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Reactivity of chlorodimethylsilyl-η^5-cyclopentadienyltrichlorotitanium with nitrogen based donors. X-ray molecular structure of $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}Cl_2]$

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Abstract

This paper reports the reactivity of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$, **1** towards nitrogen based donor reagents. Complex **1** reacts with lithium benzamidinato $Li[PhC(NSiMe_3)_2]$ to afford $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)\{PhC(NSiMe_3)_2\}Cl_2]$ **2** and with lithium amide $LiNMe_2$ to produce $[Ti(\eta^5\text{-}C_5H_4SiMe_2NMe_2)(NMe_2)_3]$ **3**. The latter compound was converted into the dihalide derivatives $[Ti(\eta^5\text{-}C_5H_4SiMe_2NMe_2)(NMe_2)X_2]$ [X = Cl (**4**) and Br (**5**)] by reaction with $SiMe_3X$ (X = Cl or Br, respectively). The constrained geometry derivatives $[Ti\{\eta^5\text{-}C_5H_4SiMe_2(\eta^1\text{-}NR)\}Cl_2]$ (R = C_6H_5 **6**, 2,6-$Me_2C_6H_3$ **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 $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}X_2]$ (X = 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 $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}MeCl]$ (**12**) by reaction with $AlMe_3$. The molecular structure of complex **7** $[Ti\{(\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}Cl_2]$ was established by X-ray crystallography.

Keywords: Titanium; Amido-silylcyclopentadienyl; Amidotitanium; Alkyltitanium

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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 $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3]$, **1** [5] which has two reactive Ti–Cl and Si–Cl bonds.

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[1] X-ray diffraction studies.

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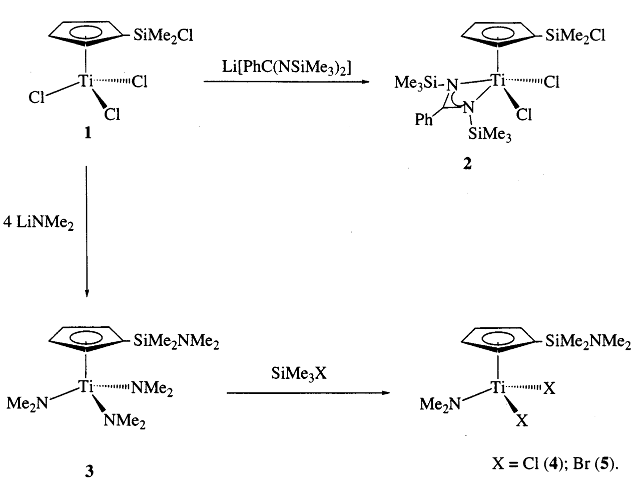
2. Results and discussion

2.1. Synthesis and NMR characterization

The reaction of [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] **1** with one equivalent of lithium benzamidinato Li[PhC($NSiMe_3$)$_2$] in toluene afforded, after extraction into hot toluene, the corresponding benzamidinato complex [Ti(η^5-$C_5H_4SiMe_2Cl$){PhC($NSiMe_3$)$_2$}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 [Ti(η^5-$C_5H_4SiMe_2NMe_2$)(NMe_2)$_3$] **3** in high yield as a yellow oil. Using a reported method [6,7], reaction of complex **3** with excess of $SiMe_3X$ (X = Cl or Br) resulted in the replacement of only two of the titanium-bonded amido groups by halogen giving the dihalo derivatives Ti(η^5-$C_5H_4SiMe_2NMe_2$)(NMe_2)X_2] (X = Cl **4** or Br **5**) in good yields with elimination of two equivalents of volatile $SiMe_3$(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.



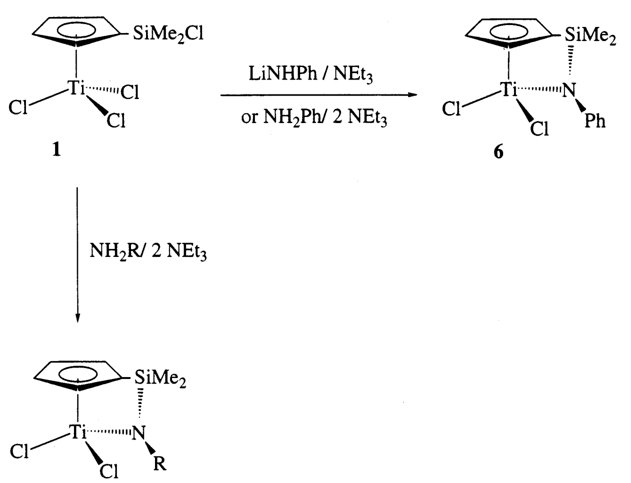
Scheme 1.

The ^{1}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}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 [Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3] **1** with primary aryl amines and their corresponding lithium salts have been studied. Treatment of **1** with one equivalent of NH_2R (R = C_6H_5, 2,6-$Me_2C_6H_3$ and 2-Me-6-^{i}Pr-C_6H_3) in the presence of two equivalents of NEt_3 gave the corresponding constrained geometry derivatives [Ti{η^5-$C_5H_4SiMe_2$(η^1-*N*R)}Cl_2], isolated as orange crystals (R = C_6H_5 **6** in ca. 30% yield) or as yellow crystals (R = 2,6-$Me_2C_6H_3$ **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 Li(NHPh) 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}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-$Me_2C_6H_3$). This behavior is confirmed by their ^{13}C-NMR spectra. However, the ^{1}H- and ^{13}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}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}C-NMR spectrum. The asymmetry is also observed in the presence of a set of doublets ($J^2_{\mathrm{HH}} = 6.6$ Hz) due to the two different methyl



R = $C_6H_3Me_2$ (**7**), $C_6H_3Me^iPr$ (**8**),

Scheme 2.

groups for the iso-propyl fragment, along with the presence of two resonances for the $SiMe_2$ group. In common with *ansa*-metallocene derivatives with bridging $-SiMe_2-$ 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.

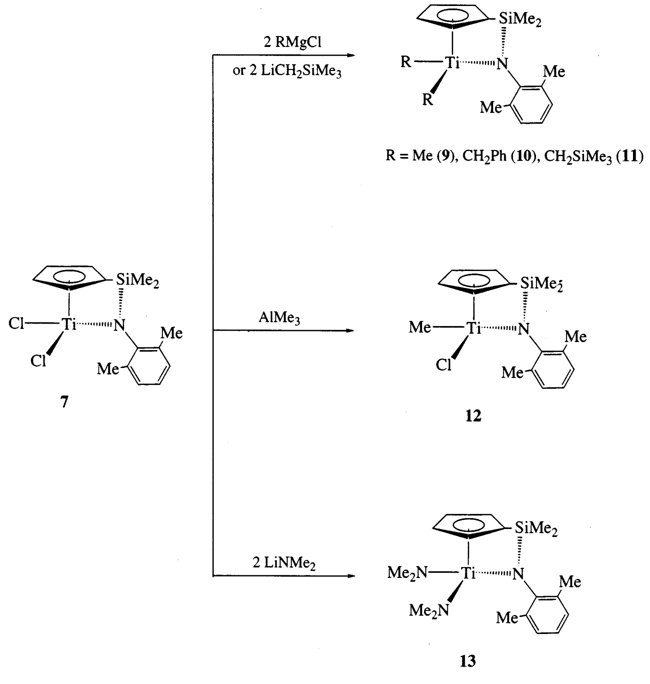
Reactions of **7** with alkylating and amido reagents have been studied. Treatment of $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}Cl_2]$ (**7**) with two equivalents of MgClMe or one equivalent of $Mg(CH_2Ph)_2 \cdot 2THF$ gave the dialkyl complexes $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}R_2]$ (R = Me **9**, CH_2Ph **10**) as yellow or red crystals, respectively, in high yield. However, the addition of two equivalents of $LiCH_2SiMe_3$ to **7** gave $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}(CH_2SiMe_3)_2]$ **11** in low yield, while the reaction with an excess of $AlMe_3$ afforded the monoalkyl derivative $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}MeCl]$ **12** as yellow crystals in 70% yield. An analogous reaction of **7** with two equivalents of $LiNMe_2$ gave the diamido complex $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}(NMe_2)_2]$ **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 $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(CH_2C_6H_5)]\}Me_2]$ 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 ^{13}C-NMR spectra. However, complex **12** shows an ABCD spin system in the ^1H-NMR spectrum and five carbon resonances in the ^{13}C-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 CH_2 protons of the benzyl group appear as two doublets at $\delta = 2.69$ and 2.22, while in the ^{13}C-NMR spectrum a triplet at $\delta = 86.2$ with $J_{CH} = 122.8$ Hz is observed.

2.2. X-ray molecular structure of $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}Cl_2]$ (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 sp^2 hybridization. The $Ti-N-C_8$ angle is 121.0 (2)°, which is smaller than that observed for the complex $[Ti\{\eta^5\text{-}C_5H_4SiMe_2(\eta^1\text{-}N^tBu)\}(NMe_2)_2]$ (128.1(4)°) with a bulkier ^{t}Bu group [6] and similar to that reported for other related compounds such as $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(CH_2C_6H_3F_2)]\}Cl_2]$ (119.7(1)°) [11] and $[Ti\{\eta^5\text{-}C_5H_4SiMe_2(\eta^1\text{-}N^iPr)\}Cl_2]$ (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.

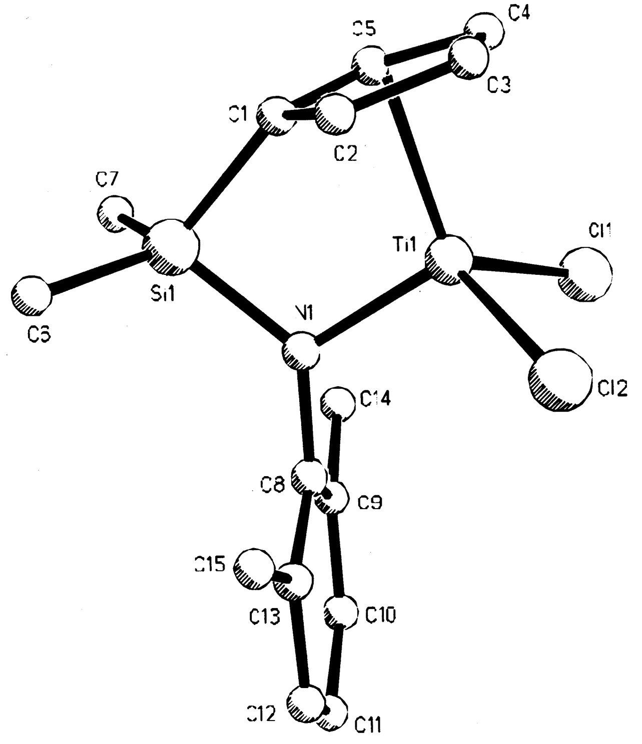


Fig. 1. Molecular structure of [Ti{η^5-$C_5H_4SiMe_2$[η^1-N($C_6H_3Me_2$)]}Cl_2] (**7**).

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 [Ti{η^5-$C_5H_4SiMe_2$(η^1-NR)}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 [Ti(η^5-C_5R_5){N(^{i}Pr)$_2$}Cl_2] (R = H 1.865(2), R = Me 1.865(5) Å) [12] and [Ti(η^5-C_5H_5){N($SiMe_3$)$_2$}Cl_2] (R = H 1.879(2) Å) [13] and chelating diamido complexes such as [Ti{[η^1-N(2,6-$^i Pr_2C_6H_3$)](CH_2)$_3$[η^1-N(2,6-$^i Pr_2C_6H_3$)]}Cl_2] (1.856(5) and 1.839(5) Å) [14] or [Ti{1,2-(η^1-NSi^{i}Pr$_3$)$_2$(C_6H_4)}Cl_2] (1,878(4) Å) [15].

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

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 C_3–C_4 bond distance of 1.389(6) Å is slightly shorter than the remaining C–C bonds within the ring. Furthermore, the Ti–C_3 and Ti–C_4 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 [Ti{(C_5H_4)$_2$SiMe$_2$}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 Ti[$C_5H_4SiMe_2N^tBu$]Cl_2 (107.0°) [6] and considerably smaller than in similar unlinked Cp–amido complexes as in [Ti(C_5H_5)(N^{i}Pr)Cl_2] (116.2°) [12] or diamido complexes such as [Ti{N($SiMe_3$)$_2$}$_2$(CH_2Ph)$_2$] (120.6°) [17]. In addition, the replacement of the amido ligand with another Cp ligand as in [Ti{(C_5H_4)$_2$SiMe$_2$}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 [Ti{η^1-N(2,6-$^i Pr_2C_6H_3$)}(CH_2)$_3${η^1-N(2,6-$^i Pr_2C_6H_3$)}Cl_2] (99.2(2)°) [14] or [Ti{1,2-(η^1-NSi^{i}Pr$_3$)$_2$(C_6H_4)}Cl_2] (92.6(2)°) [15], with six- and five-membered chelate ring, respectively.

3. Conclusions

[Ti($C_5H_4SiMe_2Cl$)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. [Ti{η^5-$C_5H_4SiMe_2$[η^1-N($C_6H_3Me_2$)]}Cl_2] is readily converted into the dialkyl and diamido complexes [Ti{η^5-$C_5H_4SiMe_2$[η^1-N(C_6H_3 Me_2)]}X_2] (X = R or NMe_2) and to the monoalkyl derivative [Ti{η^5-$C_5H_4SiMe_2$[η^1-N($C_6H_3Me_2$)]}MeCl] by salt methathesis 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 LiNHPh was prepared in hexane (in almost quantitative yield) as a solvent free solid from NH_2Ph and *n*-butyl-lithium (Aldrich, 1.6 M in hexane). The following reagents $LiNMe_2$, $SiMe_3Cl$, $SiMe_3Br$, NEt_3, MeMgCl, $Mg(CH_2Ph)_2$, $LiCH_2SiMe_3$, $AlMe_3$ and the primary amines H_2NR ($R = C_6H_5$, $C_6H_3Me_2$, $C_6H_3Me^iPr$) 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 (^{1}H-NMR at 300 MHz and ^{13}C-NMR at 75 MHz) spectrometer. ^{1}H and ^{13}C chemical shifts are reported in δ units relative to TMS standard.

4.2. Synthesis of $[Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)\{C(Ph)[N(SiMe_3)]_2\}Cl_2]$ (2)

A solution of $Li\{C(Ph)[N(SiMe_3)]_2\}$ (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 $C_{20}H_{33}N_2Si_3Ti$: C: 44.48; H: 6.15; N: 5.18. Found: C: 44.94; H: 6.00; N: 5.84%. ^{1}H-NMR (C_6D_6): δ 6.88 (m, 5H, C_6H_5), 6.84 (t, 2H, C_5H_4), 6.55 (t, 2H, C_5H_4), 1.09 (s, 6H, $SiMe_2$), −0.01 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$-NMR (C_6D_6): δ 173.5 ($Ph\underline{C}(NSiMe_3)_2$), 136.5 ($C_6H_5$), 124.0, 125.9 (CH of $\underline{C}_5H_4R$), 3.0 ($SiMe_2Cl$), 2.5 ($NSiMe_3$).

4.3. Synthesis of $[Ti(\eta^5\text{-}C_5H_4SiMe_2NMe_2)(NMe_2)_3]$ (3)

A sample of $LiNMe_2$ (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 $C_{15}H_{34}N_4SiTi$: C, 52.29; H, 10.19; N, 16.50. Found: C: 52.01; H: 9.89; N: 16.17%. ^{1}H-NMR (C_6D_6): δ 6.20 (t, 2H, C_5H_4), 6.12 (t, 2H, C_5H_4), 3.09 (s, 18H, 3 Ti–NMe_2), 2.46 (s, 6H, Si–NMe_2), 0.34 (s, 6H, $SiMe_2$). ($CDCl_3$): δ 6.17 (m, 4H, C_5H_4), 3.03 (s, 18H, 3 Ti–NMe_2), 2.42 (s, 6H, Si–NMe_2), 0.24 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 117.9 (CH of C_5H_4), 112.5(CH of C_5H_4), 44.8 (Ti–NMe_2), 38.3 (Si–NMe_2), −1.4 ($SiMe_2$).

4.4. Synthesis of $[Ti(\eta^5\text{-}C_5H_4SiMe_2NMe_2)(NMe_2)Cl_2]$ (4)

A sample of $SiMe_3Cl$ (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 $C_{12}H_{22}N_2SiCl_2Ti$: C: 40.01; H: 7.00; N: 8.48. Found: C: 40.14; H: 6.74; N: 8.51%. ^{1}H-NMR (C_6D_6): δ 6.49 (t, 2H, C_5H_4), 6.14 (t, 2H, C_5H_4), 3.25 (s, 6H, Ti–NMe_2), 2.42 (s, 6H, Si–NMe_2), 0.47 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 134.2 (C_{ipso} of C_5H_4), 125.7 (CH of C_5H_4), 119.7 (CH of C_5H_4), 52.6 (Ti–NMe_2), 38.1 (Si–NMe_2), −2.0 ($SiMe_2$).

4.5. Synthesis of $[Ti(\eta^5\text{-}C_5H_4SiMe_2NMe_2)(NMe_2)Br_2]$ (5)

In a similar way, $SiMe_3Br$ (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 $C_{12}H_{22}N_2SiBr_2Ti$: C: 31.53; H: 5.53; N: 6.68. Found: C: 31.60; H: 5.30; N: 6.70%. ^{1}H-NMR (C_6D_6): δ 6.69 (t, 2H, C_5H_4), 6.04 (t, 2H, C_5H_4), 3.30 (s, 6H, Ti–NMe_2), 2.43 (s, 6H, Si–NMe_2), 0.50 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 135.1 (C_{ipso} of C_5H_4), 125.7 (CH of C_5H_4), 119.7 (CH of C_5H_4), 53.0 (Ti–NMe_2), 38.2 (Si–NMe_2), −1.6 ($SiMe_2$).

4.6. Synthesis of $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_5)]\}Cl_2]$ (6)

Samples of H_2NPh (0.15 ml, 1.6 mmol) and NEt_3 (0.44 ml, 3.2 mmol) were added to a cooled solution (−60°C) of $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$, **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%. ^{1}H-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, C_5H_4), 6.15 (t, 2H, C_5H_4), 0.15 (s, 6H, $SiMe_2$). ($CDCl_3$): δ 7.34 (d, $2H_{ortho}$, Ph), 7.12 (t, $2H_{meta}$, Ph), 7.05 (t, $1H_{para}$, Ph), 7.14 (t, 2H, C_5H_4), 6.68 (t, 2H, C_5H_4), 0.66 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 152.3 (C_{ipso} of C_6H_5), 129.1 (C_{ortho} of C_6H_5), 126.6 (C_{meta} of C_6H_5), 125.0 (C_{para} of C_6H_5), 125.5 (CH of C_5H_4), 118.9 (CH of C_5H_4), 111.3 (C_{ipso} of C_5H_4), -2.4 ($SiMe_2$).

Following the same procedure described above using $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$, **1** (0.5 g, 1.6 mmol), LiNHPh (0.15 ml, 1.6 mmol) and NEt_3 (0.22 ml, 1.6 mmol), **6** was obtained in higher yield (0.22 g, 41% yield).

4.7. Synthesis of
$[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}Cl_2]$ (**7**)

Some $H_2N(C_6H_3Me_2)$ (0.20 ml, 1.6 mmol) and NEt_3 (0.44 ml, 3.2 mmol) were added to a cooled solution (-60°C) of $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$, **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 $C_{15}H_{19}NCl_2SiTi$: C: 50.23; H: 5.56; N: 3.91. Found: C: 50.01; H: 5.36; N: 3.88%. ^{1}H-NMR (C_6D_6): δ 7.01 (d, $2H_{meta}$, $C_6\underline{H}_3Me_2$), 6.92 (t, $1H_{para}$, $C_6\underline{H}_3Me_2$), 6.58 (t, 2H, C_5H_4), 6.15 (t, 2H, C_5H_4), 2.07 (s, 6H, $C_6H_3\underline{Me_2}$), 0.06 (s, 6H, $SiMe_2$). ($CDCl_3$): δ 7.08–6.96 (m, 3H, $C_6\underline{H}_3Me_2$), 7.17 (t, 2H, C_5H_4), 6.73 (t, 2H, C_5H_4), 2.00 (s, 6H, $C_6H_3\underline{Me_2}$), 0.56 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 147.1 (C_{ipso} of $\underline{C}_6H_3Me_2$), 129.8 (C_{ortho} of $\underline{C}_6H_3Me_2$), 128.8 (C_{meta} of $\underline{C}_6H_3Me_2$), 126.0 (C_{para} of $\underline{C}_6H_3Me_2$), 126.3 (CH of C_5H_4), 125.3 (CH of C_5H_4), 112.3 (C_{ipso} of C_5H_4), 19.7 ($C_6H_3\underline{Me_2}$), -0.7 ($SiMe_2$).

4.8. Synthesis of
$[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2\text{-}Me\text{-}6\text{-}{}^iPr\text{-}C_6H_3)]\}Cl_2]$ (**8**)

A mixture of $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ **1** (0.5 g, 1.6 mmol), $H_2N(C_6H_3Me^iPr)$ (0.25 ml, 1.6 mmol) and NEt_3 (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 $C_{17}H_{23}NCl_2SiTi$: C: 51.69; H: 6.00; N: 3.28. Found: C: 52.39; H: 5.86; N: 3.56%. ^{1}H-NMR (C_6D_6): δ 7.15–6.84 (m, 3H, $C_6\underline{H}_3Me^iPr$), 6.59 (m, 1H, C_5H_4), 6.54 (m, 1H, C_5H_4), 6.21 (m, 1H, C_5H_4), 6.15 (m, 1H, C_5H_4), 2.84 (hp, 1H, $C_6H_3Me^i\underline{Pr}$), 2.04 (s, 3H, $C_6H_3\underline{Me}^iPr$), 1.52 (d, 3H, $C_6H_3Me^i\underline{Pr}$), 1.03 (d, 3H, $C_6H_3Me^i\underline{Pr}$), 0.20 (s, 3H, $SiMe_2$), 0.05 (s, 3H, $SiMe_2$). ($CDCl_3$): δ 7.16–7.06 (m, 3H, $C_6\underline{H}_3Me^iPr$), 7.22–7.16 (m, 2H, C_5H_4), 6.77 (m, 2H, C_5H_4), 2.66 (hp, 1H, $C_6H_3Me^i\underline{Pr}$), 2.00 (s, 3H, $C_6H_3\underline{Me}^iPr$), 1.29 (d, 3H, $J_{HH} = 6.6$ Hz, $C_6H_3Me^i\underline{Pr}$), 1.01 (d, 3H, $J_{HH} = 6.6$ Hz, $C_6H_3Me^i\underline{Pr}$), 0.62 (s, 3H, $SiMe_2$), 0.58 (s, 3H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 141.5 (C_{ipso} of $\underline{C}_6H_3Me^iPr$), 129.1, 128.6, 126,5, 126,4 (rest of $\underline{C}_6H_3Me^iPr$), 126.1 (CH of C_5H_4), 126.0 (CH of C_5H_4), 125.3 (CH of C_5H_4), 124.8 (CH of C_5H_4), 112.0 (C_{ipso} of C_5H_4), 27.9, 26.5, 23.9 ($C_6H_3Me^i\underline{Pr}$), 20.7 ($C_6H_3\underline{Me}^iPr$), -0.7 ($SiMe_2$), -0.9 ($SiMe_2$).

4.9. Synthesis of
$[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}Me_2]$ (**9**)

A 2 M solution of MeMgCl (5.75 ml, 11.5 mmol) was added to a solution of $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}Cl_2]$ (**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. $C_{17}H_{25}NSiTi$: C: 63.97; H: 7.83; N: 4.38. Found: C: 63.78; H: 7.92; N: 4.34%. ^{1}H-NMR (C_6D_6): δ 7.18 (d, $2H_{meta}$, $C_6\underline{H}_3Me_2$), 7.00 (t, $1H_{para}$, $C_6\underline{H}_3Me_2$), 6.71 (t, 2H, C_5H_4), 5.95 (t, 2H, C_5H_4), 2.08 (s, 6H, $C_6H_3\underline{Me_2}$), 0.65 (s, 6H, Ti–Me), 0.11 (s, 6H, $SiMe_2$). ^{1}H-NMR ($CDCl_3$): δ 7.16–6.95 (m, 3H, $C_6\underline{H}_3Me_2$), 7.16 (t, 2H, C_5H_4), 6.36 (t, 2H, C_5H_4), 2.07 (s, 6H, $C_6H_3\underline{Me_2}$), 0.48 (s, 6H, Ti–Me), 0.36 (s, 6H, $SiMe_2$). ^{13}C-NMR ($CDCl_3$): δ 148.1 (C_{ipso} of $\underline{C}_6H_3Me_2$), 131.2 (C_{ortho} of $\underline{C}_6H_3Me_2$), 128.4 (C_{meta} of $\underline{C}_6H_3Me_2$), 123.2 (C_{para},of $\underline{C}_6H_3Me_2$), 122.5 (CH of C_5H_4), 119.6 (CH of C_5H_4), 104.2 (C_{ipso} of C_5H_4), 56.5 (Ti–Me), 19.3 ($C_6H_3\underline{Me_2}$), -0.2 ($SiMe_2$).

4.10. Synthesis of
$[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}(CH_2Ph)_2]$ (**10**)

A solution of $Mg(CH_2Ph)_2$. 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 $C_{29}H_{33}NSiTi$: C: 73.90; H: 7.00; N: 2.97. Found: C: 74.35; H: 7.10; N: 3.02%. ^{1}H-NMR (C_6D_6): δ 7.17 (d, $2H_{meta}$, $C_6\underline{H}_3Me_2$, $J_{HH} = 7.9$ Hz), 7.09 (t, $4H_{meta}$,

$CH_2C_6\underline{H}_5$, $J_{HH} = 6.1$ Hz), 7.02 (t, 1H_{para}, $C_6\underline{H}_3Me_2$, $J_{HH} = 7.9$ Hz), 6.86 (t, 4H_{para}, $CH_2C_6\underline{H}_5$, $J_{HH} = 7.3$ Hz), 6.67 (d, 4H_{ortho}, $CH_2C_6\underline{H}_5$, $J_{HH} = 7.3$ Hz), 6.35 (t, 2H, C_5H_4, $J_{HH} = 2.4$ Hz), 5.96 (t, 2H, C_5H_4, $J_{HH} = 2.4$ Hz), 2.73 (d, 2H, $C\underline{H}_2Ph$, $J_{HH} = 9.7$ Hz), 2.24 (d, 2H, $C\underline{H}_2Ph$, $J_{HH} = 9.7$ Hz), 2.14 (s, 6H, $C_6H_3\underline{Me_2}$), 0.11 (s, 6H, $SiMe_2$). ^{1}H-NMR ($CDCl_3$): δ 7.20 (d, 2H_{meta}, $C_6\underline{H}_3Me_2$), 7.12 (t, 4H_{meta}, $CH_2C_6\underline{H}_5$), 7.03 (t, 1H_{para}, $C_6\underline{H}_3Me_2$), 6.87 (t, 4H_{para}, $CH_2C_6\underline{H}_5$), 6.68 (d, 4H_{ortho}, $CH_2C_6\underline{H}_5$), 6.43 (t, 2H, C_5H_4), 6.18 (t, 2H, C_5H_4), 2.69 (d, 2H, $C\underline{H}_2Ph$), 2.24 (s, 6H, $C_6H_3\underline{Me_2}$), 2.22 (d, 2H, $C\underline{H}_2Ph$), 0.40 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 149.4 (C_{ipso} of $CH_2\underline{C}_6H_5$), 148.9 (C_{ipso} of $\underline{C}_6H_3Me_2$), 130.7 (C_{ortho} of $\underline{C}_6H_3Me_2$), 128.8 (C_{meta} of $\underline{C}_6H_3Me_2$), 128.2 (C_{ortho} of $CH_2\underline{C}_6H_5$), 125.3 (C_{meta} of $CH_2\underline{C}_6H_5$), 125.05 (C_{para} of $CH_2\underline{C}_6H_5$), 123.9 (CH of C_5H_4), 123.7 (C_{para} of $\underline{C}_6H_3Me_2$), 122.0 (CH of C_5H_4), 106.9 (C_{ipso} of C_5H_4), 86.2 ($J_{CH} = 122.8$ Hz, $\underline{C}H_2Ph$), 20.0 ($C_6H_3\underline{Me_2}$), -0.2 ($SiMe_2$).

4.11. Synthesis of *[Ti{η^5-$C_5H_4SiMe_2[\eta^1$-N(2,6-$Me_2C_6H_3$)]}($CH_2SiMe_3)_2$]* (**11**)

A solution of $LiCH_2SiMe_3$ (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 $C_{23}H_{41}NSi_3Ti$: C: 59.61; H: 8.85; N: 3.02. Found: C: 59.02; H: 8.48; N: 2.78%. ^{1}H-NMR (C_6D_6): δ 7.12–6.9 (m, 3H, $C_6\underline{H}_3Me_2$), 6.96 (t, 2H, C_5H_4), 6.27 (t, 2H, C_5H_4), 2.13 (s, 6H, $C_6H_3\underline{Me_2}$), 1.58 (d, 2H, $C\underline{H}_2SiMe_3$, $J_{HH} = 10.6$ Hz), 0.87 (d, 2H, $C\underline{H}_2SiMe_3$, $J_{HH} = 10.6$ Hz), 0.17 (s, 6H, $SiMe_2$), 0.04 (s, 18H, $CH_2Si\underline{Me_3}$). ^{1}H-NMR ($CDCl_3$): δ 7.1–6.9 (m, 3H, $C_6\underline{H}_3Me_2$), 7.09 (t, 2H, C_5H_4), 6.42 (t, 2H, C_5H_4), 2.09 (s, 6H, $C_6H_3\underline{Me_2}$), 1.48 (d, 2H, $C\underline{H}_2SiMe_3$, $J_{HH} = 10.2$ Hz), 0.75 (d, 2H, $C\underline{H}_2SiMe_3$, $J_{HH} = 10.2$ Hz), 0.32 (s, 6H, $SiMe_2$), -0.06 (s, 18H, $CH_2Si\underline{Me_3}$). ^{13}C-NMR ($CDCl_3$): δ 150.3 (C_{ipso} of $\underline{C}_6H_3Me_2$), 130.7 (C_{ortho} of $\underline{C}_6H_3Me_2$), 128.6 (C_{meta} of $\underline{C}_6H_3Me_2$), 123.0 (C_{para} of $\underline{C}_6H_3Me_2$), 121.9 (CH of C_5H_4), 117.7 (CH of C_5H_4), 105.4 (C_{ipso} of C_5H_4), 81.4 ($\underline{C}H_2SiMe_3$), 19.9 ($C_6H_3\underline{Me_2}$), 2.4 ($CH_2Si\underline{Me_3}$), -0.1 ($SiMe_2$).

4.12. Synthesis of *[Ti{η^5-$C_5H_4SiMe_2[\eta^1$-N(2,6-$Me_2C_6H_3$)]}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 $C_{16}H_{22}ClNSiTi$: C: 56.55; H: 6.52; N: 4.12. Found: C: 56.36; H: 6.51; N: 4.11%. ^{1}H-NMR (C_6D_6): δ 7.09 (d, 2H_{meta}, $C_6\underline{H}_3Me_2$), 6.97 (t, 1H_{para}, $C_6\underline{H}_3Me_2$), 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, $C_6H_3\underline{Me_2}$), 1.96 (s, 3H, $C_6H_3\underline{Me_2}$), 1.01 (s, 3H, Ti–Me), 0.07 (s, 3H, $SiMe_2$), 0.06 (s, 3H, $SiMe_2$). ^{1}H-NMR ($CDCl_3$): δ 7.28 (s, 1H, C_5H_4), 7.07 (m, 2H_{meta}, $C_6\underline{H}_3Me_2$), 6.94 (t, 1H_{para}, $C_6\underline{H}_3Me_2$), 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, $C_6H_3\underline{Me_2}$), 1.99 (s, 3H, $C_6H_3\underline{Me_2}$), 0.93 (s, 3H, Ti–Me), 0.44 (s, 3H, $SiMe_2$), 0.41 (s, 3H, $SiMe_2$). ^{13}C-NMR ($CDCl_3$): δ 147.7 (C_{ipso} of $\underline{C}_6H_3Me_2$), 130.6 (C_{ortho} of $\underline{C}_6H_3Me_2$), 130.4 (C_{ortho} of $\underline{C}_6H_3Me_2$), 128.8 (C_{meta} of $\underline{C}_6H_3Me_2$), 128.5 (C_{meta} of $\underline{C}_6H_3Me_2$), 124.4 (CH of C_5H_4), 124.0 (CH of C_5H_4), 122.4 (C_{para} of $\underline{C}_6H_3Me_2$), 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 ($C_6H_3\underline{Me_2}$), 18.9 ($C_6H_3\underline{Me_2}$), -0.2 ($SiMe_2$), -0.8 ($SiMe_2$).

4.13. Synthesis of *[Ti{η^5-$C_5H_4SiMe_2[\eta^1$-N(2,6-$Me_2C_6H_3$)]}($NMe_2)_2$]* (**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 $C_{19}H_{31}N_3SiTi$: C: 60.46; H: 8.28; N: 11.13. Found: C: 60.10; H: 7.99; N: 10.89%. ^{1}H-NMR (C_6D_6): δ 7.10–6.80 (m, 3H, $C_6\underline{H}_3Me_2$), 6.26 (t, 2H, C_5H_4, $J_{HH} = 2.2$ Hz), 6.20 (t, 2H, C_5H_4, $J_{HH} = 2.2$ Hz), 2.80 (s, 12H, NMe_2), 2.12 (s, 6H, $C_6H_3\underline{Me_2}$), 0.35 (s, 6H, $SiMe_2$). ^{1}H-NMR ($CDCl_3$): δ 7.10–6.78 (m, 3H, $C_6\underline{H}_3Me_2$), 6.63 (t, 2H, C_5H_4), 6.43 (t, 2H, C_5H_4), 3.01 (s, 12H, NMe_2), 2.12 (s, 6H, $C_6H_3\underline{Me_2}$), 0.47 (s, 6H, $SiMe_2$). ^{13}C-NMR ($CDCl_3$): δ 150.1 (C_{ipso} of $\underline{C}_6H_3Me_2$), 132.3 (C_{ortho} of $\underline{C}_6H_3Me_2$), 127.3 (C_{meta} of $\underline{C}_6H_3Me_2$), 120.8 (C_{para} of $\underline{C}_6H_3Me_2$), 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 ($C_6H_3\underline{Me_2}$), 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 $4 < 2\theta < 50°$.

Table 2
Crystal data and structure refinement for complex **7**

Empirical formula	$C_{15}H_{19}Cl_2NSiTi$
Formula weight	360.20
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.185(6)
b (Å)	7.566(2)
c (Å)	17.233(8)
β (°)	96.39(2)
Volume (Å^3)	1708(1)
Z	4
$D_{calc.}$ (g cm^{-3})	1.400
Absorption coefficient (mm^{-1})	0.873
F(000)	744
Crystal size (mm)	$0.35 \times 0.32 \times 0.28$
θ range for data collection (°)	2.00–25.00
Index ranges	$0<h<15$, $0<k<8$, $-20<l<20$
Reflections collected	3122
Independent reflections	2984 ($R_{int} = 0.0305$)
Observed reflections [$I > 2\sigma(I)$]	2063
Absorption correction	Ψ-scan
Max. and min. transmission	0.301 and 0.265
Goodness-of-fit on F^2	0.951
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.042$, $wR_2 = 0.113$
R indices (all data)	$R_1 = 0.077$, $wR_2 = 0.121$
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 $F > 4\sigma(F)$]. The values of R_1 and wR_2 are defined as $R_1 = \Sigma\|F_o| - |F_c\|/[\Sigma|F_o|]$ and $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$, 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 $U = 0.08$ Å^2.

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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