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Salt metathesis routes to homoleptic near-linear Mg(II) and Ca(II) bulky bis(silyl)amide complexes†

Ji-Dong Leng,^{a,b} Conrad A. P. Goodwin,^b Iñigo J. Vitorica-Yrezabal,^b and David P. Mills^{*b}

*Corresponding Author: david.mills@manchester.ac.uk

^aGuangzhou Key Laboratory for Environmentally Functional Materials and Technology, School of Chemistry and Chemical Engineering, Guangzhou University, 230 Wai Huan Xi Road, Guangzhou Higher Education Mega Center, Guangzhou, 510006, P. R. China.

^bSchool of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, U.K.

†CCDC 1825649-1825654 for solid state structures of **1-THF** and **2-6**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

Abstract

Herein we investigate salt metathesis reactions of the bulky bis(silyl)amide potassium salts $[K\{N(SiMe_2^tBu)_2\}]_n$, $[K\{N(SiMe_2^tBu)(Si^iPr_3)\}]_n$, $[K\{N(Si^iPr_3)_2\}]_n$ and $[K\{N(SiPh_3)_2\}]_n$ (**1**) with AeI_2 ($Ae = Mg, Ca, Sr$) in efforts to synthesise rare homoleptic two-coordinate complexes. Recrystallization of **1** from THF provided structural authentication of the solvated adduct $[K\{N(SiPh_3)_2\}(THF)_3]$ (**1-THF**). For $Ae = Mg$ we were able to identify products for three of the four bis(silyl)amides investigated: $[Mg\{N(SiMe_2^tBu)_2\}_2(THF)]$ (**2**), $[Mg\{N(SiMe_2^tBu)(Si^iPr_3)\}_2]$ (**3**) and $[Mg\{N(SiPh_3)_2\}_2]$ (**4**). Complexes **2-4** were isolated in good yields, and on one occasion during recrystallization of **2** a crystal of the heteroleptic complex $[Mg\{N(SiMe_2^tBu)_2\}(I)(THF)_2]$ (**5**) was identified by XRD. We found that these methodologies were not widely applicable for larger $Ae = Ca$ and Sr , as large quantities of the parent

bis(silyl)amines formed in reaction mixtures; however, we were able to isolate the first near-linear Ca(II) amide $[\text{Ca}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}_2]$ (**6**) from these studies. No Ae-containing products could be isolated from KC_8 /crown ether reductions of **3**, **4** and **6**. Complexes **1-4** and **6** were characterised by single crystal XRD, multinuclear NMR and FTIR spectroscopy and elemental analysis, whereas complex **5** was identified by single crystal XRD only.

Introduction

Low-coordinate complexes are desirable synthetic targets as they formally contain vacant coordination sites for substrate binding, which may lead to enhanced reactivity and improved catalytic activity.¹ Moreover, non-aqueous heavy alkaline earth (Ae = Mg, Ca, Sr, Ba) complexes are intrinsically reactive and their relatively low cost and toxicity make them ideal candidates for catalytic processes,² e.g. hydroelementation reactions.³ However, the synthesis of coordinatively unsaturated Ae complexes is challenging because their predominantly ionic bonding regimes favour maximised coordination numbers, and they are often synthesised in coordinating solvents due to starting material solubility requirements.⁴ Monodentate bulky amide ligands, $\{\text{NR}_2\}$, have proven to be adept at stabilising low-coordinate Ae complexes as their hard *N*-donor atoms are well-suited for hard Ae^{2+} cations, and the steric bulk of the two R-substituents are readily tuned to prevent oligomerisation and ethereal solvent coordination and degradation processes.⁵ Bis(silyl)amide s-block complexes form an important subset, with different ligand electronic properties resulting from the negative hyperconjugation provided by Si atoms.⁶

The archetypical bis(silyl)amide, $\{\text{N}(\text{SiMe}_3)_2\}$ (N''), has provided structurally characterised examples of four-coordinate monomeric $[\text{Ae}(\text{N}'')_2(\text{THF})_2]$ (Ae = Mg,⁷ Ca,⁸ Sr,⁸ Ba⁹) and dinuclear $[\text{Ae}(\text{N}'')_2(\mu\text{-N}'')]_2$ (Ae = Mg,¹⁰ Ca,¹¹ Sr,¹² Ba⁹) complexes, hence larger SiR_3 groups are required to obtain heavy Ae bis(silyl)amides with coordination numbers of 3 or lower in the solid state (it is noteworthy that $[\text{Ae}(\text{N}'')_2(\mu\text{-N}'')]_2$ can be monomeric in solution and the vapour phase,¹³ and that $[\text{Be}(\text{N}'')_2]$ is monomeric in solution, the vapour phase and the solid state).¹⁴ The

solid state structures of a handful of formally two-coordinate homoleptic Mg bulky silylamide complexes have been reported, including bent $[\text{Mg}\{\text{N}(\text{SiMePh}_2)_2\}_2]$,¹⁵ $[\text{Mg}\{\text{N}(\text{Si}^t\text{BuPh}_2)(\text{SiMe}_3)\}_2]$,¹⁶ and $[\text{Mg}\{\text{N}(\text{SiMe}_2\text{Ph})_2\}_2]$,¹⁷ linear $[\text{Mg}\{\text{N}(\text{Dipp})(\text{SiMe}_3)\}_2]$ (Dipp = 2,6-ⁱPr₂C₆H₃),¹⁸ and the dimetallic Mg(I) complexes $[\text{Mg}\{\text{N}(\text{Ar})(\text{SiR}_3)\}_2]$ (R = Me, ⁱPr, Ph; Ar = {C₆H₂(CHPh₂)₂R'-2,4,6}, R' = Me or ⁱPr).¹⁹ However, despite notable synthetic efforts,^{18,20} two-coordinate Ca amide complexes have not yet been structurally authenticated. Indeed, to the best of our knowledge there is only one solid state structure of a formally two-coordinate complex of a heavier Ae, $[\text{Ca}\{\text{C}(\text{SiMe}_3)_3\}_2]$.²¹ Interestingly, this complex is bent, whereas $[\text{Mg}\{\text{C}(\text{SiMe}_3)_3\}_2]$ is linear,²² which can be variously attributed to differing crystal packing effects, induced dipole stabilization and dispersion force interactions arising from the change in Ae cation.²³

Recently, we have developed synthetic routes to a series of bulky bis(silyl)amides, and we have utilised their steric effects to stabilise a series of low-coordinate *s*- and *f*-block complexes.^{24,25} Given that the largest of these ligands provided the first structurally authenticated near-linear *f*-element complexes, $[\text{Ln}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}_2]$ (Ln = Sm, Eu, Tm, Yb),^{24c-d} and the similarity of the six-coordinate ionic radii of Ca²⁺ (1.00 Å) and Yb²⁺ (1.02 Å),²⁶ we envisaged that similar complexes could be isolated for Ae metals. Previously, we found that heteroleptic Mg(II) allyl or alkyl halide precursors reacted with the potassium salts $[\text{K}\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}]_n$, $[\text{K}\{\text{N}(\text{SiMe}_2^t\text{Bu})(\text{Si}^i\text{Pr}_3)\}]_n$ and $[\text{K}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}]_n$ to give heteroleptic amido-Grignard (R₂NMgR) and Hauser base (R₂NMgCl) complexes.^{24e} Herein, we utilise the same three potassium salts, together with the related bulky bis(silyl)amide $\{\text{N}(\text{SiPh}_3)_2\}$ ²⁷ (Figure 1), in salt metathesis reactions with AeI₂ (Ae = Mg, Ca, Sr) to target homoleptic two-coordinate Ae bis(silyl)amide complexes, Ae(NR₂)₂.

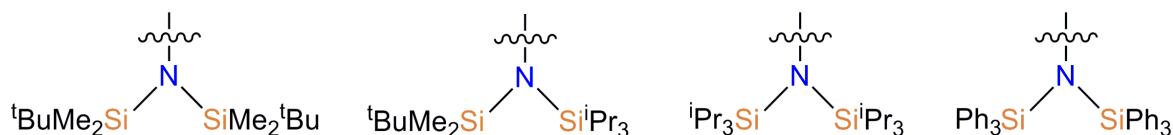


Figure 1. The bulky bis(silyl)amides used herein (l-r): $\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}$, $\{\text{N}(\text{SiPr}^i)(\text{SiMe}_2^t\text{Bu})\}$, $\{\text{N}(\text{SiPr}^i)_2\}$ and $\{\text{N}(\text{SiPh}_3)_2\}$.

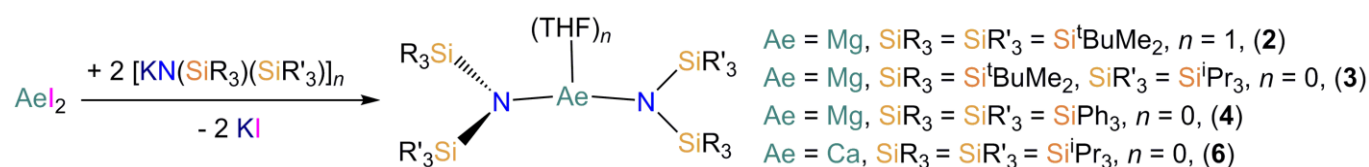
Results and discussion

Synthesis

As no K salt of $\{\text{N}(\text{SiPh}_3)_2\}$ has been reported previously,²⁷ we first reacted $\text{HN}(\text{SiPh}_3)_2$ with KH in refluxing toluene to give $[\text{K}\{\text{N}(\text{SiPh}_3)_2\}]_n$ (**1**) in 80% yield as a crude solid, by adapting synthetic procedures previously used to afford K salts of $\{\text{N}(\text{SiMe}_2\text{Ph})_2\}$ ²⁸ and $\{\text{N}(\text{SiMePh}_2)_2\}$.²⁹ Complex **1** was used without further purification, but several crystals of the solvated adduct $[\text{K}\{\text{N}(\text{SiPh}_3)_2\}(\text{THF})_3]$ (**1-THF**) were grown from a saturated THF solution to provide structural authentication (see below). Given that salt metathesis reactions of $[\text{K}\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}]_n$, $[\text{K}\{\text{N}(\text{SiMe}_2^t\text{Bu})(\text{Si}^i\text{Pr}_3)\}]_n$ and $[\text{K}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}]_n$ with metal iodide precursors to give products *via* KI elimination have proved robust,²⁴ we performed the separate reactions of 2eq. of these Group 1 transfer agents and **1** with AeI_2 (Ae = Mg, Ca, Sr) (Scheme 1). For Ae = Mg, $[\text{Mg}\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}_2(\text{THF})]$ (**2**), $[\text{Mg}\{\text{N}(\text{SiMe}_2^t\text{Bu})(\text{Si}^i\text{Pr}_3)\}_2]$ (**3**) and $[\text{Mg}\{\text{N}(\text{SiPh}_3)_2\}_2]$ (**4**) were obtained in fair yields following work-up and recrystallization, but no Mg-containing products could be isolated from the reaction of MgI_2 with $[\text{K}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}]_n$. The ^1H NMR spectrum of this latter reaction mixture showed the formation of $\text{HN}(\text{Si}^i\text{Pr}_3)_2$; this is attributed to facile cyclometallation/solvent deprotonation processes, which are common outcomes in the reactions of bis(silyl)amides with charge-dense Lewis acidic early metal halides, and tend to be more pronounced for bulkier ligands.^{5,6,25} On one occasion during the recrystallization of **2**, we identified a crystal of $[\text{Mg}\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}(\text{I})(\text{THF})_2]$ (**5**) by single crystal XRD, but analysis of the NMR spectroscopic data for different crops of **2** indicated that **5** was only a very minor component.

For Ae = Ca, $[\text{Ca}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}_2]$ (**6**) was isolated from the reaction of 2 eq. $[\text{K}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}]_n$ with CaI_2 (Scheme 1). However, no Ae-containing products could be isolated from the separate reactions of CaI_2 and SrI_2 with 2 eq. of $[\text{K}\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}]_n$, $[\text{K}\{\text{N}(\text{SiMe}_2^t\text{Bu})(\text{Si}^i\text{Pr}_3)\}]_n$ and $[\text{K}\{\text{N}(\text{SiPh}_3)_2\}]_n$ in diethyl ether, benzene, DME or THF. The ^{29}Si NMR spectra of these reaction mixtures showed the presence of large quantities of potassium bis(silyl)amide starting materials and parent bis(silyl)amine products, again presumably due to facile cyclometallation/deprotonation chemistry. It is remarkable that $[\text{K}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}]_n$ did not give an Ae-containing product for Mg, whereas this is the only Group 1 transfer agent that resulted in a product for Ca. We attribute these variable outcomes to the ideal Ca^{2+}

cation/ligand size ratio in **6** yielding a coordinating solvent-free product, as coordinated THF is polarised and more readily deprotonated. The synthesis of **6** is notable as $[\text{Ca}(\text{N}'')_2]$ and its solvated derivatives have proved to be important starting materials in organocalcium chemistry, but several synthetic routes to this vital precursor have well-documented practical issues.³⁰ Most topically, $[\text{Ca}(\text{N}'')_2]$ has recently been used as a starting material in the synthesis of dimethylcalcium, $[\text{CaMe}_2]_n$, a previously elusive reagent that has already demonstrated synthetic versatility.³¹ Finally, in efforts to synthesise Ae(I)-ate complexes the reactions of **2-4** and **6** with 1 eq. of $\text{KC}_8/18\text{-crown-6}$ were performed in diethyl ether or THF, but ^{29}Si NMR spectroscopy showed the exclusive formation of mixtures of the respective potassium bis(silyl)amides and bis(silyl)amines.



Scheme 1. Synthesis of complexes **2-4** and **6**.

The FTIR, and ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1-4** and **6** are mainly unremarkable and comparable to previously reported s-block complexes of these bis(silyl)amides.^{24,27} However, it is significant that for **2-4** and **6** the spectra are highly symmetric, indicating that any close $\text{M}\cdots\text{C}-\text{H}$ contacts observed in the solid state (see below) are not maintained in d_6 -benzene solutions at 298 K, and there is no evidence of complex aggregation. Minor impurities seen in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2-4** may be attributed to the formation of alkali metal magnesiates.³² This intriguing possibility could be verified by the rational synthesis of such complexes; whilst this is beyond the scope of this study we note that $\{\text{N}(\text{Si}^t\text{BuMe}_2)_2\}$ has previously been shown to be capable of bridging between K^+ and Ln^{2+} ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Tm}, \text{Yb}$) cations.^{24f} We examined complexes **2-4** and **6** by ^1H DOSY NMR spectroscopy in d_8 -toluene to determine if these minor impurities could be assigned to higher-order aggregates.³³ Only one diffusion coefficient was found in all cases except for **4** (Tables S1-S4, and Figures S16-S19); for **2**, **3** and **6** the calculated molecular weight approximated the anticipated formula weight, thus no higher-order species were observed. It is noteworthy that the ^1H DOSY NMR spectrum of **2** exhibits a diffusion

coefficient that corresponds to THF, suggesting that the bound THF is labile in d_8 -toluene solution. For **4**, we found a second diffusion coefficient that corresponds to a species approximately double the anticipated molecular weight of the mononuclear species. Whilst there have been no structurally characterised examples to date of $\{N(\text{SiPh}_3)_2\}$ bridging two metal centres *via* N-atoms, it is conceivable that in solution intermolecular π - π interactions between phenyl groups could also lead to higher-order aggregates. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of **1-4** and **6** provide diagnostic signals that are comparable to previously reported s-block complexes of these ligands;^{24,27} as expected only one strong resonance is observed for **1** (δ_{Si} : -34.59 ppm), **2** (δ_{Si} : -2.33 ppm), **4** (δ_{Si} : -19.80 ppm) and **6** (δ_{Si} : -7.74 ppm), whereas **3** exhibits two signals (δ_{Si} : -0.87 and -1.91 ppm) for its inequivalent SiR_3 groups. Low carbon values were consistently obtained in microanalysis experiments for **1-4** and **6**. We attribute this observation to silicon carbide formation, which can occur for silicon-rich complexes, as this has been seen reproducibly for early metal complexes that contain the bulky bis(silyl)amides in this study,²⁴ and integration of the ^1H NMR spectra of these complexes indicate only modest amounts (<5%) of protic impurities.

Structural Characterisation

Single crystal XRD experiments were performed to determine the solid state structures of **1-6** (Figures 2-7; selected bond lengths and angles are compiled in Table 1). The structure of **1** is best compared with the three-coordinate Li congener $[\text{Li}\{N(\text{SiPh}_3)_2\}(\text{THF})_2]$,^{27c} as well as the closely related four-coordinate K bis(silyl)amide THF solvate $[\text{K}\{N(\text{Si}^i\text{Pr}_3)_2\}(\text{THF})_3]$.^{24b} The K-N [2.763(2) Å] and mean K-O [2.682(5) Å] distances of **1** are similar to those seen for $[\text{K}\{N(\text{Si}^i\text{Pr}_3)_2\}(\text{THF})_3]$ [K-N: 2.739(4) Å; K-O: 2.700(12) Å mean]. The Si-N-Si angle of **1** [138.11(14)°] is larger than that seen for $[\text{Li}\{N(\text{SiPh}_3)_2\}(\text{THF})_2]$ [132.3(1)°]^{27c} and is smaller than that seen for $[\text{K}\{N(\text{Si}^i\text{Pr}_3)_2\}(\text{THF})_3]$ [143.7(2)°].^{24b} Interestingly, the two K-N-Si angles in **1** differ markedly [102.89(9)° and 118.84(3)°]. The Si-N-Si angle data indicates that $\{N(\text{SiPh}_3)_2\}$ could have a slightly smaller steric influence in metal complexes than $\{N(\text{Si}^i\text{Pr}_3)_2\}$, despite its greater size. The K coordination sphere in **1** is completed by

three close K \cdots C–H contacts from *ortho*- positions of three Ph groups [K \cdots C: 3.381(5) Å mean]; similar features were previously discussed for [K{N(SiⁱPr₃)₂}(THF)₃].^{24b}

Complex **2** contains a three-coordinate Mg centre, with a distorted trigonal planar geometry [N–Mg–N: 143.42(7)°, N–Mg–O: 108.3(13)° mean; Σ_{angles} : 360°, Mg \cdots N₂O_{plane}: 0.002(1) Å]. The mean Mg–N [2.016(3) Å] distances in **2** are similar to those seen for four-coordinate [Mg(N'')(THF)₂] [2.021(7) Å mean],⁷ whilst the Mg–O distance is relatively short [**2**: 2.0361(14) Å; [Mg(N'')(THF)₂]: 2.094(7) Å mean].⁷ In addition, the N–Mg–N angle of **2** is relatively large compared to [Mg(N'')(THF)₂] [N–Mg–N: 127.9(2)°],⁷ presumably due to the differing degrees of solvation in these complexes. The Mg coordination sphere of **2** is completed by four close Mg \cdots C–H contacts from Me groups; all other metrical parameters are unremarkable and are comparable to other Mg {N(SiMe₂^tBu)₂} complexes we have reported.^{24e} The isolation of the monomeric distorted tetrahedral complex **5** is notable as we previously disclosed the structure of dimeric [Mg{N(SiMe₂^tBu)₂}(μ -I)(THF)₂],^{24e} showing that minor differences in crystallisation conditions give variable degrees of aggregation. As expected, the terminal Mg–I distance in **5** [2.7366(10) Å] is shorter than the bridging Mg–I distances seen for [Mg{N(SiMe₂^tBu)₂}(μ -I)(THF)₂] [2.824(3) Å mean].^{24e}

The solid state structures of homoleptic two-coordinate **3**, **4** and **6** are discussed together for brevity as each complex contains an Ae bound only by two bis(silyl)amides. In the solid state structure of **3** there are two similar independent molecules in the asymmetric unit, thus we include and discuss the metrical parameters of one of these molecules, whereas tetragonal **4** contains one quarter of a molecule in the asymmetric unit. Complexes **3** [N–Mg–N: 176.32(9)°] and **6** [N–Ca–N: 172.7(1)°] exhibit near-linear geometries, whilst **4** has N–Mg–N = 180° by definition. These angles directly correlate with the torsion angles between the MgNSi₂ planes [**3**: 81.33(9)°; **4**: 90°; **6**: 47.80(2)°], which decrease as N–Ae–N angles deviate from linearity. As with **2**, complexes **3** and **4** each exhibit four close Mg \cdots C–H contacts, which are with both ⁱPr and Me groups for **3** and the *ortho*- positions of the Ph groups for **4**; the larger Ca centre in **6** exhibits six close Ca \cdots C–H contacts from both methyl and methine components of ⁱPr groups. No inter- or intra-molecular π - π stacking interactions were seen in **4**. Interestingly, **3** also exhibits two

notably different Si–N–Si angles [126.95(14) and 138.50(14)°], highlighting the flexibility of this ligand scaffold.

The steric bulk of the {N(SiPh₃)₂} ligands in linear **4** is evident by comparison of its long Mg–N distances [2.022(3) Å] with bent [Mg{N(SiMePh₂)₂}₂] [N–Mg–N: 162.8(3)°; Mg–N: 1.966(6) Å mean],¹⁵ [Mg{N(Si^tBuPh₂)(SiMe₃)₂}₂] [N–Mg–N: 140.15(6)°; Mg–N: 1.981(2) Å mean],¹⁶ and [Mg{N(SiMe₂Ph)₂}₂] [N–Mg–N: 152.28(9)°; Mg–N: 1.959(3) Å mean];¹⁷ indeed **4** is an outlier in this series by exhibiting a linear geometry, which we attribute to the high symmetry in {N(SiPh₃)₂}. To the best of our knowledge the only precisely linear Mg amide complex that has been structurally authenticated previously is [Mg{N(Dipp)(SiMe₃)₂}₂] [Mg–N: 1.919(2) Å mean].¹⁸ Conversely, **6** is the first structurally characterised near-linear Ca complex and is only the second formally two-coordinate Ca complex in the solid state after bent [Ca{C(SiMe₃)₃}₂] [C–Ca–C: 149.7(6)°].²¹ Whilst there are numerous closely related Ca bis(silyl)amide complexes in the literature,^{8,11,18,20} none are monomeric and homoleptic like **6** [Ca–N: 2.333(3) Å mean] and solvated complexes are commonplace; e.g. [Ca{N{SiMe₂^tBu}(SiMe₃)₂(py)₂}₂] [Ca–N_{amide}: 2.353(3) Å mean].²⁰ The structure of **6** is perhaps best juxtaposed with that of near-linear [Yb{N(SiⁱPr₃)₂}₂] [N–Yb–N: 166.01(14)°; Yb–N: 2.385(4) Å mean]^{24d} (six-coordinate ionic radii: Ca²⁺, 1.00 Å; Yb²⁺, 1.02 Å).²⁶

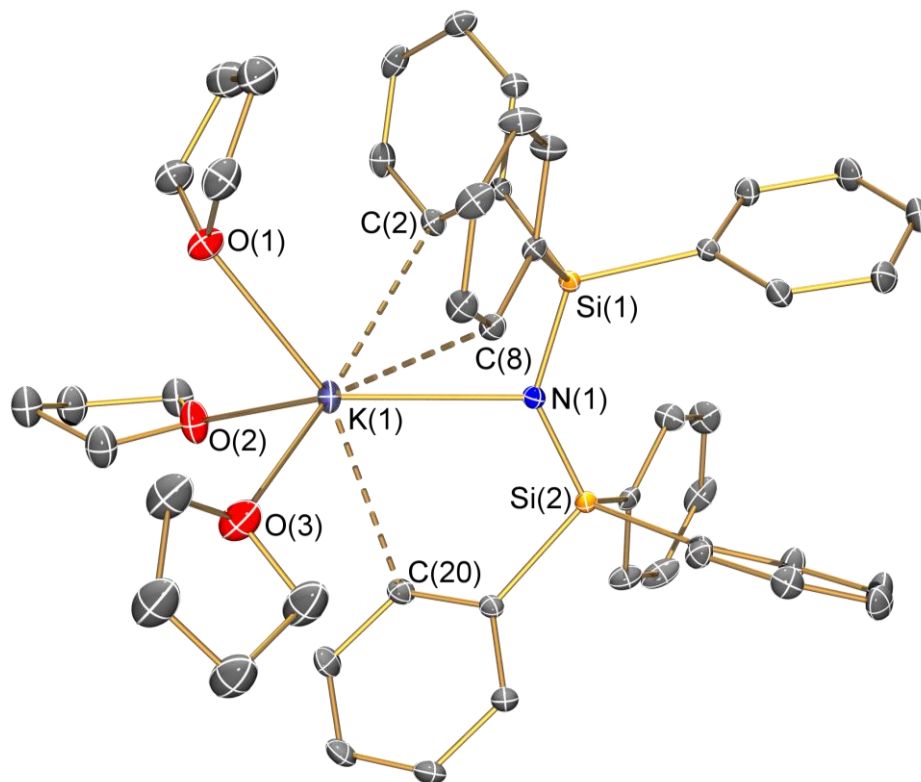


Figure 2. Molecular structure of $[\text{K}\{\text{N}(\text{SiPh}_3)_2\}(\text{THF})_3]$ (**1-THF**) with selective atom labelling. Displacement ellipsoids set at 30 % probability level and hydrogen atoms omitted for clarity.

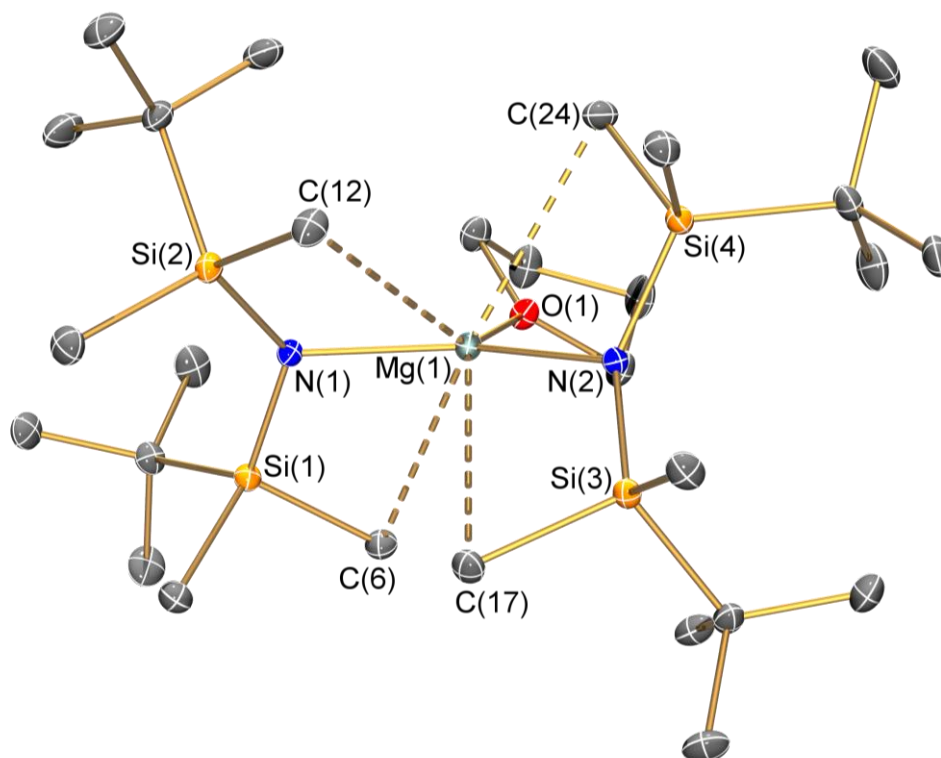


Figure 3. Molecular structure of $[\text{Mg}\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}_2(\text{THF})]$ (**2**) with selective atom labelling. Displacement ellipsoids set at 30 % probability level and hydrogen atoms omitted for clarity.

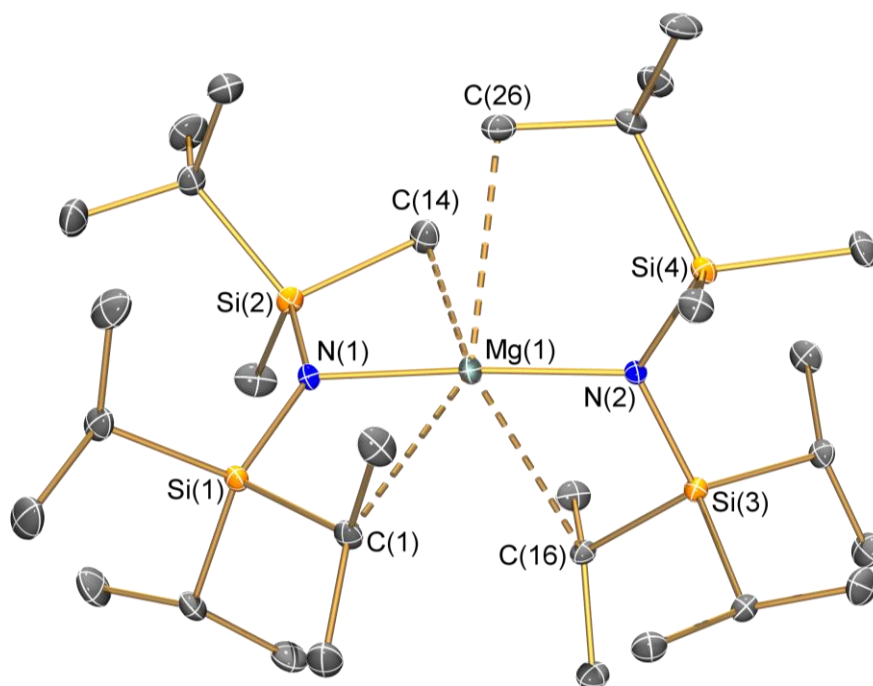


Figure 4. Molecular structure of $[\text{Mg}\{\text{N}(\text{SiMe}_2^t\text{Bu})(\text{Si}^i\text{Pr}_3)\}_2]$ (**3**) with selective atom labelling. Displacement ellipsoids set at 30 % probability level and hydrogen atoms omitted for clarity.

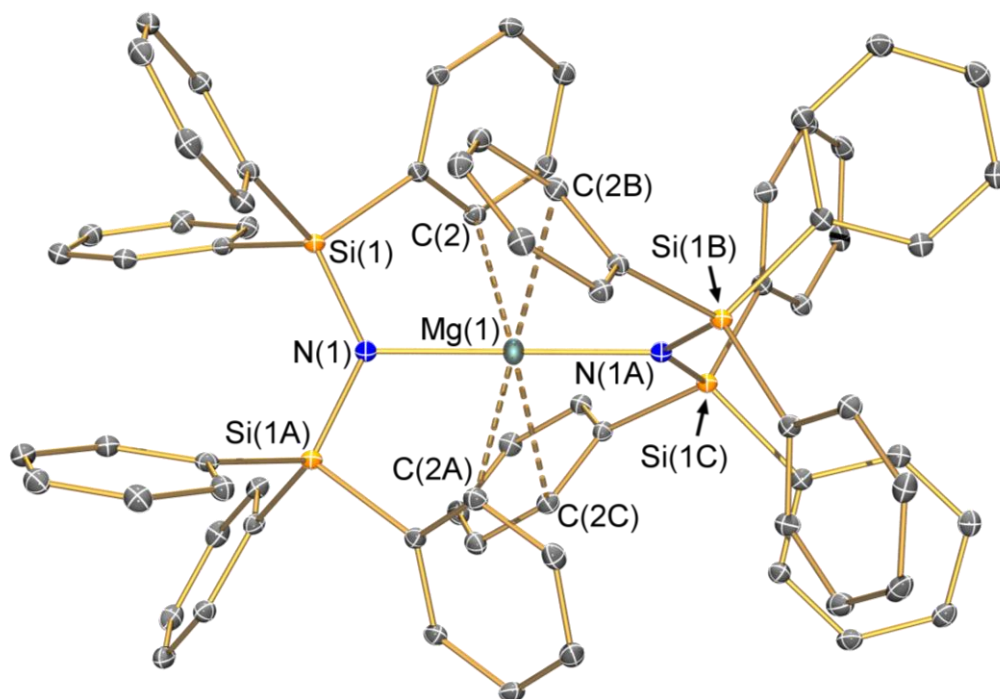


Figure 5. Molecular structure of $[\text{Mg}\{\text{N}(\text{SiPh}_3)_2\}_2]$ (**4**) with selective atom labelling. Displacement ellipsoids set at 30 % probability level and hydrogen atoms omitted for clarity. Symmetry operation to generate equivalent atoms: $x+1/2, -y+1/2, -z+1/2$.

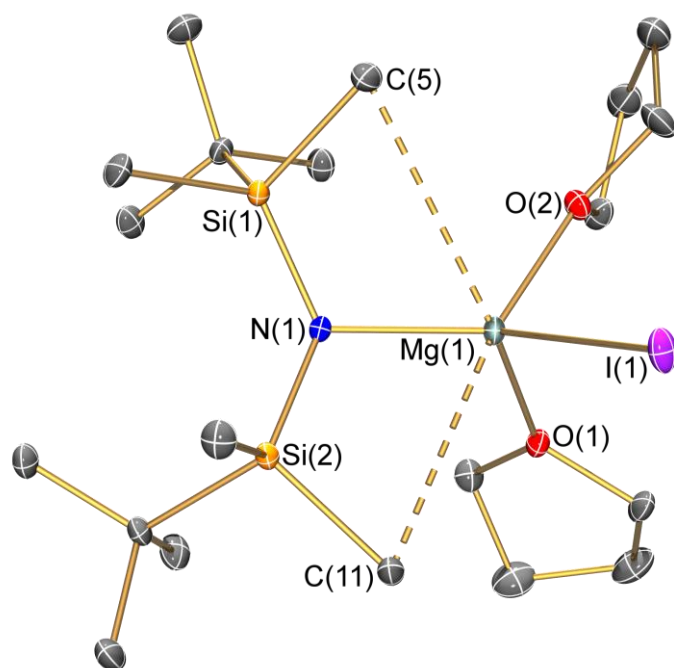


Figure 6. Molecular structure of $[\text{Mg}\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}(\text{I})(\text{THF})_2]$ (**5**) with selective atom labelling. Displacement ellipsoids set at 30 % probability level and hydrogen atoms omitted for clarity.

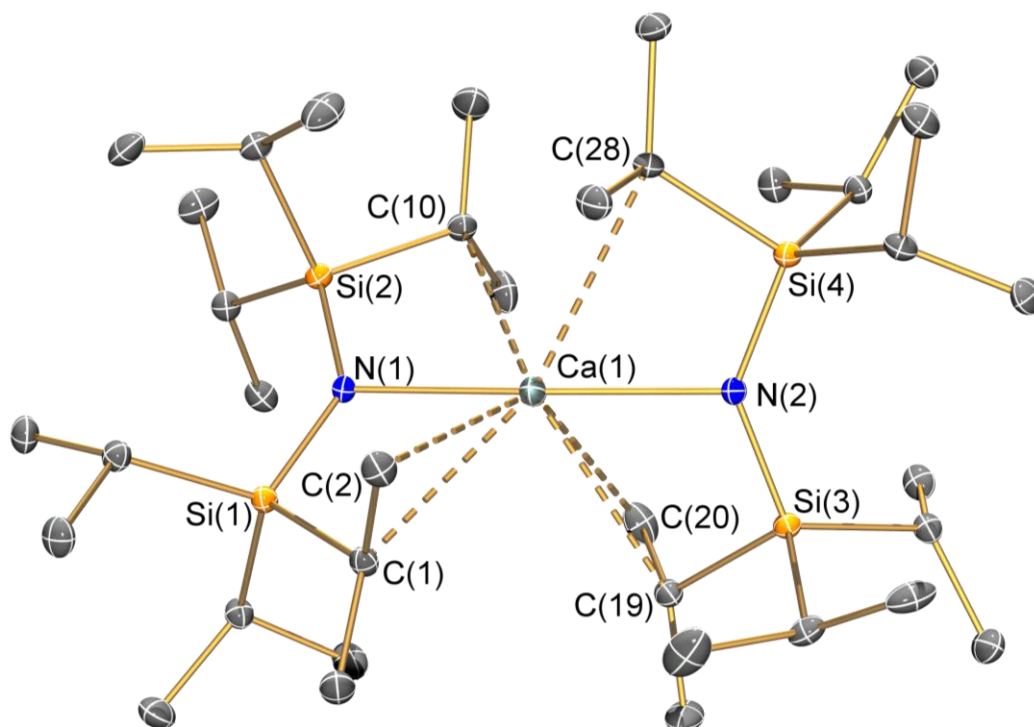


Figure 7. Molecular structure of $[\text{Ca}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}_2]$ (**6**) with selective atom labelling. Displacement ellipsoids set at 30 % probability level and hydrogen atoms omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for **1-THF** and **2-6**.

1-THF			
K(1)–N(1)	2.763(2)	N(1)–O(1)	2.700(2)
N(1)–O(2)	2.680(3)	N(1)–O(3)	2.655(3)
N(1)–Si(1)	1.656(2)	N(1)–Si(2)	1.655(2)
K(1)···C(2)	3.393(3)	K(1)···C(8)	3.508(3)
K(1)···C(20)	3.243(3)		
K(1)–N(1)–Si(1)	102.89(9)	K(1)–N(1)–Si(2)	118.84(3)
Si(1)–N(1)–Si(2)	138.11(14)		
2			
Mg(1)–N(1)	2.017(2)	Mg(1)–N(2)	2.015(2)
N(1)–Si(1)	1.715(2)	N(1)–Si(2)	1.720(2)
N(2)–Si(3)	1.712(2)	N(2)–Si(4)	1.712(2)
Mg(1)–O(1)	2.0361(14)		
Mg(1)···C(6)	2.992(2)	Mg(1)···C(12)	3.321(2)
Mg(1)···C(17)	3.239(2)	Mg(1)···C(24)	3.004(3)
N(1)–Mg(1)–N(2)	143.42(7)	Mg(1)–N(1)–Si(1)	109.92(8)
Mg(1)–N(1)–Si(2)	117.24(9)	Mg(1)–N(2)–Si(3)	116.22(10)
Mg(1)–N(2)–Si(4)	110.43(8)	Si(1)–N(1)–Si(2)	128.41(12)
Si(3)–N(2)–Si(4)	128.94(8)		
3			
Mg(1)–N(1)	1.964(2)	Mg(1)–N(2)	1.958(2)
N(1)–Si(1)	1.717(2)	N(1)–Si(2)	1.714(2)
N(2)–Si(3)	1.719(2)	N(2)–Si(4)	1.723(2)
Mg(1)···C(1)	2.921(3)	Mg(1)···C(14)	2.897(3)
Mg(1)···C(16)	3.009(3)	Mg(1)···C(26)	3.075(2)
N(1)–Mg(1)–N(2)	176.27(9)	Mg(1)–N(1)–Si(1)	111.95(10)
Mg(1)–N(1)–Si(2)	108.35(13)	Mg(1)–N(2)–Si(3)	111.93(9)
Mg(1)–N(2)–Si(4)	120.67(13)	Si(1)–N(1)–Si(2)	138.50(14)
Si(3)–N(2)–Si(4)	126.95(14)		
4			
Mg(1)–N(1)	2.022(3)	N(1)–Si(1)	1.7085(13)
Mg(1)···C(2)	2.950(3)		
N(1)–Mg(1)–N(1')	180	Mg(1)–N(1)–Si(1)	115.06(9)
Si(1)–N(1)–Si(1')	129.9(2)		
5			
Mg(1)–N(1)	2.015(3)	Mg(1)–I(1)	2.7366(10)
Mg(1)–O(1)	2.018(3)	Mg(1)–O(2)	2.051(3)
N(1)–Si(1)	1.713(3)	N(1)–Si(2)	1.712(3)
Mg(1)···C(5)	3.324(4)	Mg(1)···C(14)	3.119(4)
Si(1)–N(1)–Si(2)	127.7(2)		
6			
Ca(1)–N(1)	2.329(2)	Ca(1)–N(2)	2.337(2)
N(1)–Si(1)	1.711(3)	N(1)–Si(2)	1.709(3)
N(2)–Si(3)	1.702(3)	N(2)–Si(4)	1.708(3)
Ca(1)···C(1)	3.006(3)	Ca(1)···C(2)	3.097(4)
Ca(1)···C(10)	3.251(3)	Ca(1)···C(19)	3.033(3)
Ca(1)···C(20)	3.085(4)	Ca(1)···C(28)	3.134(3)
N(1)–Ca(1)–N(2)	172.62(11)	Ca(1)–N(1)–Si(1)	110.47(13)
Ca(1)–N(1)–Si(2)	112.55(12)	Ca(1)–N(2)–Si(3)	108.88(12)
Ca(1)–N(2)–Si(4)	112.64(12)	Si(1)–N(1)–Si(2)	136.7(2)
Si(3)–N(2)–Si(4)	138.2(2)		

The varying coordination geometries of **2-4** and **6** can be attributed to varying steric demands of the bis(silyl)amides, with $\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}$ too small to enforce a formal coordination number of 2 for Mg in the presence of THF for complex **2**. For **3**, **4**, **6** and literature two-coordinate Mg silylamide complexes, if ligand steric bulk was the only factor then one would predict that the largest ligands would give coordination geometries closest to linearity to minimise inter-ligand repulsion. However, as we have commented on previously for the near-linear lanthanide complexes $[\text{Ln}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}_2]$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Tm}, \text{Yb}$), such bulky aliphatic bis(silyl)amide ligands tend to deviate from linearity to increase the number of $\text{M}\cdots\text{H}-\text{C}$ interactions and stabilising inter-ligand interactions associated with dispersion forces.^{24c} Thus, although we could consider $\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}$ and $\{\text{N}(\text{SiMe}_2^t\text{Bu})(\text{Si}^i\text{Pr}_3)\}$ to have the largest steric effects as all C atoms bonded to Si are sp^3 -hybridised and most of these C atoms are bonded to two or more Me groups, **3** and **6** deviate considerably from linearity whilst homoleptic two-coordinate Mg complexes of $\{\text{N}(\text{SiPh}_3)_2\}$ and $\{\text{N}(\text{Dipp})(\text{SiMe}_3)\}$ ¹⁸ are precisely linear. Conversely, the Si–N–Si angles in **3**, **4** and **6** are equally important in determining coordination geometries as they influence both the metal-ligand and ligand-ligand interactions of the silyl substituents. Indeed, for these complexes the mean Si–N–Si angles follow the order **4** < **3** < **6**; this is the opposite trend to the variation in N–Ae–N angles and the size of the torsion angles between the MgNSi_2 planes (see above), though these values cannot be compared quantitatively due to differing ligand symmetries, Ae cations and complex geometries.

Conclusions

Salt metathesis reactions of AeI_2 ($\text{Ae} = \text{Mg}, \text{Ca}, \text{Sr}$) with potassium bulky bis(silyl)amides have found limited success in the synthesis of homoleptic formally two-coordinate Ae complexes. Generally, these methods are most applicable to $\text{Ae} = \text{Mg}$, whilst side-product formation predominates for the heavier Ae; however these studies have yielded rare formally two-coordinate Mg complexes and the first structurally characterised near-linear calcium complex. Given that $[\text{Ca}(\text{N}'')_2]$ is an ubiquitous starting material in organocalcium chemistry, complexes such as $[\text{Ca}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}_2]$ have potential synthetic utility in the

synthesis of novel calcium organometallics. Alternative synthetic routes to salt metathesis to install bulky bis(silyl)amides, such as alkane elimination and transmetallation, have previously been successfully employed in Ae metal silylamide chemistry.^{5,6} These routes could be investigated in future to extend the s-block chemistry of the bulky bis(silyl)amides herein to the heavier Ae metals strontium and barium.

Experimental

Materials and methods

All manipulations were conducted under argon with rigorous exclusion of oxygen and water using glove box and Schlenk techniques. Solvents were purged with UHP-grade nitrogen (Airgas) and passed through columns containing activated alumina and molecular sieves before use or were dried by refluxing over potassium and degassed before use. All solvents were stored over K mirrors or 4 Å molecular sieves (THF). NMR solvents (Cambridge Isotope Laboratories) were dried over K, degassed by three freeze-pump-thaw cycles, and vacuum-transferred before use. $\text{HN}(\text{SiPh}_3)_2$,²⁷ $[\text{K}\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}]_n$,^{24a} $[\text{K}\{\text{N}(\text{SiMe}_2^t\text{Bu})(\text{Si}^i\text{Pr}_3)_2\}]_n$ ^{24c} and $[\text{K}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}]_n$ ^{24b} were prepared according to literature procedures. MgI_2 and CaI_2 were purchased from Sigma-Aldrich and were used as received. ^1H (400.2 MHz), $^{13}\text{C}\{^1\text{H}\}$ (100.6 MHz) and $^{29}\text{Si}\{^1\text{H}\}$ (79.5 MHz) NMR spectra were obtained on a Bruker Avance III 400 MHz spectrometer at 298 K; chemical shifts are quoted in ppm and are relative to TMS. ATR-FTIR spectra were recorded as microcrystalline powders using a Bruker Tensor 27 spectrometer; other FTIR spectra were recorded as Nujol mulls in KBr discs on a PerkinElmer Spectrum RX1 spectrometer. Elemental analyses were performed by Mrs Anne Davies and Mr Martin Jennings at The University of Manchester, Manchester, U.K.

Synthetic procedures

$[\text{K}\{\text{N}(\text{SiPh}_3)_2\}]_n$ (**1**). Toluene (20 mL) was added to a mixture of $\text{HN}(\text{SiPh}_3)_2$ (15.736 g, 29.5 mmol) and KH (1.155 g, 28.8 mmol) at room temperature. The reaction mixture was refluxed for 6 hrs, forming a white precipitate, and allowed to cool to room temperature. The solution was decanted and the

remaining white solid was dried *in vacuo* to give $[\text{K}\{\text{N}(\text{SiPh}_3)_2\}]_n$ (13.424 g, 80 %). A small portion was dissolved in THF (2 mL) and stored at $-25\text{ }^\circ\text{C}$ overnight to afford several crystals of $[\text{K}\{\text{N}(\text{SiPh}_3)_2\}(\text{THF})_3]$ (**1-THF**). Anal. Calcd. for $\text{C}_{48}\text{H}_{54}\text{KNO}_3\text{Si}_2$: C, 73.15; H, 6.91; N, 1.78. Found C, 72.42; H, 6.50; N, 1.85. Data for **1**: ^1H NMR (d_6 -benzene/THF, 298 K): $\delta = 7.12$ (br m, 18H, *p*- and *m*-Ar-H), 7.91 (br m, 12H, *o*-Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_6 -benzene/THF, 298 K): $\delta = 127.71$ (Ar-CH), 127.93 (Ar-CH), 136.52 (Ar-CH), 146.58 (*ipso*-Ar-C). $^{29}\text{Si}\{^1\text{H}\}$ NMR (d_6 -benzene/THF, 298 K): $\delta = -34.59$ (SiPh₃). FTIR (Nujol, cm^{-1}): $\tilde{\nu} = 3057$ (w), 2991 (w), 1483 (w), 1426 (m), 1175 (s), 1101 (s), 993 (m), 950 (m), 736 (s), 700 (s), 508 (s), 403 (s).

[Mg{N(SiMe₂^tBu)₂]₂(THF)] (2) and [Mg{N(SiMe₂^tBu)₂](I)(THF)₂] (5). THF (20 mL) was added to a mixture of MgI₂ (0.556 g, 2.0 mmol) and $[\text{K}\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}]_n$ (1.135 g, 4.0 mmol) at $-78\text{ }^\circ\text{C}$. The reaction mixture was stirred for 48 h, forming a white precipitate. The supernatant was filtered, and volatiles were removed *in vacuo*. The resultant white solid was extracted with hexane (10 mL), reduced in volume to ca. 2 mL, and stored at $4\text{ }^\circ\text{C}$ to give **2** as colourless blocks (1.053 g, 66 %). On one occasion during recrystallization of **2** a crystal of **5** was identified by XRD. Data for **2**: Anal. Calcd. for $\text{C}_{28}\text{H}_{68}\text{MgN}_2\text{OSi}_4$: C, 57.49; H, 11.73; N, 4.79. Found C, 54.56; H, 11.75; N, 4.52. ^1H NMR (d_6 -benzene, 298 K): $\delta = 0.26$ (s, 24H, Si(CH₃)₂), 1.09 (s, 36H, SiC(CH₃)₃), 1.22 (m, 4H, THF-CH₂), 3.69 (m, 4H, THF-OCH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_6 -benzene, 298 K): $\delta = 2.92$ (Si(CH₃)₂), 20.90 (SiC(CH₃)₃), 25.33 (THF-CH₂), 28.79 (SiC(CH₃)₃), 69.87 (THF-OCH₂). $^{29}\text{Si}\{^1\text{H}\}$ NMR (d_6 -benzene, 298 K): $\delta = -2.33$ (SiMe₂^tBu); a minor impurity was seen at -21.85 , which is assigned as a silicone grease impurity. FTIR (Nujol, cm^{-1}): $\tilde{\nu} = 1060$ (m), 970 (w), 821 (m).

[Mg{N(SiMe₂^tBu)(SiⁱPr₃)₂]₂] (3). Benzene (20 mL) was added to a mixture of MgI₂ (0.556 g, 2.0 mmol) and $[\text{K}\{\text{N}(\text{SiMe}_2^t\text{Bu})(\text{Si}^i\text{Pr}_3)_2\}]_n$ (1.307 g, 4.0 mmol) at $5\text{ }^\circ\text{C}$. The reaction mixture was stirred for 48 h, forming a white precipitate. The supernatant was filtered, and volatiles were removed *in vacuo*. The resultant white solid was extracted with pentane (10 mL), reduced in volume to ca. 1 mL, and stored at $-20\text{ }^\circ\text{C}$ to give **3** as colourless blocks (1.268 g, 72 %). Anal. Calcd. for $\text{C}_{30}\text{H}_{72}\text{MgN}_2\text{Si}_4$: C, 60.36; H,

12.17; N, 4.70. Found C, 59.64; H, 11.92; N, 4.43. ^1H NMR (d_6 -benzene, 298 K): δ = 0.28 (s, 12H, $\text{Si}(\text{CH}_3)_2$), 1.03 (sept, 6H, $J_{\text{HH}} = 7.5$ Hz, $\text{SiCH}(\text{CH}_3)_2$), 1.04 (s, 18H, $\text{SiC}(\text{CH}_3)_3$), 1.22 (d, 36H, $J_{\text{HH}} = 7.5$ Hz, $\text{SiCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_6 -benzene, 298 K): δ = 2.52 (s, $\text{Si}(\text{CH}_3)_2$), 17.87 (s, $\text{SiCH}(\text{CH}_3)_2$), 20.21 (s, $\text{SiCH}(\text{CH}_3)_2$), 20.73 (s, $\text{SiC}(\text{CH}_3)_3$), 28.46 (s, $\text{SiC}(\text{CH}_3)_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (d_6 -benzene, 298 K): δ = -0.87, -1.91 (SiMe_2^tBu and Si^iPr_3). FTIR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1249 (s), 971 (m), 961 (m), 882 (m), 824 (m), 806 (m).

[Mg{N(SiPh₃)₂]₂] (4). Benzene (20 mL) was added to a mixture of MgI_2 (0.556 g, 2.0 mmol) and $[\text{K}\{\text{N}(\text{SiPh}_3)_2\}]_n$ (2.288 g, 4.0 mmol) at 4 °C. The reaction mixture was stirred for 48 h, forming a white precipitate. The supernatant was filtered, and the filtrate was reduced in volume to *ca.* 2 mL, and stored at 4 °C to give **4** as colourless blocks (1.089 g, 50 %). Anal. Calcd. for $\text{C}_{72}\text{H}_{60}\text{MgN}_2\text{Si}_4$: C, 79.38; H, 5.56; N, 2.57. Found C, 78.59; H, 5.48; N, 2.44. ^1H NMR (d_6 -benzene, 298 K): δ = 7.05 (t, 24H, $J_{\text{HH}} = 7.5$ Hz, *m*-Ar-*H*), 7.13 (t, 12H, $J_{\text{HH}} = 7.5$ Hz, *p*-Ar-*H*), 7.36 (d, 24H, $J_{\text{HH}} = 7.5$ Hz, *o*-Ar-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_6 -benzene, 298 K): δ = 128.79 (Ar-CH), 129.77 (Ar-CH), 136.58 (Ar-CH), 140.30 (*ipso*-Ar-C). $^{29}\text{Si}\{^1\text{H}\}$ NMR (d_6 -benzene, 298 K): δ = -19.80 (SiPh_3). FTIR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1286 (m), 1117 (w), 939 (m), 699 (m).

[Ca{N(Si^{*i*}Pr₃)₂]₂] (6). THF (20 mL) was added to a mixture of CaI_2 (0.588 g, 2.0 mmol) and $[\text{K}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}]_n$ (1.472 g, 4.0 mmol) at -78 °C. The reaction mixture was stirred for 48 h, forming a white precipitate. The supernatant was filtered, and volatiles were removed *in vacuo*. The white solid was extracted with hexane (10 mL), reduced in volume to *ca.* 2 mL, and stored at 4 °C to give **4** as colourless blocks (1.053 g, 76 %). Anal. Calcd. for $\text{C}_{36}\text{H}_{84}\text{CaN}_2\text{Si}_4$: C, 62.01; H, 12.15; N, 4.02. Found C, 58.24; H, 11.87; N, 3.52. ^1H NMR (d_6 -benzene, 298 K): δ = 0.91 (sept, 12H, $J_{\text{HH}} = 7.5$ Hz, $\text{SiCH}(\text{CH}_3)_2$), 1.26 (d, 72H, $J_{\text{HH}} = 7.5$ Hz, $\text{SiCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_6 -benzene, 298 K): δ = 18.49 (s, $\text{SiCH}(\text{CH}_3)_2$), 20.49 (s, $\text{SiCH}(\text{CH}_3)_2$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (d_6 -benzene, 298 K): δ = -7.71 (Si^iPr_3). FTIR (Nujol, cm^{-1}): $\tilde{\nu}$ = 969 (m), 873 (m), 704 (m), 656 (m).

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