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Supported by a Bulky, Unsymmetrical β -Diketiminato
Ligand, $[\{(Dip/TCHPNacnac)M(\beta-H)\}_2]$ (M = Mg, Ca, Sr or
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A Series of Neutral Alkaline Earth Metal Hydride Complexes Supported by a Bulky, Unsymmetrical β -Diketiminato Ligand, $[(\text{Dip}/\text{TCHP})\text{Nacnac}]\text{M}(\mu\text{-H})_2$ (M = Mg, Ca, Sr or Ba)

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A bulky, unsymmetrical β -diketiminato ligand, $[\text{HC}\{\text{MeCN}(\text{Dip})\}\{\text{MeCN}(\text{TCHP})\}]^-$ ($\text{Dip}/\text{TCHP}\text{Nacnac}$; Dip = 2,6-diisopropylphenyl, TCHP = 2,4,6-tricyclohexylphenyl), has been utilised in the preparation of a series of magnesium alkyl and calcium, strontium and barium amide complexes. Reaction of these with PhSiH_3 afforded the first complete series of β -diketiminato heavier group 2 metal hydride complexes, $[(\text{Dip}/\text{TCHP})\text{Nacnac}]\text{M}(\mu\text{-H})_2$ (M = Mg, Ca, Sr or Ba). The unsymmetrical nature of the β -diketiminato ligand seemingly promotes stabilising interactions of ligand Dip groups with the metal centres in the Ca, Sr and Ba hydride complexes.

Since the first well-defined heavier alkaline earth metal (Ae = Mg, Ca, Sr or Ba) hydride complex was reported in 2002,¹ the number, and chemistry, of such species has grown rapidly.^{2,3} This is a testament to the applicability these cheap, low toxicity metal hydrides have found in a variety of stoichiometric and catalytic synthetic transformations, many of which were previously thought to require toxic and expensive transition metal hydrides to be effective.⁴ With that said, synthetic applications of alkaline earth metal hydride complexes have been predominantly, though not exclusively,⁵ confined to soluble magnesium and calcium hydride systems.⁴ This is a result of the fact that upon descending group 2, the ionic radii of the metals increase, their electronegativity decreases, and their bonding to ligands becomes more ionic. Consequently, alkaline earth metal hydride compounds have an increasing propensity to decompose *via* Schlenk-like redistribution processes, which are thermodynamically driven by the huge

lattice energy and insolubility of the ultimate saline metal hydride products of these redistributions, *viz.* $(\text{AeH}_2)_\infty$.²

In order to kinetically stabilise Ae metal hydride complexes from undergoing Schlenk-like redistribution reactions, sterically bulky ligands are typically employed. The vast majority of these ligands are bi- or poly-dentate, which adds a degree of thermodynamic stabilisation to the complex involved. As alluded to above, these strategies have allowed the synthesis and isolation of numerous magnesium and calcium hydride complexes. Strontium and barium hydride complexes are far less common, and are confined to polynuclear cluster compounds, cationic systems incorporating neutral polydentate *N*-donor macrocycles, and neutral hydride bridged dimers.² The latter are more soluble, and perhaps offer a greater degree of synthetic utility, but so far are restricted to compounds involving the extremely bulky amidinate,⁶ β -diketiminato,⁷ tris(pyrazolyl)borate⁸ and cyclopentadienyl ligands⁹ in **I-IV** (Figure 1). We were interested in extending this series. In this respect, we have developed a bulky, unsymmetrical β -diketiminato ligand, $[\text{HC}\{\text{MeCN}(\text{Dip})\}\{\text{MeCN}(\text{TCHP})\}]^-$ ($\text{Dip}/\text{TCHP}\text{Nacnac}$; Dip = 2,6-diisopropylphenyl, TCHP = 2,4,6-tricyclohexylphenyl),¹⁰ which was recently reported to kinetically stabilise the first europium(II) hydride complex, $[(\text{Dip}/\text{TCHP})\text{Nacnac}]\text{Eu}(\mu\text{-H})_2$.¹¹ Here, we utilise the same ligand in the preparation of the first series of β -diketiminato heavier, non-radioactive alkaline earth hydride complexes.

It is well established that β -diketiminato magnesium alkyls and heavier group 2 metal amides can act as precursors to corresponding metal hydride complexes, *via* their treatment with phenylsilane.² Accordingly, a series of such complexes, **1-7** (Scheme 1), were prepared by deprotonation of β -diketimine, $\text{Dip}/\text{TCHP}\text{NacnacH}$, with $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$, $\text{MgBu}^n_2(\text{THF})_x$, $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$ (M = Sr or Ba), or $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2$ (M = Ca, Sr or Ba). In each case, elevated reaction temperatures (80–120 °C) were required for the deprotonations to proceed, in line with the considerable steric bulk of the $\text{Dip}/\text{TCHP}\text{Nacnac}$ ligand. All compounds were obtained in moderate to good isolated yields

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as colourless solids, with the exception of **5**, which is an oil at room temperature. The NMR spectra of the compounds are consistent with their proposed structures, and are emblematic of the chelating, asymmetric β -diketiminato ligand in each.

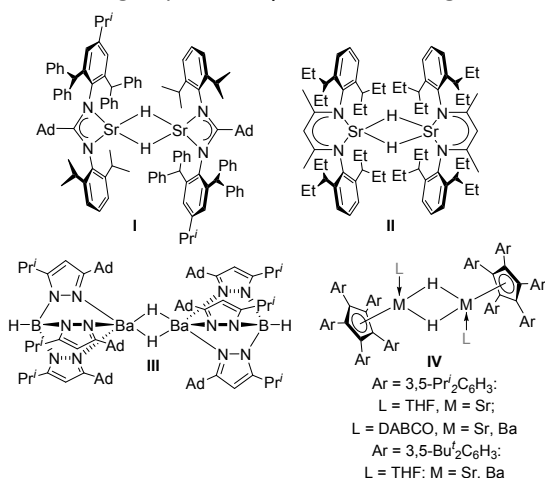
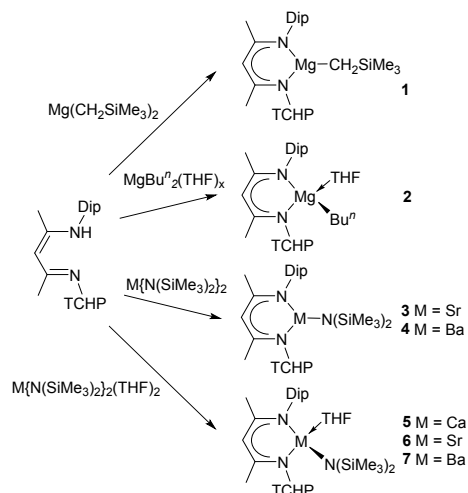


Figure 1. Previously reported neutral, hydride bridged strontium and barium complexes (Ad = 1-adamantyl, DABCO = diazabicyclo[2.2.2]octane).



Scheme 1. Synthesis of compounds 1-7.

Compounds **1**, **2** and **6** were crystallographically characterised, which revealed their structures to be very similar to those for previously reported 3- and 4-coordinate (THF ligated) magnesium alkyls¹² and 4-coordinate (THF ligated) strontium amide¹³ complexes bearing extremely bulky, symmetric β -diketiminato ligands. The molecular structures of **1** and **6** are depicted in Figure 2, while that for **2** can be found in the ESI. In all cases, the metal centre is chelated by the Dip/TCHPⁿNacnac ligand, while their metrical parameters are unremarkable, and are reminiscent of those for the aforementioned known analogous complexes.^{12,13} The structures of **1**, **2** and **6** do, however, highlight the considerable steric protection afforded to their metal centres by the β -diketiminato ligand.

With **1-7** in hand, a systematic evaluation of their reactions with phenylsilane was undertaken. Despite having a presumably electrophilic 3-coordinate magnesium centre, a benzene solution of compound **1** did not react with PhSiH₃, even when heated at 80 °C overnight. In contrast, treating **2** with

PhSiH₃ under the same reaction conditions afforded the dimeric, hydride bridged magnesium hydride complex **8** as a colourless microcrystalline solid in an isolated yield of 24% (Scheme 2). It is noteworthy that **8** is devoid of coordinated THF, which was present in the reaction mixture. This is at variance with less hindered β -diketiminato magnesium hydrides, which can form adducts with the Lewis base, e.g. as in $\{[\text{Dip}^n\text{Nacnac}](\text{THF})\text{Mg}(\mu\text{-H})_2\}_2$ (DipⁿNacnac = $[\text{HC}\{\text{MeCN}(\text{Dip})\}_2]$).¹⁴ Furthermore, when seemingly bulkier β -diketiminato ligands than Dip/TCHPⁿNacnac coordinate to the MgH fragment, dimerisation through hydride bridges can be circumvented, as in $[(\text{Ar}^*\text{Nacnac})\text{MgH}]$ ($\text{Ar}^*\text{Nacnac} = [\text{HC}\{\text{MeCN}(\text{Ar}^*)\}_2]$; $\text{Ar}^* = \text{C}_6\text{H}_2(\text{CHPh}_2)_2\text{Me-2,6,4}$).^{12(b)}

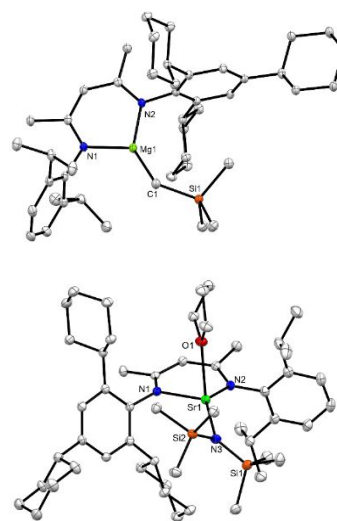
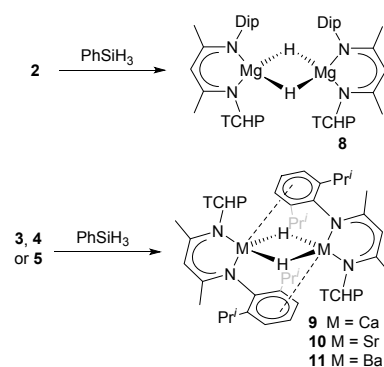


Figure 2. Molecular structures (20% thermal ellipsoids) of compounds **1** (top) and **6** (bottom).



Scheme 2. Synthesis of alkaline earth metal hydride compounds **8-11**.

Calcium hydride complex **9** was similarly prepared by treating an *in situ* generated solution of **5** with PhSiH₃, then letting the reaction solution stand for 4 days. During this time a good yield of the THF free, hydride bridged calcium hydride complex **9** deposited (Scheme 2). Related reactions involving the THF coordinated precursors **6** and **7** led to decomposition and generation of the protonated ligand, Dip/TCHPⁿNacnacH. However, reactions of the THF free precursors **3** and **4** with PhSiH₃ were successful and afforded the colourless crystalline

strontium and barium hydride complexes **10** and **11** in moderate and good isolated yields, respectively.

Magnesium hydride complex **8** is indefinitely stable in solution and the solid-state at room temperature. The ^1H NMR spectrum of the compound is reminiscent of its solid-state structure, and exhibits a hydride resonance at δ 4.06 ppm, which is in the normal region for hydrides bridging two Mg centres.² The molecular structure of the compound is depicted in Figure 3 (See Table 1). Although the structure is of relatively poor quality, the hydride ligands were located from difference maps and their positional parameters freely refined. This allowed confirmation of the dimeric nature of the compound, the metrical parameters for which are similar to those for related hydride bridged dimers, e.g. $[(^{\text{Dip}}\text{Nacnac})\text{Mg}(\mu\text{-H})_2]$.¹⁴ One point of note here is the fact that the TCHP (and Dip) substituents lie on the same side of the molecule, i.e. are *cis*-to each other, which intuitively might be expected to be less sterically favourable than the alternative *trans*-arrangement of these groups. However, DFT calculations (B3PW91) on **8** in the gas phase revealed that the geometry optimised *cis*-arrangement is indeed favoured relative to the molecule having *trans*-disposed TCHP groups, by $\Delta G^\circ_{298\text{K}} = -2.5$ kcalmol⁻¹.

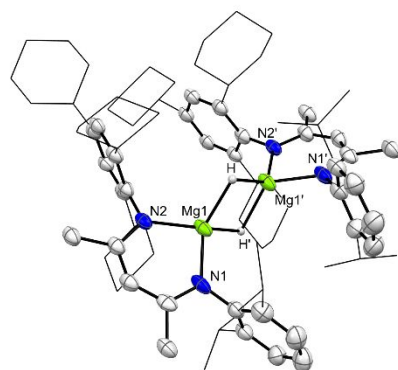


Figure 3. Molecular structure (15% thermal ellipsoids) of compound **8** (cyclohexyl and isopropyl groups shown as wireframe).

The heavier group 2 hydride complexes **9–11** are stable in the solid-state at room temperature for weeks. They are essentially insoluble in non-coordinating solvents (e.g. cyclohexane, toluene or benzene) or fluorinated arenes (e.g. 1,2-difluorobenzene). Attempts to dissolve compounds **10** and **11** in THF-*d*₈ led to their immediate decomposition to complex product mixtures, including significant amounts of $^{\text{Dip/TCHP}}\text{NacnacH}$, thus preventing the acquisition of meaningful NMR spectroscopic data for those species. Moreover, given the complexity of these product mixtures, the decomposition pathway could not be determined. In contrast, calcium hydride compound **9** will dissolve when a small amount of THF-*d*₈ is added to a suspension of the compound in benzene-*d*₆. This allowed the assignment of a signal in its ^1H NMR spectrum at δ 4.51 ppm as resulting from the hydride ligands (*cf.* δ 4.27 ppm for $[(^{\text{Dip}}\text{Nacnac})\text{Ca}(\mu\text{-H})_2]$).¹⁵

Compounds **9–11** are isostructural and isomorphous to each other, and to $[(^{\text{Dip/TCHP}}\text{Nacnac})\text{Eu}(\mu\text{-H})_2]$.¹¹ As a result, only the molecular structure of **11** is depicted in Figure 4 (see Table 1).

The metal centres in each of the hydride bridged dimers are chelated by the *N*-centres of one Nacnac ligand, while at the same time having an approximately η^3 -interaction with a Dip group on the opposing β -diketiminate. This bonding situation does not occur in the corresponding magnesium hydride complex **8**, likely because of the smaller size and lesser arenophilicity of the metal in that case. It also seems plausible that the arene interactions are enabled by the unsymmetrical nature of the ligands. That is, the smaller, *para*-substituent free, Dip groups can η^3 -coordinate to the metal centres without clashing with the TCHP group on the opposing β -diketiminate. This would not be sterically possible if the β -diketiminate was substituted with two TCHP groups. The hydride ligands of all structures were located from difference maps and their positional parameters freely refined. While of low accuracy, the M–H distances in the compounds are broadly comparable with those in related hydride bridged systems, e.g. **I–IV**^{6–9} and $[(^{\text{Dip}}\text{Nacnac})\text{Ca}(\mu\text{-H})_2]$.¹⁵ It should be noted that compound **9** co-crystallised with *ca.* 20% of the hydroxide compound $[(^{\text{Dip/TCHP}}\text{Nacnac})\text{M}(\mu\text{-OH})_2]$. Similar co-crystallisations, with corresponding hydride/hydroxide site disorders, have been previously reported for heavier group 2 hydride complexes.¹⁶

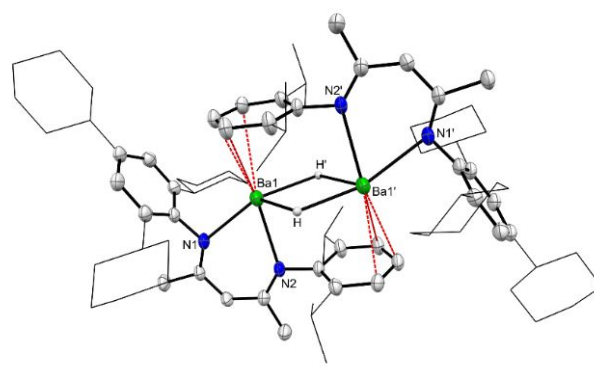


Figure 4. Molecular structure (20% thermal ellipsoids) of compound **11** (cyclohexyl and isopropyl groups shown as wireframe).

Table 1. Selected bond lengths (Å) and angles (°) for complexes **8–11**.

	8	9	10	11
M–H	2.04(4) 2.09(4)	2.16(2) 2.04(2)	2.49(6) 2.46(6)	2.43(8) 2.43(8)
M–N	2.037(8) 2.041(9)	2.404(1) 2.408(1)	2.599(3) 2.518(3)	2.741(4) 2.642(4)
Ar...M ^a	-	3.310(1)	3.047(4)	3.112(5)
N–M–N	93.4(4)	74.90(4)	69.83(9)	65.5(1)

^a The closest Dip Ar-C...M interaction is given

In summary, a bulky, unsymmetrical β -diketiminate ligand has been used to prepare a series of alkaline earth metal alkyl and amide complexes. Treating a selection of these with PhSiH₃ afforded the first complete series of β -diketiminate heavier group 2 metal hydride complexes, which includes rare examples of neutral strontium and barium hydride species. It is apparent that the unsymmetrical nature of the β -diketiminate ligand facilitates intramolecular arene interactions in the Ca, Sr and Ba hydride complexes, which likely aids in their stabilisation. We

are currently exploring the further chemistry of all prepared metal hydrides.

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Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article have been included as part of the ESI.

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Data Availability Statement

The data supporting this article have been included as part of the ESI.