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Niobium, titanium, zirconium and hafnium complexes incorporating germanium bridged *ansa* ligands. X-Ray crystal structures of $[Zr\{Me_2Ge(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ and $[M\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Zr, Hf)

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Abstract

Both the symmetric and asymmetric *ansa*-ligand precursors $Me_2Ge(C_5Me_4H)_2$ (**1**) and $Me_2Ge(C_5Me_4H)(C_5H_4R)$ (R = H (**3**), Me (**4**)) and their lithium derivatives $Li_2\{Me_2Ge(C_5Me_4)_2\}$ (**5**) and $Li_2\{Me_2Ge(C_5Me_4)(C_5H_3R)\}$ (R = H (**6**), Me (**7**)) have been prepared. The *ansa*-niobocene imido complex $[Nb(=NBu^t)\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl]$ (**8**) was synthesized by the reaction of $[Nb(=NBu^t)Cl_3(py)_2]$ with the appropriate lithiated *ansa*-precursor. The Group 4 metal complexes containing germanium bridged *ansa*-ligands $[M\{Me_2Ge(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (M = Ti (**9**), Zr (**10**), Hf (**11**)), $[M\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**12**), Zr (**13**), Hf (**14**)), and $[M\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)\}Cl_2]$ (M = Ti (**15**), Zr (**16**), Hf (**17**)) were prepared by the reaction of MCl_4 and the corresponding lithiated *ansa*-derivative. The molecular structures of **10**, **13** and **14** were determined by single-crystal X-ray diffraction studies. Preliminary results for the catalytic activity of the Group 4 *ansa*-metallocene complexes in the polymerization of ethylene and propylene are reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *ansa*-Metallocene complexes; Niobium; Titanium; Zirconium; Hafnium; Germanium; Homogeneous catalysis

1. Introduction

The use of *ansa*-cyclopentadienyl ligands has received wide attention in the chemistry of Group 4 metals [1], due mainly to their ability to impart to their complexes a selective degree of catalytic activity [2]. Recent studies have demonstrated that the incorporation of the *ansa*-bridge may have a profound influence on the behavior of the metallocene system [3]. Furthermore the use of substituted *ansa*-cyclopentadienyl ligands in the stereoselective synthesis of Group 4 metal complexes and their importance in catalysis is receiving special attention [4]. Simple ligand design, as in $Me_2Si(C_5H_3Me\text{-}3)_2$, has been shown to lead to stereoselective catalysts, eg. *rac*-$[Zr\{Me_2Si(C_5H_3Me)_2\}Cl_2]$ [5]. Some examples of asymmetric *ansa*-zirconocene complexes have been described [6], although the great majority contain indenyl or fluorenyl systems [7].

The use of silicon in the single atom *ansa*-bridge has been widely exploited, however, few examples have been reported for analogue germanium systems [8].

We have previously described the preparation of niobocene complexes containing *ansa*-ligands [9] and following from this the synthesis of niobium and zirconium systems with symmetrically and asymmetrically substituted *ansa*-ligands [9b,10]. As an extension of this work we report here the synthesis and structure of niobium, and Group 4 metal complexes incorporating

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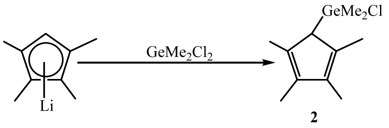
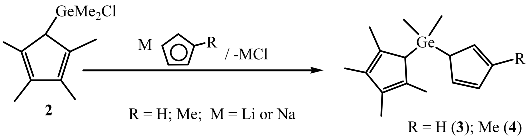
germanium bridged *ansa*-ligands and their role as catalysts in the polymerization of ethylene and propylene.

2. Results and discussion

The symmetric *ansa*-ligand precursor $Me_2Ge(C_5Me_4H)_2$ (**1**) was synthesized following the published procedure [11]. The reaction of one molar equivalent of $Li(C_5Me_4H)$ and $GeMe_2Cl_2$ gave $Me_2Ge(C_5Me_4H)Cl$ (**2**) (see Eq. (1a)). The preparation of the asymmetrically substituted *ansa*-ligands precursors $Me_2Ge(C_5Me_4H)(C_5H_4R)$ (R = H (**3**), Me (**4**)) was achieved by the reaction of $Me_2Ge(C_5Me_4H)Cl$ (**2**) and $Li(C_5H_5)$ or $Na(C_5H_4Me)$, respectively (see Eq. (1b)). **2**–**4** were characterized by ^{1}H-NMR spectroscopy and electron impact mass spectroscopy.

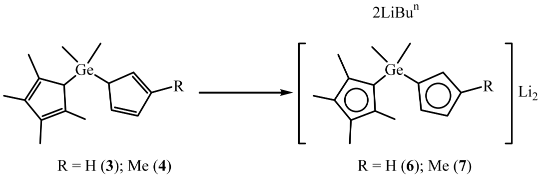


(1a)



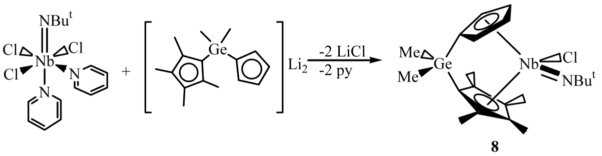
(1b)

The *ansa*-ligands **1**, **3** and **4** were lithiated in the normal manner with *n*-butyllithium giving the di-lithium derivates, $Li_2\{Me_2Ge(C_5Me_4)_2\}$ (**5**) and $Li_2\{Me_2Ge(C_5Me_4)(C_5H_3R)\}$ (R = H (**6**), Me (**7**)), in high yields (see Eq. (2)).



(2)

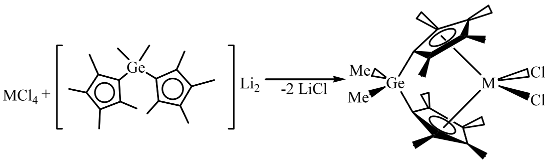
The reaction of the di-lithium derivative **6** with $[Nb(=NBu^t)Cl_3(py)_2]$ gave the niobium derivative $[Nb(=NBu^t)\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl]$ (**8**) which is the first example of a niobocene complex incorporating a germanium bridged *ansa* ligand (see Eq. (3)).



(3)

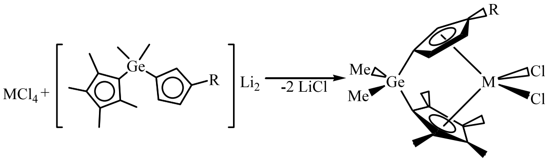
The ^{1}H-NMR spectrum of **8** shows the lack of symmetry in this chiral complex, with the four methyl groups attached to the cyclopentadienyl ring being inequivalent as are the methyl groups of the $SiMe_2$ bridge and the four protons of the unsubstituted cyclopentadienyl moiety (see Section 3). By comparison with our previous work in niobocene imido chemistry we can assume that the imido group acts as a four electron donor. **8** can, therefore, be considered as a '20 electron' complex [9b,10a,12]. However, the excess two electrons are most probably located in a ligand-based orbital as has previously been reported for similar compounds [13].

The reaction of the di-lithium derivatives **5**–**7** with either $[TiCl_4(THF)_2)]$, $ZrCl_4$ or $HfCl_4$ gave the corresponding *ansa*-metallocene dichloride complex, $[M\{Me_2Ge(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (M = Ti (**9**), Zr (**10**), Hf (**11**)), $[M\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**12**), Zr (**13**), Hf (**14**)), and $[M\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)\}Cl_2]$ (M = Ti (**15**), Zr (**16**), Hf (**17**)) (see Eq. (4)).



M = Ti (**9**); Zr (**10**); Hf (**11**)

(4a)



R = H, M = Ti (**12**); Zr (**13**); Hf (**14**)
R = Me, M = Ti (**15**); Zr (**16**); Hf (**17**)

(4b)

During the preparation of this manuscript, a similar method in preparing complexes **9**, **10**, **12** and **13** has been published [8d,8e].

9–**17** were isolated as crystalline solids and characterized spectroscopically. The ^{1}H-NMR spectra for the C_{2v} symmetric complexes **9**–**11** showed three methyl signals. Two correspond to the α- and β-methyl groups of the substituted cyclopentadienyl ligands. The third signal was assigned to the methyl groups of the $GeMe_2$ bridge (see Section 3).

The ^{1}H spectra for **12**–**14** showed the expected signals for the C_s symmetrical complexes. Thus the cyclopentadienyl ring protons H2 and H5, and H3 and H4 are equivalent and two multiplets corresponding to the AA′BB′ system between 5.20 and 7.20 ppm were observed. In addition, two singlets were observed corresponding to the methyl groups of the tetramethylcyclopentadienyl moiety. Finally, the methyl groups of the $GeMe_2$ bridging unit are equivalent and gave a unique signal (see Section 3).

The symmetry of the molecule changes from C_s to C_1 when a methyl substituent is introduced in the unsubstituted C_5 ring as is the case of the chiral complexes **15**–**17**. The ^{1}H-NMR spectra of these complexes gave three multiplets between 4.80 and 6.80 ppm for the protons of the mono substituted C_5 ring, four singlets for the non-equivalent methyl groups of the tetramethyl substituted C_5 ring and two singlets corresponding to the now inequivalent methyl groups of the $GeMe_2$ bridging unit. A further signal was observed for the methyl substituent of the mono substituted C_5 ring (see Section 3).

The molecular structures of **10**, **13** and **14** were established by X-ray crystal studies [14]. The molecular structures and atomic numbering schemes are shown in Figs. 1–3. Selected bond lengths and angles for **10**, **13** and **14** are given in Table 1.

The structures of **10**, **13** and **14** show the typical bent metallocene conformation normally observed in Group 4 metal dichloride complexes. The *ansa*-ligand chelates the metal atom and both cyclopentadienyl rings are bound to the metal in an η^5-mode. A comparison of **10** and **13** with related zirconocene and *ansa*-zirconocene complexes is given in Table 2 and shows that the molecular structures of all these complexes are essentially the same. The Cent–Zr–Cent angles of **10** and **13** are of values very similar to their silicon analogues, $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ [15] and $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ [10a] (see Table 2). The structure of the hafnocene complex **14** is also comparable with its silicon bridged *ansa*-analogue $[Hf\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ [8d] (see Table 2).

The polymerization of ethylene using **9**, **10**, **12**, **13**, **15** or **16** as catalyst with a MAO–metal catalyst ratio of 1000:1 has been carried out. The polymerization experiments were carried out at 25 °C and at olefin pressure of 1.5 bar during 30 min. The results of the experiments are given in Table 3. The titanium and zirconium *ansa*-complexes **9**, **10**, **12**, **13**, **15** and **16** exhibit activities in the polymerization of ethylene somewhat lower than that observed for the non-*ansa*-complex $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ under the same conditions. The *ansa*-zirconium complexes, as expected, show higher activities (ca. double) with respect to their titanium analogues.

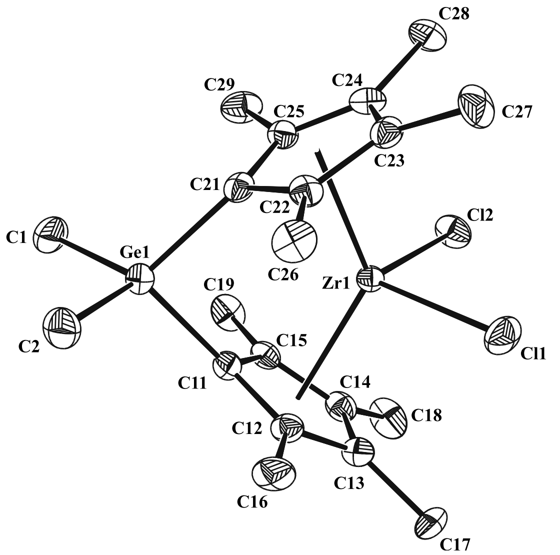


Fig. 1. Molecular structure and atom-labelling scheme for $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (**10**), with thermal ellipsoids at 30% probability.

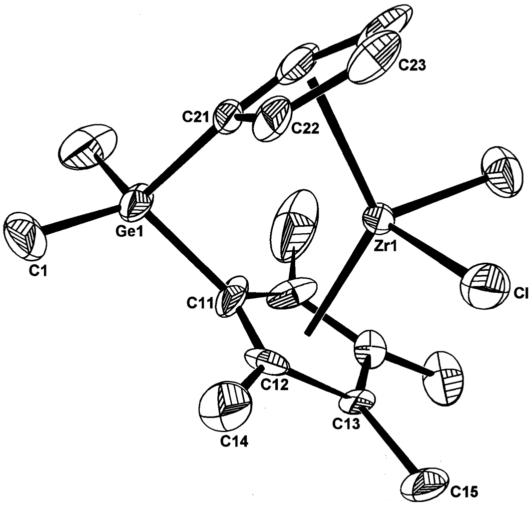


Fig. 2. Molecular structure and atom-labelling scheme for $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**13**), with thermal ellipsoids at 20% probability.

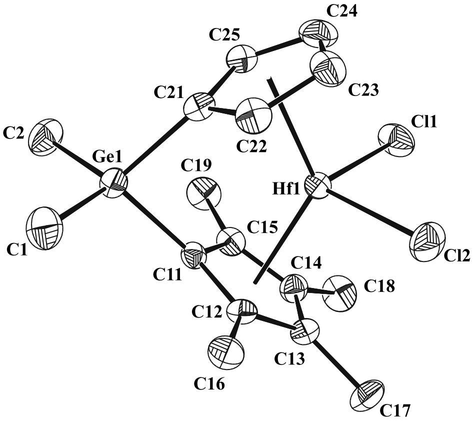


Fig. 3. Molecular structure and atom-labelling scheme for $[Hf\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**14**), with thermal ellipsoids at 30% probability.

We have also tested the *ansa*-metallocene complexes **9**, **10**, **12**, **13**, **15** and **16** as catalysts in the polymerization of propylene. The experiments were carried out at 25 °C in the presence of the appropriate *ansa*-metallocene complex and MAO co-catalyst (ratio 1/2000) and at an olefin pressure of 2 bar during 30 min. The results of the experiments are given in Table 4.

The catalytic activities for all the complexes were markedly lower than those recorded for $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$. The zirconium *ansa*-complexes gave higher

Table 1
Selected bond lengths (Å) and angles (°) for **10**, **13** and **14**

	10	**13**	**14**
Bond lengths			
M(1)–Cent(1)	2.240	2.217	2.210
M(1)–Cent(2)	2.229	2.213	2.193
av M(1)–C(Cent(1)) [a]	2.547	2.50	2.515
av M(1)–C(Cent(2)) [a]	2.529	2.51	2.495
M(1)–Cl(1)	2.437(2)	2.404(9)	2.403(3)
M(1)–Cl(2)	2.426(2)		2.414(3)
Bond angles			
Cent(1)–M(1)–Cent(2)	129.39	127.5	127.74
Ge(1)–C(11)–Cent(1)	162.78	164.9	164.38
Ge(1)–C(21)–Cent(2)	163.04	163.8	161.56
C(11)–Ge(1)–C(21)	92.7(3)	91.0(1)	91.2(3)
Cl(1)–M(1)–Cent(1)	105.95	107.8	106.54
Cl(1)–M(1)–Cent(2)	105.96	105.5	107.08
Cl(2)–M(1)–Cent(1)	106.28		106.95
Cl(2)–M(1)–Cent(2)	106.67		106.21
Cl(1)–M(1)–Cl(2)	98.35(7)	99.3(5)	98.6(1)

For **10** and **14** Cent(1) and Cent(2) are the centroids of C(11)–C(15) and C(21)–C(25), respectively. For **13** Cent(1) and Cent(2) are the centroids of C(11)–C(13) and C(21)–C(23), respectively.

[a] Average bond distance between M(1) and the carbon atoms of the C_5 ring of the corresponding cyclopentadienyl moiety.

Table 3
Ethylene polymerization results for [M{$Me_2Ge(\eta^5-C_5Me_4)_2$}Cl_2] (M = Ti (**9**), Zr (**10**)), [M{$Me_2Ge(\eta^5-C_5Me_4)(\eta^5-C_5H_4)$}$Cl_2$] (M = Ti (**12**), Zr (**13**)), [M{$Me_2Ge(\eta^5-C_5Me_4)(\eta^5-C_5H_3Me)$}$Cl_2$] (M = Ti (**15**), Zr (**16**)) and [$Zr(\eta^5-C_5H_5)_2Cl_2$] [a]

Catalyst	Activity [b]	M_w (g mol^{-1})	M_w/M_η
[Ti{$Me_2Ge(\eta^5-C_5Me_4)_2$}Cl_2] (**9**)	1734	n.d. [c]	n.d. [c]
[Zr{$Me_2Ge(\eta^5-C_5Me_4)_2$}Cl_2] (**10**)	2500	182 000	4.5
[Ti{$Me_2Ge(\eta^5-C_5Me_4)$-($\eta^5-C_5H_4$)}Cl_2] (**12**)	2734	n.d. [c]	n.d. [c]
[Zr{$Me_2Ge(\eta^5-C_5Me_4)$-($\eta^5-C_5H_4$)}Cl_2] (**13**)	5331	176 000	5.2
[Ti{$Me_2Ge(\eta^5-C_5Me_4)(\eta^5-C_5H_3Me)$}$Cl_2$] (**15**)	1667	n.d. [c]	n.d. [c]
[Zr{$Me_2Ge(\eta^5-C_5Me_4)(\eta^5-C_5H_3Me)$}$Cl_2$] (**16**)	3700	179 000	4.9
[$Zr(\eta^5-C_5H_5)_2Cl_2$]	5911	200 000	5.5

[a] At 25 °C, 1.5 bar monomer pressure, 150 ml toluene, [MAO] = 4×10^{-2} mol l^{-1}, [Ti] or [Zr] = 4×10^{-5} mol l^{-1}, t_{Pol} = 30 30 min.

[b] In kg Pol (mol (Ti or Zr) h)$^{-1}$.

[c] Not determined.

activities than their titanium analogues. The C_{2v} catalysts **9** and **10** gave the expected atactic polymers.

For **12** and **13**, the C_s symmetry should make the metallocene catalyst syndiospecific in the polymerization of propylene. However, Morokuma and co-workers have predicted, via theoretical studies, that catalytic systems based on the C_s symmetric $H_2Si(C_5Me_4)(C_5H_4)$ ligand will be substantially non enantioselective, due to repulsive interactions between the methyl group of the propylene and the methyl groups of the C_5Me_4 ligand [18]. Our results concur with this affirmation, with the polypropylene obtained using **12** and **13** as catalyst being of low stereospecificity (as observed by ^{13}C-NMR spectroscopy of the polymer). This is in agreement with previous studies conducted on the metallocene complex [Zr{$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)$}$Cl_2$] where this phenomenon was explained by the assumption that the polymer chain experiences counterbalanced steric forces exerted by the monomer methyl group on one hand and from the β-methyl cyclopentadienyl (C_5*Me*$_4$) substituents on the other [10b,19].

The *ansa*-metallocene complexes **15** and **16** exhibit C_1 symmetry. In C_1 symmetric catalysts, the two available coordination positions are non equivalent. If we assume that a chain migratory insertion mechanism is taking place and that the two coordination positions are of similar energy then these catalysts will be isospecific or syndiospecific if propylene coordination at the two coordination positions are enantioselective in favor of the same or opposite propylene enantiofaces, respectively. If propylene coordination is enantioselective in

Table 2
Selected structural data of some zirconocene and hafnocene complexes

Complex	Zr(Hf)–Cp[a]	Zr(Hf)–Cl	Cp–Zr(Hf)–Cp	Cl–Zr(Hf)–Cl	$C_{(cp)}$–Ge(Si)–$C_{(cp)}$	Reference
[$Zr(\eta^5-C_5H_5)_2Cl_2$]	2.21(1)	2.441(5)	129	97.1(2)		[15]
[Zr{$Me_2Si(\eta^5-C_5Me_4)_2$}Cl_2]	2.329	2.4334(7)	128.6	92.28	95.7(1)	[16]
[Zr{$Me_2Ge(\eta^5-C_5Me_4)_2$}Cl_2] (**10**)	2.234	2.432(2)	129.34	93.33(8)	92.7.7(3)	This work
[$Zr(\eta^5-C_5H_5)(\eta^5-C_5Me_5)Cl_2$]	2.209 Cp, 2.219 Cp*	2.442	130.01	97.78		[17]
[Zr{$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)$}$Cl_2$]	2.198(4) Cp*, 2.202(3) Cp	2.451(1)	128.10(2)	104.60(7)	95.2(2)	[10a]
[Zr{$Me_2Ge(\eta^5-C_5Me_4)(\eta^5-C_5H_4)$}$Cl_2$] (**13**)	2.208 Cp*, 2.229 Cp	2.442(4)	129.9(2)	101.7(2)	90.9(5)	This work
[Hf{$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)$}$Cl_2$]	2.193 Cp*, 2.201 Cp	2.415(2), 2.411(2)		99.96	94.1(2)	[8d]
[Hf{$Me_2Ge(\eta^5-C_5Me_4)(\eta^5-C_5H_4)$}$Cl_2$] (**14**)	2.210 Cp*, 2.193 Cp	2.408(3)	127.74	98.6(1)	91.2(3)	This work

[a] Cp refers to the C_5H_4 or C_5H_3R moiety. Cp* refers to the C_5Me_4 moiety.

Table 4
Propylene polymerization results for [M{$Me_2Ge(\eta^5\text{-}C_5Me_4)_2$}$Cl_2$] (M = Ti (**9**), Zr (**10**)), [M{$Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)$}$Cl_2$] (M = Ti (**12**), Zr (**13**)), [M{$Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)$}$Cl_2$] (M = Ti (**15**), Zr (**16**)) and [$Zr(\eta^5\text{-}C_5H_5)_2Cl_2$] [a,b]

Catalyst	Activity [c]	M_w (g mol^{-1})	M_w/M_η	M.p. (°C)
[Ti{$Me_2Ge(\eta^5\text{-}C_5Me_4)_2$}$Cl_2$] (**9**)	667	n.d. [d]	n.d. [d]	38
[Zr{$Me_2Ge(\eta^5\text{-}C_5Me_4)_2$}$Cl_2$] (**10**)	1000	15 200	10.3	33
[Ti{$Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)$}$Cl_2$] (**12**)	1100	n.d. [d]	n.d. [d]	95
[Zr{$Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)$}$Cl_2$] (**13**)	1666	190 200	8.8	99
[Ti{$Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)$}$Cl_2$] (**15**)	900	n.d. [d]	n.d. [d]	106
[Zr{$Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)$}$Cl_2$] (**16**)	1400	178 300	9.7	101
[$Zr(\eta^5\text{-}C_5H_5)_2Cl_2$]	5315	14 400	12.4	30

[a] At 25 °C, 2.0 bar monomer pressure, 150 ml toluene, [MAO] = 8×10^{-2} mol l^{-1}, [Zr] = 4×10^{-5} mol l^{-1}, t_{Pol} = 30 min.
[b] ^{13}C-NMR spectra showed essentially atactic polymers.
[c] In kg Pol (mol (Ti or Zr) h)$^{-1}$.
[d] Not determined.

only one of the coordination positions then the corresponding catalytic system will be *hemi*-isospecific.

In the case of [M{$Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)$}$Cl_2$] (M = Ti (**15**), Zr (**16**)) the catalyst is only enantioselective in one of the two coordination positions due to the fact that the β-alkyl cyclopentadienyl substituents orientated towards the more crowded position are both identically sized methyl groups (see Fig. 4). **15** and **16** should, therefore, produce *hemi*-isotactic polypropylene. However, we were unable to verify this as the ^{13}C-NMR spectrum of the polymer was complicated by the high atactic nature of this type of plastics.

The m.p. for all the polymers obtained were determined (see Table 4). The C_{2v} symmetric catalysts, **9** and **10**, produce amorphous plastics with low m.p. (33–38 °C). The C_s and C_1 metallocene catalysts, **12**, **13**, **15** and **16**, give semi-crystalline plastics with higher melting points (95–106 °C). However, in previous studies for high stereoregular isotactic polymers, melting points in the range of 140–160 °C have been observed [20].

In conclusion, we report the synthesis and structural characterization of niobium and Group 4 *ansa*-metallocene complexes and their use as catalysts in the polymerization of ethylene and propylene.

3. Experimental

3.1. Materials and procedures

All reactions were performed using standard Schlenk tube techniques in an atmosphere of dry nitrogen.

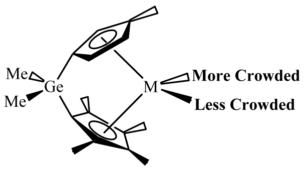


Fig. 4. Steric conditions in the metallocene catalysts **15** and **16**.

Solvents were distilled from appropriate drying agents and degassed before use.

$Me_2Ge(\eta^5\text{-}C_5Me_4H)_2$ (**1**) [11] and [Nb(=NBu^t)$Cl_3(py)_2$] [21] were prepared as described earlier. [$TiCl_4(THF)_2$], $ZrCl_4$, $HfCl_4$ and $GeMe_2Cl_2$ were purchased from Aldrich and used directly. ^{1}H- and ^{13}C-spectra were recorded on a Varian FT-300 spectrometer and referenced to the residual deuteriated solvent. Microanalyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectroscopic analyses were preformed on a Hewlett–Packard 5988A (*m*/*z* 50–1000) instrument (electron impact). Polymer melting points (m.p.) were determined using a Gallenkamp m.p. apparatus.

3.2. Synthesis of $Me_2Ge(C_5Me_4H)Cl$ (**2**)

$GeMe_2Cl_2$ (1.00 g, 5.76 mmol) in THF (50 ml) was added to a solution of $Li(C_5Me_4H)$ (0.74 g, 5.76 mmol) in THF (50 ml) at −78 °C. The reaction mixture was allowed to warm to room temperature (r.t.) and stirred for 15 h. Solvent was removed in vacuo and hexane (150 ml) was added to the resulting orange oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as a yellow oil (1.89 g, 95%). ^{1}H-NMR (300 MHz, C_6D_6) (for the predominant isomer): $-\delta$ 0.28 (s, 6H, Ge*Me*$_2$), 1.65 (6H), 1.82 (6H) (s, C_5*Me*$_4$), 3.22 (m, 1H, *H*C_5). MS electron impact (*m*/*e* (relative intensity)): 260 (10) (M^+, $Me_2Ge(C_5Me_4H)Cl^+$), 139 (10) (M^+, $-C_5Me_4H$), 121 (100) (M^+, $-Me_2GeCl$), 105 (22) (M^+, $-C_5Me_4H$, $-Cl$).

3.3. Synthesis of $Me_2Ge(C_5Me_4H)(C_5H_5)$ (**3**)

$Me_2Ge(C_5Me_4H)Cl$ (**2**) (1.50 g, 5.78 mmol) in THF (50 ml) was added to a solution of $Li(C_5H_5)$ (0.42 g, 5.78 mmol) in THF (50 ml) at −78 °C. The reaction mixture was allowed to warm to r.t. 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 (1.60 g, 96%). ^{1}H-NMR (300 MHz, C_6D_6) (for the predominant isomer): $-\delta$ 0.25 (s, 6H, Ge*Me*$_2$), 1.79 (6H), 1.85 (6H) (s, C_5*Me*$_4$), 2.84 (1H), 3.50 (1H) (m, *H*C_5), 6.52 (2H), 6.69 (2H) (m, C_5*H*$_4$). MS electron impact (*m*/*e* (relative intensity)): 289 (16) (M^+, $Me_2Ge(C_5Me_4H)(C_5H_5)^+$), 225 (100) ($M^+$, $-C_5H_5$), 169 (15) (M^+, $-C_5Me_4H$), 121 (64) (M^+, $-Me_2Ge(C_5H_5)$), 105 (13) (M^+, $-C_5Me_4H$, $-C_5H_5$).

3.4. Synthesis of $Me_2Ge(C_5Me_4H)(C_5H_4Me)$ (4)

The preparation of **4** was carried out in an identical manner to **3**. $Me_2Ge(C_5Me_4H)Cl$ (1.50 g, 5.78 mmol) and $Na(C_5H_4Me)$ (0.59 g, 5.78 mmol). Yield: 1.66 g, 95%. ^{1}H-NMR (300 MHz, C_6D_6) (for the predominant isomer): δ 0.16 (s, 6H, Ge*Me*$_2$), 1.74 (6H), 1.87 (6H) (s, C_5*Me*$_4$), 1.99 (s, 3H, C_5H_3*Me*), 3.36 (1H), 3.59 (1H) (m, *H*C_5), 6.12 (1H), 6.52 (1H), 6.56 (1H) (m, C_5*H*$_3$). MS electron impact (*m*/*e* (relative intensity)): 303 (12) (M^+, $Me_2Ge(C_5Me_4H)(C_5H_4Me)^+$), 225 (80) ($M^+$, $-C_5H_5$), 183 (57) (M^+, $-C_5Me_4H$), 121 (100) (M^+, $-Me_2Ge(C_5H_4Me)$), 105 (83) (M^+, $-C_5Me_4H$, $-C_5H_5$).

3.5. Synthesis of $Li_2\{Me_2Ge(C_5Me_4)_2\}$ (5)

LiBu^n (1.6 M in hexane) (9.1 ml, 14.48 mmol) was added via syringe to a solution of **1** (2.50 g, 7.24 mmol) in Et_2O (50 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 (2.35 g, 91%). Anal. Calc. for $C_{20}H_{30}GeLi_2$: C, 67.30; H, 8.47. Found: C, 67.11; H, 8.39%.

3.6. Synthesis of $Li_2\{Me_2Ge(C_5Me_4)(C_5H_4)\}$ (6)

The preparation of **6** was carried out in an identical manner to **5**. **3** (1.60 g, 5.54 mmol) and LiBu^n (1.6 M in hexane) (6.9 ml, 11.08 mmol). Yield: 1.53 g, 92%. Anal. Calc. for $C_{16}H_{22}GeLi_2$: C, 63.88; H, 7.37. Found: C, 63.66; H, 7.32%.

3.7. Synthesis of $Li_2\{Me_2Ge(C_5Me_4)(C_5H_3Me)\}$ (7)

The preparation of **7** was carried out in an identical manner to **5**. **4** (1.66 g, 5.48 mmol) and LiBu^n (1.6 M in hexane) (6.8 ml, 10.96 mmol). Yield: 1.56 g, 90%. Anal. Calc. for $C_{17}H_{24}GeLi_2$: C, 64.85; H, 7.68. Found: C, 64.65; H, 7.63%.

3.8. Synthesis of $[Nb(=NBu^t)\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl]$ (8)

THF (50 ml) was added to a solid mixture of $[Nb(=NBu^t)Cl_3(py)_2]$ (2.14 g, 4.99 mmol) and $Li_2\{[Me_2Ge(C_5Me_4)(C_5H_4)\}$ (**6**) (1.50 g, 4.99 mmol). The resulting brown solution was stirred for 12 h. Solvent was removed in vacuo and hexane added (75 ml) to the resulting solid. The mixture was filtered and the filtrate concentrated (10 ml) and cooled to −30 °C. The resulting yellow solid that precipitated from the solution was isolated by filtration (1.55 g, 64%). IR (Nujol) $\nu_{Nb=N}$ 1220 cm^{-1}. ^{1}H-NMR (300 MHz, C_6D_6): δ 0.29 (3H), 0.52 (3H) (s, Si*Me*$_2$), 1.01 (s, 9H, C*Me*$_3$), 1.73 (3H), 1.98 (3H), 2.02 (3H), 2.27 (3H) (s, C_5*Me*$_4$) 5.83 (1H), 5.87 (1H), 6.25 (1H), 6.60 (1H) (m, C_5*H*$_4$). ^{13}C{^{1}H}-NMR (300 MHz, C_6D_6): δ −2.2, −0.7 (Si*Me*$_2$), 11.9, 13.7, 13.8, 16.2 (C_5*Me*$_4$), 31.3 (C*Me*$_3$), 67.6 (*C*Me$_3$), 100.7, 111.9, 112.3, 115.5, 116.7 (*C*$_5H_4$), 99.7, 125.0, 126.4, 129.7, 130.2 (*C*$_5Me_4$). Anal. Calc. for $C_{20}H_{31}ClGeNNb$: C, 49.38; H, 6.42; N, 2.88. Found: C, 49.23; H, 6.36; N, 2.89%.

3.9. Synthesis of $[Ti\{Me_2Ge(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (9)

THF (50 ml) was added to a solid mixture of $[TiCl_4(THF)_2]$ (1.10 g, 3.29 mmol) and $Li_2\{Me_2Ge(C_5Me_4)_2\}$ (**5**) (1.18 g, 3.29 mmol). The resulting pale yellow 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 white crystals of the title complex (0.79 g, 52%). ^{1}H-NMR (300 MHz, C_6D_6): δ 0.61 (s, 6H, Ge*Me*$_2$), 1.61 (12H), 2.10 (12H) (s, C_5*Me*$_4$). ^{13}C{^{1}H}-NMR (300 MHz, C_6D_6): δ 2.9 (Ge*Me*$_2$), 14.0, 15.9 (C_5*Me*$_4$), 94.1, 128.9, 142.2 (*C*$_5Me_4$). Anal. Calc. for $C_{20}H_{30}Cl_2GeTi$: C, 52.01; H, 6.55. Found: C, 51.88; H, 6.48%.

3.10. Synthesis of $[Zr\{Me_2Ge(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (10)

The synthesis of **10** was carried out in an identical manner to **9**. $ZrCl_4$ (1.25 g, 5.36 mmol) and $Li_2\{Me_2Ge(C_5Me_4)_2\}$ (**5**) (1.91 g, 5.36 mmol). Yield: 1.03 g, 38%. ^{1}H-NMR (300 MHz, C_6D_6): δ 0.63 (s, 6H, Ge*Me*$_2$), 1.72 (12H), 2.03 (12H). ^{13}C{^{1}H}-NMR (300 MHz, C_6D_6): δ 3.2 (Ge*Me*$_2$), 12.7, 14.8 (C_5*Me*$_4$), 112.6, 135.0, 148.6 (*C*$_5Me_4$). Anal. Calc. for $C_{20}H_{30}Cl_2GeZr$: C, 47.55; H, 5.99. Found: C, 47.44; H, 5.93%.

3.11. Synthesis of $[Hf\{Me_2Ge(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (11)

The synthesis of **11** was carried out in an identical manner to **9**. $HfCl_4$ (1.26 g, 3.92 mmol) and $Li_2\{Me_2Ge(C_5Me_4)_2\}$ (**5**) (1.40 g, 3.92 mmol). Yield: 0.98 g, 42%. ^{1}H-NMR (300 MHz, C_6D_6): δ 0.66 (s, 6H, Ge*Me*$_2$), 1.81

(12H), 2.07 (12H) (s, $C_5\mathit{Me}_4$). $^{13}C\{^1H\}$-NMR (300 MHz, C_6D_6): δ 3.2 (GeMe_2), 12.4, 14.6 ($C_5\mathit{Me}_4$), 97.2, 120.7, 133.3 (C_5Me_4). Anal. Calc. for $C_{20}H_{30}Cl_2GeHf$: C, 40.55; H, 5.10. Found: C, 40.46; H, 5.09%.

3.12. Synthesis of $[Ti\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ *(**12**)*

The synthesis of **12** was carried out in an identical manner to **9**. $[TiCl_4(THF)_2]$ (1.20 g, 3.59 mmol) and $Li_2\{Me_2Ge(C_5Me_4)(C_5H_4)\}$ (**6**) (1.08 g, 3.59 mmol). Yield: 0.67 g, 46%. ^1H-NMR (300 MHz, C_6D_6): δ 0.34 (s, 6H, GeMe_2), 1.51 (6H), 2.07 (6H) (s, $C_5\mathit{Me}_4$), 5.20 (2H), 7.14 (2H) (m, $C_5\mathit{H}_4$). $^{13}C\{^1H\}$-NMR (300 MHz, C_6D_6): δ −1.3 (GeMe_2), 13.6, 15.7 ($C_5\mathit{Me}_4$), 99.5, 114.42, 132.62 (C_5H_4), 104.1, 126.7, 135.6 (C_5Me_4). Anal. Calc. for $C_{16}H_{22}Cl_2GeTi$: C, 47.36; H, 5.47. Found: C, 47.17; H, 5.40%.

3.13. Synthesis of $[Zr\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ *(**13**)*

The synthesis of **13** was carried out in an identical manner to **9**. $ZrCl_4$ (1.00 g, 4.29 mmol) and $Li_2\{Me_2Ge(C_5Me_4)(C_5H_4)\}$ (**6**) (1.29 g, 4.29 mmol). Yield: 0.79 g, 41%. ^1H-NMR (300 MHz, C_6D_6): δ 0.38 (s, 6H, GeMe_2), 1.63 (6H), 1.97 (6H) (s, $C_5\mathit{Me}_4$), 5.30 (2H), 6.86 (2H) (m, $C_5\mathit{H}_4$). $^{13}C\{^1H\}$-NMR (300 MHz, C_6D_6): δ −0.9 (GeMe_2), 12.4, 14.6 ($C_5\mathit{Me}_4$), 107.1, 111.7, 126.4 (C_5H_4), 112.3, 126.4, 134.8 (C_5Me_4). Anal. Calc. for $C_{16}H_{22}Cl_2GeZr$: C, 42.79; H, 4.94. Found: C, 42.55; H, 4.84%.

3.14. Synthesis of $[Hf\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ *(**14**)*

The synthesis of **14** was carried out in an identical manner to **9**. $HfCl_4$ (1.50 g, 4.68 mmol) and $Li_2\{Me_2Ge(C_5Me_4)(C_5H_4)\}$ (**6**) (1.41 g, 4.68 mmol). Yield: 0.93 g, 37%. ^1H-NMR (300 MHz, C_6D_6): δ 0.40 (s, 6H, GeMe_2), 1.72 (6H), 2.01 (6H) (s, $C_5\mathit{Me}_4$), 5.28 (2H), 6.80 (2H) (m, $C_5\mathit{H}_4$). $^{13}C\{^1H\}$-NMR (300 MHz, C_6D_6): δ −0.9 (GeMe_2), 12.2, 14.3 ($C_5\mathit{Me}_4$), 109.2, 109.6, 125.5 (C_5H_4), 111.6, 122.1, 132.9 (C_5Me_4). Anal. Calc. for $C_{16}H_{22}Cl_2GeHf$: C, 35.83; H, 4.13. Found: C, 35.70; H, 4.09%.

3.15. Synthesis of $[Ti\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)\}Cl_2]$ *(**15**)*

The synthesis of **15** was carried out in an identical manner to **9**. $[TiCl_4(THF)_2]$ (1.50 g, 4.49 mmol) and $Li_2\{Me_2Ge(C_5Me_4)(C_5H_3Me)\}$ (**7**) (1.42 g, 4.49 mmol). Yield: 0.87 g, 46%. ^1H-NMR (300 MHz, C_6D_6): δ 0.38 (3H), 0.41 (3H) (s, GeMe_2), 1.48 (3H), 1.52 (3H), 2.11 (3H), 2.13 (3H) (s, $C_5\mathit{Me}_4$), 2.38 (s, 3H, $C_5H_3\mathit{Me}$), 4.82 (1H), 5.30 (1H), 6.79 (1H) (m, $C_5\mathit{H}_3$). $^{13}C\{^1H\}$-NMR (300 MHz, C_6D_6): δ −1.0, −0.1 (GeMe_2), 12.5, 12.7, 14.6, 14.8, 15.7 ($C_5\mathit{Me}_4$, $C_5H_3\mathit{Me}$), 98.5, 112.1, 112.3, 123.9, 126.6 (C_5H_3), 105.6, 124.4, 133.2, 134.8, 138.0 (C_5Me_4). Anal. Calc. for $C_{17}H_{24}Cl_2GeTi$: C, 48.64; H, 5.76. Found: C, 48.47; H, 5.70%.

3.16. Synthesis of $[Zr\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)\}Cl_2]$ *(**16**)*

The synthesis of **16** was carried out in an identical manner to **9**. $ZrCl_4$ (1.00 g, 4.29 mmol) and $Li_2\{Me_2Ge(C_5Me_4)(C_5H_3Me)\}$ (**7**) (1.36 g, 4.29 mmol). Yield: 0.78 g, 39%. ^1H-NMR (300 MHz, C_6D_6): δ 0.41 (3H), 0.42 (3H) (s, GeMe_2), 1.59 (3H), 1.69 (3H), 2.00 (3H), 2.02 (3H) (s, $C_5\mathit{Me}_4$), 2.27 (s, 3H, $C_5H_3\mathit{Me}$), 4.95 (1H), 5.33 (1H), 6.58 (1H) (m, $C_5\mathit{H}_3$). $^{13}C\{^1H\}$-NMR (300 MHz, C_6D_6): δ −0.9, −0.8 (GeMe_2), 12.4, 12.5, 14.5, 14.8, 15.8 ($C_5\mathit{Me}_4$, $C_5H_3\mathit{Me}$), 97.8, 112.7, 112.9, 123.7, 126.6 (C_5H_3), 105.9, 124.3, 134.2, 134.6, 137.1 (C_5Me_4). Anal. Calc. for $C_{17}H_{24}Cl_2GeZr$: C, 44.09; H, 5.22. Found: C, 43.90; H, 5.15%.

3.17. Synthesis of $[Hf\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)\}Cl_2]$ *(**17**)*

The synthesis of **17** was carried out in an identical manner to **9**. $HfCl_4$ (1.40 g, 4.37 mmol) and $Li_2\{Me_2Ge(C_5Me_4)(C_5H_3Me)\}$ (**7**) (1.38 g, 4.37 mmol). Yield: 0.96 g, 40%. ^1H-NMR (300 MHz, C_6D_6): δ 0.43 (3H), 0.44 (3H) (s, GeMe_2), 1.68 (3H), 1.78 (3H), 2.04 (3H), 2.06 (3H) (s, $C_5\mathit{Me}_4$), 2.32 (s, 3H, $C_5H_3\mathit{Me}$), 4.93 (1H), 5.30 (1H), 6.50 (1H) (m, $C_5\mathit{H}_3$). $^{13}C\{^1H\}$-NMR (300 MHz, C_6D_6): δ −1.0, −0.8 (GeMe_2), 12.4, 12.5, 14.8, 15.2, 16.1 ($C_5\mathit{Me}_4$, $C_5H_3\mathit{Me}$), 100.1, 112.5, 112.9, 123.9, 125.9 (C_5H_3), 106.4, 124.9, 134.0, 134.8, 137.5 (C_5Me_4). Anal. Calc. for $C_{17}H_{24}Cl_2GeHf$: C, 37.10; H, 4.40. Found: C, 36.89; H, 4.33%.

*3.18. Polymerization of ethylene with the ansa-metallocene complexes **9–17***

The *ansa*-metallocene catalyst (6 μmol), MAO (10% in toluene) (6000 μmol) and toluene (150 ml) were mixed together in a Schlenk tube and stirred for 10 min. The N_2 pressure inside the Schlenk tube was reduced by applying vacuum. Ethylene pressure of 1.5 bar was then applied to the Schlenk tube and stirring of the mixture commenced. After exactly 30 min, stirring was halted and the ethylene pressure was released. Excess MAO was then destroyed by adding cautiously a mixture of methanol–HCl (90:10). The polymer formed was isolated by filtration and washed with ethanol and dried under vacuum at 60 °C for 12 h.

Table 5
Crystal data and structure refinement for **10**, **13** and **14**

	10	**13**	**14**
Empirical formula	$C_{20}H_{30}Cl_2GeZr$	$C_{16}H_{22}Cl_2GeZr$	$C_{16}H_{22}Cl_2GeHf$
Formula weight	505.15	449.05	536.32
Temperature (K)	250(2)	293(2)	293(2)
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorombic, *Pnma*	Triclinic, $P\bar{1}$
a (Å)	8.820(5)	10.6060(10)	8.928(2)
b (Å)	9.070(2)	13.8710(10)	9.118(3)
c (Å)	14.527(1)	12.5850(10)	12.059(3)
α (°)	93.32(2)		86.28(3)
β (°)	96.65(2)		77.27(2)
γ (°)	115.44(3)		64.37(3)
Volume (Å^3)	1034.8(7)	1851.5(3)	862.8(4)
Z, Calculated density (g cm^{-3})	2, 1.621	4, 1.611	2, 2.064
Absorption coefficient (cm^{-1})	22.14	2.464	80.51
Max./min. transmission	0.467/1.000		0.309/1.000
$F(000)$	512	896	512
Crystal size (mm)	0.4 × 0.2 × 0.2	0.3 × 0.3 × 0.4	0.3 × 0.2 × 0.1
Limiting indices	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $0 \leq l \leq 19$	$0 \leq h \leq 13$, $0 \leq k \leq 12$, $0 \leq l \leq 16$	$-11 \leq \mathrm{h} \leq 11$, $-12 \leq \mathrm{k} \leq 12$, $0 \leq l \leq 15$
Reflections collected/unique	4968/4968 [$R_{\mathrm{int}} = 0.0479$]	2229/1205 [$R_{\mathrm{int}} = 0.1455$]	4343/4148 [$R_{\mathrm{int}} = 0.0271$]
Data/restraints/parameters	4968/0/217	1205/0/97	4148/0/185
Goodness-of-fit on F^2	1.034	0.938	1.131
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0517$, $wR_2 = 0.1505$	$R_1 = 0.0746$, $wR_2 = 0.1663$	$R_1 = 0.0410$, $wR_2 = 0.1115$
R indices (all data)	$R_1 = 0.0863$, $wR_2 = 0.1833$	$R_1 = 0.2226$, $wR_2 = 0.2227$	$R_1 = 0.0594$, $wR_2 = 0.1176$
Largest difference peak and hole (e Å^{-3})	0.888 and −0.939	0.720 and −0.367	1.527 and −1.167

*3.19. Polymerization of propylene with the ansa-metallocene complexes **9–17***

The *ansa*-metallocene catalyst (6 μmol), MAO (10% in toluene) (12000 μmol) and toluene (150 ml) were mixed together in a Schlenk tube and stirred for 10 min. The N_2 pressure inside the Schlenk tube was reduced by applying vacuum. Propylene pressure of 2.0 bar was then applied to the Schlenk tube and stirring of the mixture commenced. After exactly 30 min, stirring was halted and the propylene pressure was released. Excess MAO was then destroyed by adding cautiously a mixture of methanol–HCl (90:10). The polymer formed was isolated by filtration and washed with ethanol and dried under vacuum at 60 °C for 12 h.

*3.20. X-ray structure determinations for [Zr{Me$_2$Ge(η^5-C$_5$Me$_4$)$_2$}Cl$_2$] (**10**) and [M{Me$_2$Ge(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (M = Zr (**13**), Hf (**14**))*

Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) using an ω–2θ scan technique. For **13**, the specimen diffracted weakly. The final unit cell parameters were determined from 25 well-centered and refined by least-squares method. Data were corrected for Lorentz and polarization effects but not for absorption. The space group was determined from the systematic absences and this was vindicated by the success of the subsequent solutions and refinements. The structures were solved by direct methods using SHELXS computer program [22] and refined on F^2 by full-matrix least-squares (SHELXL-97) [23]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Weights were optimized in the final cycles. Crystallographic data are given in Table 5.

4. Supplementary material

Crystallographic data for the structural analyses of **10**, **13** and **14** have been deposited with the Cambridge Crystallographic Data Center, CCDC 181459-181461. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

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