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Nickel-Catalyzed C–H Silylation of Arenes with Vinylsilanes: Rapid and Reversible β-Si Elimination

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ABSTRACT: The reaction of C_6F_5H and $H_2C{=}CHSiMe_3$ with catalytic $[^iPr_2Im]Ni(\eta^2\text{-}H_2C{=}CHSiMe_3)_2$ **(1b)** forms the C–H silylation product $C_6F_5SiMe_3$ exclusively, with ethylene as a byproduct ($[^iPr_2Im]$ = 1,3-di(isopropyl)imidazole-2-ylidene). Catalytic C–H bond silylation is facile with partially fluorinated aromatic substrates containing two ortho fluorine substituents adjacent to the C–H bond and 1,2,3,4-tetrafluorobenzene, with the less fluorinated substrates reacting slower. Under the same reaction conditions, catalytic $[IPr]Ni(\eta^2\text{-}H_2C{=}CHSiMe_3)_2$ (**1a**) ([IPr] = 1,3-bis[2,6-diisopropylphenyl]-1,3-dihydro-2H-imidazol-2-ylidene), provided only the alkene hydroarylation product $C_6F_5CH_2CH_2SiMe_3$. Mechanistic studies reveal that the C–H activation and β-Si elimination steps are reversible under catalytic conditions with both catalysts **1a** and **1b**. With catalytic **1a,** reversible ethylene loss after β-Si elimination was also observed, despite its inability to catalyze C–H silylation; the reductive elimination step to form the silylation product is much slower than reductive elimination to form the alkene hydroarylation product. Reversible ethylene loss was not reversible with **1b**, which suggests that the rate limiting step in the reaction is neither C–H activation nor β-Si elimination, but either ethylene loss, or reductive elimination of cis-disposed aryl and $SiMe_3$ moieties.

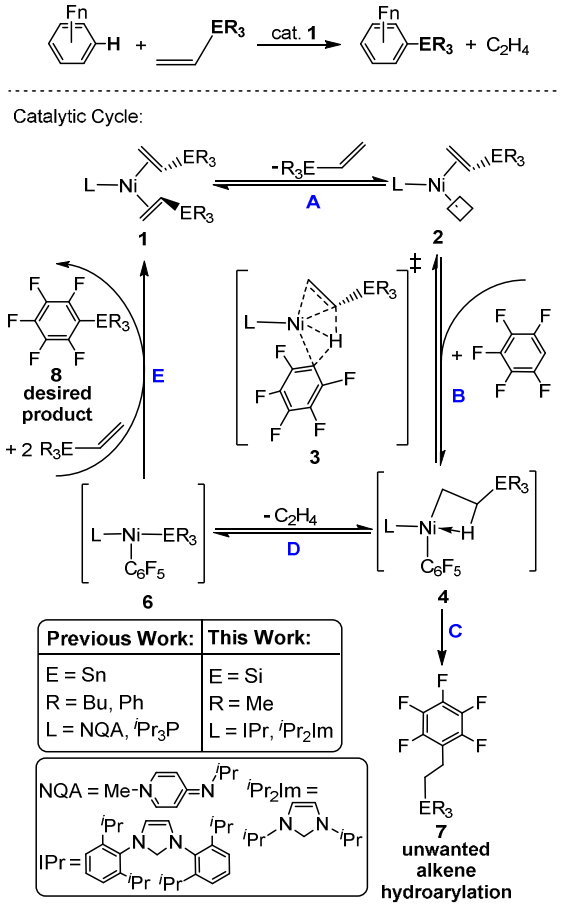
Introduction

The transition metal catalyzed functionalization of C–H bonds[1] has extensive applications for organic synthesis.[2] The silylation of aryl C–H bonds is an atom economical route to organosilicon compounds with numerous applications, such as Hiyama coupling.[3] Advances in C–H bond silylation have been the subject of several reviews;[4] however, the majority of examples require the use of noble metal complexes. Recent efforts have focused on eliminating the need for expensive heavy metals in these reactions.[5]

Our group has reported the nickel catalyzed C–H stannylation of fluorinated aromatics, as shown on the top of Scheme 1 where $ER_3 = SnBu_3$.[6] This transformation uses readily available $H_2C{=}CHSnBu_3$ to convert a plethora of partially fluorinated aromatics into organotin compounds suitable for Stille coupling,[7] with only ethylene as a byproduct. A proposed mechanistic pathway for catalysis using **1**, which is a resting state for the catalyst, is shown in Scheme 1. Step A features a reversible dissociation of the vinyl moiety to give **2**. This is followed by C–H bond activation in step B, which occurs via oxidative addition coupled with insertion through the proposed transition state **3**, alternatively viewed as a ligand to ligand hydrogen transfer.[8] The β-agostic Ni intermediate **4** can undergo two possible reaction pathways that yield different products. Reductive elimination from **4**, shown as step C, provides the unwanted alkene hydroarylation product $C_6F_5CH_2CH_2ER_3$. Alternatively, **4** can undergo β-ER_3 elimination to form $Ni(L)(C_6F_5)(ER_3)(\eta^2\text{-}C_2H_4)$ (**5**), which could lose ethylene gas to give $Ni(L)(C_6F_5)(ER_3)$ (**6**), as shown in step D. The reductive elimination step E regenerates the Ni(0) catalyst and forms the desired C–H bond functionalization product, $C_6F_5ER_3$.[6b, c, 9]

In C–H bond stannylation, competition was observed between the two mechanistic pathways, C and D, that intermediate **4** can undergo. With $E = SnBu_3$ and $L = {}^iPr_3P$ or {NQA, catalysis yielded almost exclusively the stannylation product $C_6F_5SnBu_3$. Using $SnPh_3$ with $^iPr_3P$ also led to stannylation products; however, using the {NQA} ligand with $SnPh_3$ resulted in a mixture of stannylation product and hydroarylation product, $C_6F_5CH_2CH_2SnPh_3$, with the latter being favored (95 %). Furthermore, using the IPr carbene as the ancillary ligand (IPr = 1,3-bis[2,6-diisopropylphenyl]-1,3-dihydro-2H-imidazol-2-ylidene) resulted in similar product distributions as the {NQA} ligand.[9]

Scheme 1. Proposed C–H Bond Functionalization Mechanism



A study of nickel catalyzed alkene hydroarylation reactions with IPr as the ancillary ligand provided a detailed computational mechanism, and found experimentally that the reaction of 1,3-bis(trifluoromethyl)benzene and H_2C=CHSiEt_3 provided conversion to the hydroarylation product exclusively.[10] The absence of silylation product in this reaction suggests that β-Si elimination does not occur under these conditions, possibly because it is both kinetically and thermodynamically more difficult than β-Sn elimination. Herein we report the Ni–catalyzed C–H silylation of partially fluorinated aromatics, and reexamine this assumption regarding the ease of β-Si elimination and its importance on the selectivity of these systems towards C–H silylation vs hydroarylation.

Results and Discussion

Synthesis of Nickel Complexes. To determine if silylation could be achieved under similar conditions to stannylation,[6] a 5 % loading of the previously reported[11] complex (^{i}Pr_3P)Ni(η²- H_2C=CHSiMe_3)$_2$ was reacted with H_2C=CHSiMe_3 and pentafluorobenzene at 80 °C for 24 h. The crude ^{19}F{^{1}H} NMR spectrum showed 3 % conversion to the C–H silylation product, $C_6F_5SiMe_3$ (**8**), along with unreacted starting material, but no hydroarylation product. Decomposition of the Ni catalyst was indicated by nickel metal precipitate and the observation of only ^{i}Pr_3P in the ^{31}P{^{1}H} NMR. Heating above 80 °C resulted in rapid decomposition of (^{i}Pr_3P)Ni(η²-H_2C=CHSiMe_3)$_2$. Similar temperature limitations of the catalyst were noted in our previous work with C–H stannylation.[6]

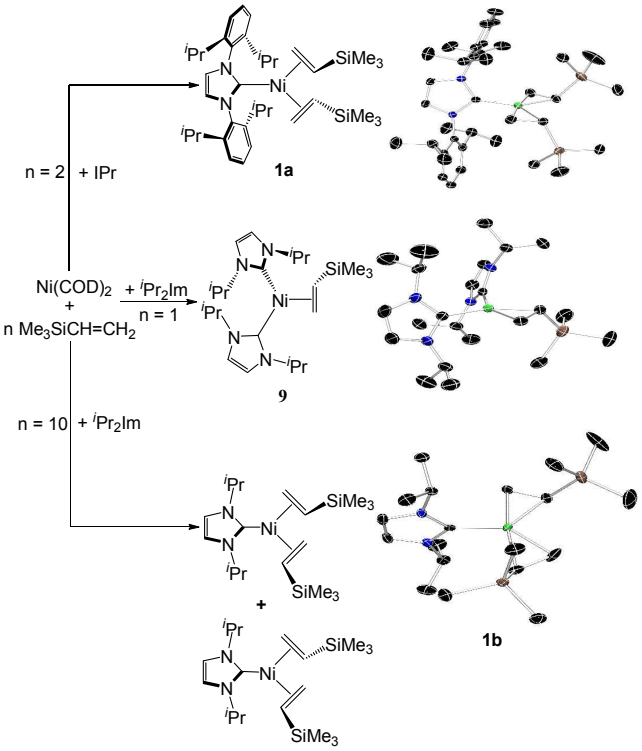


Figure 1. Syntheses and ORTEP depictions of **1a, 9,** and **1b.** Hydrogen atoms are omitted for clarity.

The use of carbene ligands in lieu of phosphines often provides more thermally robust complexes for transition metal catalysis.[12] The reaction of Ni(COD)$_2$ (COD = 1,5-cyclooctadiene) with IPr and two equivalents of H_2C=CHSiMe_3 forms the expected[10, 13] complex [IPr]Ni(η²-H_2C=CHSiMe_3)$_2$ (**1a**). The crystal structure is shown in Figure 1. A catalytic amount of **1a** was reacted with H_2C=CHSiMe_3 and pentafluorobenzene at 90 °C for 24 h, but only the alkene hydroarylation product, $C_6F_5CH_2CH_2SiMe_3$ (**7**), was formed, with no observable silylation product **8**. This is consistent with a related previous study of hydroarylation.[10]

The potential influence[14] of carbene steric bulk on catalysis led us to examine if a smaller carbene could promote selective C–H silylation instead of alkene hydroarylation. The reaction of the ^{i}Pr_2Im carbene ligand (^{i}Pr_2Im = 1,3-di(isopropyl)imidazole-2-ylidene) with Ni(COD)$_2$ and two equivalents of H_2C=CHSiMe_3 resulted in the isolation of the unanticipated bis-carbene Ni complex, [^{i}Pr_2Im]$_2$Ni(η²-H_2C=CHSiMe_3) (**9**). The reactivity of **9** towards silylation was tested with H_2C=CHSiMe_3 and a series of fluorinated substrates. Reaction with pentafluorobenzene resulted in stoichiometric conversion to the known C–F bond activation product (^{i}Pr_2Im)$_2$NiF(C_6F_4H).[15] More encouragingly, C–H silylation products were observed with the substrates 1,2,4,5-tetrafluorobenzene, 1,3,5-trifluorobenzene, and 1,3-difluorobenzene, along with C–F activation products and $FSiMe_3$. However, examination of the kinetics of these reactions revealed an incubation period, which suggested that **9** is not the active catalyst for silylation. During these reactions, two new broad peaks were observed in the ^{1}H NMR spectrum, consistent with the bis-vinyl species, [^{i}Pr_2Im]Ni(η²-H_2C=CHSiMe_3)$_2$ (**1b**).

Complex **1b** was synthesized in 90 % yield by the reaction of Ni(COD)$_2$ with 10 equivalents of H_2C=CHSiMe_3 in toluene,

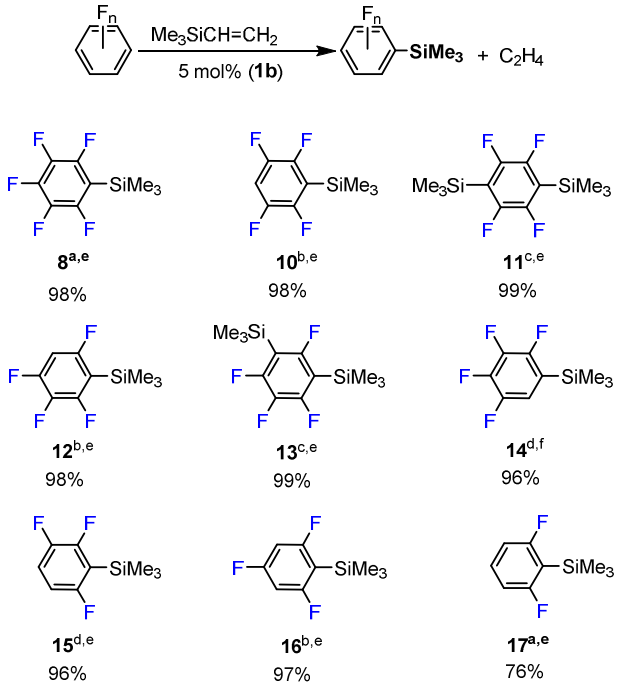
followed by the slow addition of a dilute solution of $^{i}Pr_2Im$. As shown in Figure 1, the solid-state structure of **1b** features $SiMe_3$ substituents that are on the same side of the trigonal Ni coordination plane, with one of the substituents central, and the other adjacent to the $^{i}Pr_2Im$ ligand, unlike the C_2 symmetric **1a**.[6c] At the fast exchange limit, the ^1H NMR spectrum features resonances for two isomers, shown at the bottom of Figure 1, in a 5:1 ratio, where rotation around the Ni-η^2-alkene bonds is rapid. At low temperature, these peaks decoalesce to give further rotational isomers. The presence of multiple similar energy isomers for **1b** is presumably the result of a ligand with less steric bulk.

Catalysis with 1b. To investigate the catalytic ability of **1b** for C–H silylation, experiments were carried out on a broad spectrum of fluorinated aromatics. The results are summarized in Chart 1. In initial NMR scale experiments, the C–H silylation of pentafluorobenzene was facilitated with a 5 % catalyst loading and performed at two different temperatures. Heating at 100 °C for 7 h resulted in 24 % conversion, while heating at 120 °C led to conversions of 65 %, 87 % and 98 % after 3 h, 5 h and 7 h, respectively. The reaction was also successful on larger scales, and using 1 g of pentafluorobenzene under similar conditions, the silylation product was obtained in a 70 % yield after chromatographic purification. Substrates with a C–H bond ortho to two fluorine substituents were most reactive towards silylation. The monosilylation products **8**, **10**, **12**, **14**, **15**, **16**, and **17** were made selectively using an excess of fluorinated substrate. The only impurities in these reactions were the disilylated products **11** and **13**, which could be prepared by reacting the substrate with 2.5 equivalents of $H_2C{=}CHSiMe_3$.

Kinetics modelling[16] of the rate of formation of mono- and di-silylated compounds with substrates with two equally activated sites, such as 1,2,4,5-tetrafluorobenzene, revealed that the monosilylation product **10** undergoes silylation with a rate constant about one-half of its precursor, which correlates with the number of C–H bonds in each substrate and is consistent with a minimal electronic effect of the para-$SiMe_3$ substituent in **10**. A similar approximately 2:1 ratio of silylation rate constants was found for 1,2,3,5-tetrafluorobenzene and its monosilylation product **12**, suggestive that meta-$SiMe_3$ substituents also have only a minor electronic influence. In contrast, no silylation next to an ortho-$SiMe_3$ group was observed in 1,2,3,4-tetrafluorobenzene, which can be attributed to the steric bulk of this group.

Substrates with a lesser degree of fluorination required more time to reach completion. Aryl C–H bonds with only one ortho fluorine proved to be less efficiently silylated, and required a higher catalyst loading. The silylation product of 1,2,3,4-tetrafluorobenzene was obtained in only a 30 % yield when using a 5 % loading of **1b**. When performed with a 20 % loading of **1b**, the silylation product of 1,2,3,4-tetrafluorobenzene was obtained in a 96 % yield, by integration of ^{19}F NMR spectra using an internal standard. Multinuclear NMR revealed **1b** to be the resting state of the catalyst with all these substrates. The fluoroarenes 1,2,3-trifluorobenzene, 1,2-difluorobenzene, 1,4-difluorobenzene, and fluorobenzene did not undergo efficient C–H silylation. Increasing the temperature to 140 °C resulted in the decomposition of **1b**, with the formation of a black precipitate. There are several examples of nickel catalyzed alkene hydroarylation of heterocycles,[10, 17] however, instances of C–H silylation of heterocycles with any metal are limited.[5a, 18] A previous report of Ni-catalyzed reactions of heterocycles with $H_2C{=}CHSiEt_3$, provided solely hydroarylation products;[17a] in contrast, the reaction of $H_2C{=}CHSiMe_3$ and **1b** with the heterocycle benzofuran resulted in selective silylation,[19] but a mixture of silylation and hydroarylation products with the substrates benzoxazole and benzothiazole. The latter two substrates feature very activated C–H bonds, and catalysis was observed at temperatures as low as 60 °C. Further details are provided in the Supporting Information.

Chart 1. C–H Silylation of Fluorinated Aromatics



[a] Performed with 0.498 mmol of $H_2C{=}CHSiMe_3$ and arene. [b]Performed with 0.498 mmol of $H_2C{=}CHSiMe_3$ and 10 equivalents (4.98 mmol) of arene to obtain monosilylation products. [c]Performed with 2.5 equivalents (1.25 mmol) $H_2C{=}CHSiMe_3$ relative to arene (0.498 mmol) to form disilylation product. [d]Performed with 3-5 equivalents (1.50-2.50 mmol) of arene relative to $H_2C{=}CHSiMe_3$ (0.498 mmol). [e]Reaction was carried out with 5 mol % **1b**. [f]Reaction was carried out with 20 mol % **1b**. Yields of product were determined by ^{19}F NMR and are relative to 0.062 mmol of the internal standard $FSiPh_3$.

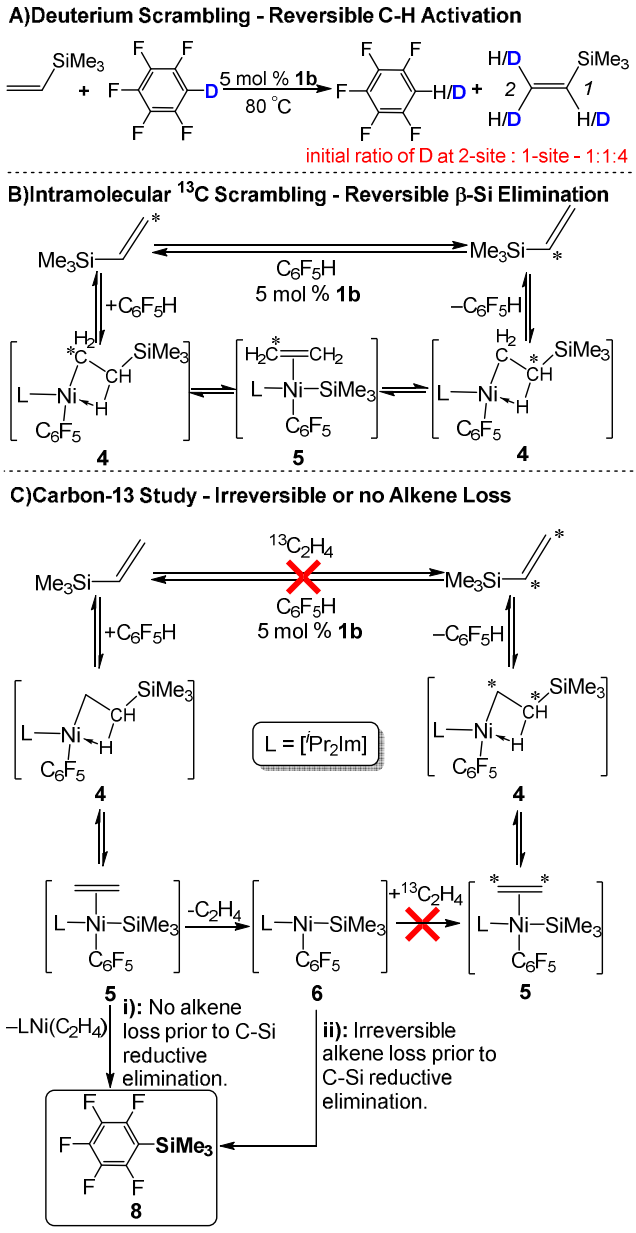
Due to the limited utility of $SiMe_3$ groups in Hiyama cross coupling reactions, additional silyl groups were investigated.[3b, 20] The reaction of $H_2C{=}CHSi(OEt)_3$ and pentafluorobenzene with a catalytic amount of $Ni(COD)_2$ and $^{i}Pr_2Im$ did not result in the silylation product. To investigate if C–H bond activation was occurring, C_6F_5D and $H_2C{=}CHSi(OEt)_3$ was reacted with a catalytic amount of $Ni(COD)_2$ and $^{i}Pr_2Im$, and heated at 120 °C for 12 h. The $^{19}F\{^1H\}$ NMR showed deuterium exchange into the arene, indicating that C–H activation still readily occurs, and so it is likely that the β-Si elimination step is not viable with the $Si(OEt)_3$ substituent. Although limited information is known about the propensity of silyl groups to undergo β-Si elimination, this result is consistent with previous studies on Ru complexes.[21] The $SiBnMe_2$ substituent, where Bn = benzyl, has also found use in coupling reactions, and seemed more likely to be capable of β-Si elimination.[22] The reaction of pentafluorobenzene and $H_2C{=}CHSiBnMe_2$ with a 5% catalyst

loading of $Ni(COD)_2$ and $^iPr_2Im$ provided the silylation product $C_6F_5SiBnMe_2$ in poorer yield than with $H_2C{=}CHSiMe_3$ (70%), but without significant byproducts. Increased catalyst loadings improved yields.

Labeling Studies with 1b. Unexpected mechanistic insights regarding β-Si elimination were obtained from a series of isotope labeling studies. The reaction of C_6F_5D and $H_2C{=}CHSiMe_3$ in the presence of catalytic **1b** at 80 °C yielded scrambling of the D label into all the sp^2 C–H bonds of the vinyl moiety, as shown in Scheme 2. This temperature is below that at which catalytic silylation is observed, and scrambling suggests that the C–H bond activation (step B in Scheme 1) is reversible and not rate limiting, in contrast to catalytic stannylation.[6c] Monitoring the reaction by ^2H NMR spectroscopy found that the initial ratio of deuterium incorporation into the two 2-sites and single 1 site of $H_2C{=}CHSiMe_3$ was 1:1:4. Two possible mechanistic explanations were considered for incorporation of D into the 2-sites:[23] The first is reversible β-Si elimination (step D in Scheme 1), where the ethylene moiety in **5** reinserts, scrambling deuterium into either the 1 or 2 sites of **4**. The second explanation is if the C–H bond activation (step B in Scheme 1) occurs with hydrogen transfer to both the 1 and 2 sites of the bound $H_2C{=}CHSiMe_3$ moiety.

Carbon-13 labeling studies were performed as a test for reversible β-Si elimination. The reaction of pentafluorobenzene and $H_2{}^{13}C{=}CHSiMe_3$ with a 5 % loading of **1b** was monitored using variable-temperature $^{13}C\{^1H\}$ NMR. At 110 °C the scrambling of labels to give $H_2C{=}{}^{13}CHSiMe_3$ was observed. A mechanism is proposed in Scheme 2. Complete ^{13}C label scrambling occurred before any silylation product was observed. This result indicates that β-Si elimination is reversible, and that alkene loss or reductive elimination is the rate determining step in the silylation reaction.

To test if alkene loss from **5** is the rate limiting step, doubly labeled $^{13}C_2H_4$ was added to a solution containing pentafluorobenzene, $H_2C{=}CHSiMe_3$ and a catalytic amount of **1b**. After undergoing 20 % conversion to silylation product, there was no observable incorporation of the ^{13}C label to give $H_2{}^{13}C{=}{}^{13}CHSiMe_3$. This suggests two possibilities for the rate determining step of C–H silylation: Either i) rate determining reductive elimination prior to ethylene loss from an isomer of **5** with cis-disposed aryl and $SiMe_3$ moieties; or ii) rate determining alkene loss from **5** before reductive elimination. Both possibilities are shown in the bottom left of Scheme 2.



Scheme 2. Isotope Labeling Studies with 1b

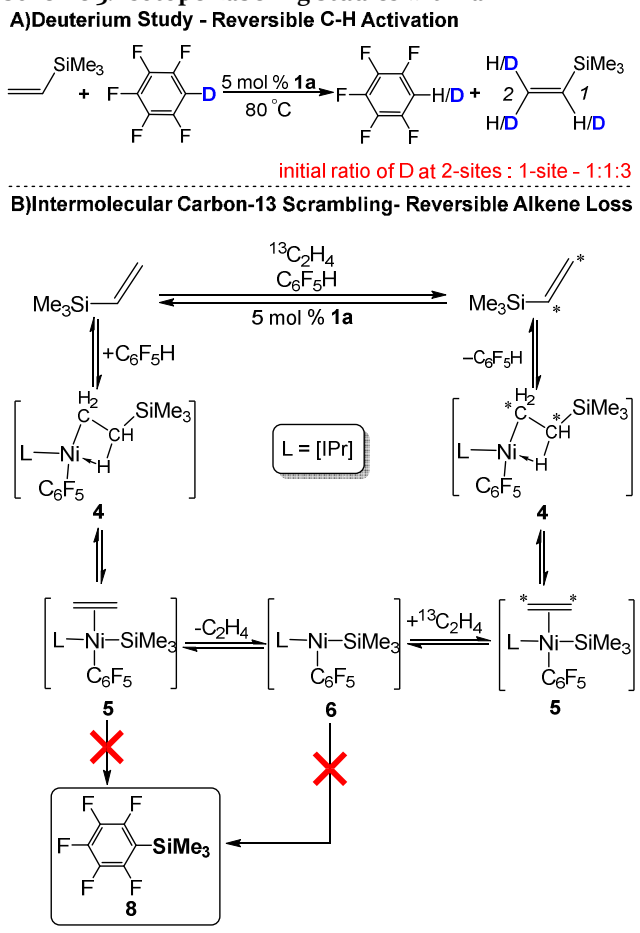
Labeling Studies with 1a. Insight into why the bulkier IPr carbene complex **1a** gives hydroarylation instead of silylation products could aid in the design of catalysts for carbon–heteroatom bond forming reactions as well as other related processes. The labeling studies using **1b** suggested that catalysis with **1a** could also feature rapid β-Si elimination, but still not give the silylation product if the reductive elimination step E (in Scheme 1) is relatively slow compared to step C.

To investigate if reversible β-Si elimination is occurring in this system, C_6F_5D and $H_2C{=}CHSiMe_3$ was reacted with a 5 % catalyst loading of **1a**. After heating at 90 °C for 5 minutes the ^2H NMR showed deuterium scrambling in both the two 2-sites and single 1-site of $H_2C{=}CHSiMe_3$ in a 1:1:3 ratio, as shown in Scheme 3. After heating the sample overnight, ^2H NMR showed statistical scrambling of deuterium into all the sp^2 C–H bonds of the alkene. Like the previous experiments conducted with **1b**, full scrambling into both the arene and

H_2C=$CHSiMe_3$ suggested C–H activation and β-Si elimination are rapidly reversible.

If β-Si elimination is reversible and not the rate limiting step for silylation with **1a**, then once again either alkene loss or the final C–Si reductive elimination could prevent silylation in this system. The reaction of pentafluorobenzene, H_2C=$CHSiMe_3$ and doubly labeled $^{13}C_2H_4$ with 5 % of **1a** at 90 °C results in intermolecular scrambling of the ^{13}C label to give $H_2{}^{13}C=^{13}CHSiMe_3$ before any hydroarylation product is observed. This result shows that not only is β-Si elimination reversible, but so is alkene loss from **5**, as shown in Scheme 3. This result is different from that obtained with catalyst **1b**. Remarkably, even though catalyst **1a** gives only alkene hydroarylation, it is not because the system does not undergo rapid β-Si elimination and subsequent reversible alkene loss to form **6**; silylation is not observed because the rate of the C–Si reductive elimination step E is much slower than C–C reductive elimination step C.

Scheme 3. Isotope Labeling Studies with 1a



Conclusions

While the application of nickel in catalysis continues to expand,[24] to the best of our knowledge, there is only one previous instance of nickel catalyzed C–H silylation, which required a reactant with a strained Si–Si bond.[25] The C–H silylation reaction reported here requires higher temperatures than analogous C–H stannylation reactions; this was expected to be due to an increased barrier to β-Si elimination, and seemed to be a likely rate-determining step for these reactions. The use of N-heterocyclic carbene donors provided more thermally stable complexes than $^{i}Pr_3P$, which afforded only trace C–H silylation, but the choice of carbene substituents plays a dramatic role in the selectivity of the reaction. The nickel complex $[^{i}Pr_2Im]Ni(\eta^2\text{-}H_2C$=$CHSiMe_3)_2$ (**1b**) performs catalytic C–H silylation of partially fluorinated aromatics with low catalyst loadings. The analogous complex **1a** using the IPr carbene gave no trace of C–H silylation, and instead gives alkene hydroarylation, as previously reported.[10] Investigations into the mechanism of the C–H bond functionalization reaction led to several key insights, the most surprising being that the β-Si elimination is rapid and reversible using both catalysts **1a** and **1b**; the IPr supported catalyst **1a** was even seen to undergo alkene exchange after β-Si elimination under catalytic conditions, despite the fact that it does not mediate C–H silylation. The possible rate determining steps for C–H silylation using **1b** are either alkene loss from **5**, or direct reductive elimination from **5** with cis disposed aryl and $SiMe_3$ groups, before ethylene loss. Relatively few catalytic systems have taken advantage of β-Si elimination for the synthesis of organosilicon compounds.[26,27]

Experimental Section

General Considerations. Unless otherwise stated, all reactions were carried out under an atmosphere of dry oxygen free dinitrogen by means of standard Schlenk or glovebox techniques. Benzene–d_6, and toluene–d_8 were degassed by three freeze-pump-thaw cycles, and subsequently dried by running through a column of activated alumina. Toluene, THF, and pentane were purchased anhydrous from Aldrich or Alfa Aesar. ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, ^2H and $^{29}Si\{^1H\}$ NMR spectra were recorded on a Bruker AMX Spectrometer operating at either 300 MHz or 500 MHz with respect to proton nuclei. ^1H NMR spectra were referenced to residual protons (C_6D_6, δ 7.15) or (tol-d_8, δ 2.17) with respect to tetramethylsilane at δ 0.00. ^{13}C $\{^1H\}$ NMR spectra were referenced relative to solvent resonances (C_6D_6, δ 128.26) or (tol-d_8, δ 21.37). ^{19}F $\{^1H\}$ NMR spectra were referenced to an external sample of 80% CCl_3F in $CDCl_3$ at δ 0.00. Benzene-d_6 and toluene-d_8 was purchased from Cambridge Isotope Laboratory. All reagents were purchased from commercial suppliers. The compounds $Ni(COD)_2$,[28] IPr,[29] $^{i}Pr_2Im$,[30] and C_6F_5D[31] were prepared according to literature procedures. Elemental analyses were carried out at the Centre for Catalysis and Materials Research, Windsor, Ontario.

General Procedure for catalytic C–H bond silylation. A solution of fluorinated arene and trimethyl(vinyl)silane in 0.6 g of toluene was added to a 5 % loading of **1b** and an internal standard, triphenylfluorosilane. The NMR tube was flame sealed under vacuum and the solution was fully immersed in an oil bath at 120 °C. Equivalents of fluorinated arene and trimethyl(vinyl)silane, and time of reaction varied upon desired product. (See Supporting Information).

$[IPr]Ni(\eta^2\text{-}H_2C$=$CHSiMe_3)_2$ (1a). $Ni(COD)_2$ (0.43 g, 1.55 mmol) was dissolved in 10 mL of toluene. Trimethyl(vinyl) silane (0.31 g, 3.10 mmol, 2 equiv) was added to the reaction mixture. The solution was added to 1,3-bis[2,6-diisopropylphenyl]-1,3-dihydro-2H-imidazol-2-ylidene) (0.60 g, 1.55 mmol), stirred for 30 minutes and evaporated in vacuo to provide a brown solid. Compound **1a** was recrystallized from pentane at –40 °C affording 0.600 g of yellow crystals (60 % yield). ^1H NMR (tol-d^8, 25 °C, 500.129 MHz): δ -0.15 (s, 18H, $Si(CH_3)_3$); 0.98 (d, 6H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.95 Hz); 1.10 (d,

6H, CH(CH_3)$_2$, $^3J_{HH}$ = 6.95 Hz); 1.16 (d, 6H, CH(CH_3)$_2$, $^3J_{HH}$ = 6.95 Hz); 1.50 (d, 6H, CH(CH_3)$_2$, $^3J_{HH}$ = 6.95 Hz); 2.35 (d, 2H, vinyl–*H*, $^2J_{HH}$ = 15.9 Hz); 2.51(dd, 2H, vinyl–*H*, $^2J_{HH}$ = 12.8 Hz, $^2J_{HH}$ = 15.9 Hz); 2.73 (d, 2H, vinyl–*H*, $^2J_{HH}$ = 12.8 Hz); 2.95 (septet, 2H, C*H*, $^3J_{HH}$ = 6.95 Hz); 3.31 (septet, 2H, C*H*, $^3J_{HH}$ = 6.95 Hz); 6.63 (s, 2H, *H*C=C*H*); 7.02 (d, 3,5–Ar–C*H*, $^3J_{HH}$ = 7.58 Hz); 7.11 (d, 3,5–Ar–C*H*, $^3J_{HH}$ = 7.58 Hz); 7.18 (t, 4–Ar–C*H*, $^3J_{HH}$ = 7.58 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 22 °C, 500.133 MHz): δ 1.2 (s, 6C, Si(*C*H_3)$_3$); 22.3 (s, isopropyl–(*C*H_3)$_2$); 22.7 (s, isopropyl–(*C*H_3)$_2$); 25.6 (s, isopropyl–(*C*H_3)$_2$); 27.0 (s, isopropyl–(*C*H_3)$_2$); 29.0 (s, isopropyl–*C*H); 30.8 (s, isopropyl–*C*H); 50.5 (s, vinyl–*C*); 53.5 (s, vinyl–*C*); 124.2 (s, H_2C=*C*H_2); 124.3 (s, H_2C=*C*H_2); 129.9 (s, Ph–*C*); 137.6 (s, Ph–*C*); 145.8 (s, Ph–*C*); 146.5 (s, Ph–*C*); 206.3 (s, Ni–*C*). ^{29}Si{^{1}H} NMR (C_6D_6, 27 °C, 59.647 MHz): δ -3.9 (s, 2Si, *Si*(CH_3)$_3$). Calcd for $C_{37}H_{60}N_2NiSi_2$: % C 68.61; % H 9.34; % N 4.32. Found: % C 66.47; % H 9.05; % N 4.31. Repeated elemental analyses gave variable but consistently low values for C, possibly due to Ni-carbide formation.

[^{i}Pr$_2$Im]Ni(η^2-H$_2$C=CHSiMe$_3$)$_2$ (1b). Ni(COD)$_2$ (1.34 g, 4.87 mmol) was dissolved in 20 mL of toluene and trimethyl(vinyl) silane (4.88 g, 48.7 mmol, 10 equiv) was added. The solution was stirred for 1 h to ensure the Ni(COD)$_2$ was fully dissolved. A solution of 1,3-di(isopropyl)imidazol-2-ylidene (0.74 g, 4.87 mmol) diluted in 3 mL of toluene was added to the reaction mixture dropwise while stirring. Solution was left to stir for 30 minutes and evaporated in vacuo to provide a light brown oil. Compound **1b** was dissolved in minimal pentane, and slow evaporation at –40 °C provided 1.54 g of a brown solid (77 % yield). Compound **1b** was recrystallized by slow evaporation at room temperature from a mixture of HMDSO and minimal benzene, affording yellow crystals. Major isomer: ^{1}H NMR (C_6D_6, 25 °C, 500.133 MHz): δ 0.21 (s, 18H, Si(*C*H_3)$_3$); 0.93 (d, 6H, CH(*C*H_3)$_2$, $^3J_{HH}$ = 6.75 Hz); 1.01 (d, 6H, CH(*C*H_3)$_2$, $^3J_{HH}$ = 6.75 Hz); 2.54 (fluxional multiplet, 2H, vinyl-*H*); 2.69 (fluxional multiplet, 2H, vinyl-*H*); 2.87 (fluxional multiplet, 2H, vinyl-*H*); 4.39 (septet, 2H, C*H*, $^3J_{HH}$ = 6.75 Hz); 6.40 (s, 2H, C*H*=C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 22 °C, 500.133 MHz): δ 1.1 (s, 6C, Si(*C*H_3)$_3$); 23.0 (s, 4C, isopropyl–*C*H_3); 23.6 (s, 2C, isopropyl–*C*H); 50.9 (s, vinyl–*C*); 52.5 (s, vinyl–*C*); 116.6 (s, H_2C=*C*H_2); 198.0 (s, Ni–*C*). ^{29}Si{^{1}H} NMR (C_6D_6, 27 °C, 59.647 MHz): δ -4.4 (s, 2Si, *Si*(CH_3)$_3$). Minor isomer: ^{1}H NMR (C_6D_6, 25 °C, 500.133 MHz): δ 0.14 (s, 18H, Si(*C*H_3)$_3$); 0.96 (d, 6H, CH(*C*H_3)$_2$, $^3J_{HH}$ = 6.75 Hz); 0.99 (d, 6H, CH(*C*H_3)$_2$, $^3J_{HH}$ = 6.75 Hz); 2.25 (dd, 2H, vinyl-*H*, $^3J_{HH}$ = 12.58 Hz, $^3J_{HH}$ = 16.20 Hz); 2.53 (d, 2H, vinyl-*H*, $^3J_{HH}$ = 16.20 Hz); 3.19 (d, 2H, vinyl-*H*, $^3J_{HH}$ = 12.58 Hz); 4.39 (septet, 2H, C*H*, $^3J_{HH}$ = 6.75 Hz); 6.41 (s, 2H, C*H*=C*H*).^{13}C{^{1}H} NMR (C_6D_6, 22 °C, 500.133 MHz): δ 0.8 (s, 6C, Si(*C*H_3)$_3$); 23.2 (s, 4C, isopropyl–*C*H_3); 23.7 (s, 2C, isopropyl–*C*H); 50.4 (s, vinyl–*C*); 50.9 (s, vinyl–*C*); 116.7 (s, H_2C=*C*H_2). ^{29}Si{^{1}H} NMR (C_6D_6, 27 °C, 59.647 MHz): δ -4.4 (s, 2Si, *Si*(CH_3)$_3$). Calcd for $C_{19}H_{40}N_2NiSi_2$: % C 55.47; % H 9.80; % N 6.81. Found: % C 52.15-54.49; % H 9.76; % N 6.92. Repeated elemental analyses gave variable but consistently low values for C, possibly due to Ni-carbide formation.

C$_6$F$_5$CH$_2$CH$_2$SiMe$_3$ (7). A solution of pentafluorobenzene (0.167 g, 0.998 mmol) and trimethyl(vinyl)silane (0.10 g, 0.998 mmol) in 0.6 g of toluene was added to **1a** (0.039 g, 0.099 mmol, 5 mol %). The solution was added to an NMR tube and placed in an oil bath at 90 °C and heated for 20 h. (60 % NMR yield). ^{1}H NMR (C_6D_6, 25 °C, 500.12 MHz): δ -0.01 (s, 9H, *Si*(CH_3)$_3$); 0.59 (second order m, 2H, C*H*$_2$SiMe$_3$); 0.23 (second order m, 2H, C*H*$_2$CH$_2$SiMe$_3$). ^{19}F{^{1}H} NMR (C_6D_6, 25 °C, 470.59 MHz): δ –146.4 (AA′MM′ second order m, 2F, 2,6–Ar–*F*); -159.6 (t, 1F, 4–Ar–*F*, $^3J_{FF}$ = 20.4 Hz); -163.8 (AA′MM′X second order m, 2F, 3,5–Ar–*F*). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 125.75 MHz): δ -1.9 (s, Si(*C*H_3)$_3$); 17.1 (s, Si*C*H$_2$); 17.5 (s, SiCH$_2$*C*H$_2$);119.2 (t, 1–Ar–*C*, $^2J_{CF}$ = 19.2 Hz); 137.8 (dm, Ar–*C*, $^1J_{CF}$ = 248.7 Hz); 145.7(dm, 4–Ar–*C*, $^1J_{CF}$ = 247.3 Hz); 150.6 (dm, Ar–*C*, $^1J_{CF}$ = 247.8 Hz).

Trimethyl(2,3,4,5,6-pentafluorophenyl)silane (8). Synthesized according to General Procedure for catalytic C–H bond silylation. Pentafluorobenzene (0.083 g, 0.498 mmol), trimethyl(vinyl)silane (0.05 g, 0.498 mmol), and **1b** (0.010 g, 0.025 mmol, 5 mol %). The NMR tube was flame sealed under vacuum and solution was fully immersed in an oil bath at 120 °C for 7 h. (98 % yield by NMR spectroscopy). ^{1}H NMR (C_6D_6, 25 °C, 500.12 MHz): δ 0.21 (t, 9H, Si(C*H*$_3$)$_3$, $^5J_{HF}$ = 1.4 Hz). ^{19}F{^{1}H} NMR (C_6D_6, 25 °C, 470.59 MHz): δ -127.8 (AA′MM′N second order m, 2F, 2,6–Ar–*F*); -152.2 (tt, 1F, 4–Ar–*F*, $^3J_{FF}$ = 20.6 Hz, $^4J_{FF}$ = 3.5 Hz); -161.5 (AA′MM′N second order m, 2F, 3,5–Ar–*F*). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 470.59 MHz): δ 0.3 (t, Si(*C*H_3)$_3$, $^4J_{CF}$ = 2.9 Hz); 111.2 (t of apparent quartets, 1–Ar–*C*, $^2J_{CF}$ = 33.2 Hz, $^3J_{CF}$ = 3.7 Hz, $^4J_{CF}$ = 3.7 Hz); 138.9 (dm, Ar–*C*, $^1J_{CF}$ = 251.3 Hz); 143.5 (dtt, 4–Ar–*C*, $^1J_{CF}$ = 253.3 Hz, $^2J_{CF}$ = 12.9 Hz, $^3J_{CF}$ = 6.2 Hz); 150.6 (dm, Ar–*C*, $^1J_{CF}$ = 253.4 Hz). ^{29}Si{^{1}H} NMR (C_6D_6, 27 °C, 59.64MHz): δ -1.4 (ttd, 1–Ar–*Si*, $^3J_{SiF}$ = 2.9 Hz, $^4J_{SiF}$ = 1.8 Hz, $^5J_{SiF}$ = 1.1 Hz).

[^{i}Pr$_2$Im]$_2$Ni(η^2-H$_2$C=CHSiMe$_3$) (9). Ni(COD)$_2$ (0.595 g, 2.16 mmol, 1 equiv) was dissolved in 10 mL of toluene. 1,3-Di(isopropyl)imidazol-2-ylidene (0.658 g, 4.32 mmol, 2 equiv) and trimethyl(vinyl) silane (0.217 g, 2.16 mmol, 1 equiv) were added and the solution was stirred for 30 minutes. The solution was evaporated in vacuo leaving 0.950 g of a bright yellow solid (95 % yield). Compound **9** was recrystallized from pentane at –40 °C. ^{1}H NMR (C_6D_6, 25 °C, 500.133 MHz): δ 0.3 (s, 9H, Si(*C*H_3)$_3$); 0.97 (broad fluxional multiplet, 12H, [CH(*C*H_3)$_2$]$_2$); 1.16 (d, 6H, CH(*C*H_3)$_2$, $^3J_{HH}$ = 6.8 Hz); 1.19 (d, 6H, CH(*C*H_3)$_2$, J_{HH} = 6.8 Hz); 1.37 (dd, 1H, vinyl–C*H*, $^3J_{HH}$ = 12.2 Hz, $^3J_{HH}$ = 13.6 Hz); 1.66 (dd, 1H, vinyl–C*H*, $^3J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 13.6 Hz); 2.16 (dd, 1H, vinyl–C*H*, $^3J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 12.2 Hz); 5.38 (septet overlapped with broad multiplet, 4H, C*H*, $^3J_{HH}$ = 6.8 Hz); 6.42 (s, 2H, *H*C=C*H*); 6.42 (s, 2H, *H*C=C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 23 °C, 75.48 MHz): δ 1.8 (s, Si(*C*H_3)$_3$); 22.7 (s, isopropyl–(*C*H_3)$_2$); 23.5 (s, isopropyl–(*C*H_3)$_2$); 28.2 (s, vinyl–*C*); 29.0 (s, vinyl–*C*); 50.7 (s, isopropyl–*C*H); 114.7 (s, H_2C=*C*H_2); 202.0 (s, Ni–*C*); 202.6 (s, Ni–*C*). ^{29}Si{^{1}H} NMR (C_6D_6, 27 °C, 59.64MHz): δ 7.39 (s, *Si*(CH_3)$_3$). Calcd for $C_{23}H_{44}N_4NiSi$: % C 59.61; % H 9.57; % N 12.09. Found: % C 59.29; % H 9.92; % N 12.07.

Reaction of C$_6$F$_5$D and 3 equivalents of H$_2$C=CHSiMe$_3$ with 5% [^{i}Pr$_2$Im]Ni(η^2-H$_2$C=CHSiMe$_3$)$_2$ (1b). A solution of C_6F_5D (0.083 g, 0.498 mmol) and trimethyl(vinyl)silane (0.150 g, 1.49 mmol, 3 equivalents) in 0.4 g of toluene was added to **1b** (0.010 g, 0.024 mmol, 5 mol %). The solution was put in a J-Young tube, heated in the NMR probe, and tracked by ^{2}H NMR. Deuterium scrambling was observed into the 1 and 2 sites of free H_2C=CHSiMe$_3$ at 90 °C after 5 minutes. The ^{2}H spectrum was modelled, and it was determined that the ratio of deuterium scrambling into the 1 and 2 sites was 4:1:1 respectively. (See supporting information Figure S1).

Reaction of C$_6$F$_5$H and H$_2$^{13}C=CHSiMe$_3$ with 35% [^{i}Pr$_2$Im]Ni(η^2-H$_2$C=CHSiMe$_3$)$_2$ (1b). A solution of C_6F_5H (0.012 g, 0.007 mmol) and H$_2$^{13}C=CHSiMe$_3$ (0.007 g, 0.070 mmol) in 0.6 g of toluene was added to **1b** (0.010 g, 0.002 mmol, 35 mol %) in a J-Young tube. The solution was heated

in the NMR probe, and after 10 minutes at 110 °C the $^{13}C\{^1H\}$ NMR showed scrambling of the carbon-13 label into H_2C=CHSiMe, forming $H_2C=^{13}CHSiMe_3$. (See supporting information, Figure S58).

Reaction of C_6F_5D and 3 equivalents of H_2C=CHSiMe$_3$ with 5% [IPr]Ni(η^2-H_2C=CHSiMe$_3$)$_2$ (1a). A solution of C_6F_5D (0.083 g, 0.498 mmol) and trimethyl(vinyl)silane (0.150 g, 1.49 mmol, 3 equivalents) in 0.4 g of toluene was added to **1b** (0.016 g, 0.024 mmol, 5 mol %). The solution was put in a J-Young tube, heated in the NMR probe, and tracked by ^2H NMR. Deuterium scrambling was observed into the 1 and 2 sites of free H_2C=CHSiMe$_3$ at 80 °C after 5 minutes. The ^2H spectrum was modelled and it was determined that the ratio of deuterium scrambling into the 1 and 2 sites was 3:1:1 respectively. (See supporting information, Figure S2).

Reaction of $H_2{}^{13}C=^{13}CH_2$ with C_6F_5H, H_2C=CHSiMe$_3$ and 5% [IPr]Ni(η^2-H_2C=CHSiMe$_3$)$_2$ (1a). Doubly labeled carbon-13 ethylene was vacuum transferred to a 5 mL flask (0.208 mmol), and subsequently vacuum transferred to a J-Young tube charged with pentafluorobenzene (0.083 g, 0.498 mmol), trimethyl(vinyl)silane (0.05 g, 0.498 mmol), and **1b** (0.016 g, 0.025 mmol, 5 mol %). The solution was heated at 90 °C for 6 h and $^{13}C\{^1H\}$ NMR showed scrambling of the carbon-13 label into H_2C=CHSiMe$_3$, forming $H_2{}^{13}C=^{13}CHSiMe_3$. (See supporting information, Figure S59).

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI:

Includes full experimental details, NMR data and spectra for new compounds, description of all catalytic and mechanistic studies.

X-ray crystallographic file for **1a**.

X-ray crystallographic file for **1b**.

X-ray crystallographic file for **9**.

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Notes

The authors declare no competing financial interest.

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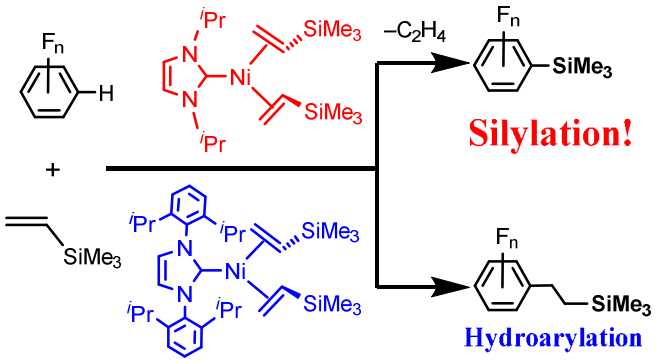
Table of Contents Artwork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