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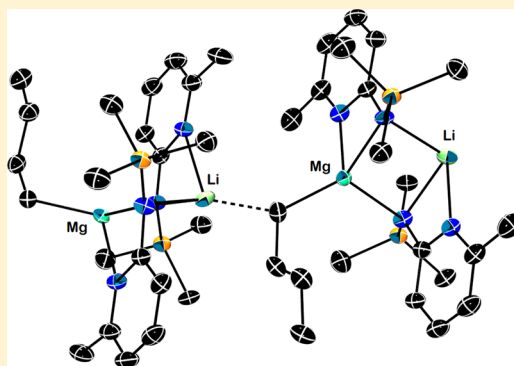
Alkaline Earth Complexes of Silylated Aminopyridinato Ligands: Homoleptic Compounds and Heterobimetallic Coordination Polymers

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S Supporting Information

ABSTRACT: The synthesis and characterization of magnesium and calcium complexes of sterically demanding aminopyridinato ligands is reported. The reaction of the 2-Me₃SiNH-6-MeC₅H₃N (L¹H), 2-MePh₂SiNH-6-MeC₅H₃N (L²H), and 2-Me₃SiNH-6-PhC₅H₃N (L³H) with KH in tetrahydrofuran (THF) yielded potassium salts L¹K(thf)_{0.5} (1), L²K (2), and L³K(thf)_{0.5} (3), which, through subsequent reaction with MgI₂ and CaI₂, afforded the homoleptic complexes (L)₂Ae(thf)_n [L = L¹, Ae = Mg, n = 1 (4); L = L², Ae = Mg, n = 0 (5); L = L³, Ae = Mg, n = 0 (6); L = L², Ae = Ca, n = 2 (7)] and heterobimetallic calciates {[L₃Ca]K}_∞ [L = L¹ (8); L = L² (9)]. The solid state structure of 8 reveals a polymeric arrangement in which the calciate units are interlocked by bridging potassium ions. Metalation reactions between L¹H or L²H and (t-Bu)₂Mg lead to the solvent-free compounds (L)₂Mg [L = L¹ (10); L = L² (5)]. The bridged butyl mixed-metal complex [(L¹)Li(μ₂-t-Bu)Mg(L¹)]_∞ (11) was also obtained via a cocomplexation reaction with t-BuLi and (t-Bu)₂Mg. 11, which adopts a monodimensional polymeric array in the solid state, is a rare example of an alkyl-bridged Li/Mg complex and the first complex to feature an unsupported bridging butyl interaction between two metals. Changing the cocomplexation reaction conditions, the order of reagents added to the reactions mixture, and with the use of a coordinating solvent (tetrahydrofuran) formed the magnesiate complex (L¹)₃MgLi(thf) (12).



■ INTRODUCTION

The study of the metalorganic chemistry of the alkaline earth (Ae) metals has gained new strength from the use of nitrogen-based ligands in the past two decades, which has made it possible to access unusual oxidation states and bonding modes for the group 2 elements and, in particular, to greatly extend the chemistry of the heavier alkaline earth elements.^{1–3} In particular, the use of bidentate ligands has facilitated the stabilization of a wide range of Ae complexes that are less likely to undergo either cleavage reactions and disproportionation through the Schlenk equilibrium.^{2,4} Such ligands have led to the stabilization of complexes that challenge the accepted knowledge of the Ae metals,^{5–8} allowing the isolation of the first Mg(I) dimer by Jones⁵ and Harder's calcium hydride “worker bee” complex.⁷ Among bidentate amide ligands, amidinates and guanidinates have gained increasing popularity over the last few decades and their wide applications in main group and transition metal chemistry have been described in several reviews on this topic.⁹ Their success has fuelled the quest for more ligand systems with similar donor properties and denticity. We have become interested in the use of aminopyridinato ligands, potential competitors to amidinates and guanidinates, owing to their similar binding modes (Figure 1).¹⁰ Although the strained model is the preferred binding mode of aminopyridinato ligands (shown in Figure 1), these

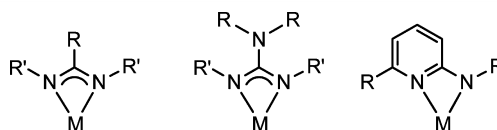


Figure 1. Amidinato (left), guanidinato (center), and aminopyridinato ligands (right).

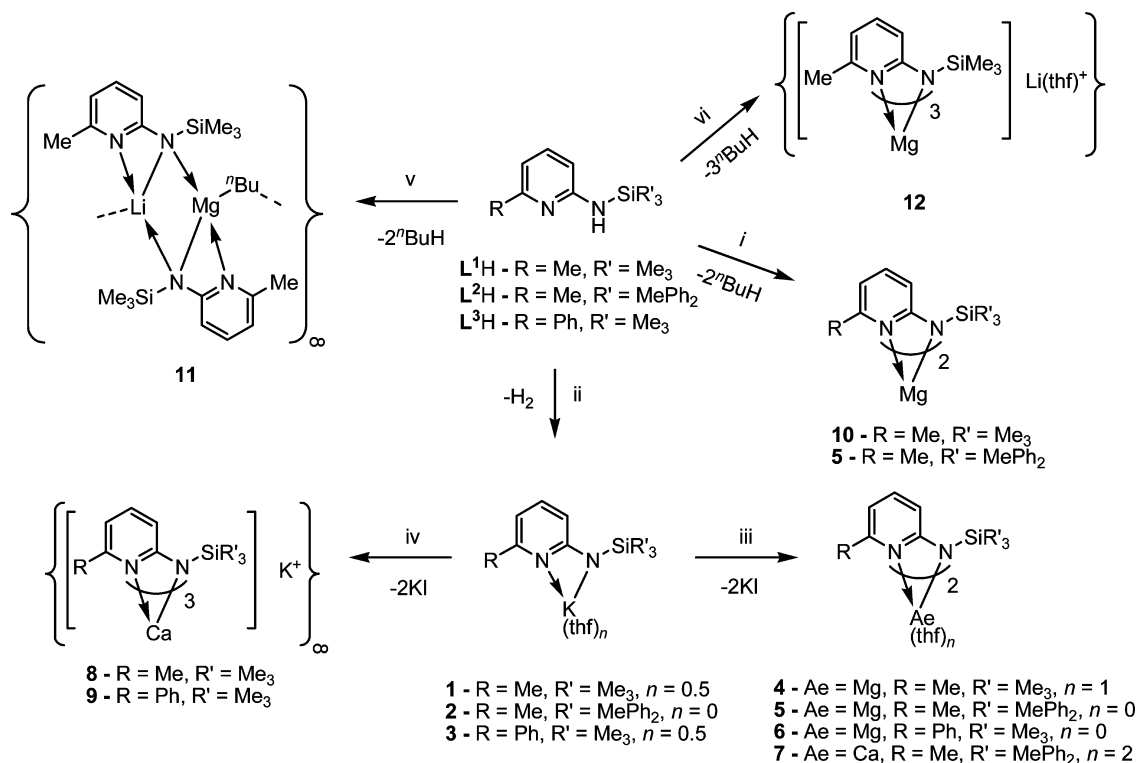
systems, unlike amidinates and guanidinates, can access a wider variety of binding modes due to their particular asymmetry.¹⁰

The ease of variation of the substituents in the 6-position of the pyridyl ring and on the amino group offers many possibilities in terms of the steric demands of these aminopyridinato ligands. This amenability to steric tuning has led to reports of a range of main group,¹¹ transition metal,¹² and f-block compounds¹³ of these ligands. Of note is the use of the sterically demanding 2-aminomesityl-6-(tripp)pyridinato ligand (tripp = 2,4,6-triisopropylphenyl) by Kempe and co-workers to stabilize a complex featuring an ultrashort Cr–Cr quintuple bond.^{12c} Despite their popularity and versatility, there are very few examples of group 2 complexes supported by aminopyridinato ligands in the literature,^{14–17} and there are none

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Scheme 1^a

^aReaction conditions: (i) 2:1 LH:(ⁿBu)₂Mg, hexane, −78 °C → room temperature, 16 h; (ii) 1:1 LH:KH, THF, −78 °C → room temperature, 16 h; (iii) 2:1 LK:AeI₂, THF, −78 °C → room temperature, 16 h; (iv) 3:1 LK:CaI₂, THF, −78 °C → room temperature, 16 h; (v) 1:1:1 LH:ⁿBuLi:(ⁿBu)₂Mg, hexane, 0 °C → room temperature, 72 h; (vi) 1:1:1 LH:ⁿBuLi:(ⁿBu)₂Mg, THF, 0 °C → room temperature, 16 h.

featuring the heavier alkaline earth elements (Ca–Ba). Isoelectronic pyridylmethylcalcium complexes have been reported by Okuda and co-workers, but these feature Ca–C bonds, as opposed to the amide linkages in aminopyridinato complexes.¹⁸ Herein we report the synthesis and isolation of magnesium and calcium complexes stabilized by silylated 2-aminopyridinato ligands; the first structurally authenticated heteroleptic and homoleptic calcium aminopyridinato complexes are described. Despite the wide range of bonding modes accessible for amidinates and guanidinates,^{9,10} the examples of coordination compounds with the group 2 metals reported in the literature are limited to species of the type (L)₂Ae(S)_n or (L)_{2n}Ae_n(S)_n (S = THF, diethyl ether),^{19–25} mixed ligand systems (L')(L'')Ae(S)_n,^{19,24–26} heteroleptic species LAeX(S) (X = halide), halide bridged dimers (LAeX)₂(S)_n,^{5,17,27} and in one case, a heteroleptic LAeR species (R = ⁱPr).²⁸ In this work, we show how aminopyridinato ligands offer further possibilities in terms of bonding modes and connectivity within alkaline earth complexes.

RESULTS AND DISCUSSION

Picoline- and phenylpyridine-based ligand precursors 2-Me₃SiNH-6-MeC₅H₃N (L¹H), 2-MePh₂SiNH-6-MeC₅H₃N (L²H), and 2-Me₃SiNH-6-PhC₅H₃N (L³H) have been synthesized in excellent yields, following previously reported methodologies.^{11a} To stabilize alkaline earth complexes, the following synthetic strategies have been employed: (i) metathesis reaction between the potassium salts of the ligand and Ae halides; (ii) metalation of the proligand with (ⁿBu)₂Mg; (iii) cocomplexation of the proligand with (ⁿBu)₂Mg and ⁿBuLi (Scheme 1).

Metathesis Reactions. The metathesis reaction between group 1 salts and an alkaline earth metal halide^{1,29} has been used as a synthetic strategy toward the synthesis of the complexes in this investigation. To this end, the potassium salts 1–3 have been synthesized in good yields according to Scheme 1. ¹H NMR spectra of 1, 2, and 3 are in a good agreement with the formulations proposed. Most of the signals in the ¹H NMR spectra are shifted with respect to the proligands. In the case of 1, the majority of the proton resonances are shifted downfield, with the exception of the CH₃ signal; the most significant shift is observed for the H³ signal (δ = 6.07 ppm, Δδ = 0.14). The same global downfield shift is observed for compound 2, besides the Si(CH₃)₃ and CH₃ signals. In this case, H⁵ undergoes the most significant shift compared to the resonance displayed by the proligand (δ = 6.40, Δδ = 0.27). The peaks of compound 3 in the ¹H NMR are all shifted with respect to the proligand: H³ shows a paramagnetic shift (δ = 6.52 ppm, Δδ = 0.40); H⁵ instead is shifted upfield (δ = 6.58 ppm, Δδ = 0.40). The reaction between 1–3 and MgI₂ afforded compounds (L¹)₂Mg(thf) (4), (L²)₂Mg (5), and (L³)₂Mg (6), respectively, according to Scheme 1. The spectroscopic and analytical data for 4–6 are in good agreement with the proposed formulations. In the case of 4, the chemical shifts of all the protons are very similar to those of the proligand, with the exception of the methyl group in the 6 position, which is shifted slightly upfield (δ = 2.30 ppm, Δδ = 0.21). For compound 5, the peaks in the ¹H NMR are significantly shifted with respect to the proligand. The signals of both methyl groups are shifted upfield (Si(CH₃)Ph₂ δ = 0.62, Δδ = 0.16; CH₃ δ = 1.84, Δδ = 0.29); similar behavior is observed for protons H³ (δ = 5.82 ppm, Δδ = 0.22), H⁴ (δ = 6.30 ppm, Δδ = 0.17), and H⁵ (δ =

6.71 ppm, $\Delta\delta = 0.15$). The proton NMR of **6** also differs from that of the proligand: the resonance of the TMS group is shifted downfield ($\delta = 0.52$ ppm, $\Delta\delta = 0.18$), as is the peak assigned to H^9 and $H^{9'}$ ($\delta = 7.76$ ppm, $\Delta\delta = 0.47$). The signal of H^3 merges with the resonances of H^5 ($\delta = 6.58$ – 6.66 ppm); the first is shifted downfield with respect to the proligand ($\Delta\delta = 0.50$), whereas for the latter, an upfield shift is observed ($\Delta\delta = 0.31$). The most significant diamagnetic shift is observed for protons H^8 and $H^{8'}$ ($\delta = 7.26$ ppm, $\Delta\delta = 0.83$) (see Experimental Section for complete numbering scheme).

The outcome of metathesis reactions between the potassium salts **1**–**3** and CaI_2 varies significantly with the steric bulk of the silyl substituent. The reaction between **2** and CaI_2 afforded $(L^2)_2Ca(thf)_2$ (**7**) with concomitant precipitation of 2 equiv of KI (Scheme 1). The 1H NMR spectra of **7** and potassium salt **2** are almost identical, showing only one significant difference in the resonance of the protons in the ortho positions on the two phenyl rings of the SiMePh₂ fragment: for **7**, the signal is a broad multiplet, which resonates at 7.82 ppm; the same signal is even broader in the case of **2**, and it resonates more upfield ($\delta = 7.59$ – 7.78 ppm). Crystals of **7** suitable for X-ray diffraction (Figure 2) were grown by the slow cooling of a saturated hot hexane solution to -30 °C. The geometry around the six-

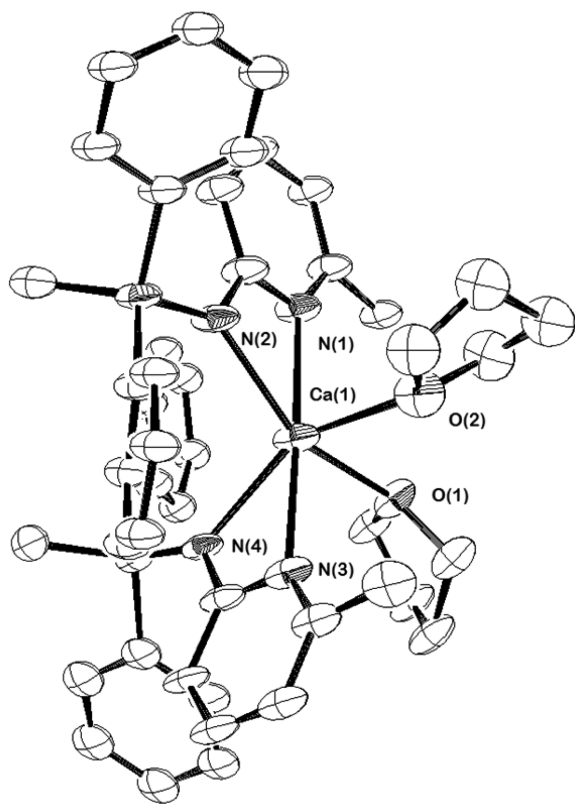


Figure 2. Molecular structure of **7**, with displacement ellipsoids set at the 50% probability level (with hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ca(1)–N(1) 2.439(7), Ca(1)–N(2) 2.412(7), Ca(1)–N(3) 2.465(7), Ca(1)–N(4) 2.415(8), Ca(1)–O(1) 2.400(4), Ca(1)–O(2) 2.404(5), N(1)–Ca(1)–N(2) 56.7(2), N(3)–Ca(1)–N(4) 56.4(2), N(2)–Ca(1)–N(3) 120.5(4), N(2)–Ca(1)–N(4) 108.0(6), N(1)–Ca(1)–N(4) 123.0(5), O(1)–Ca(1)–O(2) 82.70(15), N(1)–Ca(1)–O(1) 94.4(2), N(1)–Ca(1)–O(2) 88.7(4), N(2)–Ca(1)–O(2) 93.1(3), N(3)–Ca(1)–O(1) 88.4(4), N(3)–Ca(1)–O(2) 92.2(3), O(1)–Ca(1)–N(4) 89.4(6).

coordinate calcium atom is pseudooctahedral in a cis-type conformation, with two aminopyridinato ligands and two THF molecules completing the coordination environment. One ligand binds the metal center in the equatorial plane, together with one tetrahydrofuran (THF) and one nitrogen of the second ligand unit [N(1)–Ca(1)–N(2) = 56.7(2)°, N(1)–Ca(1)–O(1) = 94.4(2)°, N(2)–Ca(1)–N(3) = 120.5(4)°, N(3)–Ca(1)–O(1) = 88.4(4)°, $\Sigma_{L-Ca-L} = 360.0^\circ$]. The axial positions of the pseudooctahedron are occupied by one THF molecule [O(1)–Ca(1)–O(2) = 82.70(15)°, O(1)–Ca(1)–N(1) = 88.7(4)°, N(2)–Ca(1)–O(2) = 93.1(3)°, N(3)–Ca(1)–O(2) = 92.2(3)°, $\Sigma_{L-Ca-L} = 357.6^\circ$] and one nitrogen of the second ligand unit; the very acute bite angle of the bidentate aminopyridinato ligand [N(3)–Ca(1)–N(4) = 56.4(2)°] causes a significant distortion of the geometry from an ideal octahedron. As expected, the N_{amido} –Ca distances [2.412(7) and 2.415(8) Å] are slightly shorter than $N_{pyridyl}$ –Ca [2.439(7) and 2.465(7) Å]. These $N_{pyridyl}$ –Ca distances are broadly similar to those of $(thf)_3Ca(6-MeC_5H_3N-2-CH_2)_2$ [$N_{pyridyl}$ –Ca distances = 2.407(2) and 2.4331(19) Å].¹⁸ Structures with similar coordination environments have been previously reported, for example the phosphaguanidinate $(thf)_2Ca\{^iPrNC(PPh_2)N^iPr\}_2$,³⁰ guanidinate $(thf)_2Ca\{PhNC(^iPrNH)N^iPr\}_2$,³¹ and the formamidinate complex $(thf)_2Ca\{[(2,6-Me_2C_6H_3)N]_2CH\}_2$,³² but the difference between the two Ca–N bond distances is not as significant as that for **7**. The Ca–O distances for **7** [2.400(4) and 2.404(5) Å] are in the range reported for (albeit seven-coordinate) $(thf)_3Ca(6-MeC_5H_3N-2-CH_2)_2$ [2.3957(16)–2.4358(16) Å].¹⁸

The diphenylmethylsilyl group provides enough steric hindrance to stabilize the six-coordinate Ca^{2+} in **7**, with two THF molecules saturating the coordination sphere of the metal center. However, changes in the steric bulk of the silyl group significantly affect products obtained via metathesis reactions. The reactions between **1** or **3** (which feature the less sterically demanding trimethylsilyl substituent) and CaI_2 in THF afford $[(L^1)_3CaK]_\infty$ (**8**) and $[(L^3)_3CaK]_\infty$ (**9**), according to Scheme 1.

It therefore appears that the use of less bulky silyl substituents on the amido moiety allows the coordination of three ligands to the metal center: even in the presence of coordinating solvents such as THF and diethyl ether, one potassium ion is retained to balance the overall charge of the compound. 1H and $^{13}C\{^1H\}$ NMR spectra are in agreement with the formation of these new species. In the case of **8**, the proton NMR displays peaks slightly shifted with respect to the starting material **1**, with the most significant shifts observed for H^3 ($\delta = 5.81$ ppm, $\Delta\delta = 0.26$ ppm) and the methyl protons of the picoline moiety ($\delta = 1.93$ ppm, $\Delta\delta = 0.32$ ppm). Similarly, the 1H NMR spectrum of **9** is close to that of its related potassium salt **3**, in particular, the resonances of the H^{10} and $H^{9,9'}$ protons are considerably shifted upfield ($\delta = 6.90$ ppm) with respect to **3** ($\delta = 7.07$ – 7.26 ppm). For both **8** and **9**, elemental analyses support the proposed formulation. Crystals of **8** suitable for X-ray diffraction were grown from a saturated benzene-*d*₆ solution, and the final structure shows that the six-coordinate calcium compound adopts a polymeric arrangement in the solid state. The coordination polymer consists of the repetition of one calciate unit $[L^1_3Ca]^-$ and one K^+ (Figure 3) with the potassium cation facilitating the propagation of the polymeric chain by bridging between two calciate units. The K^+ ion participates in two different types of interactions: (i) an intramolecular η^6 interaction with one of the picoline ligands,

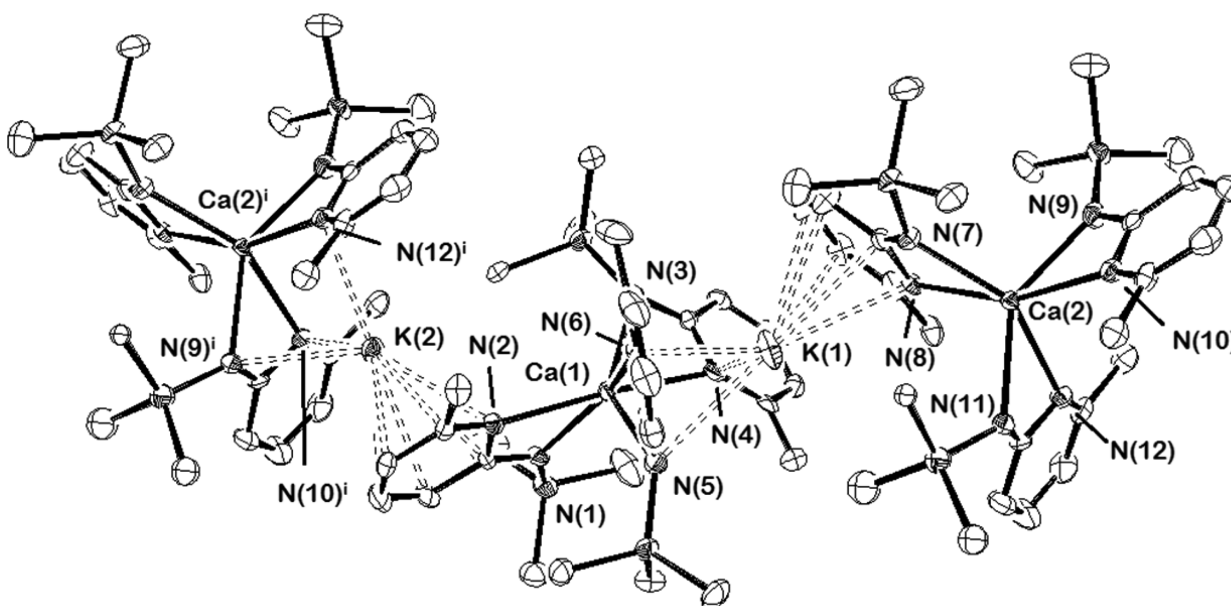


Figure 3. Molecular structure of **8** with displacement ellipsoids set at 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: (i) $x - 1/2, 1/2 + y, z$. Selected bond distances (Å) and angles (deg): Ca(1)–N(1) 2.412(5), Ca(1)–N(2) 2.455(6), Ca(1)–N(3) 2.390(6), Ca(1)–N(4) 2.492(6), Ca(1)–N(5) 2.457(6), Ca(1)–N(6) 2.542(6), K(1)···N(4) 2.910(6), K(1)···N(5) 2.968(5), K(1)···N(6) 2.776(6), K(1)···N(8) (η^6) 3.159(6), K(2)···C(4) 3.189(7), K(2)···C(5) 3.176(8), K(2)···C(6) 3.161(9), K(2)···C(7) 3.125(8), K(2)···C(8) 3.137(7), K(2)···N(2) (η^6) 3.124(6), K(2)···N(9)ⁱ 3.206(6), K(2)···N(10)ⁱ 2.778(6), K(2)···N(12)ⁱ 2.854(6), N(1)–Ca(1)–N(2) 56.23(18), N(3)–Ca(1)–N(4) 56.21(19), N(5)–Ca(1)–N(6) 54.10(17).

with K···C distances in the range 3.125(8)–3.189(7) Å; (ii) three intermolecular K···N interactions, with distances that are noticeably shorter than those for the intramolecular ones, ranging between 2.778(6)–2.968(5) Å, with the exception of K(2)···N(9) [3.206(6) Å]. The K···C distances for the η^6 interaction in **8** are short compared to those measured between K⁺ and phenyl rings in other calciate complexes, for example, in the aryloxo complex KCa{2,6-Ph₂C₆H₃O}₃ [3.155(6)–3.499(7) Å] isolated by Ruhlandt-Senge and co-workers.³³ This type of bridging role for potassium cations has been reported^{34–36} and has also been observed for Rb⁺,³⁷ but to our knowledge there are no examples of mixed-metal Ae complexes involving the η^6 interaction between a K⁺ ion and a pyridine ring. This interaction leads to one ligand being chemically different to the remaining two in the solid state, with the two Ca–N distances significantly elongated [Ca(1)–N(5) 2.457(6) Å, Ca(1)–N(6) 2.542(6) Å] compared to that for the other ligands in **7** and (thf)₃Ca(6-MeC₅H₃N-2-CH₂)₂.¹⁸ This difference is not reflected in the solution NMR spectra of **8**, which suggests that this polymeric structure may not persist in solution.

The retention of alkali metal cations in the structures of group 2 complexes has been observed in metathesis reactions,^{29,34} reduction of Ae(II) dimers with KC₈,^{6,38} and mixed metalations.³⁹ The formation of heterobimetallic species with alkali metals is more common for magnesium,^{39,40} with a tendency to form “inverse” crown complexes supported by amide ligands.³⁸ Stoichiometric control can play a key role in the formation of heterobimetallic species, and, as such, it can influence alkali metal retention.²⁹ Additionally, in some cases, the use of coordinating solvents can prevent the formation of heterobimetallic species in favor of homometallic derivatives.^{33,40} However, in the case of our compounds, we have observed that changes in the stoichiometry do not alter the formation of the final products. The reaction between **2** and

CaI₂ in a 3:1 ratio affords a mixture of **7** and unreacted **2**, which can be easily separated from the product via recrystallization from hexane, and from the reaction between potassium salts **1** or **3** with CaI₂ in a 2:1 molar ratio, the same calciate species and unreacted CaI₂ were isolated. Furthermore, the use of coordinating solvents such as diethyl ether and THF does not prevent the formation of the calciate complexes **8** and **9**.

Metalation Reactions. Direct reaction between prolignands and organoalkaline earth metal precursors is a well-established synthetic route to group 2 complexes,² with the advantage that the reactants used in these reactions (i.e., organomagnesium species and metal amides) have a good solubility in most noncoordinating solvents, facilitating access to complexes free of such coordination. We have chosen to use (tBu)₂Mg, which allows access to homoleptic compounds of the type (L)₂Mg, via the elimination of two molecules of butane⁴¹ and heteroleptic complexes (i.e., LMg(tBu) by manipulation of the reaction stoichiometry.⁴² The reaction between L¹H or L²H and (tBu)₂Mg yielded **10** and **5**, respectively (Scheme 1). The ¹H and ¹³C{¹H} NMR spectra of **10** are almost identical to those reported for **4**, differing exclusively in the absence of peaks which could be assigned to the presence of coordinated solvent. The formulation of the unsolvated compound **10** was also confirmed via elemental microanalysis.

In the case of the reaction between L¹H and (tBu)₂Mg, the coordination polymer [(L¹)Li(μ₂-tBu)Mg(L¹)]_∞ (**11**) was isolated as product in very low yields. Crystals of **11** suitable for X-ray diffraction were grown from a concentrated hexane solution at –30 °C. The solid state structure of **11** is shown in Figures 4 and 5, and relevant bond lengths and angles can be found in Figure 4. The reasons for the formation of **11** as a minor product of this reaction are unclear. It could be tentatively postulated that this polymer is formed via a mechanism that involves a reaction between (tBu)₂Mg and a Li complex such as [L¹Li]₂, which could conceivably be present

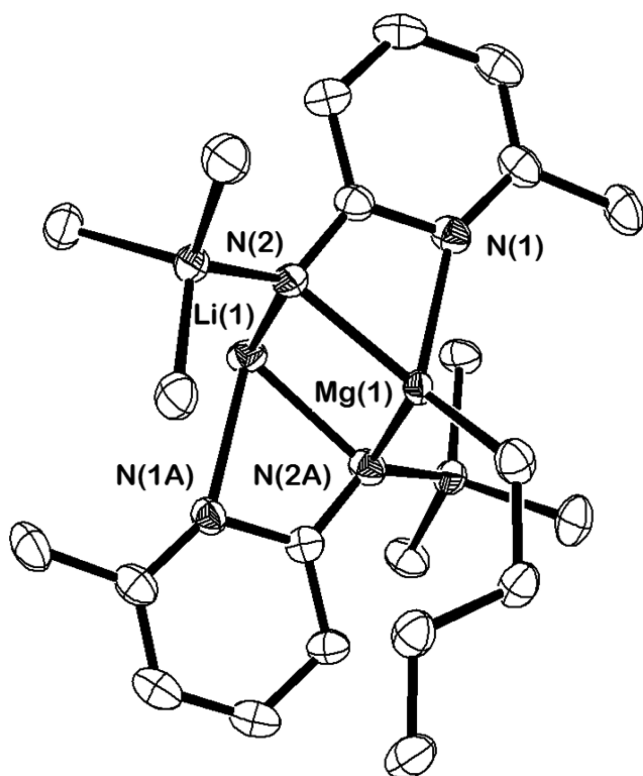


Figure 4. Molecular structure of **11** showing the monomeric unit with ellipsoids shown at 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry transformations are used to generate equivalent atoms: (i) $+x, -y, 1/2 + z$; (ii) $+x, -y, -1/2 + z$. Selected bond distances (Å) and angles (deg): Mg(1)–N(1) 2.127(7), Mg(1)–N(2) 2.159(7), Mg(1)–N(2A) 2.122(13), Li(1)–N(1A) 2.30(3), Li(1)–N(2A) 2.20(4), Li(1)–N(2) 2.22(6), Mg(1)–C(11) 2.124(13), Li(1)ⁱⁱ–C(11) 2.04(5), Mg(1)⋯Li(1) 2.90(6), Mg(1)⋯Li(1)ⁱⁱ 3.89(6), Mg(1)–N(2)–Li(1) 82.6(12), N(2)–Li(1)–N(2A) 95(2), Li(1)–N(2A)–Mg(1) 83.8(15), N(2A)–Mg(1)–N(2) 98.6(5), Mg(1)–C(11)–Li(1)ⁱⁱ 138.3(9).

in small quantities in the sample of **L¹H**. The structure of a related lithium dimer [**L¹Li(OEt₂)**]₂ has been previously reported by Raston and co-workers.^{11a} Direct addition (cocomplexation) reactions have been used by Mulvey and co-workers in the synthesis of mixed sodium and potassium alkoxide–magnesium bis(alkyl) complexes.⁴³ Magnesiate com-

pounds have been extensively studied in the past two decades, owing to their structural properties and synthetic applications.⁴⁴

In **11**, the distance between the lithium and magnesium atoms bridged by the butyl C(11) is 3.89(6) Å. The geometry around the bridging carbon is distorted pyramidal, whereas the Li and Mg centers adopt a tetrahedral geometry. In the polymeric array, a **L¹LiMgL¹** unit can be identified (Figure 4), which deviates from planarity [angle between the Mg(1)–N(2)–Li(1) and Mg(1)–N(2A)–Li(1) planes = 6.8°]. Within the **L¹LiMgL¹** unit, where the two metal atoms are situated closer to each other [2.90(6) Å], both distances between the Mg and Li centers are shorter than the sum of their van der Waals radii (4.4 Å),⁴⁵ and in the case of the shorter distance [2.90(6) Å], this is only slightly longer than a Mg–Li covalent single bond (sum of single bond covalent radii = 2.72 Å).⁴⁶ The Li and Mg atoms are formally in the 1+ and 2+ oxidation states, respectively, which is consistent with the overall charge balance of the molecule; therefore, the presence of a direct metal–metal bond can be ruled out. The polymer is perpetuated through an interaction between the lone pair on the amido nitrogen and the Mg center of the next unit (Figure 5), leading to four-coordinate environments for N(2) and N(2A). Thus, a slightly shorter distance is seen for the pyridyl nitrogen–magnesium distance than to the amide nitrogen distance: Mg(1)–N(1) = 2.121(7) Å, Mg(1)–N(2) = 2.159(7) Å. The intermolecular interaction with the nitrogen atom on the neighboring monomeric unit is similar [Mg(1)–N(2A) = 2.122(13) Å]. Complex **11** exhibits Mg–N distances that are generally within the same range as those for [Ph(2-C₅H₃N)]₂Mg(thf)₂,¹⁴ but in the latter complex, the Mg–N_{amido} distance [2.105(2) Å] is significantly shorter than the Mg–N_{pyridyl} distance [2.182(2) Å]. The M–C distances for **11** [Mg(1)–C(11) = 2.124(13) Å and Li(1)ⁱⁱ–C(11) = 2.04(5) Å] are shorter than those in [(EDBP)Mg(μ₂-ⁿBu)Li(Et₂O)]₂ [EDBP = 2,2'-ethylidenebis-(4,6-di-*tert*-butylphenoxide)] [Mg–C = 2.175(4) Å, Li–C = 2.263(7) Å], where the bridging butyl interaction is supported by a bridging phenoxide ligand.⁴⁷ Compounds containing a magnesium atom bridged to an alkali metal by a butyl group are relatively uncommon, and comparison to other examples containing a heavier alkali metal also reveals a short Mg–C bond for **11**.^{39c,43,48} Li(1)ⁱⁱ–C(11) is also shorter than the Li–C bond distances for the dimer ring in (ⁿBuLi·TMEDA)₂ [which range from 2.215(11) to 2.227(9) Å].⁴⁹ A similar agostic Li⋯C interaction was also observed in the solid state

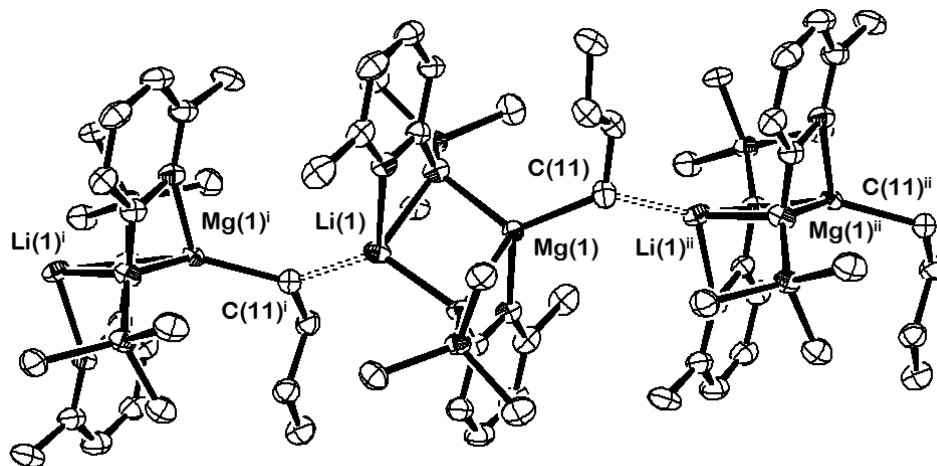


Figure 5. Molecular structure showing the polymerization of **11**. Ellipsoids are shown at 50% probability level. H atoms are omitted for clarity.

structure of the polymer $[\text{LiMg}\{\mu\text{-N}(\text{SiMe}_3)_2\}_2\text{tBu}]_\infty$, in which the metal displays a long-range interaction with a methyl carbon $[\text{Li}\cdots\text{C} = 2.563(3) \text{ \AA}]$.⁵⁰

In light of this serendipitous discovery, a rational synthetic procedure was designed with the use of a cocomplexation reaction between the proligand L^1H and a 1:1 mixture of $(^n\text{Bu})_2\text{Mg}$ and $^n\text{BuLi}$ in hexanes (Scheme 1). Following this methodology, synthesis of **11** was successfully reproduced and the compound was isolated in good yields. The characterization of **11** was completed via spectroscopic and analytical techniques. The $^7\text{Li}\{\text{H}\}$ NMR spectrum of **11** shows one broad signal at 1.29 ppm, confirming the presence of one lithium-containing species in solution. The ^1H and $^{13}\text{C}\{\text{H}\}$ NMR spectra for **11** exhibit resonances for the two different metal-bound aminopyridinato moieties: (i) two peaks can be attributed to two distinct SiMe_3 fragments, resonating at 0.32 and 0.39 ppm and integrating for a total of 18 protons; the first chemical shift value is similar to that previously reported for $[\text{L}^1\text{Li}(\text{OEt}_2)]_2$ and $[\text{L}^1\text{Li}(\text{thf})]_2$;^{11a,51} (ii) the chemical difference of the two trimethylsilyl groups is also reflected in the $^{13}\text{C}\{\text{H}\}$ NMR spectrum, which displays two different resonances at 2.0 and 2.5 ppm; (iii) the CH_3 groups of the picoline moieties resonate at 2.05 ppm, with a broad signal that partially overlaps with the resonance of a CH_2 group of the *n*-butyl chain; (iv) two different signals can be assigned to the pyridyl hydrogen H^3 , which resonate at 5.95 and 6.03 ppm; the first peak is comparable to the same resonance reported here for compounds **4** and **10**, whereas the second peak is comparable to that reported for the above-mentioned lithium dimers; (v) the signals of the pyridyl-carbon atoms C^3 and C^5 are both split into two distinct peaks, the first pair resonating at 109.8 and 112.4 ppm, and the latter resonating at 138.6 and 139.4 ppm.

Furthermore, the butyl resonances for **11** are broadly similar to those for other reported complexes, albeit containing supported butyl moieties,^{43,47,52} and are also very close to those of $(^n\text{Bu})_2\text{Mg}$. In the ^1H NMR spectrum of **11**, the resonances for the bridging carbon chain protons support the formulation of this ligand as a bridging butyl and spectroscopic data does not exhibit any resonances, which could suggest the presence of additional bridging groups in between the two metal atoms. This supports the formulation of the $\text{C}(11)\text{--C}(14)$ chain as a butyl ligand, which is also confirmed by elemental analysis run on the bulk sample, therefore confirming the proposed bimetallic nature of the coordination compound. This set of evidence leads to the conclusion that **11** is the first structurally authenticated complex to feature an unsupported bridging butyl ligand between two metal centers.⁵² Complexes featuring organic groups bridging a lithium and magnesium atom are comparatively rare, and **11** is the first to feature a bridging alkyl group not supported by another bridging ligand.^{47,53}

Changes in the reaction conditions can affect the outcome of cocomplexations. In fact, through the use of a coordinating solvent (THF) and addition of the reagents in a specific order, first $^n\text{BuLi}$ then $(^n\text{Bu})_2\text{Mg}$, to L^1H , the magnesiate complex $(\text{L}^1)_3\text{MgLi}(\text{thf})$ (**12**) was obtained (Figure 6). Crystals of X-ray quality were obtained from a concentrated solution in hexane/THF at room temperature. In the solid state, the coordination sphere of the magnesium center is saturated by three aminopyridinato ligands, adopting a distorted trigonal prismatic geometry. One of the ligands binds exclusively the magnesium atom, with magnesium–nitrogen distances within the range of

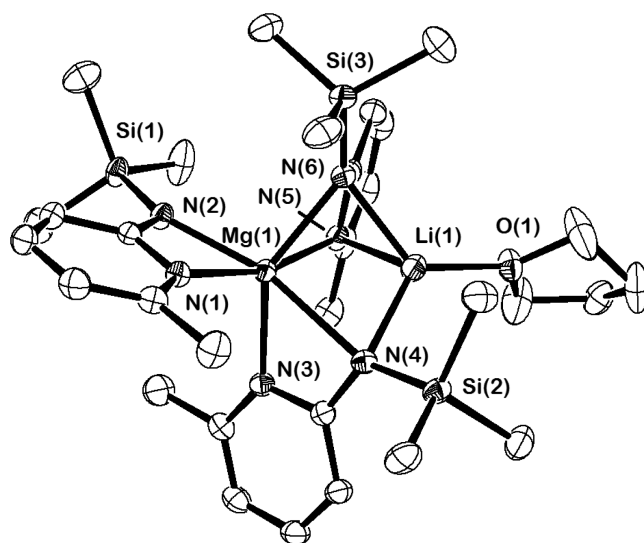


Figure 6. Molecular structure of **12**, with displacement ellipsoids set at the 50% probability level. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): $\text{Mg}(1)\text{--N}(1)$ 2.1600(12), $\text{Mg}(1)\text{--N}(2)$ 2.1402(12), $\text{Mg}(1)\text{--N}(3)$ 2.1258(12), $\text{Mg}(1)\text{--N}(4)$ 2.4619(12), $\text{Mg}(1)\text{--N}(5)$ 2.3148(12), $\text{Mg}(1)\text{--N}(6)$ 2.1796(12), $\text{Li}(1)\text{--N}(4)$ 2.022(3), $\text{Li}(1)\text{--N}(5)$ 2.282(3), $\text{Li}(1)\text{--N}(6)$ 2.061(3), $\text{Li}(1)\text{--O}(1)$ 1.921(3), $\text{Li}(1)\text{--C}(19)$ 2.337(3), $\text{Mg}(1)\cdots\text{Li}(1)$ 2.638(2), $\text{N}(1)\text{--Mg}(1)\text{--N}(2)$ 63.88(2), $\text{N}(3)\text{--Mg}(1)\text{--N}(4)$ 59.63(4), $\text{N}(5)\text{--Mg}(1)\text{--N}(6)$ 60.24(4), $\text{N}(5)\text{--Li}(1)\text{--N}(6)$ 62.41(9).

those observed for **11** [$\text{Mg}(1)\text{--N}(1) = 2.1600(12) \text{ \AA}$, $\text{Mg}(1)\text{--N}(2) = 2.1402(12) \text{ \AA}$], whereas the remaining two aminopyridinato ligands bridge between magnesium and lithium. One ligand fragment bridges via an interaction with the lone pair of the amido nitrogen [$\text{Li}(1)\text{--N}(4) = 2.022(3) \text{ \AA}$], whereas the second aminopyridinato unit bridges with both nitrogen atoms [$\text{Li}(1)\text{--N}(5) = 2.282(3) \text{ \AA}$, $\text{Li}(1)\text{--N}(6) = 2.061(3) \text{ \AA}$]. Owing to these interactions, some of the magnesium–nitrogen distances are significantly elongated compared to those with the first ligand fragment [$\text{Mg}(1)\text{--N}(4) = 2.4619(12) \text{ \AA}$, $\text{Mg}(1)\text{--N}(5) = 2.3148(12) \text{ \AA}$]. The $\text{Mg}\cdots\text{Li}$ distance for **12** [2.638(2) Å] is shorter than that displayed by **11** and is also slightly shorter than the analogous distances reported for a series of isostructural magnesiates by Mulvey and co-workers [$\text{Mg}\cdots\text{Li} = 2.679(9)\text{--}2.706(5) \text{ \AA}$].⁵⁴ Similar amido magnesiates have been previously reported in the literature, obtained with $[\text{N}(\text{Cy})_2]^-$ (Cy = cyclohexyl) and $[\text{N}(\text{SiMe}_3)_2]^-$ ligands; analogously to that observed for **12**, the previous heterobimetallic magnesiates display one terminal and two bridging amido ligands.^{50,54,55} All the previous cases of similar magnesiates were obtained with monodentate amides. Therefore, according to the previous literature, **12** is, to the best of our knowledge, the first case of a homoleptic magnesiate (considering THF as an ancillary ligand) obtained with a bidentate N-donor ligand.

Spectroscopic data obtained from the bulk sample support the formulation obtained from the crystallographic characterization. The ^1H NMR spectrum displays one set of signals for all the proton resonances, the values of the chemical shifts are very close to **11**. Moreover, two broad $\text{Si}(\text{CH}_3)_3$ and CH_3 signals ($\delta = 0.36$ and 1.94 ppm) are detected, probably due to the difference in the chemical environments between the different ligand fragments. In the $^7\text{Li}\{\text{H}\}$ NMR one broad resonance is present at 1.40 ppm, similar to that observed for

11. Finally the formulation was confirmed by elemental analysis performed on the same sample, which accounts for the presence of 1.5 molecules of THF per molecule. The same ratio of molecule and crystallization solvent could not be determined accurately in the solution ^1H NMR spectrum, due to the presence of deuterated THF in the sample.

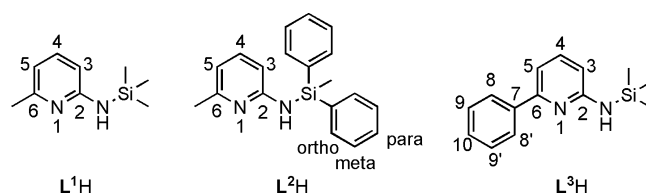
CONCLUSIONS

Aminopyridinato ligands featuring sterically demanding silyl substituents have been used to stabilize magnesium and calcium complexes, synthesized via direct metalation and metathesis reactions. The first homoleptic calcium aminopyridinato complex (7) has been isolated and structurally characterized, and two heterobimetallic calciate complexes (8 and 9) have been reported. The solid state structure of 8 reveals a monodimensional polymeric arrangement, which is, to our knowledge the first example of a calciate complex supported by a bidentate *N*-donor ligand. Complex 11 is a rare example of a mixed Li/Mg complex to feature an unsupported bridging alkyl moiety, and the first structurally authenticated complex to feature an unsupported bridging butyl ligand between two metal centers. Subtle changes in the reaction conditions of the “one-pot” reaction of L^1H , $^t\text{BuLi}$, and $^t(\text{Bu})_2\text{Mg}$ yields a different complex (12), which does not feature any butyl groups. These results show that aminopyridinato ligands can be used for the stabilization of low-coordinate group 2 complexes, and that the asymmetry in these ligands can facilitate the isolation of alkaline earth complexes featuring unusual coordination environments.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk line and glovebox techniques. Hexane was dried by passing through a column of activated 4 Å molecular sieves. Diethyl ether and THF were predried over Na wire prior to distillation from Na/K alloy (diethyl ether) or sodium–benzophenone ketyl (THF). Toluene was refluxed over and distilled from potassium. All solvents were degassed prior to use and stored over a potassium mirror (hexane, diethyl ether, toluene) or activated 4 Å molecular sieves (THF). Benzene- d_6 (Goss) was dried over potassium and THF- d_8 (Goss) was dried over CaH_2 ; both solvents were degassed with three freeze–pump–thaw cycles prior to use. Anhydrous MgI_2 (Sigma-Aldrich), CaI_2 (Alfa Aesar), and NaNH_2 (Alfa Aesar) were heated to 300 °C in vacuo overnight and stored under purified nitrogen. 2-Amino-6-methylpyridine (Alfa Aesar) was dried under vacuum overnight. 2-Amino-6-phenylpyridine (Merck) was stored over activated 4 Å molecular sieves prior to use. Di-*n*-butylmagnesium was obtained as a 1.0 M solution in heptane (Aldrich); solvent was removed in vacuo, and the compound was used as a solid. All other compounds were used as received. IR spectra were recorded as Nujol mulls on KBr discs with a Bruker Tensor 27 FTIR spectrometer. NMR spectra for all compounds were collected on Bruker DPX300, DPX400, AV400, or AV(III)400 spectrometers. Chemical shifts for ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ are quoted in ppm relative to SiMe_4 and for $^7\text{Li}\{^1\text{H}\}$ relative to $\text{LiCl/D}_2\text{O}$ solution. Elemental microanalyses were performed by Mr. Stephen Boyer at the Microanalysis Service, London Metropolitan University. The synthesis of L^1H has been previously reported in the literature; L^2H and L^3H were synthesized by adapting the same synthetic procedure.^{11a} Assignments of NMR spectra for complexes containing these ligands are according to the convention given below.

Crystallographic Method. Crystals of 7, 8, 11, and 12 were mounted on MicroMounts (MiTeGen) using YR-1800 perfluoropolyether oil and cooled rapidly to 90 or 120 K in a stream of cold nitrogen using an Oxford Cryosystems low-temperature device.⁵⁶ Data for compound 8 were collected on a Bruker SMART APEX



diffractometer, equipped with a graphite-monochromated Mo $K\alpha$ source ($\lambda = 0.71073$ Å). Absorption corrections were applied using a multiscan method (SADABS).⁵⁷ All non-H atoms were located using direct methods⁵⁸ and difference Fourier syntheses. All fully occupied non-H atoms were refined with anisotropic displacement parameters. Data for compounds 7, 11, and 12 were collected on a Oxford Diffraction SuperNova diffractometer, equipped with a mirror-monochromated Cu $K\alpha$ source ($\lambda = 1.5418$ Å). Gaussian grid face-indexed absorption correction with a beam profile correction (CrysAlis Pro)⁵⁹ were applied. Structures were solved via direct methods and refined by full matrix least-squares (SHELX-97).⁵⁸ In compound 7, extensive positional disorder was identified for both the ligand moieties. They were modeled separately over two positions: the occupancies of the two components were refined competitively, converging at a ratio of 0.617(5):0.383(5) for one ligand and 0.644(7):0.356(7) for the second one. Positional disorder also was identified for atoms C(44) and C(45): the occupancies of the two components were refined competitively, converging at a ratio of 0.606(10):0.394(10). For the two ligand moieties, restraints were applied on chemically equivalent 1,2- and 1,3-distances. Bond lengths of the two coordinated THF molecules were also restrained. Chemically equivalent Ca–donor atom distances were restrained to be approximately equal. In compound 8, positional disorder was identified for atoms C(19), C(20), and C(21): the occupancies of the two components were refined competitively, converging at a ratio of 0.54(3):0.46(3). Sensible anisotropic temperature parameters could not be refined for these atoms, so they were refined isotropically. In compound 11, the space group Cc was chosen over $C2/c$ for solving the structure, despite the two groups being both very good candidates. The proposed model was not applicable in $C2/c$, and the overall solution to a dimeric heterobimetallic model in which Mg and Li alternatively occupy the two coordination positions and the C4 chain is linked with the correct chemical occupancy. This resulted in a better overall model, which matches the spectroscopic and analytical data, and a considerable improvement in terms of residual electron density for the solution in a $C2/c$ space group. The two metals, Mg(1) and Li(1), exhibited positional disorder and their positions are partially occupied by a Li atom for the first metal and a Mg atom for the latter. The same disorder is extended also to the butyl fragment C(11)–C(14), whose occupancy is linked to the metal sites. The occupancies of the two disorder components were refined competitively, converging at a ratio of 0.720(7):0.280(7). Rigid bond restraints were applied on the chemically equivalent nitrogen–metal distances. The proximity of the hydrogen atoms H(11A) and H(11B) to Li(1) could be attributed to the presence of agostic interactions, but this cannot be rigorously confirmed as the hydrogen atoms have been positioned by symmetry using a riding model. Therefore, the very short distances [1.50 and 1.89 Å] are not reliable. Finally, global restraints were applied to the displacement parameters. In compound 12, positional disorder was identified for carbon atoms C(29) and C(30) of the THF molecule. This was modeled over two positions for each and the two components refined competitively, converging at a ratio of 0.614(10):0.386(10). CCDC 939773–939775 and 964610 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 7. $\text{C}_{46}\text{H}_{54}\text{CaN}_4\text{O}_2\text{Si}_2$, $M_r = 791.19$, $0.77 \times 0.33 \times 0.26$ mm³, monoclinic, space group $P2_1/n$, $a = 14.0740(5)$ Å, $b = 18.5192(6)$ Å, $c = 16.9551(6)$ Å, $\beta = 102.838(4)^\circ$, $V = 4300.4(3)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.222$ g cm^{−3}, $\mu = 2.112$ mm^{−1}, $F(000) = 1688$. A total of 18 733 reflections were measured, of which 7479 were unique, with $R_{\text{int}} = 0.051$. Final R_1 (wR_2) = 0.126 (0.241) with GOF = 1.08. Min

and max residual electron densities: -1.55 and $+1.14$ $\text{e}/\text{\AA}^3$, respectively.

Crystal Data for 8. $\text{C}_{54}\text{H}_{90}\text{CaK}_2\text{N}_{12}\text{Si}_6$, $M_r = 1234.28$, $0.17 \times 0.12 \times 0.07$ mm^3 , monoclinic, space group $C2/c$, $a = 30.265(4)$ \AA , $b = 11.2304(15)$ \AA , $c = 42.062(6)$ \AA , $\beta = 102.877(2)^\circ$, $V = 13\,937(3)$ \AA^3 , $Z = 8$, $D_{\text{calcd}} = 1.176$ g cm^{-3} , $\mu = 0.428$ mm^{-1} , $F(000) = 5280$. A total of 49 344 reflections were measured, of which 12 297 were unique, with $R_{\text{int}} = 0.10$. Final R_1 (wR_2) = 0.110 (0.186) with GOF = 1.26 . Min and max residual electron densities: -0.69 and $+0.60$ $\text{e}/\text{\AA}^3$.

Crystal Data for 11. $\text{C}_{22}\text{H}_{39}\text{LiMgN}_4\text{Si}_2$, $M_r = 447.00$, $0.20 \times 0.14 \times 0.10$ mm^3 , monoclinic, space group Cc , $a = 17.4769(10)$ \AA , $b = 12.6948(5)$ \AA , $c = 13.5233(8)$ \AA , $\beta = 118.782(8)^\circ$, $V = 2629.7(3)$ \AA^3 , $Z = 4$, $D_{\text{calcd}} = 1.129$ g cm^{-3} , $\mu = 1.559$ mm^{-1} , $F(000) = 968$. A total of 10 380 reflections were measured, of which 4168 were unique, with $R_{\text{int}} = 0.0421$. Final R_1 (wR_2) = 0.0476 (0.119) with GOF = 1.07 . Min and max residual electron densities: -0.20 and $+0.65$ $\text{e}/\text{\AA}^3$, respectively.

Crystal data for 12. $\text{C}_{31}\text{H}_{53}\text{LiMgN}_6\text{OSi}_3$, $M_r = 641.31$, $0.11 \times 0.15 \times 0.38$ mm^3 , monoclinic, space group $P2_1/c$, $a = 10.05140(13)$ \AA , $b = 20.2091(3)$ \AA , $c = 18.6537(2)$ \AA , $\beta = 102.1281(13)^\circ$, $V = 3704.55(8)$ \AA^3 , $Z = 4$, $D_{\text{calcd}} = 1.150$ g cm^{-3} , $\mu = 1.586$ mm^{-1} , $F(000) = 1384$. A total of 19 407 reflections were measured, of which 6866 were unique, with $R_{\text{int}} = 0.019$. Final R_1 (wR_2) = 0.0312 (0.887) with GOF = 1.04 . Min and max residual electron densities: -0.23 and $+0.30$ $\text{e}/\text{\AA}^3$, respectively.

Syntheses. **Synthesis of $\text{L}^1\text{K}(\text{thf})_{0.5}$ (1).** A solution of L^1H (2.18 g, 12.1 mmol) in THF (30 cm^3) was added slowly to a suspension of KH (0.52 g, 13.0 mmol) in THF (10 cm^3) at -78 $^\circ\text{C}$; the reaction was warmed to room temperature and stirred overnight. The reaction was filtered, the solvent was removed in vacuo, and the solid residue was washed with hexane. The resulting suspension was filtered and the residue was dried in vacuo overnight, affording **1** (1.78 g, 7.0 mmol, yield 58%) as a white solid. Compounds **2** and **3** were synthesized in an analogous procedure to that for **1**.

1. ^1H NMR (C_6D_6 , 298 K, 400.07 MHz): $\delta = 0.36$ (s, 9H , $\text{Si}(\text{CH}_3)_3$), 1.41 (m, 2H , THF), 2.25 (s, 3H , CH_3), 3.54 (m, 2H , THF), 6.07 (d, $^3J = 6.7$ Hz, 1H , $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 6.32 (d, $^3J = 8.3$ Hz, 1H , $\text{C}_5\text{H}_3\text{N}-\text{H}^5$), 7.09 (dd, $^3J = 8.5$ Hz, $^3J = 6.9$ Hz, 1H , $\text{C}_5\text{H}_3\text{N}-\text{H}^4$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 100.63 MHz): $\delta = 2.7$ ($\text{Si}(\text{CH}_3)_3$), 25.5 ($\text{CH}_3 + \text{THF}$), 67.5 (THF), 104.4 ($\text{C}_5\text{H}_3\text{N}-\text{C}^3$), 112.3 ($\text{C}_5\text{H}_3\text{N}-\text{C}^5$), 136.8 ($\text{C}_5\text{H}_3\text{N}-\text{C}^4$), 156.1 ($\text{C}_5\text{H}_3\text{N}-\text{C}^2$), 168.9 ($\text{C}_5\text{H}_3\text{N}-\text{C}^6$) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 79.51 MHz): no peaks observed. $\text{C}_{11}\text{H}_{19}\text{KN}_2\text{O}_{0.5}\text{Si}$ (254.47): calcd (%) C 51.92 , H 7.53 , N 11.01 ; found (%) C 51.86 , H 7.45 , N 10.93 . IR: $\nu = 2408(\text{w})$, $2287(\text{w})$, $1936(\text{w})$, $1805(\text{w})$, $1587(\text{w})$, $1543(\text{s})$, $1253(\text{w})$, $1241(\text{s})$, $1205(\text{m})$, $1161(\text{s})$, $1064(\text{s})$, $988(\text{s})$, $941(\text{s})$, $866(\text{s})$, $824(\text{s})$, $779(\text{s})$, $738(\text{s})$, $706(\text{m})$, $676(\text{m})$, $662(\text{m})$, $609(\text{s})$, $558(\text{m})$, $537(\text{m})$, $465(\text{m})$ cm^{-1} .

2. From 1.89 g (6.2 mmol) of L^1H was yielded 1.20 g of **2** (3.5 mmol, yield 56%). ^1H NMR (C_6D_6 , 298 K, 400.07 MHz): $\delta = 0.70$ (s, 3H , $\text{Si}(\text{CH}_3)_3$), 2.05 (s, 3H , CH_3), 6.06 (d, $^3J = 6.9$ Hz, 1H , $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 6.40 (d, $^3J = 8.4$ Hz, 1H , $\text{C}_5\text{H}_3\text{N}-\text{H}^5$), 6.93 (dd, $^3J = 8.4$ Hz, $^3J = 6.9$ Hz, 1H , $\text{C}_5\text{H}_3\text{N}-\text{H}^4$), 7.20 – 7.26 (m, 6H , $\text{Ph}-\text{CH}^{\text{meta}}$ $\text{Ph}-\text{CH}^{\text{para}}$), 7.59 – 7.78 (m, 4H , $\text{Ph}-\text{CH}^{\text{ortho}}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 100.63 MHz): $\delta = 1.1$ ($\text{Si}(\text{CH}_3)_3$), 25.1 (CH_3), 105.8 ($\text{C}_5\text{H}_3\text{N}-\text{C}^3$), 113.7 ($\text{C}_5\text{H}_3\text{N}-\text{C}^5$), 127.9 ($\text{Ph}-\text{CH}$), 128.4 ($\text{Ph}-\text{CH}$), 134.6 ($\text{Ph}-\text{CH}$), 136.7 ($\text{C}_5\text{H}_3\text{N}-\text{C}^4$), 142.9 ($\text{Ph}-\text{C}$), 155.8 ($\text{C}_5\text{H}_3\text{N}-\text{C}^2$), 169.2 ($\text{C}_5\text{H}_3\text{N}-\text{C}^6$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 79.51 MHz): $\delta = -24.8$ ($\text{Si}(\text{CH}_3)_3$) ppm. $\text{C}_{19}\text{H}_{19}\text{KN}_2\text{Si}$ (342.55): calcd (%) C 66.62 , H 5.59 , N 8.18 ; found (%) C 66.48 , H 5.59 , N 8.18 . IR: $\nu = 1580(\text{s})$, $1543(\text{w})$, $1260(\text{m})$, $1165(\text{w})$, $1103(\text{m})$, $1064(\text{w})$, $1019(\text{w})$, $992(\text{w})$, $840(\text{s})$, $788(\text{w})$, $734(\text{w})$, $705(\text{m})$, $663(\text{w})$, $540(\text{w})$ cm^{-1} .

3. From 3.43 g (14.1 mmol) of L^3H was yielded 3.42 g of **3** (10.8 mmol, yield 77%). ^1H NMR (C_6D_6 , 298 K, 400.07 MHz): $\delta = 0.32$ (s, 9H , $\text{Si}(\text{CH}_3)_3$), 1.40 (m, 2H , THF), 3.53 (m, 2H , THF), 6.52 (d, $^3J = 8.4$ Hz, 1H , $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 6.58 (d, $^3J = 6.9$ Hz, 1H , $\text{C}_5\text{H}_3\text{N}-\text{H}^5$), 7.07 – 7.26 (m, 4H , $\text{C}_5\text{H}_3\text{N}-\text{H}^4 + \text{Ph}-\text{H}^{8,9}$ + $\text{Ph}-\text{H}^{10}$), 7.69 (d, $^3J = 6.8$ Hz, 2H , $\text{Ph}-\text{H}^{8,9}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 100.63 MHz): $\delta = 2.5$ ($\text{Si}(\text{CH}_3)_3$), 25.5 (THF), 67.5 (THF), 103.8 ($\text{C}_5\text{H}_3\text{N}-\text{C}^3$), 114.6 ($\text{C}_5\text{H}_3\text{N}-\text{C}^5$), 126.6 ($\text{Ph}-\text{C}^{8,9}$), 127.6 ($\text{Ph}-\text{C}^{10}$), 128.1 ($\text{Ph}-\text{C}^{9,10}$), 128.7 ($\text{C}_5\text{H}_3\text{N}-\text{C}^4$), 136.8 ($\text{Ph}-\text{C}^7$), 156.7 ($\text{C}_5\text{H}_3\text{N}-\text{C}^2$), 169.7 ($\text{C}_5\text{H}_3\text{N}-\text{C}^6$)

ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 79.51 MHz): no peaks observed. $\text{C}_{16}\text{H}_{21}\text{KN}_2\text{O}_{0.5}\text{Si}$ (316.53): calcd (%) C 60.71 , H 6.69 , N 8.85 ; found (%) C 60.45 , H 6.51 , N 8.79 . IR: $\nu = 3062(\text{w})$, $2314(\text{w})$, $1943(\text{w})$, $1589(\text{s})$, $1572(\text{s})$, $1534(\text{s})$, $1264(\text{w})$, $1254(\text{w})$, $1241(\text{s})$, $1165(\text{s})$, $1096(\text{w})$, $1080(\text{w})$, $1044(\text{m})$, $996(\text{s})$, $950(\text{m})$, $913(\text{w})$, $848(\text{s})$, $826(\text{s})$, $799(\text{s})$, $759(\text{s})$, $736(\text{w})$, $693(\text{s})$, $672(\text{m})$, $610(\text{m})$, $557(\text{w})$, $513(\text{w})$, $468(\text{w})$ cm^{-1} .

Synthesis of $(\text{L}^1)_2\text{Mg}(\text{thf})$ (4). A solution of **1** (0.70 g, 2.7 mmol) in THF (30 cm^3) was added dropwise to a suspension of MgI_2 (0.38 g, 1.4 mmol) in THF (10 cm^3) at -78 $^\circ\text{C}$; the reaction was warmed to room temperature and stirred overnight. A white precipitate was formed with a yellow supernatant liquid. The solvent was removed in vacuo, and the oily yellow residue was extracted with hexane (10 cm^3). The mixture was filtered, and the yellow hexane solution was concentrated and stored at -80 $^\circ\text{C}$, whereupon a white precipitate formed. The suspension was filtered and dried, affording **4** (0.32 g, 0.7 mmol, yield 50%) as a white solid. ^1H NMR (C_6D_6 , 298 K, 400.07 MHz): $\delta = 0.23$ (s, 18H , $\text{Si}(\text{CH}_3)_3$), 1.12 (m, 4H , THF), 2.09 (broad, 6H , CH_3), 3.39 (m, 4H , THF), 5.95 (d, $^3J = 7.2$ Hz, 2H , $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 6.33 (d, $^3J = 8.4$ Hz, 2H , $\text{C}_5\text{H}_3\text{N}-\text{H}^5$), 6.97 (t, $^3J = 7.8$ Hz, 2H , $\text{C}_5\text{H}_3\text{N}-\text{H}^4$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 100.63 MHz): $\delta = 1.0$ ($\text{Si}(\text{CH}_3)_3$), 23.1 (CH_3), 25.5 (THF), 67.5 (THF), 109.6 ($\text{C}_5\text{H}_3\text{N}-\text{C}^5$), 139.6 ($\text{C}_5\text{H}_3\text{N}-\text{C}^4$), 156.1 ($\text{C}_5\text{H}_3\text{N}-\text{C}^2$) ppm; $\text{C}_5\text{H}_3\text{N}-\text{C}^3$ and $\text{C}_5\text{H}_3\text{N}-\text{C}^6$ not detected. $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 79.51 MHz): no peaks observed. $\text{C}_{22}\text{H}_{38}\text{N}_4\text{MgOSi}_2$ (455.04): calcd (%) C 58.07 , H 8.42 , N 12.31 ; found (%) C 58.07 , H 8.52 , N 12.40 . IR: $\nu = 3138(\text{m})$, $2462(\text{w})$, $1611(\text{s})$, $1360(\text{m})$, $1255(\text{s})$, $1243(\text{s})$, $1165(\text{s})$, $1083(\text{s})$, $1073(\text{s})$, $1036(\text{m})$, $1000(\text{m})$, $953(\text{m})$, $865(\text{s})$, $837(\text{m})$, $780(\text{m})$, $748(\text{w})$, $737(\text{w})$, $685(\text{m})$, $621(\text{m})$, $622(\text{w})$, 552 (m), $454(\text{m})$ cm^{-1} .

Synthesis of $(\text{L}^2)_2\text{Mg}$ (5). A solution of **2** (0.80 g, 2.3 mmol) in THF (30 cm^3) was added dropwise to a suspension of MgI_2 (0.32 g, 1.2 mmol) in THF (10 cm^3) at -78 $^\circ\text{C}$, and the reaction was warmed to room temperature and stirred overnight. Precipitation occurred overnight, and the solvent was removed from the suspension in vacuo. The residue was extracted with hexane (10 cm^3), and the solution was cooled to -30 $^\circ\text{C}$. The precipitate that formed was filtered and dried, affording **5** (0.43 g, 0.7 mmol, yield 57%) as a white solid. ^1H NMR (C_6D_6 , 298 K, 400.07 MHz): $\delta = 0.62$ (s, 6H , $\text{Si}(\text{CH}_3)_2$), 1.84 (s, 6H , CH_3), 5.82 (d, $^3J = 4.9$ Hz, 2H , $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 6.30 (d, $^3J = 6.7$ Hz, 2H , $\text{C}_5\text{H}_3\text{N}-\text{H}^5$), 6.71 (t, $^3J = 8.5$ Hz, 2H , $\text{C}_5\text{H}_3\text{N}-\text{H}^4$), 7.15 (m, 12H , $\text{Ph}-\text{CH}^{\text{meta}}$ $\text{Ph}-\text{CH}^{\text{para}}$), 7.68 (m, 8H , $\text{Ph}-\text{CH}^{\text{ortho}}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 100.63 MHz): $\delta = 1.2$ ($\text{Si}(\text{CH}_3)_2$), 22.6 (CH_3), 110.7 ($\text{C}_5\text{H}_3\text{N}-\text{C}^3$), 127.8 ($\text{C}_5\text{H}_3\text{N}-\text{C}^5$), 128.1 ($\text{Ph}-\text{CH}$), 129.1 ($\text{Ph}-\text{CH}$), 135.1 ($\text{Ph}-\text{CH}$), 138.2 ($\text{Ph}-\text{C}$), 138.9 ($\text{C}_5\text{H}_3\text{N}-\text{C}^4$), 155.4 ($\text{C}_5\text{H}_3\text{N}-\text{C}^2$), 166.2 ($\text{C}_5\text{H}_3\text{N}-\text{C}^6$) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 79.51 MHz): $\delta = -15.4$ ($\text{Si}(\text{CH}_3)_2$) ppm. $\text{C}_{38}\text{H}_{38}\text{N}_4\text{MgSi}_2$ (631.21): calcd (%) C 72.31 , H 6.07 , N 8.88 ; found (%) C 72.13 , H 5.91 , N 8.69 . IR: $\nu = 1594(\text{s})$, $1553(\text{m})$, $1353(\text{s})$, $1241(\text{m})$, $1166(\text{w})$, $1106(\text{s})$, $1081(\text{m})$, $1000(\text{w})$, $843(\text{s})$, $786(\text{s})$, $700(\text{s})$, $553(\text{w})$, $496(\text{w})$ cm^{-1} .

Synthesis of $(\text{L}^3)_2\text{Mg}$ (6). A solution of **3** (0.91 g, 2.9 mmol) in THF (30 cm^3) was added dropwise to a suspension of MgI_2 (0.40 g, 1.4 mmol) in THF (10 cm^3) at -78 $^\circ\text{C}$, and the reaction was warmed to room temperature and stirred overnight. A white precipitate was formed overnight, with a dark brown supernatant liquid. The solvent was removed in vacuo, and the residue was extracted with hexane (20 cm^3). The yellow hexane solution was evaporated to dryness, affording **6** (0.55 g, 1.1 mmol, yield 78%) as a white solid. ^1H NMR (C_6D_6 , 298 K, 400.07 MHz): $\delta = 0.52$ (s, 18H , $\text{Si}(\text{CH}_3)_3$), 6.58 – 6.66 (m, 4H , $\text{C}_5\text{H}_3\text{N}-\text{H}^3 + \text{C}_5\text{H}_3\text{N}-\text{H}^5$), 7.08 – 7.15 (m, 4H , $\text{C}_5\text{H}_3\text{N}-\text{H}^4 + \text{Ph}-\text{H}^{10}$), 7.26 (m, 4H , $\text{Ph}-\text{H}^{8,9}$), 7.76 (t, $^3J = 7.4$ Hz, 4H , $\text{Ph}-\text{H}^{9,10}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 100.63 MHz): $\delta = 1.4$ ($\text{Si}(\text{CH}_3)_3$), 105.8 ($\text{C}_5\text{H}_3\text{N}-\text{C}^3$), 111.6 ($\text{C}_5\text{H}_3\text{N}-\text{C}^5$), 127.4 ($\text{Ph}-\text{C}^{8,9}$), 129.0 ($\text{Ph}-\text{C}^{10}$), 129.2 ($\text{Ph}-\text{C}^{9,10}$), 138.5 ($\text{C}_5\text{H}_3\text{N}-\text{C}^4$), 140.9 ($\text{Ph}-\text{C}^7$), 156.3 ($\text{C}_5\text{H}_3\text{N}-\text{C}^2$), 162.2 ($\text{C}_5\text{H}_3\text{N}-\text{C}^6$) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 79.51 MHz): $\delta = 1.0$ ($\text{Si}(\text{CH}_3)_3$) ppm. $\text{C}_{28}\text{H}_{34}\text{N}_4\text{MgSi}_2$ (507.07): calcd (%) C 66.32 , H 6.76 , N 11.05 ; found (%) C 66.10 , H 6.61 , N 10.93 .

Synthesis of $(\text{L}^2)_2\text{Ca}(\text{thf})_2$ (7). A solution of **2** (0.80 g, 2.3 mmol) in THF (20 cm^3) was added dropwise to a suspension of CaI_2 (0.34 g, 1.2 mmol) in THF at -78 $^\circ\text{C}$; the reaction was warmed to room

temperature and stirred overnight. A white precipitate was formed overnight; the solvent was removed in vacuo, and the solid residue was washed with hot hexane (10 cm³) and extracted with THF (15 cm³). The solvent was removed in vacuo, affording **7** (0.32 g, 0.4 mmol, yield 34%) as a white solid. Crystals of X-ray quality were grown from a saturated solution of **7** in hexane at room temperature. ¹H NMR (C₆D₆, 298 K, 400.07 MHz): δ = 0.79 (s, 6H, Si(CH₃)₃), 1.20 (m, 8H, THF), 2.06 (s, 6H, CH₃), 3.46 (m, 8H, THF), 5.96 (d, ³J = 7.0 Hz, 2H, C₅H₃N-H³), 6.39 (d, ³J = 8.5 Hz, 2H, C₅H₃N-H⁵), 6.95 (dd, ³J = 8.2 Hz, ³J = 7.2 Hz, 2H, C₅H₃N-H⁴), 7.20–7.25 (m, 12H, Ph-CH^{meta}, Ph-CH^{para}), 7.82 (m, 8H, Ph-CH^{ortho}) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K, 100.63 MHz): δ = 1.2 (Si(CH₃)₃), 24.0 (CH₃), 25.0 (THF), 68.4 (THF), 106.9 (C₅H₃N-C³), 112.7 (C₅H₃N-C⁵), 127.7 (Ph-CH), 128.4 (Ph-CH), 134.9 (Ph-CH), 137.6 (C₅H₃N-C⁴), 141.5 (Ph-C), 154.3 (C₅H₃N-C²), 168.1 (C₅H₃N-C⁶) ppm. ²⁹Si{¹H} NMR (C₆D₆, 298 K, 79.51 MHz): δ = -20.7 ppm. C₄₆H₅₄N₄CaO₂Si₂ (791.20): calcd (%) C 69.83, H 6.88, N 7.08; found (%) C 69.70, H 6.69, N 6.97. IR: ν = 1957(w), 1260(s), 1093(m), 1020(m), 950(s), 798(m), 727(s), 585(s) cm⁻¹.

Synthesis of [(L¹)₃CaK]_∞ (8). A solution of **1** (0.50 g, 1.96 mmol) in THF (20 cm³) was added slowly to a suspension of CaI₂ (0.19 g, 0.65 mmol) in THF (10 cm³) at -78 °C; the reaction was warmed to room temperature and stirred overnight, whereupon a white precipitate was formed. The solvent was removed in vacuo, and the solid residue was washed with hexane (10 cm³) and extracted with diethyl ether. The ethereal solution was concentrated to ca. 2 cm³, and hexane (10 cm³) was added, causing the precipitation of a pale solid. The precipitate was filtered and dried in vacuo, affording **8** (141.0 mg, 0.23 mmol, yield 35%) as an off-white solid. Crystals of X-ray quality were grown from a saturated solution of **8** in benzene-d₆ at room temperature. ¹H NMR (C₆D₆, 298 K, 300.13 MHz): δ = 0.20 (s, 27H, Si(CH₃)₃), 1.93 (s, 9H, CH₃), 5.81 (d, ³J = 6.9 Hz, 3H, C₅H₃N-H³), 6.18 (d, ³J = 8.5 Hz, 3H, C₅H₃N-H⁵), 6.86 (dd, ³J = 8.4 Hz, ³J = 7.0 Hz, 3H, C₅H₃N-H⁴) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K, 100.63 MHz): δ = 1.8 (Si(CH₃)₃), 23.9 (CH₃), 106.0 (C₅H₃N-C³), 111.8 (C₅H₃N-C⁵), 138.0 (C₅H₃N-C⁴), 155.1 (C₅H₃N-C²), 170.3 (C₅H₃N-C⁶) ppm. ²⁹Si{¹H} NMR (C₆D₆, 298 K, 79.51 MHz): δ = -9.6 (Si(CH₃)₃) ppm. C₂₇H₄₅CaKN₆Si₃ (617.12): calcd (%) C 52.55, H 7.35, N 13.62; found (%) C 52.36, H 7.18, N 13.56. IR: ν = 2436(w), 1644(w), 1593(s), 1545(m), 1256(w), 1243(s), 1209(w), 1164(m), 1069(s), 1025(w), 992(m), 861(s), 830(m), 783(m), 758(w), 745(w), 713(w), 677(m), 618(m), 573(m), 541(m), 447(m) cm⁻¹.

Synthesis of [(L³)₃CaK]_∞ (9). A solution of **3** (0.80 mg, 2.53 mmol) in THF (30 cm³) was added slowly to a suspension of CaI₂ (0.25 g, 0.84 mmol) in THF (10 cm³) at -78 °C. The reaction was warmed to room temperature and stirred overnight, yielding a pale red precipitate with a yellow supernatant solution. The solvent was removed in vacuo, and the solid residue was washed with hexane (10 cm³) and extracted with diethyl ether. The ethereal solution was concentrated to ca. 2 cm³, and hexane (10 cm³) was added, causing the precipitation of a dark solid. The precipitate was filtered and dried in vacuo, affording **9** (152.2 mg, 0.19 mmol, yield 22%) as a brown solid. ¹H NMR (C₆D₆, 298 K, 300.13 MHz): δ = 0.31 (s, 27H, Si(CH₃)₃), 6.36 (d, ³J = 7.0 Hz, 3H, C₅H₃N-H³), 6.50 (d, ³J = 8.5 Hz, 3H, C₅H₃N-H⁵), 6.90 (broad, 9H, Ph-H^{9,9'} + Ph-H¹⁰), 7.09 (dd, ³J = 8.6 Hz, ³J = 7.0 Hz, 3H, C₅H₃N-H⁴), 7.55 (broad, 6H, Ph-H^{8,8'}) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K, 100.63 MHz): δ = 1.7 (Si(CH₃)₃), 105.2 (C₅H₃N-C³), 114.4 (C₅H₃N-C⁵), 127.2 (Ph-C^{8,8'}), 127.8 (Ph-C¹⁰), 128.6 (Ph-C^{9,9'}), 137.6 (C₅H₃N-C⁴), 142.2 (Ph-C⁷), 156.9 (C₅H₃N-C²), 171.0 (C₅H₃N-C⁶) ppm. ²⁹Si{¹H} NMR (C₆D₆, 298 K, 79.51 MHz): δ = -9.0 (Si(CH₃)₃) ppm. C₄₂H₅₁CaKN₆Si₃ (803.33): calcd (%) C 62.79, H 6.40, N 10.46; found (%) C 62.58, H 6.31, N 10.42. IR: ν = 1590(s), 1572(s), 1538(m), 1242(s), 1165(m), 1002(s), 845(s), 761(s), 704(m), 617(w) cm⁻¹.

Synthesis of (L¹)₂Mg (10). A solution of (tBu)₂Mg (1.00 g, 6.9 mmol) in hexane (6.5 cm³) was added to a solution of L¹H (1.51 g, 8.4 mmol) in hexane (20 cm³) at -78 °C; the reaction was warmed to room temperature and stirred overnight. The solvent was removed in vacuo, affording a viscous, pale yellow oil. The oil was dissolved in hexane, and a precipitate was formed overnight at -30 °C. The solid

was filtered and dried, affording **10** as a white solid (1.82 g, 4.7 mmol, yield 56%). ¹H NMR (C₆D₆, 298 K, 400.07 MHz): δ = 0.20 (s, 18H, Si(CH₃)₃), 2.09 (br s, 6H, CH₃), 5.94 (d, ³J = 7.2 Hz, 2H, C₅H₃N-H³), 6.33 (d, ³J = 8.5 Hz, 2H, C₅H₃N-H⁵), 6.96 (t, ³J = 8.3 Hz, 2H, C₅H₃N-H⁴) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K, 100.63 MHz): δ = 1.0 (Si(CH₃)₃), 23.1 (CH₃), 109.6 (C₅H₃N-C⁵), 139.6 (C₅H₃N-C⁴), 156.1 (C₅H₃N-C²) ppm; C₅H₃N-C³ and C₅H₃N-C⁶ not detected. ²⁹Si{¹H} NMR (C₆D₆, 298 K, 79.51 MHz): no peaks observed. C₁₈H₃₀N₄MgSi₂ (382.93): calcd (%) C 56.46, H 7.90, N 14.63; found (%) C 56.53, H 8.01, N 14.55. IR: ν = 1596(s), 1256(s), 1165(s), 1074(s), 1024(m), 999(m), 953(s), 866(s), 621(s), 593(m), 551(s), 454(m) cm⁻¹.

Synthesis of [(L¹)Li(μ₂-tBu)Mg(L¹)]_∞ (11). A solution of L¹H (1.00 g, 5.5 mmol) in hexane (8.0 cm³) was added dropwise to a mixture of tBuLi (4.0 mmol, 2 cm³) of a 2.5 M solution in hexanes) and (tBu)₂Mg (554.0 mg, 4.0 mmol) in hexane (20 cm³) at 0 °C. The reaction was warmed to room temperature and stirred for 72 h. During this time, a yellow precipitate was formed; the suspension was filtered, and the solid residue was dried in vacuo, affording **11** (475.0 mg, 1.1 mmol, yield 40%) as a yellow powder. Crystals of X-ray quality were grown from a saturated solution of **11** in hexane at -30 °C. ¹H NMR (C₆D₆/C₄D₈O, 298 K, 400.07 MHz): δ = -0.12 (m, 2H, butyl-CH₂), 0.32 and 0.39 (s, 18H, Si(CH₃)₃), 1.21 (t, ³J = 7.2 Hz, 3H, butyl-CH₃), 1.74 (m, 2H, butyl-CH₂), 2.02–2.15 (broad m, 8H, CH₃ + butyl-CH₂), 5.95 (d, ³J = 7.0 Hz, 1H, C₅H₃N-H³ - (L¹)Mg(tBu)), 6.03 (d, ³J = 6.9 Hz, 1H, C₅H₃N-H⁵ - (L¹)Li), 6.35 (d, ³J = 8.4 Hz, 2H, C₅H₃N-H⁴), 7.07 (t, ³J = 7.7 Hz, 2H, C₅H₃N-H⁴) ppm. ¹³C{¹H} NMR (C₆D₆/C₄D₈O, 298 K, 100.63 MHz): δ = 2.0 (Si(CH₃)₃), 2.5 (Si(CH₃)₃), 9.3 (butyl-CH₂), 15.0 (butyl-CH₃), 23.6 (CH₃), 32.8 (butyl-CH₂), 33.5 (butyl-CH₂), 107.1 (C₅H₃N-C⁵), 109.8 (C₅H₃N-C³), 112.4 (C₅H₃N-C³), 138.6 (C₅H₃N-C⁴), 139.4 (C₅H₃N-C⁴), 154.9 (C₅H₃N-C⁶), 155.2 (C₅H₃N-C⁶), 170.2 (C₅H₃N-C²) ppm. ²⁹Si{¹H} NMR (C₆D₆/C₄D₈O, 298 K, 79.51 MHz): no peaks observed. ⁷Li{¹H} NMR (C₆D₆/C₄D₈O, 298 K, 155.56): δ = 1.29 ((L¹)Li) ppm. C₂₂H₃₉LiMgN₄Si₂ (447.00): calcd (%) C 59.11, H 8.79, N 12.53; found (%) C 58.84, H 8.58, N 12.55. IR: ν = 3070(w), 3043(w), 2753(m), 2619(w), 1953(w), 1873(w), 1715(w), 1587(s), 1560(s), 1244(s), 1159(s), 1067(s), 1049(s), 1000(m), 981(w), 953(s), 854(m), 829(s), 788(m), 759(m), 741(m), 717(m), 685(m), 674(m), 625(s), 576(s), 552(s), 503(s), 461(m), 447(w) cm⁻¹.

Synthesis of (L²)₂Mg (5) via Direct Metalation. A solution of L²H (1.93 g, 6.3 mmol) in hexane (30 cm³) was added dropwise to a solution of (tBu)₂Mg (0.46 g, 3.2 mmol) in hexane (10 cm³) at -78 °C; the reaction was warmed to room temperature and stirred overnight. The solvent was removed in vacuo, and the white solid residue was recrystallized from hexane, affording **5** (785.0 mg, 1.2 mmol, yield 20%) as a white solid. Spectroscopic data were in agreement with data for the sample of **5** prepared via the metathesis route.

Synthesis of (L¹)₃MgLi(thf) (12). tBuLi (4.0 mmol, 2 cm³) of a 2.5 M in hexanes) was added via syringe to a solution of L¹H (1.20 g, 6.6 mmol) in THF (20 cm³) at 0 °C, immediately followed by addition of a solution of (tBu)₂Mg (554.0 mg, 4.0 mmol) in THF (10 cm³); the reaction was stirred at room temperature overnight. During this time, the colorless solution changed to a deep red color. The solvent was removed in vacuo, affording a brown oil, which was triturated with hexane, affording a yellow precipitate. The suspension was filtered, and the solid residue was dried in vacuo, affording **12** (751.2 mg, 1.2 mmol, yield 55%) as a red solid (chromatic change of the solid from yellow to deep red occurred after the compound was dried in vacuo for 12 h). Crystals of X-ray quality were grown from a saturated solution of **12** in hexane/THF at room temperature. ¹H NMR (C₆D₆/C₄D₈O, 298 K, 400.07 MHz): δ = 0.36 (broad, 27H, Si(CH₃)₃), 1.16 (m, 4H, THF-CH₂), 1.94 (broad 9H, CH₃), 3.29 (m, 4H, THF-OCH₂), 5.95 (d, ³J = 7.0 Hz, 3H, C₅H₃N-H³), 6.43 (d, ³J = 8.4 Hz, 3H, C₅H₃N-H⁵), 6.69 (m, 3H, C₅H₃N-H⁴) ppm. ¹³C{¹H} NMR (C₆D₆/C₄D₈O, 298 K, 100.63 MHz): δ = 2.2 (Si(CH₃)₃), 23.6 (CH₃), 31.1 (THF), 68.7 (THF), 108.7 (C₅H₃N-C⁵), 111.2 (C₅H₃N-C³), 139.3 (C₅H₃N-C⁴), 156.4 (C₅H₃N-C⁶), 170.4 (C₅H₃N-C²) ppm. ²⁹Si{¹H} NMR (C₆D₆/C₄D₈O, 298 K, 79.51 MHz): no peaks observed. ⁷Li{¹H} NMR (C₆D₆/C₄D₈O, 298 K, 155.56): δ = 1.40 ((L¹)Li) ppm. Elemental

microanalyses were performed on bulk sample, analyzed as $C_{31}H_{53}LiMgN_6OSi_3 \cdot 0.5C_4H_8O \cdot 12 \cdot (thf)_{0.5}$ (677.35): calcd (%) C 58.52, H 8.48, N 12.41; found (%) C 58.84, H 8.64, N 12.38. IR: $\nu = 2462(w), 2328(w), 2168(w), 1958(m), 1920(m), 1667(w), 1244(s), 1166(s), 1049(s), 996(m), 957(m), 824(broad\ s), 671(s), 619(m), 582(w), 550(m), 454(m)\ cm^{-1}$.

■ ASSOCIATED CONTENT

■ Supporting Information

Crystallographic data in CIF format for complexes **7**, **8**, **11**, and **12**. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

■ REFERENCES

- (1) (a) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J.; Yu, L.; Reiher, M. *Chem.—Eur. J.* **2007**, *13*, 6292. (b) Westerhausen, M. Z. *Anorg. Allg. Chem.* **2009**, 635, 13.
- (2) (a) Ruhlandt-Senge, K.; Torvisco, A.; O'Brien, A. Y. *Coord. Chem. Rev.* **2011**, *255*, 1268. (b) Ruhlandt-Senge, K.; Buchanan, W. D.; Allis, D. G. *Chem. Commun.* **2010**, 46, 4449.
- (3) Crimmin, M. R.; Barrett, A. G. M.; Hill, M. S.; Procopiou, P. A. *Proc. R. Soc. A* **2010**, 466, 927.
- (4) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 1950.
- (5) Jones, C.; Stasch, A.; Green, S. P. *Science* **2007**, *318*, 1754.
- (6) Yang, X.-J.; Liu, Y.; Li, S.; Yang, P.; Wu, B. *J. Am. Chem. Soc.* **2009**, *131*, 4210.
- (7) Harder, S.; Brettar, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 3474.
- (8) (a) Harder, S.; Spielmann, J. *Chem.—Eur. J.* **2007**, *13*, 8928. (b) Jones, C.; Bonyhady, S. J.; Green, S. P.; Nembenna, S.; Stasch, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2973. (c) Jones, C.; McDyre, L.; Murphy, D. M.; Stasch, A. *Chem. Commun.* **2010**, 46, 1511. (d) Jones, C.; Stasch, A. *Dalton Trans.* **2011**, 40, 5659.
- (9) Selected reviews on this topic: (a) Coles, M. P. *Dalton Trans.* **2006**, 985. (b) Junk, P. C.; Cole, M. L. *Chem. Commun.* **2007**, 1579. (c) Jones, C. *Coord. Chem. Rev.* **2010**, *254*, 1273.
- (10) (a) Kempe, R.; Noor, A.; Kretschmer, W. P.; Glatz, G. *Inorg. Chem.* **2011**, *40*, 4598. (b) Kempe, R. *Eur. J. Inorg. Chem.* **2003**, 791. (c) Kempe, R.; Deeken, S.; Motz, G. Z. *Anorg. Allg. Chem.* **2007**, 633, 320. (d) Kempe, R.; Qayyum, S.; Haberland, K.; Forsyth, C. M.; Junk, P. C.; Deacon, G. B. *Eur. J. Inorg. Chem.* **2008**, 557.
- (11) (a) Raston, C. L.; Junk, P. C.; Engelhardt, L. M.; Jacobsen, G. E.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1988**, 1011. (b) Raston, C. L.; Junk, P. C.; Engelhardt, L. M.; Jacobsen, G. E.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1990**, 89. (c) Aldridge, S.; Calder, R. J.; Coombs, D. L.; Jones, C.; Steed, J. W.; Coles, S.; Hursthouse, M. B. *New J. Chem.* **2002**, 26, 677. (d) Junk, P. C.; Cole, M. L. *Dalton Trans.* **2003**, 2109. (e) Kempe, R.; Scott, N. M.; Schareina, T. *Eur. J. Inorg. Chem.* **2004**, 3297.
- (12) (a) Lee, H. K.; Wong, Y.-L.; Zhou, Z.-Y.; Zhang, Z.-Y.; Ng, D. K. P.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **2000**, 539. (b) van den Ancker, T. R.; Engelhardt, L. M.; Henderson, M. J.; Jacobsen, G. E.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2004**, 689, 1991. (c) Kempe, R.; Noor, A.; Wagner, F. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 7246. (d) Kempe, R.; Noor, A.; Kretschmer, W. P.; Glatz, G. *Inorg. Chem.* **2011**, *50*, 4598.
- (13) (a) Lee, H. K.; Kui, S. C. F.; Li, H.-W. *Inorg. Chem.* **2003**, *42*, 2824. (b) Kempe, R.; Lyubov, D. M.; Döring, C.; Fukin, G. K.; Cherkasov, A. V.; Shavyrin, A. S.; Trifonov, A. A. *Organometallics* **2008**, *27*, 2905. (c) Pan, C. L.; Sheng, S.-D.; Wang, J.; Pan, Y.-S. *Mendelev Commun.* **2011**, *21*, 318. (d) Liddle, S. T.; King, D. M.; Lewis, W. *Inorg. Chim. Acta* **2012**, *380*, 167.
- (14) Mulvey, R. E.; Henderson, K. W.; Clegg, W.; O'Neil, P. A. *J. Organomet. Chem.* **1992**, 439, 237.
- (15) (a) Mulvey, R. E.; Henderson, K. W.; Clegg, W.; O'Neil, P. A. *Polyhedron* **1993**, *12*, 2535. (b) Mulvey, R. E.; Henderson, K. W.; Dorigo, A. E. *J. Organomet. Chem.* **1996**, *518*, 139.
- (16) Carpentier, J.-F.; Renaud, J.-L.; Zheng, Z.; Elmkaddem, M. K.; Fischmeister, C.; Roisnel, T.; Thomas, C. M. *New J. Chem.* **2008**, *32*, 2150.
- (17) Liu, D.-S.; Duan, X.-E.; Yuan, S.-F.; Tong, H.-B.; Bai, S.-D.; Wei, X.-H. *Dalton Trans.* **2012**, 41, 9460.
- (18) Jochmann, P.; Leich, V.; Spaniol, T. P.; Okuda, J. *Chem.—Eur. J.* **2011**, *17*, 12115.
- (19) Cameron, T. M.; Xu, C.; Dipasquale, A. G.; Rheingold, A. L. *Organometallics* **2008**, *27*, 1596.
- (20) Hill, M. S.; Barrett, A. G. M.; Crimmin, M. R.; Hitchcock, P. B.; Lomas, S. L.; Mahon, M. F.; Procopiou, P. A. *Dalton Trans.* **2010**, 39, 7393.
- (21) (a) Junk, P. C.; Boeré, R. T.; Cole, M. L. *New J. Chem.* **2005**, 29, 128. (b) Junk, P. C.; Cole, M. L. *New J. Chem.* **2005**, 29, 135.
- (22) Winter, C. H.; Sadique, A. R.; Heeg, M. J. *Inorg. Chem.* **2001**, *40*, 6349.
- (23) Arnold, J.; Schmidt, J. A. R. *J. Chem. Soc., Dalton Trans.* **2002**, 2890.
- (24) Winter, C. H.; Xia, A.; El-Kaderi, H. M.; Heeg, M. J. *J. Organomet. Chem.* **2003**, 682, 224.
- (25) Harder, S.; Feil, F. *Eur. J. Inorg. Chem.* **2005**, 4438.
- (26) Hill, M. S.; Crimmin, M. R.; Hitchcock, P. B.; Procopiou, P. A. *Dalton Trans.* **2008**, 4474.
- (27) Cheng, J. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2011**, *67*, m987.
- (28) Gibson, V. C.; Nimitsirawat, N.; Marshall, E. L.; Takolpuckdee, P.; Tomov, A. K.; White, A. J. P.; Williams, D. J.; Elsegood, M. R. J.; Dale, S. H. *Inorg. Chem.* **2007**, *46*, 9988.
- (29) Westerhausen, M.; Glock, C.; Görls, H. *Inorg. Chem.* **2009**, *48*, 394.
- (30) Westerhausen, M.; Al-Shboul, T. M. A.; Volland, G.; Görls, H. Z. *Anorg. Allg. Chem.* **2009**, 635, 1568.
- (31) Hill, M. S.; Lachs, J. R.; Barrett, A. G. M.; Crimmin, M. R.; Kociok-Köhn, G.; Mahon, M. F.; Procopiou, P. A. *Eur. J. Inorg. Chem.* **2008**, 4173.
- (32) Junk, P. C.; Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Konstas, K. *Dalton Trans.* **2006**, 3360.
- (33) Ruhlandt-Senge, K.; Zuniga, M. F.; Deacon, G. B. *Inorg. Chem.* **2008**, *47*, 4669.
- (34) (a) Westerhausen, M.; Glock, C.; Görls, H. *Dalton Trans.* **2011**, 40, 8108. (b) Hill, M. S.; Barrett, A. G. M.; Crimmin, M. R.; Hitchcock, P. B.; Kociok-Köhn, G.; Procopiou, P. A. *Inorg. Chem.* **2008**, *47*, 7366.
- (35) Roesky, P. W. *Inorg. Chem.* **2006**, *45*, 798.
- (36) Hanusa, T. P.; Quisenberry, K. T.; White, R. E.; Brennessel, W. W. *New J. Chem.* **2010**, *34*, 1579.
- (37) Ruhlandt-Senge, K.; Torvisco, A.; Decker, K.; Uhlig, F. *Inorg. Chem.* **2009**, *48*, 11459.
- (38) Zheng, W.; Pi, C.; Wan, L.; Gu, Y.; Wu, H.; Wang, C.; Weng, L.; Chen, Z.; Yang, X.; Wu, L. *Organometallics* **2009**, *28*, 5281.
- (39) (a) Mulvey, R. E.; Gallagher, D. J.; Henderson, K. W.; Kennedy, A. R.; O'Hara, C. T.; Rowlings, R. B. *Chem. Commun.* **2002**, 376. (b) Mulvey, R. E.; Hevia, E.; Kenley, F. R.; Kennedy, A. R.; Rowlings, R. B. *Eur. J. Inorg. Chem.* **2003**, 3347. (c) Mulvey, R. E.; Hevia, E.; Gallagher, D. J.; Kennedy, A. R.; O'Hara, C. T.; Talmard, C. *Chem. Commun.* **2004**, 2422. (d) Mulvey, R. E.; Andrikopoulos, P. C.; Armstrong, D. R.; Clegg, W.; Gilfillan, C. J.; Hevia, E.; Kennedy, A. R.; O'Hara, C. T.; Parkinson, J. A.; Tooke, D. M. *J. Am. Chem. Soc.* **2004**, *126*, 11612.
- (40) Ruhlandt-Senge, K.; Zuniga, M. F.; Kreutzer, J.; Teng, W. *Inorg. Chem.* **2007**, *46*, 10400.

- (41) (a) Power, P. P.; Hascall, T.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **1994**, 33, 356. (b) Mulvey, R. E.; Kennedy, A. R.; Robertson, S. D. *Dalton Trans.* **2010**, 39, 9091. (c) Winter, C. H.; El-Kaderi, H. M.; Xia, A.; Hegg, M. J. *Organometallics* **2004**, 23, 3488. (d) West-erhausen, M.; Koch, C.; Malassa, A.; Agthe, C.; Görls, H.; Bierdermann, R.; Krautscheid, H. *Z. Anorg. Allg. Chem.* **2007**, 633, 375. (e) Henderson, K. W.; Rood, J. A.; Noll, B. C. *Inorg. Chem.* **2007**, 46, 7259. (f) Winter, C. H.; Sedai, B.; Heef, M. J. *J. Organomet. Chem.* **2008**, 693, 3495. (g) Zheng, W.; Yang, D.; Ding, Y.; Wu, H. *Inorg. Chem.* **2011**, 50, 7698.
- (42) (a) Mulvey, R. E.; Hevia, E.; Kennedy, A. R.; Weatherstone, S. *Angew. Chem., Int. Ed.* **2004**, 43, 1709. (b) Mulvey, R. E.; Hevia, E.; Kennedy, A. R.; Andrikopoulos, P. C.; Armstrong, D. R.; O'Hara, C. T. *Chem. Commun.* **2005**, 1131. (c) Hill, M. S.; Barrett, A. G. M.; Casely, I. J.; Crimmin, M. R.; Lachs, J. R.; Mahon, M. F.; Procopiou, P. A. *Inorg. Chem.* **2009**, 48, 4445. (d) Jones, C.; Bonyhady, S. J.; Nembenna, S.; Stasch, A.; Edwards, A. J.; McIntyre, G. J. *Chem.—Eur. J.* **2010**, 16, 938. (e) Harder, S.; Spielmann, J.; Piesik, D. F. *Chem.—Eur. J.* **2010**, 16, 8307.
- (43) Barnett, N. D. R.; Clegg, W.; Kennedy, A. R.; Mulvey, R. E.; Weatherstone, S. *Chem. Commun.* **2005**, 375.
- (44) Mulvey, R. E.; Mongin, F.; Uchiyama, M.; Kondo, Y. *Angew. Chem., Int. Ed.* **2007**, 46, 3802.
- (45) Batsanov, S. S. *Inorg. Mater.* **2001**, 37, 871.
- (46) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, 15, 186.
- (47) Hsueh, M.-L.; Ko, B.-T.; Athar, T.; Lin, C.-C.; Wu, T.-M.; Hsu, S.-F. *Organometallics* **2006**, 25, 4144.
- (48) Kennedy, A. R.; O'Hara, C. T. *Dalton Trans.* **2008**, 4975.
- (49) Nichols, M. A.; Williard, P. C. *J. Am. Chem. Soc.* **1993**, 115, 1568.
- (50) Andrikopoulos, P. C.; Armstrong, D. R.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Rowlings, R. B.; Weatherstone, S. *Inorg. Chim. Acta* **2007**, 360, 1370.
- (51) Baldamus, J.; Cole, M. L.; Helmstedt, U.; Hey-Hawkins, E.-M.; Jones, C.; Junk, P. C.; Lange, F.; Smithies, N. A. *J. Organomet. Chem.* **2003**, 665, 33.
- (52) Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, B58, 380.
- (53) García-Álvarez, J.; Graham, D. V.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E. *Dalton Trans.* **2008**, 1481.
- (54) Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Rodger, P. J. A.; Rowlings, R. B. *J. Chem. Soc., Dalton Trans.* **2001**, 1477.
- (55) (a) Clegg, W.; Henderson, K. W.; Mulvey, R. E.; O'Neil, P. A. *J. Chem. Soc., Chem. Commun.* **1994**, 769. (b) Kennedy, A. R.; Mulvey, R. E.; Rowlings, R. B. *J. Am. Chem. Soc.* **1998**, 120, 7816.
- (56) Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, 19, 105.
- (57) Sheldrick, G. M. *SADABS, Program for Area Detector Absorption Correction*; Institute for Inorganic Chemistry, University of Göttingen: Göttingen, Germany, 1996.
- (58) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, 64, 112.
- (59) *CrysAlisPro*; Oxford Diffraction, Ltd., Agilent Technologies: Yarnton, U. K.