

Crystalline Na-Si(NN) derivatives [Si(NN) = Si{(NCH₂tBu)₂C₆H₄-1,2}]: the silylenoid [Si(NN)OMe]⁻, the dianion [(NN)Si-Si(NN)]²⁻, and the radical anion *c*-[Si(NN)]₃⁻

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Floria Antolini, Barbara Gehrhus,* Peter B. Hitchcock and Michael F. Lappert*

Department of Chemistry, School of Life Sciences, University of Sussex, Brighton, BN1 9QJ, UK.

Fax: ++44(0)1273677196; E-mail: b.gehrhus@sussex.ac.uk; m.f.lappert@sussex.ac.uk

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Experimental Section

Compound **2a**: A solution of **1** (0.26 g, 0.95 mmol) in THF (20 cm³) was added dropwise to a cooled (-50 °C) solution of [Na{μ-CH(SiMe₂OMe)(SiMe₃)}] (**5**) (0.19 g, 0.96 mmol) in THF (40 cm³). 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 hexane/THF (20/3 cm³). 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 cm³) was added dropwise to a cooled (-50 °C) solution of NaOMe (0.08 g, 1.49 mmol) in THF (30 cm³). 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 Et₂O (20 cm³). 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. C₅₀H₉₄N₄Na₂O₆Si₂ requires C, 63.2; H, 9.98; N, 5.90%), as colourless rectangular crystals, mp. (decomp.) 110 °C. ¹H NMR (C₆D₆/C₄D₈O), δ 1.06 (t, 6 H, Et₂O), 1.16 (s, 18 H, Bu^t), 1.47 (m, 4 H, THF), 2.89 (s, 3 H, MeO), 3.25 (q, 4 H, Et₂O), 3.39 (d, 4 H, CH₂), 3.54 (m, 4 H, THF), 6.74 (s, 4 H, Ph); ¹³C NMR (C₆D₆/C₄D₈O): δ 15.47 (MeO), 25.78 (THF), 29.53 (CMe₃), 34.92 (CMe₃), 47.99 (Et₂O), 57.46 (Et₂O), 65.86 (CH₂), 67.79 (THF), 106.36, 114.96 and 154.96 (Ph); ²⁹Si NMR (C₆D₆/C₄D₈O): δ 16.89; ²³Na NMR (C₆D₆/C₄D₈O): δ 9.77 (Δw^{1/2} = 2.2 KHz).

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Compound **3**: A solution of **1** (0.52 g, 1.9 mmol) in THF (30 cm³) 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

compound **3** (0.56 g, 67%). ^1H NMR (d_8 -THF) δ : 0.95 (s, 18 H, CH_3), 1.77 (m, 8 H, THF), 2.69, 2.74, 3.00 and 3.35 (AB-type, 4 H, CH_2), 3.61 (m, 8 H, THF), 5.88 (m, 2 H, phenyl) and 5.99 (m, 2 H, phenyl). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -THF) δ : 26.27 (THF), 29.8 (CMe_3), 36.4 (CMe_3), 56.7 (CH_2), 68, 103.3, 112.0 and 150.9 (phenyl). $^{29}\text{Si}\{^1\text{H}\}$ NMR (d_8 -THF) δ : 104.6. ^{23}Na NMR (d_8 -THF) δ : -6.4, $\Delta\nu_{1/2} \sim 1500$ Hz. Found: C, 64.9; H, 9.62; N, 6.23. Anal. Calc. for $\text{C}_{48}\text{H}_{84}\text{N}_4\text{Si}_2\text{O}_4\text{Na}_2$: 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 ^1H and ^{29}Si NMR to be **3**.

Compound **4**: A solution of **1** in THF (10 cm^3) 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^3). 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.