

Hydrosilylation of Dihydrosilylium Ion Stabilized by Coordination of a σ -Donating Ni(0) Ligand

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Dedication ((optional))

Abstract: The hydrosilylation reactions of dihydrosilylium ion **2**, stabilized by coordination of a σ -donating Ni(0) fragment, has been investigated. Complex **2** with two reactive sites, dihydrosilylium and Ni(0) centers, readily reacts with diphenylacetylene via a selective mono-hydrosilylation reaction to afford the corresponding Ni(0)-stabilized (hydro)(vinyl)silylium ion **6**. In the case of ethylene, three equivalents of olefin are consumed to give a cationic Ni(II)-complex **7** featuring a Bu-Si⁺-Ni^{II}-Et moiety with a NHC-supported Si atom. DFT calculations indicate that the hydrosilylation proceeds by a classical (Chalk-Harrod type) mechanism with the assistance of NHC ligand moving between Si and Ni centers according to their stabilization requirements.

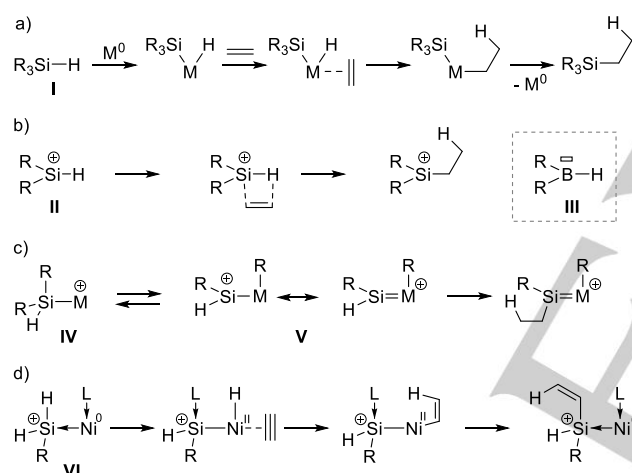
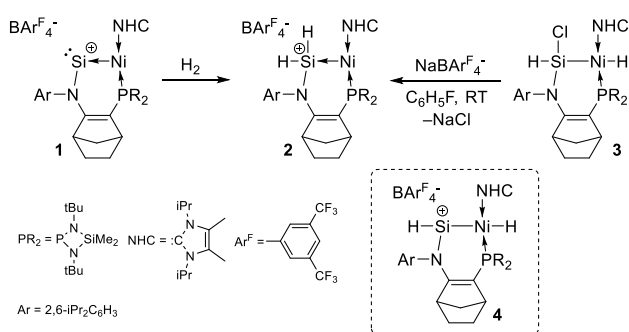


Figure 1. Hydrosilylations of unsaturated molecules with different types of silicon hydrides (I – VI).

Hydrosilylation of alkenes or alkynes,^[1] allowing to conveniently form a Si-C bond in an atom economical manner, is

a synthetically important reaction.^[2] In general, the hydrosilylation requires an activation of Si-H bond of hydrosilanes **I** by transition metal complexes such as Pt(0). Subsequent olefin insertion into M-H bond, followed by the reductive elimination of alkylated silane from the metal center complete the process of hydrosilylation (Chalk-Harrod mechanism in Figure-1a).^[3] Compared to silanes, hydrogen-substituted silylium ions **II** are attractive target molecules due to the labile Si-H bond in addition to an enhanced reactivity because of their extremely strong Lewis acid character (Figure-1b). Today, several isolable ligand-stabilized and ligand-free hydrogenosilylium ions **II** are available.^[4] However, in contrast to the isoelectronic boranes **III**, easily evolving by well-known hydroboration reactions in the presence of olefins,^[5] no examples of related hydrosilylation to unsaturated compounds have been described to date. Only limited knowledge about their reactivity as simple Lewis acids is available so far.^[4c,g,i] Of particular interest, Tilley et al. demonstrated that cationic complexes of hydrosilylated-transition metal **IV**, which reversibly isomerize into the corresponding cationic hydrosilylene complexes **V** via a 1,2-migration of R-substituent from Si to the metal center (Figure-1c),^[6,7] undergo the hydrosilylation with an alkene/alkyne directly at the strongly electrophilic Si-H fragment (**V**).^[6] Here, we report the hydrosilylation of dihydrosilylium ion **VI** stabilized by coordination of a σ -donating Ni(0) fragment, which proceeds differently from Tilley's case but similarly to the classical hydrosilylation with an assistance of donating NHC ligand (L) (Figure-1d).



Scheme 1. Synthesis of Ni(0)-stabilized dihydrosilylium ion **2** via hydride migration.

Recently, we have reported that the Ni(0)-stabilized silyliumylidene ion **1**, presenting a unique cooperative reactivity between silyliumylidene and Ni(0) sites, readily reacts with H₂ to give a Ni(0)-stabilized dihydrosilylium ion **2** (Scheme 1).^[6] This type of compound **2** can also be prepared in very good yield (71%) by the abstraction of chloride from (chloro)(hydro)silylium(II) hydride complex **3** (Scheme 1). Although no intermediate

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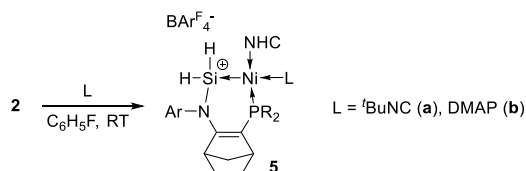
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could be detected by monitoring the reaction by ^{31}P NMR spectroscopy, the reaction probably first generates a transient silylium ion **4**, which evolves via a reductive elimination (or $\text{Ni}\rightarrow\text{Si}$ hydride migration) to give **2** which is well stabilized by the σ -donating $\text{Ni}(0)$ -ligand. Despite numerous examples of Nickel coordinating Z-type main group element complexes,^[9-12] to the best of our knowledge, no other Ni-stabilized hydrosilylium ion has been reported.



Scheme 2. Reaction of $\text{Ni}(0)$ -stabilized dihydrosilylium ion **2** with Lewis bases.

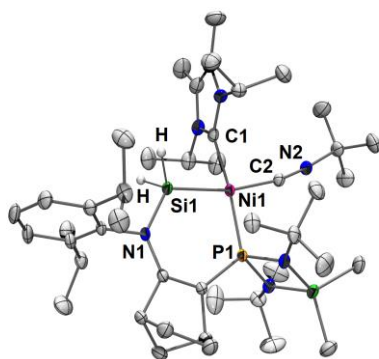
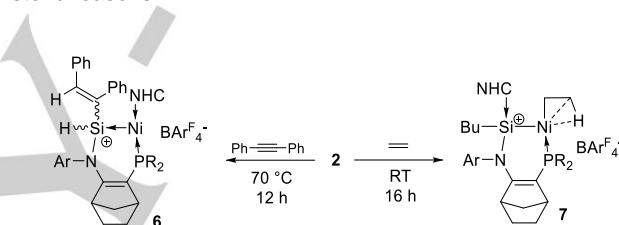


Figure 2. Molecular structure of **5a**. Thermal ellipsoids represent 30 % probability. H except for H atoms on Si1, counter anion and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-Ni1 2.210(1), N1-Si1 1.780(2), Ni1-P1 2.164(1), Ni1-C1 1.928(2), Ni1-C2 1.884(2), C2-N2 1.147(2), N1-Si1-Ni1 121.4(1), Si1-Ni1-C1 79.9(1), C1-Ni1-C2 88.2(1), C2-Ni1-P1 97.8(1), Si1-Ni1-P1 94.1(1). $\Sigma^\circ_{\text{Ni}} = 360.02^\circ$.

In order to evaluate the electrophilicity of Si and Ni centers of complex **2**, we investigated first its reaction with Lewis bases (Scheme 2). In both cases, the reaction of **2** with $t\text{BuNC}$ (**a**) or DMAP (**b**) resulted in the coordination on Ni center to afford the corresponding complexes **5a,b**, in agreement with a higher electrophilic character of Ni center (Scheme 2). The ^1H NMR spectra of **5a** and **5b** show two doublet of doublet signals at 4.20/4.59 and 4.10/4.40 ppm respectively with Si-satellites ($J_{\text{H-Si}} = 197/195$ and $191/190$ Hz respectively) for two inequivalent Si-H groups. These values are comparable to those observed for **2**^[8] (4.01 and 4.55 ppm, $J_{\text{SiH}} = 210$ and 208 Hz) and phosphine-stabilized one (5.11 ppm, $J_{\text{SiH}} = 262$ Hz).^[41] The ^{31}P NMR spectra display a singlet signal at 74.5 (**5a**) and 82.3 (**5b**) ppm in the same range as those for other $\text{Ni}(0)$ -stabilized silylium ions (68 - 82 ppm).^[8] The ^{29}Si NMR chemical shifts of **5** appear at -16.7 (**5a**) and -19.4 (**5b**) ppm, slightly up-field shifted compared to that of **2** (-6.7 ppm). The molecular structure of **5a** was determined by X-ray diffraction analysis (Figure 2).^[13] The Ni center shows distorted square planar geometry ($\Sigma^\circ_{\text{Ni}} = 360.02^\circ$) as typical for d^{10} -Nickel complexes. The Si1-Ni1 bond length

[Si1-Ni1 2.210(1) Å] is slightly elongated compared with that of precursor **2** [2.159(2) Å]^[8] probably due to a less electron-rich $\text{Ni}(0)$ center with a π -electron withdrawing isocyanide ligand.

The reaction of $\text{Ni}(0)$ -stabilized dihydrosilylium ion **2** with diphenylacetylene at 70 °C results in the hydrosilylation of alkyne to give the corresponding $\text{Ni}(0)$ -stabilized (hydrogeno)(vinyl)-silylium ion **6** (Scheme 3). While the hydrosilylation product **6** was obtained as a mixture of two diastereomers due to the chiral norbornene and cationic Si groups, the reaction proceeds in a stereospecific manner to give *E*-isomers of **6**, as indicated by X-ray diffraction analysis (Figure 3-left).^[13] The downfield-shifted ^{29}Si NMR signal (11.4 ppm) for the main diastereoisomer of **6**, compared with that of **2** (-6.7 ppm), is in good agreement with the conversion of the Si-H function to a Si-alkenyl group. Furthermore, one of the Si-H groups, which remained intact, was confirmed by the ^1H NMR signal appearing at 4.6 ppm accompanying two satellite signals with a large ^1H - ^{29}Si coupling constant ($^1J_{\text{Si-H}} = 211.7$ Hz). Further hydrosilylation of **6** in the presence of excess acetylene was not observed even at higher temperature (110 °C) probably due to steric reasons.



Scheme 3. Hydrosilylation reaction of **2** with diphenylacetylene and ethylene.

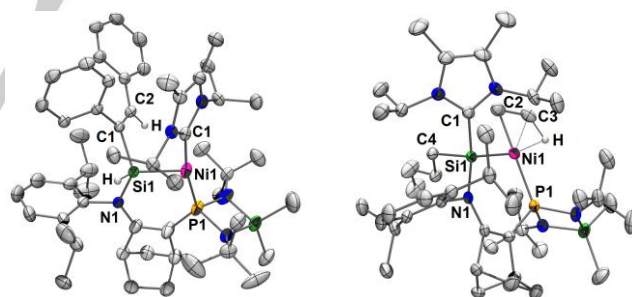


Figure 3. Molecular structure of **6** (left) and **7** (right). Thermal ellipsoids represent 30 % probability. H except for H atoms on Si1 (**6**), solvent molecule (**6**), and counter anion are omitted for clarity. Selected bond lengths [Å] and angles [°]: **6** N1-Si1 1.781(2), Si1-C2 1.884(3), C2-C3 1.343(4), Si1-Ni1 2.174(1), Ni1-C1 1.948(3), Ni1-P1 2.136(1), N1-Si1-Ni1 121.1(1), Si-Ni1-C1 97.4(1), C1-Ni1-P1 168.8(1), Si1-Ni1-P1 93.8(1); **7**: N1-Si1 1.806(3), Si1-C1 1.975(4), Si1-C4 1.890(4), Si1-Ni1 2.181(2), Ni1-C2 1.912(5), C2-C3 1.493(8), Ni1-C3 2.143(5), Ni1-P1 2.143(2), N1-Si1-Ni1 117.2(1), C1-Si1-C4 104.6(2), Si1-Ni1-C2 89.9(2), Ni1-C2-C3 76.9(3), C2-C3-Ni1 60.4(3), C3-Ni1-C2 42.7(2), Si1-Ni1-P1 100.7(1).

In contrast, with an excess of a small olefin such as ethylene (5 bar), **2** consumes three equivalents of ethylene to give the cationic $\text{Ni}(\text{II})$ complex **7**, with a NHC-supported cationic Si atom, in good yield (75 %) (Scheme 3). The ^{31}P NMR shows only one singlet signal (80.2 ppm), indicating the diastereo-selective

formation of **7** contrary to the case of **6**. In the ^{29}Si NMR, a doublet signal corresponding to the cationic Si atom was observed at 21.9 ppm (d, $^2J_{\text{Si,P}} = 40.4$ Hz). The structure of complex **7** was determined by X-ray diffraction analysis (Figure 3-right).^[13] The structure confirms the presence of the butyl group and the NHC ligand on the Si atom, as well as the ethyl group on the Ni center oriented cis to the silylium center. An agostic interaction of ethylene β -hydride with the Ni(II) center, oriented trans to the Si atom, was also observed. The Ni1-C2 bond [1.912(5) Å] shorter than Ni-C3 bond [2.143(5) Å] as well as the acute Ni-C2-C3 angle [76.9(3)°] are characteristic for the agostic interaction between β -C-H bond of ethyl group and nickel center, according to Brookhart and Green's definition.^[14] In the ^1H NMR spectrum, the signal of this agostic β -hydride was detected as a characteristic high-field shifted triplet signal at -0.82 ppm. Similar agostic interactions were observed for other alkyl-Ni(II) complexes.^[15] In the ^{13}C NMR, the signals for the Ni-CH₂-CH₃ moiety appear at 13.4 ppm (d, $^2J_{\text{CP}} = 29.0$ Hz, CH₂) and -4.8 ppm (s, CH₃). The similar NMR signal pattern has been observed for the related Et-substituted cationic Ni(II) complex.^[14a]

In order to obtain further insight into the reaction mechanism, density functional theory (DFT) calculations were carried out at M06/def2-tzvp//M06/6-31g(d) level of theory with simplified model compounds (^iPr and ^tBu group were replaced by Me group). The direct hydrosilylation of ethylene to the Si-H bond center of **2'** is unlikely and we could not find an appropriate pathway for this reaction. This is probably due to the lack of electrophilic character of Si center stabilized by the coordination of σ -donating Ni(0) fragment. We have then investigated the isomerization of **2'** via oxidative addition of Si-H to Ni(0) center (or 1,2-hydride migration) to generate a donor-free Ni(II)-substituted silylium ion **9'**. However, this process is strongly endergonic ($\Delta G_{2',9'} = 20.8$ kcal/mol) and requires an excessively high activation energy to take place ($\Delta G^\ddagger_{2',9'} = +37.1$ kcal/mol), although subsequent hydrosilylation to give the ethyl-substituted silylium ion **10'** is an exergonic process with a reasonably low energy barrier ($\Delta G_{9',10'} = -19.5$ kcal/mol and $\Delta G^\ddagger_{9',10'} = +9.0$ kcal/mol). Therefore, the direct hydrosilylation at the Si center promoted by adjacent transition metal (Glaser-Tilley mechanism Figure 1c)^[7b,c] is unlikely for our system.

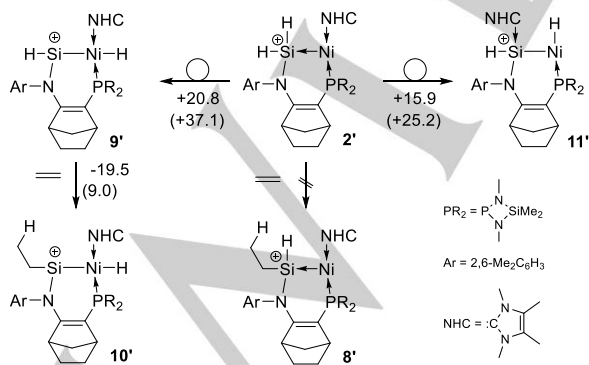


Figure 4. Calculated Gibbs free energy (ΔG in kcal·mol⁻¹) and activation energy (ΔG^\ddagger in kcal·mol⁻¹) for the oxidative addition of **2'** and hydrosilylation of **2'** and **3**.

The related isomerization of **2'** accompanied by a 1,2-migration of NHC to the Si center to give **11'** is also an unfavored process ($\Delta G_{2',11'} = 15.9$ kcal/mol, $\Delta G^\ddagger_{2',11'} = 25.2$ kcal/mol) certainly because of instable tri-coordinate environment of Ni(II) center (Figure 4). Indeed, the same rearrangement is considerably more favored for a four-coordinate Ni(II)-complex **12'** with an additional ethylene ligand ($\Delta G_{12',13'} = +1.4$ kcal/mol, $\Delta G^\ddagger_{12',13'} = +12.3$ kcal/mol in Figure 5).^[16] In addition, subsequent migratory insertion of ethylene into the Ni-H bond in the formed complex **13'** easily occurs to give the corresponding Ni-Et complex **14'** with a trans configuration between ethyl and silylium groups ($\Delta G_{13',14'} = +0.2$ kcal/mol, $\Delta G^\ddagger_{13',14'} = +3.0$ kcal/mol).^[17] The cis-trans isomerization of Ni-Et complex **14'** proceeds with relatively low energy barrier ($\Delta G_{14',15'} = -4.0$ kcal/mol and $\Delta G^\ddagger = 6.2$ kcal/mol), which is similar to previously described ones.^[15b,18] The second ethylene addition and its migratory insertion into Ni-Et bond is also easy and strongly exergonic process ($\Delta G_{14',16'} = -15.3$ kcal/mol, $\Delta G^\ddagger_{14',16'} = 14.7$ kcal/mol) and give a Ni(II)-Bu complex **16'** as a cis-isomer. In contrast to trans Ni-Et complex **14'** (or **15'**), Ni-Bu complex **16'** having a cis-configuration, easily undergoes an isomerization, after the coordination of ethylene, via H and Bu exchange on the Si and the Ni atoms to give a new Ni-hydride complex **18'** ($\Delta G_{17',18'} = -18.5$ kcal/mol, $\Delta G^\ddagger_{17',18'} = 11.6$ kcal/mol). Further evolution of **18'** via an ethylene migratory insertion into the Ni-H bond proceeds with a small barrier ($\Delta G^\ddagger_{18',7'} = 0.6$ kcal/mol), leading to the formation of **7'**_{trans}. The cis-trans isomerization of **7'**_{trans} resulted in the formation of final product **7'** ($\Delta G_{7',7'} = -4.5$ kcal/mol and $\Delta G^\ddagger = 6.0$ kcal/mol).

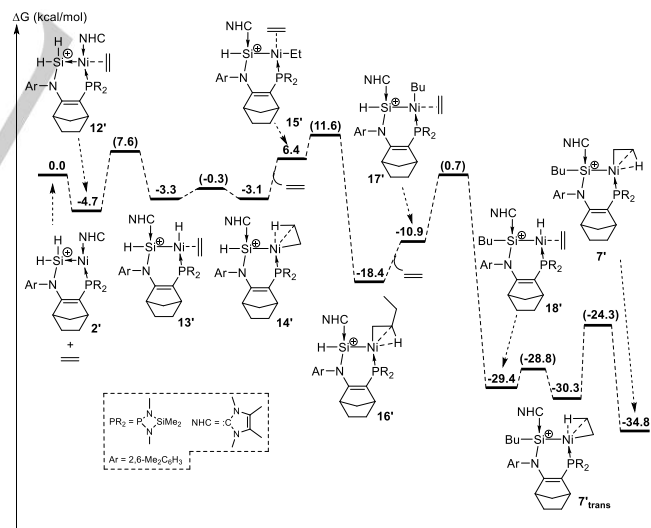


Figure 5. Calculated pathway for the reaction of **2'** with C_2H_4 (3 eq.). Gibbs energies of intermediates (and transition states) are in kcal·mol⁻¹.

The reaction of **2** with a diphenylacetylene probably proceeds in the same manner until the formation of vinyl-substituted Ni(II) complex **19**, via oxidative addition of the Si-H group to Ni(0), promoted by acetylene coordination, followed by migratory insertion of acetylene into the Ni-H bond (Figure 6).

However, certainly due to higher steric congestion, subsequent vinyl-hydride exchange on the Si and Ni centers, to generate a hindered NHC-stabilized (vinyl)(Ni-hydride) silylium ion **20**, is hampered. Instead, complex **19** evolves via a reductive elimination with concomitant migration of NHC from Si to Ni center to produce a less hindered Ni(0)-stabilized silylium ion **6**, as observed experimentally. Indeed, DFT calculations using real system indicates that the process from **19** to **20** is strongly endergonic ($\Delta G_{19,20} = +19.4$ kcal/mol) while the conversion of **19** to **6** ($\Delta G_{19,6} = -1.8$ kcal/mol) is exergonic (Figure 6). These results demonstrate that the hydrosilylation of Ni(0)-stabilized dihydrosilylium ion **2** with unsaturated compounds proceeds by a classical (Chalk-Harrod type) mechanism involving oxidative addition - alkyne/alkene migratory insertion - reductive elimination process, with a NHC ligand moving between the Si and Ni centers according to their stabilization requirements.

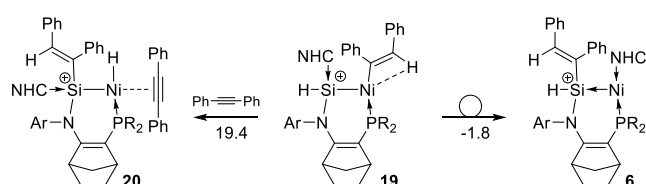


Figure 6. Calculated Gibbs free energy (ΔG in kcal·mol⁻¹) for the evolution of vinyl Ni(II)-complex **19**.

In conclusion, hydrosilylation reactions of dihydrosilylium ion **2** stabilized by coordination of a σ -donating Ni(0) ligand have been experimentally and theoretically investigated. Dihydrosilylium ion **2** with two reactive sites, dihydrosilylium and Ni(0) centers, reacts with diphenylacetylene via a selective mono-hydrosilylation reaction affording the corresponding Ni(0)-stabilized (hydro)(vinyl)silylium ion **6**. It also reacts with three equivalents of ethylene to give the Ni(II)-complex **7** with a NHC-supported cationic Si atom. DFT calculations indicate that the hydrosilylation proceeds via a classical (Chalk-Harrod-type) mechanism with NHC ligand moving between the Si and Ni centers according to their stabilization requirements. The steric hindrance of molecules is an important factor to differentiate the reaction pathways. Further applications of dihydrosilylium ion **2** are in progress.

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Keywords: Silylium ion • hydrosilylation • Nickel (0) • cooperative reaction •

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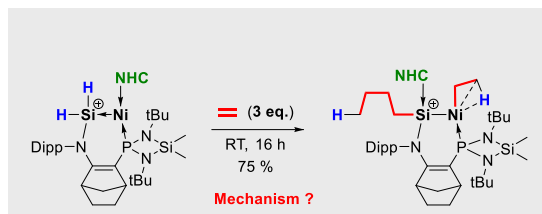
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Kato

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Hydrosilylation of Dihydrosilylium Ion
Stabilized by Coordination of a σ -
Donating Ni(0) Ligand



The hydrosilylation reactions of dihydrosilylium ion, supported by a σ -donating Ni(0) fragment, has been studied. This complex with two reactive sites, dihydrosilylium and Ni(0) centers, readily reacts with 3 equivalents of ethylene to give a cationic Ni(II)-complex featuring a Bu-Si-Ni-Et moiety. DFT calculations indicate that the hydrosilylation proceeds by a classical (Chalk-Harrod) mechanism with NHC ligand moving between Si and Ni centers according to their stabilization requirements.

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