 109 (100) $[M^+ - Zr\{CH_2CH_2Si(Et)(C_5Me_4)(C_5H_4)\}Cl_2]$. *Anal.* Calc. for $C_{24}H_{34}Cl_2Si_2Zr$: C, 53.30; H, 6.34. Found: C, 53.10; H, 6.31%.

5.36. $[Ti\{(CH_2{=}CH)Me_2SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**24a**)

From $SiMe_2(CH{=}CH_2)_2$ (0.037 g, 0.41 mmol) and $[Ti\{Et(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**17a**) (0.15 g, 0.41 mmol). Yield: 0.18 g, 93%. IR (KBr): ν_{CH} 3050, $\nu_{CH=CH_2}$ 1599 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) (for the major isomer): δ 0.18 (s, 6H, $SiMe_2$), 1.30 (3H), 1.41 (2H) (m, Si*Et*), 0.82 (2H), 1.28 (1H), 1.38 (1H) (m, CH_2CH_2), 1.86 (3H), 1.88 (3H), 2.15 (3H), 2.16 (3H) (s, C_5Me_4), 5.56 (1H), 5.58 (1H), 7.18 (2H) (m, C_5H_4), 5.76 (m, 1H, $CH_2{=}CH$), 6.11 (m, 2H, $CH_2{=}CH$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (for the major isomer): δ −3.8 ($SiMe_2$), 3.9, 4.4 (Si*Et*), 7.0, 7.1 (CH_2CH_2), 13.6, 13.7, 16.2, 16.3 (C_5Me_4), 104.0 (C^{ipso}), 116.1, 116.3, 132.8, 133.3 (C_5H_4), 98.6, 131.1, 131.7, 144.0, 144.2 (C_5Me_4), 132.5, 137.7 ($CH{=}CH_2$). $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) (for the major isomer): δ −7.9 ($Si\ C_5H_4$), −3.4 ($SiCH{=}CH_2$). MS electron impact (*m/e* (relative intensity)): 472 (38) $[M^+]$, 436 (40) $[M^+ - Cl]$, 85 (100) $[M^+ - Ti\{CH_2CH_2Si(Et)(C_5Me_4)(C_5H_4)\}Cl_2]$, 59 (87) $[M^+ - CH{=}CH_2, -Ti\{CH_2CH_2Si(Et)(C_5Me_4)(C_5H_4)\}Cl_2]$. *Anal.* Calc. for $C_{22}H_{34}Cl_2Si_2Ti$: C, 55.81; H, 7.24. Found: C, 55.55; H, 7.14%.

5.37. $[Zr\{(CH_2{=}CH)Me_2SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**24b**)

From $SiMe_2(CH{=}CH_2)_2$ (0.042 g, 0.37 mmol) and $[Zr\{Et(H)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**17b**) (0.15 g, 0.37 mmol). Yield: 0.19 g, 98%. IR (KBr): ν_{CH} 3047, $\nu_{CH{=}CH_2}$ 1591 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (for the major isomer): δ 0.18 (s, 6H, Si*Me*$_2$), 1.30 (3H), 1.41 (2H) (m, Si*Et*), 0.80 (2H), 1.22 (1H), 1.31 (1H) (m, C*H*$_2$C*H*$_2$), 1.94 (3H), 1.97 (3H), 2.06 (6H) (s, C_5*Me*$_4$), 5.67 (1H), 5.71 (1H), 7.02 (2H) (m, C_5*H*$_4$), 5.75 (m, 1H, $CH_2{=}$C*H*), 6.13 (m, 2H, C*H*$_2{=}$CH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (for the major isomer): δ −3.8 (Si*Me*$_2$), 4.1, 4.5 (Si*Et*), 6.9, 7.0 (*C*H$_2$*C*H$_2$), 12.4, 12.5, 15.0, 15.1 (C_5*Me*$_4$), 106.0 (C^{ipso}), 112.6, 112.9, 126.5, 127.0 (*C*$_5$H$_4$), 98.2, 125.7, 126.3, 135.9, 136.1 (*C*$_5$Me$_4$), 132.4, 137.8 (*C*H=*C*H$_2$). $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) (for the major isomer): δ −8.8 (*Si*C$_5$H$_4$), −3.5 (*Si*CH=CH$_2$). MS electron impact (*m*/*e* (relative intensity)): 516 (17) [M^+], 478 (5) [$M^+ - Cl$], 85 (100) [$M^+ - Zr\{CH_2CH_2Si(Et)(C_5Me_4)(C_5H_4)\}Cl_2$], 59 (89) [$M^+ - CH{=}CH_2, -Zr\{CH_2CH_2Si(Et)(C_5Me_4)(C_5H_4)\}Cl_2$]. *Anal.* Calc. for $C_{22}H_{34}Cl_2Si_2Zr$: C, 51.13; H, 6.63. Found: C, 51.09; H, 6.61%.

5.38. $[Zr\{(Et_3SiCH_2CH_2)_3SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5\text{-}Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**25b**)

From $HSiEt_3$ (0.098 g, 0.84 mmol) and $[Zr\{(CH_2{=}CH)_3SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**23b**) (0.15 g, 0.28 mmol). Yield: 0.24 g, 97%. ^1H NMR (400 MHz, $CDCl_3$) (for the major isomer): δ 0.55 (q, 18H, SiC*H*$_2$CH$_3$), 0.97 (t, 27H, SiCH$_2$C*H*$_3$), 1.28 (3H), 1.42 (2H) (m, CpSi*Et*), 0.4–1.4 (m, 16H, SiC*H*$_2$C*H*$_2$Si), 1.97 (3H), 1.98 (3H), 2.07 (6H) (s, C_5*Me*$_4$), 5.66 (1H), 5.72 (1H), 7.02 (2H) (m, C_5*H*$_4$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (for the major isomer): δ 3.6, 4.9 (CpSi*Et*), 3.0, 7.7 (Si*Et*$_3$), 2.9, 3.3, 3.6, 6.9 (*C*H$_2$*C*H$_2$), 12.4, 15.0, 15.1 (C_5*Me*$_4$), 106.6 (C^{ipso}), 112.5, 113.0, 125.5, 126.2 (*C*$_5$H$_4$), 98.3, 125.6, 127.0, 135.8, 136.2 (*C*$_5$Me$_4$). $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) (for the major isomer): δ −9.1 (*Si*C$_5$H$_4$), 8.1 (*Si*Et$_3$), 9.6 (*Si*CH$_2$CH$_2$). MS chemical ionization with CH_4 (*m*/*e* (relative intensity)): 886 (1) [M^+], 121 (34) [$M^+ - Zr\{Et_3Si(CH_2CH_2)_3SiCH_2CH_2(Et)Si(C_5H_4)\}Cl_2$], 115 (100) [$SiEt_3{}^+$], 87 (33) [$SiEt_2{}^+$]. *Anal.* Calc. for $C_{42}H_{82}Cl_2Si_5Zr$: C, 56.70; H, 9.29. Found: C, 56.66; H, 9.30%.

5.39. $[Zr\{(Et_3SiCH_2CH_2)Me_2SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**26b**)

From $HSiEt_3$ (0.034 g, 0.29 mmol) and $[Zr\{(CH_2{=}CH)Me_2SiCH_2CH_2(Et)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**24b**) (0.15 g, 0.29 mmol). Yield: 0.17 g, 91%. ^1H NMR (400 MHz, $CDCl_3$) (for the major isomer): δ 0.07 (s, 6H, Si*Me*$_2$), 0.54 (q, 6H, SiC*H*$_2$CH$_3$), 0.96 (t, 9H, SiCH$_2$C*H*$_3$), 1.27 (3H), 1.40 (2H) (m, CpSi*Et*), 0.4–1.1 (m, 8H, SiC*H*$_2$C*H*$_2$Si), 1.96 (3H), 1.97 (3H), 2.06 (6H) (s, C_5*Me*$_4$), 5.67 (1H), 5.70 (1H), 7.02 (2H) (m, C_5*H*$_4$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (for the major isomer): δ −4.3 (Si*Me*$_2$), 4.0,4.6 (CpSi*Et*), 3.0, 7.6 (Si*Et*$_3$), 3.3, 6.1, 6.8, 6.9 (*C*H$_2$*C*H$_2$), 12.3, 12.4, 15.0, 15.1 (C_5*Me*$_4$), 106.7 (C^{ipso}), 112.6, 112.9, 126.5, 126.0 (*C*$_5$H$_4$), 98.3, 125.6, 126.3, 135.9, 136.1 (*C*$_5$Me$_4$). $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) (for the major isomer): δ −9.0 (*Si*C$_5$H$_4$), 6.3 (*Si*CH$_2$CH$_2$), 8.2 (*Si*Et$_3$). MS electron impact (*m*/*e* (relative intensity)): 630 (1) [M^+], 595 (2) [$M^+ - Cl$], 515 (2) [$M^+ - Et_3Si$], 481 (4) [$M^+ - Cl, -Et_3Si$], 115 (74) [$SiEt_3{}^+$], 93 (100) [$M^+ - Zr(C_5Me_4)Cl_2, -CH_2CH_2SiMe_2(CH_2CH_2SiEt_3), -Et$]. *Anal.* Calc. for $C_{28}H_{50}Cl_2Si_3Zr$: C, 53.12; H, 7.96. Found: C, 53.44; H, 8.08%.

5.40. Synthesis of $[Ti\{Cl_2MeSiCH_2CH_2(Me)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (**29a**)

Two drops of the Karstedt catalyst (divinyltetramethylsiloxane Pt(0) in xylene (3–3.5%)) were added to a solution of $[Ti\{CH_2{=}CH(Me)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (0.30 g, 0.70 mmol) in toluene (10 mL) and the mixture was stirred for 10 min at room temperature. To this solution was added dropwise $HSiMeCl_2$ (0.08 g, 0.70 mmol) and the reaction mixture was stirred for 2 h. The mixture was filtered and volatiles removed from the filtrate under reduced pressure to give the title product as a red crystalline solid (0.37 g, 97%). ^1H NMR (400 MHz, $CDCl_3$) (for the major isomer): δ 0.43 (s, 3H, CpSi*Me*), 0.55 (s, 3H, Cl$_2$Si*Me*), 1.00 (2H), 1.31 (2H) (m, C*H*$_2$C*H*$_2$), 1.64 (6H), 1.65 (6H), 2.06 (6H), 2.09 (6H) (s, C_5*Me*$_4$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (for the major isomer): δ 0.0 (CpSi*Me*), 2.4 (Cl$_2$Si*Me*), 4.4, 9.5 (*C*H$_2$*C*H$_2$), 14.1, 14.2, 16.3, 16.5 (C_5*Me*$_4$), 92.1, 128.5, 128.7, 143.2, 143.4 (*C*$_5$Me$_4$). $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) (for the major isomer): δ −9.5 (Cp*Si*Me), 33.0 (Cl$_2$*Si*Me). MS electron impact (*m*/*e* (relative intensity)): 546 (11) [M^+], 508 (23) [$M^+ - Cl$], 493 (100) [$M^+ - Cl, -Me$], 349 (13) [$M^+ - CH_2CH_2SiMeCl_2, -Cl, -Me$], 321 (22) [$M^+ - CH_2CH_2SiMeCl_2, -Cl, -3 \times Me$], 286 (22) [$M^+ - CH_2CH_2SiMeCl_2, -2 \times Cl, -3 \times Me$]. *Anal.* Calc. for $C_{22}H_{34}Cl_4Si_2Ti$: C, 48.54; H, 6.30. Found: C, 48.33; H, 6.28%.

The preparation of **29b** and **30** was carried out in an identical manner to **29a**.

5.41. $[Zr\{Cl_2MeSiCH_2CH_2(Me)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (**29b**)

From $HSiMeCl_2$ (0.11 g, 0.10 mmol) and $[Zr\{CH_2{=}CH(Me)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (0.45 g, 0.10 mmol). Yield: 0.55 g, 96%. ^1H NMR (400 MHz, $CDCl_3$) (for the major isomer): δ 0.42 (s, 3H, CpSi*Me*), 0.55 (s, 3H, $Cl_2Si\mathit{Me}$), 0.99 (2H), 1.32 (2H) (m, $C\mathit{H_2}C\mathit{H_2}$), 1.75 (6H), 1.76 (6H), 1.99 (6H), 2.02 (6H) (s, $C_5\mathit{Me}_4$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (for the major isomer): δ 0.1 (CpSi*Me*), 0.5 ($Cl_2Si\mathit{Me}$), 4.6, 10.0 ($\mathit{C}H_2\mathit{C}H_2$), 13.0, 13.1, 15.5, 15.6 ($C_5\mathit{Me}_4$), 93.0, 124.5, 125.2, 136.1, 136.2 (C_5Me_4). $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) (for the major isomer): δ −11.0 (Cp*Si*Me), 33.1 ($Cl_2\mathit{Si}Me$). MS electron impact (*m*/*e* (relative intensity)): 586 (35) [M^+], 549 (12) [M^+ − Cl], 535 (23) [M^+ − Cl, −Me], 445 (15) [$M^+ - CH_2CH_2SiMeCl_2$], 304 (100) [$M^+ - Zr(C_5Me_4)Cl_2$], 280 (40) [$M^+ - C_5Me_4Si(Me)CH_2CH_2SiMeCl_2$]. *Anal.* Calc. for $C_{22}H_{34}Cl_4Si_2Zr$: C, 44.96; H, 5.83. Found: C, 44.58; H, 5.76%.

5.42. [$Zr\{Cl_2MeSiCH_2CH_2CH_2(Me)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2$] (**30b**)

From $HSiMeCl_2$ (0.12 g, 0.11 mmol) and [$Zr\{CH_2{=}CHCH_2(Me)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2$] (0.52 g, 0.11 mmol). Yield: 0.61 g, 92%. ^1H NMR (400 MHz, $CDCl_3$) (for the major isomer): δ 0.38 (s, 3H, CpSi*Me*), 0.67 (s, 3H, $Cl_2Si\mathit{Me}$), 0.91 (2H), 0.93 (2H), 1.27 (2H) (m, $C\mathit{H_2}C\mathit{H_2}C\mathit{H_2}$), 1.75 (6H), 1.82 (6H), 2.00 (6H), 2.01 (6H) (s, $C_5\mathit{Me}_4$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) (for the major isomer): δ 0.2 (CpSi*Me*), 2.2 ($Cl_2Si\mathit{Me}$), 17.2, 22.2, 25.9 ($\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2$), 13.0, 13.1, 15.6, 15.7 ($C_5\mathit{Me}_4$), 93.0, 124.5, 125.3, 136.1, 136.2 (C_5Me_4). $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) (for the major isomer): δ −13.5 (Cp*Si*Me), 31.5 ($Cl_2\mathit{Si}Me$). MS electron impact (*m*/*e* (relative intensity)): 598 (100) [M^+], 564 (14) [M^+ − Cl], 549 (24) [M^+ − Cl, −Me], 486 (13) [$M^+ - SiMeCl_2$], 445 (23) [$M^+ - CH_2CH_2CH_2SiMeCl_2$]. *Anal.* Calc. for $C_{23}H_{36}Cl_4Si_2Zr$: C, 45.91; H, 6.03. Found: C, 45.44; H, 6.00%.

5.43. Polymerization of ethylene

The zirconocene catalyst (6 μmol), MAO (10% in toluene) (1800 μmol) and toluene (200 mL) were mixed together for 15 min in a 1 L glass autoclave. The N_2 pressure inside the autoclave was reduced by applying a vacuum. Ethylene pressure of 2 bar was then applied and maintained to the autoclave and stirring of the mixture commenced (1000 rpm). After exactly 15 min, stirring was halted and the ethylene pressure released. Excess MAO was then destroyed by adding cautiously a mixture of methanol/HCl (90:10). The polymer was isolated by filtration and washed with ethanol and dried under vacuum at 90 °C for 16 h.

5.44. X-ray structure determination of [$Zr\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2$] (**21b**)

Data were collected on a Bruker SMART CCD-based diffractometer operating at 50 kV and 30 mA, using $\omega/2\theta$ scan-technique. Absorption corrections were applied using the SADABS program (maximum and minimum transmission coefficients 0.9608 and 0.7384). The structure was solved using the Bruker SHELXTL-PC software by direct methods and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (except H(1) which was located in a difference map), and refined in the riding mode. Weights were optimized in the final cycles. Crystallographic data are given in Table 4.

5.45. X-ray structure determination of [$Hf\{CH_2{=}CHCH_2(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2$] (**21c**)

Data were collected on a Bruker SMART CCD-based diffractometer operating at 50 kV and 100 mA, using $\omega/2\theta$ scan-technique. The structure was solved using the SHELXS-97 software by direct methods and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, and refined in the riding mode. Weights were optimized in the final cycles. Crystallographic data are given in Table 4.

Table 4
Crystal data and structure refinement for **21b** and **21c**

	21b	**21c**
Formula	$C_{21}H_{30}Cl_2SiZr$	$C_{24.5}H_{34}Cl_2HfSi$
Formula weight	472.66	606.022
T (K)	298(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2(1)/*c*
a (Å)	30.62(3)	18.43380(10)
b (Å)	8.851(10)	10.01510(10)
c (Å)	17.175(18)	26.2604(2)
β (°)	110.58(7)	91.9560(10)
V (Å^3)	4357(8)	4845.27(7)
Z	8	8
D_c (g cm^{-3})	1.441	1.650
μ (mm^{-1})	0.807	10.513
F(000)	1952	2376
Crystal dimensions (mm)	0.40 × 0.15 × 0.05	0.25 × 0.20 × 0.12
θ range (°)	2.41 to 25.92	2.40 to 70.48
hkl ranges	$-37 \leqslant h \leqslant 36$, $-9 \leqslant k \leqslant 10$, $-14 \leqslant l \leqslant 21$	$-19 \leqslant h \leqslant 22$, $-10 \leqslant k \leqslant 11$, $-30 \leqslant l \leqslant 30$
Data/parameters	4177/256	8816/495
Goodness-of-fit on F^2	0.987	1.026
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0465$, $wR_2 = 0.1026$	$R_1 = 0.0509$, $wR_2 = 0.1146$
R indices (all data)	$R_1 = 0.0905$, $wR_2 = 0.1182$	$R_1 = 0.0543$, $wR_2 = 0.1171$
Largest difference peak and hole (e Å^{-3})	0.507/−0.375	5.825/−4.816

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

6. Supplementary material

Crystallographic data for the structural analyses of **21b** and **21c** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 261467 and 261468. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http//www.ccdc.cam.ac.uk).

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