

# Hydro- and chloro-substituted silyl- and silyl- $\eta^1$ -amido- $\eta^5$ -tetramethylcyclopentadienyl titanium complexes

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## Abstract

Chlorosilyl-cyclopentadienyl titanium precursors  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeXCl})\text{Cl}_3]$  ( $X = \text{H}$  **2**,  $\text{Cl}$  **3**) were prepared by reaction of  $\text{TiCl}_4$  with the trimethylsilyl derivatives of the corresponding cyclopentadienes. Methylation of these compounds with  $\text{MgClMe}$  under appropriate conditions afforded the methyl complexes  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{R})\text{XMe}_2]$  ( $\text{R} = \text{H}$ ,  $\text{X} = \text{Cl}$  **5**,  $\text{Me}$  **6**;  $\text{R} = \text{X} = \text{Me}$  **7**). Reactions of **2** and **3** with two equivalents of  $\text{LiNH}^t\text{Bu}$  afforded the *ansa*-silyl- $\eta$ -amido compounds  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4\text{SiMeX}(\eta^1\text{-N}^t\text{Bu})\}\text{Cl}_2]$  ( $X = \text{H}$  **8**,  $\text{Cl}$  **9**). Methylation of **8** gave  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4\text{SiMeH}(\eta^1\text{-N}^t\text{Bu})\}\text{Me}_2]$  **10**. Complex **9** was also obtained by reaction of **8** with  $\text{BCl}_3$ , whereas the same reaction using alternative chlorinating agents ( $\text{TiCl}_4$ ,  $\text{HCl}$ ) resulted in deamidation to give **2**, which was also converted into **3** by reaction with  $\text{BCl}_3$ . All of the new compounds were characterized by NMR spectroscopy and the molecular structures of **2** and **4** were determined by X-ray diffraction methods.

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## 1. Introduction

Since initial studies on scandium catalysts [1], the success of  $\eta^5$ -cyclopentadienyl-silyl- $\eta^1$ -amido Group 4 metal complexes as efficient catalysts for olefin polymerization has motivated numerous studies and applications [2].

Two essential methods have been reported to isolate compounds of this type. One is based on the coordination of the cyclopentadienyl-silyl-amido  $[\text{C}_5\text{R}_4\text{-SiMe}_2\text{-NR}^t]^{2-}$  dianion after deprotonation of the corresponding amino-silyl-cyclopentadiene by basic tetra-alkyl [2a, 3] or -amido [3c, 3d, 4] metal complexes, or by initial metallation with  $\text{Li}^n\text{Bu}$  followed by reaction with metal chlorides [4f, 5]. Following the second route, simultaneous aminolysis of  $\text{Si-Cl}$  and  $\text{M-Cl}$  bonds is achieved by reaction of isolated chlorosilyl-cyclopentadienyl

metal chlorides with primary amines  $\text{R}^2\text{NH}_2$  or amides  $\text{Li}(\text{R}^2\text{NH})$  [5h, 5l, 6].

Different substituents bound to the bridging silicon atom offer reactive  $\text{Si-X}$  bonds which may provide convenient sites to introduce various functionalities that are useful precursors for supported catalysts [4h, 4k, 7]. In particular we were interested in metal complexes with chloro-silyl bridging groups for which many synthetic constraints were reported [8]. In previous work we reported [9] that chlorination of the hydro-silyl zirconium complex  $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeH-}\eta^1\text{-N}^t\text{Bu})\text{Cl}_2]$  with  $\text{BCl}_3$  is the most convenient method to isolate the pure chloro-silyl derivative  $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeCl-}\eta^1\text{-N}^t\text{Bu})\text{Cl}_2]$  in high yield. Herein we describe an extension of our studies to related titanium compounds for which we report the synthesis and structural characterization of new monocyclopentadienyl  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeHCl})\text{Cl}_3]$ ,  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeCl}_2)\text{Cl}_3]$ , silyl-amido  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeH-}\eta^1\text{-N}^t\text{Bu})\text{Cl}_2]$ ,  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeCl-}\eta^1\text{-N}^t\text{Bu})\text{Cl}_2]$  and their methylated derivatives  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{H})\text{XMe}_2]$  ( $\text{X} = \text{Cl}$ ,  $\text{Me}$ ) and  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeH-}\eta^1\text{-N}^t\text{Bu})\text{Me}_2]$ . The molecular structures

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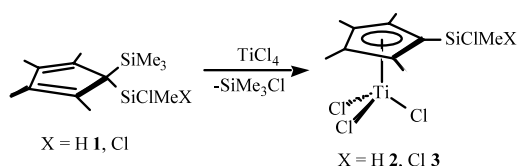
of  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeHCl})\text{Cl}_3]$  and  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Cl}_3]$  were studied by X-ray diffraction methods.

## 2. Results and discussion

### 2.1. Monocyclopentadienyl complexes

The precursor disilylated cyclopentadiene  $\text{C}_5\text{Me}_4(\text{SiMeHCl})(\text{SiMe}_3)$  **1** was isolated in 93% yield by reaction of the trimethylsilylcyclopentadienyl lithium salt [10] with  $\text{SiMeHCl}_2$  in THF. Compound **1** was isolated as a pale yellow liquid, which crystallized on cooling at  $0^\circ\text{C}$  to give colorless needles and was characterized by elemental analysis and NMR spectroscopy. The expected four signals due to the ring-methyl groups of an ABCD spin system imposed by the chiral silicon centre, along with the high field singlet due to the  $\text{SiMe}_3$  group and one doublet and one quadruplet corresponding to the coupled ( $^3J_{\text{H-H}} = 3$  Hz) methyl and hydrogen of the  $\text{SiMeH}$  group were observed in the  $^1\text{H}$ -NMR spectrum. Likewise, four ring-methyl, five ring-carbon and two silicon-methyl resonances appeared in the  $^{13}\text{C}$ -NMR spectrum.

Disilylated cyclopentadienes have been extensively used to prepare silyl-cyclopentadienyl metal complexes by reaction with appropriate metal halides. When two different silyl groups are present, electronic and steric effects control which group undergoes preferential elimination [8,11]. As shown in Scheme 1, selective elimination of the  $\text{SiMe}_3$  group took place when the disilylated cyclopentadiene **1** was reacted with one equivalent of  $\text{TiCl}_4$  in refluxing  $\text{CH}_2\text{Cl}_2$  for 3 days to give the mono-cyclopentadienyl titanium complex  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeHCl})\text{Cl}_3]$  **2**, isolated as an orange solid in 78% yield and characterized by elemental analysis and NMR spectroscopy. The  $^1\text{H}$ -NMR spectrum of **2** corresponds to that of an asymmetric molecule with a chiral centre at silicon. It shows the expected four ring-methyl singlets due to an ABCD spin system, along with the high field doublet and low field quadruplet due to the coupled methyl and hydrogen substituents of the  $\text{SiMeH}$  system ( $^3J_{\text{H-H}} = 3.3$  Hz). The  $^{13}\text{C}$ -NMR spectrum is also consistent with the proposed structure. Single orange-red crystals of **2** were obtained by cooling its  $\text{CH}_2\text{Cl}_2$  solution at  $-30^\circ\text{C}$  and its molecular structure was determined by X-ray diffraction methods.

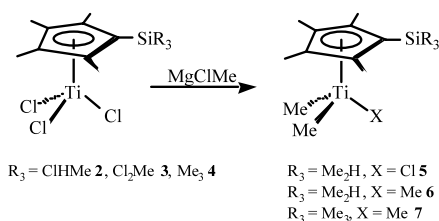
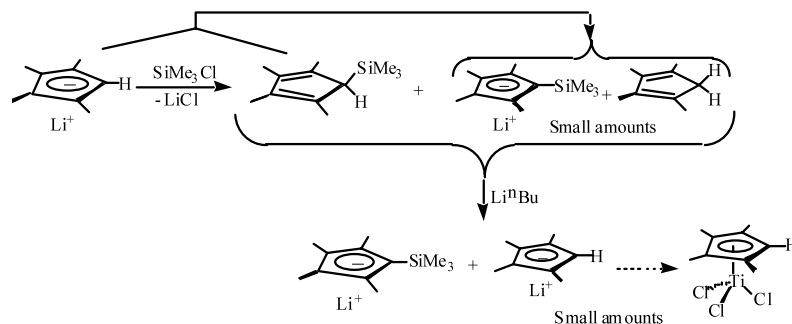


Scheme 1.

Similar reaction of the related disilylated cyclopentadiene containing the dichlorosilyl group  $\text{C}_5\text{Me}_4(\text{SiMeCl}_2)(\text{SiMe}_3)$  [9] with  $\text{TiCl}_4$  in refluxing dichloromethane for 4 days gave the corresponding mono-cyclopentadienyl titanium complex  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeCl}_2)\text{Cl}_3]$  **3**, which was isolated as an orange solid in 80% yield and characterized by elemental analysis and NMR spectroscopy. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of **3** show the expected ring-methyl signals due to an AA'BB' spin system along with the high field singlets due to the methyl-silicon group, supporting the proposed structure.

Formation of small amounts of the unsubstituted cyclopentadienyl titanium compound  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Cl}_3]$  [12] was observed in all of these reactions. To check the origin of this compound we repeated the reported [10] preparation of the titanium derivative  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Cl}_3]$  **4**, which was isolated as orange-red crystals, and we determined its molecular structure by X-ray diffraction methods. As shown in Scheme 2 we found that small amounts of  $\text{C}_5\text{Me}_4\text{H}_2$  were formed by partial acid-base exchange between the lithium salt  $\text{Li}(\text{C}_5\text{Me}_4\text{H})$  and the more acidic hydrogen of the silylcyclopentadiene  $\text{C}_5\text{Me}_4\text{H}(\text{SiMe}_3)$ , which was obtained from the reaction of the lithium salt with  $\text{SiMe}_3\text{Cl}$ . Further reaction of  $\text{C}_5\text{Me}_4\text{H}(\text{SiMe}_3)$  with  $\text{Li}^n\text{Bu}$  produces simultaneous metallation of the residual  $\text{C}_5\text{Me}_4\text{H}_2$  to give small amounts of  $\text{Li}(\text{C}_5\text{Me}_4\text{H})$  always contaminating the lithium salt  $\text{Li}[\text{C}_5\text{Me}_4(\text{SiMe}_3)]$ . This impurity was carried to the last step when it finally reacted with  $\text{TiCl}_4$  to give the observed  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Cl}_3]$  compound. It is not easy to avoid the presence of this compound, although it does not cause any difficulty as its higher solubility in all solvents allows its easy elimination.

Methylation of complex **4** with three equivalents of  $\text{MgClMe}$  in diethyl ether afforded the trimethyltitanium derivative  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Me}_3]$  **7**. As shown in Scheme 3, the totally alkylated complexes  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{H})\text{Me}_3]$  **6** and **7** were obtained under similar conditions by reaction of **2** and **3** with four and five equivalents of  $\text{MgClMe}$ , respectively. In an attempt to isolate partially methylated species from chloro complexes containing additional one (**2**) and two (**3**) Si-Cl bonds, we studied their reactions with variable molar ratios of  $\text{MgClMe}$ . Methylation of complex **3** with less than five equivalents of  $\text{MgClMe}$  and of complex **2** with less than three equivalents of  $\text{MgClMe}$  afforded irresolvable mixtures of various products resulting from the unselective alkylation at silicon and titanium. However, reaction of diethyl ether solutions of **2** with three equivalents of  $\text{MgClMe}$  gave a mixture which, after standing for 12 h at room temperature, contained the partially alkylated  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{H})\text{ClMe}_2]$  **5** and the totally alkylated  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{H})\text{Me}_3]$  **6** complexes in a molar ratio



of ca. 4/3, respectively, together with small amounts of other unidentified chloro-alkyl compounds. This mixture evolves further in a very slow reaction to transform **6** and all of the other chloro-alkyl compounds into the partially methylated **5** after several days.

Complex **5** was isolated as a yellow oil and was only characterized by NMR spectroscopy, whereas **6** and **7** were isolated as yellow solids and identified by elemental analysis and NMR spectroscopy. The  $^1\text{H}$ -NMR spectra of complexes **5**–**6** show the expected two ring-methyl singlets due to an AA'BB' spin system along with the high field doublet and low field septuplet corresponding to the two equivalent silicon-methyl groups coupled to the hydrogen of a  $\text{SiMe}_2\text{H}$  system ( $^3J_{\text{H-H}} = 3.9$  Hz) along with the singlet due to the two or three equivalent methyl-titanium groups, respectively. The  $^{13}\text{C}$ -NMR spectra are also consistent with the proposed structure. The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra of the trimethyl complex **7** follow the pattern reported [10] for the trichloro complex with one additional singlet due to the three equivalent methyl-titanium groups.

## 2.2. Description of the molecular structures of complexes **2** and **4**

A view of the molecular structures of complexes **2** and **4** are shown in Figs. 1 and 2, respectively, together with the atom-numbering schemes. Selected bond distances and angles are summarized in Table 1. The two complexes were almost isostructural, both showing the familiar piano-stool geometry with little difference in their structural features. The coordination polyhedron about the titanium atom is a distorted tetrahedron

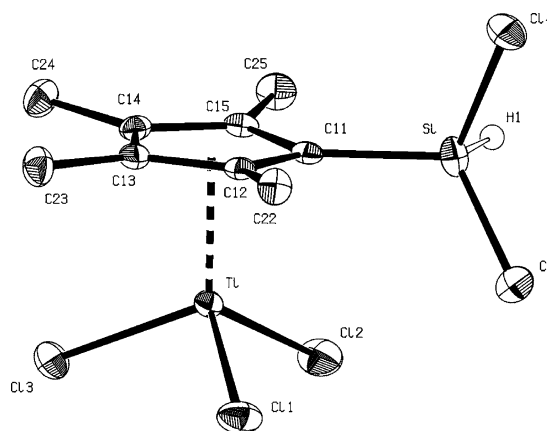


Fig. 1. ORTEP style plot of the solid state structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Shown is the main component of the disordered  $-\text{SiHClMe}$  group.

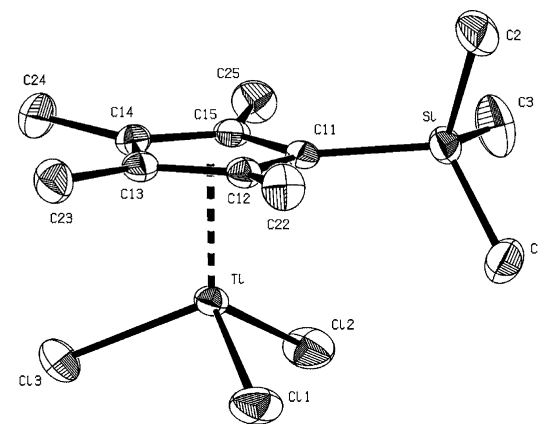


Fig. 2. ORTEP style plot of the solid state structure of **4**. Thermal ellipsoids are drawn at the 50% probability level.

formed by three Cl atoms and the centroid of the Cp ring in a  $\eta^5$ -coordination mode, with the distance between the metal and the ring centroid being 2.023 and 2.019 Å, respectively. An inspection of the bond distances and angles shows that the Cp ring in both complexes is distorted by the presence of the silyl substituents: the C–C distances involving the silyl substituted carbon atom C11 are the longest (av.

Table 1

Characteristic bond lengths (Å), angles (°), for **2**, **4** and related compounds  $\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Cl}_3$ 

	<b>2</b>	<b>4</b>	R: $-\text{C}_2\text{H}_5$ [15] <sup>a</sup>	R: $-\text{P}[\text{N}(\text{C}_2\text{H}_5)_2]^t\text{Bu}$ [16] <sup>a</sup>	R: $-(4\text{-pentenyl})$ [17] <sup>a</sup>	R: $-(2\text{-phenylethyl})$ [18] <sup>a</sup>
<i>Bond lengths</i>						
Ti–Cl1	2.2360(6)	2.2383(6)	2.238	2.235(2)	2.240(2)	2.221(3)
Ti–Cl2	2.2423(6)	2.2440(7)	2.238	2.232(2)	2.240(2)	2.245(2)
Ti–Cl3	2.2422(6)	2.2463(6)	2.254	2.235(2)	2.245(2)	2.240(2)
Ti–Cg <sup>b</sup>	2.023	2.019	2.020	2.020	2.021	2.015
C11–R	1.869(2)	1.900(2)	1.506	1.863(5)	1.499(5)	1.496(7)
<i>Bond angles</i>						
Cl1–Ti–Cl2	103.89(2)	103.94(3)	102.75	104.46(8)	103.23(5)	102.70(8)
Cl1–Ti–Cl3	101.74(2)	102.13(3)	103.42	101.90(8)	102.44(5)	103.87(8)
Cl1–Ti–Cg	115.52	115.34	115.61	116.53	115.18	115.73
Cl2–Ti–Cl3	103.66(2)	102.60(3)	103.42	100.75(8)	103.96(5)	102.10(7)
Cl2–Ti–Cg	116.66	117.44	115.61	117.68	115.08	115.28
Cl3–Ti–Cg	113.57	113.47	114.34	113.24	115.27	115.31

<sup>a</sup> The atom labels are adapted to the numbering scheme used here.<sup>b</sup> Cg denotes the centroid of the cyclopentadienyl ring.

1.436(3) Å) within the ring C–C-bonds and the C12–C11–C15 angle (107.42(15)° (**2**), 106.42(16)° (**4**)) at this carbon atom is the smallest among the internal ring angles [13]. The silicon-induced distortion in the ring also results in varying Ti–C(Cp) distances, in the range 2.309(2) Å (Ti–C11)–2.389(2) Å (Ti–C14) (**2**) and 2.322(2) Å (Ti–C11)–2.379(2) Å (Ti–C14) (**4**). The Si–Cl bond distances in complex **2** (av. 1.966 Å) is slightly shorter than that found for related chlorosilyl-cyclopentadienyl complexes [14]. The Ti–Cl bond distances (2.23–2.24 Å) and the Cl–Ti–Cl angles (102–104°) are in the typical range for compounds of this type [15–18] as shown in Table 1.

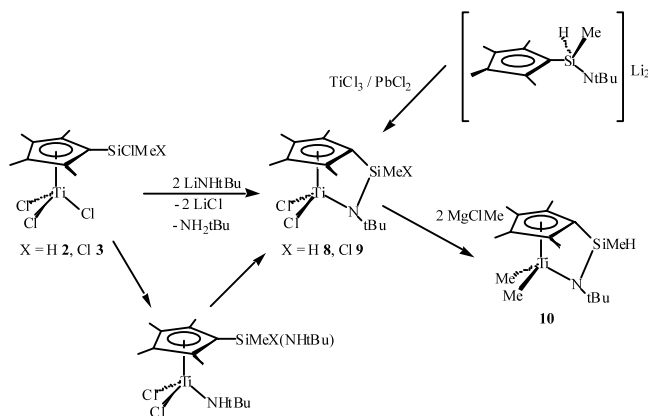
### 2.3. Cyclopentadienyl-silyl-η-amido complexes

Intramolecular formation of the silyl-η-amido bridge was easily achieved by reaction of both Si–Cl and Ti–Cl bonds of complexes **2** and **3** with two equivalent of  $\text{LiNH}^t\text{Bu}$  (see Scheme 4).

When the reaction of complex **2** was carried out at room temperature, formation of the doubly substituted

complex  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4\text{SiMeH}(\text{NH}^t\text{Bu})\}\text{Cl}_2(\text{NH}^t\text{Bu})]$  was observed. This compound was identified by NMR spectroscopy [19], although it could not be isolated as a pure compound as it always contained the silyl-η-amido impurity  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4\text{SiMeH}(\eta^1\text{-N}^t\text{Bu})\}\text{Cl}_2]$  **8**, which was the unique reaction product after standing for 6 days at room temperature or by heating the toluene solution for 12 h to 110 °C in a Teflon-sealed Schlenk tube. Therefore **8** was formed by the elimination of  $\text{NH}_2\text{Bu}$  from  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4\text{SiMeH}(\text{NH}^t\text{Bu})\}\text{Cl}_2(\text{NH}^t\text{Bu})]$ , and not by the elimination of HCl from a hypothetical monosubstituted silylamido  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4\text{-SiMeH}(\text{NH}^t\text{Bu})\}\text{Cl}_3]$  compound and its further reaction with the second equivalent of  $\text{LiNH}^t\text{Bu}$  acting as a base. A similar reaction of **3** with two equivalent of  $\text{LiNH}^t\text{Bu}$  followed the same sequence to afford the related derivative  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4\text{SiMeCl}(\text{NH}^t\text{Bu})\}\text{Cl}_2(\text{NH}^t\text{Bu})]$  [19] together with other minor amido-titanium components which were further transformed into the corresponding chlorosilyl derivative  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4\text{SiMeCl}(\eta^1\text{-N}^t\text{Bu})\}\text{Cl}_2]$  **9**. After appropriate work up of the resulting solutions, the silyl-amido titanium complexes  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeX-}\eta^1\text{-N}^t\text{Bu})\text{Cl}_2]$  (X = H **8**, Cl **9**) were isolated as yellow and orange solids in 92 and 41% yield, respectively, and were characterized by elemental analysis and NMR spectroscopy. Complexes **8** and **9** show the <sup>1</sup>H-NMR spectra expected for asymmetrical molecules with a chiral centre at silicon, exhibiting the four ring-methyl singlets typical of an ABCD spin system. In addition one doublet (**8**) or singlet (**9**) due to the methyl-silicon and the singlet due to the N<sup>t</sup>Bu groups were observed.

Alternatively complex **8** may also be prepared by reaction of the dilithium salt  $\text{Li}_2[\text{C}_5\text{Me}_4\text{SiMeH}(\text{N}^t\text{Bu})]$  [9] with an equimolar amount of  $\text{TiCl}_3(\text{THF})_3$  in THF, followed by addition of  $\text{PbCl}_2$  as oxidant [20] and appropriate work up of the resulting solution.



Scheme 4.

An alternative route to prepare complex **9** could be based on the transformation of **8** by reaction with different chlorinating agents. The titanium and zirconium derivatives  $[M(\eta^5\text{-C}_5\text{Me}_4\text{SiMeH-}\eta^1\text{-N}^t\text{Bu})\text{Cl}_2]$  show a clearly different chemical behaviour in their reactions with halogenating agents, as reported previously [4e] for reactions of related amido titanium and zirconium complexes with  $[\text{NEt}_3\text{H}]\text{Cl}$ . We reported [9] that the addition of  $\text{BCl}_3$  to a dichloromethane solution of the hydro-silyl zirconium complex afforded the chloro-silyl derivative  $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeCl-}\eta^1\text{-N}^t\text{Bu})\text{Cl}_2]$  in high yield. This result indicates that there is no interaction between the boron Lewis acid and the amido-N probably due to the low nucleophilic character imposed by the strong  $\pi$ -donation to the zirconium centre. Under these conditions preferential attack to the Si–H bond occurs leading to the chlorinated Si–Cl derivative with elimination of  $\text{BHCl}_2$  or its disproportionation products [21].

In contrast, preferential reaction at the Si– $\text{N}^t\text{Bu}$ –Ti bridging group was observed when different chlorinating agents were used. So, the reaction of **8** with one equivalent of  $\text{TiCl}_4$  in refluxing toluene gave complex **2**, recovered after filtration to remove the resulting insoluble imido-titanium product [22], which could not be identified. The same transformation was observed by  $^1\text{H-NMR}$  spectroscopy when **8** was reacted in  $\text{C}_6\text{D}_6$  with increasing amounts of a 1 M  $\text{Et}_2\text{O}$  solution of  $\text{HCl}$ . Initially mixtures of **8** and **2** were observed until **8** was totally transformed into **2** when a 1/3 molar ratio of  $\text{HCl}$  was added.

However, unexpected behaviour was observed when dichloromethane solutions of the titanium complex **8** were reacted with  $\text{BCl}_3$ . Addition of one equivalent of  $\text{BCl}_3$  at  $-78^\circ\text{C}$  and slow heating to room temperature resulted in partial loss of the amido group of **8** to give complex **9** as the major reaction product (ca. 70%) in a mixture always containing smaller amounts of complexes **2** (ca. 15%) and **3** (ca. 15%) (see Scheme 5). This result demonstrates that the nucleophilic character of the amido-N causes its interaction with the Lewis acid  $\text{BCl}_3$ , which at room temperature cleaves and chlor-

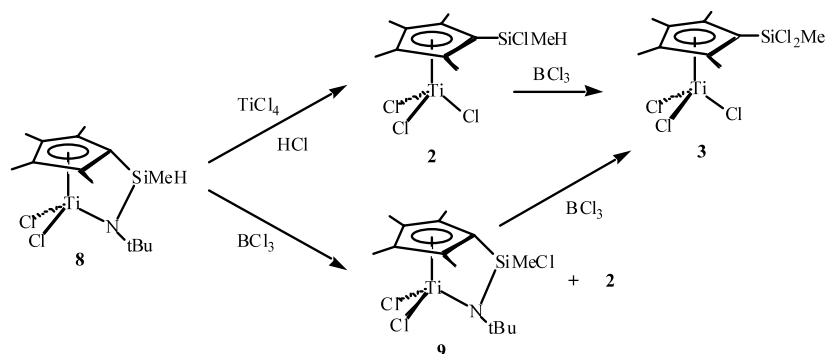
inates partially both Si–N and Ti–N bonds of complex **8** to give **2** and of complex **9** to give **3**. However, under these conditions preferential chlorination of the Si–H bond takes place to give a higher yield of the chlorosilyl complex **9**. Complex **9** was isolated as a pure compound after appropriate work up of this reaction mixture.

When no amido group was present, clean conversion of Si–H into Si–Cl by reaction with  $\text{BCl}_3$  occurred. So, further reaction of the mono-cyclopentadienyl titanium complex **2** with one equivalent of  $\text{BCl}_3$  afforded the dichlorosilyl complex **3** after heating the dichloromethane solution at  $145^\circ\text{C}$  in a Teflon-sealed Schlenk for 1 day.

As shown in Scheme 4 methylation of complex **8** with two equivalent of  $\text{MgClMe}$  in diethyl ether at room temperature afforded the dimethyl complex  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeH-}\eta^1\text{-N}^t\text{Bu})\text{Me}_2]$  **10**, isolated as an orange oil in 62% yield and characterized by elemental analysis and NMR spectroscopy. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of complex **10** follow the pattern described for the precursor dichloro complex **8** with two additional singlets due to the two non-equivalent methyl-titanium groups.

### 3. Conclusions

The *ansa*-cyclopentadienyl-chlorosilyl- $\eta$ -amido titanium complex  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4\text{SiMeCl}(\eta^1\text{-N}^t\text{Bu})\}\text{Cl}_2]$  can be isolated either by amidation with  $\text{LiNH}^t\text{Bu}$  of the dichlorosilyl-cyclopentadienyl titanium trichloride  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeCl}_2)\text{Cl}_3]$  or by chlorination of the Si–H bond of the *ansa*-hydrosilyl- $\eta$ -amido derivative  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4\text{SiMeH}(\eta^1\text{-N}^t\text{Bu})\}\text{Cl}_2]$  with one equivalent of  $\text{BCl}_3$ . However, in this reaction partial deamidation of the resulting *ansa*-chlorosilyl- $\eta$ -amido and the starting *ansa*-hydrosilyl- $\eta$ -amido compounds, gives small amounts of the corresponding trichloro titanium  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeCl}_2)\text{Cl}_3]$  and  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeHCl})\text{Cl}_3]$  compounds, respectively. Further chlorination of the last compound with  $\text{BCl}_3$  to give  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMeCl}_2)\text{Cl}_3]$  is almost quantitative when its



Scheme 5.

CH<sub>2</sub>Cl<sub>2</sub> solution is heated to 145 °C in a Teflon-sealed Schlenk tube. Similar deamidation also occurred with other chlorinating agents (TiCl<sub>4</sub>, HCl). Straightforward methylation of the precursor mono-cyclopentadienyl and *ansa*-silyl-η-amido titanium compounds allows the corresponding methyl complexes to be isolated.

## 4. Experimental

### 4.1. General comments

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox MBraun model 150B-G. Solvents were purified by distillation under argon before use by employing the appropriate drying agent (sodium for toluene, sodium–potassium alloy for hexane and pentane, phosphorus pentoxide for dichloromethane and sodium-benzophenone for diethyl ether and THF). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. LiNH<sup>t</sup>Bu was quantitatively prepared by reaction of NH<sub>2</sub><sup>t</sup>Bu with Li<sup>t</sup>Bu in hexane. TiCl<sub>4</sub> (Fluka) was distilled before use. C<sub>5</sub>Me<sub>4</sub>H<sub>2</sub> (Norquay), Li<sup>t</sup>Bu (Aldrich), SiMeHCl<sub>2</sub> (ABCR), BCl<sub>3</sub> (Aldrich), HCl (Aldrich) and MgClMe (Aldrich) were purchased from commercial sources and used without further purification. Li(C<sub>5</sub>Me<sub>4</sub>H) [23], C<sub>5</sub>Me<sub>4</sub>H(SiMe<sub>3</sub>) [10], (C<sub>5</sub>Me<sub>4</sub>)(SiMeCl<sub>2</sub>)(SiMe<sub>3</sub>) [9], [Ti(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Cl<sub>3</sub>] [12], Li<sub>2</sub>[C<sub>5</sub>Me<sub>4</sub>SiMeH(N<sup>t</sup>Bu)] [9] and TiCl<sub>3</sub>(THF)<sub>3</sub> [24] were prepared according to the literature procedures. C, H and N microanalyses were performed on a Perkin–Elmer 240B and/or Heraeus – CHN–O– rapid microanalyzer. NMR spectra, measured at 25 °C, were recorded on a Varian Unity FT-300 (<sup>1</sup>H-NMR at 300 MHz, <sup>13</sup>C-NMR at 75 MHz and <sup>29</sup>Si-NMR at 59.6 MHz). In the <sup>1</sup>H-NMR spectra, the chemical shifts refer to the residual proton signal of the solvent (δ = 7.24 ppm for chloroform and δ = 7.15 ppm for benzene), in <sup>13</sup>C-NMR spectra to the solvent signal (δ = 77.0 ppm for chloroform-d<sub>1</sub> and δ = 128.0 ppm for benzene-d<sub>6</sub>) and in <sup>29</sup>Si-NMR spectra to the resonance of external TMS (δ = 0.0 ppm).

### 4.2. Synthesis of (C<sub>5</sub>Me<sub>4</sub>)(SiMeHCl)(SiMe<sub>3</sub>) (1)

A 1.6 M solution of Li<sup>t</sup>Bu in hexane (15 ml, 24 mmol) was added dropwise, at 0 °C, to a solution of C<sub>5</sub>Me<sub>4</sub>H(SiMe<sub>3</sub>) (4.66 g, 24 mmol) in THF (250 ml). The reaction mixture was slowly warmed to room temperature (r.t.) and stirred for 16 h. After THF removal, the residue was washed with pentane (2 × 50 ml) to give Li[C<sub>5</sub>Me<sub>4</sub>(SiMe<sub>3</sub>)] as a white solid. Methyl-dichlorosilane (3.00 ml, 29 mmol) was added all at once to a solution of Li[C<sub>5</sub>Me<sub>4</sub>(SiMe<sub>3</sub>)] (4.80 g, 24 mmol) in THF (125 ml) at –78 °C. The reaction mixture was

slowly warmed to r.t. and was stirred for 20 h. After THF removal, the residue was extracted into pentane (2 × 50 ml). The pentane solvent was removed under vacuum to give **1** as a pale yellow liquid (6.08 g, 22.3 mmol, 93% yield). Anal. Calc. for C<sub>13</sub>H<sub>25</sub>Si<sub>2</sub>Cl: C, 57.20; H, 9.23. Found: C, 57.48; H, 9.25%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ –0.12 (d, 3H, SiMeHCl, *J* = 3 Hz), 0.01 (s, 9H, SiMe<sub>3</sub>), 1.81 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 1.83 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 1.97 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 2.04 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 4.97 (q, 1H, SiMeHCl, *J* = 3 Hz). <sup>13</sup>C{<sup>1</sup>H}-NMR (75 MHz, CDCl<sub>3</sub>, 25 °C): δ –3.8 (SiMeHCl), –1.0 (SiMe<sub>3</sub>), 11.3, 11.4, 14.0, 14.6 (C<sub>5</sub>Me<sub>4</sub>), 55.5 (C<sub>ipso</sub>, C<sub>5</sub>Me<sub>4</sub>), 129.9, 133.3, 138.5, 139.5 (C<sub>5</sub>Me<sub>4</sub>).

### 4.3. Synthesis of [Ti(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>SiMeHCl)Cl<sub>3</sub>] (2)

#### 4.3.1. Method (a)

A solution of **1** (6.00 g, 22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was added dropwise to a solution of TiCl<sub>4</sub> (2.5 ml, 22.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 ml) at r.t. The reaction mixture was refluxed for 3 days. The volatiles were removed under reduced pressure to yield an orange solid which was washed with hexane (2 × 25 ml). The orange solid was dried under vacuum and was characterized as **2** (6.07 g, 17.1 mmol, 78% yield). Recrystallization from CH<sub>2</sub>Cl<sub>2</sub> at –30 °C gave orange–red single crystals for X-ray diffraction. Anal. Calc. for C<sub>10</sub>H<sub>16</sub>SiCl<sub>4</sub>Ti: C, 33.93; H, 4.56. Found: C, 34.28; H, 4.73%. <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 0.73 (d, 3H, SiMeHCl, *J* = 3.6 Hz), 1.69 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 1.78 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 2.16 (2s, 6H, C<sub>5</sub>Me<sub>4</sub>), 5.52 (q, 1H, SiMeHCl, *J* = 3.6 Hz). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ 0.96 (d, 3H, SiMeHCl, *J* = 3.3 Hz), 2.31 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 2.38 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 2.52 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 2.54 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 5.52 (q, 1H, SiMeHCl, *J* = 3.3 Hz). <sup>13</sup>C{<sup>1</sup>H}-NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.7 (SiMeHCl), 13.7, 14.1, 16.5, 17.2 (C<sub>5</sub>Me<sub>4</sub>), 128.8 (C<sub>ipso</sub>, C<sub>5</sub>Me<sub>4</sub>), 141.1, 142.0, 143.6, 145.0 (C<sub>5</sub>Me<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (75 MHz, CDCl<sub>3</sub>, 25 °C): δ 1.3 (SiMeHCl), 13.8, 14.2, 16.4, 17.0 (C<sub>5</sub>Me<sub>4</sub>), 129.1 (C<sub>ipso</sub>, C<sub>5</sub>Me<sub>4</sub>), 141.4, 142.2, 143.9, 145.2 (C<sub>5</sub>Me<sub>4</sub>). <sup>29</sup>Si{<sup>1</sup>H}-NMR (59.6 MHz, CDCl<sub>3</sub>, 25 °C): δ –8.29.

#### 4.3.2. Method (b)

TiCl<sub>4</sub> (88 μl, 0.80 mmol) was added to a solution of **8** (0.28 g, 0.79 mmol) in toluene (35 ml). The reaction mixture was refluxed overnight affording a red solution and a dark red residue. The volatiles were removed under reduced pressure to yield a dark red solid which was extracted into CH<sub>2</sub>Cl<sub>2</sub> (2 × 25 ml). After filtration, the solvent was removed from the orange solution under vacuum to give **2** as an orange solid (0.26 g, 0.73 mmol, 92% yield).

#### 4.3.3. Method (c) NMR tube

A solution of **8** (0.011 g,  $3.1 \times 10^{-2}$  mmol) in  $C_6D_6$  (0.6 ml) in a Teflon-sealed NMR tube was treated with one equivalent of a 1 M solution of HCl (31  $\mu$ l,  $3.1 \times 10^{-2}$  mmol) in diethyl ether to give a mixture of **8** and **2** in a molar ratio 1.8/1. This molar ratio decreased to 1/1.3 after addition of a second equivalent and finally, a third equivalent of HCl gave **2** as the unique reaction product. Simultaneous formation of insoluble  $NH_2Bu \cdot HCl$  was observed.

#### 4.4. Synthesis of $[Ti(\eta^5-C_5Me_4SiMeCl_2)Cl_3]$ (**3**)

##### 4.4.1. Method (a)

A solution of  $(C_5Me_4)(SiMeCl_2)(SiMe_3)$  (7.68 g, 25 mmol) in  $CH_2Cl_2$  (20 ml) was added dropwise to a solution of  $TiCl_4$  (2.8 ml, 25.5 mmol) in  $CH_2Cl_2$  (20 ml) at r.t. The reaction mixture was refluxed for 4 days. The volatiles were removed under reduced pressure to yield a dark orange solid which was washed with pentane ( $2 \times 25$  ml). The orange solid was dried under vacuum and was characterized as **3** (7.77 g, 20 mmol, 80% yield). Anal. Calc. for  $C_{10}H_{15}SiCl_5Ti$ : C, 30.92; H, 3.89. Found: C, 30.93; H, 3.93%.  $^1H$ -NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta$  0.96 (s, 3H,  $SiMeCl_2$ ), 1.70 (s, 6H,  $C_5Me_4$ ), 2.23 (s, 6H,  $C_5Me_4$ ).  $^1H$ -NMR (300 MHz,  $CDCl_3$ , 25 °C):  $\delta$  1.28 (s, 3H,  $SiMeCl_2$ ), 2.34 (s, 6H,  $C_5Me_4$ ), 2.60 (s, 6H,  $C_5Me_4$ ).  $^{13}C\{^1H\}$ -NMR (75 MHz,  $C_6D_6$ , 25 °C):  $\delta$  8.8 ( $SiMeCl_2$ ), 13.6, 17.1 ( $C_5Me_4$ ), 127.3 ( $C_{ipso}$ ,  $C_5Me_4$ ), 141.4, 143.4 ( $C_5Me_4$ ).  $^{13}C\{^1H\}$ -NMR (75 MHz,  $CDCl_3$ , 25 °C):  $\delta$  8.8 ( $SiMeCl_2$ ), 14.1, 17.2 ( $C_5Me_4$ ), 127.8 ( $C_{ipso}$ ,  $C_5Me_4$ ), 141.6, 143.6 ( $C_5Me_4$ ).  $^{29}Si\{^1H\}$ -NMR (59.6 MHz,  $CDCl_3$ , 25 °C):  $\delta$  11.93.

##### 4.4.2. Method (b)

A solution of **2** (0.50 g, 1.41 mmol) in  $CH_2Cl_2$  (5 ml) was treated with one equivalent of a 1 M solution of  $BCl_3$  in heptane (1.50 ml, 1.5 mmol). The reaction mixture was warmed at 145 °C for 1 day in a Teflon-sealed Schlenk. The volatiles were removed under vacuum to yield **3** as an orange solid (0.53 g, 1.36 mmol, 97% yield).

#### 4.5. Synthesis of $[Ti(\eta^5-C_5Me_4SiMe_3)Cl_3]$ (**4**)

A solution of  $(C_5Me_4)(SiMe_3)_2$  (4.56 g, 17.1 mmol) in  $CH_2Cl_2$  (20 ml) was added dropwise to a solution of  $TiCl_4$  (1.9 ml, 17.3 mmol) in  $CH_2Cl_2$  (20 ml) at 0 °C. The reaction mixture was stirred for 20 h. The volatiles were removed under reduced pressure to yield a dark orange solid which was washed with hexane ( $2 \times 25$  ml). The orange solid was dried under vacuum and was characterized as **4** (4.16 g, 12 mmol, 70% yield). Recrystallization from  $CH_2Cl_2$  at  $-30$  °C gave orange–red single crystals for X-ray diffraction. Anal. Calc. for  $C_{12}H_{21}SiCl_3Ti$ : C, 41.46; H, 6.09. Found: C, 41.18; H,

5.94%.  $^1H$ -NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta$  0.31 (s, 9H,  $SiMe_3$ ), 1.85 (s, 6H,  $C_5Me_4$ ), 2.20 (s, 6H,  $C_5Me_4$ ).  $^1H$ -NMR (300 MHz,  $CDCl_3$ , 25 °C):  $\delta$  0.41 (s, 9H,  $SiMe_3$ ), 2.32 (s, 6H,  $C_5Me_4$ ), 2.52 (s, 6H,  $C_5Me_4$ ).  $^{13}C\{^1H\}$ -NMR (75 MHz,  $CDCl_3$ , 25 °C):  $\delta$  1.3 ( $SiMe_3$ ), 14.2, 17.6 ( $C_5Me_4$ ), 140.7 ( $C_{ipso}$ ,  $C_5Me_4$ ), 142.0, 144.5 ( $C_5Me_4$ ).

#### 4.6. Synthesis of $[Ti(\eta^5-C_5Me_4SiMe_2H)ClMe_2]$ (**5**)

A 3 M solution of  $MgClMe$  in THF (0.96 ml, 2.88 mmol) was added to a solution of **2** (0.34 g, 0.96 mmol) in diethyl ether (50 ml) cooled at  $-78$  °C. The reaction mixture was slowly warmed to r.t. and then stirred for 12 h. The volatiles were removed under reduced pressure and the residue was extracted into pentane ( $2 \times 25$  ml). After filtration, solvent was removed under vacuum to give an oily residue containing a mixture of **5** and **6** in a 4/3 molar ratio, together with small amounts of other unidentified chloro-alkyl compounds. This mixture is further transformed to give **5** as a yellow oil after 5 days (0.17 g, 0.58 mmol, 60% yield).  $^1H$ -NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta$  0.33 (d, 6H,  $SiMe_2H$ ,  $J = 3.9$  Hz), 0.81 (s, 6H,  $TiMe_2Cl$ ), 1.89 (s, 6H,  $C_5Me_4$ ), 2.15 (s, 6H,  $C_5Me_4$ ), 4.76 (h, 1H,  $SiMe_2H$ ,  $J = 3.9$  Hz).  $^{13}C\{^1H\}$ -NMR (75 MHz,  $C_6D_6$ , 25 °C):  $\delta$   $-2.1$  ( $SiMe_2H$ ), 11.9, 14.4 ( $C_5Me_4$ ), 54.9 ( $TiMe_2Cl$ ), 117.6 ( $C_{ipso}$ ,  $C_5Me_4$ ), 127.8, 129.0 ( $C_5Me_4$ ).

#### 4.7. Synthesis of $[Ti(\eta^5-C_5Me_4SiMe_2H)Me_3]$ (**6**)

A 3 M solution of  $MgClMe$  in THF (1.6 ml, 4.80 mmol) was added to a solution of **2** (0.39 g, 1.09 mmol) in diethyl ether (45 ml) cooled to  $-78$  °C. The reaction mixture was slowly warmed to r.t. and then stirred for 16 h. The volatiles were removed under reduced pressure and the residue was extracted into pentane ( $2 \times 25$  ml). After filtration, solvent was removed under vacuum to give **6** as a yellow waxy solid (0.23 g, 0.85 mmol, 78% yield). Anal. Calc. for  $C_{14}H_{28}SiTi$ : C, 61.74; H, 10.36. Found: C, 60.77; H, 10.30%.  $^1H$ -NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta$  0.23 (d, 6H,  $SiMe_2H$ ,  $J = 3.9$  Hz), 1.14 (s, 9H,  $TiMe_3$ ), 1.68 (s, 6H,  $C_5Me_4$ ), 1.95 (s, 6H,  $C_5Me_4$ ), 4.61 (h, 1H,  $SiMe_2H$ ,  $J = 3.9$  Hz).  $^{13}C\{^1H\}$ -NMR (75 MHz,  $C_6D_6$ , 25 °C):  $\delta$   $-2.1$  ( $SiMe_2H$ ), 12.0, 14.5 ( $C_5Me_4$ ), 62.7 ( $TiMe_3$ ), 118.0 ( $C_{ipso}$ ,  $C_5Me_4$ ), 127.8, 128.8 ( $C_5Me_4$ ).

#### 4.8. Synthesis of $[Ti(\eta^5-C_5Me_4SiMe_3)Me_3]$ (**7**)

##### 4.8.1. Method (a)

A 3 M solution of  $MgClMe$  in THF (2.0 ml, 6.0 mmol) was added to a solution of **3** (0.46 g, 1.18 mmol) in diethyl ether (45 ml) cooled at  $-78$  °C. The reaction mixture was slowly warmed to r.t. and then stirred for 18 h. The volatiles were removed under reduced pressure

and the residue was extracted into pentane (40 ml). After filtration, solvent was removed under vacuum to give **7** as a yellow solid (0.24 g, 0.84 mmol, 71% yield). Anal. Calc. for  $C_{15}H_{30}SiTi$ : C, 62.91; H, 10.56. Found: C, 62.60; H, 10.88%.  $^1H$ -NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta$  0.24 (s, 9H,  $SiMe_3$ ), 1.14 (s, 9H,  $TiMe_3$ ), 1.68 (s, 6H,  $C_5Me_4$ ), 1.96 (s, 6H,  $C_5Me_4$ ).  $^{13}C\{^1H\}$ -NMR (75 MHz,  $C_6D_6$ , 25 °C):  $\delta$  1.7 ( $SiMe_3$ ), 11.9, 15.0 ( $C_5Me_4$ ), 62.5 ( $TiMe_3$ ), 121.6 ( $C_{ipso}$ ,  $C_5Me_4$ ), 127.9, 128.5 ( $C_5Me_4$ ).

#### 4.8.2. Method (b)

A 3 M solution of  $MgClMe$  in THF (1.5 ml, 4.32 mmol) was added to a solution of **4** (0.50 g, 1.44 mmol) in diethyl ether (50 ml) cooled at  $-78$  °C. The reaction mixture was slowly warmed to r.t. and then stirred for 18 h. The volatiles were removed under reduced pressure and the residue was extracted into pentane ( $2 \times 25$  ml). After filtration, solvent was removed under vacuum to give **7** as a yellow solid (0.32 g, 1.12 mmol, 78% yield).

#### 4.9. Synthesis of $[Ti(\eta^5-C_5Me_4SiMeH-\eta^1-N^tBu)Cl_2]$ (**8**)

##### 4.9.1. Method (a)

Toluene (25 ml) was added to a mixture of **2** (0.35 g, 0.99 mmol) and  $LiNH^tBu$  (0.16 g, 1.98 mmol). The reaction mixture was warmed at 110 °C for 12 h in a Teflon-sealed Schlenk. After cooling to r.t., the solution was filtered through Celite and the filtrate was removed under vacuum to give **8** as a yellow solid (0.32 g, 0.91 mmol, 92% yield). Anal. Calc. for  $C_{14}H_{25}SiCl_2NTi$ : C, 47.47; H, 7.11; N, 3.95. Found: C, 47.59; H, 7.11; N, 3.91%.  $^1H$ -NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta$  0.45 (d, 3H,  $SiMe$ ,  $J = 3.3$  Hz), 1.41 (s, 9H,  $N^tBu$ ), 1.96 (2s, 6H,  $C_5Me_4$ ), 1.98 (s, 3H,  $C_5Me_4$ ), 2.10 (s, 3H,  $C_5Me_4$ ), 5.60 (q, 1H,  $SiH$ ,  $J = 3.3$  Hz).  $^1H$ -NMR (300 MHz,  $CDCl_3$ , 25 °C):  $\delta$  0.78 (d, 3H,  $SiMe$ ,  $J = 3.3$  Hz), 1.41 (s, 9H,  $N^tBu$ ), 2.14 (s, 3H,  $C_5Me_4$ ), 2.17 (s, 3H,  $C_5Me_4$ ), 2.23 (2s, 6H,  $C_5Me_4$ ), 5.61 (q, 1H,  $SiH$ ,  $J = 3.3$  Hz).  $^{13}C\{^1H\}$ -NMR (75 MHz,  $C_6D_6$ , 25 °C):  $\delta$  2.0 ( $SiMe$ ), 12.8, 13.0, 14.7, 15.9 ( $C_5Me_4$ ), 32.0 ( $N^tBu$ ), 61.9 ( $C_{ipso}$ ,  $N^tBu$ ), 100.8 ( $C_{ipso}$ ,  $C_5Me_4$ ), 138.3 (2), 140.7, 140.9 ( $C_5Me_4$ ).  $^{13}C\{^1H\}$ -NMR (75 MHz,  $CDCl_3$ , 25 °C):  $\delta$  2.3 ( $SiMe$ ), 13.3, 13.5, 14.9, 16.2 ( $C_5Me_4$ ), 32.1 ( $N^tBu$ ), 62.1 ( $C_{ipso}$ ,  $N^tBu$ ), 100.6 ( $C_{ipso}$ ,  $C_5Me_4$ ), 138.1, 138.2, 140.7, 140.9 ( $C_5Me_4$ ).  $^{29}Si\{^1H\}$ -NMR (59.6 MHz,  $CDCl_3$ , 25 °C):  $\delta$   $-40.13$ .

##### 4.9.2. Method (b)

THF (100 ml) at  $-78$  °C was added to a mixture of  $Li_2[C_5Me_4SiMeH(N^tBu)]$  (2.89 g, 11.6 mmol) and  $TiCl_3(THF)_3$  (4.30 g, 11.6 mmol) cooled to  $-78$  °C. After warming to r.t., the reaction mixture was stirred for 1 h and treated with solid  $PbCl_2$  (3.22 g, 11.6 mmol). After stirring for 15 h, the volatiles were removed under reduced pressure and the residue was stripped of

remaining THF by stirring in pentane (25 ml) which was subsequently pumped off. The residue was then extracted into hexane ( $2 \times 100$  ml). After filtration, the solution was concentrated and cooled at  $-30$  °C to give a yellow solid characterized as **8** (2.99 g, 8.44 mmol, 73% yield).

#### 4.10. Synthesis of $[Ti(\eta^5-C_5Me_4SiMeCl-\eta^1-N^tBu)Cl_2]$ (**9**)

##### 4.10.1. Method (a)

A solution of  $LiNH^tBu$  (0.16 g, 2.02 mmol) in diethyl ether (10 ml) was added to a solution of **3** (0.38 g, 0.98 mmol) in diethyl ether (50 ml) cooled to  $-78$  °C. The reaction mixture was slowly warmed to r.t. and stirred for 18 h. The volatiles were removed under reduced pressure and the residue was extracted into pentane ( $2 \times 50$  ml). After filtration, the solution was concentrated to 5 ml and cooled at  $-30$  °C to give an orange solid characterized as **9** (0.15 g, 0.40 mmol, 41% yield). Anal. Calc. for  $C_{14}H_{24}SiNTiCl_3$ : C, 43.26; H, 6.22; N, 3.60. Found: C, 43.62; H, 6.42; N, 4.04.  $^1H$ -NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta$  0.71 (s, 3H,  $SiMeCl$ ), 1.49 (s, 9H,  $N^tBu$ ), 1.86 (s, 3H,  $C_5Me_4$ ), 1.89 (s, 3H,  $C_5Me_4$ ), 1.92 (s, 3H,  $C_5Me_4$ ), 2.26 (s, 3H,  $C_5Me_4$ ).  $^1H$ -NMR (300 MHz,  $CDCl_3$ , 25 °C):  $\delta$  1.03 (s, 3H,  $SiMeCl$ ), 1.47 (s, 9H,  $N^tBu$ ), 2.16 (s, 3H,  $C_5Me_4$ ), 2.26 (s, 3H,  $C_5Me_4$ ), 2.27 (s, 3H,  $C_5Me_4$ ), 2.28 (s, 3H,  $C_5Me_4$ ).  $^{13}C\{^1H\}$ -NMR (75 MHz,  $C_6D_6$ , 25 °C):  $\delta$  8.9 ( $SiMe$ ), 13.1, 13.4, 16.1, 16.4 ( $C_5Me_4$ ), 32.7 ( $N^tBu$ ), 62.5 ( $C_{ipso}$ ,  $N^tBu$ ), 104.8 ( $C_{ipso}$ ,  $C_5Me_4$ ), 136.7, 138.9, 139.0, 142.8 ( $C_5Me_4$ ).  $^{13}C\{^1H\}$ -NMR (75 MHz,  $CDCl_3$ , 25 °C):  $\delta$  8.8 ( $SiMe$ ), 13.2, 13.4, 16.1 (2) ( $C_5Me_4$ ), 32.4 ( $N^tBu$ ), 62.4 ( $C_{ipso}$ ,  $N^tBu$ ), 104.7 ( $C_{ipso}$ ,  $C_5Me_4$ ), 136.8, 139.0, 139.2, 143.0 ( $C_5Me_4$ ).  $^{29}Si\{^1H\}$ -NMR (59.6 MHz,  $C_6D_6$ , 25 °C):  $\delta$   $-22.76$ .

##### 4.10.2. Method (b)

A solution of **8** (0.18 g, 0.51 mmol) in  $CH_2Cl_2$  (10 ml) cooled to  $-78$  °C was treated with one equivalent of a 1 M solution of  $BCl_3$  in heptane (0.55 ml, 0.55 mmol). The reaction mixture was slowly warmed to r.t. and stirred for 18 h. The solution was filtered through Celite and the filtrate was removed under vacuum to give a light orange solid characterized as a mixture containing a molar ratio 5/1/1 of **9**, **2** and **3**. Compound **9** was isolated in 52% yield after recrystallization from pentane.

#### 4.11. Synthesis of $[Ti(\eta^5-C_5Me_4SiMeH-\eta^1-N^tBu)Me_2]$ (**10**)

A 3 M solution of  $MgClMe$  in THF (1.1 ml, 3.3 mmol) was added to a solution of **8** (0.58 g, 1.64 mmol) in diethyl ether (50 ml) cooled to  $-78$  °C. The reaction mixture was slowly warmed to r.t. and then stirred for 16 h. The volatiles were removed under reduced pressure and the residue was extracted into hexane ( $2 \times 50$  ml).



After filtration, solvent was removed under vacuum to give **10** as an orange oil (0.32 g, 1.02 mmol, 62% yield). Anal. Calc. for  $C_{16}H_{31}SiNTi$ : C, 61.32; H, 9.97; N, 4.47. Found: C, 60.53; H, 9.87; N, 4.47%.  $^1H$ -NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta$  0.47 (d, 3H, SiMe,  $J = 3$  Hz), 0.51 (s, 3H, TiMe), 0.54 (s, 3H, TiMe), 1.56 (s, 9H,  $N^t$ Bu), 1.82 (s, 3H,  $C_5Me_4$ ), 1.94 (2s, 6H,  $C_5Me_4$ ), 1.96 (s, 3H,  $C_5Me_4$ ), 5.49 (q, 1H, SiH,  $J = 3$  Hz).  $^{13}C\{^1H\}$ -NMR (75 MHz,  $C_6D_6$ , 25 °C):  $\delta$  2.9 (SiMe), 11.8, 12.0, 13.5, 14.7 ( $C_5Me_4$ ), 33.9 ( $N^t$ Bu), 51.3, 52.5 (TiMe), 57.4 ( $C_{ipso}$ ,  $N^t$ Bu), 94.7 ( $C_{ipso}$ ,  $C_5Me_4$ ), 129.8, 130.1, 133.9, 134.1 ( $C_5Me_4$ ).

#### 4.12. X-ray data collection and structure determination

Crystal data and details of the structure determination are presented in Table 2. Suitable single crystals for the X-ray diffraction studies were grown by cooling a concentrated solution of **2** (**4**) in  $CH_2Cl_2$ . A clear orange–red fragment (needle)  $0.08 \times 0.20 \times 0.36$  mm ( $0.05 \times 0.05 \times 0.51$  mm) was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed and sealed. Preliminary examination and data collection were carried out on an area detecting system (KAPPA CCD; NONIUS) at the window of a rotating anode (NONIUS; Fr951) and graphite monochromated Mo– $K_\alpha$  radiation ( $\lambda = 0.71073$  Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 2809

Table 2  
Crystal data and summary of intensity data collection and structure refinement of **2** and **4**

	<b>2</b>	<b>4</b>
Formula	$C_{10}H_{16}Cl_4SiTi$	$C_{12}H_{21}Cl_3SiTi$
Formula weight	353.99	347.60
Color/shape	Orange–red fragment	Orange–red needle
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
$a$ (Å)	6.6553(1)	6.7397(1)
$b$ (Å)	23.8049(3)	24.8834(4)
$c$ (Å)	9.5519(1)	9.8788(2)
$\beta$ (°)	96.2565(5)	98.1940(6)
$V$ (Å <sup>3</sup> )	1504.28(3)	1639.83(5)
$Z$	4	4
$D_{calc}$ (g cm <sup>-3</sup> )	1.563	1.408
$\mu$ (mm <sup>-1</sup> )	1.331	1.062
Diffraction	Nonius kappaCCD	Nonius kappaCCD
$\lambda$ (Å)	Mo– $K_\alpha$ 0.71073	Mo– $K_\alpha$ 0.71073
$T$ (K)	123	173
Rflns. coll.	23 299	15 420
Independent reflections	2744	2980
Reflections observed ( $I > 2\sigma(I)$ )	2433	2537
Parameters refined	155	238
$R_1$ (observed/all data)	0.0233/0.0295	0.0280/0.0384
$wR_2$ (observed/all data)	0.0537/0.0564	0.0575/0.0612
Goodness-of-fit (observed/all data)	1.036/1.036	1.050/1.050

(3000) reflections. Data collection were performed at 123 (173) K within a  $\theta$ -range of  $1.71^\circ < \theta < 25.35^\circ$  ( $2.65^\circ < \theta < 25.30^\circ$ ); 7 (5) sets were measured in rotation scan modus with  $\Delta\varphi/\Delta\Omega = 1.0^\circ$ . A total number of 23 299 (15 420) intensities were integrated. Raw data were corrected for Lorentz, polarization, decay and absorption effects. After merging ( $R_{int} = 0.036$  (0.037)) a sum of 2744 (2980) independent reflections remained and were used for all calculations.

The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. For compound **2** all hydrogen atoms bound to the carbon atoms were calculated in ideal positions using the SHELXL riding model. The hydrogen atom at the Si-atom was found and allowed to refine freely. For compound **4** all hydrogen atoms were found in the difference Fourier maps and refined freely. Full-matrix least-squares refinements with 155 (238) parameters were carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$  with SHELXL-97 weighting scheme and stopped at shift/err < 0.001. In compound **2** a disorder 0.728(2):0.272(2) of the –SiHCIME group could be resolved clearly. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography. All calculations were performed on a DEC 3000 AXP workstation and an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SIR92, and SHELXL-97 [25].

## 5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-212781 (**2**) and CCDC-212780 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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