



Cite this: *Dalton Trans.*, 2016, **45**, 6004

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

Conrad A. P. Goodwin, Alex Smith, Fabrizio Ortu, Iñigo. J. Vitorica-Yrezabal and David P. Mills*

The preparation of silylamide Hauser base (R_2NMgX ; $X = \text{halide}$) 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 $[Mg(N^{RR})(\mu-Cl)(THF)_2]$ ($N^{RR} = \{N(Si^tBuMe_2)_2\}^-$, **1**; $\{N(Si^tBuMe_2)(Si^iPr_3)\}^-$, **2**; $\{N(Si^iPr_3)_2\}^-$, **3**) and $[Mg\{N(Si^iPr_3)_2\}(\mu-C_3H_5)]_\infty$ (**4**) identified as minor products. In contrast, salt metathesis protocols using potassium silylamides and methylmagnesium iodide gave $[Mg(N^{RR})(\mu-CH_3)_2]$ ($N^{RR} = \{N(Si^tBuMe_2)_2\}^-$, **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 $[Mg\{N(Si^tBuMe_2)_2\}(\mu-I)(THF)_2]$ (**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.

Received 3rd July 2015,
Accepted 5th August 2015

DOI: 10.1039/c5dt02535d

www.rsc.org/dalton

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) complexes⁴ 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 guanidates,^{9–11} amidinates¹² 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 ; $X = \text{halide}$),¹⁶ $[Mg(N^*)(\mu-Cl)(Et_2O)_2]$,¹⁷ which was originally prepared in 1972 by Wannagat *et al.* via a proto-

School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK. E-mail: david.mills@manchester.ac.uk

† Electronic supplementary information (ESI) available. CCDC 1408436–1408447 for **1–3**, **5a–b**, **6**, **7a–b**, **8–10** and **4**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02535d



nolysis reaction between HN^{R} and propylmagnesium chloride in diethyl ether.¹⁸ To the best of our knowledge, the heavier congener $[\text{Mg}(\text{N}^{\text{R}})(\mu\text{-Br})(\text{Et}_2\text{O})_2]$,¹⁹ together with the multi-dentate N-heterocyclic carbene (NHC) supported complexes, $[\{\text{Mg}(\text{N}^{\text{R}})\{\text{Mg}(\text{Cl})\}(\mu\text{-NHC}^3)(\mu\text{-Cl})]$ and $[\{\text{Mg}(\text{N}^{\text{R}})\}_2(\mu\text{-NHC}^3)(\mu\text{-Cl})]$ ($\text{NHC}^3 = [\text{N}\{\text{CH}_2\text{CH}_2[\text{NCHCHN}(\text{Mes})\text{C}]\}_2]$, $\text{Mes} = 2,4,6$ -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, $[\text{Mg}(\mu\text{-N}^{\text{R}})(^t\text{Bu})_2]$,²⁴ and the NHC adduct, $[\text{Mg}(\text{N}^{\text{R}})(^t\text{Bu})(\text{IPr})]$ ($\text{IPr} = 1,3$ -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 metal²⁸ and *f*-block^{28,29} complexes. These silylamides include the potassium salts $[\{\text{K}\{\mu\text{-N}(\text{SiMe}_2\text{Bu}^t)\}_2(\text{C}_7\text{H}_8)\}_\infty]$, $[\text{K}\{\text{N}(\text{SiPr}^i)_3\}\text{-}(\text{SiMe}_2\text{Bu}^t)\}_\infty]$ and $[\text{K}\{\text{N}(\text{SiPr}^i)_2\}_\infty]$ (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.

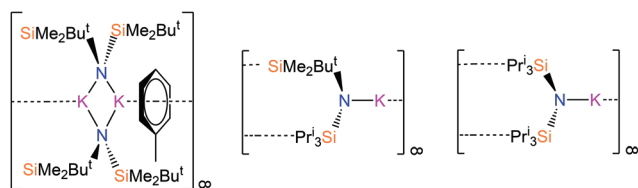


Fig. 1 The potassium silylamide complexes $[\{\text{K}\{\mu\text{-N}(\text{SiMe}_2\text{Bu}^t)\}_2(\text{C}_7\text{H}_8)\}_\infty]$, $[\text{K}\{\text{N}(\text{SiPr}^i)_3\}\text{-}(\text{SiMe}_2\text{Bu}^t)\}_\infty]$ and $[\text{K}\{\text{N}(\text{SiPr}^i)_2\}_\infty]$.²⁸

Results and discussion

Reactions of allylmagnesium chloride with silylamines and potassium silylamides

We found that the reactions of both potassium silylamides, $[\text{K}(\text{N}^{\text{RR}'})]$, and their parent silylamines with allylmagnesium chloride reproducibly gave mixtures of products and poor yields. Given that propylmagnesium chloride reacts with HN^{R} in diethyl ether to give $[\text{Mg}(\text{N}^{\text{R}})(\mu\text{-Cl})(\text{Et}_2\text{O})_2]$,^{17,18} we added allylmagnesium chloride to THF solutions of $\text{HN}(\text{Si}^t\text{BuMe}_2)_2$, $\text{HN}(\text{Si}^t\text{BuMe}_2)(\text{Si}^i\text{Pr}_3)$ and $\text{HN}(\text{Si}^i\text{Pr}_3)_2$ (Scheme 1). Work-up of the respective reaction mixtures after 8 hours reproducibly gave crystals of the chloride Hauser bases, $[\text{Mg}(\text{N}^{\text{RR}'})](\mu\text{-Cl})(\text{THF})_2$ ($\text{N}^{\text{RR}'} = \{\text{N}(\text{Si}^t\text{BuMe}_2)_2\}^-$, **1**; $\{\text{N}(\text{Si}^t\text{BuMe}_2)(\text{Si}^i\text{Pr}_3)\}^-$, **2**; $\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}^-$, **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 ¹H 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, $[\text{K}(\text{N}^{\text{RR}'})]$, did not give the expected amido-Grignard reagents, $[\text{Mg}(\text{N}^{\text{RR}'})](\text{C}_3\text{H}_5)_n$, despite several attempts at optimising the reaction conditions. However, in the attempted preparation of $[\text{Mg}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}\text{-}(\text{C}_3\text{H}_5)_n]$ several crystals of complex **3** were identified together with a crystal of $[\text{Mg}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}(\mu\text{-C}_3\text{H}_5)]_\infty$ (**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 ¹H and ¹³C{¹H} NMR spectra of **1** in *d*₆-benzene are unremarkable and not shifted considerably from those reported for $[\text{K}\{\text{N}(\text{SiMe}_2^t\text{Bu})_2\}_2]$, although the ²⁹Si{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 ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra of these complexes exhibit only minor impurity signals



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



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)	2.118(2)
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)

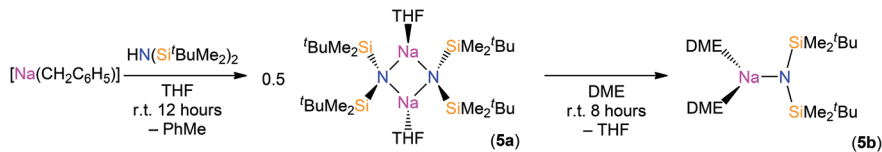
(C₃H₅)_n. However, we were not able to isolate the amido-Grignard reagent from this reaction mixture, even after 10 days of stirring, and ¹H NMR spectroscopy revealed a complex mixture of products. We concluded from these observations that allylmagnesium chloride is unsuitable for facile and reproducible 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^tBuMe₂)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{μ-N(Si^tBuMe₂)₂}]₂ (**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{μ-N(SiMe₂Bu^t)₂}]₂(C₇H₈)_∞ under vacuum yielded **6**, but this was not structurally characterised.²⁸ In the solid state, complex **6** is dimeric with a K₂N₂ 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{μ-N(SiMe₂Bu^t)₂}]₂(C₇H₈)_∞ [K–N 2.874(2) Å mean; K–N–K 78.37(5)°; N–K–N 101.63(5)°]²⁸ and [K(μ-Nⁿ)]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'})(μ-CH₃)₂]₂ (N^{RR'} = {N(Si^tBuMe₂)₂}⁻, **7a**; {N(Si^tBuMe₂)(SiⁱPr₃)₂}⁻, **8**; {N(SiⁱPr₃)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^tBuMe₂)₂}(CH₃)(DME)] (**7b**) (Scheme 3). Workup and crystallisation from





Scheme 2 Synthesis of complexes 5a–b.

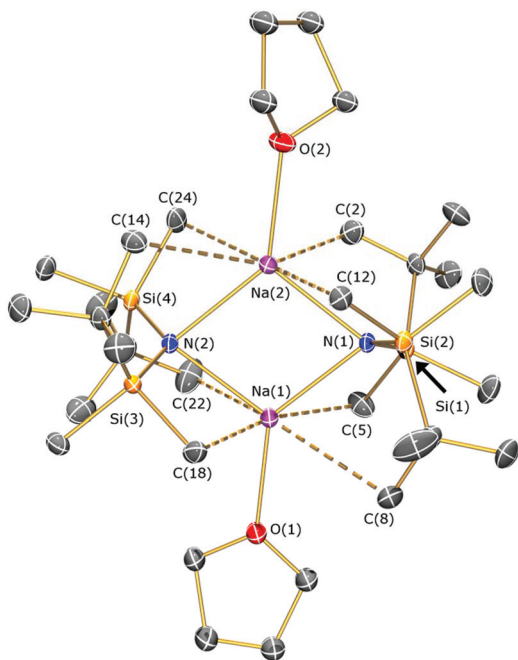


Fig. 3 Molecular structure of 5a with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity.

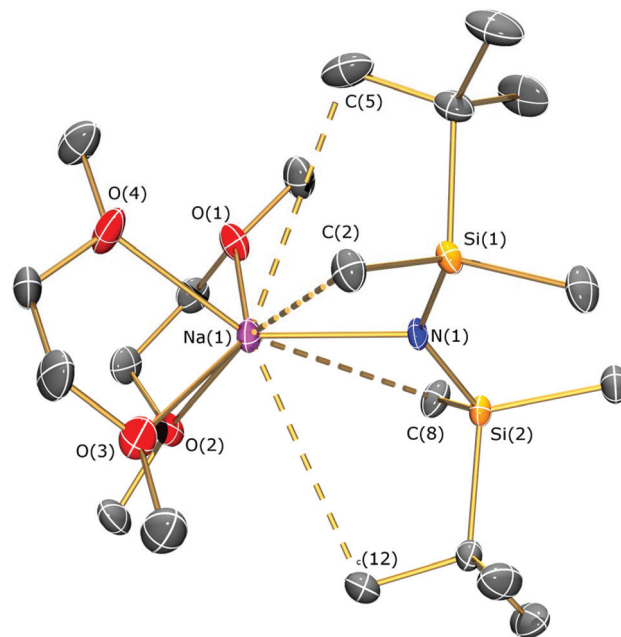
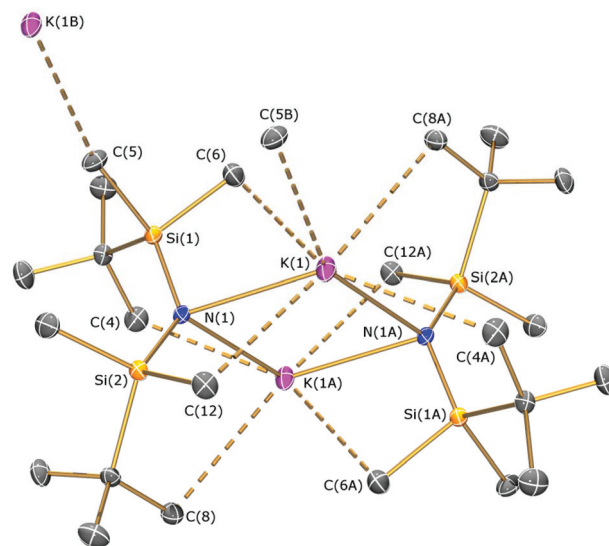
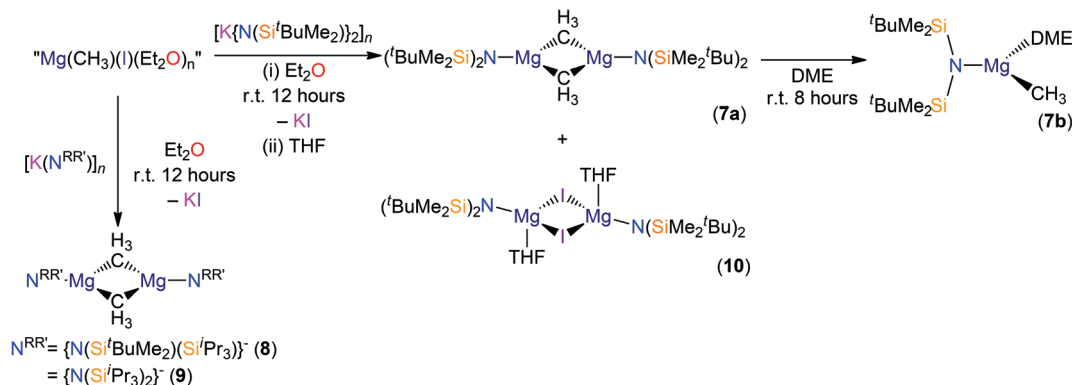


Fig. 4 Molecular structure of 5b with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity.

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 $[\text{Mg}\{\text{N}(\text{Si}^t\text{BuMe}_2)_2\}\{\mu\text{-I}(\text{THF})_2\}]_2$ (10) was obtained (4%) when attempting to isolate 7a, which has presumably formed *via* complex Schlenk equilibria.¹ Treatment of methylmagnesium iodide with $\text{HN}^{\text{RR}'}$ 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 $\text{HN}(\text{Si}^t\text{BuMe}_2)_2$ under similar forcing conditions in hexanes. Germane to this, no reaction was observed between di-*n*-butylmagnesium and $\text{HN}(\text{Si}^t\text{BuMe}_2)_2$ 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 protolysis reactions between alkylmagnesium complexes and $\text{HN}^{\text{RR}'}$. 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.

CH₃-bridged Hauser bases with monodentate N-donor ligands. Complex **7b** is unusual as it is monomeric with a terminal Mg–CH₃ group, and there are few examples of this motif in the literature.³⁸

The ¹H and ¹³C{¹H} 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 multi-dentate 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 ²⁹Si{¹H} 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 CH₃ moieties to form central Mg₂C₂ 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 MgNSi₂ fragments of all three ligands are roughly planar in **7a**, **8** and **9**; these planes are twisted relative to the central Mg₂C₂ 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

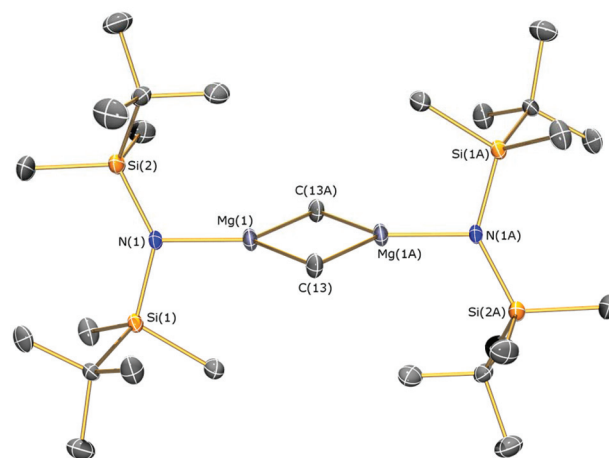


Fig. 6 Molecular structure of **7a** with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity. Symmetry operation to generate equivalent atoms: $-x, -y, -z$.

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 Mg₂I₂ 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.

Conclusions

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



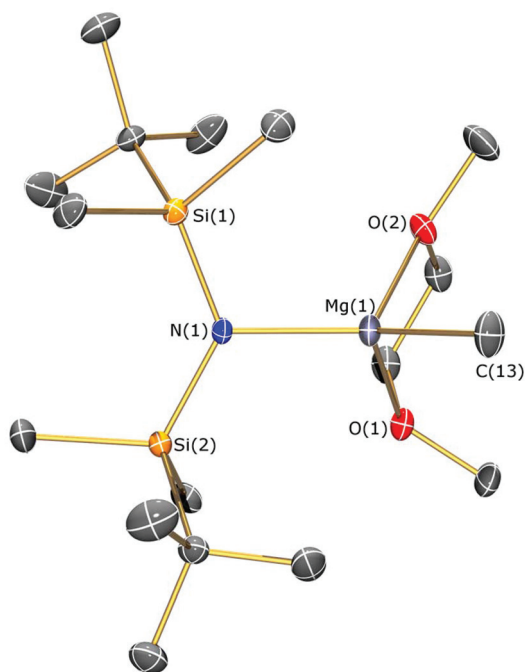


Fig. 7 Molecular structure of **7b** with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity.

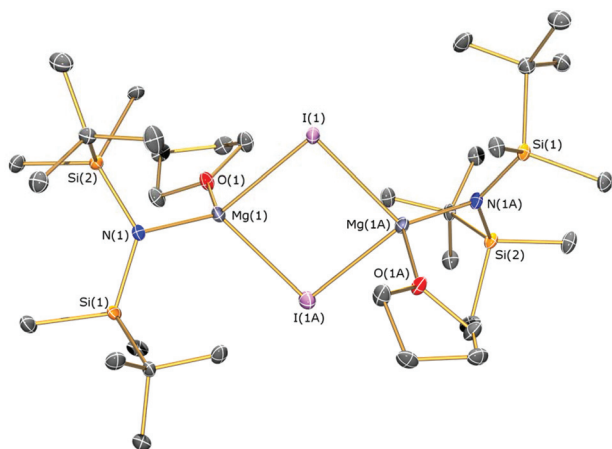


Fig. 8 Molecular structure of **10** with selective atom labelling. Displacement ellipsoids set at 30% probability level and hydrogen atoms omitted for clarity. Symmetry operation to generate equivalent atoms: $x + 1/2, -y + 1/2, z - 1/2$.

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. $[\text{K}\{\text{N}(\text{Si}^t\text{BuMe}_2)_2\}]_n$,^{29a} $[\text{K}\{\text{N}(\text{Si}^t\text{BuMe}_2)(\text{Si}^i\text{Pr}_3)_2\}]_n$,²⁸ $[\text{K}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}]_n$,^{29b} were prepared according to published procedures. $[\text{Na}(\text{CH}_2\text{C}_6\text{H}_5)]$ 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 , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ 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

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



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 C₂₃H₅₇Mg₂N₂Si₄·0.75C₇H₈: 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}

¹H NMR (*d*₆-benzene, 298 K): δ = -0.81 (s, 6H, Mg-CH₃), 0.31 (s, 12H, Si(CH₃)₂), 1.12 (m, 6H, SiCH(CH₃)₂), 1.15 (s, 18H, SiC(CH₃)₃), 1.31 (d, 18H, J_{HH} = 4 Hz, SiCH(CH₃)₂). ¹³C{¹H} NMR (*d*₆-benzene, 298 K): δ = -13.02 (Mg-CH₃), 1.82 (Si(CH₃)₂), 17.00 (SiCH(CH₃)₂), 20.14 (SiCH(CH₃)₂), 20.73 (SiC(CH₃)₃), 28.55 (SiC(CH₃)₃). ²⁹Si{¹H} NMR (*d*₆-benzene, 298 K): δ = -2.90 (Si¹Pr₃), -1.76 (Si^tBuMe₂). FTIR (Nujol, cm⁻¹): ν = 1251 (s), 1015 (s), 820 (s), 780 (s), 722 (s), 641 (m), 627 (m).

[Mg{N(SiⁱPr₃)₂}(μ-CH₃)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(SiⁱPr₃)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 C₂₀H₄₈Mg₂N₂Si₄: C, 62.00; H, 12.32; N, 3.81. Found C, 61.93; H, 12.23; N, 3.87. ¹H NMR (*d*₆-benzene, 298 K): δ = -0.80 (s, 6H, Mg-CH₃), 1.19 (m, 12H, SiCH(CH₃)₂), 1.34 (d, 36H, J_{HH} = 8 Hz, SiCH(CH₃)₂). ¹³C{¹H} NMR (*d*₆-benzene, 298 K): δ = -12.19 (Mg-CH₃), 17.44 (SiCH(CH₃)₂), 20.41 (SiCH(CH₃)₂). ²⁹Si{¹H} NMR (*d*₆-benzene, 298 K): δ = -3.15 (SiⁱPr₃). FTIR (Nujol, cm⁻¹): ν = 1000 (s), 979 (m), 878 (m), 798 (m), 739 (s), 657 (m), 617 (m).

Acknowledgements

We thank the EPSRC and The University of Manchester for generously supporting this work. This work was funded by the Engineering and Physical Sciences Research Council (grant numbers EP/K039547/1 and EP/L014416/1).

References

- G. S. Silverman and P. E. Rakita, *Handbook of Grignard Reagents*, Marcel Dekker, Inc., New York, NY, 1996.
- (a) J. K. Stille and W. J. Scott, *J. Am. Chem. Soc.*, 1986, **108**, 3033; (b) E. C. Ashby and A. B. J. Goel, *Inorg. Chem.*, 1978, **17**, 1862; (c) K. Kobayashi, M. Kawakita, S. Irisawa, H. Akamatsu, K. Sakashita, O. Morikawa and H. Konishi, *Tetrahedron*, 1998, **54**, 2691; (d) D. Bonafoux, M. Bordeau, C. Brian and P. Cazeau, *J. Org. Chem.*, 1996, **61**, 5532; (e) N. A. Van Draanen, S. Arseniyadis, M. T. Crimmins and C. H. Heathcock, *J. Org. Chem.*, 1991, **56**, 2499; (f) Y. Kondo, A. Yoshida and T. Sakamoto, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2331; (g) K. A. Swiss, C. Woo-Baeg, D. C. Liotta and A. F. Abdel-Maryanoff, *J. Org. Chem.*, 1991, **56**, 5978; (h) J. F. Allan, K. W. Henderson and A. R. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1997, 1149.
- (a) P. García-Álvarez, D. V. Graham, E. Hevia, A. R. Kennedy, J. Klett, R. E. Mulvey, C. T. O'Hara and S. Weatherstone, *Angew. Chem., Int. Ed.*, 2008, **47**, 8079; (b) R. E. Mulvey and S. D. Robertson, *Top. Organomet. Chem.*, 2013, **45**, 103; (c) A. G. M. Barrett, M. R. Crimmin, M. S. Hill and P. A. Procopiou, *Proc. R. Soc. London, Ser. A*, 2010, **466**, 927; (d) S. Harder, *Chem. Rev.*, 2010, **110**, 3852; (e) J.-F. Carpentier and Y. Sarazin, *Top. Organomet. Chem.*, 2013, **45**, 141; (f) M. R. Crimmin and M. S. Hill, *Top. Organomet. Chem.*, 2013, **45**, 191; (g) M. F. Lappert, A. Protchenko, P. P. Power and A. Seeber, *Metal Amide Chemistry*, John Wiley & Sons Ltd, Wiltshire, UK, 2009.
- (a) K. Ruhlandt-Senge, A. Torvisco and A. Y. O'Brien, *Coord. Chem. Rev.*, 2011, **255**, 1268; (b) W. D. Buchanan, D. G. Allis and K. Ruhlandt-Senge, *Chem. Commun.*, 2010, **46**, 4449.
- M. Westerhausen, *Coord. Chem. Rev.*, 2008, **252**, 1516.
- (a) M. D. Anker, M. Arrowsmith, P. Bellham, M. S. Hill, G. Kociok-Köhn, D. J. Liptrot, M. F. Mahon and C. Weetman, *Chem. Sci.*, 2014, **5**, 2826; (b) D. J. Liptrot, M. S. Hill and M. F. Mahon, *Angew. Chem., Int. Ed.*, 2014, **53**, 6224.
- Y. Sarazin, M. Schormann and M. Bochmann, *Organometallics*, 2004, **23**, 3296.
- (a) M. H. Chisholm and N. W. Eilerts, *Chem. Commun.*, 1996, 853; (b) M. H. Chisholm, N. W. Eilerts, J. C. Huffman, S. S. Iver, V. Pacol and K. Phomphrai, *J. Am. Chem. Soc.*, 2000, **122**, 11845; (c) M. H. Chisholm, J. Galluci and K. Phomphrai, *Chem. Commun.*, 2003, 48.
- S. P. Green, C. Jones and A. Stasch, *Science*, 2007, **318**, 1754.
- (a) A. Stasch and C. Jones, *Dalton Trans.*, 2011, **40**, 5659; (b) A. Stasch, *Angew. Chem., Int. Ed.*, 2014, **53**, 10200; (c) C. Jones and A. Stasch, *Top. Organomet. Chem.*, 2013, **45**, 73.
- (a) S. Krieck, L. Yu, M. Reiher and M. Westerhausen, *Eur. J. Inorg. Chem.*, 2010, 197; (b) S. Krieck and M. Westerhausen, *Chem. Unserer Zeit*, 2009, **43**, 384; (c) M. Westerhausen, *Angew. Chem., Int. Ed.*, 2008, **47**, 2185.
- G. J. Moxey, F. Ortu, L. G. Sidley, H. N. Strandberg, A. J. Blake, W. Lewis and D. L. Kays, *Dalton Trans.*, 2014, **43**, 4838, and references therein.
- L. Bourget-Merle, M. F. Lappert and J. S. Severn, *Chem. Rev.*, 2002, **102**, 3031.
- For reviews of the closely related bis(iminophospharano)-methanide ligand see: (a) T. K. Panda and P. W. Roesky, *Chem. Soc. Rev.*, 2009, **38**, 2782; (b) S. T. Liddle, D. P. Mills and A. J. Wooles, *Top. Organomet. Chem.*, 2010, **36**, 29; (c) S. T. Liddle, D. P. Mills and A. J. Wooles, *Chem. Soc. Rev.*, 2011, **40**, 2164.
- See: M. Westerhausen, *Coord. Chem. Rev.*, 1998, **176**, 157; for a review on silylamide Ae chemistry.
- (a) L. Meunier, *C. R. Hebd. Seances Acad. Sci.*, 1903, **136**, 758; (b) C. R. Hauser and H. G. Walker, *J. Am. Chem. Soc.*,



- 1947, **69**, 295; (c) C. R. Hauser and F. C. Frostick, *J. Am. Chem. Soc.*, 1949, **71**, 1350.
- 17 R. A. Bartlett, M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1994, **33**, 4800.
- 18 U. Wannagat, H. Autzen, H. Kuckertz and H.-J. Wismar, *Z. Anorg. Allg. Chem.*, 1972, **394**, 254.
- 19 K.-C. Yang, C.-C. Chang, J.-Y. Huang, C.-C. Lin, G.-H. Lee, Y. Wang and M. Y. Chiang, *J. Organomet. Chem.*, 2002, **648**, 176.
- 20 P. L. Arnold, I. S. Edworthy, C. D. Carmichael, A. J. Blake and C. Wilson, *Dalton Trans.*, 2008, 3739.
- 21 (a) P. C. Junk, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1987, 1162; (b) S. Yuan, S. Bai, D. Liu and W.-H. Sun, *Organometallics*, 2010, **29**, 2132; (c) A. S. Batsanov, P. D. Bolton, R. C. B. Copley, M. G. Davidson, J. A. K. Howard, C. Lustig and R. D. Price, *J. Organomet. Chem.*, 1998, **550**, 445; (d) D. R. Armstrong, P. García-Álvarez, A. R. Kennedy, R. E. Mulvey and J. A. Parkinson, *Angew. Chem., Int. Ed.*, 2010, **49**, 3185; (e) T. Hascall, M. M. Olmstead and P. P. Power, *Angew. Chem., Int. Ed.*, 1994, **33**, 1000; (f) J. A. Rood, S. E. Hinman, B. C. Noll and K. W. Henderson, *Eur. J. Inorg. Chem.*, 2008, 3935; (g) F. Ortu, G. J. Moxey, A. J. Blake, W. Lewis and D. L. Kays, *Chem. – Eur. J.*, 2015, **21**, 6949.
- 22 P. E. Eaton, C.-H. Lee and Y. Xiong, *J. Am. Chem. Soc.*, 1989, **111**, 8016.
- 23 (a) L. M. Engelhardt, B. S. Jolly, P. C. Junk, C. L. Raston, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1986, **39**, 1337; (b) H. Schumann, A. Steffens and M. Hummert, *Z. Anorg. Allg. Chem.*, 2009, **635**, 1041; (c) T. Y. Her, C. C. Chang, G. H. Lee, S. M. Peng and Y. Wang, *Inorg. Chem.*, 1994, **33**, 99; (d) B. Conway, E. Hevia, A. R. Kennedy, R. E. Mulvey and S. Weatherstone, *Dalton Trans.*, 2005, 1532.
- 24 A. R. Kennedy, R. E. Mulvey and S. D. Robertson, *Dalton Trans.*, 2010, **39**, 9091.
- 25 P. C. Andrikopoulos, D. R. Armstrong, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, R. B. Rowlings and S. Weatherstone, *Inorg. Chim. Acta*, 2007, **360**, 1370.
- 26 (a) D. J. Gallagher, K. W. Henderson, A. R. Kennedy, C. T. O'Hara, R. B. Rowlings and R. E. Mulvey, *Chem. Commun.*, 2002, 376; (b) E. Hevia, F. R. Kenley, A. R. Kennedy, R. E. Mulvey and R. B. Rowlings, *Eur. J. Inorg. Chem.*, 2003, 3347; (c) E. Hevia, D. J. Gallagher, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara and C. Talmard, *Chem. Commun.*, 2004, 2422; (d) P. C. Andrikopoulos, D. R. Armstrong, W. Clegg, C. J. Gilfillan, E. Hevia, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, J. A. Parkinson and D. M. Tooke, *J. Am. Chem. Soc.*, 2004, **126**, 11612; (e) K. J. Drewette, K. W. Henderson, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara and R. B. Rowlings, *Chem. Commun.*, 2002, 1176.
- 27 See, for example: (a) A. Krasovskiy, V. Krasovskaya and P. Knochel, *Angew. Chem., Int. Ed.*, 2006, **45**, 2958; (b) W. Lin, O. Baron and P. Knochel, *Org. Lett.*, 2006, **8**, 5673; (c) B. Haag, M. Mosrin, H. Ila, V. Malakhov and P. Knochel, *Angew. Chem., Int. Ed.*, 2011, **50**, 9794; (d) A. J. Martínez-Martínez, A. R. Kennedy, R. E. Mulvey and C. T. O'Hara, *Science*, 2014, **346**, 834.
- 28 C. A. P. Goodwin, K. C. Joslin, S. J. Lockyer, A. Formanuk, G. A. Morris, F. Ortu, I. J. Vitorica-Yrezabal and D. P. Mills, *Organometallics*, 2015, **34**, 2314.
- 29 (a) C. A. P. Goodwin, F. Tuna, E. J. L. McInnes, S. T. Liddle, J. McMaster, I. J. Vitorica-Yrezabal and D. P. Mills, *Chem. – Eur. J.*, 2014, **20**, 14579; (b) N. F. Chilton, C. A. P. Goodwin, D. P. Mills and R. E. P. Winpenny, *Chem. Commun.*, 2015, **51**, 101.
- 30 J. Li, A. Stasch, C. Schenk and C. Jones, *Dalton Trans.*, 2011, **40**, 10448.
- 31 Z. Rappoport and I. Marek, *The Chemistry of Organomagnesium Compounds*, John Wiley & Sons Ltd, West Sussex, UK, 2008.
- 32 P. B. Hitchcock, M. F. Lappert, L. Maron and A. V. Protchenko, *Angew. Chem., Int. Ed.*, 2008, **47**, 1488.
- 33 CSD version 5.36, November 2014, update 3 (May 2015); F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380.
- 34 (a) M. G. Davidson, G. Garcia-Vico, A. R. Kennedy, R. E. Mulvey and S. D. Robertson, *Chem. – Eur. J.*, 2011, **17**, 3364; (b) P. J. Bailey, R. A. Coxall, C. M. Dick, S. Fabre, L. C. Henderson, C. Herber, S. T. Liddle, D. Loroño-González, A. Parkin and S. Parsons, *Chem. – Eur. J.*, 2003, **9**, 4820; (c) D. Hoffmann, W. Bauer, F. Hampe, N. J. R. van Eikema Hommes, P. v. R. Schleyer, P. Otto, U. Pieper, D. Stalke, D. S. Wright and R. J. Snaith, *J. Am. Chem. Soc.*, 1994, **116**, 528; (d) M. Schlosser and J. Hartmann, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 508.
- 35 (a) M. Karl, G. Seybert, W. Massa, K. Harms, S. Agarwal, R. Maleika, W. Stelter, A. Greiner, W. Heitz, B. Neumuller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1301; (b) A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, S. D. Robertson and G. M. Robertson, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2012, **68**, m1468; (c) W. J. Evans, D. B. Rego and J. W. Ziller, *Inorg. Chem.*, 2006, **45**, 3437, and references therein.
- 36 (a) M. L. Cole, A. J. Davies, C. Jones and P. C. Junk, *J. Organomet. Chem.*, 2004, **689**, 3093; (b) C. Glock, H. Górls and M. Westerhausen, *Eur. J. Inorg. Chem.*, 2011, 5288; (c) M. L. Cole and P. C. Junk, *Dalton Trans.*, 2003, 2109; (d) P. Liu, H. Chen, Y. Zhang, M. Xue, Y. Yao and Q. Shen, *Dalton Trans.*, 2014, **43**, 5586.
- 37 K. F. Tesh, T. P. Hanusa and J. C. Huffman, *Inorg. Chem.*, 1990, **29**, 1584.
- 38 (a) V. C. Gibson, J. A. Segal, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2000, **122**, 7120; (b) P. J. Bailey, R. A. Coxall, C. M. Dick, S. Fabre and S. Parsons, *Organometallics*, 2001, **20**, 798; (c) M. Arrowsmith, B. Maitland, G. Kociok-Köhn, A. Stasch, C. Jones and M. S. Hill, *Inorg. Chem.*, 2014, **53**, 10543; (d) S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards and G. J. McIntyre, *Chem. – Eur. J.*, 2010, **16**, 938.



- 39 M. Veith, W. Frank, F. Tollner and H. Lange, *J. Organomet. Chem.*, 1987, **326**, 315.
- 40 (a) P. J. Bailey, R. A. Coxall, C. M. E. Dick, S. Fabre, S. Parsons and L. J. Yellowlees, *Chem. Commun.*, 2005, 4563; (b) T.-Y. Her, C.-C. Chang and L.-K. Liu, *Inorg. Chem.*, 1992, **31**, 2291; (c) P. J. Bailey, C. M. E. Dick, S. Fabre and S. Parsons, *J. Chem. Soc., Dalton Trans.*, 2000, 1665.
- 41 (a) M. Veith, A. Spaniol, J. Poehlmann, F. Gross and V. Huch, *Chem. Ber.*, 1993, **126**, 2625; (b) B. Lian, M. Christophe, O. L. Casagrande Jr., T. Roisnel and J.-F. Carpentier, *Polyhedron*, 2007, **26**, 3817; (c) W. Zhang, J.-P. Hu, D. Xiao-Feng, Y.-J. Wu and Z.-W. Ye, *Inorg. Chem. Commun.*, 2003, **6**, 1185; (d) M. L. H. Green, G. A. Moser, I. Packer, F. Petit, R. A. Forder and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1974, 839; (e) P. Haiss, A. Kuhn, N. Kuhn, C. Maichle-Mößmer, S. Laufer, M. Steimann and K.-P. Zeller, *Eur. J. Inorg. Chem.*, 2011, **22**, 3284.

