

## Studies Related to the Chloro Titanium and Zirconium Complexes with $[\eta^5\text{-Cyclopentadienyldi(silylamido)}]$ Ligands

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*Dedicated to Professor José Vicente on the occasion of his 60th birthday*

**Keywords:** Zirconium / Titanium / Silylamido / Cyclopentadienyl-N ligands

Trichloro complexes  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})_2]\text{Cl}_3]$   $[\text{M} = \text{Zr}$  (**2**),  $\text{Ti}$  (**3**)] have been synthesized by reaction of the corresponding chlorides  $\text{MCl}_4$  with the lithium salt  $\text{LiC}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})_2]$  (**1**). Complexes **2** and **3** react with 2 equiv. of  $\text{TiCl}_4$  in toluene at  $110^\circ\text{C}$  to afford the di(chlorosilyl) derivatives  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{Cl})_2\text{Cl}_3]$   $[\text{M} = \text{Ti}$  (**5**),  $\text{Zr}$  (**8**)]. Intermediate formation of  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{Cl})\text{Cl}_3]$  (**4**) has been proven by NMR spectroscopy. Reaction of **1** with  $\text{TiCl}_4$  (2 equiv.) in toluene at  $110^\circ\text{C}$  in the presence of excess  $\text{NEt}_3$  has yielded the chloro-silyl complex  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{Cl})(\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\text{Cl}_2]$  (**7**) through the intermediate formation of the amino-silyl derivative  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\text{Cl}_2]$  (**6**). Reactions of di-*ansa*- $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})_2\text{R}]$  and *ansa*- $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\text{R}_2]$  ( $\text{M} = \text{Ti}, \text{Zr}; \text{R} = \text{NMe}_2, \text{CH}_2\text{Ph}$ ) complexes with  $\text{NEt}_3\cdot\text{HCl}$  have afforded the dichloro

derivatives  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\text{Cl}_2]$   $[\text{M} = \text{Ti}$  (**6**),  $\text{Zr}$  (**12**)], the amine-coordinated zirconium compound  $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\text{Cl}_2(\text{NMe}_2\text{H})]$  (**9**) and the chloro-benzyl titanium complex  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\text{Cl}(\text{CH}_2\text{Ph})]$  (**11**). Formation of the mono-substituted chloro-amido zirconium complex  $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\text{Cl}(\text{NMe}_2)]$  (**10**) by the reaction of  $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\text{Cl}_2(\text{NMe}_2)]$  with  $\text{SiClMe}_3$  has been monitored in  $\text{C}_6\text{D}_6$  by NMR spectroscopy. All of the new chloro complexes have been characterized by elemental analyses and NMR spectroscopy and the X-ray crystal structure of  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})_2]\text{Cl}_3]$  (**3**) has been studied by diffraction methods.  
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### Introduction

Alkylamido-dimethylsilyl-cyclopentadienyl and indenyl group 4 metal complexes and their catalytic applications in olefin polymerization processes have been widely studied.<sup>[1–3]</sup> The most efficient method of synthesizing these compounds uses the dimetallated anion  $[\text{CpSiMe}_2(\text{NR})]^{2-}$  to transfer the  $(\eta^5\text{-Cp-}\eta^1\text{-N})$  bidentate ligand by reaction with metal chlorides  $\text{MCl}_4$  or  $\text{MCl}_2(\text{NR})_2$  to give the dichloro<sup>[1a]</sup> and diamido<sup>[4]</sup> derivatives, respectively. However, this method is not recommended in several particular cases and such anion transfers cannot be used when tridentate  $\eta^5\text{-Cp}(\eta^1\text{-N})_2$  ligands are involved in the isolation of cyclopentadienyl-bis(silyl- $\eta^1$ -amido) metal compounds of the type reported<sup>[5]</sup> by our group.

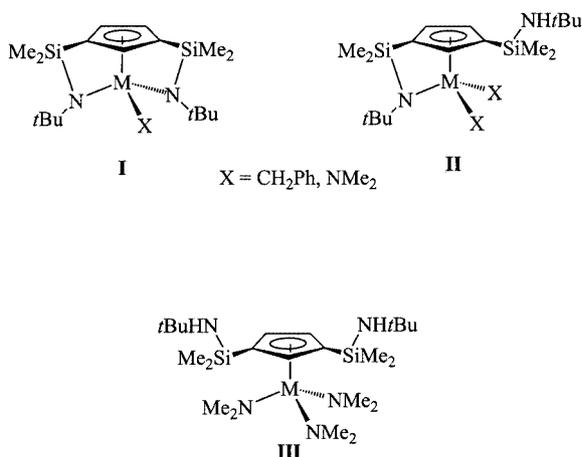
An alternative route, avoiding the metathesis step, uses the direct double deprotonation of the amino-dimethylsilyl-cyclopentadiene  $[\text{C}_5\text{H}_5\text{SiMe}_2\text{NHR}]$  with group 4 metal compounds containing strongly basic substituents. Accordingly, metal tetraamides  $\text{M}(\text{NR}_2)_4$  have been extensively used<sup>[6]</sup> to deprotonate cyclopentadienes,<sup>[7]</sup> amino-alkyl and -silylcyclopentadienes and different protonated ligands<sup>[8]</sup> with amine elimination to give amido-silyl ring-closed diamido complexes. The double deprotonation of the cyclopentadiene and the aminosilyl groups may take place in either one or two steps, depending on the acidity of the proton bound to the functional group.<sup>[9,10]</sup> Similar reactions using metal tetraalkyls<sup>[11,12]</sup> afford the corresponding dialkyl compounds and are even more useful due to their higher basicity and irreversible elimination of the resulting alkane. However, the use of these deprotonating reagents requires further metathesis of the diamido and dialkyl compounds to access the more versatile dichloro compounds.

We have reported<sup>[13]</sup> the synthesis of two types of amido and benzyl titanium and zirconium derivatives (Scheme 1), containing the bidentate  $\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})$  (**II**) and tridentate  $\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})_2$  (**I**) ligands, by deprotonation of the bis(amino-silyl)cyclopentadiene  $\text{C}_5\text{H}_4[\text{SiMe}_2(\text{NH}t\text{Bu})]_2$  with metal amides  $\text{M}(\text{NMe}_2)_4$

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and benzyls  $M(\text{CH}_2\text{Ph})_4$  ( $M = \text{Ti, Zr}$ ). To access the related chloro compounds, it is convenient to prepare a new type of monocyclopentadienyl compound **III** that may interconvert **I** – **II** – **III** by ring-closing and ring-opening reactions of the M-amidosilyl-Cp system and to compare its reactivity with complexes containing  $M\text{-Cl}$ ,  $M\text{-NMe}_2$  and  $M\text{-CH}_2\text{Ph}$  bonds.



Scheme 1

Halogenation of  $M\text{-NMe}_2$  bonds in  $[\text{M}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-NtBu})(\text{NMe}_2)_2]$  complexes with  $\text{NMe}_2\text{H}\cdot\text{HCl}$  is reported<sup>[9c]</sup> to afford the dichloro zirconium derivative, leaving the silyl- $\eta^1$ -amido bridge unaltered, whereas partial simultaneous halogenation of the  $\text{Si-N}$  bond yields the corresponding chlorosilyl- $\eta^5$ -cyclopentadienyl dichloro-amido titanium complex with amine elimination. In both cases, the liberated amine  $\text{NMe}_2\text{H}$  remained coordinated to the metal centre. Similar behaviour has also been observed for related cyclopentadienyl-alkyl- $\eta^1$ -NR zirconium and hafnium diamides<sup>[9a]</sup> and for cyclopentadienyl-Si-O-alkyl- $\eta^1$ -NR zirconium diamides.<sup>[10a]</sup> Alternatively,  $\text{SiClMe}_3$ <sup>[14,15]</sup> and  $\text{SiCl}_2\text{Me}_2$ <sup>[16]</sup> are efficient chlorinating agents that do not modify the Cp-silyl- $\eta^1$ -amido chelate.

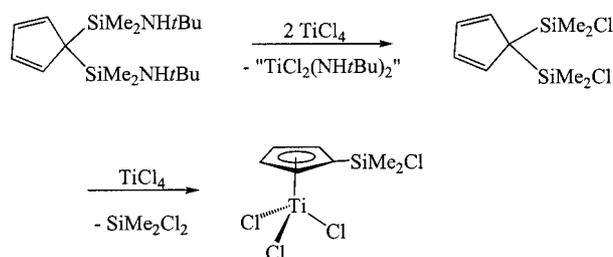
Conversion of M-alkyl into M-halide bonds in group 4  $[\text{M}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{NtBu})\}_2\text{R}_2]$  complexes without alteration of the Cp-silyl- $\eta^1$ -amido chelate is easily achieved in high yields by reactions with protic acids<sup>[17]</sup> and  $\text{I}_2$ .<sup>[18]</sup>

We describe here the results of our aim to isolate new chloro derivatives of the mono- and di-( $\eta^1$ -amidosilyl)cyclopentadienyl titanium and zirconium complexes. We report the synthesis and structural characterization of a new type of monocyclopentadienyl trichloro complex,  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NHtBu})]_2\}\text{Cl}_3]$  ( $M = \text{Ti, Zr}$ ), and studies related to its ring-closing reactions in order to coordinate the silyl-amido arms to the metal centre. We also report the transformation of the reported<sup>[5,13]</sup> *ansa*- $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NHtBu})](\text{SiMe}_2\text{-}\eta^1\text{-NtBu})\}_2\text{R}_2]$  and di-*ansa*- $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{-}\eta^1\text{-NtBu})_2\}\text{R}]$  ( $R = \text{NMe}_2, \text{CH}_2\text{Ph}$ ) complexes into the chloro compounds by reaction with chlorinating agents.

## Results and Discussion

Reactions of the bis(amidosilyl)cyclopentadiene  $\text{C}_5\text{H}_4[\text{SiMe}_2(\text{NHtBu})]_2$  with metal halides  $\text{MCl}_4$  follow different reaction pathways to those reported<sup>[13]</sup> with metal amides  $\text{M}(\text{NMe}_2)_4$  and benzyls  $\text{M}(\text{CH}_2\text{Ph})_4$  ( $M = \text{Ti, Zr}$ ). Group 4 metal halides  $\text{MCl}_4$  behave as dehalosilylating agents<sup>[19]</sup> that can cleave the  $\text{sp}^3\text{-C}(\text{Cp})\text{-SiR}_3$  bonds with the elimination of the halosilane  $\text{ClSiR}_3$ , and  $\text{TiCl}_4$  is also a useful deamidating reagent for amidosilane derivatives.<sup>[20]</sup>

The addition of 2 equiv. of  $\text{TiCl}_4$  to a dichloromethane solution of the bis(amidosilyl)cyclopentadiene produced simultaneous deamidation of the  $\text{Si-NHtBu}$  bonds and dehalosilylation with elimination of  $\text{SiMe}_2\text{Cl}_2$  to afford a mixture containing  $\text{C}_5\text{H}_4[(\text{SiMe}_2\text{Cl})_2]$ <sup>[21]</sup> and  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_3]$ <sup>[22]</sup> as major products, together with other unidentified minor components, according to  $^1\text{H}$  NMR data (Scheme 2).



Scheme 2

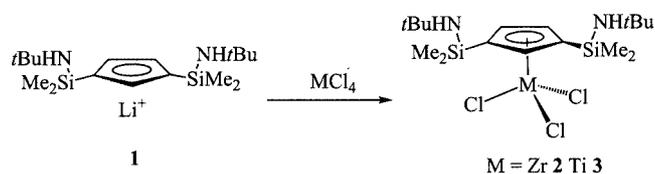
### Reactions with the $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NHtBu})]_2\}\text{Cl}_3]$ ( $M = \text{Ti, Zr}$ ) Complexes

We were first interested in isolating the trichloro  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NHtBu})]_2\}\text{Cl}_3]$  ( $M = \text{Ti, Zr}$ ) complexes to study the possible ring-closing reactions of one or both silyl-amido-metal systems that could give the dichloro( $\eta^5$ -cyclopentadienylsilyl- $\eta^1$ -amido)  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NHtBu})(\text{SiMe}_2\text{-}\eta^1\text{-NtBu})\}\text{Cl}_2]$  and chloro( $\eta^5$ -cyclopentadienyl bis(silyl- $\eta^1$ -amido))  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{-}\eta^1\text{-NtBu})_2\}\text{Cl}]$  metal complexes, respectively.

With this aim, the higher acidic character of the cyclopentadiene ring proton was used to isolate the required lithium salt  $\text{LiC}_5\text{H}_3[\text{SiMe}_2(\text{NHtBu})]_2$  (**1**) by selective metallation of the bis(amidosilyl)cyclopentadiene with 1 equiv. of  $n\text{BuLi}$  in hexane–THF for 12 h. Compound **1** was isolated as a white solid and characterized by elemental analysis and NMR spectroscopy (see Exp. Sect.).

Reaction of a toluene suspension of the lithium salt **1** with  $\text{ZrCl}_4\cdot 2\text{THF}$  afforded the trichloro complex  $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NHtBu})]_2\}\text{Cl}_3]$  (**2**), which was isolated as a yellow solid in almost quantitative yield and characterized by elemental analysis and NMR spectroscopy. However, a similar reaction of **1** with  $\text{TiCl}_4$  afforded mixtures of different products depending on the solvent, the molar ratio of both reagents and the reaction conditions (time and temperature). A hexane suspension of the lithium salt **1** reacted

with  $\text{TiCl}_4$  (1 equiv.) at room temperature to afford the trichloro derivative  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})]_2\}\text{Cl}_3]$  (**3**) as the unique reaction product. Complex **3** was isolated as an orange solid in 70% yield after purification and characterized by elemental analysis and NMR spectroscopy (Scheme 3).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of complexes **2** and **3** show the behaviour expected for  $\text{C}_s$  symmetric molecules with two equivalent aminosilyl groups and ring protons. Consequently, two singlets ( $^1\text{H}$ ) and two resonances ( $^{13}\text{C}$ ) for the diastereotopic  $\text{SiMe}_2$  methyl groups and one singlet ( $^1\text{H}$ ) and two resonances ( $^{13}\text{C}$ ) for the *tert*-butylamino substituents were observed in the NMR spectra of **2** and **3**. In addition, one doublet and one triplet ( $J_{\text{H,H}} = 2.0$  Hz) ( $^1\text{H}$ ) are observed for the  $\text{A}_2\text{B}$  spin system of the cyclopentadienyl ring protons and, consistently, three ring carbon resonances appear in the  $^{13}\text{C}$  NMR spectra. Recrystallization of **3** using pentane gave crystals appropriate for an X-ray structure determination. The molecular structure of **3** is shown in Figure 1, and selected bond lengths and angles are listed in Table 1.



Scheme 3

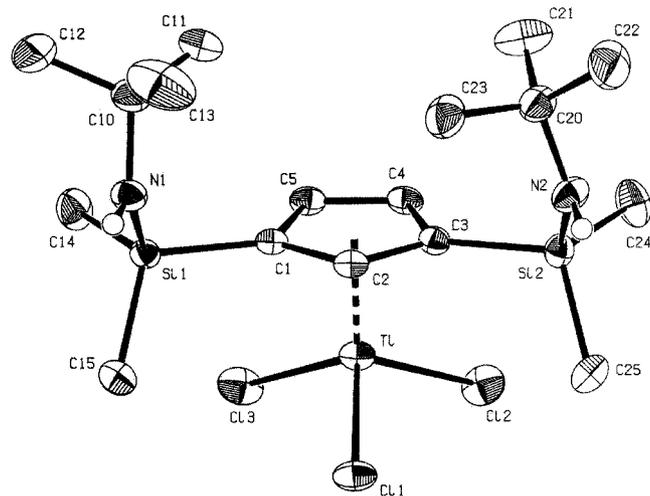


Figure 1. ORTEP drawing of the solid-state molecular structure of **3**; thermal ellipsoids drawn at the 50% probability level and hydrogen atoms are omitted for clarity except for those located at the nitrogen atoms

Complex **3** shows the titanium atom in the well-known pseudo-tetrahedral geometry defined by the centroid of the cyclopentadienyl ring and three coordinated chloro ligands, as reported for many group 4 metal monocyclopentadienyl complexes  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cl}_3]$  ( $\text{R} = \text{H}$ ,<sup>[23]</sup>  $\text{Me}$ ,<sup>[24]</sup>  $\text{CHPh}_2$ ,  $\text{CMe}_2\text{Ph}$ ,  $\text{SiMe}_2\text{Ph}$ ,<sup>[25]</sup>),  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Cl}_3]$  ( $\text{R} = t\text{Bu}$ ,<sup>[26]</sup>  $\text{CH}_2\text{CH}_2\text{Ph}$ ,<sup>[27]</sup>  $\text{SiMeClH}$ ,  $\text{SiMe}_3$ ,<sup>[20]</sup>  $[\text{Ti}(\eta^5\text{-1,3-$

Table 1. Characteristic bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_3\{\text{SiMe}_2(\text{NH}t\text{Bu})\}_2)\text{Cl}_3]$  (**3**)

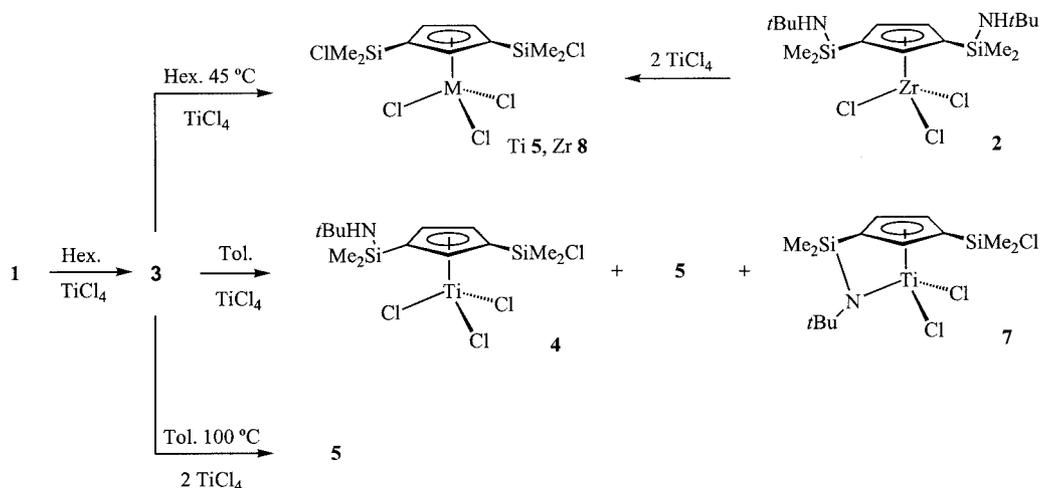
Bond lengths		Bond angles	
Ti–Cl1	2.2366(5)	Cl1–Ti–Cl2	102.69(2)
Ti–Cl2	2.2416(6)	Cl1–Ti–Cl3	103.64(2)
Ti–Cl3	2.2396(6)	Cl2–Ti–Cl3	102.45(2)
Si1–N1	1.702(2)	N1–Si1–C1	108.72(7)
Si2–N2	1.707(2)	N2–Si2–C3	110.15(8)
C1–C2	1.420(2)	Si1–N1–C10	131.96(15)
C1–C5	1.430(2)	Si2–N2–C20	133.15(14)
C2–C3	1.420(2)		
C3–C4	1.427(2)		
C4–C5	1.403(2)		

$\text{R}_2\text{C}_5\text{H}_3)\text{Cl}_3]$  ( $\text{R} = \text{SiMe}_3$ ,<sup>[28]</sup>  $t\text{Bu}$ <sup>[29]</sup>). The Cp ring in an  $\eta^5$ -coordination mode is not distorted, although the C4–C5 distance [1.403(2)]  $\text{\AA}$  is slightly shorter than the other C–C distances of 1.420(2)–1.430(2)  $\text{\AA}$ . Ti–Cl bond lengths (2.23–2.24  $\text{\AA}$ ) and the Cl–Ti–Cl angles (102–104 $^\circ$ ) are in the typical range for compounds of this type. Si–N bond lengths (1.70–1.71  $\text{\AA}$ ) are also in the range known for terminal amino–silyl bonds. Most significantly, the metal fragment and  $\text{SiMe}_2\text{NH}t\text{Bu}$  substituents are at opposite faces of the cyclopentadienyl ring, adopting a conformation that minimizes interaction with the chloro ligands and prevents the nitrogen atoms acting as  $\sigma$ -donor ligands, which would elongate the Ti–Cl bonds and close the Cl–Ti–Cl bond angles, as with  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cl}_3]$  compounds containing *O*- and *N*-functionalized R groups.<sup>[30]</sup> In addition, this structural disposition also prevents possible bridging hydrogen-bond interactions between Cl and the NH groups.

The same reaction of the lithium salt **1** with 1 equiv. of  $\text{TiCl}_4$  in hexane at 45  $^\circ\text{C}$  gave, after 1 h, the bis(chlorosilyl) derivative  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{Cl})_2\}\text{Cl}_3]$  (**5**) as the main reaction product together with a mixture containing various unidentifiable species. The presence in this mixture of the (aminosilyl)(chlorosilyl)cyclopentadienyl titanium complex  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{Cl})\}\text{Cl}_3]$  (**4**) (Scheme 4) could not be verified.<sup>4</sup>

Pure complex **5** could be isolated from this mixture as a light brown solid in very low yield (10%) after repeated recrystallizations; it was characterized by elemental analysis and NMR spectroscopy. These results demonstrate that complex **3** reacted with unchanged  $\text{TiCl}_4$  immediately after its formation, when the hexane solution was heated to 45  $^\circ\text{C}$ , producing deamidation of both amido-silane groups. Under these conditions, the preferential deamidation of complex **3** prevented the ring-closing formation of *ansa*-cyclopentadienylsilyl- $\eta^1$ -amido compounds.

Similar behaviour occurs for the same reaction with 1 equiv. of  $\text{TiCl}_4$  when using a toluene suspension of **1** at room temperature (Scheme 4). The resulting reaction product was a mixture containing almost equal molar proportions of the trichloro complexes **3**–**5**, although in this case formation of small but significant amounts of the also deamidated *ansa*-silyl- $\eta^1$ -amido complex  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{Cl})(\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{Cl}_2]$  (**7**) was also observed and



Scheme 4

identified by NMR spectroscopy (see below). The formation of complex **4**, which could not be isolated, was confirmed by a low intensity set of signals in the  $^1\text{H}$  NMR spectrum, which includes four singlets for the methyl protons of two different  $\text{SiMe}_2\text{Cl}$  and  $\text{SiMe}_2(\text{NH}t\text{Bu})$  groups, one singlet for the  $\text{NH}t\text{Bu}$  substituent and three multiplets for the non-equivalent ring protons of an asymmetric molecule (see Exp. Sect.). When this mixture containing complexes **3–5** and **7** was heated in a Teflon-sealed Schlenk tube at  $100\text{ }^\circ\text{C}$  for 5 h, compound **3** disappeared completely to give a mixture containing **7** as the major component together with **5** and traces of **4**.

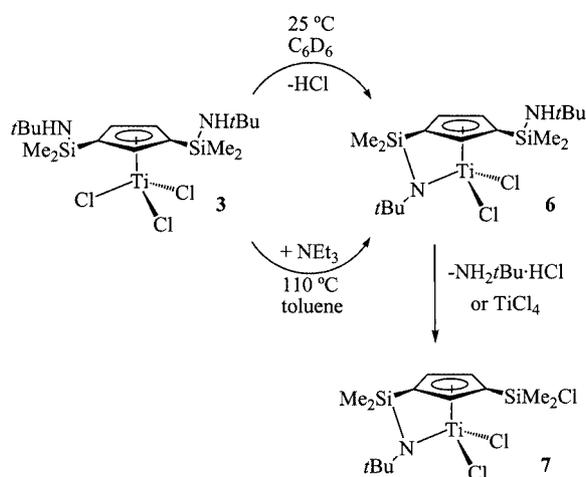
To check the deamidating role of the starting  $\text{TiCl}_4$  a toluene solution of the isolated complex **3** was reacted with 2 equiv. of  $\text{TiCl}_4$ , heating the solution at  $100\text{ }^\circ\text{C}$  for 8 h to give an insoluble green product and a solution containing **5**, which was isolated in 65% yield after purification (Scheme 4). Under similar conditions, the zirconium complex **2** did not react with excess  $\text{ZrCl}_4$  but an almost quantitative deamidation reaction occurred when its toluene solution was heated to  $110\text{ }^\circ\text{C}$  for 8 h with 2 equiv. of  $\text{TiCl}_4$ . The resulting complex  $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{Cl})_2\}\text{Cl}_3]$  (**8**) was isolated as a yellow solid in 69% yield and was characterized by elemental analysis and NMR spectroscopy. The  $^1\text{H}$  NMR spectra of complexes **5** and **8** correspond to molecules with  $C_s$  symmetry and show two  $\text{SiMe}_2$  singlets corresponding to diastereotopic methyl groups of two equivalent chlorosilyl substituents and one doublet and one triplet with relative intensity 2:1, corresponding to the  $A_2B$  spin system of the ring protons. Consistently, two  $\text{SiMe}_2$  and three ring carbon resonances appear in the  $^{13}\text{C}$  NMR spectrum (see Exp. Sect.).

$\text{TiCl}_4$  is, therefore, the deamidating agent responsible for the transformation of **3** into, successively, **4** and **5**. Moreover, in the presence of excess  $\text{TiCl}_4$ , formation of the *ansa* complexes is totally inhibited.

The thermal behaviour of **2** and **3** in the absence of  $\text{TiCl}_4$  is also important. Complex **2** is thermally stable, remaining

unaltered after heating for 6 h at  $125\text{ }^\circ\text{C}$  in a Teflon-sealed Schlenk tube. This is consistent with the known high stability of  $\text{Zr}-\text{Cl}$  bonds. However, monitoring the  $^1\text{H}$  NMR spectrum of a sample of **3**, in a Teflon-sealed NMR tube in  $\text{C}_6\text{D}_6$  at room temperature, revealed a very slow transformation that gave increasing amounts of a mixture containing one new major compound and a small amount of a second new derivative, along with traces of other components. According to  $^1\text{H}$  NMR data in the highfield  $\text{SiMe}_2$  region, the new compounds could be formulated as complexes  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{Cl}_2]$  (**6**), and  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{Cl})(\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{Cl}_2]$  (**7**) as the major and minor components, respectively (Scheme 5). This suggests that, in the absence of  $\text{TiCl}_4$ , partial formation of *ansa* complexes takes place with elimination of  $\text{HCl}$ , which, under these conditions, protonates the free amino  $\text{Si-NH}t\text{Bu}$  group of **6** to give the  $\text{Si}-\text{Cl}$  group of **7**. Some of the  $\text{HCl}$  generated in the previous reaction has to be used to neutralize the eliminated  $\text{NH}_2t\text{Bu}$ , otherwise only compound **7** should be observed. After 2 days, this transformation afforded, according to  $^1\text{H}$  NMR data, an approximately 2:1:1 molar ratio of **6**:**3**:**7**. These data confirmed that formation of the first silyl- $\eta^1$ -amido bridge occurs at room temperature albeit it is very slowly.

To favour the formation of the *ansa* compounds we studied the same reaction, heating a toluene suspension of the lithium salt **1** with 1 equiv. of  $\text{TiCl}_4$  at  $110\text{ }^\circ\text{C}$  in the presence of  $\text{NEt}_3$  (3 equiv.) (Scheme 5). Under these conditions no deamidation of complex **3** was observed – instead a mixture was obtained that contained the *ansa* complexes **7** and **6** in a molar ratio 3:1, from which complex **7** was isolated after extraction into pentane, as a yellow solid in 60% yield. Better results were obtained for the same reaction using 2 equiv. of  $\text{TiCl}_4$  because further deamidation of **6** afforded pure complex **7** as the unique reaction product. Complex **7** is a dissymmetric molecule due to the enantioface of the cyclopentadienyl ring. Its  $^1\text{H}$  NMR spectrum shows the expected four singlets for the  $\text{SiMe}_2$  groups, one



Scheme 5

singlet for the *tert*-butyl substituent and three low-field multiplets for the ring protons. Consistently, four  $SiMe_2$  resonances, two  $NtBu$  signals and five ring carbon resonances appear in the  $^{13}C$  NMR spectrum of **7** (see Exp. Sect.). Pure samples of complex **6** could not be isolated from the sticky residue, in which it was the minor component. However, complex **6** was identified by its  $^1H$  NMR spectrum, which shows the expected four  $SiMe_2$ , two *t*Bu singlets and three Cp ring proton multiplets, consistent with its proposed formulation and coincident with those of the pure complex isolated by an alternative method (see below).

Therefore, reactions in the presence of excess  $NEt_3$  yielded the *ansa* complexes, preventing deamidation of complex **3**, even when excess  $TiCl_4$  was used to favour the total deamidation of *ansa* complex **6**. However,  $NEt_3$  did not prevent protonation and deamidation of the  $Si-NHtBu$  group. Indeed, a mixture of **7** and **6** in a molar ratio 1:1 was formed when a toluene suspension of **3** was heated to  $110\text{ }^\circ\text{C}$  in the presence of 5 equiv. excess  $NEt_3$ .

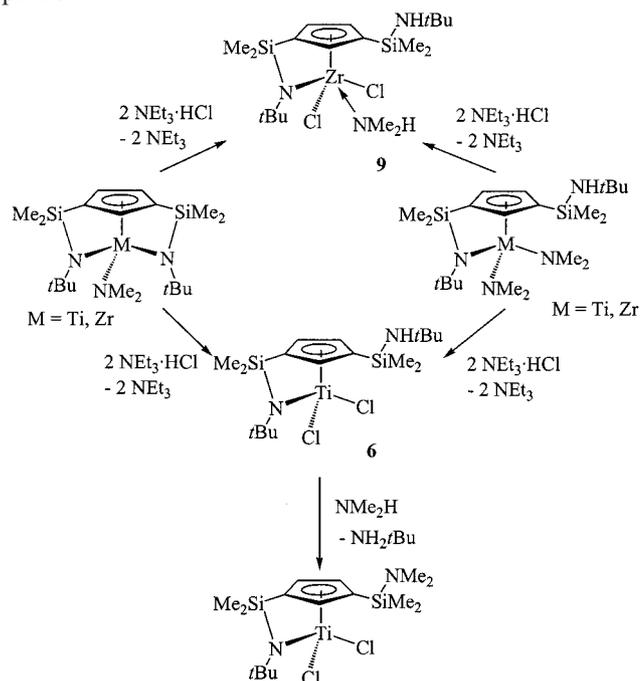
All these results suggest the following sequence of reactions: initially the reaction of  $TiCl_4$  with the lithium salt **1** gives the trichloro complex **3**, which is deamidated by excess  $TiCl_4$  to give, successively, complexes **4** and **5**. However, ring-closing reactions to give *ansa* complexes require elimination of  $HCl$ , this being favoured in the presence of  $NEt_3$ , which prevents the deamidation of complex **3** to give **6**. Complex **6** is also deamidated by excess  $TiCl_4$ , to afford pure complex **7**.

In summary, the ring-closing reaction of the first silyl- $\eta^1$ -amido arm of the trichloro complex **3** is a selective reaction in the presence of excess  $NEt_3$ , although under these conditions simultaneous deamidation of the remaining amido-silane system gives the mono-silyl- $\eta^1$ -amido complex **7**, preventing the formation of the second silyl- $\eta^1$ -amido bridge. In contrast, deamidation of both amido-silane groups of complex **3** is a selective reaction in the presence of excess  $TiCl_4$ , giving the bis(chlorosilyl) derivative **5** while suppressing the formation of silyl- $\eta^1$ -amido bridges.

### Reactions with the $[M\{\eta^5-C_5H_3(SiMe_2-\eta^1-NtBu)_2\}R]$ and $[M\{\eta^5-C_5H_3[SiMe_2(NHtBu)](SiMe_2-\eta^1-NtBu)\}R_2]$ ( $M = Ti, Zr$ ; $R = NMe_2, CH_2Ph$ ) Complexes

The amido zirconium compound  $[Zr\{\eta^5-C_5H_3(SiMe_2-\eta^1-NtBu)_2\}(NMe_2)]^{[13]}$  reacted with 1 equiv. of  $NEt_3 \cdot HCl$  in toluene at  $70\text{ }^\circ\text{C}$  to produce the simultaneous protonation of both the terminal  $Zr-NMe_2$  and one of the bridging  $Zr-NtBu-Si$  bonds, affording a mixture that contained half of the unchanged starting compound and a new zirconium complex.

The starting bis(silyl- $\eta^1$ -amido) compound was completely transformed into the new zirconium derivative, with elimination of  $NEt_3$ , when a second equiv. of  $NEt_3 \cdot HCl$  was added (Scheme 6), giving an 82% yield of a light brown solid that was characterized by elemental analysis and NMR spectroscopy as the dichloro compound  $[Zr\{\eta^5-C_5H_3[SiMe_2(NHtBu)](SiMe_2-\eta^1-NtBu)\}Cl_2(NMe_2H)]$  (**9**). Compound **9**, which contains the amine coordinated to the metal, was also obtained when the same reaction was carried out with one equiv. of  $NEt_3 \cdot HCl$  and the diamido compound  $[Zr\{\eta^5-C_5H_3[SiMe_2(NHtBu)](SiMe_2-\eta^1-NtBu)\}-(NMe_2)_2]$ .<sup>[13]</sup> The simultaneous reaction of both  $Zr-NMe_2$  bonds also occurred, leaving half of the starting complex unaltered, although one of the two amido groups could be sterically protected by the uncoordinated aminosilyl group. Probably, the increased acidity of the metal centre in the resulting chloro-amido intermediate favours the coordination of chloride with protonation and displacement of the second amido group. The reaction was complete after addition of a second equivalent of  $NEt_3 \cdot HCl$ , affording pure **9**.

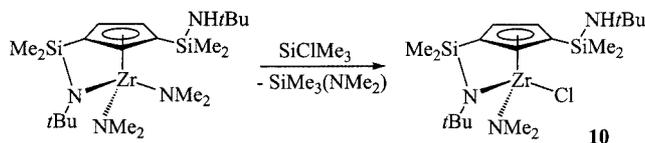


Scheme 6

Similar behaviour was observed for the titanium derivatives  $[Ti\{\eta^5-C_5H_3(SiMe_2-\eta^1-NtBu)_2\}(NMe_2)]$  and  $[Ti\{\eta^5-$

$\text{C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})(\text{NMe}_2)_2$ ]<sup>[13]</sup> However, the resulting product,  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_3\{\text{SiMe}_2(\text{NH}t\text{Bu})\}\text{-}\{\text{SiMe}_2(\eta^1\text{-N}t\text{Bu})\})\text{Cl}_2]$  (**6**), did not contain coordinated amine, and it was always accompanied by variable, small amounts of a second component that could not be isolated but was identified by NMR spectroscopy as  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NMe}_2)](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{Cl}_2]$ . This last compound resulted from a simultaneous exchange reaction between the amino-silyl Si-NH*t*Bu group of **6** and the liberated amine  $\text{NHMe}_2$ . Complex **6** was isolated as a red solid and characterized by elemental analysis and NMR spectroscopy (see Exp. Sect.).

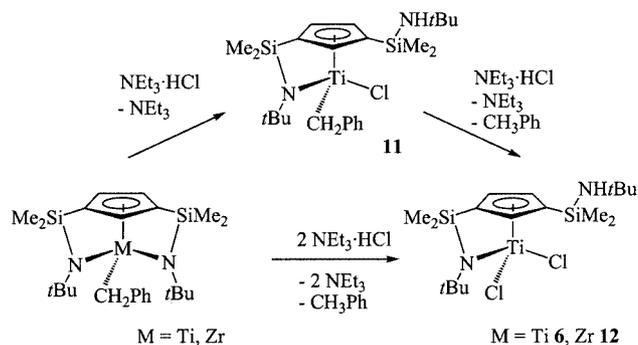
Reactions with  $\text{SiClMe}_3$  are reported<sup>[14,15]</sup> to be a convenient method of converting metal–amido into metal–chloro bonds. The reaction of the diamido zirconium complex  $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}(\text{NMe}_2)_2]$  with one equivalent of  $\text{SiClMe}_3$  was monitored by  $^1\text{H}$  NMR spectroscopy in  $\text{C}_6\text{D}_6$  at room temperature (Scheme 7). After 1 h, formation of the chloro-amido derivative  $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{-Cl}(\text{NMe}_2)]$  (**10**) with elimination of  $\text{SiMe}_3(\text{NMe}_2)$  was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. Addition of a second equiv. of  $\text{SiClMe}_3$  produced a very slow reaction, which after 4 d afforded a mixture of unidentified reaction products in which  $\text{SiMe}_3\text{-NH}t\text{Bu}$  ( $\delta_{\text{SiMe}_3} = 0.11$  ppm;  $\delta_{\text{NH}t\text{Bu}} = 1.09$  ppm) and  $\text{SiMe}_3\text{-NMe}_2$  ( $\delta_{\text{SiMe}_3} = 0.04$  ppm;  $\delta_{\text{NMe}_2} = 2.37$  ppm) were observed in the  $^1\text{H}$  NMR spectrum. This suggests that, probably, the first substitution is a fast diastereoselective reaction at the amido ligand unprotected by the noncoordinated silyl-amino group, which gives one single diastereomer (see below). However, the second substitution at the sterically protected amido ligand is very slow and exchange takes place between the amino groups bound to the silylcyclopentadienyl ligand CpSi–NH*t*Bu of **10** and the trimethylsilyl fragment of the liberated silane  $\text{Me}_3\text{Si-NMe}_2$ . Similar studies could not be extended to the related diamido titanium derivative as it was always accompanied by variable amounts of the monoamido complex.



Scheme 7

The reactivity of the benzyl derivatives was also studied (Scheme 8). When 1 equiv. of  $\text{NEt}_3\cdot\text{HCl}$  was added to a toluene solution of the benzyl titanium complex  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})_2\}(\text{CH}_2\text{Ph})]$ ,<sup>[13]</sup> one of the silyl-amido arms was protonated to afford the chloro-benzyl derivative  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{Cl}(\text{CH}_2\text{Ph})]$  (**11**), which was isolated as a red solid (77% yield) and characterized by elemental analysis and NMR spectroscopy. In this reaction the benzyl–titanium bond was unaltered although it could also be protonated with elimin-

ation of toluene when the same reaction was carried out using 2 equiv. of  $\text{NEt}_3\cdot\text{HCl}$ , at 80 °C for 12 h, to afford the dichloro derivative  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_3\{\text{SiMe}_2(\text{NH}t\text{Bu})\}\text{-}\{\text{SiMe}_2(\eta^1\text{-N}t\text{Bu})\})\text{Cl}_2]$  (**6**) described above. Reaction of the related zirconium complex  $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})_2\}(\text{CH}_2\text{Ph})]$ <sup>[13]</sup> was not selective; simultaneous protonation of the  $\eta^1$ -amido and benzyl ligands required the addition of 2 equiv. of  $\text{NEt}_3\cdot\text{HCl}$ , in toluene at 70 °C, to give the dichloro complex  $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{Cl}_2]$  (**12**), which is similar to **9** but without coordinated amine. Compound **12** was isolated as a brown solid and characterized by NMR spectroscopy. In the light of these results, the reactivity of related dibenzyl complexes  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{-}(\text{CH}_2\text{Ph})_2]$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) was not studied.



Scheme 8

The new complexes **6** and **9–12** belong to the well-known type of *ansa*-cyclopentadienylsilyl- $\eta^1$ -amido compounds with one additional noncoordinated silyl-amino substituent, which makes the face of the cyclopentadienyl ring enantiotopic. Therefore, the dichloro complexes  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{Cl}_2]$  [ $\text{M} = \text{Ti}$  (**6**),  $\text{Zr}$  (**12**)], and the amine-coordinated zirconium derivative  $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{-Cl}_2(\text{NMe}_2\text{H})]$  (**9**) are dissymmetric molecules, in agreement with the observed  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (see Exp. Sect.). The chloro-amido  $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{Cl}(\text{NMe}_2)]$  (**10**) and -benzyl  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{Cl}(\text{CH}_2\text{Ph})]$  (**11**) complexes exhibit one additional stereogenic centre at the metal, although only one isomer was formed in the diastereoselective reactions discussed above. Accordingly, the NMR spectra of **10** and **11** show the expected four Si–Me signals ( $^1\text{H}$ ,  $^{13}\text{C}$ ), two singlets ( $^1\text{H}$ ) and four signals ( $^{13}\text{C}$ ) for the *Nt*Bu groups, and three ( $^1\text{H}$ ) or five signals ( $^{13}\text{C}$ ) for the cyclopentadienyl ring proton and carbon atoms respectively, along with the typical diastereotopic  $\text{CH}_2\text{Ph}$  doublets for **11**.

All these *ansa* complexes exhibit a  $^{13}\text{C}$  signal due to the ring  $\text{C}_{ipso}$  that is shifted upfield with respect to the other ring-carbon signals,<sup>[31]</sup> and the metal–amido  $\pi$ -bonding contribution is evidenced by  $\Delta(\delta_{\text{C}_{tert}} - \delta_{\text{C}_{Me}})$ <sup>[32]</sup> of 22.8 (**10**)–30.0 (**6**) compared with those of the Si–NH*t*Bu group [15.9 (**10**)–18.5 (**9**)].

## Conclusion

Monolithium salt  $\text{LiC}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})_2]$  (**1**) reacts with the corresponding tetrachlorides  $\text{MCl}_4$  in a straightforward method of synthesizing bis(dimethylsilylamino) monocyclopentadienyl titanium and zirconium complexes  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})_2]\text{Cl}_3]$  ( $\text{M} = \text{Ti}, \text{Zr}$ ). However, simultaneous reaction of the titanium derivative with the starting  $\text{TiCl}_4$  produces partial conversion of one or both  $\text{Si-NH}t\text{Bu}$  into  $\text{Si-Cl}$  groups. This is a quantitative transformation when the isolated titanium and zirconium complexes are treated with 2 equiv. of  $\text{TiCl}_4$ .

Ring-closing coordination of one of the silyl-amido arms to the metal by elimination of  $\text{HCl}$  is very slow at room temperature for the titanium complex and does not occur for the zirconium one. However, this reaction is complete when the titanium compound is heated in toluene to  $110^\circ\text{C}$  in the presence of excess  $\text{NEt}_3$ , although simultaneous partial conversion of the free  $\text{Si-NH}t\text{Bu}$  into  $\text{Si-Cl}$  is unavoidable. Under these conditions, addition of  $\text{TiCl}_4$  gives the chloro-silyl complex  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{Cl})(\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{Cl}_2]$  in quantitative yield.

Ring-closing coordination of the second silyl-amido arm was never observed, which is consistent with the very easy ring-opening de-coordination that takes place by protonation with  $\text{NEt}_3\cdot\text{HCl}$  of one of the silyl- $\eta^1$ -amido-titanium and zirconium bonds of the cyclopentadienyl bis(silyl- $\eta^1$ -amido) di-*ansa*- $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})_2\}\text{R}]$  ( $\text{R} = \text{NMe}_2, \text{CH}_2\text{Ph}$ ) complexes. In contrast, the single silyl- $\eta^1$ -amido-titanium system of the *ansa*- $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}(\text{NMe}_2)_2]$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) derivatives remains unaltered in these protonation reactions.

Alternative methods to synthesize the elusive di-*ansa*- $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})_2\}\text{Cl}]$  complex and its alkyl derivatives are being studied and will be reported in a future paper.

## Experimental Section

**General Remarks:** All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or a dry box. Solvents were dried and freshly distilled under argon before use: tetrahydrofuran from sodium benzophenone ketyl; toluene from sodium; hexane from sodium-potassium amalgam. Unless otherwise stated, reagents were obtained from commercial sources and used as received.  $\text{C}_5\text{H}_4[\text{SiMe}_2(\text{NH}t\text{Bu})_2]$ ,  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})_2\}\text{R}]$  and  $[\text{M}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{-}\eta^1\text{-N}t\text{Bu})\}\text{R}_2]$  ( $\text{M} = \text{Ti}, \text{Zr}$ ;  $\text{R} = \text{CH}_2\text{Ph}, \text{NMe}_2$ ) were prepared by previously reported methods.<sup>[13]</sup>  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Unity VXR-300 or Varian Unity 500 Plus. Chemical shifts, in ppm, are relative to residual  $^1\text{H}$  and  $^{13}\text{C}$  resonances for  $\text{C}_6\text{D}_6$  used as solvent: 7.15 ( $^1\text{H}$ ) and 128.0 ( $^{13}\text{C}$ ), and coupling constants are in Hz. C, H and N analyses were carried out with a Perkin-Elmer 240 C analyzer.

**$\text{LiC}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})_2]$  (**1**):** A hexane solution (1.6 M) of *n*BuLi (11.0 mL, 17.6 mmol) was added dropwise to a yellow solution of  $\text{C}_5\text{H}_4[\text{SiMe}_2(\text{NH}t\text{Bu})_2]$  (5.80 g, 17.6 mmol) in a mixture of hexane

(150 mL) and THF (25 mL) at  $-78^\circ\text{C}$ . This reaction mixture was then warmed to room temperature and stirred for 12 h. The volatiles were then removed under vacuum to give **1** as a white solid, which was washed with hexane and dried under vacuum (5.72 g, 17.30 mmol, 98%).  $\text{C}_{17}\text{H}_{35}\text{LiN}_2\text{Si}_2$  (330.6): calcd. C 61.76, H 10.67, N 8.47; found C 61.02, H 10.46, N 8.27.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6/\text{NC}_6\text{D}_5$ ,  $20^\circ\text{C}$ ):  $\delta = 0.49$  (s, 12 H,  $\text{SiMe}_2$ ), 0.88 (br. s, 2 H,  $\text{NH}t\text{Bu}$ ), 1.21 (s, 18 H,  $\text{NHCMe}_3$ ), 6.75 (d,  $J_{\text{H,H}} = 2.0$  Hz, 2 H,  $\text{C}_5\text{H}_3$ ), 6.90 (t,  $J_{\text{H,H}} = 2.0$  Hz, 1 H,  $\text{C}_5\text{H}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6/\text{NC}_6\text{H}_5$ ,  $20^\circ$ ):  $\delta = 4.2$  ( $\text{SiMe}_2$ ), 34.1 ( $\text{NHCMe}_3$ ), 49.4 ( $\text{NHCMe}_3$ ), 115.2 ( $\text{C}_5\text{H}_3$ ), 115.8 ( $\text{C}_5\text{H}_3$ ), 120.4 ( $\text{C}_5\text{H}_3$ ) ppm.

**$[\text{Zr}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})_2]\text{Cl}_3]$  (**2**):** Toluene (100 mL) was added to a mixture of  $\text{ZrCl}_4\cdot 2\text{THF}$  (2.08 g, 5.52 mmol) and the lithium salt **1** (1.82 g, 5.52 mmol) at room temperature. The reaction mixture was subsequently stirred for a further 12 h. The solvent of the resulting white suspension was then removed under vacuum and the residue extracted into hexane ( $2 \times 50$  mL). After filtration and removal of the solvent, complex **2** was isolated as a light yellow solid (2.46 g, 4.33 mmol, 86%).  $\text{C}_{17}\text{H}_{35}\text{Cl}_3\text{N}_2\text{Si}_2\text{Zr}$  (521.2): calcd. C 39.17, H 6.77, N 5.37; found C 39.03, H 6.72, N 5.34.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ):  $\delta = 0.35$  (s, 6 H,  $\text{SiMe}_2$ ), 0.39 (s, 6 H,  $\text{SiMe}_2$ ), 1.02 (br. s, 2 H,  $\text{NH}t\text{Bu}$ ), 1.08 (s, 18 H,  $\text{NHCMe}_3$ ), 6.52 (d,  $J_{\text{H,H}} = 1.6$  Hz, 2 H,  $\text{C}_5\text{H}_3$ ), 7.16 (t,  $J_{\text{H,H}} = 1.6$  Hz, 1 H,  $\text{C}_5\text{H}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ):  $\delta = 1.99$  ( $\text{SiMe}_2$ ), 3.43 ( $\text{SiMe}_2$ ), 33.6 ( $\text{NHCMe}_3$ ), 49.6 ( $\text{NHCMe}_3$ ), 120.5 ( $\text{C}_5\text{H}_3$ ), 129.3 ( $\text{C}_5\text{H}_3$ ), 145.1 ( $\text{C}_5\text{H}_3$ ) ppm.

**$[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})_2]\text{Cl}_3]$  (**3**):** A colourless solution of  $\text{TiCl}_4$  (0.76 mL, 6.99 mmol) in hexane (15 mL) was cooled to  $-78^\circ\text{C}$  and added to a cooled ( $-78^\circ\text{C}$ ) stirred suspension of the lithium salt **1** (2.31 g, 6.99 mmol) in the same solvent (75 mL). The reaction mixture was then warmed slowly to room temperature and stirred for 12 h. The resulting light brown suspension was then filtered and, after removal of the solvent, complex **3** was isolated as an orange solid (2.33 g, 4.87 mmol, 70%).  $\text{C}_{17}\text{H}_{35}\text{Cl}_3\text{N}_2\text{Si}_2\text{Ti}$  (477.8): calcd. C 42.73, H 7.38, N 5.86; found C 41.92, H 7.30, N 5.73.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ):  $\delta = 0.39$  (s, 6 H,  $\text{SiMe}_2$ ), 0.48 (s, 6 H,  $\text{SiMe}_2$ ), 0.84 (br. s, 2 H,  $\text{NH}t\text{Bu}$ ), 0.94 (s, 18 H,  $\text{NHCMe}_3$ ), 6.89 (d,  $J_{\text{H,H}} = 2.0$  Hz, 2 H,  $\text{C}_5\text{H}_3$ ), 7.57 (t,  $J_{\text{H,H}} = 2.0$  Hz, 1 H,  $\text{C}_5\text{H}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ):  $\delta = 1.25$  ( $\text{SiMe}_2$ ), 1.41 ( $\text{SiMe}_2$ ), 33.7 ( $\text{NHCMe}_3$ ), 49.8 ( $\text{NHCMe}_3$ ), 132.2 ( $\text{C}_5\text{H}_3$ ), 136.6 ( $\text{C}_5\text{H}_3$ ), 149.2 ( $\text{C}_5\text{H}_3$ ) ppm.

**$[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3[\text{SiMe}_2(\text{NH}t\text{Bu})](\text{SiMe}_2\text{Cl})\}\text{Cl}_3]$  (**4**):** An orange solution of  $\text{TiCl}_4$  (0.17 mL, 1.55 mmol) in toluene (15 mL) was cooled to  $-78^\circ\text{C}$  and added to a cooled ( $-78^\circ\text{C}$ ) stirred suspension of the lithium salt **1** (0.51 g, 1.55 mmol) in the same solvent (75 mL). The reaction mixture was warmed slowly to room temperature and stirred for a further 12 h. The solvent was then removed under vacuum and the residue extracted into hexane (50 mL). After filtration and removal of the solvent, an unresolvable mixture of **3-5** and **7** was obtained. The presence of **4** was detected by NMR spectroscopy. **4**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta = 0.31$  (s, 3 H,  $\text{SiMe}_2$ ), 0.39 (s, 3 H,  $\text{SiMe}_2$ ), 0.54 (s, 3 H,  $\text{SiMe}_2$ ), 0.58 (s, 3 H,  $\text{SiMe}_2$ ), 0.92 (s, 9 H,  $\text{NHCMe}_3$ ), 6.70 (m, 1 H,  $\text{C}_5\text{H}_3$ ), 6.84 (m, 1 H,  $\text{C}_5\text{H}_3$ ), 7.47 (m, 1 H,  $\text{C}_5\text{H}_3$ ) ppm.

**$[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{Cl})_2\}\text{Cl}_3]$  (**5**) – Method A:** In a Teflon-sealed Schlenk tube,  $\text{TiCl}_4$  (0.055 mL, 0.50 mmol) was added by syringe to an orange solution of **3** (0.12 g, 0.25 mmol) in toluene (30 mL) cooled to  $-78^\circ\text{C}$ . The reaction mixture was then warmed slowly to room temperature, and subsequently heated for 12 h to  $110^\circ\text{C}$ . The volatiles were then removed under vacuum and the residue was extracted into hexane to give **5** as a light brown solid (0.089 g,

0.22 mmol, 65%).  $C_9H_{15}Cl_5Si_2Ti$  (404.5): calcd. C 26.72, H 3.74; found C 27.00, H 3.73.  $^1H$  NMR ( $CDCl_3$ , 20 °C):  $\delta$  = 0.76 (s, 6 H,  $SiMe_2$ ), 0.82 (s, 6 H,  $SiMe_2$ ), 7.33 (d,  $J_{H,H}$  = 1.8 Hz, 2 H,  $C_5H_3$ ), 7.56 (t,  $J_{H,H}$  = 1.8 Hz, 1 H,  $C_5H_3$ ) ppm.  $^{13}C$  NMR ( $CDCl_3$ , 20 °C):  $\delta$  = 2.36 ( $SiMe_2$ ), 2.81 ( $SiMe_2$ ), 131.2 ( $C_5H_3$ ), 135.0 ( $C_5H_3$ ), 139.3 ( $C_5H_{3ipso}$ ) ppm.

**Method B:** In a sealed Schlenk tube, an orange solution of  $TiCl_4$  (0.55 mL, 4.99 mmol) in toluene (15 mL) was cooled to  $-78$  °C and added to a cooled ( $-78$  °C) stirred suspension of the lithium salt **1** (0.55 g, 1.66 mmol) in the same solvent (50 mL). The reaction mixture was then warmed slowly to room temperature and then heated for 12 h to 110 °C. Volatiles were then removed under vacuum and the residue extracted into hexane to give **5** (0.66 g, 1.63 mmol, 60%).

**Method C:** Following the same procedure as method B, the similar reaction of **1** with  $TiCl_4$  in hexane (15 mL), heating to 45 °C for 1 h, gave **5** in low yield (10%) after repeated extractions into hexane.

**[Ti{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>[SiMe<sub>2</sub>(NH*r*Bu)](SiMe<sub>2</sub>- $\eta^1$ -N*r*Bu)}Cl<sub>2</sub>] (6). – Method A:** A solution of [Ti{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>[SiMe<sub>2</sub>(NH*r*Bu)](SiMe<sub>2</sub>- $\eta^1$ -N*r*Bu)}(NMe<sub>2</sub>)<sub>2</sub>] (0.60 g, 1.30 mmol) in toluene (40 mL) was added to a suspension of  $NEt_3 \cdot HCl$  (0.35 g, 2.60 mmol) in the same solvent. The mixture was then stirred for 12 h to 80 °C. After subsequent removal of the solvent under vacuum, the residue was extracted into pentane (70 mL). Following filtration and removal of the solvent, complex **6** was then isolated as a red solid (0.54 g, 1.22 mmol, 94%).  $C_{17}H_{34}Cl_2N_2Si_2Ti$  (441.4): calcd. C 46.26, H 7.76, N 6.35; found C 46.52, H 7.68, N 6.13.  $^1H$  NMR ( $C_6D_6$ , 20 °C):  $\delta$  = 0.24 (s, 3 H,  $SiMe_2$ ), 0.26 (s, 3 H,  $SiMe_2$ ), 0.45 (s, 3 H,  $SiMe_2$ ), 0.56 (s, 3 H,  $SiMe_2$ ), 1.05 (s, 9 H, NHCMe<sub>3</sub>), 1.38 (s, 9 H, NCMe<sub>3</sub>), 6.35 (m, 1 H,  $C_5H_3$ ), 6.57 (m, 1 H,  $C_5H_3$ ), 7.17 (m, 1 H,  $C_5H_3$ ) ppm.  $^{13}C$  NMR ( $C_6D_6$ , 20 °C):  $\delta$  =  $-0.1$  ( $SiMe_2$ ), 0.6 ( $SiMe_2$ ), 1.5 ( $SiMe_2$ ), 1.8 ( $SiMe_2$ ), 32.3 (NHCMe<sub>3</sub>), 33.9 (NCMe<sub>3</sub>), 49.8 (NHCMe<sub>3</sub>), 63.9 (NCMe<sub>3</sub>), 112.6 ( $C_5H_{3ipso}$ ), 126.1 ( $C_5H_3$ ), 129.4 ( $C_5H_3$ ), 129.5 ( $C_5H_{3ipso}$ ), 130.9 ( $C_5H_3$ ) ppm.

**Method B:** A solution of [Ti{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>(SiMe<sub>2</sub>- $\eta^1$ -N*r*Bu)}<sub>2</sub>](CH<sub>2</sub>Ph) (0.58 g, 1.25 mmol) in toluene (40 mL) was added to a suspension of  $NEt_3 \cdot HCl$  (0.34 g, 2.50 mmol) in the same solvent. The mixture was then stirred for 12 h at 80 °C. The solvent was then removed under vacuum and the residue extracted into hexane (40 mL). After filtration and removal of the solvent, complex **6** was then isolated as a red solid (0.31 g, 0.70 mmol, 70%).

**Method C:** **6** was formed when the method described below to prepare **7** was followed, using 1 equiv. of  $TiCl_4$ . The resulting mixture contained **6** and **7** in a 1:3 molar ratio. Pure **6** could not be isolated from this mixture.

**[Ti{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>(SiMe<sub>2</sub>Cl)(SiMe<sub>2</sub>- $\eta^1$ -N*r*Bu)}Cl<sub>2</sub>] (7):** In a sealed Schlenk tube, an orange solution of  $TiCl_4$  (0.32 mL, 2.97 mmol) in toluene (50 mL) was cooled to  $-78$  °C and added to a cooled ( $-78$  °C) stirred suspension of the lithium salt **1** (0.49 g, 1.48 mmol) in the same solvent (50 mL).  $NEt_3$  (0.62 mL, 4.45 mmol) was added to this mixture, and finally, it was warmed to room temperature and heated for 12 h to 110 °C. The volatiles were removed under vacuum and the residue was extracted into hexane. After filtration and removal of the solvent complex **7** was isolated as a yellow solid (0.44 g, 1.10 mmol, 75%).  $C_{13}H_{24}Cl_3NSi_2Ti$  (404.7): calcd. C 38.58, H 5.98, N 3.46; found C 39.07, H 6.16, N 3.46.  $^1H$  NMR ( $CDCl_3$ , 20 °C):  $\delta$  = 0.60 (s, 3 H,  $SiMe_2$ ), 0.62 (s, 3 H,  $SiMe_2$ ), 0.70 (s, 3 H,  $SiMe_2$ ), 0.79 (s, 3 H,  $SiMe_2$ ), 1.43 (s, 9 H, NCMe<sub>3</sub>), 6.53 (m, 1 H,  $C_5H_3$ ), 6.63 (m, 1 H,  $C_5H_3$ ), 7.25 (m, 1 H,  $C_5H_3$ ) ppm.  $^{13}C$  NMR

( $CDCl_3$ , 20 °C):  $\delta$  = 0.13 ( $SiMe_2$ ), 0.64 ( $SiMe_2$ ), 1.65 ( $SiMe_2$ ), 2.65 ( $SiMe_2$ ), 32.1 (NCMe<sub>3</sub>), 64.6 (NCMe<sub>3</sub>), 113.1 ( $C_5H_{3ipso}$ ), 129.4 ( $C_5H_3$ ), 130.6 ( $C_5H_3$ ), 132.1 ( $C_5H_3$ ), 135.5 ( $C_5H_{3ipso}$ ) ppm.

**[Zr{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>(SiMe<sub>2</sub>Cl)<sub>2</sub>}Cl<sub>3</sub>] (8):** In a sealed Schlenk tube,  $TiCl_4$  (0.18 mL, 1.65 mmol) was added by syringe to a cooled ( $-78$  °C) light yellow solution of complex **2** (0.43 g, 0.82 mmol) in toluene (70 mL). The reaction mixture was then warmed to room temperature, followed by heating for 12 h to 110 °C. Volatiles were then removed under vacuum and the residue extracted into hexane. After filtration and removal of the solvent, complex **8** was isolated as a light yellow solid (0.25 g, 0.56 mmol, 69%).  $C_9H_{15}Cl_5Si_2Zr$  (447.9): calcd. C 24.14, H 3.38; found C 24.01, H 3.30.  $^1H$  NMR ( $CDCl_3$ , 20 °C):  $\delta$  = 0.70 (s, 6 H,  $SiMe_2$ ), 0.75 (s, 6 H,  $SiMe_2$ ), 6.76 (d,  $J_{H,H}$  = 1.8 Hz, 2 H,  $C_5H_3$ ), 7.19 (t,  $J_{H,H}$  = 1.8 Hz, 1 H,  $C_5H_3$ ) ppm.  $^{13}C$  NMR( $CDCl_3$ , 20 °C):  $\delta$  = 2.65 ( $SiMe_2$ ), 3.83 ( $SiMe_2$ ), 121.4 ( $C_5H_3$ ), 126.6 ( $C_5H_{3ipso}$ ), 141.8 ( $C_5H_3$ ) ppm.

**[Zr{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub> [SiMe<sub>2</sub>(NH*r*Bu)](SiMe<sub>2</sub>- $\eta^1$ -N*r*Bu)}Cl<sub>2</sub>(NMe<sub>2</sub>H)] (9):** A solution of [Zr{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub> (SiMe<sub>2</sub>- $\eta^1$ -N*r*Bu)<sub>2</sub>}(NMe<sub>2</sub>)<sub>2</sub>] (0.74 g, 1.46 mmol) in toluene (40 mL) was added to a suspension of  $NEt_3 \cdot HCl$  (0.40 g, 2.92 mmol) in the same solvent. The resultant mixture was then stirred for 2 h at 70 °C. The solvent was then removed under vacuum and the residue extracted into pentane (40 mL). After filtration and removal of the solvent, complex **9** was isolated as an ochre microcrystalline solid (0.64 g, 1.21 mmol, 82%).  $C_{19}H_{41}Cl_2N_3Si_2Zr$  (529.8): calcd. C 43.07, H 7.80, N 7.93; found C 42.46, H 7.58, N 7.60.  $^1H$  NMR ( $C_6D_6$ , 20 °C):  $\delta$  = 0.27 (s, 3 H,  $SiMe_2$ ), 0.28 (s, 3 H,  $SiMe_2$ ), 0.5 (s, 3 H,  $SiMe_2$ ), 0.52 (s, 3 H,  $SiMe_2$ ), 1.06 (s, 9 H, NHCMe<sub>3</sub>), 1.50 (s, 9 H, NCMe<sub>3</sub>), 2.25 (s, 3 H, NMe<sub>2</sub>H), 2.27 (s, 3 H, NMe<sub>2</sub>H), 3.58 (s br, 1 H, NMe<sub>2</sub>H), 6.43 (m, 1 H,  $C_5H_3$ ), 6.81 (m, 1 H,  $C_5H_3$ ), 6.91 (m, 1 H,  $C_5H_3$ ) ppm.  $^{13}C$  NMR ( $C_6D_6$ , 20 °C):  $\delta$  = 1.1 ( $SiMe_2$ ), 1.4 ( $SiMe_2$ ), 1.9 ( $SiMe_2$ ), 4.2 ( $SiMe_2$ ), 31.6 (NHCMe<sub>3</sub>), 33.6 (NCMe<sub>3</sub>), 39.3 (br., NMe<sub>2</sub>H), 50.1 (NHCMe<sub>3</sub>), 58.3 (NCMe<sub>3</sub>), 114.6 ( $C_5H_{3ipso}$ ), 123.9 ( $C_5H_3$ ), 126.3 ( $C_5H_3$ ), 127.9 ( $C_5H_{3ipso}$ ), 129.4 ( $C_5H_3$ ) ppm.

**[Zr{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>[SiMe<sub>2</sub>(NH*r*Bu)](SiMe<sub>2</sub>- $\eta^1$ -N*r*Bu)}Cl(NMe<sub>2</sub>)] (10):**  $SiClMe_3$  (15.2  $\mu$ L, 0.12 mmol) was added by syringe to a solution of [Zr{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>[SiMe<sub>2</sub>(NH*r*Bu)](SiMe<sub>2</sub>- $\eta^1$ -N*r*Bu)}(NMe<sub>2</sub>)<sub>2</sub>] (0.059 g, 0.12 mmol) in  $C_6D_6$ . The  $^1H$  NMR spectrum of this solution was recorded after 1 h of reaction to confirm that **10** was the unique product.  $^1H$  NMR ( $C_6D_6$ , 20 °C):  $\delta$  = 0.30 (s, 3 H,  $SiMe_2$ ), 0.32 (s, 3 H,  $SiMe_2$ ), 0.44 (s, 3 H,  $SiMe_2$ ), 0.46 (s, 3 H,  $SiMe_2$ ), 1.04 (s, 9 H, NHCMe<sub>3</sub>), 1.27 (s, 9 H, NCMe<sub>3</sub>), 2.75 (d, 6 H, ZrNMe<sub>2</sub>), 6.28 (m, 1 H,  $C_5H_3$ ), 6.52 (m, 1 H,  $C_5H_3$ ), 7.02 (m, 1 H,  $C_5H_3$ ) ppm.  $^{13}C$  NMR ( $C_6D_6$ , 20 °C):  $\delta$  = 2.0 ( $SiMe_2$ ), 2.0 ( $SiMe_2$ ), 2.1 ( $SiMe_2$ ), 2.1 ( $SiMe_2$ ), 33.8 (NHCMe<sub>3</sub>), 34.1 (NCMe<sub>3</sub>), 43.3 (NMe<sub>2</sub>), 49.7 (NHCMe<sub>3</sub>), 56.9 (NCMe<sub>3</sub>), 111.6 ( $C_5H_{3ipso}$ ), 122.6 ( $C_5H_{3ipso}$ ), 122.9 ( $C_5H_3$ ), 125.9( $C_5H_3$ ), 127.4 ( $C_5H_3$ ) ppm.

**[Ti{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>[SiMe<sub>2</sub>(NH*r*Bu)](SiMe<sub>2</sub>- $\eta^1$ -N*r*Bu)}Cl(CH<sub>2</sub>Ph)] (11):** A solution of [Ti{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>(SiMe<sub>2</sub>- $\eta^1$ -N*r*Bu)<sub>2</sub>}(CH<sub>2</sub>Ph)] (0.58 g, 1.25 mmol) in toluene (40 mL) was added to a suspension of  $NEt_3 \cdot HCl$  (0.17 g, 1.25 mmol) in the same solvent. The resultant mixture was stirred for 2 h at 70 °C. The solvent was then removed under vacuum and the residue was extracted into pentane (40 mL). After filtration and removal of the solvent, complex **11** was isolated as a red solid (0.48 g, 0.96 mmol, 77%).  $C_{24}H_{41}ClN_2Si_2Ti$  (497.1): calcd. C 57.99, H 8.31, N 5.64; found C 58.10, H 8.03, N 5.77.  $^1H$  NMR ( $C_6D_6$ , 20 °C):  $\delta$  = 0.25 (s, 3 H,  $SiMe_2$ ), 0.30 (s, 3 H,  $SiMe_2$ ), 0.40 (s, 3 H,  $SiMe_2$ ), 0.48 (s, 3 H,  $SiMe_2$ ), 1.04 (s, 9 H, NHCMe<sub>3</sub>), 1.48 (s, 9 H, NCMe<sub>3</sub>), 2.92 (d,  $J_{H,H}$  = 9.6 Hz, 1 H, CH<sub>2</sub>Ph), 3.1 (d, 1 H, CH<sub>2</sub>Ph), 5.91 (m, 1 H,  $C_5H_3$ ), 6.39 (m, 1 H,  $C_5H_3$ ), 6.49 (m, 1 H,  $C_5H_3$ ), 6.88 (m, 1 H,  $C_6H_5$ ), 6.97 (m, 2 H,  $C_6H_5$ ), 7.18

(m, 2 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 20 °C): δ = 0.4 (SiMe<sub>2</sub>), 0.6 (SiMe<sub>2</sub>), 1.4 (SiMe<sub>2</sub>), 1.5 (SiMe<sub>2</sub>), 33.7 (NHCMe<sub>3</sub>), 33.8 (NCMe<sub>3</sub>), 49.6 (NHCMe<sub>3</sub>), 62.3 (NCMe<sub>3</sub>), 79.7 (CH<sub>2</sub>Ph), 111.4 (C<sub>5</sub>H<sub>3ipso</sub>), 122.5 (C<sub>5</sub>H<sub>3</sub>), 126.1 (C<sub>5</sub>H<sub>3ipso</sub>), 127.0 (C<sub>5</sub>H<sub>3</sub>), 128.7 (C<sub>5</sub>H<sub>4</sub>), 128.8 (C<sub>6</sub>H<sub>5</sub>), 133.1 (C<sub>6</sub>H<sub>5</sub>), 139.2 (C<sub>6</sub>H<sub>5</sub>), 149.5 (C<sub>6</sub>H<sub>5ipso</sub>) ppm.

[Zr{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>[SiMe<sub>2</sub>(NH*t*Bu)](SiMe<sub>2</sub>-η<sup>1</sup>-N*t*Bu)}Cl<sub>2</sub>] (12): A solution of [Zr{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>2</sub>-η<sup>1</sup>-N*t*Bu)<sub>2</sub>}(CH<sub>2</sub>Ph)] (0.32 g, 0.63 mmol) in toluene (40 mL) was added to a suspension of NEt<sub>3</sub>·HCl (0.17 g, 1.26 mmol) in the same solvent. The resultant mixture was stirred for 12 h at 70 °C. The solvent was then removed under vacuum and the residue extracted into pentane (70 mL). After filtration and removal of the solvent, complex 12 was isolated as a light brown solid (0.27 g, 0.58 mmol, 88%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 20 °C): δ = 0.27 (2s, 6 H, SiMe<sub>2</sub>), 0.43 (s, 3 H, SiMe<sub>2</sub>), 0.53 (s, 3 H, SiMe<sub>2</sub>), 1.05 (s, 9 H, NHCMe<sub>3</sub>), 1.30 (s, 9 H, NCMe<sub>3</sub>), 6.41 (m, 1 H, C<sub>5</sub>H<sub>3</sub>), 6.60 (m, 1 H, C<sub>5</sub>H<sub>3</sub>), 6.97 (m, 1 H, C<sub>5</sub>H<sub>3</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 20 °C): δ = 0.8 (SiMe<sub>2</sub>), 1.4 (SiMe<sub>2</sub>), 1.9 (SiMe<sub>2</sub>), 33.0 (NHCMe<sub>3</sub>), 33.9 (NCMe<sub>3</sub>), 49.8 (NHCMe<sub>3</sub>), 57.6 (NCMe<sub>3</sub>), 112.6 (C<sub>5</sub>H<sub>3ipso</sub>), 120.9 (C<sub>5</sub>H<sub>3</sub>), 126.7 (C<sub>5</sub>H<sub>3ipso</sub>), 128.3 (C<sub>5</sub>H<sub>3</sub>) ppm.

**X-ray Crystallographic Study:** Crystal data and details of the structure determination (Table 2) and bond lengths and bond angles (Table 1) are given here. Suitable single crystals for X-ray diffraction were grown from a saturated solution of 3 in pentane by standard cooling techniques. A clear orange fragment (0.41 × 0.43 × 0.48 mm) was stored under perfluorinated ether, transferred to a Lindemann capillary, fixed and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3 κ-CCD) at the window of a rotating anode (NONIUS, FR591) and graphite-monochromated Mo-K<sub>α</sub> radiation (λ = 0.71073 Å). Unit cell parameters were obtained by full-matrix

least-squares refinement of 2450 reflections. Data collection was performed at 153 K within a Θ-range of 2.77–25.35°. Nine data sets were measured in rotation scan modus with Δφ/ΔΩ = 1.0° controlled by the COLLECT software package.<sup>[33]</sup> A total of 30285 intensities were integrated. Raw data were corrected for Lorentz, polarization, and during the scaling procedure for latent decay and absorption effects. After merging (R<sub>int</sub> = 0.043), a sum of 4654 (all data) and 4560 [I > 2σ(I)] remained and all data were used.<sup>[34]</sup> The structure was solved by a combination of direct methods<sup>[35]</sup> and difference Fourier syntheses.<sup>[36]</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found in the final difference Fourier maps and allowed to refine freely with isotropic displacement parameters. Full-matrix least-squares refinements with 366 parameters were carried out by minimizing Σw(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup> with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The correct enantiomer was proved by Flack's parameter ε = 0.02(2). Final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.<sup>[37]</sup> CCDC-229361 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 2. Crystallographic data for [Ti(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>{SiMe<sub>2</sub>(NH*t*Bu)}<sub>2</sub>)Cl<sub>3</sub>] (3)

	3
Empirical formula	C <sub>17</sub> H <sub>35</sub> Cl <sub>3</sub> N <sub>2</sub> Si <sub>2</sub> Ti
Formula mass	477.87
Colour/shape	orange/fragment
Crystal size (mm)	0.41 × 0.43 × 0.48
Crystal system	monoclinic
Space group	P2 <sub>1</sub> (No. 4)
a (Å)	9.3637(1)
b (Å)	12.4297(2)
c (Å)	11.2252(1)
β (deg)	103.5551(7)
V (Å <sup>3</sup> )	1270.09(3)
Z	2
T (K)	153
ρ <sub>calcd.</sub> (g cm <sup>-3</sup> )	1.250
μ (mm <sup>-1</sup> )	0.751
F <sub>000</sub>	504
θ Range (°)	2.77–25.35
Data collected (h,k,l)	±11, ±14, ±13
No. of reflns. collected	30285
No. of indep. reflns./R <sub>int</sub>	4654 (all)/0.043
No. of obsd. reflns. (I > 2σ(I))	4560 (obsd.)
no. of parameters refined	366
R1 (obsd./all)	0.0198/0.0207
wR2 (obsd./all)	0.0450/0.0453
GO F (obsd./all)	1.093/1.093
max/min Δρ (e <sup>-</sup> Å <sup>-3</sup> )	+0.19/−0.15

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