Synthesis and characterization of bridged half-sandwich amides of titanium and zirconium

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Abstract

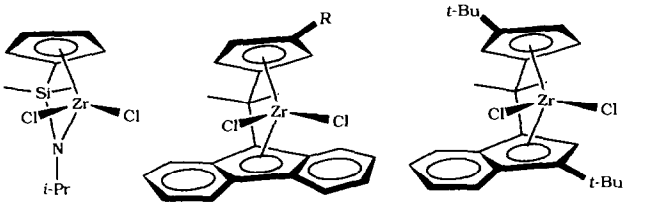
The homoleptic metal amides $Ti(NEt_2)_4$, $Ti(NMe_2)_4$, and $Zr(NEt_2)_4$ react with silyl-substituted cyclopentadienes (**1–3**) and the indene **4** to yield the new half-sandwich complexes **8–16** of type $Me_2Si[CpR][NR']M(NR''_2)_2$ (M = Ti, Zr). The new ligands have been characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, IR, and GC-MS with regard to the sigmatropic rearrangements caused by hydrogen and silicon migration. The titanium and zirconium complexes **8–16** were characterized by their ^1H, ^{13}C, and ^{29}Si NMR spectra, IR, and mass spectrometry. The capabilities and limitations of the "salt-free" procedure employed here are described.

Key words: Titanium; Zirconium; Amides; Linked cyclopentadienyl; Synthesis

1. Introduction

A new era of Ziegler-Natta polymerization has opened through the invention of the metallocene-type catalysts [1–14]. Special interest was given to the *rac*-isomers of the *ansa*-metallocenes because of their ability to produce isotactic polypropylene, and to the σ-symmetrical metallocenes for syndiospecific polymerization. Relevant parameters, *i.e.* molecular weight, activity, isospecifity, and melting point, have been optimized by modification of the ligand framework. Industrial uses of these homogeneous catalysts are in sight.

Besides the *rac*-metallocenes, new asymmetric homogeneous catalysts have also attracted considerable attention [10,11,13,15–20]. Complexes of type **I** [21], **II** [11], and **III** [18] are said to polymerize propylene isospecifically, although they do not exhibit C_2-symmetry.



I II III

While **II** and **III** are easily accessible by standard metallocene procedures, the monocyclopentadienyl complex **I** is sparsely described in the literature. We now report an efficient synthesis and the characterization of a new class of polymerization catalysts **A**. These are derived from the amidofunctionalized cyclopentadienyl complexes of titanium and zirconium.

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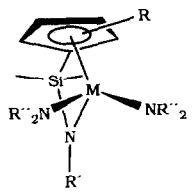
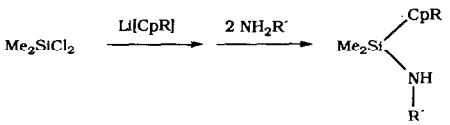


A

2. Results and discussion

2.1. Functionalized cyclopentadienes

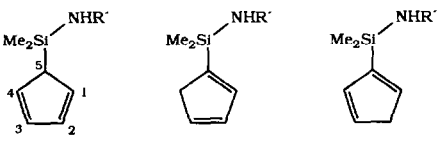
The synthesis of the divalent, bridged half-sandwich ligands **1–4** is based on a known method [22] which has been slightly modified (Scheme 1): Reaction of dichlorodimethylsilane with lithiated cyclopentadienes and its derivatives leads to the related monosubstituted compounds. In a subsequent reaction of these intermediate chlorosilanes with two equivalents of a primary amine, the silylcyclopentadienes **1–3** and the silylindene **4** are obtained as colourless, moisture-sensitive oils, that can be purified by fractional distillation.



	CpR	R′
1	C_5H_5	$C(CH_3)_3$
2	C_5H_5	C_6H_5
3	$C_5H_4CH_3$	$C(CH_3)_3$
4	C_9H_7	$C(CH_3)_3$

Scheme 1.

The cyclopentadienes **1–3** show only a slight tendency to form their Diels-Alder products. However, storage at low temperature is recommended. The ligands have been characterized by ^1H, ^{13}C, ^{29}Si NMR, IR spectroscopy, GC–MS, and elemental analyses. Gas chromatography is the most useful method for characterization with regard to the fluxional behaviour of silylated cyclopentadienylsilanes [23–29] and indenes [30–35]. **1** and **2** occur as three isomers resulting from intramolecular [1,2] sigmatropic rearrangements (≙ [1,5] shift) of the hydrogen atoms [24,36] (Scheme 2). The second pathway for isomerization represents the concerted [1,2]-silicon migration [37]. However this metallotropic shift does not yield new isomers in monosubstituted cyclopentadienes. All tautomeric structures of **1** and **2** were identified by ^1H NMR spectroscopy. The isomer ratio of **1** is 80% (5-isomer), 18% (1-isomer), and 2% (2-isomer), while the corresponding aniline derivative **2** is composed of 69% 5-isomer, 26% 1-isomer, and 5% 2-isomer (Scheme 2).



	5-Isomer	1-Isomer	2-Isomer
1 (R′ = $C(CH_3)_3$)	80 %	18 %	2 %
2 (R′ = C_6H_5)	69 %	26 %	5 %

Scheme 2.

Related cyclopentadienes with one silyl substituent exhibit ratios which were measured by ^1H NMR [38] ranging from 90:9:1 (5:1:2-isomer) for $C_5H_5Si(CH_3)_3$ to 79:19:2 for $C_5H_5Si(CH_3)_2Cl$. The isomeric ratios found in the current cyclopentadienes are therefore typical, although the content of the allylic isomer of **2** differs by about 10%.

In contrast to **1** and **2**, the fluxionality of compound **3** is caused by silicon migration even at low temperature [23,39]. At elevated temperatures, competitive prototropic rearrangement occurs and produces a large number of isomeric compounds; a detailed analysis of the NMR spectra was thus impossible [39,40].

The indene **4** also shows isomerization via a series of [1,2]-hydrogen and silicon shifts [31–33,35]. However, only three tautomeric structures **4a–c** can exist in monosilylated indenes. The allylic and vinylic species of **4** were distinguished by GC-MS (Fig. 1) and by ^1H NMR spectroscopy.

The isomer distribution corresponds to 67% of 1-isomer **4a**, 26% of 2-isomer **4b** and 7% of 3-isomer **4c**. The mixture of the related silylindene $C_9H_7Si(CH_3)_3$ contains 54% of the allylic, 28–31% and 15–17% of the vinylic isomers [31,33] respectively.

2.2. Bridged half-sandwich complexes

The half-sandwich complexes $CpTiCl_3$ [41] and $CpZrCl_3$ [42] were among the first "homogeneous" Ziegler-Natta catalysts to be found to polymerize ethylene [43]. Although the activity of the catalysts $CpTiCl_3/AlR_2Cl$ is low owing to fast reduction of the titanium, $CpMCl_3$ complexes (M = Ti, Zr) are highly active in combination with MAO (methylalumoxane) [43]. Monocyclopentadienyl complexes of formula $CpMCl_2(NRR')$ have been used as precursors of imido compounds (R = H, R′ = alkyl) and were examined by Teuben *et al.* [44], Roesky *et al.* [45], and Giolando *et al.* [46]. The tris(amides) $CpM(NR_2)_3$ [47] were first synthesized in the 1960s by Lappert *et al.*

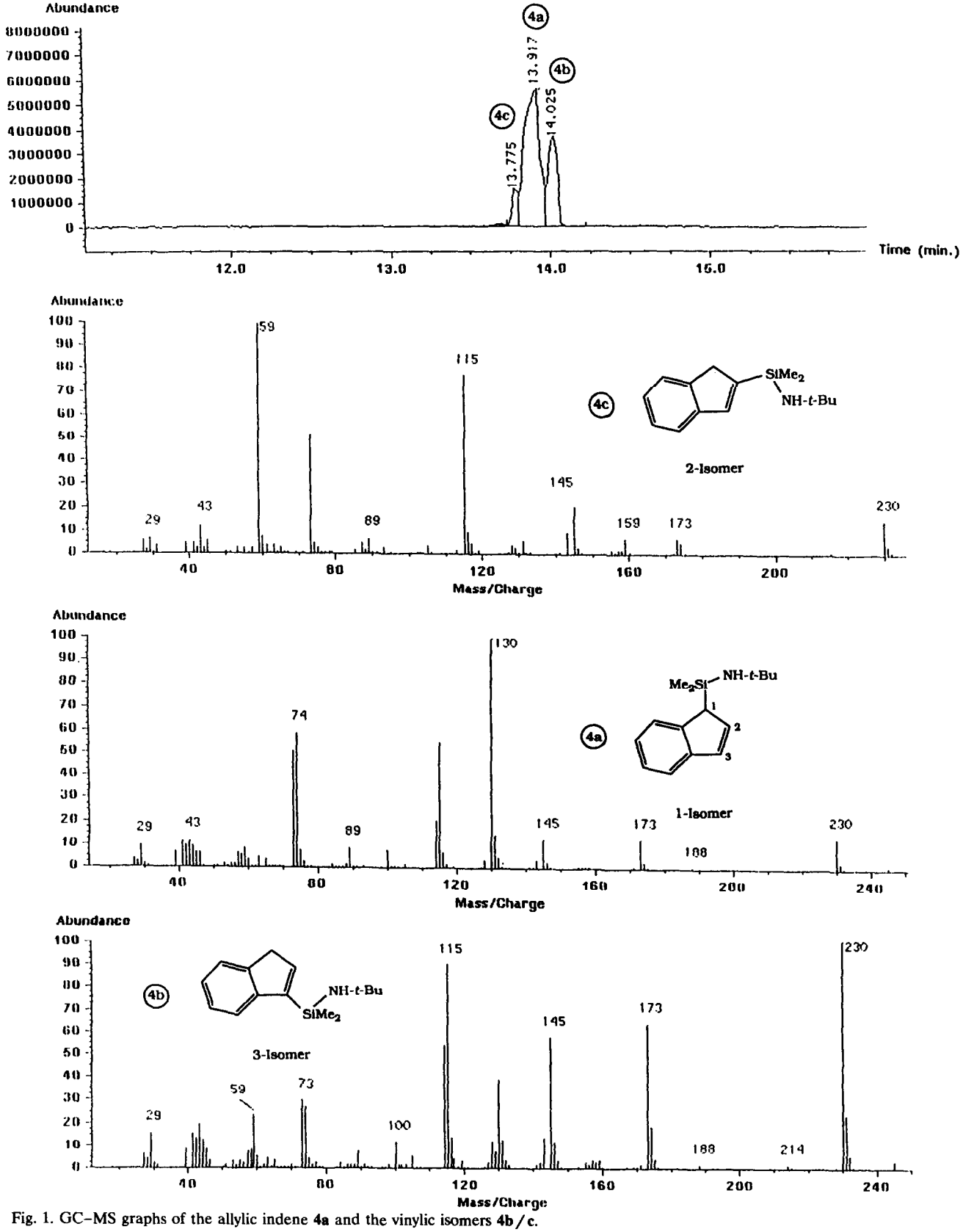


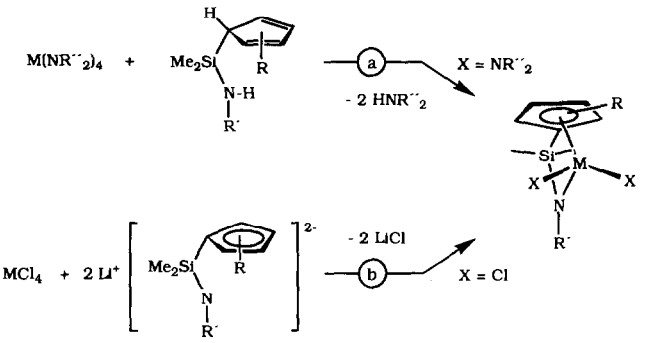
Fig. 1. GC–MS graphs of the allylic indene **4a** and the vinylic isomers **4b / c**.

[48] and then studied in the 1970s by Bürger *et al.* [49,50]. Compounds of general formula $SiMe_2[CpR][NR']MCl_n$ have been only briefly described [21] with the exception M = Sc ($n = 1$) [51] and M = Ti ($n = 2$) [22]. However, no bridged monocyclopentadienyl complexes **A** have ever been reported.

We have synthesized **A** from the homoleptic metal amides $M(NR''_2)_4$ [52–57] and the divalent cyclopentadienes **1–4** (Scheme 3, route a), with the product yields being almost quantitative. By way of contrast, the related dichloro complexes (Cl in place of X) are accessible only in poor yield [22,51,58] (route b).

The "salt-free" procedure has so far only been used with monovalent cyclopentadienes [48–50,52], apart from a previously described synthesis of a bridged half-sandwich complex [59]. This strategy represents an excellent general synthesis of this new class of compounds.

Bürger [50] has postulated that for steric reasons substituted cyclopentadienyl diethylamide complexes of titanium cannot exist, so we attempted the synthesis of bridged complexes by using tetrakis(diethylamido)-titanium $Ti(NEt_2)_4$ (**5**). This route was also checked for $Ti(NMe_2)_4$ (**6**) and $Zr(NEt_2)_4$ (**7**) to examine its limitations. If the homoleptic diethylamide **5** reacts with the ligand **1** in toluene, the half-sandwich complex **8** is formed in near quantitative yield as brown, moisture-sensitive liquids. **8** is purified by vacuum distillation. The red–brown complex **9** and the corresponding zirconium compounds **10** and **11** resulting from $Ti(NEt_2)_4$ and $Zr(NEt_2)_4$, respectively, do not require a purification step. The colour of **10** and **11** is lighter in colour than the titanium analogues, varying from yellow to yellow–brown.



Scheme 3.

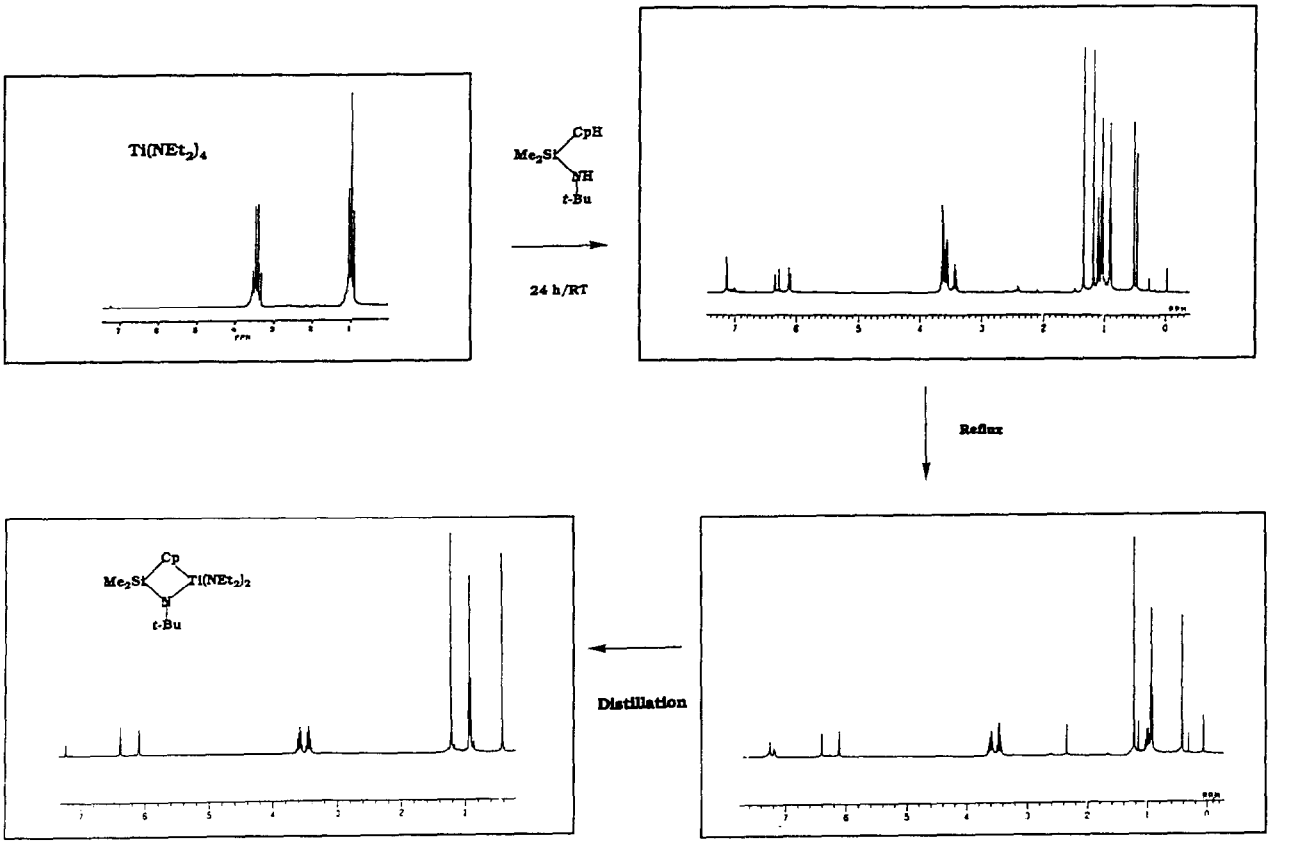
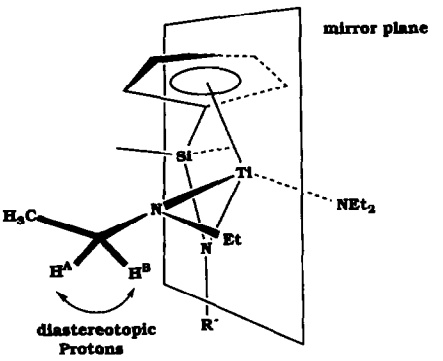
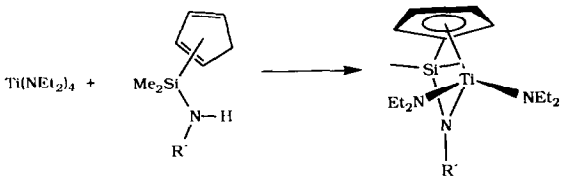


Fig. 2. The course of the reaction of the homoleptic amide **5** and the cyclopentadiene **1**.



Scheme 4.



	8	9
R'	C(CH3)3	C6H5

The reaction times mainly depend on the acidity of the amine and on steric influences.

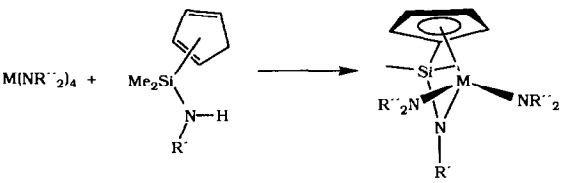
2.3. Spectroscopic characterization

The course of the reaction has been monitored by NMR spectroscopy (Fig. 2).

The metal amide $Ti(NEt_2)_4$ (**5**) shows signals at $\delta = 0.97$ (triplet, CH_3) and $\delta = 3.44$ ppm (quartet, CH_2). During the reaction the intensities of these signals diminish and new peaks arise. After stirring at room temperature for 24 h, the spectrum changes considerably. Besides the amide peaks of the starting compound there are two other triplets at $\delta = 1.00$ and overlapping multiplets at $\delta = 3.50$ ppm, suggesting the presence of other metal amides. Four triplets belonging to metal-coordinated cyclopentadienyl ligands occur at $\delta = 6$–7 ppm. Two pairs of singlets at higher field are assigned to the *tert*-butyl and the dimethylsilylene groups. After refluxing the reaction mixture the signals of **5** disappear completely; pure **8** is obtained by distillation.

The most striking feature of the NMR spectra is the coupling pattern of the methylene protons. This appearance defines the structure of the complex since the ABX_3 splitting is a typical characteristic of spectroscopically non-equivalent protons such as a X–$CH^AH^BCH_3$ function in a molecule with a prochiral centre (*e.g.* diethylacetal). Diastereotopicity of methylene protons only occurs if the complex has a mirror plane (Scheme 4).

The higher reactivity of **2** as compared with **1** is in accord with the lower acidity value of the aniline derivative. The reaction can also be accelerated by using $Ti(NMe_2)_4$ (**6**) or $Zr(NEt_2)_4$ (**7**) instead of **5**. The resulting new complexes **9**–**12** have the same structural features as **8**, as seen from the spectroscopic data (Table 1).

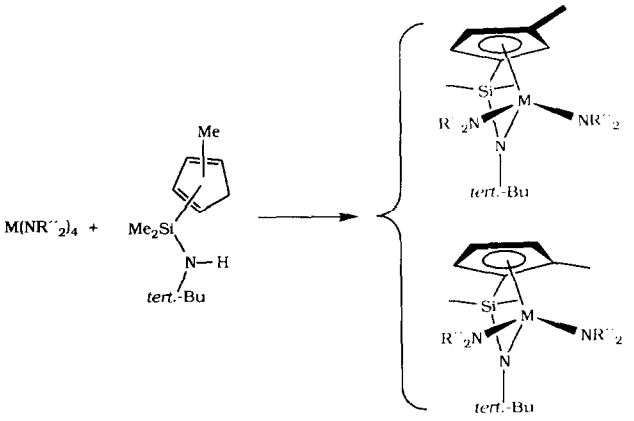


	10	11	12
M	Zr	Zr	Ti
R'	C(CH3)3	C6H5	C6H5
R''	CH2CH3	CH2CH3	CH3

TABLE 1. ^1H NMR data of the complexes **5**–**16** (chemical shifts in ppm)

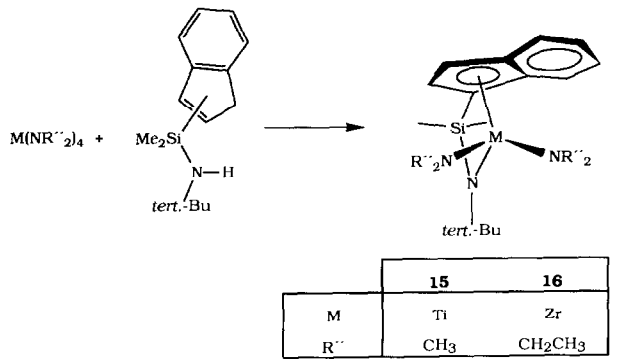
	$SiMe_2$	NR'	NR''_2	CpR
5	–	–	0.97 (CH_3), 3.44 (CH_2)	–
6	–	–	3.09	–
7	–	–	1.13 (CH_3), 3.33 (CH_2)	–
8	0.43	1.23	0.93 (CH_3), 3.45, 3.58 (CH_2)	6.09, 6.38
9	0.49	6.69, 6.90, 7.12	0.87 (CH_3), 3.34, 3.72 (CH_2)	6.23, 6.58
10	0.56	1.13	0.97 (CH_3), 3.19 (CH_2)	6.23, 6.36
11	0.55	6.81, 7.02, 7.21	0.87 (CH_3), 3.12, 3.27 (CH_2)	6.32, 6.41
12	0.52	6.86, 6.99, 7.27	2.94	6.13, 6.23
13a	0.49, 0.53	1.31	2.92, 2.99	2.05, 5.75, 5.88, 6.06
13b	0.51, 0.56	1.32	2.84, 3.08	2.06, 5.88, 5.90, 6.27
14	0.54, 0,55, 0.58, 0.62	1.34	0.93–1.02 (CH_3), 3.09–3.36 (CH_2)	2.09, 2.21, 6.01–6.27
15	0.60, 0.82	1.24	2.35, 3.06	6.27, 6.66 (olefin. CH) 6.88, 6.96, 7.48, 7.85 (aromat. CH)
16	0.63, 0.86	1.29	0.76, 0.98 (CH_3), 2.58, 3.21–3.34 (CH_2)	6.49, 6.61 (olefin. CH) 6.95–6.98, 7.48, 7.90 (aromat. CH)

Reaction of $Ti(NEt_2)_4$ (**5**) with the sterically more demanding ligands **3** and **4** entails reduced yields. Similar steric restrictions have been observed in combination with other C–H acidic ligands [48]. If **6** is used in place of **5** the methylcyclopentadienyl and the indenyl complexes **13** and **15**, respectively, are obtained quantitatively. Reactions of **7** with the divalent ligands **3**/**4** are not affected or limited by steric parameters, in striking contrast to **5**.



	13	14
M	Ti	Zr
R''	CH_3	CH_2CH_3

The methyl function of **13** and **14** destroys the σ-symmetry. The proton and carbon spectra thus become more difficult to interpret. The diastereotopic silylene protons appear as two signals and the methyl groups of the amide substituents give separate peaks, too. **13** consists of a mixture of the 1,3-(**13a**) and the 1,2-isomer (**13b**) as the related complex $[C_5H_3(Me)(SiMe_3)]Ti(NMe_2)_3$ [50]. These isomers can be determined by their NMR data and the coupling pattern of the ring protons and the methyl substituent. The assignment of signals was carried out on the basis of one- and two-dimensional ^1H and ^{13}C NMR spectra. The isomer ratio amounts to 64% of **13a** and 36% of **13b**. The zirconium complex **14** exhibit similar ratios 59% **14a** and 41% **14b**.



	15	16
M	Ti	Zr
R''	CH_3	CH_2CH_3

Although the ligand precursor **4** exists as three conformers (see above), the resulting half-sandwich metal complexes **15** and **16** each form only a single isomer. The titanium complex **15** does not exhibit a mirror plane, as indicated by the diastereotopic methyl protons of the silylene bridge at $\delta = 0.60$ and $\delta = 0.82$ ppm and of the amide groups at $\delta = 2.35$ and $\delta = 3.06$ ppm. Therefore, only the asymmetric structure of the complex shown in Eqn. (4) is present. The zirconium congener **16** also belongs to the symmetry point group C_1 as shown by the spectra (Table 1).

The mass spectra of the half-sandwich amides **8**–**16** show a rather uniform fragmentation pattern. The striking presence of the molecular ion peak in the CI spectra underlines the excellent thermal stability of these complexes. Typical fragments result from abstraction of a methyl group $[M^+ - CH_3]$ and of the amide ligands $[M^+ - n(H)NR'_2]$. Dimeric fragments such as $[2\ M^+ - 2NR'_2]$ do occasionally appear at elevated temperatures.

The IR spectra exhibit bands originating from the vibration of the cyclopentadienyl ligands at characteristic wavenumbers: 3030–3115, *ca.* 1435, *ca.* 840, and 680–700 cm^{-1} [60]. Typical features of the dimethyl- and diethylamides are the metal–nitrogen and the symmetric NC_2 stretching frequencies. The M–N frequencies of $Ti(NEt_2)_4$ (**5**), $Ti(NMe_2)_4$ (**6**), and $Zr(NEt_2)_4$ (**7**) are at 592, 610, and 577 cm^{-1} and the $\nu_{sym}(NC_2)$ absorptions occur at 950, 1003, and 1000 cm^{-1}, respectively [49,61,62]. The observed M–N bands correspond to the asymmetric stretching mode (F_2). The symmetric vibration (A_1) is only Raman-active as determined by the T_d selection rules of the TiN_4 skeleton [61]. Comparing the homoleptic metal educts with the half-sandwich complexes **8**–**16**, the metal–nitrogen stretching modes differ by about 10–20 cm^{-1} to lower frequencies (Table 2). The deviation of the $\nu(NC_2)$ bands ranges from -5 to $+10$ cm^{-1} in relation to $M(NR''_2)_4$ (Table 2). The M–N absorptions of the diethylamides

TABLE 2. Characteristic IR data of the complexes **5**–**16** (cm^{-1})

	ν(M–N)	$\nu_{sym}(NC_2)$
5	610s	1003vs
6	592s	950vs
7	577m	1000vs
8	601m	1007s
9	609m sh, 601m sh, 589m	1002m sh, 995s
10	580m	1012vs, 997 ssh
11	575m	997s
12	577m, 565m	953s, 942s
13	571m, 565m sh, 546m sh	956s, 947s
14	581m	1009s
15	571m sh, 566m, 544m sh	957s, 947s
16	585m, 564w, 553w sh	1004s

(**8–11, 16**) occur at lower wave numbers than the related dimethyl complexes (**12, 13, 15**) as observed for the homoleptic metal amides [62]. This phenomenon can only be explained in electronic terms invoking a p_π-d_π bonding in the metal-nitrogen moiety combined with the inductive effect of the alkyl substituents. If we were to consider a mass effect or a steric interaction, the opposite trend would result.

3. Conclusions

Homoleptic amides $M(NR''_2)_4$ of Group IV metals proved to be excellent sources of new π-cyclopentadienyl and π-indenyl complexes with chelate ligands owing to intramolecular amide functionalization. The precursor compounds are easily available in large amounts, procedures are one-step and straightforward, product yields are near quantitative. The new metallocene-related structures are promising candidates for polymerization of olefins. A study covering this topic is in progress.

4. Experimental section

Manipulations of organic compounds were performed in an atmosphere of pure and dry argon. The syntheses of the silyl-substituted ligands **1–4** are performed according to the literature procedure [22]. The dienes, dichlorodimethylsilane and amines were distilled under dry argon prior to use. The ligands were stored under dry argon at low temperatures. As the metal complexes are extremely air- and moisture-sensitive, manipulations of these substances were carried out either in an atmosphere of pure and dry argon, using standard high vacuum techniques or standard Schlenk procedures, or in a glovebox (N_2 atmosphere). Solvents were predried and freshly distilled or vacuum transferred from Na/K alloy. $ZrCl_4$ (Aldrich) was sublimed and $TiCl_4$ (Aldrich) was distilled under dry argon prior to use. The metal amides $M(NR''_2)_4$ **5–7** were synthezised according to literature procedures [52–57] and stored in a glovebox (N_2 atmosphere).

Elemental analyses were performed by the microanalytical laboratory of the authors' institute. The organometallic compounds gave acceptable elemental analyses in view of nitride and carbide formation [63]. IR spectra were recorded as fluid films (organic and organometallic compounds) using a Perkin-Elmer 1650 FTIR Spectrometer. Mass spectra were obtained on a Varian-MAT 90 spectrometer (CI). The organic syntheses were assisted by gas chromatographic analyses using a Beckman HP5890 instrument with mass-filter HP5970. For the analyses the following temperature programs were used: T_1: 4 min; 60°C, 15°C min^{-1}; 60–120°C, 2 min; 120°C, 35°C min^{-1}; 120–240°C, 6.5 min; 240°C. T_2: 2 min; 100°C, 15°C min^{-1}; 100–170°C, 2 min; 170°C, 35°C min^{-1}; 170–240°C, 7.8 min; 240°C, 50°C min^{-1}; 240–265°C, 2 min; 265°C, helium 200 kPa. Column: HP-1 50 m, 0.2 mm; film 0.33 mm cross-linked methylsilicone. NMR spectra were performed on a JEOL-JMN-GX 400 spectrometer.

4.1. *[(tert-Butylamino)dimethylsilyl]cyclopentadiene (1)*

Colourless liquid, bp. 61°C (1 Torr), the isomer ratio is 80% (5-isomer), 18% (1-isomer), and 2% (2-isomer). ^1H NMR (400 MHz, $CDCl_3$, 25°C): the vinyl CH signals could not be assigned exactly, 6.51–6.79 (m, vinyl C*H*); the NH protons of the 1- and 2-isomer are not visible because of the weak intensity and broad appearance. 5-Isomer: [ppm] $\delta = -0.04$ (s, 6H, $Si(CH_3)_2$), 0.61 (s, br, 1H, N*H*), 1.19 (s, 9H, $C(CH_3)_3$), 3.50 (s, broad, 1H, allyl C*H*). 1-Isomer: [ppm] $\delta = 0.21$ (s, 6H, $Si(CH_3)_2$), 1.10 (s, 9H, $C(CH_3)_3$), 3.09 (s, 1H, allyl CH_2). 2-Isomer: [ppm] $\delta = 0.22$ (s, 6H, $Si(CH_3)_2$), 1.12 (s, 9H, $C(CH_3)_3$), 3.05 (s, 1H, allyl CH_2); relative ratio 80:18:2. ^{13}C NMR (100.4 MHz, $CDCl_3$, 25°C): no exact assignment possible; [ppm] $\delta = -0.20$, 0.36, 0.66 (s, $Si(CH_3)_2$), 33.64, 33.79 (s, $C(CH_3)_3$), 43.94, 47.49 (s, $C(CH_3)_3$), 49.48, 52.08, 54.57 (s, allyl CH or CH_2), 129.99, 133.38, 133.79, 137.75, 142.00, 147.84 (s, olefin C). ^{29}Si NMR (DEPT, 79.5 MHz, $CDCl_3$, 25°C): [ppm] $\delta = -1.80$, -3.33, -4.19 (s, $Si(CH_3)_2$). IR (film): [cm^{-1}] $\tilde{\nu} = 3386$m (ν(N–H)), 3084m (ν(=C–H)), 3054m (ν(=C–H)), 3023m (ν(=C–H)), 2959vs (ν(C–H)), 2900m (ν(C–H)), 2869m sh (ν(C–H)), 1592w (ν(C=C)), 1565w (ν(C=C)), 1466m, 1378s ($\delta_{sy}(CH_3)$), 1360s ($\delta_{sy}(CH_3)$), 1249s ($\gamma(CH_3)$), 1228s ($\gamma(CH_3)$), 1076w, 1056w, 1019s, 950w, 846m ($\gamma(Si(CH_3)_2)$), 814w sh ($\gamma(Si(CH_3)_2)$), 790m, 769m, 734w, 681w, 649w, 497w, 477w, 430w. GC–MS (T_1, retention time 9.99 min): [*m*/*z*] (%) = 195 (3) [M^+], 180 (52) [$M^+ - CH_4$], 130 (100) [$Me_2SiNH - t - Bu]^+$, 123 (58), 114 (75), 100 (9), 95 (21), 74 (69), 65 (19), 59 (14), 43 (25), 39 (30), 29 (16). Anal. calc. for $C_{11}H_{21}NSi$ (196.2211). Found: C, 67.62 (67.55); H, 10.83 (11.05); Si, 14.37 (14.47)%.

4.2. *[Dimethyl(phenylamino)silyl]cyclopentadiene (2)*

Colourless liquid, mp. 15°C, bp. 107°C (1.0 Torr), the isomer ratio amounts to 69% (5-isomer), 26% (1-isomer), and 6% (2-isomer).

^1H NMR (400 MHz, $CDCl_3$, 25°C): Ph, Cp and NH protons could not be exactly assigned: [ppm] $\delta = 3.8$ (s, broad, N*H*), 6.55–7.25 (m, olefin and arom. CH). 5-Isomer: [ppm] $\delta = 0.27$ (s, 6H, $Si(CH_3)_2$), 3.17 (s, 1H, allyl C*H*). 1-Isomer: [ppm] $\delta = 0.49$ (s, 6H, $Si(CH_3)_2$), 3.42 (s, 2H, allyl CH_2). 2-Isomer: [ppm] $\delta = 0.51$ (s, 6H,

$Si(CH_3)_2$), 3.63 (s, 2H, allyl CH_2); relative ratio 69:26:5. ^{13}C NMR (100.4 MHz, $CDCl_3$, 25°C): no exact assignment possible; [ppm] $\delta = -2.45$, -2.00, -1.65 (s, $Si(CH_3)_2$), 43.69, 45.39 (s, allyl CH or CH_2), 116.50–116.80 (s, arom. CH_{ortho}), 117.30–117.80 (s, arom. CH_{para}), 129.20–129.49 (s, arom. CH_{meta}), 133.10–145.70 (s, olefin, CH and C), 147.00–147.52 (s, arom. C). ^{29}Si NMR (DEPT, 79.5 MHz, $CDCl_3$, 25°C): [ppm] $\delta = -0.74$, 1.11, 2.43 (s, $Si(CH_3)_2$). IR (film): [cm^{-1}] $\tilde{\nu}$ = 3381m (ν(N–H)), 3085m (ν(=C–H)), 3039m (ν(=C–H)), 3010m (ν(=C–H)), 2957m (ν(C–H)), 2900m (ν(C–H)), 2853m (ν(C–H)), 1601s (ν(C=C)), 1554w (ν(C=C)), 1498vs, 1476s, 1384s, 1293vs ($\delta_{sy}(Si(CH_3)_2)$), 1256s ($\delta_{sy}(Si(CH_3)_2)$), 1179m, 1154w, 1076m, 1030m, 996m, 952w, 897s (δ_{oop}(=C–H)), 828s ($\gamma(CH_3)$), 796s ($\gamma(CH_3)$), 751s (δ_{oop}(=C–H)), 692s (δ_{oop}(=C–H)), 660w, 616w, 564w, 512w, 444m. GC–MS (T_1, retention time 13.78 min): [m/z] (%) = 215 (10) [M^+], 198 (3), 150 (100) [$M^+ - C_5H_5$], 134 (12), 120 (6), 95 (5), 77 (7), 65 (8) [$C_5H_5^+$], 43 (5) [$SiMe^+$], 39 (12).

4.3. *[(tert-Butylamino)dimethylsilyl](methyl)cyclopentadiene (3)*

Colourless liquid, 58°C (0.1 Torr).

^1H NMR (400 MHz, $CDCl_3$, 25°C): [ppm] δ = 0.02, 0.25, 0.27 (s, $Si(CH_3)_2$), 0.65 (s, broad, NH), 1.17, 1.18, 1.24, 1.25 (s, $C(CH_3)_3$), 2.05, 2.10, 2.16, 2.19 (m, $C_5H_4CH_3$), 2.90, 2.99, 3.07, 3.11, 3.25, 3.45 ("s", allyl. CH or CH_2), 6.13–6.74 (m, vinyl. CH). ^{13}C NMR (100.4 MHz, $CDCl_3$, 25°C): [ppm] δ = 0.01, 0.07, 1.86 (s, $Si(CH_3)_2$), 14.75, 15.19, 16.00, 18.81 (s, $C_5H_4CH_3$), 33.80, 34.00 (s, $C(CH_3)_3$), 45.07, 47.10 (s, $C(CH_3)_3$), 48.55, 49.63, 53.63, 56.00 (s, allyl. CH or CH_2), 126.74, 128.48, 128.60, 130.43, 131.61, 131.75, 133.48, 134.55, 140.42, 142.81, 145.80, 146.86, 149.92, 150.23 (s, olefin, C). ^{29}Si NMR (DEPT, 79.5 MHz, $CDCl_3$, 25°C): [ppm] $\delta = -1.99$, -2.15, -3.19, -3.98 (s, $Si(CH_3)_2$). IR (neat): [cm^{-1}] $\tilde{\nu}$ = 3385m (ν(N–H)), 3092m (ν(=C–H)), 3046m (ν(C=C–H)) 2962vs (ν(C–H)), 2907m sh (ν(C–H)), 2861s (ν(C–H)), 1593w (ν(C=C)), 1466m, 1446w sh, 1398m, 1378s ($\delta_{sy}(CH_3)$), 1360s ($\delta_{sy}(CH_3)$), 1249s ($\gamma(CH_3)$), 1227s ($\gamma(CH_3)$), 1097w, 1020s, 971m, 955m, 905w, 847s ($\gamma(Si(CH_3)_2)$), 804s ($\gamma(Si(CH_3)_2)$), 775m, 711w, 694m, 589w, 495w, 474m, 427w. GC–MS (T_2, retention time 5.751 min): [m/z] (%) = 209 (10) [M^+], 194 (30) [$M - CH_3^+$], 137 (34), 130 (100) [Me_2SiNH–t-Bu^+], 114 (74), 100 (13), 77 (28), 74 (71), 59 (33), 43 (21). Anal. calc. for $C_{12}H_{23}NSi$ (209.4068). Found: C, 68.82 (67.60); H, 11.04 (11.24); N, 6.69 (6.82); Si, 13.41 (13.00)%.

4.4. *[(tert-Butylamino)dimethylsilyl]indene (4)*

Colourless oil, bp. 77°C (0.1 Torr), the isomer ratio is 67% (1-isomer), 26% (2-isomer), and 7% (3-isomer).

^1H NMR (400 MHz, $CDCl_3$, 25°C): 1-isomer: [ppm] $\delta = -0.04$, 0.01 (s, 3H, $SiCH_3$), 0.72 (s, 1H, NH), 1.26 (s, 9H, $C(CH)_3$), 3.67 ("t", 1H, ^3J(H,H) = 5.9 Hz, ^4J(H,H) = 1.9 Hz, allyl. CH), 6.74, 6.95 (dd, 1H, ^3J(H,H) = 6.0 Hz, olefin CH), 7.21, 7.28 (t, 1H, ^3J(H,H) = 7.4 Hz, arom. CH), 7.50, 7.59 (d, 1H, ^3J(H,H) = 7.4 Hz, arom. CH). 2-isomer: [ppm] δ = 0.42 (s, 6H, $Si(CH_3)_2$), 0.89 (s, 1H, NH), 1.20 (s, 9H, $C(CH_3)_3$), 3.45 (d, 2H, ^4J(H,H) = 1.9 Hz, allyl. CH_2), 6.85 (t, 1H, ^4J(H,H) = 1.9 Hz, olefin CH), 7.22, 7.33 ("t", 1H, ^3J(H,H) = 7.4 Hz, arom. CH), 7.54, 7.75 (d, 1H, ^3J(H,H) = 7.4 Hz, arom. CH). 3-isomer: [ppm] δ = 0.35 (s, 6H, $Si(CH_3)_2$), 1.21 (s, 9H, $C(CH_3)_3$), 3.61 (s, br, 2H; allyl. CH_2), the assignment of the vinylic and aromatic CH signals is not possible. $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, 25°C): 1-isomer: [ppm] $\delta = -1.02$, -0.26 (s, $Si(CH_3)_2$). 33.84 (s, $C(CH_3)_3$), 48.79, 49.56 (s, allyl. CH and $C(CH_3)_3$), 120.84, 122.95, 123.39, 124.58, 128.70, 136.38, 144.42, 145.22 (s, olefin and arom. CH); the assignment of the vinylic and aromatic CH signals is not possible. ^{29}Si NMR (DEPT, 79.5 MHz, $CDCl_3$, 25°C): [ppm] δ = 4.58, -2.40, -14.30 (s, $Si(CH_3)_2$). IR (neat): [cm^{-1}] $\tilde{\nu}$ = 3383m (ν(N–H)), 3115m (ν(=C–H)), 3065m (ν(=C–H)), 3014m (ν(=C–H)), 2962vs (ν(C–H)), 2903s (ν(C–H)), 2869m (ν(C–H)), 1630m (ν(C=C)), 1605w (ν(C=C)), 1579w (ν(C=C)), 1542w (ν(C=C)), 1450m, 1397w sh, 1378s ($\delta_{sy}(CH_3)$), 1360s ($\delta_{sy}(CH_3)$), 1249s ($\gamma(CH_3)$), 1226s ($\gamma(CH_3)$), 1190w sh, 1020s, 979m, 878w sh, 850s ($\nu(Si(CH_3)_2)$), 825s ($\nu(Si(CH_3)_2)$, 802s, 776s, 717m, 628w, 496w, 474w, 451m. GC–MS (T_2): 3-isomer (retention time 13.80 min, rel. intensity 7%): [m/z] (%) = 230 (15) [$M^+ - CH_3$], 173 (7) [$M^+ - NH - t - Bu$], 159 (7), 145 (21), 131 (6), 115 (78) [$C_9H_7^+$], 89 (7), 73 (52), 59 (100) [$Si(CH_3)_2^+$], 43 (13), 29(7). 1-isomer (retention time 13.90 min, rel. intensity 67%): [m/z] (%) = 245 (1) [M^+], 173 (13), 145 (13), 130 (100) [$M^+ - C_9H_7$], 115 (55), 100 (8), 89 (9), 74 (59), 59 (9), 43 (12), 29 (10). 2-isomer (retention time 14.00 min, rel. intensity 26%: [m/z] (%) = 245 (3), 230 (100), 214 (2), 188 (2), 173 (64), 159 (4), 145 (58), 130 (39), 115 (90), 100 (12), 73 (30), 59 (24), 43 (20), 29 (16). Anal. calc. for $C_{15}H_{23}NSi$ (245.4398). Found: C, 73.40 (70.54); H, 9.44 (9.24); N, 5.71 (4.98); Si, 11.44 (12.20)% .

4.5. *Bis(diethylamido){η^1 : η^5 – [(tert-butylamido)dimethylsilyl]cyclopentadienyl}titanium (8)*

Tetrakis(diethylamido)titanium (**5**) (1.72 g, 5.1 mmol) in 30 ml toluene was cooled to −60°C. The cyclopentadiene **1** (1.00 g, 5.1 mmol) was added dropwise by means of a syringe. Warming to room temperature resulted in a colour change from yellow to yellow-brown. The solution was refluxed for 7 h. The crude product was transferred to a distillation apparatus and

the byproducts were removed at 130°C (0.1 Torr) and the half-sandwich complex **8** was obtained as yellow-brown oil: yield 1.70 g (3.8 mmol, 86%).

^{1}H NMR (400 MHz, C_6D_6, 25°C): [ppm] δ = 0.43 (s, 6H, Si(CH_3)$_2$), 0.93 (t, 12H, ^3J(H,H) = 6.7 Hz, N(CH_2CH_3)$_2$), 1.23 (s, 9H, C(CH_3)$_3$), 3.45 (dt, 8H, ^3J(H,H) = 6.7 Hz, N(CH_2CH_3)$_2$), 3.58 (dt, 8H, ^3J(H,H) = 6.7 Hz, N(CH_2CH_3)$_2$), 6.09 (t, 2H, ^3J(H,H) = 2.4 Hz, olefin. C*H*), 6.38 (t, 2H, ^3J(H,H) = 2.4 Hz, olefin. C*H*). ^{13}C{^{1}H} NMR (100,4 MHz, C_6D_6, 25°C): [ppm] δ = 2.00 (s, Si(CH_3)$_2$), 13.37 (s, N(CH_2CH_3)$_2$), 34.30 (s, C(CH_3)$_3$), 48.01 (s, N(CH_2CH_3)$_2$), 59.50 (s, *C*(CH_3)$_3$), 106.26 (s, olefin. *C*), 115.95 (s, olefin. *C*H), 116.19 (s, olefin. *C*H). ^{13}C NMR (100,4 MHz, C_6D_6, 25°C): [ppm] δ = 2.01 (q, ^1J(C, H) = 119.0 Hz, Si(CH_3)$_2$), 13.35 (q, ^1J(C, H) = 125.0 Hz, N(CH_2-CH_3)$_2$) 34.03 (q, ^1J(C, H) = 124.3 Hz, ^2J(C, H) = 4.6 Hz, C(CH_3)$_3$), 48.00 (t, ^1J(C, H) = 135.5 Hz, ^1J(C, H) = 4.6 Hz, N(CH_2CH_3)$_2$), 59.50 (s, *C*(CH_3)$_3$), 106.26 (s, olefin. *C*), 115.95 (s, ^1J(C, H) = 168.6 Hz, olefin. *C*H), 116.19 (s, ^1J(C, H) = 168.8 Hz, olefin. *C*H). ^{29}Si NMR (DEPT, 79.5 MHz, C_6D_6, 25°C): [ppm] δ = −22.92 (s, *Si*(CH_3)$_2$). IR (neat): [cm^{-1}] $\tilde{\nu}$ = 3092m (ν(=C–H)), 2985vs (ν(C–H)), 2928m sh (ν(C–H)), 2880m (ν(C–H)), 2866m (ν(C–H)), 2830m (ν(C–H)), 1456m, 1442m, 1382w sh, 1366s, 1353s, 1332w, 1300w, 1246s, 1192s, 1172m sh, 1145s, 1098w, 1046m sh, 1007s (ν_{sym}(NC$_2$)), 903m, 876s, 834s, 810s, 795s, 772s, 751s, 678m, 601m (ν(M–N)), 544w, 497m, 464m. MS (CI): [*m/z*] (%) = 385 (63) [M$^+$], 370 (5) [M$^+$ − CH_3], 312 (100) [M$^+$ − $HNEt_2$], 297 (8) [M$^+$ − $HNEt_3$ − CH_3], 263 (2), 210 (4), 196 (10) [LH$^+$], 178 (20), 130 (18) [L$^+$ − C_5H_5].

4.6. *Bis(diethylamido){η^1 : η^5-[dimethyl(phenylamido)-silyl]cyclopentadienyl}titanium (9)*

The red-brown complex **9** is obtained by the same procedure (**5**: 1.00 g (3.0 mmol); **2**: 0.65 g (3.0 mmol); reflux time 6 h) as described for **8**: yield 1.20 g (3.0 mmol, 99%).

^{1}H NMR (400 MHz, C_6D_6, 25°C): [ppm] δ = 0.49 (s, 6H, Si(CH_3)$_2$), 0.87 (t, 12H, ^3J(H,H) = 6.8 Hz, N(CH_2CH_3)$_2$), 3.34 (qd, 4H, ^3J(H,H) = 6.9 Hz, N(CH_2CH_3)$_2$), 3.72 (qd, 4H, ^3J(H,H) = 6.9 Hz, N(CH_2CH_3)$_2$), 6.23 (s, 2H, olefin. C*H*), 6.58 (s, 2H, olefin. C*H*), 6.69 (t, 1H, ^3J(H,H) = 6.1 Hz, aromat. CH_{para}), 6.90 (d, 2H, ^3J(H,H) = 8.5 Hz, aromat. CH_{ortho}), 7.12 (t, 2H, ^3J(H,H) = 7.9 Hz, aromat. CH_{meta}). ^{13}C{^{1}H} NMR (100,4 MHz, C_6D_6, 25°C): [ppm] δ = −0.90 (s, Si(CH_3)$_2$), 15.16 (s, N(CH_2-CH_3)$_2$), 48.03 (s, N(CH_2CH_3)$_2$), 108.50 (s, olefin. *C*), 116.50 (s, olefin. *C*H), 119.00 (s aromat. *C*H), 120.50 (s, olefin. *C*H), 128.90 (s aromat. *C*H), 154.10 (s, aromat. *C*). ^{13}C NMR (100,4 MHz, C_6D_6, 25°C): [ppm] δ = −0.90 (q, ^1J(C, H) = 119.0 Hz, Si(CH_3)$_2$), 15.17 (qt, ^1J(C, H) = 125.4 Hz, ^2J(C, H) = 3.0 Hz, N(CH_2CH_3)$_2$), 48.00 (tq, ^1J(C, H) = 133.3 Hz, ^2J(C, H) = 4.6 Hz, N(CH_2CH_3)$_2$), 108.50 (t, ^2J(C, H) = 2.3 Hz, olefin. *C*), 116.50 (ddd, ^1J(C, H) = 170.5 Hz, ^2J(C, H) = 13.0 Hz, ^3J(C, H) = 6.1 Hz, *C*), 118.92 (d, ^1J(C, H) = 152.1 Hz, aromat. *C*H), 120.6 (ddd, ^1J(C, H) = 133.8 Hz, ^2J(C, H) = 7.6 Hz, ^3J(C, H) = 5.3 Hz, olefin. *C*H), 128.90 (ddd, ^1J(C, H) = 151.0 Hz, ^2J(C, H) = 1.5 Hz, ^3J(C, H) = 8.4 Hz, aromat. *C*H), 154.10 (t, ^1J(C, H) = 8.3 Hz aromat. *C*). ^{29}Si NMR (DEPT, 79.5 MHz, C_6D_6, 25°C): [ppm] δ = −20.47 (s, *Si*(CH_3)$_2$). IR (neat): [cm^{-1}] $\tilde{\nu}$ = 3077m (ν(=C–H)), 3046m (ν(=C–H)), 2961vs (ν(C–H)), 2931s sh (ν(C–H)) 2861s (ν(C–H)), 2831m sh (ν(C–H)), 1601m, 1588m, 1497m, 1480m, 1457w, 1444w, 1370w sh, 1366m, 1347s, 1292m, 1260s, 1245s sh, 1178w, 1145w, 1088m, 1075m, 1046s, 1027m, 1002m sh (ν_{sym}(NC$_2$)), 995s (ν_{sym}(NC$_2$)), 917s, 902m, 872m, 829s, 802s, 779s, 749s, 693m, 656m, 625m, 609m sh (ν(M–N)), 601m sh (ν(M–N)), 589m (ν(M–N)), 519w, 466w, MS (CI): [*m/z*] (%) = 405 (100) [M$^+$], 390 (4) [M$^+$ − CH_3], 373 (5), 332 (72) [M$^+$ − $HNEt_2$], 282 (10), 216 (57) [LH$^+$], 192 (10), 150 (97) [L$^+$ − C_5H_5], 133 (6), 118 (9).

4.7. *Bis(diethylamido){η^1 : η^5-[(tert-butylamido)di-methylsilyl]cyclopentadienyl}zirconium (10)*

Tetrakis(diethylamido)zirconium (**7**) (1.15 g, 3.0 mmol) was dissolved in 15 ml toluene and cooled to −60°C. **1** (0.59 g, 3.0 mmol) was injected dropwise. The light yellow solution was warmed slowly to room temperature and the colour turned to yellow. The solution was refluxed for 4 h. The volatile materials were removed *in vacuo* (0.1 Torr). The product **10** was obtained as yellow-brown liquid: yield 1.28 g (3.0 mmol, 99%).

^{1}H NMR (400 MHz, C_6D_6, 25°C): [ppm] δ = 0.56 (s, 6H, Si(CH_3)$_2$), 0.97 (t, 12H, ^3J(H,H) = 6.7 Hz, N(CH_2CH_3)$_2$), 1.31 (s, 9H, C(CH_3)$_3$), 3.19 (m, 8H, ^3J(H,H) = 6.7 Hz, N(CH_2CH_3)$_2$), 6.23 (s, 2H, olefin. C*H*), 6.36 (s, 2H, olefin. C*H*). ^{13}C{^{1}H} NMR (100,4 MHz, C_6D_6, 25°C): [ppm] δ = 2.87 (s, Si(CH_3)$_2$), 14.71 (s, N(CH_2CH_3)$_2$), 34.86 (s, C(CH_3)$_3$), 43.26 (s, N(CH_2CH_3)$_2$), 55.96 (s, *C*(CH_3)$_3$), 108.37 (s, olefin. *C*), 114.99 (s olefin. *C*H), 117.87 (s, olefin. *C*H). ^{29}Si NMR (79.5 MHz, C_6D_6, 25°C): [ppm] δ = −23.26 (s, *Si*(CH_3)$_2$). IR (neat): [cm^{-1}] $\tilde{\nu}$ = 3085m (ν(=C–H)), 3072w sh (ν(=C–H)), 2961vs (ν(C–H)), 2931s sh (ν(C–H)), 2900s sh (ν(C–H)), 2863s (ν(C–H)), 2831s (ν(C–H)), 1462m, 1424m, 1406w, 1366s sh, 1357s, 1334w, 1311w, 1261m sh, 1247s, 1225m, 1194s, 1182s, 1169s sh, 1146s, 1098m, 1041s, 1012vs (ν_{sym}(NC$_2$)), 997s sh (ν_{sym}(NC$_2$)), 900w, 866s, 835s, 807s, 798s, 771s, 751s, 717m, 679m, 580m (ν(M–N)), 537m, 496m, 455m. MS

(CI): [m/z] (%) = 428 (100) [M^+], 412 (24) [$M^+ - CH_4$], 391 (5), 356 (58) [$M^+ - NEt_2$], 341 (10) [$M^+ - NEt_2 - CH_3$], 337 (12), 267 (3) [$M^+ - 2\,HNEt_2 - CH_3$].

4.8. Bis(diethylamido){$\eta^1 : \eta^5$-[dimethyl(phenylamido)-silyl]cyclopentadienyl}zirconium (11)

The dark red complex **9** is obtained by the quantitative reaction (reflux time 3 h) of **7** (0.57 g (1.5 mmol)) and **2** (0.31 g (1.5 mmol)) as described for **10**: yield 0.66 g (1.5 mmol, 99%).

^{1}H NMR (400 MHz, C_6D_6, 25°C): [ppm] δ = 0.55 (s, 6H, $Si(CH_3)_2$), 0.87 (t, 12H, ^3J(H,H) = 6.7 Hz, $N(CH_2CH_3)_2$), 3.12 (dt, 4H, ^3J(H,H) = 6.7 Hz, $N(CH_2CH_3)_2$), 3.27 (dt, 4H, ^3J(H,H) = 6.7 Hz, $N(CH_2CH_3)_2$), 6.32 (t, 2H, ^3J(H,H) = 2.4 Hz, olefin. CH), 6.41 (t, 2H, ^3J(H,H) = 2.4 Hz, olefin. CH), 6.81 (t, 1H, ^3J(H,H) = 7.3 Hz, aromat. CH_{para}), 7.02 (d, 2H, ^3J(H,H) = 7.3 Hz, aromat. CH_{ortho}), 7.21 (t, 2H, ^3J(H,H) = 7.3 Hz, aromat. CH_{metal}). ^{13}C{^{1}H} NMR (100,4 MHz, $CDCl_3$, 25°C): [ppm] δ = 0.51 (s, $Si(CH_3)_2$), 15.57 (s, $N(CH_2CH_3)_2$), 43.46 (s, $N(CH_2CH_3)_2$), 108.86 (s, olefin. C), 115.06 (s, olefin. CH), 118.94 (s, aromat, CH_{ortho}), 121.50 (s, olefin. CH), 124.31 (s, aromat. CH_{para}), 129.21 (s, aromat. CH_{meta}), 155.34 (s, aromat, C). ^{29}Si NMR (DEPT, 79.5 MHz, C_6D_6, 25°C): [ppm] δ = −20.33 (s, $Si(CH_3)_2$). IR (neat): [cm^{-1}] $\tilde{\nu}$ = 3070m (ν(=C–H)), 3046m sh (ν(=C–H)), 2960vs (ν(C–H)), 2923s sh (ν(C–H)), 2901s sh (ν(C–H)), 2861s (ν(C–H)), 2831s sh (ν(C–H)), 1589s, 1567m sh, 1481s, 1445m, 1404w, 1367s, 1353m sh, 1335w sh, 1305w, 1260s, 1182s, 1166s, 1151s, 1098m, 1072m, 1043s, 1031m sh, 997s ($\nu_{sym}(NC_2)$), 916s, 867m, 837s, 800s, 773s, 751m, 696m, 680w sh, 621m, 609m, 575m (ν(M–N)), 510m, 459m. MS (CI): [m/z] (%) = 448 (100) [M^+], 432 (13) [$M^+ - CH_4$], 415 (4), 376 (45) [$M^+ - NEt_2$], 374 (54), 359 (2), 303 (6) [$M^+ - NEt_2 - HNEt_2$], 216 (4) [LH^+], 150 (6) [$L^+ - C_5H_5$], 129 (2), 126 (10), 116 (6), 100 (5).

4.9. Bis(dimethylamido){$\eta^1 : \eta^5$-[dimethyl(phenylamido)silyl]cyclopentadienyl}titanium (12)

To a solution of tetrakis(dimethylamido)titanium (**6**) (0.45 mg, 2.0 mmol) in 15 ml toluene the cyclopentadiene **2** (0.43 mg, 2.0 mmol) was added dropwise at −60°C. The light yellow solution was warmed slowly to room temperature and the colour turned to red–brown. The solution was stirred at room temperature for 12 h. The red–brown viscous product was dried under reduced pressure (0.1 Torr): yield 0.69 g (2.0 mmol, 99%).

^{1}H NMR (400 MHz, C_6D_6, 25°C): [ppm] δ = 0.52 (s, 6H, $Si(CH_3)_2$), 2.94 (s, 12H, $N(CH_3)_2$), 6.13 (t, 2H, ^3J(H,H) = 2.4 Hz, olefin. CH), 6.23 (t, 2H, ^3J(H,H) = 2.4 Hz, olefin. CH), 6.86 (tt, 1H, ^3J(H,H) = 8.9 Hz, ^4J(H,H) = 1.2 Hz, aromat. CH_{para}), 6.99 (d, 2H, ^3J(H,H) = 6.7 Hz, ^4J(H,H) = 0.93 Hz, aromat. CH_{ortho}), 7.27 (dd, 2H, ^3J(H,H) = 8.5/7.0 Hz, aromat. CH_{meta}). ^{13}C{^{1}H} NMR (100,4 MHz, C_6D_6, 25°C): [ppm] δ = −1.09 (s, $Si(CH_3)_2$), 48.20 (s, $N(CH_3)_2$), 108.80 (s, olefin. C), 117.21 (s, olefin. CH), 119.10 (s, aromat. CH_{ortho}), 119.72 (s, aromat. CH_{para}), 120.69 (s, olefin. CH), 129.12 (s, aromat. CH_{meta}), 153.94 (s, aromat C). ^{29}Si NMR (DEPT, 79.5 MHz, C_6D_6, 25°C): [ppm] δ = −19.97 (s, $Si(CH_3)_2$). IR (neat): [cm^{-1}] $\tilde{\nu}$ = 3067m (ν(=C–H)), 3054m (ν(=C–H)), 3015m (ν(=C–H)), 2957s (ν(C–H)), 2860s sh (ν(C–H)), 2849vs (ν(C–H)), 2809s (ν(C–H)), 2766vs (ν(C–H)), 1588m, 1562m sh, 1491m sh, 1480m, 1444m, 1415m, 1364w, 1314w, 1292m sh, 1262vs, 1246vs, 1169m, 1139m, 1117w, 1069w, 1046s, 1027m, 996m, 953s ($\nu_{sym}(NC_2)$), 942s ($\nu_{sym}(NC_2)$), 918s, 904m sh, 873m sh, 831s, 814s, 779s, 753m sh, 730m, 694s, 655m, 626m, 612w, 577m (ν(M–N)), 565m (ν(M–N)), 511w, 466m. MS (CI): [m/z] (%) = 349 (100) [M^+], 334 (1) [$M^+ - CH_3$], 304 (18) [$M^+ - NMe_2$], 303 (19) [$M^+ - HNMe_2$], 274 (1) [$M^+ - NMe_2 - 2\,CH_3$], 261 (6) [$M^+ - 2\,NMe_2$], 216 (2) [LH^+], 150 (2) [$L^+ - C_5H_5$].

4.10. Bis(dimethylamido){$\eta^1 : \eta^5$-[(tert-butylamido)dimethylsilyl]methylcyclopentadienyl}titanium (13)

Tetrakis(dimethylamido)titanium (**6**) (0.34 g, 1.5 mmol) was dissolved in 10 ml toluene and cooled to −60°C. The substituted cyclopentadiene **4** (0.31 g, 1.5 mmol) was added dropwise. The slow warming to room temperature resulted in a colour change from light yellow to dark yellow. The solution was refluxed for 5 h. The solvent was removed *in vacuo* (0.1 Torr). The product was obtained as yellow-brown oil: yield 0.51 g (1.5 mmol, 99%).

^{1}H NMR (400 MHz, C_6D_6, 25°C): 2-isomer: [ppm] δ = 0.49, 0.53 (s, 3H, $Si(CH_3)_2$), 1.31 (s, 9H, $C(CH_3)_2$), 2.05 (s, 3H, $C_5H_3CH_3$), 2.92, 2.99 (s, 6H, $N(CH_3)_2$), 5.75 (d, 1H, ^4J(H,H) = 1.4 Hz, olefin. CH), 5.88 (dd, 1H, $^{3/4}J$(H,H) = 1.9 Hz, olefin. CH), 6.06 (t, 1H, $^{3/4}J$(H,H) = 2.4/1.9 Hz, olefin. CH). 1-isomer: [ppm] δ = 0.51, 0.56 (s, 3H, $Si(CH_3)_2$), 1.32 (s, 9H, $C(CH_3)_2$), 2.06 (s, 3H, $C_5H_3CH_3$), 2.84, 3.08 (s, 6H, $N(CH_3)_2$), 5.88 (d, 1H, ^3J(H,H) = 2.0 Hz, olefin. CH), 5.90 (dd, 1H, $^{3/4}J$(H,H) = 2.9 Hz, olefin. CH), 6.27 (t, 1H, ^3J(H,H) = 2.9 Hz, olefin. CH). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25°C): 2-isomer: [ppm] δ = 1.72, 2.15 (s, $Si(CH_3)_2$), 14.49 (s, $C_5H_3CH_3$), 34.31 (s, $C(CH_3)_3$), 49.26, 49.46 (s, $N(CH_3)_2$), 60.11 (s, $C(CH_3)_2$), 106.01, 115.70, 116.86, 117.36, 118.09 (s, olefin. CH and C). 1-isomer: [ppm] δ = 2.78, 4.61 (s, $Si(CH_3)_2$), 15.56 (s, $C_5H_3CH_3$), 34.20 (s, $C(CH_3)_3$), 48.89, 49.24 (s, $N(CH_3)_2$), 59.84 (s, $C(CH_3)_2$), 105.39, 116.53, 117.93, 117.95, 118.01 (s, olefin. CH and C). ^{29}Si NMR (DEPT,

79.5 MHz, C_6D_6, 25°C): [ppm] $\delta = -24.16$ (s, $Si(CH_3)_2$). IR (neat): [cm^{-1}] $\tilde{\nu} = 3095w$ (ν(=C–H)), 3081w (ν(=C–H)), 2964vs (ν(C–H)), 2894s (ν(C–H)), 2856vs (ν(C–H)), 2806m sh (ν(C–H)), 2761s (ν(C–H)), 1460m, 1454m, 1414w, 1378m, 1354m, 1324w, 1245s, 1209m, 1193s, 1140m, 1118w, 1094m, 1050s, 1030m, 1014s, 956s ($\nu_{sym}(NC_2)$), 947s ($\nu_{sym}(NC_2)$), 920w, 835s, 809s, 796s, 771s, 753s, 684m, 652w, 571m (ν(M–N)), 565m sh (ν(M–N)), 546m sh (ν(M–N)), 500w, 478w, 463w, 421w. MS (CI): [m/z] (%) = 343 (100) [M^+], 328 (12) [$M^+ - CH_3$], 298 (36) [$M^+ - HNEt_2$], 283 (7) [$M^+ - HNEt_2 - CH_3$], 262 (2), 204 (5), 137 (2) [$L^+ - NH - t - Bu$].

4.11. Bis(diethylamido){$\eta^1 : \eta^5$-[(tert-butylamido)dimethylsilyl]methylcyclopentadienyl}zirconium (14)

Tetrakis(diethylamido)zirconium (**7**) (0.57 g, 1.5 mmol) was dissolved in 10 ml toluene and cooled to −60°C. **3** (0.31 g, 1.5 mmol) was added dropwise. The light yellow solution was warmed slowly to room temperature. The colour changed to yellow. After refluxing for 5 h the solvent was removed under reduced pressure (0.1 Torr). The product was obtained as an orange–brown viscous liquid: yield 0.66 g (1.5 mmol, 99%).

^{1}H NMR (400 MHz, C_6D_6, 25°C): [ppm] $\delta = 0.54$, 0.55, 0.58, 0.62 (s, 3H, $Si(CH_3)_2$), 0.93–1.02 (m, 24H, $N(CH_2CH_3)_2$), 1.34 (s, 18H, $C(CH_3)_3$), 2.09, 2.21 (s, 6H, $C_5H_3CH_3$), 3.09–3.36 (m, 16H, $N(CH_2CH_3)_2$), 6.01–6.27 (m, 6H, olefin. CH). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25°C): [ppm] $\delta = 2.77$, 3.07, 3.70, 5.62 (s, $Si(CH_3)_2$), 14.13, 14.51, 14.76, 14.97 (s, $N(CH_2CH_3)_2$), 16.28 (s, $C_5H_3CH_3$), 34.86 (s, $C(CH_3)_3$), 42.39, 42.92, 43.25, 44.18 (s, $N(CH_2CH_3)_2$), 55.08, 55.99 (s, $C(CH_3)_3$), 106.97, 107.04, 113.01, 114.98, 116.09, 116.72, 117.76, 117.82, 118.21 (s, olefin. CH and C). ^{29}Si NMR (79.5 MHz, C_6D_6, 25°C): [ppm] $\delta = -23.13$, −23.94 (s, $Si(CH_3)_2$). IR (neat): [cm^{-1}] $\tilde{\nu} = 3092m$ sh (ν(=C–H)), 3069m (ν(=C–H)), 2962vs (ν(C–H)), 2931s sh (ν(C–H)), 2900s sh (ν(C–H)), 2864s (ν(C–H)), 2830s (ν(C–H)), 1462m, 1444m, 1404w, 1367s sh, 1357s, 1335w, 1315w, 1274w sh, 1246s, 1226m, 1194s, 1182s sh, 1151s, 1093m, 1046m sh, 1031m, 1009s ($\nu_{sym}(NC_2)$), 954w, 923w, 867m, 837s, 810s sh, 794s, 770s, 749s, 715w, 682w, 581m (ν(M–N)), 536m, 496m, 471m, 454m. MS (CI): [m/z] (%) = 442 (30) [M^+], 426 (6) [$M^+ - CH_4$], 370 (24) [$M^+ - NEt_2$], 368 (32) [$M^+ - CH_4 - 2\ C_2H_5$], 210 (52) [LH^+], 194 (27) [$L^+ - CH_3$], 130 (100) [$L^+ - C_5H_5$].

4.12. Bis(dimethylamido){$\eta^1 : \eta^5$-[(tert-butylamido)dimethylsilyl]indenyl}titanium (15)

A solution of tetrakis(dimethylamido)titanium (**6**) (0.34 g, 1.5 mmol) in 10 ml toluene was cooled to −60°C and **4** (0.36 g, 1.5 mmol) was added dropwise. The light yellow solution was warmed slowly to room temperature and the colour changed to dark red. The solution was refluxed for 4.5 h. The solvent was removed under reduced pressure (0.1 Torr). The product **4** was obtained as dark red viscous liquid: yield 0.56 g (1.5 mmol, 99%).

^{1}H NMR (400 MHz, C_6D_6, 25°C): [ppm] $\delta = 0.60$, 0.82 (s, 3H, $Si(CH_3)_2$), 1.24 (s, 9H, $C(CH_3)_3$), 2.35 (s, 3H, $N(CH_3)_2$), 3.06 (s, 3H, $N(CH_3)_2$), 6.27, 6.66 (d, 1H, ^3J(H,H) = 2.9 Hz, olefin. CH), 6.88, 6.96 (t, 1H, ^3J(H,H) = 7.3/7.8 Hz, aromat. CH), 7.48, 7.85 (d, 1H, ^3J(H,H) = 7.8 Hz, aromat. CH). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 25°C): [ppm] $\delta = 2.78$, 4.89 (s, $Si(CH_3)_2$), 34.09 (s, $C(CH_3)_3$), 48.06, 50.39 (s, $N(CH_3)_2$), 59.97 (s, $C(CH_3)_2$), 94.11, 108.39, 123.18, 123.54, 123.77, 124.99, 125.76, 131.64, 132.36 (s, olefin. and aromat. CH/C). ^{29}Si-NMR (79.5 MHz, C_6D_6, 25°C): [ppm] $\delta = -24.02$ (s, $Si(CH_3)_2$). IR (neat): [cm^{-1}] $\tilde{\nu} = 3075m$ (ν(=C–H)), 3030w (ν(=C–H)), 2964vs (ν(C–H)), 2894s (ν(C–H)), 2849vs (ν(C–H)), 2807m sh (ν(C–H)), 2763s (ν(C–H)), 1445m, 1414m, 1382m, 1354m, 1334m, 1298w, 1245s, 1193s, 1154m, 1137s, 1049m, 1030m, 1014s, 957s ($\nu_{sym}(NC_2)$), 947s ($\nu_{sym}(NC_2)$), 834s, 809s, 771s, 756s, 741s, 670w, 642w, 571m sh (ν(M–N)), 566m (ν(M–N)), 544m (ν(M–N)), 500w, 464m, 434m, 418w. MS (CI): [m/z] (%) = 379 (47) [M^+], 364 (3) [$M^+ - CH_3$], 335 (9) [$M^+ - N(CH_3)_2$], 319 (3), 246 (68) [LH^+], 230 (100) [$L^+ - 2\ CH_3$], 215 (8) [$L^+ - 2\ CH_3$], 190 (10), 173 (7) [$L^+ - NH - t$-Bu], 130 (48) [$L^+ - C_9H_7$], 115 (4) [$L^+ - C_9H_7 - CH_3$].

4.12. Bis(diethylamido){$\eta^1 : \eta^5$-[(tert-butylamido)dimethylsilyl]indenyl}-zirconium (16)

Tetrakis(diethylamido)zirconium (**7**) (0.57 g, 1.5 mmol) was dissolved in 15 ml toluene and the indenyl **4** (0.36 mg, 1.5 mmol) was added dropwise at −60°C. The light yellow solution is warmed slowly to room temperature and the colour changed to yellow. The solution was refluxed for 4 h. The solvent was removed *in vacuo* (0.1 Torr). The product was obtained as dark orange oil: yield 0.71 g (1.5 mmol, 99%).

^{1}H NMR (400 MHz, C_6D_6, 25°C): [ppm] $\delta = 0.63$, 0.86 (s, 3H, $Si(CH_3)_2$), 0.76 (t, 6H, ^3J(H,H) = 6.7 Hz, $N(CH_2CH_3)_2$), 0.98 (t, 6H, ^3J(H,H) = 6.7 Hz, $N(CH_2CH_3)_2$), 1.29 (s, 9H, $C(CH_3)_3$), 2.58 (m, 2H, $N(CH_2CH_3)_2$), 3.21–3.34 (m, 6H, $N(CH_2CH_3)_2$), 6.49 (d, 1H, ^3J(H,H) = 3.1 Hz, olefin. CH), 6.61 (d, 1H, ^3J(H,H) = 3.1 Hz, olefin. CH), 6.95–6.98 (m, 2H, aromat. CH), 7.48 (d, 1H, ^3J(H,H) = 8.5 Hz, aromat. CH), 7.90 (d, 1H, ^3J(H,H) = 9.1 Hz, aromat. CH). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, 25°C): [ppm] δ = 3.54, 5.75 (s, $Si(CH_3)_2$), 14.33, 15.14 (s, $N(CH_2CH_3)_2$), 34.63 (s, $C(CH_3)_3$), 42.71, 43.39 (s, $N(CH_2CH_3)_2$), 56.00 (s, $C(CH_3)_2$), 94.24, 103.03, 123.18, 123.56, 124.33,

124.67, 125.25, 132.19, 132.93 (s, olefin. and aromat. *C*H/*C*). ^{13}C NMR (100.4 MHz, C_6D_6, 25°C): [ppm] δ = 3.52 (q, ^1J(C,H) = 118.5 Hz, Si(CH_3)$_2$), 5.74 (q, ^1J(C,H) = 118.57 Hz, Si(CH_3)$_2$), 14.31 (q, ^1J(C,H) = 124.8 Hz, N(CH_2CH_3)$_2$), 15.12 (q, ^1J(C,H) = 124.4 Hz, N(CH_2CH_3)$_2$), 34.62 (q, ^1J(C,H) = 125.01 Hz, C(CH_3)$_3$), 42.73 (t, ^1J(C,H) = 131.45 Hz, N(CH_2-CH_3)$_2$), 43.37 (t, ^1J(C,H) = 127.7 Hz, N(CH_2CH_3)$_2$), 55.98 (s, C(CH_3)$_3$), 94.23 (s, olefin. *C*), 103.02 (d, ^1J(C,H) = 169.13 Hz, *C*H), 123.16 (d, ^1J(C,H) = 161.78 Hz, *C*H), 123.58 (d, ^1J(C,H) = 166.38 Hz, *C*H), 124.37 (d, ^1J(C,H) = 165.4 Hz, *C*H), 124.70 (d, ^1J(C,H) = 166.4 Hz, *C*H), 125.23 (d, ^1J(C,H) = 162.7 Hz, *C*H), 132.21 (s, aromat. *C*H), 132.95 (s, aromat. *C*H). ^{29}Si NMR (DEPT, 79.5 MHz, C_6D_6, 25°C): [ppm] δ = −23.35 (s, *Si*(CH_3)$_2$). IR (neat): [cm^{-1}] $\tilde{\nu}$ = 3077m (ν(=C–H)), 3031m (ν(=C–H)), 2961vs (ν(C–H)), 2928m sh (ν(C–H)), 2864m (ν(C–H)), 2834m (ν(C–H)), 1462m, 1444m, 1404w, 1367s, 1356s, 1332m, 1277w, 1246s, 1226w, 1195s, 1180m sh, 1153s, 1100w, 1062w, 1030m sh, 1004s (ν_{sym}(NC$_2$)), 964m, 868s, 836s, 810s, 793s, 770s, 757s, 741s, 713w, 665w, 642w, 585m (ν(M–N)), 564w (ν(M–N)), 553w sh (ν(M–N)), 535m, 496m, 458m. MS (CI): [*m*/*z*] (%) = 478 (100) [M$^+$], 462 (16) [M$^+$], 406 (48) [M$^+$ − NEt$_2$], 391 (6) [M$^+$ − NEt$_2$ − CH$_3$], 319 (2) [M$^+$ − 2 NEt$_2$ − CH$_3$], 302 (4) [M$^+$ − 2 HNEt$_2$ − 2 CH$_3$], 246 (50) [LH$^+$], 230 (41) [L$^+$ − CH$_3$], 215 (2) [L$^+$ − 2 CH$_3$].

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