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We present the reactivity of the Mg–C and the β -CH bonds in the trigonal pyramidal $[(\text{pmdta})\text{Mg}(n\text{Bu})]^+$ exhibiting a weak Mg···F interaction with counter anion, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$. Instantaneous β -hydride reactivity with benzophenone, reductive alkylation of phenyl benzoate, and straightforward synthesis of $[(\text{pmdta})\text{MgH}]^+$ via metathesis with pinacolborane/phenylsilane are discussed.

Investigations on the structure and reactivity of the molecular compounds of the alkaline earth elements have been of topical interest in the 21st century.¹ Highly reactive compounds that profoundly impact organic and inorganic transformations are synthesised.² Among group 2 elements, magnesium has spurred interest in generating polar metal–carbon bonds finding utility in stoichiometric and catalytic reactions.³ Numerous examples of neutral alkyl magnesium compounds are found in the literature. Such compounds are precursors to access the corresponding alkoxides, carboxylates, amides and hydrides.^{3,4} They also find applications in the ring-opening polymerization of cyclic ethers⁵ and the catalytic reductions of carbon dioxide,⁶ carbonyls,⁷ and olefins.⁸ As compared to the neutral compounds, there are a few examples of well-characterized alkylmagnesium cations (Fig. 1).^{9–12} The Schlenk equilibrium poses a significant challenge in handling these cations in solution, limiting their reactivity studies.¹³ The selection of the ancillary ligands and the solvents significantly influences the Schlenk re-distribution.

In 2018, we reported the five-coordinate $[(\text{Me}_6\text{tren})\text{Mg}(n\text{Bu})]^+$ (Me_6tren = tris(2-dimethylaminoethyl)amine), which stoichiometrically reduced CO_2 in a Grignard-type reaction.¹⁰ We further observed the activity of the β -hydride in $[(\text{Me}_6\text{tren})\text{Mg}(n\text{Bu})]^+$ under hot conditions in toluene. Decreasing the coordination number at magnesium is expected to increase

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Reactivity of a quasi-four-coordinate butylmagnesium cation†

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the reactivity in an alkyl magnesium cation markedly.¹⁴ In this communication, we report the isolation of a four-coordinate alkylmagnesium cation, $[(\text{pmdta})\text{Mg}(n\text{Bu})]^+$ ($\text{pmdta} = N,N,N',N''\text{-pentamethyldiethylenetriamine}$) and explore its reactivity with $\text{C}=\text{O}$, $\text{B}-\text{H}$ and $\text{Si}-\text{H}$ bonds.

$[(\text{pmdta})\text{Mg}(n\text{Bu})][\text{B}\{3,5-\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]$ (**1a**) was synthesised in quantitative yields *via* slow addition of a heptane solution of di-*n*-butylmagnesium to an ether solution of pmdta and $[\text{NET}_3\text{H}][\text{B}\{3,5-\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]$ (Scheme 1). Compound **1a** was characterized by multinuclear NMR spectroscopy and elemental analysis. A characteristic peak for the α -CH₂ protons on the *n*-butyl group was observed at $\delta = 0.59$ ppm in the ¹H NMR spectrum (ESI, Fig. S1†).

Efforts to crystallize **1a** were not successful. Hence, $[(\text{pmdta})\text{Mg}(n\text{Bu})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1b**) was prepared analogous to **1a** (Scheme 1) and crystallized from a concentrated diethyl ether solution within 24 hours at -25°C . The solid-state structure

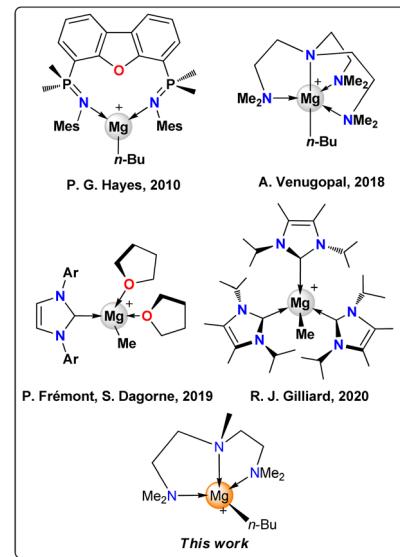
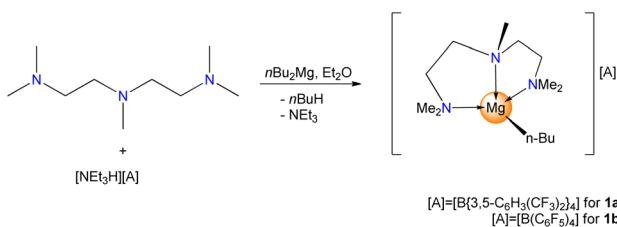


Fig. 1 Structurally characterised alkylmagnesium cations.





Scheme 1 Synthesis of cationic butylmagnesium compounds **1(a, b)**.

revealed that the cationic magnesium centre in **1b** exhibits a distorted trigonal pyramidal coordination geometry (Fig. 2). The tridentate pmdta binds to Mg1 in a κ^3 -manner with an average Mg–N distance of 2.162 Å. The central nitrogen atom, N1, in the pmdta ligand takes up the apical position of the trigonal pyramid while N2 and N3 atoms and the α -carbon, C10, of the *n*-butyl group form the distorted trigonal plane. The Mg–C distance is 2.144(19) Å. Interestingly, at the position *trans* to the Mg1–N1 bond, long Mg…F contact with the fluorine atom on the counter anion, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ is observed. The Mg1…F3 distance is observed to be 3.060(2) Å, which is slightly less than the sum of van der Waals radii of magnesium and fluorine (3.20 Å) (Fig. 2). These observations infer that the fifth coordination site at magnesium can be utilized to activate small molecules.¹⁵

Having accessed the butylmagnesium cation $[(\text{pmdta})\text{Mg}(\text{nBu})]^+$, we proceeded to test its reactivity. **1a** was treated with an equivalent amount of Ph_2CO in $\text{C}_6\text{D}_5\text{Br}$ (Scheme 2). ^1H

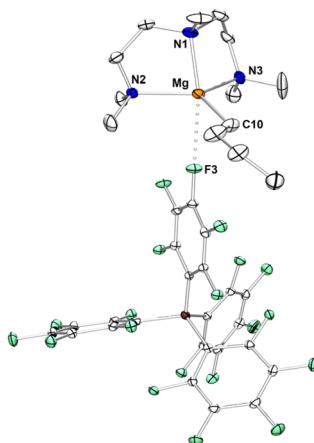
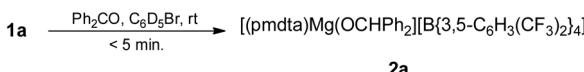


Fig. 2 Solid state structure of $[(\text{pmdta})\text{Mg}(\text{nBu})]^+$ in **1b**. H-atoms are omitted for clarity and the thermal ellipsoids are drawn at 30% probability level. Selected bond distances (Å) and angles ($^\circ$) in **1b**: Mg–N1, 2.164(3); Mg–N2, 2.160(3); Mg–N3, 2.164(3); Mg–C10, 2.144(19); N1–Mg–C10, 118.1(6); N2–Mg–C10, 108.9(4); N3–Mg–C10, 132.6(4); N1–Mg–N2, 83.76(12); N2–Mg–N3, 115.48(12); N1–Mg–N3, 83.33(14).



Scheme 2 Reduction of benzophenone by the β -hydride.

NMR studies exhibit an instantaneous transfer of the β -hydride to Ph_2CO , resulting in $[(\text{pmdta})\text{Mg}(\text{OCHPh}_2)[\text{B}\{3,5-\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]$ (**2a**) with the simultaneous release of 1-butene (Scheme 2 and ESI, Fig. S9†). The β -hydride reactivity in $[(\text{pmdta})\text{Mg}(\text{nBu})]^+$ is markedly accelerated in comparison to our previously reported $[(\text{Me}_6\text{tren})\text{MgBu}]^+$, which took 12 h at the temperature of 60 °C,¹⁰ thus underlining the advantage of lower coordination number in the former.

Attempts to crystallize **2a** in THF failed and the compound redistributed to $[\text{Mg}(\text{THF})_6][\text{B}\{3,5-\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]_2$ (**3a**) and $\text{Mg}(\text{OCHPh}_2)_2$, indicating the limitations of employing a relatively basic solvent.¹⁶ However, using diethyl ether (Et_2O) as solvent, we isolated **2a**– Et_2O in crystalline form. The formal replacement of the *n*Bu group in **1b** by the $-\text{OCHPh}_2$ moiety in **2a** is expected to increase the Lewis acidity at magnesium. Thus, an additional ether molecule is bound to the magnesium centre in **2a**, increasing its coordination number to five with a trigonal bipyramidal geometry (Fig. 3).

Once the activity of β -hydride of compound **1** was established, we moved on to explore its reactivity with ester. Grignard reagents are known to react with esters resulting in tertiary alcohols.¹⁷ Contrastingly, a reaction between phenyl benzoate (PhCOOPh) and **1a/b** in toluene resulted in the secondary alcohol, $\text{PhCH}(\text{OH})(\text{n-Bu})$, which was confirmed by NMR spectroscopy and GC-MS (Scheme 3 and ESI, Fig. S18 and S20†). **1a/b** delivers the *n*-butyl group and the β -hydride sequentially to reduce PhCOOPh to $\text{PhCH}(\text{OH})(\text{n-Bu})$. Such tandem reductive alkylation of esters has been previously performed by Grignard reagents, but requires the presence of the hydride donor $\text{Ti}(\text{O}i\text{Pr})_4$.¹⁸

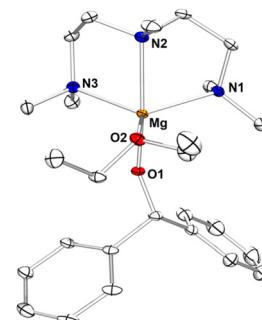
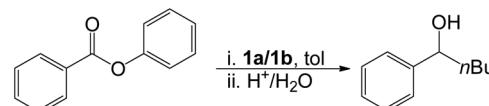


Fig. 3 Solid state structure of the cationic part in **2a**– Et_2O . H-atoms are omitted for clarity and the thermal ellipsoids are drawn at 30% probability level. Selected bond distances (Å) and angles ($^\circ$) in **2a**– Et_2O : Mg–N1, 2.184(4); Mg–N2, 2.279(4); Mg–N3, 2.205(4); Mg–O1, 1.868(3); Mg–O2, 2.098(3); N1–Mg–O1, 99.92(14); N2–Mg–O1, 171.21(15); N3–Mg–O1, 93.33(14); N1–Mg–O2, 117.10(15); N2–Mg–O2, 90.84(13); N3–Mg–O2, 120.28(14); N1–Mg–N2, 80.17(13); N2–Mg–N3, 79.07(14); N1–Mg–N3, 118.61(15); O1–Mg–O2, 96.87(13).



Scheme 3 Reductive alkylation of phenyl benzoate.



Based on the preliminary studies with the polar carbonyl compounds, we were tempted to explore the reactivity of the butylmagnesium cation **1a****1b**, with B–H and Si–H bonds. Before proceeding to experiments, we performed DFT calculations (B3PW91). For the reaction between $[(\text{pmdta})\text{Mg}(n\text{Bu})]^+$ and HBpin, the generally accepted σ -bond metathesis¹⁹ between Mg–C and H–B bonds through a four-member transition state was considered (Fig. 4). The reaction exhibits an energy barrier of 3.87 kcal mol^{−1} for the σ -bond metathesis step (Fig. 4). The formation of $[(\text{pmdta})\text{MgH}]^+$ is exothermic by −10.13 kcal mol^{−1}. We discarded an alternative reaction pathway involving the alkyl transfer from $[(\text{pmdta})\text{Mg}(n\text{Bu})]^+$ to HBpin since it involved a higher energy barrier (see ESI[†]). We further considered the reaction between $[(\text{pmdta})\text{Mg}(n\text{Bu})]^+$ and PhSiH₃ and observed that σ -bond metathesis between Mg–C and H–Si bonds displays a reaction barrier of 20.88 kcal mol^{−1} and the resulting $[(\text{pmdta})\text{MgH}]^+$ is exothermic by −7.59 kcal mol^{−1} (Fig. 4).

Prompted by the results from DFT calculations and in the efforts to access the hydridomagnesium cation, $[(\text{pmdta})\text{MgH}]^+$, we carried out a reaction between **1a** and HBpin in tetrahydrofuran under ambient conditions (Scheme 4). Cooling the reaction mixture to −25 °C led to the isolation of **3a**. Further, layering of the mother liquor with pentane resulted in the precipitation of an unprecedented hydride-rich $[(\text{pmdta})\text{MgH}]_2\{(\text{H}_3\text{BOCMe}_2\text{CMe}_2\text{O})\text{Mg}(\text{THF})_2\}_2\text{[B}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_4\}$ (**4a**). The cationic part in the solid-state structure of **4a** reveals the presence of four magnesium centres, two bridging hydride ligands, and two bridging borohydride moieties resulting from the ring-opening of HBpin (Fig. 5). ¹H NMR spectrum of **4a** in THF-D8 exhibits a characteristic peak for the Mg–H at δ 4.53 ppm (ESI, Fig. S21[†]). We did not observe a peak for the

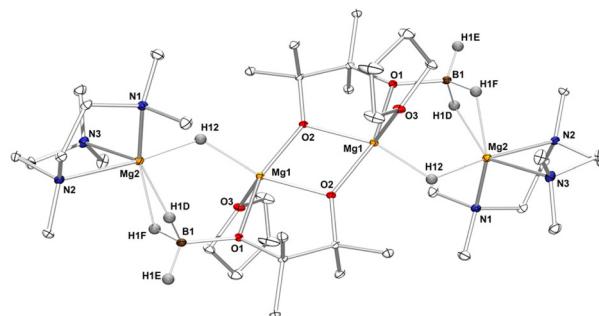


Fig. 5 Solid state structure of the cationic hydridomagnesium borohydride part in **4a**. Selected H-atoms are omitted for clarity and the thermal ellipsoids are drawn at 30% probability level. Selected bond distances (Å) and angles (°): Mg1–Mg2, 3.3557(18); Mg1–H12, 1.90(3); Mg2–H12, 1.85(3); Mg2–H(1D), 1.97(4); Mg2–H(1F), 2.06(4); N1–Mg2, 2.198(4); N2–Mg2, 2.219(4); N3–Mg2, 2.208(4); O1–Mg1, 2.081(3); O2–Mg1, 1.966(3); O3–Mg1, 2.087(3); Mg1–O2–Mg(1), 99.16(11); O2–Mg1–O1, 159.95(12); N1–Mg2–N3, 114.61(14); N1–Mg2–N2, 81.41(13); N3–Mg2–N2, 81.26(13).

B–H in the ¹H spectrum. However, a broad singlet at δ −15.42 ppm in the ¹¹B NMR spectrum can be attributed to the B–H resonance (ESI, Fig. S23[†]). There are reports of ring opening of pinacolborane by the hydrides of group 2 metals and aluminium.^{20,21} However, **4a** is a rare example of a ring-opened pinacolborane product retaining the hydride within the aggregate.

The observation of **4a** suggests an initial formation of a reactive magnesium hydride species, which subsequently breaks the B–O bond of HBpin. Stabilization of the solvated dicationic magnesium compound **3a** *via* Schlenk equilibrium might also be a factor for the formation of **4a**.²² Thus, we resorted to changing the solvent from THF to diethyl ether to access hydridomagnesium cation. Accordingly, the reaction between **1a** and HBpin was performed in diethyl ether (Scheme 5), leading to the instantaneous precipitation of a colourless solid. Analysis of the precipitated colourless solid by ¹H NMR spectroscopy in THF-D8 revealed its identity as the desired hydridomagnesium cation $[(\text{pmdta})\text{MgH}]\text{[B}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_4]$ (**5a**) with Mg–H proton signal appearing at δ 4.53 ppm (ESI, Fig. S25[†]). Compound **5a** is stable in THF-D8 for a few minutes at ambient temperature and then undergoes Schlenk redistribution resulting in **3a** and MgH₂. Subsequently, PhSiH₃ was tested as an alternative hydride

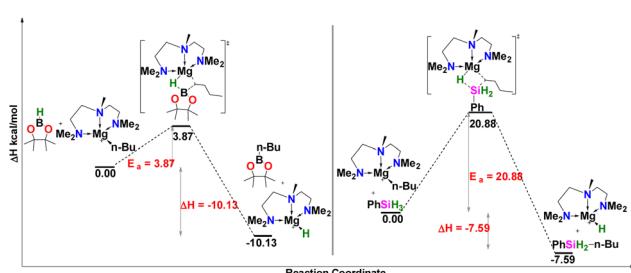
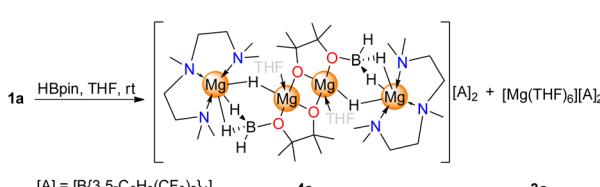
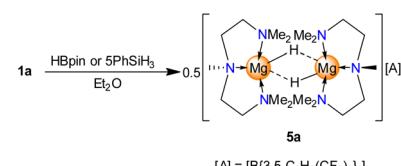


Fig. 4 Computed enthalpy profile at room temperature for the synthesis of a cationic hydridomagnesium compound from pinacolborane and phenylsilane.



Scheme 4 Ring opening of HBpin in THF to form compound **4a**.



Scheme 5 Straight-forward synthesis of cationic magnesium hydride **5a**.



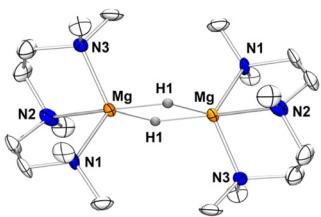


Fig. 6 Solid state structure of the cationic hydridomagnesium part in **5a**. Selected H-atoms are omitted for clarity and the thermal ellipsoids are drawn at 30% probability level. Selected bond distances (Å) and angles (°) in **5a**: Mg–H1, 1.92(8); H1...Mg, 1.98(8); N1–Mg, 2.19(2); N2–Mg, 2.217(9); N3–Mg, 2.22(3); N1–Mg–H1, 122(2); N1–Mg–N3, 113.2(7); N2–Mg–N3, 85.9(6); N1–Mg–N2, 83.1(5); N2–Mg–H1, 96(2); N2–Mg...H1, 178(2); Mg–H1...Mg, 98(4).

source for the synthesis of **5a** from **1a**. A diethyl ether solution of **1a** was layered with five-fold excess of PhSiH_3 at ambient temperature. Single crystals of **5a** were obtained after 24 h. The solid-state structure of **5a** revealed a dimeric structure with two hydrides bridged between two magnesium centres (Fig. 6). Each magnesium centre exhibits a trigonal bipyramidal geometry. One of the hydride ligands takes up the apical position, while the other is located at one of the corners of the trigonal plane. The Mg–H distances are found to be 1.92(8) and 1.98(8) Å, respectively, consistent with the other reported neutral and cationic hydridomagnesium complexes. To the best of our knowledge, this is the first report on synthesising a hydridomagnesium complex from a corresponding cationic alkyl magnesium derivative using hydridoborane and hydrosilane as hydride source.²³ Preliminary reactivity studies were performed to understand the hydridic nature of **5a**. A reaction between **5a** and Ph_2CO in C_6D_6 instantaneously resulted in **2a**. We further attempted to perform a reaction between **5a** and carbon monoxide. ^1H NMR spectrum of the reaction suggested the formation of enediolato species (ESI, Fig. S26†), which has been previously evidenced.²⁴ However, the sparingly soluble nature of the reaction mixture prevented further characterization.

The reactivity of the alkyl magnesium cations is scarcely reported in the literature. We have demonstrated the utility of the four-coordinate $[(\text{pmdta})\text{Mg}(n\text{Bu})]^+$ in the reduction of carbonyl groups and a direct route to access the hydridomagnesium cation, $[(\text{pmdta})\text{MgH}][\text{B}\{3,5-\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]$.

Conflicts of interest

There are no conflicts to declare.

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