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Main Group Chemistry

Synthesis, Characterization and Reactivity of a σ -Donating Ni^0 -Stabilized Silyliumylidene Ion

Shintaro Takahashi⁺, María Frutos⁺, Antoine Baceiredo, David Madec, Nathalie Saffon-Merceron, Vicenç Branchadell, and Tsuyoshi Kato*

Abstract: The synthesis of a silyliumylidene cation complex **2** stabilized by a Ni^0 -based donating ligand is reported. Experimental and theoretical studies demonstrate that the highly electrophilic Si^{II} center is stabilized by a dative $\text{Ni} \rightarrow \text{Si}$ σ -interaction and π -donations from the amino- and Ni-moieties. Due to the energetically close frontier orbitals localized on the Si and Ni atoms, complex **2** presents a competitive reactivity at Si and Ni sites.

Silyliumylidene ions **I**, featuring a mono-substituted Si^{II} atom with a lone pair and two vacant orbitals,^[1] are cationic silicon-based species exhibiting a peculiar high reactivity due to their highly unsaturated character (Figure 1a).^[2] The coordination of two donating ligands on the cationic silicon center (type **II**) enhances their stability, and allows to use them as useful chemical tools.^[3–6] Particularly, with strongly electron donating ligands such as NHCs, phosphazenes and NHSis, even silyliumylidene ions with small hydrogen-^[3] or halide^[4]-substituent can be isolated as stable molecules. Recently, So et al. have elegantly demonstrated that the bis(NHC)-stabilized parent silyliumylidene ion $[\text{H}-\text{Si}(\text{NHC})_2]^+$ is an efficient catalyst for the hydroboration of carbonyl compounds^[7] and for the *N*-formylation of

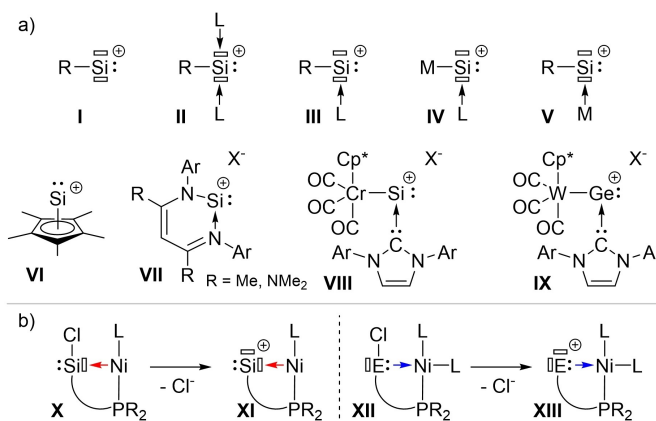


Figure 1. a) Base-stabilized silyliumylidene ions. b) Chlorine-abstraction from halo-metallylene-Ni complexes.

amines.^[8] The catalytic activity of Cp^*Si^+ cation **VI** in alkene hydrosilylation^[9] and C–O bond cleavage^[10] has also been reported. In contrast, only a few stable silyliumylidene ions supported by a single ligand (type **III**) have been described, despite an expected enhanced reactivity. Driess' and Aldridge's groups have independently reported the synthesis of imine-stabilized silyliumylidene ions **VII**.^[11] In the same vein, two metal-substituted systems of type **IV** stabilized by a NHC ligand, the silyliumylidene complex **VIII**^[12] and the germanium analogue **IX**^[13] have also been synthesized by Filippou and Tobita respectively. These derivatives are particularly reactive and present a silylene/germylene-type behavior, being able to activate small molecules such as H_2 and silanes in mild conditions. Similarly to main group element-based Lewis bases, transition metals are also known to act as Lewis bases (σ -donating ligands) toward electron deficient metallic^[14] and non-metallic species.^[15] Several σ -donating metal-supported metallylenes ($\text{M} \rightarrow \ddot{\text{E}}\text{R}_2$) have been reported to date,^[16–19] although such non-classical complexes are still less common than classical ones ($\text{R}_2\text{E} : \rightarrow \text{M}$).^[20] The related metal \rightarrow silyliumylidene complexes **V** remain elusive. Here, we would like to report the synthesis of the unprecedented silyliumylidene cation complex **2**, stabilized by a σ -donating Ni^0 ligand (Scheme 1).

A convenient way to synthesize donor-stabilized metallyliumylidene ions is the halide abstraction from the corresponding halo-metallylene derivatives, which has been used to prepare silylium- and germylium-ylidene cations

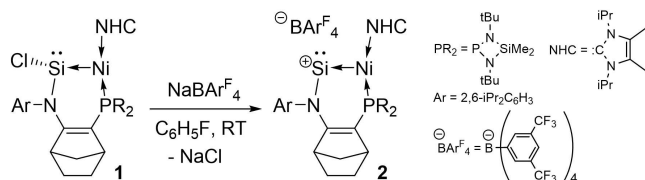
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Scheme 1. Synthesis of Ni⁰-stabilized silyliumylidene ion **2**.

VII–IX.^[11–13] Therefore, the Ni⁰→silylene complex **1**, described recently by us,^[21] featuring a pyramidalized three-coordinate Si^{II} atom with a lone pair should be an ideal precursor for such non-classical silyliumylidene complex (**X**→**XI**, Figure 1b). It should be noted that Hadlington et al. recently reported that the chloride abstraction of classical chlorometallene→Ni complexes **XII** yields the corresponding cationic metalliylidene→Ni complex **XIII** with two vacant orbitals on the E atom (E = Ge, Sn), exhibiting an appreciable catalytic activity in alkyne hydro-silylation arising from their enhanced electrophilic character.^[22]

As expected, due to its ionic character, silyliumylidene complex **2** is insoluble in nonpolar solvents (pentane, toluene), but fairly soluble in Et₂O or PhF, and slowly decomposes to unidentified products in PhF solution at room temperature (*t*_{1/2(25 °C)} = 2 days). In the ²⁹Si NMR spectrum of **2**, a doublet signal appears at 441.3 ppm (²*J*_{SiP} = 9.9 Hz), which is significantly downfield compared to the chemical shift of the chlorinated precursor **1** (123.5 ppm) and the base-stabilized silyliumylidene ions **VII** (69–80 ppm) but is still considerably upfield relative to that of NHC-stabilized metalla-silyliumylidene ion **VIII** (828.6 ppm).^[11] The high-field shift relative to **VIII** is certainly due to the stabilization of the cationic Si^{II} atom by π-donation of the amino group and the Ni⁰ fragment. The ³¹P NMR spectrum displays a singlet signal at 102.1 ppm, which is relatively downfield shifted compared with that of precursor **1** (91.4 ppm). A doublet signal observed at 173.1 ppm in the ¹³C NMR spectrum was attributed to the divalent carbon atom of the NHC ligand. The relatively large carbon-phosphorus coupling constant (²*J*_{CP} = 39.8 Hz) is in good agreement with the T-shaped geometry around the Ni atom with the NHC at the trans-position relative to the phosphine.^[21] The X-ray structure of **2**^[23] reveals a dicoordinate Si atom (Figure 2), which is part of a six-membered ring, and connected to the planar tri-coordinate N- and Ni-atoms ($\Sigma^\circ_{\text{N}} = 359.9^\circ$ and $\Sigma^\circ_{\text{Ni}} = 358.3^\circ$). The shortened Si1–N1 (1.734 Å) and Si–Ni (2.108 Å) bonds compared to those observed in the chlorinated precursor **1** (Si–N: 1.840 Å and Si–Ni: 2.178 Å) suggest their enhanced multiple bonding character due to the stabilizing π-electron donations from the amino- and Ni⁰-fragments to the cationic Si^{II} atom (resonance structures **2-B** and **2-C** in Figure 3). Similar Si–Ni bond lengths (2.065–2.120 Å) have been observed for the previously reported silylene-Ni⁰ complex with a multiple Si–Ni bond character.^[24] The structure reveals a planar and T-shaped geometry at the Ni⁰ site, with a large P–Ni–C_{1NHC} angle (151.5°). A similar T-shaped geometry around the

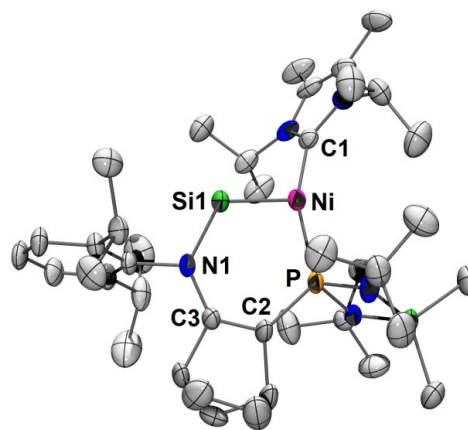


Figure 2. Molecular structure of **2**. Thermal ellipsoids represent 30% probability. H and disordered atoms and counter anion are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Si1 1.734(3), Si1–Ni 2.108(2), Ni–C1 1.979(4), Ni–P 2.146(1), P–C2 1.779(4), C2–C3 1.353(6), C3–N1 1.389(5); N1–Si1–Ni 120.8(1), Si1–Ni–C1 114.1(1), C1–Ni–P 151.5(1), Si1–Ni–P 92.7(1), Ni–P–C2 120.4(2), P–C2–C3 126.1(4), C2–C3–N1 127.6(4), C3–N1–Si1 126.2(3).

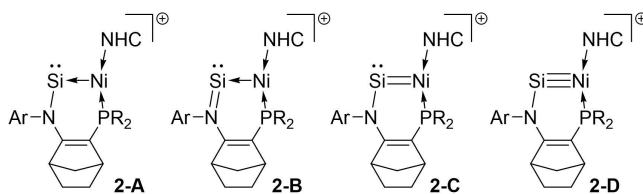


Figure 3. Possible resonance structures of **2**.

transition metal was observed for the chlorinated precursor **1** (P–Ni–C_{NHC} angle: 165.23°)^[21] and for other M⁰→metallene complexes (M = Ni, Pt)^[18,19] as well as for L₂Ni→Lewis acid complexes.^[25]

To gain more insight into the electronic structure of silyliumylidene complex **2**, DFT calculations have been performed at the M06/6-31G(d) level of theory. The optimized structure of **2** agrees quite well with the experimentally observed one (Si–Ni: 2.143 Å, Si–N: 1.761 Å, C1–Ni–P: 147.27°). The highest occupied molecular orbital (HOMO, –8.23 eV) and the lowest unoccupied bond orbital (LUMO, –4.86 eV) correspond to the in-plane lone pair orbital (*n*_σ) and p_{σSi}-type vacant orbital respectively and both are mainly localized on the Si atom similarly that of silylenes (Figure 4b,c). HOMO-2 (8.879 eV), corresponding to the d_{Ni}/π_{NHC} orbitals is mainly localized on the Ni atom and is close in energy to the HOMO. LUMO + 1 (–4.42 eV), which is only slightly higher in energy than the LUMO, corresponds to the anti-bonding σ*-orbitals of Si–Ni bond with a large contribution at the Ni atom (Figure 4a). The same type of σ*_{Si–Ni} orbital was observed as the LUMO for the chlorinated precursor **1** which can be regarded as non-classical Ni→Si^{II} complex.^[21] Due to this low-lying σ*_{Si–Ni} orbital, the Ni center of **1** presents a strongly electrophilic character. The HOMO–LUMO energy gap of **2** is calculated to be small ($\Delta E_{\text{HOMO-LUMO}}$: 3.37 eV), suggesting an enhanced

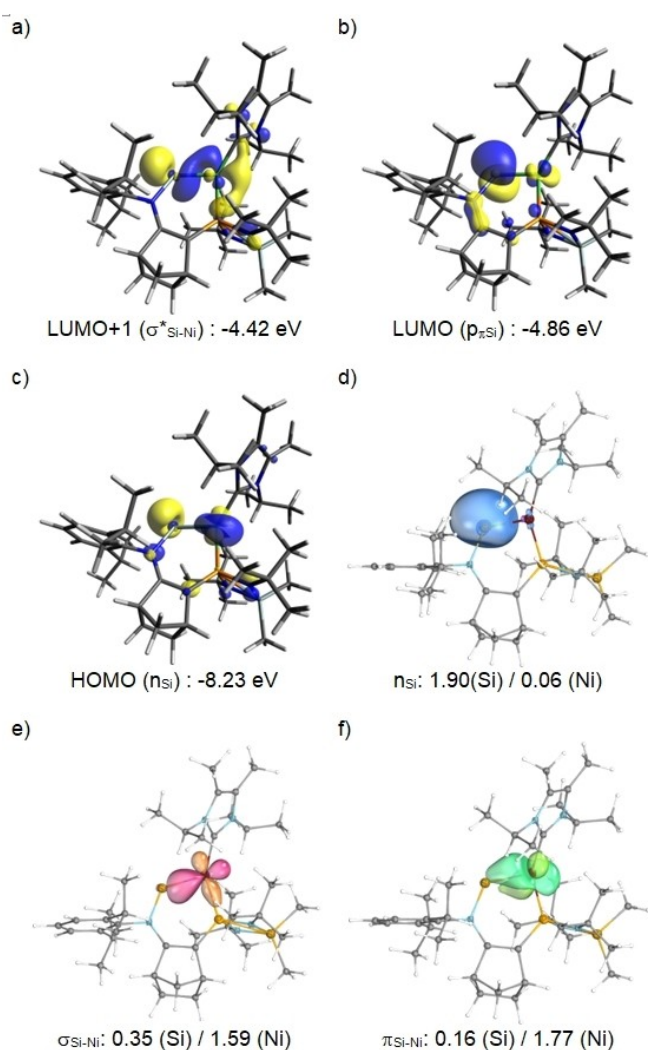


Figure 4. Frontier molecular orbitals [LUMO+1 (a), LUMO (b) and HOMO (c)] (isosurface level = ± 0.05 e/(a.u.)³) and their energy levels (eV) and selected intrinsic bond orbitals (IBOs) of [n_{Si} (d), $\sigma_{\text{Si-Ni}}$ (e) and $\pi_{\text{Si-Ni}}$ (f)] of **2**, calculated at the M06/Def2TZVP//M06/6-31G(d) level.

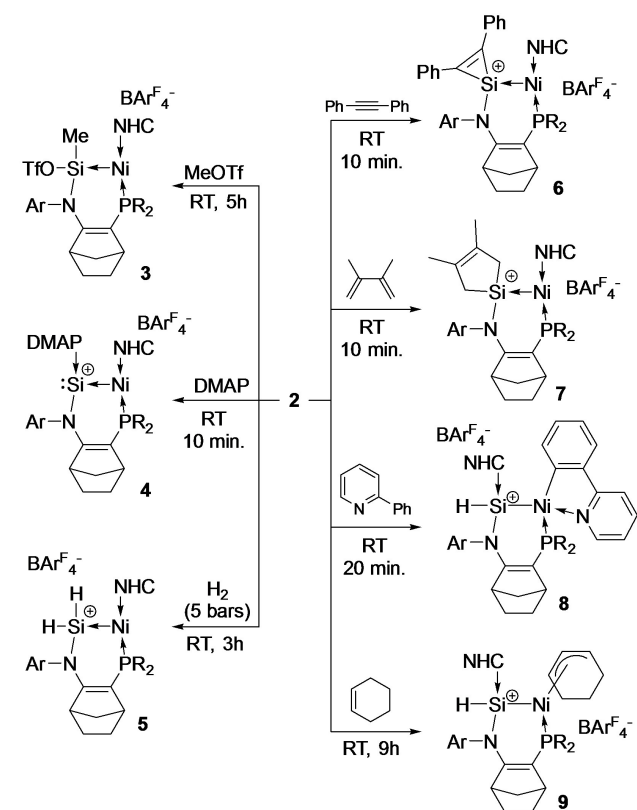
reactivity. Furthermore, the energetic proximity of silylene-type frontier orbitals localized mainly on the Si atom [LUMO ($^*\pi_{\text{Si-Ni}}$)/HOMO (n_{Si})] and those around the Ni atom [LUMO+1 ($^*\sigma_{\text{Si-Ni}}$)/HOMO-2 (d_{Ni})] suggests that the Si and Ni sites present an ambiphilic character and a competitive reactivity and also implies possible cooperative/synergetic effects of these two reactive sites, which are common in dinuclear transition metal complexes.^[26]

As expected, intrinsic bonding orbital (IBO) analysis^[27] of **2** shows the Ni–Si σ -bond with a large contribution at the Ni atom [0.35 (Si)/1.65 (Ni)], consistent with the Ni→Si bonding character. The same type of IBO was yielded for the Si–Ni σ -bond of precursor **1** [0.37 (Si)/1.58 (Ni)].^[21] The presence of a second electron-donation from Ni to Si atom via Ni–Si π -interaction (**2-C** in Figure 3) was also indicated by the IBO analysis, although such a π -interaction is considerably weak [0.16 (Si)/1.77 (Ni)] (Figure 4f). The IBO

analysis also shows the lone pair orbital on the silicon atom with a quasi-exclusive contribution on the Si atom [1.90 (Si)/0.06 (Ni)], confirming a negligible back-donation from the Si [lone pair (n_{Si}) located in the plane of the ring] to Ni atom (**2D**) due to the unfavoured in-plan π -interaction^[28] of the Si–Ni fragment within a six-membered ring with a relatively acute N1–Si1–Ni angle [120.8°]. Nevertheless, the Wiberg bond indices corresponding to Si–N (0.577) and Si–Ni (0.695) bonds are increased compared to those calculated for the chlorinated precursor **1** (Si–N: 0.460, Si–Ni: 0.539), demonstrating an increased multiple bonding character of these bonds. This is certainly due to the π -electron donations from the amino and from the Ni fragments (Resonance structures **2-B** and **2-C** in Figure 3). The extremely large s-character of the lone pair orbital on the Si atom (s: 88.3%, p: 11.6%) confirms an enhanced silyliumylidene character probably because of a weak dative Ni→silyliumylidene interaction. These results are in good agreement with a Ni-stabilized silyliumylidene ion character of **2** (**2-A** in Figure 3). As also observed in the chlorinated-precursors (**1** and **XII**), this Ni–Si bonding situation in **2** is opposite from that proposed for the related Hadlington's cationic metallylidenium–Ni⁰ complex **XIII** presenting a E→M σ -donating bond (E=Ge, Sn) and two vacant orbitals (Figure 1). The difference probably comes from the geometry around the Ni atom. Indeed, a T-shaped geometry around the Ni atom should be a crucial factor to have such Si–Ni bonding situation, since most M→electrophile complexes (M=Ni⁰, Pt⁰) exhibit this geometry.^[25] The steric repulsion between ligands (bulky phosphine and NHC) in **2**, probably favors such a geometry and thus the Ni→Si σ -donating bond. In the case of Hadlington's complexes, the use of a more flexible ligand system, leading to a larger angle at the Ge^{II} atom (132.96°), can promote the double donation of the Ni atom to stabilize such unusual species with the two vacant orbitals on the same E atom. A similar double π -back donation was also observed in the case of Driess silylene–Ni⁰ complex.^[24a]

As predicted by the MO analysis, silyliumylidene complex **2** presents an ambiphilic character at the Si center. Indeed, **2** reacts with MeOTf to form the Si-methylated product **3**, despite the slow reaction rate at room temperature (5 h) probably due to a low nucleophilicity of the silyliumylidene cation **2** with an excessively large s-character of the lone pair orbital (88.3%). The highly electrophilic silicon center of **2** was demonstrated by an immediate coordination of a Lewis base such as *N,N*-dimethylaminopyridine (DMAP) to afford the donor-acceptor complex **4**, in contrast to neutral precursor complex **1** showing an electrophilic character exclusively at the Ni atom. Placed under an atmosphere of H₂ (5 bar) silyliumylidene **2** smoothly reacts (3 h) at room temperature at the Si center leading to the Ni⁰-stabilized dihydrogenosilylium ion complex **5**. The IBO analysis of **5** indicates an enhanced covalent character of the Si–Ni σ -bond with an increased contribution at the Si atom [$\sigma_{\text{Si-Ni}}$: 0.77 (Si)/1.21 (Ni)] from that calculated for **2** [$\sigma_{\text{Si-Ni}}$: 0.35 (Si)/1.59 (Ni)]. This result implies a stronger Lewis acidic character of the silylium ion than that of silyliumylidene ion. Cycloaddition reactions also

occur in mild conditions at the Si center of **2** with diphenyl acetylene or 2,3-dimethyl-1,3-butadiene (1 eq.), affording the corresponding [2+1]- and [4+1]-cycloadducts (**6** and **7**), respectively (Scheme 2).



Scheme 2. Reactivity study of Ni-stabilized silyliumylidene ion **2**.

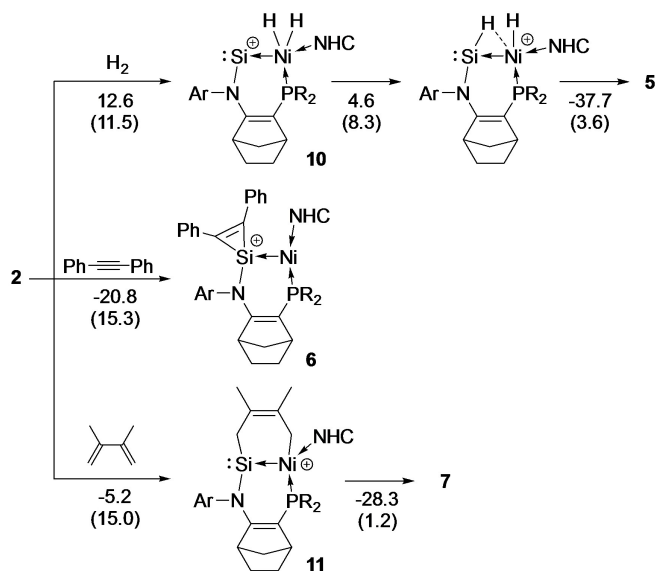


Figure 5. Calculated reaction pathways for the reactions of **2** with H_2 , PhCCPh and 2,3-dimethyl-1,3-butadiene and relative Gibbs energy ΔG (kcal mol^{-1}) of each intermediate. The calculated Gibbs energy barriers ΔG^\ddagger (kcal mol^{-1}) are in parenthesis.

Although the reactions of **2** with H_2 , diphenylacetylene, and 2,3-dimethyl-1,3-butadiene lead to the same type of products **5–7** (Ni-stabilized silylium ions),^[31] DFT calculations showed that the reactions proceed through different pathways (Figure 5). Indeed, the reaction with H_2 starts with the activation of H_2 at the Ni center to generate a dihydrogenated Ni-complex **10**, followed by stepwise isomerizations via 1,2-hydride migrations to give **5**, while the acetylene reacts at the Si center via a [2+1]-cycloaddition to give directly **6**. In contrast to these initial single-site reactions (Si or Ni), the addition of butadiene involves, in a first step, both sites (Si and Ni) to generate a transient six-membered ring **11** which readily isomerizes to the isolated product **7**. These results clearly indicate the competitive reactivity of the Si and Ni sites, which is in good agreement with the MO analysis of **2** showing the energetically very close frontier orbitals deployed at the Si and Ni atoms respectively. The reaction pathways and reactive sites, which differ according to the type of reagent used, probably rely not only on the MO symmetry/energy-level match but also on steric factors and the stability of products formed. As with many transition metals, the oxidative addition of H_2 occurs at Ni site, rather than Si center,^[32] in **2** with a low energy barrier of $11.5 \text{ kcal mol}^{-1}$, while the [2+1]-cycloaddition with an acetylene, which is a typical reaction for silylenes, takes place preferentially at the Si site to give a stable cycloadduct, instead of simple Ni-acetylene π -complex formation. In contrast, although the [4+1]-cycloaddition is generally considered to start with [2+1]-cycloaddition to generate a silirane intermediate,^[33] such a [2+1]-cycloaddition with the hindered dimethylbutadiene is unlikely. Instead, a sterically advantageous [4+2]-cycloaddition involving the Si–Ni moiety to generate **11** is predominant.

In contrast to the DMAP which simply coordinates on the Si site, the reaction of **2** with 2-phenylpyridine involves the 1,2-addition of a C–H bond across the Si–Ni fragment with the concomitant migration of the NHC ligand to the silicon center to afford the NHC-stabilized metallasilylium ion **8**. The structure of **8** was confirmed by X-ray diffraction study (Figure 6).^[23] According to DFT calculations, this reaction starts with the 1,2-migration of the NHC ligand promoted by the coordination of phenylpyridine to the Ni atom (**12**), instead of Si atom probably for steric reasons,^[34] to generate a NHC/Ni-stabilized silyliumylidene ion **13** (Figure 7). This process, being thermodynamically neutral ($\Delta G_{2-13} = 0.3 \text{ kcal mol}^{-1}$) mainly due to the instability of sterically over-congested complex **13**,^[29] can be reversible. Complex **13** evolves by the phenyl C–H bond activation at the Ni center to generate an unstable Ni^{II}-stabilized silyliumylidene complex **14** which then isomerizes via an insertion reaction of the Si center into the Ni–H bond to afford the experimentally observed complex **8**. Although the C–H activation process is endergonic ($\Delta G_{13-14} = 17.2 \text{ kcal mol}^{-1}$, $\Delta G^\ddagger_{13-14} = 26.6 \text{ kcal mol}^{-1}$), the following isomerization to afford the final product **8** is a quasi-barrierless and strongly exergonic process ($\Delta G_{14-8} = -33.3 \text{ kcal mol}^{-1}$, $\Delta G^\ddagger_{14-8} = -0.8 \text{ kcal mol}^{-1}$), which promotes the formation of **8**. This rearrangement can be related to the previously reported isomerization of phenyl-substi-

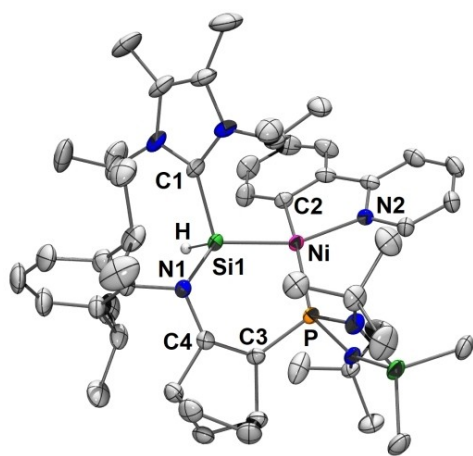


Figure 6. Molecular structure of **8**. Thermal ellipsoids represent 30% probability. H atoms, except one on the Si1 atom, counter anion, solvent molecules and the second molecule in the asymmetric unit are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C1 1.955(3), N1–Si1 1.801(2), Si1–Ni 2.178(1), Ni–C2 1.965(3), Ni–N2 1.979(2), Ni–P 2.187(1); Si1–Ni–C2 87.68(9), C2–Ni–N2 83.90(11), N2–Ni–P 99.25(7), Si1–Ni–P 94.80(3).

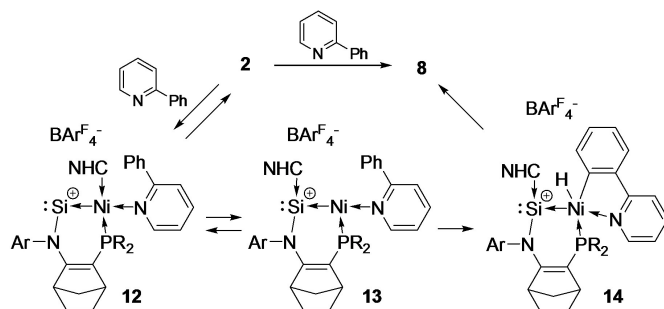


Figure 7. Proposed mechanism for the reaction of **2** with 2-phenylpyridine.

tuted silylene-Ni⁰ complex, which also proceeds through a C–H activation by Ni followed by a silylene insertion into the resulting Ni–H bond.^[21] The overall process is exergonic ($\Delta G_{2+\text{Ph-Py} \rightarrow 8} = -15.8 \text{ kcal mol}^{-1}$). In contrast to the reaction with the diphenylacetylene leading to a simple [2+1]-cycloaddition at the Si atom, the reaction with the more hindered cyclohexene affords the NHC-stabilized metalla-silylium ion **9** with a Ni^{II} fragment as a π -allyl complex (Scheme 2). The mechanism of this reaction is probably similar to that proposed for the reaction with 2-phenylpyridine (Figure 6) and, in this case, the reaction probably starts with the olefin coordination to the Ni center instead of Si atom due to the steric reasons, which leads to the NHC migration.^[30] The β -proton of activated cyclohexene is then deprotonated by the Si^{II} atom to produce the π -allyl complex **9**.

In conclusion, a cationic silyliumylidene complex **2** stabilized by a Ni⁰-based donor ligand has been successfully synthesized. Structural and theoretical analysis confirm the stabilization of the cationic Si^{II} center by double electron donations from the Ni⁰ moiety via a dative Ni→Si σ -interaction and via a π -donation in addition to the π -electron

donation of the amino substituent. Due to the presence of a lone pair (n_σ) and a vacant orbital (p_π) on the two-coordinate Si^{II} center, silyliumylidene **2** exhibits an ambiphilic character. Furthermore, due to the energetic proximity of the frontier orbitals localized on Si and on Ni respectively, silyliumylidene-Ni⁰ complex **2** exhibits competitive reactivity on Si and Ni sites. More detailed studies on its properties and reactivity are in progress.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Donor-Stabilized Species · Metallacycles · Nickel Complex · Silyliumylidene Ion · Z-Type Ligand

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