Crystalline Na–Si(NN) derivatives [Si(NN) = Si{(NCH$_2t$Bu)$_2$C$_6$H$_4$-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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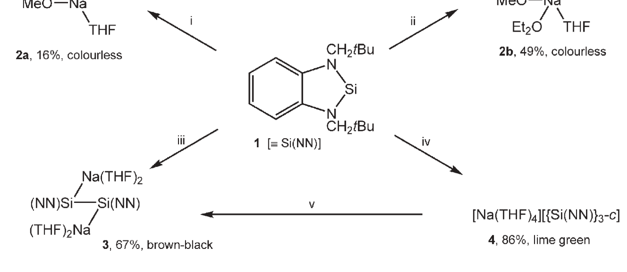
Reactions of the silylene Si[(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2], [Si(NN)], with NaOMe, excess Na or 1/3 Na yield the X-ray-characterised crystalline compounds [Na{μ-Si(NN)OMe}-(THF)(OEt$_2$)]$_2$ (2b), [Na(THF)$_2$Si(NN)]$_2$ (3) and [Na(THF)$_4$][{Si(NN)}$_3$-*c*] (4).

We wish to report the isolation of the remarkable X-ray-characterised crystalline compounds **2–4**, derived from the thermally stable bis(amino)silylene Si[(NCH$_2t$Bu)$_2$C$_6$H$_4$-1,2] (**1**) [abbreviated as Si(NN)]. These are (i) the cyclo-dimeric bis-[(solvated)sodium-bis(amino)methoxysilyls] [Na{μ-Si(NN)OMe}-(THF)L]$_2$ [L absent (**2a**), or L = OEt$_2$ (**2b**)]; (ii) the disodium disilyl [Na(THF)$_2$Si(NN)]$_2$ (**3**); and (iii) the sodium salt of a cyclotrisilane [Na(THF)$_4$][{Si(NN)}$_3$-*c*] (**4**).

As for (i), labile α-functionalised silyl anions are of considerable interest as organic synthons.[1] The silylenoids **2a** and **2b** have only a single precedent, the recently published potassium methoxybis-(trimethylsilyl)silyl.[2] Concerning (ii), compounds containing a disilyl dianion [X$_2$Si–SiX$_2$]$^{2-}$ are known[3] but only one example has previously been prepared from the appropriate silylene SiX$_2$ and one equivalent of an alkali metal (Na/K) and was characterised by a trapping reaction yielding X$_2$(Y)Si–Si(Y)X$_2$ [X = N(*t*Bu)(CH$_2$)$_2$N*t*Bu and Y = H or SiMe$_3$].[4] Reduction of SiX$_2$ with an alkali metal also led to [SiX$_2$]$^{2-}$ identified by similar trapping reactions [X = N(*t*Bu)(CH$_2$)$_2$N*t*Bu],[4] or at low temperature to the radical anion [SiX$_2$]$^-$ [X$_2$ = {C(SiMe$_3$)$_2$CH$_2$}$_2$] characterised by EPR spectroscopic data.[5] Regarding (iii), although the strained cyclotrisilanes *c*-[SiX$_2$]$_3$ have had relatively sterically demanding substituents at Si, such as *t*Bu, CH$_2t$Bu or 2,6-Me$_2$C$_6$H$_3$[6] or Si(Me)(*i*Pr)$_2$,[7] no example of X = an amino group for a neutral *c*-[SiX$_2$]$_3$ appears to have been documented; but EPR spectral data following electrochemical reduction of SiX$_2$ [X = N(*t*Bu)(CH$_2$)$_2$N*t*Bu] was consistent with the formation in solution of the corresponding cyclotrisilane radical anion *c*-[SiX$_2$]$_3$$^-$.[8] A related radical anion or dianion of the cyclotetrasilane [Si{(NEt)$_2$C$_6$H$_4$-1,2}]$_4$ with [K(THF)$_6$]$^+$ or 2[K(DME)$_3$]$^+$ as counter cation(s) is known.[9]

The syntheses of **2–4** are summarised in Scheme 1; yields refer to isolated crystalline compounds. The initial experiment, involving the interaction of Si(NN) (**1**)[10] and Na[CH(SiMe$_3$)(SiMe$_2$OMe)] (**5**)[11] led (i in Scheme 1) in modest yield to **2a**; surprisingly the Si–OMe bond of the sodium alkyl had been cleaved. The closely related compound **2b**‡ was next obtained (ii in Scheme 1) by the more direct route from **1** and NaOMe. The disodium disilyl **3**§ was prepared from **1** (iii in Scheme 1) or from **4** (v in Scheme 1) and an excess of metallic sodium in THF. The synthesis of **4**, containing the radical anion of a cyclotrisilane, involved treatment of three equivalents **1** with one equivalent sodium (iv in Scheme 1).

The thermally labile crystalline compound **2a**, isolated in low yield, was identified by a poor quality X-ray structure, which was adequate to establish that its sole components were NaOMe(THF) and Si(NN). The analogue **2b** was, however, fully characterised by microanalysis, multinuclear NMR spectroscopy, its mass spectrum and its X-ray crystal structure. In the light of the previous observation of the isolation of the lithium silyl Li[Si(NN){CH(SiMe$_3$)$_2$}](OEt$_2$) from Si(NN) and Li[CH(SiMe$_3$)$_2$],[12] it is suggested that a similar Si(NN) insertion into an M–C bond is the first step in reaction i of Scheme 1 yielding the transient intermediate **6**, which fragments yielding **2a** either directly or *via* Si(NN) and NaOMe, with an oligomeric silaethene [Me$_3$Si(H)C=SiMe$_2$]$_n$ as the presumed coproduct. In support of the proposed chelate arrangement in **6**, it is noted that the crystalline sodium alkyl [Na{CH(SiMe$_3$)(SiMe$_2$OMe)}]$_\infty$ (**5**) has a strained four-membered ring.[11] A precedent for an alkali metal methoxide extrusion reaction is found in the reaction between the lithium enamide **7** and the silylene **1** to give the ring compound **8** (Ad = 1-adamantyl).[13] In contrast to the formation (ii in Scheme 1) of the dimeric cycloadduct **2b** from NaOMe and **1** in THF, the silylene **1** and Na[N(SiMe$_3$)$_2$] gave the monomeric sodium amide Na[N(SiMe$_3$){Si(NN)SiMe$_3$}(THF)$_3$].[14]



Scheme 1 Preparation of the crystalline compounds **2a**, **2b** and **3** and **4**. Reagents: i, Na[CH(SiMe$_3$)(SiMe$_2$OMe)] (**5**), THF, crystallised from C$_6$H$_{14}$/THF; ii, NaOMe, THF, crystallised from Et$_2$O; iii, Na (excess), THF; iv, 1/3 Na, THF; v, Na (excess), THF

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† Electronic supplementary information (ESI) available: Experimental details for 2–4. See http://dx.doi.org/10.1039/b509310d

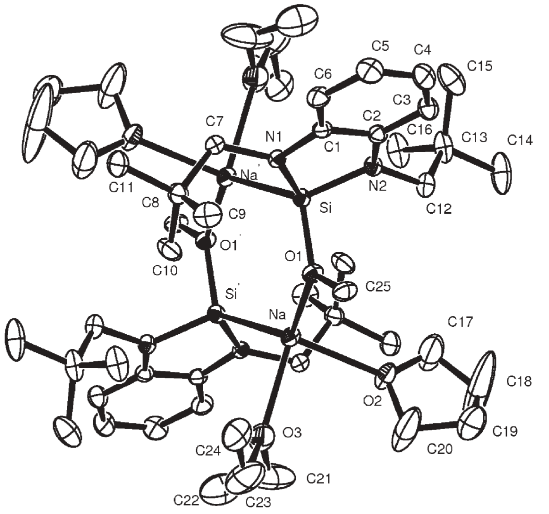
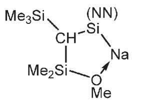


Fig. 1 ORTEP representation of **2b**. Selected bond lengths [Å] and angles [°]: Si–Na′ 3.020(2), Si–O(1) 1.731(3), Na–O(1) 2.286(3), Si–N *av.* 1.798, N(1)–Si–N(2) 87.08(15), O(3)–Na–Si′ 98.10(13), Si′–Na–O(1) 129.37(9).



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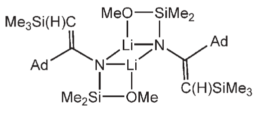

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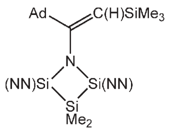

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The structure of the centrosymmetric dimeric crystalline compound **2b**[15] is shown in Fig. 1. The molecule comprises two Si(NN) units bridged by NaOMe moieties, with transoid neopentyl groups. The central core is a puckered six-membered ring of $(SiNaO)_2$ atoms, in which the oxygen atoms are out of the $(SiNa)_2$ plane by an average of 10.6°. The sodium atoms are in a distorted tetrahedral environment with a neighbouring Si and three O atoms. The Na–OMe bond distance is identical to that in $[Na\{CH(SiMe_3)(SiMe_2OMe)\}]_\infty$ (**5**),[11] but shorter than the Na–$O_{solvent}$ in **2b**, av. 2.374(5) Å. The Na–Si bond length is similar to that in $[Na(\mu\text{-}Si\textit{t}Bu_3)]_2$, 3.067(4) Å.[16] The Si–O bond is longer than in **5**, 1.6998(13) Å.[11] The Si–N distances in **2b** are significantly longer than in the free silylene **1**, av. 1.749 Å,[10] but similar to those in $[Li\{Si(NN)\textit{t}Bu\}(THF)_3]$, av. 1.807 Å.[12] Whereas in the silylene **1** the endocyclic C_6N_2Si atoms are coplanar, in **2b** the silicon atoms of each Si(NN) moiety is 0.13 Å out of the corresponding C_6N_2 plane.

Treatment of **1** with an excess of sodium afforded the brown–black crystalline compound **3**. The formation of a lime-green solid (**4**) was initially observed which subsequently went into solution. Compound **4** was obtained in high yield from the reaction of **1** and Na in a 3 : 1 ratio (iv in Scheme 1). Further reaction of **4** with sodium yielded compound **3**.

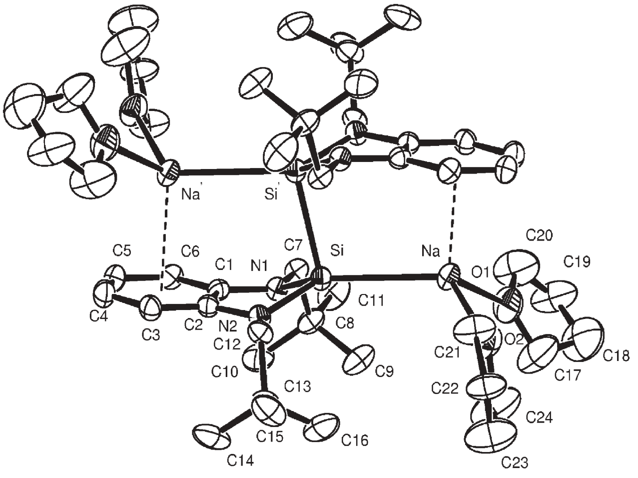

Fig. 2 ORTEP representation of **3**. Selected bond lengths [Å] and angles [°]: Na–Si 2.964(2), Na–M(1)′ 2.688(4), Si–Si′ 2.480(2), Si–N(1) 1.843(3), Si–N(2) 1.834(3); N(1)–Si–N(2) 84.73(13), N(2)–Si–Si′ 99.54(11), N(1)–Si–Si′ 99.07(10), Si′–Si–Na 100.12(6).

The structure of the centrosymmetric compound **3**[17] is illustrated in Fig. 2. Each of the four-coordinate silicon atoms is chelated by the nitrogen atoms of the puckered 5-membered ring which show considerably longer Si–N bonds, a somewhat longer C–C bond and a narrower N–Si–N′ angle than in **1** or **2b**. The sodium and silicon atoms of each Si(NN) moiety are 2.69 Å and −0.73 Å out of the attached C_6 plane. The four-coordinate sodium atoms have close contacts to two oxygen and a silicon atom and the centroid of the neighbouring C_6 ring. The Na–Si and Na···C_6H_4 distances in **3** may be compared with the Na–Si in $[Na(\mu\text{-}Si\textit{t}Bu_3)]_2$, 3.067(4) Å,[16] and the Na···C(range) in $Na_2Ar^*GeGeAr^*$, 2.049(3)–2.831(3) Å,[18] and $Na_2Ar^*SnSnAr^*$, 2.934(9)–3.084(9) Å (Ar^* = 2,4,6-Pr^i_3-C_6H_2),[18] while the Si–Si bond length in **3** is longer than in $[(NN)Si\textit{t}Bu]_2$, 2.465(7) Å,[12] but shorter than in $[(Et_2N)_2(Me_2\textit{i}PrC)\ Si]_2$, 2.539(2) Å.[19]

The structure of **4**[20] was determined by X-ray crystallography to be the THF-coordinated sodium salt of the cyclotrisilane radical *c*-$[Si(NN)]_3^-$, but having high R_1 (0.128) and wR_2 (0.366) values and data for **4** should therefore be considered with caution (Fig. 3). The poor solution of the structure is due to a disorder in the solvent as the thf ligands coordinated to Na along the 3-fold axis overlap with the next cation along the axis. Either the cations along the chain alternate between $[Na(THF)_5]$ and $[Na(THF)_3]$, or are all $[Na(THF)_4]$, with the trigonal pyramids aligned; in either case the arrangement is then disordered so as to average the structure. The anion consists of a *c*-$[Si(NN)]_3$ unit and lies on a site of a $\bar{6}$ symmetry. The Si–Si bond distances within the equilateral Si_3 triangle are slightly shorter than those found in $[K(THF)_6][\{Si(N'N')\}_4\text{-}c]$ [Si(N′N′) ≡ $Si\{(NEt)_2C_6H_4\text{-}1,2\}$]

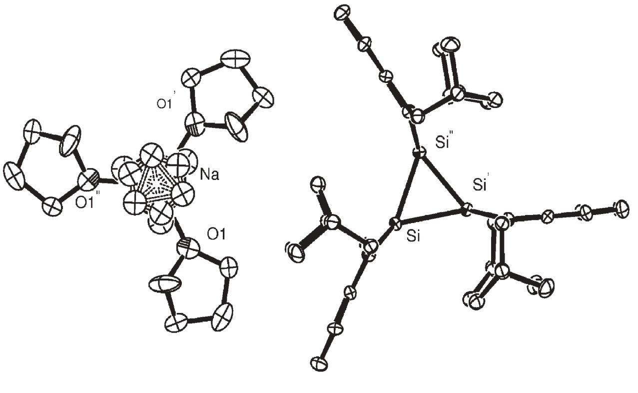

Fig. 3 ORTEP representation of **4**. Selected bond lengths [Å] and angles [°]: Si–Si′ 2.338(5), Si–N 1.784(6), N″–Si–N 86.6(4), Si–Si′–Si″ 60.

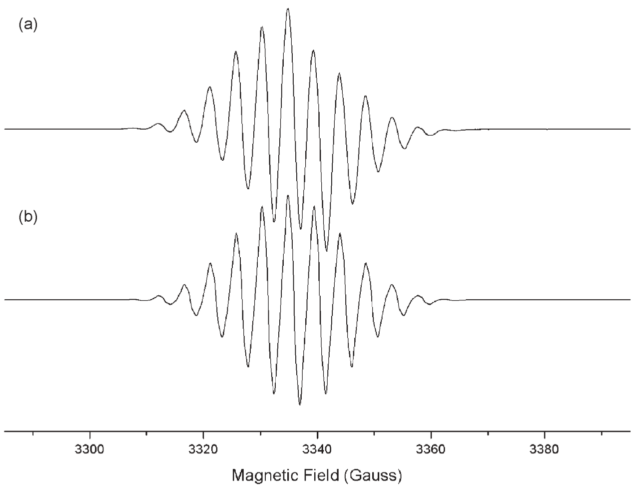

Fig. 4 The EPR spectrum of **4**: (a) experimentally observed in DME; (b) simulated, using g_{iso} 2.0045, $a(^{14}\text{N})$ 4.56(1).

[2.346(2) Å].[9] The Si–N bonds and the N–Si–N angle of **4** are somewhat longer and narrower than in the free silylene **1** [1.747(3) Å and 88.2(1)°, respectively.[10]

The EPR spectrum of **4** in DME (Fig. 4a) showed 11 of the 13 expected lines for a c-$[\text{Si(NN)}]_3^-$ radical consistent with a single electron being delocalised over the Si_3 ring and is in good agreement with the simulated spectrum ($g_{\text{iso}} = 2.0045$, $a(\text{N}) = 4.56$ G) (Fig. 4b).[21] The EPR spectrum of the related radical anion c-$[\text{Si}\{(\text{NEt})_2\text{C}_6\text{H}_4\text{-1,2}\}]_4^-$ showed 15 of the expected 17 lines.[9]

The reaction of **1** and sodium is believed to give in the first instance the intermediate $(\text{NN})\text{SiNa}_2$. Subsequently, the highly reactive silylene **1** inserts into the Si–Na bond of $(\text{NN})\text{SiNa}_2$ to yield **3**. Similarly, compound **4** is considered to be formed by reaction of **3** with an excess of **1** (from the initially high concentration of **1** in the mixture at the beginning of the reaction).

In conclusion, the isolation and characterisation of the crystalline sodium-silylene derivatives **2b**, **3** and **4** represents a significant extension to the already documented[22] wide range of reactions of thermally stable bis(amino)silylenes.

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Notes and references

‡ Selected NMR data of **2b**: ^{1}H NMR ($\text{C}_6\text{D}_6/\text{C}_4\text{D}_8\text{O}$), δ 1.06 (t, 6 H, Et_2O), 1.16 (s, 18 H, Bu^t), 1.47 (m, 4 H, THF), 2.89 (s, 3 H, MeO), 3.25 (q, 4 H, Et_2O), 3.39 (d, 4 H, CH_2), 3.54 (m, 4 H, THF), 6.74 (s, 4 H, Ph); ^{13}C NMR ($\text{C}_6\text{D}_6/\text{C}_4\text{D}_8\text{O}$): δ 15.47 (MeO), 25.78 (THF), 29.53 (C*Me*$_3$), 34.92 (*C*Me$_3$), 47.99 (Et_2O), 57.46 (Et_2O), 65.86 (CH_2), 67.79 (THF), 106.36, 114.96 and 154.96 (Ph); ^{29}Si NMR ($\text{C}_6\text{D}_6/\text{C}_4\text{D}_8\text{O}$): δ 16.89; ^{23}Na NMR ($\text{C}_6\text{D}_6/\text{C}_4\text{D}_8\text{O}$): δ 9.77 ($\Delta w_{1/2} = 2.2$ KHz).

§ Selected NMR data of **3**: ^{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). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8-THF) δ: 26.27 (THF), 29.8 (C*Me*$_3$), 36.4 (*C*Me$_3$), 56.7 (CH_2), 68,10 (THF), 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, $\Delta v_{1/2} \sim 1500$ 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%.

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15 Crystal data for **2b**: $\text{C}_{50}\text{H}_{94}\text{N}_4\text{Na}_2\text{O}_6\text{Si}_2$, $M_\text{r} = 949.45$, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.0924(4)$, $b = 11.3065(5)$, $c = 21.7705(8)$ Å, $\beta = 102.275(2)°$, $U = 2908.5(2)$ Å^3, $Z = 2$, $\mu = 0.12$ mm^{-1}, $T = 173(2)$ K, 5086 unique reflections collected, $R_1 = 0.093$ for 3587 reflections with $I > 2\sigma(I)$, $wR_2 = 0.291$ for all reflections, Data collection KappaCCD, full-matrix least squares refinement on F^2, SHELX-97. There is a problem with the THF and Et_2O ligands where unresolved residual density suggests some slight disorder between the ligands. The fact that this could not be successfully modelled is reflected in the rather high residuals. CCDC 273243 (**2b**), 273246 (**3**) and 273245 (**4**). See http://dx.doi.org/10.1039/b509310d for crystallographic data in CIF or other electronic format..

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20 Crystal data for **4**: $\text{C}_{64}\text{H}_{110}\text{N}_6\text{NaO}_4\text{Si}_3$, $M_\text{r} = 1134.84$, hexagonal, space group $P6_3/m$ (No. 176), $a = b = 15.0206(17)$, $c = 16.8690(16)$ Å, $U = 3296.1(6)$ Å^3, $Z = 2$, $\mu = 0.13$ mm^{-1}, $T = 173(2)$ K, 1467 unique reflections collected, $R_1 = 0.128$ for 1079 reflections with $I > 2\sigma(I)$, $wR_2 = 0.366$ for all reflections, Data collection KappaCCD, full-matrix least squares refinement on F^2, SHELX-97. Hydrogen atoms for all the THF ligands were omitted. The structure is disordered as the THF ligands coordinated to Na along the 3-fold axis overlap with the next cation along the axis. Either the cations along the chain alternate between $[\text{Na(THF)}_5]$ and $[\text{Na(THF)}_3]$, or are all $[\text{Na(THF)}_4]$ with the trigonal pyramids aligned; in either case the arrangement is then disordered so as to average the structure. These THF ligands are of course also disordered about the 3-fold axis.

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