# ORGANOMETALLICS

# Cooperative Si−H Addition to Side-On Ni(0)-Imine Complexes Forms Reactive Hydrosilazane Complexes

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**ABSTRACT:** Activation of a Si−H bond is commonly a critical step in catalytic hydrosilylation reactions. Herein, we investigate the cooperative reactivity of Ni(0) centers bearing a side-bound imine ligand toward silanes. Such complexes activate a Si−H bond of diphenylsilane, resulting in formal hydrosilylation of the imine backbone, which acts as a hydride acceptor. The resulting hydrosilazane motif engages either in coordination to nickel via the Si−H bond, forming an 18-electron $\eta^2$-Si−H complex, or oxidative addition to Ni to form 16-electron Ni(II) silyl/hydride complexes. DFT calculations suggest a cooperative activation of the silane via ligand-to-ligand hydride transfer. In addition, the silicon fragment readily exchanges with external hydrosilanes, showing that the Si−N bond can be reversibly cleaved under mild conditions.



## INTRODUCTION

Metal-mediated activation of Si−H bonds to form reactive silicon species such as metal silyls ($M-SiR_3$) or silylenes ($M = SiR_2$) is a critical step in homogeneously catalyzed hydrosilylation reactions.[1,2] The Si−H activation step prototypically proceeds via oxidative addition of the Si−H bond to form metal silyl/hydride complexes, but in many cases the actual activation product can best be understood as an arrested state along the oxidative addition coordinate featuring some degree of residual Si−H bonding.[3−5] In particular, addition of a Si−H bond to Ni(0) has been shown to afford either genuine Ni(II) silyl/hydride species[2,6] or Si−H sigma complexes.[1,2,7−14] Interesting dynamic processes can occur in these compounds, such as reversible Si−H reductive elimination coupled to $N_2$ uptake in PSiP pincer compounds[10] and facile σ-bond metathesis between $\eta^2$-Si−H and $\eta^2$-H−H ligands.[15]

Metal−ligand cooperation is attracting interest as a means to promote and control small-molecule activation at transition metals.[16−21] Particularly attractive for element−hydrogen bond activation are ligands than can act as hydride acceptors such as boranes as well as π-bound olefins and aromatic groups.[22−25] Such ligands can assist in the activation of silane substrates,[26] as was observed for example in a nickel complex of a diphosphine−pyridine ligand, which adds phenylsilane over a C−N bond in the ring (Figure 1).[27] In a related study, Peters and co-workers showed cooperative activation of diphenylsilane by a tridentate diphosphinoborane-nickel complex, forming a borohydrido−Ni−silyl species in which −SiPh₂H is bound to nickel and the hydride is inserted into the B−Ni bond (Figure 1).[28] The latter cooperative Si−H activation is
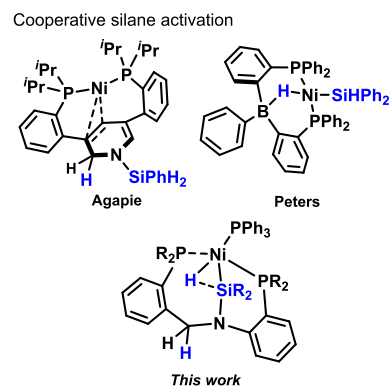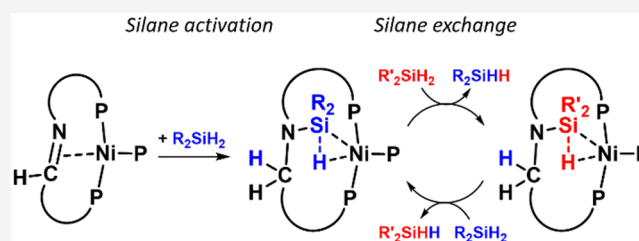


**Figure 1.** Products of cooperative silane activation at Ni complexes.

also thought to be involved in catalytic aldehyde hydrosilylation reactions.[28]

While a large number of nonclassical Si−H adducts bearing hydrocarbon substituents at silicon are known, the coordination chemistry of their N-substituted congeners, hydrosilazanes featuring an N−Si−H linkage, is surprisingly underdeveloped.[3−5,29] In this contribution, we show that reaction of a π-bound imine in the coordination sphere of Ni(0) with dihydrosilanes ($R_2SiH_2$) gives clean access to $\eta^2$-Si−H

complexes of a hydrosilazane motif (N−Si−H) or to the corresponding Ni(II) silyl/hydride depending on the number of additional coordinated ligands (Figure 1, Scheme 1). DFT

**Scheme 1. PCNP Ligands, Synthesized Ni(0) Complexes 2−4, and Products of Silane Activation 2[Si], 2[SiPhMe], 3[Si], and 4[Si]**
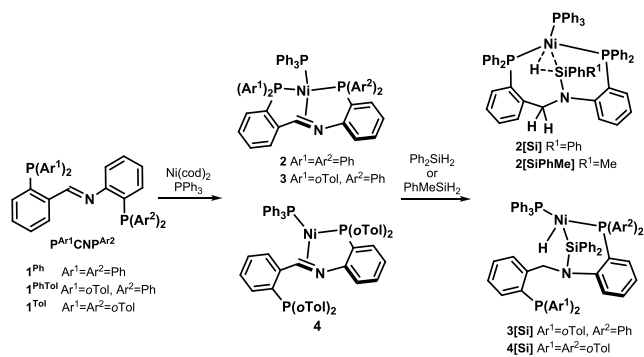


calculations suggest this activation involves a concerted, nickel-mediated ligand-to-ligand hydrogen transfer. Remarkably, the N−Si bond is readily cleaved upon exposure to an external dihydrosilane, resulting in the exchange of the whole silyl group (−SiR$_2$H).

## ◼ RESULTS AND DISCUSSION

**Silane Activation.** In the frame of our studies of phosphine-tethered C=O and C=N π-ligands,[30−34] we recently reported the Ni(0) coordination of a series of ligands consisting of an imine functionality bridged by two o-phenylene linkers with phosphine substituents (PCNP) (Scheme 1).[34] The less bulky ligands afforded tetrahedral Ni(0) complexes Ni(P$^{Ph}$CNP$^{Ph}$)PPh$_3$ (**2**) and Ni-(P$^{Ph}$CNP$^{oTol}$)PPh$_3$ (**3**) with the PCNP ligand bound via both phosphine arms and an η$^2$(C,N)-coordination of the imine moiety. In contrast, the more encumbered ligand P$^{oTol}$CNP$^{oTol}$ resulted in tricoordinate complex **4**, in which the carbon-side phosphine arm is not bound to nickel due to increased bulk on the ligand.

Treating tetracoordinate Ni PCNP complex **2** with diphenylsilane in benzene afforded a single, isolable product **2[Si]**. On the basis of multinuclear NMR data, **2[Si]** was identified as the result of formal hydrosilylation of the C=N bond, in which the N-bound −SiPh$_2$H moiety is coordinated to Ni via a σ-coordination of the Si−H bond (Scheme 1). All three phosphorus atoms are bound to nickel, as shown by three mutually coupled $^{31}$P NMR resonances at 32.8 (dd, $J_{PP}$= 3, 17 Hz), 17.1 (dd, $J_{PP}$= 17, 45 Hz) and 7.8 (dd, $J_{PP}$= 3, 45 Hz) ppm. A single hydridic $^1$H NMR signal is observed at −2.77 ppm with ddd multiplicity ($J_{HP}$ = 36, 23, 19 Hz). In a broadband, phosphorus-decoupled $^1$H NMR spectrum, this signal appears as a singlet peak with $^{29}$Si satellites ($J_{HSi}$ = 109 Hz). This coupling constant falls in the typical range for η$^2$-Si−H complexes (60−150 Hz),[8,35] while full oxidative addition of the Si−H bond to Ni to afford a Si−Ni−H complex typically results in lower coupling constants of 10−20 Hz.[2,6] The $^{29}$Si NMR spectrum contains one signal at −6.5 ppm with a ddd coupling pattern, originating from coupling with the three inequivalent $^{31}$P nuclei ($J_{SiP}$ = 3, 17, 60 Hz).[36]

Next to the hydridic and aromatic signals, the $^1$H NMR spectrum of **2[Si]** displays two doublet signals ($^2J_{HH}$= 15 Hz)

at 4.61 and 5.01 ppm, assigned to the protons of the >CH$_2$ moiety originating from hydride addition to the imine-carbon of **2**. These protons are diastereotopic due to the stereogenic tetrahedral Ni(0) center in **2[Si]**. The two signals exhibit temperature-dependent behavior, with coalescence to one broad feature at 70 °C, indicating facile racemization of the stereogenic Ni center. This likely proceeds via reversible dissociation of one of the phosphine tethers to form a planar Ni(II) silyl/hydride intermediate akin to **3[Si]** and **4[Si]** (see below). Alternative processes involving either transient Si−H dissociation and inversion of the resulting chelate macrocycle or transient Si−N bond cleavage (see below) cannot be excluded.

Analogously, the prochiral silane PhMeSiH$_2$ adds cleanly to **2** in C$_6$D$_6$. The NMR spectra exhibit two similar sets of signals with a ratio of 3:1 (Supporting Information Section 5.1), indicating that addition product **2[SiPhMe]** exists as an equilibrium mixture of two diastereomers. These likely originate from the presence of two stereocenters, one at Si and one at Ni; in other words, the silicon-bound methyl group can be orientated toward the imine−N or the imine−C atom (Figure 2). The $J_{HSi}$ coupling constants of 111 Hz for the
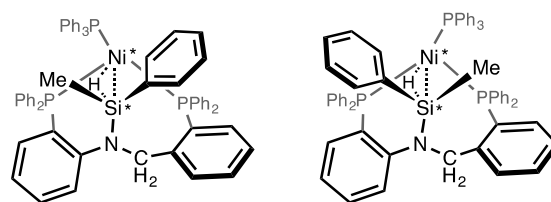


**Figure 2.** Diastereomers of **2[SiPhMe]**.

major and 102 Hz for the minor species are comparable to that in **2[Si]** and confirm analogous η$^2$-coordination of the Si−H bond to Ni. The diastereomers can readily equilibrate via epimerization of the Ni-center. Energy calculation of the equilibrium reaction between the two enantiomers of **2[SiPhMe]** in benzene (SMD model), at the M06L/def2TZVP//6-31g(d,p) level of theory, afforded a small Gibbs free energy difference of ΔG° = 0.4 kcal/mol, in agreement with experimental observations (see Supporting Information Section 6.1 for details).

Gratifyingly, **2[SiPhMe]** afforded single crystals suitable for X-ray crystal structure determination (Figure 3), confirming the structure inferred from NMR data. The structure is centrosymmetric and contains only one diastereomer: the (R,R) and (S,S) pair of enantiomers. The Ni center exhibits a tetrahedral environment, bound to all three phosphorus atoms and the N-bound Si−H moiety. The C7−N1 bond length of 1.481(2) Å is consistent with a single bond resulting from imine hydrosilylation. The N1 atom is nearly planar (sum of angles: 356.5(2)°), consistent with sp$^2$ hybridization originating from hyperconjugation with Si. The Ni−Si distance of 2.3266(5) Å is somewhat longer than those in related tetrahedral η$^2$-Si−H complexes (2.17−2.31 Å),[9,10,12,14] suggesting a relatively weak interaction.

To give insight into the effect of additional steric bulk on the ligands, the reactivities of o-tolyl-substituted complexes **3** and **4** were investigated. Addition of diphenylsilane to **3** or **4** in C$_6$D$_6$ resulted in either case a single species labeled **3[Si]** or **4[Si]**, respectively. NMR analysis of **3[Si]** shows a hydridic signal at −4.35 ppm (dd, $J_{HP}$ = 19, 92 Hz) in $^1$H NMR, and $^{29}$Si
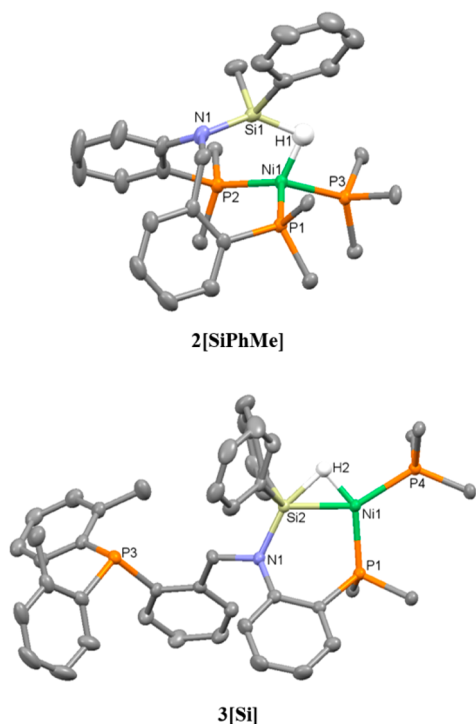
**2[SiPhMe]**



**3[Si]**

**Figure 3.** Molecular structure 2[SiPhMe] (top) and 3[Si] (bottom) in the crystal.[37] For both, a cocrystallized benzene molecule, the phenyl rings of PPh$_2$ and PPh$_3$, and all hydrogen atoms except for the Si–H are omitted for clarity, and ellipsoids are shown at 50% probability.

satellites are visible upon measuring the broadband phosphorus decoupled ^{1}H NMR spectrum at $J_{HSi}$ = 18 Hz. In stark contrast with that observed for 2[Si], the coupling constant is smaller than typical for $\eta^2$-Si–H complexes,[8] and it is likely to be mostly nickel-mediated in a Ni(II) silyl/hydride compound.[2] For 4[Si], a similar signal is observed at −5.53 ppm (dd, $J_{HP}$ = 19, 85 Hz). The observation of the [29]Si satellites corresponding to the hydride signal is complicated due to broadening of all signals, likely due to fluxionality in the structure. Approximate assignment in a broadband phosphorus decoupled ^{1}H NMR leads to a $J_{HSi}$ of ∼14 Hz. ^{31}P NMR spectra of 3[Si] and 4[Si] show in both cases three signals, located at 27, 22, and −32 ppm for 3[Si] and at 26.0, 4.8, and −31.3 ppm for 4[Si], indicating the presence of two nickel-bound and one unbound phosphine moieties. This is consistent with the hydride signals coupling with only two ^{31}P nuclei. The high sensitivity of 3[Si] precluded reliable IR investigation, but 4[Si] exhibits a band at 1862 cm$^{-1}$ that was assigned to the Ni–H vibration. Accordingly, this band disappears in the deuterated analogue formed by addition of Ph$_2$SiD$_2$ to 4, yielding 4[SiD$_2$].[38]

X-ray crystal structure determinations on single crystals of 3[Si] and 4[Si] confirm the interpretation of the spectroscopic data (Figures 3 and S29). In both complexes, a distorted square planar geometry around nickel is observed, bound to a phosphorus atom of the supporting ligand, PPh$_3$, and silyl and hydride ligands originating from the activated Si–H bond. Based on the electron density alone, P and Si atoms could not be distinguished, and the hydride could not be located in the difference electron density maps; the assignment was consequently supported by spectroscopic data. Similar structural motifs have been reported,[1,9,39−41] including reports

by the group of Radius,[2,6] where addition of Ph$_2$MeSiH to Ni($^i$Pr$_2$Im)$_2$ ($^i$Pr$_2$Im = 1,3-di-*iso* propyl-imidazolin-2-ylidene) was shown to result in a square planar hydrido silyl complex, which exhibits a $^2J_{SiH}$ coupling constant of 11 Hz.

To gain additional insight in the bonding situation, geometry optimizations using DFT were performed for 2[Si]−4[Si] at the M06*L*/6-31g(d,p) level of theory (Supporting Information Section 5). In all complexes, the Ni−H distance is similar (2[Si]: 1.55 Å, 3[Si]: 1.51 Å, 4[Si]: 1.51 Å). The Si−H distance, however, increases from 2 to 3 to 4, with calculated values of 1.71 Å for 2[Si] and 1.89 and 1.89 Å for 3[Si] and 4[Si], respectively. Moreover, the angles around nickel, specifically the ∠SiNiH ($\alpha$) and ∠ P$_{PPh_3}$NiH ($\beta$) angles, indicate the displacement of the hydride atom with respect to the Si−H bond (Figure 4). For 2[Si], the difference between
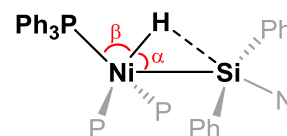


**Figure 4.** Depiction of compared angles in the Ni−HSi complexes. $\alpha$ is ∠SiNiH and $\beta$ is ∠P$_{PPh_3}$NiH.

∠$\alpha$ and ∠$\beta$ is relatively large, i.e., 50 and 86°, respectively. These angles are closer in 3[Si] and 4[Si] due to an increase of ∠SiNiH (a ∠$\alpha$ of 59 and 59° and a ∠$\beta$ of 90 and 90°) for 3[Si] and 4[Si] are obtained. This indicates a larger Ni−H character in the latter two complexes in which the hydride position is closer to bisecting the P−Ni−Si angle.

Collectively, the experimental and computational data support the assignment of structures 3[Si] and 4[Si] as Ni(II) silyl-hydride compounds with a significant secondary interaction between the silicon and hydrogen atoms (SISHA).[42] The activation of the Si−H bond by Ni significantly increases going from 18-electron complex 2[Si] to 16-electron complexes 3[Si] and 4[Si], presumably due to the electronic stabilization of the square-planar d$^8$ configuration. Similar effects in the coordination number of Ni have been documented on the degree of activation of CO$_2$[43] and alkynes.[32]

The mechanism of silane addition to the ligand C═N bond was further investigated by means of DFT calculations. First, an outer-sphere mechanism was found to be unlikely. No transition state for a direct, concerted addition of the Si−H bond to the imine could be identified, presumably because of steric hindrance, and an ionic intermediate arising from direct hydride transfer was found to be prohibitively high in energy (see Supporting Information Section 6.3.2 for detailed information). Experimentally, exposure of 1$^{Ph}$ to Ph$_2$SiH$_2$ did not result in any reaction, confirming that nickel is necessary for hydrosilylation to take place.

Next, dissociation of PPh$_3$ from Ni to form 2[I-1a], a likely first step as a result of the electronic saturation of 2, is associated with $\Delta G°$ = 19.4 kcal/mol (Figure 5). An alternative pathway in which one phosphine arm from the ligand dissociates as observed experimentally in compounds 3[Si] and 4[Si], forming 2[I-1b], is predicted to be thermodynamically more favorable ($\Delta G°$ = 12.1 kcal/mol), but 2[I-1b] was found to be too encumbered for the additional coordination of the hydrosilane (Supporting Information Section 6.2).
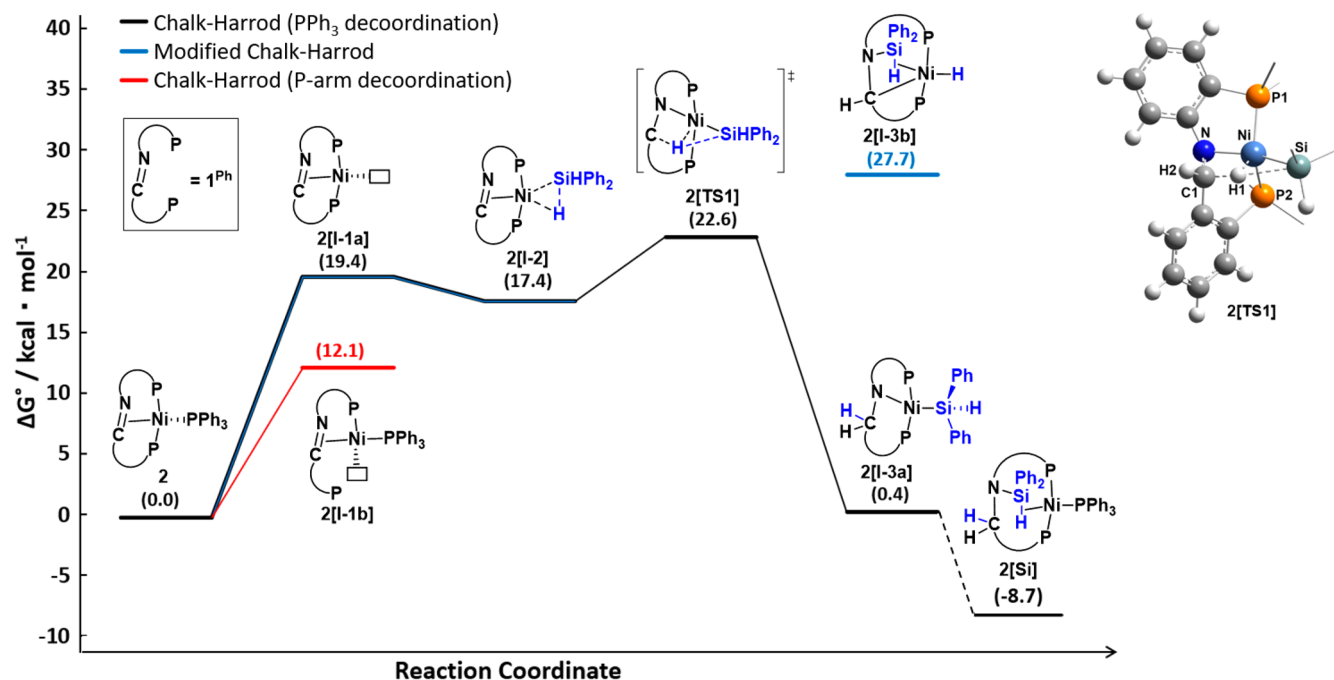
**Figure 5.** Addition of Ph$_2$SiH$_2$ to **2**. Left: Proposed energy surface, calculated at the M06L/def2TZVP//M06L/6-31g(d,p) level of theory with added dispersion correction (GD3) and the SMD benzene model. Values in parentheses are given in kcal/mol. □ represents a free coordination site. Free Ph$_2$SiH$_2$ and PPh$_3$ have been accounted for in the calculations, but were omitted for clarity in the figure. Right: TS between **2[I-2]** and **2[I-3a]**. The hydride atom is located between the Si and C1 atoms and transferred from Si to C1 via Ni-assisted hydrogen shuttling. Selected bond distances (Å): Ni−Si: 2.25, Ni−N: 1.94, Ni−H1:1.53, C1−H1:1.50, C1−H2:1.09, Si−H1:2.26, C1−N: 1.39, Si−N: 4.10. Phenyl substituents on phosphines and silicon are omitted in the figure for clarity.

Addition of the silane to Ni(0) then proceeds via initial $\eta^2$-(Si−H) bonding to form **2[I-2]**,[8] which is exergonic by −2.0 kcal/mol. Subsequently, a hydride transfer occurs from the coordinated Ph$_2$SiH$_2$ to the imine carbon atom of the ligand, resulting in the Ni-amido intermediate **2[I-3a]**. This exergonic step ($\Delta G° = -17.0$ kcal/mol) proceeds through a single concerted transition state **2[TS1]** with a $\Delta G°^{\ddagger}$ of 22.6 kcal/mol (Figure 5, right). The optimized geometry of **2[TS1]** indicates that the hydride is located between the Si and C1 atoms (Si−H1 = 2.26 Å, C1−H1 = 1.50 Å), with an additional short contact with the nickel center to assist hydride shuttling (Ni−H1 = 1.53 Å). The step corresponding to this transition state can be described as a combination of an oxidative addition of the Si−H bond to Ni and $\beta$-insertion of the C=N bond in a single step. Such transition states have been termed ligand-to-ligand hydrogen transfer by Perutz and co-workers and were proposed for C−H bond activation in Ni-catalyzed hydrofluoroarylation of alkynes.[44]

These calculations provide a plausible pathway for silane activation involving participation of both the Ni center and the $\pi$-bound imine ligand. The subsequent silyl transfer to the N atom with the formation of a $\sigma$-coordinating Si−H bond to nickel proved complicated by the accessibility of several ligand binding modes, and a detailed pathway connecting Ni(II) amido/silyl intermediate **2[I-3]** to product **2[Si]** could not be identified (Supporting Information Section 6.2). However, the experimental observation of reversible Si−N bond cleavage at room temperature (see below) in compound **2[Si]** lends credence to the accessibility of such an intermediate.

**Silane Scrambling.** The reactivity of **2[Si]** was probed using labeling experiments. First, reaction of **2** with Ph$_2$SiD$_2$ afforded **2[SiD$_2$]** (Figure 6A), which shows clean incorporation of one deuterium atom at the Si−H (100%) position,
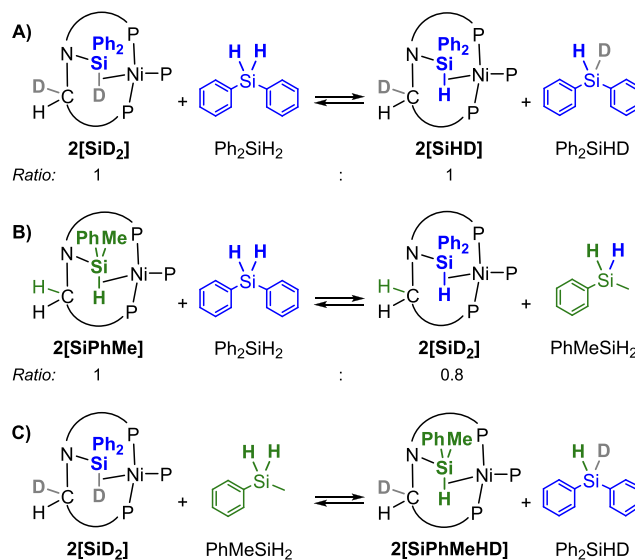


**Figure 6.** Stoichiometric reactivity of **2**. Ligand **1$^{Ph}$** is represented schematically in the figure.

the second one being equally distributed over the two (rapidly exchanging) diastereotopic >CH$_2$ positions.[36] Addition of 1 equiv of Ph$_2$SiH$_2$ to an *in situ* formed sample of **2[SiD$_2$]** resulted in the gradual appearance of the Si−H $^1$H NMR signal at −2.72 ppm. The signal integrates to 0.5 H after 1 h, indicating 50% $^1$H incorporation, i.e., statistical distribution. In contrast, no H incorporation into the backbone >CHD group was observed under the same conditions, ruling out reversible hydrosilylation as a scrambling mechanism.

H/D scrambling at the Si−H(D) position could either go via exchange of the H/D, thus via activation of the Si−H bond by Ni, or via exchange of the full $Ph_2SiH$ fragment via Si−N bond cleavage. This question was addressed by using SiPhMe as chemical label for the silicon fragment. Addition of $Ph_2SiH_2$ to an *in situ* formed sample of **2[SiPhMe]** resulted in an equilibrium mixture of **2[SiPhMe]** and **2[Si]**, with signals of both species present in a **2[SiPhMe]**:**2[Si]** ratio of 1:0.8 (Figure 6B). Performing the opposite reaction, starting from an *in situ* formed sample of **2[Si]** with the addition of $PhMeSiH_2$ results in the same product distribution after 3 h. This demonstrates reversible cleavage of the Si−N bond under the reaction conditions, allowing for scrambling of the silyl fragment.

As both the hydridic position and the silyl fragment can be exchanged, a remaining question is whether these are two distinct processes; in other words, can the hydride position be exchanged independently from the silyl fragment? To address this question, $PhMeSiH_2$ was added to an *in situ* formed sample of **2[SiD₂]** (Figure 6C). The experiment was followed by ^{1}H NMR, observing the deuterium/hydride exchange on the Si−H/Si−D position by ^{1}H NMR, and the exchange of $PhMeSiH/Ph_2SiH$ in the backbone of the Ni-complex by ^{31}P NMR. No large difference in scrambling rates was observed: After a reaction time of 10 min, ^{1}H NMR indicates a ratio of D/H (**2[SiD₂]**/**2[SiPhMe]**) of 6:1, measured by integration of the geminal −CHD signal of **2[SiD₂]** and the ingrowing Si−H of **2[SiPhMe]**. ^{31}P NMR indicates a **2[SiD₂]**/**2[SiPhMe]** ratio of 5:1 after 8 min.[45] The slight difference is likely due to the time of the measurements and error margins in the NMR signal integration, indicating very similar exchange rates for both the Si and H positions. More importantly, the observed hydride signals belong mostly to **2[SiPhMe]** at early stages, whereas the hydride signal of **2[Si]** would be expected if a competitive reaction would exchange only the hydride position. Hence, the two phenomena are best explained by a single process scrambling the entire silyl fragment.

A plausible mechanism for this reaction starts from **2[Si]** and initial dissociation of $PPh_3$ (Figure 7). Oxidative addition
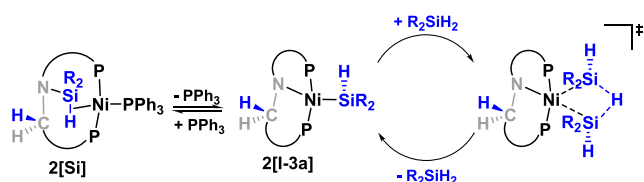


**Figure 7.** Silane scrambling mechanism. Ligand **1$^{Ph}$** is represented schematically in the figure.

of the N−SiHPh₂ bond leads to the Ni(II)-amido complex, to which $PhMeSiH_2$ can coordinate via $\eta^2$-Si−H complexation. Reversible cleavage of an Si−N bond has been observed by Calimano and Tilley in related Ir systems.[29] σ-Bond metathesis is then proposed to take place, in which a hydride is transferred from $PhMeSiH_2$ to SiHPh₂ concomitantly with Si−Ni bond formation. This is related to a phosphine−silyl−Ni(0) system reported by Peters and co-workers, in which both Si−H and H−H were reversibly bound to one Ni center, resulting in ligand exchange via σ-bond metathesis.[15,46] Dissociation of $Ph_2SiH_2$ followed by reductive elimination of the silyl and amido fragments and subsequent association of $PPh_3$ results in observed **2[SiPhMe]**.

## CONCLUSIONS

The use of a C═N bond in the coordination sphere of a metal as hydride acceptor affords an attractive way to generate reactive species from substrates containing element-hydrogen bonds. Here, the reactivity toward silanes of Ni(PCNP) complexes featuring a side-on coordinated imine moiety was studied. Complexes Ni(P$^{Ph}$CNP$^{Ph}$)PPh₃ (**2**), Ni(P$^{Ph}$CNP$^{oTol}$)-PPh₃ (**3**), and Ni(P$^{oTol}$CNP$^{oTol}$)PPh₃ (**4**) cleanly react with diphenylsilane to afford rare hydrosilazane adducts by formal hydrosilylation of the imine-backbone (**2[Si]**−**4[Si]**). DFT calculations suggest a cooperative Ni-mediated ligand-to-ligand hydrogen transfer as a key step. Interestingly, the degree of activation of the remaining Si−H bond in the product was found to strongly depend on the coordination number at Ni. Three-coordinate complex **2[Si]** is best described as an $\eta^2$(Si,H) σ-complex. However, in complexes **3[Si]** and **4[Si]** the Si−H bond is activated to a larger extent, and these are better viewed as a Ni(II) center bearing a silyl and a hydride ligand engaging in a secondary interaction.

Hydrosilazane adduct **2[Si]** additionally reacts with external hydrosilanes via reversible cleavage of the Ni−(Si−H) and Si−N bonds, resulting in net exchange of the $R_2SiH$ fragment. Metal−ligand cooperation phenomena in which an amido ($R_2N$−M) ligand (reversibly) accepts a proton are well-documented, e.g., in Ru- and Fe-catalyzed hydrogenation catalysis. The reported chemistry constitutes a rare example of metal−ligand cooperation involving the facile, reversible transfer of a molecular fragment to an amido ligand. Given the prominence of ligands containing reactive nitrogen functionalities such as imines[47] and amido[48] functionalities in nickel (pre)catalysts for hydrosilylation, the formation of related nickel hydrosilazane species under catalytic conditions should be considered, for example, as a reservoir for reactive Ni−silyl species. Investigations on the catalytic performance of these systems in hydrosilylation reactions are being conducted in our laboratories and will be reported in due course.

## ASSOCIATED CONTENT

### ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00059.

> Experimental procedures for the synthesis of new compounds, spectra (NMR, IR) and X-ray refinement data, additional discussion of NMR data, computational details (PDF)

> Computed molecular Cartesian coordinates (XYZ)

### Accession Codes

CCDC 1960190−1960192 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Author Contributions

All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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