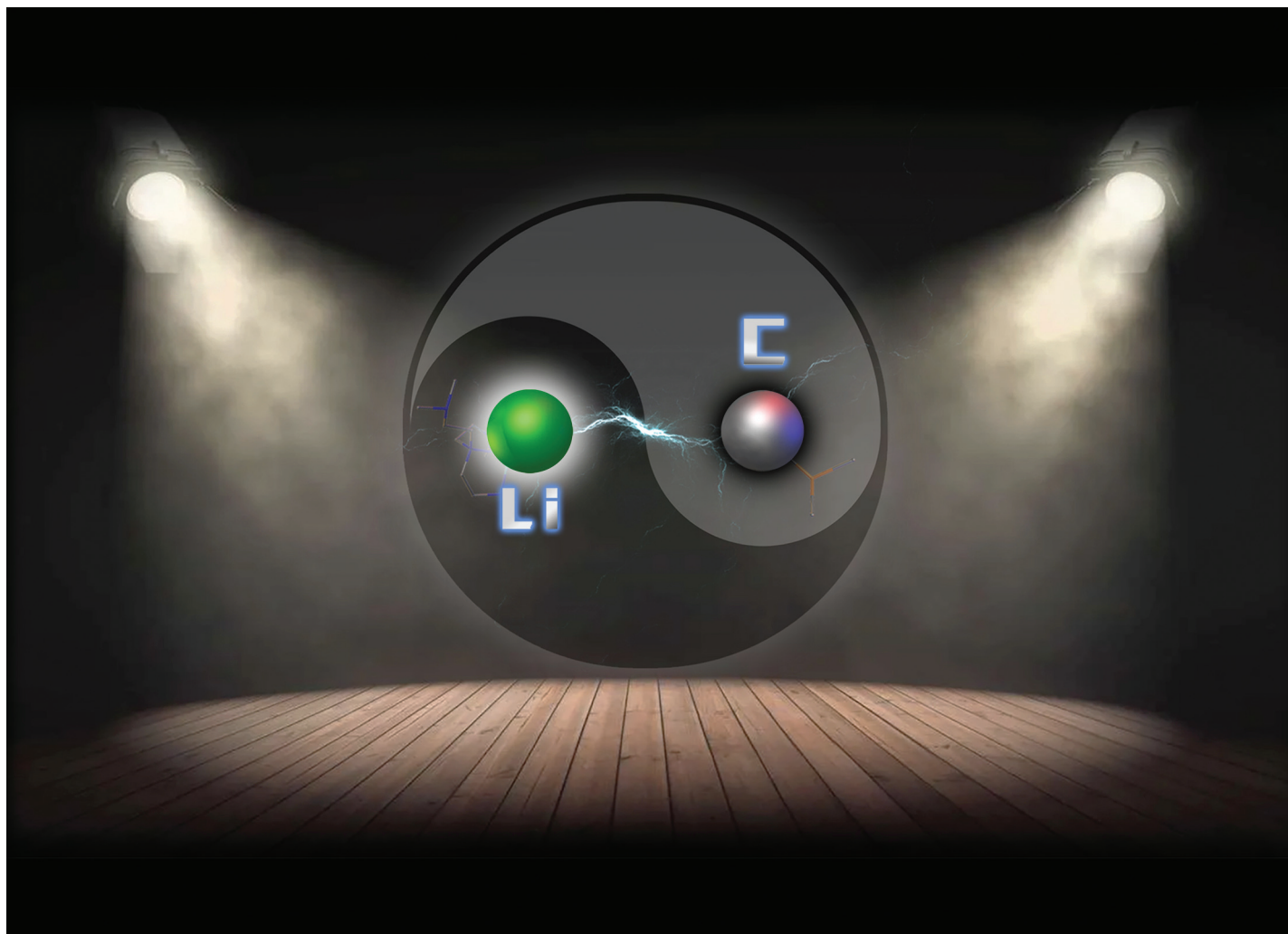


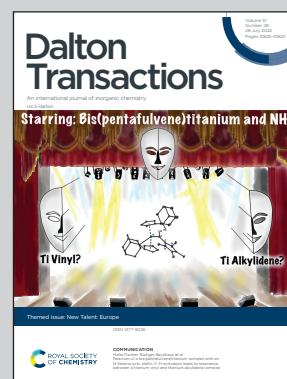


Showcasing research from Dr Erli Lu's laboratory,
Chemistry-School of Natural and Environmental Sciences,
Newcastle University, UK.

A monomeric (trimethylsilyl)methyl lithium complex:
synthesis, structure, decomposition and preliminary
reactivity studies

Organolithium reagents play vital roles in synthetic chemistry. However, surprisingly, their structure–reactivity relationship is still poorly understood. Organolithium monomers are considered as the key to providing such knowledge, but they are challenging synthetic targets. In this work, we report a rare organolithium monomer and its reactivity studies.

As featured in:



See Thomas J. Penfold, Erli Lu *et al.*,
Dalton Trans., 2022, **51**, 10707.

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A monomeric (trimethylsilyl)methyl lithium complex: synthesis, structure, decomposition and preliminary reactivity studies†

Nathan Davison, Paul G. Waddell, Casey Dixon, Corinne Wills, Thomas J. Penfold*
and Erli Lu *

Monomeric organolithium (LiR) complexes could provide enhanced Li–C bond reactivity and suggest mechanisms for a plethora of LiR-mediated reactions. They are highly sought-after but remain a synthetic challenge for organometallic chemists. In this work, we report the synthesis and characterisation of a monomeric (trimethylsilyl)methyl lithium complex, namely $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\kappa^3\text{-}N,N',N''\text{-Me}^6\text{Tren})]$ (**1**), where Me^6Tren is a tetradentate neutral amine ligand. The structure of **1** was comprehensively examined by single-crystal X-ray diffraction, variable temperature NMR spectroscopy and electron absorption spectroscopy. Complex **1** decomposes via ligand C–H and C–N activations to produce a Li amide complex **2**. Preliminary reactivity studies of **1** reveal C=O insertion and C–H activation reaction patterns.

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Introduction

Organolithium complexes (LiR; where R is alkyl or aryl) have been an indispensable tool for synthetic chemists for over a century.^{1–3} In solutions, LiR complexes form aggregates *via* bridging Li–C bonds;⁴ although this bridging behaviour stabilises the highly polar Li–C bond, it also diminishes the Li–C bond reactivity. Consequently, from the perspective of reactivity, a monomeric LiR complex with a terminal unsupported Li–C bond ought to be the most reactive version of an organolithium reagent, although exceptions have been reported.⁵ From the structure–reactivity relationship point of view, the LiR monomer is hypothesised as a key intermediate in the mechanisms of LiR-mediated reactions.⁴ Isolating the LiR monomers and studying their structure and reactivity would shed light on the mechanisms of the ubiquitous LiR-mediated reactions. For these reasons, synthetic organometallic chemists have devoted decades of effort to synthesising the LiR monomers and studying their structures and reactivity.^{5–18}

The most successful strategy to break the LiR aggregates and isolate LiR monomers is to employ neutral multidentate amines,⁴ which coordinate to the Li and kinetically stabilise the LiR monomers. Since the 1980s, this multidentate amine

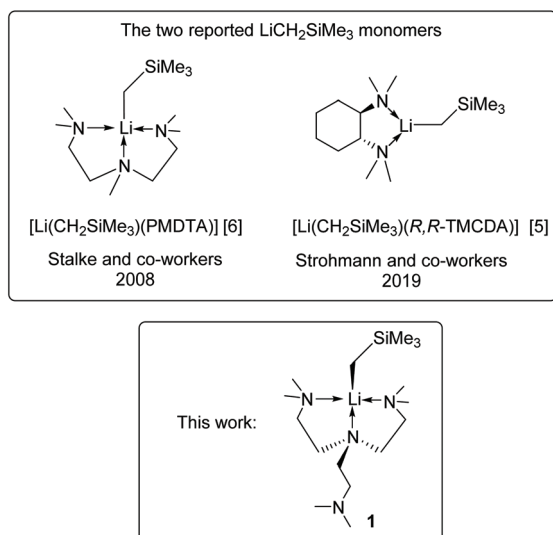
strategy has been successfully implemented by several groups to isolate a series of $[\text{Li}(\text{R})(\text{L})]$ monomers (L = multi-amine ligands; R = CH_2SiMe_3 ,^{5,6} $\text{CH}(\text{SiMe}_3)_2$,^{7,8} $t\text{Bu}$,^{9,10} $s\text{Bu}$,⁸ $i\text{Pr}$,¹¹ benzyl^{12–17}). Recently, we reported the first methyllithium monomer $[\text{Li}(\text{CH}_3)(\text{DETAN})]$, enabled by a bespoke hexa-dentate ligand $[\{\text{Et}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)\}_3]$, namely N,N',N'' -tris-(2-*N*-diethylaminoethyl)-1,4,7-triAza-cycloNonane (DETAN).¹⁸

Despite the successes, the LiR monomer is still a challenging synthetic target: most LiR monomers are highly reactive and decompose at room temperature. This is reflected by their scarcity. For instance, (trimethylsilyl)methyl lithium ($\text{LiCH}_2\text{SiMe}_3$) is a widely used and commercially available reagent. Still, there are only two reports of its monomers^{5,6} (Scheme 1), with a tridentate and a bidentate amine ligand, respectively. Developing more LiR monomers is desirable to establish a comprehensive structure–reactivity relationship.

Another knowledge gap in this field is the decomposition pathways of the LiR monomers. In most cases, the monomeric Li–C bond is reactive and could decompose at or above room temperature. However, their decomposition pathways and mechanisms are poorly understood. Our recent MeLi monomer work postulated two decomposition pathways, involving N–C/C–H cleavages and de-coordination, respectively.¹⁸ However, due to the low solubility/stability of the decomposition products, these hypothesised decomposition pathways were lacking in direct evidence; in particular, no Li-containing decomposition products were isolated and characterised. An in-depth understanding of the LiR monomer decomposition mechanisms would help synthetic chemists to design their

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(1–3) and 2120419 (4). For ESI and crystallographic data in CIF or other elec-
tronic format see DOI: 10.1039/d1dt03532k



Scheme 1 The two reported $\text{LiCH}_2\text{SiMe}_3$ monomers^{5,6} and the new $\text{LiCH}_2\text{SiMe}_3$ monomer in this work.

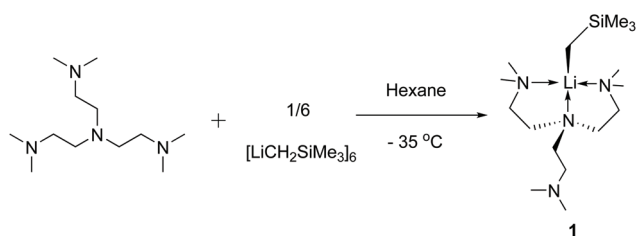
reactions by employing appropriate ligands/conditions to suppress undesired side reactions and tune the selectivity of products.

In this work, we report the synthesis and characterisation of a new $\text{LiCH}_2\text{SiMe}_3$ monomer, $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{Me}^6\text{Tren})]$ (**1**), including SCXRD and comprehensive NMR studies. Complex **1**'s decomposition and preliminary reactivity studies are also reported herein.

Results and discussion

Synthesis and characterisation of $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{Me}^6\text{Tren})]$ (**1**)

Complex **1** was synthesised *via* a reaction between the hexamer $[\text{LiCH}_2\text{SiMe}_3]_6$ and Me^6Tren in hexanes at -35°C (Scheme 2). **1** is readily soluble in hexanes, and was isolated as a white crystalline solid in 81% yield by crystallisation from concentrated hexanes solution at -35°C . **1** is stable in hexanes and benzene/ d_6 -benzene at room temperature for several hours, with observable but slow decomposition (*vide infra*). However, dissolving in toluene at room temperature leads to an immediate colour change from colourless to red, indicating chemical transformation (*vide infra*).



Scheme 2 Synthesis of the $\text{LiCH}_2\text{SiMe}_3$ monomer $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\kappa^3\text{-N,N',N''-Me}^6\text{Tren})]$ (**1**).

The ^1H NMR spectrum in C_6D_6 of **1** at 25°C exhibits two singlets at -1.61 ppm and 0.51 ppm, with an integration of 2 and 9 protons, respectively. The singlet at -1.61 ppm (2Hs) is assigned to be the two protons on the lithiated methyl $\text{LiCH}_2\text{SiMe}_3$, while the 0.51 ppm singlet (9Hs) is the protons on the trimethylsilyl $\text{LiCH}_2\text{SiMe}_3$. The NMe_2 and NCH_2CH_2 protons exhibit as a set of broad peaks in the range of 2.3 to 1.9 ppm, with a distinguishable shape and intense signal for the NMe_2 functional groups, and broader signals for the NCH_2CH_2 groups. These ^1H signals at room temperature indicate a C_{3v} symmetric coordination mode of the Me^6Tren ligand, corroborated by a single ^{13}C environment of $-\text{NMe}_2$ groups in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The symmetric NMR signals intuitively suggest that all the three sidearms of the Me^6Tren ligand coordinate to the Li, forming a C_{3v} structure. This is contrary to **1**'s solid-state structure from the single-crystal X-ray diffraction (SCXRD) study (*vide infra*). The ^7Li NMR spectrum of **1** features a singlet at 2.11 ppm.

Single crystals of **1** suitable for SCXRD study were grown from concentrated hexanes solutions at -35°C . The single-crystal diffraction data was collected at -123°C . The solid-state molecular structure of **1** is displayed in Fig. 1 with key bond lengths and angles listed in the caption. The Li–C bond length in **1** ($2.122(5)$ Å) is close to the $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{PMDTA})]$ ($2.113(2)$ Å⁶) but significantly longer than the $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{TMCDA})]$ ($2.069(3)$ Å⁵). In the solid-state structure, **1** features a partially coordinated Me^6Tren ligand in a $\kappa^3\text{-N,N',N''}$ coordination mode: two of the three sidearms coordinate to Li, while the other is coordination free. The coordination geometry around Li1 is best described as a distorted triangular pyramid: Li1, N2, N3 and C13 are nearly co-planar ($\angle\text{C13-Li1-N2} + \angle\text{C13-Li1-N3} + \angle\text{N3-Li1-N2} = 354.6^\circ$). It is intriguing that the $-\text{CH}_2\text{SiMe}_3$ alkyl group locates in a *cis*-position to the coordination-free sidearm with a $\angle\text{C13-Li1-N1}$ angle of $121.3(2)^\circ$. Similar *cis*-geometry was observed in the $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{PMDTA})]$ complex reported by Stalke and co-workers, explained by weak intermolecular interactions (intermolecular

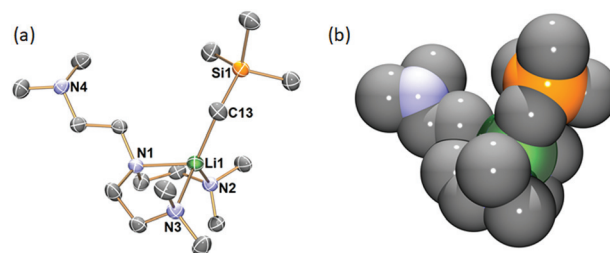


Fig. 1 (a) X-ray crystal structure of $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\kappa^3\text{-N,N',N''-Me}^6\text{Tren})]$ (**1**) at -123°C with 50% probability ellipsoids. Hydrogen atoms are omitted and only the disordered component with the highest occupancy is shown for clarity. (b) Space filling presentation of **1** (grey: carbon; green: lithium; blue: nitrogen; coral: silicon). The selected bond distances (Å) and angles ($^\circ$) are: Li1–C13 $2.122(5)$; Li1–N1 $2.177(4)$; Li1–N2 $2.167(4)$; Li1–N3 $2.189(4)$; Si1–C13–Li1 $129.77(17)$; C13–Li1–N1 $121.3(2)$; C13–Li1–N2 $127.4(2)$; C13–Li1–N3 $112.91(19)$; N2–Li1–N3 $114.29(19)$.



$\text{Li}\cdots\text{CH}_2\text{SiMe}_3$ distance: 4.6 Å).⁶ However, we could not find such weak intermolecular interactions in **1**'s lattice.

To study if the $\kappa^3\text{-N,N',N''}$ coordination mode of **1** persists in solution, where such weak intermolecular interactions in crystal lattice would be cancelled, we conducted a variable-temperature (VT) ^1H NMR study of **1** in $\text{d}_8\text{-THF}$. The ^1H NMR spectrum of **1** at room temperature, apparently, suggests that all the three sidearms are chemically equivalent (Fig. 2 25 °C), indicated by only one set of the NMe_2 (Fig. 2 25 °C, b) and the NCH_2CH_2 (Fig. 2 25 °C, a) signals. However, when cooled to -103 °C, the signals split into two sets with a 2 : 1 integral ratio (Fig. 2 -103 °C), which matches the solid-state structure in the $\kappa^3\text{-N,N',N''}$ coordination mode. Therefore, we conclude that the $\kappa^3\text{-N,N',N''}$ coordination mode persists in solution. The room temperature ^1H NMR spectrum probably results from a fast fluxional coordination and de-coordination process at the NMR time scale. The decoordination of one sidearm in the Me^6Tren ligand has been observed with bulky Li-substituents, such as $[\text{2-}^t\text{Bu-C}_5\text{H}_5\text{N}]^{-1}$ (ref. 19) or $[\text{N}(\text{SiMe}_3)_2]^{-1}$.²⁰ The $-\text{CH}_2\text{SiMe}_3$ alkyl group in **1** could rotate around the Li–C bond and features a big dynamic radius (Fig. 1(b) space-filling model), it could therefore push one of the three sidearms away and forms the observed structure of **1**.

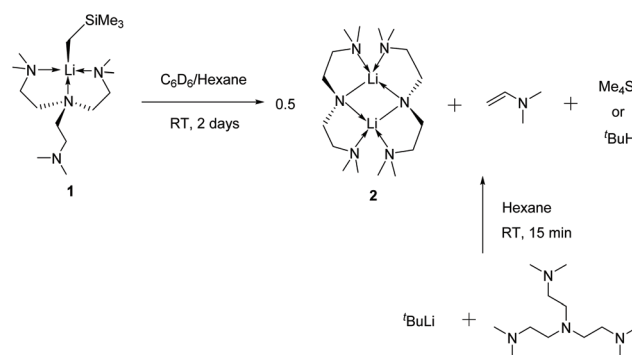
The UV/Vis spectra of organolithium complexes has been studied in the 1960s–1980s,^{21–29} in the context of photoexcited states of organic anions.³⁰ However, in more recent works, the UV/Vis spectra are missing for the isolated monomeric lithium alkyl complexes.^{4–11} We examined the UV/Vis spectrum of **1** in hexanes, and made a comparison with the parent $[\text{LiCH}_2\text{SiMe}_3]_6$ hexamer and the Me^6Tren ligand (Fig. S11†). Both complex **1** and the Me^6Tren ligand feature a strong ($>6000 \text{ L mol}^{-1} \text{ cm}^{-1}$) absorption in the deep UV region ($\sim 220 \text{ nm}$). These absorptions are probably due to electron density transitions based on the saturated amine (Me^6Tren),³¹ but a possible Li–C $\rightarrow$ N–CH₃/Si–CH₃ charge transfer was also identified by time-dependent DFT (TD-DFT) calculations

(Fig. S12†). The strong UV absorption of the Me^6Tren ligand highlights that, precaution must be taken when interpreting the UV spectrum of complexes bearing such saturated amine ligands, where the ligand-based absorption could interfere and overlap with other charge transfers.

Decomposition of $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{Me}^6\text{Tren})]$ (**1**)

Complex **1** decomposes in C_6D_6 or hexanes solutions over two days. *In situ* $^1\text{H}/^7\text{Li}$ NMR studies reveal the production of vinyl dimethyl amine ($\text{H}_2\text{C}=\text{CH}-\text{NMe}_2$), Me_4Si and a Li-containing product $[\text{Li}(\mu\text{-N-}\kappa^2\text{-N,N'-N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2)_2$ (**2**) (Scheme 3). Similar decomposition was also observed for a reaction between $^t\text{BuLi}$ and Me^6Tren (Scheme 3) (see ESI†), which is faster (completed in 15 minutes at room temperature), in line with the stronger Brønsted basicity of $^t\text{BuLi}$ compared to $\text{LiCH}_2\text{SiMe}_3$. The solid-state structure of **2** was elucidated by SCXRD (Fig. 3), and is the same as reported by Klumpp and co-workers *via* a different synthetic route.³²

The production of **2** occurs *via* C–H and N–C bond cleavages of one sidearm of the Me^6Tren ligand. Similar decomposition pathways were postulated by us for a MeLi monomer,¹⁸ and by Chen and co-workers for a scandium imido complex.³³ By ^1H NMR monitoring of **1**'s decomposition for 2 days, it is



Scheme 3 Decomposition of **1** to form **2**, vinyl dimethyl amine and tetramethylsilane.

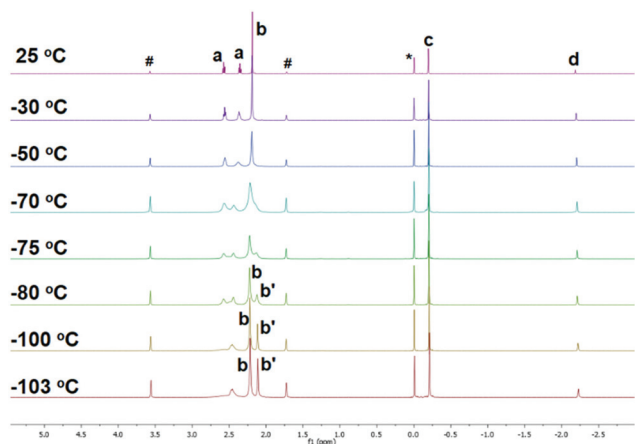


Fig. 2 Variable temperature (VT) ^1H NMR of complex **1** in $\text{d}_8\text{-THF}$. (a): NCH_2CH_2 ; b and b': NMe_2 ; c: CH_2SiMe_3 ; d: CH_2SiMe_3 ; *: Me_4Si ; #: $\text{d}_8\text{-THF}$.

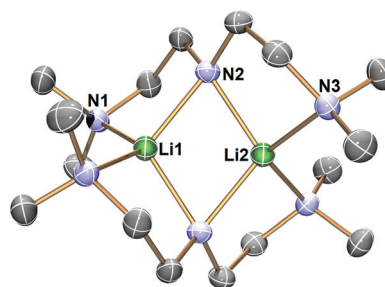


Fig. 3 X-ray crystal structure of $[\text{Li}(\mu\text{-N-}\kappa^2\text{-N,N'-N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2)_2$ (**2**) at -123 °C with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. The selected bond distances (Å) and angles (°) are: Li1–N1 2.0903(18); Li1–N2 2.0286(19); Li2–N2 2.0192(18); Li2–N3 2.0864(17); Li1⋯Li2 2.376(4); Li1–N2–Li2 71.89(9).



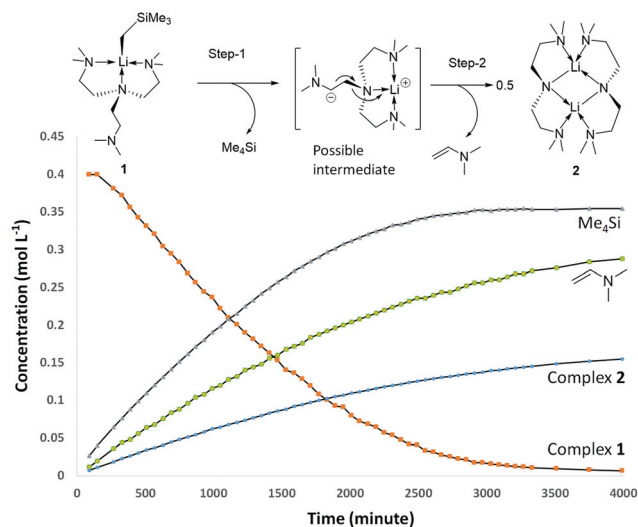
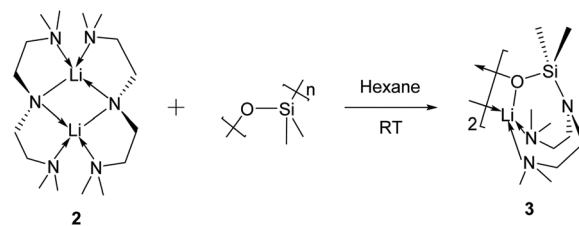


Fig. 4 Substrate concentration decay curve and products concentration increase curves for **1**'s decomposition at 25 °C (initial concentration $[1]_0 = 0.4 \text{ mol L}^{-1}$). The solid lines are for visual guidance only. The Me_4Si and vinyl dimethyl amine are volatiles, therefore their concentrations did not arrive the theoretic value of 0.4 mol L^{-1} upon **1**'s full decomposition. The postulated stepwise decomposition mechanism is presented at the top.

obvious that **1** is involved in the rate-determining step of the decomposition, as suggested by a non-linear concentration-time decay ($[1]-t$) curve (Fig. 4 orange). More information is revealed by examining the products concentration increase curves (Fig. 4 blue, green and lilac). It is evident that Me_4Si 's concentration increases more rapidly at the initial stage of the reaction, with a steeper $[c]-t$ curve from 0 to *circa* 2000 minutes. The vinyl dimethyl amine and complex **2** follow a similar increasing pattern, considering that **2** is a dimer therefore, its concentration is halved. From the data, we postulate that the decomposition of **1** follows a stepwise mechanism (Fig. 4). The step-1 is the deprotonation of the coordination-free sidearm, producing Me_4Si and an intermediate, which was not isolated. The postulated intermediate was not observed in the ^1H NMR spectra, possibly because its signals overlap with the Me^6Tren ligand signals of **1**. However, the ^1H NMR signals of the postulated intermediate do not interfere with the signals used for acquiring integrals and concentrations, namely -1.66 ppm (s, 2H, $\text{Li}-\text{CH}_2$ for **1**); 0.00 ppm (s, 12H for SiMe_4); 3.81 ppm (d, 1H, for $\text{Me}_2\text{N}-\text{CH}=\text{CH}_2$); 3.44 ppm (m, br, 8H, $\text{NCH}_2\text{CH}_2\text{N}$ for **2**). Therefore, the accuracies of the integrals and concentrations are not compromised. Step-2 was a combination of rearrangement, cleavage of an N-C bond, formation of C=C and Li-N bonds, and dimerisation into complex **2**.

The Li-N^{amide} bonds in complex **2** are reactive. **2** reacts with silicone grease to produce $[\text{Li}\{\kappa^3\text{-O}, N, N'\text{-OSiMe}_2\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2\}_2]$ (**3**) (Scheme 4) (see ESI† for details). **3** was characterised by SCXRD (Fig. 5). Silicone grease acts as a serendipitous reactant in organometallic chemistry, which could be activated by highly reactive species.^{34–36} A noticeable structural



Scheme 4 Reaction between silicone grease and complex **2**.

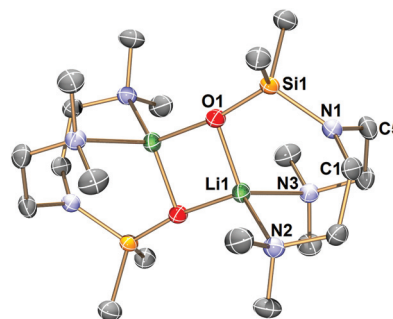


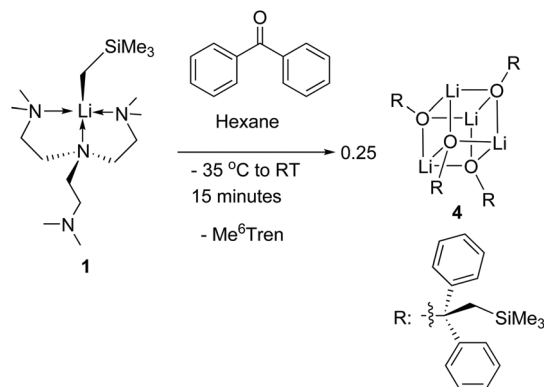
Fig. 5 X-ray crystal structure of $[\text{Li}\{\kappa^3\text{-O}, N, N'\text{-OSiMe}_2\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2\}_2]$ (**3**) at -123°C with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. The selected bond distances (Å) and angles ($^\circ$) are: $\text{Li1}-\text{O1}$ 1.851(3); $\text{Li1}-\text{N2}$ 2.213; $\text{Li1}-\text{N3}$ 2.232; $\text{Si1}-\text{O1}$ 1.5794(13); $\text{Si1}-\text{N1}$ 1.7439(16); $\text{N1}-\text{C1}$ 1.454(2); $\text{N1}-\text{C5}$ 1.454(2); $\text{Si1}-\text{N1}-\text{C5}$ 121.65(12); $\text{Si1}-\text{N1}-\text{C1}$ 123.14(12); $\text{C1}-\text{N1}-\text{C5}$ 115.21(15).

feature of **3** is the planar tertiary amine fragment (N1) ($\sum\angle = 360^\circ$). A planar amine is hypothesised to be the transition state of amine pyramidal inversion,³⁷ which plays an essential role in *N*-nucleophilic reaction, *N*-substitution and N_2 -to- NH_3 conversion (Haber-Bosch process). Therefore, a planar amine is sought-after by organic chemists as a model compound to understand the reaction mechanisms.³⁸ The formation of a planar amine in **3** is probably due to hyperconjugation between the N lone pair and the silicon atom.³⁹ In spite of the serendipitous formation of **3**, deliberate reactions between **2** and an excess amount of grease did not increase the yield of **3**, which is always a minor by-product. We conducted the stoichiometric reaction between **2** and one equivalent of hexamethyldisiloxane ($\text{Me}_3\text{Si}-\text{O}-\text{SiMe}_3$, HMDSO), which is a small molecular analogue of silicone grease, in C_6D_6 in a grease-free environment (Teflon J. Young tap NMR tube). The reaction was monitored by ^1H and ^7Li NMR spectra: we observed no reaction at room temperature (48 hours) or 60°C (48 hours).

Preliminary reactivity studies of $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{Me}^6\text{Tren})]$ (**1**)

Complex **1** reacts with benzophenone to produce an alkylolithium complex $[\text{Li}(\text{OC}(\text{CH}_2\text{SiMe}_3)\text{Ph}_2)]_4$ (**4**) as a tetramer (Scheme 5). The SCXRD structure of **4** is exhibited in Fig. 6. **4** is the result of C=O bond insertion into the Li-C bond and Me^6Tren ligand de-coordination. The free Me^6Tren ligand was observed in the ^1H NMR spectrum of the crude reaction products (see ESI†). **4** features a cubic Li_4O_4 core structure.





Scheme 5 The reaction between **1** and benzophenone to produce **4**.

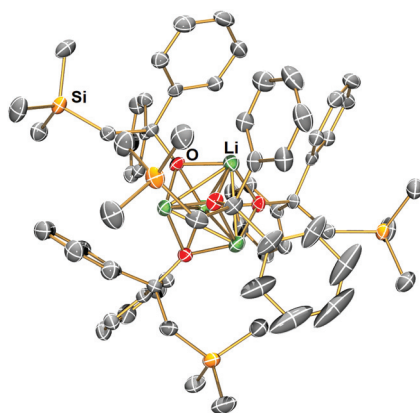
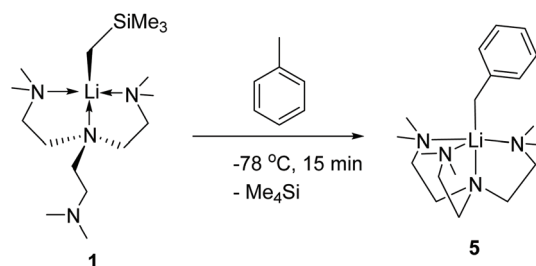


Fig. 6 X-ray crystal structure of $[\text{Li}(\text{OC}(\text{CH}_2\text{SiMe}_3)\text{Ph}_2)]_4$ (**4**) at -123°C with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.



Scheme 6 C sp^3 -H activation of toluene by the $\text{LiCH}_2\text{SiMe}_3$ monomer **1** to produce **5**.

Complex **1** readily reacts with toluene to produce $[\text{Li}(\text{CH}_2\text{Ph})(\text{Me}^6\text{Tren})]$ (**5**) (Scheme 6). The reaction was characteristic of its colour changing: upon adding toluene, the solution turned from colourless (**1**) to red within 15 minutes at -78°C . Complex **5** was identified by comparing its ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra with the authenticated spectra reported by Mulvey and co-workers in 2011.¹² In contrast with the facile C-H activation mediated by the monomer **1**, the parent $[\text{LiCH}_2\text{SiMe}_3]_6$ hexamer only reacts sluggishly with toluene at

room temperature. We attribute the enhanced C-H activation reactivity of **1** to its monomeric structure. Similar facile toluene C-H activation, induced by a $\text{LiCH}_2\text{SiMe}_3$ dimer $[\{\text{Me}_2\text{N}(\text{CH}_2)_2\text{OMe}\} \cdot (\text{LiCH}_2\text{SiMe}_3)]_2$, was reported by Stalke and co-workers.¹⁴

Conclusions

This work reports the synthesis and characterisation of a monomeric (trimethylsilyl)methyl lithium complex **1**, which is only the third member of its class. **1**'s coordination mode was elucidated by SCXRD and variable-temperature NMR spectroscopy. **1** exhibits moderate thermal stability. Its decomposition occurs *via* stepwise C-H and N-C bond cleavage, leading to a lithium amide complex **2**. The resultant lithium amide complex **2** features a highly reactive $\text{Li-N}^{\text{amide}}$ bond, which undergoes an insertion reaction with silicone grease to produce a silyl-oxo complex **3** with a planar tertiary amine centre. Preliminary reactivity studies reveals enhanced C-H activation reactivity towards the C-H bond in toluene compared to its parent $[\text{LiR}]_6$ hexamer, as well as benzophenone's C=O insertion into the Li-C bond.

This work adds a new member to the small class of structurally characterised monomeric organolithium complexes. The decomposition and reactivity studies could provide insights for organic/organometallic synthetic chemists to assist their design of reaction conditions, to achieve a fine balance between enhanced reactivity and stability.

Experimental

General procedures

All manipulations were carried out using Schlenk techniques, or a Vigor glovebox equipped with a -35°C freezer and a cold well, under an atmosphere of dry argon. Solvents were dried by sodium metal and sodium/potassium alloy, then distilled under vacuum. All solvents were stored in the glovebox over potassium mirrors except for ethers, which were stored over activated 4 Å molecular sieves. The deuterated solvents were distilled from sodium/potassium alloy, degassed by three freeze-pump-thaw cycles and stored under argon. (Trimethylsilyl)methyl lithium ($\text{LiCH}_2\text{SiMe}_3$) was prepared from refluxing chloromethyl trimethyl silane ($\text{ClCH}_2\text{SiMe}_3$) and excess lithium metal in hexanes.⁴⁰ Tris[2-(dimethylamino)ethyl]amine (Me^6Tren) was purchased from Merck and dried over 4 Å molecular sieves prior to use.

^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^7Li NMR spectra were recorded on a Bruker 300 Avance III spectrometer operating at 300.13, 75.48 and 116.64 MHz respectively. Variable temperature and kinetic ^1H NMR experiments were carried out on a Bruker 500 Avance III HD spectrometer operating at 500.15 MHz. Chemical shifts are quoted in ppm and are relative to SiMe_4 (^1H and ^{13}C) or external 0.1 M LiCl in D_2O (^7Li). The UV/Vis absorption spectrum of **1** was recorded on a Shimadzu UV-1800 spectrometer in the



wavelength range of 190 to 1100 nm using a 10 mm path-length J. Young tap quartz cuvette.

Synthesis of $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\kappa^3\text{-N,N',N''-Me}_6\text{Tren})]$ (1)

$\text{LiCH}_2\text{SiMe}_3$ (0.0942 g, 1 mmol) was dissolved in hexanes (1 ml). Me_6Tren (0.230 g, 1 mmol) was dissolved in hexanes (1 ml) and cooled to -35°C . The solution of $\text{LiCH}_2\text{SiMe}_3$ was added to the solution of Me_6Tren in one portion. The resulting pale yellow solution was left at room temperature for 5 minutes, before being placed in a -35°C freezer. After 3 days, colourless crystals suitable for single crystal X-ray diffraction resulted. The mother liquor was removed and the solid was dried *in vacuo* (81% yield). ^1H NMR (300 MHz, d_6 -benzene, 25°C): δ (ppm) 2.20–1.90 (br, 12H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.05 (s, 18H, $\text{N}(\text{CH}_3)_2$), 0.51 (s, 9H, $\text{Si}(\text{CH}_3)_3$), -1.61 (s, 2H, LiCH_2Si). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, d_6 -benzene, 25°C): δ (ppm) 57.7 ($\text{NCH}_2\text{CH}_2\text{N}$), 52.1 ($\text{NCH}_2\text{CH}_2\text{N}$), 45.9 ($\text{N}(\text{CH}_3)_2$), 7.1 ($\text{Si}(\text{CH}_3)_3$), -4.8 (LiCH_2Si). ^7Li NMR (117 MHz, d_6 -benzene, 25°C): δ (ppm) 2.10.

Synthesis of $[\text{Li}(\mu\text{-N-}\kappa^2\text{-N,N'-N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2)_2]$ (2) and $[\text{Li}\{\kappa^3\text{-O,N,N'-OSiMe}_2\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2\}_2]$ (3)

$\text{LiCH}_2\text{SiMe}_3$ (0.188 g, 2 mmol) was partially dissolved in hexanes (1 ml). Me_6Tren (0.461 g, 2 mmol) was dissolved in hexanes (1 ml). The solution of Me_6Tren was added in one-portion to the $\text{LiCH}_2\text{SiMe}_3$ solution. The resulting pale yellow solution was left at room temperature for 3 days. The volatiles were removed *in vacuo*. A pale yellow solid resulted. The solid was dissolved in hexanes (2 ml) and the solution was filtered then concentrated to 0.5 ml. The solution was placed in a -35°C freezer. After 3 days, an off-white crystalline solid resulted. The mother liquor was removed and the solid was dried *in vacuo* (60% yield).

Alternative synthesis of 2

$t\text{BuLi}$ (0.128 g, 2 mmol) was partially dissolved in hexanes (1 ml). Me_6Tren (0.461 g, 2 mmol) was dissolved in hexanes (1 ml). The solution of Me_6Tren was added in one-portion to the $t\text{BuLi}$ solution at room temperature. Immediately, a bright orange solution resulted that turned very pale within 1 minute. The solution was left at room temperature for 1 hour. The volatiles were removed *in vacuo*. A pale yellow solid resulted. The solid was dissolved in hexanes (2 ml) and the solution was filtered then concentrated to 0.5 ml. The solution was placed in a -35°C freezer. After 3 days, an off-white crystalline solid resulted. The mother liquor was removed and the solid was dried *in vacuo* (57% yield). Single crystals of 2 suitable for single crystals X-ray diffraction were grown from dissolving the crude solid in hexanes (2 ml). The solution was filtered and placed in a -35°C freezer. After 3 days, large colourless blocks resulted. ^1H NMR (300 MHz, d_6 -benzene, 25°C): δ (ppm) 3.44 (m, br, 8H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.09 (m, br, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.25 (m, br, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.04 (s, br, 24H, NCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, d_6 -benzene, 25°C): δ (ppm) 63.8 ($\text{NCH}_2\text{CH}_2\text{N}$), 58.3 ($\text{NCH}_2\text{CH}_2\text{N}$), 47.4 (br, $\text{N}(\text{CH}_3)_2$), 41.9 (br, $\text{N}(\text{CH}_3)_2$). ^7Li NMR (117 MHz, d_6 -benzene, 25°C): δ (ppm) 1.51.

Synthesis of $[\text{Li}\{\kappa^3\text{-O,N,N'-OSiMe}_2\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2\}_2]$ (3)

3 was produced as a minor side product from the reaction producing 2 when silicon grease was applied. 3 co-crystallises with 2 with similar crystal habits: both are pale yellow prismatic crystals. Due to their similar solubility in common inorganic solvents and crystallisation behaviours, it is impossible to isolate 3 from 2 by fractional crystallisation. The NMR spectra (^1H , ^7Li and ^{13}C) of the mixture suggest that 2 is the dominant ingredient with no observable 3. Therefore, we postulate that 3 is a minor serendipitous product from 2 reacting with silicon grease. Deliberate treatment of 2 with excess amount of silicon grease did not result in the increased yield of 3. In a grease-free environment (J. Young tap NMR tube), complex 2 does not react with one equivalent of hexamethyldisiloxane (HMDSO) in C_6D_6 solution at room temperature or 60°C within 48 hours.

Synthesis of $[\text{Li}(\text{OC}(\text{CH}_2\text{SiMe}_3)\text{Ph}_2)]_4$ (4)

At -35°C , a solution of 1 (0.649 g, 2 mmol) in 5 mL of hexanes was added to a solution of benzophenone (0.364 g, 2 mmol) in 5 mL of hexanes. The solution was allowed to stay at room temperature for 15 minutes, then all volatiles were removed under vacuum, to afford a white solid, which is a mixture of 4 and Me_6Tren (see the ^1H NMR spectrum, Fig. S7 in ESI†). Attempts were made to remove the Me_6Tren by washing the mixture with hexanes. However, the solubilities of 4 and Me_6Tren in hexanes are similar, even at -35°C . Due to the persisting presence of Me_6Tren , a meaningful yield of 4 is not available. However, the ^1H and ^7Li NMR spectra of the mixture suggest a clean conversion. ^1H NMR (300 MHz, d_6 -benzene, 25°C): δ (ppm) 7.38–7.27 (m, 2H, ArH), 7.22–7.15 (m, 3H, ArH), 1.49 (s, 2H, $\text{OC}(\text{Ph}_2)(\text{CH}_2\text{SiMe}_3)$), -0.19 (s, 9H, $\text{OC}(\text{Ph}_2)(\text{CH}_2\text{SiMe}_3)$). ^7Li NMR (117 MHz, d_6 -benzene, 25°C): δ (ppm) 0.43.

Synthesis of $[\text{Li}(\text{CH}_2\text{Ph})(\text{Me}_6\text{Tren})]$ (5)

Toluene (30 ml) was added to 1 (3.8904 g, 12 mmol) at room temperature. Immediately, a bright yellow solution resulted, which was stirred for 1 hour. The resulting dark orange solution was placed in a -20°C freezer. After three days, yellow needle-shaped crystals resulted. The mother liquor was removed and the crystals dried *in vacuo* to afford 5 (77% yield). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra matched the spectra reported by Mulvey and co-workers in 2011.¹²

Author contributions

N. D. and E. L. designed and conducted the experiments, synthesised and characterised the complexes. P. G. W. collected, solved, refined and analysed the crystallographic data. C. D. and C. W. designed the VT NMR and kinetic NMR experiments, collected and analysed the data. T. J. P. conducted the calculations. E. L. conceptualised the central idea, supervised the work, analysed the data and wrote the manuscript with contributions from all the authors.



Conflicts of interest

There are no conflicts to declare.

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