Journal of Organometallic Chemistry 694 (2009) 1959–1970

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

New alkenyl-substituted group 4 C-*ansa*-metallocene complexes. Reactivity of the substituent at the carbon *ansa* bridge

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ARTICLE INFO

Article history:
Received 17 December 2008
Received in revised form 20 January 2009
Accepted 21 January 2009
Available online 30 January 2009

Keywords:
Metallocenes
Zirconium
Titanium
Hydrosilylation
Hydrogenation
Hydroboration

ABSTRACT

The allyl-substituted group 4 metal complexes [M{(R)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] [M = Ti, R = $CH_2CH{=}CH_2$, (**2**); R = $CH_2C(CH_3){=}CH_2$ (**3**); M = Zr, R = $CH_2CH{=}CH_2$ (**4**), R = $CH_2C(CH_3){=}CH_2$ (**5**)] have been synthesized by the reaction of allyl *ansa*-magnesocene derivatives and the tetrachloride salts of the corresponding transition metal. The dialkyl complexes [M(R)CH(η^5-C_5Me_4)(η^5-C_5H_4)R′$_2$] [M = Ti, R = $CH_2{=}CHCH_2$, R′ = Me (**6**), R′ = CH_2Ph (**7**); R = $CH_2C(CH_3){=}CH_2$, R′ = Me (**8**), R′ = CH_2Ph (**9**); M = Zr, R = $CH_2CH{=}CH_2$, R′ = Me (**10**), R′ = CH_2Ph (**11**); R = $CH_2C(CH_3){=}CH_2$, R′ = Me (**12**), R′ = CH_2Ph (**13**)] have been synthesized by the reaction of the corresponding *ansa*-metallocene dichloride complexes **2–5** and two molar equivalents of the alkyl Grignard reagent. Compounds **2–5** reacted with H_2 under catalytic conditions (Wilkinson's catalyst or Pd/C) to give the hydrogenation products [M{(R)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] [M = Ti and R = $CH_2CH_2CH_3$ (**14**) or R = $CH_2CH(CH_3)_2$ (**15**); M = Zr and R = $CH_2CH_2CH_3$ (**16**) or R = $CH_2CH(CH_3)_2$ (**17**)]. The reactivity of **2–5** has also been tested in hydroboration and hydrosilylation reactions. The hydroboration reactions of **3**, **4** and **5** with 9-borabicyclo[3.3.1]nonane (9-BBN) yielded the complexes [M{(9-BBN)$CH_2CH(R)CH_2CH$(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] [M = Ti and R = H (**18**); M = Zr and R = H (**19**) or R = CH_3 (**20**)]. The reaction with the silane reagents $HSiMe_2Cl$ gave the corresponding [M{$ClMe_2$-$SiCH_2CHRCH_2CH$(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] [M = Ti and R = H (**21**); M = Zr and R = H (**22**) or R = CH_3 (**23**)]. The reaction of **22** with *t*-$BuMe_2SiOH$ produced a new complex [Zr{*t*-$BuMe_2SiOSi(Me_2)CH_2CH_2CH_2CH$($\eta^5$-$C_5Me_4$)($\eta^5$-$C_5H_4$)}$Cl_2$] (**24**) through the formation of Si–O–Si bonds. On the other hand, reactivity studies of some zirconocene complexes were carried out, with the insertion reaction of phenyl isocyanate (PhNCO) into the zirconium–carbon σ-bond of [Zr{(*n*-Bu)CH(η^5-C_5Me_4)(η^5-C_5H_4)}$_2Me_2$] (**25**) giving [{(*n*-Bu)CH(η^5-C_5Me_4)(η^5-C_5H_4)}]Zr{Me{κ^2-O,N-OC(Me)NPh}] as a mixture of two isomers **26a–b**. The reaction of [Zr{(*n*-Bu)(H)C(η^5-C_5Me_4)(η^5-C_5H_4)}$(CH_2Ph)_2$] (**27**) with CO also provided a mixture of two isomers [{(*n*-Bu)CH(η^5-C_5Me_4)(η^5-C_5H_4)}]Zr(CH_2Ph){κ^2-O,C-$COCH_2Ph$}] **28a–b**. The molecular structures of **4**, **11**, **16** and **17** have been determined by single-crystal X-ray diffraction studies.

1. Introduction

Group 4 metallocene complexes have been extensively investigated as catalysts for the polymerisation of α-olefin over the last few decades [1] and the *ansa*-cyclopentadienyl systems have also been at the forefront of metallocene catalysis chemistry [2]. The introduction of functional groups in the metallocene ligand system can be exploited by immobilizing the catalyst on different substrates without greatly altering the general structure of the complex [3]. Moreover, due to industrial applications [4], the current trend in the field of metallocene catalysis is moving toward supported catalysts that allow homogeneous single-site selectivity in a heterogeneous medium [5]. One route for the immobilisation of metallocene complexes is the reactivity of a C=C bond of an alkenyl substituent on the cyclopentadienido ring or at the *ansa*-bridged atom [6]. Several studies have been carried out in which hydrosilylation of the *ansa*-zirconocene complexes with vinyl or allyl groups in the silicon bridge is followed by supporting the system on silica [7], modified silica surfaces [3a] or organosilicon dendrimers [8]. In other cases, the initial modification by hydrosilylation of *ansa*-cyclopentadienyl ligands is followed by their incorporation in group 4 metallocene systems [9].

Most of the *ansa*-metallocene complexes published contain silicon as the bridging atom, and there are very few examples in which functional groups are attached to the bridgehead atom [3a,10]. Moreover, we have reported the synthesis and catalytic reactivity of group 4 metallocene complexes [11] and more recently the

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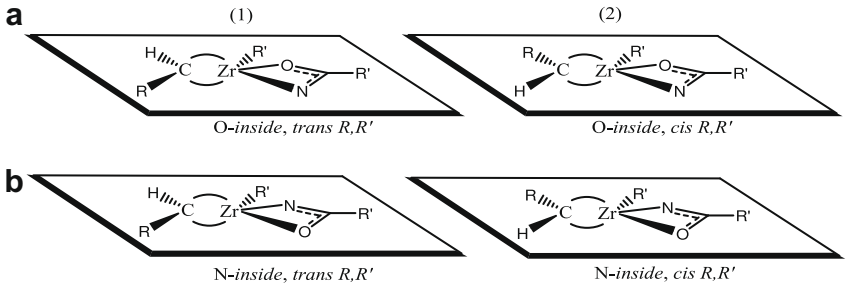
doi:10.1016/j.jorganchem.2009.01.038



Scheme 1. Different isomers for the insertion reactions of PhNCO into the chiral carbon atom-bridged dialkyl *ansa*-zirconocene complexes.

precursor K[(C_5Me_4)=CH(C_5H_4)] for the facile synthesis of *ansa*-metallocene with variable substitution at the bridging carbon atom [12]. We also described the development of new *ansa*-metallocene complexes of group 4 that have vinyl or allyl substituents at the silicon *ansa* bridge or at the cyclopentadinyl rings [13].

We report here the synthesis of new *ansa*-metallocene group 4 complexes with an allyl group on the methylene-bridge and describe its hydrogenation, hydroboration and hydrosilylation reactions. The latter reaction was performed with the aim of obtaining methylene-bridged metallocene complexes that have a chlorosilane (Si–Cl) functionality that is a suitable anchoring moiety for immobilization onto silica surfaces. The insertion reactions of PhNCO and CO into the Zr–C bond of some chiral carbon atom-bridged dialkyl *ansa*-zirconocene complexes are also described, and these generate – in addition to the different O-*inside*(a) and N-*inside*(b) configuration modes – the *trans* (1) and *cis* (2) isomers with respect to the substituent on the bridge (see Scheme 1). These results can be extrapolated to other dimethyl or dibenzyl *ansa*-zirconocene complexes with different substituents.

2. Results and discussion

Solutions of *ansa*-biscyclopentadienyl Mg{(R)CH(C_5H_4)(C_5Me_4)}-(thf)$_2$ [R = $CH_2CH{=}CH_2$ (**1a**), $CH_2C(CH_3){=}CH_2$ (**1b**)] in thf were prepared by treatment of the appropriate allyl Grignard reagent MgClR [R = $CH_2CH{=}CH_2$, $CH_2C(CH_3){=}CH_2$] in thf solution with K[(C_5Me_4)=CH(C_5H_4)] [12a] in equimolar amounts through a nucleophilic addition reaction at the exocyclic double bond. The solutions of **1a** and **1b** were used without further manipulation to prepare new *ansa*-metallocene complexes. Indeed, the subsequent addition of $MCl_4(thf)_2$ (M = Ti or Zr) to these solutions yielded the corresponding *ansa*-metallocene dichloride complexes [M{(R)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] [M = Ti and R = $CH_2CH{=}CH_2$ (**2**), $CH_2C(CH_3){=}CH_2$, (**3**); M = Zr and R = $CH_2CH{=}CH_2$, (**4**), CH_2C-$(CH_3){=}CH_2$, (**5**)] (Scheme 2).

The new chiral *ansa*-metallocene dichloride complexes **2**–**5** were isolated as crystalline solids and characterized spectroscopically by mono- (^{1}H and ^{13}C {^{1}H}) and bidimensional NMR experiments (g-COSY and g-HSQC) (see Section 4). Only signals for one compound were observed in all the spectra. The ^{1}H NMR spectra of the C_1 symmetric complexes **2**–**5** display eight signals, which are assigned to the four protons of the unsubstituted cyclopentadienyl moiety and to the four methyl groups of the tetramethylcyclopentadienyl fragment (see Section 4). The proton at the *ansa* bridge gave a triplet due to coupling to the two allyl protons in the α-position. The allyl-substituted groups, $C_\alpha H_2C_\beta R){=}C_\gamma H_2$ (R = H, CH_3), exhibited three sets of signals corresponding to the $C_\alpha H_2$ protons bonded to the carbon bridge atom, the central group protons $C_\beta R$, and the olefinic protons for the terminal $C_\gamma H_2$. The ^{13}C{^{1}H} NMR spectra showed the expected signals for the different ligand systems corresponding to the allyl-functionalized *ansa*-carbon bridgehead complexes.

The molecular structure of **4** was established by single-crystal X-ray diffraction studies. The molecular structure and atomic numbering scheme are shown in Fig. 1.

The poor quality of the crystals obtained for compound **4** preclude a detailed discussion of distances and angles for this compound.

We previously showed that some dialkylation processes of silicon-bridged *ansa*-zirconocene complexes are controlled by steric factors and that this may be due to the alkyl ligand or the substituents in the β-position of the cyclopentadienyl ring [11b,c]. The dialkyl derivatives [M(R)HC(η^5-C_5Me_4)(η^5-C_5H_4)R'_2] [M = Ti, R = $CH_2CH{=}CH_2$, R′ = Me (**6**), R′ = CH_2Ph (**7**); R = $CH_2C(CH_3){=}CH_2$,

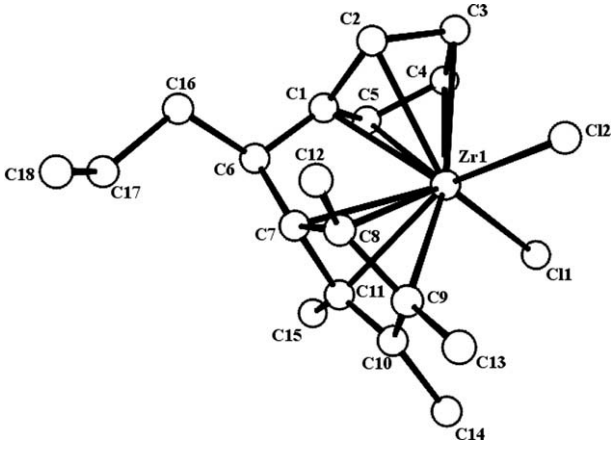
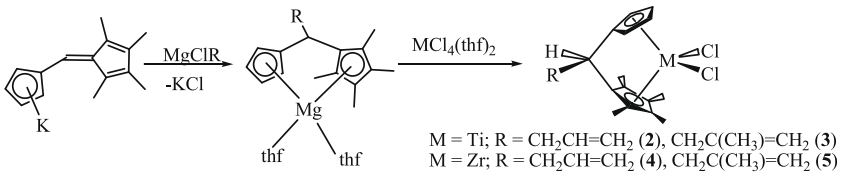
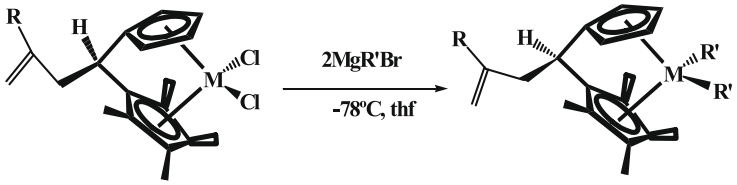


Fig. 1. View of the molecular structure and atom labelling scheme for [Zr{($CH_2{=}CHCH_2$)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**4**).



Scheme 2.



M = Ti, R = H (2); R = Me (3)

M = Zr,R = H (4); R = Me (5)

M = Ti, R = H, R' = Me (6), R' = CH_2Ph (7)
M = Ti, R = CH_3, R' = Me (8), R' = CH_2Ph (9)
M = Zr, R = H, R' = Me (10), R' = CH_2Ph (11)
M = Zr, R = CH_3, R' = Me (12), R' = CH_2Ph (13)

Scheme 3. Synthesis of the dialkyl *ansa*-metallocene complexes **6**–**13**.

R′ = Me (**8**), R′ = CH_2Ph (**9**); M = Zr, R = $CH_2CH{=}CH_2$, R′ = Me (**10**), R′ = CH_2Ph (**11**); R = $CH_2C(CH_3){=}CH_2$, R′ = Me (**12**), R′ = CH_2Ph (**13**)] were prepared by the reaction of two equivalents of the corresponding alkyl Grignard reagent and the *ansa*-zirconocene dichloride complexes **2**–**5** (Scheme 3). Compounds **6**–**13** were isolated as crystalline solids and characterized by spectroscopic methods. The alkylation reactions of the *ansa*-carbon bridged complexes were carried out as previously described for the silicon-bridged compounds [11c] since the reduction of the "*bite angle*" from the silicon to the carbon *ansa*-bridge atom does not increase the steric hindrance around the metal atom and therefore it does not disfavour the dialkylation process.

The dialkyl *ansa*-zirconocene complexes **6**–**13** were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **10**, as well as those of **6**, **8** and **12**, gave two unique signals for the metal-bonded methyl groups, thus confirming the dialkylation and the chirality of these *ansa*-metallocene complexes (see Section 4).

On the other hand, due to the chirality around the C bridge atom and the C_1 symmetry of **11**, as well as **7**, **9** and **13**, the methylene protons of the two non-equivalent benzyl ligands are diastereotopic and an AA′BB′ system was observed in the ^1H NMR spectra. This system consists of four signals, two doublets at 0.98 and 1.01 ppm ($^2J_{H-H}$ = 7.3 Hz) and another two doublets at 1.82 and 1.85 ppm ($^2J_{H-H}$ = 11.7 Hz) for H_{endo} or H_{exo} of the methylene group of the two benzyl ligands in the particular case of **11**. The $^{13}C\{^1H\}$ NMR spectra showed two resonances at 59.6 and 59.9 ppm for the two benzyl carbon atoms (CH_2) and this confirmed the non-equivalence of these groups.

The molecular structure of **11** was established by single-crystal X-ray diffraction studies, which allowed us to confirm the spectroscopic data and to compare the data with the structure obtained for complex **4**. The molecular structure and atomic numbering scheme for **11** are shown in Fig. 2 and selected bond lengths and angles are given in Table 1.

The structure of **11** is similar to that of **4**, bound by a chelating *ansa*-ligand with a bent metallocene conformation and a pseudo-tetrahedral geometry around the zirconium atom. In complex **11** the pseudo-tetrahedral environment of the zirconium atom is completed by the two benzyl groups. The two benzyl groups, which replace the two chlorine atoms, are arranged in space with the phenyl ring inclined toward the non-substituted cyclopentadienyl ring.

The reactivity of complexes **2**–**5** was tested in the hydrogenation reaction of the unsaturated bond of allyl groups. All of the complexes react under H_2 pressure in the presence of Wilkinson's catalyst $RhCl(PPh_3)_3$ at room temperature to give a single saturated *ansa*-metallocene complex $[M\{(R)CH(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ [M = Ti and R = $CH_2CH_2CH_3$ (**14**) or R = $CH_2CH(CH_3)_2$ (**15**); M = Zr and R = $CH_2CH_2CH_3$ (**16**) or R = $CH_2CH(CH_3)_2$ (**17**)] as the product (Scheme 4). However, when the hydrogenation reactions of **3** and **5**, where the 2-methylallyl group is present as the substituent on the carbon bridge, with a Pd/C catalyst were carried out under the same conditions, the final product was a 50:50 mixture of the starting material and the corresponding *n*-propyl hydrogenated product in the case of **5** and unreacted starting materials in the case of **3**. Varying the H_2 pressure or increasing the temperature gave the same results. The latter observation apparently results from a steric hindrance due to methyl group in the 2-methylallyl substituent.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **14** and **16** showed, in addition to the expected resonance for the *ansa*-ligand, signals associ-

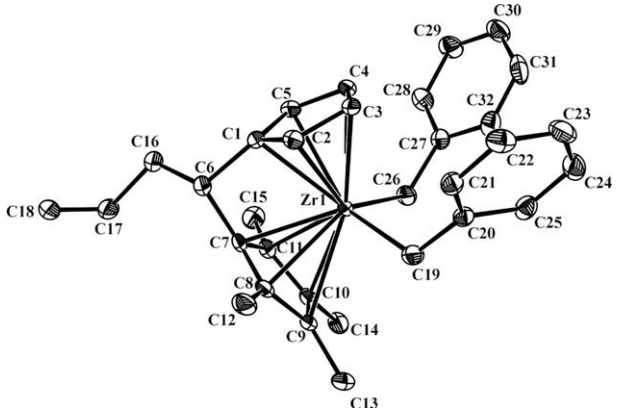
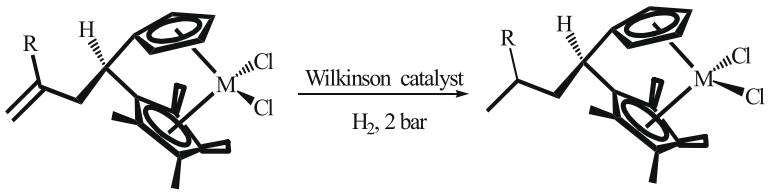


Fig. 2. Molecular structure and atom labelling scheme for $[Zr\{(CH_2{=}CHCH_2)CH(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}(CH_2Ph)_2]$ (**11**) with thermal ellipsoids at the 30% probability.

Table 1
Bond lengths (Å) and angles (°) for **11**.

11	
Zr(1)–C(19)	2.326(3)
Zr(1)–C(26)	2.297(3)
Zr(1)–Ct(1)	2.507(3)
Zr(1)–Ct(2)	2.523(3)
C(1)–C(6)	1.529(4)
C(6)–C(7)	1.531(4)
C(6)–C(16)	1.509(4)
C(16)–C(17)	1.497(4)
C(17)–C(18)	1.300(4)
C(26)–Zr(1)–C(19)	103.6(1)
Ct(1)–Zr(1)–Ct(2)	116.7(3)
C(1)–C(6)–C(16)	115.6(2)
C(7)–C(6)–C(16)	117.3(2)
C(1)–C(6)–C(7)	101.1(2)
C(6)–C(16)–C(17)	113.2(2)
C(16)–C(17)–C(18)	125.7(3)
C(20)–C(19)–Zr(1)	121.8(2)
C(27)–C(26)–Zr(1)	119.7(2)

Ct(1) is the centroid of the Cp ring and Ct(2) is the centroid of the Cp^* ring.



Scheme 4.

ated with the *n*-propyl group arising from hydrogenation of the allyl substituent (see Section 4), which were observed in the ^{1}H NMR spectrum as three signals at ca. 0.82, 1.31 and 1.81 ppm. Hydrogenation of **15** and **17** gave the *i*-butyl moieties, which gave rise to two doublets at ca. 0.82 ppm and two multiplets at ca. 1.65 and 1.91 ppm (corroborate by g-COSY experiment).

The molecular structures of **16** and **17** were established by X-ray studies. The molecular structures and atomic numbering schemes are shown in Fig. 3. Selected bond lengths and angles are given in Table 2.

Compound **16** crystallizes in the space group $P2_1/n$ and **17** crystallizes in the $P\bar{1}$ space group. It is interesting to note the bond distance between carbon atoms C17–C18 in **16** [1.498(6) Å], which is longer than the corresponding distance in complex **4** with the alkene group [1.25(4) Å]. This observation confirms that hydrogenation occurred on this bond. A similar distance between carbon atoms C17–C18 is found for complex **17** [1.470(5) Å], this data are in agreement with a saturated bond for **16** and **17** [12b]. A selection of bond distance and angles for complexes **16** and **17** is given in Table 3.

Hydroboration at the double bond of the allyl group of the *ansa*-metallocene complexes **2**–**5** was carried out in a similar manner to that published by our group [11d,f] or Erker, Piers or Alt for metallocene complexes of group 4 [14] or Schumann for lantanocene complexes [15]. 9-BBN was used as the reagent with complexes **2**–**5** to give mainly *anti*-Markonikov products [M{(9-BBN-$CH_2CH(R)CH_2$)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] [M = Ti and R = H (**18**); M = Zr and R = H (**19**) or R = CH_3 (**20**)] (Scheme 5). The reaction takes place readily at room temperature without altering the metal centre (Ti or Zr) and in all cases the borane selectively attacks the terminal olefinic carbon atom. However, when the titanocene complex with the $CH_2CH{=}CH_2$ group at the bridge was used (i.e. **2**), it was necessary to warm the reaction mixture to 60 °C. The hydroboration reaction of **3** under the same conditions did not take place.

Compounds **18**–**20** were characterized by homo- (^{1}H and ^{13}C{^{1}H}) and heteronuclear (g-COSY and g-HSQC) spectroscopic correlation techniques. The ^{1}H NMR spectra of **18**–**20** showed changes in the signals previously attributed to the allyl group (in **2**, **4** and **5**). The new propane-1,3-diyl chain generated in **18** and **19** gave three multiplets at ca. δ 1.40 (C_γ), 1.63 (C_β) and 2.00 (C_α) and the additional protons of the borane moiety gave rise to four multiplets in the range δ 1.11–1.84 (see Section 4).

In the ^{1}H NMR spectrum of **20** the signals corresponding to two different diastereoisomers were observed due to the presence of a new chiral centre at C_β of the satured chain between the carbon atom bridge and the 9-BBN group. The presence of these two iso-

Table 2
Bond lengths (Å) and angles (°) for **16** and **17**.

16		**17**	
Zr(1)–Cl(1)	2.430(1)	Zr(1)–Cl(1)	2.4437(7)
Zr(1)–Cl(2)	2.447(1)	Zr(1)–Cl(2)	2.4246(7)
Zr(1)–Ct(1)	2.492(4)	Zr(1)–Ct(1)	2.494(3)
Zr(1)–Ct(2)	2.502(3)	Zr(1)–Ct(2)	2.501(2)
C(1)–C(6)	1.540(5)	C(1)–C(6)	1.523(4)
C(6)–C(7)	1.539(5)	C(6)–C(7)	1.536(4)
C(6)–C(16)	1.493(5)	C(6)–C(16)	1.511(4)
C(16)–C(17)	1.527(5)	C(16)–C(17)	1.522(4)
C(17)–C(18)	1.498(6)	C(17)–C(18)	1.470(5)
		C(17)–C(19)	1.492(4)
Cl(1)–Zr(1)–Cl(2)	101.00(4)	Cl(1)–Zr(1)–Cl(2)	102.55(3)
Ct(1)–Zr(1)–Ct(2)	117.2(2)	Ct(1)–Zr(1)–Ct(2)	117.4(2)
C(1)–C(6)–C(16)	116.0(3)	C(1)–C(6)–C(16)	115.5(2)
C(7)–C(6)–C(16)	116.6(3)	C(7)–C(6)–C(16)	116.8(2)
C(1)–C(6)–C(7)	99.9(3)	C(1)–C(6)–C(7)	100.7(2)
C(6)–C(16)–C(17)	113.1(3)	C(6)–C(16)–C(17)	114.6(2)
C(16)–C(17)–C(18)	113.6(4)	C(16)–C(17)–C(18)	114.4(3)
		C(16)–C(17)–C(19)	111.3(3)
		C(18)–C(17)–C(19)	113.1(3)

Ct(1) is the centroid of the Cp ring and Ct(2) is the centroid of the Cp* ring.

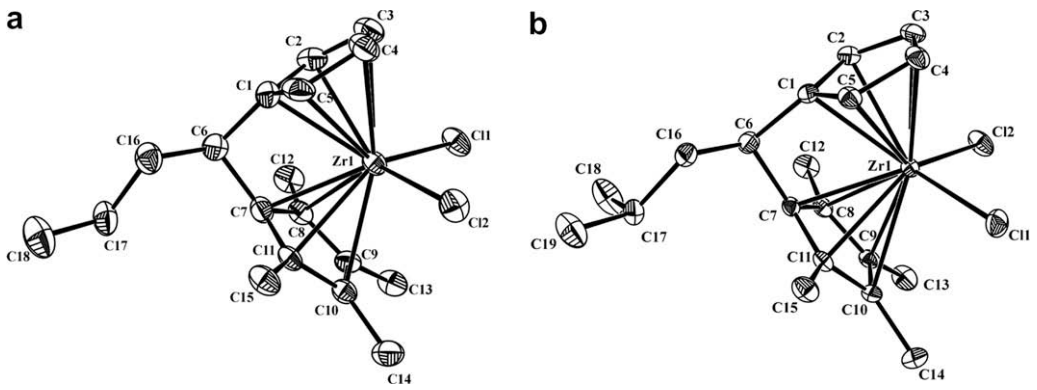
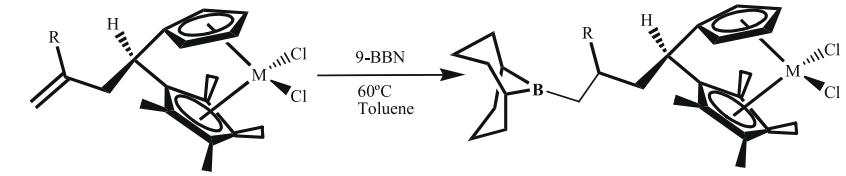


Fig. 3. Molecular structure and atom labelling scheme for (a) [Zr{($CH_3CH_2CH_2$)CH(η^5-C_5Me_4)(η^5-C_5H_4)Cl_2] (**16**) and (b) [Zr{($(CH_3)_2CHCH_2$)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**17**) with thermal ellipsoids at the 30% probability.

Table 3
Crystal data and structure refinement for **4**, **11**, **16** and **17**.

	4	**11**	**16**	**17**
Empirical formula	$C_{18}H_{22}Cl_2Zr$	$C_{32}H_{36}Zr$	$C_{18}H_{24}Cl_2Zr$	$C_{19}H_{26}Cl_2Zr$
Formula weight	400.48	511.83	402.49	416.52
T (K)	180(2)	180(2)	180(2)	180(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	9.358(5)	9.5108(7)	9.562(2)	8.6035(3)
b (Å)	11.985(6)	8.9184(7)	15.875(3)	9.3728(2)
c (Å)	15.713(8)	30.096(2)	11.795(2)	12.1372(4)
α (°)	92.128(7)			85.341(2)
β (°)	92.854(8)	98.813(1)	91.793(3)	82.416(2)
γ (°)	92.193(9)			75.784(2)
V (Å^3)	1757(2)	2522.6(3)	1789.6(6)	939.25(5)
Z	4	4	4	2
Density (calculated) (g/cm^3)	1.514	1.348	1.494	1.473
Absorption coefficient (mm^{-1})	0.921	0.454	0.905	0.865
F(000)	816	1072	824	428
Crystal size (mm^3)	0.32 × 0.27 × 0.14	0.46 × 0.32 × 0.27	0.19 × 0.15 × 0.11	0.41 × 0.19 × 0.18
Index ranges	$-11 \leqslant h \leqslant 11$	$-11 \leqslant h \leqslant 11$	$-11 \leqslant h \leqslant 11$	$-9 \leqslant h \leqslant 10$
	$-14 \leqslant k \leqslant 14$	$10 \leqslant k \leqslant 10$	$-17 \leqslant k \leqslant 18$	$-11 \leqslant k \leqslant 10$
	$-19 \leqslant l \leqslant 19$	$-34 \leqslant l \leqslant 35$	$-14 \leqslant l \leqslant 14$	$-13 \leqslant l \leqslant 14$
Reflections collected	12801	15873	9567	5891
Independent reflections [$R_{(int)}$]	6908 [0.1400]	4442 [0.0420]	3106 [0.0379]	3242 [0.0188]
Data/restraints/parameters	6908/0/209	4442/0/302	3106/0/195	3242/0/205
Goodness-of-fit on F^2	1.347	1.099	1.052	1.081
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1839	R_1 = 0.0349,	R_1 = 0.0389	R_1 = 0.0293
	wR_2 = 0.4483	wR_2 = 0.0857	wR_2 = 0.0900	wR_2 = 0.0725
Largest difference peak and hole (e Å^{-3})	2.330 and −1.383	0.507 and −0.261	0.666 and −0.477	0.399 and −0.507



Scheme 5.

mers can be clearly observed in the NMR spectrum due to the appearance of two triplets of similar intensity at 4.08 and 4.13 ppm with $^3J_{H-H}$ = 8.2 and $^3J_{H-H}$ = 8.1 Hz, respectively, which corresponds with the proton of group C*H* bridge. Moreover, for the *i*-butylene chain two sets of three multiplets at ca. δ 2.04–2.15 (C_α), 1.85–2.10 (C_β) and 1.29–1.42 (C_γ) and two doublets at ca. 0.92–0.97 ppm (CH_3) were observed for isomers I and II, respectively (see Fig. 4). The signals due to the borane moiety were observed in the same region and gave the pattern in **18**. In order to assign the signals more accurately some g-COSY and g-HSQC experiments were carried out.

Hydrosilylation reactions on metallocene compounds with a vinyl or allyl group in the bridge allow the study of the ability of these complexes to produce model molecules similar those that are probably formed by the interaction of *ansa*-metallocene complexes supported on an inorganic surface such as silica.

The hydrosilylation reactions of **2**–**5** with $HSiMe_2Cl$ were carried out in the presence of the Karstedt catalyst [platinum(0) divinyltetramethylsiloxane] at room temperature, following our previous used synthetic method [11e,13b]. These reactions gave complexes $[M\{ClMe_2SiCH_2CH(R)CH_2CH(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ [M = Ti and R = H (**21**); M = Zr and R = H (**22**) or R = CH_3 (**23**)], formed by the *anti*-Markovnikov or 1,2-addition on the double bonds of the allyl substrate (Scheme 6). Hydrosilylation reactions involving **3** did not take place.

When the Speier catalyst was used the reactions between **4** and $HSiMe_2Cl$ were carried out in toluene and with heating for 12 h at 60–80 °C. It is worth noting the lack of reactivity of **2**, **3** and **5** with this catalyst, a situation that is probably due to the steric effects of the allyl-substituted group and the poor reactivity of this catalyst.

The hydrosilylation reaction can also give the regioisomer $[M\{CH_3CH(SiMe_2Cl)CH_2CH(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (R = Me or H; M = Ti or Zr) by Markovnikov or 1,2-addition [16]. This minor product was detected in quantities of less than 5–10% by ^{1}H NMR spectroscopy.

Compounds **21**–**23** were isolated and characterized by NMR spectroscopy. The reaction leads to the loss of signals in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra corresponding to the allyl groups of the parent complexes. The NMR spectra show the expected resonances for the C_5H_4 and C_5Me_4 moieties. In addition, a set of multiplets, corresponding to the propane-1,3-diyl (**21** and **22**) or *i*-butylene (**23**) chains, and two singlets assigned to the methyl groups of $SiMe_2Cl$ were also observed. The proton of the *CH* bridge gave rise to an ABB′ system consisting of two doublets for each isomer in the ^{1}H NMR spectrum. This is due to the coupling with the two non-equivalent protons of the $C_\alpha H_2$ group. A more accurate spectroscopic NMR assignment of the signals corresponding to each isomer was made by H–H and H–C correlation experiments. Compound **23** has a new chiral centre at the carbon in the β-posi-

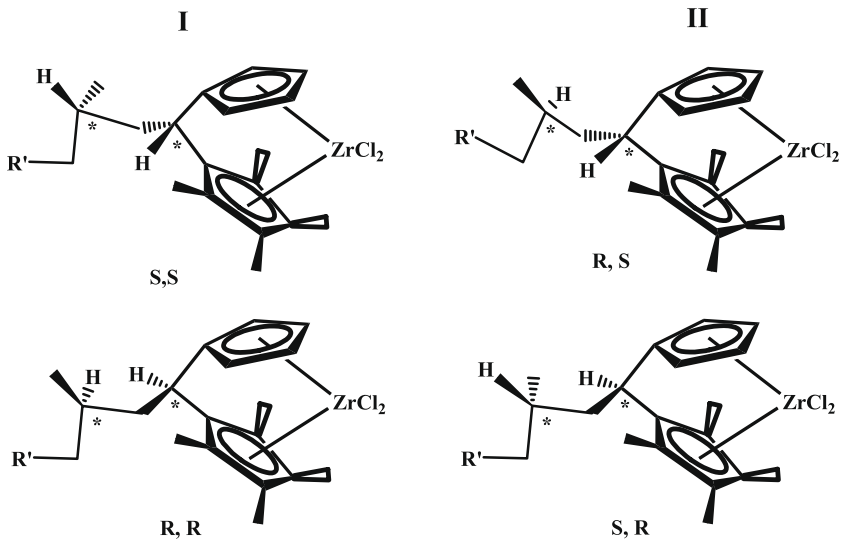
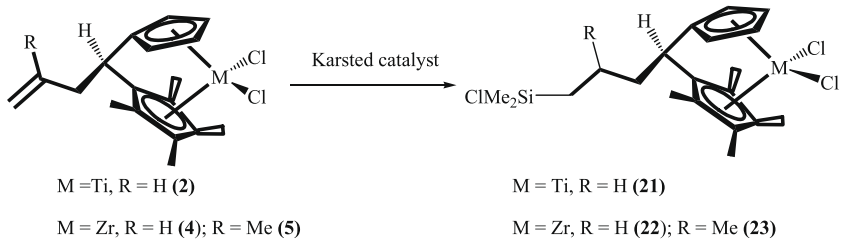


Fig. 4. Isomers of $[Zr\{R'CH_2CH(CH_3)CH_2CH(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl]_2$ R′ = $SiMe_2Cl$ or 9-BBN.



Scheme 6.

tion of the *i*-butylene moiety and this gives rise to the presence of two diastereoisomers (Fig. 4).

The $^{29}Si\{^1H\}$ NMR spectroscopic data of **21–23** confirmed the proposed structure (see Section 4), with a resonance observed at 31.02, 30.01 and 30.28 ppm for **21**, **22** and **23**, respectively, due to the new silicon atom.

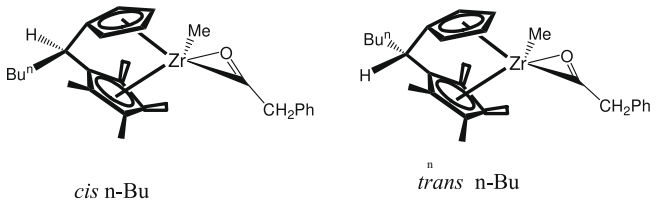
We and others have previously reported the reaction of chlorosilane metallocene compounds with silanol as surface model [13b,17]. Here is reported the ability of *ansa* hydrosilylated metallocene complex **23**, which has a Si–Cl anchor, to form Si–O–Si bonds by a homogeneous reaction with a silanol compound as a model surface support. In this way, a solution of complex **23** was reacted with *t*-$BuMe_2SiOH$ in toluene in the presence of NEt_3 at 60 °C. This reaction gave $[Zr\{t\text{-}BuMe_2SiOSi(Me_2)CH_2CH_2CH_2\text{-}CH(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**24**) as a pale yellow solid in excellent yield.

In the ^1H NMR spectra of **24**, all of the signals were shifted to lower field, a situation that could be due to the presence of an oxygen atom in the chain producing a –I effect throughout the chain. Thus, the proton of the bridge group appears at 4.15 ppm along with three multiplets at 0.71, 1.65 and 2.29 ppm for the protons of the *n*-propylene chain. The *t*-butyl protons were observed as a singlet at 1.10 ppm. The $^{29}Si\{^1H\}$ NMR spectra contained two signals at 10.11 ppm and 9.54 ppm and these are assigned to the two different silicon atoms. These observations indicate that the –OH group had reacted with the Si–Cl group. This is the first *ansa*-zirconocene complex with a methylene *ansa* bridge tethered onto a silanol surface model.

A new study on insertion reactions into the Zr–C bonds of the chiral carbon-bridged dialkyl *ansa*-zirconocene complexes was performed.

Gambarotta et al. [18] studied the insertion reactions of PhNCO into the Zr–C bond of zirconocene complexes and described the synthesis and characterization of the complex $[Cp_2Zr\{Me\}\{OC(Me)NPh\}]$. These authors proposed a κ^2-coordination mode for the phenyl isocyanate ligand on the basis of the IR and ^{13}C NMR spectroscopy and an X-ray study. The structure has a conformation in which the N atom is in an "N-*inside*" configuration and the O atom is in an "O-*outside*" configuration.

We carried out an analogous reaction of phenyl isocyanate with a solution of $[Zr\{(n\text{-}Bu)(H)C(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}_2Me_2]$ (**25**) in toluene at room temperature. In this particular case the chirality of the complex at the bridge carbon atom gives two isomers $[Zr\{(n\text{-}Bu)CH(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}(\kappa^2\text{-}O,N\text{-}C(Me)P)\}Me]$ (**26a–b**) from the insertion reactions (Scheme 1). Complexes **26a–b** were characterized by NMR and IR spectroscopy as well as mass spectrometry. The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data indicate the presence of only two of the possible conformers. For **26** the isolated product was observed not to evolve over time and therefore we tentatively propose that these are the products resulting from thermodynamic control and, as such, they adopt the N-*inside* conformation. A second insertion was not observed even when stoichiometries other than 1:1 were tested. The κ^2-coordination mode is proposed for the phenyl isocyanate ligand in **26** on the basis of IR and ^{13}C NMR data, which show the characteristic stretching vibration ν(C–O) at ca. 1705 cm^{-1} and ν(C–N) at 1660 cm^{-1} and the carbonyl



Scheme 7.

quaternary carbon atom signal at δ 180.8 and 180.9 ppm, respectively, for the two isomers. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **26** show, in addition to the expected signals for the *ansa*-metallocene protons, signals corresponding to these isomers (see Section 4).

It is known that the migratory insertion of alkyl groups towards carbon monoxide ligands allows the introduction of acyl groups that can show different coordination modes [19,11c] and this reaction pathway is well known [20]. In fact, for early transition metals the acyl group typically adopts a κ^2-coordination mode through both the oxygen and carbon atoms in an *exo* conformation. In this context we carried out the reaction of [Zr{(*n*-Bu)(H)C(η^5-C_5Me_4)(η^5-C_5H_4)}($PhCH_2$)$_2$] (**27**) with CO in toluene at room temperature. This process also provided a mixture of two isomers of the complex [{(*n*-Bu)CH(η^5-C_5Me_4)(η^5-C_5H_4)]}Zr($PhCH_2$){η^2-O,C-$COCH_2Ph$}] (**28a**–**b**) (Scheme 7). The κ^2-coordination mode is proposed for the acyl ligand in **28** on the basis of IR and ^{13}C NMR data, which show the characteristic stretching vibration ν(C–O) at ca. 1594 cm^{-1} and the carbonyl quaternary carbon atom signals at 156.5 and 156.7 ppm, respectively, for the two isomers **28a** and **28b**. The ^{1}H NMR spectra of **28** shows, in addition to the expected signals for the *ansa*-metallocene protons, signals corresponding to these isomers (see Section 4).

3. Conclusions

In this paper we report the preparation and characterization of a new family of *ansa*-metallocene group 4 complexes containing an alkenyl substituent in the carbon bridge atom. The reactivity of these compounds in catalytic hydrogenation, hydrosilylation and hydroboration processes is also described. It was observed that a steric factor is involved in the synthesis of unsaturated compounds because the face of the alkene that is tied to the catalyst could be hindered by the presence of the methyl group in the β-position.

4. Experimental

4.1. Materials and procedures

All reactions were performed using standard Schlenk tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. K[(C_5H_4)CH=(C_5Me_4)], [Zr{(*n*-Bu)CH(η^5-C_5Me_4)(η^5-C_5H_4)}$_2$$Me_2$] (**25**) and [Zr{(*n*-Bu)CH(η^5-C_5Me_4)(η^5-C_5H_4)}($PhCH_2$)$_2$] (**27**) were prepared as described earlier [12b]. MgCl(CH_2=$CHCH_2$), MgCl-(CH_2=$C(CH_3)CH_2$), MgBrMe, MgCl(CH_2Ph), 9-borabicyclo[3.3.1]-nonane (9-BBN), Wilkinson's catalyst, Pd/C (10% palladium) catalyst, $HSiMe_2Cl$, Karstedt catalyst, Spiers catalyst, *t*-$BuMe_2$-SiOH, NEt_3, [$TiCl_4$(thf)$_2$] and [$ZrCl_4$(thf)$_2$] were purchased from Aldrich and used directly. Mg{CH_2=$CHCH_2CH(C_5Me_4)(C_5H_4)$} (**1a**) and Mg{$CH_2$=$C(CH_3)CH_2CH(C_5Me_4)(C_5H_4)$} (**1b**) solutions were prepared as reported [21] and used *in situ*. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Inova FT-500 spectrometer and referenced to the residual deuteriated solvent. Microanalyses were carried out with a Perkin–Elmer 2400 microanalyzer.

4.2. Synthesis of [Ti{(CH_2=$CHCH_2$)$CH(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (**2**)

A solid mixture of [$TiCl_4$(thf)$_2$] (1.41 g, 4.23 mmol) and **1a** (1.72 g, 4.23 mmol) was added to THF (100 mL) at 0 °C. The solution was allowed to warm up to room temperature and was stirred for 15 h. The solvent was removed under reduced pressure and toluene (100 mL) was added to the resulting brown solid. The mixture was filtered, the solvent from the filtrate was removed *in vacuo* and the remaining solid was extracted into hexane (30 mL). The filtered solution was concentrated and cooled to −30 °C to give the title complex as a brown crystalline solid. Yield: 1.11 g, 73%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.27, 1.47, 1.92 (3s, 3:3:6H, C_5Me_4), 2.55 (m, 2H, CH_2=$CHCH_2$), 3.80 (t, 1H, CH, $^3J_{H-H}$ = 9.0 Hz), 4.96, 5.02 (2m, each 1H, CH_2=$CHCH_2$), 4.80, 5.00, 6.68, 6.76 (4m, each 1H, C_5H_4); 5.68 (m, CH_2=$CHCH_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 12.5, 12.8, 13.5, 15.6 (C_5Me_4), 34.2 (CH_2=$CHCH_2$), 38.09 (*C*H), 117.0 (CH_2=$CHCH_2$), 107.6, 110.1, 128.4, 129.2, 138.1 (C_5H_4); 134.9 (CH_2=$CHCH_2$), 98.7, 107.0, 123.1, 125.7, 137.4 (C_5Me_4). Mass spectrometry [electron impact *m*/*e* (*relative intensity*)]: 357 (36) [M$^+$], 321 (100) [M$^+$−Cl], 279 (21) [M$^+$−Cl−CH_2=CH_2CH_2]. Anal. Calc. for $C_{18}H_{22}Cl_2Ti$: C, 60.53; H, 6.21. Found C, 59.71; H, 6.01%.

4.3. Synthesis of [Ti{(CH_2=$C(CH_3)CH_2$)$CH(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (**3**)

The preparation of **3** was carried out in an identical manner to **2**, from a solution of **1b** (1.76 g, 4.18 mmol) and [$TiCl_4$(thf)$_2$] (1.43 g, 4.18 mmol) in thf (100 mL) Yield: 0.98 g, 63%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.31, 1.49, 1.92, 1.93 (4s, each 3H, C_5Me_4), 1.58 (s, 3H, CH_3), 2.58 (m, 2H, CH_2=CCH_3CH_2), 4.00 (t, 1H, CH, $^3J_{H-H}$ = 8.4), 4.77 (bs, 2H, CH_2=CCH_3CH_2), 4.82, 5.03, 6.68, 6.78 (4m, each 1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 12.5, 12.8, 13.4, 15.7 (C_5Me_4), 22.7 (CH_3), 37.0 (*C*H), 37.9 (CH_2=CCH_3CH_2), 98.9, 107.2, 123.2, 125.6, 137.3 (C_5Me_4), 107.6, 110.1, 126.8, 129.2, 138.2 (C_5H_4), 112.3 (CH_2=CCH_3CH_2), 142.4 (CH_2=CCH_3CH_2). Mass spectrometry [electron impact *m*/*e* (*relative intensity*)]: 371 (100) [M$^+$], 335 (84) [M$^+$−Cl], 280 (79) [M$^+$−Cl−CH_2=$C(CH_3)CH_2$]. Anal. Calc. for $C_{19}H_{24}Cl_2Ti$: C, 61.48; H, 6.52. Found C, 62.12; H, 6.24%.

4.4. Synthesis of [Zr{(CH_2=$CHCH_2$)$CH(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (**4**)

[$ZrCl_4$(thf)$_2$] (1.85 g, 4.91 mmol) in toluene (50 mL) was added to a solution of **1a** (2 g, 4.91 mmol) in Et_2O (50 mL) at −78 °C. The solution was allowed to warm up to room temperature and stirred for 10 h. The solvent was partially removed under reduced pressure and the mixture was filtered to give a deep orange solution. The filtered solution was concentrated and cooled to −30 °C to yield crystals of the title complex. Yield: 1.41 g, 72%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.45, 1.63, 1.83, 1.84 (4s, each 3H, C_5Me_4), 2.59 (m, 2H, CH_2=$CHCH_2$), 3.87 (t, 1H, CH, $^3J_{H-H}$ = 8.4 Hz), 4.95, 5.05 (2m, each 1H, CH_2=$CHCH_2$), 5.01, 5.17, 6.35, 6.45 (4m, each 1H, C_5H_4), 5.69 (m, CH_2=$CHCH_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 11.0, 11.2, 12.7, 14.7 (C_5Me_4), 35.1 (CH_2=$CHCH_2$), 39.2 (*C*H), 116.9 (CH_2=$CHCH_2$), 104.1, 114.1, 117.7, 120.3, 129.0 (C_5H_4); 135.3 (CH_2=$CHCH_2$); 104.5, 107.2, 119.8, 121.9, 129.8 (C_5Me_4). Mass spectrometry [electron impact *m*/*e* (*relative intensity*)]: 398 (60) [M$^+$], 363 (51) [M$^+$−Cl], 321 (48) [M$^+$−CH_2=$CHCH_2$−Cl]. Anal. Calc. for $C_{18}H_{22}Cl_2Zr$: C, 53.98; H, 5.54. Found: C, 51.67; H, 5.68%.

4.5. Synthesis of [Zr{(CH_2=$C(CH_3)CH_2$)$CH(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (**5**)

The preparation of **5** was carried out in an identical manner to that of **4**, from a solution of **1b** (2 g, 4.75 mmol) in Et_2O (50 mL)

and $[ZrCl_4(thf)_2]$ (1.79 g, 4.75 mmol). Yield: 1.35 g, 69%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.50, 1.66, 1.84, 1.85 (4s, each 3H, C_5Me_4), 1.58 (s, 3H, CH_2=C(CH_3)CH_2), 2.61 (m, 2H, CH_2=C(CH_3)CH_2), 4.08 (t, 1H, CH, $^3J_{H-H}$ = 8.3 Hz), 4.77 [bs, 2H, CH_2=C(CH_3)CH_2], 5.03, 5.20, 6.36, 6.47 (4m, each 1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 11.6, 11.9, 12.6, 14.9 (C_5Me_4), 23.0 (CH_2=C(CH_3)CH_2), 38.0 (CH_2=C(CH_3)CH_2), 38.8 (CH), 113.4 (CH_2=C(CH_3)CH_2), 104.5, 112.4, 119.7, 122.1, 130.0 (C_5H_4), 140.6 (CH_2=CCH_3)CH_2), 107.2, 114.5, 117.8, 120.1, 128.9 (C_5Me_4). Mass spectrometry [electron impact *m/e* (*relative intensity*)]: 412 (100) [M^+], 377 (94) [M^+–Cl], 357 (96) [M^+–CH_2=C(CH_3)CH_2], 321 (73) [M^+–CH_2=C(CH_3)CH_2–Cl]. Anal. Calc. for $C_{19}H_{24}Cl_2Zr$: C, 55.05; H, 5.84. Found: C, 55.71; H, 5.96%.

4.6. Synthesis of [Ti{(CH_2=$CHCH_2$)$CH(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Me_2] (**6**)

A 1.4 M solution of MeMgBr in thf/toluene (1.44 mL, 2.01 mmol) was added to a stirred solution of **2** (0.30 g, 0.84 mmol) in thf (50 mL) at −78 °C. The solution was allowed to warm up to room temperature and stirred for 6 h. The solvent was removed *in vacuo* and the remaining orange oil was extracted into hexane (2 × 25 mL). The solution was filtered and the solvent was removed *in vacuo* to yield the title complex as an orange solid. Yield (0.18 g, 68%). ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ *−0.12, −0.11* (2s, each 3H, TiMe_2), 1.19, 1.38, 1.94, 1.96 (4s, each 3H, C_5Me_4), 2.46 (m, 2H, CH_2=CHCH_2), 3.27 (t, 1H, CH, $^3J_{H-H}$ = 8.6 Hz), 4.61, 4.80, 6.84, 6.92 (4m, each 1H, C_5H_4), 4.95, 5.03 (2m, each 1H, CH_2=$CHCH_2$), 5.76 (m, 1H, CH_2=$CHCH_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 10.2, 10.5, 10.9, 12.9 (C_5Me_4), 33.4, 36.6 (TiMe_2), 43.6 (CH_2=$CHCH_2$), 43.7 (CH), 97.4, 104.7, 116.1, 118.5, 124.7 (C_5Me_4), 104.2, 106.5, 117.8, 119.3, 123.9 (C_5H_4), 114.9 (CH_2=$CHCH_2$), 134.9 (CH_2=$CHCH_2$). Anal. Calc. for $C_{20}H_{28}Ti$: C, 75.94; H, 8.92. Found: C, 75.31; H, 9.17%.

4.7. Synthesis of [Ti{(CH_2=$CHCH_2$)$CH(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}($CH_2Ph)_2$] (**7**)

A 2 M solution of $MgCl(CH_2Ph)$ in thf (1.00 mL, 2.01 mmol) was added to a stirred solution of **2** (0.30 g, 0.84 mmol) in thf (50 mL) at −78 °C. The solution was allowed to warm up to room temperature and stirred for 6 h. The solvent was removed *in vacuo* and the remaining red solid was extracted into hexane (2 × 25 mL). The solution was filtered and the solvent was removed *in vacuo* to yield the title complex as a red solid. Yield (0.26 g, 66%). ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.16, 1.34, 1.87, 1.88 (4s, each 3H, C_5Me_4), 1.31 (2d, each 1H, CH_2Ph, $^2J_{H-H}$ = 9.5 Hz), 1.66 (2d, each 1H, CH_2Ph, $^2J_{H-H}$ = 9.7 Hz), 2.36 (m, 2H, CH_2=CHCH_2), 3.20 (t, 1H, CH, $^3J_{H-H}$ = 8.6 Hz), 4.28, 4.51, 6.38, 6.48 (4m, each 1H, C_5H_4), 4.93, 5.01 (2m, each 1H, CH_2=$CHCH_2$), 5.69 (m, 1H, CH_2=$CHCH_2$), 6.78–7.17 (m, 10H, 2CH_2Ph). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 11.6, 11.9, 12.3, 14.3 (C_5Me_4), 34.4 (CH_2=CHCH_2), 37.8 (CH), 74.5, 74.7 ((CH_2Ph)$_2$), 95.3, 104.5, 116.9, 119.6, 126.2 (C_5Me_4), 106.9, 109.3, 123.2, 125.3, 128.5 (C_5H_4), 116.3 (CH_2=$CHCH_2$), 135.9 (CH_2=$CHCH_2$), 121.5, 121.6, 126.0, 126.3, 128.5, 128.6, 128.7, 129.3, 141.9, 155.8, 155.9 (($CH_2Ph)_2$). Anal. Calc. for $C_{32}H_{36}Ti$: C, 82.04; H, 7.75. Found: C, 82.85; H, 8.12%.

4.8. Synthesis of [Ti{(CH_2=C(CH_3)CH_2)$CH(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Me_2] (**8**)

The preparation of **8** was carried out in an identical manner to that of **6**, from a solution of **3** (0.30 g, 0.80 mmol) in thf (50 mL) and a 1.4 M solution of MgBrMe (1.38 mL, 1.92 mmol) in THF/toluene. Yield: 0.17 g, 64%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ *−0.11* (s, 6H, TiMe_2), 1.23, 1.40, 1.94, 1.96 (4s, each 3H, C_5Me_4), 1.60 (s, 3H, CH_3), 2.47 (m, 2H, CH_2=CCH_3CH_2), 3.44 (t, 1H, CH, $^3J_{H-H}$ = 8.3 Hz), 4.77 (bs, 2H, CH_2=CCH_3CH_2), 4.62, 4.82, 6.85, 6.92 (4m, each 1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 10.2, 10.5, 10.9, 13.1 (C_5Me_4), 21.5 (CH_3), 35.4 (CH), 37.1 (CH_2=CCH_3CH_2)), 43.6, 43,7 (TiMe_2), 97.7, 104.2, 116.1, 118.3, 123.9 (C_5Me_4), 104.2, 106.4, 117.7, 119.4, 124.7 (C_5H_4), 110.5 (CH_2=C(CH_3)CH_2), 142.1 (CH_2=C(CH_3)CH_2). Anal. Calc. for $C_{21}H_{30}Ti$: C, 76.36; H, 9.15. Found: C, 75.77; H, 8.64%.

4.9. Synthesis of [Ti{(CH_2=C(CH_3)CH_2)$CH(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}($CH_2Ph)_2$] (**9**)

The preparation of **9** was carried out in an identical manner to that of **7**, from a solution of **3** (0.30 g, 0.80 mmol) and a 2 M solution of $MgCl(CH_2Ph)$ (0.96 mL, 1.92 mmol). Yield: 0.31 g, 64%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.21, 1.38, 1.87, 1.90 (4s, each 3H, C_5Me_4), 1.32 (2d, each 1H, CH_2Ph, $^2J_{H-H}$ = 9.5 Hz), 1.58 (1s, 3H, CH_3), 1.68 (d, 2H, CH_2Ph, $^2J_{H-H}$ = 9.0 Hz), 2.37 (m, 2H, CH_2=C(CH_3)CH_2), 3.38 (t, 1H, CH, $^3J_{H-H}$ = 8.1 Hz), 4.30, 4.57, 6.39, 6.51 (4m, each 1H, C_5H_4), 4.77 (bs, 2H, CH_2=C(CH_3)CH_2), 6.76–7.21 (m, 10H, (2CH_2Ph)). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 11.6, 11.9, 12.2, 14.4 (C_5Me_4), 22.9 (CH_3), 36.5 (CH), 38.1 (CH_2=C(CH_3)CH_2), 74.3, 74.7 ($CH_2Ph)_2$), 95.6, 104.7, 117.0, 119.4, 126.0 (C_5Me_4), 106.9, 109.2, 122.9, 125.4, 128.2 (C_5H_4), 111.8 (CH_2=C(CH_3)CH_2), 141.9 (CH_2=C(CH_3)CH_2), 121.5, 125.8, 125.9, 126.1, 126.1, 128.3, 128.4, 128.5, 128.7, 143.2, 155.8, 155.9 (($CH_2Ph)_2$). Anal. Calc. for $C_{33}H_{38}Ti$: C, 82.14; H, 7.94. Found: C, 82.68; H, 8.09%.

4.10. Synthesis of [Zr{(CH_2=$CHCH_2$)$CH(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Me_2] (**10**)

The preparation of **10** was carried out in an identical manner with that for **6**, from a solution of **4** (0.30 g, 0.75 mmol) and a 1.4 M solution of MgBrMe (1.28 mL, 1.79 mmol). Yield: 0.20 g, 75%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ *−0.29, −0.30* (2s, each 3H, ZrMe_2), 1.44, 1.62, 1.82, 1.83 (4s, each 3H, C_5Me_4), 2.59 (m, 2H, CH_2=CHCH_2), 3.58 (t, CH, $^3J_{H-H}$ = 8.4 Hz); 5.04, 5.09 (2m, each 1H, CH_2=$CHCH_2$), 4.97, 5.11, 6.32, 6.41 (4m, each 1H, C_5H_4); 5.80 (m, CH_2=$CHCH_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 10.7, 11.1, 11.79, 13.8 (C_5Me_4), 31.1, 31.3 (ZrMe_2), 35.4 (CH_2=$CHCH_2$), 38.8 (CH), 113.2 (CH_2=$CHCH_2$), 104.1, 114.1, 117.7, 120.2, 128.9 (C_5H_4), 136.3 (CH_2=$CHCH_2$), 103.8, 106.27, 114.8, 116.3, 129.9 (C_5Me_4). Anal. Calc. for $C_{20}H_{28}Zr$: C, 66.79; H, 7.85. Found: C, 67.33; H, 8.12%.

4.11. Synthesis of [Zr{(CH_2=$CHCH_2$)$CH(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}($CH_2Ph)_2$] (**11**)

The preparation of **11** was carried out in an identical manner to that of **7**, from a solution of **4** (1.00 g, 2.50 mmol) and a 2 M solution of $MgCl(CH_2Ph)$ (2.90 mL, 5.80 mmol). Yield: 1.02 g, 81%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.98, 1.01 (2d, each 1H, CH_2Ph, $^2J_{H-H}$ = 7.3 Hz), 1.40, 1.57, 1.72, 1.73 (4s, each 3H, C_5Me_4), 1.82, 1.85 (2d, each 1H, CH_2Ph, $^2J_{H-H}$ = 11.6 Hz, 11.4 Hz), 2.50 (m, 2H, CH_2=CHCH_2), 3.52 (t, 1H, CH, $^3J_{H-H}$ = 8.5 Hz), 4.96, 5.05 (2m, each 1H, CH_2=$CHCH_2$), 4.66, 4.85, 5.65, 5.77 (4m, each 1H, C_5H_4), 5.74 (m, CH_2=$CHCH_2$), 6.77, 6.87, 7.17 (3m, 10H, 2CH_2Ph). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 10.7, 11.1, 11.8, 13.7 (C_5Me_4), 35.1 (CH_2=$CHCH_2$), 38.5 (CH), 59.5, 59.7 (($CH_2Ph)_2$), 116.4 (CH_2=$CHCH_2$), 104.4, 113.9, 117.2, 119.3, 123.1 (C_5H_4); 135.9 (CH_2=$CHCH_2$), 105.9, 106.9, 119.3, 121.8, 129.2 (C_5Me_4), 125.6, 126.0, 127.6, 127.7, 127.7, 127.9, 128.1, 128.6, 128.5, 128.6 (($CH_2Ph)_2$ Cipso not observed). Anal. Calc. for $C_{32}H_{36}Zr$: C, 75.09; H, 7.09. Found: C, 75.91; H, 7.30%.

4.12. Synthesis of [Zr{(CH_2=C(CH_3)CH_2)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Me_2] (**12**)

The preparation of **12** was carried out in an identical manner to that of **6**, from a solution of **5** (1.00 g, 2.41 mmol) and a 1.4 M solution of MgBrMe in toluene/thf (4.00 mL, 5.60 mmol). Yield: 0.63 g, 71%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ *−0.31, −0.32* (2s, each 3H, Zr*Me*$_2$), 1.49, 1.64, 1.81, 1.83 (4s, each 3H, C_5*Me*$_4$), 1.62 (s, 3H, CH_2=C(CH_3)CH_2), 2.61 (m, 2H, CH_2=C(CH_3)CH_2), 3.76 (t, C*H*, $^3J_{H-H}$ = 8.3 Hz); 4.78, 4.84 [2s, each 1H, CH_2=C(CH_3)CH_2], 4.98, 5.15, 6.31, 6.42 (4m, each 1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 9.3, 9.7, 10.4, 12.6 (C_5*Me*$_4$), 21.5 (CH_2=C(*C*H_3)CH_2), 29.7, 29.8 (Zr*Me*$_2$), 37.8 (CH_2=C(CH_3)CH_2), 36.1 (*C*H), 113.5 (*C*H_2=C(CH_3)CH_2), 103.9, 106.2, 112.0, 113.1, 114.8 (C_5H_4), 142.1 (CH_2=*C*(CH_3)CH_2), 106.8, 115.7, 118.9, 119.9, 128.3 (C_5Me$_4$). Anal. Calc. for $C_{21}H_{30}Zr$: C, 67.50; H, 8.09. Found: C, 67.78; H, 8.22%.

4.13. Synthesis of [Zr{(CH_2=C(CH_3)CH_2)CH(η^5-C_5Me_4)(η^5-C_5H_4)}(CH_2Ph)$_2$] (**13**)

The preparation of **13** was carried out in an identical manner to that of **7**, from a solution of **5** (1.00 g, 2.41 mmol) and a 2 M solution of MgBr(CH_2Ph) (2.80 mL, 5.60 mmol). Yield: 0.95 g, 75%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.98, 1.02 (2d, each 1H, C*H*$_2$Ph, $^2J_{H-H}$ = 10.4 Hz, 10.3 Hz), 1.44 [s, 3H, CH_2=C(CH_3)CH_2], 1.60, 1.72, 1.74 (3s, 6:3:3H, C_5*Me*$_4$), 1.90, 1.88 (2d, each 1H, C*H*$_2$Ph, $^2J_{H-H}$ = 11.9 Hz, 12.00 Hz), 2.57 [m, 2H, CH_2=C(CH_3)C*H*$_2$], 3.75 (t, 1H, C*H*, $^3J_{H-H}$ = 8.3 Hz), 4.87, 4.83 [2m, each 1H, CH_2=C(CH_3)CH_2], 4.72, 4.95, 5.65, 5.78 (4m, 4 each 1H C_5H_4), 6.80–7.25 (m, 10H, 2CH_2*Ph*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 10.7, 11.1, 13.9 (C_5*Me*$_4$), 11.7 (CH_2=C(*C*H_3)CH_2), 38.8 (*C*H_2=C(CH_3)CH_2), 37.3 (*C*H), 59.4, 59.7, 2*C*H_2Ph), 112.2 (CH_2=C(CH_3)CH_2), 106.9, 112.1, 117.0, 119.4, 143.2 (C_5H_4); 137.8 (CH_2=*C*(CH_3)CH_2), 114.0, 116.3, 121.7, 122.7, 143.2 (C_5Me$_4$), 125.9, 126.0, 127.9, 128.1, 128.3, 128.7, 128.5, 129.3, 151.9, 152.0 (CH_2*Ph*). Anal. Calc. for $C_{33}H_{38}Zr$: C, 75.37; H, 7.28. Found: C, 74.76; H, 7.08%.

4.14. Synthesis of [Ti{($CH_3CH_2CH_2$)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**14**)

Pd/C catalyst. Compound **2** (0.30 g, 0.84 mmol) was dissolved in toluene (25 mL) and the Pd/C (10% palladium) catalyst was added (5 mg). Hydrogen was passed through the solution at a pressure of 2 bar with stirring for 2 h at room temperature. The resulting suspension was filtered and the solvent was removed from the filtrate under reduced pressure. The remaining solid was extracted with hexane (2 × 25 mL). The solvent from the filtered solution was removed *in vacuo* to yield the title complex as a brown crystalline solid. Yield: 0.05 g, 18%.

Wilkinson's catalyst. Compound **2** (0.30 g, 0.84 mmol) was dissolved in toluene (25 mL) and Wilkinson's catalyst was added (5 mg). Hydrogen was passed through the solution at a pressure of 2 bar with stirring for 2 h at room temperature. The solvent was removed under reduced pressure and the remaining solid was extracted with hexane (2 × 25 mL). The mixture was filtered and the solvent was removed *in vacuo* to give the title complex as a brown crystalline solid. Yield: 0.23 g, 76%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.83 (t, 3H, C*H*$_3$CH$_2$CH$_2$, $^3J_{H-H}$ = 7.0 Hz), 1.28 (m, 2H, CH$_3$C*H*$_2$CH$_2$), 1.32, 1.49, 1.92 (3s, 3:3:6H, C_5*Me*$_4$), 1.78 (m, 2H, CH$_3$CH$_2$C*H*$_2$), 3.73 (t, 1H, C*H*, $^3J_{H-H}$ = 8.2 Hz), 4.83, 5.02, 6.70, 6.78 (4m, each 1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 11.3, 11.6, 12.2, 14.2 (C_5*Me*$_4$), 12.6 (*C*H$_3$CH$_2$CH$_2$), 19.5 (CH$_3$CH$_2$*C*H$_2$), 31.0 (CH$_3$*C*H$_2$CH$_2$), 37.1 (*C*H), 97.8, 106.5, 121.9, 124.5, 138.4 (C_5Me$_4$), 106.4, 109.0, 125.6, 127.9, 138.9 (C_5H_4). EI MS: *m*/*z* (%) = 358 (100) [M$^+$, [Ti{(CH_2=CHCH$_2$)HC(η^5-C_5Me$_4$)(η^5-C_5H_4)}Cl_2], 322 (79) [M$^+$−Cl], 314 (75) [M$^+$−(CH_2-CH_2CH_3)], 279 (46) [M$^+$−($CH_2CH_2CH_3$−Cl]. Anal. Calc. for $C_{18}H_{24}Cl_2Ti$: C, 60.19; H, 6.74. Found: C, 60.39; H, 6.89%.

4.15. Synthesis of [Ti {(Me_2CHCH_2)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**15**)

Compound **3** (0.30 g, 0.80 mmol) was dissolved in toluene (25 mL) and Wilkinson's catalyst was added (5 mg). Hydrogen was passed through the solution at a pressure of 3 bar with stirring for 4 h at room temperature. The solvent was removed under reduced pressure and the remaining solid was extracted into hexane (2 × 25 mL). The mixture was filtered and the filtrate was removed *in vacuo* to give the title complex as a red crystalline solid. Yield: 0.21 g, 70%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ: 0.80, 0.84 (2d, each 3H, (C*H*$_3$)$_2$CHCH$_2$), $^3J_{H-H}$ = 6.8, $^3J_{H-H}$ = 6.3 Hz), 1.34, 1.49, 1.95 (3s, 3:3:6H, C_5*Me*$_4$), 1.64 (m, 1H, (CH$_3$)$_2$C*H*CH$_2$), 1.90 (m, 2H, (CH$_3$)$_2$CHC*H*$_2$), 3.87 (t, 1H, C*H*, $^3J_{H-H}$ = 8.1 Hz), 4.83, 5.03, 6.69, 6.79 (4m, each 1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C) δ: 12.6, 12.9, 13.5, 15.7 (C_5*Me*$_4$), 22.0, 23.1 (*C*H$_3$), 26.8 ((CH$_3$)$_2$*C*HCH$_2$), 36.9 (*C*H), 39.2 ((CH$_3$)$_2$CH*C*H$_2$), 99.0, 108.0, 123.2, 125.8, 138.2 (C_5Me$_4$), 107.8, 110.3, 126.8, 129.4, 137.4 (C_5H_4). EI MS: *m*/*z* (%) = 372 (100) [M$^+$, [Ti{(CH$_3$)$_2$CHCH$_2$)HC(η^5-C_5Me$_4$)-(η^5-C_5H_4)}Cl_2], 336 (79) [M$^+$−Cl], 279 (41) [M$^+$−Cl−C_4H_9]. Anal. Calc. for $C_{19}H_{26}Cl_2Ti$: C, 61.15; H, 7.02. Found: C, 61.52; H, 7.13%.

4.16. Synthesis of [Zr{($CH_3CH_2CH_2$)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**16**)

The preparation of **16** was carried out in an identical manner to **14**.

Pd/C catalyst. From **4** (0.20 g, 0.50 mmol) Yield: 0.19 g, 95%.

Wilkinson's catalyst. From **4** (0.20 g, 0.50 mmol) Yield: 0.18 g, 93%.

^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.82 (t, 3H, C*H*$_3$CH$_2$CH$_2$, $^3J_{H-H}$ = 7.3 Hz), 1.31 (m, CH$_3$C*H*$_2$CH$_2$, 2H), 1.49, 1.65, 1.86, 1.87 (4s, each 3H, C_5*Me*$_4$), 1.81 (m, 2H, CH$_3$CH$_2$C*H*$_2$), 3.81 (t, 1H, C*H*, $^3J_{H-H}$ = 8.4 Hz), 5.04, 5.19, 6.37, 6.47 (4m, each 1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 11.4, 11.7, 12.4, 13.9 (C_5Me$_4$), 14.3 (*C*H$_3$CH$_2$CH$_2$), 20.8 (CH$_3$*C*H$_2$CH$_2$), 32.9 (CH$_3$CH$_2$*C*H$_2$), 39.1 (*C*H), 104.2, 107.3, 119.7, 121.9, 128.9 (C_5H_4), 105.6, 114.8, 117.7, 121.9, 129.7 (C_5Me$_4$). Mass spectrometry [electron impact (*m*/*e* (*relative intensity*)]: 400 (100) [M$^+$], 358 (64) [M$^+$−CH$_3$CH$_2$CH$_2$], 322 (42) [M$^+$−CH$_3$CH$_2$CH$_2$−Cl]. Anal. Calc. for $C_{18}H_{24}Cl_2Zr$: C, 53.71; H, 6.01. Found: C, 54.78; H, 6.11%.

4.17. Synthesis of [Zr{(Me_2CHCH_2)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**17**)

The preparation of **17** was carried out in an identical manner to **14**.

Pd/C catalyst. From **5** (0.20 g, 0.48 mmol) Yield: 0.10 g, 50%.

Wilkinson's catalyst. From **5** (0.20 g, 0.48 mmol) Yield: 0.19 g, 96%.

^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.80, 0.85 (2d, each 3H, (C*H*$_3$)$_2$CHCH$_2$, $^2J_{H-H}$ = 7.2 Hz), 1.43, 1.54, 1.71, 1.85, (4s, each 3H, C_5*Me*$_4$), 1.65 (m, 1H, (CH$_3$)$_2$C*H*CH$_2$), 1.91 (m, 2H, (CH$_3$)$_2$CHC*H*$_2$), 3.96 (t, 1H, C*H*, $^3J_{H-H}$ = 8.4 Hz), 5.04, 5.21, 5.28 (3m, 2:1:1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 11.7, 11.9, 12.9, 14.9 (C_5*Me*$_4$), 22.5, 23.6 ((*C*H$_3$)$_2$CHCH$_2$), 27.0 ((CH$_3$)$_2$*C*HCH$_2$), 38.1 ((CH$_3$)$_2$CH*C*H$_2$), 40.3 (*C*H), 105.1, 119.8, 119.8, 122.3, 129.1 (C_5H_4), 106.8, 107.4, 122.2, 123.5, 130.7 (C_5Me$_4$). Mass spectrometry [electron impact (*m*/*e* (*relative intensity*)]: 414 (100) [M$^+$], 379 (89) [M$^+$−Cl], 356 (90) [M$^+$−(CH$_3$)$_2$CHCH$_2$], 322 (63) [M$^+$−(CH$_3$)$_2$CHCH$_2$−Cl]. Anal. Calc. for $C_{19}H_{26}Cl_2Zr$: C, 54.79; H, 6.29. Found: C, 55.61; H, 6.41%.

*4.18. Synthesis of [Ti{(9-BBN-$CH_2CH_2CH_2$)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**18**)*

A solution of **2** (0.30 mL, 0.84 mmol) in toluene (50 mL) was added to a stirred 0.4 M solution of 9-borabicyclo[3.3.1]nonane in hexane (0.15 g, 1.26 mmol) and the solution was stirred at 60 °C for 15 h. The solvent was removed *in vacuo* and the remaining brown solid was extracted into hexane (2 × 25 mL) to give the title complex as a red solid. Yield: 0.15 g, 38%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.51 (m, 2H, 9-BBNCH_2CH$_2$CH$_2$), 1.34, 1.83 (2m, each 2H, γ-H of *9-BBN*), 1.63, 1.83 (2m, each 4H, β-H and δ-H of *9-BBN*), 1.80 (m, 2H, α-H of *9-BBN*), 1.76, 1.87, 2.10 (3s, 3:3:6H, C_5Me_4), 1.90 (m, 2H, CH$_2$CH_2CH$_2$), 2.42 (m, 2H, CH$_2$CH$_2$CH_2), 4.40 (t, 1H, C*H*, $^3J_{H-H}$ = 8.2 Hz), 5.27, 5.48, 6.86, 6.96 (4m, each 1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 12.6, 12.9, 14.0, 15.8 (C_5Me_4), 27.2 (BBN-$CH_2CH_2CH_2$), 33.7 (BBN-$CH_2CH_2CH_2$), 34.8 (BBN-$CH_2CH_2CH_2$), 39.0 (*C*H), 22.9, 23.0, 23.1, 23.2 (*9-BBN*), 99.5, 108.0, 124.2, 126.8, 138.1 (C_5Me_4), 108.3, 111.0, 127.2, 129.3, 139.0 (C_5H_4). Mass spectrometry (MALDI) [*m*/*z* (*relative intensity*)]: 479 (23) [M$^+$], 359 (100) [M$^+$−9-BBN], 327 (38) [M$^+$−9-BBN−Cl], 316 (40) [M$^+$−9-BBN−$CH_2CH_2CH_2$]. Anal. Calc. for $C_{26}H_{37}BCl_2Ti$: C, 65.17; H, 7.78. Found: C, 64.38; H, 7.55%.

*4.19. Synthesis of [Zr{(9-BBN-$CH_2CH_2CH_2$)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**19**)*

A solution of **4** (0.40 mL, 1.00 mmol) in toluene (50 mL) was added to a stirred 0.4 M solution of 9-borabicyclo[3.3.1]nonane in hexane (3.75 mL, 1.00 mmol) and the solution was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the remaining solid was washed with hexane (3 × 25 mL) to give the title compound as a yellow solid. Yield 0.44 g, 84%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ: 1.32, 1.83 (2m, each 2H, γ-H of *9-BBN*), 1.63, 1.88 (2m, each 4H, β-H and δ-H of *9-BBN*), 1.81 (m, 2H, α-H of *9-BBN*), 1.40 (m, 2H, BBN-CH_2CH$_2$CH$_2$), 1.53, 1.75, 1.86, 1.90 (4s, each 3H, C_5Me_4),1.63 (m, 2H, CH$_2$CH_2CH$_2$), 2.04 (m, 2H, CH$_2$CH$_2$CH_2), 3.95 (t, 1H, C*H*, $^3J_{H-H}$ = 8,2 Hz); 5.29, 5.10, 6.39, 6.49 (4m, each 1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C) δ: 11.3, 11.6, 12.4, 13.9 (C_5Me_4), 27.9 (9-BBNCH$_2$), 33.1 (CH$_2$CH$_2$CH$_2$), 34.2 (CH$_2$CH$_2$CH$_2$), 39.1 (*C*H), 23.2, 33.2, 33.4 (*9-BBN*), 104.3, 107.2, 119.7, 121.9, 128.9 (C_5H_4), 104.5 114.8, 117.6, 120.3, 129.9 (C_5Me_4). Mass spectrometry (MALDI) [*m*/*z* (*relative intensity*)]: 520(50) [M$^+$]; 485 (95) [M$^+$−Cl]; 357 (100) [M$^+$−(9-BBN)CH$_2$CH(CH$_3$)CH$_2$)]. Anal. Calc. for $C_{26}H_{37}BCl_2Zr$: C, 59.76; H, 7.14. Found: C, 60.35; H, 7.24%.

*4.20. Synthesis of [Zr{(9-BBN-CH_2CH(CH$_3$)CH$_2$)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**20**)*

The preparation of **20** was carried out in an identical manner to **19**, from **5** (0.40 g, 0.96 mmol) and a 0.4 M solution of 9-borabicyclo[3.3.1]nonane in hexane (3.60 mL, 0.96 mmol). Yield: 0.45 g, 87%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ: ***Isomer I*** and ***II***: 0.92, 0.97 (2d, each 3H, $^3J_{H-H}$ = 6.6 Hz, $^3J_{H-H}$ = 6.2 Hz, CH$_2$CH(C*H*$_3$)CH$_2$), 1.34, 1.82 (2m, each 4H, γ-H of *9-BBN*), 1.64, 1.87 (2m, each 8H, β-H and δ-H of *9-BBN*), 1.79 (m, 4H, α-H of *9-BBN*), 1.29, 1.42 (2m, each 2H, 9-BBNCH_2CH$_2$CH$_2$), 1.57, 1.58,1.58, 1.76, 1.78, 1.85, 1.86, 1.87 (8s, each 3H, C_5Me_4), 1.85, 2.10 (m, each 1H, CH$_2$C*H*(CH$_3$)CH$_2$), 2.04–2.15 [m, 4H, CH$_2$CH(CH$_3$)CH_2], 4.08, 4.13 (2t, each 1H, C*H*, $^3J_{H-H}$ = 8.2 Hz, $^3J_{H-H}$ = 8.1 Hz), 5.09, 5.11, 5.30, 5.32, 6.38, 6.49 (6m, 8H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C) δ: ***Isomer I*** and ***II***: 11.3, 11.4, 11.6, 11.6, 12.3, 12.4, 14.3, 14.5 (C_5Me_4), 33.4, 34.1 (CH$_2$CH(CH$_3$)CH$_2$), 23.0, 23.2, 23.6, 23.7, 25.7, 28.7, 31.7, 31.9 (*C*H$_2$, *9-BBN*), 22.6, 22.9 (*C*H$_3$), 23.5, 25.6 (*C*H$_2$CH(CH$_3$)CH$_2$), 37.4, 37.7 (*C*H), 41.6, 41.9 (CH$_2$CH(CH$_3$)*C*H$_2$), 104.7, 104.9, 115.0, 115.2, 116.8, 117.7, 120.2, 120.3, 128.8, 130.0 (*C*$_5$H$_4$), 104.5, 104.6, 107.2, 107.4, 118.7, 119.6, 122.1, 122.2, 128.9, 130.0 (*C*$_5$Me$_4$). Mass spectrometry (MALDI) [*m*/*z* (*relative intensity*)]: 534 (30) [M$^+$]; 500 (25) [M$^+$−Cl]; 373 (100) [M$^+$−(9-BBN)CH$_2$CH(CH$_3$)CH$_2$)]. Anal. Calc. for $C_{27}H_{39}BCl_2Zr$: C, 60.44; H, 7.33. Found: C, 60.71; H, 7.36%.

*4.21. Synthesis of [Ti{(ClMe$_2$SiCH$_2$CH$_2$CH$_2$)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**21**)*

To a solution of **2** (0.30 g, 0.84 mmol) in toluene (50 mL) was added dropwise HSiMe$_2$Cl (0.12 g, 1.26 mmol) in toluene (25 mL). To this solution was added three drops of the Karstedt catalyst [platinum(0) divinyltetramethylsiloxane in xylene (3–3.5%)] and the mixture was stirred for 15 h at room temperature. The solvent was removed under reduced pressure and the residue extracted with hexane (3 × 25 mL). The mixture was filtered and the filtrate was removed *in vacuo* to give the title complex as a brown solid (0.09 g, 24%). ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.40, 0.41 (2s, each 3H, Si*Me*$_2$), 0.72 (m, 2H, SiCH_2CH$_2$CH$_2$), 1.71 (m, 2H, SiCH$_2$CH_2CH$_2$), 1.75, 1.86, 2.09, 2.10 (4s, each 3H, C_5Me_4), 2.37 (m, 2H, SiCH$_2$CH$_2$CH_2), 4.36 (t, 1H, C*H*, $^3J_{H-H}$ = 8.3 Hz), 5.25, 5.46, 6.85, 6.95 (4m, each 1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 1.0 (Si*Me*$_2$); 12.6, 12.9, 14.1, 15.8 (C_5Me_4), 18.4 (SiCH$_2$CH$_2$CH$_2$), 21.7 (SiCH$_2$CH$_2$CH$_2$), 34.1 (SiCH$_2$CH$_2$CH$_2$), 38.7 (*C*H), 107.9, 108.3, 124.0, 126.7, 138.4 (*C*$_5$Me$_4$), 108.2, 110.9, 127.2, 129.3, 138.9 (*C*$_5$H$_4$). ^{29}Si{^{1}H} NMR (125 MHz, C_6D_6, 25 °C) δ 31.02 (*Si*Me$_2$Cl). Mass spectrometry (MALDI) [*m*/*z* (*relative intensity*)]: 453 (21) [M$^+$], 417 (7) [M$^+$−Cl], 357 (100) [M$^+$−SiMe$_2$Cl], 316 (32) [M$^+$−SiMe$_2$Cl−CH$_2$CH$_2$CH$_2$]. Anal. Calc. for $C_{20}H_{29}Cl_3SiTi$: C, 53.17; H, 6.47. Found: C, 53.38; H, 6.34%.

*4.22. Synthesis of [Zr{(ClMe$_2$SiCH$_2$CH$_2$CH$_2$)CH(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**22**)*

Karstedt catalyst. To a solution of **4** (0.50 g, 1.24 mmol) in toluene (50 mL) was added dropwise HSiMe$_2$Cl (0.13 g, 1.36 mmol) in toluene (25 mL). To this solution was added three drops of the Karstedt catalyst [platinum (0) divinyltetramethylsiloxane in xylene (3–3.5%)] and the mixture was stirred for 10 h at 60 °C and then cooled to room temperature. The solvent was removed under reduced pressure to give the title compound as a brown solid. Yield: 0.46 g, 76%.

H_2PtCl_6 catalyst. To a solution of **4** (0.50 g, 1.24 mmol) in toluene (50 mL) was added dropwise HSiMe$_2$Cl (0.13 g, 1.36 mmol) in toluene (10 mL). To this solution was added three drops of the H_2PtCl_6 catalyst and the mixture was stirred for 12 h at 80 °C and then cooled to room temperature. The solvent was removed under reduced pressure to give the title compound as a brown solid. Yield: 0.36 g, 60%.

^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.15 (s, 6H, Si*Me*$_2$), 0.64 (m, 2H, SiCH_2CH$_2$CH$_2$), 1.46 (m, 2H, SiCH$_2$CH_2CH$_2$), 1.51, 1.73, 1.85, 1.86 (4s, 3H, C_5Me_4), 1.95 (m, 2H, SiCH$_2$CH$_2$CH_2); 3.83 (t,1H, C*H*, $^3J_{H-H}$ = 8.3 Hz), 5.07, 5.25, 6.38, 6.48 (4m, each 1H, C_5H_4). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ 1.5 (Si*Me*$_2$); 11.6, 11.9, 12.7, 14.6 (C_5Me_4), 19.2 (SiCH$_2$CH$_2$CH$_2$), 21.6 (SiCH$_2$CH$_2$CH$_2$), 34.5 (SiCH$_2$-CH$_2$CH$_2$), 39.4 (*C*H), 14.6, 107.5, 120.1, 122.2, 129.3 (*C*$_5$H$_4$), 104.5, 114.8, 117.9, 120.6, 130.2 (*C*$_5$Me$_4$). ^{29}Si{^{1}H} NMR (125 MHz, C_6D_6, 25 °C) δ 30.01 (*Si*Me$_2$Cl). Mass spectrometry (MALDI) [*m*/*z* (*relative intensity*)]: 492 (10) [M$^+$], 458 (59) [M$^+$−Cl]. Anal. Calc. for $C_{20}H_{29}Cl_3SiZr$: C, 52.26; H, 6.36. Found: C, 51.38; H, 5.92%.

*4.23. Synthesis of [Zr{(ClMe$_2$SiCH$_2$CH(CH$_3$)CH$_2$)CH(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**23**)*

The synthesis of **23** was carried out in an identical manner to **22** with Karstedt catalyst, from **5** (0.50 g, 1.20 mmol) and HSiMe$_2$Cl (0.12 g, 1.32 mmol). Yield: 0.44 g, 71%. ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C) ***Isomer I*** and ***II*** δ: 0.16, 0.21 (s, each 6H, Si*Me*$_2$), 0.51, 0.66 (2m, each 2H, SiC*H*$_2$CH(CH$_3$)CH$_2$), 0.86, 0.93, (2d, each 3H, SiCH$_2$CH(C*H*$_3$)CH$_2$, $^3J_{H-H}$ = 6.6 Hz, $^3J_{H-H}$ = 6.5 Hz), 1.55, 1.56, 1.58, 1.74, 1.77, 1.84, 1.85, 1.86 (8s, each 3H, C$_5$*Me*$_4$), 1.73, 1.84 (2m, each 1H, SiCH$_2$C*H*(CH$_3$)CH$_2$), 2.12, 2.17 (2m, each 2H, SiCH$_2$CH(CH$_3$)C*H*$_2$), 4.00, 4.05 (2t, each 1H, C*H*, $^3J_{H-H}$ = 8.4 Hz), 5.09, 5.27, 5.32, 6.37, 6.48 (5m, each 1H, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C) ***Isomer I*** and ***II***: δ 2.4, 2.7 (Si*Me*$_2$), 11.4, 11.7, 12.0, 12.2, 12.3, 13.0, 12.3, 13.1 (C$_5$*Me*$_4$), 22.3, 23.8 (SiCH$_2$CH(CH$_3$)CH$_2$), 27.6, 28.3 (SiCH$_2$CH(CH$_3$)CH$_2$), 37.3, 37.9 (*C*H), 40.8, 41.0 (SiCH$_2$*C*H(CH$_3$)CH$_2$), 41.1, 41.3 (SiCH$_2$CH(CH$_3$)*C*H$_2$), 104.8, 105.0, 115.3, 115.5, 118.3, 118.6, 120.8, 120.9, 135.3, 137.1 (*C*$_5$H$_4$), 104.5, 105.1, 107.8, 107.9, 118.7, 120.2, 122.3, 122.7, 129.5, 130.0 (*C*$_5$Me$_4$). ^{29}Si{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C) δ 30.28 (*Si*Me$_2$Cl). Mass spectrometry (MALDI) [*m*/*z* (*relative intensity*)]: 506 (79) [M$^+$], 471(12) [M$^+$−Cl], 378 (100) [M$^+$−Me$_2$ClSi−Cl]. Anal. Calc. for C$_{21}$H$_{31}$Cl$_3$SiZr: C, 49.54; H, 6.14. Found: C, 51.02; H, 6.35%.

*4.24. Synthesis of [Zr{(t-BuMe$_2$SiOSi(Me$_2$)CH$_2$CH$_2$CH$_2$)CH(η^5-C$_5$Me$_4$)-(η^5-C$_5$H$_4$)}Cl$_2$] (**24**)*

To a solution of **4** (0.20 g, 0.40 mmol) in toluene (50 mL) was added *t*-BuMe$_2$SiOH (0.05 g, 0.40 mmol). To this solution was added NEt$_3$ (0.02 g, 0.40 mmol) and the mixture was stirred for 3 h at 60 °C and then cooled to room temperature. The resulting suspension was filtered and the solvent was removed from the filtrate under reduced pressure to give the title complex as yellow oil. Yield: 0.17 g, 75%. ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C) δ: 0.20, 0.18 (2s, each 3H, Si*Me*$_2$), 0.21 (s, 6H, ^{t}Bu*Me*$_2$Si), 0.71 (m, 2H, SiC*H*$_2$CH$_2$CH$_2$), 1.10 (s, 9H, ^{t}*Bu*MeSi), 1.65 (m, 2H, SiCH$_2$C*H*$_2$CH$_2$), 1.73, 1.74, 1.78, 1.97 (4s, each 3H, C$_5$*Me*$_4$), 2.29 (m, 2H, SiCH$_2$CH$_2$C*H*$_2$), 4.15 (t, *CH*, $^3J_{H-H}$ = 8.5 Hz), 5.42, 5.64, 6.22, 6.35 (4m, each 1H, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C) δ: −0.8, −0.8 (Si*Me*$_2$), −0.6, −0.5 (^{t}Bu*Me*$_2$Si), 25.9 ((Me$_3$)CMe$_2$Si), 26.9 ((*Me*$_3$)CMe$_2$Si), 12.0 11.1, 11.5, 13.9 (C$_5$*Me*$_4$), 19.3 (SiCH$_2$CH$_2$CH$_2$), 22.2 (SiCH$_2$CH$_2$CH$_2$), 35.2 (SiCH$_2$CH$_2$CH$_2$), 39.4 (*C*H), 101.3, 104.5, 114.4, 117.0, 134 .4 (*C*$_5$H$_4$), 112.0, 112.2, 114.8 116.9, 132.1 (*C*$_5$Me$_4$). ^{29}Si{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C) δ: 10.11, 9.54 (*Si*OSi). Anal. Calc. for C$_{22}$H$_{36}$Cl$_2$OSi$_2$Zr: C, 50.12; H, 6.96. Found: C, 49.41; H, 6.78%.

*4.25. Synthesis of [{(n-Bu)CH(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}]Zr{Me{κ^2-O,N-OC(Me)NPh}] (**26**)*

To a solution of **25** (0.50 g, 1.33 mmol) in toluene (50 mL) was added PhNCO (0.14 mL, 1.33 mmol) and the mixture was stirred for 10 h at room temperature. The resulting suspension was filtered and the solvent was removed from the filtrate under reduced pressure to give the title complex as red oil. Yield: 0.38 g, 59%. ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C) ***Isomer A*** and ***Isomer B*** δ: −0.37, −0.38 (2s, each 3H, Zr*Me*), 0.87 (m, 6H, (CH$_2$)$_3$C*H*$_3$), 1.34, 1.77, 1.93 (3m, each 4H, (*CH*$_2$)$_3$CH$_3$), 1.38, 1.41, 1.59, 1.61, 1.63, 1.73, 1.74, 2.05 (8s, each 3H, C$_5$*Me*$_4$), 2.12, 2.13 (2s, each 3H, OC(*Me*)NPh), 3.52, 3.59 (2t, each 1H, $^3J_{H-H}$ = 8.4 Hz, C*H*), 4.89, 4.93, 4.97, 5.42, 5.59, 5.78, 5.84, 5.95 (8s, each 1H, C$_5$*H*$_4$), 6.96, 7.01, 7.37 (3m, 5H, OC(Me)N*Ph*). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C) δ: 10.3, 10.7, 10.8, 11.3, 11.6, 11.6, 12.0, 13.9 (C$_5$*Me*$_4$), 14.2 ((CH$_2$)$_3$*C*H$_3$), 20.7, 20.8, 21.3, 21.4, 30.0, 30.2 ((*C*H$_2$)$_3$CH$_3$), 30.4, 30.8 (OC(*Me*)NPh), 31.3, 31.5 (Zr*Me*), 39.3, 39.4 (*C*H), 99.5, 101.9, 102.9, 105.6, 108.3, 11.6, 113.8, 115.9, 118.7, 119.4, 119.5, 119.7, 119.8, 119.9, 120.1, 129.9 (*C*$_5$Me$_4$ and *C*$_5$H$_4$), 128.8, 128.9, 129.1, 129.2, 129.3, 129.4, 129.9, 130.0 (OC-(Me)N*Ph*), 180.8, 180.9 (O*C*(Me)NPh). IR (Nujol): ν_{C-N} 1660 cm^{-1}, ν_{C-O} 1705 cm^{-1}. Anal. Calc. for C$_{28}$H$_{37}$NOZr: C, 67.96; H, 7.54. Found: C, 68.41; H, 8.17%.

*4.26. Synthesis of [{(n-Bu)CH(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]}Zr(CH$_2$Ph){η^2-O,C-COCH$_2$Ph}] (**28**)*

Compound **27** (1.00 g, 2.66 mmol) was dissolved in toluene (50 mL) and CO was passed through the solution at a pressure of 2 bar with stirring for 30 min at room temperature. Pentane (25 mL) was added to the resulting solution to obtain an orange solid and a yellow solution. The mixture was filtered and the orange solid dried *in vacuo* to give the title complex. Yield: 1.18 g, 80%. ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C) ***Isomer cis n-Bu*** and ***Isomer trans n-Bu***: δ: 0.85 (m, 6H, (CH$_2$)$_3$C*H*$_3$), 1.05, 1.08 (2s, each 2H, (C*H*$_2$Ph), 1.32, 1.55, 1.56, 1.61, 1.80, 1.84, 1.98, 2.06 (8s, each 3H, C$_5$*Me*$_4$), 1.34, 1.89, 1.92 (3m, each 4H, (*CH*$_2$)$_3$CH$_3$), 1.96, 2.00 (2d, each 2H, PhC*H*$_2$CO, $^2J_{H-H}$ = 12.0 Hz), 3.49, 3.53 (2t, each 1H, C*H*, $^3J_{H-H}$ = 8.4 Hz), 4.57, 4.70, 4.79, 5.05, 5.11, 5.15, 6.77, 6.87 (8s, each 1H, C$_5$*H*$_4$), 6.95, 7.07, 7.17, 7.42, 7.26 (5m, 10H, *Ph*CH$_2$CO). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C) δ: 9.9, 10.1, 10.4, 12.1, 12.5, 13.7, 14.0, 14.1 (C$_5$*Me*$_4$), 14.3, 14.4 ((CH$_2$)$_3$*C*H$_3$), 22.9, 23.0, 30.8, 31.0, 31.2, 31.5 ((*C*H$_2$)$_3$CH$_3$), 38.1 (PhCH$_2$CO), 39.2, 39.4 (*C*H), 47.5, 47.7 (*C*H$_2$Ph), 99.3, 100.9, 101.7, 101.9, 103.9, 107.1, 107.8, 109.6, 110.8, 113.0, 113.3, 113.6, 114.4, 115.2, 116.6, 117.7, 119.0, 119.8 (*C*$_5$Me$_4$ and *C*$_5$H$_4$), 125.1, 125.3, 125.6, 126.1, 128.7, 128.9, 129.2, 130.2, 130.3, 134.0, 134.1, 137.8, 141.9 (*Ph*CH$_2$CO), 156.5, 156.7 (PhCH$_2$*C*O). IR (Nujol): ν_{C-O} 1594 cm^{-1}. Anal. Calc. for C$_{34}$H$_{40}$OZr: C, 73.46; H, 7.25. Found: C, 75.02; H, 7.94%.

*4.27. X-ray structure determinations of [Zr{(CH$_2$=CHCH$_2$)CH(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**4**), [Zr{(CH$_2$=CHCH$_2$)CH(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}(CH$_2$Ph)$_2$] (**11**), [Zr{(CH$_3$CH$_2$CH$_2$)CH(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**16**) and [Zr{(CH$_3$)$_2$CHCH$_2$)CH(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (**17**)*

A summary of crystal data collection and refinement parameters for all compounds is given in Tables 1 and 2. The single-crystals of **4**, **11**, **16** and **17** were mounted on a glass fibre and transferred to a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite monochromated Mo Kα radiation source (λ = 0.71073 Å). Several sets of narrow data "frames" were collected using 0.3° wide ω scan frames covering the complete spheres of the reciprocal space with a crystal-to-detector distance of 6.0 cm. Data were integrated using SAINT [22] and an absorption correction was based on multiple scans with the program SADABS [23]. The software package SHELXTL version 6.12 [24] was used for space group determination, structure solution and refinement by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. The asymmetric unit of **4** contains two independent molecules. *Special features*/*exceptions*: single-crystals of **4** were obtained from a concentrated toluene solution. Despite several crystal measurements, all crystals were of very poor quality and only led to a structural solution with an *R* value of 18.4%. Only the Zr and Cl atoms were refined with anisotropic displacement parameters. Despite these poor results from the crystallographic point of view, the results obtained are sufficient to adequately establish the atom connectivity.

Acknowledgements

We gratefully acknowledge financial support from the Ministerio de Educación y Ciencia, Spain (Grant No. CTQ2006-11845), the Junta de Comunidades de Castilla La Mancha (Grant No. PCI08-0032-0957) and the program Consolider-Ingenio 2010 ORFEO CSD2007-00006.

Appendix A. Supplementary material

CCDC 710532, 710533, 710534 and 710535 contain the supplementary crystallographic data for **4**, **11**, **16** and **17**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.01.038.

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[21] Preparation of **1a** solution: a 2 M solution of $MgCl(CH_2CH{=}CH_2)$ in thf (3.80 mL, 7.60 mmol) was added to a stirred solution of $K[(C_5H_4)CH{=}(C_5Me_4)]$ (1.50 g, 6.34 mmol) in thf (100 mL) at −78 °C. The solution was allowed to warm up to room temperature and stirred for 15 h. The preparation of **1b** was carried out in an identical manner to **1a**, from a 0.5 M solution of $MgCl(CH_2C(CH_3){=}CH_2)$ in thf (15.21 mL, 7.60 mmol) and $K[(C_5H_4)CH{=}(C_5Me_4)]$ (1.50 g, 6.34 mmol) in thf (50 mL).
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