Synthesis, Structures and Reactions of New Thermally Stable Silylenes

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Two representatives **1a** and **1b** of a new series of stable but reactive bis(amino)silylenes, derived from the *N,N′*-dineopentyl-1,2-phenylenediamido ligand $RC_6H_3[N(CH_2Bu^t)]_2$, have been prepared by reductive elimination from $RC_6H_3[N(CH_2Bu^t)]_2SiCl_2$ and characterised by NMR spectroscopy and for **1a** by X-ray crystallography; the silylenes $Si[N(CH_2Bu^t)]_2C_6H_3$-1,2-R (R = H **1a** or 4-Me **1b**) readily undergo oxidative addition with EtOH or MeI.

Transient silylenes SiX_2 (X^- = a monohapto ligand) are important synthons in organosilicon chemistry, but a thermally stable analogue $Si[N(Bu^t)CHCHNBu^t]$ **I** was only recently described; the structure of gaseous **I** was established by electron diffraction.[1]

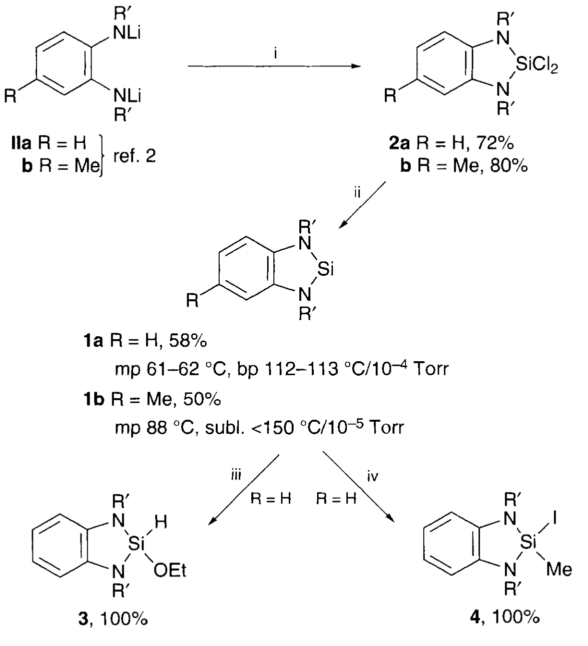
We now report on the synthesis and some oxidative addition reactions (Scheme 1) and the NMR spectroscopic characterisation[†] of two new crystalline, thermally stable, coloured, diamagnetic bis(amino)silylenes $Si[N(CH_2Bu^t)]_2C_6H_3$-1,2-R-4 (R = H **1a** or 4-Me **1b**) and the single-crystal X-ray molecular structure of **1a**,[‡] Fig. 1.

The starting material for the synthesis of silylenes **1a** and **1b** were the *N,N′*-dineopentyl-*o*-phenylenediamidodilithium compounds **IIa** and **IIb**,[2] which were converted into the bis(amino)dichlorosilanes **2a** and **2b** by treatment with silicon tetrachloride (i in Scheme 1). The dechlorination of compounds **2a** and **2b**, using potassium in refluxing tetrahydrofuran, was rather sluggish (ii in Scheme 1). By contrast the oxidative addition of ethanol or iodomethane to the silylene **1a** was fairly rapid under ambient conditions in benzene (iii in Scheme 1), as judged by the rate of discharge of the yellow colour of **1a**.

Compounds **1**–**4** gave satisfactory microanalysis, EI mass spectra (parent molecular ions) as well as ^1H, ^{13}C and ^{29}Si NMR spectra in [$^2H_6$]benzene.[†]

The yellow [λ_{max} of **1a** in C_6H_{14}: 344 (w,sh), 296 and 249 nm], crystalline, low melting, volatile (Scheme 1) bis(amino)silylenes **1a** and **b** are soluble in hydrocarbons. The molecular weight of the silylene **1a** in benzene (cryoscopy) was consistent with a monomeric structure. The ^{29}Si NMR spectral chemical shifts of the silylenes **1a** (δ +96.92) and **1b** (δ +97.72) are at higher frequency than for their dichlorosilicon(IV) precursors **2a** (δ −24.08) and **2b** (δ −24.02). These data may be compared with δ +78.3 for the silylene **I** and δ −40.7 for [**I**]Cl_2.[1] The ^{15}N NMR spectral chemical shifts for **1a** (δ −225.0) and **I** (δ −170.3) are also of similar magnitude.

The molecular structure of the crystalline silylene **1a** is shown in Fig. 1. It is evident that there are no close contacts between monomeric units, Fig. 2. The skeletal atoms $SiN_2(C_2)C_6H_4$ are essentially coplanar, with the *tert*-butyl



Scheme 1 Synthesis and reactions of the bis(amino)silylenes **1a** and **1b** (R′ = CH_2-Bu^t). *Reagents and conditions*: i, $SiCl_4$, C_6H_6, reflux 6 h; ii, 2 K, THF, reflux, 3 d; iii, EtOH, C_6D_6, 25 °C, 16 h; iv, MeI, 25 °C, 16 h.

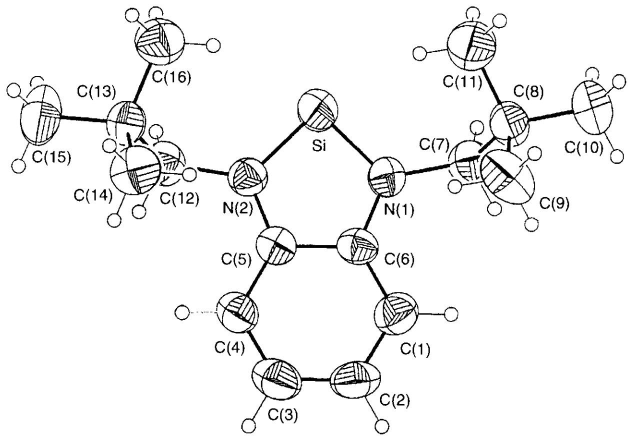


Fig. 1 The X-ray structure and atom labelling scheme for $Si[N(CH_2$-$Bu^t)]_2C_6H_4$-1,2 **1a**. Selected bond lengths (Å) and angles (°) (see also Table 1): Si–N(1)[N(2)]–C(7)[C(12)] 122.6(3) [123.7(3)], Si–N(1)[N(2)]–C(6)[C(5)] 114.1(2) [114.1(2)], C(6)[C(5)]–N(1)[N(2)]–C(7)[C(12)] 123.0(3) [121.9(3)].

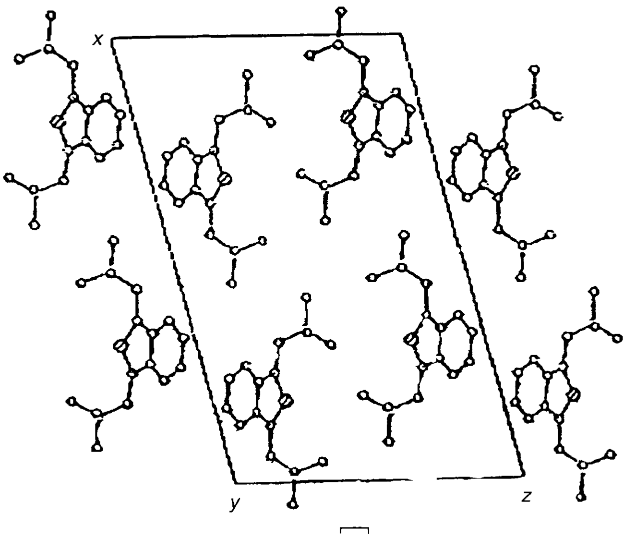


Fig. 2 A view of the unit cell of $Si[N(CH_2Bu^t)]_2C_6H_4$-1,2 **1a**

Table 1 Some comparative stuctural data for the silylenes **1a** and **I**[1,3]

Parameter	**1a** (cryst.)	**I** (gas)[1]	**I** (calc.)[1]	**I** (calc.)[3]
Si–N/Å	1.752(3), 1.747(3)	1.753(5)	1.7425	1.798
$\mathrm{N{-}C_{sp^2}}$[a]/Å	1.385(5), 1.380(5)	1.400(9)	1.3899	1.389
$\mathrm{C_{sp^2}{-}C'_{sp^2}}$[b]/Å	1.417(5)	1.347(21)	1.3325	1.362
N–Si–N′/°	88.2(1)	90.5(10)	86.04	86.5
$\mathrm{N{-}C_{sp^2}{-}C'_{sp^2}}$[b]/°	111.9(3), 111.3(3)	114.1(5)	112.20	113.4

[a] N(1)–C(6) and N(2)–C(5) for **1a**. [b] C and C′ refer to C(5) and C(6) for **1a**

fragments of the *N*,*N*′-dineopentyl groups arranged out of plane and *cis*- to one another, the nitrogen atoms being in an essentially trigonal-planar environment. The silicon atom is centred in a lipophilic pocket, which may in part account for the kinetic stability of **1a** with respect to di- or oligo-merisation or rearrangement. The C–C bond lengths in the C_6 ring are in the narrow range 1.372(6)–1.417(5) Å, showing that the aromatic character of the ring is preserved.

For the gas-phase structure of **I**, five geometric parameters were determined and compared with calculated values;[1,3] these, together with corresponding X-ray data for **1** are listed in Table 1.

The major difference in the skeletal structures of **1a** and **I** relates to the $\mathrm{C_{sp^2}{-}C'_{sp^2}}$ bond of the five-membered ring: 1.417(2) (**1a**) and 1.347(21) Å (**I**);[1] these values are fairly close to those in benzene (1.39 Å) and ethene (1.35 Å), respectively, which suggests that there is little $\mathrm{C{=}\overset{\curvearrowright}{C}{-}N}$ delocalisation, $\overset{\curvearrowright}{\ddot{\mathrm{N}}}\mathrm{{-}Si}$ being preferred, consistent with conclusions drawn from experimental and calculated $\mathrm{He^{I}}$ and $\mathrm{He^{II}}$ photoelectron spectral assignments.[3] Hence, the central $\mathrm{C_{sp^2}{-}C'_{sp^2}}$ bond may not be crucial in determining the stability of a bis(amino)silylene; however, from calculated heats of hydrogenation of the model compounds $\overline{\mathrm{SiN(H)CHCHN}}\mathrm{H}$ and $\overline{\mathrm{SiN(H)CH_2CH_2N}}\mathrm{H}$, it was estimated that the former was stabilised relative to the latter by 13.92 kcal $\mathrm{mol^{-1}}$ (1 cal = 4.184 J) [$\overline{\mathrm{SiN(Bu^t)CH_2CH_2N}}\mathrm{Bu^t}$ was said to dimerise in the solid state.[4]].

The use of bulky *N*,*N*′-disubstituted amido ligands to stabilise otherwise kinetically labile open-shell molecules dates back to 1974 and is well documented; examples include the compounds $\mathrm{M(NR_2)_2}$ (M = Ge, Sn, P or As and R = $\mathrm{SiMe_3}$), $\mathrm{M'(NR_2)_3}$ (M′ = Ge or Sn) and carbene-metal complexes having the ligand $\overline{\mathrm{CN(Me)CH_2CH_2N}}\mathrm{Me}$.[5] The most recent relevant examples relate to the crystallographically characterised molecules $\mathrm{\overline{Ge[N}(R)]_2C_6H_4\text{-}1,2}$,[6] $\mathrm{\overline{Sn[N}(R')_2C_6H_4\text{-}1,2}$[2] and $\mathrm{\{\overline{Sn[N}(R)]_2C_6H_4\text{-}1,2\}_2(tmeda)}$ (R = $\mathrm{SiMe_3}$, R′ = $\mathrm{CH_2Bu^t}$);[2] others structurally related to **I** have the formula $\mathrm{\overline{M[N(R'')CHCHN}R'']}$: M = C and R″ = adamantyl,[7a] Me,[7a] Et,[7b] $\mathrm{Pr^i}$,[7b] $\mathrm{Bu^t}$,[3] $\mathrm{C_6H_4Me}$-*p*,[7a] $\mathrm{C_6H_4Cl}$-*p*,[7a] $\mathrm{C_6H_2Me_3}$-2,4,6;[7a] M = Ge and R″ = $\mathrm{Bu^t}$;[3,7c] or $\overline{\mathrm{CN(Ph)NN(Ph)N}}\mathrm{Ph}$.[7d]

We are grateful to the Deutsche Forschungsgemeinschaft for the award of a fellowship (to B. G.).

Received, 4th July 1995; Com. 5/04347E

Footnotes

† *Selected spectroscopic data* {^{1}H NMR at 250 MHz, ^{13}C{^{1}H} NMR at 62.86 MHz, ^{15}N NMR (ref. δ $\mathrm{MeNO_2}$ = 0) at 30.4 MHz, ^{29}Si{^{1}H} NMR at 99.33 MHz; at 293 K, in [$^2\mathrm{H_6}$]benzene}. For **1a**: ^{1}H NMR δ 0.89 ($\mathrm{CMe_3}$, s), 3.58 ($\mathrm{CH_2}$, s) and 7.01 (phenyl, s); ^{13}C{^{1}H} NMR δ 28.72 ($\mathrm{C}Me_3$), 33.17 ($C\mathrm{Me_3}$), 54.91 ($\mathrm{CH_2}$), 141.48, 110.67 and 118.48 (phenyl); ^{15}N NMR δ −225.0; ^{29}Si{^{1}H} NMR δ 96.92. For **1b**: ^{1}H NMR δ 0.91 and 0.92 ($\mathrm{CMe_3}$, 2 s), 3.6 and 3.62 ($\mathrm{CH_2}$, 2 s), 2.39 ($\mathrm{CH_3}$, s) and 6.82–6.96 (phenyl, m); ^{13}C{^{1}H} NMR δ 28.76 and 28.73 ($\mathrm{C}Me_3$), 33.18 and 33.22 ($C\mathrm{Me_3}$), 55.88 and 55.01 ($\mathrm{CH_2}$), 21.53 ($\mathrm{CH_3}$), 139.59, 141.64, 127.48, 110.39, 111.36 and 119.33 (phenyl); ^{29}Si{^{1}H} NMR δ 97.72. For **2a**: ^{1}H NMR δ 0.95 ($\mathrm{CMe_3}$, s), 3.17 ($\mathrm{CH_2}$, s) and 6.67–6.77 (phenyl, m); ^{13}C{^{1}H} NMR δ 29.02 ($\mathrm{C}Me_3$), 33.67 ($C\mathrm{Me_3}$), 55.57 ($\mathrm{CH_2}$), 139.0, 119.36 and 110.53 (phenyl); ^{29}Si{^{1}H} NMR δ −24.08. For **2b**: ^{1}H NMR δ 0.95 and 0.96 ($\mathrm{CMe_3}$, 2 s), 3.17 and 3.19 ($\mathrm{CH_2}$, 2 s), 2.27 ($\mathrm{CH_3}$, s) and 6.65 (phenyl, s); ^{13}C{^{1}H} NMR δ 28.82 and 28.88 ($\mathrm{C}Me_3$), 33.61 and 33.64 ($C\mathrm{Me_3}$), 55.45 and 55.6 ($\mathrm{CH_2}$), 21.48 ($\mathrm{CH_3}$), 136.87, 139.02, 110.44, 111.61, 119.55 and 128.26 (phenyl). For **3**: ^{1}H NMR δ 0.84 ($\mathrm{CMe_3}$, s), 1.03 ($\mathrm{CH_3}$, s), 2.98 and 3.13 ($\mathrm{CH_2}$, AB-type) and 6.78–7.5 (phenyl); ^{13}C{^{1}H} NMR δ 11.94 ($\mathrm{CH_3}$), 28.85 ($\mathrm{C}Me_3$), 33.51 ($C\mathrm{Me_3}$), 55.42 ($\mathrm{CH_2}$), 110.68, 118.98 and 139.61 (phenyl); ^{29}Si{^{1}H} NMR δ −8.9. For **4**: ^{1}H NMR δ 0.93 ($\mathrm{CMe_3}$, s), 1.05 ($\mathrm{CH_3}$, t), 3.14 and 3.11 ($\mathrm{CH_2}$), 3.45 ($\mathrm{CH_2}$, q), 5.6 (SiH, s) and 6.7–7.0 (phenyl); ^{13}C{^{1}H} NMR δ 28.97 ($\mathrm{C}Me_3$), 34.35 ($C\mathrm{Me_3}$), 54.9 ($\mathrm{CH_2}$), 58.1 ($\mathrm{OCH_2}$), 117.91, 108.81 and 140.33 (phenyl); ^{29}Si{^{1}H} NMR δ −31.2.

‡ *Crystal data* for **1a** $\mathrm{C_{16}H_{26}N_2Si}$, monoclinic, space group C_2 (no. 5), a = 21.219(5), b = 5.332(3), c = 13.633(3) Å, β = 104.32(2)°, U = 1663.0(6) $\mathrm{Å^3}$, Z = 4, D_c = 1.096 g $\mathrm{cm^3}$, μ = 0.13 $\mathrm{mm^{-1}}$, T = 298 K, specimen 0.21 × 0.12 × 0.09 $\mathrm{mm^3}$, 3287 unique reflections for $3 \leqslant 2\theta \leqslant 45°$, 2097 reflections with $[F_o \geqslant 4\sigma(F)]$ used in the refinement; R = 0.0472, R_w = 0.0478. Siemens P4 4-circle diffractometer, λ(Mo-Kα) 0.71069 Å, no absorption corrections, refinement with non-hydrogen atoms anisotropic, $w^{-1} = [\sigma^2(F_o) + 0.0008\ (F_o{}^2)]$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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