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Carbene Complexes

Synthesis of Mixed Silylene–Carbene Chelate Ligands from N-Heterocyclic Silylcarbenes Mediated by Nickel**

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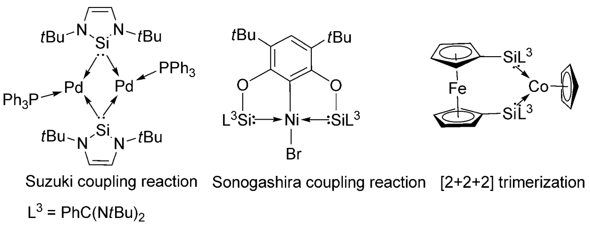
Abstract: *The Ni^{II}-mediated tautomerization of the N-heterocyclic hydrosilylcarbene $L^2Si(H)(CH_2)NHC$ **1**, where $L^2 = CH(C{=}CH_2)(CMe)(NAr)_2$, $Ar = 2,6\text{-}iPr_2C_6H_3$; NHC = 3,4,5-trimethylimidazol-2-yliden-6-yl, leads to the first N-heterocyclic silylene (NHSi)–carbene (NHC) chelate ligand in the dibromo nickel(II) complex $[L^1Si{:}(CH_2)(NHC)NiBr_2]$ **2** ($L^1 = CH(MeC{=}NAr)_2$). Reduction of **2** with KC_8 in the presence of PMe_3 as an auxiliary ligand afforded, depending on the reaction time, the N-heterocyclic silyl–NHC bromo Ni^{II} complex $[L^2Si(CH_2)NHCNiBr(PMe_3)]$ **3** and the unique Ni^0 complex $[\eta^2(Si\text{-}H)\{L^2Si(H)(CH_2)NHC\}Ni(PMe_3)_2]$ **4** featuring an agostic $Si{-}H{\rightarrow}Ni$ bonding interaction. When 1,2-bis(dimethylphosphino)ethane (DMPE) was employed as an exogenous ligand, the first NHSi–NHC chelate-ligand-stabilized Ni^0 complex $[L^1Si{:}(CH_2)NHCNi(dmpe)]$ **5** could be isolated. Moreover, the dicarbonyl Ni^0 complex **6**, $[L^1Si{:}(CH_2)NHCNi(CO)_2]$, is easily accessible by the reduction of **2** with $K(BHEt_3)$ under a CO atmosphere. The complexes were spectroscopically and structurally characterized. Furthermore, complex **2** can serve as an efficient precatalyst for Kumada–Corriu-type cross-coupling reactions.*

Silylenes are emerging as a novel class of versatile steering ligands in the coordination chemistry of the transition metals (TMs), and their complexes have demonstrated remarkable features in small-molecule activation and as precatalysts for various types of organic transformations.[1] For instance, several N-heterocyclic silylene (NHSi) TM complexes have shown to be active precatalysts for C–C bond formations,[2] [2+2+2] cyclotrimerizations,[3] borylations of arenes,[4] ketone hydrosilylations,[5] and organic amide reductions (Scheme 1).[6] These investigations demonstrate that NHSis are not simply spectator ligands, but can also tune the electronic properties of the TM centers and ultimately change the reactivity and selectivity of the emerging TM complexes.[4]



Scheme 1. Selected NHSi–transition-metal complexes that can serve as precatalysts for organic transformations.

N-Heterocyclic carbenes (NHCs) have been one of the most widely utilized supporting ligands in TM chemistry in the last decades.[7] These complexes exhibit numerous superior activities in comparison to phosphine complexes owing to the stronger σ-donor ability of NHC ligands.[8] According to previous studies, both NHCs and NHSis can drastically exceed the σ-donor ability of phosphines and feature a strong *trans* effect. Combining these two ligand types in one chelate molecule could enable new coordination features at TMs. Moreover, the presence of both strong σ-donating moieties might facilitate the coordination and dissociation of other ligands, thereby improving the reactivity or catalytic performance of respective TM complexes. Until now, no such mixed silylene–carbene ligand system or a respective TM complex has been reported. The difficulty to synthesize a mixed NHSi–NHC chelate ligand is most likely due to the reactive nature of NHSi groups, which can react with NHCs via $C{:}{\rightarrow}Si^{II}$ coordination or insertion of the Si^{II} atom of the NHSi into a C–H bond of the NHC, precluding the formation of a NHSi–NHC chelate ligand.[9]

In 2010, we reported the silicon(II)-based (metal-free) sp^3 C–H activation of the 1,3,4,5-tetramethylimidazol-2-ylidene by the zwitterionic NHSi $L^2Si{:}$,[10] affording the N-heterocyclic hydrosilylcarbene **1**, $L^2Si(H)(CH_2)NHC$ ($L^2 = CH(C{=}CH_2)(CMe)(NAr)_2$, $Ar = 2,6\text{-}iPr_2C_6H_3$; NHC = 3,4,5-trimethylimidazol-2-yliden-6-yl).[11] Herein we describe the unexpectedly facile formation of the first mixed NHSi–NHC chelate complex $[L^1Si{:}(CH_2)(NHC)NiBr_2]$ **2** ($L^1 = CH(MeC{=}NAr)_2$) through the hydrogen-atom migration (tautomerization) from the silicon atom to the exocyclic methylene group in **1** mediated by $NiBr_2$. Remarkably, the reduction of **2** with KC_8 in the presence of PMe_3 does not lead to the expected NHSi–NHC $(Me_3P)_2Ni^0$ complex but to the silyl-NHC bromo Ni^{II} complex **3** and the hydrosilyl–NHC(Ni^0) complex **4** with an agostic $Si{-}H{\rightarrow}Ni$ bonding interaction, respectively (Scheme 2). However, the analogous reduction of **2** in the presence of 1,2-bis(dimethylphosphino)ethane (DMPE) furnishes the first mixed NHSi–NHC(DMPE)Ni^0 complex **5**

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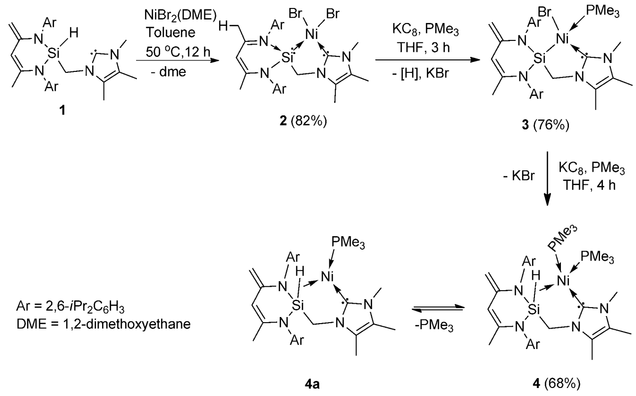
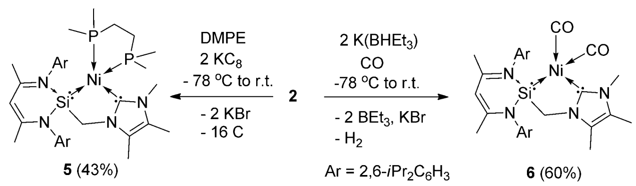


Scheme 2. Synthesis of the mixed NHSi–NHC Ni^{II} complex **2**, and its stepwise reduction with KC_8 in the presence of PMe_3 to form **3** and **4**, respectively.



Scheme 3. Reductions of **2** in the presence of DMPE and CO to afford the Ni^0 complexes **5** and **6**, respectively.

(Scheme 3). Moreover, we further report the remarkably high catalytic activity of **2** for Kumada–Corriu-type cross-coupling reactions.

Treatment of **1** with $[NiBr_2(dme)]$ (dme = 1,2-dimethoxyethane) in toluene at 50 °C afforded the mixed NHSi–NHC-stabilized Ni^{II} complex $[L^1Si{:}(CH_2)(NHC)NiBr_2]$ **2** which was isolated as dark red crystals in 82 % yield (Scheme 2). We propose that the formation of **2** proceeds first via the coordination of the NHC moiety in **1** to $NiBr_2$, which then triggers the hydride migration from the Si–H moiety to the terminal CH_2 group. This affords the silylene species that spontaneously coordinates to the nickel(II) center yielding complex **2**, bearing the chelate NHSi–NHC ligand $[L^1Si{:}(CH_2)(NHC)]$ **1a**. The proposed process is further supported by density functional theory (DFT) calculations, which reveal that the coordination of the NHC to $NiBr_2$ and the subsequent formation of complex **2** are energetically favorable (−4.2 kcal mol^{-1} and −29.1 kcal mol^{-1}, respectively; see the Supporting Information for details).

Compound **2** is highly soluble in CH_2Cl_2 and THF, and moderately soluble in toluene. The protons at the methyl groups of the β-diketiminato ligand are observed at $\delta = 1.57$ and 1.66 ppm as singlet resonance signals in the ^1H NMR spectrum in CD_2Cl_2 solutions. Interestingly, the resonance signals of the methine protons of the *i*Pr groups exhibit two septet signals at $\delta = 2.95$ and 5.03 ppm with one being shifted significantly downfield. This is likely a consequence of intramolecular hydrogen bonding between the methine protons with one of the bromide atoms attached to the nickel center, which is consistent with respective metric parameters in the molecular structure determined by single-crystal X-ray diffraction analysis (see below). The ^{29}Si resonance signal appears at $\delta = 8.3$ ppm in the $^{29}Si\{^1H\}$ NMR spectrum, which is shifted upfield when compared to that of the pincer-type bis(NHSi) Ni^{II} complex ($\delta = 20.2$ ppm) depicted in Scheme 1.[2d]

Single crystals of **2** suitable for X-ray diffraction analysis were obtained from concentrated toluene solutions at −20 °C (Figure 1).[12] The complex crystallizes in the orthorhombic space group $P2_12_12_1$. Noteworthy is that the nickel center exhibits a somewhat distorted square-planar geometry, with a sum of the angles around nickel of 365.03°. The short distances of Br1 with the H15 and H24 atoms (2.884 and 2.990 Å) from the *i*Pr groups indicate strong intramolecular hydrogen bonding, which can be attributed to the drastically downfield-shifted resonance signal for the methine protons in the ^1H NMR spectrum (see above). This also rationalizes the slight distortion of the nickel configuration. The Ni1–Si1 distance of 2.1553(8) Å is similar to those in a pincer-type bis(NHSi) Ni^{II} complex (2.1737(7) Å; Scheme 1),[2d] whereas it is longer than those in NHSi-supported $Ni^0(\eta^6\text{-arene})$ complexes (2.0369(6)–2.0936(10) Å), which have a somewhat stronger $Ni \rightarrow Si^{II}$ π back-donation.[13] The substantially longer Ni1–Br2 distance of 2.4437(6) Å in comparison to that of Ni1–Br1 (2.3538(5) Å) might be attributed to a stronger *trans* effect of the NHSi compared to that of the NHC moiety.

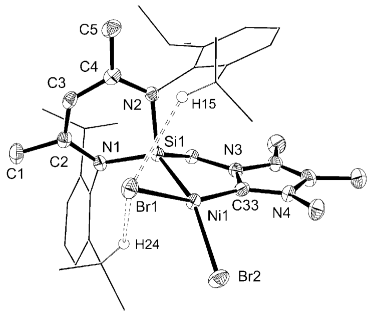


Figure 1. Molecular structure of compound **2**. Ellipsoids are set at 50% probability; all hydrogen atoms (except H15 and H24) and solvent molecules (toluene) are omitted for clarity.

Compound **2** is the first TM complex stabilized by a chelate NHSi–NHC ligand, which encouraged us to investigate its reduction to isolable Ni^0 complexes. The desired debromination of **2** with two molar equivalents of KC_8 in the presence of PMe_3 as an exogenous ligand was carried out in THF. Unexpectedly, after a reaction time of 3 h at room temperature, only the new silyl-NHC monobromo Ni^{II} complex **3**, $[L^2Si(CH_2)NHCNi(Br)(PMe_3)]$, could be isolated in 76 % yield (Scheme 2). Complex **3** was formed through dehydrobromination of **2**; a similar dehydrobromination occurred in the preparation of L^2SiBr_2, which is the dibromo precursor for synthesizing $L^2Si{:}$.[10] After a prolonged reaction time at room temperature (4 h), the reduction resulted in the formation of the unprecedented hydrosilyl-NHC Ni^0 complex $[\eta^2(Si\text{-}H)][L^2Si(H)(CH_2)NHCNi(PMe_3)_2]$ **4** with an agostic $Si{-}H \rightarrow Ni$ interaction, which could be isolated in 68 % yield (Scheme 2). The mechanism for the formation of **4** is unknown but might proceed via the Ni^I species [L^2Si-

$(CH_2)NHCNi^I(PMe_3)]$, generated by one-electron reduction of **3**. However, the latter intermediate is expected to be highly reactive, and can likely abstract a hydrogen atom from the environment (THF or other sources).[14] Subsequent reductive elimination of the Si–H moiety, would yield the Ni^0 complex **4** as the final product.

Compound **3** was isolated as red crystals from concentrated *n*-hexane solutions; it exhibits good solubility in *n*-hexane, benzene, and toluene. Akin to complex **2**, owing to the hydrogen bonding between the bromide atom and the methine hydrogen atoms, two downfield-shifted proton resonance signals ($\delta = 4.52$ and 5.44 ppm) could be observed in the ^{1}H NMR spectrum in [D$_6$]benzene solutions. The protons of PMe$_3$ resonate at $\delta = 1.64$ ppm as a doublet ($^2J_{H,P} = 8.0$ Hz), while the corresponding ^{31}P resonance signal is observed at $\delta = -14.9$ ppm in the $^{31}P\{^1H\}$ NMR spectrum. Owing to the coupling with the ^{31}P nucleus, the ^{29}Si signal results in a doublet at $\delta = 12.2$ ppm ($^2J_{Si,P} = 45.9$ Hz) in the $^{29}Si\{^1H\}$ NMR spectrum, which is shifted downfield in comparison to that of complex **2** ($\delta = 8.3$ ppm). Complex **3** is the first example of any nickel complex containing a chelate silyl-NHC ligand. It is noteworthy that silyl-functionalized NHC cobalt and iron complexes have recently been reported by Deng and co-workers.[15]

The molecular structure of complex **3** is portrayed in Figure 2. It crystallizes in the monoclinic space group $P2_1/c$. The C1–C2 bond (1.360(2) Å) is significantly shorter than the C4–C5 distance (1.496(2) Å), indicating its double-bond character. The Ni1–Si1 bond (2.2273(4) Å) is slightly longer than the Si–Ni dative bond (2.1553(8) Å) in **2**, whereas the value is comparable to those in the silyl nickel complexes $[(2,4,6\text{-}Me_3C_6H_2)B(o\text{-}Ph_2PC_6H_4)_2)(\mu\text{-}H)NiE]$ (E = SiH$_2$Ph, 2.2379(4) Å; SiHPh$_2$, 2.2479(7) Å).[16]

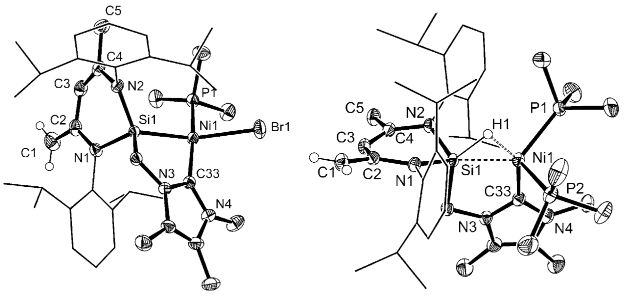


Figure 2. Molecular structures of **3** (left) and **4** (right). Ellipsoids are set at 50% probability; all hydrogen atoms (except those at C1 and Si1) are omitted for clarity.

The NMR spectra of complex **4** in [D$_6$]benzene or [D$_8$]toluene solutions at room temperature are rather complex and are consistent with the coexistence of the two species **4** and **4a** in solutions owing to the coordination and dissociation of one of the PMe$_3$ ligands (Scheme 2). This is exemplified by one sharp ($\delta = -18.8$ ppm) and two broad resonances ($\delta = -27.9$ and -31.3 ppm) for PMe$_3$ groups in the $^{31}P\{^1H\}$ NMR spectrum in [D$_8$]toluene solutions, of which belong to **4a** and **4**, respectively. In analogy, the $^{29}Si\{^1H\}$ NMR spectrum reveals one doublet signal ($\delta = -19.2$ ppm, $^2J_{Si,P} = 8.8$ Hz) for **4a** and a broad signal around $\delta = 2.5$ ppm for **4**. The variable temperature NMR spectroscopic studies show that the two broad ^{31}P resonance signals for **4** are converted into two doublet signals with a coupling constant of 35.4 Hz when the sample is cooled down to −20 °C. The broad ^{29}Si resonance signal of **4** becomes a triplet signal with a coupling constant of 71.5 Hz at −79 °C owing to the coupling with two ^{31}P nuclei of two chemically equivalent PMe$_3$ moieties.

The hydride signal is observed at $\delta = -7.8$ ppm in the ^{1}H NMR spectrum with ^{29}Si satellites ($J_{Si,H} = 87.5$ Hz), which is shifted substantially upfield compared to that of the $[\eta^2(Si\text{–}H)Ni^0(PPh_3)]$ complex ($\delta = -2.9$ ppm).[17] This might be due to the stronger σ-donating property of the ligand **1**. The coupling constant of $^1J_{Si,H} = 87.5$ Hz is much higher than the typical values for Si–M–H complexes (< 20 Hz) with oxidative addition of Si–H bonds to TM centers. The large value of the minimum T_1 (1319 ms) determined by T_1 measurement for Si–H hydride at 298 K and 400 MHz clearly indicates a η^2(Si–H) coordination to the nickel center in **4**.[18] The stretching frequency for the Si–H bond is observed at $\nu = 1746\ cm^{-1}$ in the IR spectrum, which is in the range of the frequency for an σ-silane TM complex ($\nu = 1650$–$1800\ cm^{-1}$).[19] The Si1–H1 bond length (1.738(19) Å) of **4** (Figure 2) is also in the range of those reported for η^2(Si–H) TM complexes (1.70–1.90 Å). Therefore, complex **4** can best be described as a $\eta^2(Si\text{–}H)Ni^0$ complex with an agostic Si–H→Ni bonding interaction.

In an attempt to isolate the chelate NHSi–NHC stabilized Ni^0 complex, we further probed to utilize the chelate diphosphine ligand DMPE and CO as additional supporting ligands. Accordingly, the reduction of **2** with KC$_8$ was carried out in THF in the presence of one molar equivalent of DMPE. In contrast to the case of PMe$_3$ as an exogenous ligand, the reaction afforded the desired Ni^0 complex **5**, $[L^1Si\!:\!(CH_2)NHCNi^0(dmpe)]$, in 43 % yield as dark-green crystals (Scheme 3). This result shows that the ligand **1a** is also capable of stabilizing Ni^0 species. The $^{31}P\{^1H\}$ resonance of **5** is revealed as a singlet signal at $\delta = 15.8$ ppm with ^{29}Si satellites ($^2J_{Si,P} = 30.9$ Hz) in [D$_6$]benzene solutions. Correspondingly, a triplet signal ($\delta = 60.0$ ppm, $^2J_{Si,P} = 30.9$ Hz) is observed in the $^{29}Si\{^1H\}$ NMR spectrum owing to the coupling with two chemically equivalent ^{31}P nuclei from the DMPE ligand.

The nickel center of **5** (Figure 3) exhibits a tetrahedral geometry, and the Ni–Si bond (2.1740(18) Å) is slightly shorter than those in $[L^3Si\!:\!(O)\!:\!SiL^3Ni(cod)]$ (L^3 = PhC-

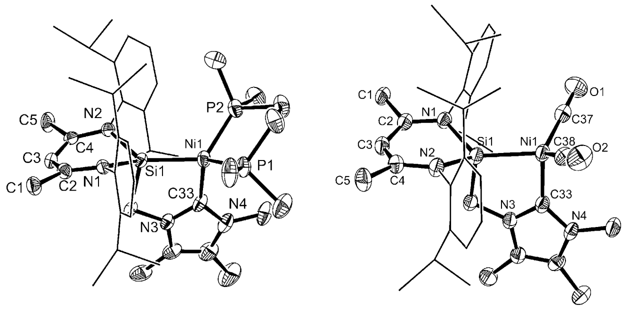


Figure 3. Molecular structures of **5** (left) and **6** (right). Ellipsoids are set at 50% probability; all hydrogen atoms are omitted for clarity.

(N*t*Bu)$_2$; cod = cyclooctadiene) (2.1908(7) and 2.1969(7) Å).[20] DFT calculations revealed a significant π back-donation from the nickel center to both silicon and carbon centers, as indicated by the highest-occupied molecular orbital (HOMO). Furthermore, a π-type bonding orbital (HOMO−1) is present and this orbital appears to be delocalized over the Si−Ni−C framework of complex **5** (Supporting Information, Figure S28). To understand the electron-donating property of the ligand **1a**, we further synthesized the carbonyl complex [L^{1}Si:(CH$_2$)NHCNi(CO)$_2$] **6**.

Reduction of **2** with two molar equivalents of K(BHEt$_3$) under an atmosphere of CO afforded complex **6** as brown crystals in 60 % yield (Scheme 3).[21] The ^{13}C resonances of CO and carbene ligands are observed at $\delta = 198.8$ and 206.2 ppm, respectively, which are comparable to those of [(NHC^{Cy})$_2$Ni(CO)$_2$] ($\delta = 198.3$ and 205.2 ppm; NHC^{Cy} = (CHNCy)$_2$C:, Cy = cyclohexyl).[23] The ^{29}Si nucleus resonates at $\delta = 66.8$ ppm in the ^{29}Si{^{1}H} NMR spectrum, which is shifted downfield when compared to that of **5** ($\delta = 60.0$ ppm). This is likely due to the stronger π-acidity of CO than phosphine ligands, which also results in decreasing the π back-donation from the Ni center to the silicon and NHC carbon centers. This consequently leads to longer Ni1−Si1 (2.2131(13) Å) and Ni1−C33 (1.947(4) Å) bond lengths of **6** (Figure 3) in comparison to those in **5** (2.1740(18) and 1.918(7) Å, respectively). The IR stretching vibrations for the CO ligands are observed at $\nu = 1952$ and 1887 cm^{-1}, which are blue-shifted in comparison to those observed in [{(dmpm)Ni(CO)$_2$}$_2$] ($\nu = 1991$ and 1927 cm^{-1}; dmpm = bis(dimethylphosphino)methane)[22] and [(NHC^{Mes})$_2$Ni(CO)$_2$] ($\nu = 2050$ and 1877 cm^{-1}, NHC^{Mes} = (CHNMes)$_2$C:, Mes = 2,4,6-Me$_3$C$_6$H$_2$).[23] This suggests that the NHSi–NHC ligand **1a** is a stronger σ-donor than two phosphine or NHC ligands.

To highlight the influences of the chelate NHSi–NHC ligand **1a** on the reactivity of the nickel center, we further tested the catalytic performance of **2** in Kumada–Corriu-type cross-coupling reactions (Scheme 4).[24] It was found that complex **2** can efficiently catalyze the cross-coupling reactions of 4-MeC$_6$H$_4$MgCl with aromatic halides (yields: > 99 %) bearing Me, *t*Bu, CF$_3$, and Me$_2$N groups at *para* positions, respectively. Moreover, the effect of the halide leaving group was studied, showing excellent yields with I, Br, Cl (**7a–e**, > 99 %). With 2,4,6-Me$_3$C$_6$H$_2$Br as the substrate, a significant decrease in the yield is observed which might be a result of the steric hindrance from the mesityl group (**7g**, 29 %).

Complex **2** is also capable of catalyzing the cross-coupling reactions of the heterocyclic bromides with 4-MeC$_6$H$_4$MgCl with yields of more than 99 % (**7h**) and 58 % (**7i**). Strikingly, a 86 % yield for the sp^3–sp^2 C−C bond formation with 1-octyl bromide and 4-MeC$_6$H$_4$MgCl was obtained (**7j**), whereas no cross-coupling product was detected when the chelate bis(NHSi) Ni complex [L^{3}Si:(O):SiL^{3}Ni(cod)] was used as the precatalyst.[2c] When *t*BuMgCl was employed, the coupling reaction with 4-MeOC$_6$H$_4$Br gave 31 % yield along with 69 % yield of the hydrodehalogenation product anisole (**7k**). Overall, complex **2** shows very good performance for Kumada–Corriu-type cross-coupling reaction and moreover highlights the promising potential of the NHSi–NHC ligand supported TM complexes for other organic transformations.

In summary, with the assistance of Ni^{II}, the reaction of ligand **1** with NiBr$_2$ afforded the first mixed NHSi–NHC supported Ni^{II} complex **2**. Its reduction by KC$_8$ in the presence of PMe$_3$ afforded the silyl-NHC bromo Ni^{II} complex **3** and the η^2(Si−H)Ni^0 complex **4** depending on the reaction time. Using DMPE as the auxiliary ligand, the analogous reduction smoothly furnishes Ni^0 complex **5**. The substantially low IR stretching frequencies of **6** suggest that **1a** is a better σ-donor than two phosphine or NHC ligands. Moreover, complex **2** is a highly efficient precatalysts for Kumada–Corriu-type cross-coupling reaction. Exploring new complexes for other catalytic transformations of organic substrates and the coordination features of **1** and **1a** toward other TMs are currently under investigation in our laboratory.

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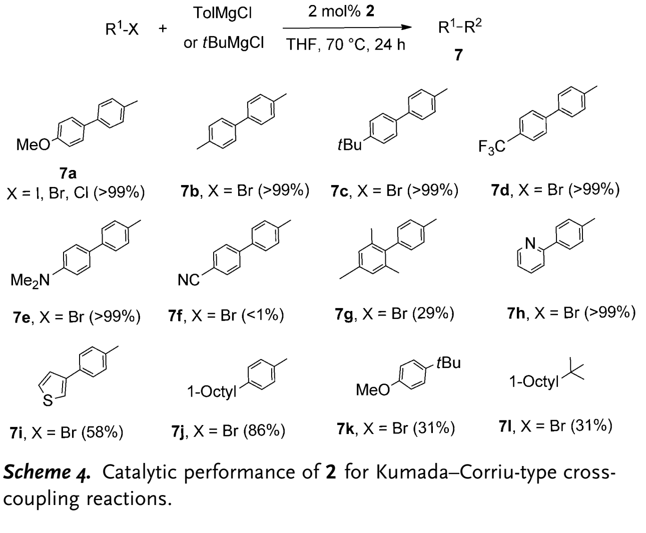

Scheme 4. Catalytic performance of **2** for Kumada–Corriu-type cross-coupling reactions.

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