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Synthesis, characterization, and thermal properties of volatile 1,4-dialkyl-5-silatetrazolines: nitrogen-rich silicon heterocycles as possible CVD precursors for silicon nitride†

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We describe the synthesis, thermal properties, and volatilities of three 1,4-dialkyl-5-silatetrazolines of the form (L)Si(N₄R₂), where R = Et (**2**), ⁱPr (**3**), or ^tBu (**4**) and L is the 1,4-diazabutenediyl chelate ^tBuNCHCHN^tBu. The compounds were characterized by NMR and IR spectroscopy and X-ray crystallography. Volatility studies show that compound **2**, the 1,4-diethyl-5-silatetrazoline compound, is the most volatile of the three new compounds, exhibiting a 1 Torr vapor pressure at 95 °C and subliming at 65 °C and 5 mTorr. These compounds are of interest as possible low temperature CVD precursors for the growth of silicon nitride (SiN_x) thin films.

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Introduction

Silicon nitride (SiN_x) thin films have multiple applications in the manufacturing of microelectronic devices, ranging from gate dielectrics^{1–3} to encapsulation layers and diffusion barriers.^{4,5} These applications impose strict requirements on the growth process and the film quality, including good dielectric properties, high physical density, and low etch rate in hydrofluoric acid.^{2–5} In back-end processes, SiN_x films must be deposited at temperatures below 400 °C to avoid device degradation caused by interfacial reactions, and the films must be grown conformally, which has become more difficult as the sizes of device features decrease and the aspect ratios of vias and trenches increase.^{6–8} The back-end applications for SiN_x films include etch stop layers, conformal spacers, and seamless gapfill of trenches or vias, depending on the device integration scheme. Gapfill with SiO₂ is already available and the development of a SiN_x process at comparable temperatures is of interest because it will provide etch contrast vs. SiO₂.

Atomic layer deposition (ALD) has been used successfully to grow conformal films of SiN_x at temperatures within the thermal budget.^{3,6,7,9} ALD typically affords films with excellent conformality, but also has disadvantages, such as typically requiring two separate precursors, each containing a com-

ponent of the desired film composition, which are alternately passed over the growth surface with chamber purge steps in between each exposure. These factors result in slow deposition rates (often ~1 Å per cycle), which lead to increased processing time and higher manufacturing costs.^{10,11} In comparison, chemical vapor deposition (CVD) can afford films much more quickly than ALD, and under the right conditions this method can afford highly conformal films.¹² Furthermore, CVD allows for the use of single-source precursors tailored to the desired film, simplifying the deposition process. In addition, CVD has some capabilities that ALD lacks, such as the ability to afford superconformal films in which growth is faster at the bottom of a deep feature.¹² This capability has become increasingly important as feature sizes on integrated circuits decrease with each new device generation.

Of the various CVD precursors for silicon nitride, some of the most interesting are single-source molecular silicon azides. Several such compounds have been studied as CVD/ALD precursors; however, some are explosive and therefore unsafe to work with, especially on a larger industrial scale.^{13–16} In addition, many of the silicon azides that have been used as CVD precursors also contain silicon–carbon bonds, which inevitably lead to carbon incorporation in the resulting films; for example, films grown from an alkyl-triazido silane, SiEt(N₃)₃, contain approximately 10% carbon.¹³

The design of new CVD precursors for the deposition of SiN_x films presents an interesting challenge. The precursor must be thermally stable at and above room temperature, volatile enough to ensure efficient vapor-phase transport into the CVD chamber, but reactive enough to deposit the desired film within the 400 °C thermal budget. An ideal single-source CVD

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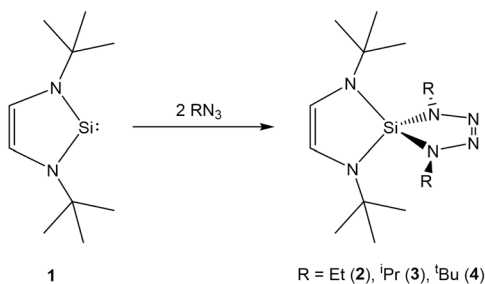


Fig. 1 Reaction of silylene **1** with the alkyl azides studied in the current paper.

precursor for SiN_x should contain only silicon–nitrogen bonds, so as to minimize the incorporation of heteroatoms such as carbon.

The isolation of the thermally stable *N*-heterocyclic silylene 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene (**1**) by West and co-workers was followed by several reports of the reactions of this silylene toward a variety of inorganic, organic, and organometallic reagents.^{17–19} Of interest in the context of the current paper is that **1** reacts with several organic azides (see Fig. 1) to afford 1,4-disubstituted 5-silatetrazolines with bulky substituents ($\text{R} = \text{Ph}$, *p*-tolyl, adamantyl, CPh_3 , SiPh_3 , or a substituted 1,3,2-diazaboryl group).^{18,20} Except for the large substituents, which greatly reduce the volatility of these compounds, these nitrogen-rich silatetrazolines have many of the attributes needed for a good silicon nitride CVD precursor.

Here we report the synthesis of three new spirocyclic 1,4-dialkyl-5-silatetrazolines by treatment of silylene **1** with low molecular weight alkyl azides. The new compounds have been characterized by NMR and IR spectroscopy and X-ray crystallography. In addition, we have investigated their thermal properties to assess their suitability as CVD precursors for the deposition of SiN_x films at low temperatures.

Results and discussion

Synthesis of 1,4-dialkyl-5-silatetrazoline compounds

Following the same method used to prepare silatetrazoline compounds ($^t\text{BuNCHCHN}^t\text{BuSi}(\text{N}_4\text{R}_2)$) with bulky R groups,¹⁸ we have found that treatment of silylene **1** with ethyl-, *iso*-propyl, or *tert*-butyl azide^{21,22} in pentane (Fig. 1) affords three new 1,4-dialkyl-5-silatetrazolines of the form ($^t\text{BuNCHCHN}^t\text{BuSi}(\text{N}_4\text{R}_2)$), where $\text{R} = \text{Et}$ (**2**), *i*Pr (**3**), or *t*Bu (**4**). The mechanism of this reaction has previously been proposed to involve coordination of the first equiv. of the azide to the silylene, followed by loss of N_2 to form an iminosilane, ($^t\text{BuNCHCHN}^t\text{BuSi}=\text{NR}$), which reacts with the second equivalent of the azide by a [3 + 2] cycloaddition to form the silatetrazoline product.²³ Compounds **2** and **3** are best obtained by removing the solvent and subliming the product under vacuum (5 mTorr) at 65–75 °C; the isolated yields are 43% and 75%, respectively. Compound **4** precipitates from solution as a

white solid with excellent purity and 30% yield. It sublimes at 115 °C under vacuum.

We did not attempt to prepare the methyl-substituted analog due to the explosive nature of the methyl azide starting material.²⁴

Crystal structures of the new 1,4-dialkyl-5-silatetrazoline compounds

Crystal data for the new 1,4-dialkyl-5-silatetrazolines are listed in Table S1† and views of the molecules are given in Fig. 2. The ethyl compound **2** crystallizes in the space group *Pna*2₁, with one molecule (residing on a general position) per asymmetric unit. The *iso*-propyl compound **3** crystallizes in the space group *P1*, with 2 molecules of similar geometry per asymmetric unit. The *tert*-butyl compound **4** crystallizes in the space group *Cmcm*, with one-fourth molecule (*mm*2 site symmetry) per asymmetric unit.

Selected bond distances and angles for compounds **2–4** are listed in Tables S2–S4.† In all compounds, the silicon atom is bound to one 1,4-di(*tert*-butyl)-1,4-diazabutenediyl (DAD) ligand and one 1,4-dialkyltetrazenediyl (TET) ligand. DAD ligands are potentially redox non-innocent: the backbone C–C unit is a double bond in the dianionic state and a single bond in the neutral state.²⁵ The DAD ligands in **2–4** are clearly dianions, as shown by the backbone C–C bond lengths of 1.338(2) Å in **2**, 1.332(4) Å in **3**, and 1.343(3) Å in **4**.

In all three compounds, the average Si–N distances of the DAD ligand are similar to the Si–N distances of the TET ligand: 1.725(2) Å vs. 1.729(1) Å for **2**, 1.718(3) Å vs. 1.732(3) Å for **3**, and 1.726(1) Å vs. 1.735(1) Å for **4**. The N–Si–N angle between the two nitrogen atoms of the TET ligand is 85.62(7)°, 85.92(12)°, and 86.71(7)° for **2–4**, respectively.

The Si–N distances between the silicon and nitrogen atoms in the TET ligands range from 1.729 to 1.735 Å. These bond distances are very similar to those of 1.735(2)–1.740(2) Å and 1.740(3)–1.746(3) Å reported for two other 5-silatetrazoline compounds, the 1,4-diphenyl-5-silatetrazoline molecule, ($^t\text{BuNCH}=\text{CHN}^t\text{BuSi}(\text{N}_4\text{Ph}_2)$), and the 1,4-bis(triphenylsilyl)-5-silatetrazoline molecule, ($^t\text{BuNCH}=\text{CHN}^t\text{BuSi}[\text{N}_4(\text{SiPh}_3)_2]$).¹⁸ The N–Si–N angles in these two compounds are also very similar to those in compounds **2–4**: 85.53(11)° for the 1,4-diphenyl compound and 88.72(13)° for the 1,4-bis(triphenylsilyl) compound.¹⁸

Spectroscopic properties

In the ^1H NMR spectra of **2–4**, the DAD ligand shows singlets at δ 5.55, 5.57, and 5.59, respectively, for the backbone CH protons and at δ 1.19, 1.14, and 1.11, respectively, for the *tert*-butyl groups. The alkyl groups of the TET ligand appear as a quartet at δ 3.45 and a triplet at δ 1.25 for the ethyl groups in **2**, a septet at δ 3.81 and a doublet at δ 1.37 for the *iso*-propyl groups in **3**, and at δ 1.49 for the *tert*-butyl groups in **4**. The latter resonances are significantly deshielded with respect to those for the *tert*-butyl groups of the DAD ligand. $^{13}\text{C}\{^1\text{H}\}$ NMR data for all three compounds can be found in the Experimental section.



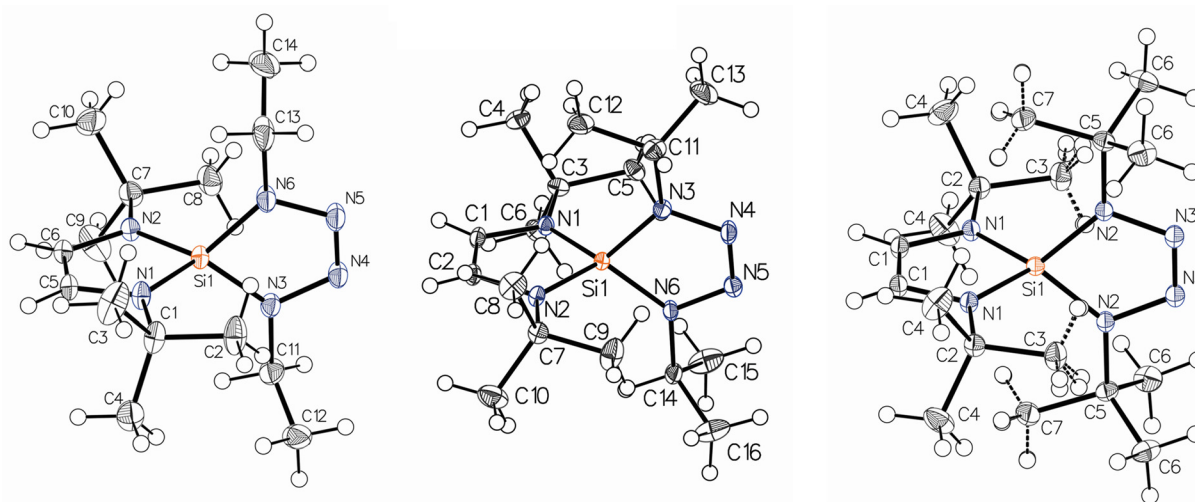


Fig. 2 Crystal structures of the 1,4-diethyl-, 1,4-di(*iso*-propyl)-, and 1,4-di(*tert*-butyl)-5-silatetrazoline compounds **2–4**. Ellipsoids are drawn at the 50% probability level. In **4**, because of the mirror symmetry, some of the methyl hydrogen atoms are disordered, as indicated by the dotted lines.

Comparisons of the IR spectra of **2–4** with that of the silylene compound **1** (which lacks the TET group) show some additional bands whose frequencies are largely independent of the alkyl group on the tetrazene ring. One of these bands appears at 1117 cm^{-1} and the other appears between 993 and 1007 cm^{-1} ; we tentatively assign these bands to N–N stretches within the tetrazene ring.

Air sensitivity, thermal properties, and volatility

Samples of **2–4** were exposed as solids to air for 1 day and subsequently analyzed by ^1H NMR spectroscopy. The *tert*-butyl compound **4** showed little decomposition even after being exposed to air for 3 days (Fig. S15[†]). In contrast, all of the ethyl compound **2** and half of the *iso*-propyl compound **3** decompose over this period. For both **2** and **3**, the principal decomposition product and only identifiable species is 1,4-di(*tert*-butyl)-1,4-diazabutadiene, which results from the hydrolysis and oxidation of the DAD ligand (Fig. S9[†]). For **2**, there is no sign of the ethyl groups of the TET ligand or their possible decomposition product, ethylene; these species, if formed, evidently volatilized out of the sample during sample handling. For **3**, several multiplets at δ 2.80–3.23 and several small doublets at δ 0.75–1.55 are due to the *iso*-propyl groups derived from the tetrazene ring (Fig. S12[†]), but the identities of the species responsible for these peaks are uncertain.

Because nitrogen-rich compounds have the potential to be explosive, we conducted shock tests. No sparks, fires, fumes, or noises were observed when compounds **2–4** were shocked. This assessment was supported by TGA data for **2–4** and silylene **1** (Table 1). When the compounds are heated under N_2 in a temperature ramp from room temperature to $600\text{ }^\circ\text{C}$, no anomalies appear in the TGA curves that would indicate a tendency to explode (Fig. 3). Instead, compounds **2–4** all evaporate smoothly without decomposition, as shown by the small residual masses of 0.3% (**2**), 0.4% (**3**), and 1.4% (**4**).

Table 1 TGA data for silylene **1** and the 1,4-dialkyl-5-silatetrazoline compounds **2–4**

	(1)	(2)	(3)	(4)
Sample amount, mg	7.67	8.82	8.44	7.21
Onset temperature for evaporation, $^\circ\text{C}$	114	179	201	210
Peak evaporation temperature, $^\circ\text{C}$	143	215	236	237
Residual mass, %	3.7 ^a	1.4	0.8	0.3

^a Elevated owing to oxidation during sample loading.

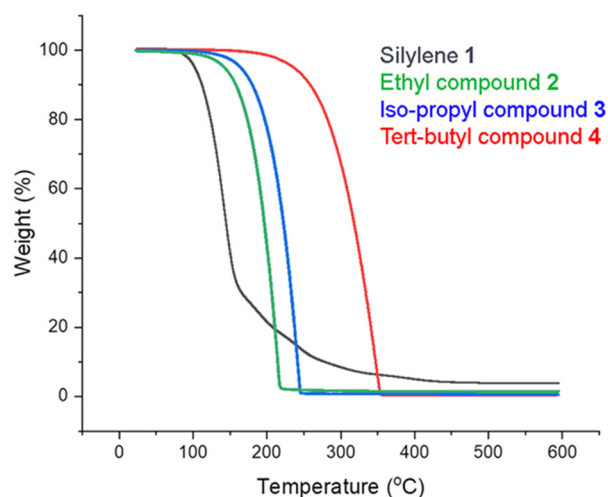


Fig. 3 TGA plots for the 1,4-dialkyl-5-silatetrazoline compounds **2–4** under 1 atm of nitrogen at ramp rates of $10\text{ }^\circ\text{C min}^{-1}$.

The onset and peak temperatures for evaporation increase in the order $2 < 3 < 4$ as expected from the increase in the size and molecular weight of the substituents on the TET ring. In contrast to the smooth volatilization seen for **2–4**, silylene **1**



shows a decrease in the slope of its TGA curve above 150 °C. This slope change could reflect adventitious oxidation of a portion of this highly air-sensitive compound during the loading of the sample into the TGA instrument, but could also indicate the onset of decomposition, for example by addition of C–H bonds to the silicon(II) center. The residual mass of 3.7% is small, however, indicating that most of **1** volatilizes rather than decomposes.

Isothermal TGA data were also collected for the ethyl compound **2** (Fig. S3†). After 18 mg of **2** was heated to 60 °C under 1 atm of N₂ for 4 h, 95% of the sample remained, which was shown to be unreacted **2** by NMR spectroscopy. These results indicate that, even when heated over an extended period of time, compound **2** continues to volatilize smoothly without decomposition. A series of isothermal TGA experiments (Fig. S3†) at different set temperatures, analyzed by Price's method,²⁶ showed that compound **2** has a room temperature vapor pressure of 5.11 ± 0.04 mTorr, a 1 Torr vapor pressure at 94.6 ± 0.2 °C, and an enthalpy of vaporization (ΔH_{vap}) of 69.1 ± 0.2 kJ mol^{−1}.

Conclusions

Three silicon 1,4-dialkyl-5-silatetrazoline compounds of the form (tBuNCHCHNtBu)Si(N₄R₂), where R = Et (**2**), iPr (**3**), or tBu (**4**), have been synthesized by treatment of silylene **1** with 2 equiv. of an alkyl azide. The R groups on the tetrazenediyl ligand are smaller than those in previously reported compounds, and as a result compounds **2–4** are appreciably volatile.

The synthesis, thermal properties, and volatilities of these compounds suggest that they may serve as precursors for the low temperature CVD of SiN_x films. Of the three new compounds reported here, the 1,4-diethyl-5-silatetrazoline compound **2** shows the most promise as a CVD precursor because it is the most volatile. It sublimates at 65 °C and 5 mTorr, and TGA studies show an onset of volatility at 179 °C under 1 atm of N₂. Isothermal TGA studies show that **2** has a room temperature vapor pressure of 5 mTorr and a 1 Torr vapor pressure temperature of 95 °C.

Experimental section

All experiments were carried out under vacuum or under argon by using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium/benzophenone immediately before use. The silylene compound **1** (1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene)²⁷ and organic azides^{21,22} were prepared through literature routes. Microanalyses were performed by the University of Illinois Microanalytical Laboratory using combustion techniques. The microanalytical results for **2–4** are about 1% low in nitrogen, for reasons that are unclear. The spectroscopic results suggest that the isolated samples are pure.

¹H NMR data were collected using a Varian Unity Inova spectrometer at 400 MHz and ¹³C NMR data were collected using a Bruker Avance III HD 500 NMR spectrometer; ¹H and ¹³C NMR chemical shifts are reported in δ units (positive chemical shifts to higher frequencies) relative to tetramethylsilane (TMS). The IR spectra were recorded using a Nicolet Impact 410 instrument as Nujol mulls between KBr plates.

Caution: Catenated nitrogen compounds often present explosion hazards. Although we have not experienced any problems in the synthesis, characterization, sublimation, or handling of the compounds described here, their energetic properties have not been fully investigated and therefore they should be handled using standard safety precautions for explosive materials (safety glasses, face shield, blast shield, puncture resistant gloves, and ear protection).

[1,4-Di(*tert*-butyl)-1,4-diazabut-2-ene-1,4-diyl][1,4-diethyltetraaz-2-ene-1,4-diyl]silane, 6,9-di-*tert*-butyl-1,4-diethyl-1,2,3,4,6,9-hexaaza-5-silaspiro[4.4]nona-2,7-diene, **2**

To a solution of ethyl azide (2.8 mmol) in pentane was added dropwise a solution of silylene **1** (0.275 g, 1.40 mmol) in pentane (20 mL). The solution was stirred at room temperature for 4 days. The colorless solution was evaporated to dryness under vacuum, resulting in a white microcrystalline solid. Yield: 0.340 g (78%). Crystals suitable for single-crystal XRD were grown from concentrated solutions of pentane at −20 °C. Anal. calcd for C₁₄H₃₀N₆Si: C, 54.2; H, 9.74; N, 27.1. Found: C, 54.2; H, 9.76; N, 26.0. ¹H NMR (C₆D₆, 20 °C): 5.59 (s, CH, 2 H), 3.45 (q, ³J_{HH} = 7.2 Hz, 4 H, CH₂), 1.25 (t, ³J_{HH} = 7.3 Hz, 6 H, CH₃), 1.11 (s, 18 H, tBu). ¹³C{¹H} NMR (C₆D₆, 20 °C): 109.58 (s, CH), 51.70 (s, CH₂), 41.41 (s, C), 30.63 (s, CH₃ of tBu), 15.62 (s, CH₃ of Et). IR (cm^{−1}): 1314 m, 1267 s, 1226 s, 1197 w, 1152 w, 1117 m, 1097 m, 1060 w, 1006 s, 750 s.

[1,4-Di(*tert*-butyl)-1,4-diazabut-2-ene-1,4-diyl][1,4-di(*iso*-propyl)tetraaz-2-ene-1,4-diyl]silane, 6,9-di-*tert*-butyl-1,4-di(*iso*-propyl)-1,2,3,4,6,9-hexaaza-5-silaspiro[4.4]nona-2,7-diene, **3**

To a solution of *iso*-propyl azide (3.22 mmol) in pentane was added dropwise a solution of silylene **1** (0.317 g, 1.61 mmol) in pentane (20 mL). The solution was allowed to stir at room temperature for 4 days. The colorless solution was evaporated to dryness under vacuum, resulting in a white microcrystalline solid. Yield: 0.412 g (75%). Crystals suitable for single-crystal XRD were grown from concentrated solutions of pentane at −20 °C. Anal. calcd for C₁₆H₃₄N₆Si: C, 56.8; H, 10.1; N, 24.8. Found: C, 56.7; H, 10.2; N, 23.7. ¹H NMR (C₆D₆, 20 °C): 5.57 (s, 2 H, CH of DAD), 3.81 (sep, ³J_{HH} = 6.5 Hz, 2 H, CH of iPr), 1.37 (d, ³J_{HH} = 6.6 Hz, 12 H, CH₃ of iPr), 1.14 (s, 18 H, CH₃ of tBu). ¹³C{¹H} NMR (C₆D₆, 20 °C): 109.09 (s, CH of DAD), 51.83 (s, CH of iPr), 48.49 (s, C of tBu), 30.54 (s, CH₃ of tBu), 22.96 (s, CH₃ of iPr). IR (cm^{−1}): 1267 m, 1226 m, 1117 m, 1096 w, 1063 w, 1007 m, 745 s.



[1,4-Di(*tert*-butyl)-1,4-diazabut-2-ene-1,4-diyl][1,4-di(*tert*-butyl)tetraaz-2-ene-1,4-diyl]silane, 6,9-di-*tert*-butyl-1,4-di(*tert*-butyl)-1,2,3,4,6,9-hexaaza-5-silaspiro[4.4]nona-2,7-diene, 4

To a solution of *tert*-butyl azide (5.09 mmol) in pentane was added dropwise a solution of silylene **1** (0.500 g, 2.55 mmol) in pentane (15 mL). The solution was allowed to stir at room temperature for 4 days. The colorless solution was evaporated to dryness under vacuum, resulting in a white microcrystalline solid. Yield: 0.284 g (30%). Crystals suitable for single-crystal XRD were grown from concentrated solutions of pentane at $-20\text{ }^{\circ}\text{C}$. Anal. calcd for $\text{C}_{18}\text{H}_{38}\text{N}_6\text{Si}$: C, 59.0; H, 10.4; N, 22.9. Found: C, 58.6, H, 10.4; N, 22.2. ^1H NMR (C_6D_6 , $20\text{ }^{\circ}\text{C}$): 1.19 (s, 18 H, CH_3 of DAD ^tBu), 1.49 (s, 18 H, CH_3 of TET ^tBu), 5.55 (s, 2H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , $20\text{ }^{\circ}\text{C}$): 108.83 (s, CH), 54.45 (s, C of TET ^tBu), 52.05 (s, C of DAD ^tBu), 30.49 (s, CH_3 of TET ^tBu), 30.11 (s, CH_3 of DAD ^tBu). IR (cm^{-1}): 1267 m, 1222 s, 1117 m, 1093 w, 1041 w, 993 m, 731 m.

Thermogravimetric studies

TGA experiments were performed on Pt sample pans in a TA Instruments Q50 analyzer. Because the TGA instrument was not inside a glovebox, a sample preparation protocol was followed to limit the exposure of these air- and moisture-sensitive compounds to the atmosphere during the sample loading process. In an argon-filled glovebox, weighed 7–9 mg and 11–18 mg samples were loaded into sealable vials for ramp and isothermal experiments, respectively. At the TGA instrument, the sample was quickly transferred from the vial into the ceramic cup, and the cup was placed on the Pt sample pan and immediately loaded into the TGA instrument.

For ramp experiments, the samples were heated under a flow of N_2 to $600\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The onset of volatilization was measured as the intersection of the tangents of the initial plateau and the point in the TGA curve at which the mass loss rate is the greatest. The residual masses of 0.3% (**2**), 0.4% (**3**), and 1.4% (**4**) for these compounds are very low, suggesting that these compounds volatilize smoothly with little decomposition.

For the isothermal time-study experiment, 18 mg of sample was heated under a flow of N_2 to $60\text{ }^{\circ}\text{C}$ and held at this temperature. In the stepwise isothermal experiment, 11 mg of sample was heated under a flow of N_2 with dwell times of 10 minutes in $10\text{ }^{\circ}\text{C}$ steps with a ramp rate between steps of $10\text{ }^{\circ}\text{C min}^{-1}$.

General crystallographic procedures

All crystals were mounted on a Nylon loop with Krytox oil and immediately cooled to $-173\text{ }^{\circ}\text{C}$ in a cold nitrogen gas stream on the diffractometer. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations (esds) by correction for background, scan speed, and Lorentz and polarization effects. No corrections for crystal decay were necessary, but multi-scan absorption corrections were applied for **2** and **3**. Systematically absent reflections were

deleted and symmetry equivalent reflections were averaged to yield the set of unique data.

All structures were solved by direct methods (SHELXS) and correct positions for all the non-hydrogen atoms were deduced from an E-map and subsequent least-squares refinement and difference Fourier calculations. The analytical approximations to the scattering factors were used and all structure factors were corrected for both real and imaginary components of anomalous dispersion. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen major site atoms. Unless otherwise stated in the ESI,[†] hydrogen atoms were placed in idealized positions; the displacement parameters for all hydrogen atoms were set equal to 1.2 times U_{eq} for the attached carbon. A final analysis of variance between the observed and calculated structure factors showed no apparent errors. Final refinement parameters are given in Table S1.[†] Aspects of the refinement unique to each structure are reported in the ESI.[†]

Data availability

The data supporting this article have been included as part of the ESI.[†]

Crystallographic data for compounds **2**, **3**, and **4** have been deposited at the Cambridge Crystallographic Data Centre under accession codes CCDC 2347929, 2347931, and 2347934.[†]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- 1 G. R. Nowling, S. E. Babayan, V. Jakovic and R. F. Hicks, Remote Plasma-Enhanced Chemical Vapour Deposition of



- Silicon Nitride at Atmospheric Pressure, *Plasma Sources Sci. Technol.*, 2002, **11**, 97–103.
- 2 G. D. Wil, R. M. Wallace and J. M. Anthony, High-k Gate Dielectrics: Current Status and Materials Properties Considerations, *J. Appl. Phys.*, 2001, **89**, 5243–5275.
 - 3 X. Meng, Y. Byun, H. S. Kim, J. S. Lee, A. T. Lucero, L. Cheng and J. Kim, Atomic Layer Deposition of Silicon Nitride Thin Films: A Review of Recent Progress, Challenges, and Outlooks, *Materials*, 2016, **9**, 1–20.
 - 4 C. Dussarrat, J. Girard, T. Kimura, N. Tamoki and Y. Sato, Methods for Producing Silicon Nitride Films and Silicon Oxynitride Films by Thermal Chemical Vapor Deposition, *U.S. Patent* 7192626B2, March 20, 2007.
 - 5 F. L. Rily, Silicon Nitride and Related Materials, *J. Am. Ceram. Soc.*, 2000, **83**, 245–265.
 - 6 T. Faraz, M. Drunen, H. C. M. Knoops, A. Mallikarjunan, I. Buchanan, D. M. Hausmann, J. Henri and W. M. M. Kessels, Atomic Layer Deposition of Wet-Etch Resistant Silicon Nitride Using Di(sec-butylamino)silane and N₂ Plasma on Planar and 3D Substrate Topographies, *ACS Appl. Mater. Interfaces*, 2017, **9**, 1858–1869.
 - 7 R. A. Ovanesyan, N. Leick, K. M. Kelchner, D. M. Hausmann and S. Agarwal, Atomic Layer Deposition of SiC_xN_y Using Si₂Cl₆ and CH₃NH₂ Plasma, *Chem. Mater.*, 2017, **29**, 6269–6278.
 - 8 R. S. Iyer, S. M. Seutter, S. Tandon, E. A. C. Sanchez and S. Wang, Method for Silicon Nitride Chemical Vapor Deposition, *US* 7365029B2, April 29, 2008.
 - 9 C. A. Murray, S. D. Elliott, D. Hausmann, J. Henri and A. LaVoie, Effect of Reaction Mechanism on Precursor Exposure Time in Atomic Layer Deposition of Silicon Oxide and Silicon Nitride, *ACS Appl. Mater. Interfaces*, 2014, **6**, 10534–10541.
 - 10 W.-J. Lee and Y.-H. Choa, Novel Plasma Enhanced Chemical Vapor Deposition of Highly Conformal SiN Films and their Barrier Properties, *J. Vac. Sci. Technol., B*, 2018, **36**, 022201.
 - 11 M. Leskelä and M. Ritala, Atomic Layer Deposition (ALD): From Precursors to Thin Film Structures, *Thin Solid Films*, 2002, **409**, 138–146.
 - 12 J. R. Abelson and G. S. Girolami, New Strategies for Conformal, Superconformal, and Ultrasoother Films by Low Temperature Chemical Vapor Deposition, *J. Vac. Sci. Technol., A*, 2020, **38**, 030802.
 - 13 D. A. Roberts, A. K. Hochberg, D. L. O'Meara, F. Rusnak and H. Hockenhull, The LPCVD of Silicon Nitride Films from Alkylazidosilanes, *Mater. Res. Soc. Symp. Proc.*, 1991, **24**, 515–520.
 - 14 A. K. Hochberg, S. Beach, D. L. O'Meara and D. A. Roberts, Deposition of Silicon Nitride Films from Azidosilane Sources, *U.S. Patent* 4992299A, February 12, 1991.
 - 15 M. Ishikawa, H. Machida and H. Sudo, Film Forming Material, Film Forming Method and Device, *Japanese Patent* JP2011009479A, January 1, 2011.
 - 16 A. LaVoie, M. J. Saly, R. D. Odedra and R. Kanjolia, Precursors for Plasma Activated Conformal Film Deposition, *U.S. Patent* US20130210241A1, August 15, 2013.
 - 17 N. J. Hill and R. West, Recent Developments in the Chemistry of Stable Silylenes, *J. Organomet. Chem.*, 2004, **689**, 4165–4183.
 - 18 N. J. Hill, D. F. Moser, I. A. Guzei and R. West, Reactions of Stable Silylenes with Organic Azides, *Organometallics*, 2005, **24**, 3346–3349.
 - 19 A. C. Tomasik, A. Mitra and R. West, Synthesis and Reactivity of Three New N-Heterocyclic Silylenes, *Organometallics*, 2009, **28**, 378–381.
 - 20 K. Yuvaraj and C. Jones, Synthesis and Reactivity of Boryl Substituted Silaimines, *Dalton Trans.*, 2019, **48**, 11961–11965.
 - 21 J. C. Bottaro, P. E. Penwell and R. J. Schmitt, Expedient Synthesis of t-Butyl Azide, *Synth. Commun.*, 1997, **27**, 1465–1467.
 - 22 M. Swetha, P. V. Ramana and S. G. Shirodkar, Simple and Efficient Method for the Synthesis of Azides in Water-THF Solvent System, *Org. Prep. Proced. Int.*, 2011, **43**, 348–353.
 - 23 R. West and M. Denk, Stable silylenes: Synthesis, Structure, Reactions, *Pure Appl. Chem.*, 1996, **68**, 785–788.
 - 24 J. Chae, Methyl Azide, in *Encyclopedia of Reagents for Organic Synthesis*, John Wiley and Sons, 2008.
 - 25 E. N. Nikolaevskaya, N. O. Druzhkov, M. A. Syroeshkin and M. P. Egorov, Chemistry of Diazadiene Type Ligands with Extra Coordination Groups. Prospects of Reactivity, *Coord. Chem. Rev.*, 2020, **417**, 213353.
 - 26 D. M. Price, Vapor Pressure Determination by Thermogravimetry, *Thermochim. Acta*, 2001, **367–368**, 253–262.
 - 27 M. Haaf, A. Schmiedl, T. A. Schmedake, D. R. Powell, A. J. Millevolte, M. Denk and R. West, Synthesis and Reactivity of a Stable Silylene, *J. Am. Chem. Soc.*, 1998, **120**, 12714–12719.

