Synthesis, structural and thermal characterisation of titanium silylamido complexes

Samuel D. Coshama, Andrew L. Johnsona,*, Gabriele Kociok-Köhnb, Kieran C. Molloya

Abstract

The titanium silylamido complexes \([\{R_2Si(NR' Bu)_2\}_2 Ti \} (R = Me (3) and R = Ph (4)); \{[(R, Si(NR' Bu)_2)Ti(\{2- NBU\})_2] (R = Me (5) and R = Ph (6) have been synthesised from the reaction of the lithio-silylamide ligands \([R_2Si(NR' Bu)_2]_2 (R = Me; (1), R = Ph; (2)) with TiCl4 and \{Ti(NR' Bu)Cl(\{2) \} respectively. In the case of complexes 2, 3 and 5 the complexes have been structurally characterised by single crystal X-ray diffraction. The thermal profiles of the four silylamido (3–6) complexes have also been investigated by thermogravimetric analysis.

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Introduction

As the size downscaling of microelectronics continues, and the use of copper as an interconnect material in integrated circuitry has increased [1], the need for materials that can inhibit the fast diffusion of copper into the underlying silicon layers, and prohibit the formation of highly resistive materials such as CuSi, has also increased in turn [2]. Thin films of materials, based around early transition metal (Groups 4–6) nitrides, and specifically Ti–N, and produced by chemical vapour deposition (CVD) [3], or more recently atomic layer deposition (ALD) [4] has been an area of significant interest to those in the microelectronics industry for the last three decades and has continually been cited in the International Roadmap for Semiconductors as an area of considerable interest [5]. More recently materials such as Hf–N, Zr–N, Ta–N, Nb–N and W–N [3,6] which combine properties such as, high conductivity, thermal stability and chemical inertness, have become increasingly important as diffusion barrier layers in ultra-large scale integration devices (ULSI).

However, one of the drawbacks of crystalline barrier materials, such as Ti–N, is the diffusion of Cu along grain boundaries [2,7]. Grain boundaries can also have a significant effect on properties such as conductivity, thermal stability and chemical inertness. As a result there is increasing attraction towards amorphous ternary materials such as M–Si–N (M = Ti, Ta, W, Mo) [8] and, to a lesser extent, M–B–N [9].

The efficacy of these films is sensitive to the relative M:N:Si ratios, with a high N content raising the temperature at which crystallization commences [10], while excessive amounts of Si encourages the formation of regions of resistive Si3N4 within the films [8b,11].

Ternary Ti–Si–N films have largely been deposited by physical techniques such as cathodic arc ion plating [12], or sputtering in a nitrogen atmosphere [13], although variations on CVD methods such as MOCVD [8a,11,14], PECVD [15], LPCVD [16], ALD [17] and various others [18] have all been performed using multiple source precursors.

We have previously reported the development of metal silylamido complexes as single-source precursors for the production of M–Si–N materials (M = Group 4 metals [3e] and Zn [18]). Several examples of possible precursors which claim the use of metal complexes of bidentate silylamides i.e. \([R_2Si(NR' N)MNR' N]_2\), for the formation of M–Si–N thin film materials using CVD methods for a range of metals from Groups 4–6 are found in the patent literature [20]. However, details of the characterization of these complexes were not included in these patents. It is important to note that a successful single source precursor capable of depositing carbon and oxygen-free early transition metal MN or M–Si–N films has yet to be reported in a non-patent report. It is also important to note that precursors typically also require an external/additional
reactive source of nitrogen (e.g. ammonia or hydrazine) to produce Ti–N or Ti–Si–N thin films. It is for these reasons that the development of new single source precursors represents a significant challenge.

Our interest in this area is the synthesis and development of single source precursors that contain pre-formed M–N–Si linkages for CVD purposes [21]. While there is a paucity of complexes developed specifically for utilization in CVD applications, it is important to note there are a wide range of complexes reported in the literature that have been developed for catalytic purposes [22] which contain both pre-formed M–N–Si linkages and an {MN₄} core: a key feature of precursor materials which has previously been reported to favour formation of M–N materials on decomposition [3e,23].

In this paper, we report on the reactions of both TiCl₄ and [Ti(N₆Bu)Cl₂(Py)₂] respectively with lithio-silylamides [(R₃Si(NBu₂)]L₂ [R = Me (1), R = Ph (2)] and the structural and spectroscopic characterisation of the products. Thermogravimetric analysis has also been used in order to assess the potential utility of these complexes to form amorphous Ti–Si–N films.

**Experimental**

**General information**

All operations were performed under an atmosphere of dry argon using standard Schlenk line and glovebox techniques. Hexanes and toluene solvents were dried using commercially available solvent purification system (Innovative Technology Inc.) and degassed under argon prior to use. Deuterated benzene (C₆D₆) and THF (d₈-THF) NMR solvents were purchased from Fluorochem and dried over potassium before isolating in vacuo.

**Synthesis of [Ph₂Si(NLi₄Bu)₂] (1)**

A stirred hexane (100 ml) solution of [Ph₂Si(NLi₄Bu₂)] (9.78 g, 30 mmol) was treated with nBuLi (2.5 M, 24 ml, 60 mmol) at −78 °C. The solution was allowed to warm to room temperature, then slowly refluxed for 30 min. Volatiles were then removed in vacuo. Recrystallisation of the residue from hexane at −28 °C yielded [Ph₂Si(NLi₄Bu₂)], as colourless crystals. Yield 7.72 g, 76%. ¹H NMR (300 MHz, C₆D₆): δH 8.14 (m, 2H, meta-C₆H₅), 7.47–7.27 (br m, 3H, ortho- and para-C₆H₅), 1.25 (s, 9H, N₆Bu). ¹³C{¹H} NMR (75.5 MHz, C₆D₆); δC 138.0, 135.7, 130.2, 129.5, 61.0, 36.8. Analysis: calc for C₂₈H₆₆N₆Si₂Ti₂: C 52.65, H 10.41, N 13.16%; found: C 52.86, H 10.38, N 13.30.

**Synthesis of [Me₂Si(N₆Bu₂)₂Ti(C₆H₅)N] (2)**

Slow addition of TiCl₄ (0.54 ml, 5 mmol) to a stirred Et₂O (60 ml) solution of [Me₂Si(N₆Bu₂)₂], 4 (3.38 g, 10 mmol) at −78 °C afforded a precipitate. After stirring for 24 h the solution was filtered and dried in vacuo. Isolation of the residue from toluene at −28 °C yielded [[Me₂Si(N₆Bu₂)₂]Ti(C₆H₅)N]]; as a green powder. Yield 2.89 g, 83%. ¹H NMR (300 MHz, C₆D₆): δH 8.98 (s, 1H, meta-C₆H₅), 7.66 (m, 3H, ortho- and para-C₆H₅), 1.32 (s, 9H, N₆Bu). ¹³C{¹H} NMR (75.5 MHz, C₆D₆); δC 138.0, 135.7, 130.2, 129.5, 61.0, 36.8. Analysis: calc for C₃₈H₇₄N₆Si₂Ti: C 69.83, H 8.10, N 8.04%; found: C 69.11, H 8.19, N 8.07%.

**Synthesis of [[Me₂Si(N₆Bu₂)₂]Ti(t₂-N₆Bu₂)₅] (5)**

Slow addition of a Et₂O (20 ml) solution of [Ti(N₆Bu₂)Cl₂(Py)₂], 3 (5.30 g, 10 mmol) to a stirred Et₂O (60 ml) solution of [Me₂Si(N₆Bu₂)₂], 4 (2.17 g, 10 mmol) at −78 °C afforded a precipitate. After stirring for 24 h the solution was filtered and dried in vacuo. Recrystallisation of the residue from toluene at −28 °C yielded [[Me₂Si(N₆Bu₂)₂]Ti(t₂-N₆Bu₂)₅]; as green crystals. Yield 2.30 g, 72% (base on Ti). ¹H NMR (300 MHz, C₆D₆): δH 1.61 (s, 6H, N₆Bu), 1.32 (s, 9H, N₆Bu), 0.46 (s, 2H, SiMe), ¹³C{¹H} NMR (75.5 MHz, C₆D₆); δC 69.0, 59.8, 36.4, 6.4, 14. ²⁷Si NMR (99.35 MHz, C₆D₆): δSi −45.9. Analysis: calc for C₅₂H₇₂N₆Si₂Ti₂: C 52.65, H 10.41, N 13.16%; found: C 51.31, H 9.57, N 12.89.

**Crystallography**

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in Table 1. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using MoKα radiation (λ = 0.71073 Å). Structure solution was followed by full-matrix least squares refinement and was
performed using the WinGX-1.70 suite of programmes [29]. Specific details: Compound 2: The asymmetric unit consists of one half of the molecular dimer, consisting of two lithium atoms and two independent halves of the \( \text{Ph}_2\text{Si}[\text{N(Bu)}_2] \) ligand, the complete molecule being generated by symmetry operator \(-x + 1, y, z + \frac{1}{2}\). Compound 3 sits on an inversion centre such that only one half of the molecule forms the asymmetric unit, the second half of the molecule being generated by the symmetry operator \(-x, y, z\). In addition, the molecule exhibits disorder within the \( ^3\text{Bu} \) groups due to rotation about the \([\text{N}(1)-\text{C}(3)]\) and \([\text{N}(2)-\text{C}(4)]\) bonds. Consequently, the associated methyl groups are refined over two positions \([\text{C}(3A)-\text{C}, \text{C}(3D)-\text{F}, \text{C}(4A)-\text{C}, \text{C}(4D)-\text{F}]\), the relative proportions of which are defined by a free variable, the sum of which is equal to 1. Compound 5 sits on an inversion centre and the asymmetric unit corresponds to one half of the molecular entity.

**Results and discussion**

**Synthesis and discussion**

The synthsins \( \text{R}_2\text{Si}[\text{N(Li)}_2]\text{Bu}_2 \) \([\text{R} = \text{Me} (1), \text{Ph} (2)]\) were prepared following the reported procedure for 1 [21b,24] from the corresponding protonated ligands (Eqn. 1):

\[
\begin{align*}
\text{Me}_2\text{SiCl}_2 + 4\text{BuNH}_2 & \rightarrow \text{R}_2\text{Si}[\text{H}(\text{Bu})_2]_2 \quad & (\text{Eqn. 1}) \\
\text{Ph}_2\text{SiCl}_2 + 2\text{Bu}(\text{H})\text{Li} & \rightarrow \text{R}_2\text{Si}[\text{N}(\text{H})\text{Bu}_2]_2 \quad & (\text{Eqn. 1})
\end{align*}
\]

However, the synthesis of \( \text{Ph}_2\text{Si}[\text{N(H)}_2]\text{Bu}_2 \) cannot be achieved by direct reaction of \( \text{Ph}_2\text{SiCl}_2 \) and \( ^3\text{BuNH}_2 \) (unlike analogous compounds with smaller substituents), and requires pre-formation of \( ^3\text{Bu}(\text{H})\text{Li} \), in a protocol analogous to that required for the synthesis of \( \text{Ph}_2\text{Si}[\text{N}(\text{H})(\text{CH}_3)\text{Pr}_2-2,6]_2 \) [28].

The molecular structure of the dimeric complex 2 is shown in Fig. 1 and is reminiscent of related disililo-silyl/diamide complexes reported previously [30] in that the primary coordination of the lithium atoms is provided by the nitrogen centres, such that each lithium maintains a pseudo trigonal pyramidal geometry coordinated by three nitrogen atoms. Each lithium atom has two longer and one shorter Li–N contacts such that while the core of the complex can be viewed as central \([\text{Li}_4]\) core in each of the \([\text{Li}_4]\) faces are essentially capped by a nitrogen atom, the distortion is such that the interlocked \([\text{Li}_4]\) and \([\text{N}_4]\) tetrahedra form a distorted \([\text{N}_4\text{Li}_4]_2\)-square antiprism.

Despite the fact that the reaction was carried out in diethyl ether, a Lewis base solvent which favourably coordinates to lithium via the lone pairs on the oxygen, no solvent molecules are observed within the crystal structure. This is possibly due to aggregation of the monomer being favoured over solvation in addition to steric hindrance from peripheral \( ^3\text{Bu} \) groups retarding solvent coordination to the lithium atoms. Reaction of 1 and 2 in a 2:1 ratio with \( \text{TiCl}_4 \) yields the titanium silylamides 3 and 4 (Eqn. 2).

\[
\begin{align*}
\text{Me}_2\text{SiCl}_2 + 4\text{BuNH}_2 & \rightarrow \text{R}_2\text{Si}[\text{H}(\text{Bu})_2]_2 \quad & (\text{Eqn. 1}) \\
\text{Ph}_2\text{SiCl}_2 + 2\text{Bu}(\text{H})\text{Li} & \rightarrow \text{R}_2\text{Si}[\text{N}(\text{H})\text{Bu}_2]_2 \quad & (\text{Eqn. 1})
\end{align*}
\]

\[
\begin{align*}
\text{R} = \text{Me} (1), & \quad \text{Ph} (2) \\
\text{R} = \text{Me} (3), & \quad \text{Ph} (4)
\end{align*}
\]

The titanium complex \([\text{(Me}_2\text{Si}[\text{N}(\text{Bu})_2]_2)\text{Ti}]_2 \) (3) and its zirconium analogue [25] as well as the hafnium and vanadium(IV) analogues [31], have previously been prepared by Brauer et al. The reaction of
N(2) Si Å N(2) colour change is uncertain. Analysis of the 1H NMR spectrum for the under an atmosphere of nitrogen over a period of several weeks in our hands complex this work represent a new modi
eisolated and characterised by Brauer are reported to be yellow-
significantly in the original publication by Brauer et al. complex 
Ti(III), suggesting degradation of orange crystals shows it to be identical to the initial spectrum for 
thermal ellipsoids are at the 30% probability level. Selected data: Ti–N(1) 1.915(5), Ti–N(2) 1.912(6), Ti–N(3) 1.925(5), Ti–N(3') 1.938(5), Si–N(1) 1.760(6), Si–N(2) 1.757(5) Å; N(1)–Ti–N(2) 83.8(2), N(1)–Ti–N(3) 126.6(2), N(1)–Ti–N(3') 119.49(18), N(2)–Ti–N(3) 125.49(17), N(2)–Ti–N(3') 119.3(2), N(3)–Ti–N(3') 86.44(18), N(1)–Si–N(2) 93.3(3), N(1)–Si–C(1) 114.7(3), N(1)–Si–C(2) 113.5(3), N(2)–Si–C(1) 114.3(3), N(2)–Si–C(2) 112.4(3), C(1)–Si–C(2) 108.2(4)°. Symmetry operation: 1 – x, 1 – y, – z.

1 with TiCl4 in a 1:1 ratio has also been used to yield the mono-
substituted complex [(Me2Si(NBu)2)TiCl2] [22b]. Curiously, although 3 was initially isolated as green crystals, when stored under an atmosphere of nitrogen over a period of several weeks these crystals were observed to turn orange. The cause of this colour change is uncertain. Analysis of the 1H NMR spectrum for the orange crystals shows it to be identical to the initial spectrum for the complex, whilst both spectra show no broadening of the resonances due to the presence of Ti(III), suggesting degradation of the complex seems unlikely. In addition, the 1H NMR spectrum of the green crystals of 3 showed no trace of resonances attributed to residual solvent. However, it is interesting to note that crystals isolated and characterised by Brauer are reported to be yellow–orange in colour [25], while the green crystals analysed as part of this work represent a new modification of this compound. More significantly in the original publication by Brauer et al. complex 3 is described as crystallising in the orthorhombic space group P212121; in our hands complex 3 crystallises in the monoclinic space group C2/c with almost identical (within experimental error) unit cell parameters to the zirconium analogue [(Me2Si(NBu)2)Zr2] [25]. Since the geometric data for this new crystallographic modification were calculated from a data set recorded at 150 K (cf. 283–303 K for the Brauer modification), significant bond lengths and angles in the complex are different to those previously reported.

The molecular structure of 3 along with selected bond lengths and angles is shown in Fig. 2. At the centre of the spirocyclic complex is a distorted [TiN₄] core, with approximate D₂ᵥ symmetry at the Ti-metal centre, with two [Me₂Si(NBu)₂] moieties bonded to each titanium atom, resulting in the formation of two approximately perpendicular planar [TiN₂Si] rings [Ti(1), N(1), Si(1), N(2); Ti(1), N(1’), Si(1’), N(2’)] fused at the central titanium atom.

The Ti–N distances [1.9281(15) Å] are longer than those found in other four-coordinate titanium silyldiamide and titanium cyclic diamide complexes, which are in the 1.820–1.906 Å range [22c,32]. It is of note that both the Ti–N bond lengths and N–Ti–N bite angle [81.71(7)°] in 3 is different to those reported by Brauer. In addition, the N–Ti–N and N–Si–N [92.78(7)°] bond angles observed in 3 is significantly different to comparable bond angles in the titanium (cyclic)silyldiamide complexes reported by Kang et al. which display much more acute N–Si–N [ca. 89.4°] and obtuse N–Ti–N [ca. 85°] than those observed in 3, which is somewhat counterintuitive given the general reasoning that geometry constraints provided by the (Cyc)Si link of the diamide ligand should result in a reduction of both the N–Si–N and N–Ti–N angles.

In contrast complex 4 was isolated in very low yield and characterised solely by NMR, which, due to its simplicity (C₆H₅:8 . 10, 7.66 ppm; tC₄H₉: (1.10 ppm) suggests a structure analogous to that of 3.

Similarly, reaction of 1 & 2 with (Py)₂Cl₂Ti = NBu in a 1:1 ratio afforded the novel species 5, 6, as green and orange–brown crystals, respectively (Eqn. (3)).

\[
R = \text{Me (1), Ph (2)}
\]

\[
(\text{Py})_2\text{Cl}_2\text{Ti} + \text{NBU} \xrightarrow{-2 \text{LiCl}} R = \text{Me (5), Ph (6)}
\]

(Eqn. 3)

The 1H NMR spectrum for 5 shows it to be comparable to the 1H NMR spectrum for 1, although the resonance attributed to the tert-butyl groups of the diaminosilane is observed to be shifted slightly
downfield (1.61 and 1.34 ppm for 5 & 1, respectively). Furthermore, an additional singlet is observed (1.32 ppm) that may be assigned to the t-butyl protons of the [N3Si] imido group bonded to the titanium. Integration of the resonances attributed to the tert-buty1 groups of the {Me3Si(NBu)2} and (TiNBut) moieties show them to be present in a 2:1 ratio; similar observations are made concerning the 1H NMR spectra for 6. Interestingly no resonances are observed within the 1H NMR spectra of 5 and 6 that may be attributed to coordinated pyridine molecules. Consequently these observations are consistent with the formation of titanium imido species with the empirical formula [(R3Si(NBu))2Ti(NBu)], which may exist as monomeric complexes in which the titanium atom adopts a three coordinate geometry, or alternatively as a coordinatively more satisfied dimeric complex containing the titanium atoms in a more favourable 4-coordinate environment. The molecular structure of 5 (Fig. 3) confirms the latter scenario.

The titanium atoms within 5 occupy a four-coordinate pseudo-tetrahedral environment with one {Me3Si(NBu)2} moiety bonded to each titanium atom, resulting in the formation of two planar [TN2Si] rings [Ti(1), N(1), Si(1), N(2); Ti(1’), N(1’), Si(1’), N(2’)]. The methyl groups bonded to the silicon occupy a plane perpendicular to the plane of the [TN2Si] ring [inter-planar angle: 89.76(31)°]. The two [TN2Si] rings are linked through the titanium atoms via a planar four-membered [TiN2Si] ring [Ti(1), N(3), Ti(1’), N(3’)] that is observed to be perpendicular [89.95(32)°] to the plane of the two [TN2Si] four-membered rings. This [TiN2Si] ring is similar to that observed within a number of imido bridged complexes of the general form [(R’R’N)xTi(j2-NR)]2 reported by ourselves [3e] and others [3d,33]. Each of the three nitrogen atoms adopts a planar geometry [S(bond angles): 359.9 N(1); 359.3 N(2); 360° N(3)], suggesting possible π-overlap between the lone pair and an available orbital on titanium [33a].

Finally, and most unexpectedly, reaction of two equivalents of (Me3Si)Li with (Py)2Cl2Ti = NBut yielded not the anticipated product (Py)2(Me3Si)LiTi(NBut) = NBut but rather the metallacyclodibutane species [((Me3SiN(SiMe3)2)Ti(j2-NBu))2] (7) resulting from a C–H bond activation within the methyl group of one silylamine (Eqn. (4)) in low yield (<25%).

The (TiNSiC) rings observed in 7 arise from the elimination of a single hydrogen from one of the {Me3Si} groups of a [N(SiMe3)2] ligand, with the resultant {Me3SiNSiMe3CH2} moiety bonding to the titanium in a bidentate manner through the nitrogen and methylene carbon atoms. While single hydrogen γ elimination from a coordinated [(Me3Si)2N] group [34] or a β-elimination from a {Me2N} or [Et2N] group are known C–H activation/thermal decomposition pathways [35], for metal amide complexes the number of isolated and structurally characterised complexes containing these metallacyclocarbocations is small, compared to metal silylamide systems. This γ-hydrogen elimination within [N(SiMe3)2] ligands and subsequent formation of a (MNSiC) ring has previously been reported for several Group 4 metal complexes [34a,b,36]. In particular, Cp2Ti((CH3)2Si-Me2NSiMe3) has been prepared by a similar reaction to that for the synthesis of 7 through the addition of two equivalents of LiN(SiMe3)2 to a solution of Cp2TiCl2 and whose mechanism of formation has been discussed by Andersen et al. [34b] The molecular structure of complex 7 along with selected bond lengths and bond angles is provided in the supporting Supplementary data associated with this paper.

Any formation of the speculative bis-amide species [(Me3Si)2N2]Ti = NBut cannot be established as the reaction of the metal chloride species with (Me3Si)Li results in the formation of a complex reaction mixture as determined by 1H NMR spectroscopy, and suggests the presence of multiple species. Despite multiple attempts using various solvents and work-up procedures the yield of complex 7 could not be improved upon and the precise identity side products from this reaction could not be further illuminated.

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Thermogravimetric analysis

Thermogravimetric analysis (TGA) of complexes 3–6 were performed in order to gain insight into their relative volatilities and thermal stabilities (Fig. 4).

This analysis was carried out with an instrument that was housed in a nitrogen filled purge-box in order to minimize reaction with atmospheric moisture/air. Compounds 3 and 5 were found to undergo mass loss to yield stable residues of 16% (110–350 °C) and 25% (110–400 °C) respectively. In the case of complex 3 the residual mass % is lower lower than the expected values for TiSiN (~20%) suggesting of a degree of volatilisation in the complex. This is consistent with observations made by Brauer et al. who have
reported the sublimation of 3 occurring under similar conditions (70 °C/0.08 mmHg) [25]. Curiously, a patent filed by Air Products and Chemicals Inc. reports the structurally similar complex \([\text{[H}_2\text{Si(NBu)}_3]_2\text{Ti}\)] to be volatile, with a residual mass of 1.64% observed within the TGA being less than may be expected for titanium metal alone (12.2%) [20b].

In contrast, complex 5 begins to lose mass at ~110 °C, which is comparable to complex 3, although significant mass loss (>10%) does not occur until the sample has reached a temperature of 250 °C (50 °C higher than complex 3). At ~400 °C complex 5 ceases to lose mass leaving a residual mass of ~25%; this residual mass is greater than that expected for TiN (9.7%), TiS (11.9%) TiSiN (14%), TiSi2N2 (16.3%) or Ti2SiN2 (21%), but is in fact between the mass residues expected for Ti2SiN2 (24%) and Ti2Si2N2 (25.9%). Despite the uncertainty of the identity of the residual mass the TGA curve shows that between 400 and 600 °C there is no further mass loss from complex 5.

TGA curves for the complexes containing phenyl groups (4 and 6) show very clearly more than one thermal event occurring; as with complexes 3 and 5 the onset of thermal degradation begins at about 110 °C with a small mass loss (~2%). Mass loss then continues at a steady rate until both samples reach approx. 400 °C when there is further mass loss. In both cases, formation of a stable decomposition product is not observed within the temperature range analysed, an observation that has been made previously with other phenyl-silyl derivatives [3e,19].

Conclusions

A range of spirocyclic Ti-silylamide complexes have been prepared and structurally characterised. Thermogravimetric analysis has been used in order to assess the potential of these materials as prospective Ti–Si–N precursors. Analysis of the thermogravimetric traces reveal that the phenyl derivatives (4 & 6) decompose via a complicated pathway leaving residual masses which are greater than the desired Ti–Si–N materials. Of the complexes examined the \([\text{Me}_2\text{Si}]_2\text{ derivatives 3 and 5 show the most promise although only complex 5 leaves mass residues which are less than, but approaching that of, Ti–Si–N. The reduced residual mass observed for complex 3, suggests a degree of volatility in the complex desirable in prospective CVD precursors. Work directed towards the use of complex 3 in the production of thin films is under way, the results of which will form the basis of future publications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.08.026.

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