Crystalline Na-Si(NN) derivatives [Si(NN) = Si{(NCH₂Bu)₂C₆H₄-1,2}]: the silylenoid [Si(NN)OMe]⁻, the dianion [(NN)Si-Si(NN)]₂⁻, and the radical anion c-[Si(NN)]₃⁻

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

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, But), 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 (Δw½ = 2.2 KHz).

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%). $^1$H 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). $^{13}$C{$^1$H} NMR (d$_8$-THF) δ: 26.27 (THF), 29.8 (CMe$_3$), 36.4 (CMe$_3$), 56.7 (CH$_2$), 68,10 (THF), 103.3, 112.0 and 150.9 (phenyl). $^{29}$Si{$^1$H} NMR (d$_8$-THF) δ: 104.6. $^{23}$Na NMR (d$_8$-THF) δ: -6.4, $\Delta$ν$_{1/2}$~1500 Hz. Found: C, 64.9; H, 9.62; N, 6.23. Anal. Calc. for C$_{48}$H$_{84}$N$_4$Si$_2$O$_4$Na$_2$: C, 65.3; H, 9.58; N, 6.34%.

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 $^1$H 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 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.