Probing the metallating ability of a polybasic sodium alkylmagnesiate supported by a bulky bis(amido) ligand: deprotomagnesiation reactions of nitrogen-based aromatic substrates

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Experimental Section

General Procedure. All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. THF and hexane, purchased from Sigma Aldrich, were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^{1}H, and 100.62 MHz for ^{13}C{^{1}H}. BuNa was prepared by reaction of equimolar amounts of ^{n}BuLi and NaO^{t}Bu in hexane according to the literature method.[1] 2,6-diisopropyl aniline was dried with CaH_2 and distilled under argon at reduced pressure prior to use. $\{Ph_2Si(NHAr^*)_2\}$ and $[\{Na(THF)_6\}^+\{(Ph_2Si(NAr^*)_2)Mg(Bu)(THF)\}^-]$ (**1**) were prepared following our previously described method.[9] Elemental analyses were attempted using a Perkin Elmer 2400 elemental analyzer; however, due to the extreme air-sensitivity of the compounds, satisfactory analyses could not be obtained. Owing to the traces of **5** present in the crystalline sample of **3**, elemental analysis values for this compound did not match the theoretical values.

X-ray crystallography. Crystallographic data were collected at 123(2) K on Oxford Diffraction diffractometers with Mo Kα (λ = 0.71073 Å) radiation. Structures were solved using SHELXS-97,[2] and refined to convergence on F^2 against all independent reflections by the full-matrix least-squares method using the SHELXL-97 program.[2] The structure of **3** contained non-metal-bound disordered THF. The SQUEEZE routine implemented from within the program PLATON[3] was used to model this. A total of 44 electrons were estimated in a volume of 345 Å^3. This corresponds to approximately 1 THF molecule per unit cell. **3** also contained three further THF groups that were modelled as disordered, each over two sites. Appropriate restraints on bond lengths and displacement parameters were required to give chemically sensible values. Four disordered THF molecules were

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[1] W. Bauer, C. Schade and P. v. R. Schleyer, *J. Organomet. Chem.*, 1985, **295**, C25.
[2] G. M. Sheldrick, *Acta Crystallogr.*, 2007, **A64**, 112.
[3] A. L. Spek, *Acta Crystallogr.*, 2009, **D65**, 148

similarly treated in the model of structure **4**. Selected crystallographic data are presented in Table S1 in the ESI and full details in cif format are available from the CCDC (CCDC 960101-960103). These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Selected crystallographic and refinement parameters.

	2	**3**	**4**[a]
empirical formula	$C_{128}H_{182}Mg_2N_8Na_2O_{10}Si_2$	$C_{56}H_{77}MgN_4NaO_3Si$	$C_{92}H_{145}MgN_4NaO_8Si$
M_r	2143.60	926.61	1510.51
crystal system	monoclinic	monoclinic	monoclinic
space group	P 2_1/c	P 2_1/c	P 2_1/n
T(K)	150(2)	123(2)	123(2)
a [Å]	19.3321(10)	10.4287(6)	11.0261(7)
b [Å]	17.1557(8)	38.3533(18)	18.0103(11)
c [Å]	19.9580(11)	14.3444(7)	44.259(2)
β [°]	113.694(6)	104.314(5)	94.473(6)
V [$Å^3$]	6061.2(5)	5559.3(5)	8762.4(9)
Z	2	4	4
ρ_{calcd} [g cm^{-3}]	1.175	1.111	1.145
reflns measured	41345	39077	-[a]
unique reflns	12833	13477	38363
observed reflns	4767	9627	17297
R_{int}	0.0921	0.0410	-[a]
GooF	0.767	1.055	1.048
R [on F, obs rflns only]	0.0533	0.0665	0.1028
wR [on F^2, all data]	0.1275	0.1707	0.3128
Largest diff. peak/hole [$eÅ^{-3}$]	0.476/-0.281	0.604/-0.357	0.782/-0.426

[a] After initial refinement, the program Rotax suggested the presence of twinning for **4**. A matrix corresponding to a 180 ° rotation about 1 0 0 was applied to give a new hklf5 formatted dataset. Refinement against this dataset improved the fit of the model. A batch scale factor for the ratio of the twin components refined to 0.1716(15).[4]

Synthesis of [(THF)$_2$NaMg(NC$_4$H$_4$)$_3$] (5). Pyrrole (0.21 ml, 3 mmol) was added to a solution of sodium magnesiate **1** (1.14 g, 1 mmol) in hexane (3 mL), affording a suspension which was stirred at room temperature for one hour affording a white suspension. THF (6 ml) was introduced and the suspension gently heated until all the solid was dissolved affording a pale yellow solution. The resulting solution was transferred to the freezer (-30°C) and colourless crystals were obtained after 24 hours. Compound **5** was isolated as a colourless crystalline solid in a 49% yield (0.19 g).[5] ^{1}H NMR (D$_8$-THF, 298K) δ 6.91 [s, 6H, α-CH, Mg-NC$_4$H$_4$], 6.01 [s, 6H, β-CH, Mg-NC$_4$$H_4$], 3.62 [m, 8H, O-C$H_2$, THF], 1.78 [m, 8H, C$H_2$, THF]. ^{13}C{^{1}H} NMR (C_6D_6, 298K) 127.8 [α-CH, MgNC$_4$H$_4$], 107.7 [β-CH, MgNC$_4$H$_4$], 68.1 [O-CH$_2$,THF], 26.1 [CH$_2$,THF].

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[4] Rotax, R. I. Cooper; R. O. Gould; S. Parsons; D. J. Watkin, *J. Appl. Cryst.*, 2005, *35*, 168.

[5] Compound **5** was isolated as a crystalline solid along with trace amounts of bis(amine) $Ph_2Si(NHAr^*)_2$ which is the byproduct resulting from the reaction of **1** with 3 molar equivalents of pyrrole. ^{1}H NMR integration indicated that this impurity is present in an approximately 5%.

Table S2: ^{1}H and ^{13}C NMR chemical shifts (δ in ppm) for free pyrrole and pyrrolyl ligands in compounds **3** and **5** in C_6D_6 solution.

Compound	δ(^{1}H) *α*-H	δ(^{1}H) *β*-H	δ(^{13}C) *α*-CH	δ(^{13}C) *β*-CH
pyrrole	6.37	6.31	117.5	108.4
3	6.50	6.13	136.6	128.5
5	7.69	6.61	127.8[a]	107.7[a]

[a] ^{13}C NMR spectrum recorded in deuterated THF due to the low solubility of **5** in C_6D_6.

Reactions of [{Na(THF)$_6$}$^+${(Ph$_2$Si(NAr*)$_2$)Mg(Bu)(THF)}$^-$] (1) with 2,6-diisopropylaniline

(a) Reaction of 1 with 3 equivalents of NH$_2$Ar*: Synthesis of [{Na(THF)$_6$}$^+${Mg(NHAr*)$_3$}$^-$] (7). 2,6-diisopropylaniline (0.57 mL, 3 mmol) was added to a solution of sodium magnesiate **1** (1.14 g, 1 mmol) in hexane (5 mL), affording a colourless solution which was allowed to stir at room temperature for 1 hour. Approximately half of the volume was removed *in vacuo*. The resulting yellow solution was transferred to the freezer at -28ºC. A crop of colourless crystals of Ph$_2$Si(NHAr*)$_2$ was formed after 48 hours which were isolated by filtration and analyzed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. ^{1}H NMR (C_6D_6, 298 K) δ7.71 [m, 4H, Ph], 7.12 [m, 6H, Ph], 7.05 [m, 6H, Ar*], 3.51 [s, 2H, N*H*], 3.38 [m, 4H, C*H*, ^{i}Pr, Ar*], 1.00 [d, 24H, CH_3, ^{i}Pr, Ar*]. ^{13}C{^{1}H} NMR (C_6D_6, 298K) δ145.2, 138.7, 136.3, [$C_{\text{quarternay}}$, Ph and Ar*], 136.0, 135.9, 129.8, 123.9, 123.5 [*C*H, Ph and Ar*], 23.4 [*C*H, ^{i}Pr, Ar*], 29.1 [*C*H$_3$, ^{i}Pr, Ar*]. The volatiles from the filtrate solution were removed under vacuum affording **7** as a colourless oil which was characterised by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR (C_6D_6, 298K) δ 7.02 [d, 6H, Ar*], 6.56 [t, 3H, Ar*], 3.54 [m, 6H, CH, ^{i}Pr, Ar*], 3.25 (s, 3H, N*H*), 3.14 [m, 24H, OCH_2, THF], 1.30 [d, 36H, CH_3, ^{i}Pr, Ar*], 1.55 [m, 24H, CH_2, THF] ^{13}C{^{1}H} NMR (C_6D_6, 298K) δ 154.2, 142.7, 135.4 [C quarternary, Ar*], 132.3, 123.7, 112.4 [*C*H, Ar*], 68.2 [O*C*H$_2$,THF], 28.1 [*C*H, ^{i}Pr, Ar*], 25.3 [*C*H$_2$, THF], 23.9 [*C*H$_3$, ^{i}Pr, Ar*].

(b) Reaction of 1 with 1 equivalent of NH$_2$Ar*: Formation of [{Na(THF)$_6$}$^+${(Ph$_2$Si(NAr*)$_2$)Mg(NHAr*)(THF)}$^-$] (6.) Sodium magnesiate **1** (0.29 g, 0.25 mmol) was charged in an NMR tube and 0.5 mL of C_6D_6 were added affording a colourless solution. NH$_2$Ar* (47 µL, 0.25 mmol) were introduced and the solution was allowed to rest at room temperature for 15 minutes. ^{1}H NMR of the solution showed the almost quantitative formation of **6** along with some trace amounts of **4** (see Figure S1b). ^{1}H NMR (C_6D_6, 298K) δ 7.71 [d, 4H, Ar], 7.18 [d, 4H, Ar], 7.07 [m, 6H, Ar], 6.61[t, 1H, NHAr*], 3.91 [m, 4H, CH, ^{i}Pr, Ar*], 3.34 [m, 24H, OCH_2, THF], 3.22 (s, 1H, N*H*Ar*), 3.15 (m, 2H, , CH, ^{i}Pr, Ar*], 1.19 [bs, 36H,THF and CH_3, ^{i}Pr, Ar*], 1.11 [bs, 24H, CH_3, ^{i}Pr, Ar*].^{13}C{^{1}H} NMR (C_6D_6, 298K) δ 152.2, 142.6, 139.2, 135.9 [$C_{\text{quarternary}}$], 135.2 [*C*H, Ph], 132.1 [$C_{\text{quarternary}}$], 129.9, 127.8, 123.6, 123.5, 122.9, [*C*H, Ph and Ar*], 112.4 [*C*H, Ar*], 68.09 [O*C*H$_2$, THF], 31.80 [*C*H, ^{i}Pr, Ar*], 28.30 [*C*H, ^{i}Pr, Ar*], 25.24 [*C*H$_2$, THF], 23.88, 23.69 [*C*H$_3$, ^{i}Pr, Ar*]. Despite being a minor product in this reaction, after 24 hours a few colourless crystals of **4** deposited in the NMR tube which were used for an X-ray crystallographic study.

(c) Reaction of 1 with 2 equivalents of NH$_2$Ar*. Sodium magnesiate **1** (0.29 g, 0.25 mmol) was charged in an NMR tube and 0.5 mL of C_6D_6 were added affording a colourless solution. NH$_2$Ar* (94 µL, 0.50 mmol) were introduced and the solution was allowed to rest at room temperature for 15 minutes. ^{1}H NMR of the solution showed a complex mixture of products, comparison of this spectrum with those recorded for **6**, **7** and

$Ph_2Si(NHAr^*)_2$ (see Figure S1b and S2), revealed that these three species are present in solution along with some unreacted starting material **1**. Close inspection of the aromatic region between 7 and 6.5 ppm showed the presence of a third species containing NHAr* amido ligands, which was attributed to $[\{Na(THF)_6\}^+\{(Ph_2Si(NAr^*)(NHAr^*))Mg(NHAr^*)_2(THF)\}^-]$ (**4**) (Figure S1c and Figure S2). The same species is a minor component in the reaction mixture of **1** with 1 equivalent of NH_2Ar (Figure S1b). Although the ^1H spectrum of the 1:2 reaction is quite complicated, with significant overlapping of most of the signals, the resonances for the *para*-H of the NHAr* ligands are well resolved (see Figure S2) and their integration can be used to estimate the ratio present in solution of products **4**, **6** and **7**, showing that these three different amination products **4**, **6** and **7** are formed in a 1:2.1:1.1 ratio. Similarly, when the reaction of **1** was carried out using 1.5 equivalents of NH_2Ar^* (70 μL, 0.37 mmol) afforded a mixture of products where the single-amination product **6** was the major species present in solution (the **4**:**6**:**7** ratio was found to be 1.1:5:1, see Figure S1c). The complexity of these NMR spectra contrasts with the relatively straightforward spectra obtained when 3 equivalents of the aniline are employed, highlighting the difficulty to control the polybasic behaviour of butyl magnesiate **1** in the presence of substoichiometric amounts of the amine.

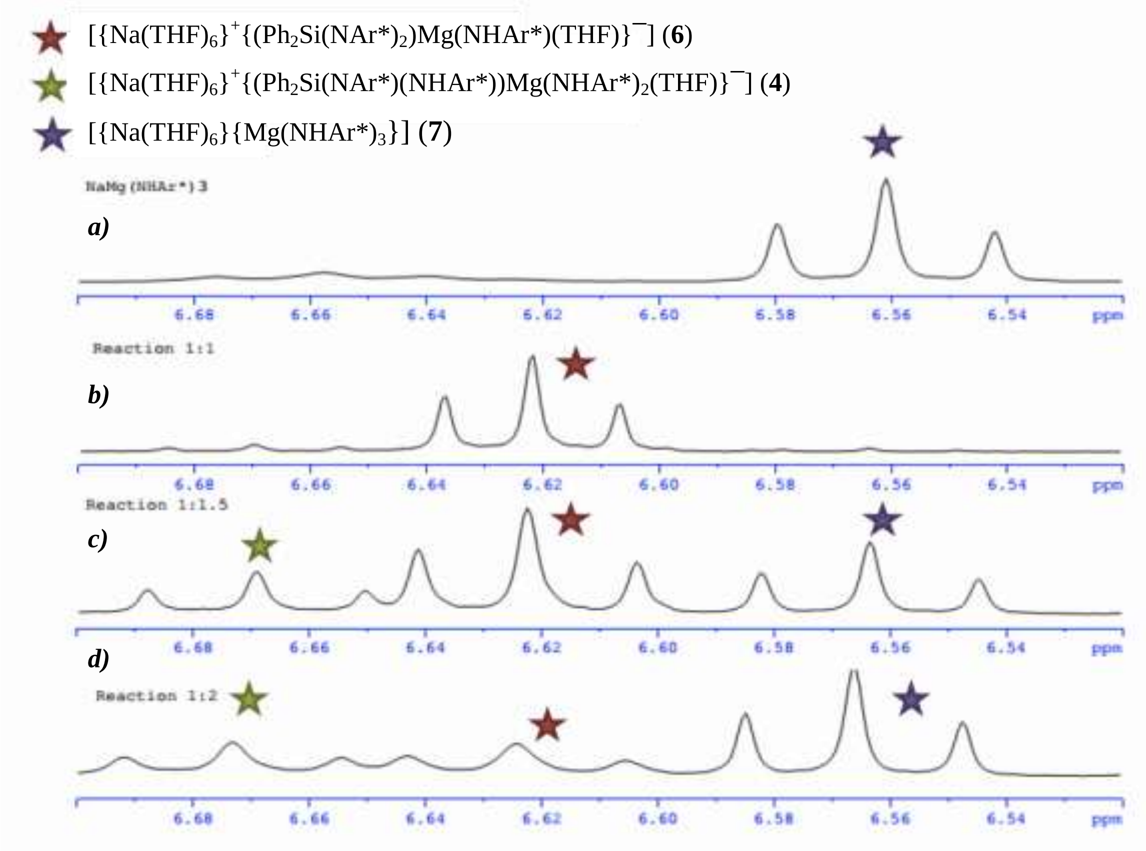


Figure S1. Comparison of the resonances for the *para*-H of the NHAr* amido ligands in the ^1H NMR spectra in deuterated benzene solutions of: a) isolated $[(THF)_4NaMg(NHAr^*)_3]$ (**7**); b) reaction of **1** with one equivalent of NH_2Ar; c) reaction of **1** with 1.5 equivalents of NH_2Ar^*; and d) reaction of **1** with 2 equivalents of NH_2Ar^*.

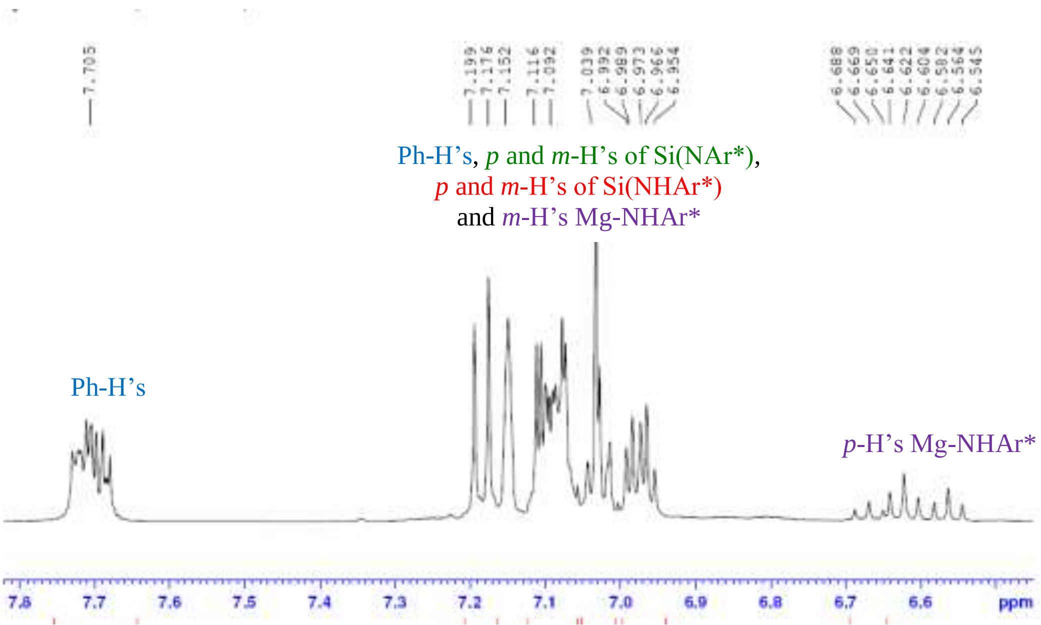
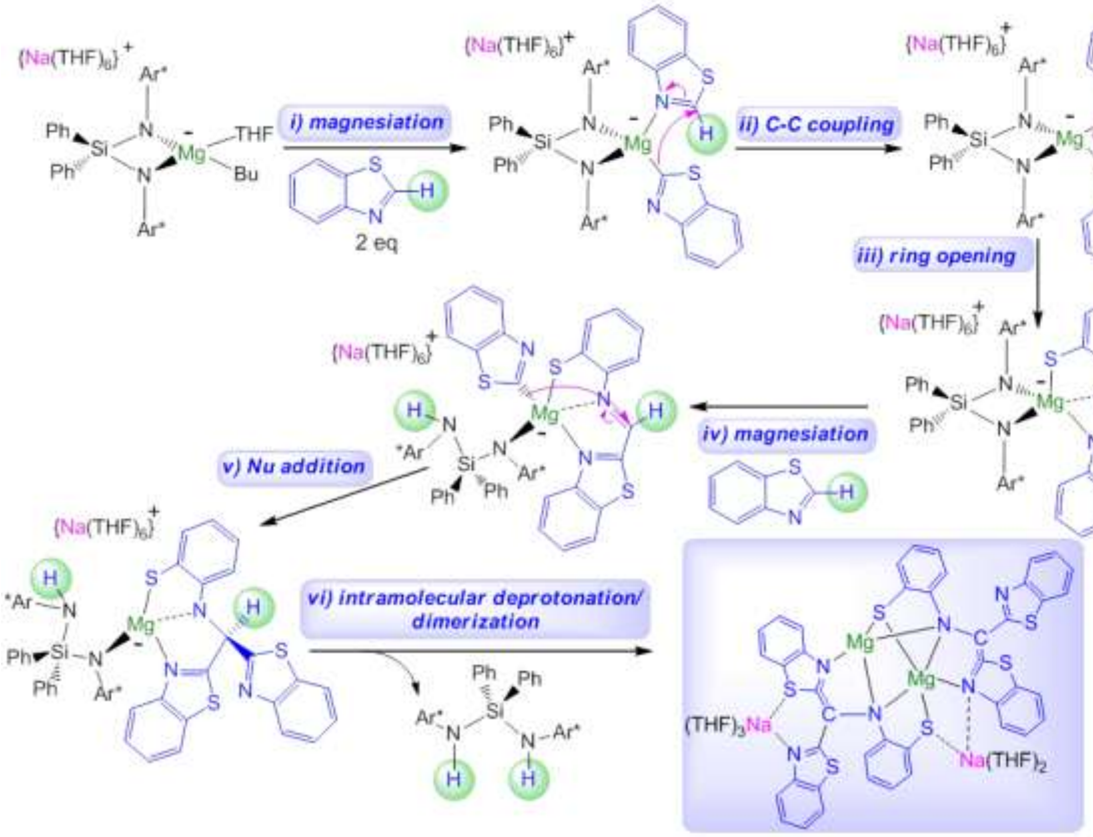


Figure S2. Expansion of the aromatic region of the ^{1}H NMR spectrum of the reaction of **1** with 2 equivalents of NH_2Ar^*in C_6D_6.



Scheme S1. Proposed mechanism for the formation of $[Na_2Mg_2(L1)_2(THF)_5]$ (solvating THF molecules on Mg are omitted for clarity).[6]

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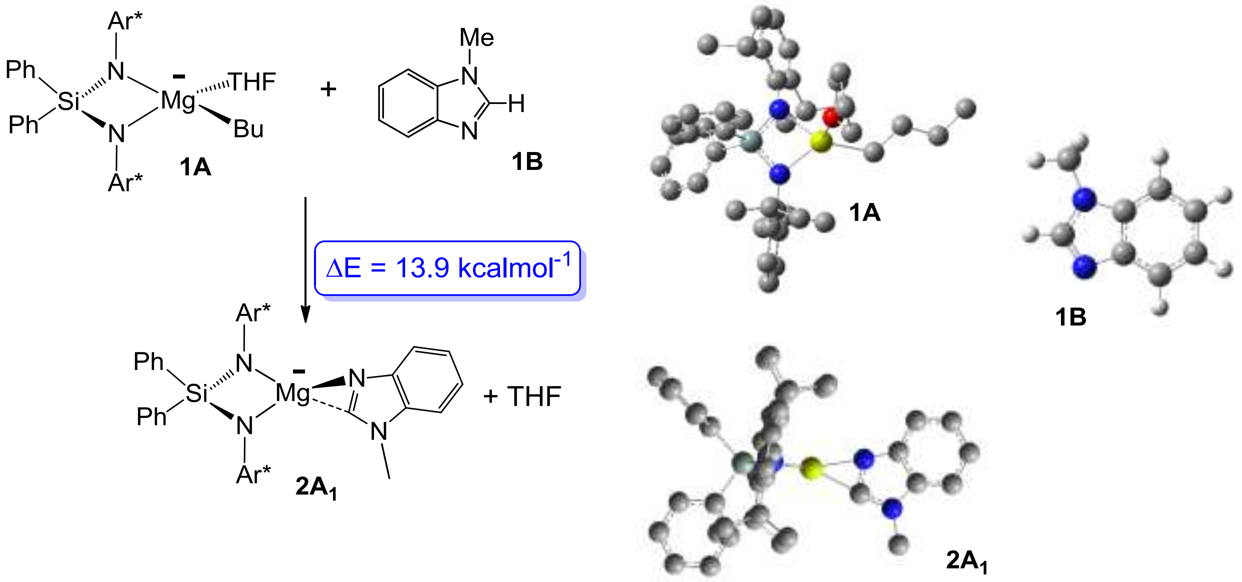
6. V. L. Blair, W. Clegg, A. R. Kennedy, Z. Livingstone. L. Russo, E. Hevia, *Angew. Chem*, *Int. Ed.* 2011, **50**, 9857.

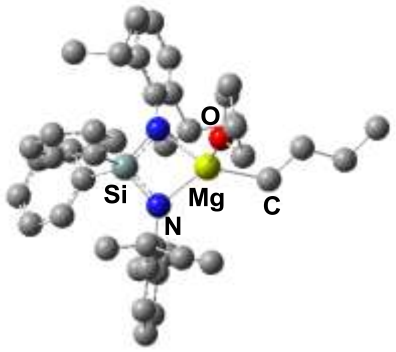
Computational Details

Density Functional Theory (DFT) calculations[7] were performed using the Gaussian computational package G03.[8] In this series of calculations the geometries of the molecules and ions were optimised by employing the B3LYP density functionals[9,10] and the 6-311G** basis set.[11,12]



Scheme S2: DFT study on the energy of the reaction of model systems **1A** and **1B** to afford **2A$_1$**

Geometry optimisation of 1A



(E = -2388.4409237 a.u.)

Principal bond lengths (Å)

Mg-O	2.223
Mg-C	2.173
Mg-N	2.119 2.081
N-Si	1.727 1.724

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[7]. W. Kohn, A. D. Becke and R.G. Parr, J. Phys. Chem., **1996**, *100*, 12974.

[8]. Gaussian 03, Revision B.0.5, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

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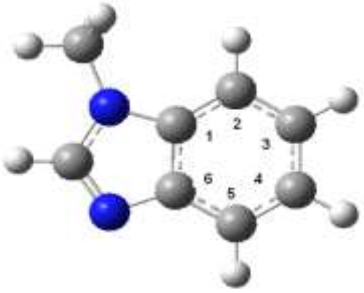
[11]. A. D. McLean and G. S. Chandler, J. Chem. Phys., **1980**, 72, 5639.

[12]. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, J. Chem. Phys., **1980**, *72*, 650.

Geometry optimisation of 1B

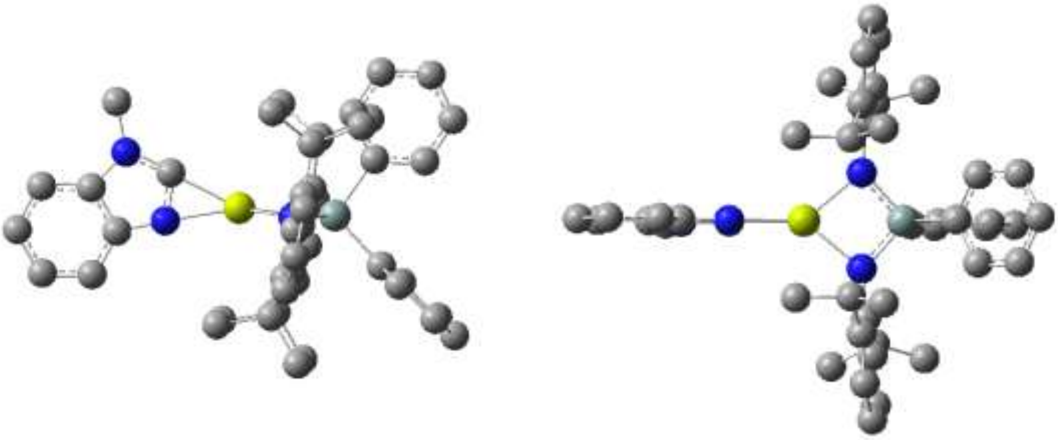


(E = -419.2809335 a.u.)

Principal bond lengths (Å)

N_{Me}-C_{Me}	1.449	N_{Me}-C	1.378
N_{Me}-C_1	1.384	N-C	1.305
N-C_6	1.387	C_1-C_2	1.395
C_2-C_3	1.390	C_3-C_4	1.407
C_4-C_5	1.389	C_5-C_6	1.398
C_1-C_6	1.415		

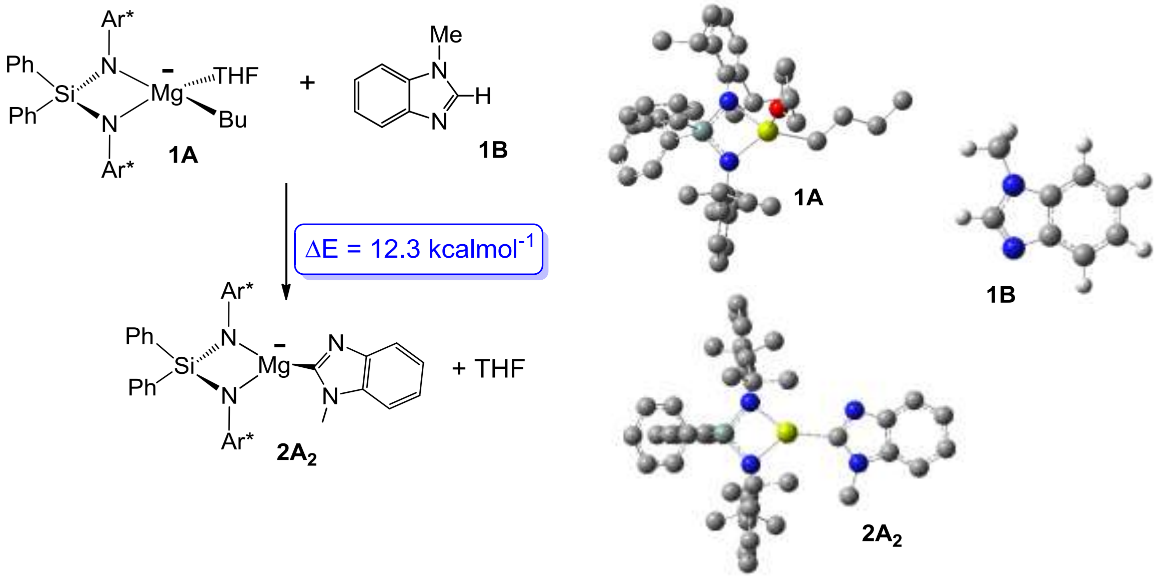
Geometry optimisation of $2A_1$



(E = -2416.7252498 a.u.)

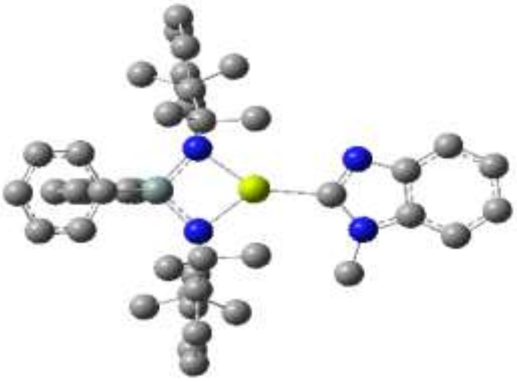
Principal bond lengths (Å) and angles (°)

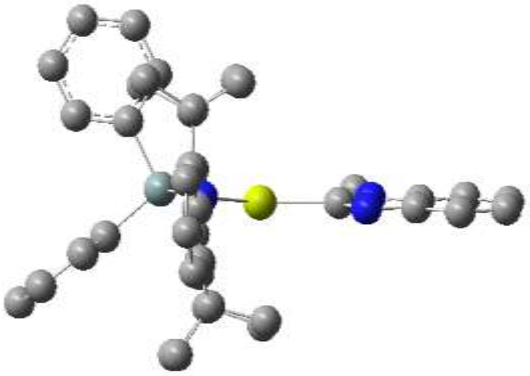
Inner 3-membered ring		*Inner 4-membered ring*		
N-C	1.354	N-Mg	2.044	2.044
N-Mg	2.099	Si-Mg	1.729	1.729
C-Mg	2.163	N-Mg-N	79.4	
C-N-Mg	74.1	N-Si-N	98.1	
N-Mg-C	37.0	Mg-N-Si	90.8	90.8
Mg-C-N	68.9			



Scheme S3: DFT study on the energy of the reaction of model systems **1A** and **1B** to afford **$2A_2$**

Geometry optimisation of $2A_2$





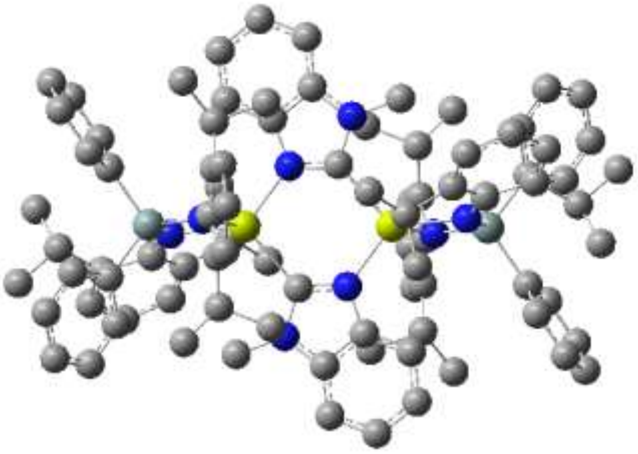
(E = -2416.7228618 a.u.)

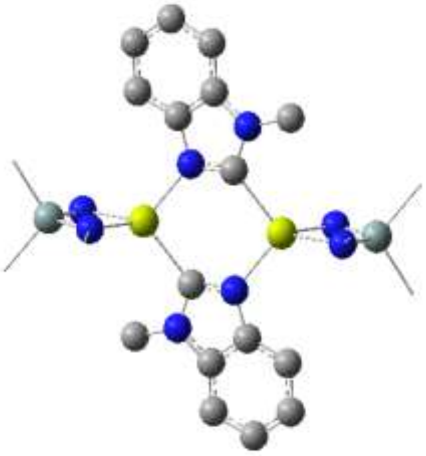
Principal bond lengths (Å) and angles (º)

Inner 4-membered ring		
N-Mg	2.040	2.024
Si-Mg	1.733	1.731
N-Mg-N	80.0	
N-Si-N	97.9	
Mg-N-Si	90.7	91.2

Mg-imidazolyl	
Mg-C	2.133
C-N	1.333
C-N_{Me}	1.400
Mg-C-N	117.5
Mg-C-N_{Me}	132.6
N-C-N_{Me}	109.9

Geometry optimisation of dianion 2B





(E = -4833.4144145 a.u.)

Principal bond lengths (Å) and angles (°)

Inner 6-membered ring		*Outer 4-membered rings*	
Mg-N	2.144	Mg-N	2.210 2.082
N-C	1.357	Si-N	1.721 1.741
Mg-C	2.270	N-Mg-N	76.4
C-Mg-N	100.8	Mg-C-N	117.5
Mg-N-C	125.2	Si-N-Mg	94.2 89.3
N-C-Mg	127.2		

Dimerization energy: When considering only the magnesiate anions, the dimerization process was found to be endothermic(**2A$_1$** → 0.5 **2B**; ΔE = +22.6 kcal mol^{-1}). However when taking into account the effect of the Na cations, into consideration, the reaction was found to be exothermic by 71.4 kcal mol^{-1}. This value was estimated using the resulting point energies of placing the Na cations 15 Å away from their anionic counterparts, using the Mg atoms as the origin. This approximation was made in order to simulate the solvent-separated ion-pair structure found experimentally for **2**