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A crystalline carbene–silylene adduct 1,2-$C_6H_4[N(R)]_2C$-$Si[N(R)]_2C_6H_4$-1,2 (R = CH_2Bu^t); synthesis, structure and bonding in model compounds†

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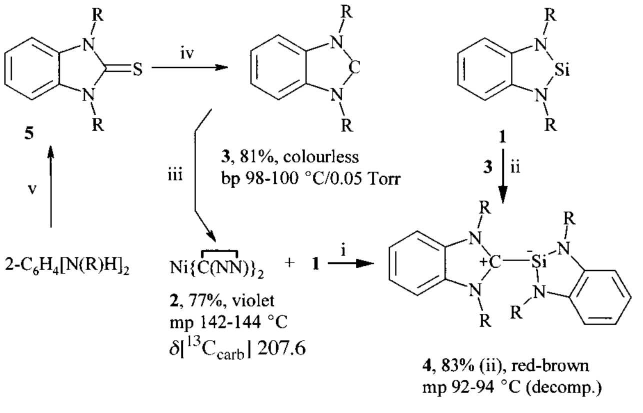
The red–brown, crystalline carbene–silylene adduct, 1,2-$C_6H_4[N(R)]_2C$-$Si[N(R)]_2C_6H_4$-1,2 (R = CH_2Bu^t) 4, was obtained from its factors, the carbene 3 and silylene 1, or from Ni{C[N(R)]$_2$C$_6$H$_4$-1,2}$_2$ and 1; the X-ray structure of 4 shows a long C–Si bond [2.162(5) Å] and NMR spectral data indicate significant C^+–Si^- bond polarity, features consistent with DFT calculations at the B3LYP/6-311+G level on [(CH)$_2$(NH)$_2$]C–Si[(NH)$_2$(CH)$_2$], ($H_2N)_2C$–$Si(NH_2)_2$ or even [(CH)$_2$(NH)$_2$]C–SiH$_2$ and ($H_2N)_2C$–SiH_2, but not H_2C=$Si(NH_2)_2$ or H_2C=Si[(NH)$_2$(CH)$_2$].**

Recently we reported on the coordination chemistry of the stable silylene Si[N(CH_2Bu^t)]$_2C_6H_4$-1,2 **1** [abbreviated as Si(NN)]. The crystalline, diamagnetic complexes [Ni(PPh$_3$)-{Si(NN)}$_3$], [Ni{Si(NN)}$_4$] or *trans*-[Pt{Si(NN)Cl}$_2$-{Si(NN)}$_2$] were obtained from **1** and [NiCl$_2$(PPh$_3$)$_2$], [Ni(cod)$_2$] or [PtCl$_2$(PPh$_3$)$_2$].[1] An attempt to synthesise a mixed carbene(silylene)–nickel complex was the starting point of the present investigation.

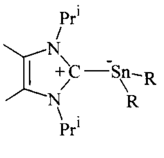
The new bis(carbene)nickel(0) complex **2** {obtained from [Ni(cod)$_2$] and the carbene **3** (*cf.* ref. 2)} with 2 equiv. of **1** afforded the crystalline carbene-silylene adduct **4** in good yield, accompanied by a deposit of Ni; an intermediate may have been a transient Ni{C(NN)}{Si(NN)} complex. Compound **4** was also prepared directly from its factors **1** and **3**. Compound **3** was synthesised from the thiourea **5** and C$_8$K at ambient temperature (*cf.* ref. 3). These data are summarised in Scheme 1.

Each of the new compounds **2**–**5** gave satisfactory microanalytical and NMR spectroscopic data. The $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectral signals for **4** in [^{2}H]$_8$toluene or [^{2}H]$_6$benzene at ambient temperature were at *ca.* 15 ppm lower frequency compared to the values in the free carbene **3**, δ_C 231.6, or silylene **1**, δ_{Si} 96.9.[4] However, these chemical shifts for **4** rose in frequency with increasing temperature, steadily approaching those for **3** and **1**, indicative of a dissociative equilibrium: **4** ⇄ **1** + **3**. Nonetheless, the EI mass spectrum of **4** at 70 eV showed the molecular ion [**4**]$^+$ at *m/z* 532 as the highest peak present in substantial abundance (46%).

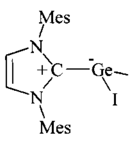


Scheme 1 Synthesis of the carbene-silylene adduct **4** and compounds **2**, **3** and **5** (R = CH_2Bu^t). *Reagents and conditions* (at *ca.* 20 °C): i or ii, C$_6$H$_6$; iii, [Ni(cod)$_2$], C$_6$H$_6$; iv, 2 C$_8$K, thf; v, C(S)Cl$_2$, 2 NEt$_3$.

Crystalline **4** is a monomer, Fig. 1.‡ There is a long central bond of 2.162(5) Å between the three-coordinate C and Si atoms, the carbon atom being in an almost planar but the silicon in a pyramidal environment: the sum of the angles at C(1) being 351.4° and at Si 291.6°. This may be compared with the C=Si bond length in the silenes Ad(Me$_3$SiO)C=Si(SiMe$_3$)$_2$ [1.764(3) Å, twist angle 14.6°][5] and Bu$^t_2$(Me)Si(Me$_3$Si)C=SiMe$_2$ [1.702(5) Å, twist angle 1.6°][6] having the essentially planar double bond geometry; the sum of the three angles at Si or C is 360°. In **4**, the fold angles are 28° at C(1) and 77° at Si. There is significant torsion of the N$_2$CSiN$_2$ skeleton as evident by the dihedral angles N(1)–C(1)–Si–N(4) of 75° and N(2)–C(1)–Si–N(3) of 128.1°. We infer that the CSi bond in **4** is dipolar, with the silicon being the negative end of the dipole, a C=Si double bond being ruled out. This conclusion is supported by DFT calculations on model compounds (see below), as well as by analogy with suggestions on the nature of the di(amino)-carbene–tin(II) and –germanium(II) complexes **6**,[7] **7**,[8] and **8**.[9]



6 R = C$_6$H$_2$Pr$^i_3$-2,4,6
7 R = Cl



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The silylene $\overline{M[N(Bu^t)(CH)_2N}Bu^t]$ (M = Si) failed to react with the carbene (M = C), germylene (M = Ge) or CO.[10] By contrast, **1** not only forms the adduct **4** with **3**, but also reacts with the heavier group 14 carbene analogues M′[N(SiMe$_3$)$_2$]$_2$ (M′ = Ge, Sn or Pb),[11] although we now report that it did not react with CO in supercritical xenon at > 20 atm at 25 °C.[12]

Density functional calculations[13] were performed on the parent silene H$_2$C=SiH$_2$ **9** and derivatives X$_2$CSiY$_2$ **10**–**15** (X$_2$

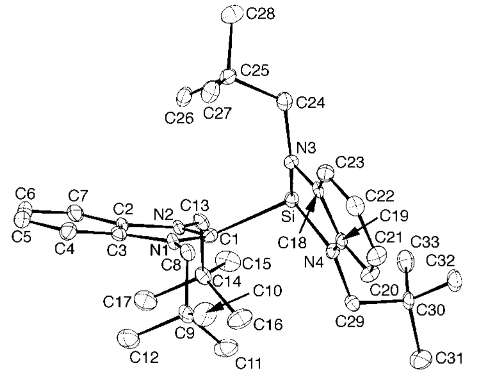


Fig. 1 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Si–C(1) 2.162(5), C(1)–N(1) 1.362(5), C(1)–N(2) 1.362(5), Si–N(3) 1.791(4), Si–N(4) 1.790(4), N(1)–C(1)–N(2) 105.6(4), N(3)–Si–N(4) 87.5(2).

and Y_2 are hydrogens or nitrogen functions, Table 1). The structures, illustrated by **9**, **10**, **12** and **15** in Fig. 2, separate into two distinct groups. The model compounds $H_2C{=}SiY_2$ **9–11** all have CSi double bonds with distances near 1.70 Å, planar or nearly planar geometries and large association energies. The second group, **12–15**, like **4**, have longer SiC distances (1.93–2.02 Å, compared with 1.885 Å in $H_3C{-}SiH_3$),[14] strongly pyramidal geometries at silicon, and weaker association energies.

The dramatic structural changes produced by substituting the hydrogens at carbon by amino groups are clarified by natural bond order analysis. The N–C–N unit delocalises the positive charge on carbon. The polarities of **12–15** are reversed (*cf.* **9** and **10**) and the SiY_2 moieties are negative (Fig. 2). The π-delocalisation causes amino groups on carbon, but not on silicon, to be co-planar (or nearly so). The silicon substituents bond through the silicon p orbitals at angles approaching 90°.

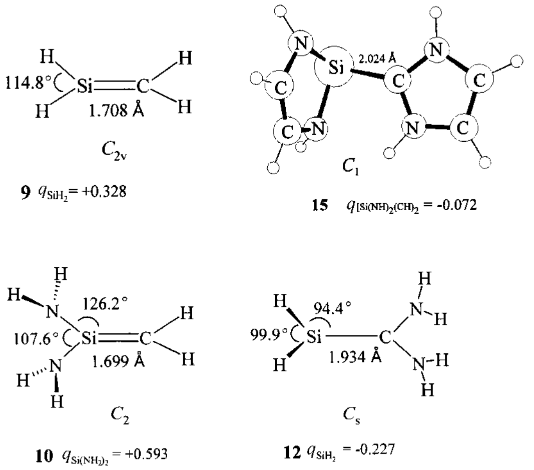
The association energies for the model compounds **9–15** (Table 1) are highly revealing. These are based on the energies of the process $X_2C\colon + \colon SiY_2 \longrightarrow X_2CSiY_2$ [using the $\colon CH_2$ ($^1A_1$) energy for uniformity as the other carbenes and silylenes are ground state singlets]. The association energies vary remarkably, from 116.5 kcal mol^{-1} for the parent silene **9** to only 3.2 kcal mol^{-1} for **15**, the model closest to **4**. These energies reflect the changes in carbene and silylene stability due to their substituents. The C=Si bond in the parent silene **9** is weakened markedly by NH_2 substitution, much more on C than on Si. The effects on C and Si are roughly additive. The aromaticity conferred by the five-membered $Si[(NH)_2(CH)_2]$ ring in **11** (*vs.* **10**) has a much greater effect on lowering the association energy than that due to the $C[(NH)_2(CH)_2]$ ring in **13** (*vs.* **12**).[15]

The structures of **4** and **12–15** can best be considered as donor–acceptor complexes in which the carbene lone pair interacts with the formally vacant silicon p orbital, as suggested for the $H_2Si{-}CO$ complex which also has pronounced pyramidalisation at silicon.[16] The polarisation of the parent silene **9** is reversed by amino substitution at the carbon and the SiY_2 moiety assumes anionic character. The lowering of the association energy in **12–15** also results in longer CSi separations. The difference between the CSi distance in **15** (2.02 Å) from that in **4** (2.16 Å) is not significant in view of the weakness of these complexes. The computed torsion barrier for **15** is only 1 kcal mol^{-1} and, like **4**, has a significantly twisted energy minimum.

Table 1 Carbene–silylene association energies[a]

			r_{CSi}/Å	$-\Delta H_0$/ kcal mol^{-1}
9	$H_2C{=}SiH_2$	C_{2v}	1.708	116.5
10	$H_2C{=}Si(NH_2)_2$	C_2	1.699	89.3
11	$H_2C{=}Si[(NH)_2(CH)_2]$	C_{2v}	1.698	74.7
12	$(H_2N)_2C{-}SiH_2$	C_s	1.934	47.6
13	$[(CH)_2(HN)_2]C{-}SiH_2$	C_s	1.927	46.4
14	$(H_2N)_2C{-}Si(NH_2)_2$	C_s	1.960	15.8
15	$[(CH)_2(HN)_2]C{-}Si[(NH)_2(CH)_2]$	C_1	2.024	3.2

[a] B3LYP/6-311+G(d, p) optimised data, with zero-point energy obtained at B3LYP/6-31G* scaled by 0.96 for $-\Delta H_0$ (1 kcal = 4.182 kJ).



9 q_{SiH_2} = +0.328

15 $q_{[Si(NH)_2(CH)_2}$ = -0.072

10 $q_{Si(NH_2)_2}$ = +0.593

12 q_{SiH_2} = -0.227

Fig. 2 Optimized structures at B3LYP/6-311+G** level for silenes **9**, **10**, **12** and **15** (Mulliken charges are given).

In a full paper, we shall report on the synthesis and structures of the heavier group 14 analogues of the carbene–silylene complex **4**.

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Notes and references

† No reprints available.

‡ *Crystal data for* **4**: $C_{33}H_{52}N_4Si$, M = 532.9, monoclinic, space group $P2_1/n$ (no. 14), a = 10.212(4), b = 16.231(5), c = 19.776(8) Å, β = 101.73(3)°, U = 3209(2) Å^3, Z = 4, D_c = 1.10 g cm^{-3}, μ(Mo-Kα) = 0.1 mm^{-1}, T = 173(2) K, Final residuals were R_1 = 0.075 for the 3093 reflections with $I > 2\sigma(I)$ and wR_2 = 0.198 for all reflections. Intensities were measured in the ω–2θ mode in the range $2 < \theta < 25°$ on an Enraf-Nonius CAD4 diffractometer. Full-matrix least-squares refinement, on all F^2, with SHELXL-93, H atoms in riding mode and non-H atoms anisotropic. CCDC 182/1199. See http://www.rsc.org/.suppdata/cc/755/ for crystallographic files in .cif format.

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