Electronic Supplemental Information

Low-Nuclearity Magnesium Hydride Complexes Stabilized by N-Heterocyclic Carbenes

Lucas A. Freeman,^a Jacob E. Walley,^a Diane A. Dickie,^a Robert J. Gilliard, Jr*^a

Department of Chemistry, University of Virginia, 409 McCormick Rd. / PO Box 400319, Charlottesville, VA 22904 *Correspondence Email: rjg8s@virginia.edu

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Experimental Procedures

General Considerations - All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques or a MBRAUN LABmaster glovebox operating at <0.1 ppm H₂O and O_2 and equipped with a -39 °C freezer. All reaction solvents were distilled over sodium/benzophenone. Deuterated solvents were purchased Cambridge Isotope Laboratories dried over sodium/benzophenone or Na/K alloy. Glassware was oven-dried at 190 °C overnight. The NMR spectra were recorded at room temperature on a Bruker Avance 600 MHz (¹H: 600.13 MHz, ¹³C: 150.90 MHz). Proton and carbon chemical shifts are reported in ppm and are referenced using the residual proton and carbon signals of the deuterated solvent (¹H; C₆D₆, δ 7.16, ¹³C; C₆D₆, δ 128.06). Solid-state FTIR spectra were recorded on an Agilent Cary 630 FT-IR equipped with a diamond ATR unit in an argon-filled glovebox. Crystallographic data for 1-5 are summarized in Table S1. Satisfactory elemental analysis results could not be obtained for new compounds. Problems with determining the purity of group 2 compounds using elemental analysis are well documented. Because of the extreme air and moisture sensitivity associated with these compounds, they were unable to survive the shipping, handling, and sample preparation associated with the process. Bulk purity of samples was instead assessed by a combination of ¹H and ¹³C NMR, and the FTIR data were obtained for each compound. Phenylsilane (PhSiH₃) was purchased from Millipore Sigma and used as received. Free I¹Pr^{Me2} was prepared according to a literature procedure and recrystallized from *n*-hexane prior to use.¹

Synthesis of $[Mg(N(SiMe_3)_2)_2]_2$ - Hexamethyldisilazane (25 mL, 120 mmol) was added to a 250 mL Schlenk round-bottomed flask fitted with a reflux condenser. To this flask, a 1.0 M solution of di-*n*-butylmagnesium (60 mL, 60 mmol) was added slowly at RT. The resulting solution was stirred vigorously and heated to 75 °C for 3 d. All volatiles were removed under vacuum at 40 °C (to remove as much unreacted amine and heptane as possible) until a sticky white solid was obtained. The solid was redissolved in minimal *n*-hexane and kept at –39 °C, yielding the product as a highly pure, completely colorless crystalline solid. Further reduction in volume and recrystallization of the supernatant was necessary to retrieve remaining product (13.455 g, 65%). ¹H NMR (600 MHz, C₆D₆) δ 0.45 (s, 36H), 0.37 (s, 36H).

Synthesis of $[Mg(N[SiMe_2(CH_2)]_2)_2]_2$, (1) – Compound 1 was prepared via a similar procedure to $[Mg(N(SiMe_3)_2)_2]_2$, using 2 eq of HN[SiMe_2(CH_2)]_2)_2 (10 mL, 52.83 mmol). The product was obtained after recrystallization from hexane at –39 °C as a colorless crystalline solid. Further reduction in volume and recrystallization of the supernatant was necessary to retrieve remaining product (6.296 g, 70%). ¹H NMR (600 MHz, C₆D₆) δ 0.95 (s, 8H, Si(CH_3)₂(CH₂)₂), 0.81 (s, 8H, Si(CH₃)₂(CH₂)₂), 0.36 (s, 24H, Si(CH₃)₂(CH₂)₂) 0.32 (s, 24H, Si(CH₃)₂(CH₂)₂); ¹³C NMR (150.90 MHz, C₆D₆) δ 12.0, 10.0, 5.8, 5.2. m.p.: 138-140 °C.

Synthesis of $(I^{i}Pr^{Me2})Mg(HMDS)_2$ (2) - Crystalline IⁱPr^{Me2} (0.523 g, 2.9 mmol) and Mg(HMDS)_2 (1.000 g, 2.9 mmol) were combined in a 100 mL Schlenk round-bottomed flask, dissolved in a minimal amount of *n*-hexane (approx. 40 mL), yielding a colorless solution which was stirred for 16 h at RT. All volatiles were removed under vacuum and the resulting solids collected, yielding the product (1.305 g, 86% yield) as a bright white free-flowing powder. ¹H NMR (600 MHz, C₆D₆) δ 5.25 (hept, 2H, (CH₃)₂CH), 1.49 (s, 6H, C_{backbone}(CH₃)), 1.23 (d, 12H, (CH₃)CH), 0.29 (s, 36H, Si(CH₃)₃); ¹³C NMR (150.90 MHz, C₆D₆) δ 179.7 (C_{carbene}), 125.5, 53.0, 22.4, 10.0, 6.5. m.p.: 116-118 °C.

Synthesis of $(I^{i}Pr^{Me2})Mg(ASCP)_{2}$ (3) - Crystalline IⁱPr^{Me2} (0.500 g, 2.77 mmol) and 1 (0.946 g, 2.77 mmol) were combined in a 100 mL Schlenk round-bottomed flask, dissolved in a minimal amount of *n*-hexane (approx. 40 mL), yielding a colorless solution which was stirred for 16 h at RT. All volatiles were removed under vacuum and the resulting solids collected, yielding the product (1.278 g, 89% yield) as a bright white free-flowing powder. ¹H NMR (600 MHz, C₆D₆) δ 4.19 (hept, *J*= 6.8 Hz, 2H, (CH₃)₂CH), 1.41 (s, 6H, C_{backbone}(CH₃)), 1.30 (d, *J* = 6.8 Hz, 12H, (CH₃)CH), 1.07 (s, 8H, Si(CH₃)₂(CH₂)₂), 0.32 (s, 24H, Si(CH₃)₂(CH₂)₂); ¹³C NMR (150.90 MHz, C₆D₆) δ 177.0 (C_{carbene}), 125.0, 51.8, 23.3, 12.3, 9.1, 5.1. m.p.: 149-151 °C.

Synthesis of $[(I^{i}Pr^{Me2})Mg(\mu-H)(HMDS)]_2$ (4) – Compound 2 (133 mg, 0.25 mmol) was added to a small Schlenk pressure tube equipped with a stir bar and dissolved in minimal *n*-hexane (8 mL). PhSiH₃ (58 mg, 0.54 mmol) was added at RT, and the tube was sealed before heating at 65 C for 16 h. A small amount of white precipitate was observed, which was removed via filtration through a 0.45 µm PTFE syringe filter. The filtrate was kept at –39 °C to yield clear, colorless, rectangular block-like crystals of the product suitable for X-ray diffraction (68 mg, 73%). ¹H NMR (600 MHz, C₆D₆) δ 5.30 (hept, *J*= 6.9 Hz, 4H, (CH₃)₂CH), 4.29 (s, 2H, MgH), 1.64 (s, 12H, C_{backbone}(CH₃)), 1.42 (d, *J* = 7.0 Hz, 36H, (CH₃)CH) 0.37 (s, 36H, Si(CH₃)₃); ¹³C NMR (150.90 MHz, C₆D₆) δ 182.0 (C_{carbene}), 125.0, 53.4, 22.6, 9.9, 6.4. m.p.: 178-180 °C.

Synthesis of $[(I^{i}Pr^{Me2})Mg(\mu-H)(ASCP)]_2$ (5) – Compound **3** (521 mg, 1.00 mmol) was added to a Schlenk pressure tube along with a stir bar and dissolved in a minimal amount of n-hexane (approx. 25 mL). PhSiH₃ (217 mg, 2.00 mmol) was added to the solution at RT. The flask was sealed and heated while stirring at 40 °C for 16 h, yielding a bright white precipitate. The suspension was filtered over a medium frit and the solids were collected, yielding the product as a highly pure, bright white powder (241 mg, 66%). Clear, colorless, rhombohedral single crystals suitable for X-ray diffraction were obtained by keeping the filtrate at –39 °C. ¹H NMR (600 MHz, C₆D₆) δ 4.93 (hept, J = 6.8 Hz, 4H, (CH₃)₂CH), 4.31 (s, 2H, MgH), 1.59 (s, 12H, C_{backbone}(CH₃)), 1.45 (d, J = 7.0 Hz, 24H, (CH₃)CH), 1.10 (s, 8H, Si(CH₃)₂(CH₂)₂)), 0.22 (s, 24H, Si(CH₃)₂(CH₂)₂); ¹³C NMR (150.90 MHz, C₆D₆) δ 180.9 (C_{carbene}), 124.8, 52.9, 23.0, 12.6, 9.6, 4.7. m.p.: 218-220 °C.



Figure S1. Molecular Structure of **1** (thermal ellipsoids set at 50% probability, H atoms omitted for clarity.

NMR Spectra





Figure S3. ${}^{13}C{}^{1}H$ NMR spectrum of 1 in C₆D₆ at 298 K.



Figure S4. ¹H NMR spectrum of 2 in C₆D₆ at 298 K.



Figure S5. ¹³C NMR spectrum of 2 in C₆D₆ at 298 K.



Figure S6. ¹H NMR spectrum of **3** in C_6D_6 at 298 K.



Figure S7. ${}^{13}C{}^{1}H$ NMR spectrum of 3 in C₆D₆ at 298 K.



Figure S8. ¹H NMR spectrum of 4 in C_6D_6 at 298 K.



Figure S9. ¹³C NMR spectrum of **4** in C_6D_6 at 298 K.



Figure S10. ¹H NMR spectrum of 5 in C₆D₆ at 298 K.



Figure S11. ¹³C NMR spectrum of 5 in C₆D₆ at 298 K.





Figure S12. FTIR spectrum of 2.



Figure S13. FTIR spectrum of 3.







Figure S15. FTIR spectrum of 5

Crystallographic Refinement Details

General Considerations. Single crystal X-ray diffraction data were collected on a Bruker Kappa APEXII Duo diffractometer running the APEX3² software suite. The structures were solved and refined using the Bruker SHELXTL Software Package³ within OLEX2.⁴ Non-hydrogen atoms were refined anisotropically. The Mg-H atoms in 4 and 5, as well as the H atoms on C10 in 3 were located in the diffraction map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with $U_{iso} = 1.2U_{equiv}$ of the parent atom ($U_{iso} = 1.5U_{equiv}$ for methyl). Compound 5 was refined as a two component twin. The TWINROTMAT feature of Platon⁵ was used to identify the two-fold rotation around the (0 1 -1) axis. The resulting twin law was -1.000 0.000 0.000 / 0.000 -1.000/ 0.000 -1.000 0.000, and the BASF refined to 0.43253. The relative occupancies of each disordered site in 3 and 5 were freely refined. Constraints and restraints were used as need on the anisotropic displacement parameters of the disordered atoms, and the disordered bonds, respectively.

Compound	1	2	3	4	5
Chemical formula	C24 H64 Mg2 N4 Si8	C ₂₃ H ₅₆ MgN ₄ Si ₄	C ₂₃ H ₅₂ MgN ₄ Si ₄	C34H78Mg2N6Si4	$C_{68}H_{148}Mg_4N_{12}Si_8$
Formula weight (g/mol)	682.13	525.38	521.35	732.00	1455.94
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal size (mm)	0.298 x 0.396 x 0.856	0.541 x 0.695 x 0.748	0.406 x 0.465 x 0.597	0.160 x 0.163 x 0.428	0.338 x 0.448 x 0.493
Crystal habit	colorless block	colorless rod	colorless block	colorless rod	colorless block
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	P212121	$P2_1/n$	P -1	P -1
a (Å)	11.5402(9)	10.0360(7)	15.8930(12)	11.699(2)	a = 12.0227(15)
b (Å)	16.7067(13)	18.3530(14)	12.1252(10)	12.225(2)	b = 20.662(3)
c (Å)	20.9436(17)	18.4828(13)	17.9168(13)	18.044(3)	c = 20.675(3)
α (°)	90	90	90	103.803(6)	$\alpha = 67.026(4)$
β (°)	98.891(2)	90	113.009(2)	102.534(6)	$\beta = 79.336(4)$
γ (°)	90	90	90	99.630(6)	$\gamma = 79.418(4)$
Volume (Å ³)	3989.4(5)	3404.4(4)	3178.0(4)	2380.2(7)	4611.5(10)
Ζ	4	4	4	2	2
Density (calculated) (g/cm ³)	1.136	1.025	1.090	1.021	1.049
μ (mm ⁻¹)	0.321	0.209	0.224	0.179	0.184
Theta range (°)	1.567 to 31.571	1.56 to 29.57	2.08 to 28.31	1.21 to 29.67	1.21 to 26.12
	$-16 \le h \le 16$	$-13 \le h \le 13$	$-20 \le h \le 21$	$-16 \le h \le 16$	$-14 \le h \le 14$
Index ranges	$-24 \le k \le 24$	$-25 \le k \le 21$	$-16 \le k \le 16$	$-16 \le k \le 16$	$-24 \le k \le 25$
-	$-30 \le 1 \le 30$	$-25 \le 1 \le 21$	$-23 \le 1 \le 23$	$-25 \le 1 \le 25$	$-25 \le 1 \le 25$
Reflections collected	59939	45442	35995	96663	78270
Independent	13286 [R(int) =	9532 [R(int) =	7891 [R(int) =	13415 [R(int) =	18246 [R(int) =
reflections	0.0292]	0.0291]	0.0235]	0.0716]	0.0526]
Data / restraints / parameters	13286 / 0 / 359	9532 / 0 / 307	7891 / 0 / 345	13415 / 0 / 447	18246 / 18 / 910
Goodness-of-fit on F ²	1.133	1.051	1.044	1.009	1.022
$R_1[I > 2\sigma(I)]$	0.0441	0.0308	0.0287	0.0443	0.0544
wR ₂ [all data]	0.1065	0.0826	0.0774	0.1148	0.1508

Table S1. Crystallographic details for compounds 1-5.

References

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