Titanium(IV) complexes incorporating the aminodiamide ligand [(SiMe$_3$)N{CH$_2$CH$_2$N(SiMe$_3$)}$_2$]$^{2-}$(L); the X-ray crystal structures of [TiMe$_2$(L)] and [TiCl{CH(SiMe$_3$)$_2$}(L)] [☆]

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Abstract

The reaction of the lithium salt of the aminodiamide ligand Li$_2$[(SiMe$_3$)N{CH$_2$CH$_2$N(SiMe$_3$)}$_2$] (Li$_2$L) (1) with [TiCl$_4$(THF)$_2$] (THF = tetrahydrofuran) forms [TiCl$_2$(L)] (2), from which Ti^{IV} mono and dialkyl complexes are accessible. The treatment of 2 with Me$_2$Mg, LiCH$_2$(SiMe$_3$) or LiCH(SiMe$_3$)$_2$ results in the formation of [TiMe$_2$(L)] (3), [Ti{CH$_2$(SiMe$_3$)}$_2$(L)] (4) or [TiCl{CH(SiMe$_3$)$_2$}(L)] (5) respectively, in which only partial coordination of the amino-nitrogen is observed in solution and the solid state. The X-ray crystal structures of 3 and 5, and an improved synthesis of 1, are described.

Keywords: Titanium; Amide; Alkyl complex; X-ray structure; NMR spectroscopy; Mass spectroscopy

1. Introduction

Non-metallocene complexes of Group IV metals have recently attracted considerable attention as possible alternatives for olefin polymerisation catalysts, employing N$_4$-macrocycles [1,2], porphyrins [3], tripodal amides [4,5], mixed cyclopentadienyl-amides [6], -phosphines [7] or -benzamidines [8], and Schiff bases [9] as spectator ligands.

We have recently described the synthesis of some zirconium complexes that incorporate the sterically demanding, tridentate diamide ligand [(Me$_3$Si)N{CH$_2$-CH$_2$N(SiMe$_3$)}$_2$]$^{2-}$ (1) as an alternative to cyclopentadienyl-based ligands [10], and so sought to extend this to titanium. Herein we report a high yield, one-pot synthesis to the triply-silylated triamine, and the preparation of Ti^{IV} chloro, and mono and dialkyl complexes incorporating 1.
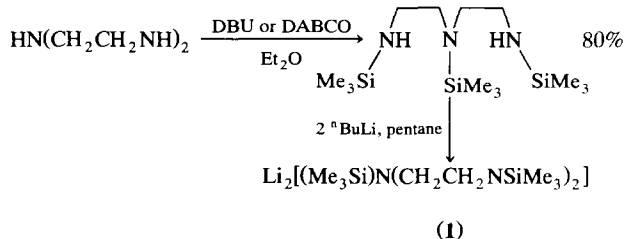
2. Results and discussion

2.1. Improved synthesis of (Me$_3$Si)N{CH$_2$CH$_2$NH(SiMe$_3$)}$_2$

The synthesis of the triply-silylated amine (Me$_3$Si)N{CH$_2$CH$_2$NH(SiMe$_3$)}$_2$ as a precursor to 1 was previously effected in two steps, viz. silylation of the primary amines of diethylenetriamine using NH(SiMe$_3$)$_2$, with the central secondary amine silylated by a low-temperature lithiation route [10]. It has since been found that this amine can be synthesised in a one-pot process from diethylenetriamine and SiMe$_3$Cl using a stoichiometric amount of either 1,4-diazabicyclo[2.2.2]octane (DABCO) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base (Scheme 1), in a similar manner to that employed in the generation of ^{t}BuMe$_2$Si derivatives of amines [11]. This route is not viable when using weaker bases such at NEt$_3$.

The addition of diethylenetriamine to a stirred mixture of SiMe$_3$Cl and DBU (or DABCO) in Et$_2$O results in the immediate deposition of the base–hydrochloride salt. Evaporation of the Et$_2$O filtrate affords essentially pure amine in high yield (80% using DBU, after distilla-

$HN(CH_2CH_2NH)_2$ $\xrightarrow[\text{Et}_2\text{O}]{\text{DBU or DABCO}}$ 80%

2 ^{n}BuLi, pentane

$Li_2[(Me_3Si)N(CH_2CH_2NSiMe_3)_2]$

(1)

Scheme 1. Improved synthesis of $Li_2[(Me_3Si)N(CH_2CH_2NSiMe_3)_2]$ (1).

tion), which is easily converted into the dilithio salt **1** by reaction with ^{n}BuLi in pentane [10].

2.2. Synthesis of [TiCl₂(L)] (2)

The reaction between $[TiCl_4(THF)_2]$ (THF = tetrahydrofuran) and **1** in Et_2O at $-78°C$ results in the generation of a brown slurry affording, after evaporation, extraction into toluene and cooling to $-50°C$, orange crystals of **2** in moderate yield (Scheme 2). Attempts to grow crystals that were suitable for X-ray diffraction were unsuccessful. Elemental analysis was consistent with the proposed formulation of **2** as $[TiCl_2(L)]_n$. It is probable that **2** is monomeric, with the ligands arranged in a pseudo-trigonal bipyramidal manner, similar to the structurally characterised complex $[TiCl_2\{CH(2-C_5H_4N)(CH_2NSiMe_3)_2\}]$ that incorpo-

rates a less sterically demanding aminodiamido ligan [12]. The ^1H NMR spectrum is similar to those for] coordinated to zirconium [10], with resonances in a 2: ratio at δ 0.33 and 0.08 ppm for the amido and amin SiMe₃ groups respectively, and four signals due to th backbone protons, indicating some coordination of th amino-nitrogen. The broad nature of these latter peak ($w_{1/2} = 50$ Hz) is indicative of a fluxional proces involving dissociation of the amino-nitrogen from th titanium centre, a feature which will be discussed late with reference to the dimethyl complex **3**.

2.3. Synthesis of the dialkyl complexes [TiR₂(L)][R = Me (3), CH₂SiMe₃ (4)]

The dichloride complex **2** proved to be a versatil precursor to organotitanium complexes via halide dis placement reactions with alkyllithium or alkylmagne sium reagents. The reaction between **2** and a sligh excess of dimethylmagnesium in Et_2O at $-78°C$ re sulted in the formation of the moderately thermall sensitive dimethyl complex $[TiMe_2(L)]$ **(3)** as large yellow prisms in good yield (Scheme 2). No microanal ysis of this complex was obtained due to its therma instability above 298 K. However, complex **3** is volatil and sublimes at $40°C/10^{-5}$ mbar, although some de composition is observed. The formation of the dimethy complex **3** was found to be sensitive to the alkylatin

$[TiCl_4(THF)_2] + (1) \xrightarrow{Et_2O}$
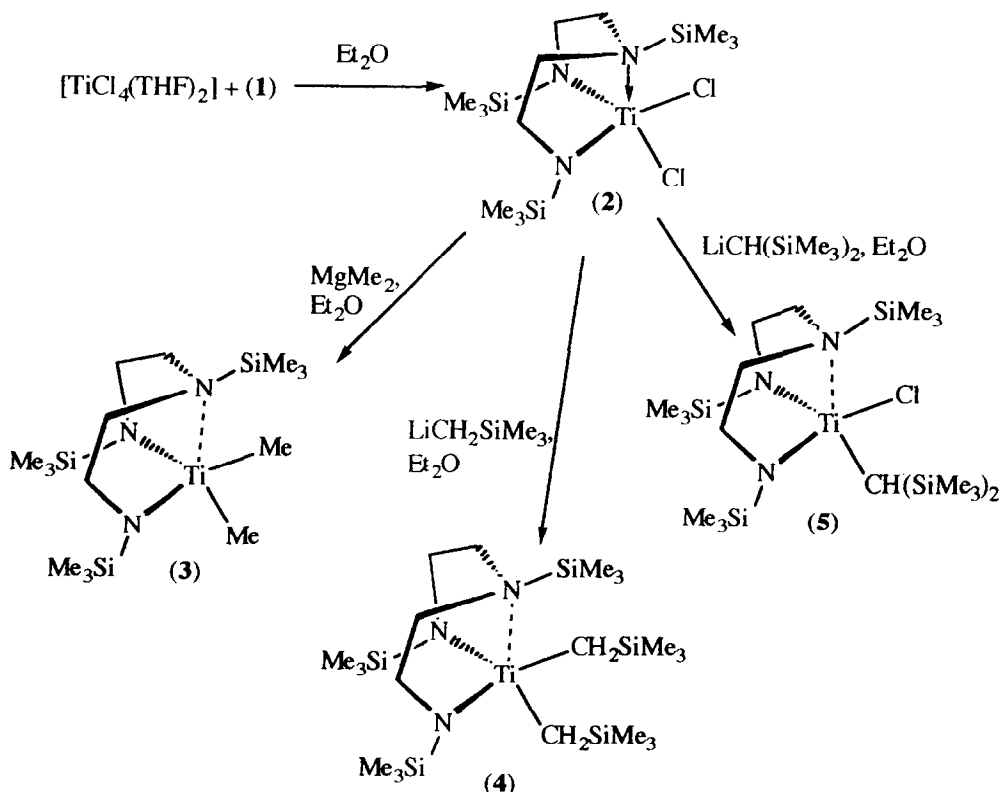
Scheme 2. The synthesis of Ti^{IV} alkyl and alkyl chloride complexes.
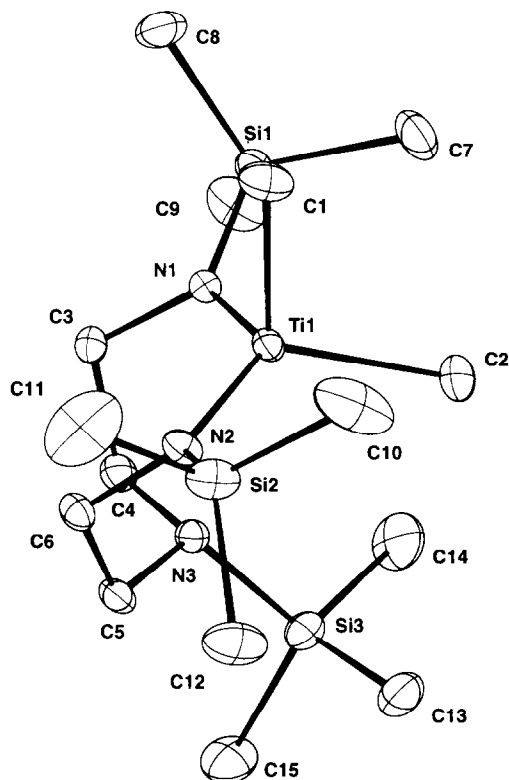
Fig. 1. The molecular structure of [TiMe$_2$(L)] (3).

Table 2
Fractional atomic coordinates for [Ti(Me)$_2$(L)] (3)

Atom	x	y	z
Ti	0.20501(5)	0.38247(2)	0.66483(3)
Si1	0.25754(8)	0.37974(3)	0.45841(4)
Si3	0.08394(9)	0.19087(4)	0.66386(5)
Si2	0.08841(10)	0.42397(4)	0.85074(5)
N1	0.1427(2)	0.3684(1)	0.5405(1)
N3	−0.0023(2)	0.2724(1)	0.6378(1)
N2	0.0531(2)	0.3922(1)	0.7431(1)
C1	0.2955(4)	0.4836(2)	0.6621(2)
C2	0.4251(3)	0.3329(2)	0.7248(2)
C3	−0.0347(3)	0.3530(1)	0.5111(2)
C4	−0.0702(3)	0.2822(1)	0.5428(2)
C5	−0.1200(3)	0.2927(1)	0.6943(2)
C6	−0.1172(3)	0.3685(1)	0.7118(2)
C7	0.4823(3)	0.3720(2)	0.5058(2)
C8	0.2165(4)	0.4649(2)	0.4049(2)
C9	0.2026(4)	0.3124(2)	0.3719(2)
C10	0.3085(5)	0.4460(3)	0.8920(2)
C11	−0.0389(6)	0.5017(2)	0.8558(3)
C12	0.0312(5)	0.3578(2)	0.9263(2)
C13	0.1833(4)	0.1880(2)	0.7829(2)
C14	0.2386(5)	0.1736(2)	0.5926(3)
C15	−0.0840(4)	0.1250(2)	0.6436(2)

reagent, as the reaction between the dichloride complex 2 and LiMe resulted in a mixture of products (amongst which 3 was present), in a similar manner to that observed by Andersen in alkylation reactions of [ZrCl$_2$\{N(SiMe$_3$)$_2$\}$_2$] [13]. The low-temperature, solid-state structure determined by X-ray crystallography is shown in Fig. 1, with selected bond lengths and angles detailed in Table 1, fractional atomic coordinates in Table 2 and crystal data in Table 3. The ligand arrange-

ment around the Ti centre can be described as either distorted tetrahedral, or if the influence of N3 is taken into account, as pseudo-trigonal bipyramidal, with N1, N2 and C2 in the equatorial plane and C1 and N3 axial. The bond angles between the atoms in the equatorial plane suggest that the latter description is more apt, unlike that for the complex [TiMe$_2$\{N(c-C$_6$H$_{11}$)$_2$\}$_2$] which was observed to be distorted tetrahedral in the solid state [14].
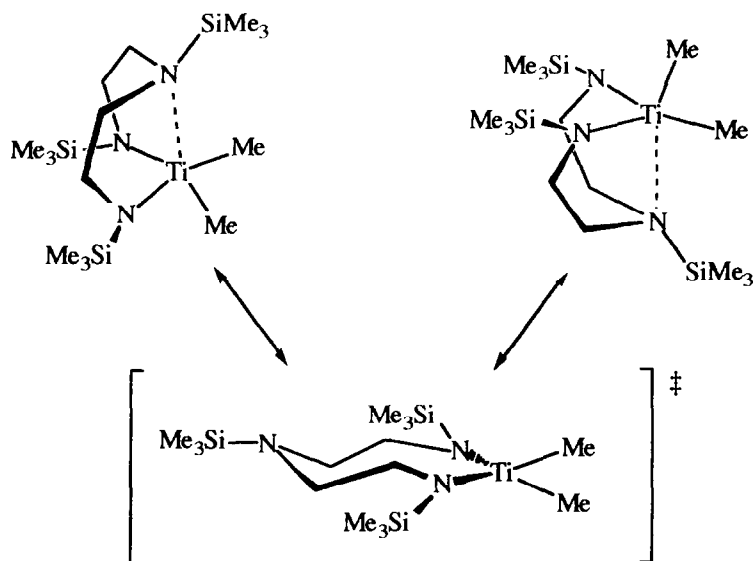
The distance of 2.732(2) Å between Ti1 and N3 is too long to be described as bonding, although the remainder of the structure appears distorted to accom-

Table 1
Selected bond distances (Å) and angles (°) for [Ti(Me)$_2$(L)] (3) and [TiCl\{CH(SiMe$_3$)$_2$(L)\}] (5)

3		5	
N1–Ti–N2	124.67(9)	N3–Ti–N1	119.8(2)
N1–T1–C2	114.56(12)	N3–Ti–C14	103.0(3)
N2–Ti–C2	112.51(11)	N1–Ti–C14	106.4(3)
N1–Ti–C1	98.19(10)	N3–Ti–Cl	111.4(2)
N2–Ti–C1	101.23(10)	N1–Ti–Cl	110.6(2)
C2–Ti–C1	99.40(13)	C14–Ti–Cl	104.0(2)
N1–Ti···N3	72.18(7)		
N2–Ti···N3	73.06(7)		
C2–Ti···N3	99.35(11)		
C1–Ti···N3	161.15(10)		
Ti–N1	1.905(2)	Ti–N3	1.894(5)
Ti–N2	1.910(2)	Ti–N1	1.905(5)
Ti–C2	2.105(3)	Ti–C14	2.119(7)
Ti–C1	2.120(3)	Ti–Cl	2.250(2)
Ti···N3	2.732(2)	Ti···N2	2.909(6)

Table 3
Crystal data for the complexes [TiMe$_2$(L)] (3) and [TiCl\{CH(SiMe$_3$)$_2$\}(L)] (5)

	5	3
Formula	C$_{20}$H$_{54}$ClN$_3$Si$_5$Ti	C$_{15}$H$_{41}$N$_3$Si$_3$Ti
M	560.5	395.7
Crystal system	orthorombic	monoclinic
Space group	Pna2$_1$ (No. 33)	P2$_1$/n (non-standard No. 14)
a (Å)	16.056(6)	8.237(5)
b (Å)	11.728(3)	19.590(6)
c (Å)	17.705(4)	15.418(4)
β (°)		101.21(4)
U (Å^3)	3334(2)	2440(2)
z	4	4
D (g cm^{-3})	1.12	1.08
F(000)	1216	864
λ (Å)	0.71073	0.71073
μ (cm^{-1})	5.3	5.0
T (K)	293	173

Scheme 3. Facile amino-nitrogen dissociation in [TiMe$_2$(L)] (3).

modate N3 in a partially bonding manner. Elongated Zr–N$_{amino}$ bond lengths were also observed in the structurally characterised complexes [Zr(η^3-BH$_4$)$_2$(L)] and [ZrCl{CH(SiMe$_3$)$_2$}(L)] [10]. The Ti1–N1, Ti1–N2,

Ti1–C1 and Ti1–C2 bond distances are similar to those observed for [TiMe$_2${N(c-C$_6$H$_{11}$)$_2$}$_2$] [14]. As alluded to earlier, it is apparent that a dynamic process is occurring in solution. The ^{1}H NMR spectrum at 298 K
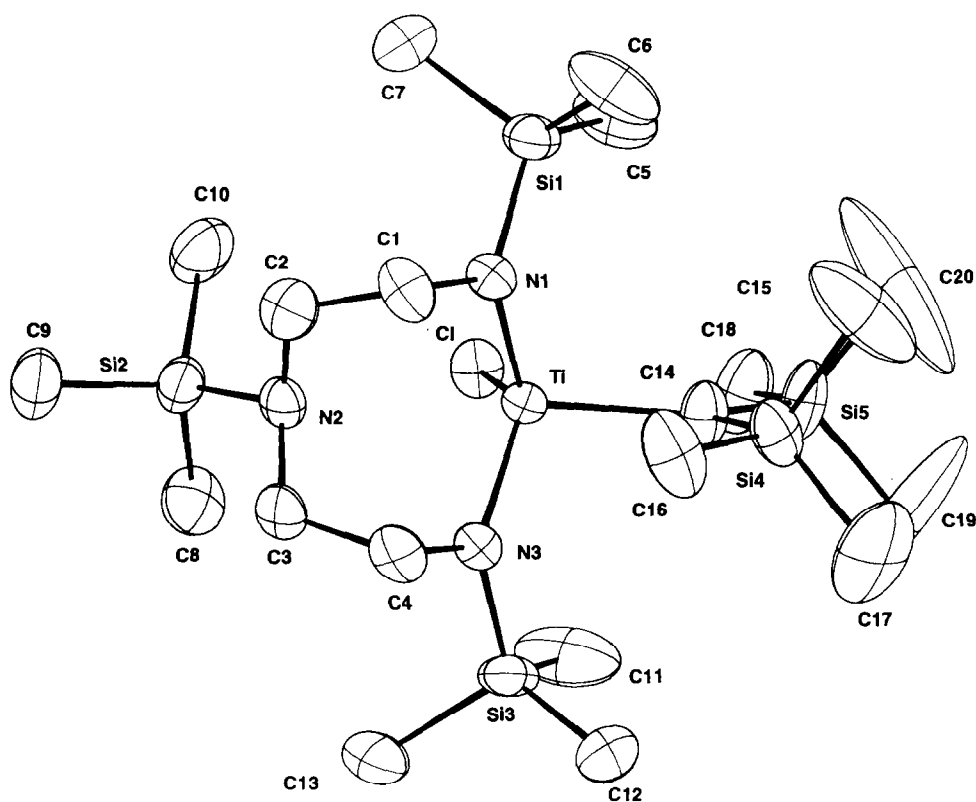
Fig. 2. The molecular structure of [TiCl{CH(SiMe$_3$)$_2$}(L)] (5).

displays the expected 2:1 singlets at δ 0.35 and 0.08 ppm for the amido– and amino–SiMe$_3$ groups, respectively. However, only one resonance at δ 0.79 ppm is observed for the two methyl ligands and the backbone protons are seen as two broad signals at δ 3.27 and 2.21 ppm for 4H each. On cooling the sample to 268 K, the low-temperature limiting spectrum is observed, with two separate resonances for the methyl protons at δ 0.93 and 0.88 ppm, consistent with axial and equatorial methyl groups in a trigonal bipyramidal structure. At this temperature, the backbone protons are observed as four multiplets for 2H each, which is indicative of facial coordination of the aminodiamido ligand, so supporting partial ligation of the amino-nitrogen to the Ti^{IV} centre. On warming the sample to 318 K, the backbone multiplets coalesce into two triplets at δ 3.30 and 2.26 ppm (J_{HH} = 8.0 Hz). A mechanism involving the dissociation of the amino-nitrogen, so equilibrating the geminal protons of the backbone, is described in Scheme 3.

In a similar manner to that above, the reaction of the dichloride 2 with LiCH$_2$SiMe$_3$ in Et$_2$O at −78°C resulted in the formation of the dialkyl complex [Ti(CH$_2$SiMe$_3$)$_2$(L)] (4) as yellow plates in moderate yield (Scheme 2). In this case, the incorporation of the sterically large CH$_2$SiMe$_3$ groups (as compared to CH$_3$) results in a solution structure more akin to the high-temperature limit observed by NMR spectroscopy for the dimethyl complex 3. In the ^{1}H NMR spectrum at 298 K, the backbone protons are observed as two triplets and the SiMe$_3$ protons as 2:1 singlets. The alkyl ligand SiMe$_3$ protons resonate as a singlet at δ 0.08 ppm, with the methylene protons observed at δ 1.43 ppm. Mass spectrometry suggests that complex 4 is monomeric in the solid state, with fragments seen for M − Me, M − CH$_2$SiMe$_3$ and M − 2(CH$_2$SiMe$_3$).

2.4. Synthesis and structural characterisation of [TiCl{CH(SiMe$_3$)$_2$}(L)] (5)

A further increase in the steric influence of the alkyl group, i.e. by using LiCH(SiMe$_3$)$_2$ as the alkylating reagent, is found to inhibit the formation of the dialkyl complex, resulting in the formation of the monoalkyl chloride complex [TiCl{CH(SiMe$_3$)$_2$}(L)] (5) only (Scheme 2). Complex 5 was isolated in moderate yield due to reduction of the Ti^{IV} species by the organolithium reagent to a second, blue Ti^{III} complex [15]. The mass spectrum indicates that complex 5 is monomeric in the solid state, with a fragment observed for [M − Me]$^+$, which is supported by an X-ray crystallographic study described in Fig. 2. Bond lengths and angles are detailed in Table 1, crystal data are displayed in Table 3 and atomic coordinates are shown in Table 4. Unlike the dimethyl complex 3, the geometry at the Ti^{IV} centre is best described as distorted tetrahedral, with the amino-nitrogen atom N2 pendant, although the bite

Table 4
Fractional atomic coordinates for [TiCl(CH(SiMe$_3$)$_2$)(L)] (5)

Atom	x	y	z
Ti	0.39923(6)	0.13410(9)	0.55831(6)
Cl	0.5092(1)	0.1651(2)	0.4823(1)
Si1	0.4751(2)	0.2829(2)	0.7006(1)
Si2	0.3779(1)	0.4232(2)	0.4320(2)
Si3	0.2841(2)	−0.0029(2)	0.4333(1)
Si4	0.3518(2)	−0.0721(2)	0.6851(2)
Si5	0.5191(2)	−0.1177(2)	0.6000(2)
N1	0.3961(3)	0.2439(5)	0.6375(3)
N2	0.3262(3)	0.3447(5)	0.5022(3)
N3	0.3016(3)	0.1031(4)	0.5019(3)
C1	0.3235(5)	0.3226(8)	0.6420(5)
C2	0.3225(5)	0.4036(7)	0.5757(5)
C3	0.2471(4)	0.2959(6)	0.4785(5)
C4	0.2297(4)	0.1807(6)	0.5122(5)
C5	0.5725(5)	0.2038(10)	0.6828(7)
C6	0.4403(7)	0.2584(14)	0.7991(5)
C7	0.5010(10)	0.4378(8)	0.6914(9)
C8	0.3860(6)	0.3352(8)	0.3463(5)
C9	0.3189(6)	0.5554(7)	0.4103(6)
C10	0.4831(6)	0.4669(8)	0.4642(7)
C11	0.3842(7)	−0.0634(12)	0.4022(8)
C12	0.2111(6)	−0.1126(7)	0.4717(6)
C13	0.2331(8)	0.0629(9)	0.3490(6)
C14	0.4259(5)	−0.0248(7)	0.6099(5)
C15	0.3970(8)	−0.0729(17)	0.7804(6)
C16	0.2569(6)	0.0196(9)	0.6099(5)
C17	0.3115(8)	−0.2173(10)	0.6675(10)
C18	0.5937(6)	−0.0835(8)	0.5251(7)
C19	0.4934(12)	−0.2648(10)	0.5788(20)
C20	0.5782(14)	−0.1301(25)	0.6844(11)

angle of the amido chelate [N1–Ti–N3 = 119.8(2)°C] is still larger than expected for a tetrahedral ligand arrangement. The Ti–N2 bond length of 2.909(6) Å implies that there is no or little interaction between these two atoms. This may be expected, as the zirconium analogue [ZrCl{CH(SiMe$_3$)$_2$}(L)] was seen to have an elongated Zr–N$_{amino}$ bond, although in this case the bond length of 2.770(5) Å was deemed to be partially bonding [10]. The remaining Ti–ligand bond distances are unremarkable. However, the methyne carbon C14 is apparently planar; the H-atom bonded to it (see later) could not be located and was therefore omitted. The molecule has a non-crystallographic mirror symmetry and it is possible that the C14 alkyl group is disordered across this plane with overlapping C14 positions which are not resolved. In solution, a similar structure is inferred by NMR spectroscopy. As with 3 and 4, the SiMe$_3$ protons are observed as singlets in a 2:1 ratio. The backbone protons resonate as three multiplets at δ 3.98, 3.20 and 2.37 ppm, the latter resonance for 4H due to the inequivalence of the geminal protons imposed on this molecule by the presence of the dissimilar Cl and CH(SiMe$_3$)$_2$ groups. The methyne proton of the alkyl group is observed as a singlet at δ 2.59 ppm.

3. Experimental details

3.1. General considerations

All experiments were carried out under pure argon using Schlenk techniques, or in a mBraun glove box under an atmosphere of dinitrogen (< 2 ppm H_2O, < 1 ppm O_2). Diethyl ether, tetrahydrofuran (THF) and n-pentane were pre-dried over sodium wire, distilled from sodium/potassium alloy and stored over potassium mirrors. Deuteriated solvents (toluene-d_8 and benzene-d_6) were refluxed over potassium and trap-to-trap distilled prior to use. ^{n}BuLi in hexanes (2.5 M), diethylenetriamine, trimethylsilyl chloride and DBU were purchased from Aldrich and used without further purification. The compounds $[TiCl_4(THF)_2]$ [16], $MgMe_2$ [17], $LiCH_2SiMe_3$ [18] and $LiCH(SiMe_3)_2$ [9] were prepared according to literature methods. NMR spectra were recorded on Bruker AMX-500, WM-360 and AC-250 instruments at 298 K unless otherwise stated, and were referenced internally to residual solvent resonances. The mass spectra were recorded on solid samples using a Kratos MS80RF spectrometer. Elemental analyses were carried out by the Canadian Microanalytical Service Ltd, Canada.

3.2. Improved preparation of N,N',N''-tris(trimethyl-silyl)diethylenetriamine, [(Me₃Si)N{CH₂CH₂NH-SiMe₃}₂]

To a stirred mixture of DBU (50 g, 0.33 mol) in diethyl ether (500 ml) was added chlorotrimethylsilane (46 ml, 0.36 mol) resulting in the immediate formation of a white precipitate. The reactants were left to stir for 1 h, after which time diethylenetriamine (11.35 ml, 0.1 mol) was added dropwise resulting in the immediate thickening of the white precipitate. The mixture was left to stir at room temperature for 12 h after which time the solution was filtered off via cannula, the solid washed with diethyl ether (100 ml) and the filtrates combined. The solvent was removed in vacuo and the residual pale yellow oil distilled at 0.5 mbar to give the product as a clear, colourless oil at 72–75°C (yield, 28.6 g; 82%). The dilithium salt $Li_2[(Me_3Si)N\{CH_2CH_2N(SiMe_3)_2\}]$, (Li_2L), (1), was prepared as previously described [10].

3.3. Preparation of [Ti(L)Cl₂] (2)

To a yellow stirred suspension of $[TiCl_4(THF)_2]$ (0.59 g, 1.8 mmol) in diethyl ether (30 ml) at $-78°C$ was added a colourless solution of $[Li_2L]$ (0.58 g, 1.8 mmol) in diethyl ether (20 ml), dropwise over 10 min. The orange/brown reaction mixture was then stirred at room temperature for 2 h. The solvent was removed in vacuo, the solid extracted with toluene and filtered through Celite on a glass frit to afford a deep

orange/brown solution. The filtrate was concentrated in vacuo and stored in a freezer at $-50°C$ overnight to afford orange/brown microcrystals which were isolated and dried in vacuo (yield, 0.48 g; 62%). ^1H NMR (C_6D_6) δ: 4.19 (br, 2H, CH_2); 3.11 (br, 2H, CH_2); 2.62 (br, 2H, CH_2); 2.22 (br, 2H, CH_2); 0.33 (s, 18H, $SiMe_3$); 0.08 (s, 9H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR ($CD_3C_6D_5$) δ: 57.08 (CH_2); 55.15 (CH_2); 0.87 ($SiMe_3$); -0.98 ($SiMe_3$) ppm. Anal. Calc. for $C_{13}H_{35}ClN_3Si_3Ti$: C, 35.77; H, 8.08; N, 9.63%. Found: C, 35.29; H, 8.04; N, 9.50%.

3.4. Preparation of [Ti(L)Me₂] (3)

In a Schlenk was placed 2 (2 g, 4.6 mmol) and $MgMe_2$ (0.28 g, 4.8 mmol). The Schlenk was cooled to $-78°C$ and diethyl ether (30 ml) added dropwise with stirring. The reaction mixture was allowed to warm to room temperature whereupon a yellow colouration developed together with the formation of a white precipitate. After 1 h, the solvent was removed in vacuo, the residue extracted with pentane and then filtered through Celite on a glass frit. The yellow filtrate was concentrated in vacuo and cooled slowly to $-50°C$ whereupon large yellow crystals formed after several days, which were isolated and dried in vacuo (yield, 1.09 g; 67%). ^1H NMR (C_6D_6) δ: 3.27 (br, 4H, CH_2); 2.21 (br, 4H, CH_2); 0.79 (s, 6H, CH_3); 0.35 (s, 18H, $SiMe_3$); -0.08 (s, 9H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR ($CD_3C_6D_5$) δ: 54.58 (CH_2); 52.58 (CH_2); 1.24 ($SiMe_3$); -1.17 ($SiMe_3$) ppm. No micro-analysis was possible due to the thermally unstable nature of the compound. MS (EI) m/z: 395 (10, $[M]^+$); 380 (55, $[M - Me]^+$); 364 (100, $[M - 2Me]^+$).

3.4.1. Crystallographic study of 3

Data were collected on an Enraf-Nonius CAD4 diffractometer using a crystal of dimensions $0.40 \times 0.40 \times 0.30$ mm mounted in mineral oil at 173 K. A total of 7540 unique reflections were measured for $2° < 2\theta < 30°$, 5076 reflections with $|F^2| > 2\sigma(F^2)$ being used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04i)^2]^{0.5}/L_p$. An absorption correction (maximum 1.00, minimum 0.87) was applied. The structure was solved using SHELXS with non-H atoms refined anisotropically by full-matrix least squares. Hydrogen atoms were refined in riding mode with $U_{iso}(H) = 1.3U_{eq}(C)$ or $1.5U_{eq}(C)$ for Me_3Si groups. The methyl groups were fixed at idealised geometry but with the torsion angle defining the hydrogen atom positions refined with $U_{iso}(H) = 1.5U_{eq}(C)$. The final residuals were $R = 0.053$, $R' = 0.139$ and $S = 1.063$.

3.5. Preparation of [Ti(L)(CH₂SiMe₃)₂] (4)

To an orange solution of 2 (0.56 g, 1.3 mmol) in diethyl ether (20 ml) was added dropwise a colourless

solution of [Li(CH$_2$SiMe$_3$)] (0.24 g, 2.6 mmol) in diethyl ether (20 ml) at $-78°C$. The stirred reaction mixture was allowed to warm to room temperature whereupon a yellow colouration was seen to develop along with formation of a white precipitate. After stirring for 18 h, the solvent was removed in vacuo, the solid extracted into pentane and filtered through Celite on a glass frit to afford a yellow solution. Concentration of the filtrates in vacuo and slow cooling to $-50°C$ resulted in yellow plate-like crystals, which were isolated and dried in vacuo (yield, 0.37 g; 55%). ^{1}H NMR (C$_6$D$_6$) δ: 3.34 (t, 4H, CH$_2$, $J_{HH} = 5.5$ Hz); 2.21 (t, 4H, CH$_2$, $J_{HH} = 5.5$ Hz); 1.43 (s, 4H, CH_2SiMe$_3$); 0.4 (s, 18H, CH$_2$SiMe_3); 0.08 (s, 18H, SiMe$_3$); -0.06 (s, 9H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (CD$_3$C$_6$D$_5$) δ: 75.07 (CH_2SiMe$_3$); 54.13 (CH$_2$); 53.99 (CH$_2$); 3.24 (SiMe$_3$); 2.35 (SiMe$_3$); -0.93 (SiMe$_3$) ppm. Analysis: Calc. for C$_{21}$H$_{57}$N$_3$Si$_5$Ti: C, 46.71; H, 10.64; N, 7.78%. Found: C, 46.62; H, 10.31; N, 8.10%. MS (EI) m/z: 524 (4, [M $-$ Me]$^+$); 452 (50, [M $-$ CH$_2$SiMe$_3$]$^+$); 364 (80, [M $-$ 2CH$_2$SiMe$_3$]$^+$).

3.6. Preparation of [Ti(L)(CH(SiMe$_3$)$_2$)Cl] (5)

A colourless solution of [Li(CH(SiMe$_3$)$_2$)] (0.22 g, 1.33 mmol) in diethyl ether (15 ml) was added dropwise to an orange, stirred solution of 2 (0.6 g, 1.39 mol) in diethyl ether (30 ml) at $-78°C$. The reaction mixture was allowed to warm to room temperature whereupon an apple green colour developed along with a white precipitate. After stirring for a further 18 h, the solvent was removed in vacuo, the remaining solid extracted into pentane and filtered through Celite on a glass frit. Concentration of the solution in vacuo and slow cooling to $-50°C$ afforded a mixture of blue and yellow crystals. The mother liquor was decanted off and the crystals dried in vacuo. The yellow crystals of 5 were isolated by hand in a glove box (yield, 0.27 g; 34%). ^{1}H NMR (C$_6$D$_6$) δ: 3.98 (m, 2H, CH$_2$); 3.20 (m, 2H, CH$_2$); 2.59 [s, 1H, CH(SiMe$_3$)$_2$]; 2.37 (m, 4H, CH$_2$); 0.39 (s, 18H, SiMe$_3$); 0.38 (s, 18H, SiMe$_3$); 0.10 (s, 9H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (CD$_3$C$_6$D$_5$) δ: 88.0 [CH($SiMe_3$)$_2$]; 57.43 (CH$_2$); 52.82 (CH$_2$); 5.40 (SiMe$_3$); 1.87 (SiMe$_3$); -0.91 (SiMe$_3$) ppm. Anal. Calc. for C$_{20}$H$_{54}$ClN$_3$Si$_5$Ti: C, 42.86; H, 9.71; N, 7.50%. Found: C, 43.05; H, 9.59; N, 7.96%. MS (EI) m/z: 544 (5, [M $-$ Me]$^+$).

3.6.1. Crystallographic study of 5

Data were collected on an Enraf-Nonius CAD4 diffractometer using a crystal of dimensions 0.40 × 0.20 × 0.20 mm mounted in a Lindeman capillary under nitrogen. A total of 4139 unique reflections were measured for $2° < 2\theta < 28°$, 2404 reflections with $|F^2| > 2\sigma(F^2)$ being used in the refinement, where $\sigma(F^2) =$ $[\sigma^2(I) + (0.04i)^2]^{0.5}/L_p$. An absorption correction (maximum 1.00, minimum 0.97) was applied. The structure was solved using SHELXS with non-H atoms refined anisotropically by full-matrix least squares. Hydrogen atoms were refined in riding mode with U_{iso}(H) of $1.2U_{eq}$(C) for $-$CH$_2$ or $1.5U_{eq}$(C) for $-$CH$_3$. The final residuals were $R = 0.0591$, $R' = 0.1103$ and $S = 1.046$.

4. Conclusion

The improvement of the synthesis of (Me$_3$Si)N(CH$_2$-CH$_2$NHSiMe$_3$)$_2$(L) leading to Li$_2$(L) (1) has allowed the early transition metal chemistry of this ligand to be further explored. The synthesis of the titanium dichloride complex 2 provides an entry into organotitanium(IV) chemistry via halide displacement reactions, leading to novel dialkyl (3), (4) and alkyl halide (5) complexes. The amino-nitrogen in these complexes has been shown to be labile by NMR spectroscopy and X-ray diffraction, engaging in differing degrees of coordination depending upon the size of the alkyl group(s). We are currently undertaking studies in the catalytic activity of these complexes and cationic complexes derived from them.

References

[1] R. Uhrhammer, D.G. Black, T.G. Gardner, J.D. Olsen and R.F. Jordan, J. Am. Chem. Soc., 115 (1993) 8493.

[2] L. Giannini, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, Angew. Chem., Int. Ed. Engl., 33 (1993) 2204; C. Floriani, S. Ciurli, A. Chiesi-Villa and C. Guastini, Angew. Chem., Int. Ed. Engl., 26 (1987) 70.

[3] H. Brand, J.A. Capriotti and J. Arnold, Organometallics, 13 (1994) 4469.

[4] M. Kol, R.R. Schrock, R. Kempe and W.M. Davies, J. Am. Chem. Soc., 116 (1994) 4382, and references therein.

[5] S. Friedrich, L.H. Gade, A.J. Edwards and M. McPartlin, Chem. Ber., 126 (1993) 1797.

[6] A.K. Hughes, A. Meetsma and J.H. Teuben, Organometallics, 12 (1993) 1936.

[7] M.D. Fryzuk, S.S.H. Mao, P.B. Duval and S.J. Rettig, Polyhedron, 14 (1995) 11.

[8] R. Gomez, M.L.H. Green and J.L. Haggit, J. Chem. Soc., Chem. Commun., (1994) 2607; A.N. Chernega, R. Gomez and M.L.H. Green, J. Chem. Soc., Chem. Commun., (1993) 1415.

[9] E.B. Tjaden, D.C. Swenson, R.F. Jordan and J.L. Peterson, Organometallics, 14 (1995) 371.

[10] F.G.N. Cloke, P.B. Hitchcock and J.B. Love, J. Chem. Soc., Dalton Trans., (1995) 25.

[11] J.M. Aizpurua and C. Palomo, *Tetrahedron Lett.*, 26 (1985) 475.

[12] S. Friedrich, L.H. Gade, A.J. Edwards and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1993) 2861.

[13] R.A. Andersen, *Inorg. Chem.*, 18 (1979) 2928.

[14] L. Scoles, R. Minhas, R. Duchateau, J. Jubb and S. Gambarotta, *Organometallics*, 13 (1994) 4978.

[15] H.C.S. Clark, F.G.N. Cloke, P.B. Hitchcock and J.B. Love, unpublished results.

[16] L.E. Manzer, *Inorg. Synth.*, 21 (1982) 136.

[17] R.A. Andersen and G. Wilkinson, *Inorg. Synth.*, 19 (1979) 262.

[18] C. Tessier-Youngs and O.T. Beachley, *Inorg. Synth.*, 24 (1985) 95.

[19] N. Wiberg and G. Wagner, *Chem. Ber.*, 119 (1986) 1462.