# Supplementary Material (ESI) for Chemical Communications

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Crystalline Na-Si(NN) derivatives  $[Si(NN) = Si\{(NCH_2tBu)_2C_6H_4-1,2\}]$ : the silylenoid  $[Si(NN)OMe]^-$ , the diamion  $[(NN)Si-Si(NN)]^{2-}$ , and the radical amion c- $[Si(NN)]_3^{--}$ 

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## **Experimental Section**

Compound **2a**: A solution of **1** (0.26 g, 0.95 mmol) in THF (20 cm<sup>3</sup>) was added dropwise to a cooled (- 50 °C) solution of  $[Na{\mu-CH(SiMe_2OMe)(SiMe_3)}]$  (**5**) (0.19 g, 0.96 mmol) in THF (40 cm<sup>3</sup>). The

15 mixture was allowed to warm to ambient temperature and stirred for 16 h. The volatiles were removed *in vacuo* and the residue was extracted into hexane/THF (20/3 cm<sup>3</sup>). The mixture was concentrated *in vacuo* and cooled to -25 °C to afford compound **2a** (as the bis-THF derivative) (0.14 g, 16%), mp. (decomp.) 190 °C.

Compound **2b**: A solution of **1** (0.41 g, 1.49 mmol) in THF (20 cm<sup>3</sup>) was added dropwise to a cooled 20 (- 50 °C) solution of NaOMe (0.08 g, 1.49 mmol) in THF (30 cm<sup>3</sup>). The mixture was allowed to warm to ambient temperature and stirred for 16 h. The volatiles were removed *in vacuo* and the residue was extracted into Et<sub>2</sub>O (20 cm<sup>3</sup>). The extract was filtered and the filtrate concentrated and stored at ambient temperature to yield compound **2b** (0.32 g, 49%) (Found: C, 62.5; H, 9.75; N, 6.19. C<sub>50</sub>H<sub>94</sub>N<sub>4</sub>Na<sub>2</sub>O<sub>6</sub>Si<sub>2</sub> requires C, 63.2; H, 9.98; N, 5.90%), as colourless rectangular crystals, mp 25 (decomp.) 110 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>/C<sub>4</sub>D<sub>8</sub>O), δ 1.06 (t, 6 H, Et<sub>2</sub>O), 1.16 (s, 18 H, Bu<sup>t</sup>), 1.47 (m, 4 H, THF), 2.89 (s, 3 H, MeO), 3.25 (q, 4 H, Et<sub>2</sub>O), 3.39 (d, 4 H, CH<sub>2</sub>), 3.54 (m, 4 H, THF), 6.74 (s, 4 H, Ph); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>/C<sub>4</sub>D<sub>8</sub>O): δ 15.47 (MeO), 25.78 (THF), 29.53 (*CMe<sub>3</sub>*), 34.92 (*CMe<sub>3</sub>*), 47.99 (Et<sub>2</sub>O), 57.46 (Et<sub>2</sub>O), 65.86 (CH<sub>2</sub>), 67.79 (THF), 106.36, 114.96 and 154.96 (Ph); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>/C<sub>4</sub>D<sub>8</sub>O): δ 16.89; <sup>23</sup>Na NMR (C<sub>6</sub>D<sub>6</sub>/C<sub>4</sub>D<sub>8</sub>O): δ 9.77 (Δw<sup>1</sup>/<sub>2</sub> = 2.2 KHz).

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Compound **3**: A solution of **1** (0.52 g, 1.9 mmol) in THF (30 cm<sup>3</sup>) was stirred with an excess of Na. Initially a green precipitate formed which disappeared with continued stirring (16 h). Unreacted metal was removed from the black-brown solution. Crystallization at -25 °C yielded dark-brown crystals of

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compound **3** (0.56 g, 67%). <sup>1</sup>H NMR (d<sub>8</sub>-THF) δ: 0.95 (s, 18 H, CH<sub>3</sub>), 1.77 (m, 8 H, THF), 2.69, 2.74, 35 3.00 and 3.35 (AB-type, 4 H, CH<sub>2</sub>), 3.61 (m, 8 H, THF), 5.88 (m, 2 H, phenyl) and 5.99 (m, 2 H, phenyl). <sup>13</sup>C{<sup>1</sup>H} NMR (d<sub>8</sub>-THF) δ: 26.27 (THF), 29.8 (*CMe<sub>3</sub>*), 36.4 (*CMe<sub>3</sub>*), 56.7 (CH<sub>2</sub>), 68,10 (THF), 103.3, 112.0 and 150.9 (phenyl). <sup>29</sup>Si{<sup>1</sup>H} NMR (d<sub>8</sub>-THF) δ: 104.6. <sup>23</sup>Na NMR (d<sub>8</sub>-THF) δ: - 6.4, Δv<sub>1/2</sub> ~1500 Hz. Found: C, 64.9; H, 9.62; N, 6.23. Anal. Calc. for C<sub>48</sub>H<sub>84</sub>N<sub>4</sub>Si<sub>2</sub>O<sub>4</sub>Na<sub>2</sub>: C, 65.3; H, 9.58; N, 6.34%.

40 Alternatively, in an NMR-scale reaction a suspension of **4** in  $d_8$ -THF was treated with Na for several days. A dark solution was obtained which was identified by <sup>1</sup>H and <sup>29</sup>Si NMR to be **3**.

Compound 4: A solution of 1 in THF (10 cm<sup>3</sup>) was stirred with excess Na. The reaction was stopped after a green precipitate had formed. Unreacted sodium was removed and the suspension was filtered 45 leaving a lime-green solid. X-ray suitable crystals were obtained from hot THF.

Alternatively, sodium (0.0292 g, 1.269 mmol) was added to a solution of **1** (1.04 g, 3.81 mmol) in THF (10 cm<sup>3</sup>). The mixture was stirred for 16 h during which time a solid had formed. Filtration and drying of the solid *in vacuo* afforded compound **4**, as a lime-green solid (1.23 g, 86%). Crystals suitable for X-ray analysis were grown from hot THF. The EPR spectrum of **4** was recorded from a 50 sample of **4** dissolved in DME.