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Electronic Supporting Information

Complexity in Seemingly Simple Sodium Magnesiate Systems

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General Methods

All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane was dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. ^{n}BuNa was prepared according to the literature procedure.[1] Na(HMDS) and $^{n}Bu_2Mg$ were purchased from Sigma Aldrich Chemicals and used as received. TMCDA was prepared according to the literature procedure and distilled prior to use.[2] TMEDA was distilled over CaH_2 prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer. All ^{13}C NMR spectra were proton decoupled. 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.

Synthesis of [Na(μ-HMDS)$_2$Mg(^{n}Bu)]$_\infty$ (1). BuNa (2 mmol, 0.16 g) was added to a Schlenk tube under inert atmosphere, and suspended in 8 ml hexane, followed by 4 mmol HMDS(H) and allowed to stir for 1 hour. To this was added 2 ml (2 mmol) $^{n}Bu_2Mg$ (1M, in heptane), forming a slight white suspension after stirring. Addition of toluene (19 mmol, 2 mL) and gentle heating and subsequent slow cooling overnight in a hot water dewar afforded a large amount of colourless crystalline material (0.732 g, 81%). ^{1}H NMR (400.13 MHz, 298 K, C_6D_6): δ (ppm) 0.08 (2H, t, Mg-CH_2, Bu), 0.21 (36H, s, Si(CH_3)$_3$), 1.26 (3H, t, $^{3}J_{HH}$ = 7.2 Hz, CH_3, Bu), 1.79 (2H, m, CH_2, Bu), 2.05 (2H, m, CH_2, Bu). ^{13}C{^{1}H} NMR (100.62 MHz, 298K, C_6D_6): δ (ppm) 6.1 (Si(CH$_3$)$_3$), 12.1 (CH$_3$, Bu), 14.6 (Mg-CH$_2$, Bu), 32.2 (CH$_2$, Bu), 33.2 (CH$_2$, Bu).

Synthesis of [Na(TMEDA)$_2$]$^+$[Mg(HMDS)$_3$]$^-$ (2). To a suspension of **1** (0.5 g, 1.17 mmol) in hexane (10 mL), was added TMEDA (0.17 mL, 1.17 mmol). After stirring for 1 hour, the solution was heated giving a clear solution, and the Schlenck tube was slowly cooled overnight in a hot water dewar affording a large amount of colourless crystalline material

plus amorphous solid (0.28 g of 60 % pure **2**). ^{1}H NMR (400.13 MHz, 298 K, C_6D_{12}): δ (ppm) 0.13 (54H, s, Si(C*H*$_3$)$_3$), 2.25 (24H, s, N(C*H*$_3$)$_2$, TMEDA), 2.36 (8H, s, NC*H*$_2$, TMEDA). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C_6D_{12}): δ (ppm) 7.0 (Si(*C*H$_3$)$_3$), 45.8 (N(*C*H$_3$)$_2$, TMEDA), 57.5 (N*C*H$_2$, TMEDA). Only the NMR resonances corresponding to **2** are indicated.

Synthesis of [{(TMEDA)$_2$·Na}(μ-^{n}Bu)Mg(HMDS)$_2$] (4). To a suspension of **1** (0.5 g, 1.17 mmol) in hexane (10 mL), was added TMEDA (0.35 mL, 2.34 mmol). After stirring for 1 hour, the solution was heated giving a clear solution, and the Schlenck tube was slowly cooled down overnight in a hot water dewar affording a colourless crystalline material (0.13 g, 17%). ^{1}H NMR (400.13 MHz, 298 K, C_6D_6): δ (ppm) -0.63 (2H, m, Mg-C*H*$_2$, Bu), 0.40 (36H, s, Si(C*H*$_3$)$_3$), 1.17 (3H, t, $^3J_{HH}$ = 7.5 Hz, C*H*$_3$, Bu), 1.62-1.67 (2H, m, C*H*$_2$, Bu), 1.92 (26H, m, N(C*H*$_3$)$_2$, TMEDA and C*H*$_2$, Bu), 1.96 (8H, s, NC*H*$_2$, TMEDA). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C_6D_6): δ (ppm) 6.25 (Si(*C*H$_3$)$_3$), 6.76 (Mg-*C*H$_2$, Bu), 12.97 (*C*H$_3$, Bu), 14.26 (*C*H$_2$, Bu), 31.82 (*C*H$_2$, Bu), 45.72 (N(*C*H$_3$)$_2$, TMEDA), 57.43 (N*C*H$_2$, TMEDA).

Synthesis of [{Na(μ-HMDS)}$_2$Mg(μ-^{n}Bu)$_2$·(TMEDA)]$_\infty$ (5). To a suspension of Na(HMDS) (0.37 g, 2 mmol) in hexane (5 mL), ^{n}Bu$_2$Mg (1 mL of a 1 M solution in heptane, 1 mmol) was added to produce a slightly clear solution. At this stage TMEDA (0.12 mL, 1 mmol) was added. After stirring for 1 hour, the solution was heated giving a clear solution, and the Schlenck tube was transferred to the freezer (-30 °C). After 6 days colourless crystals suitable for X-ray diffraction deposited (0.25g, yield 43%). ^{1}H NMR (400.13 MHz, 298 K, C_6D_{12}): δ (ppm) -0.66 (4H, t, $^3J_{HH}$ = 8 Hz, Mg-C*H*$_2$, Bu), 0.07 (36H, s, Si(C*H*$_3$)$_3$), 0.91 (6H, t, $^3J_{HH}$ = 7.2 Hz, C*H*$_3$, Bu), 1.28-1.38 (4H, m, C*H*$_2$, Bu), 1.60-1.65 (4H, m, C*H*$_2$, Bu), 2.32 (12H, s, N(C*H*$_3$)$_2$, TMEDA), 2.40 (4H, s, NC*H*$_2$, TMEDA). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C_6D_{12}): δ (ppm) 5.73 (Si(*C*H$_3$)$_3$), 10.64 (Mg-*C*H$_2$, Bu), 13.91 (*C*H$_3$, Bu), 31.26 (*C*H$_2$, Bu), 32.02(*C*H$_2$, Bu), 46.10 (N(*C*H$_3$)$_2$, TMEDA), 57.56 (N*C*H$_2$, TMEDA).

Synthesis of [{Na(HMDS)}$_2$Mg(μ-^{n}Bu)$_2$·{(*R*,*R*)-TMCDA}]$_\infty$ **(6).** To a suspension of Na(HMDS) (0.37 g, 2 mmol) in hexane (5 mL), ^{n}Bu$_2$Mg (1 mL of a 1 M solution in heptane, 1 mmol) was added to produce a slightly clear solution. At this stage TMCDA (0.19 mL, 1

mmol) was added. After stirring for 1 hour, the solution was heated giving a clear solution, and the Schlenck tube was transferred to the freezer (-30 °C). After 2 days colourless crystals suitable for X-ray diffraction were deposited (0.45g, yield 66%). ^{1}H NMR (400.13 MHz, 298 K, C_6D_{12}): δ (ppm) -0.62 (2H, m, Mg-C*H*$_2$, Bu),0.07 (36H, s, Si(C*H*$_3$)$_3$), 0.90 (3H, t, $^3J_{HH}$ = 7.2 Hz, C*H*$_3$, Bu), 1.15-1.18 (4H, m, C*H*$_2$, TMCDA), 1.30-1.36 (4H, m, C*H*$_2$, Bu), 1.58-1.65 (4H, m, C*H*$_2$, Bu), 1.82-1.97 (m, 4H, C*H*$_2$, TMCDA), 2.35 (12H, s, N(C*H*$_3$)$_2$, TMCDA), 2.44 (2H, s, NC*H*$_2$, TMCDA). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C_6D_{12}): δ (ppm) 5.57 (Si(*C*H$_3$)$_3$), 8.31 (Mg-*C*H$_2$, Bu), 13.97 (*C*H$_3$, Bu), 21.33 (2x*C*H$_2$, TMCDA), 21.84 (*C*H$_2$, TMCDA), 24.58 (*C*H$_2$, TMCDA), 31.52 (*C*H$_2$, Bu), 32.80(*C*H$_2$, Bu), 44.45 (N(*C*H$_3$), TMCDA), 63.98 (N*C*H$_2$, TMCDA).

NMR Chemical Shits of Starting Materials in C_6D_6

Starting Material	^{1}H δ / ppm
Na(HMDS)	0.11 (SiC*H*$_3$)
Mg^{n}Bu$_2$	1.79-1.74 (4H, m, *Bu*), 1.58-1.50(4H, m, *Bu*), 1.25-1.03 (6H, m, *Bu*), 0.12--0.16 (4H, m, Mg-C*H*$_2$)
HMDS(H)	0.09 (SiC*H*$_3$)
TMEDA	2.35 (4H, s, C*H*$_2$), 2.12 (12H, s, C*H*$_3$)
Na(HMDS) + TMEDA	2.00 (4H, s, C*H*$_2$,TMEDA), 1.98 (12H, s, C*H*$_3$, TMEDA), 0.27 (18H, s, SiC*H*$_3$)
Mg^{n}Bu$_2$ + TMEDA	2.11-2.08 (4H, m, *Bu*), 2.07-1.80 (16H, m, *Bu* and C*H*$_3$, TMEDA), 1.57 (4H, br, C*H*$_2$,TMEDA), 1.33-1.30 (6H, m, *Bu*), -0.17--0.14 (4H, t, Mg-C*H*$_2$)

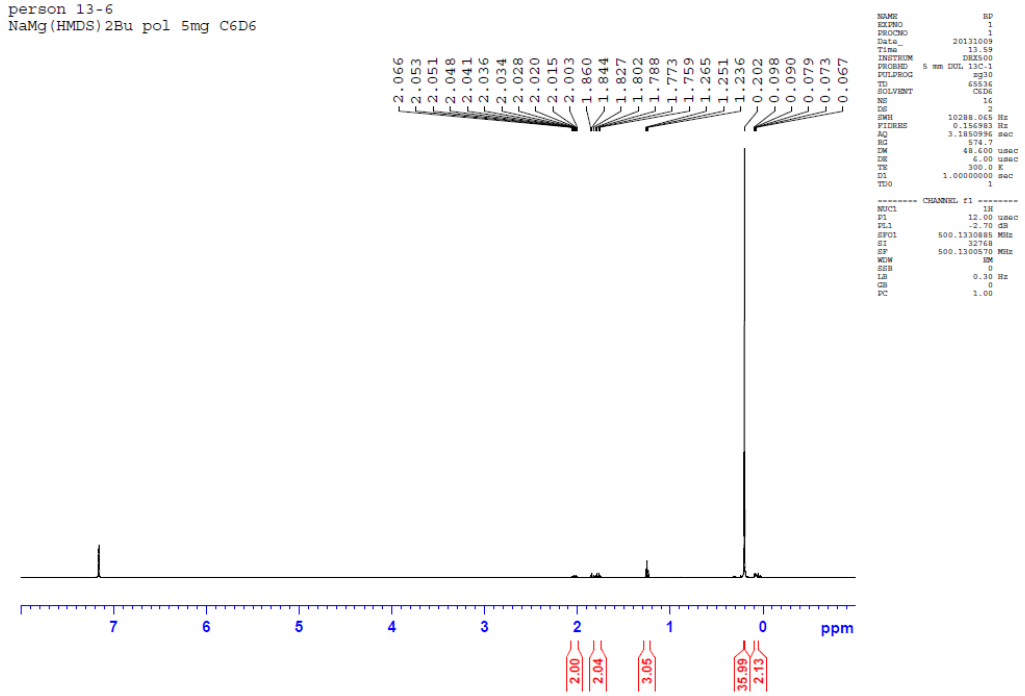

Figure S1. ^{1}H NMR of $[Na(\mu\text{-HMDS})_2Mg(^{n}Bu)]_\infty$ (**1**) in C_6D_6.

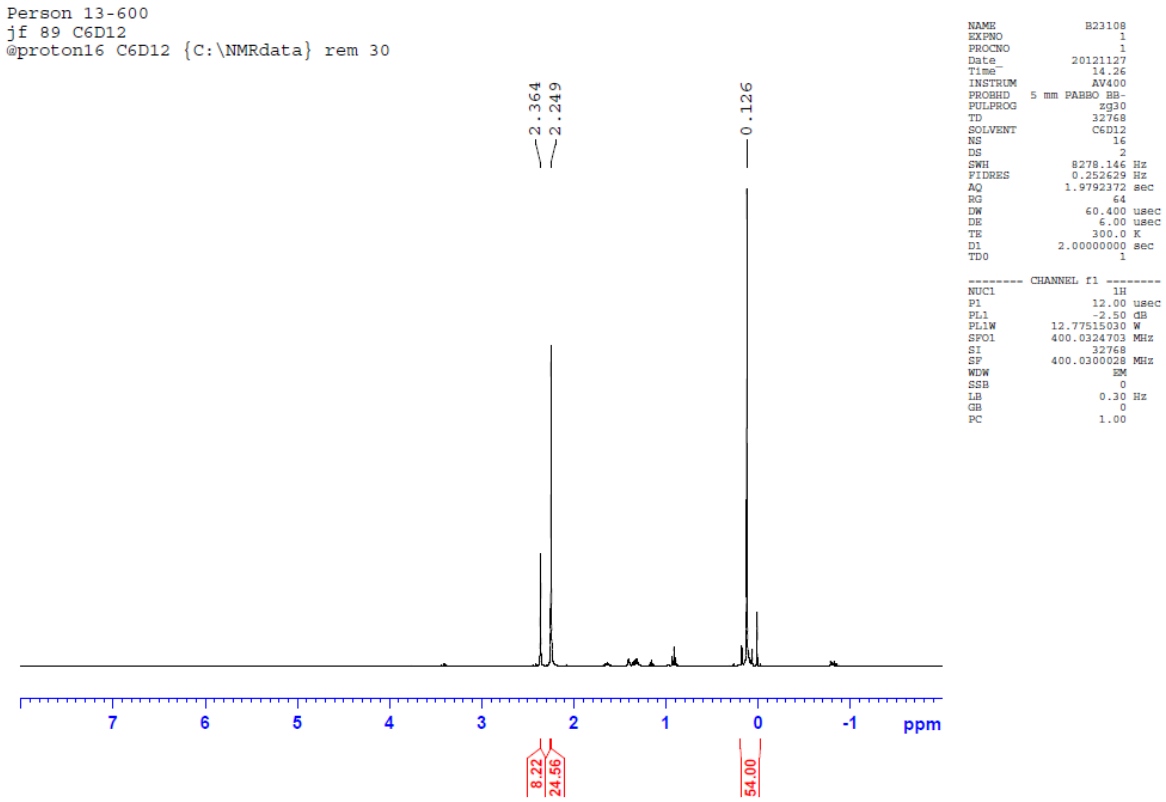

Figure S2. ^{1}H NMR of 60 % pure $[Na(TMEDA)_2]^{+}[Mg(HMDS)_3]^{-}$ (**2**) in C_6D_{12}.

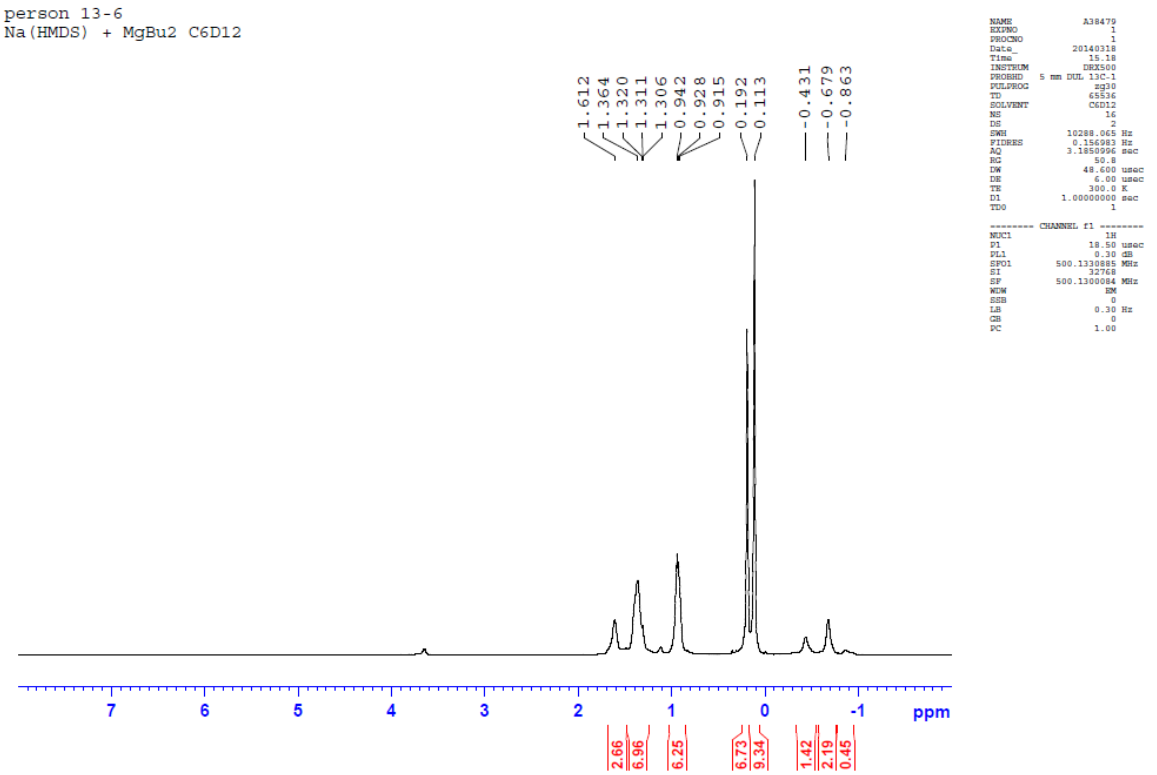

Figure S2b. ^{1}H NMR of a mixture of Na(HMDS) and $^{n}Bu_2Mg$ in C_6D_{12}.

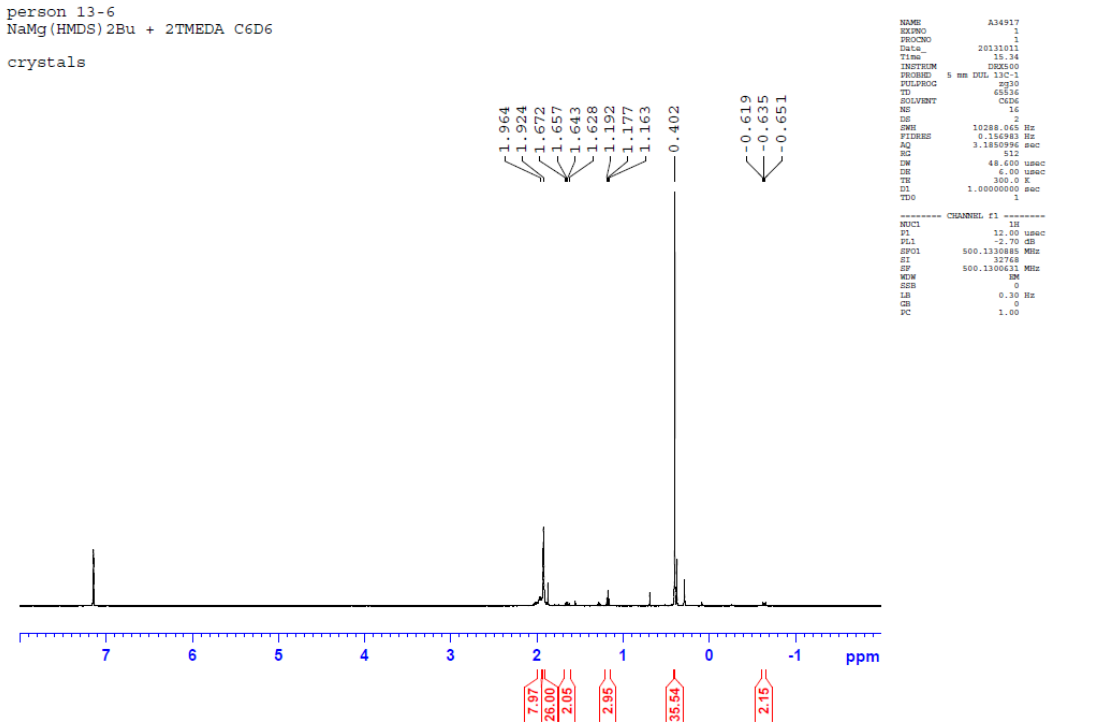

Figure S3. ^{1}H NMR of [{(TMEDA)$_2$·Na}(μ-^{n}Bu)Mg(HMDS)$_2$] (**4**) in C_6D_6.

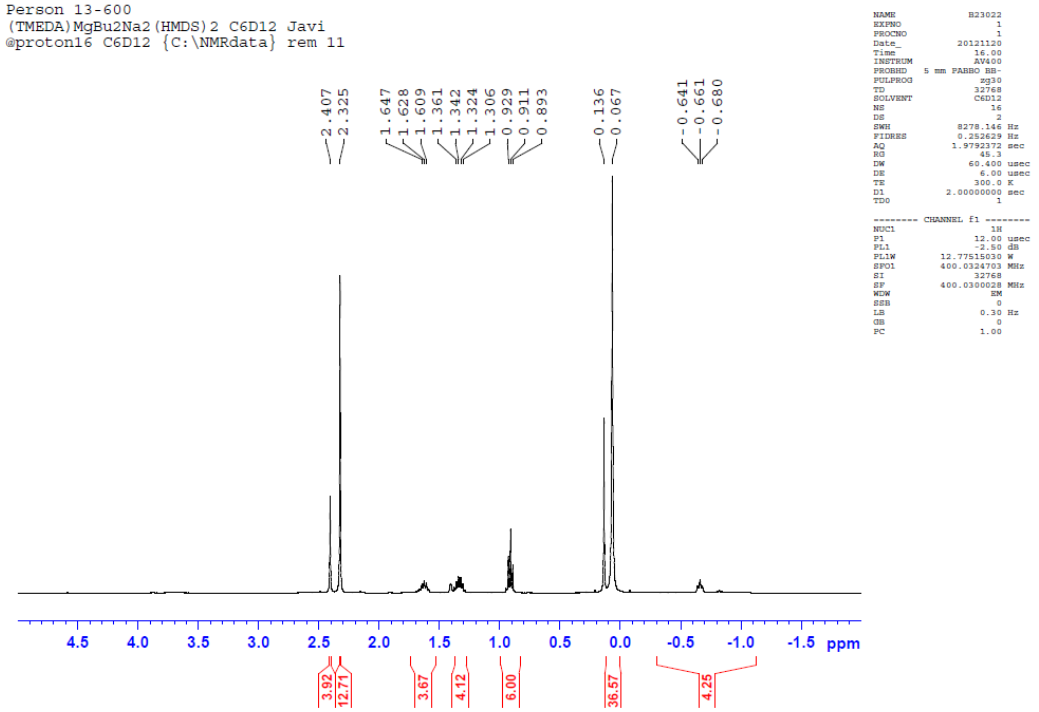

Figure S4. ^{1}H NMR of [{Na(μ-HMDS)}$_2$Mg(μ-^{n}Bu)$_2$·(TMEDA)]$_\infty$ (**5**) in C_6D_{12}.

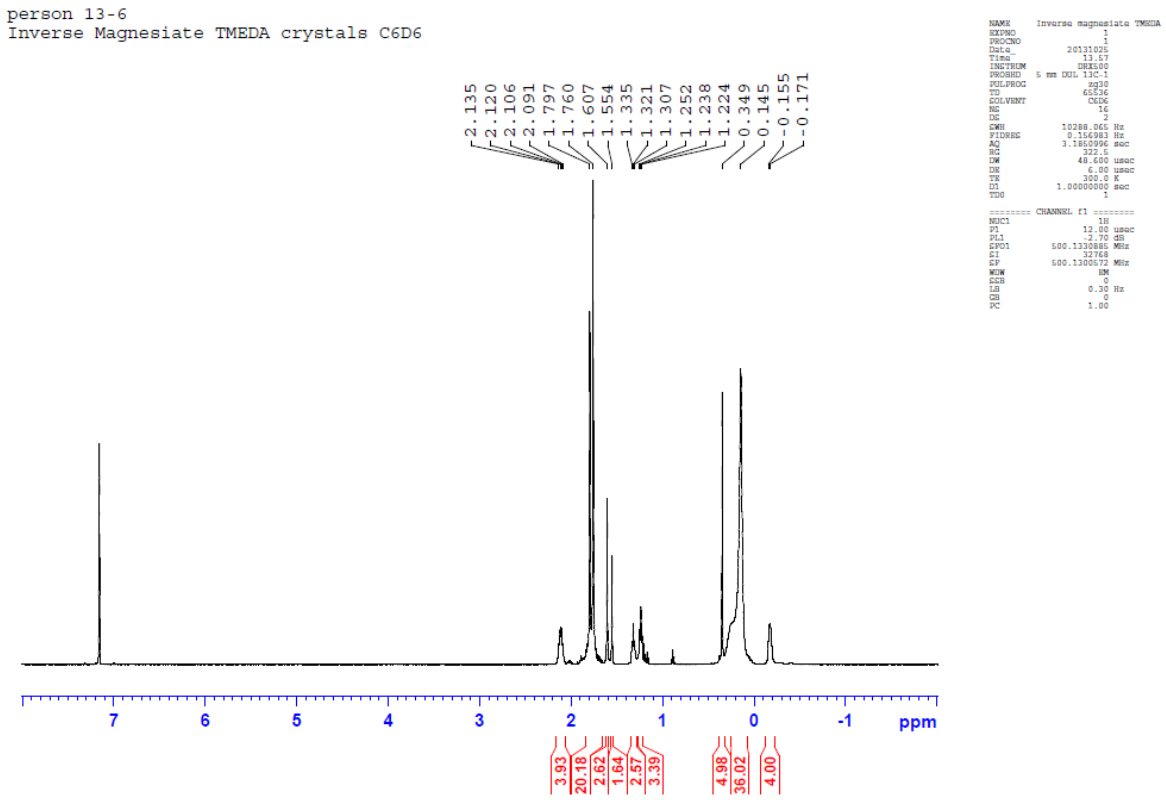

Figure S4b. ^{1}H NMR of [{Na(μ-HMDS)}$_2$Mg(μ-^{n}Bu)$_2$·(TMEDA)]$_\infty$ (**5**) in C_6D_6.

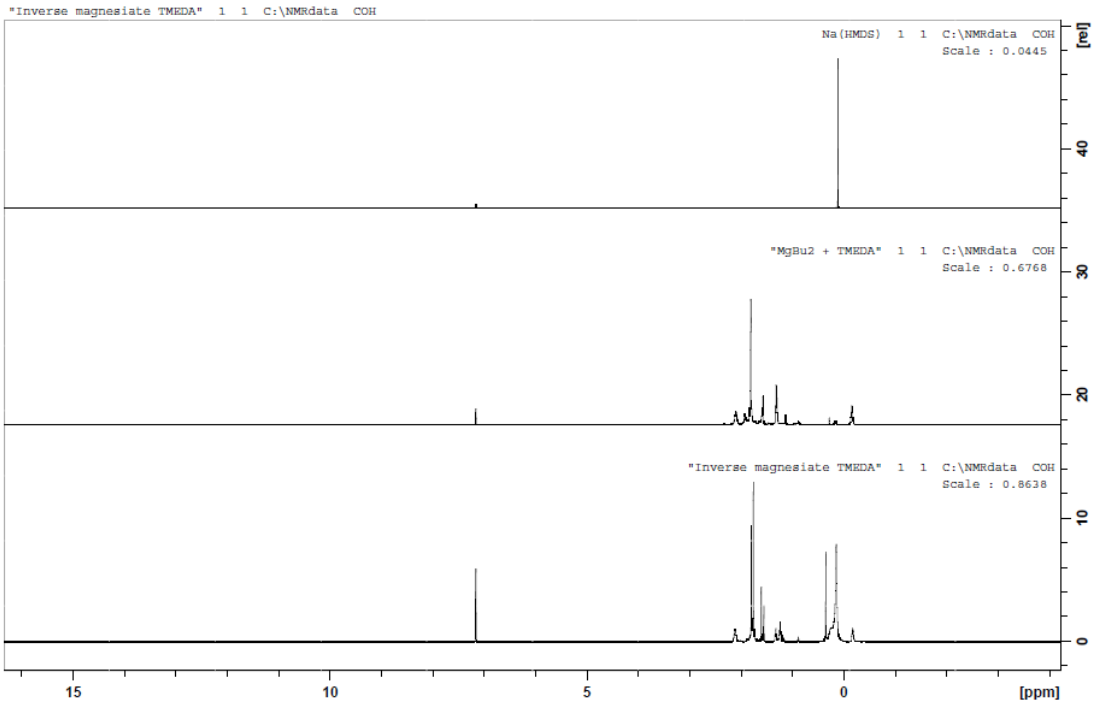

Figure S4c. ^{1}H NMR comparison of $[\{Na(\mu\text{-}HMDS)\}_2Mg(\mu\text{-}^nBu)_2\cdot(TMEDA)]_\infty$ (**5**) (bottom) with a mixture of $MgBu_2$ + TMEDA (middle) and Na(HMDS) (top) in C_6D_6.

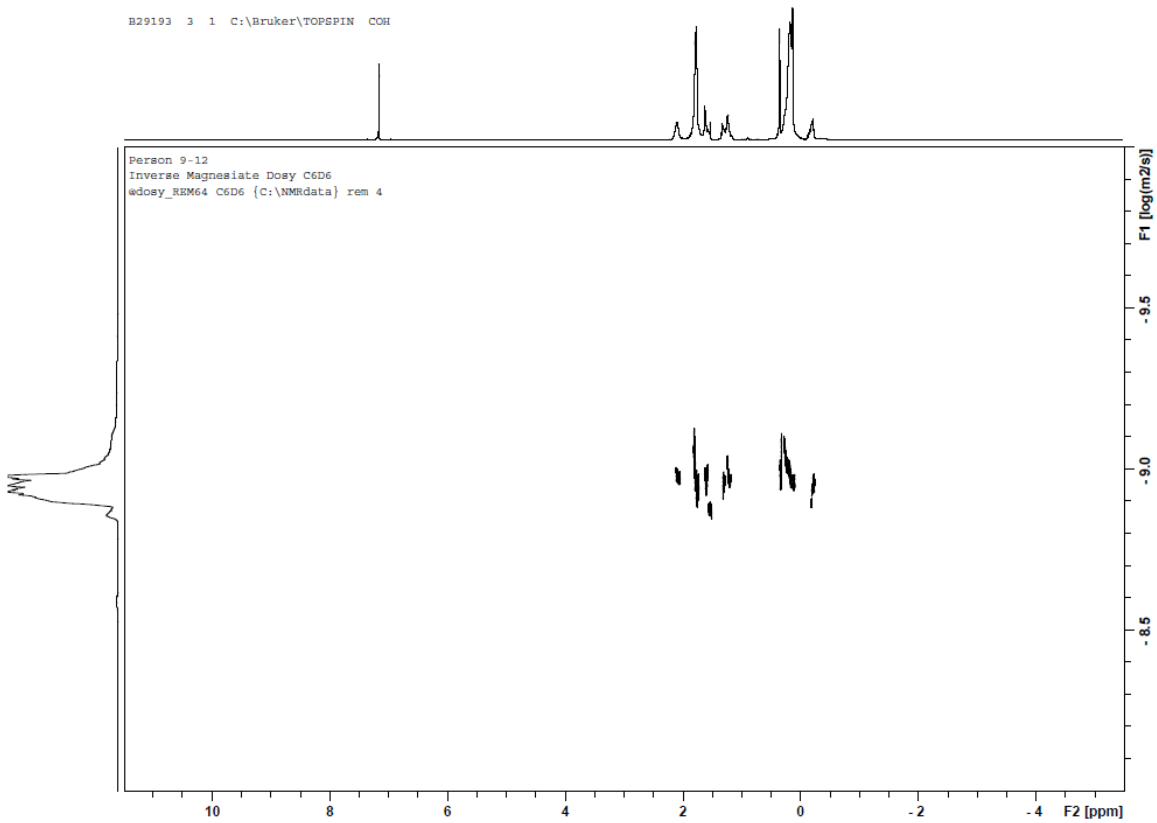

Figure S4d. ^{1}H DOSY NMR of $[\{Na(\mu\text{-}HMDS)\}_2Mg(\mu\text{-}^{n}Bu)_2\cdot(TMEDA)]_\infty$ (**5**) in C_6D_6.

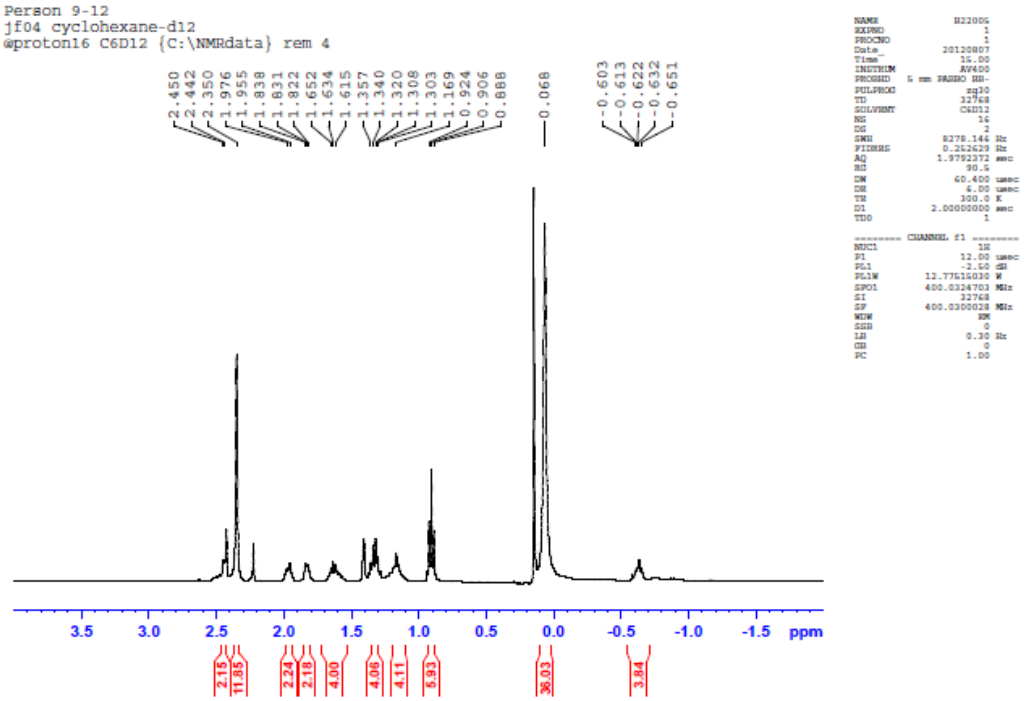

Figure S5. ^{1}H NMR of [{Na(HMDS)}$_2$Mg(μ-^{n}Bu)$_2$·{(*R*,*R*)-TMCDA}]$_\infty$ (**6**) in C_6D_{12}.

Table S1: Key crystallographic and refinement parameters for compounds **1-2**

	$[NaMg(^nBu)(HMDS)_2]$ (**1**)	$[Na(TMEDA)_2]^+[Mg(HMDS)_3]^-$ (**2**)
Empirical formula	$C_{16}H_{45}MgN_2NaSi_4$	$C_{30}H_{83}MgN_7NaSi_6$
Molecular Weight	425.20	757.87
Temperature (K)	123.0	123.0
Wavelenght (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P\,2_1/n$	P-1
a (Å)	9.2943(2)	11.8176(10)
b (Å)	20.5586(5)	11.9680(11)
c (Å)	13.8977(3)	18.4164(16)
α (°)		94.913(7)
β (°)	96.463(2)	99.478(7)
γ (°)		103.922(8)
Cell volume (Å^3)	2638.67(10)	2472.2(4)
Z	4	2
ρ_{calc} (g.cm^{-3})	1.070	1.018
μ (mm^{-1})	0.269	0.216
Index ranges	-9<=h<=12 -25<=k<=27 -18<=l<=18	-15<=h<=16 -16<=k<=16 -25<=l<=25
2θmax (°)	59.42	58.00
Reflections collected	16297	24497
Reflections unique	6593	13120
|Reflections obs [I>2σ(I)]	5257	7499
R_{int}	0.0271	0.0438
No. Parameters	238	454
Goodnes of fit on F^2 (GOF)	1.087	0.864
Final R indices [I>2σ(I)]	R1 = 0.0486 wR2 = 0.1126	R1 = 0.0467 wR2 = 0.0944
R indices (all data)	R1 = 0.0671 wR2 = 0.1217	R1 = 0.0927 wR2 = 0.1015
Largest diff. peak and hole (e Å^{-3})	0.896 and -0.527	0.585 and -0.296

Table S2: Key crystallographic and refinement parameters for compounds **4-5**

	$[(TMEDA)_2Na(^nBu)Mg(HMDS)_2]$ (**4**)	$[\{(TMEDA)Na_2(^nBu)_2Mg(HMDS)_2\}_\infty]$ (**5**)
Empirical formula	C_{28} H_{77} Mg N_6 Na Si_4	C_{26} H_{70} Mg N_4 Na_2 Si_4
Molecular Weight	657.62	621.51
Temperature (K)	123.0	123.0
Wavelenght (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*P n a* 2_1	*P* 2_1 / *n*
a (Å)	39.1203(11)	9.2182(2)
b (Å)	8.7705(3)	22.7925(6)
c (Å)	25.6241(7)	19.7071(5)
β (°)		93.215(2)
Cell volume ($Å^3$)	8791.7(5)	4134.06(18)
Z	8	4
ρ_{calc} ($g.cm^{-3}$)	0.994	0.999
μ (mm^{-1})	0.183	0.199
Index ranges	-48<=h<=47 -10<=k<=11 -28<=l<=34	-11<=h<=10 -29<=k<=29 -25<=l<=25
2θmax (°)	57.78	55.00
Reflections collected	32190	25085
Reflections unique	16630	9466
|Reflections obs [I>2σ(I)]	13362	6276
R_{int}	0.0407	0.0438
No. Parameters	838	419
Goodnes of fit on F^2 (*GOF*)	1.076	1.016
Final *R* indices [I>2σ(I)]	R1 = 0.0652 wR2 = 0.1235	R1 = 0.0501 wR2 = 0.1064
R indices (all data)	R1 = 0.0838 wR2 = 0.1322	R1 = 0.0919 wR2 = 0.1223
Largest diff. peak and hole (e $Å^{-3}$)	0.365 and -0.444	0.374 and -0.350
Flack	0.01(10)	

Table S3: Key crystallographic and refinement parameters for compound **6**

	$[\{(TMCDA)Na_2(^nBu)_2Mg(HMDS)_2\}_\infty]$ (**6**)
Empirical formula	$C_{30}\ H_{76}\ Mg\ N_4\ Na_2\ Si_4$
Molecular Weight	675.60
Temperature (K)	123.0
Wavelenght (Å)	0.71073
Crystal system	Tetragonal
Space group	$P\ 4_2\ 2_1\ 2$
$a = b$ (Å)	23.5623(5)
c (Å)	15.9256(5)
Cell volume (Å^3)	8841.6(4)
Z	8
ρ_{calc} (g.cm^{-3})	1.015
μ (mm^{-1})	0.191
Index ranges	-31<=h<=31 -31<=k<=18 -21<=l<=21
2θmax (°)	57.98
Reflections collected	52309
Reflections unique	11587
|Reflections obs [I>2σ(I)]	8277
R_{int}	0.0709
No. Parameters	404
Goodnes-of-fit-on F^2 (*GOF*)	1.033
Final R indices [I>2σ(I)]	R1 = 0.0598 wR2 = 0.1073
R indices (all data)	R1 = 0.0987 wR2 = 0.1222
Largest diff. peak and hole (e Å^{-3})	0.507 and -0.268
Flack	-0.13(12)

1. C. Schade, W. Bauer and P. v. R. Schleyer, *J. Organomet. Chem.*, 1985, **295**, C25-C28.
2. J.-C. Kizirian, N. Cabello, L. Pinchard, J.-C. Caille and A. Alexakis, Tetrahedron, 2005, **61**, 8939.