

Amido- and imido-ethylpyridine titanium complexes. Crystal structure of $\{\text{Ti}[\text{NCH}_2\text{CH}_2\text{py}]\text{Cl}_2(\text{THF})\}_2$

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Abstract

Compounds of general formula $\text{N}(\text{R}_1)(\text{R}_2)\text{CH}_2\text{CH}_2\text{py}$ ($\text{py} = \text{C}_5\text{H}_4\text{N}$; $\text{R}_1 = \text{R}_2 = \text{SiMe}_3$, **1a**; $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{Si}^i\text{BuMe}_2$, **1b**; $\text{R}_1 = \text{SiMe}_3$, $\text{R}_2 = \text{Si}^i\text{BuMe}_2$, **1c**; $\text{R}_1 = \text{SiMe}_3$, $\text{R}_2 = \text{Ph}$, **5**) were synthesised. They readily reacted with TiCl_4 to afford the corresponding amidoaminotrichlorides $\{\text{Ti}[\text{N}(\text{R}_2)(\text{CH}_2\text{CH}_2\text{py})]\text{Cl}_3\}$ ($\text{R}_2 = \text{SiMe}_3$, **2a**; $\text{R}_2 = \text{Si}^i\text{BuMe}_2$, **2b**; $\text{R}_2 = \text{Ph}$, **6**). The related imido derivatives $\{\text{Ti}[\text{N}(\text{CH}_2\text{CH}_2\text{py})]\text{Cl}_2\}_n$ (**3b**) and $\{\text{Ti}[\text{N}(\text{CH}_2\text{CH}_2\text{py})](\text{L})\text{Cl}_2\}_2$ ($\text{L} = \text{THF}$, **3c**; PMe_3 , **3d**) were isolated upon heating and reaction with L , respectively. Reaction of **6** with THF afforded the corresponding adduct, $\{\text{Ti}[\text{N}(\text{Ph})(\text{CH}_2\text{CH}_2\text{py})](\text{THF})\text{Cl}_3\}$ (**7**). Compound **3b** reacted with LiNMe_2 to give asymmetrical $\{\text{Ti}_2[\text{N}(\text{CH}_2\text{CH}_2\text{py})][\text{N}(\text{CH}_2\text{CH}_2\text{py})']\text{Cl}_4\}$ (**4a**). Compound $\{\text{CpTi}[\text{N}(\text{CH}_2\text{CH}_2\text{py})]\text{Cl}\}_n$ (**4b**), was formed when **3b** reacted with NaCp . Analogous studies with **2a** and **6** led to Cp_2TiCl_2 . $\{\text{Cp}_2\text{Ti}_2[\mu\text{-N}(\text{Ph})]\text{Cl}_2\}$ (**8**) was isolated as the product of CpTiCl_3 and $\text{Na}[\text{N}(\text{Ph})\text{CH}_2\text{CH}_2\text{py}]$. The molecular structure of **3c** was determined by X-ray single crystal diffraction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Titanium; Amido; Imido; 2'-Aminoethyl-2-pyridyl derivatives

1. Introduction

Nitrogen-based ligands offer a great diversity of structural frameworks that have been used as ancillary ligands in several studies of organometallic chemistry [1–7], including Group 4 metal complexes with activity in olefin polymerisation [8–11]. Relevant results include bis(amido)titanium (IV) complexes that carry out the living polymerisation of olefins [12–14].

The amido/amine donor set has attracted the interest of several researchers. Pyridyl-substituted 1-azaallyl ligands have been successfully co-ordinated to zirconium to give octahedral complexes that show high activity in ethylene polymerisation [15,16]. Recent studies on Group 4 aminopyridinato complexes emphasise the importance of the amido nitrogen substituents on the control of metal–ligand stoichiometry and reactivity [5,15,17,18].

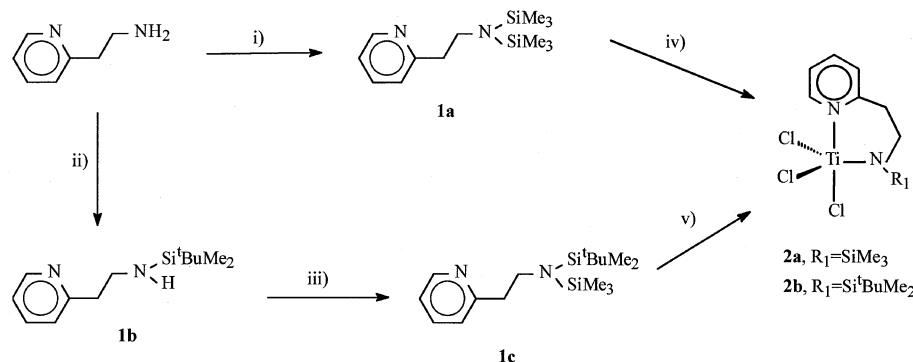
The particular features that dictate the performance of polyfunctional nitrogen compounds as catalysts are still not fully understood [10,19]. Thus, the study of Group 4 complexes with ancillary *N*-donor ligands is a topic of current interest [20–24]. We report the synthesis, characterisation and reactivity of new Ti(IV) complexes containing amido- and imido-ethylpyridine ligands.

2. Results and discussion

Silylated amine derivatives are useful reagents as they are easy to synthesise and because they react with metal chlorides to give R_3SiCl which, being volatile, are easily eliminated from the reaction media. These features, associated with efficient steric bulk, partially explain their extensive use in synthesis and the large number of co-ordination compounds containing such ligands [1,5,9,25,26]. Silylated derivatives of 2'-aminoethyl-2-pyridine are no exception. Compounds **1a–1c** were isolated in good yields (>90%) and in multigram

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Scheme 1. (i) SiMe_3Cl ; (ii) $\text{Si}^t\text{BuMe}_2\text{Cl}$; (iii) $\text{CF}_3\text{SO}_3\text{SiMe}_3$; (iv) TiCl_4 ; (v) TiCl_4 .

quantities (Scheme 1). **1a** was obtained as a colourless oil from the reaction of 2'-aminoethyl-2-pyridine with three equivalents of SiMe_3Cl in dichloromethane. The reaction of primary amines with Me_3SiCl usually gives monosilylated products. The synthesis of bis-silylated compounds often requires the use of strong electrophiles or catalysts [27]. The mild experimental conditions used in the preparation of **1a** suggest the assistance of the pyridyl fragment in N–H intramolecular bond activation of the $\text{N}(\text{H})(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{py}$ intermediate. In similar conditions, the use of a bulky reagent ($\text{Si}^t\text{Bu}(\text{Me})_2\text{Cl}$) led to a pale-yellow oil, $\text{N}(\text{H})(\text{Si}^t\text{BuMe}_2)\text{CH}_2\text{CH}_2\text{py}$ (**1b**) that was converted by $\text{CF}_3\text{SO}_3\text{SiMe}_3$ to the bis-silylated compound $\text{N}(\text{SiMe}_3)(\text{Si}^t\text{BuMe}_2)\text{CH}_2\text{CH}_2\text{py}$ (**1c**).

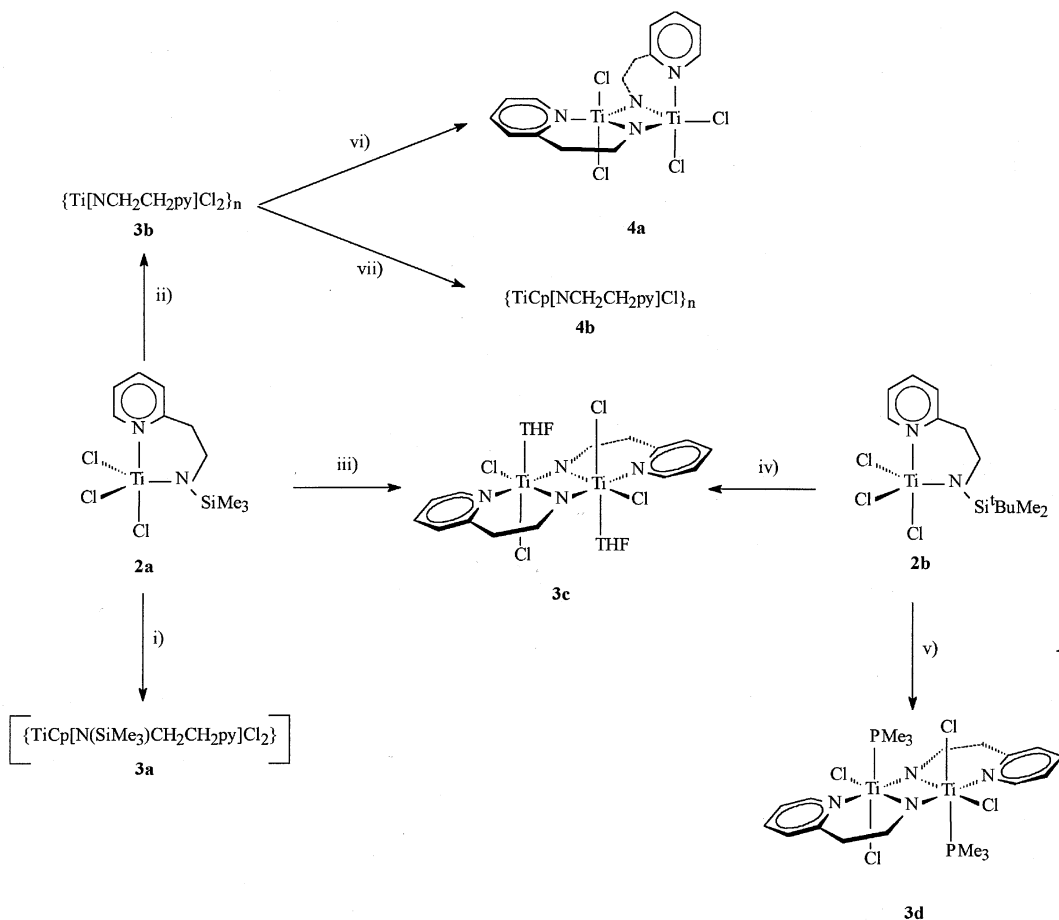
Compounds **1a** and **1c** readily react with TiCl_4 , in toluene, to afford the expected trichlorides, $\{\text{Ti}[\text{N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{py}]\text{Cl}_3\}$ (**2a**) and $\{\text{Ti}[\text{N}(\text{Si}^t\text{BuMe}_2)\text{CH}_2\text{CH}_2\text{py}]\text{Cl}_3\}$ (**2b**) as dark-orange and bright-red microcrystalline solids, respectively, which precipitate out of solution in essentially quantitative yields (Scheme 1). The use of SiMe_3Cl as a leaving group proved to be the best way to carry out these reactions. Attempts to use monosilylated compounds in the presence of a base to neutralise the HCl formed, or the more common procedures involving lithium or sodium salts [5,26], led to mixtures of unidentified products. The outcome of the reactions also depends on the solvent used. When carried out in dichloromethane, ^1H - and ^{13}C -NMR spectra show the formation of **2a** and ethylpyridine (3:1), which is assumed to be co-ordinated to the metal centre in view of the low field shifted resonances of the *ortho*-pyridyl (δ 8.92) and CH_2 aliphatic protons (δ 4.99). The ^1H -NMR spectra of both compounds attest the chelating co-ordination of the ligands to the titanium since all the proton resonances are shifted low field in relation to the corresponding values in the ligand precursors. Particularly sensitive to the metal co-ordination are the α -nitrogen chain protons (δ 3.17, **1a** vs. 4.63 **2a**; 3.22, **1c** vs. 4.74, **2b**) and the *ortho*-pyridyl protons (δ 8.52, **1a** vs. 8.75 **2a**; 8.52, **1c** vs. 8.71, **2b**). The chain carbons adjacent to

the pyridyl are slightly shielded (δ 44.8, **1a** vs. 39.0 **2a** and 44.4, **1c** vs. 40.0, **2b**). The very low solubilities of **2a** and **2b** in non-co-ordinating solvents make their formulation most probably as dimers or other higher-order aggregates [24,28]. Unfortunately, the poor-quality crystals grown in dichloromethane prevented the obtention of their molecular solid state structures. Also, all the attempts to obtain mass spectra (EI and FAB) were unfruitful.

Compounds **2a** and **2b** proved to be unstable under a variety of conditions (Scheme 2). In order to increase their solubility, attempts were made to introduce a second ligand into the metal co-ordination sphere. No reaction was observed, however, when **2a** was mixed with one equivalent of $\text{N}(\text{SiMe}_3)_2\text{CH}_2\text{CH}_2\text{py}$ (**1a**). The reaction of **2a** with NaCp gave a mixture of compounds (as shown later). These results are probably due to the lability of the N–Si bond, a fact well illustrated by the formation of compounds **3b–3d**.

In the presence of L-type donors (THF and PMe_3), or upon heating in 1,2-dichloroethane, *N*-bridging imides are formed as a result of N–Si bond cleavage. The dissolution of **2a**, **2b** in THF affords $\{\text{Ti}_2[\mu\text{-NCH}_2\text{CH}_2\text{py}]_2\text{Cl}_4(\text{THF})_2\}$ (**3c**) as a bright-red crystalline material in quantitative yield. Suitable X-ray crystals were thus obtained from the reaction media. Fig. 1 depicts the molecular structure of **3c**. Selected bond lengths and angles are presented in Table 1.

The molecule is a dimer, with two titanium centres linked by *N*-imido bridges and related by a centre of symmetry lying in the plane defined by the Ti_2N_2 ring. Each titanium atom is located in a distorted octahedral environment, with angles ranging from 82.02(10) to 97.10(13)°. The $\text{N}(1)\text{--Cl}(1)\text{--N}(2)\text{--N}(1\text{A})$ atoms are almost co-planar, (maximum deviation, 0.0021 Å), with the titanium atom 0.118(2) Å away from this plane, in the direction of the axial chloride. The nitrogen atoms of the pyridyl-imido ligand occupy equatorial positions, with each *N*-imido co-ordinated *trans* to the *N*-pyridyl atom of the other ligand. The THF group occupies an axial position and thus both chloride atoms are *cis* to each other. The $\text{Ti}\cdots\text{Ti}$ distance (2.848(2) Å) falls in the



Scheme 2. (i) NaCp; (ii) 1,2-dichloroethane, Δ ; (iii) THF; (iv) THF; (v) PMe_3 ; (vi) LiNMe_2 ; (vii) NaCp.

usual range for this type of binuclear Ti(IV) complexes [29–32]. The four-membered ring is rather planar with different Ti–N bonding distances ($\text{Ti}(1)\text{--N}(1) = 1.932(4)$, $\text{Ti}(1)\text{--N}(1A) = 1.868(4)$ Å), which are within the values usually found for Ti–N bridging imido complexes (1.86–2.17 Å) [30,33,34]. For complexes containing chelating μ -N-imido ligands, the stereochemical constraint imposed by the chelating ligand can induce considerable lengthening of the Ti–N bonds (2.04–2.17 Å) [33]. This increase is not observed for **3c**, where the chelating effect is reflected in the enlargement of the aliphatic chain bond angles ($\text{N}(1)\text{--C}(1)\text{--C}(2)$ ($112.5(5)^\circ$) and $\text{C}(1)\text{--C}(2)\text{--C}(3)$ ($115.1(5)^\circ$)). The small distortion observed for the Ti_2N_2 core, with a difference of 0.064 Å between the $\text{Ti}(1)\text{--N}(1)$ and $\text{Ti}(1)\text{--N}(1A)$ distances, is comparable to that reported for other compounds containing μ -N-imido ligands and a centre of inversion [30,34]. As expected on the basis of the *trans* effect associated to imido ligands, the equatorial $\text{Ti}(1)\text{--Cl}(1)$ bond (2.4074(16) Å) is longer than the axial $\text{Ti}(1)\text{--Cl}(2)$ distance (2.3271(18) Å). The same effect may be responsible for the value of 2.304(4) Å for the $\text{Ti}(1)\text{--N}(2)$ bond, that is slightly higher than the mean distance reported for the Ti–pyridine bond (2.279 Å) [35].

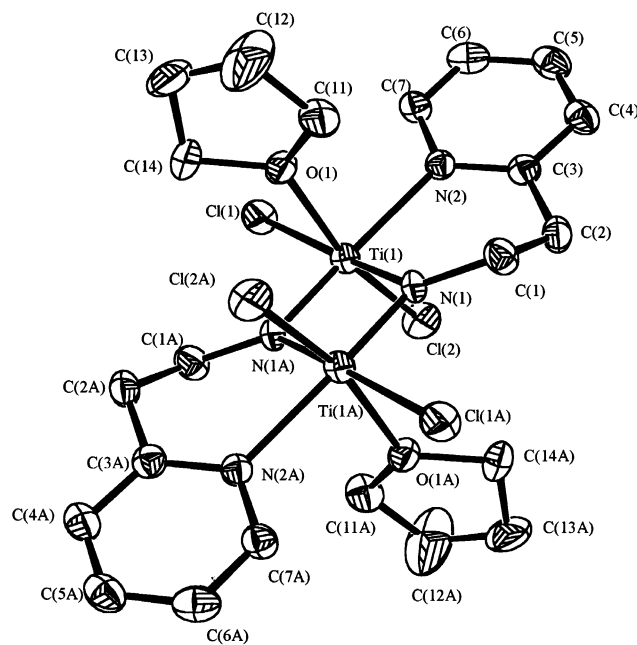


Fig. 1. ORTEP diagram of **3c** showing thermal ellipsoids at 40% probability level. Hydrogens are omitted for clarity.

Table 1
Bond lengths (Å) and angles (°) for **3c**

Bond lengths (Å)		Bond angles (°)	
Ti(1)–N(1)	1.868(4)	N(1)–Ti(1)–Cl(2)	100.79(14)
Ti(1)–O(1)	2.167(4)	O(1)–Ti(1)–Cl(2)	162.40(11)
Ti(1)–Cl(2)	2.3271(18)	N(1)–Ti(1)–Cl(1)	97.10(13)
Ti(1)–Ti(1A)	2.848(2)	O(1)–Ti(1)–Cl(1)	82.02(10)
N(1)–Ti(1A)	1.932(4)	Cl(2)–Ti(1)–Cl(1)	89.08(6)
C(2)–C(1)	1.534(7)	C(1)–N(1)–Ti(1)	133.2(3)
Ti(1)–N(2A)	2.304(4)	Ti(1)–N(1)–Ti(1A)	97.07(18)
Ti(1)–Cl(1)	2.4074(16)	N(1)–C(1)–C(2)	112.7(5)
N(1)–C(1)	1.462(6)	N(2)–C(3)–C(2)	118.8(5)
C(2)–C(3)	1.486(7)	C(3)–N(2)–Ti(1A)	122.9(3)
N(2)–Ti(1A)	2.304(4)	N(1)–Ti(1)–N(1A)	82.93(18)
		N(1A)–Ti(1)–O(1)	91.64(15)
		N(1A)–Ti(1)	85.93(16)
		–N(2A)	

(A) Generated by symmetry operation $-x+1, -y+1, -z+2$.

A similar 14-electron structure is assumed for $\{\text{Ti}_2[\mu\text{-NCH}_2\text{CH}_2\text{py}]_2\text{Cl}_4(\text{PMe}_3)_2\}$ (**3d**) that precipitated out of toluene as a yellow microcrystalline solid as the reaction of the in situ generated **2b** and PMe_3 proceeded.

When heated in 1,2-dichloroethane, **2a** afforded quantitatively a red microcrystalline solid, which analyses for $\text{TiC}_7\text{H}_8\text{N}_2\text{Cl}_2$. In the absence of an L-donor ligand, we propose that the imido-bridged core is maintained (that is, after all, the most common arrangement in this type of compounds [29,33,34,36,37]). The 14-electron titanium centres may be achieved by chloride bridges, leading to the polymeric structure proposed above for **3b**. Similar linkages have been reported for $[\text{Ti}(\mu\text{-NSiMe}_3)\text{Cl}_2]_8$ [37].

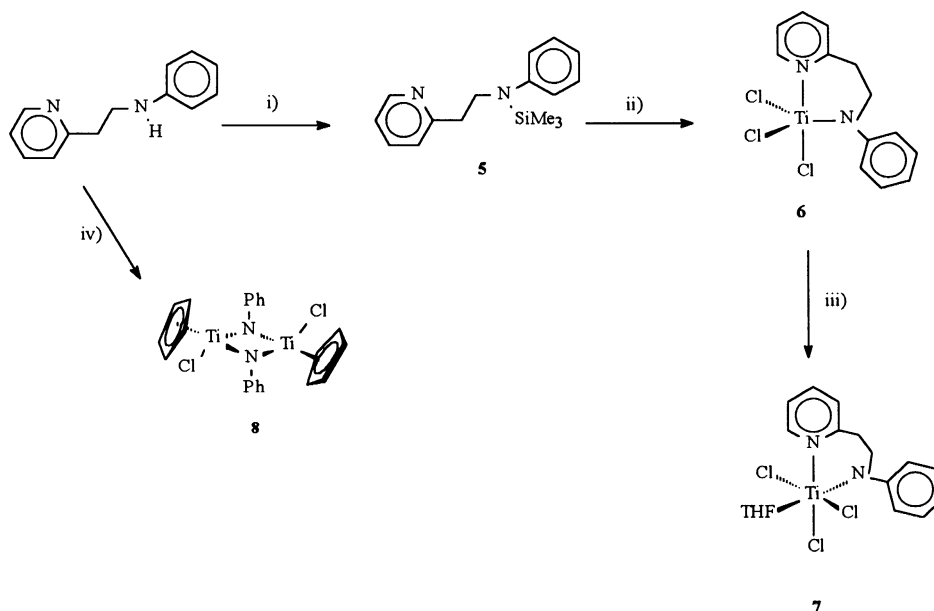
In order to get some insight into the structure of **3b**, several attempts were made to replace one chloride by a bulkier ligand, as represented in Scheme 2. Efforts to introduce an alkyl group (Me or CH_2Ph) in the titanium co-ordination sphere were unsuccessful, leading to unidentified products. Treatment of **3b** with one equivalent of NaCp afforded a brown microcrystalline sample of **4b** in poor yield (< 5%). This compound analysed for $\{\text{CpTi}[\text{NCH}_2\text{CH}_2\text{py}]\text{Cl}\}_4$ and showed in its mass spectrum a parent ion corresponding to a tetramer (i.e. $\{\text{CpTi}[\text{NCH}_2\text{CH}_2\text{py}]\text{Cl}\}_4$), reflecting the trend of these compounds to form higher-order aggregates, possibly to cope with the acidic titanium centres. A similar reaction with **3c** did not allow the isolation of well-defined compounds. The reaction of equimolar amounts of LiNMe_2 and **3b**, in toluene, did not afford the desired substitution compound, $\{\text{Ti}[\text{NCH}_2\text{CH}_2\text{py}](\text{NMe}_2)\text{Cl}\}$. Instead, it appears to have broken the polymeric structure of **3b** leading to a dark-red solid **4a**, in ca. 27% reproducible yield. The ^1H -NMR spectrum at room temperature shows a total absence of NMe_2 groups and two inequivalent ligands, with different signals for the pyridyl and the chain protons. Two sets

of resonances are observed for both pyridyl protons (e.g. δ 9.45 H_6 and 8.27 H_6) and aliphatic chains (δ 2.33, 2.93, 4.99, 5.78 and 2.77, 3.48, 4.72, 5.41). The diastereotopic pattern displayed by the methylenic chain protons indicates co-ordination of both imido and pyridyl moieties. Similarly, there are two sets of signals in the ^{13}C -NMR spectrum. Two-dimensional (2D) NMR experiments, $^1\text{H}\{^1\text{H}\}$ 2D correlations (COSY, NOESY and TOCSY) and $^{13}\text{C}\{^1\text{H}\}$ single bond correlation (HETCOR) allowed the assignment of all the resonances. Variable-temperature NMR experiments showed no ligand exchange in the range -50 to $+60^\circ\text{C}$. The NMR is consistent with the formulation of **4a** as a dimer with two bridging *N*-imido ligands between the titanium atoms. The structure has no inversion centre, suggesting that the two ligands are arranged differently around the Ti_2N_2 core. As represented in Scheme 2, one of the pyridyl fragments co-ordinates in the Ti_2N_2 plane while the other occupies a position out of this plane. Two different co-ordination geometries may be envisaged for the titanium atoms, namely trigonal-bipyramidal or quadrangular-pyramidal. Although our results do not allow an unequivocal assignment, the lack of reported X-ray characterised trigonal-bipyramidal structures for $\text{Ti}(\text{IV})$ μ -imido complexes makes the quadrangular pyramidal arrangement more probable [33,34,36]. The limited stability of complex **4a** in toluene and THF (observed after 2 days, even at -20°C) prevented its characterisation by X-ray diffraction studies.

Attempts to increase the stability of the amido complexes led us to the replacement of the silyl group by phenyl (Scheme 3).

Compound $\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{py}$ (**5**) was obtained in good yield (94%) as an orange oil, when the in situ generated lithium salt of 2'-(*N*-phenylamino)ethyl-2-pyridine reacted with SiMe_3Cl in *n*-hexane. The equimolar reaction of compound **5** with TiCl_4 proceeds similarly as for **1a** or **1c** to afford $\{\text{Ti}[\text{N}(\text{Ph})\text{CH}_2\text{CH}_2\text{py}]\text{Cl}_3\}$ (**6**) in quantitative yield. As previously observed, the α -nitrogen chain protons are deshielded upon co-ordination (δ 3.81, **5** vs. 4.80, **6**), as well as the *ortho*-pyridyl proton (δ 8.59, **5** vs. 8.90, **6**). As expected, **6** is more robust than its silylated analogues, since no ligand cleavage is observed in the presence of THF. In fact, dissolution of **6** in THF gave the corresponding adduct, $\{\text{Ti}[\text{N}(\text{Ph})\text{CH}_2\text{CH}_2\text{py}]\text{Cl}_3(\text{THF})\}$ (**7**), in quantitative yield. The introduction of THF in the metal co-ordination sphere does not induce significant changes in the ^1H - and ^{13}C -NMR resonances.

Our studies pursued the synthesis of mixed cyclopentadienyl-amidoamino complexes of general formula $\{\text{CpTi}[\text{N}(\text{R})\text{CH}_2\text{CH}_2\text{py}]\text{Cl}_3\}$. With this aim in mind, $\{\text{Ti}[\text{N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{py}]\text{Cl}_3\}$ (**2a**) was allowed to react with one equivalent of NaCp in THF to give a dark-red



Scheme 3. (i) 1-*n*-LiBu, 2-SiMe₃Cl; (ii) TiCl₄; (iii) THF; (iv) 1-NaH, 2-CpTiCl₃.

material soluble in toluene. The NMR data suggests the presence of the desired product {CpTi[N(SiMe₃)-CH₂CH₂py]Cl₂} (**3a**) as the major component, as evidenced by the signals at δ 6.19 (Cp), 8.44 (Py H₆), 4.58 and 3.14 (CH₂N and CH₂py, respectively) and 0.24 (SiMe₃). The simultaneous formation of Cp₂TiCl₂ (yield < 5%) was inferred by the resonance at δ 5.91. Unfortunately the compound resisted all recrystallisation attempts, leading to a mixture of insoluble materials. The analogous reaction of equimolar amounts of **6** and NaCp gave Cp₂TiCl₂, in very low yield, as the only identified product. A different approach was attempted when CpTiCl₃ was mixed with N(SiMe₃)₂CH₂CH₂py (**1a**). No reaction was observed, however. The reaction of CpTiCl₃ with the sodium salt of 2'-(*N*-phenylamino)ethyl-2-pyridine led to ligand cleavage and afforded the already known complex {Cp₂Ti₂[μ -N(Ph)]Cl₂} (**8**) [30,38], in poor yield (< 10%), according to Scheme 3. This was confirmed by the re-determination of its molecular structure by X-ray diffraction of crystals grown from diethylether.¹

The results described above are very surprising in view of the stability of several titanium cyclopentadienylamido complexes [39,40] that have been prepared by one of the two synthetic approaches tried in this work. However, the cleavage of an α -carbon nitrogen bond of the amido ligands has previously been reported

in the literature for strongly acidic metal centres [41–43]. The greater stability of bis-Cp titanium complexes when compared to their Cp-amido analogues is probably a considerable driving force for the observed outcome of these reactions.

3. Conclusions

N(SiMe₃)(R)(CH₂CH₂)py reacts readily with TiCl₄ to give the corresponding trichlorides, {Ti[N(R)-(CH₂CH₂)py]Cl₃}. The study of their chemistry is hampered by the high reactivity of the N–R bond that often leads to the formation of *N*-bridged imido complexes, and by the inability of amidoethylpyridine ligands to offer steric protection to the metal centres. The lack of rigidity conferred by the C₂ chain does not impose a constrained co-ordination mode of the ligand, a feature that may be crucial in the stabilisation of the amido complexes [5,26]. The formation of *N*-bridged imido compounds dominated the reactivity pattern observed.

The reactivity of amido and/or imido compounds with alkylating reagents and Cp[−] proved to be rather disappointing. The high insolubility of these complexes prevented the stereochemical control of subsequent reactions, making them poor starting materials and leading to surprising results, as the formation of {Ti₂[μ -N(CH₂CH₂)py][μ -N(CH₂CH₂)py]'Cl₄} with two different imido-pyridyl ligands disposed in a rarely observed arrangement.

¹ Crystal data obtained at room temperature: **8** crystallised in the orthorhombic system, space group *Pbca*, with cell parameters $a = 8.697(2)$, $b = 14.593(2)$, $c = 17.158(2)$ Å, final $R_1 = 0.0454$ and $wR_2 = 0.1115$.

4. Experimental

All manipulations, except stated otherwise, were carried out under N₂, using either standard Schlenk-line or dry-box techniques. Solvents were pre-dried using 4 Å molecular sieves and refluxed over sodium-benzophenone (Et₂O, THF and C₆H₅CH₃) or CaH₂ (CH₂Cl₂, 1,2-dichloroethane and *n*-hexane) under an atmosphere of N₂, and collected by distillation. Deuterated solvents were dried with molecular sieves and freeze–pump–thaw–degassed prior to use. ¹H- and ¹³C-NMR spectra were recorded in a Varian Unity 300, at 298 K unless otherwise stated, referenced internally to residual protons (solvent (¹H) or solvent (¹³C) resonances and reported relative to TMS (δ 0). Assignments were supported by NOE spectra (1- and 2D) experiments and by one bond ¹³C{¹H} hetero-correlations, as appropriate. Mass spectra were performed at IST, Lisbon, Portugal and Université de Rouen, Rouen, France. Elemental analyses were obtained from the Laboratório de Análises do IST (Fisons Instrument 1108).

CF₃SO₃SiMe₃, PMe₃ (1.0 mol dm^{−3} in C₆H₅CH₃), LiNMe₂, aminoethylpyridine, Et₃N, SiMe₃Cl, Si^{*i*}BuMe₂Cl, *n*-LiBu (1.6 mol dm^{−3} in hexanes), TiCl₄ and NaH (60% dispersion in mineral oil) were purchased from Aldrich. CF₃SO₃SiMe₃, PMe₃ and LiNMe₂ were used as received. 2'-Aminoethyl-2-pyridine was purified by distillation over potassium hydroxide. Triethylamine was pre-dried with molecular sieves, refluxed over CaH₂ and collected by distillation. SiMe₃Cl was purified by removal of residual HCl (by bubbling nitrogen through for ca. 15 min.) and then distilled trap-to-trap. Si^{*i*}BuMe₂Cl was freeze–pump–thaw–degassed prior to use. The *n*-LiBu solution was titrated by usual methods before use. TiCl₄ was freeze–pump–thaw–degassed and then distilled trap-to-trap. NaH was washed with THF prior to use. The compounds NaC₅H₅ [44], CpTiCl₃ [45] and 2'-(*N*-phenylamino)ethyl-2-pyridine [46] were prepared according to literature methods.

4.1. Synthesis of *N*(SiMe₃)₂CH₂CH₂py (**1a**)

To a solution of 2'-aminoethyl-2-pyridine (12.35 g, 101.1 mmol) in CH₂Cl₂ (200 ml), Et₃N (50 ml, 358.7 mmol) was added. The mixture was cooled to 0°C and SiMe₃Cl (40.0 ml, 315.2 mmol) was added dropwise. A white precipitate appeared immediately. The mixture was stirred for 15 h at room temperature (r.t.). The volatiles were removed under vacuum. The residue was extracted with *n*-hexane. The solvent was removed under reduced pressure leaving 25.93 g of a colourless oil (96% yield). ¹H-NMR (C₆D₆, 300 MHz): δ = 8.48 (m, 1H, Py H₆), 7.04 (td, 1H, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.8 Hz, Py H₄), 6.75 (d, 1H, ³J_{HH} = 7.8 Hz, Py H₃), 6.61 (m, 1H, Py H₅), 3.27 (m, 2H, CH₂N), 2.89 (m, 2H, CH₂py),

0.20 (s, 18H, Si(CH₃)₃). ¹H-NMR (CD₂Cl₂, 300 MHz): δ = 8.52 (m, 1H, Py H₆), 7.57 (td, 1H, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 2.1 Hz, Py H₄), 7.10 (m, 2H, Py H₃ + Py H₅), 3.17 (m, 2H, CH₂N), 2.84 (m, 2H, CH₂py), 0.22 (s, 18H, Si(CH₃)₃). ¹³C-NMR (C₆D₆): δ = 160.5 (Py C₂), 149.9 (Py C₆), 135.7 (Py C₄), 122.7 (Py C₅), 121.0 (Py C₃), 46.5 (CH₂N), 44.7 (CH₂py), 2.2 (Si(CH₃)₃). ¹³C-NMR (CD₂Cl₂): δ = 160.8 (Py C₂), 149.9 (Py C₆), 136.4 (Py C₄), 123.3 (Py C₃ or Py C₅), 121.5 (Py C₃ or Py C₅), 46.5 (CH₂N), 44.8 (CH₂py), 2.4 (Si(CH₃)₃). Anal. Found: C, 58.53; H, 9.94; N, 10.53. Calc. for C₁₃H₂₆N₂Si₂: C, 58.58; H, 9.83; N, 10.51%. MS: 266 (80) [M⁺]; 251 (20) [M⁺ − CH₃]; 193 (10) [M⁺ − SiMe₃].

4.2. Synthesis of *N*(H)(Si^{*i*}BuMe₂)CH₂CH₂py (**1b**)

Triethylamine (90 ml, 645.7 mmol) was added to a solution of 2'-aminoethyl-2-pyridine (15.66 g, 128.2 mmol) in 150 ml of CH₂Cl₂. The mixture was heated to 35°C and a solution of Si^{*i*}BuMe₂Cl (21.27 g, 141.0 mmol) in CH₂Cl₂ was added dropwise. The mixture was refluxed for 2 h. The volatiles were removed under vacuum and the residue extracted with *n*-hexane. The solvent was removed under reduced pressure leaving 27.88 g of a pale-yellow oil (92% yield). ¹H-NMR (C₆D₆, 300 MHz): δ = 8.46 (m, 1H, Py H₆), 7.07 (td, 1H, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.8 Hz, Py H₄), 6.76 (d, 1H, ³J_{HH} = 7.8 Hz, Py H₃), 6.64 (m, 1H, Py H₅), 3.17 (m, 2H, CH₂N), 2.77 (m, 2H, CH₂py), 0.50 (s, 1H, N(H)), 0.88 (s, 9H, Si(CH₃)₃), −0.048 (s, 6H, Si(CH₃)₂). ¹³C-NMR (C₆D₆): δ = 161.0 (Py C₂), 149.7 (Py C₆), 135.5 (Py C₄), 123.3 (Py C₅), 120.9 (Py C₃), 43.7 (CH₂N), 42.9 (CH₂py), 26.6 (Si(CH₃)₃), 18.56 (Si(CH₃)₃), −4.9 (Si(CH₃)₂). Anal. Found: C, 63.40; H, 10.59; N, 11.83. Calc. for C₁₃H₂₄N₂Si: C, 66.04; H, 10.23; N, 11.85%. MS: 237 (95) [M⁺]; 221 (20) [M⁺ − Me]; 179 (100) [M⁺ − ^{*i*}Bu]; 123 (12) [M⁺ − Si^{*i*}BuMe₂].

4.3. Synthesis of *N*(SiMe₃)(Si^{*i*}BuMe₂)CH₂CH₂py (**1c**)

A solution of **1b** (27.89 g, 118.0 mmol) in 200 ml of Et₂O was cooled to 0°C and Et₃N (50 ml, 358.7 mmol) was added. CF₃SO₃SiMe₃ (23.5 ml, 129.8 mmol) was added dropwise and the mixture was stirred for 4 days at r.t. A mixture of two phases was formed: a pink heavy phase, containing the triflate salts, and a yellow phase, containing **1b**. The lighter phase was decanted and the volatiles were removed under vacuum. The resulting residue was extracted with *n*-hexane and the solvent evaporated under reduced pressure, leaving a pale-yellow oil (36.0 g, 98.9% yield). ¹H-NMR (C₆D₆, 300 MHz): δ = 8.45 (m, 1H, Py H₆), 7.05 (td, 1H, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.8 Hz, Py H₄), 6.75 (d, 1H, ³J_{HH} = 7.8 Hz, Py H₃), 6.61 (m, 1H, Py H₅), 3.36 (m, 2H, CH₂N), 2.94 (m, 2H, CH₂py), 0.92 (s, 9H,

$\text{SiC}(\text{CH}_3)_3$, 0.25 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.22 (s, 6H, $\text{Si}(\text{CH}_3)_2$). ^1H -NMR (CD_2Cl_2 , 300 MHz): δ = 8.52 (m, 1H, Py H₆), 7.58 (td, 1H, $^3J_{\text{HH}} = 7.80$ Hz, $^4J_{\text{HH}} = 1.80$ Hz, Py H₄), 7.10 (m, 2H, Py H₃ + Py H₅), 3.22 (m, 2H, CH_2N), 2.89 (m, 2H, CH_2py), 0.93 (s, 9H, $\text{SiC}(\text{CH}_3)_3$), 0.25 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.23 (s, 6H, $\text{Si}(\text{CH}_3)_2$). ^{13}C -NMR (C_6D_6): δ = 160.5 (Py C₂), 149.9 (Py C₆), 135.8 (Py C₄), 122.6 (Py C₃ or Py C₅), 121.1 (Py C₃ or Py C₅), 47.6 (CH_2N), 44.4 (CH_2py), 27.8 ($\text{SiC}(\text{CH}_3)_3$), 20.2 ($\text{SiC}(\text{CH}_3)_3$), 3.1 ($\text{Si}(\text{CH}_3)_3$), –2.2 ($\text{Si}(\text{CH}_3)_2$). ^{13}C -NMR (CD_2Cl_2): δ = 160.7 (Py C₂), 149.9 (Py C₆), 136.5 (Py C₄), 123.1 (Py C₃), 121.5 (Py C₅), 47.6 (CH_2N), 44.4 (CH_2py), 28.0 ($\text{SiC}(\text{CH}_3)_3$), 20.4 ($\text{SiC}(\text{CH}_3)_3$), 3.2 ($\text{Si}(\text{CH}_3)_3$), –2.2 ($\text{Si}(\text{CH}_3)_2$). Anal. Found: C, 61.91; H, 10.59; N, 9.32. Calc. for $\text{C}_{16}\text{H}_{32}\text{N}_2\text{Si}_2$: C, 62.27; H, 10.45; N, 9.07%. MS: 309 (100) [M^+]; 293 (30) [$\text{M}^+ - \text{CH}_3$]; 235 (30) [$\text{M}^+ - \text{SiMe}_3$]; 251 (100) [$\text{M}^+ - \text{tBu}$].

4.4. Synthesis of $\{\text{Ti}[\text{N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{py}]\text{Cl}_3\}$ (**2a**)

TiCl_4 (2.1 ml, 19.26 mmol) in 100 ml of $\text{C}_6\text{H}_5\text{CH}_3$ was cooled to -80°C . A solution of **1a** (5.132 g, 19.26 mmol) in $\text{C}_6\text{H}_5\text{CH}_3$ was added dropwise. The mixture was allowed to warm slowly to r.t. while stirring for 19 h. A dark-orange microcrystalline precipitate formed and was filtered off. The solid was washed with *n*-hexane and dried under dynamic vacuum (4.161 g, 62% yield). A second crop of dark-orange crystals (1.795 g) was obtained by keeping the mother liquor at -20°C for 2 days (global yield: 89%). ^1H -NMR (CD_2Cl_2 , 300 MHz): δ = 8.75 (m, 1H, $^3J_{\text{HH}} = 6.0$ Hz, $^4J_{\text{HH}} = 0.8$ Hz, Py H₆), 7.90 (td, 1H, $^3J_{\text{HH}} = 7.7$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, Py H₄), 7.43 (m, 2H, Py H₃ + Py H₅), 4.63 (m, 2H, CH_2N), 3.41 (m, 2H, CH_2py), 0.47 (s, 9H, $\text{Si}(\text{CH}_3)_3$). ^{13}C -NMR (CD_2Cl_2): δ = 157.1 (Py C₂), 149.2 (Py C₆), 140.2 (Py C₄), 125.8 (Py C₃), 122.7 (Py C₅), 48.8 (CH_2N), 39.0 (CH_2py), 0.19 ($\text{Si}(\text{CH}_3)_3$). Anal. Found: C, 34.45; H, 4.95; N, 8.14. Calc. for $\text{TiC}_{10}\text{H}_{17}\text{N}_2\text{SiCl}_3$: C, 34.56; H, 4.93; N, 8.06%.

4.5. Synthesis of $\{\text{Ti}[\text{N}(\text{Si}^t\text{BuMe}_2)\text{CH}_2\text{CH}_2\text{py}]\text{Cl}_3\}$ (**2b**)

TiCl_4 (0.275 ml, 2.50 mmol) in 40 ml of $\text{C}_6\text{H}_5\text{CH}_3$ was cooled to -80°C and solution of **1c** (0.773 g, 2.50 mmol) in $\text{C}_6\text{H}_5\text{CH}_3$ was added dropwise. The mixture was allowed to warm slowly to r.t. as it stirred overnight. A bright-red precipitate formed quantitatively and was filtered off. The solid was washed with *n*-hexane and dried under dynamic vacuum. ^1H -NMR (CD_2Cl_2 , 300 MHz): δ = 8.71 (m, 1H, Py H₆), 7.91 (td, 1H, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, Py H₄), 7.43 (m, 2H, Py H₃ + Py H₅), 4.74 (m, 2H, CH_2N), 3.45 (m, 2H, CH_2py), 1.02 (s, 9H, $\text{SiC}(\text{CH}_3)_3$), 0.55 (s, 6H, $\text{Si}(\text{CH}_3)_2$). ^{13}C -NMR (CD_2Cl_2): δ = 156.9 (Py C₂), 149.2 (Py C₆), 140.6 (Py C₄), 126.0 (Py C₃), 123.1 (Py C₅), 49.5 (CH_2N), 40.0 (CH_2py), 28.2 ($\text{SiC}(\text{CH}_3)_3$), 25.8

($\text{SiC}(\text{CH}_3)_3$), –1.94 ($\text{Si}(\text{CH}_3)_2$). Anal. Found: C, 39.84; H, 6.01; N, 7.18. Calc. for $\text{TiC}_{13}\text{H}_{23}\text{N}_2\text{SiCl}_3$: C, 40.07; H, 5.95; N, 7.19%.

4.6. Reaction of $\{\text{Ti}[\text{N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{py}]\text{Cl}_3\}$ (**2a**) with NaCp

To a solution of **2a** (0.511 g, 1.47 mmol) in 40 ml of THF, cooled to -95°C , a solution of NaCp (0.138 g, 1.57 mmol) in ca. 15 ml of THF was added dropwise. The mixture was stirred for 5.5 h as it slowly warmed to r.t. A white solid precipitated out of a deep-red solution, and was filtered off. Volatiles were removed and the residue was washed with *n*-hexane and then extracted with Et_2O . Upon solvent removal, a brownish solid was obtained in 65% yield. ^1H -NMR (C_6D_6 , 300 MHz): δ = 8.44 (m, 1H, Py H₆), 7.07 (m, 1H, Py H), 6.58 (m, 2H, Py H), 6.19 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 5.91 (s, ($\eta^5\text{-C}_5\text{H}_5$)₂TiCl₂), 4.58 (m, 2H, CH_2N), 3.14 (m, 2H, CH_2py), 0.24 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

4.7. Synthesis of $\{\text{Ti}[\text{NCH}_2\text{CH}_2\text{py}]\text{Cl}_2\}_n$ (**3b**)

A solution of TiCl_4 (0.50 ml, 4.53 mmol) in 1,2-dichloroethane at 0°C , was added dropwise to a solution of **1a** (1.206 g, 4.53 mmol) in 1,2-dichloroethane. The mixture was stirred for 48 h at 80°C . A bright-red solid was filtrated and washed with *n*-hexane and Et_2O . The solid was dried under dynamic vacuum (0.968 g, 89% yield). Anal. Found: C, 34.85; H, 3.42; N, 11.85. Calc. for $\text{TiC}_7\text{H}_8\text{N}_2\text{Cl}_2$: C, 35.18; H, 3.37; N, 11.72%.

4.8. Synthesis of $\{\text{Ti}_2[\mu\text{-NCH}_2\text{CH}_2\text{py}]_2\text{Cl}_4(\text{THF})_2\}$ (**3c**)

The dissolution of **2a** or **2b** in THF at r.t. affords overnight a bright-red crystalline insoluble solid in almost quantitative yield. Crystals suitable for X-ray diffraction were obtained. Anal. Found: C, 41.63; H, 5.41; N, 8.81. Calc. for $\text{Ti}_2\text{C}_{22}\text{H}_{32}\text{N}_4\text{O}_2\text{Cl}_4$: C, 42.47; H, 5.18; N, 9.01%.

4.9. Synthesis of $\{\text{Ti}_2[\mu\text{-NCH}_2\text{CH}_2\text{py}]_2\text{Cl}_4(\text{PMe}_3)_2\}$ (**3d**)

To a solution of **2b**, prepared in situ as described in Section 4.6 and left stirring for 12 h, one equivalent of PMe_3 was added dropwise. The mixture was stirred for 5 h at r.t. and a yellow solid precipitated in almost quantitative yield. Anal. Found: C, 37.72; H, 5.58; N, 8.63. Calc. for $\text{Ti}_2\text{C}_{20}\text{H}_{34}\text{N}_4\text{P}_2\text{Cl}_4$: C, 37.75; H, 5.44; N, 8.89%.

4.10. Reaction of $\{Ti[NCH_2CH_2py]Cl_2\}_n$ (**3b**) with $LiNMe_2$

A solution of $LiNMe_2$ (0.231 g, 4.60 mmol) in ca. 30 ml of THF was added dropwise to a suspension of **3b** in 100 ml of THF (1.08 g, 4.52 mmol), previously cooled to -60°C . The mixture was allowed to warm slowly to r.t. After 15 h, there is a white solid suspended in a dark-red solution. The solvent was evaporated and the residue extracted with $C_6H_5CH_3$. The solvent was removed and the resulting red solid dried under dynamic vacuum (0.302 g, 27.9% yield). $^1\text{H-NMR}$ (C_6D_6 , 300 MHz): δ = 9.45 (m, 1H, Py H₆), 8.27 (m, 1H, Py H₆), 6.77 (td, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, Py H₄), 6.68 (td, 1H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz, Py H₄), 6.41 (m, 2H, Py H₃ + Py H₅), 6.34 (m, 2H, Py H₃ + Py H₅), 5.80 (m, 1H, CH_2N'), 5.41 (m, 1H, CH_2N), 4.99 (m, 1H, CH_2N'), 4.72 (m, 1H, CH_2N), 3.48 (m, 1H, CH_2py), 2.93 (m, 1H, CH_2py'), 2.77 (m, 1H, CH_2py), 2.33 (m, 1H, CH_2py'). $^{13}\text{C-NMR}$ (C_6D_6): δ = 160.5 (Py C₂ or Py C_{2'}), 160.1 (Py C₂ or Py C_{2'}), 152.4 (Py C₆), 150.9 (Py C₆), 138.3 (Py C₄), 137.8 (Py C₄), 124.8 (Py C₃), 124.0 (Py C₃), 121.8 (Py C₅ + Py C_{5'}), 69.2 (CH_2N or CH_2N'), 59.5 (CH_2N or CH_2N'), 42.6 (CH_2py or CH_2py'), 40.5 (CH_2py or CH_2py'). Anal. Found: C, 39.52; H, 4.65; N, 12.05; Ti, 17.3. Calc. for $TiC_7H_8N_2Cl_2$: C, 35.19; H, 3.37; N, 11.72; Ti, 20.0%.

4.11. Synthesis of $\{CpTi[NCH_2CH_2py]Cl\}_n$ (**4b**)

A solution of $NaCp$ (0.265 g, 3.01 mmol) in THF was added dropwise to a suspension of **3b** (0.693 g, 2.90 mmol) in THF at -30°C . After stirring for 5 h as it warmed slowly to r.t., a dark-red solution formed. The solvent was evaporated and the residue washed with *n*-hexane and Et_2O . The residue was then extracted with $C_6H_5CH_3$, giving a dark-red solution. After solvent removal a dark-red solid was obtained. Redissolution in $C_6H_5CH_3$ yield, at r.t., a dark microcrystalline solid that did not redissolve (yield < 5%). Anal. Found: C, 53.73; H, 4.87; N, 10.32. Calc. for $TiC_{12}H_{13}N_2Cl$: C, 53.66; H, 4.88; N, 10.43%. MS:² 1177 (0.5) [$5M^+ - 2Cp - Cl$]; 1074 (1) [$4M^+$]; 973 (0.5) [$4M^+ - Cp - Cl$]; 939 (0.75) [$M^+ - Cp - 2Cl$]; 895 (0.75) [$4M^+ - Cp - 2Cl - py$]; 828 (0.75) [$4M^+ - 2Cp - 2Cl - py$]; 700 (1.5) [$3M^+ - pyCH_2CH_2$]; 599 (10) [$3M^+ - Cp - pyCH_2CH_2$]; 403 (20) [$2M^+ - L - N$]; 195 (10) [$M^+ - py$].

4.12. Synthesis of $N(SiMe_3)(C_6H_5)CH_2CH_2py$ (**5**)

Fourty-four millilitres of *n*-LiBu in hexanes (1.6 mol dm⁻³, 70.4 mmol) was added dropwise to a suspension of *N*-phenyl-2'-aminoethyl-2-pyridine (11.42 g,

56.46 mmol) in 200 ml of *n*-hexane at -60°C . The mixture was allowed to warm slowly to r.t. After 40 min at r.t. a yellow solution was formed. $SiMe_3Cl$ (14 ml, 110 mmol) was added dropwise at r.t. The reaction vessel was closed and the mixture was heated at 30°C overnight. The volatiles were removed under vacuum and the residue extracted with *n*-hexane. The solvent was evaporated under reduced pressure leaving 14.69 g of an orange oil (94.4% yield). $^1\text{H-NMR}$ (C_6D_6 , 300 MHz): δ = 8.49 (m, 1H, Py H₆), 7.19 (m, 2H, H_m), 7.01 (m, 3H, Py H₄ + H_o), 6.86 (m, 1H, H_p), 6.61 (m, 2H, Py H₃ + Py H₅), 3.81 (t, 2H, $^3J_{HH}$ = 7.2 Hz, CH_2N), 2.90 (t, 2H, $^3J_{HH}$ = 7.2 Hz, CH_2py), 0.07 (s, 9H, $Si(CH_3)_3$). $^1\text{H-NMR}$ (CD_2Cl_2 , 300 MHz): δ = 8.59 (m, 1H, Py H₆), 7.58 (td, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, Py H₄), 7.31 (m, 2H, H_m), 7.10 (m, 4H, Py H₃ + Py H₅ + H_o), 6.94 (m, 1H, H_p), 3.81 (t, 2H, $^3J_{HH}$ = 7.2 Hz, CH_2N), 2.96 (t, 2H, $^3J_{HH}$ = 7.2 Hz, CH_2py), 0.20 (s, 9H, $Si(CH_3)_3$). $^{13}\text{C-NMR}$ (C_6D_6): δ = 160.8 (Py C₂), 149.8 (Py C₆), 149.1 (C_{ipso}), 135.6 (Py C₄), 129.1 (C_m), 123.7 (Py C₅), 122.0 (C_o), 121.0 (Py C₃), 120.5 (C_p), 47.8 (CH_2N), 38.3 (CH_2py), 0.8 ($Si(CH_3)_3$). $^{13}\text{C-NMR}$ (CD_2Cl_2): δ = 160.8 (Py C₂), 149.8 (Py C₆), 149.1 (C_{ipso}), 136.3 (Py C₄), 129.2 (C_m), 124.0 (Py C₅), 121.6 (Py C₃ or C_o), 121.5 (Py C₃ or C_o), 120.2 (C_p), 48.0 (CH_2N), 38.6 (CH_2py), 1.0 ($Si(CH_3)_3$). Anal. Found: C, 70.78; H, 8.22; N, 10.20. Calc. for $C_{16}H_{22}N_2Si$: C, 71.06; H, 8.20; N, 10.36%. MS: 271 (15) [M^+]; 255 (10) [$M^+ - CH_3$]; 199 (25) [$M^+ - SiMe_3$]; 194 (10) [$M^+ - Ph$]; 178 (80) [$M^+ - Me - Ph$].

4.13. Synthesis of $\{Ti[N(Ph)CH_2CH_2py]Cl_3\}$ (**6**)

A solution of **5** (1.239 g, 4.58 mmol) in $C_6H_5CH_3$ was added dropwise to a solution of $TiCl_4$ (0.5 ml, 4.58 mmol) in $C_6H_5CH_3$ (100 ml) previously cooled to -60°C . The mixture was allowed to warm slowly to r.t. while stirring for 15 h. A brown precipitate formed and was filtered off. The solid was washed with Et_2O and $C_6H_5CH_3$ and dried under dynamic vacuum (1.446 g, 90% yield). $^1\text{H-NMR}$ (CD_2Cl_2 , 300 MHz): δ = 8.90 (m, 1H, Py H₆), 7.93 (m, 1H, Py H₄), 7.33 (m, 7H, H_{arom} + Py H₃ + Py H₅), 4.80 (m, 2H, CH_2N), 3.62 (m, 2H, CH_2py). $^{13}\text{C-NMR}$ (CD_2Cl_2): δ = 157.4 (Py C₂), 153.7 (C_{ipso}), 149.7 (Py C₆), 140.4 (Py C₄), 129.6 (C_{arom}), 127.7 (C_{arom}), 125.8 (Py C₃), 123.0 (Py C₅), 119.9 (C_{arom}), 47.4 (CH_2N), 35.9 (CH_2py). Anal. Found: C, 44.73; H, 4.02; N, 7.49. Calc. for $TiC_{13}H_{13}N_2Cl_3$: C, 44.42; H, 3.73; N, 7.97%.

4.14. Synthesis of $\{Ti[N(Ph)CH_2CH_2py]Cl_3(THF)\}$ (**7**)

The dissolution of **6** in THF at r.t. affords a dark-brown solution. After removal of the solvent, a yellowish solid was obtained in quantitative yield. $^1\text{H-NMR}$ (CD_2Cl_2 , 300 MHz): δ = 8.86 (m, 1H, Py H₆), 7.92 (td, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, Py H₄), 7.43 (m, 6H, H_{arom} + Py H₃ + Py H₅), 7.22 (t, 1H, $^3J_{HH}$ = 7.2 Hz,

² M = $TiC_{12}H_{13}N_2Cl$; py = C_5H_4N ; Cp = C_5H_5 ; L = NCH_2CH_2py .

H_p), 4.75 (m, 2H, CH₂N), 3.80 (m, 4H, THF OCH₂CH₂), 3.66 (m, 2H, CH₂py), 1.85 (m, 4H, THF OCH₂CH₂). ¹³C-NMR (CD₂Cl₂): δ = 157.7 (Py C₂), 152.1 (C_{ipso}), 149.6 (Py C₆), 140.4 (Py C₄), 129.5 (C_{arom}), 127.6 (C_{arom}), 125.9 (Py C₃), 123.0 (Py C₅), 120.2 (C_{arom}), 69.3 (OCH₂-THF), 49.8 (CH₂N), 36.2 (CH₂py), 25.9 (CH₂-THF). Anal. Found: C, 47.56; H, 5.04; N, 6.73. Calc. for TiC₁₇H₂₁N₂OCl₃: C, 48.20; H, 5.00; N, 6.61%.

4.15. Reaction of {Ti[N(Ph)CH₂CH₂py]Cl₃(THF)} (7) with NaCp

Compound **6** (0.405 g, 1.15 mmol) was dissolved in ca. 40 ml of THF and the deep-red solution obtained was cooled to –50°C. NaCp (0.166 g, 1.89 mmol) in ca. 20 ml of THF was added dropwise. The mixture was allowed to warm to r.t. as it stirred for 5 h. The volatiles were then removed and the residue was extracted with C₆H₅CH₃. The solution obtained was concentrated and placed at –20°C. Bright-red crystals of Cp₂Cl₂ formed overnight (yield < 10%). ¹H-NMR (C₆D₆, 300 MHz): δ = 5.91 (s, η⁵-C₅H₅). Anal. Found: C, 48.43; H, 3.89. Calc. for TiC₁₀H₁₀Cl₂: C, 48.24; H, 4.05%.

Table 2
Crystal data and structure refinement for **3c**

Empirical formula	C ₁₁ H ₁₆ Cl ₂ N ₂ O ₂
Formula weight	311.06
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	
<i>a</i> (Å)	8.735(3)
<i>b</i> (Å)	13.975(3)
<i>c</i> (Å)	11.888(3)
α (°)	90
β (°)	111.67(2)
γ (°)	90
<i>V</i> (Å ³)	1348.6(6)
<i>Z</i>	4
<i>D</i> _{calc} (Mg Å ^{–3})	1.532
Absorption coefficient (mm ^{–1})	1.016
<i>F</i> (000)	640
Crystal size (mm)	0.50 × 0.40 × 0.20
Theta range for data collection (°)	2.35–25.97
Index ranges	–10 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 17, –14 ≤ <i>l</i> ≤ 14
Reflections collected	5280
Independent reflections	2644 [<i>R</i> _{int} = 0.0823]
Reflections observed (>2σ)	1543
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2644/6/154
Goodness-of-fit on <i>F</i> ²	1.048
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0579, <i>wR</i> ₂ = 0.1107
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1176, <i>wR</i> ₂ = 0.1401
Largest difference peak and hole (e Å ^{–3})	0.544 and –0.413

4.16. Synthesis of {Cp₂Ti₂[μ-NPh]Cl₂} (8)

N-Phenylaminoethyl-2-pyridine (0.449 g, 2.27 mmol) was dissolved in 20 ml of THF and added dropwise to a suspension of NaH in 50 ml of THF. After 15 h at 50°C, a red solution was obtained. After being cooled to –50°C, the solution was filtered to a schlenk containing CpTiCl₃ (0.504 g, 2.30 mmol). After the addition, the solution becomes darker and a white solid precipitates as the temperature rises gently over 7 h. The volatiles were evaporated and the residue, a dark-red solid, was washed with *n*-hexane. This solid was extracted with Et₂O and the solution placed at –20°C, from which orange crystals grew overnight. (Yield < 10%). ¹H-NMR (C₆D₆, 300 MHz): δ = 7.00 (td, 2H, ³*J*_{HH} = 7.8 Hz, H_m), 6.78 (m, 2H, H_o), 6.75 (m, 1H, H_p), 6.08 (s, 5H, η⁵-C₅H₅). ¹³C-NMR (C₆D₆): δ = 129.3 (C_m), 125.4 (C_p), 121.2 (C_o), 118.5 (η⁵-C₅H₅). Anal. Found: C, 54.03; H, 4.12; N, 5.18. Calc. for Ti₂C₂₂H₂₀N₂Cl₂: C, 55.16; H, 4.21; N, 5.85%.

4.17. X-ray crystallographic study

Crystal data for compound **3c** was collected in a MACH 3 (Enraf–Nonius) diffractometer using graphite monochromated Mo–K_α radiation (λ = 0.71069 Å) by the ω–2θ scan-mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections (18 < θ < 20°). Data was corrected for Lorentz polarisation and linear decay (no linear decay was detected) as well as empirically for absorption using MOLEN software [47].

The molecular and crystal structure was solved by a combination of direct methods and Fourier difference synthesis and the refinement was based on *F*². Non-hydrogen atoms were refined with anisotropic thermal parameter, atom C12 showing a high thermal vibration. All hydrogens were inserted in idealised positions and allowed to refine riding in the parent C atom, with thermal parameter 1.2 times those to which they are bonded. All remaining crystal data and refinement parameters are presented in Table 2.

Calculations were done using SHELXS-97 [48] and SHELXL-97 [49]. Graphic presentations were prepared with ORTEP-III [50]. All of these programs are included in OSCAIL, version 8 [51].

5. Supplementary material

Experimental details, atomic coordinates, bond lengths and angles for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 157363 for compound **3c**. Copies of data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK

(Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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