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Chloro- and Alkyltitanium Complexes of a New Dianionic Ancillary Ligand: A Linked Amidinate–Amide^[‡]

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The lithium amidinate [Me₃SiNC(Ph)N(CH₂)₃N(Me)SiMe₃]-Li(THF) (**2**), with a pendant methyl(trimethylsilyl)amine functionality, was prepared and found to react with [TiCl₄(THF)₂] to give the titanium amidinate–amide dichloride complex [η²,η¹-Me₃SiNC(Ph)N(CH₂)₃NMe]TiCl₂ (**3**) by elimination of LiCl and Me₃SiCl. The elimination of Me₃SiCl from the cyclopentadienyl derivative Cp[η²-Me₃SiNC(Ph)N(CH₂)₃N(-SiMe₃)Me]TiCl₂ (**5**) to give Cp[η²,η¹-Me₃SiNC(Ph)N-

(CH₂)₃NMe]TiCl (**4**) is much less favorable, and was found to be readily reversible. Dialkyltitanium complexes [η²,η¹-Me₃SiNC(Ph)N(CH₂)₃NMe]Ti(CH₂R)₂ [R = Ph (**6**), SiMe₃ (**7**)] were prepared, but could not be activated for catalytic ethene polymerization.

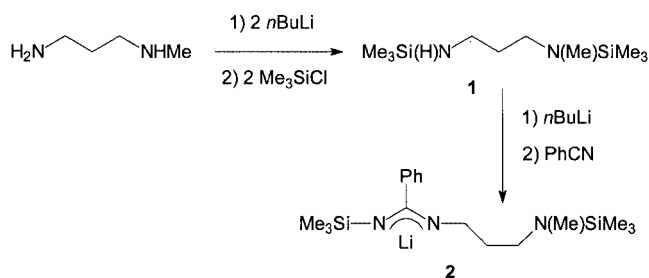
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Introduction

Amidinate monoanions [RC(NR')₂]⁻ (R = aryl, alkyl; R' = aryl, alkyl, SiMe₃) form a group of versatile ancillary ligands (binding predominantly in an *N,N'*-bidentate fashion) that have been employed extensively in main-group and transition-metal coordination chemistry, organometallic chemistry and catalysis.^[1–5] They can also be incorporated as a functionality in polydentate ligand systems. Examples have been reported recently of the synthesis and complexation chemistry of monoanionic tridentate amidinate Lewis base^[6–9] and dianionic tetradentate bis(amidinate) ligands.^[10–12] One way to prepare amidinate-based polydentate ligands is the reaction of functionalized trimethylsilylamides with nitriles.^[6,8,9,12] Here we report the use of this method to prepare the amidinate [Me₃SiNC(Ph)N(CH₂)₃N(SiMe₃)Me]⁻ with a pendant alkyl(trimethylsilyl)amine functionality. Reaction of the Li salt of this amidinate with titanium chlorides leads to the formation of titanium complexes of the new dianionic amidinate–amide tridentate ligand [Me₃SiNC(Ph)N(CH₂)₃NMe]²⁻ by sequential salt metathesis and Me₃SiCl elimination reactions. The synthesis, structure and reactivity of two of these titanium complexes, [Me₃SiNC(Ph)N(CH₂)₃NMe]TiCl₂ and Cp[Me₃SiNC(Ph)N(CH₂)₃NMe]TiCl, are described.

Results and Discussion

The Li salt of an amidinate with a pendant alkyl(trimethylsilyl)amine group, [Me₃SiNC(Ph)N(CH₂)₃N(SiMe₃)Me]⁻, was prepared by the deprotonation of the diamine Me₃Si-N(H)(CH₂)₃N(Me)SiMe₃ (**1**) with *n*BuLi/hexane in THF, followed by reaction with benzonitrile (Scheme 1). After recrystallization from pentane, the resulting Li amidinate was obtained analytically pure as its THF solvate [Me₃SiNC(Ph)N(CH₂)₃N(Me)SiMe₃Li(THF)] (**2**) in 55% isolated yield. The presence of THF in **2** probably indicates that the pendant methyl(trimethylsilyl)amine functionality is not coordinated to the Li ion, in contrast to the THF-free Li amidinate–amine [Me₃SiNC(Ph)N(CH₂)₃NMe₂]Li, which was found to adopt a dimeric structure with a coordinated amine functionality.^[9]



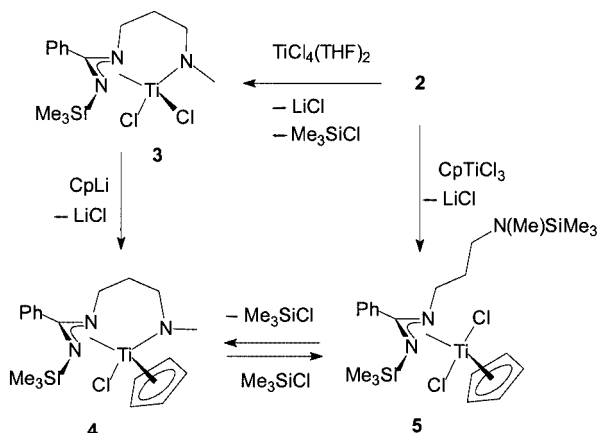
Scheme 1

The Li amidinate **2** reacts with [TiCl₄(THF)₂] in THF to give the titanium amidinate–amide complex [η²,η¹-Me₃SiNC(Ph)N(CH₂)₃NMe]TiCl₂ (**3**) by elimination of LiCl and

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Me_3SiCl (Scheme 2). After recrystallization from diethyl ether, complex **3** was obtained as orange-red crystals, analytically pure, in 56% yield.



Scheme 2

A single-crystal X-ray structure determination of **3** (Figure 1) showed that the amidinate moiety of the ligand is N,N' -dihapto bound to the metal center [$\text{Ti}-\text{N}(1) = 2.077(2) \text{ \AA}$ and $\text{Ti}-\text{N}(2) = 2.059(2) \text{ \AA}$]. The $\text{Ti}-\text{N}$ distance to the amido nitrogen atom is significantly shorter [$\text{Ti}-\text{N}(3) = 1.863(2) \text{ \AA}$] than those to the amidinate nitrogen atoms, probably in response to an amide $\text{N}(p) \pi$ -donation to $\text{Ti}(d)$. The amidinate nitrogen atom linked to the alkylamide moiety deviates somewhat from planarity [the sum of the angles around $\text{N}(2)$ is 353.8°], but this deviation is not as pronounced as in the vanadium amidinate–amine complex [$\eta^2, \eta^1\text{-Me}_3\text{SiNC}(\text{Ph})\text{N}(\text{CH}_2)_2\text{NMe}_2\text{VCl}_2(\text{THF})$] in which the sum of the angles around N is 336.4° ^[6] and where the amidinate–amine tridentate ligand clearly adopts a *fac* coordination geometry. The amide nitrogen atom in **3** is planar [the sum of the angles around $\text{N}(3)$ is 360.0°], again indicative of efficient amide-to-metal π -donation. The angles around this atom show significant asymmetry, with the $\text{Ti}-\text{N}-\text{C}$ angle within the six-membered ring [$\text{Ti}-\text{N}(3)-\text{C}(13) = 137.0(2)^\circ$] being significantly larger than the $\text{Ti}-\text{N}-\text{C}(\text{Me})$ angle [$\text{Ti}-\text{N}(3)-\text{C}(14) = 110.2(2)^\circ$]. The solution NMR spectra of **3** are consistent with C_s symmetry, indicating that the amidinate–amide acts as a meridional-type ligand, and that the six-membered TiN_2C_3 ring, which adopts a boat-like conformation in the crystal structure, readily inverts.

The rapid formation in high yield of the amidinate–amide complex **3** in the reaction of $\text{TiCl}_4(\text{THF})_2$ with the Li amidinate **2** indicates that the Me_3SiCl elimination reaction from $[\eta^2\text{-Me}_3\text{SiNC}(\text{Ph})\text{N}(\text{CH}_2)_3\text{N}(\text{SiMe}_3)\text{Me}]\text{TiCl}_3$, the likely primary product of the salt metathesis reaction, is facile. The reverse reaction – formation of group-4 metal chlorides by reaction of group-4 metal amides with an excess of Me_3SiCl – was reported as a clean, salt-free route to generate group-4 metallocene dichlorides from their corresponding bis(amides).^[13–15] Apparently, in our case the chelate effect

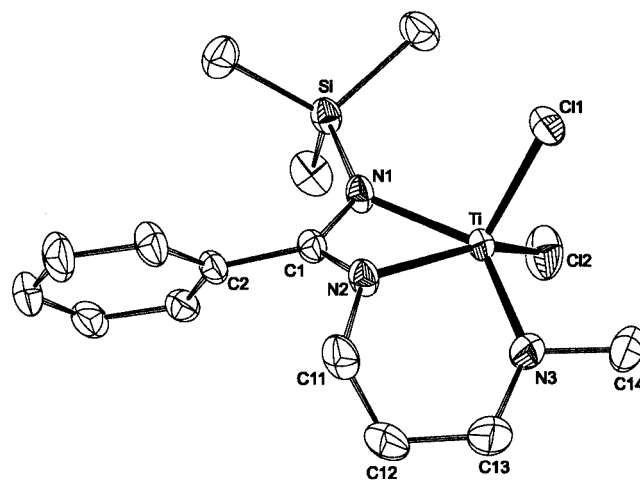


Figure 1. Molecular structure of compound **3**; thermal ellipsoids are drawn at the 50% probability level; $\text{Ti}-\text{Cl}(1) 2.2464(6)$, $\text{Ti}-\text{Cl}(2) 2.2954(7)$, $\text{Ti}-\text{N}(1) 2.077(2)$, $\text{Ti}-\text{N}(2) 2.059(2)$, $\text{Ti}-\text{N}(3) 1.863(2) \text{ \AA}$; $\text{Cl}(1)-\text{Ti}-\text{Cl}(2) 107.26(2)$, $\text{N}(1)-\text{Ti}-\text{N}(2) 64.03(6)$, $\text{N}(1)-\text{Ti}-\text{N}(3) 139.40(7)$, $\text{N}(2)-\text{Ti}-\text{N}(3) 84.08(7)$, $\text{N}(3)-\text{Ti}-\text{Cl}(1) 107.72(6)$, $\text{N}(3)-\text{Ti}-\text{Cl}(2) 100.83(6)$, $\text{Ti}-\text{N}(3)-\text{C}(13) 137.0(2)$, $\text{Ti}-\text{N}(3)-\text{C}(14) 110.2(2)^\circ$

leads to a thermodynamically favored elimination of Me_3SiCl and formation of the metal–amide bond in **3**.

The reaction of $[\text{CpTiCl}_3]$ with the Li amidinate **2** in THF, followed by extraction with, and crystallization from, diethyl ether, resulted only in a low isolated yield (13%) of the corresponding amidinate–amide complex $\text{Cp}[\eta^2, \eta^1\text{-Me}_3\text{SiNC}(\text{Ph})\text{N}(\text{CH}_2)_3\text{NMe}]\text{TiCl}$ (**4**), which was characterized by single-crystal X-ray diffraction (vide infra). Workup of the reaction mixture was made more difficult by the presence of a substantial amount of an orange oil, which appeared to be the major product of the reaction, but which defied crystallization. Investigation of the reaction between $[\text{CpTiCl}_3]$ and **2** in $[\text{D}_8]\text{THF}$ at ambient temperature initially showed rapid formation of a primary product, identified as $\text{Cp}[\eta^2\text{-Me}_3\text{SiNC}(\text{Ph})\text{N}(\text{CH}_2)_3\text{N}(\text{SiMe}_3)\text{Me}]\text{TiCl}_2$ (**5**) from its NMR characteristics (which are identical to those of the orange oil observed in the reaction on preparative scale). This initial reaction is followed by slow release of Me_3SiCl and concomitant formation of the amidinate–amide complex **4** (Scheme 2). Characteristic for the latter are the significant downfield shift of the NMR resonances associated with the NMe group (^1H : $\delta = 3.21 \text{ ppm}$; ^{13}C : $\delta = 51.0 \text{ ppm}$) relative to those in **5** (^1H : $\delta = 2.29 \text{ ppm}$; ^{13}C : $\delta = 35.3 \text{ ppm}$). The secondary reaction can be accelerated by increasing the reaction temperature ($50\text{--}80^\circ\text{C}$), but this is then accompanied by the formation of unidentified degradation products. The Me_3SiCl elimination reaction appears to be noticeably faster when the reaction is performed in C_6D_6 rather than in the Lewis basic solvent $[\text{D}_8]\text{THF}$, proceeding readily at ambient temperature. The reaction was observed to reach an equilibrium (in C_6D_6 and 25°C within 30 min), suggesting that the reaction is readily reversible in the mono(cyclopentadienyl)titanium system. Indeed, upon addition of Me_3SiCl to C_6D_6 solutions of the amidinate–amide complex **4** the formation

of **5** could be observed. Examination of C_6D_6 solutions of **4** of known concentration to which 1, 2 or 3 equiv. of Me_3SiCl were added allowed a determination of the equilibrium constant at 25 °C of the equilibrium of **4** + Me_3SiCl with **5** as $K = [5]/([4] + [Me_3SiCl]) = 32(3) \text{ L mol}^{-1}$. Compound **4** was also prepared independently, in 38% isolated yield, by the reaction of the dichloride **3** with $CpLi$, in which this equilibrium is avoided. This reaction appears to suffer from some reduction of the metal center, as seen from the dark residue left after extraction of the reaction mixture with hexane and the relatively modest isolated yield.

The molecular structure of **4** (Figure 2) shows a fully symmetrically bound η^5 -cyclopentadienyl ligand and an η^2, η^1 -amidinate–amide ligand in which the TiN_2C_3 ring now adopts a twisted conformation. The amidinate nitrogen atom attached to the alkylamide moiety is significantly less planar [sum of the angles around N(2) is 340.6°] than in **3**. The angles around the (planar) amide nitrogen atom are again highly asymmetric, but in the opposite direction than in **3**: the Ti–N–C angle within the six-membered ring [Ti–N(1)–C(7) = $105.6(2)^\circ$] is now significantly smaller than the Ti–N–C(Me) angle [Ti–N(1)–C(6) = $141.6(2)^\circ$]. This is probably in response to the twisted conformation of the six-membered ring. It also reduces the steric interaction of the amide methyl group with the cyclopentadienyl ligand, towards which it is pointing. Overall, the metal–ligand distances in **4** are larger than those in **3** [especially the Ti–Cl distance of 2.4038(7) Å, compared to 2.2464(6) and 2.2954(7) Å in **3**] but the metal–amide distances are similar [1.887(2) Å in **4**, 1.863(2) Å in **3**], indicating the importance of the amide-to-metal π -donation.

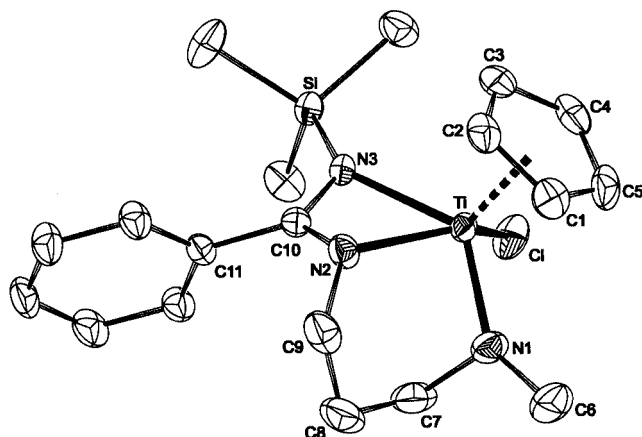
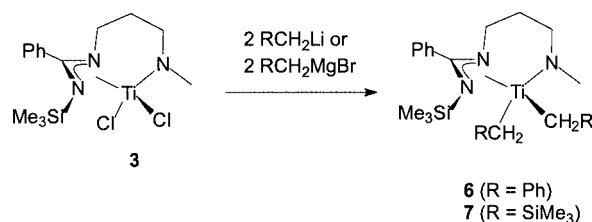


Figure 2. Molecular structure of compound **4**; thermal ellipsoids are drawn at the 50% probability level; Ti–Cl 2.4038(7), Ti–N(1) 1.887(2), Ti–N(2) 2.095(2), Ti–N(3) 2.170(2) Å; N(1)–Ti–N(2) $85.12(7)^\circ$, N(1)–Ti–N(3) $128.61(7)^\circ$, N(2)–Ti–N(3) $61.96(6)^\circ$, N(1)–Ti–Cl $93.96(6)^\circ$, Ti–N(1)–C(6) $141.6(2)^\circ$, Ti–N(1)–C(7) $105.6(2)^\circ$

The amidinate–amide dichloride **3** may be converted into the corresponding dialkyltitanium amidinate–amide complexes, which are precursors to cationic monoalkyl species that are interesting as potential olefin polymerization catalysts. Reaction of **3** with 2 equiv. of either $PhCH_2MgBr$ or Me_3SiCH_2Li results in the formation of

the dialkyl complexes $[\eta^2, \eta^1-Me_3SiNC(Ph)N(CH_2)_3NMe]Ti(CH_2R)_2$ [$R = Ph$ (**6**), $SiMe_3$ (**7**); Scheme 3]. Compound **6** was obtained in 74% yield as yellow crystals by crystallization from pentane, whereas **7** is an extremely soluble oil that only gradually solidifies on standing. The compounds are thermally rather labile, and are best handled and stored below 0 °C. Their solution NMR spectra are consistent with an average C_s symmetry, and each show two doublets for the diastereotopic alkyl methylene protons in the 1H NMR spectrum (**6**: $\delta = 2.75$ and 3.09 ppm, $^2J_{H,H} = 9.0$ Hz; **7**: $\delta = 1.56$ and 1.86 ppm, $^2J_{H,H} = 11.0$ Hz).



Scheme 3

The dibenzyl complex **6** was treated with the Lewis acid $B(C_6F_5)_3$ in C_6D_6 and in $[D_5]$ bromobenzene solvents in order to effect the abstraction of a benzyl anion. As the ligand system is sterically not very demanding, the formation of a contact ion pair with an η^6 - $PhCH_2B(C_6F_5)_3$ interaction might be anticipated, as was observed recently for titanium in the reaction of $[(2,6\text{-diphenylphenoxy})_2Ti(CH_2Ph)_2]$ with $B(C_6F_5)_3$.^[16,17] However, in both solvents rapid decomposition to a mixture of unidentified products was observed, even when the reaction in $[D_5]$ bromobenzene was performed at -20 °C. Attempts at catalytic ethene polymerization (5 bar of ethene, 150 mL of toluene solvent, 50 °C, 15 μ mol of Ti) by treating **6** with $B(C_6F_5)_3$ or **7** with $[PhNMe_2H][B(C_6F_5)_4]$ in the presence of monomer did not result in ethene uptake, suggesting that the decomposition of the cationic species generated is rapid. It is likely that the present amidinate–amide ligand is either reactive itself and/or provides insufficient steric protection to the highly electron-deficient metal center.

Conclusion

Titanium complexes of the new dianionic η^2, η^1 -amidinate–amide ligand can be prepared by sequential salt metathesis and Me_3SiCl elimination reactions that occur upon combining titanium chlorides with a lithium amidinate containing a pendant (trimethylsilyl)amide functionality. The Me_3SiCl elimination reaction forming the titanium–amide bond is thermodynamically favored by its intramolecular nature, but it is reversible, and the equilibrium is dependent on what is probably a combination of electronic and steric factors. The formation of the TiN_2C_3 six-membered ring is clearly less favorable in the more electron-rich and sterically more encumbered $[Cp(\text{amidinate})TiCl_2]$ species **5** than in the $(\text{amidinate})TiCl_3$ intermediate

proposed in the formation of **3**. The dialkyltitanium derivatives [η^2, η^1 -Me₃SiNC(Ph)N(CH₂)₃NMe]Ti(CH₂R)₂ (R = Ph, SiMe₃) are readily prepared but are thermally rather labile, and could not be converted into well-defined cationic alkyl compounds that are active in catalytic olefin polymerization. Possibly the present substitution pattern of the ligand (SiMe₃ on the amidinate nitrogen atom, Me on the amido nitrogen atom) renders it incapable of stabilizing such highly reactive species, and sterically more demanding substituents may be required for catalytic activity.

Experimental Section

General Remarks: All experiments were carried out under purified dinitrogen using standard Schlenk and glove-box techniques. Solvents were distilled from Na/K alloy (THF, diethyl ether, pentane, hexane) or sodium (toluene) under nitrogen before use. Deuterated solvents were either dried with Na/K alloy and vacuum-transferred before use (C₆D₆, [D₈]THF) or degassed and stored over 4-Å molecular sieves ([D₅]bromobenzene). [TiCl₄(THF)₂]^[18] and [CpTiCl₃]^[19] were prepared according to published procedures. Benzonitrile, *n*BuLi/hexane, Me₃SiCl and MeNH(CH₃)₃NH₂ were purchased and used as received. NMR spectra were recorded with Varian Gemini 200, VXR 300 and Unity 500 spectrometers. The ¹H NMR spectra were referenced to the resonances of residual protons in the deuterated solvent. Chemical shifts (δ) are given relative to tetramethylsilane (downfield shifts are positive). Elemental analyses were performed at the Microanalytical Department of the University of Groningen. All values are the average of at least two independent determinations.

Synthesis of Me₃SiN(H)(CH₂)₃N(Me)SiMe₃ (1): This compound was prepared according to a modification of a published procedure.^[20] A 2.5 M solution of *n*BuLi in hexane (160 mL, 0.40 mol) was slowly added to a solution of MeNH(CH₃)₃NH₂ (20.9 mL, 0.20 mol) in 50 mL of hexane. After refluxing for 2.5 h, Me₃SiCl (50.5 mL, 0.40 mol) was added dropwise, and the mixture was subsequently refluxed for one more hour. From the resulting deep orange suspension, the volatiles were flash-distilled at 90 °C and 0.05 Torr. Subsequent vacuum distillation of this liquid (14 Torr) yielded the product as a spectroscopically pure colorless liquid at 98–101 °C (29.3 g, 0.126 mol, 63%). ¹H NMR (300 MHz, C₆D₆): δ = 0.09 (s, 18 H, SiMe₃), 1.46 (m, 2 H, CH₂CH₂CH₂), 2.39 (s, 3 H, NCH₃), 2.70 (t, ³J_{H,H} = 7.7 Hz, 2 H, HNCH₂), 2.64 (t, ³J_{H,H} = 7.0 Hz, 2 H, MeNCH₂) ppm. ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 0.2 [Si(CH₃)₃], 34.0 (CH₂CH₂CH₂), 34.1 (NCH₃), 39.8 (HNCH₂), 49.0 (MeNCH₂) ppm. IR (neat, KBr): $\tilde{\nu}$ = 3420 (br. w), 2969 (s), 2854 (m), 2795 (w), 1453 (w), 1400 (m), 1375 (w), 1330 (w), 1253 (s), 1189 (w), 1144 (m), 1110 (m), 1020 (w), 980 (w), 943 (w), 835 (s), 746 (m), 677 (m) cm⁻¹.

Synthesis of [Me₃SiNC(Ph)N(CH₂)₃N(Me)SiMe₃]Li(THF) (2): A solution of **1** (4.2 mL, 18 mmol) in 50 mL of THF was cooled to -80 °C after which a 2.5 M solution of *n*BuLi in hexane (8 mL, 20 mmol) was added dropwise. The solution was allowed to warm to room temperature and was subsequently stirred for 2 h. The light yellow mixture was cooled to -80 °C and benzonitrile (1.8 mL, 17 mmol) was added, after which the mixture was allowed to warm to room temperature. The volatiles from the orange-yellow mixture were removed in vacuo, and the solid residue was recrystallized twice from pentane. Yield: 4.13 g (9.93 mmol, 55%) of a light yellow solid. ¹H NMR (300 MHz, C₆D₆): δ = -0.08 [s, 9 H,

Si(CH₃)₃], -0.03 [s, 9 H, Si(CH₃)₃], 1.28 (m, 4 H, THF β-H), 1.58 (m, 2 H, CH₂CH₂CH₂), 2.44 (s, 3 H, NCH₃), 2.47 (t, ³J_{H,H} = 7.0 Hz, 2 H, NCH₂), 2.98 [t, ³J_{H,H} = 7.3 Hz, 2 H, N(Me)CH₂], 3.58 (m, 4 H, THF α-H), 7.0–7.2 (m, 5 H, Ph) ppm. ¹³C{¹H} NMR (50 MHz, C₆D₆): δ = -0.9 and 3.6 [Si(CH₃)₃], 25.7 (THF β-C), 32.6 (CH₂CH₂CH₂), 34.3 (NCH₃), 48.4 and 49.3 (NCH₂), 68.3 (THF α-C), 126.9, 127.8, 128.1 (Ph CH), 143.3 (Ph C), 177.5 (NCN) ppm. C₂₁H₄₀N₃LiOSi₂ (413.68): calcd. C 60.97, H 9.75, N 10.16; found C 61.17, H 9.60, N 10.45.

Synthesis of [Me₃SiNC(Ph)N(CH₂)₃NMe]TiCl₂ (3): A solution of **2** (2.45 g, 5.93 mmol) and TiCl₄(THF)₂ (1.98 g, 5.93 mmol) in 70 mL of THF was stirred overnight at room temperature. The dark red solution was stirred for another 8 h, during which the flask was periodically briefly evacuated. The volatiles were removed in vacuo, and the residue was freed of residual THF by stirring twice with diethyl ether (15 mL), which was subsequently removed in vacuo. The residue was extracted three times with diethyl ether (30 mL) after which the extract was concentrated and cooled to -80 °C, yielding microcrystalline orange-red **3** (1.26 g, 3.31 mmol, 56%). Crystals suitable for X-ray diffraction were obtained by cooling a solution of **3** in diethyl ether to -20 °C. ¹H NMR (300 MHz, C₆D₆): δ = 0.24 [s, 9 H, Si(CH₃)₃], 1.35 (m, 2 H, CH₂CH₂CH₂), 2.60 (m, 2 H, NCH₂), 2.99 (m, 2 H, MeNCH₂), 3.74 (s, 3 H, NCH₃), 6.93–6.99 (m, 5 H, Ph) ppm. ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 0.2 [Si(CH₃)₃], 31.8 (CH₂CH₂CH₂), 43.0 (NCH₂), 46.6 (NCH₃), 61.8 (NCH₂), 126.8, 127.7, 130.4 (Ph CH), 132.7 (Ph C) ppm; NCN signal not observed. C₁₄H₂₃Cl₂N₃SiTi (380.23): calcd. C 44.22, H 6.10, N 11.05, Ti 12.60; found C 44.36, H 6.03, N 11.12, Ti 12.50.

Synthesis of Cp[Me₃SiNC(Ph)N(CH₂)₃NMe]TiCl (4). Method 1: A solution of **2** (1.07 g, 2.56 mmol) in 40 mL of THF was cooled to -80 °C, after which CpTiCl₃ (0.57 g, 2.59 mmol) was added. The solution was allowed to warm to room temperature, during which time the color changed from yellow to orange-red. After stirring for 2 h, the volatiles were removed in vacuo and the residual THF was removed by stirring the mixture in pentane, which was subsequently pumped off. The residue was extracted twice with diethyl ether (20 mL). Concentrating and cooling the extract to -20 °C yielded red crystalline **4** (0.14 g, 0.34 mmol, 13%). Crystals suitable for X-ray diffraction were obtained by cooling a concentrated solution of **4** in diethyl ether from room temperature to 7 °C. **Method 2:** Hexane (15 mL) was condensed onto a mixture of solid **3** (0.11 g, 0.28 mmol) and CpLi (20 mg, 0.28 mmol), frozen in liquid nitrogen. The mixture was allowed to thaw and warm to room temperature. After stirring for one more hour, the suspension was filtered and the volatiles were removed from the filtrate in vacuo. Extraction of the residue with hexane, and concentrating and cooling the extract to -20 °C, yielded microcrystalline **4** (54 mg, 0.13 mmol, 38%). ¹H NMR (500 MHz, C₆D₆): δ = 0.17 [s, 9 H, Si(CH₃)₃], 1.13, 1.33 (m, 1 H each, CH₂CH₂CH₂), 2.43 (ddd, ²J_{H,H} = 12.4, ³J_{H,H} = 8.8, 5.7 Hz, 1 H, NCHH), 2.65 (ddd, ²J_{H,H} = 14.8, ³J_{H,H} = 6.2, 4.4 Hz, 1 H, MeNCHH), 3.03 (ddd, overlapped, 1 H, NCHH), 3.04 (s, 3 H, NCH₃), 3.38 (ddd, ²J_{H,H} = 14.8, ³J_{H,H} = 7.6, 4.3 Hz, 1 H, NCHH), 6.24 (s, 5 H, C₅H₅), 6.98–7.03 (m, 5 H, Ph) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆): δ = 2.6 [Si(CH₃)₃], 29.8 (CH₂CH₂CH₂), 44.8 (MeNCH₂), 49.8 (NCH₃), 58.6 (NCH₂), 114.5 (C₅H₅), 127.0, 128.6, 129.3 (Ph CH), 135.0 (Ph C), 174.3 (NCN) ppm. C₁₉H₂₈ClN₃SiTi (409.89): calcd. C 55.68, H 6.89, N 10.25; found C 55.10, H 6.89, N 9.75.

Reaction of [CpTiCl₃] with **2 in [D₈]THF:** Separately prepared solutions of [CpTiCl₃] (17 mg, 0.08 mmol) and **2** (33 mg, 0.08 mmol), each in 0.4 mL of [D₈]THF, were mixed at ambient temperature,

resulting in a rapid color change from light yellow to orange, and the mixture was added into an NMR tube, equipped with a Teflon valve. The ^1H and ^{13}C NMR spectra indicated formation of $\text{Cp}[\text{Me}_3\text{SiNC}(\text{Ph})\text{N}(\text{CH}_2)_3\text{N}(\text{Me})\text{SiMe}_3]\text{TiCl}$ (**5**). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$): $\delta = -0.11, -0.05$ [s, 9 H each, $\text{Si}(\text{CH}_3)_3$], 1.66 (m, 2 H, CH_2), 2.29 (s, 3 H, NCH_3), 2.52 (t, $^3J_{\text{H,H}} = 6.8$ Hz, 2 H, MeNCH_2), 3.03 (m, 2 H, NCH_2), 6.83 (s, 5 H, C_5H_5), 7.33 (m, 2 H, Ph *m*-H), 7.45 (m, 3 H, Ph *o*-H and *p*-H) ppm. ^{13}C (APT) NMR (75 MHz, $[\text{D}_8]\text{THF}$): $\delta = 0.4, 3.3$ [$\text{Si}(\text{CH}_3)_3$], 31.6 (CH_2), 35.3 (NCH_3), 49.8, 52.2 (NCH_2), 122.0 (C_5H_5), 128.7, 130.4, 131.5 (Ph CH), 135.2 (Ph C), 172.2 (NCN) ppm. Upon standing at ambient temperature or 50°C , gradual formation of **4** and Me_3SiCl was observed. At 50°C a maximum conversion of 34% was reached (after 24 h, with concomitant formation of some degradation products). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, characteristic resonances): $\delta = -0.11$ [s, $\text{Si}(\text{CH}_3)_3$], 3.21 (s, 3 H, NCH_3), 6.30 (s, 5 H, C_5H_5) ppm. ^{13}C (APT) NMR (75 MHz, $[\text{D}_8]\text{THF}$): $\delta = 51.0$ (NCH_3), 116.1 (C_5H_5) ppm.

Reaction of 4 with Me_3SiCl : Three NMR tubes were charged each with a solution of **4** in C_6D_6 to which measured amounts of a stock solution of Me_3SiCl in C_6D_6 was added. Initial concentrations of $[\mathbf{4}]/[\text{Me}_3\text{SiCl}]$ in the three tubes were: 0.030:0.035, 0.029:0.069 and 0.029:0.100 mol L^{-1} . After 30 min at 25°C , the relative amounts of **4**, **5** and Me_3SiCl were determined by ^1H NMR spectroscopy. Observed ratios after 1 h were the same, indicating that equilibrium had been reached. Values determined for $K = [\mathbf{5}]/([\mathbf{4}] + [\text{Me}_3\text{SiCl}])$ were 32, 33 and 33(2) L mol^{-1} , respectively, for the three samples. $\text{Cp}[\text{Me}_3\text{SiNC}(\text{Ph})\text{N}(\text{CH}_2)_3\text{N}(\text{Me})\text{SiMe}_3]\text{TiCl}_2$ (**5**): ^1H NMR (500 MHz, C_6D_6): $\delta = -0.04$ [s, 9 H, $\text{Si}(\text{CH}_3)_3$], 0.04 [s, 9 H, $\text{Si}(\text{CH}_3)_3$], 1.63 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.27 (s, 3 H, NCH_3), 2.49 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 2 H, NCH_2), 3.22 (m, 2 H, NCH_2), 6.55 (s, 5 H, C_5H_5), 6.70–6.95 (m, 5 H, Ph) ppm.

Synthesis of $[\text{Me}_3\text{SiNC}(\text{Ph})\text{N}(\text{CH}_2)_3\text{NMe}]\text{Ti}(\text{CH}_2\text{Ph})_2$ (6**):** A solution of **3** (0.316 g, 0.83 mmol) in 30 mL of diethyl ether was cooled to -100°C and a 1.56 M solution of PhCH_2MgBr in diethyl ether (1.07 mL, 1.66 mmol) was slowly added. The solution was allowed to warm to -15°C , at which temperature the mixture was stirred for 2 h. During workup the temperature of the mixture was kept at or below -15°C . The volatiles were removed in vacuo and the mixture was stirred twice with 10 mL of precooled pentane, which was subsequently pumped off. The residue was extracted with pentane, after which the extract was concentrated and cooled to -60°C . This yielded crystalline **6** (0.302 g, 0.62 mmol, 74%). ^1H NMR (300 MHz, C_6D_6): $\delta = 0.26$ [s, 9 H, $\text{Si}(\text{CH}_3)_3$], 1.07 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.63 (m, 2 H, NCH_2), 2.75, 3.09 (d, $^2J_{\text{H,H}} = 9.0$ Hz, 2 H each, TiCH_2), 3.80 (s, 3 H, NCH_3), 6.9–7.2 (m, 15 H, Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): $\delta = 3.0$ [$\text{Si}(\text{CH}_3)_3$], 31.2 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 40.8 (MeNCH_2), 45.4 (NCH_3), 59.9 (NCH_2), 84.5 (TiCH_2), 122.2, 126.5, 127.2, 128.6, 128.8, 129.3 (Ph CH), 134.6 (Ph C), 144.4 ($\text{CH}_2\text{Ph C}$), 177.4 (NCN) ppm. $\text{C}_{28}\text{H}_{37}\text{N}_3\text{SiTi}$ (491.59): calcd. C 68.41, H 7.59, N 8.55; found C 68.32, H 7.53, N 8.44.

Synthesis of $[\text{Me}_3\text{SiNC}(\text{Ph})\text{N}(\text{CH}_2)_3\text{NMe}]\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$ (7**):** Pentane (30 mL) was condensed into a vessel containing a solid mixture of **3** (0.31 g, 0.81 mmol) and $\text{Me}_3\text{SiCH}_2\text{Li}$ (0.15 g, 1.63 mmol) that was frozen in liquid nitrogen. The solution was allowed to thaw and warm to -15°C , at which temperature it was stirred for 2 h. The solution was filtered and the residue was extracted with 30 mL of pentane. From the combined filtrates the volatiles were removed in vacuo to leave **7** as a yellow oil that slowly solidified on standing. Attempts to recrystallize this material from pentane were unsuccessful due to the extreme solubility of the product. The yield of the material (> 95% pure by NMR spectroscopy) was essentially quantitative. ^1H NMR (300 MHz, C_6D_6): $\delta = 0.18$ [s, 18 H,

Table 1. Crystallographic data for compounds **3** and **4**

	3	4
Empirical formula	$\text{C}_{14}\text{H}_{23}\text{Cl}_2\text{N}_3\text{SiTi}$	$\text{C}_{19}\text{H}_{28}\text{ClN}_3\text{SiTi}$
Molecular mass	380.21	409.86
Temperature [K]	130	130
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions	$a = 11.570(1) \text{ \AA}$ $b = 8.992(1) \text{ \AA}$ $c = 18.177(1) \text{ \AA}$ $\beta = 94.129(5)^\circ$	$a = 12.130(1) \text{ \AA}$ $b = 15.168(1) \text{ \AA}$ $c = 12.278(1) \text{ \AA}$ $\beta = 112.607(6)^\circ$
Volume	$1886.2(3) \text{ \AA}^3$	$2805.4(3) \text{ \AA}^3$
Z	4	4
Density (calculated)	1.339 Mg/m^3	1.305 Mg/m^3
Absorption coefficient	0.8 mm^{-1}	0.6 mm^{-1}
$F(000)$	792	864
Crystal size	$0.25 \times 0.30 \times 0.61 \text{ mm}$	$0.08 \times 0.38 \times 0.50 \text{ mm}$
θ range for data collection	$1.12\text{--}28.0^\circ$	$1.34\text{--}27.0^\circ$
Index ranges	$-15 \leq h \leq 1$ $0 \leq k \leq 11$ $-23 \leq l \leq 23$	$-14 \leq h \leq 10$ $0 \leq k \leq 19$ $-15 \leq l \leq 0$
Reflections collected	5514	4934
Independent reflections	4529	4531
Data/restraints/parameters	4529/0/282	4531/0/338
Goodness-of-fit on F^2	1.012	1.067
Final R indices	$R_1 = 0.0352, wR_2 = 0.1012$	$R_1 = 0.0326, wR_2 = 0.0827$
Largest difference peak and hole [e \AA^{-3}]	0.59 and $-0.51(7)$	0.42 and $-0.27(5)$

$\text{CH}_2\text{Si}(\text{CH}_3)_3$, 0.22 [s, 9 H, $\text{Si}(\text{CH}_3)_3$], 1.54 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.56, 1.86 (d, $^2J_{\text{H,H}} = 11.0$ Hz, 2 H each, TiCH_2), 2.87 (m, 2 H, MeNCH_2), 3.05 (m, 2 H, NCH_2), 3.69 (s, 3 H, NCH_3), 7.1–7.3 (m, 5 H, Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): $\delta = 2.6$ [$\text{CH}_2\text{Si}(\text{CH}_3)_3$], 2.7 [$\text{NSi}(\text{CH}_3)_3$], 32.4 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 42.4 (MeNCH_2), 45.5 (NCH_3), 60.0 (NCH_2), 78.3 (TiCH_2), 126.5, 128.8, 129.6 (Ph CH), 134.9 (Ph C), 180.5 (NCN) ppm.

X-ray Crystallographic Study: Single crystals of **3** and **4** were mounted on a glass fibre in a nitrogen-filled glove-box and transferred to the cold nitrogen stream of an Enraf–Nonius CAD-4F diffractometer (graphite-monochromated $\text{Mo-K}\alpha$ radiation, $\lambda = 0.71073$ Å) using inert-gas handling techniques. The structures were solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.^[21] All hydrogen atoms were located from the difference Fourier map and refined with isotropic displacement parameters. Final refinements on F^2 were carried out by full-matrix least-squares techniques (SHELXL-97^[22]). CCDC-183877 (**3**) and -183876 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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