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

Silylenenickel(0) or Silyl(silylene)platinum(II) Complexes by Reaction of Si[(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2] with [NiCl$_2$(PPh$_3$)$_2$], [Ni(cod)$_2$], or [PtCl$_2$(PPh$_3$)$_2$]

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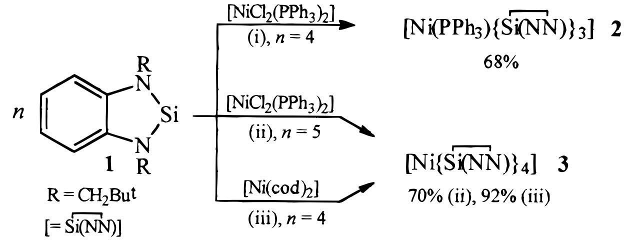
*Summary: The stable silylene Si[(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2] [abbreviated as Si(NN)] (**1**) (4 equiv) with 1 equiv each of [NiCl$_2$(PPh$_3$)$_2$], [Ni(cod)$_2$], or [PtCl$_2$(PPh$_3$)$_2$] in benzene affords the crystalline diamagnetic complex [Ni(PPh$_3$){Si(NN)}$_3$] (**2**), [Ni{Si(NN)}$_4$] (**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.*

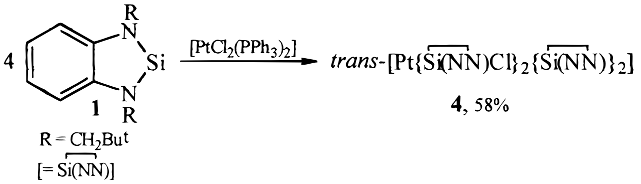
The chemistry of transient silylenes SiX$_2$ (X$^-$ being a monodentate anionic ligand) has been extensively studied, but there is no record of the trapping of such a silylene on a transition metal (M), generating [M(SiX$_2$)$_n$(L)$_m$]. Details have appeared on just two cases of a stable divalent silicon compound, the silylene SiN(Bu^t)(CH)$_2$NBu^t or Si(η^5-C$_5$Me$_5$)$_2$, functioning as a ligand yielding [Ni(CO)$_2${SiN(Bu^t)(CH)$_2$NBu^t}$_2$][1] or [AuCl{Si(η^1-C$_5$Me$_5$)(η^5-C$_5$Me$_5$)}][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$_5$Me$_5$)(PMe$_3$)$_2$(SiX$_2$)]$^+$ (X = SEt,[3a] SC$_6$H$_4$Me-4,[3b] Me,[3b] or Ph[3b]) and *trans*-[PtH{P(C$_6$H$_{11}$-c)$_3$}$_2$(SiX$_2$)]$^+$ (X = SEt).[4]

We now report that the thermally stable silylene Si[(NCH$_2$Bu^t)$_2$C$_6$H$_4$-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$_2$X′]$^-$ 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 (^{1}H, ^{29}Si{^{1}H}, ^{195}Pt{^{1}H}) as well as ^{1}H 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.

Scheme 1



Scheme 2



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

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[1] (a) Denk, M.; Hayashi, R. K.; West. R. *J. Chem. Soc., Chem. Commun.* **1994**, 33. (b) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, *68*, 785.

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[5] Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1931. Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. *J. Organomet. Chem.* **1996**, *521*, 211.

[6] Selected data for **2**: Yellow crystals, mp 106−108 °C (decomp). NMR (C$_6$D$_6$, 293 K): ^{1}H δ 0.78 (s, 54 H), 3.26 (s, 12 H), 6.96 (m, 21 H), 7.7 (m, 6 H); ^{13}C{^{1}H} δ 29.46 (C*Me*$_3$), 34.08(*C*Me$_3$), 52.47 (CH$_2$), 110.99, 117.52, 141.22 (phenyl); ^{31}P{^{1}H} δ 47.31 (s); ^{29}Si{^{1}H} δ 136.19.

[7] Selected data for **3**: Yellow crystals, mp 84−86 °C (decomp). NMR (C$_6$D$_6$, 293 K): ^{1}H δ 0.87 (s, 72 H), 3.76 (s, 16 H), 6.96 (m, 8 H), 7.08 (m, 8 H); ^{13}C{^{1}H} δ 29.94 (C*Me*$_3$), 34.32 (*C*Me$_3$), 52.96 (CH$_2$), 110.84, 118.06 and 141.30 (phenyl); ^{29}Si{^{1}H} δ 145.9.

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

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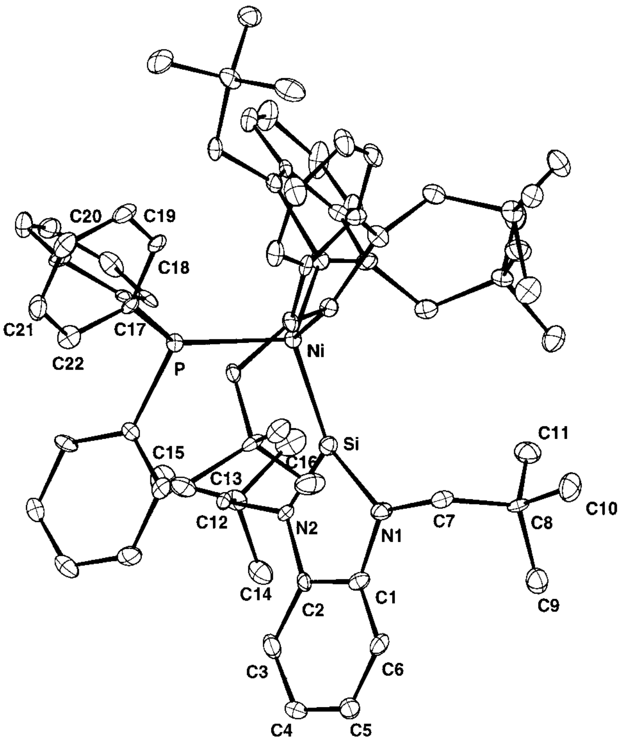
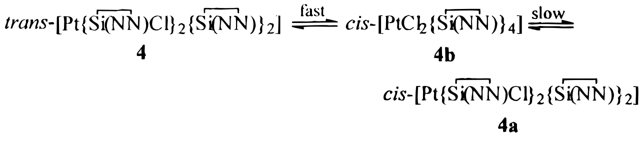


Figure 1.



Scheme 3

trans-[Pt{$\overline{\mathrm{Si(NN)}}$Cl}$_2${$\overline{\mathrm{Si(NN)}}$}$_2$] $\xrightleftharpoons{\text{fast}}$ *cis*-[PtCl$_2${$\overline{\mathrm{Si(NN)}}$}$_4$] $\xrightleftharpoons{\text{slow}}$ *cis*-[Pt{$\overline{\mathrm{Si(NN)}}$Cl}$_2${$\overline{\mathrm{Si(NN)}}$}$_2$]

4 **4b** **4a**

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 $\overline{\mathrm{Si(NN)}}Cl_2$[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 $\overline{\mathrm{Si(NN)}}$ 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 $^1J(^{29}\mathrm{Si}{-}^{195}\mathrm{Pt})$ = 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)$_2${$\overline{\mathrm{SiN(Bu^t)(CH)_2NBu^t}}$}$_2$] ($\delta$ 97.5)[1] and $\overline{\mathrm{SiN(Bu^t)(CH)_2NBu^t}}$ (δ 78.4).[9] The ^{29}Si NMR spectral chemical shift attributed to the [$\overline{\mathrm{Si(NN)}}$Cl]$^-$ ligand in **4** and **4a** was at δ 53.7 and 57.3 [with $^1J(^{29}\mathrm{Si}{-}^{195}\mathrm{Pt})$ = 957 and 934 Hz] and may be compared with $\delta(^{29}\mathrm{Si})$ values for the [$\overline{\mathrm{Si(NN)}}$X]$^-$ ligand in Sn(Ar){$\overline{\mathrm{Si(NN)}}$Ar} [$\delta$ 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.

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)$_2${$\overline{\mathrm{SiN(Bu^t)(CH)_2NBu^t}}$}$_2$][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

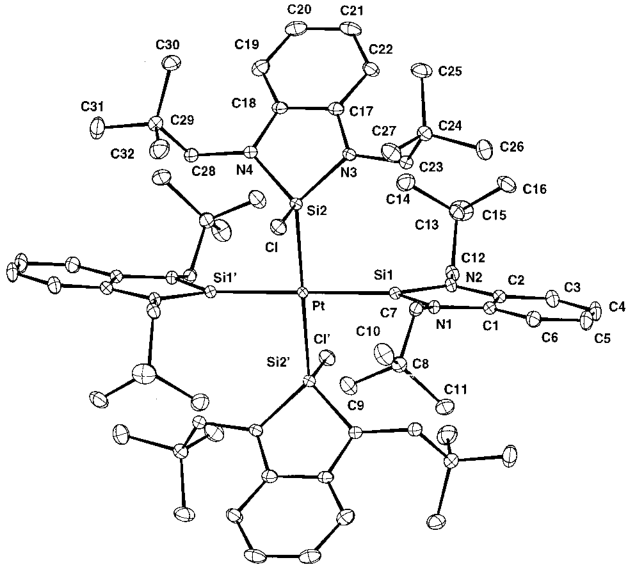


Figure 2.

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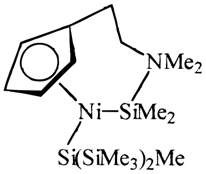
(9) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691.

(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 (λ = 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*-$[\mathrm{PtH\{P(C_6H_{11}\text{-}c)_3\}_2\{Si(SEt)_2\}}]^+$.[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 $[\mathrm{Pt(OPr^i)(SiBu^t{}_2OH)\{(PMe_2CH_2)_2\}}]$[14]}, as is the Si−Cl, 2.100(1) Å.

Crystalline $[\mathrm{Ni\{\overline{Si(NN)}\}_4}]$ (**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 $[\mathrm{Ni\{In\{C(SiMe_3)_3\}_4\}}]$[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 $[\mathrm{M(CX_2)_2}]$[19] and the three-coordinate $[\mathrm{M'(GeX'_2)_3}]$[20] and $[\mathrm{M'(SnX'_2)_3}]$,[20] prepared from the appropriate $[\mathrm{M(cod)_2}]$, $[\mathrm{M'(cod)Cl_2}]$, 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′ = $\mathrm{N(SiMe_3)_2}$]. 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.

Acknowledgment. We are grateful for support from EPSRC and the Royal Society, especially for the fellowships for B.G. (EPSRC) and H.M. (Royal Society-NATO), and to Dr. A. G. Avent for valuable NMR spectroscopic data on **4**.

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**: $C_{64}H_{104}Cl_2N_8PtSi_4\cdot5(C_6H_6)$, $M = 1754.4$, 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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