Silylene Complexes from a Stable Silylene and Metal Carbonyls: Synthesis and Structure of $[Ni\{(Bu^tN–CH=CH–NBu^t)Si\}_2(CO)_2]$, a Donor-free Bis-silylene Complex

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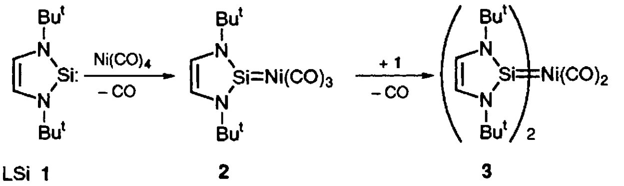
$[Ni(LSi)_2(CO)_2]$ **3**; the first silylene complex of nickel, has been obtained from the stable silylene 1,3-di-*tert*-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene (LSi) **1** and tetracarbonylnickel; complex **3** was characterized by single crystal X-ray diffraction and NMR spectroscopy (^1H, ^{13}C, ^{29}Si).

Silylenes, like carbenes, have been shown to form stable metal complexes.[1–3] Unlike the carbene complexes, silylene complexes usually require additional stabilization by a Lewis base coordinated to silicon. The structure of the first base-free silylene complex has only recently been reported.[3]

The synthesis of 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene **1**,[4] a stable silylene,[5] provided the possibility to obtain silylene complexes by CO substitution from metal carbonyls. Reaction of **1** with $Ni(CO)_4$ gave the bis-silylene complex **3** in nearly quantitative yield.[†] Compound **3** is the first silylene complex of nickel as well as the first bis-silylene complex without Lewis base stabilization. It is highly air- and moisture-sensitive but quite stable thermally (mp 160 °C, decomp.). No monosubstitution product **2** was observed on changing the reaction conditions [inverse addition of **1** to a large excess of $Ni(CO)_4$ at −80 °C] or on the attempted comproportionation of **3** with $Ni(CO)_4$[7] (Scheme 1).

The structure of **3**, determined by single crystal X-ray diffraction,[‡] shows a slightly distorted tetrahedral arrangement of two silylene and two carbonyl ligands around nickel. The C_2N_2Si units of both silylene ligands are planar. The coordination geometry of nickel in **3** is similar to that of the CC saturated germanium analogue.[6]



Scheme 1

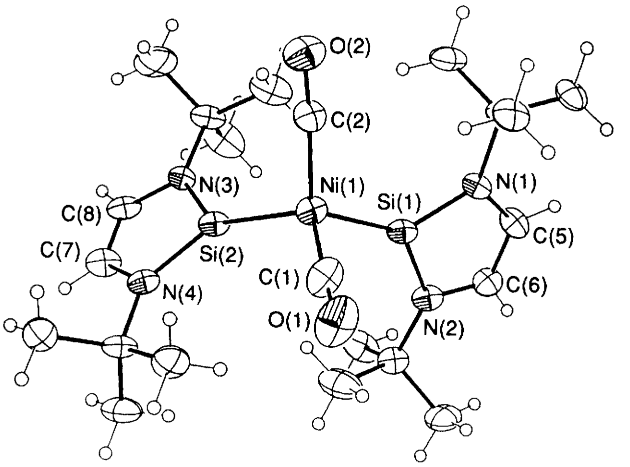


Fig. 1 Molecular structure of $[Ni\{Bu^t–NCH=CHN–Bu^t)Si\}_2(CO)_2]$ **3**. ORTEP view with hydrogen atoms omitted for clarity. Thermal ellipsoids are at the 50% probability level. Selected bond distances (pm) and bond angles (°) as follows: Ni(1)–Si(1) 220.7(2), Ni(1)–Si(2) 221.6(2), Ni(1)–C(1) 177.8(7), Ni(1)–C(2) 176.1(6), C(1)–O(1) 113.9(9), C(2)–O(2) 115.7(7), Si(1)–N(1) 174.5(5), Si(1)–N(2) 174.3(5), Si(2)–N(3) 174.9(5), Si(2)–N(4) 174.5(5), N(1)–C(5) 138.6(7), N(2)–C(6) 140.2(9), N(3)–C(8) 139.7(8), N(4)–C(7) 139.3(9), C(5)–C(6) 134.4(8), C(7)–C(8) 133.0(9), Si(1)–Ni(1)–Si(2) 108.4(1), Si(1)–Ni(1)–C(1) 103.5(2), Si(1)–Ni(1)–C(2) 112.5(2), Si(2)–Ni(1)–C(1) 115.3(3), Si(2)–Ni(1)–C(2) 106.2(2), C(1)–Ni(1)–C(2) 111.1(3). N(1)–Si(1)–N(2) 90.0(2), N(3)–Si(2)–N(4) 89.9(2).

The N–Si–N angle of **3** is remarkably small (90°), its value being close to what was predicted[7] for free silylenes. The Si–Ni bond is short; bond lengths reported for silylene complexes of iron, chromium and manganese[1] are typically 10–15 pm longer than the Si–Ni bond in **3**. A recent theoretical study predicts a Si–Ni bond length of 229 pm.[8]

The CO stretching frequencies and the chemical shift, $\delta(^{13}C)$, of the carbonyl groups of **3** are both nearly identical with the values reported for the phosphine complex $[Ni(Ph_3P)_2(CO)_2]$ [ν/cm^{-1},[9] 2000 (A_1) and 1941 (B_1); $\delta(^{13}CO)$,[10] 199.4].

Silicon NMR studies show the silicon nucleus to experience moderate deshielding upon coordination (**1** + 78.4 ppm, **3** + 97.5 ppm);[§] all other NMR shifts show little change. No satellites due to coupling to ^{61}Ni could be detected.

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Footnotes

[†] Synthesis of **3**: compound **1** (0.158 ml, 1.22 mmol) was added to a solution of $Ni(CO)_4$ (480 mg, 2.44 mmol) in *n*-hexane (5 ml) at room temperature. After CO evolution ceased (*ca.* 5 min) stirring was continued for 1 h. Cooling to +5 °C (2 h) then −25 °C (1 day) gave 576 mg (93%) of **3** after filtration and drying.

[‡] *Crystal data* for **3**: $C_{22}H_{40}N_4NiSi_2O_2$, $M = 507.5$, crystal size = 0.1 × 0.2 × 0.2 mm, monoclinic, space group $P2_1/c$, $a = 9.4873(15)$, $b = 16.374(2)$, $c = 17.8784(15)$ Å, $\beta = 105.245(11)°$, $V = 2679.5(5)$ Å^3, $Z = 4$, $D_c = 1.258$ g cm^{-3}, λ(Cu-Kα) = 1.54178 Å, μ(Cu-Kα) = 2.087 mm^{-1}, $F(000) = 1088$, scan type $2\theta–\theta$, $T = 113(2)$ K, $4.0 < 2\theta$ 114.0°, total unique data 3571 (R_{int} = 10.6%), no. of observations [$(F) > 4\sigma(F)$] 2745, observations/variables 9.7, $R = 0.068$, $R_w = 0.089$, maximum peak in final Fourier difference synthesis 1.13 e Å^{-3}. Data were collected on a Siemens P4 diffractometer. No absorption correction was applied. Lorentz and polarisation corrections were applied. Systematically absent reflexions were rejected and equivalent reflexions were merged. The heavy-atom positions were determined by direct methods. Subsequent difference Fourier synthesis revealed the positions of all other non-hydrogen atoms; organic hydrogen atoms were put into idealized position. The non-hydrogen atoms were refined by the full-matrix least-squares method with the hydrogen atoms 'riding' on their supporting carbon atoms. A weighting scheme [$w^{-1} = \sigma^2(F) + 0.001F^2$] was applied and the data were corrected for the effects of anomalous dispersion and seondary extinction. Crystallographic calculations were carried out using the Siemens SHELXTL PLUS program[11] on a Silicon Graphics Indigo system.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[§] NMR data were recorded at room temperature in C_6D_6 solution at 200 MHz (^1H), 126 MHz (^{13}C) and 99.3 MHz (^{29}Si). *Selected spectroscopic data for* **1**: ^1H NMR δ 1.40 (18 H, s, CMe_3) and 6.74 (2 H, s); ^{13}C NMR δ 30.3 (^1J 125.7 Hz, CMe_3), 54.0 (CMe_3) and 120.0 (dd, ^1J 176.1 Hz, ^2J 11.0 Hz, =CH); ^{29}Si NMR δ +78.4 (s).

For **3**: ^{1}H NMR: δ 1.46 (18 H, s, CMe$_3$) and 6.57 (2 H, s); ^{13}C NMR δ 33.3 (^1J 125.7 Hz, C*Me*$_3$), 55.2 (*C*Me$_3$), 119.1 (dd, ^1J 179.5 Hz, ^2J 9.0 Hz, =CH) and 201.0 (CO); ^{29}Si NMR δ +97.5 (s); IR (CsBr, Nujol) ν/cm^{-1} 2011w, 2001s, 1995m, 1983w, 1945s, 1366s, 1260s, 1212m, 1144w, 1096mbr, 1022sbr, 806s, 729m, 671m, 510w and 461 w.

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