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Synthesis, characterization and polymerization potential of *ansa*-metallocene dichloride complexes of titanium, zirconium and hafnium containing a Si–N–Si bridging unit

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Abstract

Five new Si–N–Si bridged metallocene dichloride complexes of the type $[Cp–SiMe_2N(R)SiMe_2–Cp]MCl_2$ ($Cp = C_5H_4$, C_9H_6; R = alkyl, M = Ti, Zr, Hf) were synthesized using a new type of amine elimination reaction. All complexes were characterized by ^1H-, ^{13}C-, ^{15}N- and ^{29}Si-NMR spectroscopy. An X-ray structure analysis was performed for complex $[C_5H_4–SiMe_2N(^nBu)SiMe_2–C_5H_4]HfCl_2$ (**4**) © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Group IV metal; Amino silyl cyclopentadienyl; Indenyl; *ansa*-Metallocene dichloride; Ethylene polymerization

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1. Introduction

ansa-Metallocene dichloride complexes with group four metals have been used as potential catalyst precursors in olefin polymerization for quite some time. Until now, mainly methylene ($–CH_2–$) [1–3], isopropylidene ($–CMe_2–$) [4,5], dimethylsilylene ($–SiMe_2–$) [6–10], dimethylstannylene groups ($–SnMe_2–$) [11,12] and oxygen atoms (–O–), or a combination of these elements were used to bridge the aromatic ligands (Fig. 1) [13–16].

Most studies have been done on *ansa*-metallocene dichloride complexes with one or two bridging atoms. Bridged metallocene dichloride complexes of zirconium with three bridging atoms are an exception [1,13,15,17].

Up to now these complexes were synthesized by the reaction of the bidentate ligand precursor with the metal tetrachloride. The distance between the five-membered ring ligands is predetermined by the number of bridging atoms. Unfavorable stereochemistry and difficulties during ligand synthesis may limit the formation of such *ansa*-complexes (Scheme 1).

2. Results and discussion

For the first time reported the element nitrogen has been used as a bridging atom in *ansa*-metallocene dichloride complexes. The syntheses of *ansa*-metallocene dichloride complexes of titanium, zirconium and hafnium with a Si–N–Si bridging unit are possible by a new elimination reaction not previously reported, followed by a cyclization of the already existing ligand sphere of the amino silyl functionalized unbridged metallocene dichloride complexes.

The bidentate ligand precursors of the type $C_5H_5–SiMe_2–NHR$ (R = alkyl) are suited for the synthesis of *ansa*-halfsandwich dichloride complexes of the type $[C_5H_4–SiMe_2–NR]MCl_2$ with group four metals, as well as for the synthesis of unbridged and bridged metallocene dichloride complexes. These ligand precursors are especially useful due to their two protons with different acidity. The proton of a cyclopentadiene ring has a pK_a-value of about 15–16 [18], which is approximately a factor of 10^{20} more acidic than that of a nitrogen bonded proton ($pK_a \approx 35$) [19,20], This acidity difference facilitates the selective lithiation of the five-

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membered ring. Only the five-membered ring proton is abstracted when the ligand precursor C_5H_5–$SiMe_2$–NH^nBu (**a**) is reacted with an equimolar amount of butyllithium.

The corresponding metallocene dichloride complex $(C_5H_4$–$SiMe_2$–$NH^nBu)_2ZrCl_2$ (**1**) is formed almost quantitatively by reacting the singly deprotonized ligand precursor $Li[C_5H_4SiMe_2$–$NH^nBu]$ (**b**) with half an equivalent of $ZrCl_4$. The ^{1}H-NMR spectrum of 1 exhibits two virtual triplets of an AA′BB′ spin system for the aromatic protons, one multiplet for the methylene protons on the nitrogen atom of the *n*-butyl group and one singlet for the protons of the dimethylsilyl group with an integral ratio of 4:4:4:12. The amino proton signals collapse with the proton signals of the *n*-butyl group. In the infrared spectrum of **1** a medium strong absorption band is observed at 3396 cm^{-1} for the N–H stretching vibration of the amino protons.

By reacting complex **1** with another equivalent of zirconium tetrachloride an immediate ring closure occurs with intramolecular elimination of the amine adduct $ZrCl_4 \cdot H_2N^nBu$ to form the new *ansa*-zirconocene complex $[C_5H_4SiMe_2$–$N(^nBu)SiMe_2$–$C_5H_4]ZrCl_2$ (**2**). Complex **2** is produced in quantitative yield via this reaction. The ^{1}H-NMR spectrum of **2** is similar to the spectrum of the unbridged complex **1**, except for differences in integrals. The *ansa*-complex **2** has an integral distribution of 4:4:2:12 for the protons α-$CH_{arom.}$:β-$CH_{arom.}$:N–CH_2:$Si(CH_3)_2$. Another difference is the low field shifted ^{29}Si signal of the *ansa*-complex **2**. The ^{29}Si-NMR signal of **1** at $\delta = -7.3$ ppm is observed at $\delta = -3.7$ ppm after cyclization.

The synthesis of Si–N–Si bridged complexes can also be performed in a convenient 'one-pot reaction'. The organo lithium ligand precursor **b** is reacted with a stoichiometric amount of zirconium tetrachloride. The intermediary formed unbridged zirconium dichloride complex **1** reacts with excess zirconium tetrachloride. The Si–N–Si bridged zirconocene dichloride complex **2** is formed after intramolecular amine elimination as the zirconium tetrachloride adduct $ZrCl_4 \cdot H_2NR$. The corresponding *ansa*-titanocene complex **3** and the *ansa*-hafnocene dichloride complex **4** can also be formed by varying the amount of metal tetrachloride.

It was possible to perform an X-ray structure analysis of hafnium complex **4**. Complex **4** exhibits a disorder regarding the conformation of the *n*-butyl group in the solid state. The hafnium atom is in a distorted tetrahedral environment. It is surrounded by the cyclopentadienyl rings bridged by a Si–N–Si chain and both chloro ligands (Fig. 2).

The bond lengths between the single five-membered ring carbon atoms and the center metal suggests η^5-coordination of the five-membered ring ligands. The sterical influence of the Si–N–Si bridge is only reflected in slightly altered bond lengths. Per aromatic ligand, the distances between the carbon atoms and hafnium vary by approximately 6 pm. The angle between the center metal and the centers of both Cp rings is 130.8°. This angle is identical to that found in the unbridged metallocene dichloride complex $(C_5H_5)_2ZrCl_2$ (130.9°) [21] (Table 1).

The nitrogen atom of the hafnium complex is surrounded in a trigonal planar manner by both silicon atoms, Si(1) and Si(2), and the carbon atom C(15) of the *n*-butyl group (angle sum = 355.9°). The sp^2-hybridization of the N atom is indicative for a p_π–d_π interaction between the p_z atom orbital of its free electron pair with the atom orbitals of the neighboring Si atom.

The reaction of the single deprotonized indenyl ligand precursor, $Li[C_9H_6$–$SiMe_2$–$NH^nBu]$, with one equivalent of $ZrCl_4$ gives the *ansa*-complex $[C_9H_6$–$SiMe_2N(^nBu)SiMe_2$–$C_9H_6]ZrCl_2$ (**5**) as an isomer mixture of the *rac* and *meso* forms (Fig. 3). As expected, the sterical repulsion for both six-membered rings of the indenyl ligand is higher for the *rac* form than for the *meso* form (55:45). Therefore, the *meso* form is slightly preferred to the *rac* form. The separation of the *rac* and the *meso* form was not possible by crystallisation at various temperatures.

Analogous to the unbridged zirconium dichloride complexes, the Si–N–Si bridged zirconocene dichloride complex **2** reacts with two equivalents of methyllithium with elimination of LiCl to form the *ansa*-dimethyl complex **6** almost quantitatively (Scheme 2).

The amino silyl substituted complex **1** and the *ansa*-metallocene dichloride complexes **2**–**5**, in combination with MAO, are highly active olefin polymerization catalysts (Table 2).

Compared to unbridged metallocene dichloride complexes of group four metals the Si–N–Si bridged complexes differ mainly in their higher activities and the higher molecular weights of the polyethylenes they form.

The influence of the transition metal of the *ansa*-complexes on the polymerization behavior is similar to that observed for the corresponding unbridged metallocene derivatives. As expected, the activities of the *ansa*-complexes increase in the order Hf < Ti < Zr. Due to the lower stability of the Zr–C bond compared to the Hf–C bond, the ethylene insertion rate into the forming polymer chain is higher for zirconium. This rate increase for the growth of the polymer chain results in higher activities for the zirconium complexes.

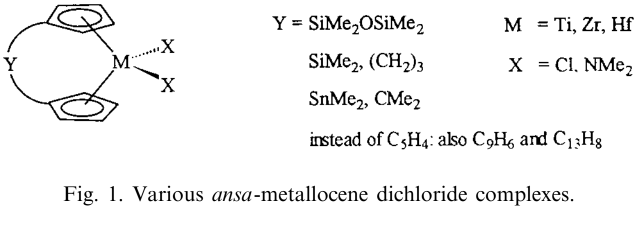
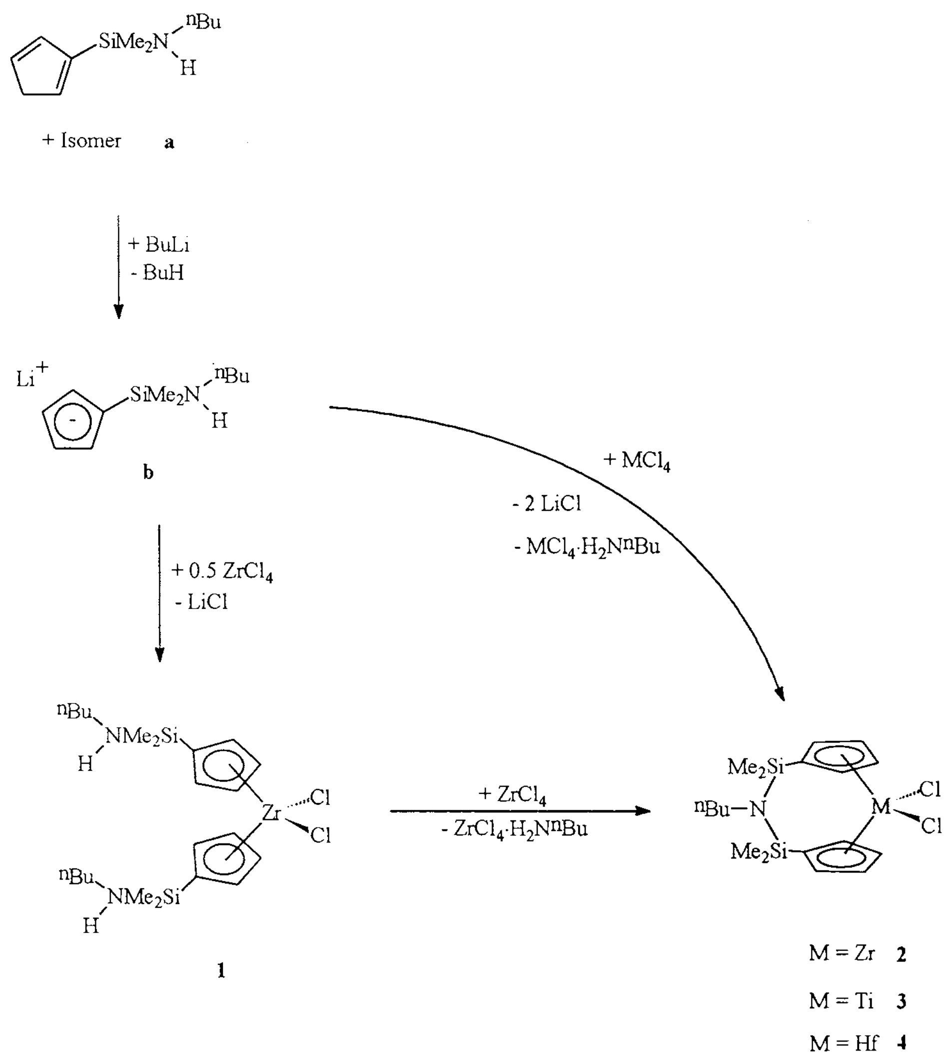


Fig. 1. Various *ansa*-metallocene dichloride complexes.



Scheme 1.

At the same time, one can expect that the weaker Zr–C bonds are responsible for a quicker chain termination via β hydrogen transfer than the Hf–C bonds. The molecular weights of the obtained polymer samples confirm this behavior: The polyethylene molecular weights decrease as the transition metal varies from the heaviest to the lightest element. The hafnium complex **4** produces polyethylene with the highest molecular weight (1.65×10^3 kg mol^{-1}). The molecular weight of the polymer decreases by approximately 75% on going from Hf to Zr (**2**) and by 92% on going from Hf to Ti (**3**).

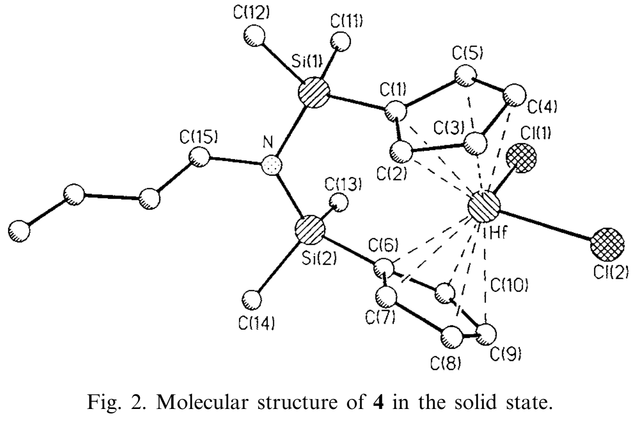


Fig. 2. Molecular structure of **4** in the solid state.

3. Experimental

All operations were carried out using the Schlenk technique under exclusion of air and moisture. Purified and dried argon was used as inert gas (BTS catalyst, molecular sieve). The solvents used were dried over Na/K alloy (Et_2O, toluene, *n*-pentane) or over P_2O_5 and subsequently over CaH_2 (CH_2Cl_2).

The NMR spectra were recorded in deuterated solvents at 25°C using a Bruker ARX 250 spectrometer. In ^{1}H-NMR spectra the chemical shifts refer to the residual proton signal of the solvent ($\delta = 7.24$ ppm for

Table 1
Selected bond lengths (pm) and angles (°) of 4

Hf–CI(1)	241.4(2)	Si(l)–N	173.9(6)	Si(2)–N	173.7(5)
Hf–CI(2)	241.7(3)	Si(1)–C(1)	186.2(8)	Si(2)–C6)	186.7(8)
Si(l)–C(11)	186.7(10)	Si(2)–C(14)	186.5(10)	N–C(15)	147.2(12)
Hf–C(1)	244.9(6)	Hf–C(2)	247.0(6)	Hf–C(3)	249.8(7)
Hf–C(4)	250.8(7)	Hf–C(5)	248.4(7)	Hf–C(6)	247.1(7)
Hf–C(7)	248.2(7)	Hf–C(8)	250.2(7)	Hf–C(9)	253.2(6)
Hf–C(10)	250.2(7)				
Cl(1)–Hf–Cl(2)	96 9(1)	Si(2)–N–C(15)	115.1(5)	Si(l)–N–Si(2)	125.1(4)
Si(1)–N–C(15)	115.7(4)	Cp(l)–Hf–Cp(2)	130.8		

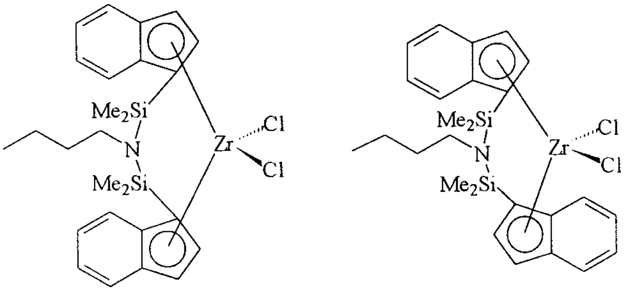
chloroform), in ^{13}C-NMR spectra to the solvent signal ($\delta = 77.0$ ppm for chloroform-d_1), in ^{15}N-NMR spectra to the resonance of nitromethane (external reference, $\delta = 0.0$ ppm) and in ^{29}Si NMR spectra to the resonance of TMS (external reference, $\delta = 0.0$ ppm).

EI mass spectra were recorded using a Varian MAT CH7 mass spectrometer (direct inlet, EI = 70 eV).

Ethylene (dried over Alox) was polymerized in a 1 l metal Büchi autoclave (model 280 BEP). Complexes were activated by adding a 1000-fold molar excess of MAO (30 wt.% in toluene; Witco). The autoclave was filled with 500 ml pentane and 3 ml MAO and stirred for 10 min to dry pentane. After adding the activated complex (ca. 1 mg) the polymerizations were performed under an ethylene pressure of 10 bar and at a temperature of 60°C over a period of 1 h. The polymer samples were subsequently washed with MeOH/HCl and dried under high vacuum.

Molecular weight determinations of the polyethylene samples were performed using an Ubbelohde precision capillary viscometer in *cis*/*trans* decalin at 135 ± 0.1°C. Calibration curves for three different polymer concentrations were available ($c = 0.03$, 0.1 and 3.0 g dl^{-1}) to determine $\bar{M}_\eta$.

A Netzsch DSC 200 was available to determine thermal characteristics of the polyethylene samples. Approximately 5 mg PE were fused in standard aluminum pans and measured using the following temperature program: (1) Heating phase (20°C min^{-1}) from 40 to 200°C, isothermal phase (3 min) at 200°C, cooling phase (-20°C min^{-1}) to 40°C; (2) heating phase (20°C min^{-1}) from 40 to 200°C. The melting points were measured during the second heating phase.



meso *rac*

Fig. 3. *rac* and *meso* forms of the *ansa*-bisindenyl complex **5**.

3.1. $C_5H_5SiMe_2NH^nBu$ (*a*)

At 0°C 10 mmol Li[NH^{n}Bu] are added in portions to 10 mmol $C_5H_5SiMe_2Cl$ dissolved in 100 ml Et_2O. After the addition is completed the mixture is stirred for an additional 12 h. Subsequently it is filtered over Na_2SO_4, the solvent is removed and the remaining crude product is distilled (56–58°C, membrane vacuum, yield 70–80%). EI-MS: $m/e = 195$ (M$^+$).

3.2. $Li[C_5H_4SiMe_2NH^nBu]$ (*b*)

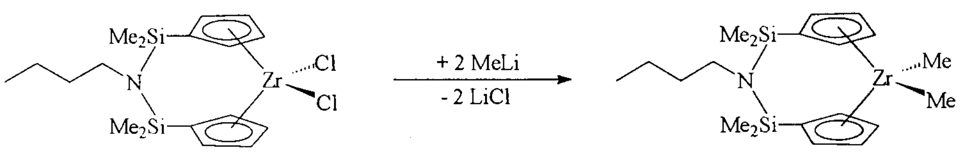
At -78°C 5 mmol ligand precursor **a** in 50 ml diethylether are mixed with 5 mmol BuLi (1.6 M in hexane). The mixture is brought to room temperature and stirred for 12 h.

^{1}H-NMR: δ (ppm, THF-d_8) 5.84 (m, 2H), 5.73 (m, 2H), 2.76 (m, 2H), 1.37 (m, 4H), 0.90 (m, 3H), 0.51 (br, 1H), 0.11 (s, 6H). ^{13}C{^{1}H}-NMR: δ (ppm, THF-d_8) 112.1 (CH), 106.9 (CH), 110.3 (C_q), 42.7 (CH_2), 38.2 (CH_2), 20.9 (CH_2), 14.5 (CH_3), 1.1 (CH_3). ^{29}Si{^{1}H}-NMR: δ (ppm, THF-d_8) -11.9. ^{15}N{^{1}H}-NMR: δ (ppm, THF-d_8) -355.0.

3.3. $(C_5H_4\text{–}SiMe_2\text{–}NH^nBu)_2ZrCl_2$ (*1*)

At RT 2.5 mmol $ZrCl_4$ are added in portions to 5 mmol ligand precursor **b** in 50 ml diethylether. After the addition is completed the mixture is stirred for an additional 12 h. Subsequently, the reaction mixture is dried in vacuo. Complex **1** is dissolved in pentane and filtered over Na_2SO_4. The solution is then reduced in volume, and the complex crystallized at -30°C (yield 75%).

^{1}H-NMR: δ (ppm, C_6D_6) 6.54 (m, 4H), 6.11 (m, 4H), 2.65 (m, 4H), 1.25 (m, 8H), 0.83 (m, 8H), 0.37 (m, 12H). ^{13}C{^{1}H}-NMR: δ (ppm, C_6D_6) 127.6 (C_q)7 126.7 (CH), 115.9 (CH), 41.9 (CH_2), 37.2 (CH_2), 20.2 (CH_2), 14.1 (CH_3), 0.1 (CH_3). ^{29}Si{^{1}H}-NMR: δ (ppm, C_6D_6)



2 **6**

Scheme 2.

− 7.3. ^{15}N$\{^1$H$\}$-NMR: δ (ppm, C_6D_6) − 354.3. EI-MS: *m/e* = 548 (M^+).

3.4. [C_5H_4–$SiMe_2N(Bu)SiMe_2$–C_5H_4]$ZrCl_2$ (**2**)

Procedure A: 1 mmol of complex **1** is dissolved in 20 ml diethylether, mixed with 1 mmol $ZrCl_4$ at RT and stirred for 12 h. Subsequently, the reaction batch is brought to dryness in vacuo, the complex dissolved in pentane and the solution filtered over Na_2SO_4. After the solvent removal *ansa*-complex **2** is obtained quantitatively.

Procedure B: At − 78°C 5 mmol ligand precursor *a* in 50 ml diethylether are mixed with 5 mmol BuLi (1.6 M in hexane). The mixture is brought to room temperature and stirred for 12 h. Five millimoles of $ZrCl_4$ are added to the suspension and it is stirred for further 12 h. Subsequently, the reaction batch is brought to dryness in vacuo and complex **2** dissolved in pentane. The pentane solution is filtered over Na_2SO_4 and reduced in volume, and the complex is crystallized at − 30°C (yield 90%).

^{1}H-NMR: δ (ppm, $CDCl_3$) 6.67 (m, 4H), 6.61 (m, 4H), 2.95 (m, 2H), 1.50 (m, 2H), 1.27 (m, 2H), 0.93 (m, 3H), 0.31 (s, 12H). ^{13}C$\{^1$H$\}$-NMR: δ (ppm, $CDCl_3$) 124.0 (CH), 123.1 (CH), 117.2 (C_q), 45.1 (CH_2), 37.6 (CH_2), 20.3 (CH_2), 13.9 (CH_3), 1.6 (CH_3). ^{29}Si$\{^1$H$\}$-NMR: δ (ppm, $CDCl_3$) − 3.7. ^{15}N$\{^1$H$\}$-NMR: δ (ppm, $CDCl_3$) − 354.8. EI-MS: *m/e* = 475 (M^+)

Table 2
Polymerization experiments and polymer characteristics

Complex	Activity[a] (kg PE mmol^{-1} [M] h)	$\bar{M}_\eta$[b] (kg mol^{-1})	T^c_{m2} (°C)
Cp_2ZrCl_2	110	300	139.9
1	68	260	141.2
2	215	420	140 4
3	45	130	132 2
4	14	1650	138.3
5[d]	140	1150	138.9

[a] T_p = 60°C; solvent, 500 ml pentane; $p(C_2H_4)$ = 10 bar; [M]/[Al] = 1:5000.

[b] Average molar weight determined by viscosimetry.

[c] Maximum of the melting peak during second heating course (DSC).

[d] Mixture of *meso* and *rac* forms.

3.5. [C_5H_4–$SiMe_2N(^nBu)SiMe_2$–C_5H_4]$TiCl_2$ (**3**)

The synthesis is analogous to the procedure of **2** (Procedure B). Only 0.7 equivalents $TiCl_4$ are used (yield: 60%).

^{1}H-NMR: δ (ppm, $CDCl_3$) 6.76 (m, 4H), 6.64 (m, 4H), 2.89 (m, 2H), 1.45 (m, 2H), 1.27 (m, 2H), 0.89 (m, 3H), 0.27 (s, 12H). ^{13}C$\{^1$H$\}$-NMR: δ (ppm, $CDCl_3$) 127.8 (CH), 125.5 (CH), 119.9 (C_q)7 44.3 (CH_2), 37.0 (CH_2), 20.1 (CH_2), 13.5 (CH_3), 116 (CH_3). ^{29}Si$\{^1$H$\}$-NMR: δ (ppm, $CDCl_3$) − 3.3. ^{15}N$\{^1$H$\}$-NMR: ~ δ (ppm, $CDCl_3$) − 355.6. EI-MS: *m/e* = 433 (M^+)

3.6. [C_9H_4–$SiMe_2N(^nBu)SiMe_2$–C_5H_4]$HfCl_2$ (**4**)

The synthesis is analogous to the procedure of **2** (Procedure B; yield: 90%).

^{1}H-NMR: δ (ppm, $CDCl_3$) 6.60 (m, 4H), 6.51 (m, 4H), 2.98 (m, 2H), 2.47 (m, 2H), 1.31 (m, 2H), 0.96 (m, 3H), 0.33 (s. 12H). ^{13}C$\{^1$H$\}$-NMR: δ (ppm, $CDCl_3$) 125.2 (CH), 123.2 (CH), 115.2 (C_q)7 45 0 (CH_2), 37.6 (CH_2), 20.3 (CH_2), 13.9 (CH_3), 1.6 (CH_3). ^{29}Si$\{^1$H$\}$-NMR: 0 (ppm, $CDCl_3$) − 3.8. ^{15}N$\{^1$H$\}$-NMR: δ (ppm, $CDCl_3$) − 354.8. EI-MS: *m/e* = 565 (M^+).

3.7. [C_9H_6–$SiMe_2N(^nBu)SiMe_2$–C_9H_6]$ZrCl_2$ (**5**)

The synthesis is analogous to the procedure of **2** (Procedure B) with C_9H_7–$SiMe_2NH(^nBu)$ as ligand precursor (yield: 85%).

The NMR signals are not assigned to both isomers. ^{1}H-NMR: δ (ppm, $CDCl_3$) 7.80 (m), 7.67 (m), 7.45 (m), 7.33 (m), 7.19 (m), 6.94 (m), 6.61 (m), 6.15 (m), 3.31 (m), 1.67 (m), 1.50 (m), 1.00 (m), 0.55 (s), 0.50 (s). 0.49 (s), 0.39 (s). ^{13}C$\{^1$H$\}$-NMR: δ (ppm, $CDCl_3$) 135.0 (C_q), 132.4 (C_q), 131.0 (CH), 130.7 (CH), 130.2 (CH), 127.1 (CH), 127.0 (CH), 126.5 (CH), 126.3 (CH), 126.2 (CH), 126.0 (CH)125.8 (CH), 113.7 (CH), 112.6 (CH), 105 87(C_q)7 105.1 (C_q)7 45.7 (CH_2), 45.1 (CH_2) 38.1 (CH_2), 37.7 (CH_2), 20.5 (CH_2), 20 4 (CH_2), 14.1 (CH_3), 14.0 (CH_3), 3.3 (CH_3), 2.2 (CH_3), 1.7 (CH_3). ^{29}Si$\{^1$H$\}$-NMR: δ (ppm, $CDCl_3$) − 2.5, − 3.1. ^{15}N$\{^1$H$\}$-NMR: δ (ppm, $CDCl_3$) − 352.9, − 354.6. EI-MS: *m/e* = 551 (M^+).

3.8. *$[C_5H_4–SiMe_2N(^nBu)SiMe_2–C_5H_4]ZrMe_2$* (**6**)

At −78°C 1.5 mmol of **2** in 20 ml diethylether are mixed with 3 mmol MeLi (1.6 M in Et_2O). The mixture is brought to room temperature and stirred for 2 h. Subsequently, the reaction batch is brought to dryness under vacuum, the complex dissolved in pentane, the pentane solution filtered over Na_2SO_4, the solution reduced in volume, and the product crystallized at −30°C (yield: 95%).

^{1}H-NMR: δ (ppm, $CDCl_3$) 6.57 (m, 4H), 6.12 (m, 4H), 2.87 (m, 2H), 1.61 (m, 2H), 1.30 (m, 2H), 0.94 (m, 3H), 0.24 (s, 12H), −0.39 (s, 6H). $^{13}C\{^1H\}$-NMR: δ (ppm, $CDCl_3$) 118.2 (CH), 116.2 (CH), 112.0 (C_q), 45.0 (CH_2), 37.6 (CH_2), 28.9 (CH_3), 20.3 (CH_2), 14.0 (CH_3), 1.6 (CH_3). $^{29}Si\{^1H\}$-NMR: δ (ppm, $CDCl_3$) −4.3. $^{15}N\{^1H\}$-NMR: δ (ppm, $CDCl_3$) −354.1. EI-MS: $m/e = 435$ (M^+).

3.9. *Crystal structure determination of* **4**

Crystal structure analysis was performed on a Siemens P4 diffractometer, wherein Mo–K_α radiation with a wavelength of 0.71073 Å was used (graphite monochromator). The software package SIEMENS SHELXTL PLUS (VMS) was used to resolve the structure.

X-ray structure analysis: $C_{18}H_{29}Cl_2HfNSi_2$ (**4**), yellow small tiles in the dimension 0.40 × 0.35 × 0.10 mm, triclinic; space group $P\bar{1}$; $a = 7.106(2)$ Å, $b = 10.998(2)$ Å and $c = 15.447(2)$ Å; $\alpha = 69.71(2)°$, $\beta = 112.97(2)°$, $\gamma = 85.07(2)$; $V = 1127.5(4)$ Å^3; $Z = 2$, $M = 565.0$ g mol^{-1}, $D_{calc.} = 1.664$ Mg m^{-3}, absorption coefficient: 4.970 mm^{-1}, $F(000) = 556$, measuring temperature: 296 K, measuring range: $3.0 \leq 2\theta \leq 60.0°$, measured reflexions: 7740, independent reflexions: 6346 ($R_{int} = 4.87\%$), observed reflexions: 5737 ($F > 3.0\sigma$ (F)), refined parameter: 210, absorption correction: semi-empirical (Ψ-scans), minimum transmission 0.2610, maximum transmission 0.9664, R-value: $R = 4.29\%$, wR-value ($w^{-1} = \sigma^2$ (F)): 4.62%, maximum of the residual electron density: 1.50 e Å^{-3}, minimum of the residual electron density −3.22 e Å^{-3}.

Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-408526 (**4**), the names of the authors and the journal citation.

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