

A Silylene Stabilized by a σ -Donating Nickel(0) Fragment

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Abstract: A donor-stabilized silylene **4** featuring a Ni(0)-based donating ligand was synthesized. Complex **4** exhibits a pyramidalized and nucleophilic Si(II) center and shows a peculiar behavior due to the cooperative reactivity of Si and Ni centers. Calculations indicate that the orientation of Ni-ligands with respect to the silylene moiety is crucial in determining the role of Ni-fragment (Lewis acid or Lewis base) towards silylene. Indeed, a simple 90° rotation of Si-Ni-bond, reverses the role of Ni, and transforms a classical silylene→Ni(0) complex into an unprecedented Ni(0)→silylene complex.

Transition metals basically act as Lewis acids and thus form various complexes **I** interacting with Lewis base ligands. Despite less common, transition metals also act as Lewis bases^[1] to interact with Lewis acids (A) to form non-classical M→A complexes **II**. This non-classical mode of interaction (known as Z-ligands^[2] or metal-only Lewis pairs^[3]) leads to new methods to tune/improve properties of transition metals.^[4] Singlet divalent group-14 species **III** such as carbenes and their heavier analogues (R₂E, E = C, Si, Ge...), featuring a divalent E center with a lone pair orbital (n_E) and a vacant orbital (p_E), present an ambiphilic character. Consequently, like in the case of transition metals, there are potentially two coordination modes *via* σ -electron donation: (i) either from R₂E to metal [R₂E→M] **IV** or, (ii) from metal to ER₂ [M→ER₂] **V**. Classical R₂E→M complexes **IV**, presenting a planar E atom, categorized as Fischer- or Schrock-types complexes,^[5] are ubiquitous and play an important role in synthetic chemistry. In contrast, and not surprisingly, M→ER₂ complexes **V**, characterized by a strongly pyramidalized E center as base-stabilized metallylene **VI**, are less common and only a few examples are known. How could the formation of such non-classical complexes **V** be promoted? On descending a group in the periodic table, the nucleophilicity of divalent atom (E) decreases (increasing s-character of lone pair) and the unoccupied p_E orbital becomes more Lewis acidic. Therefore, heavier divalent species (E = Ge, Sn, Pb) present stronger tendency to form M→ER₂ complexes **V**. Indeed, to

date, the only known compounds of this type **V** are germylene-, stannylene- and plumbylene-based complexes (**VII–X**).^{6789 [6–9]} DFT calculations predicted that, although germynes and stannylenes are able to form complexes of type **V**, lighter analogues (silylenes and carbenes) tend to form classical R₂E→M complexes **IV**,^[7] although several methanediide-TM complex, featuring a pyramidalized carbon centre, have been described.^{10[10]} To the best of our knowledge, complexes **V** involving a silylene fragment M→SiR₂ remain elusive, and no clear synthetic access has been proposed, despite their potential usefulness as an extended model of Lewis base-stabilized silylenes **VI**.

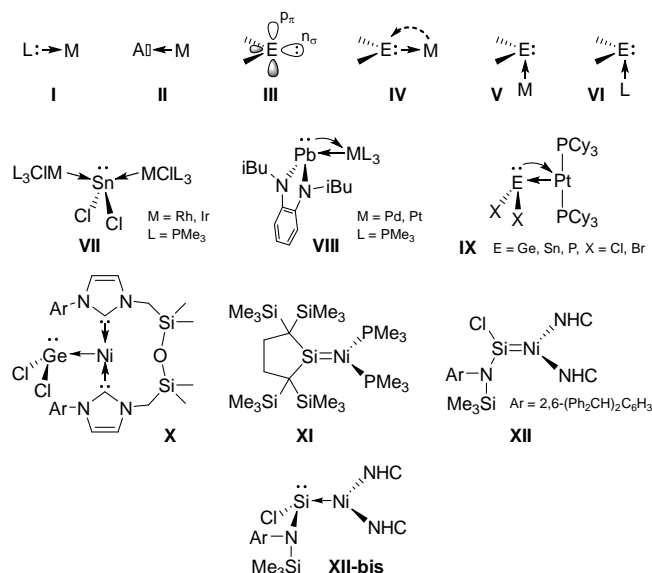


Figure 1. Classical and non-classical metallylene complexes

Here, we would like to report the synthesis of an unusual 16e-nickel(0)-silylene complex **4**, presenting a strongly pyramidalized and nucleophilic divalent silicon center, which can be regarded as a silylene complex stabilized by coordination of σ -donating Ni(0) ligand. DFT calculations indicate that the orientation of Ni-ligands relative to silylene fragment is crucial in determining the coordination mode of R₂Si-Ni⁰L₂ complexes, and a simple 90° rotation of Si-Ni bond reverses the role of Ni-fragment which turns from Lewis acid to Lewis base (**IV** → **V**).

16e-Ni(0) complexes featuring silylene ligands (**XI**, **XII**) usually present a short Si=Ni double bond and two trigonal planar Si and Ni centers which are perpendicular to each other.^{11 [11]} We have computationally studied Ni⁰-silylene complexes by hypothesizing that the Si=Ni π -bond can be broken through a rotational distortion around SiNi-bond axis and thus changing the coordination mode. Calculations predict that such a 90° SiNi-bond rotation in complex model H₂Si=Ni(PMe₃)₂ **1**, affording rotamer **2**, is only moderately exergonic ($\Delta G_{1\rightarrow 2}$ = 6.6 kcal/mol) and leads to a dramatic geometrical modification (Figure 2). Indeed, rotamer **2** exhibits a strongly

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pyramidalized Si center ($\Sigma^\circ_{\text{Si}} = 305.9^\circ$) and a considerably elongated Si-Ni bond (2.249 Å) compared to that of **1** (2.118 Å). This structural feature of **2** is in agreement with a Si atom holding a lone pair of electrons and a reduced Si-Ni multiple bonding character. Indeed, it was found that the negative charge of H₂Si fragment in **2** [-0.40 (H₂Si) / +0.40 (Ni(PMe₃)₂)] is increased from that in **1** [-0.17 (H₂Si) / +0.17 (Ni(PMe₃)₂)] and that the Wiberg and Mayer bond orders of the Si-Ni bond of **2** (0.602 and 0.812) are smaller than those calculated for **1** (0.820 and 1.163). Furthermore, intrinsic bond orbital (IBO) analysis^{[12]12} of **1** clearly indicates the presence of a Si=Ni double bond constituted of R₂Si→Ni σ-donation (Si-Ni σ-bonding orbital with a main occupancy at Si, Figure 1a) and π-back donation from Ni to Si (π-bonding orbital with a main occupancy at Ni, Figure-1b). In marked contrast, in the case of rotamer **2**, a large part of Si-Ni σ-bonding electrons is localized at the Ni atom (0.38 at Si and 1.60 at Ni, Figure-1c), in agreement with a Ni→Si σ-donation. Furthermore, the IBO analysis also indicates the presence of a lone pair localized on the Si atom in **2** with no contribution at Ni (1.90 at Si and 0.00 at Ni, Figure-1d), instead of π-bonding orbital. These results demonstrate that a 90° rotation of Si-Ni bond in **1** induces, not only the SiNi-π-bond breaking but also the reversal of the role of Ni(0)-fragment: from Lewis acid (coordination center) to Lewis base (coordinating ligand).

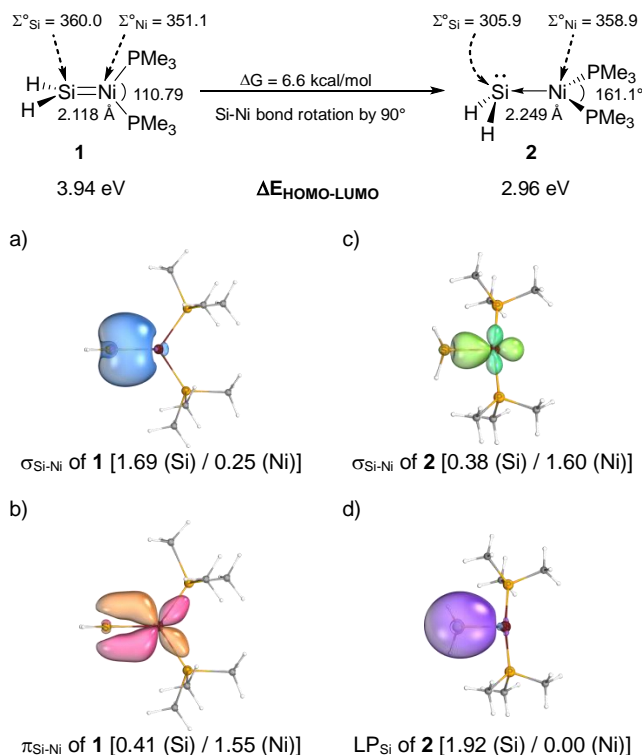
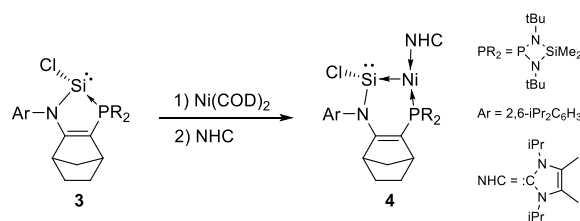


Figure 2. Calculated free energy ΔG (kcal/mol) for the isomerization of silylene-Ni(0) complex **1** to the corresponding rotamer **2** by a 90° rotation of Si-Ni bond as well as the geometry and selected intrinsic bond orbitals (IBOs) of each rotamer (**1** and **2**). Values in parenthesis are the contributions of Si-Ni σ- and π-bonding electrons at Si and Ni atoms.

Driess' complex **XII**^[11b] undergoes a similar isomerization with a relatively small energy ($\Delta G_{\text{XII} \rightarrow \text{XII-bis}} = 12.1 \text{ kcal/mol}$) affording rotamer **XII-bis** (Figure 1) with a strongly pyramidalized Si center ($\Sigma^\circ_{\text{Si}} = 337.73^\circ$) and a single Si-Ni bond (2.244 Å). Of particular interest, such geometrical and electronic modifications of silylene-nickel complexes (**1**→**2** and **XII**→**XII-bis**) induce a considerable

decrease of HOMO-LUMO energy gaps ($\Delta E_{\text{HOMO-LUMO}}$: 3.49 eV for **1** vs 2.96 eV for **2** and 4.19 eV for **XII** vs 2.73 eV for **XII-bis**), and therefore an increased reactivity of the non-classical complexes (type **V**) compared to classical ones (type **IV**). In contrast, in the case of the corresponding carbene complexes [R₂C-Ni(PMe₃)₂, R = H, F], such a geometrical change was not observed by the C-Ni bond rotation and the classical carbene→Ni complex (with a planar carbon center and a short C=Ni double bond) was calculated to be the only stable isomer.

In order to verify the theoretical results, we have considered the use of a rigid planar bridging system connecting silylene- and metal-fragments which imposes such a bond rotated geometry of silylene-Ni complex of non-classical complexes of type **V**. For this purpose, we employed the phosphine-stabilized (amino)(chloro)silylene **3**^[13] as a precursor, in which the amino substituent and the phosphine ligand are linked by a planar olefin bridge. Similarly to the synthesis of complex **XII**,^[11b] the two successive additions of equimolar amounts of Ni(COD)₂, and N-heterocyclic carbene (NHC), to chlorosilylene **3**, in fluorobenzene at RT, afford silylene-Ni(0) complex **4** (Scheme 1). The reaction probably proceeds *via* the insertion of Ni into the Si(II)-P-bond followed by the COD ligand substitution by NHC at the Ni center. Complex **4** was isolated as air-sensitive crystals from a THF solution at RT (yield 70 %).



Scheme 1. Synthesis of Ni-stabilized silylene **4**

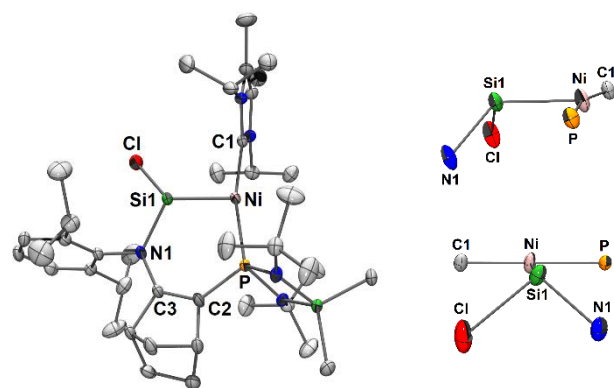


Figure 3. Molecular structures of **4**. Thermal ellipsoids represent 30% probability. H and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-Ni 2.178(1), N1-Si1 1.840(2), Si1-Cl 2.196(1), Ni-C1 1.934(2), Ni-P 2.126(1), P-C2 1.762(2), C2-C3 1.359(3), C3-N1 1.360(2), Cl-Si1-N1 95.35(6), Cl-Si1-Ni 110.94(4), N1-Si1-Ni 115.29(6), Si1-Ni-C1 101.53(6), C1-Ni-P 164.51(6), Si1-Ni-P 93.87(2), Ni-P-C2 117.05(7), P-C2-C3 129.90(16), C2-C3-N1 129.62(18), C3-N1-Si1 117.17(13). $\Sigma^\circ_{\text{Si}} = 321.58^\circ$. Torsion angles: C1-Ni-Si1-Cl = 33.16(7)°, P-Ni-Si1-N1 = 38.21(7)°.

Even though silylene complex **4** slowly decomposes in solution (THF, fluorobenzene) ($t_{1/2} = 2$ days at RT, and $t_{1/2} = 2$ h, at 80 °C), it was characterized by NMR spectroscopy. In the ²⁹Si-NMR spectrum, a doublet signal appears at 138.1 ppm ($^2J_{\text{SiP}} = 71.8 \text{ Hz}$) in the region of that of the related acyclic (chloro)aminosilylene-Ni(0) complex

XII ($\delta = 123.2$ ppm)^[11b] but significantly downfield compared to the starting phosphine-stabilized silylene **3** (-10.5 ppm).^[13] The ³¹P-NMR spectrum displays a singlet signal at 91.4 ppm, also downfield shifted compared to **3** (75.0 ppm). A doublet signal observed at 186.7 ppm in ¹³C-NMR spectrum was attributed to the divalent carbon of NHC ligand. The relatively large carbon-phosphorus coupling constant ($^2J_{CP} = 50.4$ Hz) is in good agreement with the T-shaped geometry around the Ni atom with the NHC ligand in a trans-position relative to the phosphine.^[8c]

The molecular structure of **4**^[14] reveals a strongly pyramidalized Si1 center ($\Sigma^\circ_{Si} = 321.58^\circ$) similarly to the case of the phosphine-stabilized silylene **3** ($\Sigma^\circ_{Si} = 292.0^\circ$)^[13] and an elongated Si-Ni bond (2.178 Å) compared to other Ni(0)-silylene complexes (2.075 - 2.133 Å) (Figure 3).^[10] This value is within the range of Ni-Si single bonds.^[15] These structural data of **4** are in agreement with a non-classical complex **V** (Ni→silylene) with a lone pair on the Si atom and a reduced Si-Ni multiple bonding character. The Ni(0) site presents a planar and T-shaped geometry ($\Sigma^\circ_{Ni} = 359.91^\circ$) with a large P-Ni-Cl_{NHC} angle (164.51°), in contrast to the case of silylene-Ni(NHC)₂ complex **XII** with a trigonal planar Ni site (C_{NHC} -Ni- $C_{NHC} = 111.4^\circ$).^[11] A similar geometry was observed for other M(0)→metallylene complexes **IX-X** (M = Ni, Pt)^[8,9] as well as for L₂Ni→Lewis acid complexes.^[16]^[16]

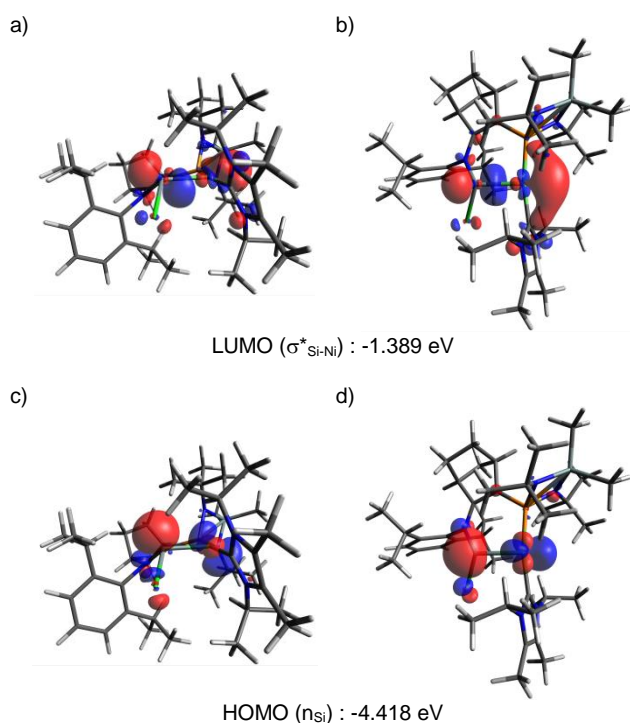
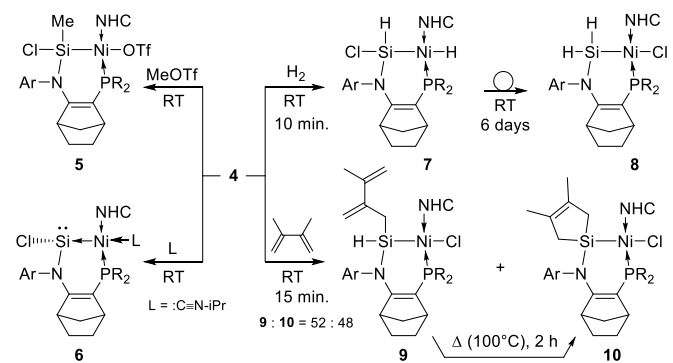


Figure 4. Frontier molecular orbitals [LUMO (a, b) and HOMO (c, d)] of **4** (isosurface level = ± 0.05 e/(a.u.)³) and their energy levels (eV) calculated at the M06/Def2TZVP level.

To gain more insight into the electronic structure of Ni⁰→silylene complex **4**, DFT calculations have been performed at the M06/Def2TZVP//M06/6-31G(d) level of theory (Figure 4). The optimized structure of **4** agrees quite well with the experimentally observed one (Si-Ni: 2.227 Å, Si-N: 1.831 Å, Si-Cl: 2.19 Å, C1-Ni-P: 169.47°, $\Sigma^\circ_{Si} = 319.37^\circ$). The highest occupied molecular orbital (HOMO, -4.418 eV) corresponds to the lone pair orbital mainly localized on the Si atom and the lowest unoccupied bond orbital

(LUMO, -1.389 eV) corresponds to the anti-bonding σ^* -orbital of Si-Ni bond with a large coefficient on the Ni atom. Similar to the case of **XII-bis**, the HOMO-LUMO energy gap of **4** ($\Delta E_{HOMO-LUMO}$: 3.03 eV) is calculated to be small, suggesting an enhanced reactivity. As expected, IBO analysis of **4** show the same pattern of Ni→Si σ -bond and Si-lone pair (n_{Si}) orbitals as those calculated for **2** (Figure-1c,d) (see the supporting information).



Scheme 2. Reactions of Ni-stabilized chlorosilylene complex **4**

In agreement with the MO analysis, contrary to other silylene-Ni complexes presenting an electrophilic character at the Si atom,^[11a,17] silylene complex **4** presents a nucleophilic Si center, which has been demonstrated by the immediate reaction with MeOTf, leading to Si-methylated Ni(II) complex **5** (Scheme 2). In contrast, a Lewis base such as *iso*-propyl isocyanide coordinates on the metal center to form a tetra-coordinate Ni⁰ complex **6**. A less pyramidalized Si(II) center ($\Sigma^\circ_{Si} = 349.69^\circ$) and a shorten Si-Ni bond [2.1108(5) Å] in **6** compared to those of **4** [$\Sigma^\circ_{Si} = 321.58^\circ$, Si-Ni: 2.1780(7) Å] suggest an enhanced Si→Ni π -back donation in **6** probably due to the geometrical modification at Ni(0) center (T-shape → distorted tetrahedral).

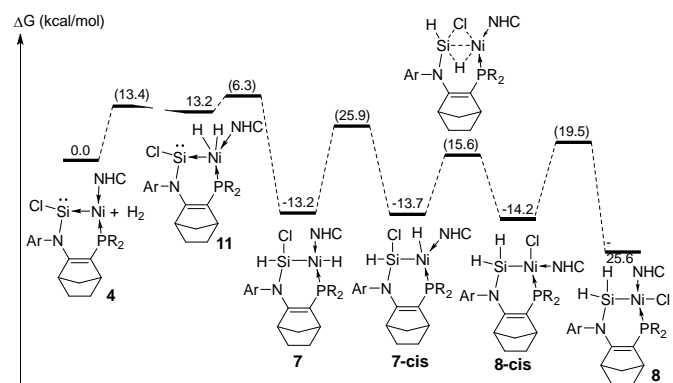


Figure 5. Calculated reaction pathways for the hydrogenation of **4** and calculated relative Gibbs energies ΔG (kcal/mol) of each intermediate and product **8** from that of **4**+H₂. In parenthesis are calculated Gibbs energy barriers ΔG^\ddagger (kcal/mol).

Silylene complex **4** also readily reacts with H₂ at RT to afford a formal 1,2-dihydrogen adduct **7** which slowly isomerizes to the corresponding isomer **8** by the substituent exchange of H and Cl on the Si and Ni atoms respectively (Scheme 2). Although intermediate **7** could not be isolated, the two ¹H-NMR signals corresponding to the Si-H (4.92 ppm, $J_{HH} = 6.5$ Hz, $J_{PH} = 5.6$ Hz, $J_{SiH} = 176.5$ Hz) and Ni-H (-6.49 ppm, $J_{HH} = 6.5$ Hz, $J_{PH} = 56.5$ Hz, $J_{SiH} = 86.0$ Hz) appearing

in the characteristic regions indicate its formation. Typically, the large trans coupling-constants ($^2J_{\text{Si-H}} = 86.0$ Hz, $^2J_{\text{P-C(NHC)}} = 82.8$ Hz) suggest a square planar geometry around the Ni^{II} atom in **7** with the Ni-H function at the trans-position relative to the Si atom. The structure of dihydrosilane-Ni(II) complex **8** was confirmed by X-ray diffraction analysis.^[14]

Silylene-Ni **4** complex also readily reacts with 2,3-dimethyl-1,3-butadiene at RT to give a mixture of two $\text{Si}^{\text{VI}}\text{-Ni}^{\text{II}}$ complexes (**9** and **10**) with a 1 : 1 ratio, which are formally formed by either a C-H insertion or a [4+1] cycloaddition at the Si center followed by a 1,2-migration of chlorine atom to the Ni center, respectively (Scheme 2). Of particular interest, complex **9** isomerizes at 100 °C to give cycloadduct **10** in 2 h. Calculations predict that both reactions start with a formal 1,2-addition of butadiene to the Si-Ni moiety, either *via* an ene-type reaction of the allylic C-H group, or by a [4+2]-cycloaddition reaction, followed by the isomerization of the resulting intermediates *via* 1,2-migrations of the ligands onto the Si and Ni atoms to give the experimentally obtained **9** and **10** (see Supporting Information). In both cases, the first step is the most costly step (1,2-addition or [4+2]-cycloaddition), with very similar energy barriers ($\Delta G^\ddagger = 21.3$ and 20.7 kcal/mol, respectively), which is consistent with the formation of **9** and **10** in the same proportions. Calculations also indicate that the isomerization of **9** to **10** proceeds *via* a tautomerization of **9** to generate a zwitterionic intermediate **12** that cyclizes to give **10** (Figure 6). The experimental thermal activation required for this isomerization (100 °C) is in agreement with a considerably high energy barrier ($\Delta G^\ddagger_{9 \rightarrow 12} = 37.9$ kcal/mol) and the endergonic nature of the tautomerization step ($\Delta G_{9 \rightarrow 12} = 30.3$ kcal/mol).

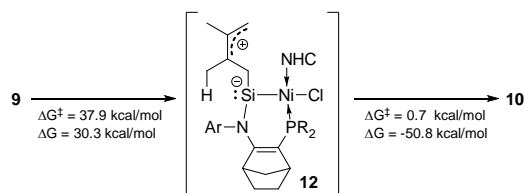
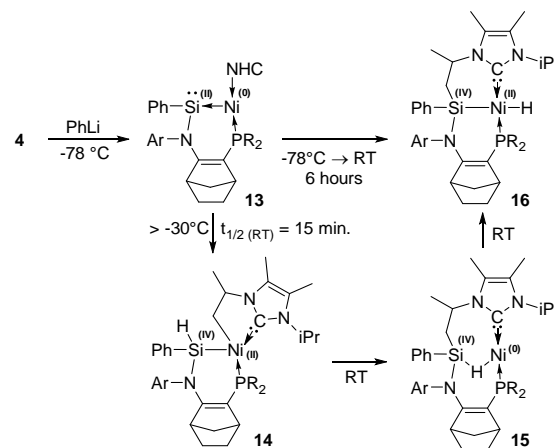


Figure 6. Calculated reaction pathway for the isomerization of **9** to **10**.

In order to check the substituent effect on the reactivity/stability of the Ni→Si complexes, we have also tested the substitution of chloride on the Si atom in **4** by PhLi. The reaction of **4** with PhLi (1 eq.) proceeds smoothly at -80 °C to generate the corresponding phenyl-substituted silylene complex **13** (Scheme 3). The formation of **13** was indicated by the characteristic ^{29}Si -NMR chemical shift for the Si(II) atom ($\delta = 154.2$ ppm, $J_{\text{SiP}} = 85.6$ Hz). However, phenylsilylene complex **13** is less stable than its precursor **4** and starts evolving above -30 °C *via* a 1,2-addition of the C-H moiety of NHC ligand across the Si-Ni fragment to give the silyl hydride $\text{Si}^{\text{IV}}\text{-Ni}^{\text{II}}$ complex **14** (isomerization completed within 30 min at RT). The formation of **14** is supported by the characteristic signals observed for the Si-H group in the ^1H -NMR spectrum ($\delta = 5.36$ ppm, $^3J_{\text{HP}} = 5.2$ Hz, $^1J_{\text{SiH}} = 153.1$ Hz) and for the $\text{CH}_2\text{-Ni}$ moiety in the ^{13}C -NMR spectrum ($\delta = 45.0$ ppm, $^2J_{\text{CP}} = 12.8$ Hz).^{[18][18]} The decreased HOMO-LUMO energy gap (2.72 eV) calculated for **13** compared to **4** (3.03 eV) is in good agreement with its lower stability. Furthermore, at RT, complex **14** isomerizes further by exchange of ligands (H and CH_2) on the Si and Ni centers to give a stable pincer-type nickel(II) hydride complex **16**.^[14] Contrary to the related isomerization of **7** to **8**, proceeding *via* two simultaneous 1,2-migrations of ligands on the Si and Ni atoms (Figure 5), in the case of **14**, the isomerization proceeds

in two steps: i) reductive elimination at the Ni center and formation of a Si-C bond to generate a $\text{Si}^{\text{IV}}\text{-Ni}^0$ complex **15** with the Si-H moiety interacting with the Ni(0) center, and then ii) oxidative addition of the Si-H moiety to the Ni center to give the final nickel(II)-hydride complex **16**. Although clean NMR spectra of **14** could not be obtained due to the similar kinetics of the two isomerization steps (**14** → **15** and **15** → **16**), careful NMR analysis of the reaction mixture allowed to detect characteristic signals for the Si-H-Ni moiety of **15** in the ^1H -NMR spectrum ($\delta = -3.48$ ppm, $^2J_{\text{PH}} = 4.8$ Hz, $^1J_{\text{SiH}} = 104.1$ Hz)^[19] and in the ^{29}Si -NMR spectrum ($\delta = -15.8$ ppm, $^2J_{\text{SiP}} = 28.6$ Hz),^{[20][20]} strongly supporting the formation of **15** as an intermediate.



Scheme 3. Synthesis of phenyl-substituted silylene **13** and its isomerization.

In conclusion, a donor-stabilized silylene complex **4** with a Ni(0)-based donating ligand ($\text{Ni}^0 \rightarrow \text{silylene}$ complex) was successfully synthesized. Complex **4**, exhibiting a pyramidalized and nucleophilic Si(II) center, shows a peculiar chemical behavior due to the cooperative reactivity of the Si and Ni centers. Of particular interest, calculations demonstrate that the orientation of Ni-ligands with respect to the silylene moiety is a crucial factor in determining the role of Ni-fragment (Lewis acid or Lewis base) towards silylene, and a simple 90° rotation of the Si-Ni bond reverses the role of Ni, transforming a classical silylene→Ni(0) complex into an original Ni(0)→silylene complex. In addition, calculations also predict that the energy difference between both complex isomers is relatively small and, therefore, such a transformation can occur in solution for models without structural restrictions to prevent the Si-Ni bond rotation and alter their reactivity. More detailed studies on their properties and reactivity are under investigation.

Acknowledgements

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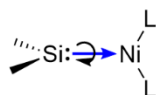
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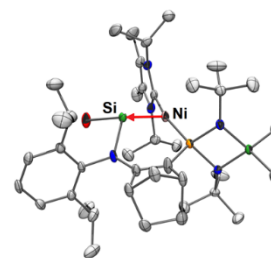
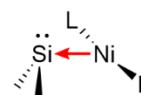
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A Silylene stabilized by σ -Donating Nickel(0) Fragment



90° rotation
at Si-Ni bond axis



A silylene complex stabilized by a Ni(0)-based donating ligand was successfully synthesized. This complex exhibits a pyramidalized and nucleophilic Si(II) atom and shows a peculiar chemical behavior due to the cooperative reactivity of the Si and Ni centers. DFT calculations demonstrated that a simple rotation of 90° on the Si-Ni bond reverses the role of Ni, transforming a classical silylene→Ni(0) complex into the corresponding Ni(0)→silylene complex.

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