Synthesis and Reactivity of Alkali Metal Hydrido-Magnesiate Complexes which Exhibit Group 1 Metal Counter-Cation Specific Stability

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Abstract

Reactions of the series of alkali metal amides M(HMDS) (M = Li – Cs; HMDS = $[N(SiMe_3)_2]^-$) with the neutral magnesium(II) hydride compound $[Mg(BDI^{Dipp})(\mu\text{-}H)]_2$ (BDI^{Dipp} = $[CH\{C(Me)NDipp\}_2]^-$, Dipp = 2,6-^{i}Pr$_2$-C$_6$H$_3$) have been carried out. When M = Li or Na the reactions yielded $Mg(BDI^{Dipp})(HMDS)$ and MH as the primary products. In the sodium amide reaction $[Na_2(HMDS)][\{Mg(BDI^{Dipp})\}_2(H)_3]$ was obtained as a low-yield by-product. When M = K–Cs, the reactions gave the group 1 metal hydrido-magnesiates

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$M_2[Mg(BDI^{Dipp})(HMDS)(H)]_2\cdot(benzene)_n$ (n = 0 or 1), the thermal stability of which increases with increasing molecular weight of the alkali metal involved. Reactions of $Cs_2[Mg(BDI^{Dipp})(HMDS)(H)]_2\cdot(benzene)$ with 18-crown-6 and CO gave the first monomeric alkali metal hydrido-magnesiate $[Cs(18\text{-crown-6})][Mg(BDI^{Dipp})(HMDS)(H)]$ and the ethenediolate complex $Cs_2[\{Mg(BDI^{Dipp})(HMDS)\}_2(\mu\text{-}C_2H_2O_2)]$, respectively. The new synthetic route to alkali metal hydrido-magnesiates described herein may facilitate further reactivity studies of this rare compound class.

Keywords: magnesium, hydride, alkali metal, carbon monoxide, homologation

Introduction

Organoalkali reagents, which provide access to an array of reactive nucleophiles, are used extensively in academic chemical research and in industry.[1] Similarly, combinations of alkali metal cations with binary main-group (p-block) element hydride anions (e.g. $LiAlH_4$ and $NaBH_4$) can act as highly nucleophilic and bottleable mixed-metal hydride reagents.[2,3] Such group 1 metal/p-block hydride combinations have been widely applied in, for example, the reduction of unsaturated substrates including ketones, imines and azides.[4] Despite the popularity and widespread use of these reagents, examples of well-defined purely s-block metal hydride complexes are relatively rare. This is perhaps surprising, given that the s-block elements include some of the most abundant and environmentally benign metals, and as such are attractive for inclusion in reagents for the sustainable transformation of organic substrates. With that said, homometallic s-block metal hydride compounds have received increasing attention over the past few decades, as reagents for the stoichiometric and catalytic reduction of unsaturated organic substrates.[2,3] From group 2, magnesium(II) hydrides complexes such as $[Mg(BDI^{Dipp})(\mu\text{-}H)]_2$ ($BDI^{Dipp} = [CH\{C(Me)NDipp\}_2]^-$

, Dipp = 2,6-$^{i}Pr_2$-C_6H_3), have played a pivotal role.[5-18] In contrast, only a handful of well-defined heterobimetallic s-block magnesium(II) hydride systems have been reported, and their chemistry poorly investigated (Figure 1).

The first reports of structurally characterized mixed s-block magnesium(II) hydrides detailed the inverse crown complexes **I** (M = Na or K). These were prepared by Mulvey and co-workers from the reaction of *n*-butylsodium or benzylpotassium with *n*-,*sec*-dibutylmagnesium and diisopropylamine.[19-21] This work was extended by Hill and co-workers with the preparation of **II** by addition of phenylsilane to “K[Mg(HMDS)$_2$(Bu)]” (HMDS = $[N(SiMe_3)_2]^-$). Related reactions involving the lighter congeners “M[Mg(HMDS)$_2$(Bu)]” (M = Na or Li) led to the cluster compound $[Mg_6Na_6(HMDS)_8H_{10}]$, or an intractable mixture of products, respectively.[22] Independent reports by Guan[23] and Mulvey[24] indicated that complex **II** is a feasible intermediate in the catalytic hydrogenation of alkenes using Mg(HMDS)$_2$/KH/H_2 or K{Mg(HMDS)$_3$}/1,4-cyclohexadiene reagent mixtures. Hicks and co-workers later demonstrated that the reduction of Mg(NON^{Dipp}) (NON^{Dipp} = 4,5-bis(Dipp)-2,7-di-*tert*-butyl-9,9-dimethyl-xanthene) with potassium metal, or the addition of KH (excess) to Mg(NON^{Dipp}), in both cases provided K$_2$[Mg(NON^{Dipp})(H)]$_2$ (**III**) in moderate yields.[25] The analogous calcium hydride system, K$_2$[Ca(NON^{Dipp})(H)]$_2$, was also prepared using this approach. Both **III** and its calcium hydride analogue reduced CO to ethenediolate ($C_2H_2O_2^{2-}$), as has been previously shown to be possible using neutral and cationic magnesium and calcium hydride complexes.[14-16,25,26] Most recently, Hill and co-workers reported that the activation of H_2 by the dimagnesium(I) complex, [Na{(SiN^{Dipp})Mg}]$_2$ (SiN^{Dipp} = {CH_2SiMe_2N(Dipp)}$_2$), affords **IV** at 40 °C over 3 days. The hydrogenation reaction is complicated by accompanying decomposition processes.[27] Despite these advances, simple methods to readily access well-defined mixed s-block magnesium(II) metal hydride complexes remain limited.

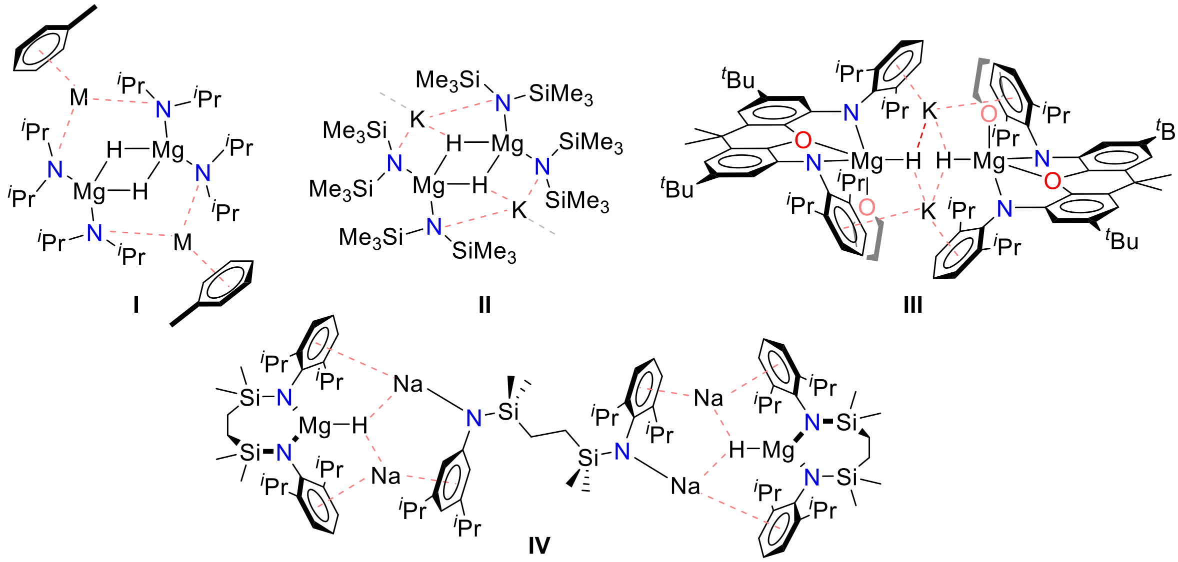


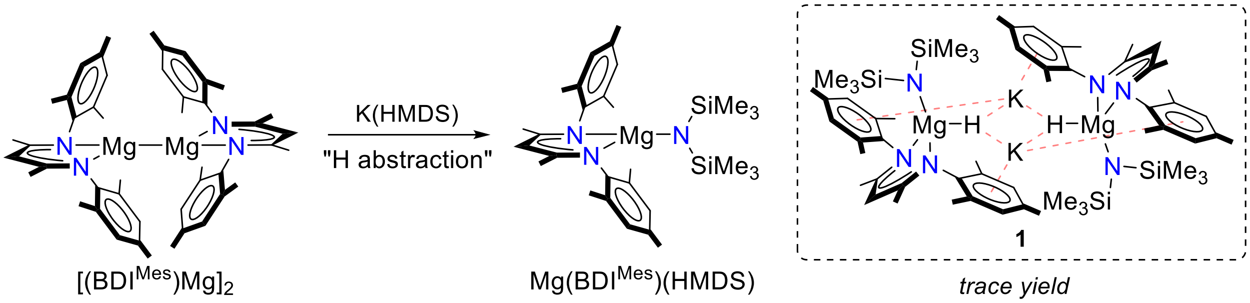
Figure 1: Selected examples of mixed s-block magnesium(II) hydride contact ion assemblies (**I**–**IV**, M = Na or K).

In this contribution, we extend the rich chemistry of neutral $[Mg(BDI^{Dipp})(\mu\text{-}H)]_2$ by exploring its reactions with the group 1 amide compounds, M(HMDS) (M = Li–Cs). Reactions with the heavier group 1 amides (M = K-Cs) gave the alkali metal magnesium hydride contact ion assemblies, $M_2[Mg(BDI^{Dipp})(HMDS)(H)]_2\cdot(benzene)_n$ (n = 0 or 1). Reactions with the lighter group 1 amides (M = Li or Na) likely proceed *via* analogous species, $M_2[Mg(BDI^{Dipp})(HMDS)(H)]_2$ (M = Li or Na), though these are unstable, decomposing to $(BDI^{Dipp})Mg(HMDS)$ and MH. Accordingly, it is shown that the thermal stability of the series $M_2[Mg(BDI^{Dipp})(HMDS)(H)]_2$ increases with the size of the alkali metal involved. Reactions of the most stable compound, $Cs_2[Mg(BDI^{Dipp})(HMDS)(H)]_2\cdot(benzene)$, with 18-crown-6 and CO lead to dimer dissociation and ethenediolate formation, respectively.

Results and Discussion

In previous work, our group has shown that coordination of neutral Lewis bases to dimagnesium(I) complexes induces elongation and polarization of the Mg–Mg bonds in the formed adducts, e.g. $(BDI^{Dipp})(DMAP)Mg$-$Mg(BDI^{Dipp})$ (DMAP = 4-dimethylaminopyridine).[5,28-31] This markedly increases the reactivity of the magnesium(I) complexes by enhancing the nucleophilic character of their 3-coordinate Mg center, thus allowing them to reductively activate normally inert molecules such as CO. In the current study, we initially explored similar reactivity with the anionic N-donor ligand $[N(SiMe_3)_2]^-$ in order to see if related activated anionic magnesium(I) compounds could be formed. To this end, the reaction between $[(BDI^{Mes})Mg]_2$ ($BDI^{Mes} = [CH\{C(Me)NMes\}_2]^-$, Mes = mesityl),[30,32] and K(HMDS) (1 equiv.) was carried out. However, the predominant product in the reaction mixture was shown by an ^1H NMR spectroscopic analysis to be the known magnesium(II) amide $Mg(BDI^{Mes})(HMDS)$ (Scheme 1).[33] A black precipitate also formed in the reaction (presumably elemental magnesium), thus indicating that the reaction proceeds *via* a disproportionation process. Repeating the reaction at low temperature (-80 °C) in toluene, or with different reactant stoichiometries, provided similar outcomes.

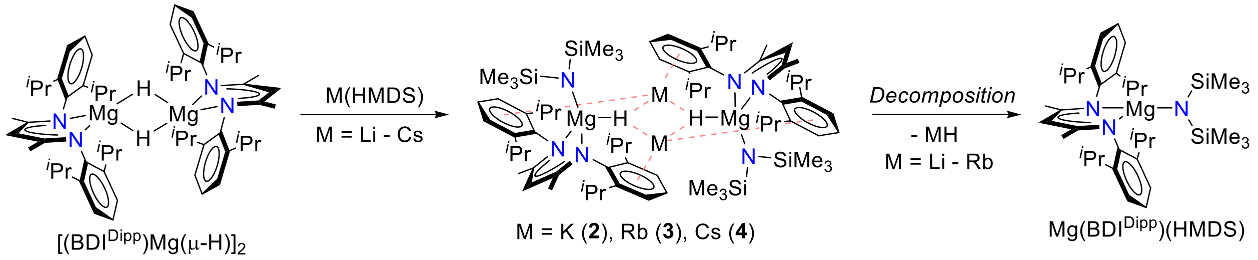
Upon work-up of the initial reaction mentioned above, a few colorless crystals of another product, **1**, were formed, presumably *via* hydrogen abstraction associated with the aforementioned disproportionation pathway (Scheme 1). Due to the very low yield of the compound, and the fact that **1** decomposes to $Mg(BDI^{Mes})(HMDS)$ in solution over *ca.* 10 minutes, no solution state spectroscopic data could be acquired. In the solid state, the crystal structure of **1** (see SI) shows it to be dimeric and essentially isostructural to several anionic magnesium hydride compounds described below. Consequently, no further discussion of its solid-state structure will be given here.



Scheme 1: Synthesis of Mg(BDI^{Mes})(HMDS) and **1**.

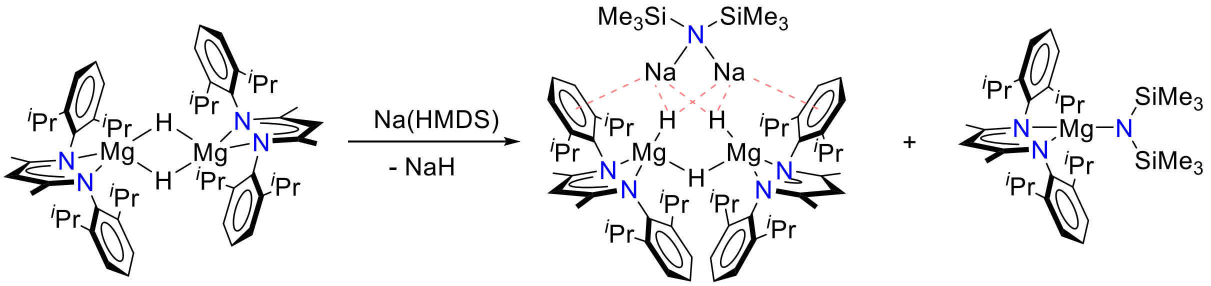
As **1** is a rare example of an anionic magnesium hydride, which are typically difficult to access, we sought to prepare a series of such compounds *via* a more rational and high yielding synthetic route. It seemed to us that reaction of known magnesium hydride compounds, [(BDI)Mg(μ-H)]$_2$, with alkali metal HMDS salts, *viz.* M(HMDS) (M = Li-Cs), might prove successful. However, given the fact that [(BDI^{Mes})Mg(μ-H)]$_n$ exists in solution as a mixture of oligomeric species,[34] the well-defined solution and solid-state dimer [(BDI^{Dipp})Mg(μ-H)]$_2$,[30] which incorporates a bulkier β-diketiminate ligand, was chosen as the magnesium hydride source in this study.

Addition of M(HMDS) (2 equiv., M = Li-Cs) to toluene solutions of [(BDI^{Dipp})Mg(μ-H)]$_2$ at –78 °C led to differing outcomes that were dependent on the alkali metal involved. The major product from reactions with Li(HMDS) and Na(HMDS) was the known magnesium amide, Mg(BDI^{Dipp})(HMDS) (Scheme 2).[35] The presumed by-products in these reactions are LiH and NaH respectively. In contrast, reactions employing the heavier amide salts, M(HMDS) (M = K-Cs), afforded moderate to good yields of the anticipated products **2-4** as colorless crystalline solids. Interestingly, **2** is unstable at room temperature, and decomposes in solution (over *ca.* 8 hours) or the solid-state (over *ca.* 5 days) to give Mg(BDI^{Dipp})(HMDS) and KH. The analogous rubidium salt **3** is more stable, but similarly decomposes to Mg(BDI^{Dipp})(HMDS) and RbH when solutions of the compound are left to stand for days at room temperature. Compound **4** is the most stable of the series, in that it is indefinitely stable at room temperature in the solid state, but will slowly decompose to Mg(BDI^{Dipp})(HMDS) and CsH when its solutions are heated at 80 °C overnight.



Scheme 2: Reactions of M(HMDS) with [(BDI^{Dipp})Mg(μ-H)]$_2$ to give compounds **2**-**4** and/or Mg(BDI^{Dipp})(HMDS). The depiction of the dimeric constructs for **2** and **4** are drawn as that observed in the solid-state for **3** for sake of simplicity.

It seems very likely that the reactions of Li(HMDS) and Na(HMDS) with [(BDI^{Dipp})Mg(μ-H)]$_2$ proceed *via* Li and Na analogues of **2**-**4**, but these intermediates are too short-lived to be observed spectroscopically, and readily decompose to Mg(BDI^{Dipp})(HMDS). Some evidence for this proposal comes from the fact that the reaction involving Na(HMDS) gave a low isolated yield of the mixed metal hydride "cluster" compound **5** as a colorless crystalline solid, in addition to Mg(BDI^{Dipp})(HMDS) (Scheme 3). It can be envisaged that **5** forms by complexation of [(BDI^{Dipp})Mg(μ-H)]$_2$ with a mixture of Na(HMDS) and NaH, where the latter is generated by decomposition of the suspected intermediate Na$_2$[Mg(BDI^{Dipp})(HMDS)(H)]$_2$. It is evident from this work that there is a clear increase in stability of the magnesium hydride complexes, M$_2$[Mg(BDI^{Dipp})(HMDS)(H)]$_2$ (M = Li-Cs), with increasing molecular weight of the alkali metal counter-cation. This is possibly due to the increasing areneophilicity of the alkali metal cations down group 1, which leads to a greater stabilizing effect of the intramolecular M···arene interactions in the compound series.



5 (*minor*) (*major*)

Scheme 3: Reaction of Na(HMDS) with $[(BDI^{Dipp})Mg(\mu\text{-}H)]_2$ yielding $Mg(BDI^{Dipp})(HMDS)$ and mixed metal hydride "cluster" **5**.

The ^1H NMR spectra of the compound series **2-4** are broadly consistent with their proposed structures. Of most note from these spectra is the trend towards lower field chemical shifts for the Mg-*H* fragments with increasing size of the group 1 cation, *viz.* (**2** δ_H 3.23, **3** δ_H 3.63, **4** δ_H 4.50 ppm; *cf.* δ_H 4.03 ppm for $[(BDI^{Dipp})Mg(\mu\text{-}H)]_2$[30]). However, all of these signals lie in the normal range for magnesium hydride compounds.[18] The observed trend does suggest that the alkali metal cations, all of which hydride bridge to Mg centers, directly influence the chemical environment of the hydride ligands. It cannot be certain what the origin of this cation influence is, but it is known that hydride resonance de-shielding increases with increasing molecular weight of metal hydrides, including those of the s- and p-block. This has been ascribed to Heavy Atom Light Atom Spin-Orbit coupling effects (HALA-SO).[36] In the solid-state, no Mg-H stretching bands could be confidently identified in the FTIR spectra of **2-5**. This is not surprising as it is well established that such stretching bands associated with Mg-H-M fragments occur in the fingerprint region of IR spectra and are difficult to deconvolute from complex ligand absorptions in that region.[33]

The X-ray crystal structures of **2**, **3** and **4**·(benzene) were determined, and their molecular structures are depicted in Figure 2. As far as we are aware, compound **4**·(benzene) represents the first crystallographically characterized cesium/magnesium hydride complex.[37] Compounds **2** and **3** are centrosymmetric dimers while two crystallographically independent dimers lie in the asymmetric unit of the crystal structure of **4**·(benzene). The Mg centers in each system are four coordinate and display distorted tetrahedral geometries, with each $[(BDI^{Dipp})(HMDS)Mg(H)]^-$ unit linked by M···H and M···π(Dipp) interactions that vary with the size of the group 1 cation. For **2** and **3**, the coordination sphere of the alkali metal cations are completed by two M···H and one or two flanking M···π(Dipp) contacts (K-centroid: 2.8757(11) Å, Rb-centroid: 3.1456(10) and 3.5161(9) Å), respectively. In contrast, the Cs cations in **4**·(benzene) adopt different coordination environments that cause asymmetry within the dimeric framework. Atom Cs(1) is bound by two flanking Cs···π(Dipp) (Cs-centroid: 3.2569(13) and 3.4093(14) Å) and two Cs···H interactions, while Cs(2) is capped by a benzene molecule (Cs···π(C_6H_6) centroid: 3.338(2) Å) that results in only one Cs···π(Dipp) (Cs-centroid: 3.3432(13) Å) and one Cs···H interaction in this case. These structures are quite similar to those of **III**[25] and **IV**,[27] where there are also considerable separations of the Mg–H units due to the influence of the group 1 cation.

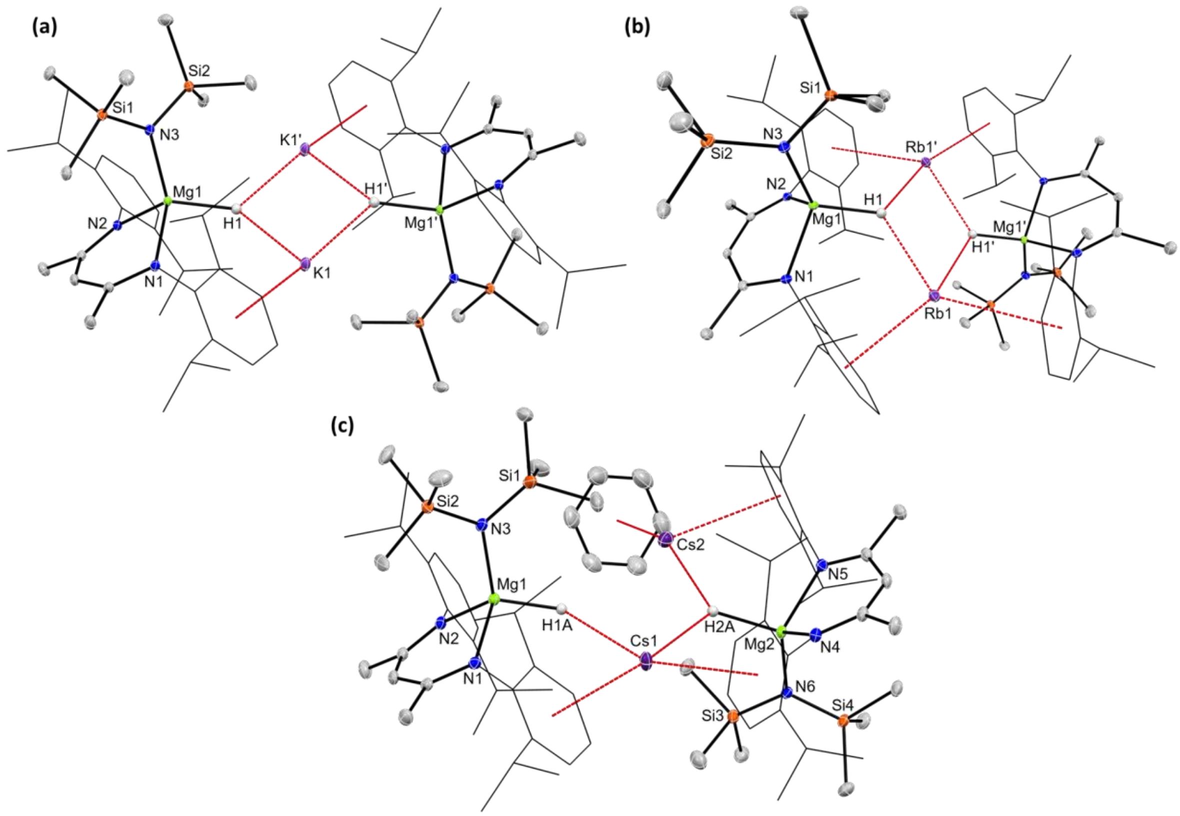


Figure 2: Molecular structures of (a) **2**, (b) **3** and (c) **4**·(benzene). Thermal ellipsoids shown at 20% probability; hydrogen atoms, except hydrides, omitted; Dipp groups shown as wireframe for clarity). Selected bond lengths (Å) and angles (°): (**2**) Mg1–H1 1.957(17), K1···H1 2.704(17), K1···H1' 2.669(18), K1-H1-K1' 90.5(4), H1-K1-H1' 89.1(4); (**3**) Mg1–H1 1.907(18), Rb1···H1 2.87(2), Rb1···H1' 2.787(15), Rb1-H1-Rb1' 107.7(6), H1-Rb1-H1' 75.5(6); (**4**·(benzene)) Mg1–H1A 1.86(3), Mg2–H2A 1.89(4), Cs1···H1A 3.04(3), Cs1···H2A 2.97(4), Cs2···H2A 2.99(4).

The molecular structure of **5** is shown in Figure 3. The compound is monomeric with each Mg center adopting a distorted tetrahedral geometry, supported by the BDI$^{\mathrm{Dipp}}$ ligand and two hydride ligands. While one hydride bridges two Mg centers (giving an Mg–H–Mg fragment), the remaining two hydrides form a heterometallic bridge between the Mg and Na atoms (giving Mg–

H···Na fragments). Both of the Na centers additionally have η^6-interactions with BDI^{Dipp} aryl groups, and are bridged by a $N(SiMe_3)_2$ unit.

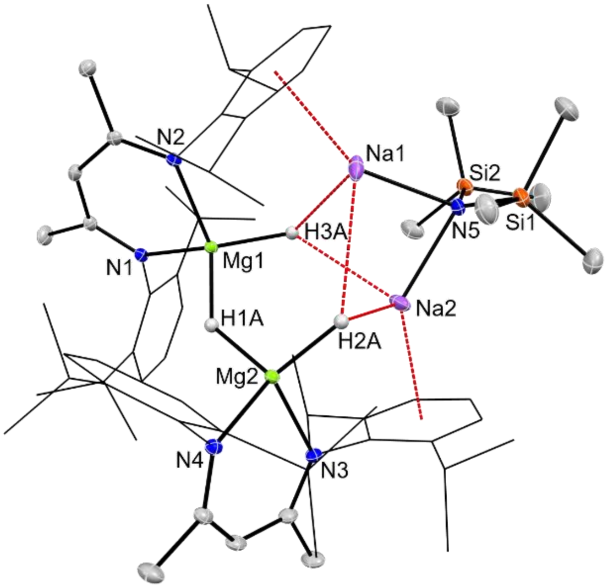
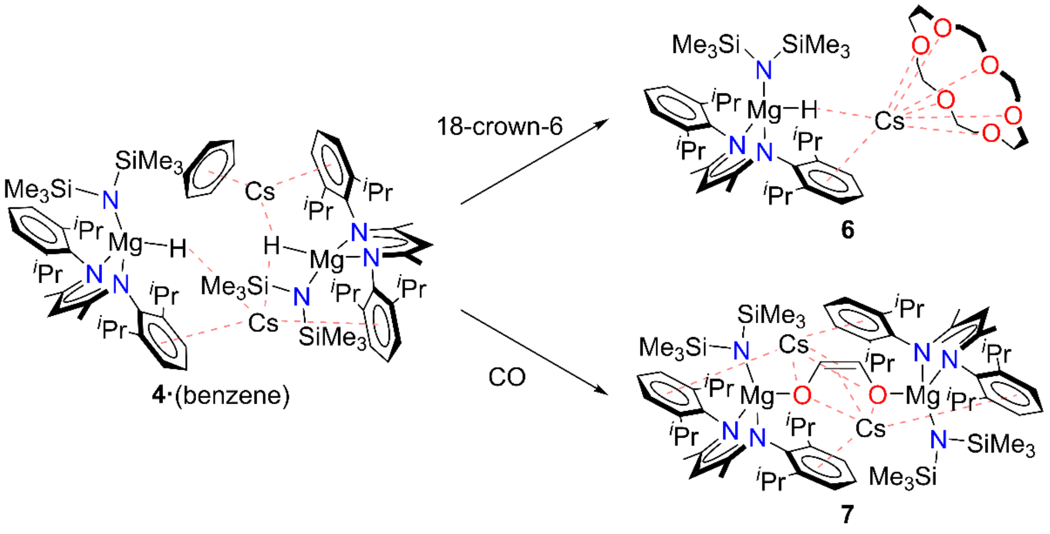


Figure 3: Molecular structure of **5**. Thermal ellipsoids shown at 20% probability; hydrogen atoms, except hydrides, omitted; Dipp groups shown as wireframe for clarity. Selected bond lengths (Å) and angles (°): Mg1–H1A 1.87(4), Mg1–H3A 1.79(2), Mg2–H1A 1.78(4), Mg2–H2A 1.74(2), Na1···H2A 3.24(3), Na1···H3A 2.24(2), Na2···H2A 2.22(3), Na2···H3A 2.79(3), Na1-N5 2.348(2), Na2-N5 2.351(2), Mg1-H1-Mg2 137.1(2), Na1-N5-Na2 81.07(5).

Studies involving the reactivity of alkali metal salts of anionic magnesium hydride complexes are rare, especially when the heavier alkali metals are involved. In the current study, all but the cesium salt **4**·(benzene) showed significant degrees of decomposition to Mg(BDI^{Dipp})(HMDS) in solution, which was more prominent for the lighter alkali metal salts. This has impeded examinations of the further reactivity of those compounds. However, given the relative stability of **4**·(benzene), preliminary reactivity studies were undertaken. In the first instance, and in an attempt to dismantle the dimeric structure of **4**·(benzene), the isolated or *in situ* generated compound was treated with two equivalents of 18-crown-6 which led to good yields (up to 63%) of the monomeric contact ion pair compound **6** as a colorless crystalline solid after reaction work-up (Scheme 4). This compound is the first example of a monomeric alkali metal-hydridomagnesiate complex to be reported. In solution, the ^{1}H NMR spectrum of **6** shows a Mg–*H* resonance at δ_H 4.69 ppm, which is only slightly down-field from that observed for **4**·(benzene) (δ_H 4.50 ppm). As expected, the chemical environments of the BDI$^{\mathrm{Dipp}}$ and HMDS ligands have also been affected by the change in structure, with an additional signal at δ_H 3.04 corresponding to the coordinated 18-crown-6 molecule. The ^{133}Cs NMR spectrum of **6** exhibits a broad resonance at δ_{Cs} 25.8 ppm, which is downfield from the equivalent resonance in the spectrum of **4**·(benzene), δ_{Cs} 7.2 ppm.



Scheme 4: Synthesis of compounds **6** and **7**.

In recent years, neutral, anionic and cationic magnesium hydride complexes have been shown to effect the reductive dimerisation, trimerization and catalytic transformation of the normally inert diatomic molecule, CO, under mild reaction conditions.[14-16,25,26] In order to explore if similar chemistry is accessible with **4**·(benzene), a benzene solution of the compound was placed under an atmosphere of CO (*ca.* 1 bar) at room temperature. A reaction occurred over 18 hours, yielding the ethenediolate complex **7** as pale-yellow crystals after reaction work-up (11% yield). Although it could not be determined what the other products of this reaction are, the formation of **7** is reproducible. This reaction is closely related to several prior magnesium hydride induced transformations of CO to ethenediolate, the first of which was reported by our group in 2015.[16] In solution, the ^{1}H and ^{13}C NMR spectra of **7** exhibit broad resonances for the $C_2H_2O_2^{2-}$ fragment at δ_H 5.07 and δ_C 129.7 ppm, respectively. In contrast, the resonances for the BDI^{Dipp} and HMDS ligands remain well-resolved. Samples of **7** decompose in solution (over several hours) and the solid-state (over several days) to give largely intractable mixtures of products, which include significant amounts of hexamethyldisilazane (HMDSH). The instability of **7** frustrated an examination of its reactivity with, for example, electrophiles.

Both **6** and **7** were crystallographically characterized, and their molecular structures can be found in Figure 4. That for **6** confirms its monomeric nature and shows it to possess a distorted tetrahedral Mg center which bridges to a cesium atom through H1. The cesium atom is η^6-coordinated by a Dipp group, while being κ^6-ligated by an 18-crown-6 unit. Both the Mg-H and Cs···H distances are in the reported ranges for such interactions.[37] Compound **6** is dinuclear and contains two Cs cations which are η^4-coordinated to a bridging $C_2H_2O_2^{2-}$ fragment, while being additionally η^6-ligated by two Dipp groups. Each Mg(BDI^{Dipp})(HMDS) unit coordinates to a terminal oxygen atom of the $C_2H_2O_2^{2-}$ ligand, which renders a distorted tetrahedral geometry for the Mg atoms. The mode of coordination to the $C_2H_2O_2^{2-}$ fragment and its bonding metrics are indicative of an electronically delocalized unit, and are closely comparable to those of a potassium-magnesium ethenediolate complex (C–O: 1.366(8) Å, C–C: 1.349(11) Å)[25] recently reported by Hicks and co-workers.

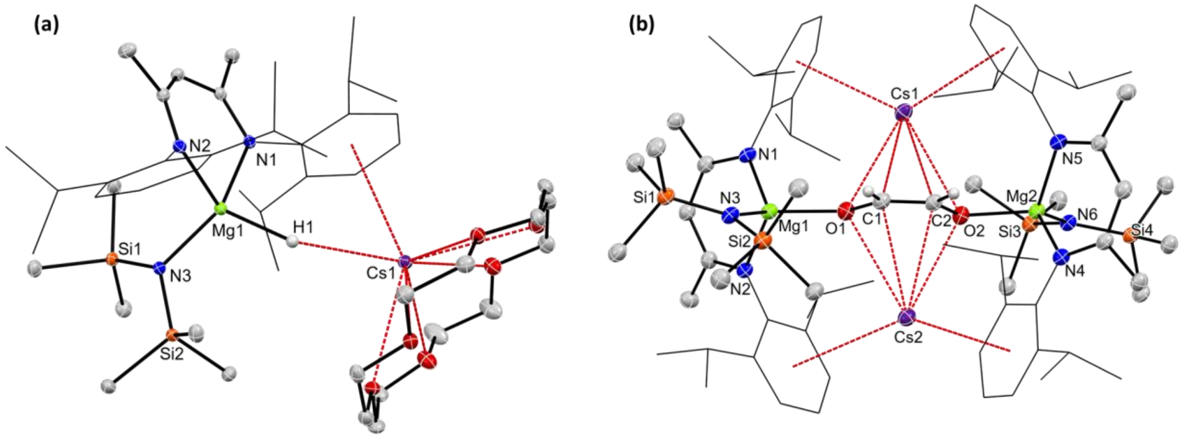


Figure 4: Molecular structures of (a) **6** and (b) **7**. Thermal ellipsoids shown at 20% probability; hydrogen atoms, except hydrides, omitted; Dipp groups shown as wireframe for clarity. Selected bond lengths (Å) and angles (°): (**6**) Mg1–H1 1.889(16), Cs1···H1 3.150(16), Mg1-N3 2.075(2), Mg1-H1-Cs1 132.3 (4); (**7**) Mg1–O1 1.980(4), Mg2–O2 1.976(4), O1–C1 1.356(7), C1–C2 1.345(8), C2–O2 1.352(6), Cs1-O1 3.167(4), Cs1-O2 3.179(4), Cs2-O1 3.177(4), Cs2-O2 3.010(4).

Conclusions

In summary, we have described reactions of the complete series of non-radioactive group 1 amide complexes M(HMDS) (M = Li – Cs) with $[Mg(BDI^{Dipp})(\mu\text{-}H)]_2$. Those where M = Li or Na are thought to proceed *via* alkali metal hydrido-magnesiate compounds, $M_2[Mg(BDI^{Dipp})(HMDS)(H)]_2$, which cannot be isolated, and decompose to $Mg(BDI^{Dipp})(HMDS)$ and group 1 metal hydrides, MH. A low yield of the trimetallic mixed metal hydride “cluster” $[Na_2(HMDS)][\{Mg(BDI^{Dipp})\}_2(H)_3]$ **5** was additionally isolated from the reaction involving Na(HMDS). Reactions involving the heavier group 1 amides all led to the alkali metal magnesiates,

$M_2[Mg(BDI^{Dipp})(HMDS)(H)]_2$·(benzene)$_n$ (n = 0, M = K **2**, Rb **3** or n = 1, Cs **4**·(benzene)), the thermal stability of which increases with the molecular weight of the alkali metal cation. These complexes were spectroscopically and crystallographically characterized, though the thermal instability of **2** and **3** plagued attempts to obtain analytically pure solids in those cases. Compound **4**·(benzene) represents the first structurally characterized cesium hydrido-magnesiate. Reactions of **4**·(benzene) with 18-crown-6 and CO yielded the first monomeric alkali metal hydrido-magnesiate [Cs(18-crown-6)][$Mg(BDI^{Dipp})(HMDS)(H)$] **6** and the ethenediolate complex $Cs_2[\{Mg(BDI^{Dipp})(HMDS)\}_2(C_2H_2O_2)]$ **7**, respectively. This study has provided a new synthetic route to alkali metal hydrido-magnesiates, which has the potential to facilitate further reactivity studies on this rare compound class.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Hexane, benzene and toluene were distilled over molten potassium. ^{1}H, $^{13}C\{^{1}H\}$ and ^{133}Cs NMR spectra were recorded on either Bruker DPX300, Bruker AvanceIII 600 or Bruker AvanceIII 400 spectrometers and were referenced to the resonances of the solvent used or external 0.1 M $CsNO_3$ in D_2O. FTIR spectra were collected for solid samples as Nujol mulls on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Microanalyses were carried out at by the Elemental Analysis Service at London Metropolitan University. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. M(HMDS) (M = Li, Na, K and Cs[38]), $[(BDI^{Mes})Mg]_2$[32] and $[(BDI^{Dipp})Mg(\mu\text{-}H)]_2$[30] were prepared according to literature procedures. $[Mg(BDI^{Dipp})(HMDS)]$[35]

was identified by its characteristic NMR spectrum. Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used as received.

Synthesis of Rb(HMDS). In an adaption to the literature procedure,[38] a 1.6 M solution of *n*-butyllithium (14.95 mL, 24 mmol) in hexane was added to bis(trimethylsilyl)amine (5.01 mL, 24 mmol) in hexane and allowed to stir for 2 hours. Rubidium fluoride was added *via* a solid addition Schlenk and the resulting mixture heated at reflux for 16 hours. Volatiles were removed *in vacuo* and the residue extracted in toluene (60 mL), then filtered *via* cannula. The extract was dried *in vacuo* to give the product as a white powder that was used without further purification. NMR data match those reported in the literature.[39] Yield 4.00 g, 68 %.

Synthesis of $K_2[Mg(BDI^{Mes})(HMDS)(H)]_2$ 1. A solution of K(HMDS) (42 mg, 0.21 mmol) and $[(BDI^{Mes})Mg]_2$ (150 mg, 0.21 mmol) in C_6D_6 (*ca.* 1 mL) was prepared and transferred to a J. Youngs fitted NMR tube. The resulting red/black suspension was allowed to stand at room temperature for 30 minutes affording colorless crystals. Yield 12 mg (mixture with $Mg(BDI^{Mes})(HMDS)$). The thermal instability of the sample in solution and the solid-state prevented the acquisition of any meaningful spectroscopic data. The bulk sample contained $Mg(BDI^{Mes})(HMDS)$ as the primary decomposition product.

Synthesis of $K_2[Mg(BDI^{Dipp})(HMDS)(H)]_2$ 2. A solution of K(HMDS) (36 mg, 0.18 mmol) in toluene (*ca.* 2 mL) was added to a solution of $[(BDI^{Dipp})Mg(\mu\text{-}H)]_2$ (80 mg, 0.09 mmol) in toluene (*ca.* 2 mL) at –78 °C. The solution was reduced to *ca.* 1 mL *in vacuo* and stored at –30 °C overnight to give colorless crystals of **2.** The mother liquor was decanted and the crystals dried *in vacuo*.

Yield 60 mg, 52 %. M.p. 184–186 °C (dec). ^{1}H NMR (400 MHz, C_6D_6) δ 0.07 (br s, 18H, Si(C*H*$_3$)$_2$), 0.54 (br s, 18H, Si(C*H*$_3$)$_2$), 1.12 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.18 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.32 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.50 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.62 (s, 12H, NCC*H*$_3$), 3.23 (s, 2H, Mg*H*), 3.37 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 4.04 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 4.98 (s, 2H, NCC*H*), 6.96 – 6.87 (m, 8H, Ar-*H*), 7.06 (d, *J* = 7.2 Hz, 4H, Ar-*H*). I.R. (v/cm^{-1}, Nujol): 746 (s), 792 (m), 819 (s), 840 (m), 888 (m), 926 (m), 999 (s), 1109 (w), 1171 (m), 1508 (m), 1552 (w). The poor solubility of the product in aliphatic and aromatic solvents, along with its decomposition in solution and the solid-state at room temperature to Mg(BDI$^{\mathrm{Dipp}}$)(HMDS), prevented full spectroscopic characterisation and the acquisition of a reliable elemental analysis.

Synthesis of Rb$_2$[Mg(BDI$^{\mathrm{Dipp}}$)(HMDS)(H)]$_2$ 3. A solution of Rb(HMDS) (100 mg, 0.41 mmol) in toluene (*ca.* 2 mL) was added to a solution of [Mg(BDI$^{\mathrm{Dipp}}$)(μ-H)]$_2$ (180 mg, 0.21 mmol) in toluene (*ca.* 2 mL) at –78 °C. The reaction mixture was reduced in volume to *ca.* 1 mL, and the resultant solution stored at –30 °C overnight to give colorless crystals. The mother liquor was decanted and the crystals dried *in vacuo*. Yield 102 mg (mixture with Mg(BDI$^{\mathrm{Mes}}$)(HMDS)). M.p. 173–175 °C (dec). ^{1}H NMR (400 MHz, C_6D_6) δ 0.21 (s, 36H, Si(C*H*$_3$)$_2$), 1.09 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.19 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.35 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.49 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.59 (s, 12H, NCC*H*$_3$), 3.33 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 3.63 (s, 2H, Mg*H*), 4.06 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 4.97 (s, 2H, NCC*H*), 6.98 (d, *J* = 4.6 Hz, 8H, Ar-*H*), 7.10 – 7.15 (m, 4H, Ar-*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 6.6 (Si(C*H*$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 25.3 (NC*C*H$_3$), 25.4, 25.4, 27.0 (CH(*C*H$_3$)$_2$), 27.5, 27.7 (*C*H(CH$_3$)$_2$), 98.0 (NC*C*H), 123.9, 124.3, 124.6, 143.5, 149.5 (Ar-*C*), 167.5 (N*C*); ^{29}Si NMR (80 MHz, C_6D_6) δ -11.0

(*Si*(CH_3)$_2$); I.R. (ν/cm^{-1}, Nujol): 695 (w), 751 (m), 792 (m), 817 (m), 840 (m), 882 (m), 925 (m), 997 (s), 1015 (w), 1168 (m), 1506 (m), 1551 (w). Slow decomposition of the compound in the solid-state at room temperature to Mg(BDI^{Dipp})(HMDS), prevented the acquisition of a reliable elemental analysis.

Synthesis of Cs_2[Mg(BDI^{Dipp})(HMDS)(H)]$_2$·(benzene) 4·(benzene). A solution of Cs(HMDS) (33 mg, 0.11 mmol) in benzene (*ca.* 0.5 mL) was added to a J. Youngs fitted NMR tube containing [Mg(BDI^{Dipp})(μ-H)]$_2$ (50 mg, 0.05 mmol) at room temperature. The mixture was allowed to stand for *ca.* 30 minutes, during which time colorless crystals deposited. The mother liquor was then decanted and the crystals dried *in vacuo*. Yield 30 mg, 36%. M.p. 194–196 °C (dec). Anal. calcd. for $C_{70}H_{120}Cs_2Mg_2N_6Si_4$ (1472.53): C, 57.10; H, 8.21; N, 5.71 %. found: C, 56.79; H, 8.20; N, 5.43 %. The microanalysis results indicate loss of benzene of solvation and coordination upon drying the crystalline material under vacuum. ^{1}H NMR (400 MHz, C_6D_6) δ 0.18 (br s, 18H, Si(C*H*$_3$)$_3$), 0.62 (br s, 18H, Si(C*H*$_3$)$_3$), 1.13 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.23 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.37 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.51 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.62 (s, 12H, NCC*H*$_3$), 3.40 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 4.10 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 4.50 (s, 2H, Mg*H*), 4.99 (s, 2H, NCC*H*), 7.00 – 6.92 (m, 8H, Ar-*H*), 7.14 – 7.10 (m, 4H, Ar-*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 7.0, 8.6 (br, Si(*C*H$_3$)$_3$), 24.4 (CH(*C*H$_3$)$_2$), 25.2 (NC*C*H$_3$), 25.4, 25.4, 26.9 (CH(*C*H$_3$)$_2$), 27.6, 27.8 (*C*H(CH$_3$)$_2$). 97.9 (NC*C*H), 124.0, 124.3, 124.5, 128.6, 143.7, 145.0, 150.1 (Ar-*C*), 167.4 (N*C*); ^{29}Si NMR (79 MHz, C_6D_6) δ -10.9 (*Si*(CH$_3$)$_3$); ^{133}Cs NMR (52 MHz, C_6D_6) δ 7.2; I.R. (cm^{-1}, Nujol): 753 (m), 795 (m), 818 (m), 838 (m), 882 (m), 923 (m), 994 (s), 1059 (w), 1113 (w), 1 1513 (m), 1542 (m), 1625 (w).

Synthesis of [Na_2(HMDS)][{Mg(BDI^{Dipp})}$_2$(H)$_3$] 5. A solution of Na(HMDS) (41 mg, 0.22 mmol) in toluene (*ca*. 2 mL) was added to a solution of [Mg(BDI^{Dipp})(μ-H)]$_2$ (100 mg, 0.11 mmol) in toluene (*ca*. 2 mL) at –78 °C. The reaction mixture was reduced in volume to *ca*. 1 mL, and the resultant solution stored at –30 °C overnight to give colorless crystals. The mother liquor was decanted and the crystals dried *in vacuo*. Yield 45 mg (mixture with Mg(BDI^{Dipp})(HMDS)). M.p. 218 – 220 °C (dec). ^{1}H NMR (400 MHz, C_6D_6) δ 0.13 (s, 18H, Si(C*H*$_3$)$_3$), 0.44 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.94 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.06 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.21 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.35 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.36 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.40 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.58 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.59 (s, 6H, NCC*H*$_3$), 1.61 (s, 6H , NCC*H*$_3$), 2.78 – 2.98 (m, 5H, C*H*(CH$_3$)$_2$, Mg*H*), 3.25 (sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.33 (sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.55 (sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 4.79 (s, 2H, NCC*H*), 6.84 – 6.98 (m, 4H, Ar-*H*), 7.08 – 7.15 (m, 8H, Ar-*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 6.8 (Si(*C*H$_3$)$_3$), 24.0, 24.2, 24.3, 24.3, 24.4, 24.5, 24.6, 25.1, 25.2, 26.7 (CH(*C*H$_3$)$_2$, NC*C*H$_3$), 27.5, 28.3, 28.4, 28.7 (*C*H(CH$_3$)$_2$), 95.1 (NC*C*H), 124.0, 124.2, 124.5, 124.6, 125.4, 125.7, 142.8, 143.7, 144.2, 144.8, 146.2, 147.9 (Ar-*C*), 166.6, 168.5 (N*C*); ^{29}Si NMR (79 MHz, C_6D_6) δ -14.0 (*Si*(CH$_3$)$_3$); I.R. (ν/cm^{-1}, Nujol): 731 (m), 754 (m), 795 (s), 815 (s), 883 (m), 930 (m), 1015 (s), 1035 (m), 1100 (m), 1175 (m),1518 (m), 1542 (m). Decomposition of the compound in solution and the solid-state at room temperature to Mg(BDI^{Dipp})(HMDS) prevented the acquisition of a reliable elemental analysis.

Synthesis of [Cs(18-crown-6)][Mg(BDI^{Dipp})(HMDS)(H)] 6. *Method 1:* A benzene-*d*$_6$ solution of 18-crown-6 (18 mg, 0.07 mmol) was added to a J Youngs NMR tube containing compound **4**·(benzene) (50 mg, 0.03 mmol) at room temperature. The mixture was agitated to afford a pale yellow solution. The solution was allowed to stand for *ca.* 24 hours to give colorless crystals. The mother liquor was decanted and the crystals dried *in vacuo*. Yield 12 mg, 17 %. *Method 2*: [Mg(BDI^{Dipp})(μ-H)]$_2$ (410 mg, 0.46 mmol), Cs(HMDS) (271 mg, 0.92 mmol) and 18-crown-6 (294 mg, 0.92 mmol) were dissolved in toluene (*ca.* 3 mL), and the reaction mixture agitated to give a homogenous solution. This was stored at –30 °C for 18 hours to give colorless crystals of the title compound Yield 610 mg, 63 %. Anal. calcd. for $C_{47}H_{84}CsMgN_3O_6Si_2$ (1000.58): C, 56.42; H, 8.46; N, 4.20 %. found: C, 56.34; H, 8.43; N, 3.64 %. M.p. 152–154 °C (dec); ^{1}H NMR (400 MHz, C_6D_6) δ 0.38 (br s, 9H, Si(C*H*$_3$)$_2$), 0.73 (br s, 9H, Si(C*H*$_3$)$_2$), 1.37 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.42 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.52 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.70 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.80 (s, 6H, NCC*H*$_3$), 3.04 (s, 24H, crown-C*H*$_2$), 3.74 (sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 4.36 (sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 4.69 (s, 1H, Mg*H*), 5.12 (s, 1H, NCC*H*), 7.08 (t, *J* = 7.6 Hz, 2H, Ar-*C*), 7.19 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.28 (d, *J* = 7.6 Hz, 2H, Ar-*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 7.1, 7.7 (Si(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 25.4 (NC*C*H$_3$), 25.7, 26.1, 26.9 (CH(*C*H$_3$)$_2$), 27.8, 27.8 (CH(*C*H$_3$)$_2$), 69.8 (crown-*C*H$_2$), 97.8 (NC*C*H), 123.4, 123.8, 124.1, 143.6, 144.7, 150.1 (Ar-*C*), 166.9 (N*C*). ^{133}Cs NMR (52 MHz, C_6D_6) δ 25.8; I.R. (*ν*/cm^{-1}, Nujol): 679 (m), 706 (w), 733 (m), 763 (m), 791 (m), 821 (s), 883 (m), 927 (m), 959 (m), 1005 (s), 1111 (s), 1509 (m), 1544 (w).

Synthesis of Cs$_2$[{Mg(BDI^{Dipp})(HMDS)}$_2$(μ-C$_2$H$_2$O$_2$)] 7. Compound **4**·(benzene) (270 mg, 0.18 mmol) and benzene (~5 mL) were added to a Schlenk flask. The solution was degassed, the flask evacuated, then back-filled with CO (*ca.* 1 bar, dried over P_2O_5). The resulting red solution was allowed to stir at room temperature for 18 hours. The volume of the reaction mixture was reduced to *ca.* 1 mL, then stored at 8 °C overnight to afford large pale-yellow crystals of the title compound. Yield 30 mg, 11 %. M.p. > 260 °C (dec). ^{1}H NMR (400 MHz, C_6D_6) δ 0.30 (s, 18H, Si(C*H*$_3$)$_2$), 0.57 (s, 18H, Si(CH_3)$_2$), 1.11 (d, *J* = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.19 (d, *J* = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.24 (d, *J* = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.39 (d, *J* = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.65 (s, 12H, NCCH_3), 2.11 (s, 6H, toluene), 3.17 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 4.14 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 4.94 (s, 2H, NCC*H*), 5.07 (br s, 2H, MgC*H*O), 6.73 – 7.10 (m, 22H, Ar-*H*, toluene); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 7.2, 9.1 (Si(CH_3)$_2$), 21.4 (toluene), 25.0, 25.3 (CH(*C*H$_3$)$_2$), 26.1 (NC*C*H$_3$), 26.2 (CH(*C*H$_3$)$_2$), 27.6 (*C*H(CH$_3$)$_2$), 27.7 (CH(*C*H$_3$)$_2$), 97.9 (NC*C*H), 123.7, 124.0, 124.2, 124.3, 124.9 (Ar-*C*), 125.7 (toluene-*C*), 128.1 (Ar-*C*), 128.7, 129.3 (toluene-*C*), 129.7 (Mg*C*HO, very broad signal tentatively assigned), 136.1 (toluene-*C*), 139.9, 144.5, 145.0, 149.7 (Ar-*C*), 168.3 (N*C*); ^{133}Cs NMR (52 MHz, C_6D_6) δ -92.5. I.R. (ν/cm^{-1}, Nujol): 695 (w), 752 (m), 793 (s), 821 (m), 836 (m), 884 (m), 924 (m), 956 (m), 1014 (m), 1106 (m), 1509 (m), 1544 (w), 1584 (w), 1619 (w), 2868 (m), 2924 (m), 2957 (m), 3055 (w). Decomposition of the compound in solution and the solid-state at room temperature led to the poor yield, and prevented the acquisition of a reliable elemental analysis.

X-ray Crystallography

Crystals suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Rigaku Xtalab Synergy Dualflex using a graphite monochromator with Cu Kα (1.54180 Å) or Mo Kα (0.71073 Å), or the MX1 beamline of the Australian Synchrotron ($\lambda = 0.71090$ Å). The software package Blu-Ice[40] was used for synchrotron data acquisition, while the program XDS[41] was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX-16[42]) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model). However, the hydride ligands of all structures were located from difference maps, and their positional and isotropic displacement parameters freely refined. Two crystallographically independent molecules of **4**·(benzene), **6** and **7** were refined in the asymmetric units of the crystal structures of those compounds. No significant geometrical differences were found between the two molecules in each case. Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S1 in the Supporting Information.

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The authors declare no competing financial interests.

Supporting Information Available: NMR and IR spectra, and further details of the crystallographic studies.

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Reactions of a series of alkali metal amides with a neutral magnesium(II) hydride compound have given a range of group 1 metal hydrido-magnesiates, the thermal stability of which increases with the molecular weight of the group 1 metal involved. Reactions of the structurally unprecedented cesium hydrido-magnesiate towards 18-crown-6 and CO have been explored.