

Reactivity of chlorodimethylsilyl- η^5 -cyclopentadienyltrichlorotitanium with nitrogen based donors. X-ray molecular structure of $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\eta^1\text{-N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]\}\text{Cl}_2]$

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Abstract

This paper reports the reactivity of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_3]$, **1** towards nitrogen based donor reagents. Complex **1** reacts with lithium benzamidinato $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$ to afford $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}_2]$ **2** and with lithium amide LiNMe_2 to produce $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{NMe}_2)(\text{NMe}_2)_3]$ **3**. The latter compound was converted into the dihalide derivatives $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{NMe}_2)(\text{NMe}_2)\text{X}_2]$ [$\text{X} = \text{Cl}$ (**4**) and Br (**5**)] by reaction with SiMe_3X ($\text{X} = \text{Cl}$ or Br , respectively). The constrained geometry derivatives $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-NR})\}\text{Cl}_2]$ ($\text{R} = \text{C}_6\text{H}_5$ **6**, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ **7** and 2-Me-6- i -Pr- C_6H_3 **8**) have been synthesized by treatment of **1** with the corresponding primary aryl amines H_2NR . Complex **7** was readily converted into the dialkyl and diamido compounds $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\eta^1\text{-N}(\text{C}_6\text{H}_3\text{Me}_2)]\}\text{X}_2]$ ($\text{X} = \text{Me}$ (**9**), CH_2Ph (**10**), CH_2SiMe_3 (**11**) or NMe_2 (**13**)) by metathesis using Grignard or organolithium reagents and into the monoalkyl derivative $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\eta^1\text{-N}(\text{C}_6\text{H}_3\text{Me}_2)]\}\text{MeCl}]$ (**12**) by reaction with AlMe_3 . The molecular structure of complex **7** $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\eta^1\text{-N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]\}\text{Cl}_2]$ was established by X-ray crystallography. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Amido-silylcyclopentadienyl; Amidotitanium; Alkyltitanium

1. Introduction

The organometallic chemistry of Ti(IV) is dominated by complexes with ancillary cyclopentadienyl (Cp) ligands [1]. More recently, there has been considerable interest in the use of alternative ligands either with or in place of the Cp moieties. Replacement of one of the Cp rings in dicyclopentadienyl derivatives by a less electron donating and less sterically demanding anionic ligand of the same charge allows the investigation of its influence on the chemical reactivity and catalytic activity of the metal center.

In particular, the use of nitrogen based donors is receiving considerable attention for both synthetic and catalytic purposes. In addition to the amido chemistry [2], research effort has been devoted to the synthesis of pendant nitrogen functionalized Cp complexes and constrained geometry derivatives of Group 4 metals [3,4].

As part of our current research, we were interested in the synthesis of 12- and 14-electron Cp Group 4 metal complexes in order to compare their reactivity with the analogous 16-electron dicyclopentadienyl derivatives. We herein report the synthesis and characterization of a number of monocyclopentadienyl titanium complexes with a second ancillary ligand in their coordination environment in which the new ligand can be either linked or unlinked to the Cp group. The starting material for our investigations was $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_3]$, **1** [5] which has two reactive Ti–Cl and Si–Cl bonds.

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¹ X-ray diffraction studies.

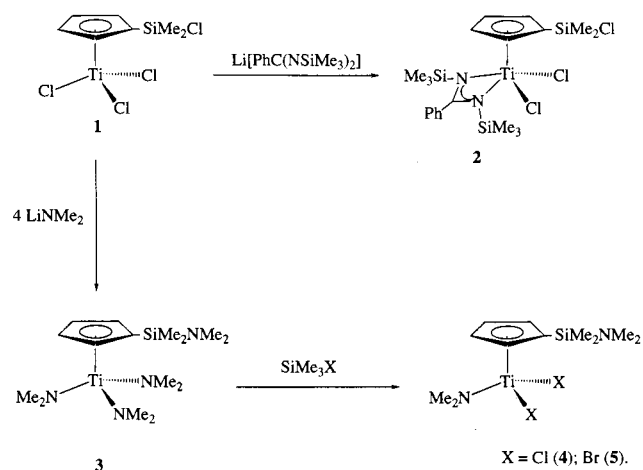
2. Results and discussion

2.1. Synthesis and NMR characterization

The reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_3]$ **1** with one equivalent of lithium benzamidinato $\text{Li}[\text{PhC}(\text{NSiMe}_3)_2]$ in toluene afforded, after extraction into hot toluene, the corresponding benzamidinato complex $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}_2]$ **2** as red crystals in ca. 50% isolated yield. Complex **2** is scarcely soluble in hexane and diethyl ether, soluble in hot toluene and very soluble in THF and chlorinated solvents. Compound **2** is moisture sensitive and decomposes slowly both in solution and in the solid state with elimination of SiMe_3Cl to give unidentified products.

Reaction of complex **1** with four equivalents of LiNMe_2 in diethyl ether at room temperature (r.t.) followed by extraction into hexane afforded the tetraamido derivative $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{NMe}_2)(\text{NMe}_2)_3]$ **3** in high yield as a yellow oil. Using a reported method [6,7], reaction of complex **3** with excess of SiMe_3X ($\text{X} = \text{Cl}$ or Br) resulted in the replacement of only two of the titanium-bonded amido groups by halogen giving the dihalo derivatives $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{NMe}_2)(\text{NMe}_2)_2\text{X}_2]$ ($\text{X} = \text{Cl}$ **4** or Br **5**) in good yields with elimination of two equivalents of volatile $\text{SiMe}_3(\text{NMe}_2)$. Compounds **3–5** are air- and moisture-sensitive but thermally stable. Whilst the oily complex **3** is very soluble in hexane or pentane, the reddish derivatives **4** and **5** are insoluble in hydrocarbon solvents but soluble in toluene and more soluble in THF and chlorinated solvents. Attempts to react compound **1** with one, two or three equivalents of LiNMe_2 led to mixtures of complexes formed by unselective partial substitution of Ti-Cl and Si-Cl bonds.

The NMR data and analytical composition of complexes **2–5** (see Section 4) are consistent with the structures shown in Scheme 1.



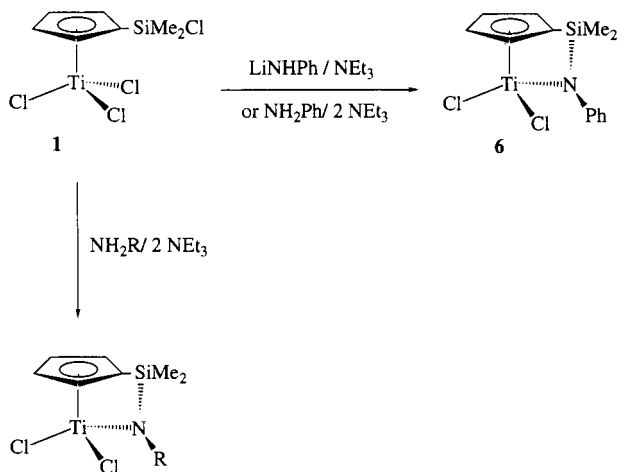
Scheme 1.

The $^1\text{H-NMR}$ spectra of compounds **2–5** show the expected AA'BB' spin system for the four ring protons. The methyl resonances of the Ti-NMe_2 group are shifted down field in relation to the methyl signal due to the silicon-bound amido group. In addition, the chemical shift of the Si-NMe_2 protons is slightly affected by the metal substituents. The assignment of the $^{13}\text{C-NMR}$ spectra for these compounds is also straightforward and consistent with the presence of three different types of ring carbon atoms. The *ipso*-carbon atom signal, when observed, appears at lower field than the other two resonances.

Reactions of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_3]$ **1** with primary aryl amines and their corresponding lithium salts have been studied. Treatment of **1** with one equivalent of NH_2R ($\text{R} = \text{C}_6\text{H}_5$, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ and 2-Me-6-*i*-Pr- C_6H_3) in the presence of two equivalents of NEt_3 gave the corresponding constrained geometry derivatives $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-NR})\}\text{Cl}_2]$, isolated as orange crystals ($\text{R} = \text{C}_6\text{H}_5$ **6** in ca. 30% yield) or as yellow crystals ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ **7** and 2-Me-6-*i*-Pr- C_6H_3 **8** in 90 and 20% yield, respectively), after standard work-up. A slightly better yield (41%) was obtained for compound **6** using the lithium amide $\text{Li}(\text{NPh})$ in the presence of one equivalent of NEt_3 . All attempts to prepare the related 2,6-diiso-propylphenyl derivative failed under these conditions. Complexes **6–8** are thermally stable in C_6D_6 after 24 h at 120°C , but extremely oxygen and moisture sensitive. It is worth noting that compound **6** is the most moisture sensitive; the steric hindrance afforded by the bulkier 2,6-dimethylphenyl or 2-methyl-6-iso-propylphenyl substituents probably impedes the decomposition of **7** and **8**. Compounds **6–8** were scarcely soluble in hexane, soluble in toluene and very soluble in THF and chlorinated solvents. The larger branched aryl ligands give greater solubility than the unsubstituted aryl ligand.

The structures proposed for the new complexes **6–8** are shown in Scheme 2 and their spectroscopic and analytical data are collected in Section 4.

The $^1\text{H-NMR}$ spectra of complexes **6** and **7** show the expected AA'BB' spin system for the C_5H_4 ring protons and one singlet for the SiMe_2 group. The presence of a plane of symmetry is also consistent with the chemical shifts observed for the freely rotating aryl amido substituents (C_6H_5 and 2,6- $\text{Me}_2\text{C}_6\text{H}_3$). This behavior is confirmed by their $^{13}\text{C-NMR}$ spectra. However, the ^1H - and $^{13}\text{C-NMR}$ spectra of complex **8** are indicative of the asymmetric structure imposed by the two different aryl substituents which make all the Cp proton and carbon atoms chemically nonequivalent. The $^1\text{H-NMR}$ spectrum shows an ABCD coupling pattern for the ring protons and five resonances for the corresponding carbon atoms are observed in the $^{13}\text{C-NMR}$ spectrum. The asymmetry is also observed in the presence of a set of doublets ($J_{\text{HH}}^2 = 6.6$ Hz) due to the two different methyl



R = C₆H₃Me₂ (**7**), C₆H₃MeⁱPr (**8**),

Scheme 2.

groups for the iso-propyl fragment, along with the presence of two resonances for the SiMe₂ group. In common with *ansa*-metallocene derivatives with bridging –SiMe₂– groups [8] and other similar compounds [9,10], the ring C_{ipso} resonance for compounds **6–8** appears at higher field than those of the other carbon atoms, consistent with the dimethylsilyldicyclopentadienyl and amidosilylcyclopentadienyl ligands being in a chelate coordination mode with the metal center.

Reactions of **7** with alkylating and amido reagents have been studied. Treatment of [Ti{η⁵-C₅H₄SiMe₂[η¹-N(C₆H₃Me₂)]Cl₂] (**7**) with two equivalents of MgClMe or one equivalent of Mg(CH₂Ph)₂·2THF gave the dialkyl complexes [Ti{η⁵-C₅H₄SiMe₂[η¹-N(C₆H₃Me₂)]R₂] (R = Me **9**, CH₂Ph **10**) as yellow or red crystals, respectively, in high yield. However, the addition of two equivalents of LiCH₂SiMe₃ to **7** gave [Ti{η⁵-C₅H₄SiMe₂[η¹-N(C₆H₃Me₂)](CH₂SiMe₃)₂] **11** in low yield, while the reaction with an excess of AlMe₃ afforded the monoalkyl derivative [Ti{η⁵-C₅H₄SiMe₂[η¹-N(C₆H₃Me₂)]MeCl] **12** as yellow crystals in 70% yield. An analogous reaction of **7** with two equivalents of LiNMe₂ gave the diamido complex [Ti{η⁵-C₅H₄SiMe₂[η¹-N(C₆H₃Me₂)](NMe₂)₂] **13** as a brown oil. All of these compounds are thermally stable but extremely moisture sensitive. The thermal stability of complex **9** with the bulkier 2,6-dimethylphenyl fragment contrasts with the analogous complex [Ti{η⁵-C₅H₄SiMe₂[η¹-N(CH₂C₆H₅)]Me₂] which decomposes in a few hours at r.t. [11]. The structures proposed for the new complexes **9–13** are shown in Scheme 3 and their spectroscopic and analytical data are collected in Section 4.

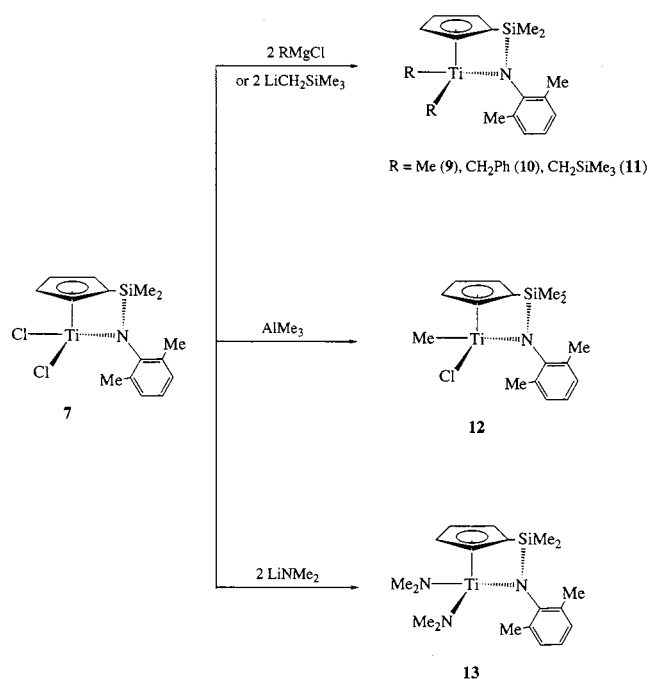
The ¹H-NMR spectra of complexes **9–11** and **13** show the expected AA'BB' spin system for the Cp ring protons and three resonances for the corresponding

carbon atoms are observed in their ¹³C-NMR spectra. However, complex **12** shows an ABCD spin system in the ¹H-NMR spectrum and five carbon resonances in the ¹³C-NMR spectrum. The asymmetry of this molecule results in the presence of different signals assigned to the methyl groups bound to the aryl fragment and to the silicon atom. In complex **10**, the diastereotopic CH₂ protons of the benzyl group appear as two doublets at δ = 2.69 and 2.22, while in the ¹³C-NMR spectrum a triplet at δ = 86.2 with J_{CH} = 122.8 Hz is observed.

2.2. X-ray molecular structure of [Ti{η⁵-C₅H₄SiMe₂[η¹-N(C₆H₃Me₂)]Cl₂] (**7**)

Crystals of **7** suitable for X-ray diffraction were obtained by slow cooling of its THF solution. The molecular structure of **7** is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1.

The titanium atom is in a pseudo-tetrahedral environment defined by one silylamido σ-*N* coordinated Cp ligand and two chloro ligands. The amido nitrogen is planar (the sum of bond angles around N atom is 360°) with sp² hybridization. The Ti–N–C₈ angle is 121.0 (2)°, which is smaller than that observed for the complex [Ti{η⁵-C₅H₄SiMe₂(η¹-N^{*t*}Bu)}(NMe₂)₂] (128.1(4)°) with a bulkier ^{*t*}Bu group [6] and similar to that reported for other related compounds such as [Ti{η⁵-C₅H₄SiMe₂[η¹-N(CH₂C₆H₃F₂)]Cl₂] (119.7(1)°) [11] and [Ti{η⁵-C₅H₄SiMe₂(η¹-N^{*i*}Pr)}Cl₂] (117.4(1)°) [11]. The Ti–N distance (1.914(3) Å) is consistent with a π-bonding contribution from an interaction between the nitro-



Scheme 3.

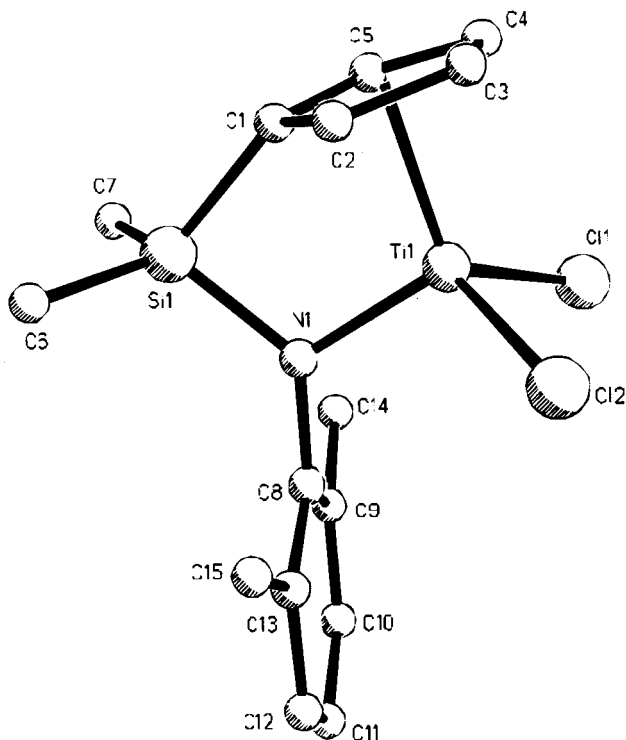


Fig. 1. Molecular structure of $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\eta^1\text{-N}(\text{C}_6\text{H}_3\text{Me}_2)]\}\text{Cl}_2]$ (**7**).

gen p_π orbital with the appropriate vacant metal d_π orbital [2]. However, the magnitude of this interaction is controlled both by the constrained geometry of the molecule and by the electronic and steric properties of the amido substituent, as observed in other complexes of this type $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\eta^1\text{-NR})\}\text{Cl}_2]$ [6,11]. The Ti–N bond distance found in compound **7** is longer and therefore the π -bonding contribution smaller than

that found in Cp–amido derivatives such as $[\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\{\text{N}(\text{Pr})_2\}\text{Cl}_2]$ (R = H 1.865(2), R = Me 1.865(5) Å) [12] and $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\{\text{N}(\text{SiMe}_3)_2\}\text{Cl}_2]$ (R = H 1.879(2) Å) [13] and chelating diamido complexes such as $[\text{Ti}\{\eta^1\text{-N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}(\text{CH}_2)_3\{\eta^1\text{-N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}\text{Cl}_2]$ (1.856(5) and 1.839(5) Å) [14] or $[\text{Ti}\{1,2\text{-}(\eta^1\text{-NSi}^i\text{Pr}_3)_2(\text{C}_6\text{H}_4)\}\text{Cl}_2]$ (1.878(4) Å) [15].

An examination of the structural parameters associated with the Cp ring indicates a significant π -bonding contribution from an η^3 -allyl- η^2 -olefin resonance structure of the normal η^5 -coordination mode. The C₃–C₄ bond distance of 1.389(6) Å is slightly shorter than the remaining C–C bonds within the ring. Furthermore, the Ti–C₃ and Ti–C₄ bond distances are slightly longer than the rest. This contribution, probably determined by the dimethylsilyl bridge, has also been observed in the *ansa*-metallocene derivative $[\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{SiMe}_2\}\text{X}_2]$ [8,16].

The Cp–Ti–N angle of 105.1° observed in **7** is slightly smaller than that found in the analogous constrained geometry derivative $\text{Ti}[\text{C}_5\text{H}_4\text{SiMe}_2\text{N}^i\text{Bu}]\text{Cl}_2$ (107.0°) [6] and considerably smaller than in similar unlinked Cp–amido complexes as in $[\text{Ti}(\text{C}_5\text{H}_5)(\text{N}^i\text{Pr})\text{Cl}_2]$ (116.2°) [12] or diamido complexes such as $[\text{Ti}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{CH}_2\text{Ph})_2]$ (120.6°) [17]. In addition, the replacement of the amido ligand with another Cp ligand as in $[\text{Ti}\{(\text{C}_5\text{H}_4)_2\text{SiMe}_2\}\text{Cl}_2]$ produces a significant increase in the corresponding Cp–M–Cp bond angle to 128.7° [8]. However, the Cp–Ti–N angle in **7** is larger than the N–Ti–N angle observed in bidentate diamide derivatives of the type $[\text{Ti}\{\eta^1\text{-N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}(\text{CH}_2)_3\{\eta^1\text{-N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}\text{Cl}_2]$ (99.2(2)°) [14] or $[\text{Ti}\{1,2\text{-}(\eta^1\text{-NSi}^i\text{Pr}_3)_2(\text{C}_6\text{H}_4)\}\text{Cl}_2]$ (92.6(2)°) [15], with six- and five-membered chelate ring, respectively.

Table 1
Selected bond lengths (Å) and angles (°) for complex **7**

Bond length (Å)			
Ti(1)–N(1)	1.914(3)	Ti(1)–Cl(1)	2.264(1)
Ti(1)–Cl(2)	2.273(1)	Ti(1)–C(1)	2.320(4)
Ti(1)–C(5)	2.325(4)	Ti(1)–C(2)	2.327(4)
Ti(1)–C(4)	2.374(4)	Ti(1)–C(3)	2.386(4)
Si(1)–N(1)	1.755(3)	Si(1)–C(1)	1.869(4)
N(1)–C(8)	1.435(4)	C(1)–C(5)	1.419(5)
C(1)–C(2)	1.431(5)	C(2)–C(3)	1.412(6)
C(3)–C(4)	1.389(6)	C(4)–C(5)	1.410(6)
Ti(1)–Cp(1)	2.016		
Bond angle (°)			
N(1)–Ti(1)–Cl(1)	108.6(1)	N(1)–Ti(1)–Cl(2)	108.5(1)
Cl(1)–Ti(1)–Cl(2)	101.1(1)	N(1)–Si(1)–C(1)	89.2(2)
C(8)–N(1)–Si(1)	131.1(2)	C(8)–N(1)–Ti(1)	121.0(2)
Si(1)–N(1)–Ti(1)	108.0(1)	Cp(1)–Ti(1)–Cl(1)	116.7
Cp(1)–Ti(1)–Cl(2)	116.6	Cp(1)–Ti(1)–N(1)	105.1

3. Conclusions

$[\text{Ti}(\text{C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_3]$ **1** is a very versatile starting material for preparing new monocyclopentadienyl titanium derivatives. In particular, reactions of **1** with nitrogen based donor reagents gave amido–titanium and –silicon compounds. New constrained geometry amidosilylcyclopentadienyl derivatives containing aryl groups bound to nitrogen have been synthesized by reacting complex **1** with an appropriate primary aryl amine in the presence of NEt_3 . $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\eta^1\text{-N}(\text{C}_6\text{H}_3\text{Me}_2)]\}\text{Cl}_2]$ is readily converted into the dialkyl and diamido complexes $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\eta^1\text{-N}(\text{C}_6\text{H}_3\text{Me}_2)]\}\text{X}_2]$ (X = R or NMe_2) and to the monoalkyl derivative $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\eta^1\text{-N}(\text{C}_6\text{H}_3\text{Me}_2)]\}\text{MeCl}]$ by salt metathesis using Grignard, organolithium or organoaluminium reagents.

4. Experimental section

4.1. General considerations

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox model HE-63 or MBraun. Solvents were purified by distillation under argon from an appropriate drying agent (sodium for toluene, sodium–potassium alloy for hexane and sodium–benzophenone for diethyl ether). The lithium benzamidinate salt was prepared by a known procedure [18] and LiNHPPh was prepared in hexane (in almost quantitative yield) as a solvent free solid from NH₂Ph and *n*-butyl-lithium (Aldrich, 1.6 M in hexane). The following reagents LiNMe₂, SiMe₃Cl, SiMe₃Br, NEt₃, MeMgCl, Mg(CH₂Ph)₂, LiCH₂SiMe₃, AlMe₃ and the primary amines H₂NR (R = C₆H₅, C₆H₃Me₂, C₆H₃Me^{*i*}Pr) were purchased from Aldrich. 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 300 (¹H-NMR at 300 MHz and ¹³C-NMR at 75 MHz) spectrometer. ¹H and ¹³C chemical shifts are reported in δ units relative to TMS standard.

4.2. Synthesis of

[Ti(η⁵-C₅H₄SiMe₂Cl){C(Ph)[N(SiMe₃)₂}Cl₂] (2)

A solution of Li{C(Ph)[N(SiMe₃)₂]} (0.87 g, 3.20 mmol) in toluene (15 ml) was added to a solution of **1** (1.00 g, 3.20 mmol) in toluene (40 ml) at –30°C. The reaction mixture was warmed to r.t. and stirred for 12 h. The solution was filtered and the volume of the filtrate reduced to ca. 20 ml and cooled to –40°C to give **2** as red–orange crystals (0.40 g, 50% yield). Anal. Calc. for C₂₀H₃₃N₂Si₃Ti: C: 44.48; H: 6.15; N: 5.18. Found: C: 44.94; H: 6.00; N: 5.84%. ¹H-NMR (C₆D₆): δ 6.88 (m, 5H, C₆H₅), 6.84 (t, 2H, C₅H₄), 6.55 (t, 2H, C₅H₄), 1.09 (s, 6H, SiMe₂), –0.01 (s, 18H, SiMe₃). ¹³C{¹H}-NMR (C₆D₆): δ 173.5 (PhC(NSiMe₃)₂), 136.5 (C₆H₅), 124.0, 125.9 (CH of C₅H₄R), 3.0 (SiMe₂Cl), 2.5 (NSiMe₃).

4.3. Synthesis of [Ti(η⁵-C₅H₄SiMe₂NMe₂)(NMe₂)₃] (3)

A sample of LiNMe₂ (0.34 g, 6.70 mmol) was added to a diethyl ether solution (40 ml) of **1** (0.50 g, 1.60 mmol) at –78°C. After warming to r.t., the reaction mixture was stirred for 12 h. The volatiles were removed under reduced pressure and the residue was extracted into hexane (40 ml). After filtration, solvent was removed under vacuum to give **3** as an analytically pure yellow–green oil (0.44 g, 80% yield). Anal. Calc. for C₁₅H₃₄N₄SiTi: C, 52.29; H, 10.19; N, 16.50. Found: C: 52.01; H: 9.89; N: 16.17%. ¹H-NMR (C₆D₆): δ 6.20

(t, 2H, C₅H₄), 6.12 (t, 2H, C₅H₄), 3.09 (s, 18H, 3 Ti–NMe₂), 2.46 (s, 6H, Si–NMe₂), 0.34 (s, 6H, SiMe₂). (CDCl₃): δ 6.17 (m, 4H, C₅H₄), 3.03 (s, 18H, 3 Ti–NMe₂), 2.42 (s, 6H, Si–NMe₂), 0.24 (s, 6H, SiMe₂). ¹³C{¹H}-NMR (CDCl₃): δ 117.9 (CH of C₅H₄), 112.5 (CH of C₅H₄), 44.8 (Ti–NMe₂), 38.3 (Si–NMe₂), –1.4 (SiMe₂).

4.4. Synthesis of [Ti(η⁵-C₅H₄SiMe₂NMe₂)(NMe₂)Cl₂] (4)

A sample of SiMe₃Cl (0.4 ml, 3.1 mmol) was added to a solution of **3** (0.20 g, 0.58 mmol) in THF at –70°C. The mixture was warmed to r.t. and then stirred for 2 h. Volatiles were removed in vacuo giving **4** as a red solid (0.14 g, 75% yield). Recrystallization from toluene at –40°C afforded red microcrystals suitable for analysis. Anal. Calc. for C₁₂H₂₂N₂SiCl₂Ti: C: 40.01; H: 7.00; N: 8.48. Found: C: 40.14; H: 6.74; N: 8.51%. ¹H-NMR (C₆D₆): δ 6.49 (t, 2H, C₅H₄), 6.14 (t, 2H, C₅H₄), 3.25 (s, 6H, Ti–NMe₂), 2.42 (s, 6H, Si–NMe₂), 0.47 (s, 6H, SiMe₂). ¹³C{¹H}-NMR (CDCl₃): δ 134.2 (C_{ipso} of C₅H₄), 125.7 (CH of C₅H₄), 119.7 (CH of C₅H₄), 52.6 (Ti–NMe₂), 38.1 (Si–NMe₂), –2.0 (SiMe₂).

4.5. Synthesis of [Ti(η⁵-C₅H₄SiMe₂NMe₂)(NMe₂)Br₂] (5)

In a similar way, SiMe₃Br (0.4 ml, 3.0 mmol) was added to a solution of **3** (0.20 g, 0.58 mmol) in THF at –70°C. The mixture was warmed to r.t. and then stirred for 2 h. The volatiles were removed in vacuo giving **5** as a red dark solid (0.18 g, 76% yield). Recrystallization from toluene at –40°C afforded red microcrystals suitable for analysis. Anal. Calc. for C₁₂H₂₂N₂SiBr₂Ti: C: 31.53; H: 5.53; N: 6.68. Found: C: 31.60; H: 5.30; N: 6.70%. ¹H-NMR (C₆D₆): δ 6.69 (t, 2H, C₅H₄), 6.04 (t, 2H, C₅H₄), 3.30 (s, 6H, Ti–NMe₂), 2.43 (s, 6H, Si–NMe₂), 0.50 (s, 6H, SiMe₂). ¹³C{¹H}-NMR (CDCl₃): δ 135.1 (C_{ipso} of C₅H₄), 125.7 (CH of C₅H₄), 119.7 (CH of C₅H₄), 53.0 (Ti–NMe₂), 38.2 (Si–NMe₂), –1.6 (SiMe₂).

4.6. Synthesis of [Ti{η⁵-C₅H₄SiMe₂[η¹-N(C₆H₅)]}Cl₂] (6)

Samples of H₂NPh (0.15 ml, 1.6 mmol) and NEt₃ (0.44 ml, 3.2 mmol) were added to a cooled solution (–60°C) of Ti(η⁵-C₅H₄SiMe₂Cl)Cl₃, **1** (0.50 g, 1.6 mmol) in toluene (50 ml). The reaction mixture was slowly warmed to r.t. and stirred for 10 h, giving an orange solution with a white residue. After filtration, the solution was concentrated and cooled to –30°C to give orange crystals. Concentration of the mother liquor (10 ml) and subsequent cooling to –30°C gave

a second crop of product which was characterized as **6**. (0.16 g, 30% yield). Anal. Calc. for $C_{13}H_{15}NCl_2SiTi$: C: 46.47; H: 4.56; N: 4.12. Found: C: 47.01; H: 4.55; N: 4.21%. 1H -NMR (C_6D_6): δ 7.27 (d, 2H_{ortho}, Ph), 7.15 (t, 2H_{meta}, Ph), 6.83 (t, 1H_{para}, Ph), 6.53 (t, 2H, C₅H₄), 6.15 (t, 2H, C₅H₄), 0.15 (s, 6H, SiMe₂). (CDCl₃): δ 7.34 (d, 2H_{ortho}, Ph), 7.12 (t, 2H_{meta}, Ph), 7.05 (t, 1H_{para}, Ph), 7.14 (t, 2H, C₅H₄), 6.68 (t, 2H, C₅H₄), 0.66 (s, 6H, SiMe₂). $^{13}C\{^1H\}$ -NMR (CDCl₃): δ 152.3 (C_{ipso} of C₆H₅), 129.1 (C_{ortho} of C₆H₅), 126.6 (C_{meta} of C₆H₅), 125.0 (C_{para} of C₆H₅), 125.5 (CH of C₅H₄), 118.9 (CH of C₅H₄), 111.3 (C_{ipso} of C₅H₄), -2.4 (SiMe₂).

Following the same procedure described above using Ti(η^5 -C₅H₄SiMe₂Cl)Cl₃, **1** (0.5 g, 1.6 mmol), LiNHPH (0.15 ml, 1.6 mmol) and NEt₃ (0.22 ml, 1.6 mmol), **6** was obtained in higher yield (0.22 g, 41% yield).

4.7. Synthesis of

[Ti{ η^5 -C₅H₄SiMe₂}[η^1 -N(2,6-Me₂C₆H₃)]Cl₂] (**7**)

Some H₂N(C₆H₃Me₂) (0.20 ml, 1.6 mmol) and NEt₃ (0.44 ml, 3.2 mmol) were added to a cooled solution (-60°C) of Ti(η^5 -C₅H₄SiMe₂Cl)Cl₃, **1** (0.5 g, 1.6 mmol) in 50 ml of toluene. The reaction mixture was slowly warmed to r.t. and stirred for 10 h, giving an orange solution with a white residue. After filtration, the solution was concentrated and cooled to -30°C to give yellow crystals of **7**. (0.52 g, 90% yield). Anal. Calc. for C₁₅H₁₉NCl₂SiTi: C: 50.23; H: 5.56; N: 3.91. Found: C: 50.01; H: 5.36; N: 3.88%. 1H -NMR (C_6D_6): δ 7.01 (d, 2H_{meta}, C₆H₃Me₂), 6.92 (t, 1H_{para}, C₆H₃Me₂), 6.58 (t, 2H, C₅H₄), 6.15 (t, 2H, C₅H₄), 2.07 (s, 6H, C₆H₃Me₂), 0.06 (s, 6H, SiMe₂). (CDCl₃): δ 7.08–6.96 (m, 3H, C₆H₃Me₂), 7.17 (t, 2H, C₅H₄), 6.73 (t, 2H, C₅H₄), 2.00 (s, 6H, C₆H₃Me₂), 0.56 (s, 6H, SiMe₂). $^{13}C\{^1H\}$ -NMR (CDCl₃): δ 147.1 (C_{ipso} of C₆H₃Me₂), 129.8 (C_{ortho} of C₆H₃Me₂), 128.8 (C_{meta} of C₆H₃Me₂), 126.0 (C_{para} of C₆H₃Me₂), 126.3 (CH of C₅H₄), 125.3 (CH of C₅H₄), 112.3 (C_{ipso} of C₅H₄), 19.7 (C₆H₃Me₂), -0.7 (SiMe₂).

4.8. Synthesis of

[Ti{ η^5 -C₅H₄SiMe₂}[η^1 -N(2-Me-6-*i*-Pr-C₆H₃)]Cl₂] (**8**)

A mixture of Ti(η^5 -C₅H₄SiMe₂Cl)Cl₃, **1** (0.5 g, 1.6 mmol), H₂N(C₆H₃Me^{*i*}Pr) (0.25 ml, 1.6 mmol) and NEt₃ (0.44 ml, 3.2 mmol) in hexane (50 ml) were allowed to stir at r.t. for 15 h and the color of the solution gradually changed to red brown. The solution was filtered off and the residue was extracted into diethyl ether (2 × 25 ml). After filtration, the solution was cooled to -30°C affording **8** as yellow crystals (0.12 g, 19% yield). Anal. Calc. for C₁₇H₂₃NCl₂SiTi: C: 51.69; H: 6.00; N: 3.28. Found: C: 52.39; H: 5.86; N: 3.56%. 1H -NMR (C_6D_6): δ 7.15–6.84 (m, 3H, C₆H₃Me^{*i*}Pr), 6.59 (m, 1H, C₅H₄), 6.54 (m, 1H, C₅H₄), 6.21 (m, 1H,

C₅H₄), 6.15 (m, 1H, C₅H₄), 2.84 (hp, 1H, C₆H₃Me^{*i*}Pr), 2.04 (s, 3H, C₆H₃Me^{*i*}Pr), 1.52 (d, 3H, C₆H₃Me^{*i*}Pr), 1.03 (d, 3H, C₆H₃Me^{*i*}Pr), 0.20 (s, 3H, SiMe₂), 0.05 (s, 3H, SiMe₂). (CDCl₃): δ 7.16–7.06 (m, 3H, C₆H₃Me^{*i*}Pr), 7.22–7.16 (m, 2H, C₅H₄), 6.77 (m, 2H, C₅H₄), 2.66 (hp, 1H, C₆H₃Me^{*i*}Pr), 2.00 (s, 3H, C₆H₃Me^{*i*}Pr), 1.29 (d, 3H, J_{HH} = 6.6 Hz, C₆H₃Me^{*i*}Pr), 1.01 (d, 3H, J_{HH} = 6.6 Hz, C₆H₃Me^{*i*}Pr), 0.62 (s, 3H, SiMe₂), 0.58 (s, 3H, SiMe₂). $^{13}C\{^1H\}$ -NMR (CDCl₃): δ 141.5 (C_{ipso} of C₆H₃Me^{*i*}Pr), 129.1, 128.6, 126.5, 126.4 (rest of C₆H₃Me^{*i*}Pr), 126.1 (CH of C₅H₄), 126.0 (CH of C₅H₄), 125.3 (CH of C₅H₄), 124.8 (CH of C₅H₄), 112.0 (C_{ipso} of C₅H₄), 27.9, 26.5, 23.9 (C₆H₃Me^{*i*}Pr), 20.7 (C₆H₃Me^{*i*}Pr), -0.7 (SiMe₂), -0.9 (SiMe₂).

4.9. Synthesis of

[Ti{ η^5 -C₅H₄SiMe₂}[η^1 -N(2,6-Me₂C₆H₃)]Me₂] (**9**)

A 2 M solution of MeMgCl (5.75 ml, 11.5 mmol) was added to a solution of [Ti{ η^5 -C₅H₄SiMe₂}[η^1 -N(2,6-Me₂C₆H₃)]Cl₂] (**7**) (2.0 g, 5.5 mmol) in diethylether (100 ml) and the reaction mixture was stirred at r.t. for 12 h in the glovebox. After the solvent was completely removed under vacuum, the green solid was extracted into hexane (100 ml) and the solution filtered. The solution was concentrated and cooled to -40°C to give yellow green crystals of **9** (1.21 g, 69%). Anal. Calc. for C₁₇H₂₅NSiTi: C: 63.97; H: 7.83; N: 4.38. Found: C: 63.78; H: 7.92; N: 4.34%. 1H -NMR (C_6D_6): δ 7.18 (d, 2H_{meta}, C₆H₃Me₂), 7.00 (t, 1H_{para}, C₆H₃Me₂), 6.71 (t, 2H, C₅H₄), 5.95 (t, 2H, C₅H₄), 2.08 (s, 6H, C₆H₃Me₂), 0.65 (s, 6H, Ti-Me), 0.11 (s, 6H, SiMe₂). 1H -NMR (CDCl₃): δ 7.16–6.95 (m, 3H, C₆H₃Me₂), 7.16 (t, 2H, C₅H₄), 6.36 (t, 2H, C₅H₄), 2.07 (s, 6H, C₆H₃Me₂), 0.48 (s, 6H, Ti-Me), 0.36 (s, 6H, SiMe₂). ^{13}C -NMR (CDCl₃): δ 148.1 (C_{ipso} of C₆H₃Me₂), 131.2 (C_{ortho} of C₆H₃Me₂), 128.4 (C_{meta} of C₆H₃Me₂), 123.2 (C_{para} of C₆H₃Me₂), 122.5 (CH of C₅H₄), 119.6 (CH of C₅H₄), 104.2 (C_{ipso} of C₅H₄), 56.5 (Ti-Me), 19.3 (C₆H₃Me₂), -0.2 (SiMe₂).

4.10. Synthesis of

[Ti{ η^5 -C₅H₄SiMe₂}[η^1 -N(2,6-Me₂C₆H₃)](CH₂Ph)₂] (**10**)

A solution of Mg(CH₂Ph)₂. 2THF (0.97 g, 2.77 mmol) in diethyl ether (15 ml) was added to another solution of **7** (1.0 g, 2.77 mmol) in diethylether (50 ml) and the reaction mixture was stirred at r.t. for 12 h in the glovebox. After the solvent was completely removed under vacuum, the red solid was extracted into hexane (100 ml) and the solution filtered. The solution was concentrated and cooled to -40°C to give complex **10** (0.85 g, 65%) as red crystals. Anal. Calc. for C₂₉H₃₃NSiTi: C: 73.90; H: 7.00; N: 2.97. Found: C: 74.35; H: 7.10; N: 3.02%. 1H -NMR (C_6D_6): δ 7.17 (d, 2H_{meta}, C₆H₃Me₂, J_{HH} = 7.9 Hz), 7.09 (t, 4H_{meta},

$\text{CH}_2\text{C}_6\text{H}_5$, $J_{\text{HH}} = 6.1$ Hz), 7.02 (t, 1H_{para}, $\text{C}_6\text{H}_3\text{Me}_2$, $J_{\text{HH}} = 7.9$ Hz), 6.86 (t, 4H_{para}, $\text{CH}_2\text{C}_6\text{H}_5$, $J_{\text{HH}} = 7.3$ Hz), 6.67 (d, 4H_{ortho}, $\text{CH}_2\text{C}_6\text{H}_5$, $J_{\text{HH}} = 7.3$ Hz), 6.35 (t, 2H, C_5H_4 , $J_{\text{HH}} = 2.4$ Hz), 5.96 (t, 2H, C_5H_4 , $J_{\text{HH}} = 2.4$ Hz), 2.73 (d, 2H, CH_2Ph , $J_{\text{HH}} = 9.7$ Hz), 2.24 (d, 2H, CH_2Ph , $J_{\text{HH}} = 9.7$ Hz), 2.14 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 0.11 (s, 6H, SiMe_2). ¹H-NMR (CDCl_3): δ 7.20 (d, 2H_{meta}, $\text{C}_6\text{H}_3\text{Me}_2$), 7.12 (t, 4H_{meta}, $\text{CH}_2\text{C}_6\text{H}_5$), 7.03 (t, 1H_{para}, $\text{C}_6\text{H}_3\text{Me}_2$), 6.87 (t, 4H_{para}, $\text{CH}_2\text{C}_6\text{H}_5$), 6.68 (d, 4H_{ortho}, $\text{CH}_2\text{C}_6\text{H}_5$), 6.43 (t, 2H, C_5H_4), 6.18 (t, 2H, C_5H_4), 2.69 (d, 2H, CH_2Ph), 2.24 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 2.22 (d, 2H, CH_2Ph), 0.40 (s, 6H, SiMe_2). ¹³C{¹H}-NMR (CDCl_3): δ 149.4 (*C*_{ipso} of $\text{CH}_2\text{C}_6\text{H}_5$), 148.9 (*C*_{ipso} of $\text{C}_6\text{H}_3\text{Me}_2$), 130.7 (*C*_{ortho} of $\text{C}_6\text{H}_3\text{Me}_2$), 128.8 (*C*_{meta} of $\text{C}_6\text{H}_3\text{Me}_2$), 128.2 (*C*_{ortho} of $\text{CH}_2\text{C}_6\text{H}_5$), 125.3 (*C*_{meta} of $\text{CH}_2\text{C}_6\text{H}_5$), 125.05 (*C*_{para} of $\text{CH}_2\text{C}_6\text{H}_5$), 123.9 (CH of C_5H_4), 123.7 (*C*_{para} of $\text{C}_6\text{H}_3\text{Me}_2$), 122.0 (CH of C_5H_4), 106.9 (*C*_{ipso} of C_5H_4), 86.2 ($J_{\text{CH}} = 122.8$ Hz, CH_2Ph), 20.0 ($\text{C}_6\text{H}_3\text{Me}_2$), -0.2 (SiMe_2).

4.11. Synthesis of

$[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\eta^1\text{-N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]\}(\text{CH}_2\text{SiMe}_3)_2]$ (**11**)

A solution of $\text{LiCH}_2\text{SiMe}_3$ (0.27 g, 2.94 mmol) in diethylether (15 ml) was added to a solution of **7** (0.5 g, 1.4 mmol) in diethylether (40 ml) and the reaction was stirred at r.t. for 12 h in the glovebox. After the solvent was completely removed under vacuum, the product was extracted with hexane (50 ml) and the solution filtered. The solution was concentrated and cooled to -40°C to afford the complex **11** (0.35 g, 59%) as dark green solid. Anal. Calc. for. $\text{C}_{23}\text{H}_{41}\text{NSi}_3\text{Ti}$: C: 59.61; H: 8.85; N: 3.02. Found: C: 59.02; H: 8.48; N: 2.78%. ¹H-NMR (C_6D_6): δ 7.12–6.9 (m, 3H, $\text{C}_6\text{H}_3\text{Me}_2$), 6.96 (t, 2H, C_5H_4), 6.27 (t, 2H, C_5H_4), 2.13 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 1.58 (d, 2H, CH_2SiMe_3 , $J_{\text{HH}} = 10.6$ Hz), 0.87 (d, 2H, CH_2SiMe_3 , $J_{\text{HH}} = 10.6$ Hz), 0.17 (s, 6H, SiMe_2), 0.04 (s, 18H, CH_2SiMe_3). ¹H-NMR (CDCl_3): δ 7.1–6.9 (m, 3H, $\text{C}_6\text{H}_3\text{Me}_2$), 7.09 (t, 2H, C_5H_4), 6.42 (t, 2H, C_5H_4), 2.09 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 1.48 (d, 2H, CH_2SiMe_3 , $J_{\text{HH}} = 10.2$ Hz), 0.75 (d, 2H, CH_2SiMe_3 , $J_{\text{HH}} = 10.2$ Hz), 0.32 (s, 6H, SiMe_2), -0.06 (s, 18H, CH_2SiMe_3). ¹³C-NMR (CDCl_3): δ 150.3 (*C*_{ipso} of $\text{C}_6\text{H}_3\text{Me}_2$), 130.7 (*C*_{ortho} of $\text{C}_6\text{H}_3\text{Me}_2$), 128.6 (*C*_{meta} of $\text{C}_6\text{H}_3\text{Me}_2$), 123.0 (*C*_{para} of $\text{C}_6\text{H}_3\text{Me}_2$), 121.9 (CH of C_5H_4), 117.7 (CH of C_5H_4), 105.4 (*C*_{ipso} of C_5H_4), 81.4 (CH_2SiMe_3), 19.9 ($\text{C}_6\text{H}_3\text{Me}_2$), 2.4 (CH_2SiMe_3), -0.1 (SiMe_2).

4.12. Synthesis of

$[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\eta^1\text{-N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]\}\text{MeCl}]$ (**12**)

A 2 M solution of AlMe_3 in toluene (1 ml, 2 mmol.) was added to a solution of **7** (0.5 g, 1.4 mmol) in 40 ml of toluene at r.t. and the mixture stirred for 12 h. The yellow solution was then filtered, concentrated and cooled overnight to -40°C to give complex **12** (0.30 g, 62%) as

yellow crystals. Anal. Calc. for. $\text{C}_{16}\text{H}_{22}\text{ClNSiTi}$: C: 56.55; H: 6.52; N: 4.12. Found: C: 56.36; H: 6.51; N: 4.11%. ¹H-NMR (C_6D_6): δ 7.09 (d, 2H_{meta}, $\text{C}_6\text{H}_3\text{Me}_2$), 6.97 (t, 1H_{para}, $\text{C}_6\text{H}_3\text{Me}_2$), 6.63 (t, 1H, C_5H_4), 6.45 (t, 1H, C_5H_4), 6.02 (t, 2H, C_5H_4), 2.19 (s, 3H, $\text{C}_6\text{H}_3\text{Me}_2$), 1.96 (s, 3H, $\text{C}_6\text{H}_3\text{Me}_2$), 1.01 (s, 3H, Ti–Me), 0.07 (s, 3H, SiMe_2), 0.06 (s, 3H, SiMe_2). ¹H-NMR (CDCl_3): δ 7.28 (s, 1H, C_5H_4), 7.07 (m, 2H_{meta}, $\text{C}_6\text{H}_3\text{Me}_2$), 6.94 (t, 1H_{para}, $\text{C}_6\text{H}_3\text{Me}_2$), 6.86 (s, 1H, C_5H_4), 6.56 (s, 1H, C_5H_4), 6.45 (s, 1H, C_5H_4), 2.06 (s, 3H, $\text{C}_6\text{H}_3\text{Me}_2$), 1.99 (s, 3H, $\text{C}_6\text{H}_3\text{Me}_2$), 0.93 (s, 3H, Ti–Me), 0.44 (s, 3H, SiMe_2), 0.41 (s, 3H, SiMe_2). ¹³C-NMR (CDCl_3): δ 147.7 (*C*_{ipso} of $\text{C}_6\text{H}_3\text{Me}_2$), 130.6 (*C*_{ortho} of $\text{C}_6\text{H}_3\text{Me}_2$), 130.4 (*C*_{ortho} of $\text{C}_6\text{H}_3\text{Me}_2$), 128.8 (*C*_{meta} of $\text{C}_6\text{H}_3\text{Me}_2$), 128.5 (*C*_{meta} of $\text{C}_6\text{H}_3\text{Me}_2$), 124.4 (CH of C_5H_4), 124.0 (CH of C_5H_4), 122.4 (*C*_{para} of $\text{C}_6\text{H}_3\text{Me}_2$), 122.0 (CH of C_5H_4), 120.7 (CH of C_5H_4), 108.15 (*C*_{ipso} of C_5H_4), 62.0 (Ti–Me), 20.1 ($\text{C}_6\text{H}_3\text{Me}_2$), 18.9 ($\text{C}_6\text{H}_3\text{Me}_2$), -0.2 (SiMe_2), -0.8 (SiMe_2).

4.13. Synthesis of

$[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2[\eta^1\text{-N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]\}(\text{NMe}_2)_2]$ (**13**)

A solution of LiNMe_2 (0.15 g, 2.8 mmol) in diethylether (20 ml) was added to a solution of **7** (0.5 g, 1.4 mmol) in diethylether (40 ml) and the reaction mixture was stirred at r.t. for 12 h in the glovebox. After the solvent was completely removed under vacuum, the compound was extracted with hexane (50 ml) and the solution filtered. The solvent was removed under vacuum to give complex **13** (0.35g, 66%) as black, viscous oil. Anal. Calc. for. $\text{C}_{19}\text{H}_{31}\text{N}_3\text{SiTi}$: C: 60.46; H: 8.28; N: 11.13. Found: C: 60.10; H: 7.99; N: 10.89%. ¹H-NMR (C_6D_6): δ 7.10–6.80 (m, 3H, $\text{C}_6\text{H}_3\text{Me}_2$), 6.26 (t, 2H, C_5H_4 , $J_{\text{HH}} = 2.2$ Hz), 6.20 (t, 2H, C_5H_4 , $J_{\text{HH}} = 2.2$ Hz), 2.80 (s, 12H, NMe_2), 2.12 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 0.35 (s, 6H, SiMe_2). ¹H-NMR (CDCl_3): δ 7.10–6.78 (m, 3H, $\text{C}_6\text{H}_3\text{Me}_2$), 6.63 (t, 2H, C_5H_4), 6.43 (t, 2H, C_5H_4), 3.01 (s, 12H, NMe_2), 2.12 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 0.47 (s, 6H, SiMe_2). ¹³C-NMR (CDCl_3): δ 150.1 (*C*_{ipso} of $\text{C}_6\text{H}_3\text{Me}_2$), 132.3 (*C*_{ortho} of $\text{C}_6\text{H}_3\text{Me}_2$), 127.3 (*C*_{meta} of $\text{C}_6\text{H}_3\text{Me}_2$), 120.8 (*C*_{para} of $\text{C}_6\text{H}_3\text{Me}_2$), 119.1 (CH of C_5H_4), 117.5 (CH of C_5H_4), 109.9 (*C*_{ipso} of C_5H_4), 47.9 (Ti– NMe_2), 19.4 ($\text{C}_6\text{H}_3\text{Me}_2$), 0.8 (SiMe_2).

4.14. X-ray structure determination of **7**

A yellow crystal of compound **7** crystallized from THF was mounted in a glass capillary in a random orientation on an Enraf-Nonius Cad4 four-circle automatic diffractometer with graphite-monochromated Mo–K α radiation ($\lambda = 0.7073$ Å). Crystallographic and experimental details of **7** are summarized in Table 2. Data were collected at r.t. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. Intensity measurements were performed by $\omega - 2\theta$ scans in the range $4 < 2\theta < 50^\circ$.

Table 2
Crystal data and structure refinement for complex 7

Empirical formula	C ₁₅ H ₁₉ Cl ₂ NSiTi
Formula weight	360.20
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	13.185(6)
<i>b</i> (Å)	7.566(2)
<i>c</i> (Å)	17.233(8)
β (°)	96.39(2)
Volume (Å ³)	1708(1)
<i>Z</i>	4
<i>D</i> _{calc.} (g cm ⁻³)	1.400
Absorption coefficient (mm ⁻¹)	0.873
<i>F</i> (000)	744
Crystal size (mm)	0.35 × 0.32 × 0.28
θ range for data collection (°)	2.00–25.00
Index ranges	0 < <i>h</i> < 15, 0 < <i>k</i> < 8, –20 < <i>l</i> < 20
Reflections collected	3122
Independent reflections	2984 (<i>R</i> _{int} = 0.0305)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	2063
Absorption correction	Ψ-scan
Max. and min. transmission	0.301 and 0.265
Goodness-of-fit on <i>F</i> ²	0.951
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.042, <i>wR</i> ₂ = 0.113
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.077, <i>wR</i> ₂ = 0.121
Weighting scheme	Calc. $w = 1/[\sigma^2(F_o^2) + (0.081P)^2]^a$
Largest difference peak and hole (e Å ⁻³)	0.432 and –0.325

$$^a P = (F_o^2 + 2F_c^2)/3.$$

The structure was solved by direct methods (SHELXS-90) [19] and refined by least-squares against *F*² (SHELXL-93) [20]. Of the 3122 measured reflections, 2984 were independent; *R*₁ = 0.042 and *wR*₂ = 0.113 [for 2063 reflections with *F* > 4σ(*F*)]. The values of *R*₁ and *wR*₂ are defined as $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.081P)^2]$, $P = (F_o^2 + 2F_c^2)/3$ and σ was obtained from counting statistics. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced in the last cycle of refinement from geometrical calculations and refined using a riding model with thermal parameters fixed at *U* = 0.08 Å².

5. Supplementary material available

The supplementary material includes a list of the positional parameters and their standard deviations, a complete list of bond lengths and angles, anisotropic displacement parameters, the calculated fractional coordinates of the hydrogen atoms and a list of observed and calculated structure factors. This is available on request from the authors.

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