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Amidomagnesium cations†

Sumanta Banerjee,[a] Ankur,[a] Alex P. Andrews,[a] Babu Varghese[b] and Ajay Venugopal*[a]

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We report the synthesis, structure and reactivity of molecular amidomagnesium cations bearing tris{2-(di-methylamino)-ethyl}amine (Me_6TREN). Me_6TREN binds to the cationic magnesium centre exhibiting κ^4 and κ^3 coordination modes in $[Me_6TREN\text{-}Mg\text{-}N(SiHMe_2)_2]^+$ and $[Me_6TREN\text{-}Mg\text{-}N(SiMe_3)_2]^+$ respectively. $[Me_6TREN\text{-}Mg\text{-}N(SiHMe_2)_2]^+$ reacts with benzophenone resulting in the insertion of the carbonyl group across β-SiH bond. The reaction between $[Me_6TREN\text{-}Mg\text{-}N(SiMe_3)_2]^+$ and CO_2 leads to $[Me_6TREN\text{-}Mg\text{-}OSiMe_3]^+$, while the reaction with H_2O results in $[Me_6TREN\text{-}Mg\text{-}OH]_2^{2+}$. Attempts to prepare hydridomagnesium cations from $[Me_6TREN\text{-}Mg\text{-}N(SiMe_3)_2]^+$ using KH resulted in the precipitation of MgH_2 and the isolation of $[(Me_6TREN)K(THF)_3]^+$.

Introduction

Amidomagnesium reagents are an important class of compounds in synthetic chemistry.[1] The first report of these compounds dates back to 1903 by Meunier, although the advent of Hauser bases [$(R_2N)MgX$ and $(R_2N)_2Mg$] in the late forties set the wheels in motion for further research in the area.[2–4] A wide range of organic ligands have been used to generate structurally diverse amidomagnesium complexes.[5] Bidentate β-diketaminate[6–12] and amidinate,[13,14] tridentate trispyrazolylborate[15] and the tetradentate tetraazacyclododecane[16,17] ligands have been employed to generate monomeric amidomagnesium species. The steric and electronic effects provided by these ligands decide the reactivity of the complexes. Amidomagnesium compounds have the potential to function as reagents in various organic transformations,[5,18] catalysts for ring opening polymerisation of lactides,[5,19] and also as precursors for isolating synthetically important novel magnesium compounds like molecular magnesium hydrides.[20,21]

A cationic magnesium centre ought to change the chemistry of magnesium on account of increased Lewis acidity on the metal. Extensive and systematic experiments with cationic magnesium complexes have remained scarce except for a few examples in literature (Fig. 1).[22–26] Synthetic access to cationic complexes of magnesium is challenging, mainly due to aggregation in the solid state and Schlenk equilibrium operative in solution. Consequently, the choice of ligand becomes critical to stabilise molecular magnesium cations. The year 2018 witnessed a renewed interest in the isolation of reactive magnesium cations.[24–26] A highly electrophilic β-diketaminate stabilised magnesium cation has been shown to have strong interactions with alkynes and arenes triggering the interest in hydrocarbon functionalisation by s-block compounds.[25–31]

Mulvey and co-workers have pioneered the use of tris{2-(di-methylamino)-ethyl}amine (Me_6TREN) to stabilise monomeric alkali metal complexes.[32–41] This motivated us to employ

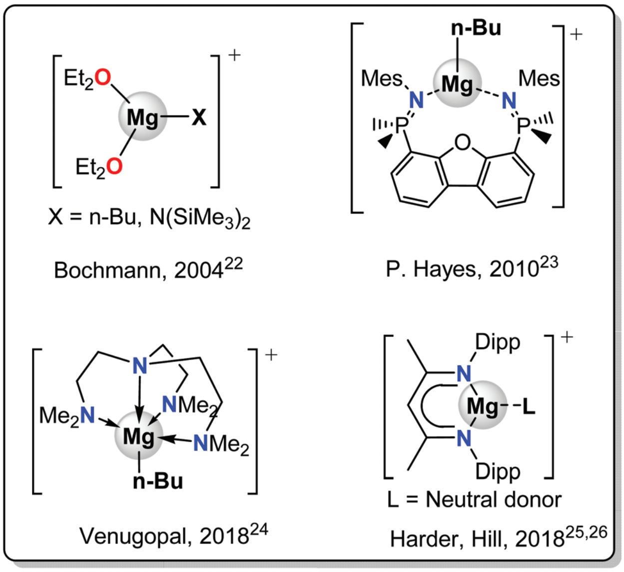

Fig. 1 Structurally characterised molecular magnesium cations.

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[a] *School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, Vithura, Thiruvananthapuram 695551, India. E-mail: venugopal@iisertvm.ac.in*

[b] *Sophisticated Analytical Instrument Facility, Indian Institute of Technology Madras, Chennai 600036, India*

† Electronic supplementary information (ESI) available: Experimental data, CIF for **1**, **2a**, **2b**, **4–6**. CCDC 1886056, 1886058–1886062 and 1886412. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt05095c

Me_6TREN in the investigations on molecular magnesium cations. We have recently demonstrated the reactivity of butylmagnesium cation ($[Me_6TREN\text{-}Mg\text{-}n\mathrm{Bu}][B(C_6F_5)_4]$) with electrophiles and found that the β-CH of the alkyl group bound to magnesium could be used to quantitatively reduce benzophenone in non-polar medium.[24] In this report, we describe the synthesis and structural features of cationic magnesium amides that can act as potential precursors for further reactions, thereby expanding the chemistry of cationic magnesium complexes.

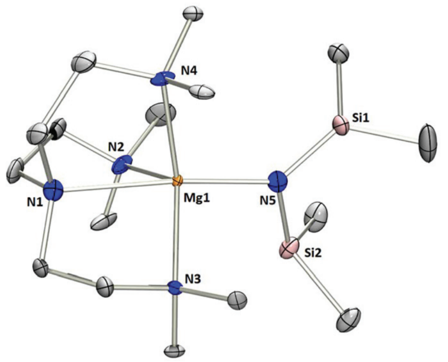
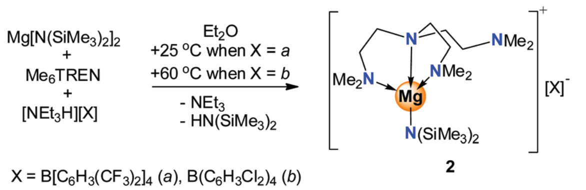


Fig. 2 Solid state structure of the cationic moiety of **1**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) are provided in Table 1.



Scheme 2 Synthesis of bis(trimethylsilyl)amidomagnesium cation (**2**).

Results and discussion

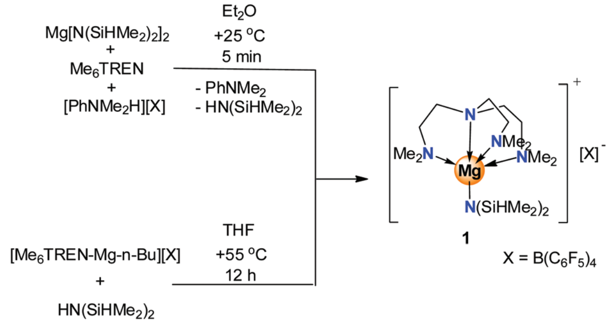
$[Mg\{N(SiHMe_2)_2\}_2]$[42] and $[Mg\{N(SiMe_3)_2\}_2]$[43] were chosen as precursors to access the amidomagnesium cations. $[Mg\{N(SiHMe_2)_2\}_2]$ was treated with Me_6TREN in diethyl ether followed by the addition of $[PhNMe_2H][B(C_6F_5)_4]$ to obtain $[Me_6TREN\text{-}Mg\text{-}N(SiHMe_2)_2][B(C_6F_5)_4]$ (**1**, Scheme 1). Colourless crystals of **1** were isolated from a solvent mixture of diethyl ether and *n*-hexane at −30 °C. **1** was characterised by NMR spectroscopy (see ESI, Fig. S1–S4†), elemental analysis and single crystal X-ray diffraction (XRD) studies. Compound **1** could also be prepared from the reaction between $[Me_6TREN\text{-}Mg\text{-}n\text{-}Bu][B(C_6F_5)_4]$ and tetramethyldisilazane in tetrahydrofuran at 55 °C (Scheme 1). The reaction was accompanied by the evolution of *n*-butane, which was confirmed by ^1H NMR spectroscopy (see ESI, Fig. S5†).

NMR spectroscopy and solid state structure analysis of **1** (Fig. 2) reveal κ^4-coordination mode of Me_6TREN to the magnesium centre similar to the one observed in $[Me_6TREN\text{-}Mg\text{-}n\text{-}Bu][B(C_6F_5)_4]$. The overall geometry around magnesium in **1** is trigonal bi-pyramidal.

The reaction between $[Mg\{N(SiMe_3)_2\}_2]$, Me_6TREN and $[NEt_3H][B\{C_6H_3(CF_3)_2\}_4]$ led to the formation of $[Me_6TREN\text{-}Mg\text{-}N(SiMe_3)_2][B\{C_6H_3(CF_3)_2\}_4]$ (**2a**, Scheme 2) in quantitative yields. We observed that **2** could be obtained by employing diethyl ether as the solvent. Changing the solvent to tetrahydrofuran results in the formation of magnesium dication $[(THF)_6Mg][B\{C_6H_3Cl_2\}_4]_2$ (see ESI, Fig. S24†) strongly suggesting the existence of Schlenk equilibrium in relatively polar aprotic solvents. Isolation and structural characterisation of such magnesium dications have precedence in the literature.[44,45]

^1H NMR spectroscopy suggests a dynamic coordination mode of Me_6TREN with the magnesium centre in **2** in solution. Chemical shifts of Me_6TREN could not be resolved even at low temperatures (see ESI, Fig. S14†). Single crystal XRD experiment on **2** revealed the κ^3 coordination mode of Me_6TREN to the magnesium centre (Fig. 3) in contrary to the observation made in $[Me_6TREN\text{-}Mg\text{-}n\text{-}Bu][B(C_6F_5)_4]$ and **1**.

As evident from the solid state structure analysis, the binding mode of Me_6TREN is different in **1** and **2**. While a trigonal bipyramid geometry is observed in **1**, a tetrahedral geometry is found at magnesium centre in **2**. The reason for the different coordination numbers is due to the increased sterics at the amide in **2** leading to a κ^3 coordination of Me_6TREN. Such a coordination mode is observed in the lithium



Scheme 1 Synthesis of bis(dimethylsilyl)amidomagnesium cation (**1**).

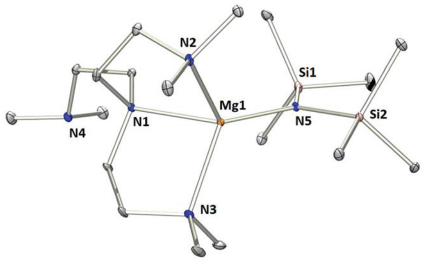


Fig. 3 Solid state structure of the cationic moiety of **2a**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) are provided in Table 1.

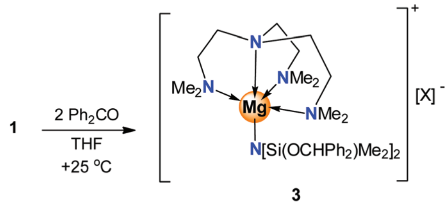
Table 1 Selected bond distances (Å) and angles (°)

Bond lengths (Å) and angles (°)	[Me$_6$TREN-Mg-n-Bu]$^+$	**1**	**2a**
Mg1–N1	2.304(6)	2.294(11)	2.205(3)
Mg1–N2	2.239(6)	2.316(6)	2.181(4)
Mg1–N3	2.223(6)	2.232(5)	2.169(4)
Mg1–N4	2.208(7)	2.279(6)	
Mg1–E	2.148(7)	2.048(4)	1.970(4)
N1–Mg1–E	177.9(3)	174.8(2)	126.6(1)
N1–Mg1–N2	77.1(2)	77.1(3)	84.2(1)
N1–Mg1–N3	77.7(2)	78.5(2)	83.6(1)
N2–Mg1–N3	114.5(2)	114.3(2)	113.1(2)

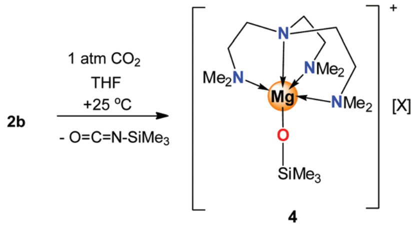
E = C13 ([Me$_6$TREN-Mg-n-Bu]$^+$), N5 (**1**,**2**).

complex [(Me$_6$TREN)Li{N(SiMe$_3$)$_2$}].[46] Table 1 provides a comparative data of selected bond lengths and angles of [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$], **1** and **2a**. Analysis of the average Mg-N(Me$_6$TREN) distances indicate that they are shortest in **2a**. The decreased coordination number in **2a** results in shortening of the Mg-N(Me$_6$TREN) distances. Additionally, Mg-N(SiMe$_3$)$_2$ distance in **2a** is shorter than the corresponding Mg-N(SiHMe$_2$)$_2$ distance in **1** as well as Mg–C distance in [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$]. Decrease in the coordination number from five in **1** to four in **2** results in increased electrophilicity at the magnesium centre in the latter as evident from the bond distances. Hence, one may expect **2** to be more reactive than **1**, but the steric constraints in **2** may pose a challenge to its reactivity.

To verify our proposition on the reactivity of **1** and **2**, we considered the reaction between amidomagnesium cations and benzophenone (Ph$_2$C=O) expecting the insertion of the latter across Mg–N bond. However, hydrosilylation of Ph$_2$C=O was observed upon treating with **1** (**3**, Scheme 3), while **2b** showed no reactivity. The formation of **3** can best be described as β-hydride abstraction followed by Si–O bond formation and is reminiscent of the "disguised" hydride reactivity of [Me$_6$TREN-Mg-n-Bu]$^+$ during the reduction of benzophenone.[24] In the same category falls the reactivity of DIPPnacnacMgBu, which reacts with Ph$_3$C$^+$ by β-hydride elimination giving butane and Ph$_3$CH.[25] Interestingly, [Me$_6$TREN-Mg-n-Bu]$^+$ reacts with H{N(SiHMe$_2$)$_2$}$_2$ as a carbanion source and not as a hydride donor, exhibiting dual reactivity of a Mg-bound butyl anion. The steric hindrance caused by the SiMe$_3$ groups prevents the reaction of **2b** with benzophenone.



Scheme 3 Reactivity of **1** with benzophenone.



Scheme 4 Reactivity of **2b** with CO$_2$.

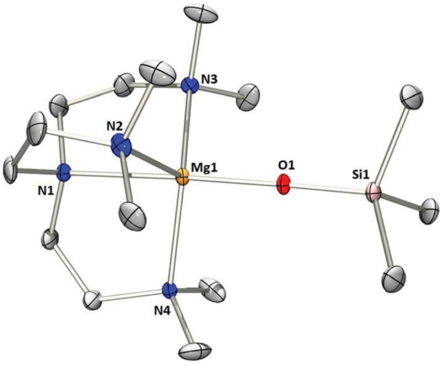
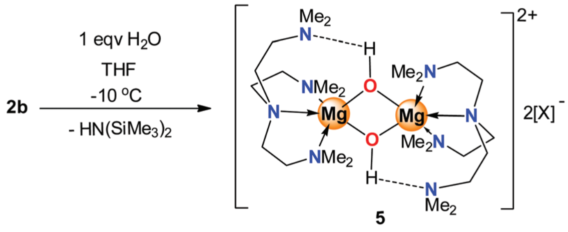


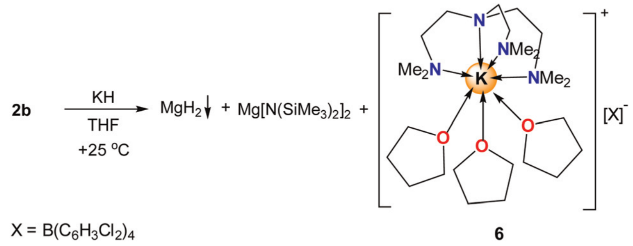
Fig. 4 Solid state structure of the cationic moiety of **4**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Mg1–N1 2.243(3), Mg1–N2 2.187(5), Mg1–N3 2.190(4), Mg1–N4 2.233(3), Mg1–O1 1.833(3), O1–Si1 1.579(3), Mg1–O1–Si1 179.0(2), N1–Mg1–O1 177.9(2), O1–Mg1–N2 101.5(2), O1–Mg1–N4 98.6(1), O1–Mg1–N3 100.9(2).

Having observed no reactivity with Ph$_2$C=O, we proceeded to check the reactivity of **2b** with a smaller electrophile, carbon dioxide (CO$_2$). Accordingly, **2b** was treated with CO$_2$ (1 bar) in tetrahydrofuran. A siloxomagnesium cation, [Me$_6$Tren-Mg-OSiMe$_3$][B(C$_6$H$_3$Cl$_2$)$_4$] (**4**, Scheme 4 and Fig. 4) was the only magnesium compound isolated from this reaction mixture. Insertion of CO$_2$ in neutral amidomagnesium compounds are known to follow the path of carbamate formation followed by subsequent elimination of isocyanate eventually forming strong Si–O bonds.[47] A similar mechanism operates in the formation of **4**. It can also be concluded from Scheme 4, that a reactivity at Mg–N bond in **2** can be expected with small electrophilic molecules like CO$_2$.

We observed that **2b** is extremely sensitive to both air and moisture. Controlled reactions of **2b** with H$_2$O was performed to explore the possible products. When a dilute solution of **2b** in THF was treated with 1 equivalent of degassed H$_2$O and stored at 5 °C for seven days, colourless microcrystals were obtained (Scheme 5). Single crystal XRD analysis (Fig. 5) revealed a hydroxomagnesium cation [Me$_6$TREN-Mg-OH]$_2$[B(C$_6$H$_3$Cl$_2$)]$_2$ (**5**). To the best of our knowledge, there are no reports of hydroxomagnesium cations in the literature. The five-coordinate magnesium centre in **5** adopts a distorted trigonal bipyramidal geometry with O1–O1′–N1′ constituting the equatorial plane. The free arm of the ligand is



Scheme 5 Reactivity of **2b** with H_2O.



Scheme 6 Ligand transfer reaction of **2b** with KH.

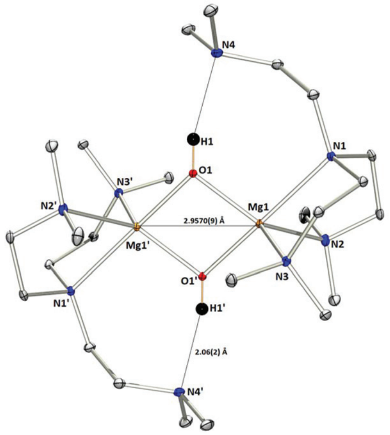


Fig. 5 Solid state structure of the cationic moiety of **5**. Hydrogen atoms except the hydroxyl groups have been omitted for clarity. Selected bond distances (Å) and angles (°): Mg1–N1 2.324(2), Mg1–N2 2.242(2), Mg1–N3 2.207(2), Mg1–O1 1.92(2), Mg1–O1′ 1.950(2), Mg1–Mg1′ 2.959(2), O1–Mg1–O1′ 81.05(7), Mg1–O1–Mg1′ 99.04(8), O1–Mg1–N1 175.17(8), O1–Mg1–N2 97.87(7), O1–Mg1–N3 103.96(8).

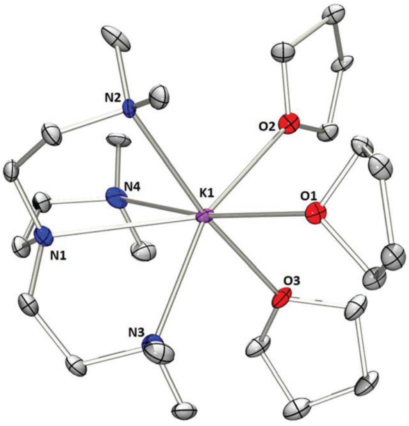


Fig. 6 Solid state structure of the cationic moiety of **6**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): K1–N1 2.988(16), K1–N2 2.932(13), K1–N3 2.919(17), K1–N4 2.877(15), K1–O1 2.754(13), K1–O2 2.915(11), K1–O3 2.932(13), K1–O3 2.830(15), O1–K1–N1 139.1(6), O1–K1–N4 157.6(6), O3–K1–N2 171.2(7), O2–K1–N3 163.9(6), N1–K1–N4 62.8(5).

effectively pulled towards the hydroxide group by hydrogen bonding as depicted in Fig. 5.

Attempted synthesis of magnesium hydride

Our interest in accessing hydridomagnesium cation prompted us to explore **1** and **2** as possible synthetic precursors. Initially, a THF solution of **1** was heated under reflux conditions for several days to check the possibility of the β-SiH migration to the magnesium centre. But the solution remained stable without exhibiting any reactivity. We further checked the reaction of **1** and **2** with H_2 as well as $PhSiH_3$ without any success. We then employed KH as a hydride source and carried out a reaction with **2b.** In contrast to our expectation of a molecular magnesium hydride, redistribution took place resulting in the precipitation of MgH_2. The filtered solution was found to contain $[Mg\{N(SiMe_3)_2\}_2]$ and $[(Me_6TREN)K(THF)_3][B(C_6H_3Cl_2)_4]$ (**6**, Scheme 6). Our search for molecular hydridomagnesium cations continues.

Compound **6** was characterised by NMR spectroscopy, single crystal XRD and elemental analysis. It is the first Me_6TREN stabilised potassium cation without any interaction with the anion. The potassium centre in **6** (Fig. 6) has a coordination number of seven and the average K–N distance is 2.929 Å similar to the ones found in $(Me_6TREN)KSiPh_3$,[48] $(Me_6TREN)KCH_2Ph$,[32] $(Me_6TREN)K(HBPh_3)$[41] and $\{Me_6TREN\}K\{BPh_3N(SiHMe_2)\}$.[49]

Conclusions

Me_6TREN supported amidomagnesium cations have been successfully prepared and well characterised. The variation in the coordination mode of Me_6TREN depending on the nitrogen substituents in the amide generates diverse reactivity which is manifested in the isolation of several cationic magnesium complexes. These cations can serve as precursors for further exploration in the chemistry of s-block elements.

Experimental

All reactions were performed under argon atmosphere using standard Schlenk techniques or in a glovebox under argon atmosphere. Prior to use, glasswares were dried at 200 °C and solvents were dried, distilled and degassed using standard methods.[50] Me_6TREN,[51] $[HNEt_3][B\{C_6H_3(CF_3)_2\}_4]$[52]

and [HNEt$_3$][B(C$_6$H$_3$Cl$_2$)$_4$]^{53} were synthesised according to the literature procedures. ([PhNMe$_2$H][B(C$_6$F$_5$)$_4$]), O$_2$ (99.990% purity) and CO$_2$ (99.990% purity) were purchased from commercial sources. The gases were passed through a column of molecular sieves dried overnight at 200 °C before performing the reaction. ^{1}H, ^{13}C, ^{11}B, ^{19}F and DEPT NMR spectra were recorded on a Bruker 500 MHz spectrometer. Chemical shifts (δ in ppm) in the ^{1}H and^{13}C NMR spectra were referenced to the residual signals of the deuterated solvents. ^{11}B NMR spectra were referenced to NaBH$_4$ signal in D$_2$O. ^{19}F spectra were referenced to CFCl$_3$ signal. Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintuplet), sext (sextet), sep (septet), br (broad). Samples for elemental analysis were rigorously dried *in vacuo* at 10^{-3} mbar pressure. Elemental analyses were performed on an Elemental Vario Micro Cube machine. Crystals were layered with paraffin oil before mounting on the X-ray diffractometer. X-ray diffraction data were collected on a Bruker Kappa Apex-II CCD diffractometer at 150 K and with Mo-Kα irradiation (λ = 0.71073 Å). Single crystal diffraction data for **1** (CCDC 1886056), **2a** (CCDC 1886061), **2b** (CCDC 1886062), **4** (CCDC1886058), **5** (CCDC 1886060), **6** (CCDC 1886059) and [(THF)$_6$Mg][B{C$_6$H$_3$Cl$_2$}$_4$]$_2$ (CCDC 1886412)† is reported in crystallographic information files (CIF) accompanying this document. Details on data collection, reduction and refinement can be found in the individual CIFs.

Synthesis of 1 [Me$_6$TREN-Mg-N(SiHMe$_2$)$_2$][B(C$_6$F$_5$)$_4$]

Me$_6$TREN (0.150 mL, 0.561 mmol) was added to [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (0.432 g, 0.561 mmol) in 5 mL of dry diethyl ether in a vial inside the glove box to form a clear solution. A solution of Mg[N(SiHMe$_2$)$_2$]$_2$ (0.161 g, 0.561 mmol) in 5 mL of dry diethyl ether was added slowly to the above solution and stirred at room temperature for 20 minutes. Colourless crystals were obtained in quantitative yield on layering the ether solution with *n*-hexane and storage at −30 °C. Anal. calc. for Mg$_1$B$_1$Si$_2$N$_5$F$_{20}$C$_{40}$H$_{44}$ (%): C – 45.07, H – 4.13, N – 6.57. Anal. found: (%): C – 44.89, H – 4.02, N – 6.45; ^{1}H NMR [500 MHz, 300 K, CD$_2$Cl$_2$]: δ (d, 0.20 ppm, 12H, MgN(SiH*Me*$_2$)$_2$), δ (s, 2.55 ppm, 18H, Me$_6$TREN-N(CH$_2$CH$_2$N*Me*$_2$)$_3$), δ (t, 2.64 ppm, 6H, Me$_6$TREN-N(CH$_2$C*H*$_2$NMe$_2$)$_3$), δ (t, 2.83 ppm, 6H, Me$_6$TREN-N(C*H*$_2$CH$_2$NMe$_2$)$_3$), δ (quin, 4.72 ppm, 2H, MgN(Si*H*Me$_2$)$_2$), δ (t, 1.14 ppm, residual Et$_2$O), δ (q, 3.43 ppm, residual Et$_2$O); ^{13}C NMR: δ (0.11 and 4.57 ppm, MgN(SiH*Me*$_2$)$_2$), δ (46.98 ppm, Me$_6$TREN-N(CH$_2$CH$_2$N*Me*$_2$)$_3$), δ (56.18 ppm, Me$_6$TREN-N(CH$_2$C*H*$_2$NMe$_2$)$_3$), δ (58.98 ppm, Me$_6$TREN-N(C*H*$_2$CH$_2$NMe$_2$)$_3$), δ (65.64 ppm, residual Et$_2$O), δ (15.07 ppm, residual Et$_2$O), δ (137.25 ppm, *ipso*-C), δ (149.13 ppm, *o*-CF), δ (147.22 ppm, *m*-CF), δ (139.18 ppm, *p*-CF); ^{19}F: δ (−133.03 ppm, *o*-C*F*), δ (−167.75 ppm, *m*-C*F*), δ (−163.58 ppm, *p*-C*F*); ^{11}B: δ (s, −13.50 ppm, B(C$_6$F$_5$)$_4$).

Synthesis of 2a [Me$_6$TREN-Mg-N(SiMe$_3$)$_2$][B{C$_6$H$_3$(CF$_3$)$_2$}$_4$]

Me$_6$TREN (0.1 mL, 0.36 mmol) was added to [HNEt$_3$][B{C$_6$H$_3$(CF$_3$)$_2$}$_4$] (0.360 g, 0.36 mmol) in 1 mL of dry diethyl ether inside the glove box to form a clear colourless solution. A solution of Mg[N(SiMe$_3$)$_2$]$_2$ (0.129 g, 0.36 mmol) in 1 mL of dry diethyl ether was added slowly to the above solution and stirred well for a few minutes. The colourless solution was then layered with dry *n*-hexane and stored at −30 °C inside the glove box. Colourless crystals were obtained after four days in quantitative yield. Anal. calc. for Mg$_1$B$_1$Si$_2$N$_5$F$_{24}$C$_{50}$H$_{66}$ (%): C – 46.77, H – 5.14, N – 5.46. Anal. found: (%): C – 46.71, H – 5.01, N – 5.32; ^{1}H NMR [500 MHz, 300 K, THF(D8)]: δ (d, 0.05 ppm, 18H, MgN(Si*Me*$_3$)$_2$), δ (m, 2.15–2.65 ppm, 30H, Me$_6$Tren-N(C*H*$_2$C*H*$_2$N*Me*$_2$)$_3$), δ (s, 7.58 ppm, 4H, *p*-C*H*), δ (s, 7.79 ppm, 8H, *o*-C*H*); ^{13}C NMR: δ (−2.20, 0.89, 1.82 ppm, MgN(Si*Me*$_3$)$_2$), δ (41.40 ppm, Me$_6$TREN-N(CH$_2$CH$_2$N*Me*$_2$)$_3$), δ (54.39 ppm, Me$_6$TREN-N(CH$_2$C*H*$_2$NMe$_2$)$_3$), δ (49.63 ppm, Me$_6$TREN-N(C*H*$_2$CH$_2$NMe$_2$)$_3$), δ (158.13 ppm, *ipso*-C), δ (130.72 ppm, *o*-CH), δ (125.28 ppm, *m*-C(CF$_3$)), δ (113.31 ppm, *p*-CH); δ (119.56 ppm, CF$_3$) ^{19}F: δ (−65.26 ppm, *m*-CF$_3$); ^{11}B: δ (s, −8.37 ppm, B(C$_6$H$_3$(CF$_3$)$_2$)$_4$).

Synthesis of 2b [Me$_6$TREN-Mg-N(SiMe$_3$)$_2$][B(C$_6$H$_3$Cl$_2$)$_4$]

Me$_6$TREN (0.05 mL, 0.18 mmol) was added to [HNEt$_3$][B(C$_6$H$_3$Cl$_2$)$_4$] (0.125 g, 0.18 mmol) in 20 mL of dry diethyl ether in a solvent bulb inside the glove box to form an insoluble solution. A solution of Mg[N(SiMe$_3$)$_2$]$_2$ (0.064 g, 0.18 mmol) in 5 mL of dry diethyl ether was added slowly to the above solution and stirred well at 60 °C for 12 hours or until the formation of a clear solution. Colourless blocks of crystals were obtained in quantitative yield on storing the solution at −30 °C. On scaling up the reaction, the final product precipitates from the solution and can be used as such for further experiments after washing it with dry *n*-hexane and drying *in vacuo*. Anal. calc. for Mg$_1$B$_1$Si$_2$N$_5$Cl$_8$C$_{42}$H$_{66}$ (%): C – 49.66, H – 6.50, N – 6.90. Anal. found: (%): C – 49.52, H – 6.41, N – 6.84; ^{1}H NMR [500 MHz, 300 K, THF(D8)]: δ (s, 0.04 ppm, 18H MgN(Si*Me*$_3$)$_2$), δ (m, 2.15–2.63 ppm, 30H, Me$_6$TREN-N(C*H*$_2$C*H*$_2$N*Me*$_2$)$_3$), δ (s, 7.03 ppm, 8H, *o*-C*H*), δ (s, 6.98 ppm, 4H, *p*-C*H*); ^{13}C NMR: δ (45.29 ppm, Me$_6$TREN-N (CH$_2$CH$_2$N*Me*$_2$)$_3$), δ (53.52 ppm, Me$_6$TREN-N(CH$_2$C*H*$_2$NMe$_2$)$_3$), δ (58.28 ppm, Me$_6$TREN-N(C*H*$_2$CH$_2$NMe$_2$)$_3$), δ (1.69 and 4.83 ppm, MgN(Si*Me*$_3$)$_2$), δ (164.44 ppm, *ipso*-C), δ (133.12 ppm, *o*-CH), δ (132.86 ppm, *m*-C(Cl)), δ (122.86 ppm, *p*-CH); ^{11}B: δ (s, −6.9 ppm, B(C$_6$H$_3$Cl$_2$)$_4$).

Synthesis of 3 [Me$_6$TREN-Mg-N[Si(OCHPh$_2$)Me$_2$]$_2$][B(C$_6$F$_5$)$_4$]

Crystals of **1** [Me$_6$TREN-Mg-N(SiHMe$_2$)$_2$][B(C$_6$F$_5$)$_4$] (0.100 g, 0.094 mmol) and Ph$_2$C═O (0.034 g, 0.188 mmol) were taken in a vial and 3 mL of THF was added to it. The solution was allowed to stir for 12 hours. After washing with n-hexane the resultant precipitate was stored in the glovebox. ^{1}H NMR [500 MHz, 300 K, THF(D8)]: δ (s, −0.04 ppm, 12H, Mg-N[Si(OCHPh$_2$)*Me*$_2$]$_2$), δ (m, 2.40–2.95 ppm, 30H, Me$_6$TREN), δ (s, 5.90 ppm, 2H, Mg-N[Si(OC*H*Ph$_2$)Me$_2$]$_2$), δ (m, 0.85–2.15 ppm, residual *n*-hexane), δ (m, 7.13–7.39 ppm, 20H, Mg-N[Si(OCHP*h*$_2$)Me$_2$]$_2$); ^{13}C NMR: δ (77.01 ppm, Mg-N[Si(O*C*HPh$_2$)*Me*$_2$]$_2$); ^{19}F: δ (−132.71 ppm, *o*-C*F*), δ (−168.42 ppm, *m*-C*F*), δ (−164.91 ppm, *p*-C*F*).

Synthesis of 4 $[\mathrm{Me_6TREN\text{-}Mg\text{-}OSiMe_3}][\mathrm{B(C_6H_3Cl_2)_4}]$

Crystals of **2b** $[\mathrm{Me_6TREN\text{-}Mg\text{-}N(SiMe_3)_2}][\mathrm{B(C_6H_3Cl_2)_4}]$ (0.050 g, 0.050 mmol) were dissolved in THF in a reaction flask and pressurised with carbon dioxide (1 atm) at 0 °C which was slowly raised to room temperature. The solution was stirred for 12 hours. Upon layering the THF solution with pentane and storage at −25 °C colourless crystals were obtained with quantitative yield. Anal. calc. for $\mathrm{Mg_1B_1O_1Si_1N_4Cl_8C_{39}H_{57}}$ (%): C – 49.58, H – 6.04, N – 5.93. Anal. found: (%): C – 49.49, H – 5.94, N – 5.82. ^{1}H NMR [500 MHz, 300 K, THF(D8)]: δ (s, −0.04 ppm, 9H, $\mathrm{Mg\text{-}OSi}\mathit{Me}_3$), δ (s, 2.45 ppm, 18H, $\mathrm{Me_6TREN\text{-}N(CH_2CH_2N}\mathit{Me}_2)_3$), (s, 2.68 ppm, 6H, $\mathrm{Me_6TREN\text{-}N(CH_2C}\mathit{H}_2\mathrm{NMe_2)_3}$), (s, 2.76 ppm, 6H, $\mathrm{Me_6TREN\text{-}N(C}\mathit{H}_2\mathrm{CH_2NMe_2)_3}$), δ (s, 6.98 ppm, 4H, *p*-C*H*), δ (s, 7.04 ppm, 8H, *o*-C*H*); ^{13}C NMR: δ (44.82 ppm, $\mathrm{Me_6TREN\text{-}N(CH_2CH_2N}\mathit{Me}_2)_3$), δ (49.35 ppm, $\mathrm{Me_6TREN\text{-}N(CH_2C}\mathit{H}_2\mathrm{NMe_2)_3}$), δ (54.95 ppm, $\mathrm{Me_6TREN\text{-}N(C}\mathit{H}_2\mathrm{CH_2NMe_2)_3}$), δ (3.43 ppm, $\mathrm{Mg\text{-}OSi}\mathit{Me}_3$), δ (164.83 ppm, *ipso*-C), δ (133.11 ppm, *o*-CH), δ (132.79 ppm, *m*-C(Cl)), δ (122.86 ppm, *p*-CH);^{11}B: δ (s, −6.9 ppm, $\mathrm{B(C_6H_3Cl_2)_4}$).

Synthesis of 5 $[\mathrm{Me_6TREN\text{-}Mg\text{-}OH}]_2[\mathrm{B(C_6H_3Cl_2)_4}]_2$

25 mL of dry THF was condensed on to the crystals of **2b** $[\mathrm{Me_6TREN\text{-}Mg\text{-}N(SiMe_3)_2}][\mathrm{B(C_6H_3Cl_2)_4}]$ (0.050 g, 0.050 mmol) in a 100 mL Schlenk flask. 30 mL of dry THF (contaminated with 1 µL of degassed water) was added dropwise to the above solution at −25 °C using an additional funnel. After stirring for a few minutes the solution was concentrated to 25 mL and kept for crystallisation in the in the refrigerator at 5 °C. Colourless crystals were obtained after one week. Anal. calc. for $\mathrm{Mg_2B_2O_2N_8Cl_{16}C_{72}H_{98}}$ (%): C – 49.54, H – 5.62, N – 6.42. Anal. found: (%): C – 49.38, H – 5.54, N – 6.31; ^{1}H NMR [500 MHz, 300 K, THF(D8)]: δ (s, 2.47 ppm, 18H, $\mathrm{Me_6TREN\text{-}N(CH_2CH_2N}\mathit{Me}_2)_3$), δ (s, 2.66 ppm, 6H, $\mathrm{Me_6TREN\text{-}N(CH_2C}\mathit{H}_2\mathrm{NMe_2)_3}$), δ (s, 2.72 ppm, 6H, $\mathrm{Me_6TREN\text{-}N(C}\mathit{H}_2\mathrm{CH_2NMe_2)_3}$), δ (quin, 6.96 ppm, 8H, *o*-C*H*), δ (t, 7.03 ppm, *p*-C*H*).

Synthesis of 6 $[\mathrm{Me_6TREN\text{-}K\text{-}(THF)_3}][\mathrm{B(C_6H_3Cl_2)_4}]_2$

Crystals of **2b** $[\mathrm{Me_6TREN\text{-}Mg\text{-}N(SiMe_3)_2}][\mathrm{B(C_6H_3Cl_2)_4}]$ (0.050 g, 0.050 mmol) were dissolved in THF and excess KH (0.008 g, 0.195 mmol) was added to it. The turbid solution was stirred at room temperature for 2 days. The solution was filtered and the resultant yellow filtrate was dried and dry diethyl ether was added to it. The solution was filtered and the filtrate was kept for crystallisation after layering with hexane at −25 °C. Colourless crystals were obtained in quantitative yield after 2 days. Anal. calc. for $\mathrm{K_1B_1O_3N_4Cl_8C_{48}H_{72}}$ (%): C – 53.04, H – 6.63, N – 5.16. Anal. found: (%): C – 52.95, H – 6.55, N – 5.11; ^{1}H NMR [500 MHz, 300 K, THF(D8)]: δ (s, 2.15 ppm, 18H, $\mathrm{Me_6TREN\text{-}N(CH_2CH_2N}\mathit{Me}_2)_3$), δ (t, 2.30 ppm, 6H, $\mathrm{Me_6TREN\text{-}N(CH_2C}\mathit{H}_2\mathrm{NMe_2)_3}$), δ (t, 2.55 ppm, 6H, $\mathrm{Me_6TREN\text{-}N(C}\mathit{H}_2\mathrm{CH_2NMe_2)_3}$), δ (quin, 6.96 ppm 8H, *o*-C*H*($\mathrm{BAr_4^{Cl}}$)), δ (t, 7.03 ppm, 4H, *p*-C*H*($\mathrm{BAr_4^{Cl}}$)).

Conflicts of interest

There are no conflicts to declare.

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