Novel sandwich complexes of zirconium [C9H5(SiMe3)2](C5Me4R)ZrCl2 (R = CH3, CH2CH2NMe2): Synthesis and reduction behavior

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Abstract

Novel half-sandwich [C9H5(SiMe3)2]ZrCl3 (**3**) and sandwich [C9H5(SiMe3)2](C5Me4R)ZrCl2 (R = CH3 (**1**), CH2CH2NMe2 (**2**)) complexes were prepared and characterized. The reduction of **2** by Mg in THF lead to $(\eta^5$-C9H5(SiMe3)2)$[\eta^5:\eta^2(C,N)$-C5Me4CH2CH2N(Me)CH2]ZrH (**7**). The structure of **7** was proved by NMR spectroscopy data. Hydrolysis of **2** resulted in the binuclear complex ([C5Me4CH2CH2NMe2]ZrCl2)2O (**6**). The crystal structures of **1** and **6** were established by X-ray diffraction analysis.
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1. Introduction

Sandwich complexes of Zr(II) have been studied intensively as they are able to activate inert C–H bonds. However, the extreme reactivity of the "naked" [Cp2Zr(II)] centers and their pronounced tendency to undergo self-degradation into Zr(III) or Zr(IV) inactive complexes makes the practical application of the divalent "zirconocenes" top problematic. From this viewpoint, the choice of an appropriate ligand environment that could provide a compromise between the thermal stability and reactivity of the Zr(II) species appears to be one of the possible solutions of the problem. Among the known alternatives, the sterically hindered indenyl ligands [1,2] seem to be good candidates due to their ability to reversibly stabilize Zr(II) center by "toggling" between η^5, η^6 and η^9 coordination modes (see Scheme 1). Like other Zr(II) derivatives, these complexes are able to activate C–H bonds [3].
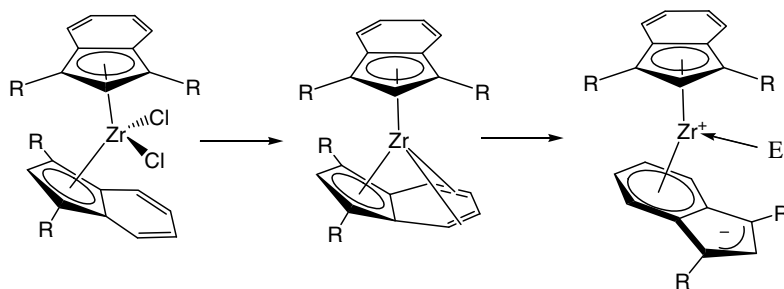
To date, bis(indenyl) compounds have been more thoroughly explored then their mixed analogues containing both indenyl and pentamethylcyclopentadienyl ligands. Few examples of (Cp*)(Ind)ZrCl2 complexes are known [4–6]. Synthesis and investigation of (Cp*)(Ind)ZrCl2 derivatives bearing side-chain functional groups are of particular interest. We herein report the synthesis and redox behavior of mixed sandwich complexes [C9H5(SiMe3)2]-(C5Me4R)ZrCl2 (R = CH3, CH2CH2NMe2).

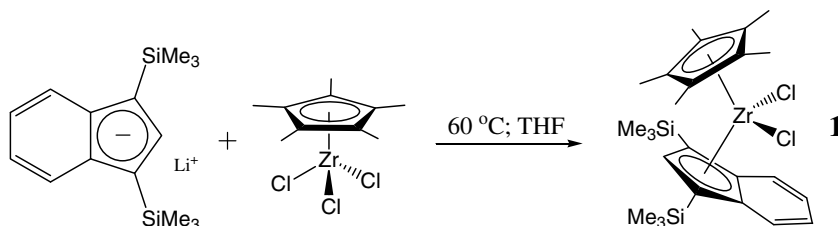## 2. Results and discussion

2.1. Synthesis of complexes

Sandwich complex (Ind^{Si2})Cp*ZrCl2 (**1**) (Ind^{Si2} = C9H5-(SiMe3)2) was synthesized by reaction of Ind^{Si2}Li with Cp*ZrCl3 (Scheme 2). The pure product was characterized by NMR spectroscopy and X-ray analysis.
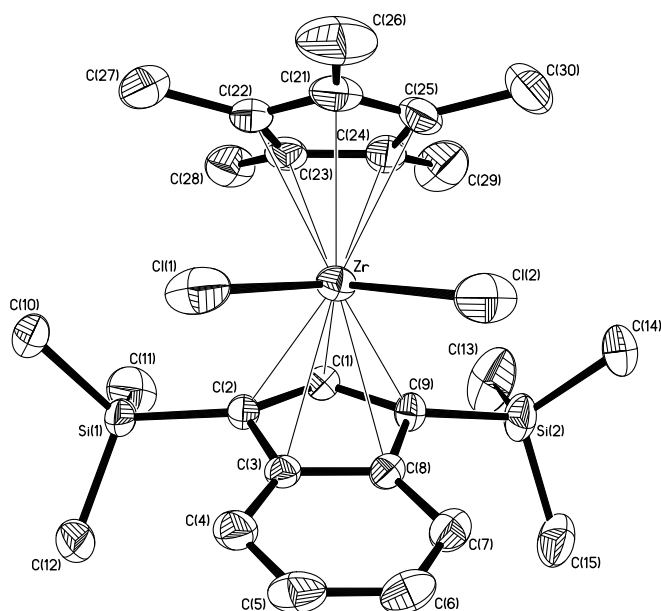
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Scheme 1.

Scheme 2.

Fig. 1. Molecular structure of **1**.

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

Zr–Cl(2)	2.4136(10)
Zr–Cl(1)	2.4298(13)
Zr–C(1)	2.521(2)
Zr–C(2)	2.552(3)
Zr–C(9)	2.574(3)
Zr–C(3)	2.627(3)
Zr–C(8)	2.644(3)
Zr–C(21)	2.525(3)
Zr–C(22)	2.553(3)
Zr–C(23)	2.526(3)
Zr–C(24)	2.527(3)
Zr–C(25)	2.545(3)
Zr–Pl(1)[a]	2.233(2)
Zr–Pl(2)[a]	2.276(2)
Si(1)–C(2)	1.880(3)
Si(2)–C(9)	1.883(3)
Cl(2)–Zr–Cl(1)	96.40(4)
Pl(1)–Pl(2)[a]	48.7(1)

[a] Pl(1) and Pl(2) denote the planes of five–membered cyclopentadienyl and indenyl rings.

In crystalline form, sandwich complex **1** possesses approximate mirror-plane symmetry (Fig. 1). The conformation of η^5-C_5 rings is staggered and **1** can be treated as a class II zirconocene [7]. In **1** the indenyl ligand has its phenylene moiety oriented towards the front side of metallocene wedge. Such a conformation was not observed previously for mixed (cyclopentadienyl)(indenyl)zirconocenedichlorides [5,6,8,9]. The metrical parameters of **1** (Table 1) are close to those found for other silyl-substituted indenyl zirconium sandwiches [1].

Complex **2**, with an amino-functionalized cyclopentadienyl ligand Cp^{*N} ($Cp^{*N} = C_5Me_4CH_2CH_2NMe_2$), was prepared by treatment of $(Ind^{Si2})ZrCl_3$ (**3**) with $Cp^{*N}Li$.

Halfsandwich **3** was obtained previously [1] as an adduct with Et_2O and LiCl by the reaction of $Ind^{Si2}Li$ with $ZrCl_4$ in ether. We developed an alternative two-step synthesis of **3** starting from indene. In the first step, indene was silylated with an excess of Me_3SiCl in the presence of lithium diisopropylamide (Scheme 3). A novel silane, $C_9H_5(SiMe_3)_3$ (**4**), was formed in a good yield. Prolonged heating of **4** with $ZrCl_4$ in toluene at 140 °C resulted in solvent free complex **3** with a total yield of 56% (based on indene).

Unexpectedly, reaction of **3** with $Cp^{*N}Li$ in THF at either ambient or elevated (up to 100 °C) temperatures, resulted in formation of an equimolar mixture of the known halfsandwich complex $(Cp^{*N})ZrCl_3$ (**5**) [10] and lithium salt $Ind^{Si2}Li$ (NMR data; see Scheme 4). Thus, in THF medium, Ind^{Si2}
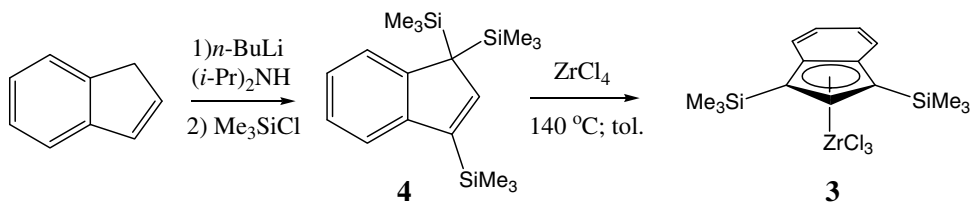
Scheme 3.
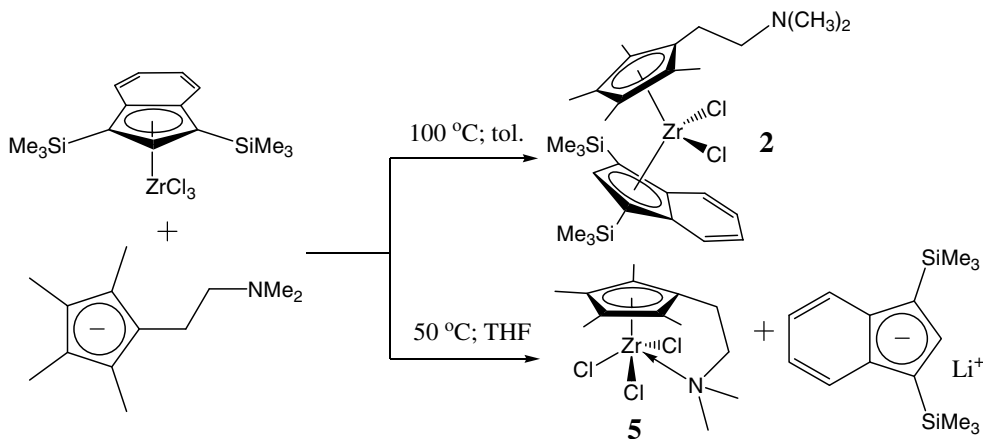
Scheme 4.

anion appears to be a better leaving group than Cl⁻. At the temperature range around 100 °C formation of the THF cleavage products also took place.

Complex **2** was obtained by prolonged heating (40 h) of **3** and **4** in toluene. It should be noted, that after 10 h of heating, considerable amount of **5** (~30%) was also detected in the reaction mixture.

As with other cyclopentadienyl derivatives of the Group 4 metals which contain the pendant amino-group, **2** is extre-

mely moisture sensitive [11]. Thus, exposure of the hexane mother liquor (the rests after isolation of **2**) to humid air resulted in formation of ([C₅Me₄CH₂CH₂NMe₂]ZrCl₂)₂O (**6**) as single crystals.

The dimeric molecule of **6** lies on crystallographic two-fold axis passing through oxygen atom (Fig. 2, Table 2). Both zirconium atoms possess a distorted octahedral coordination assuming the Cp-ring occupies one site. The cyclopentadienyl rings and one of the bridging Cl atoms lie in the
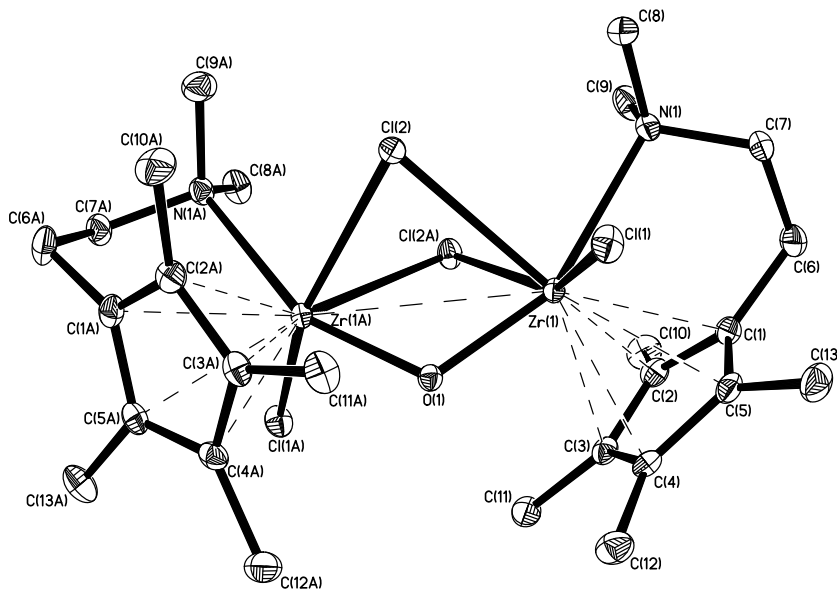

Fig. 2. Molecular structure of **6**.

Table 2
Selected bond lengths (Å) and angles (°) for **6**

Zr(1)–O(1)	1.9581(9)
Zr(1)–Cl(1)	2.4867(5)
Zr(1)–Cl(2)	2.7825(5)
Zr(1)–Cl(2A)[a]	2.6037(5)
Zr(1)–N(1)	2.5441(15)
Zr(1)–Pl[b]	2.2274(8)
Zr(1)–Zr(1A)	3.3100(5)
Zr(1)–Cl(2)–Zr(1A)	75.756(14)
Zr(1)–O(1)–Zr(1A)	115.39(9)

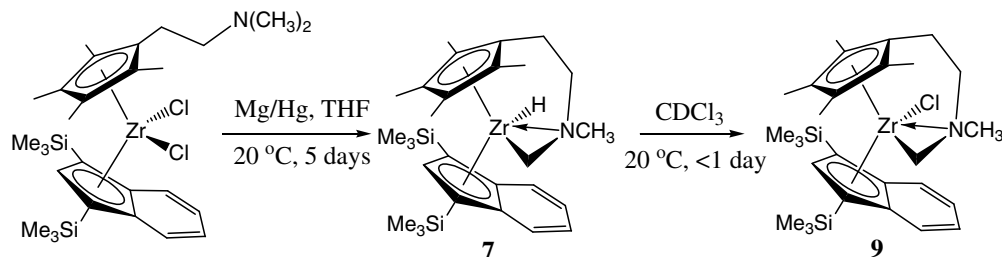[a] Symmetry transformation: $-x, y, -z + 1/2$.
[b] Pl denote the plane of cyclopentadienyl ring.

apical positions while the amino-groups, terminal Cl atoms and bridging oxygen atom occupy equatorial ones. The apical bridging bond Zr(1)–Cl(2) is significantly longer (2.7825(5) Å) than equatorial bridging Zr(1)–Cl(2A) bond (2.6037(5) Å). We have previously observed the same effect for related dimeric structures $[(\eta^5:\eta^1-C_5Me_4CH_2CH_2EMe)ZrCl_3]_2$, (E = O, S) [12,13]. The Zr(1)–Cl(1) distance (2.4867(5) Å) is of ordinary value for terminal Zr–Cl bonds [14]. In **6**, Zr–N bond length (2.5441(15) Å) is somewhat shorter than in closely related complex $(\eta^5:\eta^1-C_5Me_4CH_2CH_2NMe_2)(THT)ZrCl_3 - 2.594(3)$ Å [10]. To the best of our knowledge, **6** is the second example of the structure with central $Zr_2(\mu_2\text{-}Cl)_2(\mu_2\text{-}O)$ fragment [15]. However, Zr–O distance (1.9581(9) Å) is close to the average value for zirconoxanes retrieved from Cambridge Structural Database (ver. 5.28, May 2007) [16] – 1.977 Å (60 refcodes).

2.2. Reduction of complexes

The reduction of **1** and **2** was performed in order to prepare mixed Zr(II) complexes containing both η^9 or η^6-indenyl and Cp* or Cp*[N] ligands. However, we found that in both cases no low valent species were formed. The reduction of **1** with Mg in THF or with Na/Hg in toluene resulted only in the decomposition of metallocene structure and the corresponding magnesium or sodium indenide signals were observed in NMR spectra. This result differs drastically from that reported for $(\eta^9\text{-}C_9H_5(^iPr)_2)Cp^*ZrCl_2$[4], which reacts with Na/Hg in benzene giving $(\eta_9\text{-}C_9H_5(^iPr)_2)Cp^*Zr$. The latter can be explained by the higher stability of Ind[Si2−] anion in comparison with diisopropylindene anion.

The reduction of **2** with Mg in THF lead to the intramolecular CH-activation product **7** (Scheme 5).

However, the traces of Ind[Si2−] were also found (7%). Recently, we reported the synthesis of closely related complex $(\eta^5\text{-}C_5Me_5)[\eta^5:\eta^2(C,N)\text{-}C_5Me_4CH_2CH_2N(Me)CH_2]$-ZrH (**8**) (Scheme 6) [17]. The similar cyclic products of the intramolecular CH-activation of NCH_2-H bonds have been obtained by Erker and coworkers [18,19] via d^0 Zr(IV) cationic intermediates. In contrast we observed the reaction proceeds via d^2 Zr(II) intermediate.

^{1}H and ^{13}C NMR spectra for $[\eta^5:\eta^2(C,N)\text{-}C_5Me_4CH_2\text{-}CH_2N(Me)CH_2]$ZrH fragment in **7** were similar to those of $(\eta^5\text{-}C_5Me_5)[\eta^5:\eta^2(C,N)\text{-}C_5Me_4CH_2CH_2N(Me)CH_2]$ZrH (**8**) [17], including the splitting of CH_2CH_2 proton multiplets. As in case of **8** [17], in the spectra of **7** through-space spin–spin interaction between hydride ligand and the adjacent methyl group of Cp-ring ($J_{H-ZrH} = 1.7$ Hz, $J_{C-ZrH} = 6.5$ Hz) was observed. The corresponding cross-peaks also appeared in COSY spectra. The only one significant difference in the ^{1}H spectra of these complexes was found: in **8**, the methyl group at the N atom has a "normal" chemical shift value ($\delta = 2.24$ ppm), while for **7** this signal is strongly shifted upfield ($\delta = 1.17$ ppm). The assignment of these signals was achieved by selective decoupling in ^{13}C-spectrum. The aforementioned low value can be explained by the shielding of NMe-group by the benzene ring of the bulky indenyl ligand.

Complex **7** readily exchanges a hydride ligand for a chlorine when dissolved in $CDCl_3$ as does $Cp^*_2ZrH(\eta^2 - \kappa C,N\text{-}C_5H_4N)$ [20], quantitatively forming **9** within several hours. The ^{1}H and ^{13}C spectra of **7** and **9** are also quite similar (differing in the absence of ZrH signal and splitting of $CH_3{}^5$ group signal in ^{1}H spectrum of **9**). Unfortunately, no crystal structures were obtained for **7** or **9**, however, the comparison of NMR spectra with those of **8** and $(\eta^5\text{-}C_5Me_5)[\eta^5:\eta^2(C,N)\text{-}C_5Me_4CH_2CH_2N(Me)CH_2]$ZrCl (for which NOE and X-ray analysis data are available) allows us to confirm the structures of **7** and **9** unambiguously.
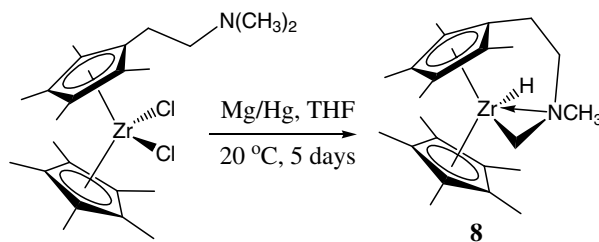
Scheme 6.

Scheme 5.

3. Experimental part

3.1. General remarks

All procedures were performed either under high purity argon or in sealed-off evacuated glass vessels. Solvents were dried and distilled from conventional drying agents [21] prior to use. $Cp^{*N}Li$ and Cp^*ZrCl_3 were prepared according to the reported techniques [10,22]. $ZrCl_4$, Me_3SiCl and indene were purchased from commercial suppliers and used without further purification. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400 and 100 MHz, respectively. For ^1H and ^{13}C spectra, the solvent resonances $\delta_H = 7.15$ and $\delta_C = 128.0$ (C_6D_6), $\delta_H = 1.73$ and $\delta_C = 25.3$ (THF-d_8) were used as the internal reference standards.

Elemental analyses were performed on the Carlo-Erba automated analyzer.

3.2. Preparation of tris(trimethylsilyl)indene (4)

To a solution of indene (11.6 g, 0.1 mol) and diisopropylamine (35 g, 0.35 mol) in 50 ml of THF, a 2.45 M solution of butyllithium in hexane (143 ml, 0.35 mol) was added dropwise at $-5\,°C$ within 1 h. The mixture was stirred for another 90 min at room temperature. Later, two-thirds of solvent were removed in vacuo and THF (50 ml) was added. On cooling to $-5\,°C$ Me_3SiCl (40 g, 0.37 mol) was added dropwise within 30 min and the mixture was stirred for 4 h at reflux. Removal of solvent in vacuo followed by extraction of product with hexane, washing with water, drying over $MgSO_4$, concentration and vacuum distillation (120 °C/2–3 mm Hg) yielded tris(trimethylsilyl)indene (22.7 g, 70%) as a colorless oil, which solidifies slowly on standing. Calc. for $C_{18}H_{32}Si_3$ C, 64.98; H, 9.69. Found: C, 65.01; H, 9.96%. ^1H NMR (27 °C, C_6D_6): $\delta = -0.09$ [s, 18H, $>C(SiMe_3)_2$]; 0.36 (s, 9 H, $=CSiMe_3$); 6.94 (s, 1H, H^2); 7.20, 7.26 (each t, 1H, $^3J_{HH} = 7.5$ Hz, $H^{5,6}$); 7.56, 7.71 (each d, 1H, $^3J_{HH} = 7.5$ Hz, $H^{4,7}$). $^{13}C\{^1H\}$ NMR (27 °C, C_6D_6): $\delta = -1.01$ [$>C(SiMe_3)_2$]; -0.63 ($=CSiMe_3$); 52.00 (C^3); 122.67, 123.44, 123.55, 124.45 (CH^{4-7}); 141.18 (C^1); 147.24 (CH^2); 148.32, 149.00 ($C^{3a,7a}$).

3.3. Preparation of (η^5-$C_9H_5(SiMe_3)_2$)$ZrCl_3$ (3)

A mixture of $C_9H_5(SiMe_3)_3$ (7.8 g, 0.023 mol) and $ZrCl_4$ (5.55 g, 0.024 mol) was heated in 150 ml of toluene for 16 h at 140 °C. After removal of solvent in vacuo, the product was extracted twice with CH_2Cl_2, the solution was concentrated to dryness and the residue was washed twice with hexane and dried in vacuum to give $C_9H_5(SiMe_3)_2ZrCl_3$ (6.15 g, 80%) as a yellow-orange solid. Anal. Calc. for $C_{15}H_{23}Si_2Cl_3Zr$: C, 39.41; H, 5.07. Found: C, 39.39; H, 5.18%. ^1H NMR (27 °C, C_6D_6): $\delta = 0.40$ (s, 18H, $SiMe_3$); 6.99, 7.80 (each m, 2H, CH^{4-7}); 7.39 (s, 1H, H^2). $^{13}C\{^1H\}$ NMR (27 °C, C_6D_6): $\delta = 0.16$ ($SiMe_3$); 125.78 ($C^{1,3}$); 127.47, 127.59 (CH^{4-7}); 135.49 ($C^{3a,7a}$); 136.73 (CH^2).

3.4. Preparation of (η^5-$C_9H_5(SiMe_3)_2$)(η^5-C_5Me_5)$ZrCl_2$ (1)

Solution of Cp^*ZrCl_3 (0.57 g, 1.7 mmol) and $C_9H_5(SiMe_3)_2Li$ (0.56 g, 2.1 mmol) in THF was heated at 80 °C for 40 h. On removal of THF by recondensation the same amount of ether–hexane mixture (1:1) was entered and the solution was separated from the precipitate by decantation. After removal of solvent and drying in vacuum $C_9H_5(SiMe_3)_2Cp^*ZrCl_2$ (0.4 g, 42%) was obtained as a light-yellow solid. Anal. Calc. for $C_{25}H_{38}Si_2Cl_2Zr$: C, 53.92; H, 6.88. Found: C, 54.18; H, 7.01%. ^1H NMR (27 °C, THF-d_8): $\delta = 0.38$ (s, 18H, $SiMe_3$); 2.04 (s, 15H, C_5Me_5); 6.73 (s, 1H, H^2); 7.20, 7.75 (each m, 2H, CH^{4-7}). $^{13}C\{^1H\}$ NMR (27 °C, THF-d_8): $\delta = 1.46$ ($SiMe_3$); 13.39 (C_5Me_5); 118.68 ($C^{1,3}$); 125.41, 129.23 (CH^{4-7}); 126.00 (C_5Me_5); 135.82 (CH^2); 139.15 ($C^{3a,7a}$). ^1H NMR (27 °C, C_6D_6): $\delta = 0.35$ (s, 18H, $SiMe_3$); 1.90 (s, 15H, C_5Me_5); 6.64 (s, 1H, H^2); 7.12, 7.84 (each m, 2H, CH^{4-7}).

3.5. Preparation of (η^5-$C_9H_5(SiMe_3)_2$)(η^5-$C_5Me_4CH_2$-CH_2NMe_2)$ZrCl_2$ (2)

A mixture of $C_9H_5(SiMe_3)_2ZrCl_3$ (0.971 g, 2.1 mmol) and $Cp^{*N}Li$ (0.44 g, 2.2 mmol) was heated in toluene at 80–100 °C for 40 h. Solution was separated from precipitate, solvent was removed *in vacuo* and the residue was washed with hexane to give $C_9H_5(SiMe_3)_2Cp^{*N}ZrCl_2$ (0.8 g, 62%) as a yellow solid. Satisfactory elemental analysis data was not obtained due to the extremely moisture sensitivity of the product. ^1H NMR (27 °C, THF-d_8): $\delta = 0.42$ (s, 18H, $SiMe_3$); 2.04, 2.12 (each s, 6H, C_5Me_4); 2.18 (m, 2H, CH_2CH_2N); 2.23 (s, 6H, NMe_2); 2.72 (m, 2H, CH_2N); 6.76 (s, 1H, H^2); 7.21, 7.76 (each m, 2H, CH^{4-7}). $^{13}C\{^1H\}$ NMR (27 °C, THF-d_8): $\delta = 1.62$ ($SiMe_3$); 13.41, 13.56 (C_5Me_4); 27.80 (CH_2CH_2N); 45.84 (NMe_2); 60.12 (CH_2N); 118.66 ($C^{1,3}$); 125.36, 129.22 (CH^{4-7}); 125.47, 126.99 (CCH_3); 126.85 (CCH_2CH_2N); 135.42 (CH^2); 139.20 ($C^{3a,7a}$). ^1H NMR (27 °C, C_6D_6): $\delta = 0.37$ (s, 18H, $SiMe_3$); 1.92, 2.07 (each s, 6H, C_5Me_4); 2.11 (s, 6H, NMe_2); 2.11 (m, 2H, CH_2CH_2N); 2.85 (m, 2H, CH_2N); 6.70 (s, 1H, H^2); 7.13, 7.86 (each m, 2H, CH^{4-7}). $^{13}C\{^1H\}$ NMR (27 °C, C_6D_6): $\delta = 1.41$ ($SiMe_3$); 13.21, 13.36 (C_5Me_4); 27.25 (CH_2CH_2N); 45.45 (NMe_2); 59.72 (CH_2N); 118.31 ($C^{1,3}$); 125.00 (CCH_3); 126.30 (CCH_3, CCH_2CH_2N); 125.44, 128.88 (CH^{4-7}); 134.47 (CH^2); 138.89 ($C^{3a,7a}$).

3.6. Reduction of (η^5-$C_9H_5(SiMe_3)_2$)(η^5-$C_5Me_4CH_2CH_2$-NMe_2)$ZrCl_2$ (preparation of complex 7)

Stirring of $Ind^{Si2}Cp^{*N}ZrCl_2$ (350 mg) with an excess of Mg in THF at room temperature for one week resulted in formation of deep red solution. Solvent was removed, hexane was added to the residue and hexaneous solution was filtered from precipitate of $MgCl_2$ and Mg. After evaporation of hexane a colorless crystalline product 7 (235 mg, 76%) was

Table 3
Crystal and structure refinement data for **1** and **6**

	1	6
Empirical formula	$C_{25}H_{38}Cl_2Si_2Zr$	$C_{26}H_{44}Cl_4N_2O_1Zr_2$
Formula weight	556.85	724.87
Color, habit	Yellow needle	Colourless plate
Crystal size (mm)	$0.40 \times 0.10 \times 0.10$	$0.40 \times 0.20 \times 0.05$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
Cell dimensions		
a (Å)	10.040(2)	9.4793(10)
b (Å)	15.834(7)	14.7680(16)
c (Å)	17.997(5)	21.224(2)
β (°)	104.15(2)	99.309(2)
V (Å^3)	2774.2(16)	2932.0(5)
Z	4	4
D_{calc} (g cm^{-3})	1.333	1.642
μ (mm^{-1})	0.686	1.098
$F(000)$	1160	1480
Diffractometer	Enraf-Nonius CAD4	Bruker SMART APEX
Temperature (K)	293(2)	120(2)
θ Range (°)	2.13–25.48	1.94–30.00
Index ranges	$-12 \leqslant h \leqslant 12$	$-13 \leqslant h \leqslant 13$
	$-3 \leqslant k \leqslant 19$	$-20 \leqslant k \leqslant 13$
	$-3 \leqslant l \leqslant 21$	$-29 \leqslant l \leqslant 29$
Reflections collected	7804	11440
Independent reflections ($R_{int} =$)	5150 (0.0247)	4206 (0.0269)
Data/restraints/parameters	5150/0/282	4206/0/247
Reflections with $I > 2\sigma(I)$	3226	3737
Goodness-of-fit on F^2	0.990	1.038
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0289$, $wR_2 = 0.0697$	$R_1 = 0.0279$, $wR_2 = 0.0647$
R indices (all data)	$R_1 = 0.0831$, $wR_2 = 0.0777$	$R_1 = 0.0327$, $wR_2 = 0.0666$
Largest difference in peak/hole (e Å^{-3})	0.338/−0.287	0.878/−0.565

3.7. $(\eta^5-C_9H_5(SiMe_3)_2)[\eta^5:\eta^2(C,N)-C_5Me_4CH_2CH_2N(Me)CH_2]ZrCl$ (**9**)

Complex **7** was dissolved in CDCl$_3$ and after 1 day NMR spectra were recorded.

^{1}H NMR (27 °C, CDCl$_3$): $\delta = 0.29$, 0.37 (each s, 9H, SiMe$_3$); 0.68 (d, 1H, $^2J_{HH} = 8.4$ Hz, ZrCHHN); 1.14 (s, 3H, NCH$_3$); 1.88 (d, 1H, $^2J_{HH} = 8.4$ Hz, ZrCHHN); 1.95, 1.97, 2.10, 2.13 (each s, 3H, CH$_3^{2-5}$); 2.26 (m, 2 H, CH$_2$CH$_2$N); 2.91 (m, 1 H, CH$_2$CHHN); 3.34 (m, 1H, CH$_2$CHHN); 6.11 [s, 1H, H^2(Ind)]; 6.97 [m, 2H, H^{5,6}(Ind)]; 7.41, 7.66 [each d, 1H, $^3J_{HH} = 8.0$ Hz, H^{4,7}(Ind)]. ^{13}C{^{1}H} NMR (27 °C, CDCl$_3$): $\delta = 0.52$, 0.87 (SiMe$_3$); 11.95, 12.61, 13.52, 13.63 (CH$_3^{2-5}$); 20.98 (CH$_2$CH$_2$N); 45.35 (NCH$_3$); 57.86 (ZrCH$_2$N); 65.95 (CH$_2$CH$_2$N); 103.37, 104.98, 111.22, 114.48, 114.84, 122.45, 123.27, 136.66, 138.13 [C$^{1-5}$, C^{1,3,3a,7a}(Ind)]; 121.94, 123.24, 123.96, 129.67, 132.88 [CH$^{2,4-7}$(Ind)].

3.8. X-ray crystallography for **1** and **6**

Crystal and structure refinement parameters are listed in Table 3. Experimental data were measured using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods [23] and refined by full matrix least-squares on F^2 [24] with anisotropic thermal parameters for all non-hydrogen atoms. In the structure of **1**, all hydrogen atoms were placed in calculated positions and refined using a riding model. In **6**, all hydrogen atoms were found from difference Fourier synthesis and refined isotropically (see Table 3).

4. Supplementary material

CCDC 649963 and 649964 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

obtained. ^{1}H NMR (27 °C, THF–d_8): $\delta = 0.22$ (d, 1H, $^2J_{HH} = 8.3$ Hz, ZrCHHN); 0.37, 0.42 (each s, 9H, SiMe$_3$); 1.17 (s, 3H, NCH$_3$); 1.28 (d, 1H, $^2J_{HH} = 8.3$ Hz, ZrCHHN); 1.88, 1.98, 2.05 (each s, 3H, CH$_3^{2-4}$); 1.97 (m, 2H, CH$_2$CH$_2$N); 2.26 (d, 3H, $J_{H-ZrH} = 1.7$ Hz, CH$_3^5$); 2.77 (br s, 1H, ZrH); 2.90 (m, 1H, CH$_2$CHHN); 3.38 (m, 1H, CH$_2$CHHN); 5.55 [s, 1H, H^2(Ind)]; 6.73, 6.84 [each t, 1H, $^3J_{HH} = 7.5$ Hz, H^{5,6}(Ind)]; 7.36, 7.46 [each d, 1H, $^3J_{HH} = 8.4$ Hz, H^{4,7}(Ind)]. ^{13}C NMR (27 °C, THF–d_8): $\delta = 1.18$, 1.78 (each q, $^1J_{CH} = 119$ Hz, SiMe$_3$); 12.34, 12.65, 12.67 (each q, $^1J_{CH} = 126$ Hz, CH$_3^{2-4}$); 15.61 (qd, $^1J_{CH} = 126$ Hz, $J_{C-ZrH} = 6.5$ Hz, CH$_3^5$); 21.64 (t, $^1J_{CH} = 127$ Hz, CH$_2$CH$_2$N); 49.84 (q, $^1J_{CH} = 136$ Hz, NCH$_3$); 50.16 (t, $^1J_{CH} = 143$ Hz, ZrCH$_2$N); 68.25 (t, $^1J_{CH}$ 136 Hz, CH$_2$CH$_2$N); 102.30, 103.60, 107.10, 112.29, 113.45, 115.16, 120.68, 133.65, 134.50 [each s, C$^{1-5}$, C^{3a,7a}(Ind), C^{1,3}(Ind)]; 121.88, 127.53 (each dd, $^1J_{CH} = 159$ Hz), 123.03, 124.68 (each dd, $^1J_{CH} = 158$ Hz) [CH$^{4-7}$(Ind)]; 127.26 [d, $^1J_{CH} = 163$ Hz, CH^2(Ind)].

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