

# Methylbenz[*e*]indenyl asymmetric *ansa*-metallocene and silylamido zirconium complexes

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Dedicated to Professor Pierre Braunstein

## Abstract

2-(2-Methylbenz[*e*]indenyl)-2-cyclopentadienyl-propane [MeC<sub>13</sub>H<sub>8</sub>–CMe<sub>2</sub>–C<sub>5</sub>H<sub>5</sub>] (**1**) (MBI–CMe<sub>2</sub>–Cp), was synthesized by reaction of LiMBI with 6,6-dimethylfulvene. The silyl derivatives [MeC<sub>13</sub>H<sub>8</sub>–SiMeRCl] (R = Me **2**, H **4**) were isolated by reaction of 2-methylbenz[*e*]indene (LiMBI) with SiMeRCl<sub>2</sub> and further reactions of **2** and **4** with NaCp afforded the silyl-bridged compounds [MeC<sub>13</sub>H<sub>8</sub>–SiMeR–C<sub>5</sub>H<sub>5</sub>] (R = Me **3**, H **5**). Metallation of **1** and **3** with 2 equiv. of LiBu gave the dilithium salts Li<sub>2</sub>[MeC<sub>13</sub>H<sub>7</sub>–EMe<sub>2</sub>–C<sub>5</sub>H<sub>4</sub>] (E = C **6**, Si **7**) which were reacted with ZrCl<sub>4</sub>(THF)<sub>2</sub> to obtain the *ansa*-metallocenes [Zr(MeC<sub>13</sub>H<sub>7</sub>–EMe<sub>2</sub>–C<sub>5</sub>H<sub>4</sub>)Cl<sub>2</sub>] (E = C **8**, Si **9**). A similar reaction of **5** with 2 equiv. of LiBu provided a mixture of the two diastereomers [Zr{MeC<sub>13</sub>H<sub>7</sub>–SiMeBu–C<sub>5</sub>H<sub>4</sub>}Cl<sub>2</sub>] (**10a**, **10b**). Analogous metallation of [MeC<sub>13</sub>H<sub>8</sub>–SiMe<sub>2</sub>(NH-*t*-Bu)] gave Li<sub>2</sub>[MeC<sub>13</sub>H<sub>7</sub>–SiMe<sub>2</sub>(N-*t*-Bu)] which was used to prepare the amidosilyl derivatives [M{MeC<sub>13</sub>H<sub>7</sub>–SiMe<sub>2</sub>–η-(N-*t*-Bu)}Cl<sub>2</sub>] (M = Zr **11**, Ti **12**) by reaction with ZrCl<sub>4</sub>(THF)<sub>2</sub> and TiCl<sub>3</sub>(THF)<sub>3</sub> and further oxidation with PbCl<sub>2</sub> (Ti). All of the new complexes were characterized by elemental analysis and NMR spectroscopy, and the molecular structures of complexes **9** and **10a** were studied by X-ray diffraction methods.

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**Keywords:** *ansa*-Metallocenes; Methylbenz[*e*]indenyl silylamido; Titanium; Zirconium

## 1. Introduction

The rational design of new types of Group 4 and other transition metal catalysts for olefin polymerization has been the objective of a considerable amount of scientific work. These efforts have achieved further improvements not only in the activity and productivity of the polymerization process but also notably in the thermal stability and selectivity of the catalytic systems, as well as providing a more profound knowledge of their catalytic behavior. It has been extensively demonstrated [1] that the clever selection of an appropriate ligand is a decisive step in achieving the best results from the catalytic system. It is well known that the presence of

aromatic six-membered rings in indenyl ligands and their derivatives induces a remarkable increase in the catalytic activity of indenyl metallocenes, and that the introduction of a 2-alkyl substituent in these molecules hinders the β-elimination that favors the production of polymers of higher molecular weight [2,3].

The symmetry of the catalyst precursor also plays an important role in determining the stereoselectivity of the polymerization processes. C<sub>2</sub> symmetric *ansa*-metallocenes produce highly isotactic polypropylene [4–6], whereas C<sub>1</sub> analogues give thermoplastic elastic polypropylenes in homogeneous processes both at low and ambient temperature [7,8]. The monocyclopentadienyl-amido so called ‘constrained geometry’ catalysts have been shown to be very efficient catalysts for copolymerization of ethylene and other larger olefins [9–11].

In this work we report the use of the 2-methylbenz[*e*]indenyl ligand to synthesize the new mixed *ansa*-zirconocenes [Zr(MeC<sub>13</sub>H<sub>7</sub>–EMe<sub>2</sub>–C<sub>5</sub>H<sub>4</sub>)Cl<sub>2</sub>] (E = C,

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Si) and  $[\text{Zr}\{\text{MeC}_{13}\text{H}_7\text{-SiMeBu-C}_5\text{H}_4\}\text{Cl}_2]$  and the related 2-methylbenz[*e*]indenyl-silylamido derivatives  $[\text{M}\{\text{MeC}_{13}\text{H}_7\text{-SiMe}_2\text{-}\eta\text{-(N-t-Bu)}\}\text{Cl}_2]$  ( $\text{M} = \text{Zr, Ti}$ ).

## 2. Results and discussion

The ligands required to prepare the desired *ansa*-mixed-metalloenes of the type (MBI-B-Cp)MCl<sub>2</sub> with various B bridging groups were prepared using the lithium salt of the 2-methylbenz[*e*]indene (LiMBI). The method previously reported [12] was followed to prepare a mixture of the 1-H and 3-H isomers of the LiMBI, and its lithiated derivative was formed by reaction with LiBu and isolated as a pale yellow solid which can be stored for long time under an inert atmosphere.

As shown in Scheme 1 the reaction of LiMBI with 6,6-dimethylfulvene in THF afforded, after appropriate manipulation (see Section 3), the -CMe<sub>2</sub>- bridged 2-cyclopentadienyl-2-(2-methylbenz[*e*]indenyl) propane  $[\text{MeC}_{13}\text{H}_8\text{-CMe}_2\text{-C}_5\text{H}_5]$  (**1**) as a pale yellow oil in 86% yield. Compound **1** was characterized by <sup>1</sup>H NMR spectroscopy as a mixture of two isomers. All attempts to make similar reactions using 6,6-diphenylfulvene with the lithium, sodium and potassium MBI salts at various temperatures were unsuccessful.

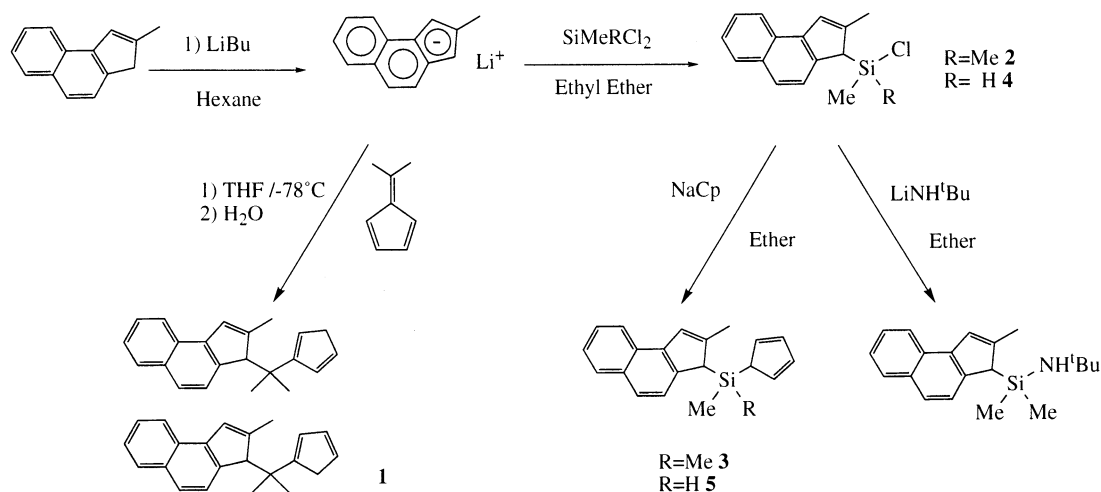
The known -SiMe<sub>2</sub>-bridged homolog  $[\text{MeC}_{13}\text{H}_8\text{-SiMe}_2\text{Cl}]$  (**2**) was prepared using LiMBI following the method reported [2] for related silanes. Further reaction of a diethylether solution of **2** with NaCp dissolved in the minimum amount of THF afforded  $[\text{MeC}_{13}\text{H}_8\text{-SiMe}_2\text{-C}_5\text{H}_5]$  (**3**) as a colorless viscous oil in 93% yield. Compound **3** was identified by <sup>1</sup>H NMR spectroscopy as a unique 1-silyl asymmetric component, for which none of the Si-Me and ring protons are equivalent (see Section 3). The same procedure was used to prepare the silicon-chiral derivative using SiMeHCl<sub>2</sub>, which afforded  $[\text{MeC}_{13}\text{H}_8\text{-SiMeHCl}]$  (**4**) as a colorless viscous

oil in quantitative yield. When **4** was reacted with a THF solution of NaCp the silyl-bridged  $[\text{MeC}_{13}\text{H}_8\text{-SiMeH-C}_5\text{H}_5]$  (**5**) was isolated as a colorless viscous oil in 87% yield. The <sup>1</sup>NMR spectra of **4** and **5** show the presence of two pairs of diastereomers as expected for molecules which possess two chiral centers at carbon and silicon (see Section 3).

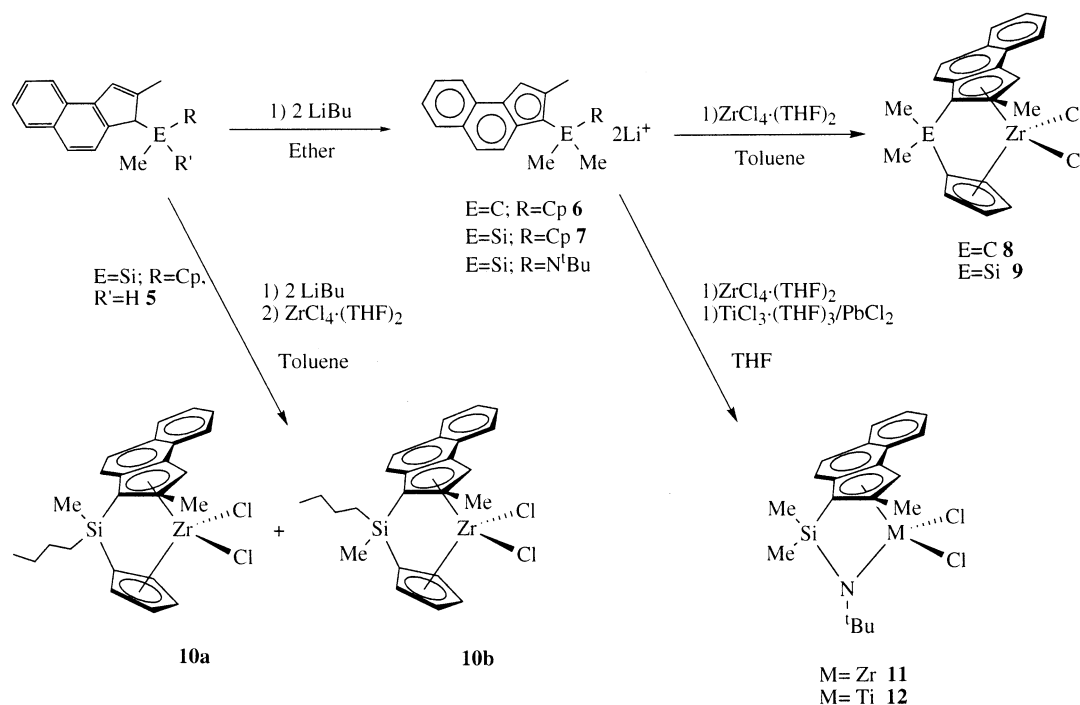
With the aim of isolating cyclopentadienyl-silyl-amido compounds, we carried out the reaction of **2** with NH<sub>2</sub>-t-Bu following the previously reported [13] method to prepare the already known amino derivative  $[\text{MeC}_{13}\text{H}_8\text{-SiMe}_2(\text{NH-t-Bu})]$ .

Double deprotonation of compounds **1**, **3** and  $[\text{MeC}_{13}\text{H}_8\text{-SiMe}_2(\text{NH-t-Bu})]$  by reaction with 2 equiv. of LiBu afforded the dilithium salts  $\text{Li}_2[\text{MeC}_{13}\text{H}_7\text{-EMe}_2\text{-C}_5\text{H}_4]$  ( $\text{E} = \text{C}$  **6**,  $\text{Si}$  **7**) and  $\text{Li}_2[\text{MeC}_{13}\text{H}_7\text{-SiMe}_2(\text{N-t-Bu})]$  which were used to transfer the ligand to the Group 4 metal chloride. Reaction of **6** and **7** with a toluene suspension of ZrCl<sub>4</sub>(THF)<sub>2</sub> afforded the zirconium metalloenes  $[\text{Zr}\{\text{MeC}_{13}\text{H}_7\text{-EMe}_2\text{-C}_5\text{H}_4\}\text{Cl}_2]$  ( $\text{E} = \text{C}$  **8**,  $\text{Si}$  **9**) isolated after purification as yellow crystalline solids in 20 and 23% yield, respectively (see Scheme 2). Complexes **8** and **9** were identified by elemental analysis and NMR spectroscopy and a single crystal of **9** was studied by X-ray diffraction methods.

The NMR spectra of complexes **8** and **9** correspond to asymmetric molecules (see Fig. 1) and show one singlet for the MBI methyl substituent, two singlets for the EMe<sub>2</sub> groups (<sup>1</sup>H and <sup>13</sup>C), shifted highfield for silicon (**9**) and four multiplets (<sup>1</sup>H) or singlets (<sup>13</sup>C{<sup>1</sup>H}) due to the cyclopentadienyl C<sub>5</sub>H<sub>4</sub> ring. The resonance due to the ring C<sub>ipso</sub> atom is shifted highfield with respect to the other ring carbon atoms as expected [14] for this type of *ansa*-metalloenes. All of the remaining MBI non-equivalent protons give the set of signals shown in Fig. 1, the MBI-3-H proton appearing as one singlet at δ 7.10 and 7.21 for **8** and **9**, respectively.



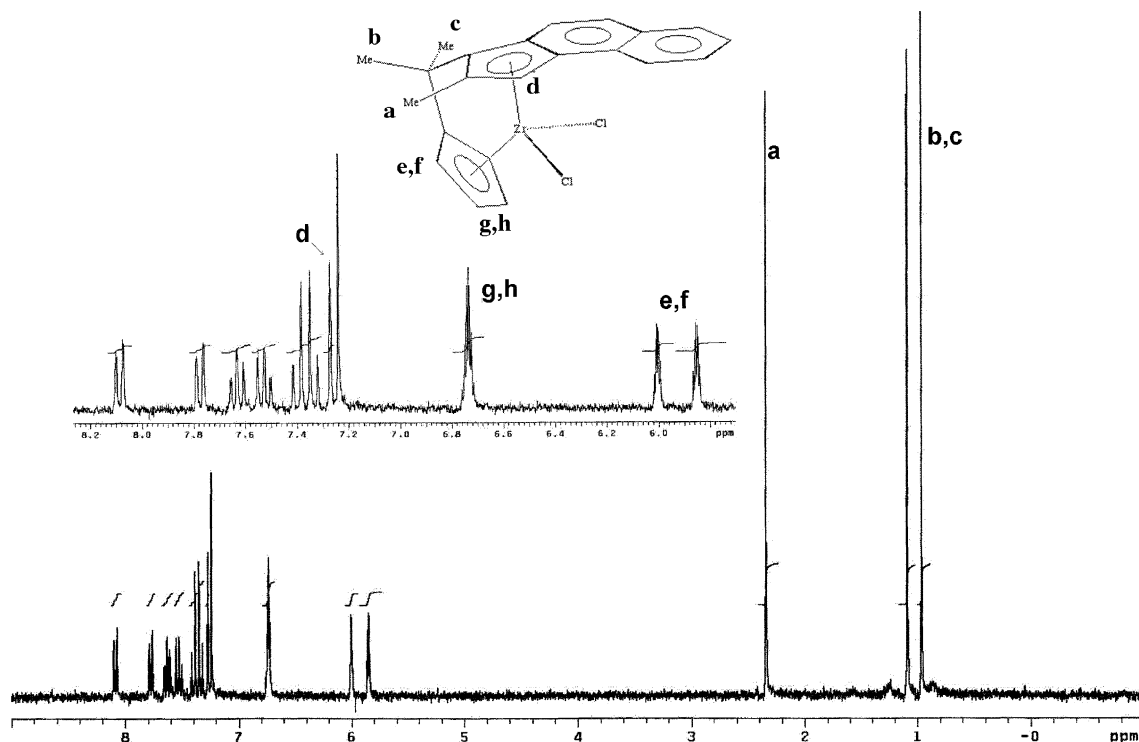
Scheme 1.



Scheme 2.

Single crystals of **9** appropriate for X-ray diffraction studies were formed by slowly cooling its toluene–hexane solution. A view of the molecular structure of complex **9** is shown in Fig. 2(a) together with the atomic labeling system. Selected bond distances and angles for **9** are given in Table 1 and the structural data reported for

related indenyl compounds is summarized in Table 2. Coordination around the zirconium atom is defined by the two chlorine atoms and the centroids of the five membered Cp and MBI rings arranged in the pseudo-tetrahedral geometry typically found in metallocene complexes. The presence of the fused aromatic rings

Fig. 1.  $^1H$  NMR for **9** in  $CDCl_3$ . The spectrum shows the normal pattern of signals for MBI-E-CpZrCl<sub>2</sub> complexes.

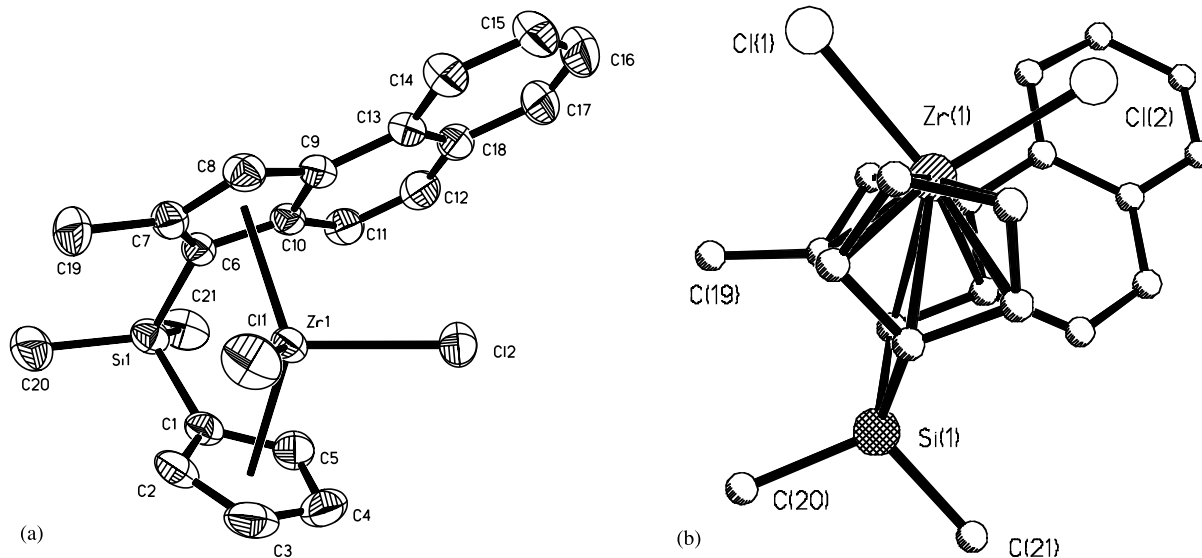


Fig. 2. ORTEP representation of molecular structure of compound **9**. Thermal ellipsoids are drawn at the 50% probability level. (a) The H atoms were removed for clarity. (b) Top view perpendicular to the  $ZrCl_2$  plane.

Table 1  
Selected interatomic distances (Å) and angles (°) for complexes **9** and **10a**· $C_7H_8$

	<b>9</b>	<b>10a</b>
<i>Interatomic distances</i>		
Zr–Cl1	2.4396(11)	2.4414(4)
Zr–Cl2	2.4216(11)	2.4237(4)
Zr–C1	2.481(3)	2.487(1)
Zr–C2	2.477(4)	2.497(2)
Zr–C3	2.559(4)	2.572(2)
Zr–C4	2.581(6)	2.564(2)
Zr–C5	2.488(5)	2.472(2)
Zr–C6	2.482(3)	2.474(2)
Zr–C7	2.505(4)	2.483(2)
Zr–C8	2.569(4)	2.555(2)
Zr–C9	2.614(3)	2.626(1)
Zr–C10	2.531(3)	2.552(1)
Zr–Cp1	2.213(6)	2.212
Zr–Cp2	2.233(5)	2.229
Si–C1	1.868(3)	1.880(2)
Si–C6	1.877(4)	1.883(2)
Si–C20	1.855(5)	1.861(2)
Si–C21	1.846(5)	1.875(2)
<i>Bond angles</i>		
Cl1–Zr–Cl2	99.34(4)	99.27(2)
Cl1–Zr–Cp1	106.2(1)	106.05
Cl1–Zr–Cp2	107.4(1)	107.27
Cl2–Zr–Cp1	106.2(1)	107.39
Cl2–Zr–Cp2	108.0(1)	107.04
Cp1–Zr–Cp2	126.2(2)	126.54
C1–Si–C6	94.0(1)	93.64(6)
C1–Si–C20	116.2(2)	109.99(8)
C1–Si–C21	113.4(1)	114.14(7)
C6–Si–C20	116.2(2)	114.35(7)
C6–Si–C21	113.4(1)	112.13(7)
C20–Si–C21	110.0(2)	111.50(8)

Cp1/2 denotes the centroids of the five membered Cp (C1–C5) and MBI (C6–C10) rings.

does not modify the structural parameters of the indenyl system. The  $CE(Cp)-Zr-CE(MBI)$  angle ( $126.2(2)^\circ$ ) is slightly more closed than that observed for related *ansa*- $SiMe_2$ -bridged di-MBI, di-indenyl and Cp-Indenyl compounds. The  $CE(Cp)-Zr$  distance is slightly longer than the  $CE(MBI)-Zr$ . The projection of the structure in the equatorial plane represented in Fig. 2 shows the ring methyl group in the  $\alpha$  position with respect to the bridge, far from the nearest Cl(1) atom located in a free region, whereas the second Cl(2) is located below the benzene ring of the MBI ligand, with the nearest ring carbon atoms located at distances longer than 3.85 Å. The steric protection afforded by the benzene ring on the Cl(2) atom may affect its reactivity. The  $Zr-Cl(2)$  bond distance ( $2.4217(11)\text{Å}$ ) is slightly shorter than that found for  $Zr-Cl(1)$  ( $2.4391(11)\text{Å}$ ) and the  $Cl(1)-Zr-Cl(2)$  angle is in the range reported for indenyl homologues.

Similar deprotonation of the mixture of diastereomers **5** with 2 equiv. of LiBu in toluene provided a solid assumed to be the dilithium salt. Reaction of this product with  $ZrCl_4(THF)_2$  in refluxing toluene did not give the corresponding zirconocene but afforded only a small amount of a yellow crystalline solid that did not contain hydrogen but unexpectedly contained butyl bonded to silicon [ $Zr\{MeC_{13}H_7-SiMeBu-C_5H_4\}Cl_2$ ] (**10a**, **10b**). The presence of the silicon chiral center together with the enantiotopic MBI face generates two pairs of diastereomers **10a** and **10b**. The  $^1H$  NMR spectrum shows the presence of two similar sets of signals in a molar ratio of approximately 1/1. The two diastereomers were separated after repeated recrystallization in toluene, and a single crystal of **10a** was

Table 2  
Comparison of structural parameters for *ansa*-[Zr{R1(SiMe<sub>2</sub>)R2}Cl<sub>2</sub>] complexes

	R1 = R2 Ind [3]	R1 = R2 MeInd [3]	R1, R2 Cp, Ind [7]	R1 = R2 MBI [12]	<b>9</b>	<b>10a</b>
Zr–Cl <sup>a</sup> (Å)	2.431	2.419	2.43	2.423	2.431	2.433
Cl–Zr–Cl (°)	98.76(1)	99.06	97.1(1)	99.2(1)	99.34(4)	99.72(2)
Zr–Ind <sup>b</sup> (Å)	2.241(1)	2.244 <sup>a</sup>	2.227(5)	2.247	2.233(5)	2.229
Zr–Cp <sup>b</sup> (Å)			2.198(5)		2.213(6)	2.212
Zr–C(Ind) min (Å)	2.470(1)	2.462(3)	2.455(4)	2.474	2.482(3)	2.474(2)
Zr–C(Ind) max (Å)	2.659(1)	2.663(5)	2.573(5)	2.648	2.614(3)	2.626(1)
Cp–Zr–Cp (°)	127.81(1)	128.11(1)	126.9(1)	127.9	126.2(2)	126.54
E1–E2 <sup>c</sup> (°)	61.94	61.39		60.8	60.58	60.01(7) <sup>d</sup>

<sup>a</sup> Average.

<sup>b</sup> Centroid of rings.

<sup>c</sup> Interplanar angle of indenyl rings.

<sup>d</sup> Interplanar angle of Cp and indenyl/MBI rings.

obtained from a toluene–hexane solution and used to determine its molecular structure by X-ray diffraction.

A view of the molecular structure of complex **10a** is shown in Fig. 3 together with the atomic labeling system. The unit cell contains both enantiomers of **10a** together with one toluene solvent molecule. Selected bond distances and angles for **10a** are given in Table 1 and a comparison of the structural data reported for related indenyl compounds is summarized in Table 2. The molecular geometry of **10a** is very close to compound **9** and therefore requires no detailed discussion (see above for **9**).

A similar reaction of Li<sub>2</sub>[MeC<sub>13</sub>H<sub>7</sub>–SiMe<sub>2</sub>(N-t-Bu)] with ZrCl<sub>4</sub>(THF)<sub>2</sub> afforded the silylamido complex [Zr{MeC<sub>13</sub>H<sub>7</sub>–SiMe<sub>2</sub>–η-(N-t-Bu)}Cl<sub>2</sub>] (**11**) which was isolated as a pale yellow solid in 32% yield after purification and identified by elemental analysis and NMR spectroscopy. When the same reaction was carried out using TiCl<sub>3</sub>(THF)<sub>3</sub> and the resulting product was oxidized with PbCl<sub>2</sub>, the corresponding titanium derivative [Ti{MeC<sub>13</sub>H<sub>7</sub>–SiMe<sub>2</sub>–η-(N-t-Bu)}Cl<sub>2</sub>] (**12**) was isolated as a dark-red solid in 26% yield. The preparation of this compound by a different method has

been reported [1] previously. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds **11** and **12** correspond to asymmetric molecules and show one singlet (<sup>1</sup>H) and two resonances (<sup>13</sup>C) for the t-Bu group along with the same pattern of signals described above for compounds **8** and **9**. The value observed for  $\Delta\delta = \delta_{\text{quat}} - \delta_{\text{Me}}$  of 23.9 in the <sup>13</sup>C NMR spectrum of **11** demonstrates a significant  $\pi$ -bonding contribution [15] from the amido ligand in spite of the donor capacity of the MBI substituent.

### 3. Experimental

#### 3.1. General methods

All manipulations were performed under an inert atmosphere of argon using standard Schlenk and high-vacuum line techniques or a glove box model HE-63. The solvents were pre-dried over sodium wire before purification by distillation under argon employing the appropriate drying/deoxygenated agent: toluene, hexane and pentane (sodium–potassium alloy) and diethyl ether, THF (sodium–benzophenone). After being col-

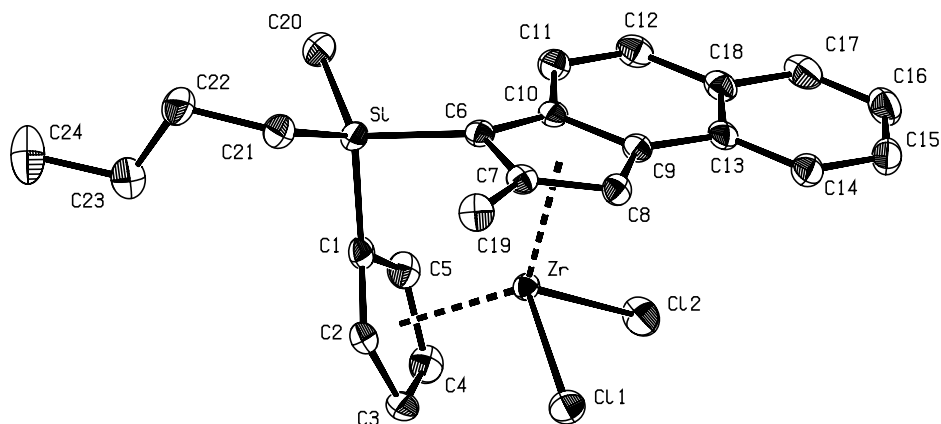


Fig. 3. ORTEP representation of complex **10a** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.



lected, the dried solvents were stored under argon in ampoules over potassium mirrors or 4 Å molecular sieves (THF). Deuterated solvents from Scharlau were dried, degassed, and stored over molecular sieves.  $\text{TiCl}_4$  (Fluka) was distilled before use,  $\text{ZrCl}_4$  (Fluka),  $\text{SiMe}_2\text{Cl}_2$  (Aldrich), 6,6'-dimethylfulvene (Aldrich) were used without further purifications and  $\text{NH}_2\text{-t-Bu}$  (Aldrich) was distilled before use and stored over 4 Å molecular sieves.  $\text{LiNH-t-Bu}$  was quantitatively prepared by reaction of  $\text{NH}_2\text{-t-Bu}$  with  $\text{Li-n-Bu}$  in hexane.  $\text{ZrCl}_4\cdot(\text{THF})_2$  was prepared following the literature method [16]. C, H and N microanalyses were performed on a Perkin–Elmer 240C and/or Heraeus CHN-O-Rapid microanalyzer. NMR spectra, measured at 25 °C, were recorded on a Varian Unity VXR-300 ( $^1\text{H}$  NMR at 300 MHz,  $^{13}\text{C}$  NMR at 75 MHz) or 500 Plus ( $^1\text{H}$  NMR at 500 MHz,  $^{13}\text{C}$  NMR at 125 MHz) spectrometer and chemical shifts are referenced to the residual protons or carbons of the deuterated solvents.

### 3.2. Preparation of 2-cyclopentadienyl-2-(2-methylbenz[e]indenyl)propane (**1**)

A solution of 6,6-dimethylfulvene (5 ml, 4.4 g, 41 mmol) in THF (20 ml) was added dropwise at 0 °C to a solution of lithium 2-methylbenz[e]indenyl (7.72 g, 41 mmol) in THF (100 ml) at the same temperature. The reaction mixture was allowed to warm to room temperature (r.t.) and stirred for 12 h to produce a dark red solution. The mixture was then hydrolyzed with 200 ml of saturated aqueous ammonium chloride and extracted into 150 ml of diethyl ether. The solvent was removed from the organic phase and the remaining brown yellow oil was dissolved in pentane, dried over anhydrous sodium sulfate and filtered through celite. The solvent was removed under reduced pressure to produce **1** (10.1 g, 35 mmol, 86% yield) as a pale yellow oil.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  1.02 (s, 3H,  $\text{CMe}_2$ ), 1.06 (s, 3H,  $\text{CMe}_2$ ), 1.14 (s, 3H,  $\text{CMe}_2$ ), 1.25 (s, 3H,  $\text{CMe}_2$ ), 1.90 (s, 3H,  $\text{CMe}$ ), 1.92 (s, 3H,  $\text{CMe}$ ), 2.78 (s, 2H,  $\text{C}_5\text{H}_4$ ), 2.79 (s, 2H,  $\text{C}_5\text{H}_4$ ), 3.37 (s, 1H,  $\text{C}_{13}\text{H}_7$ ), 3.51 (s, 1H,  $\text{C}_{13}\text{H}_7$ ), 5.8 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.07 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.28 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.44 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.53 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.64 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.93 (m, 1H,  $\text{C}_5\text{H}_4$ ), 6.95 (m, 1H,  $\text{C}_5\text{H}_4$ ), 7.19 (s, 1H,  $\text{C}_{13}\text{H}_7$ ), 7.22 (s, 1H,  $\text{C}_{13}\text{H}_7$ ), 7.29 (m, 5H,  $\text{C}_{13}\text{H}_7$ ), 7.50 (m, 3H,  $\text{C}_{13}\text{H}_7$ ), 7.74 (m, 2H,  $\text{C}_{13}\text{H}_7$ ), 8.02 (m, 2H,  $\text{C}_{13}\text{H}_7$ ). *Anal.* Calc. for  $\text{C}_{22}\text{H}_{22}$ : C, 92.26; H, 7.74. Found: C, 92.53; H, 7.47%.

### 3.3. Preparation of (chlorodimethyl)(2-methylbenz[e]indenyl)silane (**2**)

A solution of lithium 2-methylbenz[e]indenyl in 100 ml of diethyl ether was added drop wise to a stirred solution of dichlorodimethylsilane in 100 ml of diethyl ether cooled to 0 °C. After the yellow mixture was

stirred for 6 h, the solvent and excess dichlorodimethylsilane was removed under vacuum. The product was extracted into 200 ml of hexane, the resulting solution filtered through celite and the solvent completely removed to give a colorless viscous oil. The yield was almost quantitative and the product was employed without further purification. *Anal.* Calc. for  $\text{C}_{16}\text{H}_{17}\text{SiCl}$ : C, 73.15; H, 6.47. Found: C, 73.42; H, 6.62%.

### 3.4. Preparation of (cyclopentadienyl)dimethyl(2-methylbenz[e]indenyl)silane (**3**)

A solution of cyclopentadienyl sodium (3.17 g, 37 mmol), prepared using the least amount of THF (20 ml) to achieve dissolution, was added to a solution of **2** (10 g, 37 mmol) in diethyl ether (200 ml) cooled to 0 °C. The reaction mixture was stirred overnight and the solvent was removed under vacuum. The product was extracted into 200 ml of hexane, the resulting solution filtered throughout celite and the solvent removed to give **3** (10.1, 33 mmol, 93% yield) as colorless viscous oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  -0.55 (s, 3H,  $\text{SiMe}$ ), -0.49 (s, 3H,  $\text{SiMe}$ ), 2.01 (s, 3H,  $\text{CMe}$ ), 3.32 (s, 1H,  $\text{C}_5\text{H}_4$ ), 6.23 (m, 4H,  $\text{C}_5\text{H}_4$ ), 7.28 (s, 1H,  $\text{C}_{13}\text{H}_7$ ), 7.46 (m, 4H,  $\text{C}_{13}\text{H}_7$ ), 7.86 (m, 1H,  $\text{C}_{13}\text{H}_7$ ), 8.12 (m, 1H,  $\text{C}_{13}\text{H}_7$ ). *Anal.* Calc. for  $\text{C}_{21}\text{H}_{22}\text{Si}$ : C, 83.38; H, 7.33. Found: C, 83.76; H, 7.58%.

### 3.5. Preparation of chloromethyl(2-methylbenz[e]indenyl)silane (**4**)

A solution of lithium 2-methylbenz[e]indenyl (6 g, 32 mmol) in diethyl ether (50 ml) at 0 °C was added drop wise to a stirred solution of dichloromethylsilane (6.7 ml, 7.41 g, 64 mmol) in diethyl ether (100 ml) cooled to 0 °C. After the yellow mixture was stirred for 6 h, the solvent and excess dichloromethylsilane was removed under vacuum. The product was extracted into 200 ml of hexane, the resulting solution filtered through celite and the solvent removed to give **4** (8.28 g, 32 mmol, 100% yield) as a colorless viscous oil. The yield was almost quantitative and the product was employed without further purification.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  -0.32 (d,  $J=2.8$  Hz, 3H,  $\text{SiMe}$ ), -0.29 (d,  $J=2.8$  Hz, 3H,  $\text{SiMe}$ ), 2.02 (s, 3H,  $\text{CMe}$ ), 2.18 (s, 3H,  $\text{CMe}$ ), 3.44 (s, 2H,  $\text{C}_{\text{sp}^3}\text{-H}$ ,  $\text{C}_{13}\text{H}_7$ ), 4.80 (q, 1H,  $\text{Si-H}$ ), 4.90 (q, 1H,  $\text{Si-H}$ ), 7.00 (s, 2H,  $\text{C}_{13}\text{H}_7$ ), 7.25–8.02 (m, 12H,  $\text{C}_{13}\text{H}_7$ ). *Anal.* Calc. for  $\text{C}_{15}\text{H}_{15}\text{SiCl}$ : C, 69.61; H, 5.84. Found: C, 70.18; H, 6.09%.

### 3.6. Preparation of (cyclopentadienyl)methyl(2-methylbenz[e]indenyl)silane (**5**)

A solution of cyclopentadienyl sodium (2.81 g, 32 mmol), prepared using the least amount of THF (20 ml) to achieve dissolution, was added to a solution of **4** (8.28

g, 32 mmol) in diethyl ether (200 ml) cooled at 0 °C. The reaction mixture was stirred overnight and the solvent was removed under vacuum. The product was extracted into 200 ml of hexane, filtered throughout celite and the solvent removed to give **5** (8.03 g, 28 mmol, 87% yield) as a colorless viscous oil. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ -0.16 (d, *J* = 2.8 Hz, 3H, SiMe), 0.09 (d, *J* = 2.8 Hz, 3H, SiMe), 2.05 (s, 3H, CMe), 2.24 (s, 3H, CMe), 3.56 (s, 2H, C<sub>sp<sup>3</sup></sub>-H, C<sub>13</sub>H<sub>7</sub>), 4.76 (q, *J* = 2.8 Hz, 1H, Si-H), 4.82 (q, *J* = 2.8 Hz, 1H, Si-H), 6.16–6.28 (m, 8H, C<sub>5</sub>H<sub>4</sub>), 7.12 (s, 2H, C<sub>13</sub>H<sub>7</sub>), 7.25–8.02 (m, 12H, C<sub>13</sub>H<sub>7</sub>). *Anal.* Calc. for C<sub>20</sub>H<sub>20</sub>Si: C, 83.28; H, 6.99. Found: C, 84.02; H, 7.28%.

### 3.7. Preparation of dilithium[propylidene-2-cyclopentadienyl-2-(2-methylbenz[e]indenyl)] (**6**)

n-Butyllithium 1.6 M in hexane (53 ml, 84 mmol) was added drop wise to a solution of **1** (12 g, 42 mmol) in diethyl ether (300 ml) cooled to -78 °C. After the solution was stirred for 1 h at -78 °C, it was gradually warmed to r.t. and subsequently stirred overnight. The solvent was removed under vacuum and the product was washed with hexane (2 × 30 ml) and dried under vacuum to produce the dilithium salt **6** (13.1 g, 41 mmol, 99% yield) as a pale yellow powder. The product was used without further purification.

### 3.8. Preparation of dilithium(cyclopentadienyl)-dimethylsilyl(2-methylbenz[e]indenyl) (**7**)

In a procedure analogous to that described above for **6** a solution of **3** (15 g, 50 mmol) in diethyl ether (300 ml) cooled at -78 °C was reacted with n-butyllithium 1.6 M in hexane (62 ml, 100 mmol) to yield a pale yellow powder characterized as the dilithium salt **7** (15.72 g, 50 mmol, 100% yield). The product was used without further purification.

### 3.9. Preparation of zirconium [propylidene-2-η<sup>5</sup>-cyclopentadienyl-2-(2-methyl-η<sup>5</sup>-benz[e]indenyl)] dichloride (**8**)

Toluene (300 ml) was added to a mixture of **6** (6 g, 20 mmol) and ZrCl<sub>4</sub>·(THF)<sub>2</sub> (7.58 g, 20 mmol) and the resulting suspension was refluxed with stirring for 20 h. The solution was filtered, concentrated under vacuum (150 ml) and cooled to -35 °C. After 3 days, the precipitate formed was collected by filtration and washed with hexane (2 × 15 ml), yielding pure complex **8** (1.8 g, 4 mmol, 20% yield) as a yellow powder. Recrystallization from toluene-hexane gave **8** as a yellow microcrystalline solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ 2.13 (s, 3H, CMe), 2.44 (s, 3H, CMe), 2.93 (s, 3H, CMe), 5.87 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 6.51 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 7.10 (s, 1H, C<sub>13</sub>H<sub>7</sub>), 7.25 (m, 1H, C<sub>13</sub>H<sub>7</sub>),

7.51 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 7.59 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 7.66 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 7.73 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 8.06 (m, 1H, C<sub>13</sub>H<sub>7</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 25 °C): δ 20.8 (CMe), 27.6 (CMe), 28.7 (CMe), 41.3 (C<sub>ipso</sub>, CMe<sub>2</sub>), 101.8 (C<sub>ipso</sub>, C<sub>5</sub>H<sub>4</sub>), 103.0, 106.7, 115.1, 120.9 (C<sub>5</sub>H<sub>4</sub>), 121.2, 122.2, 123.5, 127.3, 127.7, 127.9, 128.5 (C<sub>13</sub>H<sub>7</sub>), 117.8, 120.7, 126.4, 128.3, 128.9, 131.3 (C<sub>ipso</sub>, C<sub>13</sub>H<sub>7</sub>). *Anal.* Calc. for C<sub>22</sub>H<sub>20</sub>ZrCl<sub>2</sub>: C, 59.18; H, 4.15. Found: C, 59.36; H, 4.31%.

### 3.10. Preparation of zirconium [(η<sup>5</sup>-cyclopentadienyl)dimethylsilyl(2-methyl-η<sup>5</sup>-benz[e]indenyl)] dichloride (**9**)

In a procedure analogous to that described above for **8** a mixture of **6** (10 g, 32 mmol) and ZrCl<sub>4</sub>·(THF)<sub>2</sub> (12 g, 32 mmol) were reacted in toluene (300 ml) to yield a yellow microcrystalline solid characterized as **9**. (3.4 g, 7 mmol, 23% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ 0.93 (s, 3H, SiMe), 1.06 (s, 3H, SiMe), 2.31 (s, 3H, CMe), 5.82 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 5.97 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.71 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 7.21 (s, 1H, C<sub>13</sub>H<sub>7</sub>), 7.30 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 7.36 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 7.5 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 7.6 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 7.74 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 8.06 (m, 1H, C<sub>13</sub>H<sub>7</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 25 °C): δ -1.2 (SiMe), -0.28 (SiMe), 18.8 (CMe), 91.1 (C<sub>ipso</sub>, C<sub>5</sub>H<sub>4</sub>), 110.1, 115.7, 118.5, 120.6 (C<sub>5</sub>H<sub>4</sub>), 124.4, 125.3, 127.3, 127.5, 127.7, 128.6, 128.9 (C<sub>13</sub>H<sub>7</sub>), 107.1, 122.7, 129.6, 131.9, 134.1, 134.5 (C<sub>ipso</sub>, C<sub>13</sub>H<sub>7</sub>). *Anal.* Calc. for C<sub>21</sub>H<sub>20</sub>ZrSiCl<sub>2</sub>: C, 54.52; H, 4.36. Found: C, 54.81; H, 4.64%.

### 3.11. Preparation of zirconium [(η<sup>5</sup>-cyclopentadienyl)butylmethylsilyl(2-methyl-η<sup>5</sup>-benz[e]indenyl)] dichloride (**10**)

In a procedure analogous to that described above for **6** a solution of **5** (15 g, 50 mmol) in diethyl ether (300 ml) cooled at -78 °C was reacted with n-butyllithium 1.6 M in hexane (62 ml, 100 mmol) to yield a pale yellow powder (15.72 g, 50 mmol, 100% yield). The product was used without further purification. In a procedure analogous to that described above for **8** a mixture of the resulting pale yellow powder (10 g, 32 mmol) and ZrCl<sub>4</sub>·(THF)<sub>2</sub> (12 g, 32 mmol) were reacted in toluene (300 ml) to yield after concentration, a small amount of a yellow microcrystalline solid characterized as a mixture of two isomers **10a** and **10b**. After recrystallization in toluene several times pure **10a** was isolated. Compound **10a**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ 1.00 (t, 3H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.07 (s, 3H, SiMe), 1.38–1.72 (m, 6H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 2.36 (s, 3H, CMe), 5.84 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 5.97 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.74 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 7.28 (s, 1H, C<sub>13</sub>H<sub>7</sub>), 7.33 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 7.41 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 7.52 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 7.63 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 7.77 (m, 1H, C<sub>13</sub>H<sub>7</sub>), 8.09 (m, 1H, C<sub>13</sub>H<sub>7</sub>). <sup>1</sup>H NMR (300 MHz,

$C_6D_6$ , 25 °C):  $\delta$  0.58 (s, 3H, SiMe), 0.86–1.04 (m, 3H,  $(CH_2)_3CH_3$ ), 1.30–1.38 (m, 3H,  $(CH_2)_3CH_3$ ), 2.14 (s, 3H, CMe), 5.41 (m, 1H,  $C_5H_4$ ), 5.66 (m, 1H,  $C_5H_4$ ), 6.57 (m, 2H,  $C_5H_4$ ), 7.19 (m, 3H,  $C_{13}H_7$ ), 7.35 (m, 1H,  $C_{13}H_7$ ), 7.41 (m, 1H,  $C_{13}H_7$ ), 7.61 (m, 1H,  $C_{13}H_7$ ), 7.95 (m, 1H,  $C_{13}H_7$ ).  $^{13}C\{^1H\}$  NMR (75 MHz,  $CDCl_3$ , 25 °C):  $\delta$  -2.8 (SiMe), -13.8 ( $CH_2Me$ ), 13.9 ( $CH_2$ ), 25.2 ( $CH_2$ ), 26.4 ( $CH_2$ ), 18.8 (CMe), 91.1 ( $C_{ipso}$ ,  $C_5H_4$ ), 110.5, 115.5, 118.8, 120.7 ( $C_5H_4$ ), 124.4, 125.7, 127.3, 127.5, 127.7, 128.6, 128.6 ( $C_{13}H_7$ ), 107.0, 123.2, 129.6, 131.7, 134.0, 134.2 ( $C_{ipso}$ ,  $C_{13}H_7$ ). Compound **10b**:  $^1H$  NMR (300 MHz,  $CDCl_3$ , 25 °C):  $\delta$  0.94 (s, 3H, SiMe), 0.84 (m, 3H,  $(CH_2)_3CH_3$ +2H,  $(CH_2)_3CH_3$ ), 1.24 (m, 4H,  $(CH_2)_3CH_3$ ), 2.34 (s, 3H, CMe), 5.84 (m, 1H,  $C_5H_4$ ), 6.01 (m, 1H,  $C_5H_4$ ), 6.74 (m, 2H,  $C_5H_4$ ), 7.19–7.95 (m, 7H,  $C_{13}H_7$ ). Anal. Calc. for  $C_{24}H_{26}ZrSiCl_2$ : C, 57.12; H, 5.19. Found: C, 56.54; H, 5.33%.

### 3.12. Preparation of zirconium [ $(\eta^1$ -*tert*-butylamido)dimethylsilyl(2-methyl- $\eta^5$ -benz[e]indenyl)] dichloride (**11**)

In a procedure analogous to that described above for **8**, a mixture of dilithium (*tert*-butylamido)dimethylsilyl(2-methylbenz[e]indenyl) (7 g, 22 mmol) and  $ZrCl_4 \cdot (THF)_2$  (7.58 g, 20 mmol) was reacted in toluene (300 ml) to yield a pale yellow powder characterized as **11** (3.3 g, 7 mmol, 32% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ , 25 °C):  $\delta$  0.73 (s, 3H, SiMe), 0.90 (s, 3H, SiMe), 1.35 (s, 9H, *t*-Bu), 2.47 (s, 3H, CMe), 7.37 (s, 1H,  $C_{13}H_7$ ), 7.52 (m, 2H,  $C_{13}H_7$ ), 7.60 (m, 2H,  $C_{13}H_7$ ), 7.82 (m, 1H,  $C_{13}H_7$ ), 8.15 (m, 1H,  $C_{13}H_7$ ).  $^{13}C\{^1H\}$  NMR (75 MHz,  $CDCl_3$ , 25 °C):  $\delta$  5.7 (SiMe), 6.0 (SiMe), 18.3 (CMe), 32.9 (*t*-Bu), 56.8 ( $C_{ipso}$ , *t*-Bu), 112.5, 122.1, 123.5, 127.4, 127.7, 129.0, 129.1 ( $C_{13}H_7$ ), 95.0, 128.2, 129.0, 132.0, 132.8, 140.2 ( $C_{ipso}$ ,  $C_{13}H_7$ ). Anal. Calc. for  $C_{20}H_{25}Cl_2NSiZr$ : C, 51.15; H, 5.37; N, 2.98. Found: C, 50.99; H, 5.46; N, 2.94%.

### 3.13. Preparation of titanium [ $(\eta^1$ -*tert*-butylamido)dimethylsilyl(2-methyl- $\eta^5$ -benz[e]indenyl)] dichloride (**12**)

Dilithium (*tert*-butylamido)dimethylsilyl(2-methylbenz[e]indenyl) (3.7 g, 11.5 mmol) in THF was added to a stirred solution of  $TiCl_3 \cdot (THF)_3$  (4.27 g, 11.5 mmol) in the same solvent (40 ml) at -78 °C. The reaction mixture was allowed to reach r.t. and stirred for a further 2 h. A suspension of  $PbCl_2$  (3.2 g, 5.75 mmol) in THF was then added and the mixture stirred for 6 h. The solvent was removed under vacuum and the product was extracted into 100 ml of hexane. The hexane solution was filtered through celite, concentrated (30 ml), and cooled to -35 °C to give **12** (1.26 g, 3 mmol, 26% yield) as a red solid. Anal. Calc. for

$C_{20}H_{25}Cl_2NSiTi$ : C, 56.38; H, 5.87; N 3.29. Found: C, 56.52; H, 6.04; N, 3.45%.

### 3.14. X-ray structure determination of [ $Zr\{MeC_{13}H_7-SiMe_2-C_5H_4\}Cl_2$ ] (**9**) and [ $Zr\{MeC_{13}H_7-SiMeBu-C_5H_4\}Cl_2$ ] **10a**· $C_7H_8$

Details of the X-ray experiments, data reduction, and final structure refinement calculations for **9** and **10a** are summarized in Table 3.

Crystals of compound **9** were obtained by crystallization from toluene–hexane. Suitable sized crystal was sealed in a Lindemann tube under argon atmosphere and mounted in an Enraf–Nonius CAD 4 automatic four-circle diffractometer with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). Data were collected at r.t. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structures were

Table 3  
Crystallographic data for [ $Zr\{MeC_{13}H_7-SiMe_2-C_5H_4\}Cl_2$ ] (**9**) and [ $Zr\{MeC_{13}H_7-SiMeBu-C_5H_4\}Cl_2$ ] **10a**· $C_7H_8$

	<b>9</b>	<b>10a</b>
Formula	$C_{21}H_{24}Cl_2SiZr \cdot 1/2C_7H_8$	$C_{24}H_{26}Cl_2SiZr \cdot C_7H_8$
M	550.68	596.79
Color/shape	yellow/prismatic	yellow/fragment
Crystal size (mm)	0.35 × 0.30 × 0.27	0.46 × 0.46 × 0.46
Crystal system	triclinic	triclinic
Space group	<i>P</i> 1	<i>P</i> 1
<i>a</i> (Å)	9.735(1)	9.0732(1)
<i>b</i> (Å)	11.299(1)	11.7460(1)
<i>c</i> (Å)	11.833(1)	13.6474(2)
$\alpha$ (°)	64.68(1)	87.3199(4)
$\beta$ (°)	74.11(1)	84.3596(4)
$\gamma$ (°)	81.20(1)	70.7054(8)
<i>V</i> (Å <sup>3</sup> )	1130.62(18)	1365.96(3)
<i>Z</i> (formula units)	2	2
<i>T</i> (K)	293	153
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.618	1.451
$\mu$ (mm <sup>-1</sup> )	0.791	0.661
<i>F</i> (000)	560	616
$\lambda$ (Å)	0.71073	0.71073
Device/scan method	CAD4/ $\omega$ - $\theta$	KCCD/ $\varphi$ - and $\omega$ -movement
$\theta$ Range (°)	2.16–24.99	1.50–25.34
Data collected ( <i>h</i> , <i>k</i> , <i>l</i> )	0/11, -13/13, -13/14	-10/10, -14/14, -16/16
Reflections collected	4236	33411
Independent reflections	3979	4991 (all data)
Observed reflections	3428 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4800 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]
Parameters	246	452
<i>R</i> <sub>int</sub>	0.011	0.026
<i>R</i> <sub>1</sub> (all data)/[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0501/0.0368	0.0201/0.0190
<i>wR</i> <sub>2</sub> (all data)/[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1160/0.1019	0.0465/0.0459
Goodness-of-fit (all data)/ <i>I</i> > 2 $\sigma$ ( <i>I</i> )	1.125/1.125	1.089/1.089
Weights <i>a/b</i>	0.0652/0.9487	0.0144/0.8041
$\Delta\rho_{max/min}$ (e Å <sup>-3</sup> )	1.14/-0.568	+0.29/0.24



solved by combination of direct methods and Fourier syntheses and refined by least-squares against  $F^2$  (SHELXL 97)[20]. All non hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined with fixed thermal parameters.

Crystals of complex **10a** suitable for an X-ray single crystal structure determination were obtained from toluene–hexane. Preliminary examination and data collection were carried out on a kappa-CCD device (Nonius) at the window of a rotating anode (NONIUS FR591; 50 kV; 60 mA; 3.0 kW) and graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). [17] The unit cell parameters were obtained by full-matrix least-squares refinement of 4988 reflections. Data collection were performed at 153 K with an exposure time of 20 s per frame (nine sets; 528 frames; phi and omega scans; 2° scan-width). A total of 33411 reflections were integrated. Raw data were corrected for Lorentz and polarization effects. If necessary, corrections for absorption and decay effects were applied during the scaling procedure. [18] After merging, a sum of 4991 independent reflections remained, and was used for all calculations. All non-hydrogen atoms of the compound were refined anisotropically. The structure was solved by a combination of direct methods [19] and difference-Fourier syntheses. [20] All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were found in the final Fourier maps and refined with isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$  with SHELXL-97 weighting scheme and stopped at maximum shift/err < 0.001. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from international tables for crystallography. All other calculations (including ORTEP graphics) were done with the program PLATON. [21]

#### 4. Supporting information available

Supporting information available: crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC Nos. 200905 and 200895 (**10a**·C<sub>7</sub>H<sub>8</sub>). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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