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Supplementary Information for

Beryllium-Centred C-H Activation of Benzene

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Synthetic Details

General Considerations

CAUTION: Beryllium and its compounds are extremely toxic. Suitable precautions (e.g., use of protective clothing, breathing apparatus, and a well-ventilated fume cupboard) should be taken for all manipulations involving these species.¹

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of argon. NMR experiments were conducted in J-Young tap NMR tubes prepared in a glovebox. NMR spectra were recorded on a Bruker BioSpin GmbH spectrometer operating at 400.13 MHz (¹H), 100.62 MHz (¹³C) and 56.2 MHz (⁹Be) or on an Agilent ProPulse spectrometer operating at 194.3 MHz (⁷Li). Elemental analyses were performed at Elemental Microanalysis Ltd., Okehampton, Devon, UK. Solvents were dried by passage through a commercially available solvent purification system and stored under argon in ampoules over 4 Å molecular sieves. BeCl₂ was originally purchased from Sigma-Aldrich Ltd. C₆D₆ was purchased from Merck, dried over a potassium before distilling and storage over molecular sieves. {CH₂SiMe₂N(H)Dipp}₂,² Li/LiCl and Na/NaCl were synthesised according to literature procedures.^{3,4}

Synthesis of [{CH₂SiMe₂NDipp}₂BeClLi]₂(8)

ⁿButyl Lithium (2.5 M, 1.61 cm³, 4.02 mmol) was slowly added dropwise to a pre-cooled (0 °C) hexanes solution (*ca.* 20 cm³) of {CH₂SiMe₂N(H)Dipp}₂ (1 g, 2.01 mmol), resulting in a colourless suspension. The reaction mixture was stirred for 30 minutes at 0 °C, before being allowed to warm to ambient temperature and stir for a further 120 minutes. Next, BeCl₂ (0.16 g, 2.01 mmol) was slowly added resulting in a slight exotherm, and the reaction mixture was left to stir for 16 hours. After filtration the volatiles were removed under reduced pressure, resulting in a colourless solid. Yield: 0.66 g, 58%.

¹H NMR (C₆D₆): $\delta = 6.95$ (d, *m*-C₆H₃, ³*J*_{*HH*} = 7.31 Hz, 4H), 6.79 (t, *p*-C₆H₃, ³*J*_{*HH*} = 7.31 Hz, 2H), 3.85 (sept, C<u>H</u>(CH₃)₂, ³*J*_{*HH*} = 6.94 Hz, 4H), 1.26 (d, CH(C<u>H</u>₃)₂, ³*J*_{*HH*} = 6.99 Hz, 12H), 1.12 (s, SiCH₂, 4H), 1.08 (d, CH(C<u>H</u>₃)₂, ³*J*_{*HH*} = 6.99 Hz, 12H), 0.21 (s, SiCH₃, 12H).

¹³C{¹H} NMR (C₆D₆) δ = 152.4 (*i*-C₆H₃), 146.7 (*o*-C₆H₃), 144.9 (*o*-C₆H₃), 123.1 (*m*-C₆H₃), 121.8 (*p*-C₆H₃), 27.8 (<u>C</u>H(CH₃)₂), 25.1 (CH(<u>C</u>H₃)₂), 24.3 (CH(<u>C</u>H₃)₂), 14.2 (SiCH₂), 0.6 (SiCH₃).

⁷Li NMR (C₆D₆) $\delta = -6.6$ (s).

⁹Be NMR (C₆D₆) δ = 8.2 (br s, $\omega_{1/2}$ = 314 Hz).

Anal. Calc. for Be₁N₂Si₂Cl₂Li₂C₃₀H₅₀ -: C, 65.96; H, 9.23; N, 5.13. Found: C, 66.49; H, 9.45; N, 4.89.

Synthesis of {CH₂SiMe₂NDipp}₂Be (9)

[{**CH**₂**SiMe**₂**NDipp**}₂**BeClLi**]₂ (0.2 g, 0.35 mmol) was dissolved in the minimum amount of benzene and heated at 40 °C for 16 hours. After filtration the volatiles were removed under reduced pressure to afford a colourless solid. Yield: 0.17 g, 98 %. The reaction can be performed faster at 50 or 60 °C.

¹H NMR (C₆D₆): δ = 7.11-7.00 (m, Ar-H, 6H), 3.75 (sept, C<u>H</u>(CH₃)₂, ³*J*_{HH} = 6.92 Hz, 4H), 1.27 (d, CH(C<u>H</u>₃)₂, ³*J*_{HH} = 6.95 Hz, 12H), 1.15 (s, SiCH₂, 4H), 1.09 (d, CH(C<u>H</u>₃)₂, ³*J*_{HH} = 6.95 Hz, 12H), 0.15 (s, SiCH₃, 12H).

¹³C{¹H} NMR (C₆D₆) δ = 144.9 (*i*-C₆H₃), 140.0 (*o*-C₆H₃), 124.1 (*m*-C₆H₃), 123.5 (*p*-C₆H₃), 28.1 (<u>C</u>H(CH₃)₂), 25.1 (CH(<u>C</u>H₃)₂), 24.3 (CH(<u>C</u>H₃)₂), 9.35 (SiCH₂), -0.25 (SiCH₃).

⁹Be NMR (C₆D₆) δ = 11.6 (br s, $\omega_{1/2}$ = 266 Hz).

Despite multiple attempts, no satisfactory elemental analyses were obtained. Anal. Calc. for $Be_1N_2Si_2C_{30}H_{50}$ -: C, 71.50; H, 10.00; N, 5.56. Found: C, 60.76; H, 9.14; N, 4.39.

Synthesis of [{CH₂SiMe₂NDipp}₂Be-C₆D₅][Na] (10-d)

 C_6D_6 (0.6 cm³) was added to a J-Young's NMR tube containing 5 wt% Na/NaCl (80 mg) and { CH_2SiMe_2NDipp }₂Be (10 mg, 0.02 mmol) and the reaction mixture was heated to 100 °C for 2 days. Two species present spectroscopically, after filtration into a vial colourless crystals were grown from a saturated C_6D_6 solution, allowing for the crystallographic identification of [{ CH_2SiMe_2NDipp }₂Be- C_6H_5][Na]. Mass: 11 mg.

⁹Be NMR (C₆D₆) δ = 11.8 (br s, $\omega_{1/2}$ = 327 Hz).

Synthesis of [{CH₂SiMe₂NDipp}₂Be-C₆D₅][Li] (11-d)

 C_6D_6 (0.6 cm³) was added to a J-Young's NMR tube containing 5 wt% Li/LiCl (66 mg) and { CH_2SiMe_2NDipp }₂Be (10 mg, 0.02 mmol) and the reaction mixture was heated to 100 °C for 5 days. Multiple species present spectroscopically, after filtration into a vial colourless crystals were grown from the slow evaporation of C_6D_6 , single crystal XRD confirms the identification of [{ CH_2SiMe_2NDipp }Be-C₆H₅][Li]. Mass: 7 mg.

⁹Be NMR (C₆D₆) δ = 11.6 (br s, $\omega_{1/2}$ = 180 Hz).

Synthesis of [{CH₂SiMe₂NDipp}₂Be-C₆H₅][Na] ((10-h)

 C_6H_6 (0.6 cm³) was added to a J-Young's NMR tube containing 5 wt% Na/NaCl (80 mg) and { CH_2SiMe_2NDipp }₂Be (10 mg, 0.02 mmol) and the reaction mixture was heated to 100 °C for 2 days. The solution was filtered into a fresh NMR tube and concentrated resulting in a colourless solid. Colourless crystals grown from benzene/hexane solvent system, the identification of [{ CH_2SiMe_2NDipp }_2Be-C₆H₅][Na] was confirmed crystallographically. Mass: 18 mg. ⁹Be NMR (C₆D₆) = 11.8 (br s, $\omega_{1/2}$ = 327 Hz).

Control Reactions

Attempted reduction of C₆D₆ with Na/NaCl

 C_6D_6 (0.6 cm³) was added to a J-Young's NMR tube containing 5 wt% Na/NaCl (80 mg) and the reaction mixture was heated to 100 °C for 2 days. No reaction was observed.

Attempted reduction of C₆D₆ with Li/LiCl

 C_6D_6 (0.6 cm³) was added to a J-Young's NMR tube containing 5 wt% Li/LiCl (80 mg) and the reaction mixture was heated to 100 °C for 5 days. No reaction was observed.

Reaction of {CH₂SiMe₂N(Dipp)Li}₂with Be metal and Na/NaCl

 C_6D_6 (0.6 cm³) was added to a J-Young's NMR tube containing 5 wt% Na/NaCl (100 mg), Be powder (2 mg, 0.22 mmol) and {CH₂SiMe₂NDippLi}₂.OEt₂ (12.6 mg, 0.02 mmol) and the reaction mixture was heated to 100 °C for 2 days. No new Be species were formed, as confirmed by ⁹Be NMR spectrum and the only observed product was the dimeric the lithiated starting material, the connectivity of which was identified by single crystal X-ray analysis (see Figure S41).

Reaction of BeCl₂ and Na/NaCl

 C_6D_6 (0.6 cm³) was added to a J-Young's NMR tube containing 5 wt% Na/NaCl (80 mg) and BeCl₂ (5 mg, 0.06 mmol) and the reaction mixture was heated to 100 °C for 2 days. No Reaction was observed.



Figure S2. ¹³C{¹H} NMR Spectrum (C₆D₆, 298 K, 100.62 MHz) for [{CH₂SiMe₂NDipp}₂BeClLi]₂.



Figure S3. ¹H-¹³C HSQC trace (C₆D₆, 298 K, 400.13, 100.62 MHz) for [{CH₂SiMe₂NDipp}₂BeClLi]₂.



Figure S4. ¹H-¹³C HMBC trace (C₆D₆, 298 K, 400.13, 100.62 MHz) for [{CH₂SiMe₂NDipp}₂BeClLi]₂.







Figure S6. 9Be NMR Spectrum (C6D6, 298 K, 56.2 MHz) for [{CH₂SiMe₂NDipp}₂BeClLi]₂.



Figure S7. ¹H NMR Spectrum (C₆D₆, 298 K, 400.13 MHz) for {CH₂SiMe₂NDipp}₂Be. * = [{CH₂SiMe₂NDipp}₂BeClLi]₂.



Figure S8. ¹³*C*{¹*H*} *NMR Spectrum (C*₆*D*₆*, 298 K, 100.62 MHz) for {CH*₂*SiMe*₂*NDipp*}*2Be.*



Figure S9. ¹H-¹³C HSQC trace (C₆D₆, 298 K, 400.13, 100.62 MHz) for {CH₂SiMe₂NDipp}₂Be.



Figure S10. ¹H-¹³C HMBC trace (C₆D₆, 298 K, 400.13, 100.62 MHz) for {CH₂SiMe₂NDipp}₂Be.



Figure S11. ⁹Be NMR Spectrum (C₆D₆, 298 K, 56.2 MHz) for {CH₂SiMe₂NDipp}₂Be.



Figure S12. ¹*H NMR Spectrum (C*₆*D*₆, 298 K, 400.13 MHz) for reaction between {*CH*₂*SiMe*₂*NDipp*}2*Be* and 5 wt% *Na/NaCl.*



Figure S14. ¹*H*-¹³*C HSQC trace* (*C*₆*D*₆, 298 K, 400.13, 100.62 MHz) for reaction between {*CH*₂*SiMe*₂*NDipp*}2*Be* and 5 wt% *Na/NaCl*.



Figure S15. ¹*H*-¹³*C HMBC* trace (C₆D₆, 298 K, 400.13, 100.62 MHz) for reaction between {*CH*₂*SiMe*₂*NDipp*}2*Be* and 5 *wt% Na/NaCl*.



Figure S16. ⁹Be NMR Spectrum (C₆D₆, 298 K, 56.2 MHz) for reaction between {CH₂SiMe₂NDipp}₂Be and 5 wt% Na/NaCl.



Figure S17. ¹H NMR Spectrum (C₆D₆, 298 K, 400.13 MHz) for reaction between {CH₂SiMe₂NDipp}₂Be and 5 wt% Li/LiCl.



Figure S18. ¹³C{¹H} NMR Spectrum (C₆D₆, 298 K, 100.62 MHz) for reaction between {CH₂SiMe₂NDipp}₂Be and 5 wt% Li/LiCl.



Figure S19. ¹*H*-¹³*C HSQC trace (C₆D₆, 298 K, 400.13, 100.62 MHz) for reaction between {<i>CH*₂*SiMe*₂*NDipp*}*2Be and 5 wt% Li/LiCl.*



Figure S20. ¹*H*-¹³*C HMBC trace* (*C*₆*D*₆, 298 K, 400.13, 100.62 MHz) *for reaction between* {*CH*₂*SiMe*₂*NDipp*}2*Be and* 5 *wt*% *Li*/*LiCl*.



Figure S22. ⁹Be NMR Spectrum (C₆D₆, 298 K, 56.2 MHz) for reaction between {CH₂SiMe₂NDipp}₂Be and 5 wt% Li/LiCl.



Figure S23. ¹H NMR Spectrum (C₆D₆, 298 K, 400.13 MHz) for reaction between {CH₂SiMe₂NDipp}₂Be and 5 wt% Na/NaCl in C₆H₆.



Figure S24. ¹³C{¹H} NMR Spectrum (C₆D₆, 298 K, 100.62 MHz) for reaction between {CH₂SiMe₂NDipp}₂Be and 5 wt% Na/NaCl in C₆H₆.



Figure S25. ¹*H*-¹³*C HSQC trace* (*C*₆*D*₆, 298 K, 400.13, 100.62 MHz) *for reaction between* {*CH*₂*SiMe*₂*NDipp*}*2Be and* 5 *wt% Na/NaCl in C*₆*H*₆.



Figure S26. ¹*H*-¹³*C HMBC* trace (C₆D₆, 298 K, 400.13, 100.62 MHz) for reaction between {CH₂SiMe₂NDipp}₂Be and 5 wt% Na/NaCl in C₆H₆.



Figure S27. ⁹Be NMR Spectrum (C₆D₆, 298 K, 56.2 MHz) for reaction between {CH₂SiMe₂NDipp}₂Be and 5 wt% Na/NaCl in C₆H₆.

Reaction Monitoring the Formation of {CH₂SiMe₂NDipp}₂Be

Separate NMR scale reactions were undertaken, heating [{CH₂SiMe₂NDipp}₂BeClLi]₂ at 40, 45, 50 and 60 °C. Each reaction was monitored over 16 hours, recording a ¹H NMR spectrum at 5-minute intervals for the first hour and subsequently a ¹H NMR spectrum was recorded every 30 minutes for the remaining 15 hours.



Figure S28. ¹*H NMR Spectrum (C*₆D₆, 313.1 K, 400.13 MHz) monitoring the conversion of [{CH₂SiMe₂NDipp}₂BeClLi]₂ to {CH₂SiMe₂NDipp}₂Be over 16 hours.



Figure S29. ¹*H NMR Spectrum (C*₆*D*₆*, 313.1 K, 400.13 MHz) monitoring the conversion of [{CH₂SiMe₂NDipp}₂BeClLi]₂ to {CH₂SiMe₂NDipp}₂Be over 16 hours, zoomed in on the methine resonance.*



Figure S30. ¹H NMR Spectrum (C₆D₆, 318.1 K, 400.13 MHz) monitoring the conversion of [{CH₂SiMe₂NDipp}₂BeClLi]₂ to {CH₂SiMe₂NDipp}₂Be over 16 hours.



Figure S31. ¹*H NMR Spectrum (C*₆*D*₆*, 323.1 K, 400.13 MHz) monitoring the conversion of [{CH*₂*SiMe*₂*NDipp*}₂*BeClLi*]₂ to {*CH*₂*SiMe*₂*NDipp*}₂*Be over 16 hours.*



Figure S32. ¹H NMR Spectrum (C₆D₆, 333.1 K, 400.13 MHz) monitoring the conversion of [{CH₂SiMe₂NDipp}₂BeClLi]₂ to {CH₂SiMe₂NDipp}₂Be over 16 hours.

NMR Spectra from Control Reactions



Figure S33. ¹H NMR Spectrum (C₆D₆, 298 K, 400.13 MHz) from heating Na/NaCl at 100 °C for 2 days.



Figure S34. ¹H NMR Spectrum (C₆D₆, 298 K, 500.06 MHz) from heating Li/LiCl at 100 °C for 5 days.

19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10 -11 -12 -13 -14 -15 -16 -17 -18 -19 fl (ppm)

Figure S35. ⁷Li NMR Spectrum (C₆D₆, 298 K, 194.3 MHz) from heating Li/LiCl at 100 °C for 5 days.





n i populari i dina hal i ni nakiliki di mi lan rima di akira wa karia 45 40 30 20 50 35 25 15 10 5 f1 (ppm) 0 -5 -10 -15 -20 -25 -30 -35 -40

Figure S37. ⁹Be NMR Spectrum (C₆D₆, 298 K, 56.2 MHz) from heating Na/NaCl with Be metal and {CH₂SiMe₂NDippLi}₂.OEt₂ at 100 °C for 2 days.



Figure S38. ⁷Li NMR Spectrum (C₆D₆, 298 K, 194.3 MHz) from heating Na/NaCl with Be metal and {CH₂SiMe₂NDippLi}₂.OEt₂ at 100 °C for 2 days.



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 fl (ppm)

Figure S39. ¹H NMR Spectrum (C₆D₆, 298 K, 500.06 MHz) from heating Na/NaCl with BeCl₂ at 100 °C for 2 days.

— 2.12 — 1.29



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Figure S40. 9Be NMR Spectrum (C6D6, 298 K, 56.2 MHz) from heating Na/NaCl with BeCl2 at 100 °C for 2 days.



Figure S41. Molecular structure of the dimerised starting material ({CH₂SiMe₂NDippLi}₂), crystallised from the reaction of heating Na/NaCl with Be metal at 100 °C for 2 days. Displacement ellipsoids at the 50 % probability level and hydrogen atoms omitted for clarity.

Crystallographic Details

Single Crystal X–ray diffraction data for compounds **8** – **11** were collected on a SuperNova, EosS2 diffractometer using CuK α ($\lambda = 1.54184$ Å) radiation throughout. The crystals were maintained at 150 K during data collection. Using Olex2,⁵ the structures were solved with the olex2.solve⁶ structure solution program or ShelXT and refined with the ShelXL⁷ refinement package using Least–Squares minimization.

The gross structure of 10 is dominated by 1-D polymers that assemble along the *a*-axis and which, in turn, generate channels along *b*.

There are 2 crystallographically independent molecules in the asymmetric unit of **11**.

Compound	8	9	10	11
Empirical formula	C ₃₀ H ₅₀ BeClLiN ₂ Si ₂	C30H50BeN2Si2	C36H55BeN2NaSi2	C72H110Be2Li2N4Si4
Formula weight	546.30	503.91	604.00	1175.89
Crystal system	monoclinic	tetragonal	orthorhombic	monoclinic
Space group	$P2_{1}/n$	<i>I</i> -4	$Pca2_1$	Cc
a/Å	16.6788(3)	25.5602(1)	18.5743(4)	12.7041(2)
b/Å	10.6255(0)	25.5602(1)	11.9001(3)	16.8932(3)
c/Å	19.9196(3)	9.4309(1)	16.6826(4)	33.7442(5)
a/°	90	90	90	90
β°	106.774(2)	90	90	92.349(1)
$\gamma/^{\circ}$	90	90	90	90
Volume/Å ³	3379.96(9)	6161.43(8)	3687.46(15)	7235.9(2)
Ζ	4	8	4	4
$\rho_{\text{calc}} \text{g/cm}_3$	1.074	1.086	1.088	1.079
μ/mm^{-1}	1.808	1.173	1.162	1.059
F(000)	1184.0	2208.0	1312.0	2560.0
Crystal size/mm ³	$0.36 \times 0.266 \times 0.164$	$0.268 \times 0.2 \times 0.164$	$0.095 \times 0.069 \times 0.056$	$0.11 \times 0.102 \times 0.1$
2θ range /°	8.184 to 145.204	6.916 to 145.3	7.428 to 145.298	8.714 to 146.572
Index ranges	$-20 \le h \le 20,$	$-31 \le h \le 31,$	$-22 \le h \le 22,$	$-15 \le h \le 14$,
	$-5 \le k \le 13,$	$-31 \le k \le 31,$	$-14 \le k \le 13,$	$-20 \le k \le 20,$
	$-22 \le l \le 24$	$-11 \le l \le 7$	$-16 \le l \le 20$	$-41 \le l \le 41$
Reflections collected	23705	38933	36978	39607
Independent reflections [<i>R</i> _{int} , <i>R</i> _{sigma}]	6684 [0.0325, 0.0342]	6102 [0.0210, 0.0141]	6374 [0.0574, 0.0409]	11846 [0.0537, 0.0402]
Data/restraints/parameters	6684/0/346	6102/0/328	6374/1/392	11846/2/781
Goodness–of–fit on F^2	1.029	1.036	1.036	1.059
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0435, wR_2 = 0.1139$	$R_1 = 0.0222, wR_2 = 0.0598$	$R_1 = 0.0375, wR_2 = 0.0867$	$R_1 = 0.0606, wR_2 = 0.1600$
Final <i>R</i> indexes [all data]	$R_1 = 0.0479, wR_2 = 0.1188$	$R_1 = 0.0224, wR_2 = 0.0600$	$R_1 = 0.0448, wR_2 = 0.0909$	$R_1 = 0.0635, wR_2 = 0.1632$
Largest diff. peak/hole (e Å ⁻³⁻)	0.46/-0.33	0.17/-0.17	0.19/-0.15	0.52/-0.29
Flack parameter		-0.002(3)	0.48(3)	0.066(18)

Table S1: Crystal data and structure refinement for compounds 8 - 11.



Figure S42. Displacement ellipsoid (30% probability) plot of compound **8**. Hydrogen atoms are removed and silylmethyl and *iso*propyl Dipp substituents are shown as wireframe for clarity. Selected bond lengths (Å) and angles (°): Cl1-Be1 2.1121(18), Cl1-Li1¹ 2.350(3), Cl1-Li1 2.388(3), N1-Be1 1.595(2), N2-Be1 1.578(2), Be1-Cl1-Li1¹ 169.50(9), Be1-Cl1-Li1 104.91(8), Li1¹-Cl1-Li1 83.89(10), N1-Be1-Cl1 111.47(10), N2-Be1-Cl1 113.92(10), N2-Be1-N1 134.58(13). Symmetry operators to generate primed (¹) atoms, 1-*x*, 1-*y*, 1-*z*.



Figure S43: Displacement ellipsoid (30% probability) plot of the Be1-containing molecule of compound **11**-*d*. Hydrogen atoms are removed and Dipp substituents, apart from C5-C10, are shown as wireframe for clarity. Selected bond lengths (Å) and angles (°): N1-Be1 1.644(7), N2-Be1 1.622(7), C31-Be1 1.787(7), N1-Be1-C31 115.0(4), N2-Be1-N1 126.4(4), N2-Be1-C31 118.4(4).

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