

Titanium imido complexes of pendant arm functionalised benzamidinate ligands

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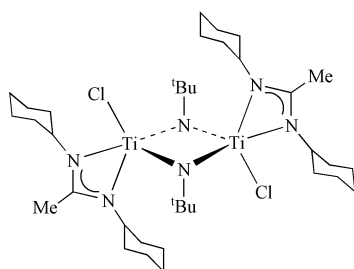
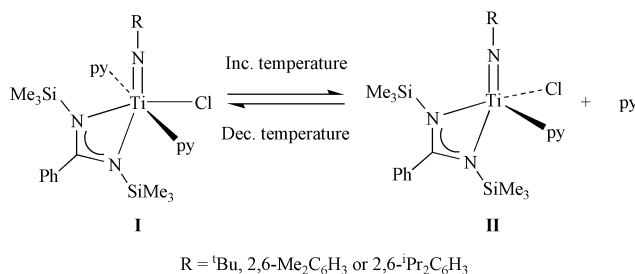
Reactions of the lithiated pendant arm functionalised benzamidinates $\text{Li}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}$ and $\text{Li}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}$ with the compounds $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$ ($\text{R} = \text{'Bu}$, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$, 2,6- $\text{iPr}_2\text{C}_6\text{H}_3$) afforded five-coordinate $[\text{Ti}(\text{NR})\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\text{Cl}]$ **1–3** and $[\text{Ti}(\text{NR})\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\text{Cl}]$ **4–6**, respectively. Reaction of $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\text{Cl}]$ **4** with $\text{C}_6\text{F}_5\text{NH}_2$ gave elimination of $^t\text{BuNH}_2$ and the corresponding perfluoroarylimido complex **7**. The X-ray crystal structures of $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\text{Cl}]$ **1** and $[\text{Ti}(\text{N}-2,6\text{-R}_2\text{C}_6\text{H}_3)\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\text{Cl}]$ ($\text{R} = \text{Me}$ **5** or ^iPr **6**) have been determined. Reaction of either **1** or **4** with $\text{H}_2\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3$ in C_6D_6 afforded the corresponding arylimido compounds **2** and **5**, but this route is not amenable to easy scale-up. For better evaluation of the effects of the pendant NMe_2 donor group in **1–6**, the bis(pyridine) compound $[\text{Ti}(\text{N}^t\text{Bu})\{\text{MeCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\text{Cl}(\text{py})_2]$ **9** was prepared from $\text{Li}\{\text{MeCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}$ **8** and $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_3]$. The compounds **1–3** with two-carbon pendant arms are quite sensitive to adventitious protonation, and the X-ray crystal structures of the products of two such reactions, namely $[\text{Ti}_2\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=\text{C}(\text{Ph})\text{N}(\text{H})\text{SiMe}_3\}_2(\text{N}^t\text{Bu})_2\text{Cl}_2(\mu\text{-Cl})_2]$ **10** and $[\text{Ti}_2(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)_2\text{Cl}_2(\mu\text{-O})\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}=\text{C}(\text{Ph})\text{N}(\text{H})\text{SiMe}_3\}_2]$ **11**, have been determined. Both possess amidine ligands that show interesting intramolecular $\text{N-H} \cdots \text{X}$ ($\text{X} = \mu\text{-Cl}$ or $\mu\text{-O}$) hydrogen bonds.

Introduction

Transition metal imido complexes continue to provide a rich seam of reactivity, both at the $\text{M}=\text{NR}$ bond itself and with the imido group acting as a supporting ligand.^{1,2a,b} We have been interested in developing the chemistry of titanium imido compounds² in both of these regards. As part of these studies we previously prepared a series of amidinate-supported complexes^{3,4} starting from the appropriate chloride derivatives $[\text{Ti}(\text{NR})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$ (**I**, $\text{R} = \text{'Bu}$ or aryl) or $[\text{Ti}_2(\mu\text{-NBu}^t)_2\{\text{MeC}(\text{NC}_6\text{H}_{11})_2\}_2\text{Cl}_2]$ **III** as presented in Chart 1.⁵ As shown, compounds **I** exist in temperature- and R group-

dependent equilibria with five-coordinate **II**, whilst **III** is dinuclear with bridging imido ligands. Accessible from **I/II** via chloride ligand metathesis reactions are alkyl, cyclopentadienyl, amide, aryloxy and borohydride derivatives,⁶ and so the amidinate–imide combination is a useful supporting ligand set. Furthermore, on revisiting recently some cyclopentadienyl–amidinate supported imido systems and their homologues we found that the complexes $[\text{Ti}(\text{NR})(\eta\text{-C}_5\text{Me}_5)\{\text{MeC}(\text{N}^i\text{Pr})_2\}]$ ($\text{Ar} =$ substituted phenyl groups) react with CO_2 (via an initial cycloaddition reaction) to form $[\text{Ti}(\eta\text{-C}_5\text{Me}_5)\{\text{MeC}(\text{N}^i\text{Pr})_2\}\text{O}(\text{CO})\text{N}(\text{Ar})(\text{CO})\text{O}]$; the double CO_2 activation reaction leading to these compounds was the first example for any transition metal imide.⁷

We have therefore been interested to open up further the chemistry of amidinate-supported imido compounds. A well-established strategy that we have recently employed in titanium imido chemistry with considerable success^{2b} is the use of hemilabile ligands, specifically those having pendant donor groups that can stabilise an otherwise reactive $\text{Ti}=\text{NR}$ moiety, potentially decoordinate during a reaction sequence, and stabilise as required any $\text{Ti}=\text{NR}$ coupling product so-formed. With this in mind we noted with interest recent reports by Hessen and Teuben and coworkers⁸ and Lappert *et al.*⁹ of the pendant arm functionalised benzamidinate ligands $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3$ and $\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3$. The lithiated derivatives (dimeric for the three-carbon arm system and presumably also dimeric for the other, two-carbon homologue) of these ligands are readily available in good yields. Complexes of lithium (dinuclear), aluminium, gallium, cerium (dinuclear with chloride bridges), yttrium (and a dinuclear yttrium–lithium “ate” complex) and vanadium have so far been reported and crystallographically characterised. The $\text{Me}_2\text{N}(\text{CH}_2)_n\text{NC}(\text{Ph})\text{NSiMe}_3$ ($n = 2$ or 3) ligands have shown both *mer*- and *fac*-tridentate coordination modes, as well as bidentate ones with the pendant NMe_2 nitrogen non-coordinated; The dinuclear compounds with bridging amidinate ligands have had



III
Chart 1

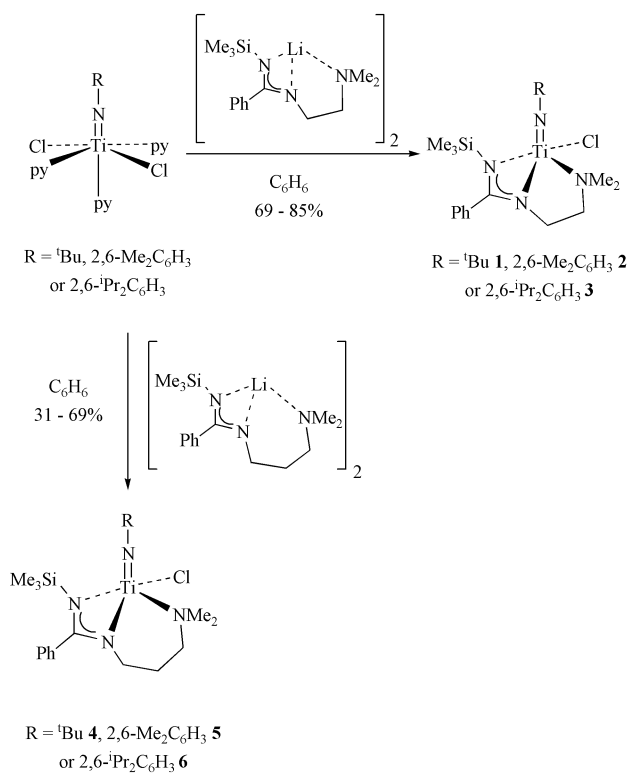
the PhC(NSiMe₃)N moiety bound to one metal (yttrium in the case of the mixed metal dinuclear Y–Li complex) and the NMe₂ donor bound to the second metal centre.

Given the lack of any Group 4¹⁰ or metal–ligand multiply-bonded derivatives of these ligands, and of the potential use of such hemi-labile amidinate ligands in titanium imido chemistry in general, we set out to prepare titanium imido complexes of both Me₂N(CH₂)_nNC(Ph)NSiMe₃ (*n* = 2 or 3) ligands, and this is the subject of our present contribution.¹¹

Results and discussion

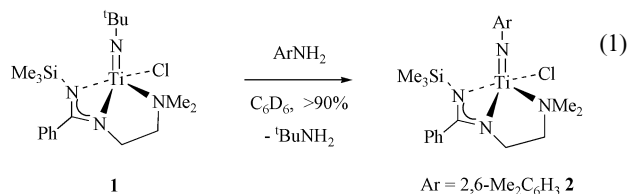
Syntheses

In our previous work in titanium imido chemistry we have found that chloride and/or pyridine substitution reactions of the compounds [Ti(NR)Cl₂(py)₃] (R = ^tBu or aryl)¹² is a very reliable route to new imido complexes. The reactions between [Ti(NR)Cl₂(py)₃] (R = ^tBu, 2,6-Me₂C₆H₃ or 2,6-ⁱPr₂C₆H₃) and the lithiated ligands Li{Me₂NCH₂CH₂NC(Ph)NSiMe₃}⁸ and Li{Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}⁹ (prepared as reported previously by Hessen and Teuben, and Lappert) are summarised in Scheme 1.



Scheme 1

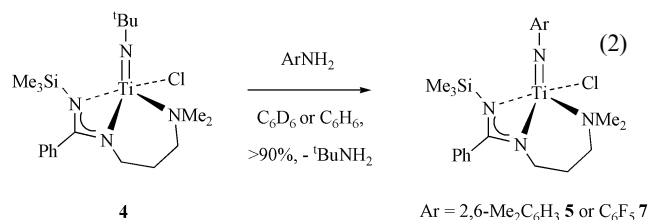
The compounds [Ti(NR)Cl₂(py)₃] (R = ^tBu or aryl) react with Li{Me₂NCH₂CH₂NC(Ph)NSiMe₃} smoothly in benzene at room temperature to form [Ti(NR){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] (R = ^tBu **1**, 2,6-Me₂C₆H₃ **2** or 2,6-ⁱPr₂C₆H₃ **3**) as benzene-soluble, air- and moisture-sensitive compounds in 69–85% yield. These are the first metal–ligand multiply-bonded ligand complexes of any pendant arm functionalised amidinate ligand. The *tert*-butylimido compound **1** can be recrystallised from cold pentane yielding diffraction-quality crystals from which the X-ray structure of **1** has been determined (see below) and which supports the structures proposed for **1**–**3**. The arylimido analogues **2** and **3** do not easily crystallise, but can be sublimed at high vacuum in low yields (<20%) to yield analytically pure samples. However, the initial products of reaction, after extraction to separate **1**–**3** from the LiCl side-product, are sufficiently pure to use in further reactions.



In several previous studies^{2,12} we have found that arylimido compounds [Ti(NAr)(L)_n] (L_n is a supporting ligand or ligand set) can be prepared from the *tert*-butylimido homologues [Ti(N^tBu)(L)_n] by reaction of the latter with the appropriate aniline, ArNH₂. An NMR tube scale reaction between [Ti(N^tBu){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] **1** and H₂N-2,6-Me₂-C₆H₃ in C₆D₆ showed quantitative formation of **2** and the expected *tert*-butylamine side-product. However, attempts to scale this reaction up were always hampered by problems of separation of the product **2** from residual amines (presumably because of weak coordination to the remaining vacant site in five-coordinate **2**).

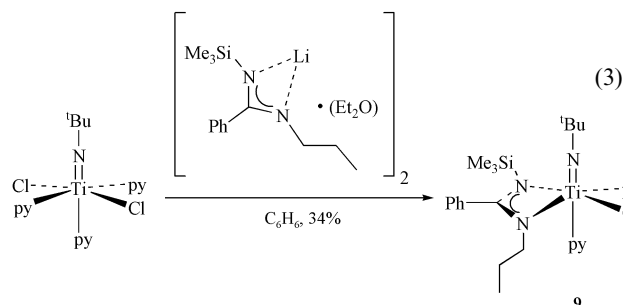
The ¹H and ¹³C NMR spectra for the new compounds **1**–**3** support the proposed structures and confirm that the CH₂CH₂NMe₂ arm is coordinated to the metal centre. In all of these compounds, each of the four diastereotopic methylene hydrogens gives rise to an individual ¹H NMR multiplet, and the two methyl groups appear as inequivalent sharp singlets in the ¹H and ¹³C spectra. The imido N-substituents give rise to the expected resonances. The methyl groups of the aryl ring *iso*-propyl substituents in **3** are inequivalent as required by the absence of a molecular mirror plane in this compound.

The corresponding reactions (Scheme 1) of [Ti(NR)Cl₂(py)₃] with the lithiated three-carbon pendant arm ligand similarly afforded five-coordinate complexes, namely [Ti(NR){Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] (R = ^tBu **4**, 2,6-Me₂C₆H₃ **5** or 2,6-ⁱPr₂C₆H₃ **6**) in 67, 31 and 69% yields, respectively. The physical and spectroscopic properties of these new compounds are analogous to those of **1**–**3**. The NMR spectra suggest firm coordination of the NMe₂ moiety to titanium, with sharp resonances arising from each of the six inequivalent arm methylene protons and the two inequivalent NMe₂ methyl groups (as confirmed by the X-ray structures of **5** and **6** discussed in a later section). Full assignment of these resonances was possible from 2-dimensional ¹H–¹H, ¹H–¹³C and ROESY NMR spectra; one reason for carrying this out this being the observation of a low-field shifted resonance (δ ca. 2.9 ppm) for one of the hydrogens of the methylene linkage next to the NMe₂ group in **5** and **6** (but not in **4** or the two-carbon arm complexes **1**–**3**); the other H atom of this methylene group appears at δ ca. 1.6 ppm in **5** and **6**. The unusual shift is unambiguously assigned to the axial H atom (*i.e.* oriented “up”, more or less parallel to the Ti=NAr bond) which apparently feels some anisotropic deshielding effects from the arylimido groups in **5** and **6**.



As with [Ti(N^tBu){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] **1**, the three-carbon arm system **4** undergoes quantitative and facile *tert*-butylimido/aniline exchange with H₂N-2,6-Me₂C₆H₃ on an NMR tube scale in C₆D₆ to form **5** (eqn. (2)). Again it is more convenient on scale-up to prepare **5** directly from the dichloride [Ti(N-2,6-Me₂C₆H₃)Cl₂(py)₃] and Li{Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}.

We were also interested to prepare perfluoroarylimido analogues of **4–6** to compare their reactivity and determine their X-ray structures (we have very recently found that perfluoroarylimido complexes can feature interesting π -stacked supramolecular solid state structures).^{2c} Unfortunately we have so far been unable to prepare in suitably pure form the required synthon $[\text{Ti}(\text{NC}_6\text{F}_5)\text{Cl}_2(\text{py})_3]$, and so reaction of this with $\text{Li}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}$ (as for **4–6**) was not a possible route. The target complex $[\text{Ti}(\text{NC}_6\text{F}_5)\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\text{Cl}]\textbf{7}$ therefore had to be prepared by the *tert*-butylimido/perfluoroaniline exchange method summarised in eqn. (2). The reaction proceeds in a very good crude yield of over 90%. But while >90% spectroscopically pure, samples of **7** were always contaminated with residual amine. Pure samples were obtained in less than 5% yield by high vacuum tube sublimation and, disappointingly, it has not been possible to obtain diffraction-quality crystals of **7**. The ¹H NMR spectrum of **7**, like those of **5** and **6**, showed very different chemical shifts (δ 2.99 and 1.71 ppm) for the two hydrogen atoms of the methylene group adjacent to NMe_2 .



As mentioned above and summarised in Chart 1, the benzamidinate-supported imidotitanium complexes $[\text{Ti}(\text{NR})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$ (**I**, R = 'Bu or aryl) exist in dynamic equilibrium with the 5-coordinate, mono-pyridine complexes **II**. The compounds **1–7** clearly do not bind pyridine (present in the reaction mixtures) tightly, an observation that can be attributed to features of the $\text{Me}_2\text{N}(\text{CH}_2)_n\text{NC}(\text{Ph})\text{NSiMe}_3$ ($n = 2$ or 3) pendant arms, coupled with the *trans*-labilising effect of the imido ligands themselves. To make a better comparison of the complexes **1–7** with the non-pendant arm species **I/II** we prepared eqn. (3) a sterically comparable benzamidinate compound $[\text{Ti}(\text{N}^t\text{Bu})\{\text{MeCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\text{Cl}(\text{py})_2]$ **9** by reaction of $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_3]$ with $\text{Li}\{\text{MeCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\cdot(\text{Et}_2\text{O})$ **8**. † The ligand $\text{MeCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3$ in **9** is in all regards comparable to the NMe_2 -functionalised ones, apart from obviously not having the additional pendant donor group.

The structure proposed for **9** (eqn. (3)) is fully consistent with the NMR data. Thus, in addition to expected resonances for the N^tBu and $\text{MeCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3$ ligands, the ¹H NMR spectrum shows two very different pyridine ligand environments. The *ortho* hydrogen resonances for these two chemically distinct ligands appear at δ 9.55 and *ca.* 8.7 ppm. All the ¹H resonances for the pyridine associated with the more downfield *ortho* resonance are sharp, whereas those for the other pyridine are rather broad. ROESY NMR spectra of **9** established that the two pyridines are in dynamic exchange on the NMR timescale, and a weak nOe between the SiMe_3 group of $\text{CH}_3\text{CH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3$ and the sharp *ortho* hydrogen at δ 9.55 ppm suggested that these two groups are probably mutually *cis* to each other. The chemical shifts of the broad pyridine resonances suggest that this ligand lies opposite the very *trans*-labilising *tert*-butylimido group. With the N^tBu and two

Table 1 Selected bond distances (Å) and angles (°) for $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\text{Cl}]\textbf{1}$

Ti(1)–N(1)	1.688(2)	Ti(1)–Cl(1)	2.3231(6)
Ti(1)–N(2)	2.126(2)	N(2)–Si(1)	1.735(2)
Ti(1)–N(3)	2.095(2)	N(2)–C(5)	1.339(3)
Ti(1)–N(4)	2.248(2)	N(3)–C(5)	1.325(3)
Ti(1)–N(1)–C(1)	175.0(2)	N(1)–Ti(1)–Cl(1)	109.42(6)
N(1)–Ti(1)–N(2)	116.07(8)	N(1)–Ti(1)–N(4)	106.08(8)
N(1)–Ti(1)–N(3)	107.85(8)	N(3)–Ti(1)–N(4)	73.89(6)
N(2)–Ti(1)–N(3)	63.14(6)	N(2)–C(5)–N(3)	112.1(2)
Ti(1)–N(2)–C(5)	88.7(1)	Ti(1)–N(2)–Si(1)	138.62(9)
Si(1)–N(2)–C(5)	132.3(1)	Ti(1)–N(3)–C(5)	90.4(1)
Ti(1)–N(3)–C(12)	123.8(1)	C(5)–N(3)–C(12)	125.7(2)

pyridine ligands thus lying in a meridional coordination mode, the remaining $\text{MeCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3$ and chloride ligands must adopt the relative coordination sites shown for **9** in eqn. (3), with both N donors of the benzamidinate ligand being *cis* to the imido ligand. The structure of **9** is in contrast to the six-coordinate complexes $[\text{Ti}(\text{NR})\{\text{PhC}(\text{NSiMe}_3)_2\}\text{Cl}(\text{py})_2]$ **I** in which the two chemically equivalent pyridine ligands are mutually *trans* (and *cis* to the imido group), with one of the benzamidinate nitrogens being *cis* to NR and one approximately *trans*, presumably to minimise the number of $\text{N}^t\text{Bu}/\text{NSiMe}_3$ *cis*-interactions. Finally we note that **9** is not particularly stable in solution. Solutions of **9** in C_6D_6 in sealed tubes under N_2 show significant signs of degradation to unknown product(s) after one or two hours at ambient temperature, and this thwarted attempts to obtain an analytically pure sample. This instability provides further evidence for the importance of the pendant arm coordination in the comparatively stable complexes **1–7**.

X-Ray structures of **1**, **5** and **6**

The X-ray crystal structure of $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\text{Cl}]\textbf{1}$ is shown in Fig. 1 and selected bond distances and angles are given in Table 1. Molecules of **1** have a square base pyramidal geometry. The atoms N(2), N(3), N(4) and Cl(1) form the square base with Ti(1) lying 0.75 Å out of the least squares best-fit plane containing these atoms. The N(1)–Ti(1)– L_{base} angles are in excess of 105° which is a feature of metal–ligand multiply-bonded compounds of this kind.¹³ The Ti=N_{imide} and Ti–Cl distances are at the short end of the range of values found for imidotitanium compounds,¹⁴ but consistent with the 14 valence electron count. The $\text{Me}_2\text{NCH}_2\text{CH}_2$ –

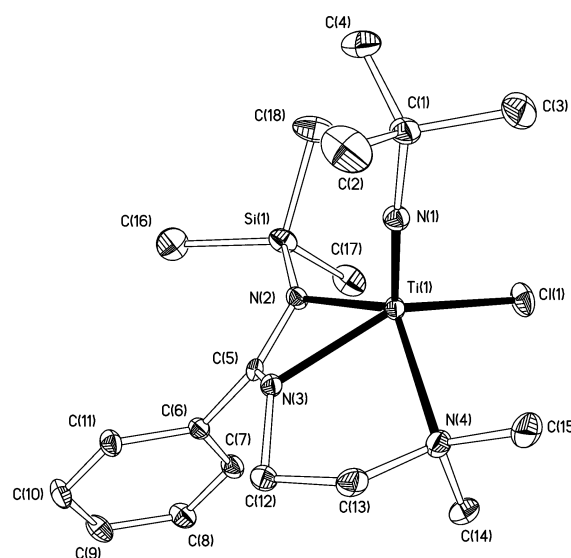


Fig. 1 Molecular structure of $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{NC}(\text{Ph})\text{NSiMe}_3\}\text{Cl}]\textbf{1}$. Displacement ellipsoids are drawn at the 25% probability level. H atoms omitted for clarity.

† Note added at proof: molecules of **8** possess a dinuclear structure in the solid state. C. L. Boyd, B. R. Tyrrell and P. Mountford, *Acta Crystallogr., Sect. E*, 2002, **58**, m597.

Table 2 Selected bond distances (Å) and angles (°) for [Ti(N-2,6-Me₂C₆H₃)₂{Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] **5** and [Ti(N-2,6-ⁱPr₂C₆H₃)₂{Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] **6**

	5	6
Ti(1)–N(1)	1.713(1)	1.713(3)
Ti(1)–N(2)	2.124(1)	2.110(2)
Ti(1)–N(3)	2.080(1)	2.085(2)
Ti(1)–N(4)	2.223(1)	2.228(3)
Ti(1)–Cl(1)	2.3234(4)	2.3386(9)
N(2)–Si(1)	1.734(1)	1.735(3)
N(2)–CPh	1.337(2)	1.340(4)
N(3)–CPh	1.316(2)	1.317(4)
Ti(1)–N(1)–C(1)	178.58(9)	175.0(2)
N(1)–Ti(1)–N(2)	104.53(4)	109.03(12)
N(1)–Ti(1)–N(3)	110.09(5)	107.30(11)
N(1)–Ti(1)–N(4)	98.13(4)	102.19(11)
N(2)–Ti(1)–N(3)	63.71(4)	63.51(9)
N(3)–Ti(1)–N(4)	83.16(14)	82.7(1)
N(1)–Ti(1)–Cl(1)	113.67(4)	111.32(9)
Ti(1)–N(2)–CPh	89.77(7)	91.2(2)
Ti(1)–N(2)–Si(1)	129.04(6)	133.83(13)
Si(1)–N(2)–CPh	131.58(8)	134.5(2)
Ti(1)–N(3)–CPh	92.26(7)	92.9(2)
Ti(1)–N(3)–CH ₂	138.75(8)	139.9(2)
PhC–N(3)–CH ₂	125.4(1)	126.9(2)

NC(Ph)NSiMe₃ ligand adopts a κ^3 -coordination geometry with the pendant arm firmly coordinated as indicated above by the solution ¹H and ¹³C NMR data. Interestingly the benzamidinate nitrogen donors feature different degrees of planarity, with N(3) being distinctly pyramidalised. This is apparent from visual inspection of the molecular structure, but is also quantified by the sums of the angles subtended at N(2) (359.5(3)°, *i.e.* planar within error) and at N(3) (339.9(4)°). The pyramidalisation of N(3) can be attributed to distortions required to achieve coordination of the pendant NMe₂ group. Despite the pyramidalisation of N(3) the Ti(1)–N(2) distance is significantly longer than Ti(1)–N(3) (difference = 0.031(3) Å). Factors contributing to this observation could be unfavourable steric interactions arising from the SiMe₃ group, and the additional binding through N(4) which would favour closer coordination of N(3). There is a small and marginally significant difference between the N(2)–C(5) (longer) and N(3)–C(5) bond lengths (difference = 0.014(4) Å).

It was important to be able to compare solid state structures of complexes of the three-carbon pendant arm ligand Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃ with that of **1**. We were not able to grow diffraction-quality crystals of the *tert*-butylimido system [Ti(N^tBu){Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] **4** (or indeed of **2** or **3**) which would have allowed the best comparison. However, we have been able to determine the X-ray structures of the two arylimido compounds [Ti(N-2,6-R₂C₆H₃)₂{Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] (R = Me **5** or ⁱPr **6**). The molecular structures are shown in Fig. 2 and selected bond distances and angles are summarised and compared in Table 2. The structures of **5** and **6** are broadly analogous to that of **1**. The Ti=N_{imido} distances are somewhat longer in the arylimido systems as is usually the case.^{12,13} The titanium atoms in **5** and **6** lie 0.64 and 0.67 Å out of the least-squares plane of the {N(2),N(3),N(4),Cl(1)} donor set (corresponding value in **1** is 0.75 Å) suggesting that the three-carbon atom arm ligand allows for a more comfortable accommodation of the Ti=NR moiety. The N(3) atoms in **5** and **6** are effectively planar with the sums of the angles subtended at these atoms being 356.5(4) and 359.7(6)°, respectively. The longer chain pendant arm leads to increased N(4)–Ti(1)–N(3) angles of 83.16(14) and 82.7(1)° in **5** and **6** compared to a more acute angle of 73.89(6)° in **1**. As in compound **1** the Ti(1)–N(2) distances in **5** and **6** are significantly longer than the Ti(1)–N(3) distances, presumably for the same reasons. As also in **1**, the N(2)–CPh distances are slightly

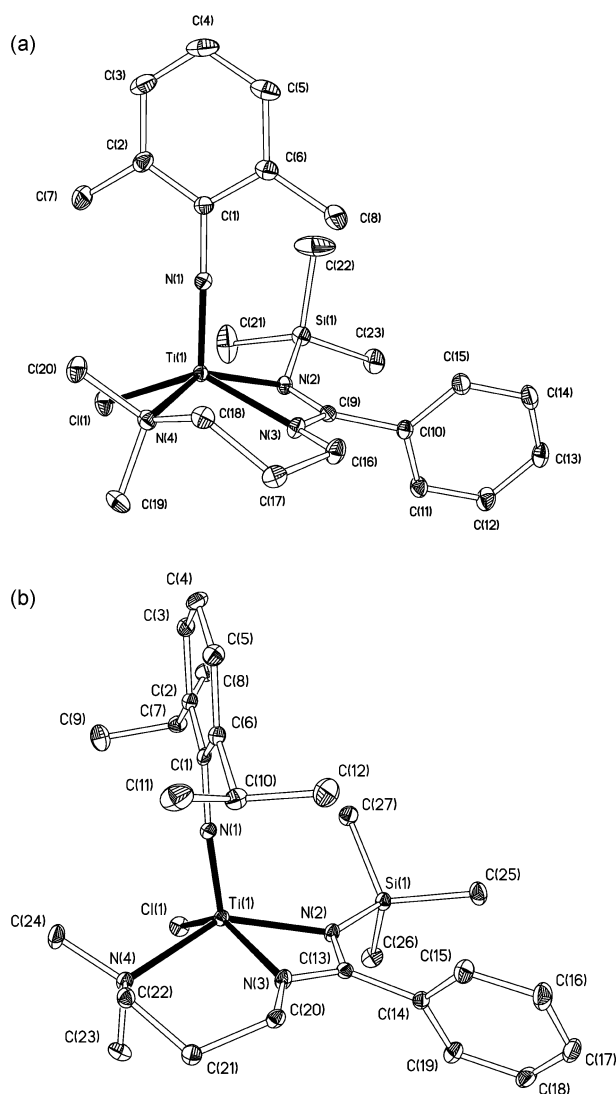


Fig. 2 Molecular structures of (a) [Ti(N-2,6-Me₂C₆H₃)₂{Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] **5** (25% probability ellipsoids) and (b) [Ti(N-2,6-ⁱPr₂C₆H₃)₂{Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] **6** (20% probability) with H atoms omitted for clarity.

longer than those for N(3)–CPh (differences 0.021(3) and 0.023(6) Å for **5** and **6**, respectively). These small but persistent differences may be attributable (directly or indirectly) to steric factors associated with the SiMe₃ group.

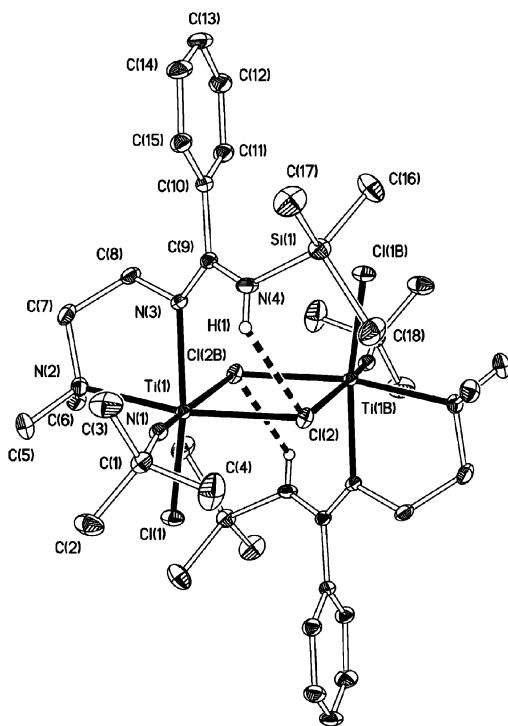
Products of trace hydrolysis in the two-carbon pendant arm systems

Perhaps unsurprisingly in the light of the somewhat strained structure discussed for **1**, all three compounds [Ti(NR){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] **1–3** are significantly more sensitive to adventitious protonation-hydrolysis than their three-carbon arm homologues. We include here two X-ray structures of these hydrolysis compounds since they (i) show interesting molecular features; (ii) demonstrate potential drawbacks of pendant arm amidinates with arms that are too short; (iii) suggest possible uses of the parent amidine ligands Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃ in supramolecular chemistry.

Fig. 3 shows the molecular structure of [Ti₂{Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂(N^tBu)₂Cl₂(μ-Cl)₂] **10**; selected bond lengths and angles are listed in Table 3. Compound **10** is dinuclear with bridging chloride ligands and crystallographically imposed C_i symmetry. It is evidently the product of formally inserting HCl (presumably from hydrolysis of a Ti–Cl bond of **1**) into the Me₃SiN–Ti bond of [Ti(N^tBu)–

Table 3 Selected bond distances (Å) and angles (°) for [Ti₂{Me₂-NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂(N^tBu)₂Cl₂(μ-Cl)₂] **10**

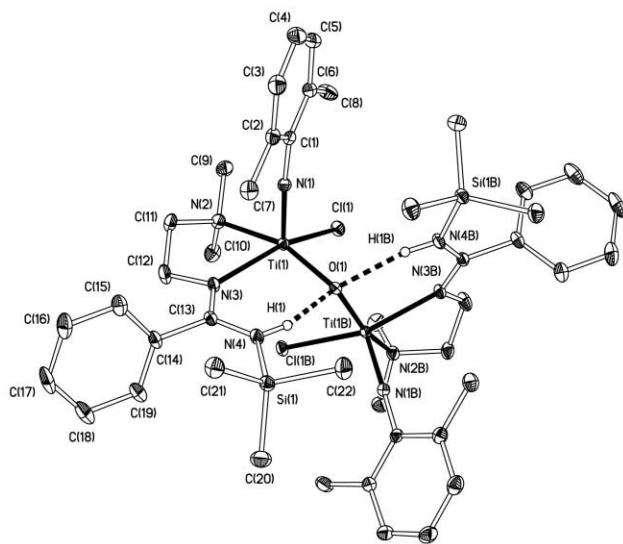
Ti(1)–N(1)	1.694(1)	N(3)–C(9)	1.307(2)
Ti(1)–N(2)	2.318(1)	N(4)–C(9)	1.349(2)
Ti(1)–N(3)	2.192(1)	N(4)–H(1)	0.80(2)
Ti(1)–Cl(1)	2.3685(4)	N(4)–Si(1)	1.771(2)
Ti(1)–Cl(2)	2.4223(5)	Cl(2) ⋯ H(1)	2.75(2)
Ti(1)–Cl(2B)	2.8539(5)		
<hr/>			
Ti(1)–N(1)–C(1)	169.8(1)	Ti(1)–Cl(2)–Ti(1B)	103.630(15)
N(1)–Ti(1)–N(2)	98.44(6)	Cl(1)–Ti(1)–Cl(2B)	85.556(15)
N(1)–Ti(1)–N(3)	97.46(6)	N(4)–H(1) ⋯ Cl(2)	127(2)
Cl(1)–Ti(1)–N(1)	99.11(5)	C(9)–N(4)–Si(1)	132.7(1)
Cl(2)–Ti(1)–N(1)	97.61(5)	C(9)–N(4)–H(1)	112(2)
Cl(2B)–Ti(1)–N(1)	172.81(5)	H(1)–N(4)–Si(1)	112(2)

**Fig. 3** Molecular structure of [Ti₂{Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂(N^tBu)₂Cl₂(μ-Cl)₂] **10**. Displacement ellipsoids are drawn at the 25% probability level. H atoms bound to C are omitted and H(1) is drawn as a sphere of arbitrary radius. Atoms carrying the suffix 'B' are related to their counterparts by the symmetry operator $[-x, -y, 1 - z]$.

{Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] **1**, and indeed can be prepared, albeit in impure form, by the addition of NH₂Me₂Cl (a source of HCl) to **1**. Compound **10** contains the “parent” amidine ligand Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃. While a large number of non-pendant arm amidine complexes have been reported^{3,14} only one crystallographically characterised pendant arm amidine derivative has been previously described, this being the cation [Co{H₂NCH₂CH₂N=C(NH₂)CH₂NH₂}-(tmeda)Cl]⁺.¹⁵ The N(3)–C(9) distance of 1.307(2) Å in **10** is significantly shorter than the N(4)–C(9) value of 1.349(2) Å, suggesting that N(3) is best considered as an imino nitrogen and N(4) as an amino nitrogen. The Lewis base coordination of the amidine moiety of the Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃ ligand through the imino rather than amino nitrogen is highly typical of amidine ligands.¹⁴ In **10** coordination through N(3) is particularly favoured by further coordination through the dimethylamino nitrogen N(2). The possibility of coordination through N(2) might also contribute to the explanation of why it is N(4) that ends up with the added proton rather than the presumably more basic (and distorted in the X-ray structure of **1**) N(3) atom. Indeed N(3) might well be the kinetic site of electrophilic attack by H⁺ on **1** but we have no evidence either way for this hypothesis.

The Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃ amidine ligand in **10** could potentially be interesting in supramolecular type applications, it being simultaneously a dual Lewis base donor (through the amidine imino and pendant arm amino nitrogens) and a hydrogen bond donor through the Me₃SiN–H group. In **10** this group forms an intramolecular N(4)–H(1) ⋯ Cl(2) hydrogen bond, the refined H(1) ⋯ Cl(2) distance of 2.75(2) being in the acceptable range for such interactions.^{2e,16} However, it is not clear if the hydrogen bonds in **10** have an important role in setting the structural features of this compound or are simply opportunistic consequences of the coordination geometry. The role of an analogous hydrogen bond in the binuclear complex [Ti₂(N-2,6-C₆H₃Me₂)₂Cl₂(μ-O){Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂] **11** (see below) is much less ambiguous. Hughes, Wade *et al.* have recently reported a mononuclear complex of a non-pendant arm amidine ligand that shows a close intramolecular hydrogen bond, the hydrogen bond donor being the amino nitrogen of the amidine ligand.¹⁷

Attempted crystallisation of [Ti(N-2,6-Me₂C₆H₃){Me₂-NCH₂CH₂NC(Ph)NSiMe₃}Cl] **2** gave a small number of crystals of [Ti₂(N-2,6-C₆H₃Me₂)₂Cl₂(μ-O){Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂] **11**. The molecular structure is shown in Fig. 4, and selected bond lengths and angles are listed in Table

**Fig. 4** Molecular structure of [Ti₂(N-2,6-C₆H₃Me₂)₂Cl₂(μ-O){Me₂-NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂] **11**. Displacement ellipsoids are drawn at the 30% probability level. H atoms bound to C are omitted and H(1) is drawn as a sphere of arbitrary radius. Atoms carrying the suffix 'B' are related to their counterparts by the symmetry operator $[\frac{1}{2} - x, -y, \frac{3}{2} - z]$.

4. The solution ¹H NMR spectrum of **11** is consistent with the solid state structure. In particular a broad resonance at δ 10.6 ppm (integral 2 H per dimeric molecule) is assigned to the N–H ⋯ O hydrogen atoms. Molecules of **11** (which lie on crystallographic two-fold axes) apparently form from reaction of adventitious H₂O with two molecules of **2**, with the O–H bonds formally inserting into the Ti–NSiMe₃ bonds of **2**. Again the neutral Me₂NCH₂CH₂N=C(Ph)NSiMe₃ amidine ligand shows shorter N(3)–C(13) [1.308(3) Å] than N(4)–C(13) [1.352(3) Å] distances, consistent with N(3) being an imino nitrogen and N(4) an amino nitrogen. Like **10**, the amidine ligand acts as a Lewis base through the pendant NMe₂ and imino nitrogens, and a hydrogen bond donor through the Me₃SiN–H group, this time to a bridging oxo ligand. The geometry at O(1) is close to tetrahedral and the N–H ⋯ O distances and angles are consistent with the formation of strong intramolecular hydrogen bonds.¹⁴ Very interestingly, the Ti(1)–O(1)–Ti(1B) angle has the highly acute value of 113.7(1)°. Over 60 bridging mono-oxo complexes [(L_n)Ti(μ-O)Ti(L_n)] have been crystallographically characterised and the mean Ti–O–Ti angle

Table 4 Selected bond distances (Å) and angles (°) for [Ti₂(N-2,6-C₆H₃Me₂)₂Cl₂(μ-O){Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂] **11**

Ti(1)–N(1)	1.729(2)	N(3)–C(13)	1.308(3)
Ti(1)–N(2)	2.307(2)	N(4)–C(13)	1.352(3)
Ti(1)–N(3)	2.198(2)	N(4)–H(1)	0.88(3)
Ti(1)–Cl(1)	2.4103(6)	N(4)–Si(1)	1.767(2)
Ti(1)–O(1)	1.8808(11)	O(1) ⋯ H(1)	2.02(3)
Ti(1)–N(1)–C(1)	174.4(2)	Ti(1)–O(1) ⋯ H(1)	96(1)
N(1)–Ti(1)–N(2)	96.62(7)	Ti(1)–O(1)–H(1B)	116(1)
N(1)–Ti(1)–N(3)	101.45(7)	H(1) ⋯ O(1) ⋯ H(1B)	121(2)
Cl(1)–Ti(1)–N(1)	104.44(6)	C(13)–N(4)–H(1)	113(2)
O(1)–Ti(1)–N(1)	106.21(7)	Si(1)–N(4)–H(1)	116(2)
Ti(1)–O(1)–Ti(1)B	113.7(1)	C(13)–N(4)–Si(1)	131.64(14)
N(4)–H(1) ⋯ O(1)	161(3)		

is 171(7)° (range *ca.* 152–180°).¹⁴ This preference for linearity stems from a requirement to minimise steric interactions between the two titanium centres and to maximise O_{2π}→Ti_{3dπ} π interactions. It seems very likely that the two strong N–H ⋯ O interactions cause the highly bent Ti–O–Ti linkage in **11**.

Conclusions

We have prepared in good yield the first transition metal imido complexes of pendant arm functionalised amidinate ligands. Three of these complexes have been structurally characterised. The pendant arm allows the isolation of well-defined five-coordinate amidinate–imido complexes of a type not previously possible with non-pendant arm amidinates. It is likely that these compounds will form the starting point for further exploring titanium imido chemistry. Two products arising from protonation–hydrolysis have been structurally characterised, and the μ-oxo compound **11** in particular shows an unusual geometry attributed to the hydrogen bond donor ability of the parent amidine ligand Me₂NCH₂CH₂N=C(Ph)NSiMe₃.

Experimental

General methods and instrumentation

The compounds Li{Me₂NCH₂CH₂NC(Ph)NSiMe₃}⁸, Li{Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}⁹ and [Ti(NR)Cl₂(py)₃] (R = ^tBu, 2,6-Me₂C₆H₃, 2,6-¹Pr₂C₆H₃)¹² were prepared as reported previously.

General methods and instrumentation

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Solvents were predried over activated 4 Å molecular sieves and were refluxed over appropriate drying agents under a dinitrogen atmosphere and collected by distillation. Deuterated solvents were dried over appropriate drying agents, distilled under reduced pressure, and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ¹H, ¹³C{¹H}, ¹³C and ¹⁹F NMR spectra were recorded on Varian Unity Plus 500 and Varian Mercury spectrometers. ¹H and ¹³C assignments were confirmed when necessary with the use of NOE, DEPT-135, DEPT-90, DEPT-45, and two dimensional ¹H–¹H and ¹³C–¹H NMR experiments. All spectra were referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz (Hz). Infrared spectra were prepared as Nujol mulls between NaCl or KBr plates or as KBr discs and were recorded on Perkin-Elmer 1600 and 1700 series spectrometers. Infrared data are quoted in wavenumbers (cm⁻¹). Mass spectra were recorded by the mass spectrometry service of the University of Oxford's Inorganic Chemistry Laboratory. Combustion analyses were recorded by the analytical services of the University of Oxford's Inorganic Chemistry Laboratory.

[Ti(N^tBu){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] (**1**)

To a stirred solution of [Ti(N^tBu)Cl₂(py)₃] (1.01 g, 2.35 mmol) in benzene (40 ml) was added a solution of Li{Me₂NCH₂CH₂NC(Ph)NSiMe₃} (0.63 g, 2.35 mmol) in benzene (20 ml) dropwise over 15 min. The orange solution became orange–yellow in colour and a white precipitate formed. Volatiles were removed under reduced pressure and extracted into benzene (50 ml). The waxy orange residue was recrystallised at –80 °C from pentane (20 ml), yielding [Ti(N^tBu){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] as an orange–yellow powder with some single diffraction-quality crystals. Yield: 0.68 g (69%).

¹H NMR data (CD₂Cl₂, 500.0 MHz, 293 K): δ 7.5–7.3 (5 H, m, C₆H₅), 3.75 (1 H, m, CN₂CH₂), 3.31 (1 H, m, Me₂NCH₂), 3.03 (3 H, s, NMe₂), 3.01 (1 H, m, CN₂CH₂), 2.36 (1 H, m, Me₂NCH₂), 2.16 (3 H, s, NMe₂), 1.02 (9 H, s, CMe₃), 0.90 (9 H, s, SiMe₃). ¹³C–{¹H} NMR data (CD₂Cl₂, 125.7 MHz, 289 K): δ 173.74 (CN₂), 134.25 (*ipso*-C₆H₅), 130.41, 128.50, 127.86, 123.8, 123.60 (5 CH of C₆H₅), 70.31 (CMe₃), 62.71 (Me₂NCH₂), 50.18 (NMe₂), 46.12 (CN₂CH₂), 46.12 (NMe₂), 32.10 (CMe₃), 1.48 (SiMe₃). IR data (KBr plates, Nujol mull, cm⁻¹): 2727 (w), 1603 (w), 1578 (w), 1505 (w), 1349 (m), 1329 (w), 1245 (m), 1204 (m), 1176 (w), 1153 (w), 1134 (w), 1087 (w), 1073 (w), 1046 (w), 1023 (w), 950 (w), 933 (w), 869 (m), 836 (m), 793 (w), 776 (w), 757 (w), 723 (w), 702 (w), 627 (w), 594 (w), 563 (w), 515 (w), 500 (w), 442 (w) cm⁻¹. Anal. found (calc. for C₁₈H₃₃ClN₄SiTi): C 51.7 (51.9), H 7.5 (8.0), N 13.4 (13.4)%.

[Ti(N-2,6-Me₂C₆H₃){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] (**2**)

To a stirred solution of [Ti(N-2,6-Me₂C₆H₃)Cl₂(py)₃] (0.54 g, 1.14 mmol) in benzene (30 ml) was added a solution of Li{Me₂NCH₂CH₂NC(Ph)NSiMe₃} (0.31 g, 1.14 mmol) in benzene (15 ml) dropwise over 10 min. The solution remained brown in colour and a white precipitate formed. Volatiles were removed under reduced pressure and extracted into benzene (30 ml). The residue was triturated with pentane (20 ml) giving **2** as a brown solid. Yield: 0.38 g (72%). An analytically pure sample was obtained by sublimation at 1 × 10⁻⁶ mbar and 160 °C to yield [Ti(N-2,6-Me₂C₆H₃){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] as a red–brown oil which hardened to a red–brown solid upon standing at rt. Sublimed yield: 59 mg (16%).

An attempt to crystallise [Ti(N-2,6-Me₂C₆H₃){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] **2** yielded a small quantity of crystals of [Ti₂(N-2,6-C₆H₃Me₂)₂Cl₂(μ-O){Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂] (**11**). Data for [Ti(N-2,6-Me₂C₆H₃){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] (**2**). ¹H NMR (C₆D₆, 500.0 MHz, 293 K): δ 7.17 (2 H, d of d, *ortho*-C₆H₅, ²J = 7.8, ³J = 1.5), 6.98–7.03 (5 H, m, *meta*- and *para*-C₆H₅ and *meta*-C₆H₃Me₂), 6.73 (1 H, t, *para*-C₆H₃Me₂, ²J = 7.3), 3.10 (1 H, m, CN₂CH₂), 2.86 (6 H, s, C₆H₃Me₂), 2.63 (1 H, m, CN₂CH₂), 2.43 (3 H, s, NMe), 2.27 (1 H, m, CH₂NMe₂), 2.00 (3 H, s, NMe), 1.63 (1 H, m, CH₂NMe₂), 0.18 (9 H, s, SiMe₃). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 293 K): δ 174.43 (CN₂), 160.30 (*ipso*-C₆H₃Me₂), 134.67 (*ipso*-C₆H₅), 132.59 (*ortho*-C₆H₃Me₂), 130.53 (*meta*- or

para-C₆H₅ or *meta*-C₆H₃Me₂), 128.65 (*meta*- or *para*-C₆H₅ or *meta*-C₆H₃Me₂), 127.87 (*ortho*-C₆H₅), 127.38 (*meta*- or *para*-C₆H₅ or *meta*-C₆H₃Me₂), 120.68 (*para*-C₆H₃Me₂), 62.92 (CH₂-NMe₂), 49.45 (NMe), 47.78 (NMe), 45.97 (CN₂CH₂), 20.17 (C₆H₃Me₂), 2.22 (SiMe₃). IR (Nujol mull, KBr plates): 1892 (w, br), 1828 (w), 1770 (w), 1606 (w), 1582 (m), 1504 (w), 1404 (s), 1342 (m), 1312 (s), 1250 (m), 1198 (m), 1172 (w), 1158 (w), 1088 (m), 1076 (m), 1062 (w), 1050 (w), 1024 (w), 984 (w), 966 (w), 946 (m), 930 (w), 864 (s), 842 (s), 808 (w), 792 (w), 778 (w), 758 (m), 738 (m), 722 (w), 628 (w), 616 (w, br), 582 (w), 562 (w), 498 (w), 476 (w), 444 (w), 422 (w) cm⁻¹. Accurate mass EI-MS for [Ti(N-2,6-Me₂C₆H₃){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl]⁺. Found (calc. for C₂₂H₃₃N₄ClSiTi): *m/z* = 464.1630 (464.1643). Anal. found (calc. for C₂₂H₃₃N₄ClSiTi): C 56.6 (56.8), H 7.3 (7.2), N 12.2 (12.1)%.

Data for [Ti(N-2,6-C₆H₃Me₂)Cl(μ-O){Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂ (11). ¹H NMR (C₆D₆, 500.0 MHz, 293 K): δ 10.61 (2 H, s, NH), 7.48–7.57 (6 H, m, *meta*- and *para*-C₆H₅), 7.40 (2 H, d, *ortho*-C₆H₅, ²*J* = 7.3), 7.27 (2 H, d, *ortho*-C₆H₅, ²*J* = 7.3), 6.69 (4 H, d, *meta*-C₆H₃Me₂), 6.33 (2 H, t, *para*-C₆H₃Me₂), 3.51, 3.41, 3.20 (3 × 2 H, m, CH of pendant arm), 2.88 (6 H, s, C₆H₃Me₂), 2.61 (6 H, s, C₆H₃Me₂), 2.33–2.54 (14 H, overlapping br s and m, NMe₂ and CH of pendant arm), 0.04 (18H, s, SiMe₃).

NMR tube scale reaction of [Ti(N^tBu){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] (1) with 2,6-dimethylaniline

A solution of **1** (6.8 mg, 0.016 mmol) in C₆D₆ (0.5 ml) in a 5 mm NMR tube was treated with *ca.* 1.0 equiv. of 2,6-dimethylaniline at rt. The ¹H NMR spectrum after 10 min showed quantitative formation of **2** together with a new resonance attributable to ^tBuNH₂.

[Ti(N-2,6-ⁱPr₂C₆H₃){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] (3)

To a stirred solution of [Ti(N-2,6-ⁱPr₂C₆H₃)Cl₂(py)₃] (0.68 g, 1.29 mmol) in benzene (30 ml) was added a solution of Li{Me₂NCH₂CH₂NC(Ph)NSiMe₃} (0.35 g, 1.29 mmol) in benzene (15 ml) dropwise over 10 min. The solution remained brown in colour and a white precipitate formed. Volatiles were removed under reduced pressure and extracted into benzene (20 ml). The residue was triturated with pentane (30 ml) giving **3** as a brown solid. Yield: 0.51 g (85%). An analytically pure sample was obtained by sublimation at 7 × 10⁻⁶ mbar and 100 °C to yield [Ti(N-2,6-ⁱPr₂C₆H₃){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] as a brown oil which hardened to a brown solid on standing at rt. Sublimed yield: 63 mg (19%).

¹H NMR (C₆D₆, 500.0 MHz, 293 K): δ 7.19–7.22 (2 H, m, br, *ortho*-C₆H₅), 7.09 (2 H, app d, *meta*-C₆H₃ⁱPr₂, app ²*J* = 7.3), 7.00–7.05 (3 H, m, br, *meta*- and *para*-C₆H₅), 6.90 (1 H, t, *para*-C₆H₃ⁱPr₂, ²*J* = 7.3), 4.71 (2 H, septet, CHMe₂, ²*J* = 6.8), 3.16 (1 H, m, CN₂CH₂), 2.60 (1 H, m, CN₂CH₂), 2.49 (3 H, s, NMe), 2.37 (1 H, m, CH₂NMe₂), 1.97 (3 H, s, NMe), 1.61 (1 H, m, CH₂NMe₂), 1.54 (6 H, d, CHMe₂, ²*J* = 6.8), 1.49 (6 H, d, CHMe₂, ²*J* = 6.8), 0.19 (9 H, s, SiMe₃). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 293 K): δ 176.36 (CN₂), 157.73 (*ipso*-C₆H₃ⁱPr₂), 143.18 (*ipso*-C₆H₅), 134.78 (*ortho*-C₆H₃ⁱPr₂), 130.55 (*meta*- or *para*-C₆H₅), 128.72 (*meta*- or *para*-C₆H₅), 127.85 (*ortho*-C₆H₅), 122.25 (*meta*-C₆H₃ⁱPr₂), 121.58 (*para*-C₆H₃ⁱPr₂), 62.92 (CH₂-NMe₂), 49.32 (NMe), 47.68 (NMe), 45.99 (CN₂CH₂), 28.62 (CHMe₂), 25.01 (CHMe₂), 24.54 (CHMe₂), 2.24 (SiMe₃). IR (Nujol mull, NaCl plates): 1916 (w), 1582 (w), 1504 (m), 1328 (s), 1378 (s), 1290 (s), 1250 (s), 1200 (s), 1174 (w), 1158 (w), 1140 (w), 1088 (m), 1048 (m), 1022 (m), 982 (m), 948 (s, br), 848 (s), 790 (s), 758 (s), 704 (m), 692 (m), 632 (w), 562 (m), 408 (s, br) cm⁻¹. Accurate mass EI-MS for [Ti(N-2,6-ⁱPr₂C₆H₃){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl]⁺. Found (calc. for C₂₆H₄₁N₄ClSiTi): *m/z* = 520.2105 (520.2083). Anal. found (calc. for C₂₆H₄₁N₄ClSiTi): C 59.6 (59.9), H 7.7 (7.9), N 11.0 (10.8)%.

[Ti(N^tBu){Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] (4)

To a stirred solution of [Ti(N^tBu)Cl₂(py)₃] (0.98 g, 2.30 mmol) in benzene (60 ml) was added a solution of Li{Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃} (0.65 g, 2.30 mmol) in benzene (20 ml), dropwise over 10 min. The resulting orange–yellow solution was stirred for 3 days. Volatiles were removed under reduced pressure and extracted into benzene (40 ml). The product was triturated with pentane (20 ml). Upon standing at rt a waxy orange solid formed. Yield: 0.66 g (67%).

¹H NMR data (C₆D₆, 500.0 MHz, 293 K): δ 7.4–7.0 (5 H, m, C₆H₅), 3.10 (2 H, m, CN₂CH₂), 2.83 (3 H, s, NMe₂), 2.04 (1 H, m, Me₂NCH_{2(ax)}), 1.87 (3 H, s, NMe₂), 1.82 (1 H, m, Me₂-NCH_{2(eq)}), 1.38 (1 H, m, CH₂CH₂CH_{2(ax)}), 1.23 (9 H, s, CMe₃), 0.95 (1 H, m, CH₂CH₂CH_{2(eq)}), 0.28 (9 H, s, SiMe₃). ¹³C-{¹H} NMR data (C₆D₆, 125.7 MHz, 293 K): 174.60 (CN₂), 136.04 (*ipso*-C₆H₅), 129.00, 128.6, 128.19, 127.80, 126.63 (5 CH of C₆H₅), 70.77 (CMe₃), 62.95 (Me₂NCH₂), 52.35 (NMe₂), 47.49 (CN₂CH₂), 43.94 (NMe₂), 32.65 (CMe₃), 25.84 (CH₂CH₂CH₂), 2.42 (SiMe₃). IR data (KBr plates, Nujol mull, cm⁻¹): 2724 (w), 1593 (w, br), 1466 (s, br), 1347 (m), 1302 (m), 1262 (w), 1244 (m), 1205 (s), 1154 (m), 1131 (w), 1109 (w), 1062 (w), 1016 (m), 978 (w), 946 (m), 923 (w), 897 (m), 857 (w), 841 (m), 818 (m), 786 (m), 764 (w), 721 (w), 707 (w), 629 (w), 597 (w), 547 (m), 510 (w), 455 (w), 435 (w) cm⁻¹. Anal. found (calc. for C₁₉H₃₃ClN₄SiTi): C 53.0 (53.0), H 7.8 (8.2), N 12.8 (13.0)%.

[Ti(N-2,6-Me₂C₆H₃){Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] (5)

To a stirred solution of [Ti(N-2,6-Me₂C₆H₃)Cl₂(py)₃] (0.56 g, 1.18 mmol) in benzene (40 ml) was added a solution of Li{Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃} (0.33 g, 1.18 mmol) in benzene (20 ml) dropwise over 10 min. The brown solution became red–brown in colour and a white precipitate formed. Volatiles were removed under reduced pressure and extracted into benzene (30 ml). The brown oily residue was recrystallised at rt from CH₂Cl₂ (5 ml) and hexane (30 ml), yielding **5** as red–brown diffraction-quality crystals. Yield: 0.18 g (31%).

¹H NMR (C₆D₆, 500.0 MHz, 293 K): δ 7.26–7.20 (2 H, d, br, *ortho*-C₆H₅, ²*J* = 4.9), 7.10–7.02 (3 H, m, br, *meta*- and *para*-C₆H₅), 6.99 (2 H, app d, *meta*-C₆H₃Me₂, app ²*J* = 7.3), 6.71 (1 H, t, *para*-C₆H₃Me₂, ²*J* = 7.8), 3.02 (1 H, m, CN₂CH_{2(ax)}), 2.95 (1 H, m, CN₂CH_{2(eq)}), 2.87 (1 H, app t, Me₂NCH_{2(ax)}, app ²*J* = 12.7), 2.82 (6 H, s, C₆H₃Me₂), 2.59 (3 H, s, NMe_{2(eq)}), 1.90 (3 H, s, NMe_{2(ax)}), 1.62 (1 H, d of d, Me₂NCH_{2(eq)}, ²*J* = 12.7, ³*J* = 5.4), 1.21 (1 H, m, CH₂CH₂CH_{2(ax)}), 0.87 (1 H, br d, CH₂CH₂CH_{2(eq)}, ²*J* = 15.6), 0.12 (9 H, s, SiMe₃). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 293 K): δ 174.95 (CN₂), 160.30 (*ipso*-C₆H₃Me₂), 134.97 (*ipso*-C₆H₅), 132.58 (*ortho*-C₆H₃Me₂), 129.24 (*meta*- or *para*-C₆H₅), 128.47 (*meta*- or *para*-C₆H₅), 127.70 (*meta*-C₆H₃Me₂), 127.28 (*ortho*-C₆H₅), 120.65 (*para*-C₆H₃Me₂), 62.18 (CH₂NMe₂), 52.70 (NMe_{2(eq)}), 45.90 (CN₂CH₂), 45.87 (NMe_{2(ax)}), 25.50 (CH₂CH₂CH₂), 20.16 (C₆H₃Me₂), 2.20 (SiMe₃). IR (Nujol mull, KBr plates): 2360 (w), 2338 (w), 1946 (w), 1894 (w), 1876 (w), 1830 (w), 1650 (w), 1604 (w), 1582 (w), 1506 (m), 1444 (s, br), 1412 (s, br), 1342 (s), 1316 (s), 1244 (s), 1204 (m), 1228 (m), 1176 (w), 1154 (w), 1128 (w), 1104 (m), 1058 (m), 1026 (w), 1008 (m), 978 (m), 946 (w), 916 (w), 892 (s), 838 (s), 818 (s), 780 (m), 734 (m), 698 (m), 628 (w), 554 (w), 514 (m), 494 (w), 436 (w), 412 (m) cm⁻¹. Accurate mass EI-MS for [Ti(N-2,6-Me₂C₆H₃){Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl]⁺. Found (calc. for C₂₃H₃₅N₄ClSiTi): *m/z* = 478.1816 (478.1799). Anal. found (calc. for C₂₃H₃₅N₄ClSiTi): C 57.6 (57.7), H 7.4 (7.4), N 11.5 (11.7)%.

NMR tube scale reaction of [Ti(N^tBu){Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] (4) with 2,6-dimethylaniline

A solution of **4** (7.0 mg, 0.016 mmol) in C₆D₆ (0.5 ml) in a 5 mm NMR tube was treated with *ca.* 1.0 equiv. of 2,6-dimethyl-

aniline at rt. The ^1H NMR spectrum after 10 min showed quantitative formation of **5** together with a new resonance attributable to $^t\text{BuNH}_2$.

[Ti(N-2,6- i -Pr $_2$ C $_6$ H $_3$) $\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC(Ph)NSiMe}_3\}\text{Cl}\}$ (6)

To a stirred solution of $[\text{Ti}(\text{N}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{Cl}_2(\text{py})_3]$ (0.63 g, 1.18 mmol) in benzene (30 ml) was added a solution of $\text{Li}\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC(Ph)NSiMe}_3\}$ (0.34 g, 1.18 mmol) in benzene (30 ml) dropwise over 10 min. The solution remained brown in colour and a white precipitate formed. Volatiles were removed under reduced pressure and extracted into benzene (30 ml). The brown oily residue was recrystallised at -30°C from hexanes (40 ml), yielding $[\text{Ti}(\text{N}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC(Ph)NSiMe}_3\}\text{Cl}]$ as a beige powder. Yield: 0.44 g (69%). Diffraction-quality crystals of **6** were obtained by diffusion of a solution of **6** in hexanes into paraffin oil.

^1H NMR (C_6D_6 , 500.0 MHz, 293 K): δ 7.20–7.32 (2 H, m, br, *ortho*-C $_6$ H $_5$), 7.10–7.03 (3 H, m, br, *meta*- and *para*-C $_6$ H $_5$), 7.05 (2 H, app d, *meta*-C $_6$ H $_5$ $^i\text{Pr}_2$, app $^2J = 7.8$), 6.88 (1 H, t, *para*-C $_6$ H $_5$ $^i\text{Pr}_2$, $^2J = 7.8$), 4.80 (2 H, septet, CHMe $_2$, $^2J = 6.8$), 2.99–3.18 (3 H, m, CN $_2$ CH $_{2\text{ax}}$, CN $_2$ CH $_{2\text{eq}}$, CH $_2$ NMe $_{2\text{ax}}$), 2.65 (3 H, s, NMe $_{\text{eq}}$), 1.90 (3 H, s, NMe $_{\text{ax}}$), 1.67 (1 H, d of d, CH $_2$ NMe $_{2\text{eq}}$, $^2J = 12.7$, $^3J = 4.9$), 1.48 (12 H, app t, CHMe $_2$, app $^2J = 6.8$), 1.19 (1 H, m, CH $_2$ CH $_2$ CH $_{2\text{ax}}$), 0.88 (1 H, m, CH $_2$ CH $_2$ CH $_{2\text{eq}}$), 0.15 (9 H, s, SiMe $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz, 293 K): δ 175.17 (CN $_2$), 157.57 (*ipso*-C $_6$ H $_5$ $^i\text{Pr}_2$), 143.48 (*ipso*-C $_6$ H $_5$), 135.05 (*ortho*-C $_6$ H $_5$ $^i\text{Pr}_2$), 129.47 (*meta*- or *para*-C $_6$ H $_5$ or *meta*-C $_6$ H $_5$ $^i\text{Pr}_2$), 128.18 (*meta*- or *para*-C $_6$ H $_5$ or *meta*-C $_6$ H $_5$ $^i\text{Pr}_2$), 127.85 (*ortho*-C $_6$ H $_5$), 122.34 (*meta*- or *para*-C $_6$ H $_5$ or *meta*-C $_6$ H $_5$ $^i\text{Pr}_2$), 121.87 (*para*-C $_6$ H $_5$ $^i\text{Pr}_2$), 62.17 (CH $_2$ NMe $_2$), 52.86 (NMe $_{\text{eq}}$), 46.24 (NMe $_{\text{ax}}$), 45.86 (CN $_2$ CH $_2$), 28.12 (CHMe $_2$), 25.70 (CH $_2$ CH $_2$ CH $_2$), 25.03 (CHMe $_2$), 25.00 (CHMe $_2$), 2.44 (SiMe $_3$). IR (Nujol mull, KBr plates): 2722 (w), 2678 (w), 2624 (w), 1958 (w), 1894 (w), 1842 (w), 1606 (w), 1576 (w), 1514 (s), 1426 (s, br), 1336 (s), 1288 (s), 1244 (s), 1212 (s), 1174 (w), 1156 (s), 1110 (m), 1058 (m), 1012 (w), 980 (s), 942 (w), 918 (w), 898 (s), 842 (s), 818 (m), 786 (s), 750 (s), 720 (m), 702 (m), 672 (w), 632 (w), 594 (w), 632 (w), 516 (m), 496 (w), 446 (w) cm^{-1} . Accurate mass EI-MS for $[\text{Ti}(\text{N}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC(Ph)NSiMe}_3\}\text{Cl}]^+$. Found (calc. for $\text{C}_{27}\text{H}_{43}\text{N}_4\text{ClSiTi}$): $m/z = 534.2433$ (534.2425). Anal. found (calc. for $\text{C}_{27}\text{H}_{43}\text{N}_4\text{ClSiTi}$): C 60.1 (60.6), H 8.3 (8.1), N 10.4 (10.5)%.

[Ti(NC $_6$ F $_5$) $\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC(Ph)NSiMe}_3\}\text{Cl}\}$ (7)

To a stirred solution of $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC(Ph)NSiMe}_3\}\text{Cl}]$ (0.98 g, 2.27 mmol) in benzene (20 ml) was added a solution of pentafluoroaniline (0.42 g, 2.27 mmol) in benzene (20 ml), dropwise over 10 min. The orange solution darkened in colour. After stirring for 15 h, volatiles were removed under reduced pressure to yield $[\text{Ti}(\text{NC}_6\text{F}_5)\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC(Ph)NSiMe}_3\}\text{Cl}]$ as an orange oil. Yield: 1.14 g (93%). An analytically pure sample of **7** was obtained by sublimation at 3×10^{-6} mbar and 130°C in poor yield.

^1H NMR data (C_6D_6 , 500.0 MHz, 293 K): δ 7.01–7.06 (5 H, m, br, C $_6$ H $_5$), 2.99 (1 H, app t, CH $_2$ NMe $_2$, app $^2J = 12.7$), 2.91 (2 H, br d, CN $_2$ CH $_2$, $^2J = 5.9$), 2.65 (3 H, s, NMe), 1.88 (3 H, s, NMe), 1.71 (1 H, br d, CH $_2$ NMe $_2$, $^2J = 11.7$), 1.24 (1 H, m, CH $_2$ CH $_2$ CH $_2$), 0.85 (1 H, br d, CH $_2$ CH $_2$ CH $_2$, $^2J = 15.6$), 0.16 (9 H, s, SiMe $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR data (C_6D_6 , 75.5 MHz, 293 K): 177.19 (CN $_2$), 152.43, 145.87, 142.72, 139.61, 137.35, 134.95, 133.78 (6 C of C $_6$ F $_5$ and *ipso*-C $_6$ H $_5$), 129.57 (*para*-C $_6$ H $_5$), 128.79 (*ortho*- or *meta*-C $_6$ H $_5$, 2 overlapping), 126.50 (*ortho*- or *meta*-C $_6$ H $_5$, 2 overlapping), 62.92 (CH $_2$ NMe $_2$), 53.17 (NMe), 47.78 (CN $_2$ CH $_2$), 45.72 (NMe), 26.28 (CH $_2$ CH $_2$ CH $_2$), 2.24 (SiMe $_3$). ^{19}F NMR data (C_6D_6 , 300.0 MHz, 293 K): $-\text{154.90}$ (2 F, *ortho*-C $_6$ F $_5$), $-\text{167.09}$ (2 F, *meta*-C $_6$ F $_5$), $-\text{171.03}$ (1 F, *para*-C $_6$ F $_5$). IR data (KBr disc, cm^{-1}): 2956 (s), 2924 (s), 2362 (w), 2344 (w), 1670 (w), 1618 (m, br), 1580 (w), 1522 (s), 1504 (s), 1446 (m), 1404 (m), 1392 (m), 1344 (w), 1326 (w), 1304 (w), 1246 (m, br),

1198 (w), 1178 (w), 1158 (w), 1098 (w), 1042 (m), 1010 (s), 982 (s), 946 (m), 888 (m), 840 (s), 785 (m), 746 (m), 700 (s), 660 (m), 632 (w). Accurate mass EI-MS for $[\text{Ti}(\text{N}-\text{C}_6\text{F}_5)\{\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC(Ph)NSiMe}_3\}\text{Cl}]$: found (calculated for $\text{C}_{21}\text{H}_{26}\text{N}_4\text{ClF}_5\text{SiTi}$): 540.0989 (540.1015).

Li $\{\text{CH}_3\text{CH}_2\text{CH}_2\text{NC(Ph)NSiMe}_3\}\cdot\text{Et}_2\text{O}$ (8)

To a solution of propylamine (8.63 g, 0.15 mol) in Et $_2$ O (100 ml) at -78°C was added 1.6 M $^n\text{BuLi}$ /hexanes solution (91 ml, 0.15 mol) over 30 min. A white precipitate formed and the mixture was stirred for 16 h at rt. The reaction mixture was cooled to -78°C , trimethylsilylchloride (19 ml, 0.146 mol) added and the mixture stirred for a further 16 h at rt. The mixture was filtered and the white precipitate washed with 3×20 ml Et $_2$ O. The combined filtrates were cooled to -78°C and 1.6 M $^n\text{BuLi}$ /hexanes solution (91 ml, 0.15 mol) was added over 30 min. The mixture was stirred at rt for 16 h. Volatiles were removed under reduced pressure yielding $\text{Li}\{\text{CH}_3\text{CH}_2\text{CH}_2\text{NSiMe}_3\}$ as a pale yellow oil. A portion of $\text{Li}\{\text{CH}_3\text{CH}_2\text{CH}_2\text{NSiMe}_3\}$ (8.04 g, 59 mmol) was dissolved in Et $_2$ O (70 ml) and cooled to -78°C . Benzonitrile (6.04 g, 59 mmol) was added over 15 min. The resulting orange solution was stirred at rt for 16 h. Volatiles were removed under reduced pressure and the orange residue extracted into hexane (40 ml). The mixture was filtered and the white precipitate washed with hexane (3×15 ml). The filtrates were combined and the volatiles removed under reduced pressure to give a yellow oil. This was recrystallised from a mixture of Et $_2$ O (10 ml) and pentane (30 ml) at -80°C yielding **8** as a pale yellow powder. Yield: 2.90 g (7%).

^1H NMR data (C_6D_6 , 500.0 MHz, 293 K): 7.29 (2 H, d, br, *ortho*-C $_6$ H $_5$), 7.22 (2 H, app t, *meta*-C $_6$ H $_5$, app $^2J = 7.8$), 7.08 (1 H, t, *para*-C $_6$ H $_5$, $^2J = 7.8$), 3.29 (2 H, q, CH $_3$ CH $_2$ O, $^2J = 7.3$), 3.18 (2 H, m, br, CN $_2$ CH $_2$), 1.70 (2 H, m, br, CH $_3$ CH $_2$), 1.13 (3 H, t, CH $_3$ CH $_2$ O, $^2J = 7.3$), 0.84 (3 H, s, br, CH $_3$), 0.11 (9 H, s, br, SiMe $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR data (C_6D_6 , 75.5 MHz, 293 K): 128.10 (*meta*-C $_6$ H $_5$), 127.68 (*para*-C $_6$ H $_5$), 126.92 (*ortho*-C $_6$ H $_5$), 66.26 (CH $_3$ CH $_2$ O), 52.92 (NCH $_2$), 27.74 (CH $_3$ CH $_2$), 16.20 (CH $_3$ CH $_2$ O), 12.98 (CH $_3$), 4.14 (SiMe $_3$). IR data (KBr plates, Nujol mull, cm^{-1}): 3584 (w), 3328 (w), 3058 (m), 3020 (m), 2730 (w), 2690 (w), 2632 (w), 2318 (w), 1946 (w), 1888 (w), 1808 (w), 1774 (w), 1622 (m), 1600 (m), 1578 (w), 1402 (s), 1138 (s), 1292 (m), 1246 (s), 1172 (m), 1148 (w), 1126 (w), 1102 (w), 1054 (s), 1018 (s), 928 (m), 876 (s), 830 (s), 1782 (m), 754 (s), 678 (w), 630 (m), 410 (s). Anal. found (calc. for $\text{C}_{13}\text{H}_{21}\text{LiN}_2\text{Si}$) for Et $_2$ O-free **8**: C 64.2 (65.0), H 8.7 (8.8), N 11.8 (11.6)%. A satisfactory mass spectrum could not be obtained for this compound.

[Ti(N t Bu) $\{\text{CH}_3\text{CH}_2\text{CH}_2\text{NC(Ph)NSiMe}_3\}\text{Cl(py)}_2\]$ (9)

To a stirred solution of $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_3]$ (0.46 g, 1.09 mmol) in benzene (30 ml) was added a solution of $\text{Li}\{\text{CH}_3\text{CH}_2\text{CH}_2\text{NC(Ph)NSiMe}_3\}\cdot 0.5\text{Et}_2\text{O}$ (0.30 g, 1.09 mmol) in benzene (30 ml) dropwise over 10 min. The resulting orange mixture was stirred for 16 h. Volatiles were removed under reduced pressure and the resulting orange oil extracted into benzene (20 ml). The orange oily residue was triturated with pentane (20 ml) yielding **9** as an orange solid. The product was recrystallised at -80°C from a mixture of hexane (30 ml) and CH $_2$ Cl $_2$ (20 ml). Yield: 172 mg (34%).

^1H NMR data (C_6D_6 , 500.0 MHz, 293 K): 9.55 (2 H, d, br, *cis*-*o*-C $_5$ H $_5$ N, $^2J = 4.9$), 8.67 (2 H, s, br, *trans*-*o*-C $_5$ H $_5$ N), 7.09 (2 H, m, *meta*-C $_6$ H $_5$), 7.02 (3 H, m, *ortho*- and *para*-C $_6$ H $_5$), 6.93 (1 H, s, br, *trans*-*p*-C $_5$ H $_5$ N), 6.78 (1 H, t, br, *cis*-*p*-C $_5$ H $_5$ N, $^2J = 7.8$), 6.63 (2 H, s, br, *trans*-*m*-C $_5$ H $_5$ N), 6.53 (2 H, app t, br, *cis*-*m*-C $_5$ H $_5$ N, app $^2J = 6.8$), 3.94 (2 H, m, CN $_2$ CH $_2$), 2.14 (2 H, m, MeCH $_2$), 1.42 (9 H, s, CMe $_3$), 0.98 (3 H, t, MeCH $_2$, $^2J = 7.3$), 0.14 (9 H, s, SiMe $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR data (C_6D_6 , 75.5 MHz, 293 K): 165.24 (CN $_2$), 135.93 (*ipso*-C $_6$ H $_5$), 152.22 (*cis*-*o*-C $_5$ H $_5$ N), 137.92 (*cis*-*p*-C $_5$ H $_5$ N), 129.34 (*ortho*- or *para*-C $_6$ H $_5$), 128.55 (*ortho*- or *para*-C $_6$ H $_5$), 126.62 (*meta*-C $_6$ H $_5$), 123.62

Table 5 X-Ray data collection and processing parameters for [Ti(N^tBu){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] **1**, [Ti(N-2,6-Me₂C₆H₃)-{Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] **5**, [Ti(N-2,6-¹Pr₂C₆H₃){Me₂NCH₂CH₂CH₂NC(Ph)NSiMe₃}Cl] **6**, [Ti(N^tBu)Cl(μ-O){Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂] **10** and [Ti(N-2,6-Me₂C₆H₃)Cl(μ-O){Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂] **11**

	1	5	6	10	11
Formula	C ₁₈ H ₃₃ ClN ₄ SiTi	C ₂₃ H ₃₅ ClN ₄ SiTi	C ₂₇ H ₄₃ ClN ₄ SiTi	C ₃₆ H ₆₈ Cl ₄ N ₈ Si ₂ Ti ₂	C ₄₄ H ₆₈ Cl ₂ N ₈ O ₂ Si ₂ Ti ₂
Formula weight	416.93	479.00	535.10	906.78	931.96
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	11.7460(3)	8.8806(1)	16.0613(5)	8.8140(3)	13.9462(2)
<i>b</i> /Å	9.9836(3)	11.2263(1)	11.3483(4)	11.6000(5)	10.0038(2)
<i>c</i> /Å	20.1557(7)	15.0212(2)	17.5211(6)	12.6200(5)	17.9894(3)
<i>a</i> ^o	90	70.6889(7)	90	89.420(2)	90
<i>β</i> ^o	90.265(1)	88.3802(5)	112.749(2)	107.252(2)	96.337(1)
<i>γ</i> ^o	90	66.8105(5)	90	105.453(2)	90
<i>V</i> /Å ³	2363.6(1)	1290.11(3)	2945.1(2)	1184.4(1)	2494.45(7)
<i>Z</i>	4	2	4	1	2
<i>μ</i> (Mo-Kα)/mm ⁻¹	0.53	0.50	0.433	0.64	0.51
Total reflections	7790	11005	10922	11043	9895
Observed reflections ^a	3204	4948	3325	4422	3931
<i>R</i> ^b , <i>R</i> _w ^c	0.0329, 0.0366	0.0308, 0.0318	0.0411, 0.0254	0.0459, 0.0348	0.0351, 0.0399

^a For reflections with *I* > 3σ(*I*); ^b *R* = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|; ^c *R*_w = √{Σw(|*F*_o| - |*F*_c||)²/Σw|*F*_o|²}.

(*cis-m*-C₅H₅N), 67.46 (CMe₃), 53.90 (CN₂CH₂), 31.30 (CMe₃), 26.62 (MeCH₂), 11.91 (MeCH₂), 2.93 (SiMe₃). IR data (KBr plates, Nujol mull, cm⁻¹): 2610 (w), 1604 (w), 1510 (w), 1444 (s), 1400 (s), 1356 (m), 1296 (w), 1244 (m), 1194 (m), 1178 (w), 1158 (w), 1070 (m), 1042 (w), 1020 (m), 1002 (w), 918 (w), 902 (m), 868 (s), 842 (s), 780 (w), 764 (m), 702 (m), 636 (s), 412 (s). A satisfactory analysis and mass spectrum could not be obtained for this compound.

[Ti₂{Me₂NCH₂CH₂NC(Ph)N(H)SiMe₃}₂(N^tBu)₂Cl₂(μ-Cl)₂] (**10**)

To a stirred solution of [Ti(N^tBu){Me₂NCH₂CH₂NC(Ph)NSiMe₃}Cl] (0.113 g, 0.271 mmol) in pyridine (10 ml) was added a solution of NH₂Me₂Cl (19.9 mg, 0.244 mmol) in pyridine (20 ml) dropwise over 15 min. The resulting mixture was refluxed at 80 °C for 9 h. A pure product was not isolable upon layering with pentane, but resonances visible in the NMR spectrum of the crystals of [Ti₂{Me₂NCH₂CH₂NC(Ph)N(H)SiMe₃}₂(N^tBu)₂Cl₂(μ-Cl)₂] were also visible in the NMR spectrum of the crude reaction mixture.

¹H NMR data (C₆D₆, 300.0 MHz, 293 K): δ 2.33 (6 H, s, NMe₂), 1.27 (9 H, s, CMe₃), -0.03 (9 H, s, SiMe₃). Assignment of other peaks not possible due to overlaps with impurities. IR data (KBr plates, Nujol mull, cm⁻¹): 3268 (w), 2955 (m), 1608 (w), 1590 (m), 1574 (m), 1494 (w), 1353 (m), 1342 (w), 1288 (m), 1244 (m), 1208 (w), 1171 (w), 1147 (w), 1123 (w), 1081 (m), 1060 (m), 1037 (w), 1007 (m), 953 (m), 932 (m), 846 (s), 797 (m), 770 (m), 757 (m), 733 (m), 709 (m), 626 (w), 597 (w), 565 (w), 525 (w), 471 (w), 448 (w) cm⁻¹. Anal. found (calc. for C₃₆H₆₈Cl₄N₈Si₂Ti₂): C 46.6 (47.7), H 8.0 (7.6), N 11.8 (12.4)%.

Crystal structure determinations for [Ti(N^tBu){Me₂NCH₂CH₂-NC(Ph)NSiMe₃}Cl] (**1**), [Ti(N-2,6-R₂C₆H₃){Me₂NCH₂CH₂-CH₂NC(Ph)NSiMe₃}Cl] (**R** = Me **5** or ¹Pr **6**), [Ti₂{Me₂NCH₂-CH₂N=C(Ph)N(H)SiMe₃}₂(N^tBu)₂Cl₂(μ-Cl)₂] (**10**) and [Ti₂(N-2,6-C₆H₃Me₂)₂Cl₂(μ-O){Me₂NCH₂CH₂N=C(Ph)N(H)SiMe₃}₂] (**11**)

Crystal data collection and processing parameters are given in Table 5. Crystals were immersed in a film of perfluoropolyether oil on a glass fibre and transferred to an Enraf-Nonius DIP2000 or KappaCCD diffractometer equipped with an Oxford Cryo-systems low-temperature device.¹⁸ Data were collected at low temperature using Mo-Kα radiation; equivalent reflections were merged and the images were processed with the DENZO and SCALEPACK programs.¹⁹ Corrections for Lorentz-polarisation effects and absorption were performed and the structures were solved by direct methods using SIR92.²⁰ Subsequent difference Fourier syntheses revealed the positions of

all other non-hydrogen atoms. Carbon bound hydrogen atoms were placed geometrically except for in **7** for which they were located from difference syntheses and refined in a riding model. In both **7** and **8** the H atom bound to N(4) was located from difference syntheses and refined isotropically. Extinction corrections²¹ and a weighting scheme were applied as appropriate. Crystallographic calculations were performed using SIR92²⁰ and CRYSTALS.²²

CCDC reference numbers 190460–190464.

See <http://www.rsc.org/suppdata/dt/b2/b207184c/> for crystallographic data in CIF or other electronic format.

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