Alkaline Earth Complexes of a Sterically Demanding Guanidinate Ligand

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Abstract

The synthesis of the guanidine MesN{C(NCy$_2$)}N(H)Mes (**L**H; Mes = 2,4,6-Me$_3$C$_6$H$_2$, Cy = cyclohexyl), and its use as a proligand for the synthesis of alkaline earth metal complexes are reported. Described herein are (i) an unusual Hauser base cubane, (ii) a homoleptic and a base-stabilized magnesium complex featuring the same guanidinate ligands, and (iii) the comparison of a series of alkaline earth (Mg, Ca, Sr, Ba) *bis*(guanidinate) complexes, which allows the opportunity to compare the changing trends in bonding as the Group is descended. The reaction between **L**H and MeMgI(OEt$_2$)$_2$ yields the Hauser base as a mixture of the tetramer [Mg$_4$**L**$_4$(μ$_3$-I)$_4$] (**1a**) and dimer [Mg$_2$**L**$_2$(μ-I)$_2$(OEt$_2$)$_2$] (**1b**), and the reaction with two equivalents of Mg^{n}Bu$_2$ leads to the formation of four-coordinate [Mg**L**$_2$] (**2**), which features a square-planar geometry for the magnesium cation, or five-coordinate [Mg**L**$_2$(THF)] (**3**), depending on the solvent used. **1a** is the first crystallographically-characterized cubane structure to consist of four LAeX (L = ligand, X = halide) units. The complexes [Ae**L**$_2$(THF)$_2$] (Ae = Ca, **4**; Ae = Sr, **5**) and [Ba**L**$_2$] (**6**) were synthesized *via* redox transmetallation/ligand exchange reactions. Complex **6** is the first example

of a homoleptic, monomeric barium complex of the NCN ligand family, with the structure stabilized by a number of barium-arene interactions in the solid state.

1. Introduction

Although the metal-organic chemistry of magnesium has been long explored, the related chemistry of the heavier alkaline earth elements (Ca, Sr, Ba) has only recently started to gain momentum,[1] driven by a wealth of potential applications in the catalysis of reactions such as hydroamination,[2] hydrosilylation,[3] styrene polymerization,[4] the Tishchenko reaction,[5] and in the formation of thin films for solid state devices.[6] Despite this potential, a number of issues impede the quest for new complexes featuring the heavier alkaline earth metals, such as low compound stability, aggregation to form low solubility oligomers and Schlenk equilibrium reactions. In the chemistry of strontium and barium, large ionic radii and low charge density exacerbate such issues.

Sterically demanding, bidentate ligand systems such as β-diketiminates and the related amidinate and guanidinate ligands have been used to great effect in the stabilization of complexes featuring hitherto unknown oxidation states and bonding modes, such as the Mg(I) species [RMg–MgR] (R = $[(Dipp)NC(Me)]_2CH$ and $DippN\{CN({}^{i}Pr)_2\}NDipp$, where Dipp = 2,6-${}^{i}Pr_2C_6H_3$).[7] These sterically bulky bidentate anions effectively shield the alkaline earth cations, thereby minimizing aggregation and coordination by extraneous Lewis bases, and to increase the stability of the resultant complexes towards air and moisture. The delocalization of the negative charge reduces the nucleophilicity of the anion, and therefore the likelihood of side reactions such as Schlenk equilibrium reorganization and ether degradation reactions.[8-10]

Given the renewed interest in alkaline earth chemistry, and the requirement to develop an understanding of highly reactive Group 2 complexes which have potential applications in materials science and catalysis, a systematic study of the solution and solid state structures of the alkaline earth *bis*(guanidinates) will inform further developments in this area. Herein, we describe the synthesis and structural characterization of a series of alkaline earth metal complexes of guanidinate ligands, which offer the opportunity for comparative studies of related magnesium complexes and of the properties of guanidinate complexes as Group 2 is descended.

2. Results and Discussion

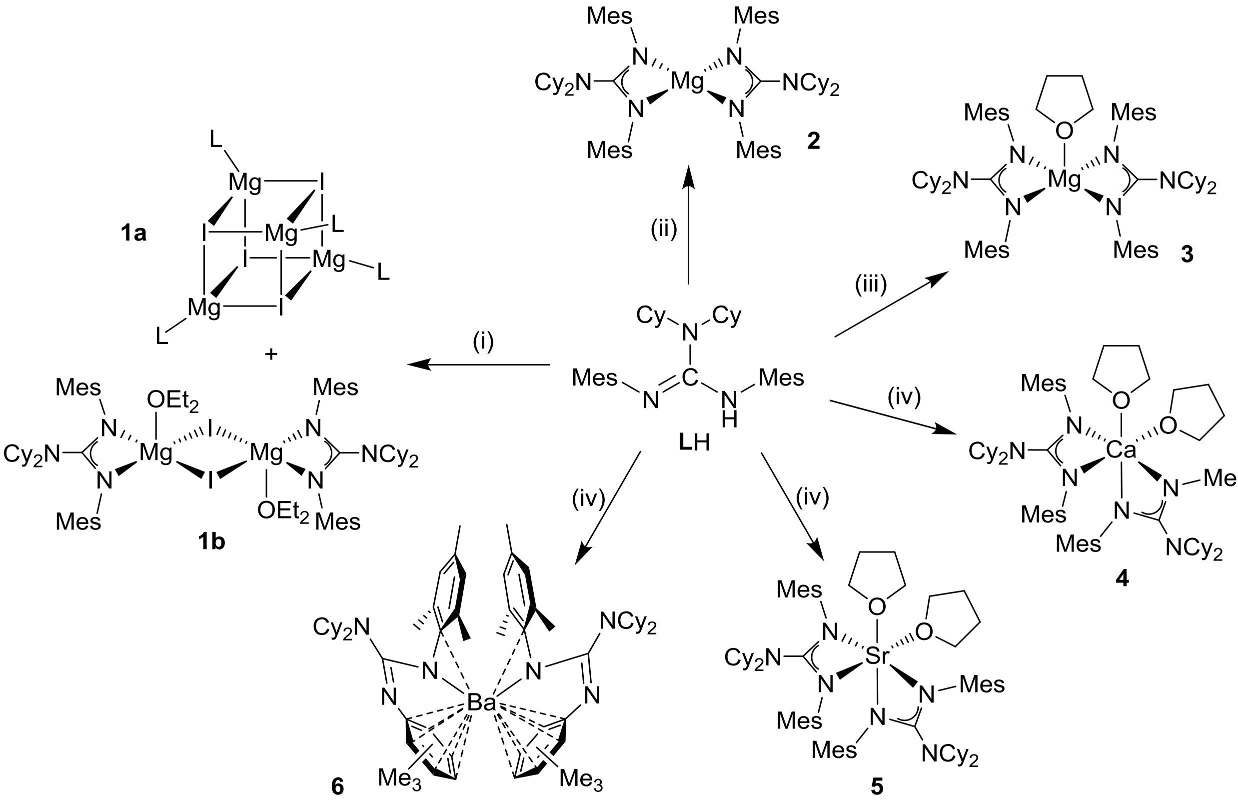
2.1 Synthesis and Spectroscopic Characterization

The guanidine MesN{C(NCy_2)}N(H)Mes (**L**H) (Scheme 1) was synthesized in good yield *via* minor modification of existing literature methods for the synthesis of these compounds.[11] In the ^{1}H NMR spectra, the N-H resonance is at 4.9 ppm, and in the $^{13}C\{^{1}H\}$ NMR spectra, the guanidine backbone N*C*N resonance is at 149.9 ppm, which is in the range reported for amidines and guanidines.[12-15] In contrast with amidines such as Dipp{C(*p*-Tol)}N(H)Dipp,[12] there is no evidence of more than one isomeric form of **L**H in solution.

The syntheses of alkaline earth metal complexes **1**-**6** from proligand **L**H are detailed in Scheme 1. The reaction between the **L**H and the Grignard reagent $MeMgI(OEt_2)_2$ yielded the corresponding Hauser base **L**MgI, as a mixture of the tetramer [Mg_4**L**$_4(\mu_3\text{-}I)_4$] (**1a**) and dimer [Mg_2**L**$_2(\mu\text{-}I)_2(OEt_2)_2$] (**1b**), the latter complex also featuring additional coordination of a molecule of diethyl ether per magnesium cation. Hauser bases are magnesium amide bases, first described by Hauser and Walker in 1947.[16]

The mixture of crystals of **1a** and **1b** could not be separated by hand picking, but the microanalysis result, as well as the ^{1}H NMR integration ratio of diethyl ether to guanidinate ligand in d_6-benzene, indicates a 1:1 mixture of **1a** and **1b**. Fragmentation of cubanes into monomers or lower aggregates in solution and under mass spectrometry conditions has been observed previously within our research group.[17] The use of d_8-THF as a solvent leads to a simplification of the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, and only one ligand environment is observed, due to the formation of a single species in solution. Based on the findings of Mulvey and co-workers on TMP (TMP = 2,2,6,6-tetramethylpiperidide) Hauser bases, it is likely that this is a THF-stabilized dimer, as seen in the formation of [{(TMP)Mg(THF)Cl}$_2$] in THF solution.[18] A study on alkylmagnesium alkoxides by Coates and co-workers revealed that in non-coordinating solvents such as benzene, the unsolvated tetramers and oligomers (depending on the steric demands of the alkoxide) are preferred, but in coordinating solvents such as THF and diethyl ether, dimeric solvate structures are formed.[19,20]

Complexes **2**-**6** are monomeric and readily soluble in hydrocarbon solvents. The reaction between **L**H and Mg^{n}Bu$_2$ in DME (DME = 1,2-dimethoxyethane) or THF leads to the formation of four-coordinate [Mg**L**$_2$] (**2**) or five-coordinate [Mg**L**$_2$(THF)] (**3**), respectively, in good yields with concomitant evolution of *n*-butane. These compounds have been analyzed by NMR spectroscopy and the empirical formulae confirmed by elemental analysis. From the similarities between the ^{1}H and ^{13}C{^{1}H} NMR spectra for **2** and **3**, the additional coordination of a THF molecule has little effect on the solution structures of these complexes.



Scheme 1 Synthesis of complexes **1**-**6**. *Reagents and Conditions:* (i) 1 eq. MeMgI(OEt$_2$)$_2$, diethyl ether, –78 °C → room temperature, overnight, –MeH (complexes **1a** and **1b** obtained in a 1:1 ratio). (ii) 0.5 eq. Mg^{n}Bu$_2$, DME, –78 °C → room temperature, overnight, –^{n}BuH. (iii) 0.5 eq. Mg^{n}Bu$_2$, THF, –78 °C → room temperature, overnight, –^{n}BuH. (iv) 2 eq. M (M = Ca, Sr, Ba), 0.5

eq. $HgPh_2$, THF, room temperature, overnight, –PhH, –0.5 eq. Hg. **L** = $[MesN\{C(NCy_2)\}NMes]^-$.

The *bis*(guanidinate) complexes [Ca**L**$_2$(THF)$_2$] (**4**), [Sr**L**$_2$(THF)$_2$] (**5**) and [Ba**L**$_2$] (**6**) were synthesized *via* the redox transmetallation/ligand exchange reaction between **L**H, the finely divided metal and $HgPh_2$ in THF solution, which has been reported for complexes featuring amidinate and pyrazolates, for example.[21] Although this is the first time that this methodology has been applied to the synthesis of alkaline earth-guanidinate complexes, the reactions were very clean, and yielded the products in moderate to good yields. Satisfactory microanalyses could not be obtained for compounds **4-6**: this is a recognized problem within the literature for alkaline earth metal complexes,[22] and the proposed formulations have been confirmed by NMR spectroscopy and mass spectrometry (in the case of **5** and **6** it was possible to obtain high resolution mass spectra). The NMR spectra of **4** and **5** indicate the presence of one ligand environment in solution, along with two molecules of THF. The NMR spectra for **6** indicate the presence of one ligand environment in solution, and confirm the absence of coordinated solvent. In the ^{1}H NMR spectrum of **6** the resonance for the *ortho*-methyl substituents of the mesityl groups is broadened and significantly shifted in comparison to that for the other *bis*(guanidinate) complexes; the resonance of δ_H 2.16 ppm in **6** is upfield compared to values of δ_H 2.36-2.48 ppm for **2-5**, which is conceivably due to an interaction with these aryl rings in solution, similar to that observed in the solid state (*vide infra*).

2.2 Crystallographic Characterization

Crystals of **L**H of suitable quality for X-ray diffraction studies were grown by the slow cooling of a saturated hexane solution to –30 °C. In the solid state, **L**H exists exclusively in the Z_{anti} configuration, and there is a significant difference of *ca.* 0.107 Å in the lengths of the C–N and the C=N bonds, which is similar to that for other guanidines such as DippN{C(NCy_2)}N(H)Dipp.[23]

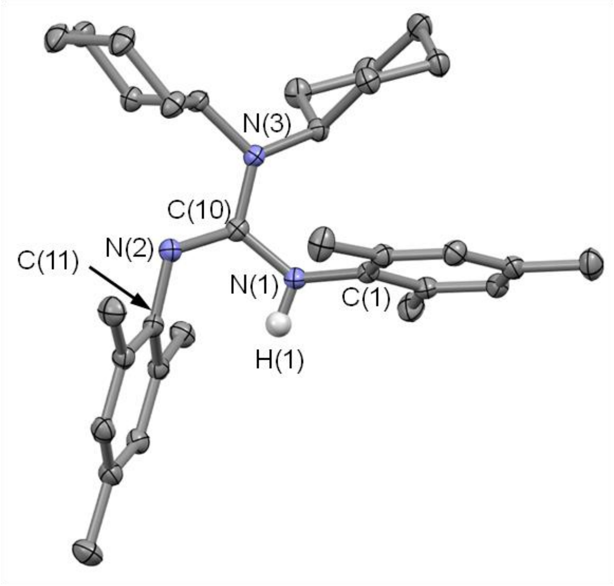


Figure 1: Molecular structure of **L**H with displacement ellipsoids set at 50% probability level. With the exception of H(1) all hydrogen atoms have been omitted for clarity. Relevant bond lengths (Å) and angles (°): N(1)–C(10) 1.3977(12), N(2)–C(10) 1.2912(13), N(3)–C(10) 1.3819(12), N(1)–C(1) 1.4312(12), N(2)–C(11) 1.4127(12), N(1)–C(10)–N(2) 122.53(9), C(1)–N(1)–C(10) 128.50(8), C(10)–N(2)–C(11) 120.14(8).

The investigation of the structures of (i) an unusual Hauser base cubane, (ii) a homoleptic *vs*. a base-stabilized magnesium complex, and (iii) a series of alkaline earth complexes from Mg-Ba featuring the same ligand, provides invaluable information about the trends in the coordination and structural chemistry of these elements.

Colorless crystals of the cubane [Mg_4**L**$_4$(μ_3-I)$_4$] (**1a**) were grown *via* the slow cooling of a saturated toluene solution to –30 °C and were interspersed with a colorless microcrystalline material identified as dimer **1b**. The structures of **1a**, along with relevant bond lengths and angles can be found in Figure 2. Structurally authenticated compounds featuring a cubane with an Ae_4X_4

(X = halide) core are as yet unreported; **1a** is the first crystallographically-characterized cubane structure to consist of a tetramer of four LAeX (L = ligand, X = halide) units.[24] The solid state characterization of a tetrameric complex in **1a** is in contrast to that observed for [DippN{CN(^{i}Pr)$_2$}NDippMg(μ-I)]$_2$, presumably due to the greater steric demands of the Dipp-substituted guanidinate ligand.[7] There remains significant interest in the aggregation characteristics of Grignards and related complexes[25] and the resulting implication for their reactivity. Related compounds featuring Mg_4O_4 cores are notable for finding use as single-source starting materials for the deposition of MgO thin films and nanoparticles.[26] Within **1a** each magnesium cation is five-coordinate in a distorted square pyramidal geometry, with the metal coordinated to one guanidinate ligand and three iodide anions. The Mg−I distances vary in the range 2.8343(15)-2.9587(15) Å, with one of these being significantly longer than the other two, leading to distortion of the cube. Concomitant with this are the differing internal angles within the cube which vary from 86.24(4)° (narrowest Mg−I−Mg angle) to 93.87(4)° (widest I−Mg−I angle). Due to lower steric demands in **1a**, the Mg−N distances [2.013(11), 2.037(4) Å], are shorter than those in **3** [2.1286(15), 2.1134(15) Å], which also features a five-coordinate Mg center; concomitant with this are slightly more obtuse N−Mg−N angles in **1a** [65.7(5)°] *vs.* **3** [63.49(6)°].

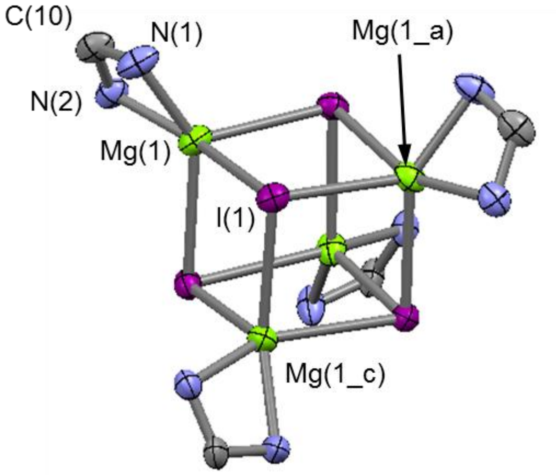


Figure 2: Molecular structure of **1a** with displacement ellipsoids set at 50% probability level. Hydrogen atoms are omitted for clarity. Of the guanidinate ligand, only the CNC backbone is

displayed. Relevant bond lengths (Å) and angles (°): Mg(1)–N(1) 2.013(11), Mg(1)–N(2) 2.037(4), Mg(1)–I(1) 2.8579(15), Mg(1_a)–I(1) 2.9587(15), Mg(1_c)–I(1) 2.8343(15), N(1)–C(10) 1.356(12), N(2)–C(10) 1.357(6), N(3)–C(10) 1.361(12), N(1)–Mg(1)–N(2) 65.7(3), I–Mg–I 89.89(4)-93.87(4), Mg–I–Mg 86.24(4)-89.88(4). Symmetry operation: a = $-\frac{3}{4} + y$, $\frac{3}{4} - x$, $\frac{3}{4} - z$; c = $\frac{3}{4} - y$, $\frac{3}{4} + x$, $\frac{3}{4} - z$.

Single crystals of **2** [Mg**L**$_2$] and **3** [Mg**L**$_2$(THF)] suitable for X-ray diffraction were obtained from the slow cooling of hot hexane solutions of the complexes to room temperature. The structures of **2** and **3**, along with relevant bond lengths and angles can be found in Figures 3 and 4, respectively. In both complexes, the magnesium center is bound by two chelating guanidinate ligands, and in the case of **3** this coordination is supplemented by the additional coordination of a molecule of THF, highlighting that, in the absence of coordinating solvents the guanidinate ligand **L**$^-$ is sufficiently sterically demanding to stabilize homoleptic species. Compound **2** [Mg**L**$_2$] is a four-coordinate monomer, with the magnesium center in a square planar configuration (Σ angles around Mg = 360.1°). This square planar geometry remains highly unorthodox for magnesium, and the few examples of this are complexes of rigid porphryins,[27] Lappert's 1-azallyl complex [Mg(Me$_3$SiNC(^{t}Bu)C(H)SiMe$_3$)$_2$],[28] Junk's *bis*(amidinate) [Mg{DippN{C(*p*-Tol)}NDipp}$_2$],[29] rigid [{2,6-[DippNC(CH$_3$)$_2$]$_2$(C$_5$H$_3$N)}Mg(THF)][30] and some *bis*(amido)silane 'ate' complexes.[31] With the exception of Junk's *bis*(amidinate), these coordination environments are enforced by intramolecular interactions or by sufficiently rigid ligand frameworks. The near linear C(10)···Mg(1)···C(41) arrangement of the two guanidinate ligands around the magnesium center in **2** [173.92(10)°] would appear to minimize the steric repulsion around the metal.

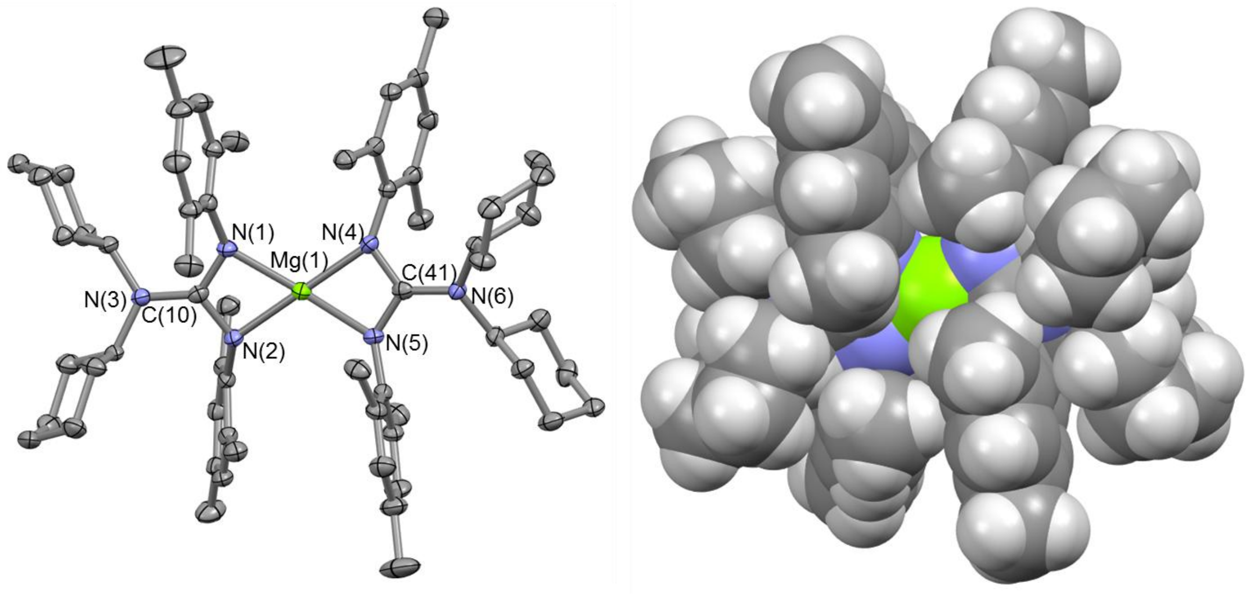


Figure 3: Left: Molecular structure of **2** with displacement ellipsoids set at 50% probability level. All hydrogen atoms have been omitted for clarity. Right: space-filling diagram of **2** (colors used: Mg = green, N = blue, C = gray, H = light gray). Relevant bond lengths (Å) and angles (°): Mg(1)–N(1) 2.049(3), Mg(1)–N(2) 2.049(3), Mg(1)–N(4) 2.049(3), Mg(1)–N(5) 2.052(2), N(1)–C(10) 1.364(4), N(2)–C(10) 1.350(4), N(3)–C(10) 1.377(4), N(4)–C(41) 1.360(4), N(5)–C(41) 1.359(4), N(6)–C(41) 1.369(4), N(1)–Mg(1)–N(2) 65.90(10), N(4)–Mg(1)–N(5) 65.92(9), N(1)–Mg(1)–N(4) 113.87(10), N(2)–Mg(1)–N(5) 114.37(13), N(1)–C(10)–N(2) 110.3(2), N(4)–C(41)–N(5) 110.3(2).

It has been suggested that the square planar disposition of the amidinate ligands around the magnesium center in [Mg{DippN{C(*p*-Tol)}NDipp}$_2$] avoids unfavorable interactions between the sterically demanding Dipp substituents.[29] Examination of the space-filling diagram (Figure 3) indicates that this analogous arrangement is adopted by **2** in order to avoid unfavorable interactions between the sterically demanding mesityl substituents in **2**. From this diagram it also appears that the steric demands on the magnesium center are lower in **2** than in [Mg{DippN{C(*p*-Tol)}NDipp}$_2$]. By performing the synthesis of magnesium complexes in a coordinating, monodentate solvent such as THF, it is also possible to also yield the analogous five-coordinate complex **3**. Crystals of **3** were grown by the slow cooling of a hot hexane solution to room temperature: the solid state structure and relevant bond lengths and angles are shown in Figure 4. Complex **3** features the magnesium center in a distorted square pyramidal geometry (Σ angles around base = 347.2°), with the Addison parameter $\tau = 0.17$ [defined as $(\beta-\alpha)/60$), where β = N(1)–Mg(1)–N(1') and α = N(2)–Mg(1)–N(2'), with a value which varies from 0 (regular square-based pyramidal) to 1 (trigonal bipyramidal geometry)].[32] The THF ligand occupies the apical position of the square-based pyramid. The presence of a coordinated THF molecule pushes the ligands away from a planar configuration, with the magnesium cation sitting 0.49 Å out of the plane defined by the four metal-bound nitrogen atoms.

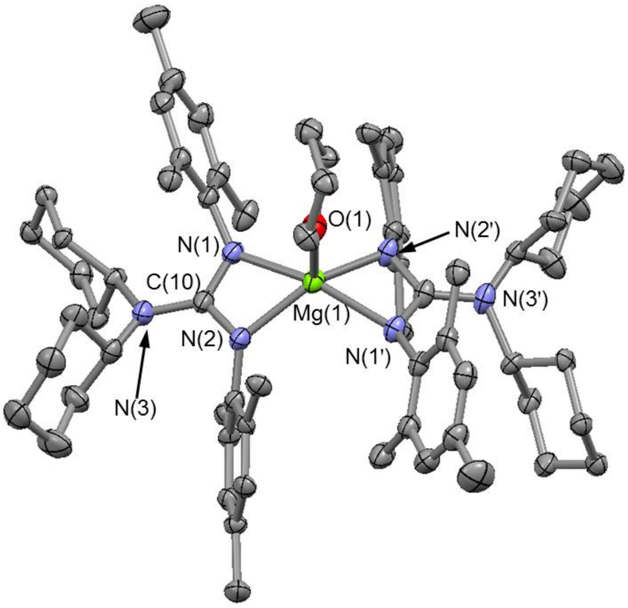


Figure 4: Molecular structure of **3** with displacement ellipsoids set at 50% probability level. Hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (°): Mg(1)–N(1) 2.1286(15), Mg(1)–N(2) 2.1134(15), N(1)–C(10) 1.343(2), N(2)–C(10) 1.358(2), N(3)–C(10) 1.398(2), Mg(1)–O(1) 2.119(2), N(1)–Mg(1)–N(2) 63.49(6), N(1)–Mg(1)–N(2') 110.13(6), N(1)–Mg(1)–N(1') 158.57(9), N(2)–Mg(1)–N(2') 148.11(10), N(1)–C(10)–N(2) 111.44(16), N(1)–Mg(1)–O(1) 100.72(5), N(2)–Mg(1)–O(1) 105.95(5). Symmetry operation: ' = $1-x$, $+y$, $^{3}/_{2}-z$.

Shorter Mg–N distances are observed for four-coordinate **2** [range = 2.049(3)-2.052(2) Å] compared to five-coordinate **3** [2.1286(15), 2.1134(15) Å]; these distances are in line with typical Mg–N bonds within four-coordinate amidinate complexes and five-coordinate guanidinate and amidinate complexes.[15,29,33,34] The steric strain from the additionally coordinated THF in the five-coordinate structure leads to slightly more acute N−Mg−N angles in **3** [63.49(6)°] compared to **2** [65.90(10)° and 65.92(9)°], and a C(10)···Mg(1)···C(10') angle that deviates significantly from linearity [149.92(9)°].

Single crystals of **4** [Ca**L**$_2$(THF)$_2$] and **5** [Sr**L**$_2$(THF)$_2$] suitable for X-ray diffraction study were obtained by the slow cooling of hot hexane solutions of the complexes to room temperature. In these structures, the metal center is bound by two chelating guanidinate ligands, supplemented by the additional coordination of two mutually *cis*-oriented molecules of THF. There is no dimerization in the solid state structures of **4** and **5** as has been observed in the solid state for the Sr complex $[\{(\eta^2\text{-}\{^i\text{PrNC(NMe}_2)\text{N}^i\text{Pr}\})\text{Sr}\}_2(\mu_2,\eta^2\text{:}\eta^2\text{-}\{^i\text{PrNC(NMe}_2)\text{N}^i\text{Pr}\})(\mu_2,\eta^1\text{:}\eta^1\text{-}\{^i\text{PrNC(NMe}_2)\text{N}^i\text{Pr}\})]$.[11] The structure of **5** is shown in Figure 5, and relevant bond lengths and angles for **4** and **5** can be found in Table 1.

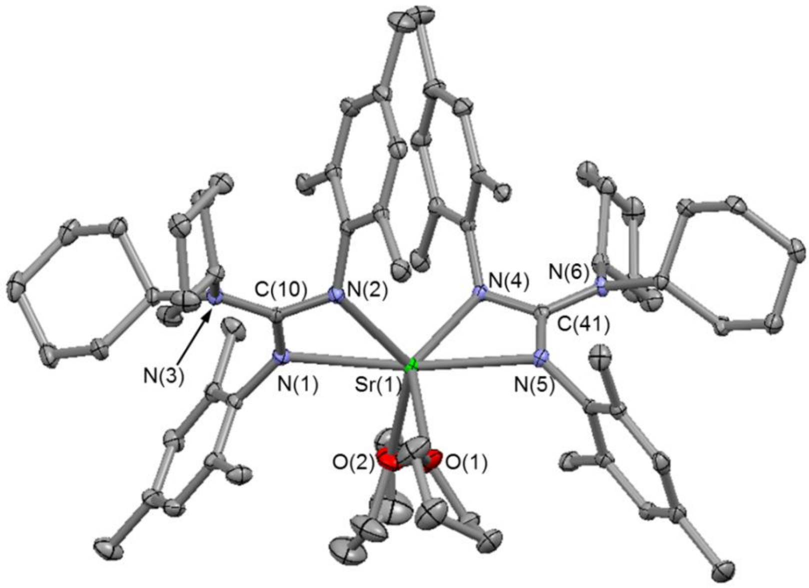


Figure 5: Molecular structure of one of the crystallographically independent molecules of **5** with displacement ellipsoids set at 50% probability level. Hydrogen atoms are omitted for clarity. Complex **4** is isostructural with **5** in the solid state.

Table 1. Selected distances (Å) and angles (°) for **4** and **5**.

	4 (M = Ca)	**5** (M = Sr)
M–N	2.463(2), 2.454(2), 2.450(3), 2.445(2), 2.452(2), 2.432(2), 2.447(2), 2.451(2)	2.5729(16), 2.5616(16), 2.5695(16), 2.5871(16), 2.5613(16), 2.5784(16), 2.5574(16), 2.5709(16)
M–O	2.429(2), 2.455(2), 2.428(2), 2.448(2)	2.5773(18), 2.5563(18) 2.5705(17), 2.5509(17)
N–C (guanidinate)	1.333(3), 1.356(3), 1.361(4), 1.340(4), 1.330(4), 1.363(4), 1.352(3), 1.337(3)	1.332(3), 1.359(2), 1.352(2), 1.334(3), 1.346(2), 1.336(2), 1.363(2), 1.329(2)
N–M–N (ligand)	54.71(7), 55.01(8), 55.00(8), 55.09(7)	52.20(5), 52.12(5), 52.28(5), 52.32(5)
N–C–N	114.3(2), 113.6(3), 113.7(2), 114.8(2)	114.13(16), 114.98(15), 115.17(16), 114.27(15)
O–M–O	86.49(8), 85.77(7)	86.93(6), 84.72(5)

The M−N distances for **4** [2.432(2)-2.463(2) Å] and **5** [2.5574(16)-2.5784(16) Å] occur in relatively narrow ranges, similar to those for other six-coordinate calcium and strontium amidinate and guanidinate complexes.[10,21c,35] The M−O(THF) distances are also relatively consistent within the crystal structures of each complex. Within the individual molecules of **4** and **5** there is little variation between the guanidinate bite angles [for **4** N−M−N = 54.71(7)-55.09(7)°; for **5** N−M−N = 52.12(5)-52.32(5)°]. More acute N−M−N angles are observed for **5** than in **4**, despite the larger ionic radius of Sr^{2+} (1.18 Å) compared to Ca^{2+} (1.00 Å).[36] This trend has been observed for analogous Ca^{2+} and Sr^{2+} guanidinate complexes,[4c,35e] and has been ascribed previously to a guanidinate bite angle which is largely invariant to the metal.[35e]

Single crystals of [Ba**L**$_2$] (**6**) suitable for X-ray diffraction study were grown by slow cooling of a hot hexane solution to room temperature. This complex crystallizes with half a molecule of *iso*-hexane in the unit cell, and the structure of **6·0.5**$\mathbf{C_6H_{14}}$ is shown in Figure 6, along with relevant bond lengths and angles. In this homoleptic complex, the barium center is coordinated by two guanidinate ligands through one amide linkage, with the coordination sphere completed by long-range C···Ba interactions between the central metal and the nitrogen-bound mesityl substituents. Complex **6** is, to the best of our knowledge, the first example of a homoleptic, monomeric barium complex of the NCN ligand family. The lack of solvent coordination in **6** is remarkable; evidently these arene rings compete with the THF for coordination of Ba^{2+}, thereby facilitating the isolation of a homoleptic, monomeric derivative. Other examples of barium amidinate or guanidinate complexes feature either coordination of additional ancillary ligands[35e,37] or dimerization through the formation of bridging amides.[11] No evidence of dimerization for **6** is seen in solution *via* NMR spectroscopy: it is precluded by the encapsulation of the barium center by the guanidinate ligands.

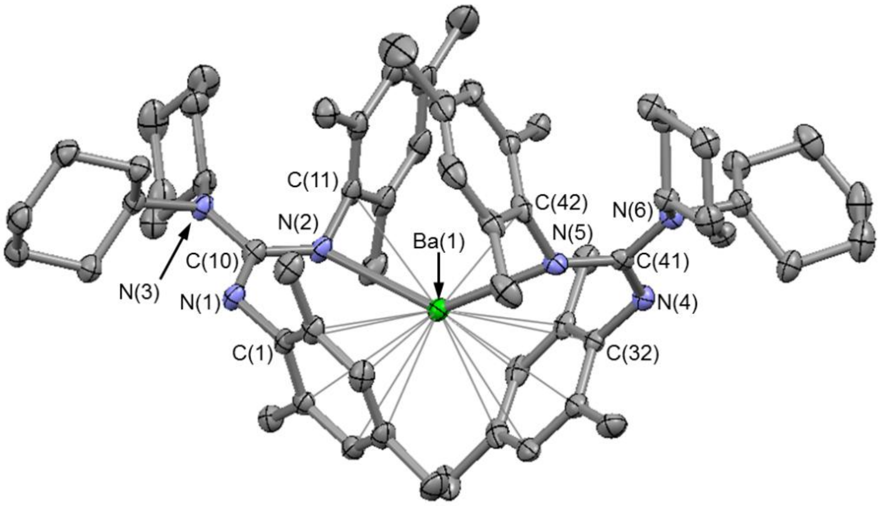


Figure 6: Molecular structure of **$6\cdot0.5C_6H_{14}$** with displacement ellipsoids set at 50% probability level. Hydrogen atoms and the *iso*-hexane solvent of crystallization omitted for clarity. Relevant bond lengths (Å) and angles (°): Ba(1)–N(2) 2.7215(19), Ba(1)–N(5) 2.7055(19), N(1)–C(10) 1.314(3), N(2)–C(10) 1.361(3), N(3)–C(10) 1.404(3), N(4)–C(41) 1.323(3), N(5)–C(41) 1.356(3), N(6)–C(41) 1.403(3), Ba(1)···C(11) 3.256(2), Ba(1)···C(42) 3.157(2), Ba(1)···C[C(1)arene] 3.138(2)-3.303(3), Ba(1)···C[C(32)arene] 3.163(2)-3.337(3), N(2)–Ba(1)–N(5) 135.50(6), N(1)–C(10)–N(2) 121.59(19), N(4)–C(41)–N(5) 121.51(19).

The barium-nitrogen distances differ significantly from each other [Ba(1)–N(2) = 2.7215(19) Å, Ba(1)–N(4) 2.7055(19) Å], presumably reflecting small variations in the coordination environments provided by the two guanidinate ligands. Although there are only three structurally authenticated barium complexes featuring two NCN ligands in the literature,[11,35c,37] they represent a relatively wide range of Ba–N distances [Ba–N = 2.685(3)-2.837(7) Å for non-bridging interactions], and the Ba–N bond lengths for **6** fall comfortably at the lower end of this range, despite a considerably higher effective coordination number for the barium center in **6** than in the other barium complexes of this type. Short Ba···C distances are observed between the barium center and the *ipso*-carbon atoms of the nitrogen-bound mesityl group on each guanidinate ligand, Ba(1)···C(11) 3.256(2) Å, Ba(1)···C(42) 3.157(2) Å. There are also η^6-arene interactions with the other nitrogen-bound mesityl substituents, which occur in the following ranges: C(1) mesityl: Ba(1)···C = 3.138(2)-3.303(3) Å, C(32) mesityl: Ba(1)···C = 3.163(2)-3.337(3) Å. These can be considered as significant interactions,[1d] and are, overall shorter than those in [M(C_6F_5){N_3(Mes)(Trip)}] [Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$; Ba···C(Mes) = 3.327-3.430 Å; Ba···C(Trip) = 3.386-3.406 Å[38] and [Ba{N_3(Dmp)Tph}$_2$] [Dmp = 2,6-Mes$_2$C$_6$H$_3$; Tph = 2-TripC$_6$H$_4$; Ba···C = 3.312(5)-3.424(5) Å].[39] Such interactions have also been observed in Ba aryloxide chemistry.[40,41]

The N–Ba–N unit deviates considerably from linearity [N(2)–Ba(1)–N(5) 135.50(6)°]: such a deviation is also seen in the monodentate amide complexes [Ba{N(SiMe$_3$)(Mes)}$_2$(THF)$_3$] [123.19(6)°][42] and [Ba{N(Si(H)Me$_2$)$_2$}$_2$(THF)$_4$] [129.92(9)°],[43] which admittedly feature differing coordination environments to that exhibited by the Ba^{2+} in **6**. Using high-level *ab initio* methods, Kaupp and Schleyer have calculated that, from an orbital-oriented viewpoint, barium amides should display significant bending of the N–Ba–N angle due to covalent σ-bonding contributions involving the metal d-orbitals[44] and the polarization of the Ba^{2+} cation by the anionic ligands.[45] The differences between the N–C distances for the metal-bound nitrogen atoms

[N(2)–C(10) 1.361(3) Å, N(5)–C(41) 1.356(3) Å] and the non-coordinating nitrogen atoms [N(1)–C(10) 1.314(3) Å, N(4)–C(41) 1.323(3) Å], suggests that the level of delocalization in **6** is low.[46]

2.3 Overview of the Structures of 2-6

No evidence for the formation of oligomers is seen in solution or solid state measurements on **2**-**6**. The steric demands of $\mathbf{L}^{-}$ are sufficient to stabilize a four-coordinate homoleptic species (**2**), although performing the synthesis of [Mg$\mathbf{L}_2$] in the presence of THF affords the five-coordinate species (**3**) and a change in structure from square planar to square pyramidal in the solid state. Increase of the cation size from Mg^{2+} (ionic radius = 0.57 Å for four-coordinate, 0.66 Å for five-coordinate) to Ca^{2+} (1.00 Å)[36] yields a six-coordinate metal center through the η^2-coordination of two guanidinate ligands and two molecules of THF. Larger Sr^{2+} (1.18 Å) also adopts a six-coordinate structure, analogous to that for calcium. Finally, on moving down the group to larger barium cation (1.61 Å for twelve-coordinate Ba^{2+}),[36] the ligand coordination changes yielding a homoleptic species: the guanidinates only bond through one nitrogen atom each, with the coordination sphere of the metal being completed by the formation of two η^1-arene and two η^6-arene interactions. η^1(N); η^6(arene) interactions have been observed recently in lanthanide-formamidinate chemistry.[47] No solvent coordination is seen, despite the reaction being performed in THF, which differs significantly from the lighter congeners – magnesium, calcium and strontium.

Remarkably, four-coordinate **2** adopts a square planar geometry around the metal center, which occurs in order to minimize the steric repulsion between the mesityl substituents, with the two ligands being almost coplanar (NCN/NCN dihedral angle = 12.4°). The additional coordination of THF in five-coordinate **3** leads to disruption of the planar MgN_4 core [Σ angles around Mg = 360.1° in (**2**) and 347.2° in (**3**)], with the dihedral angle between the two mean planes of the two NCN moieties in **3** being 28.7°. The isostructural complexes **4** and **5** adopt six-coordinate metal geometries in a *cis*oid configuration of the THF ligands. In these complexes the two guanidinate ligands are almost orthogonal to each other, with their NCN planes forming dihedral angles of 81.3° (average for **4**) and 80.1° (average for **5**), presumably due to the complexes adopting a geometry which is closer to octahedral. This geometry is significantly different to that exhibited in the formaminidate complexes $[M(DippN\{CH\}NDipp)_2(THF)_2]$ (M = Ca, Sr), where NCN/NCN angles of 33.9(4)° (M = Ca) and 31.8(4)° (M = Sr) are observed.[35c] The dihedral angle between the NCN planes in **6** (88.5°) represents a near-orthogonal arrangement, presumably in order to minimize steric repulsion and to maximize the barium-arene interactions.

As shown by the similarities in the magnesium-bound N–C bond distances, there is significant delocalization across the guanidinate ligands in the bidentate complexes **2** and **3**. There are slight differences between the shorter and longer metal-bound N–C distances within the crystal structures of **4** and **5** (Table 1). A more significant difference between the metal-bound nitrogen atoms [1.361(3) Å and 1.356(3) Å] and the non-coordinating nitrogen atoms [1.314(3) Å and 1.323(3) Å], suggests that the level of NCN delocalization in **6** is lower than in the bidentate complexes. There is a wider NCN angle in **6** [121.59(19), 121.51(19) Å], compared to the bidentate complexes **2**-**5** [range = 110.3(2)-115.17(16)° depending on metal coordination number], the more obtuse angle in **6** being more akin to the analogous N–C–N angle in the proligand **L**H [122.53(9)°].

3. Conclusions

The new sterically demanding guanidine $[MesN\{C(NCy_2)\}N(H)Mes]$ (**L**H) has been synthesized and used to form complexes of the alkaline earth metals, in particular; an unusual Hauser base cubane, a homoleptic *vs*. base-stabilized magnesium guanidinate complex and a series of alkaline earth complexes from magnesium to barium featuring the same ligand motif. The Hauser base **L**MgI exists as a mixture of the tetramer $[Mg_4\mathbf{L}_4(\mu_3\text{-}I)_4]$ (**1a**), which is the first crystallographically characterized cubane structure to consist of a tetramer of four LAeX (L = ligand, X = halide) units, and dimer $[Mg_2\mathbf{L}_2(\mu\text{-}I)_2(OEt_2)_2]$ (**1b**). Such complexes are of importance due to continued significant interest in the aggregation characteristics of Grignards and related complexes and the resulting implication for their reactivity. The reaction with two equivalents of Mg^nBu_2 leads to the formation of four-coordinate $[Mg\mathbf{L}_2]$ (**2**), which features an unusual square-planar magnesium cation, or five-coordinate $[Mg\mathbf{L}_2(THF)]$ (**3**), depending on the solvent. The heavier alkaline earth (Ca, Sr, Ba) complexes were synthesized *via* redox transmetallation/ligand exchange reactions. The calcium and strontium complexes $[Ae\mathbf{L}_2(THF)_2]$ (Ae = Ca, **4**; Ae = Sr, **5**) are isostructural, and $[Ba\mathbf{L}_2]$ (**6**) is the first example of a homoleptic, monomeric barium complex of the NCN ligand family, the structure presumably stabilized by a number of barium-arene interactions in the solid state. The synthesis and crystallographic characterization of a series of Ae complexes (Ae = Mg, Ca, Sr, Ba) enables an analysis of the trends in bonding as Group 2 is descended.

4. Experimental Section

Experimental Section

All manipulations were performed under an argon or dinitrogen atmosphere using standard Schlenk line or glove box techniques. Hexane was dried by passing through a column of activated 4 Å molecular sieves. Diethyl ether, THF, DME and toluene were pre-dried over Na wire and freshly distilled over Na/K alloy (diethyl ether), sodium benzophenone ketyl (THF and DME) or potassium (toluene) under nitrogen. All solvents were degassed and stored over a potassium mirror (hexane, diethyl ether and toluene) or activated 3 Å molecular sieves (THF and DME) prior to use. Benzene-d_6 (Goss) was dried over potassium and THF-d_8 (Goss) was dried over CaH_2. Both were degassed with three freeze-pump-thaw cycles prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AV 400, DPX 400 or DPX 300 spectrometers. Chemical shifts are quoted in ppm relative to TMS. Mass spectra were measured by the the EPSRC UK National Mass Spectrometry Facility at Swansea University, and by the departmental service at the School of Chemistry, University of Nottingham. Elemental analyses were performed by Mr Stephen Boyer, London Metropolitan University. Despite repeated attempts, satisfactory microanalyses could not be obtained for compounds **4**, **5** and **6**, reflecting an acknowledged issue in alkaline earth metal chemistry.[22] Di-*n*-butylmagnesium was obtained from Aldrich as a 1.0 M solution in heptane. The solvent was removed *in vacuo* and the $^{n}Bu_2Mg$ was stored as a solid in the glove box. $MeMgI(OEt_2)_2$ was prepared by treating activated magnesium metal with iodomethane in refluxing diethyl ether, followed by filtration, concentration of the solvent under reduced pressure and controlled cooling of the solution to −30 °C. The resultant crystalline $MeMgI(OEt_2)_2$ was isolated, dried under vacuum and stored in the glove box. Ca, Sr and Ba metals were obtained commercially as turnings or chunks, which were freshly filed under nitrogen prior to use. MesN=C=NMes was prepared following a literature procedure.[48] All other reagents were obtained from commercial sources and used without further purification. Yields refer to purified products and are not optimized.

Syntheses

Caution! Diphenylmercury and mercury metal are toxic requiring well-ventilated or fully-contained handling methods. Residues should be consigned to heavy metal waste or the Hg metal recycled.

Synthesis of [MesN{C(NCy$_2$)}N(H)Mes] (LH). $^{n}BuLi$ (5.81 mL of a 1.6 M solution in hexanes, 9.3 mmol), was added dropwise to a stirred solution of dicyclohexylamine (1.72 g, 1.89 mL, 9.5 mmol) in THF (20 mL). After 2 hours of stirring, a solution of MesN=C=NMes (2.51 g, 9.0 mmol) in THF (20 mL) was added dropwise, and the reaction mixture was heated to reflux for 2 hours, then cooled to room temperature and stirred overnight. The solvent was removed *in vacuo*, and the residue was treated with diethyl ether (80 mL) and water (80 mL). The organic phase was separated and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic fractions were dried over magnesium sulfate, filtered, and the solvent removed *in vacuo*. The residue was extracted with hot hexane. Following concentration and cooling to –30 °C, colorless crystals of **L**H were obtained. A second crop of crystals was obtained by further concentration and subsequent cooling of the mother liquor. Total yield 3.52 g, 84 %. ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz): δ 1.01-1.07 (m, 6H, Cy-CH_2), 1.53-1.61 (m, 6H, Cy-CH_2), 1.70-1.73 (m, 4H, Cy-CH_2), 2.05-2.13 (m, 4H, Cy-CH_2), 2.26-2.29 (m, 18H, CH_3), 3.07-3.11 (m, 2H, Cy-C*H*N), 4.90 (s, 1H, N*H*), 6.82 (s, 2H, Ar*H*), 6.89 (s, 2H, Ar*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, 100 MHz): δ 18.8 (*C*H_3), 19.1 (*C*H_3), 20.63 (*C*H_3), 20.7 (*C*H_3), 25.9 (Cy-*C*H_2), 27.0 (Cy-*C*H_2), 32.6 (Cy-*C*H_2), 57.9 (Cy-*C*HN), 129.1-129.4 (Ar*C*H), 129.8 (Ar*C*), 130.0 (Ar*C*), 134.5 (Ar*C*), 135.0 (Ar*C*), 136.4 (Ar*C*), 145.2 (Ar*C*), 149.9 (*C*N_3). Elemental analysis: Calcd for $C_{31}H_{45}N_3$: C 80.99, H 9.87, N 9.14; found C 80.87, H 9.88, N 9.04. Mass spec. accurate mass (ESI): Calcd for $C_{31}H_{46}N_3$ $[M + H]^+$: 460.3686; found 460.3698.

Synthesis of [$Mg_4L_4(\mu_3\text{-}I)_4$] (1a) and [$Mg_2L_2(\mu\text{-}I)_2(OEt_2)_2$] (1b). A solution of $MeMgI(OEt_2)_2$ (0.31 g, 1.0 mmol) in diethyl ether (20 mL) was cooled to –78 °C, and a solution of **L**H (0.46 g, 1.0 mmol) in diethyl ether (10 mL) was added dropwise with stirring. The reaction mixture was slowly warmed to room temperature and stirred overnight, affording in a white precipitate. The solution was filtered and the resultant white solid was washed with hexane (2 × 5 mL), and extracted with toluene. Concentration (to *ca.* 5 mL) and controlled cooling to –30 °C afforded colorless crystals of **1a** suitable for single crystal X-ray diffraction interspersed with a colorless microcrystalline material identified as **1b**. The mixture of crystals could not be separated by handpicking (0.54 g combined yield). The microanalysis result, as well as the ^{1}H NMR (run in

C_6D_6) integration ratio of diethyl ether to guanidinate ligand, indicates a 1:1 mixture of **1a** and **1b**. ^{1}H NMR (underlined values are for **1b**) (C_6D_6, 298 K, 400 MHz): δ 0.90-0.95 (m, 24H + $\underline{12H}$, Cy-C*H*$_2$ + $\underline{12H}$, Et$_2$O-C*H*$_3$), 1.41-1.61 (m, 56H + $\underline{28H}$, Cy-C*H*$_2$), 2.32 (s, $\underline{12H}$, C*H*$_3$), 2.33 (s, 24H, C*H*$_3$), 2.37 (s, $\underline{24H}$, C*H*$_3$), 2.65 (s, 48H, C*H*$_3$), 3.43-3.50 (m, $\underline{8H}$, Et$_2$O-C*H*$_2$), 3.61-3.72 (m, 8H + $\underline{4H}$, Cy-C*H*N), 6.92 (s, $\underline{8H}$, Ar*H*), 6.94 (s, 16H, Ar*H*). ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 100 MHz): δ 13.9 (Et$_2$O-*C*H$_3$), 19.1 (*C*H$_3$), 20.1 (*C*H$_3$), 20.7 (*C*H$_3$), 21.2 (*C*H$_3$), 26.0 (Cy-*C*H$_2$), 26.1 (Cy-*C*H$_2$), 27.5 (Cy-*C*H$_2$), 27.6 (Cy-*C*H$_2$), 36.2 (Cy-*C*H$_2$), 36.4 (Cy-*C*H$_2$), 59.8 (Cy-*C*HN), 60.0 (Cy-*C*HN), 66.6 (Et$_2$O-O*C*H$_2$), 129.1 (Ar*C*H), 129.3 (Ar*C*H), 130.6 (Ar*C*), 130.8 (Ar*C*), 131.9 (Ar*C*), 132.3 (Ar*C*), 144.8 (Ar*C*), 144.9 (Ar*C*), 169.3 (*C*N$_3$), 170.0 (*C*N$_3$). ^{1}H NMR (C_4D_8O, 298 K, 300 MHz): δ 0.72-0.82 (m, 36H, Cy-C*H*$_2$), 1.12 (t, 12H, Et$_2$O-C*H*$_3$, *J* = 6.9 Hz,), 1.34-1.43 (m, 84H, Cy-C*H*$_2$), 2.17 (s, 36H, C*H*$_3$), 2.40 (s, 72H, C*H*$_3$), 3.35-3.44 (m, 20H, Et$_2$O-C*H*$_2$ + Cy-C*H*N), 6.74 (s, 24H, Ar*H*). ^{13}C{^{1}H} NMR (C_4D_8O, 298 K, 75 MHz): δ 12.9 (Et$_2$O-*C*H$_3$), 18.5 (*C*H$_3$), 18.7 (*C*H$_3$), 24.1 (Cy-*C*H$_2$), 25.5 (Cy-*C*H$_2$), 34.5 (Cy-*C*H$_2$), 57.7 (Cy-*C*HN), 63.5 (Et$_2$O-*C*H$_2$), 126.7 (Ar*C*H), 127.5 (Ar*C*), 130.4 (Ar*C*), 144.2 (Ar*C*), 166.4 (*C*N$_3$). Elemental analysis: Calcd for $C_{194}H_{284}I_6Mg_6N_{18}O_2$ (1:1 mixture of **1a** and **1b**): C 61.19, H 7.52, N 6.62; found C 60.98, H 7.23, N 6.78.

Synthesis of [MgL$_2$] (2). A solution of di-*n*-butylmagnesium (0.07 g, 0.5 mmol) in DME (10 mL) was added dropwise to a solution of **L**H (0.46 g, 1.0 mmol) in DME (10 mL) at –78 °C with stirring. The reaction mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed *in vacuo*, and the residue was extracted with hot hexane (*ca.* 5 mL) and filtered. Slowly cooling the solution to room temperature afforded colorless crystals of **2** of suitable quality for single crystal X-ray diffraction. Yield 0.34 g, 72 %. ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ 0.88-0.96 (m, 12H, Cy-C*H*$_2$), 1.40-1.55 (m, 28H, Cy-C*H*$_2$), 2.32 (s, 12H, C*H*$_3$), 2.36 (s, 24H, C*H*$_3$), 3.64 (m, 4H, Cy-C*H*N), 6.91 (s, 8H, Ar*H*). ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 75

MHz): δ 19.3 (CH$_3$), 20.7 (CH$_3$), 25.6 (Cy-CH$_2$), 27.1 (Cy-CH$_2$), 36.2 (Cy-CH$_2$), 59.8 (Cy-CHN), 129.3 (ArCH), 130.5 (ArC), 131.9 (ArC), 144.9 (ArC), 169.9 (CN$_3$). Elemental analysis: Calcd for $C_{62}H_{88}MgN_6$: C 79.08, H 9.42, N 8.92; found C 79.00, H 9.54, N 8.87.

Synthesis of [MgL$_2$(THF)] (3). A solution of di-*n*-butylmagnesium (0.07 g, 0.5 mmol) in THF (10 mL) was added dropwise to a solution of **L**H (0.46 g, 1.0 mmol) in THF (10 mL) at –78 °C with stirring. The reaction mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed *in vacuo*, and the residue was extracted with hot hexane (*ca.* 5 mL) and filtered. Slowly cooling the solution to room temperature afforded colorless crystals of **3** of suitable quality for single crystal X-ray diffraction. Yield 0.39 g, 76 %. ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ 0.82-0.99 (m, 12H, Cy-CH_2), 1.40-1.58 (m, 32H, Cy-CH_2 + THF-CH_2), 2.35 (s, 12H, CH_3), 2.36 (s, 24H, CH_3), 3.65 (m, 4H, Cy-CHN), 3.79 (m, 4H, THF-OCH_2), 6.93 (s, 8H, ArH). ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 75 MHz): δ 19.4 (CH$_3$), 20.7 (CH$_3$), 25.6 (Cy-CH$_2$), 26.1 (THF-CH$_2$), 27.6 (Cy-CH$_2$), 36.2 (Cy-CH$_2$), 59.8 (Cy-CHN), 68.7 (THF-OCH$_2$), 129.0 (ArCH), 130.1 (ArC), 132.1 (ArC), 145.7 (ArC), 169.4 (CN$_3$). Elemental analysis: Calcd for $C_{66}H_{96}MgN_6O$: C 78.19, H 9.54, N 8.29; found C 78.08, H 9.69, N 8.17.

Synthesis of [CaL$_2$(THF)$_2$] (4). A Schlenk flask was charged with Ca metal (0.08g, 2.0 mmol), **L**H (0.46 g, 1.0 mmol), diphenylmercury (0.18 g, 0.5 mmol) and THF (30 mL). The reaction mixture was stirred at room temperature overnight, giving a pale yellow solution. The reaction mixture was filtered to remove mercury and unreacted calcium metal, and the solvent was removed *in vacuo*. The residue was extracted with hot hexane (*ca.* 10 mL); the solution was filtered and slowly cooled to room temperature, affording colorless crystals of **4** of suitable quality for single crystal X-ray diffraction. Yield 0.41 g, 74 %. ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ 0.85-1.14 (m, 12H, Cy-CH_2), 1.35 (m, 8H, THF-CH_2), 1.40-1.68 (m, 28H, Cy-CH_2), 2.39 (s, 12H, C*H*$_3$), 2.41 (s, 24H, C*H*$_3$), 3.49 (m, 8H, THF-OC*H*$_2$), 3.59 (m, 4H, Cy-C*H*N), 6.93 (s, 8H, Ar*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 298 K, 75 MHz): δ 19.4 (*C*H$_3$), 20.6 (*C*H$_3$), 25.2 (Cy-*C*H$_2$), 26.4 (THF-*C*H$_2$), 27.9 (Cy-*C*H$_2$), 36.7 (Cy-*C*H$_2$), 59.6 (Cy-*C*HN), 68.1 (THF-O*C*H$_2$), 128.4 (Ar*C*), 129.0 (Ar*C*H), 130.7 (Ar*C*), 148.0 (Ar*C*), 168.6 (*C*N$_3$). Mass spec. (EI): *m/z*: 1056 ([M - 3Me]$^+$, 0.1%), 873 ([M - 2THF - Cy]$^+$, 0.2%), 760 ([M - 2THF - 2Me - 2Cy]$^+$, 0.1%), 459 ([LH]$^+$, 1.1%), 376 ([LH - Cy]$^+$, 20.4%).

Synthesis of [SrL$_2$(THF)$_2$] (5). Sr metal (0.18 g, 2.0 mmol), **L**H (0.46 g, 1.0 mmol) and diphenylmercury (0.18 g, 0.5 mmol) were stirred in THF (30 mL) at ambient temperature overnight. The resulting pale yellow solution was filtered, and the solvent removed *in vacuo*. The residue was extracted with a mixture of hot hexane (*ca.* 10 mL) and THF (*ca.* 1 mL), the solution was filtered and slowly cooled to room temperature. Colorless crystals of **5** of suitable quality for single crystal X-ray diffraction were obtained. Yield 0.39 g, 68 %. ^{1}H NMR (C$_6$D$_6$, 298 K, 300 MHz): δ 0.92-1.25 (m, 12H, Cy-C*H*$_2$), 1.31 (m, 8H, THF-C*H*$_2$), 1.50-1.79 (m, 28H, Cy-C*H*$_2$), 2.37 (s, 12H, C*H*$_3$), 2.48 (s, 24H, C*H*$_3$), 3.35 (m, 8H, THF-OC*H*$_2$), 3.51 (m, 4H, Cy-C*H*N), 6.92 (s, 8H, Ar*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 298 K, 75 MHz): δ 20.2 (*C*H$_3$), 20.7 (*C*H$_3$), 25.0 (Cy-*C*H$_2$), 26.6 (THF-*C*H$_2$), 28.0 (Cy-*C*H$_2$), 36.3 (Cy-*C*H$_2$), 59.3 (Cy-*C*HN), 67.9 (THF-O*C*H$_2$), 128.1 (Ar*C*), 129.3 (Ar*C*H), 130.8 (Ar*C*), 149.7 (Ar*C*), 167.3 (*C*N$_3$). Mass spec. (EI): *m/z*: 1004 ([M - 2THF]$^+$, 0.1%), 921 ([M - 2THF - Cy]$^+$, 0.9%), 459 ([LH]$^+$, 25%), 376 ([LH - Cy]$^+$, 100%). Mass spec. (CI): *m/z*: 1005 ([M - 2THF + H]$^+$, 0.1%), 460 ([LH + H]$^+$, 100%. Accurate mass (EI): Calcd for $C_{56}H_{77}N_6{}^{86}Sr$ [M - 2THF - Cy]$^+$: 919.5297; found 919.5295.

Synthesis of [BaL$_2$] (6). Ba metal (0.27 g, 2.0 mmol), **L**H (0.46 g, 1.0 mmol), diphenylmercury (0.18 g, 0.5 mmol) and THF (30 mL) were stirred at room temperature overnight. The yellow solution was filtered, the solvent removed *in vacuo*, and the residue extracted with hot hexane (*ca.* 10 mL). The solution was filtered and slowly cooled to room temperature, affording colorless crystals of **$6{\cdot}0.5C_6H_{14}$** which were of suitable quality for single crystal X-ray diffraction Yield 0.34 g, 64 %. ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ 1.18 (br s, 12H, Cy-CH_2), 1.62 (br s, 4H, Cy-CH_2), 1.78-1.82 (m, 16H, Cy-CH_2), 2.16 (br s, 24H, CH_3), 2.28 (s, 12H, CH_3), 2.41 - 2.44 (m, 8H, Cy-CH_2), 3.08 (m, 4H, Cy-C*H*N), 6.82 (s, 8H, Ar*H*). ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 75 MHz): δ 19.8 (*C*H_3), 20.7 (*C*H_3), 26.3 (Cy-*C*H_2), 27.4 (Cy-*C*H_2), 33.4 (Cy-*C*H_2), 57.4 (Cy-*C*HN), 130.6 (Ar*C*H), 132.5 (Ar*C*), 152.5 (Ar*C*), 157.5 (*C*N_3) (one Ar*C* obscured by solvent peak). Mass spec. (EI): *m/z*: 1054 ([M]$^+$, 1%), 971 ([M - Cy]$^+$, 5%), 459 ([LH]$^+$, 25%), 376 ([LH - Cy]$^+$, 100%). Accurate mass (APCI): Calcd for $C_{62}H_{89}{}^{134}BaN_6$ [M + H]$^+$: 1051.6188; found 1051.6196.

Crystallographic methods

Crystals were mounted on MicroMounts™ (MiTeGen) using YR-800 perfluoropolyether oil and cooled rapidly to 90 or 120 K in a stream of cold nitrogen using an Oxford Cryosystems low-temperature device.[49] Data for **L**H, **1a**, **2-4** and **$6{\cdot}0.5C_6H_{14}$** were collected on a Bruker SMART APEX diffractometer (90 K) equipped with graphite-monochromated Mo-*K*α source (λ = 0.71073 Å) and data for **5** were collected on Oxford Diffraction SuperNova diffractometer (90 K), equipped with a mirror-monochromated Cu-*K*α source (λ = 1.5418 Å). Programs used were CrysAlisPro[50] and Bruker AXS SMART[51] (control), CrysAlisPro[50] and Bruker AXS SAINT[51] (integration), and SHELXS,[52] SHELXL[52] and OLEX2[53] (structure solution, structure refinement and molecular graphics). In **1a**, the N-mesityl N(1), C(1)-C(9) and N-cyclohexyl N(3), C(20)-C(25) show correlated disorder over two orientations. The occupancies of these two orientations were refined competitively, converging at a ratio of 0.50:0.50. Chemically equivalent bonds of the disordered nitrogen atoms were restrained to be approximately equal. Enhanced rigid bond and similarity restraints were applied to the thermal parameters of the disordered atoms. A large region of disordered solvent could not be sensibly modelled, and so the structure was treated with

PLATON SQUEEZE.[54] The solvent region equated to 32 molecules of toluene, the solvent used for crystallization. These solvent molecules were included in the formula, and calculation of derived parameters. In **3** the coordinated THF molecule is disordered across the twofold rotation axis; bonds to symmetry equivalents were suppressed (PART -1). The mesityl group C(11)-C(19) is disordered over two orientations. The occupancies of the two components were refined competitively, converging at a ratio of 0.49:0.51. The cyclohexyl groups are coherently disordered over two positions, and the occupancies of the two components were refined competitively, converging at a ratio of 0.51:0.49. Chemically equivalent bonds of these groups were restrained to be approximately equal. For **4**, atoms C(64), C(68) and C(139) of the coordinated THF molecules were disordered over two positions. The occupancies of each were refined competitively, converging at ratios of 0.93:0.07, 0.67:0.33 and 0.86:0.14, respectively. Chemically equivalent bonds of the disordered atoms were restrained to be approximately equal. Atom C(68A) was refined anisotropically, with enhanced rigid bond restraints, while atoms C(64A) and C(13A) were refined isotropically, with similarity restraints. Each of the THF molecules exhibits disorder of one of the backbone carbon atoms. For **5**, the occupancies of these disordered carbon atoms were refined competitively, converging at ratios of 0.81:0.19, 0.88:0.12, 0.83:0.17 and 0.95:0.05. Chemically equivalent bonds of each THF were restrained to be approximately equal. The minor component carbon atoms were refined isotropically. In the case of $\mathbf{6{\cdot}0.5C_6H_{14}}$, the molecule of *iso*-hexane is disordered across the center of inversion. Equivalent bond lengths and angles of this molecule were restrained to be approximately equal, and the Me–Me distance was restrained to ~2.5 Å. The thermal parameters were fixed to a common refining anisotropic thermal parameter. CCDC-1417988-1417994 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. The crystal data for these complexes are summarized in Table 2.

Table 2 Crystal data for compounds **L**H, **1a** and **2-6·0.5C$_6$H$_{14}$**.

	LH	**1a**	**2**	**3**	**4**	**5**	**6·0.5C$_6$H$_{14}$**
Formula	$C_{31}H_{45}N_3$	$C_{124}H_{176}I_4Mg_4N_{12}$	$C_{62}H_{88}MgN_6$	$C_{66}H_{96}MgN_6O$	$C_{70}H_{104}CaN_6O_2$	$C_{70}H_{104}N_2O_2Sr$	$C_{65}H_{95}BaN_6$
FW	459.70	3176.67	941.69	1013.79	1101.67	1149.21	1097.80
Space Group	*P*-1	$I4_1/a$	*P*-1	*C*2/*c*	$P2_1/n$	$P2_1/n$	*P*-1
a [Å]	8.8649(5)	23.6923(3)	13.1927(7)	18.305(3)	18.7146(17)	18.7969(2)	11.7684(13)
b [Å]	8.9541(5)	23.6923(3)	15.7582(9)	14.781(2)	16.7213(15)	16.9120(2)	15.8372(18)
c [Å]	17.9377(11)	31.9372(9)	15.8336(9)	22.812(3)	40.918(4)	40.8173(5)	16.1624(18)
α [°]	85.378(1)	90	97.748(3)	90	90	90	91.173(2)
β [°]	77.101(1)	90	113.293(2)	98.946(3)	100.333(2)	100.598(1)	102.272(2)
γ [°]	83.860(1)	90	106.026(2)	90	90	90	92.588(2)
Vol [Å^3]	1377.59(14)	17947.4(7)	2792.7(3)	6097.1(15)	12597(2)	12754.2(3)	2939.1(6)
Z	2	4	2	4	8	8	2
D_{calc} [g cm^{-3}]	1.108	0.903	1.120	1.104	1.162	1.197	1.240
μ [mm^{-1}]	0.064	0.759	0.075	0.074	0.149	1.537	0.720
F(000)	504	5056	1028	2216	4816	4960	1166
No. of indep. reflns ($R_{int)}$	6226 (0.014)	12117 (0.100)	9852 (0.052)	5944 (0.035)	28893 (0.069)	25465 (0.033)	13352 (0.054)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0458, 0.1238	0.0695, 0.1886	0.0725, 0.1836	0.0495, 0.1196	0.0879, 0.1672	0.0421, 0.1032	0.0350, 0.0845
Min. and max. electron density [e/Å^3]	–0.27, 0.27	–0.61, 1.47	–0.26, 0.85	–0.47, 0.18	–0.28, 0.64	–0.56, 2.08	–0.68, 1.20

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Supporting Information Available: Crystallographic data for **L**H, **1a** and **2-6**. This material is available free of charge *via* the Internet at http://dx.doi.org/10.1002/ejic.201501239.

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