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Salt metathesis *versus* protonolysis routes for the synthesis of silylamide Hauser base (R_2NMgX; X = halogen) and amido-Grignard (R_2NMgR) complexes†

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The preparation of silylamide Hauser base (R_2NMgX; X = halide) and amido-Grignard (R_2NMgR) complexes from simple Grignard reagents using $[K\{N(SiMe_2{}^tBu)_2\}]_n$, $[K\{N(SiMe_2{}^tBu)(Si^iPr_3)\}]_n$ and $[K\{N(Si^iPr_3)_2\}]_n$, and their parent silylamines, was explored. Both salt metathesis and protonolysis routes proved ineffective with allylmagnesium chloride as a starting material due to complex Schlenk equilibria, with $[Mg(N^{RR'})(\mu\text{-Cl})(THF)]_2$ ($N^{RR'}$ = $\{N(Si^tBuMe_2)_2\}^-$, **1**; $\{N(Si^tBuMe_2)(Si^iPr_3)\}^-$, **2**; $\{N(Si^iPr_3)_2\}^-$, **3**) and $[Mg\{N(Si^iPr_3)_2\}(\mu\text{-}C_3H_5)]_\infty$ (**4**) identified as minor products. In contrast, salt metathesis protocols using potassium silylamides and methylmagnesium iodide gave $[Mg(N^{RR'})(\mu\text{-}CH_3)]_2$ ($N^{RR'}$ = $\{N(Si^tBuMe_2)_2\}^-$, **7a**; $\{N(Si^tBuMe_2)(Si^iPr_3)\}^-$, **8**; $\{N(Si^iPr_3)_2\}^-$, **9**) and $[Mg\{N(Si^tBuMe_2)_2\}(CH_3)(DME)]$ (**7b**), with $[Mg\{N(Si^tBuMe_2)_2\}(\mu\text{-I})(THF)]_2$ (**10**) isolated as a side-product during the preparation of **7a**. Unusually, methylmagnesium iodide, di-*n*-butylmagnesium and **7–9** did not react with $HN^{RR'}$ under the conditions we employed. The synthesis of $[Na\{N(Si^tBuMe_2)_2\}(THF)]_2$ (**5a**) and $[Na\{N(Si^tBuMe_2)_2\}(DME)_2]$ (**5b**) from benzyl sodium and $HN(Si^tBuMe_2)_2$, and a solvent-free structure of $[K\{N(Si^tBuMe_2)_2\}]$ (**6**), are also reported. Complexes **1**, **5b**, **7a**, **7b**, **8**, **9** and **10** are fully characterised by single crystal XRD, multinuclear NMR and IR spectroscopy and elemental analysis, whereas complexes **2–4**, **5a** and **6** were identified by XRD only.

Introduction

Grignard reagents are widely utilised due to their facile preparation and broad applicability in organic synthesis,[1,2] yet in stark contrast the synthetic potential of Hauser bases, amido analogues with a N–Mg bond instead of a C–Mg bond, is only starting to be realised.[3] This is remarkable as N-donor groups are harder than C-donors and a wider variety of synthetic routes are available to access homo- and heteroleptic N-donor alkaline earth (Ae) complexes[4] than Ae organometallics.[1,4,5] Furthermore, highly reactive heteroleptic magnesium complexes with N-donors, such as alkyls and hydrides, are desirable and useful reagents, as they can undergo σ-bond metathesis or protonolysis with a number of substrates, thereby providing access to various synthetic heterofunctionalisations.[3f,6]

Sterically demanding N-donor ligands are commonly employed in Ae solution chemistry as they impede oligomerisation, complex Schlenk equilibria and other unwanted degradation pathways in ethereal solvents, particularly for the heavier Ae metals.[4,5] Bochmann and co-workers have shown that cationic magnesium complexes with bulky amido ligands such as $[Mg(N'')(Et_2O)_3][BAr^F]$ ($N'' = \{N(SiMe_3)_2\}^-$, $BAr^F = \{B(C_6F_5)_4\}^-$) can act as potent ring opening polymerisation catalysts,[7] an industrially significant process in which Chisholm and others have shown magnesium catalysts have great promise.[8] In seminal work by Jones, bulky N-donor ligands have been used to stabilise the first examples of structurally characterised Mg(I) complexes,[9] which have since proven their utility as selective one-electron reducing agents in a number of diverse transformations.[10]

Multidentate ligands such as guanidinates,[9–11] amidinates[12] and β-diketiminates[6,9–11,13,14] dominate N-donor magnesium chemistry and there are relatively few examples of monodentate complexes.[3b,e,9,15] In 1994 Power disclosed the first crystallographically authenticated Hauser base complex (R_2NMgX; X = halide),[16] $[Mg(N'')(\mu\text{-Cl})(Et_2O)]_2$,[17] which was originally prepared in 1972 by Wannagat *et al. via* a proto-

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nolysis reaction between HN″ and propylmagnesium chloride in diethyl ether.[18] To the best of our knowledge, the heavier congener $[Mg(N'')(\mu\text{-}Br)(Et_2O)]_2$,[19] together with the multidentate N-heterocyclic carbene (NHC) supported complexes, $[\{Mg(N'')\}\{Mg(Cl)\}(\mu\text{-}NHC^3)(\mu\text{-}Cl)]$ and $[\{Mg(N'')\}_2(\mu\text{-}NHC^3)(\mu\text{-}Cl)]$ (NHC^3 = $[N\{CH_2CH_2[NCHCHN(Mes)C]\}_2]$, Mes = 2,4,6-trimethylphenyl),[20] are the only other structurally characterised Hauser bases supported by silylated amides. Furthermore, expanding the search to halide Hauser bases of any monodentate amide yields only a handful more examples.[3a,21]

Amido-Grignard complexes, (R_2NMgR),[22] are better represented in the literature, but again there are few examples that contain silylamides.[23] Recently, Mulvey reported the dimeric complex, $[Mg(\mu\text{-}N'')(^tBu)]_2$,[24] and the NHC adduct, [Mg(N″)-(^{n}Bu)(IPr)] (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene);[25] however, in general heteroleptic magnesium silylamide complexes remain relatively rare. Amido-Grignard complexes are key intermediates in the formation of monoalkyl-bis(amido) group 1/group 2 bimetallic systems, which are typically formed directly from secondary amines in the presence of alkali metal and organomagnesium reagents.[26] Mulvey and co-workers have widely used such mixed metalation reactions with Hauser bases to prepare bimetallic systems with various degrees of complexity, ranging from simple heterobimetallic compounds to more elaborate architectures, *e.g.* inverse crown ethers.[26] Such systems have been employed in synergic deprotonative metalation chemistry, providing a powerful tool for a number of transformations, and this pioneering work has recently been reviewed by Knochel and co-workers.[3b,27] It follows that facile synthetic routes to a wider range of silylamide Hauser bases need to be developed in order to enable their future exploitation.

Recently, we have reported a series of bulky silylamines and we have utilised these starting materials to synthesise homo- and heteroleptic alkali metal[28] and *f*-block[28,29] complexes. These silylamides include the potassium salts $[\{K[\mu\text{-}N(SiMe_2Bu^t)_2]\}_2(C_7H_8)]_\infty$, $[K\{N(SiPr^i_3)(SiMe_2Bu^t)\}]_\infty$ and $[K\{N(SiPr^i_3)_2\}]_\infty$ (Fig. 1),[28] which are used as starting materials herein. Jones and co-workers have also developed synthetic routes to bulky silylamide s-block complexes that are useful ligand transfer agents.[30] In this paper, we report the reactions of bulky alkali metal silylamides and parent silylamines with commercially available Grignard reagents to afford a novel series of Hauser base and amido-Grignard complexes.

Results and discussion

Reactions of allylmagnesium chloride with silylamines and potassium silylamides

We found that the reactions of both potassium silylamides, $[K(N^{RR'})]$, and their parent silylamines with allylmagnesium chloride reproducibly gave mixtures of products and poor yields. Given that propylmagnesium chloride reacts with HN″ in diethyl ether to give $[Mg(N'')(\mu\text{-}Cl)(Et_2O)]_2$,[17,18] we added allylmagnesium chloride to THF solutions of $HN(Si^tBuMe_2)_2$, $HN(Si^tBuMe_2)(Si^iPr_3)$ and $HN(Si^iPr_3)_2$ (Scheme 1). Work-up of the respective reaction mixtures after 8 hours reproducibly gave crystals of the chloride Hauser bases, $[Mg(N^{RR'})(\mu\text{-}Cl)(THF)]_2$ ($N^{RR'}$ = $\{N(Si^tBuMe_2)_2\}^-$, **1**; $\{N(Si^tBuMe_2)(Si^iPr_3)\}^-$, **2**; $\{N(Si^iPr_3)_2\}^-$, **3**), which were minor components of intractable mixtures of products. Complexes **1–3** were structurally characterised (see below) but they could not be separated from the bulk material, which was shown to be a mixture of products by ^{1}H NMR spectroscopy. By increasing the reaction time to 10 days, we were able to improve the crystalline yield of complex **1** to 19%. Improved yields of **2–3** were not achieved by this method so further analysis of these complexes could not be obtained. On the other hand, the attempted salt metathesis reactions between allylmagnesium chloride and the corresponding potassium amides, $[K(N^{RR'})]$, did not give the expected amido-Grignard reagents, $[Mg(N^{RR'})(C_3H_5)]_n$, despite several attempts at optimising the reaction conditions. However, in the attempted preparation of $[Mg\{N(Si^iPr_3)_2\}(C_3H_5)]_n$ several crystals of complex **3** were identified together with a crystal of $[Mg\{N(Si^iPr_3)_2\}(\mu\text{-}C_3H_5)]_\infty$ (**4**) by single crystal XRD (see below). These observations suggested that complex Schlenk equilibria processes are taking place in these reaction mixtures.[1,31]

The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **1** in d_6-benzene are unremarkable and not shifted considerably from those reported for $[K\{N(SiMe_2{}^tBu)_2\}]_2$, although the $^{29}Si\{^1H\}$ NMR spectrum of **1** exhibits a single resonance (δ: −0.40 ppm) that is shielded in comparison to the related potassium complex (δ: −15.72 ppm).[29a] Microanalysis was performed multiple times on discrete crystalline samples of complex **1** and consistently low C values were obtained despite good agreement between measured and expected H and N content. This phenomenon was also encountered for complexes **5b**, **7b** and **9** (see below), even though the ^{1}H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra of these complexes exhibit only minor impurity signals

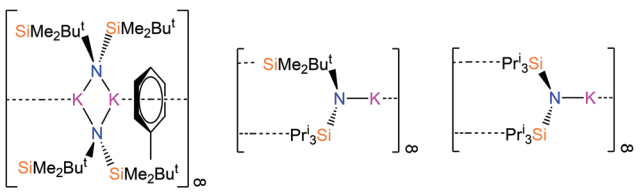
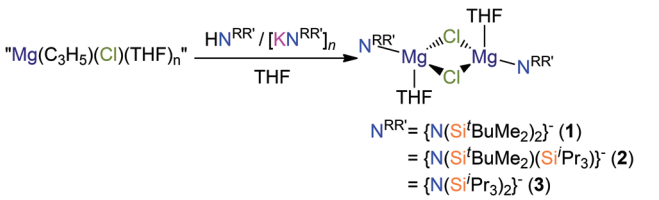


Fig. 1 The potassium silylamide complexes $[\{K[\mu\text{-}N(SiMe_2Bu^t)_2]\}_2(C_7H_8)]_\infty$, $[K\{N(SiPr^i_3)(SiMe_2Bu^t)\}]_\infty$ and $[K\{N(SiPr^i_3)_2\}]_\infty$.[28]



Scheme 1 Synthesis of complexes **1–3**.

(see ESI Fig. S1–S9†). Similar amounts of trace impurities were detected in the NMR spectra of other structurally characterised complexes reported herein, yet these have excellent agreement between predicted and observed microanalysis values. Therefore, we attribute these discrepancies to carbide formation, which has been cited previously as a recurring phenomenon in elemental analyses of silicon-rich complexes.[29a,32]

The identities of **1–4** were determined by single crystal XRD experiments (the molecular structure of **1** is depicted in Fig. 2; see ESI Fig. S10–S12† for the structures of **2–4**. Selected bond lengths and angles are compiled in Table 1). The dataset obtained for **4** is of poor quality as the crystals were weakly diffracting. Therefore no discussion of the geometric parameters of **4** is given here, but as the connectivity is clear-cut the structure is included for completeness. The magnesium centres in **4** are 3-coordinate, which is rare for magnesium amide structures and even more so for monodentate ligands.[21g,33] They are each bridged by two allyls, which generates an infinite 1D polymer comprised of two parallel-bridged chains. Complexes **1–3** exhibit similar motifs in the solid state, therefore only the structure of **1** is discussed for brevity. Complex **1** is dimeric with a central Mg_2Cl_2 rhomboid [Mg–Cl–Mg 92.15(6)°; Cl–Mg–Cl 87.85(6)°] and two 4-coordinate magnesium centres that are each bound by THF. The Mg–Cl [2.418(2) and 2.411(2) Å] and Mg–O [2.018(4) Å] distances are longer than those in $[Mg(N'')(\mu\text{-}Cl)(Et_2O)]_2$ [Mg–Cl 2.401(1) and 2.405(1) Å; Mg–O 2.000(3) Å],[17] which we attribute to the increased steric demands of $\{N(Si^tBuMe_2)_2\}^-$. Each magnesium coordination sphere of **1–3** is completed by two short Mg···C–H contacts [mean Mg···C 3.3485(8) Å (**1**); 3.192(4) Å (**2**); 3.267(6) Å (**3**)] and several short Mg···H distances [range Mg···H 2.71–2.75 Å (**1**); 2.63–3.02 Å (**2**); 2.56–2.67 Å (**3**)], where only one close Mg···C–H contact is present in $[Mg(N'')(\mu\text{-}Cl)(Et_2O)]_2$ [Mg···C 3.207(5) Å; mean Mg···H 3.02 Å].[17]

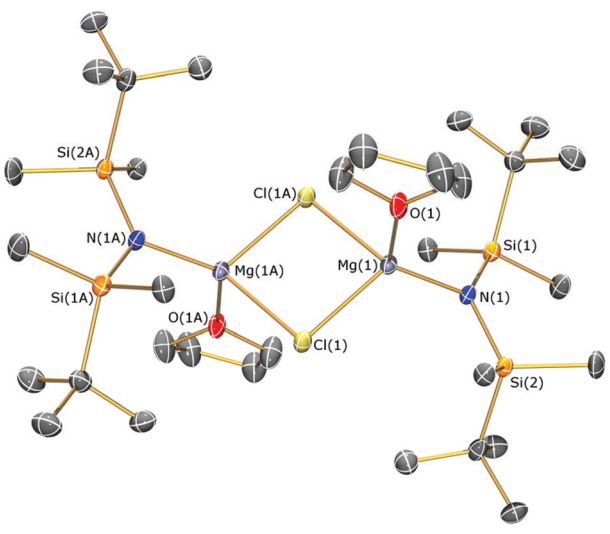


Fig. 2 Molecular structure of **1** with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity. Symmetry operation to generate equivalent atoms: $x - 1/2$, $-y - 1/2$, $z - 1/2$.

Reactions of allylmagnesium chloride with sodium silylamides

The reaction of sodium silylamides, $[Na(N^{RR'})]$, with allylmagnesium chloride did not give improved yields of the expected amido-Grignard complexes. During the course of these studies, we considered that sodium silylamides could be employed as alternative ligand transfer agents that may be less susceptible to byproduct formation. $HN(Si^tBuMe_2)_2$ was treated with an excess of sodium hydride in THF, but this deprotonation strategy was laborious and only 30% conversion was observed by ^1H NMR spectroscopy after 72 h reflux. In contrast, the deprotonation of $HN(Si^tBuMe_2)_2$ with benzyl sodium[34] in THF proceeded at room temperature to give $[Na\{N(Si^tBuMe_2)_2\}(THF)_n]$ as a dark oil following work-up (Scheme 2). Attempted crystallisation from pentane gave only several crystals of $[Na\{\mu\text{-}N(Si^tBuMe_2)_2\}(THF)]_2$ (**5a**); therefore the residue was treated with DME and recrystallised from pentane to afford $[Na\{N(Si^tBuMe_2)_2\}(DME)_2]$ (**5b**) as a beige solid in fair yield (65%). The NMR spectra of **5b** exhibit similar features to the potassium salt $[K\{N(SiMe_2{}^tBu)_2\}]_n$,[29a] although **5b** contains two additional resonances for coordinated DME in both the ^1H (δ = 2.80 and 2.88 ppm) and ^{13}C (δ = 59.21 and 71.30 ppm) NMR spectra. $^{29}Si\{^1H\}$ NMR spectroscopy shows a single resonance for **5b** (δ = −13.89 ppm; *cf.* $[K\{N(SiMe_2{}^tBu)_2\}]_n$ δ = −15.73 ppm).[29a]

The solid state structures of **5a** and **5b** are depicted in Fig. 3 and 4 respectively, and selected bond lengths and angles are shown in Table 1. Both complexes exhibit bond metrics typical of silylamide group 1 salts.[28,35] Complex **5a** is dimeric, with a central Na_2N_2 solvent-capped core and a mean Na–N distance of 2.4903(6) Å, which is longer than the mean $Na\text{–}N_{silylamide}$ bond lengths in $[Na\{\mu\text{-}N(SiMe_3)_2\}(THF)]_2$ [2.399(2) Å],[35a] $[\{Na[\mu\text{-}N(SiMe_3)_2]\}_2(\mu\text{-TMEDA})]_\infty$ (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) [2.4433(10) Å][35b] and $[Na\{\mu\text{-}N(SiMe_2Ph)_2\}(THF)]_2$ [2.440(4) Å].[35c] This can be attributed to the increased steric demands of the silylamide ligands in **5a**. The sodium coordination spheres in **5a** are completed by multiple short Na···C–H/Na···H distances [Na···C range 2.827(4)–3.028(4) Å; Na···H range 2.48–2.88 Å], in common with the potassium salt $[\{K[\mu\text{-}N(SiMe_2Bu^t)_2]\}_2(C_7H_8)]_\infty$, which exhibits analogous K···C–H/K···H contacts.[28] Complex **5b** is monomeric in the solid state, with a 5-coordinate sodium centre and exhibits shorter Na–N distances [2.350(3) Å] than those in **5a**, as would be expected for a terminally bound silylamide. The Na–O distances of **5b** [range 2.425(3)–2.567(4) Å] are within the range of those for Na–DME interactions in the literature [2.402(9)–2.658(7) Å].[36] To the best of our knowledge, $[Sm\{[N(Ar)C(CH_2)]_2CHC(N^iPr)_2Na(DME)_2\text{-}\kappa^3\text{-}N,N',N''\}\{N(SiMe_3)_2\}]$ (Ar = $C_6H_3{}^iPr_2$-2,6)[36d] is the only other literature example containing a terminal, DME-capped N–Na bond. As with **5a**, the coordination sphere of sodium in **5b** is also completed by short Na···H contacts [range Na···H 2.84–3.06 Å].

The reaction of **5b** with allylmagnesium chloride in THF was performed in an attempt to synthesise $[Mg\{N(SiMe_2Bu^t)_2\}$-

Table 1 Selected bond lengths (Å) and angles (°) for **1–3** and **5–10**

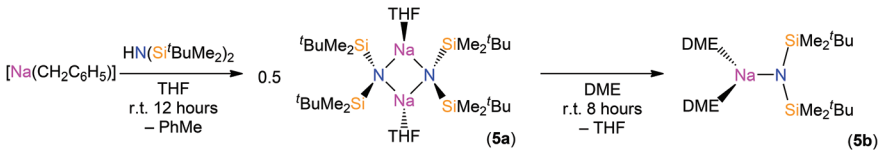
1			
N(1)–Mg(1)	1.998(4)	Mg(1)–Cl(1)	2.4178(17)
Mg(1)–Cl(1A)	2.411(2)	N(1)–Si(1)	1.722(4)
N(1)–Si(2)	1.711(4)	Mg(1)–O(1)	2.018(4)
Mg(1)···Mg(1A)	3.478(4)	Cl(1)–Mg(1)–Cl(1A)	87.85(6)
Mg(1)–Cl(1)–Mg(1A)	92.15(6)	N(1)–Mg(1)–O(1)	118.33(16)
N(1)–Mg(1)–Cl(1)	123.38(13)	N(1)–Mg(1)–Cl(1A)	125.18(14)
Si(1)–N(1)–Si(2)	126.8(2)		
2			
N(1)–Mg(1)	2.005(2)	Mg(1)–Cl(1)	2.4098(11)
Mg(1)–Cl(1A)	2.4073(11)	N(1)–Si(1)	1.717(2)
N(1)–Si(2)	1.707(2)	Mg(1)–O(1)	2.031(2)
Mg(1)···Mg(1A)	3.4324(16)	Cl(1)–Mg(1)–Cl(1A)	89.11(4)
Mg(1)–Cl(1)–Mg(1A)	90.89(4)	N(1)–Mg(1)–O(1)	122.77(9)
N(1)–Mg(1)–Cl(1)	125.72(7)	N(1)–Mg(1)–Cl(1A)	117.93(7)
Si(1)–N(1)–Si(2)	133.73(13)		
3			
N(1)–Mg(1)	2.028(3)	Mg(1)–Cl(1)	2.4169(14)
Mg(1)–Cl(1A)	2.4376(15)	N(1)–Si(1)	1.726(3)
N(1)–Si(2)	1.724(3)	Mg(1)–O(1)	2.046(3)
Mg(1)···Mg(1A)	3.504(3)	Cl(1)–Mg(1)–Cl(1A)	87.60(5)
Mg(1)–Cl(1)–Mg(1A)	92.40(5)	N(1)–Mg(1)–O(1)	121.27(13)
N(1)–Mg(1)–Cl(1)	121.88(10)	N(1)–Mg(1)–Cl(1A)	124.92(10)
Si(1)–N(1)–Si(2)	134.07(19)		
5a			
N(1)–Na(1)	2.472(3)	N(2)–Na(2)	2.499(3)
Na(1)–O(1)	2.333(3)	Na(2)–O(2)	2.361(3)
N(1)–Na(2)	2.502(3)	N(2)–Na(1)	2.485(3)
N(1)–Si(1)	1.697(3)	N(1)–Si(2)	1.692(3)
N(2)–Si(3)	1.692(3)	N(2)–Si(4)	1.698(3)
Na(1)···Na(2)	2.998(2)	Na(1)···C(5)	3.027(4)
Na(1)···C(8)	3.373(5)	Na(1)···C(18)	2.942(4)
Na(1)···C(22)	3.484(5)	Na(2)···C(2)	3.595(4)
Na(2)···C(12)	2.828(4)	Na(2)···C(14)	3.449(4)
Na(2)···C(24)	2.921(4)	N(1)–Na(1)–N(2)	106.61(10)
Na(1)–N(1)–Na(2)	73.95(8)	Si(1)–N(1)–Si(2)	126.85(16)
Si(3)–N(2)–Si(4)	126.28(16)	N(1)–Na(1)–O(1)	133.44(10)
N(2)–Na(2)–O(2)	134.31(10)		
5b			
N(1)–Na(1)	2.350(3)	Na(1)–O(1)	2.505(4)
Na(1)–O(2)	2.428(3)	Na(1)–O(3)	2.567(4)
Na(1)–O(4)	2.425(3)	N(1)–Si(1)	1.671(3)
N(1)–Si(2)	1.665(3)	Na(1)···C(2)	3.557(5)
Na(1)···C(5)	3.713(5)	Na(1)···C(8)	3.578(5)
Na(1)···C(12)	3.621(5)	Si(1)–N(1)–Si(2)	133.65(19)
6			
N(1)–K(1)	2.848(2)	N(1)–K(1A)	2.864(3)
K(1)···K(1A)	3.461(2)	N(1)–Si(1)	1.677(3)
N(1)–Si(2)	1.696(3)	K(1)···C(4A)	3.343(3)
K(1)···C(5B)	3.188(4)	K(1)···C(6)	3.309(3)
K(1)···C(8A)	3.482(4)	K(1)···C(12)	3.289(4)
N(1)–K(1)–N(1A)	105.41(6)	K(1)–N(1)–K(1A)	74.59(6)
Si(1)–N(1)–Si(2)	130.75(16)		
7a			
N(1)–Mg(1)	1.956(3)	Mg(1)–C(13)	
Mg(1)–C(13A)	2.212(4)	Mg(1)···Mg(1A)	2.692(2)
N(1)–Mg(1)–C(13)	129.50(13)	N(1)–Mg(1)–C(13A)	125.28(13)
Mg(1)–C(13)–Mg(1A)	74.80(12)	C(13)–Mg(1)–C(13A)	105.20(12)
Si(1)–N(1)–Si(2)	132.02(15)		
7b			
N(1)–Mg(1)	2.0293(15)	Mg(1)–C(13)	2.118(2)
Mg(1)–O(1)	2.1213(14)	Mg(1)–O(2)	2.1259(16)
N(1)–Mg(1)–C(13)	133.97(8)	Si(1)–N(1)–Si(2)	127.60(9)
8			
N(1)–Mg(1)	1.9658(18)	Mg(1)–C(16)	2.241(3)
Mg(1)–C(16A)	2.231(2)	Mg(1)···Mg(1A)	2.7200(14)
N(1)–Mg(1)–C(16)	130.90(9)	N(1)–Mg(1)–C(16A)	123.91(9)
Mg(1)–C(16)–Mg(1A)	74.93(8)	C(16)–Mg(1)–C(16A)	105.06(9)
Si(1)–N(1)–Si(2)	132.51(10)		
9			
N(1)–Mg(1)	1.977(2)	Mg(1)–C(19)	2.251(4)
Mg(1)–C(19A)	2.212(3)	Mg(1)···Mg(1A)	2.739(2)
N(1)–Mg(1)–C(19)	128.97(11)	N(1)–Mg(1)–C(19A)	126.47(14)
Mg(1)–C(19)–Mg(1A)	75.72(11)	C(19)–Mg(1)–C(19A)	104.28(13)
Si(1)–N(1)–Si(2)	135.93(15)		
10			
N(1)–Mg(1)	1.985(5)	Mg(1)–I(1)	2.8280(18)
Mg(1)–I(2)	2.8187(19)	Mg(1)–O(1)	2.010(4)
Mg(1)···Mg(1A)	4.068(4)	Mg(1)–I(1)–Mg(1A)	91.99(7)
Mg(1)–I(2)–Mg(1A)	92.38(7)	I(1)–Mg(1)–I(2)	87.81(5)
N(1)–Mg(1)–O(1)	111.85(19)	Si(1)–N(1)–Si(2)	128.6(3)

$(C_3H_5)]_n$. However, we were not able to isolate the amido-Grignard reagent from this reaction mixture, even after 10 days of stirring, and ^{1}H NMR spectroscopy revealed a complex mixture of products. We concluded from these observations that allylmagnesium chloride is unsuitable for facile and reproducible synthetic routes to $N^{RR'}$-containing Hauser bases, at least in the reaction conditions employed, and therefore we switched our attention to a different organomagnesium starting material (see below).

Reactions of methylmagnesium iodide with silylamines and potassium silylamides

Methylmagnesium iodide reacts with potassium silylamides, $[K(N^{RR'})]$, to give amido-Grignard complexes in fair yields, but protonolysis reactions with the parent silylamines were unsuccessful. As the reaction of $[K\{N(Si^tBuMe_2)_2\}]_n$ or **5b** with allylmagnesium chloride is slow and gives poor yields of **1** (see above), we selected methylmagnesium iodide as an alternative starting material, which has been extensively used in the literature as a reagent for the preparation of L–Mg–X and L–Mg–R complexes.[6,9–14,36] In the course of synthesising potassium silylamide precursors for this study, crystals of $[\{K[\mu\text{-}N(Si^tBuMe_2)_2]\}_2]_\infty$ (**6**) were obtained and identified by single crystal XRD (Fig. 5, selected bond lengths and angles are shown in Table 1). We previously reported that desolvation of $[\{K[\mu\text{-}N(SiMe_2Bu^t)_2]\}_2(C_7H_8)]_\infty$ under vacuum yielded **6**, but this was not structurally characterised.[28] In the solid state, complex **6** is dimeric with a K_2N_2 core. K···C–H agostic interactions [K···C 3.188(4) Å] between the dimers form a 1D chain and numerous other K···C–H/K···H agostic and anagostic interactions are also present. Each potassium centre in **6** is close to two nitrogen atoms, with N–K distances [2.856(3) Å mean] and K–N–K [74.59(6)°] and N–K–N [105.41(6)°] angles that are comparable to those in $[\{K[\mu\text{-}N(SiMe_2Bu^t)_2]\}_2(C_7H_8)]_\infty$ [K–N 2.874(2) Å mean; K–N–K 78.37(5)°; N–K–N 101.63(5)°][28] and $[K(\mu\text{-}N'')]_2$ [K–N 2.787(3) Å mean; K–N–K 85.53(9)°; N–K–N 94.47(9)°].[37]

The amido-Grignard complexes $[Mg(N^{RR'})(\mu\text{-}CH_3)]_2$ ($N^{RR'}$ = $\{N(Si^tBuMe_2)_2\}^-$, **7a**; $\{N(Si^tBuMe_2)(Si^iPr_3)\}^-$, **8**; $\{N(Si^iPr_3)_2\}^-$, **9**) were obtained by salt-metathesis reactions using the appropriate potassium amides and methylmagnesium iodide in diethyl ether, and treatment of **7a** with DME gave $[Mg\{N(Si^tBuMe_2)_2\}(CH_3)(DME)]$ (**7b**) (Scheme 3). Workup and crystallisation from



Scheme 2 Synthesis of complexes **5a–b**.

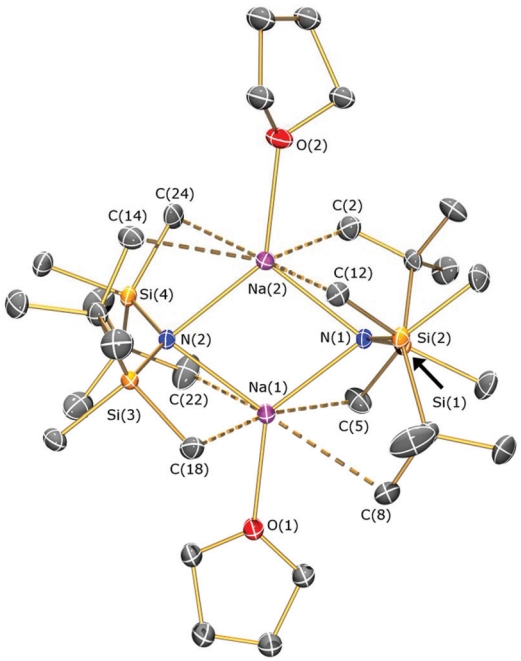


Fig. 3 Molecular structure of **5a** with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity.

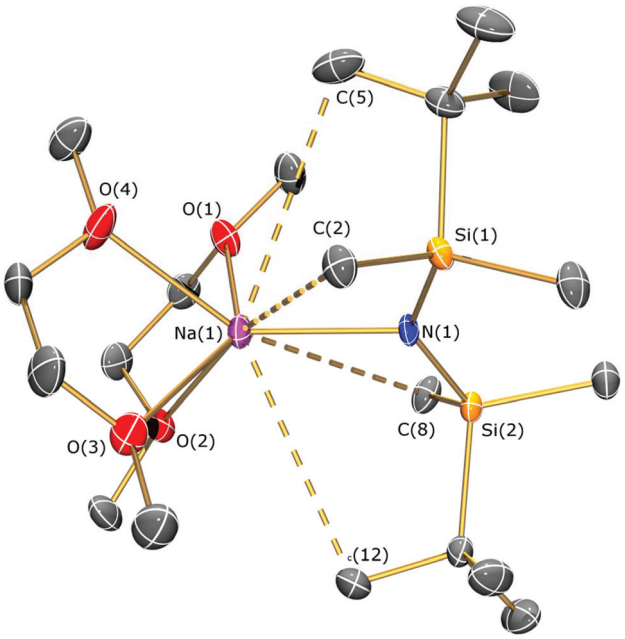


Fig. 4 Molecular structure of **5b** with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity.

hot toluene afforded colourless crystals in poor (**7a** and **7b**), fair (**9**) and excellent (**8**) yields, respectively. On one occasion a small crop of the Hauser base $[Mg\{N(Si^tBuMe_2)_2\}(\mu\text{-}I)(THF)]_2$ (**10**) was obtained (4%) when attempting to isolate **7a**, which has presumably formed *via* complex Schlenk equilibria.[1] Treatment of methylmagnesium iodide with $HN^{RR'}$ in diethyl ether gave no reaction even after extended reaction times (>3 days at room temperature) or heating the reaction mixture under reflux for three hours. Furthermore, we found that **7a** does not react with $HN(Si^tBuMe_2)_2$ under similar forcing conditions in hexanes. Germane to this, no reaction was observed between di-*n*-butylmagnesium and $HN(Si^tBuMe_2)_2$ in a mixture of heptane and hexanes. Refluxing this reaction mixture for extended periods gave an intractable mixture of products. Together, these experiments illustrate the sluggishness of protonolysis reactions between alkylmagnesium complexes and $HN^{RR'}$. Complexes **7–10** were characterised by single crystal XRD studies (see below), elemental analysis and NMR and IR spectroscopies. To the best of our knowledge, **7a**, **8** and **9** are the first examples of structurally characterised dimeric

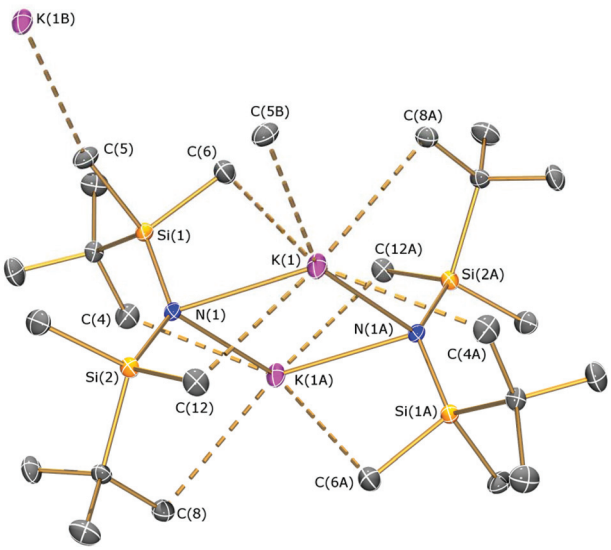
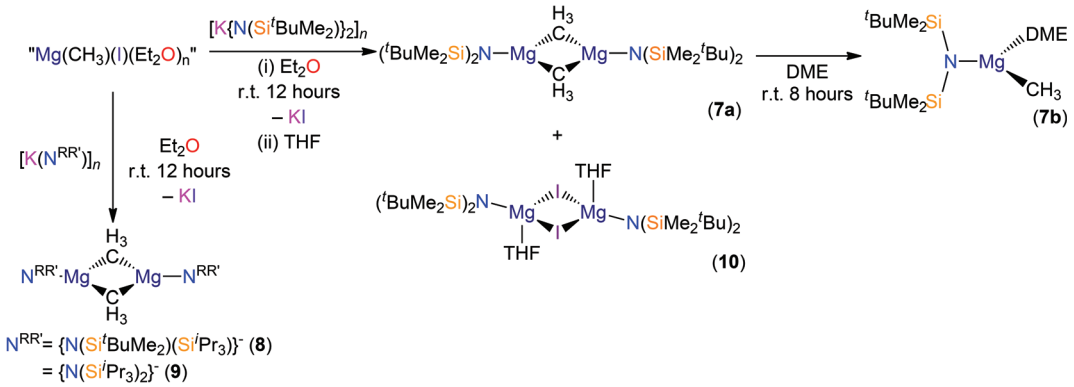


Fig. 5 Molecular structure of **6** with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity. Symmetry operation to generate equivalent atoms: *–x, –y, –z*.



Scheme 3 Synthesis of complexes **7–10**.

CH_3-bridged Hauser bases with monodentate N-donor ligands. Complex **7b** is unusual as it is monomeric with a terminal Mg–CH_3 group, and there are few examples of this motif in the literature.[38]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **7–10** contain unremarkable silylamide ligand resonances, but the shielded methyl resonances in **7–9** [δ_H: −0.71 ppm (**7a**); −0.99 ppm (**7b**); −0.81 ppm (**8**); −0.80 ppm (**9**); δ_C: −10.04 ppm (**7a**), −13.65 ppm (**7b**), −13.02 ppm (**8**), −12.19 ppm (**9**)] are in agreement with those of structurally characterised examples in the literature (δ_H range −2.00 ppm to −0.67 ppm).[38] The similarity of the methyl group chemical shifts in **7–9** with multidentate N-donor complexes in the literature suggests that the spectator ligand does not greatly influence these values.[6,39,40] One resonance is observed in the ^{29}Si{^{1}H} NMR spectra of **7a**, **7b**, **9** and **10** and two resonances were found for **8** [δ_{Si}: −1.93 ppm (**7a**); −2.43 ppm (**7b**); −2.90 and −1.76 ppm (**8**); −3.15 ppm (**9**); −1.19 ppm (**10**)], correlating with the number of unique silicon environments.

The identities of **7a**, **7b**, **8**, **9** and **10** were determined by single crystal XRD and are depicted herein (**7a**: Fig. 6; **7b**: Fig. 7; **10**: Fig. 8; see ESI Fig. S13 and S14† for the structures of **8** and **9**), with selected bond lengths and angles compiled in Table 1. The structures of **7a**, **8** and **9** are broadly similar, with 3-coordinate Mg centres and bridging CH_3 moieties to form central Mg_2C_2 rhomboids with centres of inversion. The Mg–N distances [**7a**: 1.956(3) Å, **8**: 1.9658(18) Å; **9**: 1.977(2) Å] are slightly shorter than in **1**, **2**, and **3** respectively, which is a reflection of the absence of coordinated solvent molecules in **7–9**. The mean Mg–C bond lengths in **7a**, **8** and **9** are comparable [**7a**: 2.217(6) Å; **8**: 2.236(3) Å; **9**: 2.232(5) Å] and are typical of methylmagnesium amides [previously reported range Mg–C 1.977(3)–2.434(13) Å].[33] The $MgNSi_2$ fragments of all three ligands are roughly planar in **7a**, **8** and **9**; these planes are twisted relative to the central Mg_2C_2 plane by differing amounts [**7a**: 74.38(11)°; **8**: 63.95(8)°; **9**: 67.77(10)°] with no clear trend. In the dimeric unit, the two ligand Si–N–Si fragments are also co-planar with each other (to within 0.1°) for all three structures. The coordination spheres of the magnesium centres in **7a**, **8** and **9** are completed by a number of short Mg···C–H/Mg···H distances. Complex **7b** is monomeric due to the coordinated DME molecule and the Mg–N [2.0293(15) Å] and Mg–C [2.118(2) Å] bonds are correspondingly shorter than those in **7a**. However, the coordination sphere of the magnesium centre is again completed by short Mg···C–H/Mg···H distances. Complex **10** exhibits a near-square Mg_2I_2 central motif, with the sum of the four internal angles calculated at 359.99(12)°. The two Mg–I bond lengths in **10** [2.8280(18) and 2.8187(19) Å] are similar to those observed for literature examples that contain N–Mg–I moieties and bridging iodide ligands [range 2.7766(12)–2.901(3) Å].[6,19,41] Finally, in common with **1–3**, the coordination sphere of Mg is completed by a THF molecule [Mg–O 2.010(4) Å] and multiple short Mg···C–H/Mg···H distances.

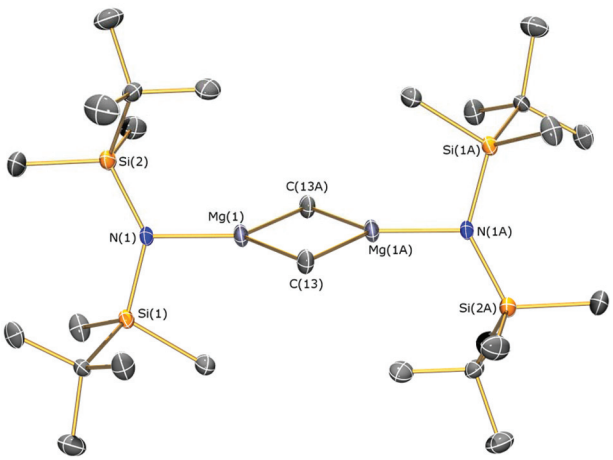


Fig. 6 Molecular structure of **7a** with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity. Symmetry operation to generate equivalent atoms: *–x, –y, –z*.

Conclusions

We have structurally characterised a series of silylamide Hauser bases during our exploration of straightforward syn-

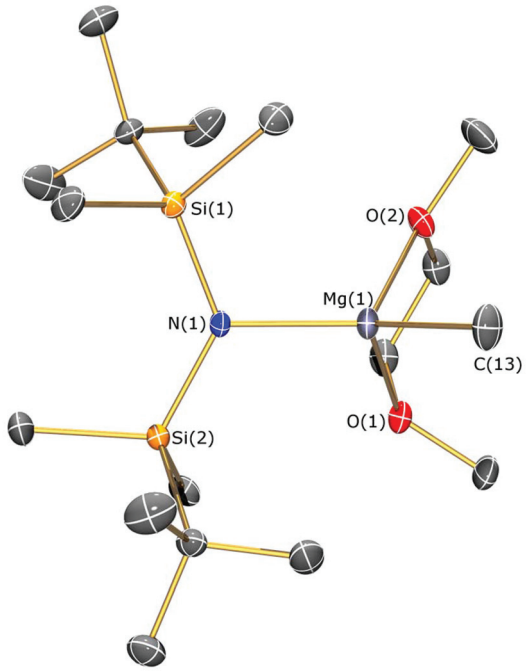


Fig. 7 Molecular structure of **7b** with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity.

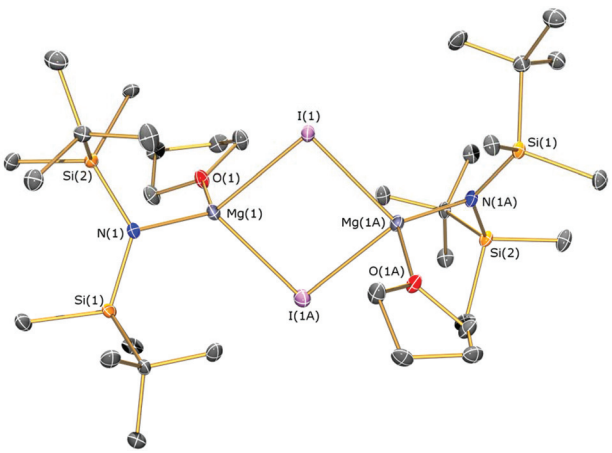


Fig. 8 Molecular structure of **10** with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity. Symmetry operation to generate equivalent atoms: $x + 1/2, -y + 1/2, z - 1/2$.

thetic routes to these complexes. Protonolysis routes to Hauser base complexes by treating allylmagnesium chloride, di-*n*-butylmagnesium or methylmagnesium iodide with a series of silylamines were found to be slow and prone to complex Schlenk equilibria. A fully characterised isolated product, **1**, was achieved on only one occasion by using extended reaction times. The salt metathesis reactions of allylmagnesium chloride with potassium silylamides, and the novel sodium silylamide, **5b**, gave intractable mixtures. We concluded from these studies that, using these ligand systems and methodologies, allylmagnesium chloride is unsuitable as a starting material for reproducible syntheses of silylamide Hauser base and amido-Grignard complexes.

Salt metathesis reactions of potassium silylamides with methylmagnesium iodide were found to be a far more successful strategy, giving modest to excellent yields of the amido-Grignard complexes **7–9**. The isolation of a small amount of the iodide Hauser base complex **10** indicated that complex Schlenk equilibria also operate in these reaction mixtures, slightly reducing the yields of the target complexes. Despite these side-reactions, facile synthetic routes to amido-Grignard complexes of three different silylamide ligands have been achieved. We envisage that such amido-Grignard complexes could be useful reagents for heterofunctionalisation reactions. Additionally, such compounds could pave the way for the preparation of novel bimetallic systems with alkali metals, which could potentially be employed in synergic metalation reactions.

Experimental

Materials and methods

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of dry argon. Solvents were dried by refluxing over potassium and degassed before use. All solvents were stored over potassium mirrors (with the exception of THF and DME which were stored over activated 4 Å molecular sieves). Deuterated solvents were distilled from potassium, degassed by three freeze–pump–thaw cycles and stored under argon. $[K\{N(Si^tBuMe_2)_2\}]_n$,[29a] $[K\{N(Si^tBuMe_2)(Si^iPr_3)_2\}]_n$,[28] $[K\{N(Si^iPr_3)_2\}]_n$,[29b] were prepared according to published procedures. $[Na(CH_2C_6H_5)]$ was prepared *via* a modification of published procedures.[34] All other chemicals were used as purchased and stored appropriately. Most solid reagents were dried under vacuum for four hours and most liquid reagents were dried over 4 Å molecular sieves and distilled before use. ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were recorded on a spectrometer operating at 400.2, 100.6 and 79.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to TMS. FTIR spectra were recorded as Nujol mulls in KBr discs on a Perkin Elmer Spectrum RX1 spectrometer. Elemental microanalyses were carried out by Mr Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK.

Synthetic procedures

$[Mg\{N(Si^tBuMe_2)_2\}(\mu\text{-}Cl)(THF)]_2$ (1). Allylmagnesium chloride (1.5 mL, 2.0 M in THF, 3 mmol) was added dropwise to a precooled solution −78 °C) of $HN(Si^tBuMe_2)_2$ (0.74 g, 3 mmol) in THF (20 mL). The reaction mixture was allowed to warm to room temperature, forming a white precipitate which redissolved to give a colourless solution. After 10 days stirring at room temperature volatiles were removed *in vacuo* to leave a

white solid which was washed with hexanes (4 mL). The solid residue was dried *in vacuo* and extracted with hot toluene (15 mL). Storage of the toluene solution at −20 °C for 24 hours gave **1** as colourless crystals (0.44 g, 19%). Anal. Calcd for $C_{32}H_{76}Cl_2Mg_2N_2O_2Si_4$: C, 41.92; H, 8.85; N, 3.06. Found C, 40.48; H, 8.60; N, 3.38 (low C value attributed to **1** being a silicon-rich molecule, as has been observed previously).[29a,32] ^{1}H NMR (d_6-benzene, 298 K): δ = 0.38 (s, 24H, Si(CH_3)$_2$), 1.18 (s, 36H, SiC(CH_3)$_3$), 1.24 (m, 8H, THF–CH_2) 3.84 (m, 8H, THF–OCH_2). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ = 2.72 (Si(CH_3)$_2$), 20.98 (SiC(CH$_3$)$_3$), 25.16 (THF–CH_2), 29.32 (SiC(CH_3)$_3$), 71.19 (THF–OCH_2). ^{29}Si{^{1}H} NMR (d_6-benzene, 298 K): δ = −0.40 (Si^{t}BuMe$_2$). FTIR (Nujol, cm^{-1}): ν = 1259 (s), 1246 (s), 1019 (s), 983 (s), 844 (m), 829 (s), 795 (s), 722 (m), 660 (m).

[Mg{N(Si^{t}BuMe$_2$)(Si^{i}Pr$_3$)}(μ-Cl)(THF)]$_2$ (2). Allylmagnesium chloride (1.5 mL, 2.0 M in THF, 3 mmol) was added dropwise to a precooled −78 °C) solution of HN(Si^{t}BuMe$_2$)(Si^{i}Pr$_3$) (0.73 g, 3 mmol) in THF (20 mL). The reaction mixture was allowed to warm to room temperature, forming a white precipitate which re-dissolved to give a colourless solution. After 8 hours stirring at room temperature volatiles were removed *in vacuo* to leave a white solid which was extracted with hot toluene (2 mL). Storage of the toluene solution at −20 °C for 24 hours afforded **2** as colourless crystals in an intractable mixture of products.

[Mg{N(Si^{i}Pr$_3$)$_2$}(μ-Cl)(THF)]$_2$ (3) and [Mg{N(Si^{i}Pr$_3$)$_2$}(μ-C$_3$H$_5$)]$_\infty$ (4). Allylmagnesium chloride (1.5 mL, 2.0 M in THF, 3 mmol) in THF (10 mL) was added dropwise to a precooled −78 °C) solution of [KN(Si^{i}Pr$_3$)$_2$]$_n$ (1.10 g, 3 mmol) in THF (15 mL) at. The reaction mixture was allowed to warm to room temperature and stirred for 24 hours. Removal of volatiles *in vacuo* gave a white solid which was extracted with hot toluene (2 mL). Storage at −20 °C for 24 hours afforded **3** and **4** as colourless crystals in an intractable mixture of products.

[Na{μ-N(Si^{t}BuMe$_2$)$_2$}(THF)$_2$]$_2$ (5a) and [Na{N(Si^{t}BuMe$_2$)$_2$}(DME)$_2$] (5b). HN(Si^{t}BuMe$_2$)$_2$ (2.65 g, 10.8 mmol) in THF (10 mL) was added dropwise to a pre-cooled −78 °C) slurry of benzylsodium (1.23 g, 10.8 mmol) in THF (15 mL). The reaction was allowed to warm to room temperature and stirred for 12 hours to form a dark orange solution. Volatiles were removed *in vacuo* to give a dark brown oil which was dissolved in pentane (5 mL). Storage at −20 °C afforded several colourless crystals of **5a**. Volatiles were removed *in vacuo* and the resultant oil was dissolved in dimethoxyethane (5 mL) and stirred for 8 hours. Volatiles were removed *in vacuo* and this oil was dissolved in pentane (5 mL) and stored at −20 °C to afford colourless crystals of **5b**. These were washed with cold pentane (5 mL) and dried *in vacuo* to give a beige powder (3.15 g, 65%). Anal. Calcd for $C_{20}H_{50}NNaO_4Si_2$: C, 53.68; H, 11.26; N, 3.13. Found C, 48.64; H, 11.02; N, 3.41 (low C value attributed to **5b** being a silicon-rich molecule, as has been observed previously).[29a,32] ^{1}H NMR (d_6-benzene, 298 K): δ = 0.30 (s, 12H, Si(CH_3)$_2$), 1.28 (s, 18H, SiC(CH_3)$_3$), 2.80 (s, 8H, DME–OCH_2), 2.88 (s, 12H, DME–OCH_3); ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ = 2.17 Si(CH_3)$_2$), 20.79 (SiC(CH$_3$)$_3$), 28.72 (SiC(CH_3)$_3$), 59.21 (DME–OCH_3), 71.30 (DME–OCH_2). ^{29}Si{^{1}H} NMR (d_6-benzene, 298 K): δ = −13.89 (Si^{t}BuMe$_2$). FTIR (Nujol, cm^{-1}): ν = 1117 (s), 1086 (s), 1030 (s), 819 (s), 802 (s), 637 (m).

[K{N(Si^{t}BuMe$_2$)$_2$}]$_2$ (6). Crystallisation of a small portion (1.00 g, 3.5 mmol) of the previously reported compound [{K[μ-N(Si^{t}BuMe$_2$)$_2$]}$_2$(C$_7$H$_8$)]$_\infty$[28,29a] from hexane gave **6** as large colourless blocks.

[Mg{N(Si^{t}BuMe$_2$)$_2$}(μ-CH$_3$)]$_2$ (7a), [Mg{N(Si^{t}BuMe$_2$)$_2$}(CH$_3$)(DME)}] (7b) and [Mg{N(Si^{t}BuMe$_2$)$_2$}(μ-I)(THF)]$_2$ (10). Methylmagnesium iodide (2 mL, 3 M in diethyl ether, 6 mmol) was added dropwise to a pre-cooled −78 °C) solution of [KN(Si^{t}BuMe$_2$)$_2$]$_n$ (1.70 g, 6 mmol) in diethyl ether (20 mL). The reaction was allowed to warm to room temperature and stirred for 8 hours, forming a white precipitate. Filtration and removal of volatiles *in vacuo* gave a colourless oil. Crystallisation from toluene (20 mL) at room temperature yielded **7a** (0.91 g, 32%). During the synthesis and attempted crystallisation of **7a** from THF, we obtained a small crop of **10** (0.10 g, 4%). Following isolation and characterisation of **7a** and **10**, the extracts were recombined and volatiles were removed *in vacuo*. Dimethoxyethane (5 mL) was added and the resultant light yellow solution was stirred for 2 hours. The volatiles were removed *in vacuo* to leave a white crystalline solid that was dissolved in toluene (3 mL). The reaction was transferred to a −20 °C freezer for 24 hours to form colourless crystals of **7b** (1.03 g, 46%). Data for **7a**: Anal. Calcd for $C_{26}H_{66}Mg_2N_2Si_4$: C, 55.00; H, 11.72; N, 4.93. Found C, 54.96; H, 11.79; N, 4.90. ^{1}H NMR (d_6-benzene, 298 K): δ = −0.64 (s, 6H, Mg–CH_3), 0.16 (s, 24H, Si(CH_3)$_2$), 1.01 (s, 36H, SiC(CH_3)$_3$). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ = −10.04 (Mg–CH_3), 0.86 (Si(CH_3)$_2$), 19.92 (SiC(CH$_3$)$_3$), 27.79 (SiC(CH_3)$_3$). ^{29}Si{^{1}H} NMR (d_6-benzene, 298 K): δ = −1.93 (Si^{t}BuMe$_2$). FTIR (Nujol, cm^{-1}): ν = 1250 (s), 1211 (s), 1077 (m), 1030 (s), 936 (m), 824 (s), 753 (m), 642 (m). Data for **7b**: Anal. Calcd for $C_{17}H_{43}MgNO_2Si_2{\cdot}0.1C_7H_8$: C, 55.47; H, 11.52; N, 3.66. Found C, 49.79; H, 11.44; N, 3.75 (low C value attributed to **7b** being a silicon-rich molecule, as has been observed previously).[29a,32] ^{1}H NMR (d_6-benzene, 298 K): δ = −0.99 (s, 3H, Mg-CH_3), 0.34 (s, 12H, Si(CH_3)$_2$), 1.18 (s, 18H, SiC(CH_3)$_3$), 2.72 (s, 4H, OCH_2), 2.79 (s, 6H, OCH_3). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ = −13.65 (Mg-CH_3), 2.19 (Si(CH_3)$_2$), 21.10 (SiC(CH$_3$)$_3$), 29.00 (SiC(CH_3)$_3$), 58.79 (OCH_3), 68.48 (OCH_2). ^{29}Si{^{1}H} NMR (d_6-benzene, 298 K): δ = −2.43 (Si^{t}BuMe$_2$). FTIR (Nujol, cm^{-1}): ν = 1246 (s), 1047 (s), 1015 (s), 822 (s), 791 (s), 649 (m). Data for **10**: Anal. Calcd for $C_{32}H_{76}I_2Mg_2N_2O_2Si_4$: C, 41.56; H, 8.19; N, 2.96. Found C, 40.95; H, 8.24; N, 3.02. ^{1}H NMR (d_6-benzene, 298 K): δ = 0.36 (s, 24H, Si(CH_3)$_2$), 1.24 (s, 36H, SiC(CH_3)$_3$), 1.40 (m, 8H, THF-CH_2), 3.59 (m, 8H, THF-OCH_2). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ = 3.44 (Si(CH_3)$_2$), 21.29 (SiC(CH$_3$)$_3$), 25.93 (THF-CH_2), 29.75 (SiC(CH_3)$_3$), 68.60 (THF–OCH_2). ^{29}Si{^{1}H} NMR (d_6-benzene, 298 K): δ = −1.19 (Si^{t}BuMe$_2$). FTIR (Nujol, cm^{-1}): ν = 1253 (s), 1016 (s), 981 (s), 823 (s), 795 (s), 645 (m).

[Mg{N(Si^{i}Pr$_3$)(Si^{t}BuMe$_2$)}(μ-CH$_3$)]$_2$ (8). Methylmagnesium iodide (1 mL, 3 M in diethyl ether, 3 mmol) was added dropwise to a pre-cooled −78 °C) solution of [KN(Si^{t}BuMe$_2$)(Si^{i}Pr$_3$)]$_n$ (1.95 g, 3 mmol) in diethyl ether (15 mL). The reaction was allowed to warm to room temperature and stirred for 8 hours,

forming a white precipitate. Filtration and removal of volatiles *in vacuo* yielded a white powder. This was dissolved in hot toluene (15 mL) and colourless crystals of **8** formed at room temperature (1.46 g, 93%). Anal. Calcd For $C_{23}H_{57}Mg_2N_2Si_4 \cdot 0.75C_7H_8$: C, 62.05; H, 11.74; N, 3.89. Found C, 49.23; H, 11.81; N, 3.82 (low *C* value attributed to **8** being a silicon-rich molecule, as has been observed previously).[29a,32] ^{1}H NMR (d_6-benzene, 298 K): δ = −0.81 (s, 6H, Mg–CH_3), 0.31 (s, 12H, Si(CH_3)$_2$), 1.12 (m, 6H, SiCH(CH$_3$)$_2$), 1.15 (s, 18H, SiC(CH_3)$_3$), 1.31 (d, 18H, J_{HH} = 4 Hz, SiCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ = −13.02 (Mg-*C*H$_3$), 1.82 (Si(*C*H$_3$)$_2$), 17.00 (SiCH(*C*H$_3$)$_2$), 20.14 (Si*C*H(CH$_3$)$_2$), 20.73 (Si*C*(CH$_3$)$_3$), 28.55 (SiC(*C*H$_3$)$_3$). ^{29}Si{^{1}H} NMR (d_6-benzene, 298 K): δ = −2.90 (*Si*^{i}Pr$_3$), −1.76 (*Si*^{t}BuMe$_2$). FTIR (Nujol, cm^{-1}): ν = 1251 (s), 1015 (s), 820 (s), 780 (s), 722 (s), 641 (m), 627 (m).

[Mg{N(Si^{i}Pr$_3$)$_2$}(μ-CH$_3$)]$_2$ (9). Methylmagnesium iodide (1 mL, 3 M in diethyl ether, 3 mmol) was added dropwise to a pre-cooled −78 °C) solution of [KN(Si^{i}Pr$_3$)$_2$]$_n$ (1.10 g, 3 mmol) in diethyl ether (15 mL). The mixture was allowed to warm to room temperature and stirred for 8 hours, forming a white precipitate. Filtration and removal of volatiles *in vacuo* yielded a white powder. This was dissolved in hot toluene (15 mL) and colourless crystals of **9** formed at room temperature (0.77 g, 61%). Anal. Calcd for $C_{20}H_{48}Mg_2N_2Si_4$: C, 62.00; H, 12.32; N, 3.81. Found C, 61.93; H, 12.23; N, 3.87. ^{1}H NMR (d_6-benzene, 298 K): δ = −0.80 (s, 6H, Mg–CH_3), 1.19 (m, 12H, SiCH(CH$_3$)$_2$), 1.34 (d, 36H, J_{HH} = 8 Hz, SiCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ = −12.19 (Mg–CH_3), 17.44 (SiCH(*C*H$_3$)$_2$) 20.41 (Si*C*H(CH_3)$_2$). ^{29}Si{^{1}H} NMR (d_6-benzene, 298 K): δ = −3.15 (*Si*^{i}Pr$_3$). FTIR (Nujol, cm^{-1}): ν = 1000 (s), 979 (m), 878 (m), 798 (m), 739 (s), 657 (m), 617 (m).

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