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Si–Cl Bond Activations at Ni(0) to Give Bimetallic Ni(I) $\mu_{1,2}$-Cl–SiR^{1}R^2 Complexes that Undergo Selective Hydrogenolyses to R^{1}R^{2}SiH$_2$ Dihydrosilanes

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ABSTRACT: Chlorosilanes are cheap and abundant raw materials as crucial building blocks in silicon chemistry, yet the metal-mediated activation and functionalization of Si–Cl bonds typically require precious metal sources due to their thermodynamic inertness. Herein, we report the stoichiometric, facile activation and hydrogenolysis of chlorosilanes mediated by a series of low-valent NHC-Ni (NHC = *N*-heterocyclic carbene) complexes. Treatment of a Ni(0) complex (IPr)Ni(η^6-toluene) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) with chlorosilanes (R^{1}R^{2}SiCl$_2$, R^1 = Cl, R^2 = Cl, Me, Ph, or R^1 = R^2 = Me, Et, Ph, 4-MePh) rapidly afforded di-Ni(I) complexes with a bridging silyl ligand ([(IPr)Ni]$_2$(μ-SiR^{1}R^{2}Cl)(μ-Cl), **1**^{R1,R2}) in high yields. Use of a bulkier chlorosilane, Ph$_2$SiCl$_2$, allowed the isolation of the mono-Ni(II) silyl complex (IPr)Ni(SiPh$_2$Cl)Cl (**2**^{Ph}) as an intermediate generated *via* Si–Cl oxidative addition, which underwent comproportionation with (IPr)Ni(η^6-toluene) to form **1**^{Ph,Ph} in nearly quantitative yield. Interestingly, **1**^{R1,R2} were found to react with H$_2$ at room temperature to form mono- or di-hydrosilanes in moderate to high yields, and the product selectivity was found to be highly dependent on the identity of substituents on Si. These results demonstrate a novel example of facile Si–Cl activation and hydrogenolysis mediated by low-valent mono- and di-nuclear NHC-Ni complexes under mild conditions.

INTRODUCTION

Chlorosilanes are annually produced on a very large scale,[1] as desired or side products in the industrial manufacture of silicon compounds.[2-5] Considering the tremendous scale associated with these technologies, chlorosilanes represent potentially abundant resources as chemical intermediates to more valuable silicon-based products such as methyl- and hydro-silanes. In this context, there has been considerable interest in finding strategies to achieve the cleavage of Si–Cl bonds as a key step for catalytic conversions. However, the controlled activation of Si–Cl bond represents a famously challenging goal in metal-silicon chemistry, given the thermodynamic inertness of the Si–Cl bond (bond dissociation energy (BDE) of 113 kcal/mol, compared to ~81 kcal/mol for a C–Cl bond), which originates from the strong electrostatic interaction between the Si and Cl atoms.[6]

The oxidative addition of an Si–Cl bond to a transition metal center has been mainly associated with electron-rich complexes. The first unambiguous example was achieved by a low-valent Ir system reported by Milstein in 1989,[7] with the five-coordinate Ir(I) complex (coe)Ir(PMe$_3$)$_3$Cl (coe = cyclooctene), which readily activates the Si–Cl bond of methyltrichlorosilane *via* oxidative addition to yield a well-defined Ir(III) silyl complex (Figure 1, top left). Further examples of stoichiometric Si–Cl bond activation have since been reported,[8-11] most of which use electron-rich platinum-group metals such as Ru, Rh, and Pt, and the activation of an Si–Cl bond typically occurs *via* a two-electron oxidative addition pathway, yielding monometallic silyl chloride complexes. Notably, the subsequent functionalization of the resulting metal silyl complexes, however, has remained comparatively underexplored.[11] More recently, significant advances in catalytic Si–Cl bond transformations are based on zero-valent nickel precatalysts that cross-couple chlorosilanes with

electrophilic organic substrates.[12-16] In these applications, the Si–Cl bond activation is thought to occur *via* oxidative addition to Ni(I) or Ni(0) intermediates, and the resulting Ni-silyl species are often postulated as key intermediates that mediate C–Si coupling reactions.[14-16] A related chlorosilane activation at nickel proceeds via initial Si–H oxidative addition as reported by Johnson *et al*., with reaction of Ph_2SiHCl and a Ni(0) source, $[(^iPr_3P)_2Ni]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$, to give a dinuclear Ni(I) μ-silyl complex $[(^iPr_3P)Ni(\mu\text{-}SiHPh_2)]_2$ in 19% yield (Figure 1, bottom left).[17]

Very recently, Nakajima *et al.* reported the activation of $SiCl_4$ using an Fe(0) complex supported by a phenanthroline-based ligand, through two steps of single-electron transfer to form an Fe(II)($SiCl_3$)(Cl) complex.[18] Interestingly, Si–H bond formation was observed when the Fe(0) starting material was treated with $SiCl_4$ in the presence of 9,10-dihydroanthracene as a H-atom donor (Figure 1, top right), in a process attributed to the intermediacy of a transient radical-type species generated during the Si–Cl bond activation.

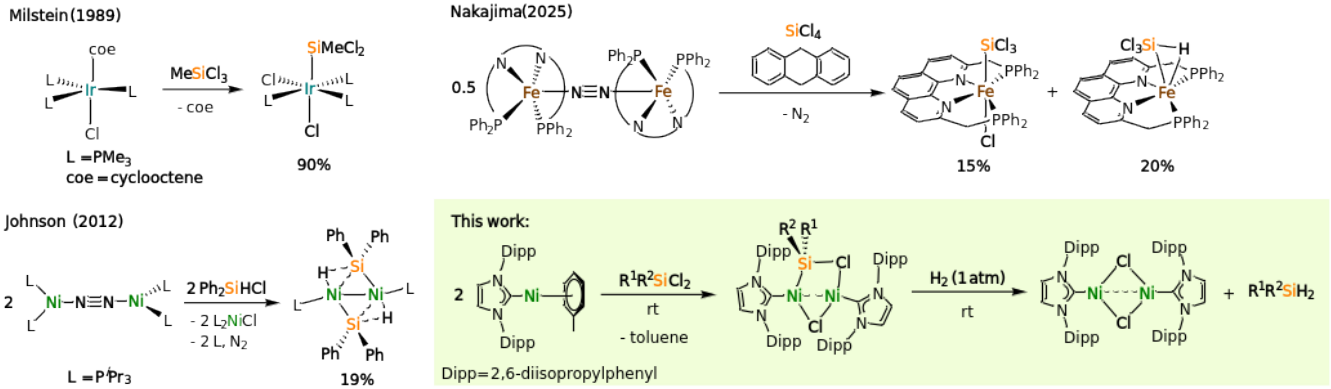


Figure 1. Selected examples of transition metal-mediated Si–Cl bond activation.

Interest in the activation of Si–Cl bonds stems from the possible utility of such processes in allowing the conversion of chlorosilanes to more valuable organo- or hydrosilanes from readily available, cost-efficient reagents. The conversion of chlorosilanes to hydrosilanes using H_2 as the ideal hydrogen source, however, is thermodynamically unfavorable due to the formation of weak Si–H bond (Figure 2).[19-20] Indeed, the reaction of $SiCl_4$ and H_2 only occurs at elevated temperature (>1000 °C) to give $HSiCl_3$ and HCl.[21] The Schneider group first reported the direct hydrogenations of chloromethylsilanes to hydromethyl silanes at room temperature, using a (PNP)RuH_2(CO) catalyst activated by $Na[B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)]_4$.[22] Subsequently, reports have appeared on the hydrogenolysis of Si–Cl bonds using iridium hydride-based catalysts.[23-25] The Cantat group has also developed a metal-free approach to catalytic chlorosilane hydrogenolysis using metal-free systems employing borane-based catalysts.[26-27] Notably, these systems typically require use of a strong base to assist the Si–Cl bond cleavage,[25] and no evidence for a pathway that involves the hydrogenolysis of a metal-silyl intermediate was observed for the metal-catalyzed transformations.

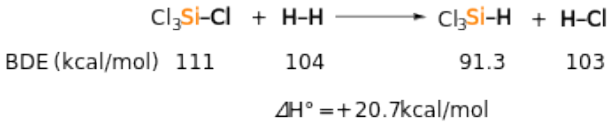


Figure 2. Thermodynamics of reaction between $SiCl_4$ and H_2. All values are given at 298 K.

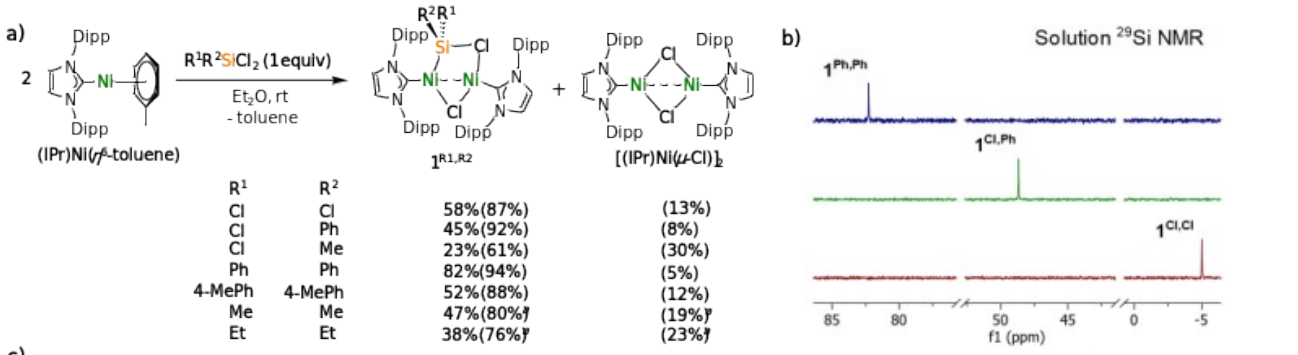
The Tilley laboratory has investigated unusual reaction steps associated with low-coordinate Ni complexes,[28-33] and their generally high reactivity toward small molecules suggested the possibility of chlorosilane activations. This contribution describes studies focused on Si–Cl bond activations by a sterically protected Ni(0) complex supported by an *N*-heterocyclic carbene (NHC) ligand, (IPr)Ni(η^6-toluene) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene, Figure 1, bottom right), which has previously been found to activate inert C–C, C–O and C–N bonds[34-37] and can be readily prepared in large quantities.[38] Reactions of (IPr)Ni(η^6-toluene) with chlorosilanes produce well-defined di-Ni(I), μ-silyl complexes with unusual Ni–Si–Cl–Ni bridging interactions, which form *via* initial Si–Cl oxidative addition at Ni(0) to form a mono-Ni(II) silyl complex, followed by comproportionation with another equivalent of Ni(0). Remarkably, treatment of the di-Ni(I) μ-silyl complexes with H_2 rapidly affords the corresponding dihydrosilanes and a known dimeric Ni(I) μ-Cl complex $[(IPr)Ni(\mu\text{-}Cl)]_2$[39] in excellent yields. These results provide a rare example of the facile hydrogenolysis of Si–Cl bonds under mild conditions, in the selective production of dihydrosilanes with formation of two Si–H bonds.

RESULTS AND DISCUSSION

Activation of the simplest chlorosilane, $SiCl_4$, was initially investigated by treatment of a benzene-d_6 solution of (IPr)Ni(η^6-toluene) with 0.5 equiv of $SiCl_4$ at room temperature, which resulted in a gradual color change from dark reddish brown to green over 1.5 h. A ^{1}H NMR spectroscopic analysis of the reaction mixture indicated formation of $[(IPr)Ni(\mu\text{-}Cl)]_2$ (13%) along with a new diamagnetic product formed in 87% spectroscopic yield (Figure 3, top left). The ^{29}Si NMR spectrum of the reaction mixture revealed the full conversion of $SiCl_4$ and the sole appearance of a resonance at -5.00 ppm (benzene-d_6, 298 K) associated with the new product.

Cooling a Et_2O/*n*-pentane solution of this product at -35 °C afforded dark green crystals suitable for X-ray diffraction analysis, which characterized the complex as possessing two Ni centers with a bridging trichlorosilyl ligand, [(IPr)Ni]$_2$(μ-$SiCl_3$)(μ-Cl) (**1**^{Cl,Cl}, Figure 3, bottom left). The Ni–Ni distance of 2.497(6) Å is longer than the sum of single-bond covalent radii of two nickel atoms (2.20 Å),[40] which is consistent with weak Ni–Ni bonding or antiferromagnetic coupling to give the observed diamagnetism. The Ni–Si distances of 2.105(9) and 2.530(1) Å support the presence of only one Ni–Si bond, consistent with the four-coordinate silicon atom bearing a distorted tetrahedral geometry. Interestingly, the μ-$SiCl_3$ ligand was found to bridge two IPr-Ni moieties in a $\mu_{1,2}$-Si–Cl fashion, an unusual coordination mode with little precedent.[41] The Si–Cl$_\mu$ bond is considerably longer (2.194(1) Å) than those of the two terminal Si–Cl bonds (2.086(1), 2.097(1) Å), apparently as a result of back donation from both Ni atoms into the Si–Cl σ* orbital, which is further supported by the acute Si-Cl$_\mu$-Ni angle (∠Si-Cl1-Ni2 = 69.61(4)°). A similar bond elongation was reported for a diruthenium complex bearing a Ru–Si–Cl–Ru linkage (Si–Cl$_\mu$ = 2.311(2) Å).[41]

The complex (IPr)Ni(η^6-toluene) mediated rapid Si–Cl activations in other chlorosilanes ($R^1R^2SiCl_2$, R^1 = Cl, R^2 = Me, Ph; R^1 = R^2 = Me, Et, Ph, 4-MePh) to afford the corresponding di-Ni(I) μ-silyl complexes [(IPr)Ni]$_2$(μ-SiR^1R^2Cl)(μ-Cl) (**1**^{R1,R2}) in high spectroscopic and moderate isolated yields (Figure 3a). In each case, the product gives rise to a single, sharp ^{29}Si NMR resonance that is associated with each product, which is downfield shifted with respect to that of **1**^{Cl,Cl} (Figure 3b. Selected examples of ^{29}Si NMR shifts: **1**^{Ph,Ph}, 82.27 ppm; **1**^{Cl,Ph}, 48.66 ppm; **1**^{Cl,Cl}, -5.00 ppm; also see Supporting Information). X-ray structural



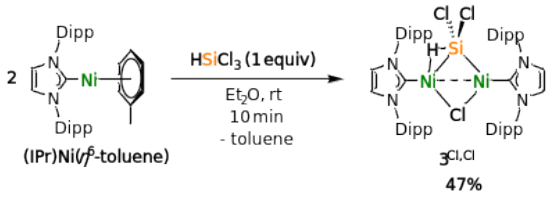
R^1	R^2		
Cl	Cl	58%(87%)	(13%)
Cl	Ph	45%(92%)	(8%)
Cl	Me	23%(61%)	(30%)
Ph	Ph	82%(94%)	(5%)
4-MePh	4-MePh	52%(88%)	(12%)
Me	Me	47%(80%)[a]	(19%)[a]
Et	Et	38%(76%)[a]	(23%)[a]

	1^{Cl,Cl}	**1**^{Cl,Ph}	**1**^{Ph,Ph}
Ni1–Si (Å)	2.105(9)	2.110(8)	2.142(6)
Si–Cl1 (Å)	**2.194(1)**	**2.245(1)**	**2.295(7)**
Ni2–Cl1 (Å)	2.239(1)	2.288(7)	2.216(6)
Ni1–Ni2 (Å)	2.497(6)	2.466(7)	2.488(7)
Ni1–C1 (Å)	1.889(3)	1.883(2)	1.873(1)
Ni2–C2 (Å)	1.950(4)	1.928(2)	1.951(1)

Figure 3. a): Si–Cl activation of chlorosilanes by an IPr-Ni(0) complex to form di-Ni(I) μ-silyl complexes. Both isolated and spectroscopic yields (in brackets) are shown. b): Overlay of ^{29}Si NMR spectra (119 MHz, benzene-d_6, 298 K) of **1**^{Cl,Cl} (bottom), **1**^{Cl,Ph} (middle), and **1**^{Ph,Ph} (top). c): Crystal structures of **1**^{Cl,Cl} (left), **1**^{Cl,Ph} (middle), and **1**^{Ph,Ph} (right) with thermal ellipsoids at 50% probability level and comparison of selected bond length. Hydrogen atoms are omitted for clarity. All spectroscopic yields were obtained from NMR experiments conducted in benzene-d_6 with an internal standard. *a*: Spectroscopic yield obtained from reactions in cyclohexane-d_{12} due to slow reaction rate in benzene-d_6.

analyses confirm the dimeric structures of complexes **1**^{R1,R2} with a bridging chloride ligand and a $\mu_{1,2}$-Si–Cl bridge (Figure 3c). Most notably, change of the substituents on Si from Cl to Ph results in considerable elongation of the Si–

Cl_μ bond from 2.194(4) Å (**1**^{Cl,Cl}) to 2.245(1) Å (**1**^{Cl,Ph}) and 2.295(7) Å (**1**^{Ph,Ph}), accompanied by a slight increase in the Ni–Si distance and relatively minor changes in Ni–Cl, Ni–C and Ni–Ni distances (Figure 2, bottom). The further elongation of the Si–Cl_μ bond likely results from electronic substituent effects on the orbitals of silicon. Formation of a small amount of [(IPr)Ni(μ-Cl)]$_2$ was observed in all cases, which likely results from the competing side reactions of the reaction intermediates involved (see below).



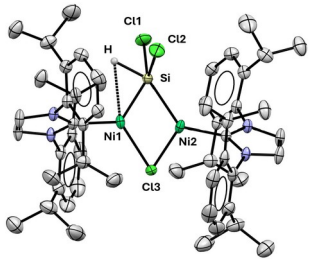
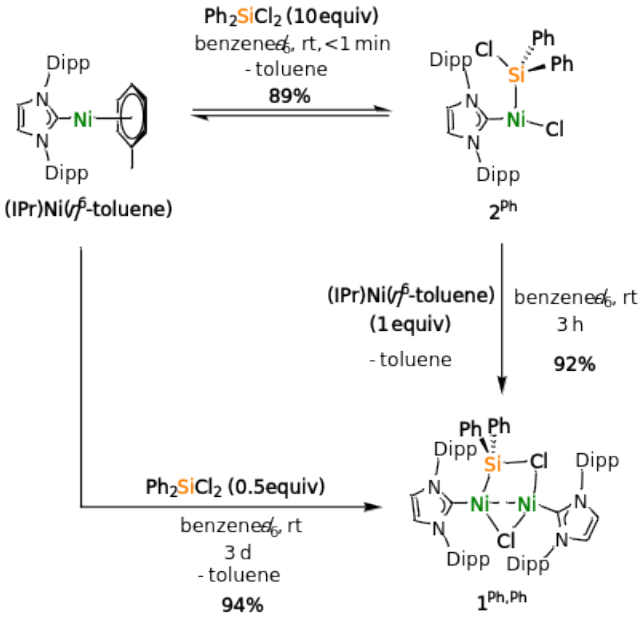


Figure 4. Top: Formation of a di-Ni(I) μ-silyl complex (**3**^{Cl,Cl}) bearing a μ-η^2(Si–H) silyl ligand from Si–Cl bond activation of $HSiCl_3$ by (IPr)Ni(η^6-toluene). Bottom: Crystal structure of **3**^{Cl,Cl}. Hydrogen atoms except for the Si–H are omitted for clarity. Selected bond length and angles: Ni1–Si = 2.0354(9) Å, Ni2–Si = 2.3233(9) Å, Ni–Cl3 = 2.282(1) Å, Ni2–Cl3 = 2.070(1) Å, Si–H = 1.50(4) Å, Ni1–H = 2.44(4) Å, ∠Ni1-Si-Ni2 = 65.97(4)°.

Interestingly, the reaction of (IPr)Ni(η^6-toluene) with $HSiCl_3$ under the same conditions resulted in selective Si–Cl bond cleavage to afford [(IPr)Ni]$_2$(μ-$SiHCl_2$)(μ-Cl) (**3**^{Cl,Cl}) as the major product (Figure 4). By X-ray crystallography, the bridging silyl ligand is bound in an η^2(Si–H), μ-fashion with Ni–H–Si 3-center

Scheme 1. Isolation of a mono-Ni(II) silyl complex (**2**^{Ph}) as an intermediate to di-Ni(I) μ-silyl complex (**1**^{Ph,Ph}).



bonding. Notably, there is no $\mu_{1,2}$-Si–Cl interaction in this case. The formation of **1**^{Cl,Cl} as a minor side product was observed, likely *via* competing Si–H activation of $HSiCl_3$, followed by H/Cl exchange between Ni centers.

The formation of a di-Ni(I) μ-silyl complex from a mono-Ni(0) complex suggests the operation of an unusual reaction pathway. While no intermediates were observed in the reactions of (IPr)Ni(η^6-toluene) with either stoichiometric or excess amounts of $RSiCl_3$ (R = Cl, Me, Ph), reaction with diphenyldichlorosilane (Ph_2SiCl_2) allowed observation and isolation of a presumed key intermediate. Treatment of a benzene-d_6 solution of (IPr)Ni(η^6-toluene) with 0.5 equiv of Ph_2SiCl_2 resulted in gradual formation of the di-Ni(I) μ-silyl complex [(IPr)Ni]$_2$(μ-$SiPh_2Cl$)(μ-Cl) (**1**^{Ph,Ph}) over 3 d in 94% spectroscopic yield (Scheme 1). Inspection of the reaction progress revealed the initial formation of a diamagnetic intermediate, which further converted to **1**^{Ph,Ph} over time. The ^{1}H NMR integration indicated that this intermediate contained one Ph_2SiCl_2 equivalent per IPr ligand. When a large excess of Ph_2SiCl_2 was used, rapid conversion of (IPr)Ni(η^6-toluene) to this intermediate was achieved in 89% spectroscopic yield along with only a trace amount of **1**^{Ph,Ph}. Cooling a saturated Et_2O solution of this intermediate at -35 °C afforded large purple blocks suitable for X-ray diffraction analysis, which revealed its identity as the mono-Ni(II) chlorodiphenylsilyl complex ((IPr)Ni($SiPh_2Cl$)Cl, **2**^{Ph}, Figure 5). A crystallographic study of **2**^{Ph} revealed a three-coordinate, "T-shaped" Ni(II) center, with the silyl group in a *cis* position relative to IPr and Cl due to its strong *trans* influence.

In benzene-d_6, **2**^{Ph} thermally decomposed over 2 d to a mixture of products including **1**^{Ph,Ph}, [(IPr)Ni(μ-Cl)]$_2$, (IPr)Ni(η^6-C_6D_6) and free Ph_2SiCl_2 (Figure S40), indicating reversibility of the Si–Cl activation. Finally, treatment of a benzene-d_6 solution of (IPr)Ni(η^6-toluene) with a stoichiometric amount of **2**^{Ph} smoothly afforded **1**^{Ph,Ph} in 92% spectroscopic yield over 3 h (Scheme 1). These results suggest a two-step reaction pathway for the formation of **1**^{Ph,Ph}, in which the chlorosilane oxidatively adds to an equimolar amount of (IPr)Ni(0) to form the mono-Ni(II) silyl complex **2**^{Ph}, which then combines with another equivalent of (IPr)Ni(0) to form the di-Ni(I) μ-silyl complex **1**^{Ph,Ph}. In reactions with $SiCl_4$ and $HSiCl_3$, the latter step may be fast enough to prevent observation of the corresponding mono-Ni(II) silyl intermediate, possibly due to less steric demand from the silyl group.

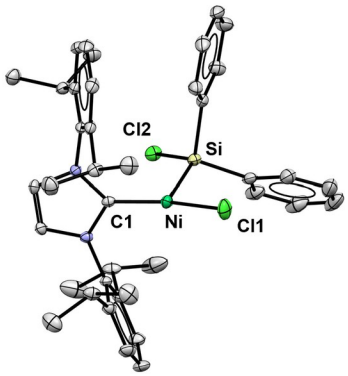


Figure 5. Crystal structure of **2**^{Ph} with thermal ellipsoids at 50% probability level. Hydrogen atoms and co-crystallized solvent molecule are omitted for clarity. Selected bond length and angles: Ni–Si = 2.176(6) Å, Ni–Cl1 = 2.099(6) Å, Ni–C1 = 1.852(2) Å, Si–Cl2 = 2.103(8) Å, ∠C1-Ni-Cl1 = 164.07(7)°, ∠C1-Ni-Si = 99.52(3)°, ∠Cl1-Ni-Si = 95.97(6)°.

Computational analysis afforded further information on the reaction mechanism, with the toluene complex (IPr)Ni(η^6-toluene) simplified to (IPr)Ni(η^6-benzene). For the reaction of $SiCl_4$ with (IPr)Ni(η^6-benzene), two distinct pathways were located, each with one rate-limiting transition state (Figure 6). The full potential energy surfaces for both parts contain many minor features not essential to the kinetics or outcome of the reaction; only selectivity and/or rate-determining features shown in Figure 6. Both paths connect (IPr)Ni(η^6-benzene) with **1**^{Cl,Cl} and have rate-limiting transition states of roughly equal barrier height that correspond to the initial docking of $SiCl_4$ to Ni, changing the coordination of benzene from η^6 to η^2. Of the two available paths, proceeding through **TSA1** gives the lower effective free energy barrier of $\Delta G^{\ddagger}$ = 22.3 kcal/mol. As per the Eyring equation ($k = k_B*T/h \exp(-G^{\ddagger}/RT)$), this value is in good qualitative agreement with experimental observations tracking the gradual conversion of (IPr)Ni(η^6-toluene) to **1**^{Cl,Cl} at room temperature. **TSB1** is found to be a structurally similar transition state to **TSA1** with a slightly higher barrier (24.1 kcal/mol). While Path A results directly in the most stable Si-Cl activation product **2**^{Cl}, Path B proceeds through an intermediate complex (**B1**) in which both Cl atoms bind equally, which then rearranges to the thermodynamically stable **2**^{Cl}. No equivalent to **2**^{Cl} appears to exist for

(IPr)Ni($SiCl_3$)Cl in which the $SiCl_3$ moiety is coordinated *trans* to the carbene.

Formation of the antiferromagnetically coupled Ni-Ni species $\mathbf{1}^{Cl,Cl}$ from $\mathbf{2}^{Cl}$ and (IPr)Ni(η^6-benzene) is strongly exergonic (-34.3 kcal/mol). Notably, assignment of $\mathbf{1}^{Cl,Cl}$ as a closed-shell singlet Ni(0)–Ni(II) species instead raised the energy by 9.1 kcal/mol. Additionally, Loewdin spin orbital population analysis of $\mathbf{1}^{Cl,Cl}$ reveals a spin density of +0.764 on the Ni bonded to Si and –0.801 on the other Ni (Figure S59). These data together further support the antiferromagnetic coupling nature of $\mathbf{1}^{Cl,Cl}$. The process is formally a comproportionation in which $\mathbf{2}^{Cl}$ undergoes a one-electron reduction to Ni(I) and (IPr)Ni(η^6-benzene) is oxidized to Ni(I).

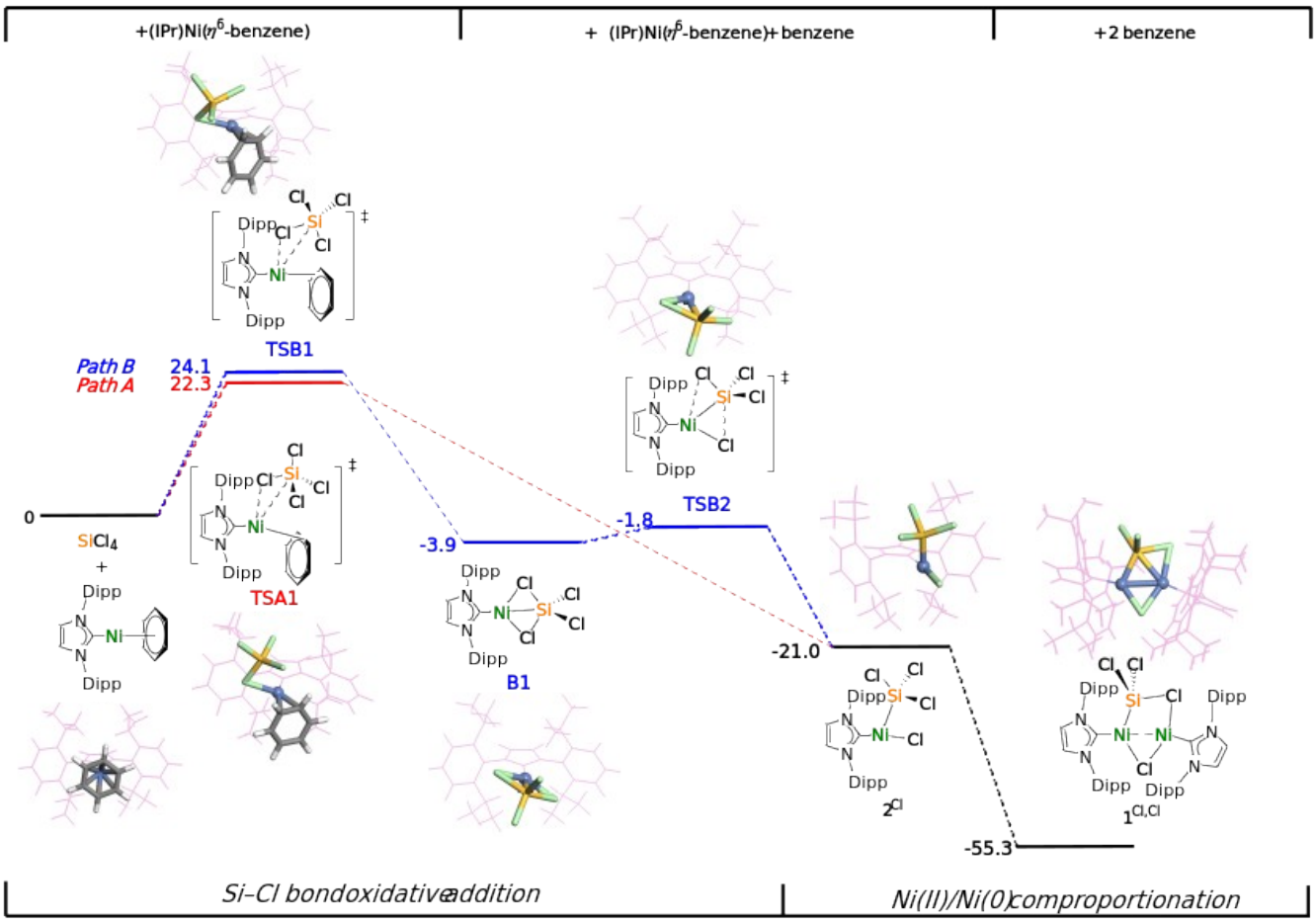
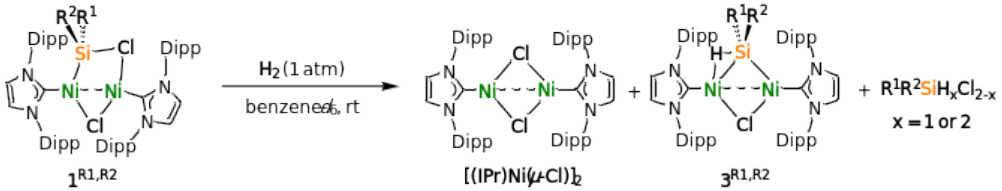


Figure 6. Reaction profile of the computed relative Gibbs free energies (kcal/mol) for the reaction of (IPr)Ni(η^6-benzene) with $SiCl_4$ to give $\mathbf{1}^{Cl,Cl}$. Two distinct pathways to the intermediate $\mathbf{2}^{Cl}$ are shown in red (Path A) and blue (Path B).

With Si–Cl activation products in hand, their reactions with H_2 were investigated. Hydrogenolysis of Si–Cl bonds is of particular interest as an appealing approach for production of more valuable hydrosilanes using H_2 as a cheap and clean H atom source. It was found that treatment of a benzene-d_6 solution of $\mathbf{1}^{R1,R2}$ with 1 atm of H_2 resulted in rapid conversion under mild conditions (Figure 7, Figure S41–47), and ^{1}H NMR spectroscopic analysis revealed different reaction outcomes depending on the identity of the substituents on Si. Remarkably, reactions of $\mathbf{1}^{R,R}$ (R = Ph, 4-MePh, Et, Entries 1-3) with H_2 led to rapid conversion of starting material with formation of [(IPr)Ni(μ-Cl)]$_2$ and R_2SiH_2 in high spectroscopic yields (Figure S41-43). Substitution of D_2 for H_2 in the reaction with $\mathbf{1}^{Ph,Ph}$ furnished Ph_2SiD_2 with 97% deuterium incorporation (Figure S56), clearly assigning the origin of the formed silicon hydrides as from H_2. Minimal formation of R_2SiHCl was observed upon full conversion of $\mathbf{1}^{R,R}$, although a slow transformation of R_2SiH_2 to R_2SiHCl was observed as a subsequent, side reaction over 3-4 d. This is attributed to a further H/Cl exchange between [(IPr)Ni(μ-Cl)]$_2$ and R_2SiH_2, which was confirmed *via* independent reaction studies (see below). Reaction of $\mathbf{1}^{Me,Me}$ with H_2 also resulted in rapid conversion to [(IPr)Ni(μ-Cl)]$_2$ and Me_2SiH_2 as major products, yet subsequent formation of a considerable amount of $\mathbf{3}^{Me,Me}$ and Me_2SiHCl (19% and 15%, respectively, Entry 4, Figure S44) was observed upon complete conversion of starting material, and these products continued to accumulate over time likely due to a faster subsequent H/Cl exchange reaction.

Interestingly, although hydrogenolysis of $\mathbf{1}^{R,R}$ (R = Ph, 4-MePh, Me, Et) resulted in the selective conversion to dihydrosilanes, for other derivatives bearing chloro

substituents on Si, product mixtures containing mostly *mono*hydrosilicon species were obtained. Reactions of $\mathbf{1}^{Cl,R2}$ (R^2 = Cl, Ph, Me) with H_2 generated a mixture of products containing [(IPr)Ni]$_2$(μ-SiClR^{2}H)(μ-Cl) ($\mathbf{3}^{Cl,R2}$), [(IPr)Ni(μ-Cl)]$_2$ and the corresponding monohydrosilane, R^2SiHCl_2, in moderate yields (Figure 7, Entry 5-7, Figure S45-47). Formation of $HSiCl_3$ was initially observed in the reaction of $\mathbf{1}^{Cl,Cl}$ with H_2, but $HSiCl_3$ further reacted with [(IPr)Ni(μ-Cl)]$_2$ to give an unidentified product, thereby preventing accurate yield determination. The ostensible chlorodihydrosilane product ClR^2SiH_2 (R^2 = Cl, Me, Ph) was not observed as a final product in any of the reactions of $\mathbf{1}^{Cl,R2}$ with H_2. Given the rapid formation of dihydrosilanes and the subsequent conversion to monohydrosilanes observed in Entries 1-4, it is hypothesized that the hydrogenolyses in Entries 5-7 result from analogous reaction pathways (Figure 8) in which $\mathbf{1}^{Cl,R2}$ initially react with H_2 to form the corresponding dihydrosilane R^2ClSiH_2, followed by a relatively rapid secondary reaction with the byproduct [(IPr)Ni(μ-Cl)]$_2$ involving chloride-transfer to silicon.



Entry	R^1,R^2	Time (min)	[(IPr)Ni(μ-Cl)]$_2$ (%)	$\mathbf{3}^{R1,R2}$ (%)	$R^1R^2SiH_2$ (%)	R^1R^2SiHCl (%)
1	Ph,Ph	5	84	0	74	0
2	4-MePh,4-MePh	5	97	0	93	0
3	Et,Et	5	91	8	68	7
4	Me,Me	5	74	19	38	15
5	Cl,Ph	240	34	43	0	30
6	Cl,Me	240	65	34	0	31
7	Cl,Cl	240	15	61	0	7[a]

Figure 7. Hydrosilane formation via hydrogenolysis of di-Ni(I) μ-silyl complexes ($\mathbf{1}^{R1,R2}$). All yields are spectroscopic and were determined by the use of an internal standard. *a*: Maximum yield as an intermediate.

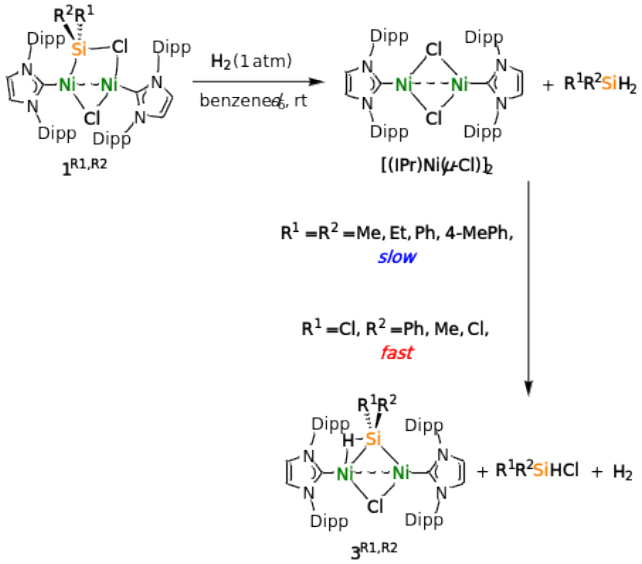
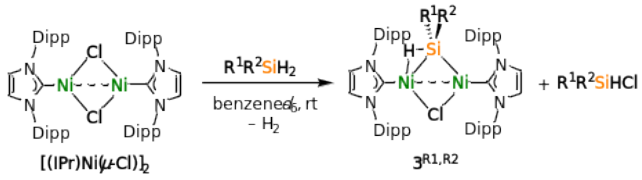


Figure 8. Proposed kinetic formation of dihydrosilanes followed by a secondary reaction to form monohydrosilanes.

To test this hypothesis, the reaction of [(IPr)Ni(μ-Cl)]$_2$ with dihydrosilanes was investigated (Figure 9). A benzene-d_6 solution of [(IPr)Ni(μ-Cl)]$_2$ was treated with 1 equiv of H_2SiCl_2 (used as stock solution in *n*-heptane), to give an instant color change from pale yellow to dark green. Indeed, NMR spectroscopic analysis revealed *ca.* 73% conversion of [(IPr)Ni(μ-Cl)]$_2$ and formation of a product mixture containing $\mathbf{3}^{Cl,Cl}$ and $HSiCl_3$ (Figure 9, Figure S49 Entry 1), consistent with the observed product mixture from the reaction of $\mathbf{1}^{Cl,Cl}$ with H_2. Use of 2 equiv of H_2SiCl_2 resulted in complete conversion of [(IPr)Ni(μ-Cl)]$_2$ to $\mathbf{3}^{Cl,Cl}$ in nearly doubled yield (Figure 9, Figure S50, Entry 2), suggesting a 1:2 reaction stoichiometry between [(IPr)Ni(μ-Cl)]$_2$ and H_2SiCl_2. Formation of $HSiCl_3$ was not observed in this case, likely due to a faster side reaction with Ni species under this condition. In contrast to the instantaneous reaction with H_2SiCl_2, treatment of a benzene-d_6 solution of [(IPr)Ni(μ-Cl)]$_2$ with Et_2SiH_2 led to a slow color change to green over 4 d, ^{1}H NMR spectroscopic analysis indicates the major conversion of both reactants to $\mathbf{3}^{Et,Et}$ and Et_2SiHCl in high yields (Figure 9, Figure S51, Entry 3, also see Supporting Information for isotopic labelling experiment). Notably, the formation of H_2 was observed in all experiments, suggesting that silane dehydrocoupling is a likely side reaction.



Entry	R^1,R^2	Silane Equiv	Time	Conv. (%)	$3^{R1,R2}$ (%)	R^1R^2SiHCl (%)
1	Cl,Cl	1	<1 min	73	39	5
2	Cl,Cl	2	<1 min	100	75	N.O.
3	Et,Et	2	4 d	86	79	74

Figure 9. Investigation of the secondary reaction between $[(IPr)Ni(\mu\text{-}Cl)]_2$ and dihydrosilanes. Formation of H_2 was observed by ^1H NMR spectroscopy in all entries.

These findings imply that $[(IPr)Ni(\mu\text{-}Cl)]_2$ and the corresponding dihydrosilane are the primary kinetic products from hydrogenolyses of all $\mathbf{1}^{R1,R2}$ complexes. While the secondary reaction of $[(IPr)Ni(\mu\text{-}Cl)]_2$ with non-chlorinated dihydrosilanes are relatively slow, such reactions with a chlorodihydrosilane ClR^2SiH_2 appear to occur rapidly (Figure 8). The faster rates for the latter reactions account for the observed depletion of chlorodihydrosilane products as the reactions proceed, presumably by a faster H/Cl exchange between the nickel and silicon centers. Clearly, chlorinated silanes are more reactive toward $[(IPr)Ni(\mu\text{-}Cl)]_2$ and this has a significant effect on the observed product distribution.

These hydrogenolyses represent unusual reactions of a metal silyl complex that selectively form two Si–H bonds of a dihydrosilane. While metal silyl complexes are known to react with H_2 to form the corresponding monohydrosilane and a concomitant metal hydride complex,[42] reactions with H_2 to form two Si–H bonds have typically been observed for silylene compounds or metal silylene complexes. Examples include two acyclic silylene compounds Si[N(SiMe$_3$)Dipp]L (L = Si(SiMe$_3$)$_3$, B(NDippCH)$_2$) reported by Aldridge *et al.*,[43-44] which rapidly reacted with H_2 to generate the corresponding dihydrosilanes H_2Si[N(SiMe$_3$)Dipp]L under mild conditions, and a Ni^0-stabilized silyliumylidene ion reported by Kato *et al.*,[45] which underwent hydrogenolysis under 5 bar of H_2 to form a dihydrosilylium ion. Interestingly, although both reaction types produce two Si–H bonds, they appear to proceed by different mechanisms. In the former case, DFT calculations and experimental studies suggest a concerted, bimolecular H_2 addition to a free silylene, while in the latter case DFT supports a pathway involving H_2 activation at Ni to initially generate a nickel dihydride which then undergoes stepwise 1,2-hydride migrations to form the Si–H bonds.

The facile hydrogenolysis of $\mathbf{1}^{R1,R2}$ complexes to dihydrosilanes implies silylene-type reactivity of the bridging chlorosilyl ligands and may point the way to other interesting functionalizations at Si. Indeed, heating a benzene-d_6 solution of $\mathbf{1}^{Ph,Ph}$ in the presence of 10 equiv of the trapping agent 2,3-dimethylbutadiene (DMB)[46] at 60 °C for 3 d led to the formation of the corresponding silacyclopent-3-ene product in 53% spectroscopic yield (Figure S53–54), indicating silylene transfer. However, an attempt to trap a silylene intermediate during the hydrogenolysis, by treatment of a DMB solution of $\mathbf{1}^{Ph,Ph}$ with H_2 at room temperature, resulted in rapid conversion to Ph_2SiH_2 as the major Si-containing product, with no formation of silacyclopent-3-ene detected by ^1H and ^{29}Si NMR spectroscopy (Figure S55). This suggests that a pathway involving direct addition of H_2 to a silylene intermediate is unlikely.

Given the latter result, mechanisms involving activation of H_2 at the nickel center(s) are currently favored. While a well-defined intermediate resulting from direct H_2 activation has not been observed experimentally, or successfully optimized by DFT, it is reasonable to assume that this would lead to a fleeting oxidative addition product that would rapidly undergo H migrations to silicon and elimination of the observed dihydrosilane kinetic product. Another possible mechanistic scenario would involve reductive elimination of HCl, to form $\mathbf{3}^{R1,R2}$, which might then rapidly combine to give the dihydrosilane and $[(IPr)Ni(\mu\text{-}Cl)]_2$. To test the latter hypothesis, the hydrogenolysis of $\mathbf{1}^{Ph,Ph}$ was carried out in the presence of NEt_3, which afforded Ph_2SiH_2 and $[(IPr)Ni(\mu\text{-}Cl)]_2$ in comparable yields and reaction rate (< 3 min) to that of the reaction occurring in the absence of base, with no $[HNEt_3]Cl$ formation observed (Figure S52). This result suggests that HCl is not formed as a kinetic product in hydrogenolysis and this mechanism can be ruled out.

CONCLUSION

In conclusion, a low-valent NHC-Ni system was found to mediate the facile activation and hydrogenolysis of a broad range of chlorosilane substrates, *via* a class of novel dinuclear Ni(I) μ-silyl complexes bearing a $\mu_{1,2}$-Si–Cl moiety. The Si–Cl activation initially occurs by a classical two-electron oxidative addition to give a Ni(II) silyl chloride intermediate. Critically, this species is rapidly trapped by another equivalent of the Ni(0) starting material to produce an unusual, bimetallic Ni(I) complex with a $\mu_{1,2}$-Si–Cl bridge. This bonding mode involving the interaction of two Ni centers with an Si–Cl bond appears to significantly weaken the Si–Cl bond and permit its cleavage by hydrogenolysis, enabling selective formation of dihydrosilanes *via* an unusual double Si–H bond formation pathway. Future efforts will further explore the use of this bond activation in promoting stochiometric and catalytic silicon-element bond formations.

ASSOCIATED CONTENT

Supporting Information.
The Supporting Information is available free of charge at XX.

Experimental data, including synthesis and characterization of nickel complexes and NMR spectra (PDF)

Optimized structures and transition states used in DFT calculations (XYZ)

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Notes

T.L., P.M., D.E.K and T.D.T. are inventors on a patent application describing a method of preparing hydrosilanes filed by the Dow Chemical Company and University of California, Berkeley. The authors declare no other competing interests.

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