Organometallics **1998,** *17,* 5599−5601

Silylenenickel(0) or Silyl(silylene)platinum(II) Complexes by Reaction of Si[$(NCH_2Bu^t)_2C_6H_4$-1,2] with [$NiCl_2(PPh_3)_2$], [Ni(cod)$_2$], or [$PtCl_2(PPh_3)_2$]

Barbara Gehrhus, Peter B. Hitchcock, Michael F. Lappert,* and Hieronim Maciejewski

The Chemistry Laboratory, University of Sussex, Brighton, BN1 9QJ U.K.

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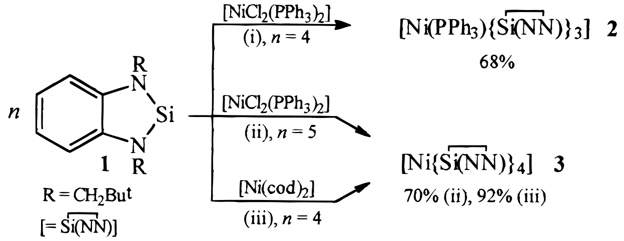
*Summary: The stable silylene Si[$(NCH_2Bu^t)_2C_6H_4$-1,2] [abbreviated as Si(NN)] (**1**) (4 equiv) with 1 equiv each of [$NiCl_2(PPh_3)_2$], [Ni(cod)$_2$], or [$PtCl_2(PPh_3)_2$] in benzene affords the crystalline diamagnetic complex [Ni(PPh_3){Si(NN)}$_3$] (**2**), [Ni{Si(NN)}$_4$] (**3**), or trans-[Pt{Si(NN)Cl}$_2${Si(NN)}$_2$] (**4**), while from **1** (5 equiv) and [$NiCl_2(PPh_3)_2$] the product was **3**. The diversity of behavior of **1**, functioning as (i) a neutral ligand, (ii) a reducing agent, and/or (iii) a source of the anionic ligand [Si(NN)Cl]$^-$ is noteworthy.*

The chemistry of transient silylenes SiX_2 (X^- being a monodentate anionic ligand) has been extensively studied, but there is no record of the trapping of such a silylene on a transition metal (M), generating [M$(SiX_2)_n$(L)$_m$]. Details have appeared on just two cases of a stable divalent silicon compound, the silylene SiN(Bu^t)(CH)$_2$NBu^t or Si(η^5-C_5Me_5)$_2$, functioning as a ligand yielding [Ni(CO)$_2${SiN(Bu^t)(CH)$_2$NBu^t}$_2$][1] or [AuCl{Si(η^1-C_5Me_5)(η^5-C_5Me_5)}][2] from [Ni(CO)$_4$] or [Au(Cl)CO], respectively; also mentioned have been the crystalline [Fe(CO)$_4${SiN(Bu^t)(CH)$_2$NBu^t}] and [Cr(CO)$_2$(Mes){SiN(Bu^t)(CH)$_2$NBu^t}].[1b] There are a few other examples of metal (Ru(II) or Pt(II)) complexes containing three-coordinate silicon (but these were invariably obtained from a tetravalent silicon precursor): [Ru(η^5-C_5Me_5)(PMe_3)$_2$(SiX_2)]$^+$ (X = SEt,[3a] SC_6H_4Me-4,[3b] Me,[3b] or Ph[3b]) and *trans*-[PtH{P(C_6H_{11}-c)$_3$}$_2$(SiX_2)]$^+$ (X = SEt).[4]

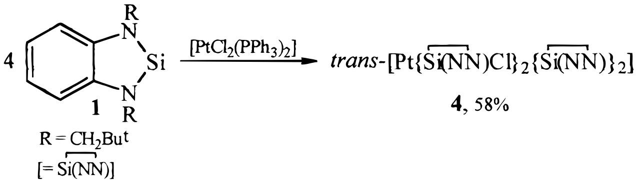
We now report that the thermally stable silylene Si[$(NCH_2Bu^t)_2C_6H_4$-1,2] [abbreviated as Si(NN)][5] (**1**) can behave with a suitable transition metal complex not only as (i) an SiX_2 ligand but also as (ii) a reducing agent and/or (iii) a source of an [SiX_2X']$^-$ ligand. This diversity is illustrated by the isolation of the three X-ray-authenticated crystalline complexes [Ni(PPh_3){Si(NN)}$_3$] (**2**),[6] [Ni{Si(NN)}$_4$] (**3**),[7] and *trans*-[Pt{Si(NN)Cl}$_2${Si(NN)}$_2$] (**4**),[8] obtained from **1** and [$NiCl_2(PPh_3)_2$] (**2** and **3**), [Ni(cod)$_2$] (**3**), or [$PtCl_2(PPh_3)_2$] (**4**), Schemes 1 and 2. Thus, **1** (i) is a nucleophile, displacing triphenylphosphine or cycloocta-1,4-diene from a group 10 metal; (ii) reduces a Ni(II) chloride to the Ni(0) complex **3**; and (iii) inserts into two Pt−Cl bonds of [$PtCl_2(PPh_3)_2$] in yielding **4**. Variable-temperature, multinuclear (^1H, $^{29}Si\{^1H\}$, $^{195}Pt\{^1H\}$) as well as ^1H saturation transfer (at 213 K) and 2D EXSY (at 243 K) NMR spectroscopic experiments on **4** in $CDCl_3$, to be described in the full paper, revealed that the compound underwent fluxional processes, involving as major components **4**, its *cis*-analogue **4a**, and the six-coordinate isomer *cis*-[$PtCl_2${Si(NN)}$_4$] (**4b**), Scheme 3.

The outcome of the reaction between the silylene **1** and [$NiCl_2(PPh_3)_2$] (1 equiv) was stoichiometry-dependent. Complex **2** was obtained from **1** (4 equiv), whereas

Scheme 1



Scheme 2



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(6) Selected data for **2**: Yellow crystals, mp 106−108 °C (decomp). NMR (C_6D_6, 293 K): ^1H δ 0.78 (s, 54 H), 3.26 (s, 12 H), 6.96 (m, 21 H), 7.7 (m, 6 H); $^{13}C\{^1H\}$ δ 29.46 (CMe_3), 34.08(CMe_3), 52.47 (CH_2), 110.99, 117.52, 141.22 (phenyl); $^{31}P\{^1H\}$ δ 47.31 (s); $^{29}Si\{^1H\}$ δ 136.19.

(7) Selected data for **3**: Yellow crystals, mp 84−86 °C (decomp). NMR (C_6D_6, 293 K): ^1H δ 0.87 (s, 72 H), 3.76 (s, 16 H), 6.96 (m, 8 H), 7.08 (m, 8 H); $^{13}C\{^1H\}$ δ 29.94 (CMe_3), 34.32 (CMe_3), 52.96 (CH_2), 110.84, 118.06 and 141.30 (phenyl); $^{29}Si\{^1H\}$ δ 145.9.

(8) Compound **4**: Orange crystals, mp 158−160 °C (decomp).

10.1021/om980818h CCC: $15.00
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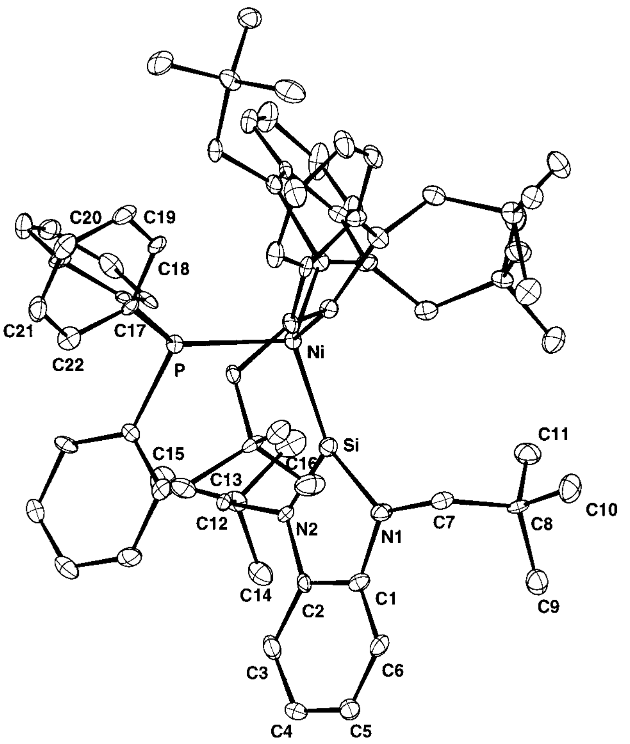
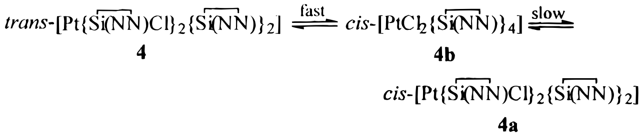


Figure 1.

Scheme 3



formation of **3** required the use of 5 equiv of **1**. The homoleptic nickel(0) silylene complex **3** was also accessible from [Ni(cod)$_2$] (1 equiv) and **1** (4 equiv). Each of these high-yield reactions was accomplished in benzene at ambient temperature. The coproduct of these reactions were $\overline{\text{Si(NN)}}$Cl$_2$[5] and PPh$_3$ (i or ii in Scheme 1) and cycloocta-1,4-diene (iii in Scheme 1).

In contrast to reaction ii of Scheme 1 involving [NiCl$_2$(PPh$_3$)$_2$], the isoleptic platinum compound was not reduced by **1** under similarly mild conditions, but instead underwent insertion into each of the Pt−Cl bonds, affording stereoselectively (Scheme 2) the crystalline *trans*-bis(chlorosilyl)bis(silylene)platinum(II) product **4**. It is therefore possible that a transient (chlorosilyl)-nickel(II) compound may have been an intermediate in the reduction (i or ii of Scheme 1) of the nickel(II) chloride. Experiments to test this hypothesis are in hand.

The yellow (**2**[6] or **3**[7]) or orange (**4**),[8] crystalline, diamagnetic complexes gave satisfactory analyses, multinuclear NMR, and mass (parent ion observed) spectra. Single-crystal X-ray diffraction data established their molecular structures, shown in Figures 1 (for **2**) and 2 (for **4**); the structure of **3** will appear in the full paper.

The ^{29}Si{^{1}H} NMR spectra showed that the ^{29}Si chemical shift of the $\overline{\text{Si(NN)}}$ ligand in **2** (δ 136.2), **3** (δ 145.9), and the three isomers **4**, **4a**, and **4b** [**4**/**4a**: δ 142.5 and 146.9 with $^1J(^{29}\text{Si}-^{195}\text{Pt}) = 2265$ and 2259 Hz, respectively; **4b**: δ 143.0 and 146.5 (coupling not resolved)] of **4** in CDCl$_3$/toluene at 213 K was at a significantly higher frequency than in the free silylene **1** (δ 96.92);[5] this shift is substantially greater than that between [Ni(CO)$_2${$\overline{\text{SiN(Bu}^t\text{)(CH)}_2\text{NBu}^t}$}$_2$] ($\delta$ 97.5)[1] and $\overline{\text{SiN(Bu}^t\text{)(CH)}_2\text{NBu}^t}$ (δ 78.4).[9] The ^{29}Si NMR spectral chemical shift attributed to the [$\overline{\text{Si(NN)}}$Cl]$^-$ ligand in **4** and **4a** was at δ 53.7 and 57.3 [with $^1J(^{29}\text{Si}-^{195}\text{Pt}) =$ 957 and 934 Hz] and may be compared with $\delta(^{29}\text{Si})$ values for the [$\overline{\text{Si(NN)}}$X]$^-$ ligand in Sn(Ar){$\overline{\text{Si(NN)}}$Ar} [δ 48.1, Ar = C$_6$H$_3$(NMe$_2$)$_2$-2,6].[10] The ^{195}Pt{^{1}H} NMR spectrum of the crystalline **4** in CDCl$_3$/toluene at 213 K showed two major signals at δ −5474 and −5497 attributed to **4**/**4a** and one minor signal (**4b**) at δ −5540.

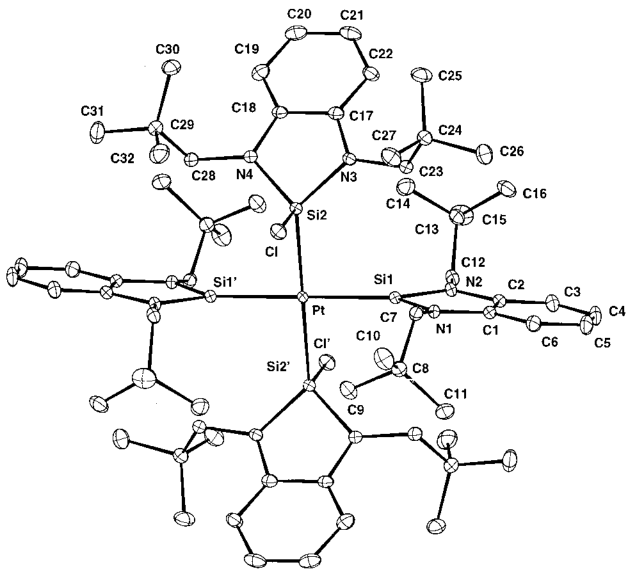


Figure 2.

Crystalline complex **2**[11] (Figure 1) lies on a crystallographic 3-fold axis, the central Ni atom being almost tetrahedrally surrounded by the three silicons and the phosphorus of the four ligands, the Si−Ni−P angles of 106.4(1)° being somewhat narrower than the Si−Ni−Si′ of 112.4(1)°. The Si−Ni bond distances of 2.165(2) Å are between the 2.207(2) Å of [Ni(CO)$_2${$\overline{\text{SiN(Bu}^t\text{)(CH)}_2\text{NBu}^t}$}$_2$][1] (the only other base-free silylenenickel complex) and the 2.137(1) Å for the Ni−SiMe$_2$ bond in the base-stabilized silylene(silyl)nickel(II) complex **5**, the Ni−Si(SiMe$_3$)$_2$Me bond length in **5** being 2.240(1) Å.[12] Each silicon atom in **2** is slightly (0.214 Å) out of the

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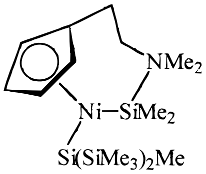
[9] Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691.

[10] Drost, C.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1997**, 1845.

[11] Crystal data for **2**: C$_{66}$H$_{93}$N$_6$NiPSi$_3$, $M = 1216.6$, cubic, space group $Pa\bar{3}$ (No. 205), $a = 23.841(4)$ Å, $U = 13551(4)$ Å^3, $F(000) = 5264$, $Z = 8$, $D_c = 1.19$ Mg m^{-3}, μ(Mo Kα) = 0.41 mm^{-1}, specimen 0.3 × 0.2 × 0.2 mm, 2119 independent reflections [R(int) = 0.0468], R1 = 0.060 for 1248 reflections with $I > 2\sigma(I)$, wR2 = 0.15 (for all data). Intensities were measured on $\theta_{\max}$ 20° on an Enraf-Nonius CAD4-diffractometer [$T = 173(2)$ K] using monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Full-matrix least-squares refinement, on all F^2, with SHELXL-93, H atoms in riding mode and all non-H atoms anisotropic. There are two molecules of pentane solvate disordered across the crystallographic $\bar{3}$ site.

[12] Nlate, S; Herdtweck, E; Fischer, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1861.

corresponding NiN_2 plane, which, together with the small deviation from trigonal planarity at Si (sum of angles at each Si 355.8°), points to imperfect Ni−Si π-bonding. The Ni−P bond length of 2.210(4) Å is unexceptional.



5 [12]

The centrosymmetric, crystalline Pt(II) complex **4**[13] (Figure 2) has a square-planar coordination environment for Pt, Si(1)−Pt−Si(1)′ 180.0°, Si(1)−Pt−Si(2) 90.86(3)°. In each silylene ligand, the neopentyl substituents are *trans*-disposed to one another (in contrast to their being *cis* in **1**),[5] probably in order to accommodate the mutually *trans* chlorines on the $[\overline{\mathrm{Si(NN)}}\mathrm{Cl}]^-$ ligands. The three-coordinate silicons, Si(1), are in a planar environment (sum of angles at Si, 359.9°), with the average N−Si(1)−Pt bond angle being 133.3° and Si only 0.04 Å out of the PtNN′ plane. The Pt−Si(1) bond length, 2.266(1) Å, is almost identical to the 2.270(2) Å in the cationic Pt(II) complex *trans*-$[PtH\{P(C_6H_{11}\text{-c})_3\}_2\{Si(SEt)_2\}]^+$.[4] The geometric parameters within the silylene are somewhat different from those (shown successively in parentheses) for the $[\overline{\mathrm{Si(NN)}}\mathrm{Cl}]^-$ ligand of **4**, **2**, and the free silylene **1**:[5] N−Si−N′ 93.2(1)° [89.7(1), 89.5(3), 88.2(1)°], Si−N 1.713(2) Å [1.76(1), 1.75(1), 1.75(1) Å], N−C 1.41(1) Å [1.41(1), 1.40(1), 1.38(1) Å], and C−C 1.405(4) Å [1.407(4), 1.40(1), 1.415(5) Å]. The four-coordinate silicons, Si(2), of **4** are in a distorted tetrahedral environment, the Pt−Si(2) bond length of 2.426(1) Å being unexceptional {e.g., 2.401(3) Å in $[Pt(OPr^i)(SiBu^t{}_2OH)\{(PMe_2CH_2)_2\}]$[14]}, as is the Si−Cl, 2.100(1) Å.

Crystalline $[Ni\{\overline{\mathrm{Si(NN)}}\}_4]$ (**3**) is a new member of the rare class of homoleptic four-coordinate nickel(0) complexes and only the second (cf.[15] a homoleptic stannylene−Ni complex) having a group 14 element-centered ligand, joining the recently described $[Ni\{In\{C(SiMe_3)_3\}_4\}]$[16] in extending the boundaries of such complexes to the left of the group 15 elements. The coordination chemistry of the heavier group 14 element carbene congeners $M'X_2$ (M′ = Ge, Sn, or Pb) is well-established,[17] as is that of carbenes[18a,b] or their dimers.[18c] Related homoleptic d^{10} metal complexes to **3** are the two-coordinate $[M(CX_2)_2]$[19] and the three-coordinate $[M'(GeX'_2)_3]$[20] and $[M'(SnX'_2)_3]$,[20] prepared from the appropriate $[M(cod)_2]$, $[M'(cod)Cl_2]$, and CX_2, GeX'_2, or SnX'_2 [M = Ni or Pt, M′ = Pd or Pt, $CX_2 = \overline{\mathrm{CN(C_6H_2Me_3\text{-}2,4,6)CHCHN}}\mathrm{C_6H_2Me_3\text{-}2,4,6}$, X′ = $N(SiMe_3)_2$]. The different coordination numbers for these complexes and **3** are probably largely controlled by steric effects.

The present results, together with those of refs 1 and 2, thus complete the series and offer a prelude of the significant extensions that will surely follow.

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Supporting Information Available: Tables giving X-ray diffraction data for **2** and **4** (22 pages). Ordering information is given on any current masthead page.

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(13) Crystal data for **4**: $C_{64}H_{104}Cl_2N_8PtSi_4 \cdot 5(C_6H_6)$, $M = 1754.4$, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.755(2)$ Å, $b = 13.857(4)$ Å, $c = 13.999(3)$ Å, $\alpha = 85.36(2)°$, $\beta = 60.89(2)°$, $\gamma = 77.61(2)°$, $U = 2275.7(9)$ Å^3, $F(000) = 922$, $Z = 1$, $D_c = 1.28$ Mg m^{-3}, μ(Mo Kα) = 1.70 mm^{-1}, specimen 0.3 × 0.25 × 0.25 mm, 7994 independent reflections, R1 = 0.025 for 7819 reflections with $I > 2\sigma(I)$, wR2 = 0.058 (for all data). Intensities were measured on θ_{max} 25° on an Enraf-Nonius CAD4-diffractometer [$T = 173(2)$ K] using monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Full-matrix least-squares refinement, on all F^2, with SHELXL-93, H atoms in riding mode and all non-H atoms anisotropic. There is a molecule of the platinum complex on an inversion center, two ordered benzene solvate molecules in general positions, and one disordered benzene solvate molecule on an inversion center.

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