10-5-2017

Catalytic C–H Bond Functionalization by Nickel(0) N-Heterocyclic Carbene Complexes: Influence of Ligand Sterics on Selective Silylation

Matthew Ryan Elsby
University of Windsor

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Catalytic C–H Bond Functionalization by Nickel(0) N-Heterocyclic Carbene Complexes: Influence of Ligand Sterics on Selective Silylation

By

Matthew Ryan Elsby

A Thesis
Submitted to the Faculty of Graduate Studies
Through the Department of Chemistry and Biochemistry
In Partial Fulfillment of the Requirements for
The Degree of Masters of Science
At the University of Windsor

Windsor, Ontario, Canada

2017

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Catalytic C–H Bond Functionalization by Nickel(0) N-Heterocyclic Carbene Complexes: Influence of Ligand Sterics on Selective Silylation

by

Matthew Ryan Elsby

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S. Johnson, Advisor
Department of Chemistry and Biochemistry

August 21, 2017
DECLARATION OF CO-AUTHORSHIP / PREVIOUS PUBLICATION

I. Co-Authorship

I hereby declare that this thesis incorporates material that is result of joint research, as follows: Chapter 2 contains results published in an article titled “Nickel-Catalyzed C–H Silylation of Arenes with Vinylsilanes: Rapid and Reversible β-Si Elimination” (Elsby, M. R.; Johnson, S. A. J. Am. Chem. Soc. 2017, 139(27), 9401-9407. I performed all of the synthesis and mechanistic studies presented in this publication, and co-authored it with my advisor Dr. Samuel A. Johnson. I have obtained written permission to include this work in my thesis.

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<th>Publication status</th>
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ABSTRACT

The reaction of $C_6F_5H$ and $H_2C=CHSiMe_3$ with catalytic amounts of the Ni(0) complex, $[^{1}Pr_2Im]Ni(\eta^2-H_2C=CHSiMe_3)_2$, forms the C–H silylation product $C_6F_5SiMe_3$ exclusively, with ethylene as a byproduct ($[^{1}Pr_2Im] = 1,3$-(diisopropyl)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. The analogous reaction with $[IPr]Ni(\eta^2-H_2C=CHSiMe_3)_2$ provided only the alkene hydroarylation product $C_6F_5CH_2CH_2SiMe_3$ ($[IPr] = 1,3$-bis[2,6-diisopropylphenyl]-1,3-dihydro-2H-imidazol-2-ylidene]. Mechanistic studies show that the C–H activation and $\beta$-Si elimination steps are reversible under catalytic conditions with both Ni(0) catalysts, and tuning steric bulk on the ancillary carbene ligand plays a major role in reactivity of the catalysts.

The IBn and IMes carbene ligands have similar electronic parameters to IPr and $[^{1}Pr_2Im$, but varied $\% V_{bb}$ [$(IBn) = 1,3$-dibenzyl-1,3-dihydro-2H-imidazol-2-ylidene], [$(IMes) = 1,3$-bis[2,4,6-trimethylphenyl]-1,3-dihydro-2H-imidazol-2-ylidene]. Studies were performed by reacting $C_6F_5H$ and $H_2C=CHER_3$ ($ER_3 = SnBu_3$, SnPh_3, GePh_3, SiMe_3) with catalytic amounts of Ni(COD)_2 and the carbene ligands IPr, IMes, IBn, and $[^{1}Pr_2Im$. Catalytic C–H stannylation was facile with all ligands except for one anomaly. The correspondingly more difficult C–H germylation and C–H silylation reactions could form selective germylation and silylation products by using the small IBn and $[^{1}Pr_2Im$ carbene ligands. Using the larger IPr or IMes carbenes resulted in either a mixture of germylation/silylation and hydroarylation products, or exclusive conversion to the hydroarylation product.
ACKNOWLEDGEMENTS

My mother, Maria, for the unconditional love and support; for all the tea that fuelled me; for selflessly always putting me first; and for everything you have ever done and will do for me.

My father, Rick, for your unwavering trust and belief in my pursuits; for all the road trips, the battles of wit, and sarcastic comments; for the years of an unfathomable amount of hard work to provide me with any life I could have possibly imagined; and for molding me into the man I am today.

Dr. Sam Johnson, for taking in a second-year undergrad; for always having your door open; for your guidance and infectious enthusiasm for our work; for teaching me how to write, how to think, and how to intelligently approach any problem I face; and for being a true mentor.

Manar, for all the coffees and memories in the lab; for always going above and beyond to help me with any problem I came across; for chemistry talks that led to new ideas and kept me inspired; and for being the ideal role model and someone I will always aspire to emulate.

The Johnson Group, for the comradery developed over the years that made the research group a genuine pleasure to be a part of.

Dr. Charles Macdonald, for being on my committee and being a great professor over the course of my undergraduate and graduate studies.

Dr. Matt Revington, for diligently helping me when the NMR spectrometers were down, and for always being available for my inquiries.

Marlene, for making this whole process happen despite the tight timeline
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<tr>
<td>q</td>
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qd quartet of doublets (NMR spectroscopy)
R hydrocarbyl
$R$ reliability factor (X-ray crystallography)
Reflns reflections (X-ray crystallography)
$\sigma$ estimated standard deviation (X-ray crystallography), or sigma-bonding
s singlet
t triplet (NMR spectroscopy)
td triplet of doublets (NMR spectroscopy)
tm triplet of multiplets (NMR spectroscopy)
tt triplet of triplets (NMR spectroscopy)
T temperature in Kelvin or °C
THF tetrahydrofuran
TMS trimethylsilane
TON turnover number
V unit cell volume
$W_{1/2}$ width at half height
X halide substituent (or donor with negative charge)
Z asymmetric units per unit cell (X-ray crystallography)
Chapter 1 – Towards Catalytic C–H Bond Silylation with Inexpensive Nickel Catalysts

1.1 C–H Bond Activation & Functionalization

1.1.1 General Introduction and Brief History

A challenge in chemistry is the discovery of novel pathways for the conversion of inert compounds into more reactive species for utilization in pharmaceutical, agrochemical, petrochemical, and polymer industries.¹ Synthetic chemistry is traditionally based on the formation of carbon–carbon bonds to construct complex organic frameworks.² Reactions that facilitate the formation of carbon–carbon or carbon–heteroatom bonds³ are some of the most ubiquitous and useful chemical processes, such as Pd-catalyzed cross-coupling,⁴ shown in Scheme 1.1, which was awarded the Nobel Prize in Chemistry in 2010. This process occurs through the reaction of an organic electrophile with an organometallic
nucleophile facilitated by a palladium catalyst, and offers an efficient route towards organic complexes.

\[
\text{R} \rightarrow [\text{M}] + \text{R}_1\text{X} \xrightarrow{\text{Pd catalyst}} \text{R} - \text{R}_1 + [\text{M}] - \text{X}
\]

\( R = \text{alkyl, aryl} \)
\( X = \text{Cl, Br, I, OTf} \)

<table>
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<tr>
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<tr>
<td>Mg/Li</td>
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<tr>
<td>Zn/Al/Zr</td>
<td>Negishi</td>
</tr>
<tr>
<td>Sn</td>
<td>Stille</td>
</tr>
<tr>
<td>B</td>
<td>Suzuki-Miyaura (base activated)</td>
</tr>
<tr>
<td>Si</td>
<td>Hiyama-Denmark (base/flouride activated)</td>
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**Scheme 1.1.** General reaction scheme for Pd-catalyzed cross coupling reaction.

Over the past 50 years the direct functionalization of C–H bonds via transition metal catalysis has emerged as an invaluable technique for the installation of a plethora of functional groups for further reactivity.\(^5\) The activation and functionalization of conventionally inert C–H bonds offers an atom economical path towards organic reagents with numerous applications, such as cross coupling chemistry.\(^{1a, 5f, 6}\) The high bond dissociation energy of C–H bonds (110 kcal/mol) makes direct activation difficult.\(^7\) Traditional methods for activation typically require a prefunctionalization, such as halogenation.\(^{1f}\) Alternatively, an electron withdrawing group (EWG) proximal to a C–H bond makes it acidic enough for classic deprotonation, generating a nucleophile to further react with an electrophile, forming new carbon–heteroatom bonds. Furthermore, C–H bonds can be cleaved by a variety of radicals, or electrophilic aromatic substitutions can install functional groups at the C–H site.\(^{1g}\)
C–H bond activation is the cleavage of a C–H bond via a sigma-adduct intermediate resulting in the formation of a new M–C and M–H bond, also known as an oxidative addition reaction, shown in Scheme 1.2. Other mechanisms of C–H activation, shown in Scheme 1.2, include electrophilic activation, and ligand to ligand hydrogen transfer (LLHT). The distinguishing feature of C–H activation is the key formation of the sigma-adduct intermediate through which the reaction proceeds. Jones and coworkers showed that stronger aryl C–H bonds (110 kcal/mol) are preferentially activated over weaker alkane C–H bonds (96-102 kcal/mol). This is due to the propensity of stronger C–H bonds to form even stronger M–C bonds yielding the overall reaction more thermodynamically favorable.

Scheme 1.2. General mechanisms for C–H bond activation via: A) electrophilic activation, B) oxidative addition, C) ligand to ligand hydrogen transfer (LLHT).
Chapter 1 – Towards Catalytic C–H Bond Silylation with Inexpensive Nickel Catalysts

The first report of C–H activation is often credited to Chatt. In 1965, he observed the oxidative addition of a C–H bond in naphthalene forming a Ru(0) phosphine complex, [Ru(dmpe)_2], shown in Scheme 1.3, (dmpe = 1,2-bis(dimethylphosphino)ethane). This was followed with several advances by Shilov and Shulpin, who reported the platinum-catalyzed halogenations of alkanes. Simultaneously, Fujiwara was independently investigating the formation of carbon–carbon bonds via C–H cleavage of aromatic and aliphatic C–H bonds. Despite these developments, C–H activation did not garner much interest until the 1980’s following Bergman’s breakthrough report of the first transition metal catalyzed intermolecular C–H activation of unactivated and saturated hydrocarbons, shown in Scheme 1.3. Photolysis of Cp*Ir(PMe_3)H_2 facilitates the oxidative addition of hexane to form the activated iridium-alkyl hydride species, Cp*Ir(PMe_3)HR, where R = hexane. These early examples of stoichiometric C–H bond activation laid the groundwork for future experimental design.
Scheme 1.3. A) Stoichiometric C–H activation of naphthalene by a ruthenium complex. B) Stoichiometric C–H activation of hexane with an iridium complex.

1.1.2 Challenges of C–H Bond Activation & Functionalization: Recent Advances

The pursuit of catalytically functionalizing C–H bonds is often justified as a movement towards green and sustainable chemistry.\textsuperscript{1g} Though there are several examples of C–H bond functionalization which eliminate the need for two functionalized reagents,\textsuperscript{12} few cases truly demonstrate a green synthetic approach. This is because most C–H functionalization reactions require one or several of the following: silver or copper oxidants; additives such as salts, acids, or bases which remain as by-products; commercially available, but expensive ligands; or high loadings of expensive catalysts with complex ligands. There are several further problems in C–H functionalization.\textsuperscript{1h} Often a molecule contains more than one C–H bond, leading to multiple possible activation sites. Monofunctionalization of a C–H bond would greatly aid in the ability to design and synthesize compounds. Correspondingly, the capability to control site selectivity is desired.
A system that can functionalize one C–H bond is likely reactive enough to functionalize multiple sites, leading to a mixture of products. Another challenge is the functionalization of unactivated C–H bonds. Many instances of C–H activation exploit a variety of possible factors that activate the C–H bond, making it stronger and therefore easier to functionalize. Despite these current limitations, C–H bond functionalization remains a viable and cutting edge synthetic strategy for the preparation of complex molecules or smaller building blocks in fewer steps than would be required by traditional methods.13

Despite these common problems, the functionalization of C–H bonds has steadily evolved into a powerful technique commonly utilized by the synthetic community. This has lead to constant improvement to subvert the challenges of C–H functionalization. To expand the scope so that directing groups are not needed, carboxylic acids are used as traceless directing groups which can be removed in a one pot synthesis following C–H functionalization.14 Larrosa et al reported the ruthenium catalyzed C–H arylation of perfluoroarenes and selectivity relied upon electronic and steric factors.15 The discovery of frustrated lewis pairs (FLP’s) has given rise to a new pursuit of “transition metal free catalysis” to replace catalysis by expensive heavy metal complexes. 16 Fontaine et al. demonstrated the C–H bond activation and subsequent dehydrogenative borylation of a series of heteroarenes catalyzed by the borane (1-TMP-2-BH2-C6H4)2.17 Although these reports provide great ingenuity, they still take advantage of activated C–H bonds. To continue to make progress towards a truly green synthetic approach by using abundant and inexpensive atom economical catalysts, with mild reaction conditions and great selectivity, to produce versatile functionalized products; new strategies must be employed.
1.1.3 Challenge in Using Inexpensive 1st Row Transition Metals

While the past 50 years have brought forth countless instances of C–H functionalization, the majority of examples employ expensive 2nd and 3rd row transition metals such as Pt, Pd, Rh, and Ir. Developing efficient methodologies for C–H activation with 1st row transition metals is more sustainable and economically beneficial, however, this prospect faces a fundamental challenge. The thermodynamic driving force of C–H bond activation relies on the formation of strong M–C bonds. The strength of M–C bonds with 1st row transition metals are significantly lower than that of their heavier congeners. There has been an increase in the use of 1st row metals in C-H bond functionalization, however, the field is still dominated by the heavier transition metals.

1.2 Overview of Nickel Chemistry

1.2.1 Properties of Nickel

Nickel is an abundant group 10 first row transition metal and is approximately 2000 and 10,000 times cheaper than its heavier congeners, palladium and platinum. Nickel is a relatively electropositive late transition metal, aiding in facile oxidative addition; however, the microscopic reverse reductive elimination is correspondingly more difficult. Nickel has 10 d-electrons in a neutral Ni(0) species and can exist in several oxidation states. Catalytic cycles generally utilize nickel in its most common oxidation states, Ni(0) and Ni(II). Though less common, Ni(I) and Ni(III) are accessible oxidation states that allow different mechanisms of reactivity. Though rare, there have also been reports of Ni(IV) species. Nickel in the Ni(II) oxidation state adopts a variety of geometries, with the most common being square planar and octahedral; less common arrangements like trigonal planar are also utilized in catalysis. Reactions using nickel...
frequently proceed through either a 16 or 18 electron species. For instance, the oxidative addition of a substrate to a 14 electron Ni(0) complex forms a stable 16 electron square planar Ni(II) complex, which is perfectly suited for subsequent reductive elimination. Figure 1.1 displays examples of nickel complexes in a variety of geometries and oxidation states.

Figure 1.1. Isolable nickel complexes in a variety of oxidation states and coordination geometries: A) Nickel in the common Ni(0) and Ni(II) oxidation states. B) Nickel in the more rare Ni(I), Ni(III), and Ni(IV) oxidation states.

1.2.2 Nickel in C–H Bond Activation: Thermodynamic Considerations

Though oxidative addition with nickel compounds is more facile than related palladium and platinum complexes for certain processes, this trend does not apply to the
mechanistically distinct C–H activation reaction. A seminal computational study evaluated and quantified the thermodynamic barrier towards C–H activation with a hypothetical Ni(0) complex. The DFT results demonstrated that the activation barrier for oxidative addition of the C–H bond of benzene to a Ni(H₂PCH₂CH₂PH₂) complex is 21.3 kcal mol⁻¹, with the overall reaction being disfavored by 20.4 kcal mol⁻¹, shown in Figure 1.2.

*Figure 1.2.* Summary of DFT calculations for the oxidative addition of benzene to Ni Ni(H₂PCH₂CH₂PH₂), showing activation barrier and overall reaction energies. Adapted from ref. 28.

The DFT study provides an intrinsically significant comparison to the analogous C–F bond activation reaction. It was shown that though the oxidative addition of C₆F₆ to Ni(H₂PCH₂CH₂PH₂) is ultimately favored by −19.7 kcal mol⁻¹; the calculated activation barrier is 22.5 kcal mol⁻¹. There are numerous literature examples of facile C–F bond activation facilitated by Ni(0) complexes, in stark contrast to those of C–H activation. The activation barrier for C–F activation in this instance is slightly higher than that of the corresponding C–H activation, suggesting that despite the high activation energy of the reaction, nickel C–H bond activation products should be kinetically accessible.

9

*References being on page 24*
1.2.2.1 – Observing C–H Bond Activation by a Ni(0) Complex: The ortho-Fluorine Effect

In 2008 the Johnson group investigated the reactivity of the Ni(PEt$_3$)$_2$ moiety towards C–H bond activation. The reduction of NiBr$_2$(PEt$_3$)$_2$ in the presence of phenanthrene provided a synthon for the reactive Ni(0) moiety (1). The reaction of 1 with 1,2,4,5-tetrafluorobenzene provided conversion to the C–F activation products, however, investigating the early stage of the reaction showed an initial equilibrium producing the kinetic C–H activation product, Ni(PEt$_3$)$_2$(H)(2,3,5,6-C$_6$F$_4$H) (2), shown in Scheme 1.4.$^{30}$ Despite observing the kinetic C–H oxidative addition product by NMR, the product was not isolable since it existed in an equilibrium of mononuclear and dinuclear species and reactants. It was later shown that increasing the steric bulk of the phosphine ancillary ligand, making compound (3), and performing the analogous reaction allowed for the isolation of the C–H bond oxidative addition Ni-complex trans-(P$^{i}$Pr$_3$)$_2$NiH(2,3,5,6-C$_6$F$_4$H) (4), as seen in Scheme 1.4.$^{31}$
A) 
\[(\text{Et}_3\text{P})_2\text{Ni}(\eta^2\text{-C}_{14}\text{H}_{10}) + \text{F}_2\text{C}_6\text{F}_4\text{H}_2 \rightleftharpoons \text{F}_2\text{C}_6\text{F}_4\text{H}_2\quad \text{Ni-H} \]

\[\eta^2\text{-C}_{14}\text{H}_{10} = \begin{array}{c}
\text{} \\
\text{} \\
\end{array}\]

B) 
\[(\text{Pr}_3\text{P})_2\text{Ni}(\eta^2\text{-C}_{14}\text{H}_{10}) + \text{F}_2\text{C}_6\text{F}_4\text{H}_2 \rightarrow \text{RT, 6 h} \]

\[\eta^2\text{-C}_{14}\text{H}_{10} = \begin{array}{c}
\text{} \\
\text{} \\
\end{array}\]

**Scheme 1.4.** A) Early observation of C–H activation of 1,2,4,5-C_{6}F_{4}H_{2} with (Et_{3}P)_{2}Ni(\eta^{2}\text{-C}_{14}\text{H}_{10}); B) Analogous C–H activation of 1,2,4,5-C_{6}F_{4}H_{2}, except with (Et_{3}P)_{2}Ni(\eta^{2}\text{-C}_{14}\text{H}_{10}) to allow for the isolation of \text{trans-}(\text{Pr}_{3}P)_{2}\text{NiH}(2,3,5,6-\text{C}_{6}F_{4}H).

These examples made use of a highly fluorinated aromatic substrate, as opposed to benzene, which makes use of several factors regarding the thermodynamic and kinetic propensity for C–H bonds to undergo oxidative addition. It is well documented that C–H bonds in fluorinated aromatics are more reactive towards oxidative addition than those in benzene.\textsuperscript{1b, 32} It has been shown that C–H bonds bearing ortho-fluorine substituents are strongly activated, making oxidative addition more thermodynamically accessible.\textsuperscript{33} This is because C–H bonds with ortho-fluorines have higher bond dissociation energies, and after C–H bond activation via an oxidative addition pathway, even stronger M–C bonds are made, yielding the overall reaction more thermodynamically favorable. Although the

References being on page 24
previous examples took advantage of highly activated C–H bonds in 1,2,4,5-C₆F₄H₂, the work provided early proof that Ni(0) was indeed capable of C–H bond activation, and should also be able to facilitate functionalization.

1.2.3 Potential Application of C–H Bond Functionalization of Fluorinated Aromatics

The selective activation and functionalization of C–H bonds in partially fluorinated aromatics catalyzed by transition metal complexes is a potential route towards synthesis of partially fluorinated organics which have extensive use in pharmaceuticals and agrochemicals. Fluorine atoms are only slightly larger than hydrogen, and while the substitution of a fluorine atom in place of a hydrogen has minor effects on the size and conformation of molecules, it has the potential to dramatically impact the physical properties of a compound.

The benefits of partial fluorination on the efficacy of pharmaceutical drugs is well documented. Upon introduction of a fluorine atom into a compound, the physical properties observed to have been affected include: slowed metabolism, improved lipophilicity, and changes in acidity and basicity.

Several examples of common fluorine containing pharmaceuticals are shown in Figure 1.3. Pharmaceuticals containing a single fluorine substituent on an aryl moiety are the most common, however, there are examples of drugs containing two fluorine atoms, such as Fluconazole, where fluorine substituents are in the 2,4- position. Furthermore, there are numerous drugs with anticancer properties that contain aromatic rings bearing
two fluorines in the 2,6- or 3,4- positions such as sitagliptin, a drug used by individuals with Type 2 diabetes.\textsuperscript{37}

![Fluorouracil, sitagliptin, Fluconazole, and Fluconazole](image)

**Figure 1.3.** Four examples of fluorinated organics with medicinal applications, including Fluconazole, a compound with two fluorine substituents.

Transition metal catalysts have potential to facilitate the selective conversion of commercially available fluorinated substrates into these versatile pharmaceutical compounds via C–H bond functionalization.\textsuperscript{32} These reactions are traditionally facilitated by the expensive 2\textsuperscript{nd} and 3\textsuperscript{rd} row transition metals, however, it has been shown that cheaper alternative 1\textsuperscript{st} row metals such as nickel are capable of performing C–H bond activation. The example discussed previously (Section 1.2.2.1) takes advantage of two fluorine substituents ortho to the activated C–H bond. While these aromatic substrates with a higher degree of fluorination do not offer the same widespread application as those with a lesser degree of fluorination, intelligent catalyst design can lead to the functionalization of these desired substrates with more economical metals.
1.2.4 Catalytic C–H Bond Functionalization with Nickel

In 2010, Johnson et al provided the first instance of Ni-catalyzed C–H bond stannylation of a plethora of perfluoroarenes, shown in Scheme 1.5. The reaction of stoichiometric amounts of a fluorinated arene and H₂C=CHSnBu₃ with catalytic amounts of Ni(COD)₂ and iPr₃P at 80 °C, results in the functionalized stannylation product with only ethylene as a byproduct, shown in Scheme 1.5 (COD = 1,5-bis-cyclooctadiene). Ligand choice significantly impacts the reaction conditions and scope, with the zwitterionic neutral quasi amido donor [NQA] ligand capable of facilitating the stannylation reaction at room temperature with a limited scope, and iPr₃P performing stannylation of a wider substrate scope at elevated temperatures. This reaction provides an efficient route towards organostannanes desired for their utility in Stille coupling.

![Scheme 1.5. Ni-catalyzed C–H bond stannylation of fluorinated aromatics.](image)

It was found that the resting state of the catalyst is the Ni(0) complex, [iPr₃PNi[η²-(H₂C=CHSnBu₃)₂]] (C1). A proposed mechanism for the C–H bond stannylation reaction is shown in Scheme 1.6. The first step A is the reversible dissociation of the vinyl moiety to give C2. This is followed by C–H activation, step B, via LLHT which is proposed to proceed through the transition state C3. The Ni intermediate C4 featuring a β-agostic hydrogen undergoes β-Sn elimination step C, resulting in the loss of ethylene gas and the
formation of C5. Final reductive elimination step D forms the silylation product, and regenerates the Ni(0) catalytic species.

Scheme 1.6. Proposed mechanism for catalytic C–H bond stannylation of C6F5H.

Follow up work in expanding the R substituents on the vinyl tin moiety led to unexpected results. The reaction of Ni(COD)2 and the NQA ligand with 2 equivalents of H2C=CHSnPh3 led to the expected Ni(0) complex [NQA]Ni[η2-(H2C=CHSnPh3)] (C1Ph).

Upon reaction of catalytic amounts of C1Ph with C6F5H and H2C=CHSnPh3, the resulting product was the alkene hydroarylation product, C6F5CH2CH2SnPh3.40 Whereas previous work with H2C=CHSnBu3 and 1Pr3P, or NQA, led to exclusively silylation products, the
combination of the [NQA] ligand with a different R group led to a completely different product. The results are summarized in Scheme 1.7. This reaction was proposed to occur via direct C–C reductive elimination from intermediate C4 along the proposed catalytic pathway shown in Scheme 1.6.

Scheme 1.7. General reaction of C₆F₅H and H₂C=CHSnPh₃ with the nickel catalyst [L]Ni[η²-(H₂C=CHSnR₃)]₂ leading to either C–H stannylation product, or alkene hydroarylation product.

A mechanistically similar instance of Ni-catalyzed C–H bond functionalization was reported in 2015 by Hartwig et al.⁴¹ They reported the alkene hydroarylation of a series of olefins with arenes featuring unactivated C–H bonds, selectively forming a linear alkyl arene functionalized product, shown in Scheme 1.8. The reaction occurred at 100 °C for 5-12 h and also used Ni(COD) as the Ni(0) source starting material with the N-heterocyclic-carbene (NHC) ligand IPR-HCl (IPr = 1,3-bis[2,6-diisopropylphenyl]-1,3-dihydro-2H-imidazol-2-ylidene). Furthermore, a similar resting catalyst state was found when using norbornene as the olefin source. This methodology was then extended to allow the
hydroarylation of a multitude of heteroarenes featuring activated C–H bonds. These examples offer a unique mechanistic manifold under which C–H bond functionalization can occur.

\[ \text{F}_3\text{C} \quad + \quad \text{n-hex} \quad \xrightarrow{20\% \text{ Ni(COD)}_2, 40\% \text{IPr-HCl, Na}^+\text{BuO, THF, 100 °C, 16 h}} \quad \text{F}_3\text{C} \quad \text{n-hex} \]

Scheme 1.8. Ni-catalyzed alkene hydroarylation of olefins to unactivated arenes.

1.3 C–H Bond Silylation

1.3.1 General Overview

The transition metal catalyzed functionalization of C–H bonds provides an efficient route from inactivated organic stock feeds to functionalized compounds.\textsuperscript{1f, 8} The catalytic silylation of C–H bonds enables preparation of an array of organosilicon compounds desired because, as opposed to tin, they are environmentally benign, economical, and have great utility in Hiyama-Denmark cross coupling reactions.\textsuperscript{43} Formation of C–Si bonds traditionally use either organolithium or Grignard reagents with silicon electrophiles. This option has low functional group tolerance making the use of protecting groups necessary. Alternatively, aryl silanes can be prepared by transition metal catalyzed cross coupling of aryl halides with hydrosilanes or disilanes. While this approach circumvents the functional group tolerance issue, it requires the prefuctionalization of the aryl substrate, limiting regioselectivity of the subsequent silylation.\textsuperscript{44}
The general mechanism for C–H bond silylation catalyzed by transition metals from traditionally Groups 8 and 9, is shown in Scheme 1.6. Following oxidative addition of the C–H bond by the metal-silyl fragment, step A, reductive elimination step B forms the desired silylation product. Addition of the H–Si (or Si–Si) bond to the metal regenerates the metal silyl species, step C, and the catalyst is reformed after the hydrogen byproduct is either directly eliminated or transferred to a sacrificial hydrogen acceptor, step D.

Scheme 1.9. General mechanism for silylation of C–H bonds.

The widespread application of C–H bond silylation to synthetic chemistry has been limited by the inefficiency of the reaction. Many instances of catalytic silylation depend on the use of a stoichiometric amount of sacrificial hydrogen acceptor. Furthermore, numerous examples require a large excess of substrate relative to the silane, or harsh reaction conditions. Finally, as with C–H bond activation, selectivity of the reaction is either
dependent upon a directing group or using steric's to allow only one possible site for functionalization

1.3.2 Aryl C–H Bond Silylation

The first report of C–H bond silylation in 1982 by Curtis et al. showed the Ir-catalyzed silylation of the C–H bond in benzene with hydrosilanes to yield phenyloxysilanes. This seminal work demonstrated the potential to create new organosilane compounds via transition metal catalyzed C–H functionalization. The last 30 years have brought forth many advances in the field of C–H silylation which have been the topic of several reviews. There are 3 main types of silylation of aryl C–H bonds: Intramolecular, directed intermolecular, and undirected intermolecular. Intramolecular C–H silylation is generally efficient and does not need excess of any reagents, however, it often requires the use of a tether to connect the silane to the arene substrate. Intermolecular silylation of C–H bonds requires the pre-coordination of a directing group on the arene, but does not require tethering the silane to the arene. The majority of examples are limited to ortho selectivity. Furthermore, the directing group is not always a part of the desired product and often must be removed, diminishing step economy. The undirected intermolecular silylation of aryl C–H bonds is the most desired, however, it frequently requires harsh reaction conditions and large excess of arene substrate, with most examples yielding trialkylsilanes products which have limited utility. Example of all three classes of transition metal catalyzed C–H silylation of arenes are shown in Scheme 1.10.
The most active catalysts for C–H bond silylation are generally rhodium complexes of hindered arylbisphosphines with biaryl backbones, or iridium complexes supported by phenanthroline ligands. In 2014 Hartwig reported the Ir-catalyzed C–H silylation reaction of arenes and heteroarene with HSiMe(OSiMe$_3$)$_2$, supported by a phenanthroline derivative ancillary ligand, shown in Scheme 1.7. The reaction occurs with high...
selectivity for the most sterically accessible C–H bond and has a high functional group tolerance. Harsh reaction conditions along with requirement of sacrificial hydrogen acceptor show that despite the rapid development of this field, the most cutting-edge examples of C–H silylation still cannot overcome all of these fundamental issues.

Scheme 1.11. Ir-catalyzed C–H silylation of arenes and heteroarenes.

A mechanistically distinct example of C–H silylation was discovered by Murai and co-workers. They describe the Ru-catalyzed silylation of heteroarenes directed by a carbonyl group which uses a vinylsilane as the silicon source, as opposed to traditional hydro- or disilanes, shown in Scheme 1.8. The authors ascertain that the reaction occurs via insertion of the vinyl moiety into the Ru–H bond after C–H activation, followed by deinsertion of ethylene. The proposed mechanism through which this reaction occurs bears a strong resemblance to the Ni-catalyzed C–H bond stannylation and Ni-catalyzed alkene hydroarylation reactions previously discussed (See Scheme 1.6), perhaps indicating that the methodology in these catalytic systems could be potentially extended towards C–H silylation.
1.3.3. Research Goal: Towards C–H Bond Silylation with Nickel Catalysts

The majority of C–H bond silylation reactions are carried out by expensive noble metal catalysts.\textsuperscript{44,46} There are instances of silylation being performed by 1\textsuperscript{st} row transition metals (scandium and nickel), however, these examples require specialized circumstances.\textsuperscript{48a,52} A recent breakthrough by Grubbs \textit{et al} describes the potassium catalyzed C–H silylation of a broad scope of heteroarenes.\textsuperscript{53} While this novel report shows great promise, the extension of C–H bond silylation to cheaper and more abundant 1\textsuperscript{st} row transition metals is still its infancy. The goal of this thesis is to apply the methodology used in the Ni-catalyzed C–H stannylation reactions, and optimize the Ni(0) catalyst to extend the work into catalytic C–H bond silylation for the synthesis of organosilicon compounds, which have many benefits over their tin counterparts.

\textit{Scheme 1.12}. Ru-catalyzed C–H silylation of heteroarenes with vinyltrimethylsilane as Si source.
1.4 Scope of Thesis

This thesis contains two additional chapters that discuss C–H bond functionalization reactions with N-heterocyclic carbene supported Ni(0) catalysts and investigation into the mechanism and selectivity of these reactions. Chapter 2 details the synthesis of a nickel complex capable of facilitating the catalytic C–H silylation of partially fluorinated arenes containing two ortho-fluorine substituents, using a N-heterocyclic carbene as the ancillary ligand, which provides more thermally robust compounds. It describes a series of isotopic labelling studies that elucidate key insight into the rapid reversibility of the β-Si elimination step, leading to a greater understanding of possible rate limiting steps in the catalytic cycle. Chapter 3 discusses the effect that carbene steric bulk has on the selectivity of product formation in the catalytic system. A screening of NHC ligands is carried out to probe this phenomenon, and the affect is further investigated in analogous C–H stannylation and C–H germylation reactions. Finally, it also provides logical follow-up experiments and projects that should be conducted.
1.5 References


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Chapter 2 – Nickel-Catalyzed C–H Silylation of Arenes with Vinylsilanes: Rapid and Reversible \( \beta \)-Si Elimination

2.1 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 \( \text{ER}_3 = \text{SnBu}_3 \).\(^6\) This transformation uses readily available \( \text{H}_2\text{C} = \text{CHSnBu}_3 \) to convert a plethora of partially fluorinated aromatics
into organotin compounds suitable for Stille coupling, 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. 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 C₆F₅CH₂CH₂ER₃. Alternatively, 4 can undergo β-ER₃ elimination to form Ni(L)(C₆F₅)(ER₃)(η²-C₂H₄) (5), which could lose ethylene gas to give Ni(L)(C₆F₅)(ER₃) (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, C₆F₅ER₃.

In C–H bond stannylation, competition was observed between the two mechanistic pathways, C and D, that intermediate 4 can undergo. With E = SnBu₃ and L = iPr₃P or NQA, catalysis yielded almost exclusively the stannylation product C₆F₅SnBu₃. Using SnPh₃ with iPr₃P also led to stannylation products; however, using the [NQA] ligand with SnPh₃ resulted in a mixture of stannylation product and hydroarylation product, C₆F₅CH₂CH₂SnPh₃, with the latter being favored (95 %). Furthermore, using the IPr carbene as the ancillary ligand (IPr = 1,3-bis[2,6-diisoproplyphenyl]-1,3-dihydro-2H-imidazol-2-ylidene) resulted in similar product distributions as the {NQA} ligand.
Chapter 2 – Nickel-Catalyzed C–H Silylation of Arenes with Vinysilanes: Rapid and Reversible β-Si Elimination

\[
\text{Scheme 2.1. Proposed C–H Bond functionalization mechanism.}
\]

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Chapter 2 – Nickel-Catalyzed C–H Silylation of Arenes with Vinilsilanes: Rapid and Reversible β-Si Elimination

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 H₂C=CHSiEt₃ 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.

2.2 Results and Discussion

2.2.1 Synthesis of Nickel Complexes.

To determine if silylation could be achieved under similar conditions to stannylation,⁶ a 5 % loading of the previously reported¹¹ complex (iPr₃P)Ni(η²-H₂C=CHSiMe₃)₂ was reacted with H₂C=CHSiMe₃ and pentafluorobenzene at 80 °C for 24 h. The crude F{¹H} NMR spectrum showed 3 % conversion to the C–H silylation product, C₆F₅SiMe₃ (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 iPr₃P in the ³¹P{¹H} NMR. Heating above 80 °C resulted in rapid decomposition of (iPr₃P)Ni(η²-H₂C=CHSiMe₃)₂. Similar temperature limitations of the catalyst were noted in our previous work with C–H stannylation.⁶
The use of carbene ligands in lieu of phosphines often provides more thermally robust complexes for transition metal catalysis. The reaction of Ni(COD)$_2$ (COD = 1,5-cyclooctadiene) with IPr and two equivalents of H$_2$C=CHSiMe$_3$ forms the expected $^{10,13}$

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complex [IPr]Ni(η^2-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 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 iPr_2Im carbene ligand (iPr_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, [iPr_2Im]_2Ni(η^2-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 (iPr_2Im)_2NiF(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 ^1H NMR spectrum, consistent with the bis-vinyl species, [iPr_2Im]Ni(η^2-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 iPr_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 iPr2Im ligand, unlike the C2 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-η2-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.

2.2.2 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 H2C=CHSiMe3.
Kinetics modelling\textsuperscript{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\textsubscript{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\textsubscript{3} substituents also have only a minor electronic influence. In contrast, no silylation next to an ortho-SiMe\textsubscript{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 \textsuperscript{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,\textsuperscript{10, 17} however, instances of C–H silylation of heterocycles with any metal are limited.\textsuperscript{5a, 18} A previous report of Ni-catalyzed reactions of heterocycles

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with H₂C=CHSiEt₃, provided solely hydroarylation products;¹⁷a in contrast, the reaction of H₂C=CHSiMe₃ 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.

![Chart 2.1. C–H Silylation of fluorinated aromatics](chart)

Due to the limited utility of SiMe₃ groups in Hiyama cross coupling reactions, additional silyl groups were investigated.³b, ²⁰ The reaction of H₂C=CHSi(OEt)₃ and pentafluorobenzene with a catalytic amount of Ni(COD)₂ and iPr₂Im did not result in the

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silylation product. To investigate if C–H bond activation was occurring, C₆F₅D and H₂C=CHSi(OEt)₃ was reacted with a catalytic amount of Ni(COD)₂ and iPr₂Im, and heated at 120 °C for 12 h. The 19F{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 SiBnMe₂ 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 H₂C=CHSiBnMe₂ with a 5% catalyst loading of Ni(COD)₂ and iPr₂Im provided the silylation product C₆F₅SiBnMe₂ in poorer yield than with H₂C=CHSiMe₃ (70%), but without significant byproducts. Increased catalyst loadings improved yields.

### 2.2.3 Labeling Studies with 1b.

Unexpected mechanistic insights regarding β-Si elimination were obtained from a series of isotope labeling studies. The reaction of C₆F₅D and H₂C=CHSiMe₃ in the presence of catalytic 1b at 80 °C yielded scrambling of the D label into all the sp² 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 H₂C=CHSiMe₃ 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

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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 H₂C=CHSiMe₃ moiety.

Carbon-13 labeling studies were performed as a test for reversible β-Si elimination. The reaction of pentafluorobenzene and H₂¹³C=CHSiMe₃ with a 5 % loading of 1b was monitored using variable-temperature $^{13}$C{¹H} NMR. At 110 °C the scrambling of labels to give H₂C=¹³CHSiMe₃ 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 $^{13}$C₂H₄ was added to a solution containing pentafluorobenzene, H₂C=CHSiMe₃ 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 H₂¹³C=¹³CHSiMe₃. 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 SiMe₃ moieties; or ii) rate determining alkene loss from 5 before reductive elimination. Both possibilities are shown in the bottom left of Scheme 2.
Chapter 2 – Nickel-Catalyzed C–H Silylation of Arenes with Vinysilanes: Rapid and Reversible β-Si Elimination

A) Deuterium Scrambling - Reversible C–H Activation

\[
\text{SiMe}_3 + \overset{\text{D}}{\text{C}} \rightarrow \overset{\text{H/D}}{\text{C}} + 2 \overset{\text{H/D}}{\text{H}}
\]

initial ratio of D at 2-site : 1-site - 1:4

B) Intramolecular $^{13}\text{C}$ Scrambling - Reversible β-Si Elimination

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \overset{\text{H}_2}{\longrightarrow} \overset{\text{Me}_3\text{Si}}{\longrightarrow} \\
\text{C}_6\text{F}_5\text{H} & \quad 5 \text{ mol % } \overset{1\text{b}}{\longrightarrow} \overset{-\text{C}_6\text{F}_5\text{H}}{\longrightarrow} \\
\text{L} & \quad \overset{\text{Ni}}{\longrightarrow} \overset{\text{Ni}}{\longrightarrow} \\
\text{C}_6\text{F}_5 & \quad 4 \quad 5 \quad 4
\end{align*}
\]

C) Carbon-13 Study - Irreversible or no Alkene Loss

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \overset{\text{H}_2}{\longrightarrow} \overset{\text{Me}_3\text{Si}}{\longrightarrow} \\
\text{C}_6\text{F}_5\text{H} & \quad 5 \text{ mol % } \overset{1\text{b}}{\longrightarrow} \overset{-\text{C}_6\text{F}_5\text{H}}{\longrightarrow} \\
\text{L} & \quad \overset{[\text{Pr}_2\text{Im}]}{\longrightarrow} \overset{[\text{Pr}_2\text{Im}]}{\longrightarrow} \\
\text{C}_6\text{F}_5 & \quad 4 \quad 4 \quad 4
\end{align*}
\]

i): No alkene loss prior to C-Si reductive elimination.

\[
\begin{align*}
\text{L} & \quad \overset{\text{Ni}}{\longrightarrow} \overset{\text{Ni}}{\longrightarrow} \\
\text{C}_6\text{F}_5 & \quad 5 \\
\text{L} & \quad \overset{[\text{Pr}_2\text{Im}]}{\longrightarrow} \overset{[\text{Pr}_2\text{Im}]}{\longrightarrow} \\
\text{C}_6\text{F}_5 & \quad 4
\end{align*}
\]

ii): Irreversible alkene loss prior to C-Si reductive elimination.

\[
\begin{align*}
\text{F} & \quad \overset{\text{SiMe}_3}{\longrightarrow} \\
\text{F} & \quad \overset{\text{F}}{\longrightarrow} \\
\text{F} & \quad \overset{\text{F}}{\longrightarrow} \\
\text{SiMe}_3 & \quad 8
\end{align*}
\]

\[\text{Scheme 2.2. Isotope Labeling Studies with 1b.}\]

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2.2.4 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, C₆F₅D and H₂C=CHSiMe₃ 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 H₂C=CHSiMe₃ 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 sp² C–H bonds of the alkene. Like the previous experiments conducted with 1b, full scrambling into both the arene and H₂C=CHSiMe₃ 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, H₂C=CHSiMe₃ and doubly labeled ¹³C₂H₄ with 5 % of 1a at 90 °C results in intermolecular scrambling of the ¹³C label to give H₂¹³C=¹³CHSiMe₃ 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

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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 2.3. Isotope Labeling Studies with 1a.
2.3 Conclusions

While the application of nickel in catalysis continues to expand, 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. 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 1Pr\textsubscript{3}P, 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 [\textit{i}Pr\textsubscript{2}Im]Ni(\textit{η}\textsubscript{2}H\textsubscript{2}C=CHSiMe\textsubscript{3})\textsubscript{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.\textsuperscript{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\textsubscript{3} groups, before ethylene loss. Relatively few catalytic systems have taken advantage of β-Si elimination for the synthesis of organosilicon compounds.\textsuperscript{26,27}
2.4 Experimental

2.4.1 Materials and Methods

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–d₆, and toluene–d₈ 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, ¹³C{¹H}, ¹⁹F{¹H}, ²H and ²⁹Si{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 (C₆D₆, δ 7.15) or (toluene-d₈, δ 2.17) with respect to tetramethylsilane at δ 0.00. ¹³C{¹H} NMR spectra were referenced relative to solvent resonances (C₆D₆, δ 128.26) or (toluene-d₈, δ 21.37). ¹⁹F{¹H} NMR spectra were referenced to an external sample of 80% CCl₃F in CDCl₃ at δ 0.00. Benzene–d₆ and toluene–d₈ was purchased from Cambridge Isotope Laboratory. All reagents were purchased from commercial suppliers. The compounds Ni(COD)₂, ²⁸IPr, ²⁹IPr₂Im, ³⁰ and C₆F₅D₃₁ were prepared according to literature procedures.

2.4.2 Synthesis, Characterization, Reactivity of Complexes, and Mechanistic Studies

Synthesis of [IPr]Ni(η²-H₂C=CHSiMe₃)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 (toluene-d₈,
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25 °C, 500.129 MHz): δ -0.15 (s, 18H, Si(CH$_3$)$_3$); 0.98 (d, 6H, CH(CH$_3$)$_2$; $^3$J$_{HH}$ = 6.95 Hz); 1.10 (d, 6H, CH(CH$_3$)$_2$; $^3$J$_{HH}$ = 6.95 Hz); 1.16 (d, 6H, CH(CH$_3$)$_2$; $^3$J$_{HH}$ = 6.95 Hz); 1.50 (d, 6H, CH(CH$_3$)$_2$; $^2$J$_{HH}$ = 6.95 Hz); 2.35 (d, 2H, vinyl–H, $^2$J$_{HH}$ = 15.9 Hz); 2.51(dd, 2H, vinyl–H, $^2$J$_{HH}$ = 15.9 Hz, $^2$J$_{HH}$ = 12.8 Hz); 2.73 (d, 2H, vinyl–H, $^2$J$_{HH}$ = 12.8 Hz); 2.95 (septet, 2H, C$_2$H$_3$); 3.31 (septet, 2H, C$_2$H$_3$); 6.63 (s, 2H, H=C=CH$_2$); 7.02 (d, 3,5–Ar–C$_2$H$_3$; $^3$J$_{HH}$ = 7.58 Hz ); 7.11 (d, 3,5–Ar–C$_2$H$_3$; $^3$J$_{HH}$ = 7.58 Hz); 7.18 (t, 4–Ar–C$_2$H$_3$; $^3$J$_{HH}$ = 7.58 Hz).

$^{13}$C{$_1^1$H} NMR (C$_6$D$_6$, 22 °C, 125.75 MHz): δ 1.2 (s, 6C, Si(CH$_3$)$_3$); 22.3 (s, isopropyl–(CH$_3$)$_2$); 22.7 (s, isopropyl–(CH$_3$)$_2$); 25.6 (s, isopropyl–(CH$_3$)$_2$); 27.0 (s, isopropyl–(CH$_3$)$_2$); 29.0 (s, isopropyl–CH); 30.8 (s, isopropyl–CH); 50.5 (s, vinyl–C); 53.5 (s, vinyl–C); 124.2 (s, H$_2$C=CH$_2$); 124.3 (s, H$_2$C=CH$_2$); 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{$_1^1$H} NMR (C$_6$D$_6$, 27 °C, 59.647 MHz): δ -4.1 (s, 2Si, Si(CH$_3$)$_3$). Calcd for C$_{37}$H$_{60}$N$_2$NiSi$_2$: % 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.

Synthesis of [iPr$_2$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 all Ni(COD)$_2$ was fully dissolved. A solution of 1,3-di(isopropyl)imidazol-2-ylidene (0.74 g, 4.87 mmol) was diluted in 3 mL of toluene, and added to the reaction mixture dropwise while stirring. The solution was stirred 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 solution of HMDSO and minimal benzene, affording yellow crystals.

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Major isomer: $^1$H NMR (C$_6$D$_6$, 25 °C, 500.133 MHz): δ 0.21 (s, 18H, Si(CH$_3$)$_3$); 0.93 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH} = 6.75$ Hz); 1.01 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH} = 6.75$ Hz); 2.54 (fluxional multiplet, 2H, vinyl-$_H$); 2.69 (fluxional multiplet, 2H, vinyl-$_H$); 4.39 (septet, 2H, CH$_3$); 6.40 (s, 2H, CH=CH$_2$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 22 °C, 500.133 MHz): δ 1.1 (s, 6C, Si(CH$_3$)$_3$); 23.0 (s, 4C, isopropyl–CH$_3$); 23.6 (s, 2C, isopropyl–CH); 50.9 (s, vinyl–C); 116.6 (s, H$_2$C=CH$_2$); 198.0 (s, Ni–C). $^{29}$Si{$^1$H} NMR (C$_6$D$_6$, 27 °C, 59.647 MHz): δ -4.4 (s, 2Si, Si(CH$_3$)$_3$).

Minor isomer: $^1$H NMR (C$_6$D$_6$, 25 °C, 500.133 MHz): δ 0.14 (s, 18H, Si(CH$_3$)$_3$); 0.96 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH} = 6.75$ Hz); 0.99 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH} = 6.75$ Hz); 2.25 (dd, 2H, vinyl-$_H$, $^3$J$_{HH} = 12.58$ Hz, $^3$J$_{HH} = 16.20$ Hz); 2.53 (d, 2H, vinyl-$_H$, $^3$J$_{HH} = 16.20$ Hz); 3.19 (d, 2H, vinyl-$_H$, $^3$J$_{HH} = 12.58$ Hz); 4.39 (septet, 2H, CH$_3$); 6.41 (s, 2H, CH=CH$_2$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 22 °C, 500.133 MHz): δ 0.8 (s, 6C, Si(CH$_3$)$_3$); 23.2 (s, 4C, isopropyl–CH$_3$); 23.7 (s, 2C, isopropyl–CH); 50.9 (s, vinyl–C); 116.7 (s, H$_2$C=CH$_2$); 198.0 (s, Ni–C). $^{29}$Si{$^1$H} NMR (C$_6$D$_6$, 27 °C, 59.647 MHz): δ -4.4 (s, 2Si, Si(CH$_3$)$_3$).

Calcd for C$_{19}$H$_{40}$N$_2$NiSi$_2$: % 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.

**Synthesis of [($i$Pr$_2$Im)$_2$Ni(η$_2$-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$_6$D$_6$, 25 °C, 500.133 MHz): δ 0.3 (s, 9H, Si(CH$_3$)$_3$); 0.97 (broad

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fluxional multiplet, 12H, [CH(CH$_3$)$_2$]$_2$; 1.16 (d, 6H, CH(CH$_3$)$_2$, $^3J_{HH} = 6.8$ Hz); 1.19 (d, 6H, CH(CH$_3$)$_2$, $^1J_{HH} = 6.8$ Hz); 1.37 (dd, 1H, vinyl–CH, $^3J_{HH} = 12.2$ Hz, $^3J_{HH} = 13.6$ Hz); 1.66 (dd, 1H, vinyl–CH, $^3J_{HH} = 2.8$ Hz, $^3J_{HH} = 13.6$ Hz); 2.16 (dd, 1H, vinyl–CH, $^3J_{HH} = 2.8$ 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, CH=C=CH$_2$); 6.42 (s, 2H, CH=C=CH$_2$).

$^{13}$C{$^1$H} NMR (C$_6$D$_6$, 23 °C, 75.48 MHz): δ 1.8 (s, Si(CH$_3$)$_3$); 22.7 (s, isopropyl–(CH$_3$)$_2$); 23.5 (s, isopropyl–(CH$_3$)$_2$); 28.2 (s, vinyl–C); 29.0 (s, vinyl–C); 50.7 (s, isopropyl–CH); 114.7 (s, H$_2$C=CH$_2$); 202.0 (s, Ni–C); 202.6 (s, Ni–C). $^{29}$Si{$^1$H} NMR (C$_6$D$_6$, 27 °C, 59.64MHz): δ 7.39 (s, Si(CH$_3$)$_3$).

Calcd for C$_{23}$H$_{44}$N$_4$NiSi: % C 59.61; % H 9.57; % N 12.09. Found: % C 59.29; % H 9.92; % N 12.07.

Synthesis of 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 0.6g of toluene was added to 1a (0.039 g, 0.099 mmol, 5 mol %) and triphenyfluorosilane (0.017 g, 0.062 mmol), which was used as an internal standard. The solution was heated at 90 °C for 20 h (60 % yield by NMR spectroscopy). $^1$H NMR (C$_6$D$_6$, 25 °C, 500.12 MHz): δ 0.06 (s, 9H, Si(CH$_3$)$_3$); 0.71 (second order m, 2H, C$_H$SiMe$_3$); 2.47 (second order m, C$_H$CH$_2$SiMe$_3$).

$^{19}$F{$^1$H} NMR (C$_6$D$_6$, 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$_6$D$_6$, 25 °C, 125.75 MHz): δ -1.9 (s, Si(CH$_3$)$_3$); 17.1 (s, SiCH$_2$); 17.5 (s, SiCH$_2$CH$_2$); 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).

Synthesis of trimethyl(2,3,4,5,6-pentafluorophenyl)silane (8). A solution of pentafluorobenzene (0.083 g, 0.498 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol)
in 0.6 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and triphenylfluorosilane (0.017 g, 0.062 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 7 h. (98% yield by NMR spectroscopy). $^1$H NMR (C$_6$D$_6$, 25 °C, 500.12 MHz): $\delta$ 0.21 (t, 9H, Si(CH$_3$)$_3$, $^5$J$_{HF}$ = 1.4 Hz). $^{19}$F{$^1$H} NMR (C$_6$D$_6$, 25 °C, 470.59 MHz): $\delta$ -127.8 (AA‘MM’N second order m, 2F, 2,6–Ar–F); -152.2 (tt, 1F, 4–Ar–F, $^3$J$_{FF}$ = 20.6 Hz, $^4$J$_{FF}$ = 3.5 Hz); -161.5 (AA‘MM’N second order m, 2F, 3,5–Ar–F). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 25 °C, 125.75 MHz): $\delta$ 0.3 (t, Si(CH$_3$)$_3$, $^4$J$_{CF}$ = 2.9 Hz); 111.2 (triplet of coincident quartets, 1–Ar–C, $^2$J$_{CF}$ = 33.2 Hz, $^3$J$_{CF}$ = 3.7 Hz, $^4$J$_{CF}$ = 3.7 Hz); 138.9 (dm, Ar–C, $^1$J$_{CF}$ = 251.3 Hz); 143.5 (dtt, 4–Ar–C, $^1$J$_{CF}$ = 253.3 Hz, $^2$J$_{CF}$ = 12.9 Hz, $^3$J$_{CF}$ = 6.2 Hz); 150.6 (dm, Ar–C, $^1$J$_{CF}$ = 253.4 Hz). $^{29}$Si{$^1$H} NMR (C$_6$D$_6$, 27 °C, 59.64MHz): $\delta$ -1.4 (tt, 1–Ar–Si, $^3$J$_{SIF}$ = 2.9 Hz, $^4$J$_{SIF}$ = 1.8 Hz, $^5$J$_{SIF}$ = 1.1 Hz).

**Synthesis of trimethyl(2,3,4,5,6-pentafluorophenyl)silane (8) on a 1 g Scale.** A solution of pentafluorobenzene (0.700 g, 4.15 mmol) and trimethyl(vinyl)silane (0.416 g, 4.15 mmol) in 10 g of toluene was added to 1b (0.084 g, 0.207 mmol, 5 mol %). Solution was put into a 50 mL high pressure Schlenk flask, and immersed in an oil bath at 120 °C for 20 h. The solution was then subjected to flash chromatography through silica, and all volatiles were removed in vacuo to afford 0.714 g of a yellow oil (71% yield).

**Synthesis of trimethyl(2,3,5,6-tetrafluorophenyl)silane (10).** A solution of 1,2,4,5-tetrafluorobenzene (0.745 g, 4.98 mmol, 10 equiv) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.4 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and triphenylfluorosilane (0.017 g, 0.062 mmol), which was used as an internal standard. The
NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 7h. (98% yield by NMR spectroscopy). $^1$H NMR (C$_6$D$_6$, 25 °C, 500.12 MHz): δ 0.22 (t, 9H, Si(CH)$_3$), $^5$J$_{HF} = 1.4$ Hz); 6.27 (tt, 1H, 4–Ar–H, $^3$J$_{HF} = 7.4$ Hz, $^4$J$_{HF} = 9.4$ Hz). $^{19}$F{$_1$H} NMR (C$_6$D$_6$, 25 °C, 470.59 MHz): δ -129.4 (AA‘MM’ second order m, 2,6–Ar–F); -139.8 (AA‘MM’ second order m, 3,5–Ar–F). $^{13}$C{$_1$H} NMR (C$_6$D$_6$, 25 °C, 125.75 MHz): δ 0.3 (t, Si(CH)$_3$), $^4$J$_{CF} = 3.05$ Hz); 108.0 (tt, 4–Ar–C, $^2$J$_{CF} = 23.6$ Hz, $^3$J$_{CF} = 1.59$ Hz); 118.2 (tt, 1–Ar–C, $^2$J$_{CF} = 30.9$ Hz, $^3$J$_{CF} = 2.2$ Hz); 146.9 (dm, 2,6–Ar–C, $^1$J$_{CF} = 250.5$ Hz); 149.9 (dm, 3,5–Ar–C, $^1$J$_{CF} = 243.5$ Hz). $^{29}$Si{$_1$H} NMR (C$_6$D$_6$, 27 °C, 59.64 MHz): δ -1.7 (tt, 1–Ar–Si, $^3$J$_{SiF} = 2.37$ Hz, $^4$J$_{SiF} = 3.45$ Hz).

**Synthesis of 2,3,5,6-tetrafluorophenyl-1,4-bis(trimethylsilane) (11).** A solution of 1,2,4,5-tetrafluorobenzene (0.075 g, 0.498 mmol) and trimethyl(vinyl)silane (0.125 g, 1.25 mmol, 2.5 equiv) in 0.6 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and triphenylfluorosilane (0.017 g, 0.062 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 20 h. (99% yield by NMR spectroscopy). $^1$H NMR (C$_6$D$_6$, 25 °C, 500.12 MHz): δ 0.27 (virtual pentet, 18H, SiCH$_3$, apparent $J = 0.73$ Hz). $^{19}$F{$_1$H} NMR (C$_6$D$_6$, 25 °C, 470.59 MHz): δ -129.2 (s, 2,3,5,6–Ar–F). $^{13}$C{$_1$H} NMR (C$_6$D$_6$, 25°C, 125.75 MHz): δ 0.3 (virtual pentet, Si(CH)$_3$), apparent $J = 1.43$ Hz); 118.2 (AA‘A’A”‘X second order m, 1,4–Ar–C); 149.5 (dm, 2,3,5,6–Ar–C, $^1$J$_{CF} = 245.8$ Hz). $^{29}$Si{$_1$H} NMR (C$_6$D$_6$, 27 °C, 59.64 MHz): δ -2.1 (virtual pentet, 1,4–Ar–Si, apparent $J = 2.85$ Hz).

**Synthesis of trimethyl(2,3,4,6-tetrafluorophenyl)silane (12).** A solution of 1,2,3,5-tetrafluorobenzene (0.745 g, 0.498 mmol, 10 equiv) and trimethyl(vinyl)silane (0.05 g,
0.498 mmol) in 0.4 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and triphenylfluorosilane (0.017 g, 0.062 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 7 h. (98% yield by NMR spectroscopy). \(^1\)H NMR (C\(_6\)D\(_6\), 25 °C, 500.12 MHz): \(\delta 0.21 \text{ (t, 9H, Si(CH\(_3\)_3), } J_{HF} = 1.54 \text{ Hz) ; } 6.02 \text{ (ddddd, 1H, 5–Ar–H, } J_{HF} = 10.83 \text{ Hz, } J_{HF} = 8.36 \text{ Hz, } J_{HF} = 5.23 \text{ Hz, } J_{HF} = 2.45 \text{ Hz).} \(^19\)F\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 25 °C, 470.59 MHz): \(\delta -102.5 \text{ (dd, 6–Ar–F, } J_{FF} = 3.92 \text{ Hz, } J_{FF} = 12.21 \text{ Hz); -122.1 \text{ (dd, 4–Ar–F, } J_{FF} = 8.21 \text{ Hz, } J_{FF} = 23.0 \text{ Hz); -132.4 \text{ (dd, 2–Ar–F, } J_{FF} = 3.92 \text{ Hz, } J_{FF} = 8.21 \text{ Hz, } J_{FF} = 20.32 \text{ Hz); -167.7 \text{ (dd, 3–Ar–F, } J_{FF} = 12.21 \text{ Hz, } J_{FF} = 23.0 \text{ Hz).} \(^{13}\)C\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 25 °C, 125.75 MHz): \(\delta 0.4 \text{ (t, Si(CH\(_3\)_3), } J_{CF} = 2.7 \text{ Hz); 101.6 \text{ (ddd, 5–Ar–C, } J_{CF} = 33.3 \text{ Hz, } J_{CF} = 20.9 \text{ Hz, } J_{CF} = 2.9 \text{ Hz); 111.5 \text{ (tm, 1–Ar–C, } J_{CF} = 35.7 \text{ Hz); 152.6 \text{ (dm, Ar–C, } J_{CF} = 251.9 \text{ Hz); 155.3 \text{ (dm, Ar–C, } J_{CF} = 244.2 \text{ Hz); 161.2 (dm, Ar–C, } J_{CF} = 241.5 \text{ Hz).} \(^{29}\)Si\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 27 °C, 59.64MHz): \(\delta -2.7 \text{ (ddddd, 1–Ar–Si, } J_{SIS} = 4.5 \text{ Hz, } J_{SIF} = 3.4 \text{ Hz, } J_{SIF} = 1.6 \text{ Hz, } J_{SIF} = 0.9 \text{ Hz).}

**Synthesis of 2,4,5,6-tetrafluorophenyl-1,3-bis(trimethylsilane) (13).** A solution of 1.2,4,5-tetrafluorobenzene (0.075 g, 0.498 mmol) and trimethyl(vinyl)silane (0.125 g, 1.25 mmol, 2.5 equiv) in 0.6 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and triphenylfluorosilane (0.017 g, 0.062 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 20 h. (99% yield by NMR spectroscopy). \(^1\)H NMR (C\(_6\)D\(_6\), 25 °C, 500.12 MHz): \(\delta 0.26 \text{ (ddd, 18H, 1,3–Ar–Si(CH\(_3\)_3), } J_{HF} = 1.49 \text{ Hz, } J_{HF} = 1.49 \text{ Hz, } J_{HF} = 0.68 \text{ Hz).} \(^19\)F\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 25 °C, 470.59 MHz): \(\delta -88.1 \text{ (dt, 2–Ar–F, } J_{FF} = 2.0 \text{ Hz, } J_{FF} = 13.2 \text{ Hz); -120.3 \text{ (dd, 4,6–Ar–F, } J_{FF} = 23.0 \text{ Hz, } J_{FF} = 2.0 \text{ Hz); -167.0 \text{ (td, 5–Ar–F, } J_{FF} = 23.0 \text{ Hz, } J_{FF} =

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13.2 Hz). $^{13}$C$^1$H NMR (C$_6$D$_6$, 25 °C, 125.75 MHz): 0.3 (dd, Si(CH$_3$)$_3$), $^4$J$_{CF}$ = 4.6 Hz, $^4$J$_{CF}$ = 1.7 Hz); 111.1 (ddd, 1,3–Ar–C, $^2$J$_{CF}$ = 44.0 Hz, $^2$J$_{CF}$ = 34.5 Hz, $^3$J$_{CF}$ = 3.6 Hz); 152.3 (dm, 5–Ar–C, $^1$J$_{CF}$ = 251.9 Hz); 156.0 (ddd, 4,6–Ar–C, $^1$J$_{CF}$ = 246.3 Hz, $^2$J$_{CF}$ = 16.4 Hz, $^3$J$_{CF}$ = 9.9 Hz, $^3$J$_{CF}$ = 6.3 Hz); 164.8 (dtd, 2–Ar–C, $^1$J$_{CF}$ = 236.0 Hz, $^3$J$_{CF}$ = 16.4 Hz, $^4$J$_{CF}$ = 4.5 Hz). $^{29}$Si$^1$H NMR (C$_6$D$_6$, 27 °C, 59.64 MHz): δ -3.2 (AA’XX’YZ second order m, 1,3–Ar–Si).

**Synthesis of trimethyl(2,3,4,5-tetrafluorophenyl)silane (14).** A solution of 1,2,3,4-tetrafluorobenzene (0.420 g, 2.79 mmol, 4 equiv) and trimethyl(vinyl)silane (0.07 g, 0.698 mmol) in 0.4 g of toluene was added to 1b (0.040 g, 0.099 mmol, 20 mol %). Triphenylfluorosilane was used as an internal standard (0.017 g, 0.062 mmol). The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 7 h. (96% yield by NMR spectroscopy). $^1$H NMR (C$_6$D$_6$, 25 °C, 500.12 MHz): δ 0.14 (t, 9H, Si(CH$_3$)$_3$), $^5$J$_{HF}$ = 1.10 Hz, $^5$J$_{HF}$ = 0.90 Hz); 6.56 (dddd, 1H, 6–Ar–H, $^3$J$_{HF}$ = 9.70 Hz, $^4$J$_{HF}$ = 8.60 Hz, $^4$J$_{HF}$ = 3.80 Hz, $^5$J$_{HF}$ = 2.80 Hz). $^{19}$F$^1$H NMR (C$_6$D$_6$, 25 °C, 470.59 MHz): δ -128.3 (ddd, 1F, 2–Ar–F, $^3$J$_{FF}$ = 21.6 Hz, $^4$J$_{FF}$ = 4.4 Hz, $^5$J$_{FF}$ = 15.1 Hz); -139.4 (ddd, 1F, 5–Ar–F, $^3$J$_{FF}$ = 23.3 Hz, $^4$J$_{FF}$ = 4.8 Hz, $^5$J$_{FF}$ = 15.1 Hz); -154.4 (ddd, 1F, 3–Ar–F, $^3$J$_{FF}$ = 21.6 Hz, $^3$J$_{FF}$ = 20.3 Hz, $^4$J$_{FF}$ = 4.8 Hz); -155.9 (ddd, 1F, 4–Ar–F, $^3$J$_{FF}$ = 23.3 Hz, $^3$J$_{FF}$ = 20.3 Hz, $^4$J$_{FF}$ = 4.4 Hz). $^{13}$C$^1$H NMR (C$_6$D$_6$, 25 °C, 125.75 MHz): δ 0.6 (s, Si(CH$_3$)$_3$); 115.7 (ddd, 6–Ar–C, $^3$J$_{CF}$ = 20.1 Hz, $^4$J$_{CF}$ = 12.2 Hz, $^4$J$_{CF}$ = 4.3 Hz, $^5$J$_{CF}$ = 3.4 Hz); 123.4 (ddd, 1–Ar–C, $^3$J$_{CF}$ = 30.0 Hz, $^4$J$_{CF}$ = 6.1 Hz, $^4$J$_{CF}$ = 3.2 Hz); 141.5 (dm, Ar–C, $^1$J$_{CF}$ = 256.3 Hz); 142.4 (dm, Ar–C, $^1$J$_{CF}$ = 254.0 Hz); 148.5 (dm, Ar–C, $^1$J$_{CF}$ = 248.8 Hz); 152.0 (Ar–C, $^1$J$_{CF}$ = 239.0 Hz). $^{29}$Si$^1$H NMR (C$_6$D$_6$, 27 °C, 59.64 MHz): δ -2.5 (ddd, 1–Ar–Si, $^3$J$_{SiF}$ = 5.4 Hz, $^4$J$_{SiF}$ = 3.0 Hz, $^4$J$_{SiF}$ = 1.3 Hz, $^5$J$_{SiF}$ = 1.3 Hz).
Synthesis of trimethyl(2,3,6-trifluorophenyl)silane (15). A solution of 1,2,4-trifluorobenzene (0.197 g, 1.50 mmol, 3 equiv) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.5 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and triphenylfluorosilane (0.017 g, 0.062 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 20 h. (96% yield by NMR spectroscopy). 1H NMR (C₆D₆, 25 °C, 500.12 MHz): δ 0.27 (t, 9H, Si(CH₃)₃, JHF = 1.57 Hz); 6.2 (dddd, 1H, 4–Ar–H, JHF = 10.9 Hz, JHH = 7.7 Hz, JHF = 3.2 Hz, JHF = 1.8 Hz); 6.4 (ddd, 1H, 5–Ar–H, JHF = 18.3 Hz, JHH = 7.7 Hz, JHF = 5.1 Hz). 19F{1H} NMR (C₆D₆, 25 °C, 470.59 MHz): δ -104.2 (dd, 6–Ar–F, JFF = 16.8 Hz, JFF = 1.0 Hz); -123.1 (dd, 3–Ar–F, JFF = 23.3 Hz, JFF = 1.0 Hz); -144.1 (dd, 2–Ar–F, JFF = 23.3 Hz, JFF = 16.8 Hz). 13C{1H} NMR (C₆D₆, 25 °C, 125.75 MHz): δ 0.4 (t, Si(CH₃)₃, JCF = 2.9 Hz); 111.6 (ddd, 4–Ar–C, JCF = 29.8 Hz, JCF = 5.6 Hz, JCF = 3.8 Hz); 116.8 (ddd, 1–Ar–C, JCF = 36.5 Hz, JCF = 29.8 Hz, JCF = 2.2 Hz); 119.2 (ddd, 5–Ar–C, JCF = 19.7 Hz, JCF = 10.8 Hz, JCF = 1.9 Hz); 147.9 (ddd, 6–Ar–C, JCF = 246.0 Hz, JCF = 10.6 Hz, JCF = 3.8 Hz); 154.5 (ddd, 2–Ar–C, JCF = 244.4 Hz, JCF = 16.5 Hz, JCF = 13.0 Hz); 162.4 (ddd, 3–Ar–C, JCF = 239.8 Hz, JCF = 13.4 Hz, JCF = 2.6 Hz). 29Si{1H} NMR (C₆D₆, 27 °C, 59.64MHz): δ -3.2 (ddd, 1–Ar–Si, JSiF = 3.8 Hz, JSiF = 3.8 Hz, JSiF = 2.1 Hz).

Synthesis of trimethyl(2,4,6-trifluorophenyl)silane (16). A solution of 1,3,5-trifluorobenzene (0.655 g, 4.98 mmol, 10 equiv) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.4 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and triphenylfluorosilane (0.017 g, 0.062 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 21 h. (98% yield by NMR spectroscopy). 1H NMR (C₆D₆, 25 °C, 500.12 MHz): δ 0.31 (t, 9H,
Synthesis of trimethyl(2,6-difluorophenyl)silane (17). A solution of 1,3-difluorobenzene (0.057 g, 0.498 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.6 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and triphenylfluorosilane (0.017 g, 0.062 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 36 h. (75% yield by NMR spectroscopy).

\[ ^1H \text{NMR (C}_6\text{D}_6, 25 \degree \text{C, 500.12 MHz): } \delta \text{ 0.39 (t, 9H, Si(CH}_3)_3, } ^5J_{HF} = 1.52 \text{ Hz); 6.51 (AA’MM’N second order m, 2H, 3,5–Ar–H); 6.71 (tt, 1H, 4–Ar–H, } ^3J_{HH} = 8.02 \text{ Hz, } ^4J_{HF} = 6.77 \text{ Hz).} \]

\[ ^19F\{^1H\} \text{NMR (C}_6\text{D}_6, 25 \degree \text{C, 470.59 MHz): } \delta \text{ 97.2 (s, 2,6–Ar–F).} \]

\[ ^13C\{^1H\} \text{NMR (C}_6\text{D}_6, 25 \degree \text{C, 125.75 MHz): } \delta \text{ 0.0 (t, Si(CH}_3)_3, } ^4J_{CF} = 2.6 \text{ Hz); 100.0 (ddd, 3,5–Ar–C, } ^2J_{SIF} = 32.3 \text{ Hz, } ^2J_{SIF} = 24.3 \text{ Hz, } ^4J_{SIF} = 3.7 \text{ Hz); 109.5 (td, 1–Ar–C, } ^2J_{SIF} = 4.2 \text{ Hz, } ^4J_{SIF} = 31.2 \text{ Hz); 165.7 (dt, 4–Ar–C, } ^1J_{SIF} = 250.0 \text{ Hz, } ^3J_{SIF} = 17.4 \text{ Hz); 168.6 (dd, 2,6–Ar–C, } ^1J_{SIF} = 244.7 \text{ Hz, } ^3J_{CF} = 14.4 \text{ Hz, } ^3J_{CF} = 19.6 \text{ Hz).} \]

\[ ^29Si\{^1H\} \text{NMR (C}_6\text{D}_6, 27 \degree \text{C, 59.64MHz): } \delta \text{ 4.2 (td, 1–Ar–Si, } ^3J_{SIF} = 3.9 \text{ Hz, } ^5J_{SIF} = 0.6 \text{ Hz).} \]

Synthesis of dimethylbenzyl(2,3,4,5,6-pentafluorophenyl)silane. A solution of pentafluorobenzene (0.047 g, 0.284 mmol) and dimethylbenzyl(vinyl)silane (0.05 g, 0.284 mmol) in 0.6 g of toluene was added to Ni(COD)$_2$ (0.004 g, 0.014 mmol, 5 mol %), 1,3-
di(isopropyl)imidazol-2-ylidene (0.002 g, 0.014 mmol, 5 mol %), and triphenylfluorosilane (0.019 g, 0.071 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 9 h. $^{19}$F{$^1$H} NMR showed 70% conversion to silylation product with no significant byproducts. $^1$H NMR ($C_6D_6$, 25 °C, 500.12 MHz): δ 0.17 (t, 6H, Si(CH$_3$)$_3$, $^5$J$_{HF}$ = 1.7 Hz); 2.19 (s, 2H, CH$_2$Ph); 6.83 (m, 2H, Ph–H); 6.98 (m, 2H, Ph–H); 7.07 (m, 1H, Ph–H). $^{19}$F{$^1$H} NMR ($C_6D_6$, 25 °C, 470.59 MHz): δ -127.0 (AA’MM’N second order m, 2F, 2,6–Ar–F); -151.5 (tt, 1F, 4–Ar–F, $^3$J$_{FF}$ = 20.5 Hz, $^4$J$_{FF}$ = 3.5 Hz); -161.2 (AA’MM’N second order m, 2F, 3,5–Ar–F). $^{13}$C{$^1$H} NMR ($C_6D_6$, 25 °C, 125.75 MHz): δ -2.1 (t, Si(CH$_3$)$_3$, $^4$J$_{CF}$ = 3.3 Hz); 25.9 (t, Si(CH$_2$), $^4$J$_{CF}$ = 2.1 Hz); 112.6 (triplet of coincident quartets, 1–Ar–C, $^2$J$_{CF}$ = 33.2 Hz, $^3$J$_{CF}$ = 3.6 Hz, $^4$J$_{CF}$ = 3.6 Hz); 126.4 (s, Ph–C); 128.7 (s, Ph–C); 128.8 (s, Ph–C); 138.1 (s, Ph–C); 137.6 (dm, Ar–C, $^1$J$_{CF}$ = 251.9 Hz); 142.0 (dm, 4–Ar–C, $^1$J$_{CF}$ = 251.9 Hz); 149.2 (dm, Ar–C, $^1$J$_{CF}$ = 245.1 Hz). $^{29}$Si{$^1$H} NMR ($C_6D_6$, 27 °C, 59.64MHz): δ -1.5 (ttd, 1–Ar–Si, $^3$J$_{SIF}$ = 2.7 Hz, $^4$J$_{SIF}$ = 1.6 Hz, $^5$J$_{SIF}$ = 1.4 Hz).

Synthesis of 2-ethyltrimethylsilylbenzothiazole. A solution of benzothiazole (0.067 g, 0.498 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.6 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and ferrocene (0.011 g, 0.059 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 60 °C for 2 h. $^1$H NMR showed decomposition of 1b, along with a mixture of silylation product, 2-trimethylsilylbenzthiazole, and hydroarylation product, 2-ethyltrimethylsilylbenzothiazole, and catalytic turnovers of 4 and 2 respectively. The silylation product decomposed upon contact with silica and could not be isolated, however NMR shifts were consistent with literature values. The resulting solution was filtered.

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through a plug of silica and rinsed with EtOAc. To the filtrate was added 0.250 g of silica, and all volatiles were removed in vacuo. The hydroarylation product was purified by flash chromatography (ethyl acetate–hexane = 6:4). $^1$H NMR (C$_6$D$_6$, 25 °C, 500.12 MHz): δ - 0.10 (s, 9H, Si(CH$_3$)$_3$); 1.03 (second order m, 2H, CH$_2$SiMe$_3$); 2.92 (second order m, CH$_2$CH$_2$SiMe$_3$); 7.01 (ddd, 1H, 7–Ar–H, $^3$J$_{HH}$ = 8.13 Hz, $^3$J$_{HH}$ = 7.35 Hz, $^4$J$_{HF}$ = 1.20 Hz); 7.15 (ddd, 1H, 6–Ar–H, $^3$J$_{HH}$ = 8.13 Hz, $^3$J$_{HH}$ = 7.35 Hz, $^4$J$_{HF}$ = 1.20 Hz); 7.50 (ddd, 1H, 8–Ar–H, $^3$J$_{HH}$ = 7.94 Hz, $^3$J$_{HH}$ = 1.20 Hz, $^5$J$_{HH}$ = 0.67 Hz); 8.06 (dd, 1H, 8–Ar–H, $^3$J$_{HH}$ = 7.94 Hz, $^4$J$_{HH}$ = 1.20 Hz, $^5$J$_{HH}$ = 0.67 Hz). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 25 °C, 125.75 MHz): δ - 1.9 (s, Si(CH$_3$)$_3$); 16.9 (s, CH$_2$SiMe$_3$); 18.5 (s, CH$_2$CH$_2$SiMe$_3$); 121.6 (s, 6–Ar–C); 123.2 (s, 3–Ar–C); 124.7 (s, 5–Ar–C); 126.1 (s, 4–Ar–C); 135.8 (s, 7–Ar–C); 154.4 (s, 2–Ar–C); 174.1 (s, 1–Ar–C).

**Synthesis of 2-ethyltrimethylsilylbenzoxazole.** A solution of benzoxazole (0.059 g, 0.498 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.6 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and ferrocene (0.011 g, 0.059 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 60 °C for 2 h. $^1$H NMR showed decomposition of 1b, along with a mixture of silylation product, 2-trimethylsilylbenzoxazole, and hydroarylation product, 2-ethyltrimethylsilylbenzoxazole, and catalytic turnovers of 4 and 2 respectively. The silylation product decomposed upon contact with silica and could not be isolated, however NMR shifts were consistent with literature values. The resulting solution was filtered through a plug of silica and rinsed with EtOAc. To the filtrate was added 0.250 g of silica, and all volatiles were removed in vacuo. The hydroarylation product was purified by flash chromatography (ethyl acetate–hexane = 4:6). $^1$H NMR (C$_6$D$_6$, 25 °C, 500.12 MHz): δ -
Synthesis of 2-trimethylsilylbenzofuran. A solution of benzofuran (0.059 g, 0.498 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.6 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and ferrocene (0.011 g, 0.059 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 12 h. $^1$H NMR showed no indication of hydroarylation or other products, and 6 catalyst turnovers resulting in 2-trimethylsilylbenzofuran. NMR shifts were consistent with literature values.  

Reaction of 1,2,3,4-tetrafluorobenzene and trimethyl(vinyl)silane and 5% 1b. A solution of 1,2,4,5-tetrafluorobenzene (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 120 °C for 20 h resulting in a 30 % NMR yield of 14 with no significant byproducts. Increasing catalyst loading improved yields.
1:1 Reaction with 1,2,3,5-tetrafluorobenzene. A solution of 1,2,3,5-tetrafluorobenzene (0.078 g, 0.520 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.6 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and triphenylfluorosilane (0.017 g, 0.062 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 3 h. The resulting integrals were converted to relative concentrations and modeled in a kinetics simulator. The rate constants of formation for monosilylation product vs disilylation product were in a 2.5:1 ratio respectively. Mechanism and conditions used are shown in Table 2.1. Final calculated and modeled concentrations, and rate constants are shown in Table 2.2.

Table 2.1. Mechanism description input for 1:1 reaction of H₂C=CHSiMe₃ and 1,2,3,5-C₆F₄H₂ and 5 mol % 1b.

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<th>Di</th>
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Table 2.2. Final calculated and modeled concentrations, and rate constants of formation for monosilylation and disilylation products of 1,2,3,5-C₆F₄H₂.

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<td>4.21E-03</td>
<td>0.47</td>
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1:1 Reaction with 1,2,4,5-tetrafluorobenzene. A solution of 1,2,4,5-tetrafluorobenzene (0.078 g, 0.520 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.6 g of toluene was added to 1b (0.010 g, 0.025 mmol, 5 mol %) and triphenylfluorosilane (0.017 g, 0.062 mmol), which was used as an internal standard. The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 3 h. The resulting integrals were converted to relative concentrations and modeled in a kinetics simulator. The rate constants of formation for monosilylation product vs disilylation product were in a 2.3:1 ratio respectively. Mechanism and conditions used are shown in Table 2.3. Final calculated and modeled concentrations, and rate constants are shown in Table 2.4.

**Table 2.3.** Mechanism description input for 1:1 reaction of H2C=CHSiMe3 and 1,2,4,5-C6F4H2 and 5 mol % 1b.

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Chapter 2 – Nickel-Catalyzed C–H Silylation of Arenes with Vinylsilanes: Rapid and Reversible \( \beta \)-Si Elimination

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Chapter 2 – Nickel-Catalyzed C–H Silylation of Arenes with Vinysilanes: Rapid and Reversible \( \beta \)-Si Elimination

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Table 2.4. Final calculated and modeled concentrations, and rate constants of formation for monosilylation and disilylation products of 1,2,4,5-C\( _6 \)F\( _4 \)H\(_2 \).

Reaction of C\( _6 \)F\( _5 \)D and H\(_2 \)C=CHSiMe\(_3 \) with 5\% Ni(COD)\(_2 \) and \( ^{i} \)Pr\(_3 \)P. A solution of pentafluorobenzene (0.083 g, 0.498 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.6 g of toluene was added to Ni(COD)\(_2 \) (0.006 g, 0.025 mmol, 5 mol \%) and \( ^{i} \)Pr\(_3 \)P (0.004 g, 0.025 mmol, 5 mol \%). Solution was added to an NMR tube and placed in an oil bath at 80 °C and heated 24 h. Crude \( ^{19} \)F NMR showed conversion to C-H silylation product
8 in a 3 % yield. Heating solution for 48 h resulted in no further conversion to product. Heating solution past 80°C resulted in rapid decomposition of catalyst.

**Reaction of C₆F₅H and H₂C=CHSi(OEt)₃ with 5% Ni(COD)₂ and tPr₂Im.** A solution of pentafluorobenzene (0.083 g, 0.498 mmol) and triethoxy(vinyl)silane (0.093 g, 0.498 mmol) in 0.6 g of toluene was added to Ni(COD)₂ (0.006 g, 0.025 mmol, 5 mol %) and tPr₂Im (0.004 g, 0.025 mmol, 5 mol %). The NMR tube was flame sealed under vacuum and solution was heated at 120 °C for 24 h. ¹⁹F NMR showed no reaction.

**Reaction of C₆F₅D and H₂C=CHSi(OEt)₃ with 5% Ni(COD)₂ and tPr₂Im.** A solution of C₆F₅D (0.083 g, 0.498 mmol) and triethoxy(vinyl)silane (0.093 g, 0.498 mmol) in 0.6 g of toluene was added to Ni(COD)₂ (0.006 g, 0.025 mmol, 5 mol %) and tPr₂Im (0.004 g, 0.025 mmol, 5 mol %). The solution was put in a J-Young tube and heated at 120 °C for 12 h. The ¹⁹F NMR showed full H/D scrambling into the pentafluorobenzene, forming C₆F₅H/D, indicating that C–H activation is rapid and reversible.

**Reaction of 1,3-difluorobenzene and H₂C=CHSiMe₃ with 5% of (9).** A solution of trimethyl(vinyl)silane (0.050 g, 0.498 mmol), C₆F₅H₄ (0.057 g, 0.498 mmol) in 0.6 mL of toluene was added to 9 (0.012 g, 0.025 mmol, 5 mol %). The NMR tube was flame sealed under vacuum and heated at 140 °C periodically at 20 minute intervals during the first hour, and 30 minute intervals subsequently. During the first 60 minutes of the reaction small amounts of both FSiMe₃ and C–F activation [(F)(tPr₂Im)₂Ni(C₆FH₄)] byproducts are observed with no indication of silylation product. At the 120-min mark, there is approximately 0.8% conversion to silylation product, while production of FSiMe₃ and C–
F activation byproducts ceases. The rate of conversion to silylation product continues to increase to 3%, 5%, and 9% at the 180, 240, and 300-minute mark respectively.

**Chart 2.2.** Kinetic Studies of catalysis with 9.

![Chart 2.2. Kinetic Studies of catalysis with 9.](image)

**Reaction of 1,2,4,5-C₆F₄H₂ and H₂C=CHSiMe₃ with 50% [Pr₂Im]Ni(η²-H₂C=CHSiMe₃)₂ (1b) – Attempted Intermediate Observation.** A solution of 1,2,4,5-tetrafluorobenzene (0.074 g, 0.498 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.4 g of toluene was added to 1b (0.102 g, 0.249 mmol, 50 mol%). The solution was heated at 95 °C for 5 h total. ¹⁹F{¹H} NMR spectra were taken at 30 minutes, 1 hour, 2 hours, and 5 hours. No intermediates were observed.

**Reaction of C₆F₅D and 3 equivalents of H₂C=CHSiMe₃ with 5% [Pr₂Im]Ni(η²-H₂C=CHSiMe₃)₂ (1b).** A solution of C₆F₅D (0.083 g, 0.498 mmol) and trimethyl(vinyl)silane (0.150 g, 1.49 mmol) 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 site of free H$_2$C=CHSiMe$_3$ at 90 °C after 5 minutes. The $^2$H spectrum was modelled to determine the relative ratio of deuterium in each site. It was determined that the initial ratio of deuterium scrambling into the 1 and 2 sites was 4:1:1 respectively.

**Reaction of C$_6$F$_5$D and 3 equivalents of H$_2$C=CHSiMe$_3$ with 5% [IPr]Ni(η$^2$-H$_2$C=CHSiMe$_3$)$_2$ (1a).** A solution of C$_6$F$_5$D (0.083 g, 0.498 mmol) and trimethyl(vinyl)silane (0.150 g, 1.49 mmol) in 0.4 g of toluene was added to 1a (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 $^2$H NMR. Deuterium scrambling was observed into the 1 and 2 site of free H$_2$C=CHSiMe$_3$ at 80 °C after 5 minutes. The $^2$H spectrum was modelled to determine the relative ratio of deuterium in each site. It was determined that the initial ratio of deuterium scrambling into the 1 and 2 sites was 3:1:1 respectively, as shown in Figure 2.3.

**Preparation of H$_2^{13}$C=CHSiMe$_3$ and Carbon-13 labeling experiment.** A solution of trichloro(vinyl)silane (0.017 g, 0.108 mmol) in 2 mL of toluene was added to Grubbs 1st generation (0.002 g, 0.002 mmol, 2.5 mol %). Carbon-13 labelled ethylene was vacuum transferred to a 5 mL flask, and subsequently vacuum transferred to a J-young tube containing the reaction mixture. Solution was heated at 40 °C for 1h and crude $^{13}$C($^1$H) NMR showed the transfer of the carbon-13 label to the vinyl site, making H$_2^{13}$C=CHSiCl$_3$. Solution was subsequently added to a vial charged with methylmagnesium chloride (0.051 g, 0.432 mmol, 4 equiv) and stirred overnight to afford H$_2^{13}$C=CHSiMe$_3$. Solution was vacuum transferred to a J-young tube containing pentafluorobenzene (0.012 g, 0.071 mmol) and 1b (0.002 g, 0.004 mmol, 5 mol %) in toluene-d$_8$. At 110 °C the carbon-13 label
being transferred to the other vinyl site was observed, forming $\text{H}_2\text{C}=^{13}\text{CHSiMe}_3$. $^{19}\text{F}(^{1}\text{H})$ NMR showed no conversion to the silylation product.

**Reaction of $\text{H}_2^{13}\text{C}=^{13}\text{CH}_2$ with $\text{C}_6\text{F}_5\text{H}$, $\text{H}_2\text{C}=\text{CHSiMe}_3$ and 5% [IPr]Ni($\eta^2$-$\text{H}_2\text{C}=\text{CHSiMe}_3)_2$ (1a).** Carbon-13 labeled 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 1a (0.016 g, 0.025 mmol, 5 mol %). The solution was heated at 90 °C for 6 h, $^{13}\text{C}(^{1}\text{H})$ NMR showed scrambling of the carbon-13 label into free $\text{H}_2\text{C}=\text{CHSiMe}_3$, forming $\text{H}_2^{13}\text{C}=^{13}\text{CHSiMe}_3$.

### 2.5 X-ray Crystallography

#### 2.5.1. Crystallographic Data

*Table 2.5.* Crystal data and structure refinement for [IPr]Ni($\eta^2$-$\text{H}_2\text{C}=\text{CHSiMe}_3)_2$ (1a)

- **Empirical formula**: C$_{37}$H$_{60}$N$_2$NiSi$_2$
- **Formula weight**: 647.76
- **Temperature**: 150(2) K
- **Wavelength**: 0.71073 Å
- **Crystal system**: Orthorhombic
- **Space group**: Pbc a
- **Unit cell dimensions**:
  - $a = 18.4342(10)$ Å, $\alpha = 90^\circ$
  - $b = 19.3195(12)$ Å, $\beta = 90^\circ$
  - $c = 21.7657(12)$ Å, $\gamma = 90^\circ$
- **Volume**: 7751.6(8) Å$^3$
Density (calculated) 1.110 g/cm³
Absorption coefficient 0.587 mm⁻¹
F(000) 2816
Crystal size 0.240 x 0.210 x 0.180 mm³
Theta range for data collection 2.896 to 29.999°.
Index ranges -25 ≤ h ≤ 25, -27 ≤ k ≤ 27, -30 ≤ l ≤ 25
Reflections collected 104107
Independent reflections 11291 [R(int) = 0.0621]
Completeness to theta = 29.999° 99.9 %
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 11291 / 0 / 417
Goodness-of-fit on F² 1.019
Final R indices [I>2sigma(I)] R1 = 0.0422, wR2 = 0.0847
R indices (all data) R1 = 0.0768, wR2 = 0.0979
Largest diff. peak and hole 0.895 and -0.719 e.Å⁻³

Table 2.6. Crystal data and structure refinement for [iPr2Im]Ni(η²-H₂C=CHSiMe₃)₂ (1b).

Empirical formula C₁₉H₄₀N₂NiSi₂
Formula weight 411.42
Temperature 173(2) K
Wavelength 0.71073 Å

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Crystal system
Monoclinic

Space group
P 21/c

Unit cell dimensions
\[ a = 11.9002(17) \text{ Å} \quad \alpha = 90^\circ. \]
\[ b = 11.0146(15) \text{ Å} \quad \beta = 97.281(3)^\circ. \]
\[ c = 18.542(2) \text{ Å} \quad \gamma = 90^\circ. \]

Volume
2410.8(6) Å\(^3\)

Z
4

Density (calculated)
1.134 Mg/m\(^3\)

Absorption coefficient
0.908 mm\(^{-1}\)

F(000)
896

Theta range for data collection
2.848 to 27.500°.

Index ranges
\[-15 \leq h \leq 15, \quad -14 \leq k \leq 14, \quad -24 \leq l \leq 24\]

Reflections collected
33188

Independent reflections
5527 [R(int) = 0.0588]

Completeness to theta = 27.500°
99.7 %

Refinement method
Full-matrix least-squares on F\(^2\)

Data / restraints / parameters
5527 / 0 / 251

Goodness-of-fit on F\(^2\)
1.235

Final R indices [I>2\(\sigma(I)\)]
R1 = 0.0762, wR2 = 0.1163

R indices (all data)
R1 = 0.0986, wR2 = 0.1247

Largest diff. peak and hole
0.448 and -0.504 e.Å\(^{-3}\)
### Table 2.7. Crystal data and structure refinement for $[i^2\text{Pr}2\text{Im}]_2\text{Ni}(\eta^2\text{H}_2\text{C}=\text{CHSiMe}_3)$ (9).

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2.6 References


References being on page 71
Chapter 2 – Nickel-Catalyzed C–H Silylation of Arenes with Vinylsilanes: Rapid and Reversible β-Si Elimination


References being on page 71


Chapter 2 – Nickel-Catalyzed C–H Silylation of Arenes with Vinysilanes: Rapid and Reversible β-Si Elimination


23. An alternate mechanism, a type 1 Ni/Si dyotropic rearrangement in 4 with L = [iPr2Im] cannot be ruled out experimentally, but fails to explain the incorporation of 13C2H4 in the case of 1a (vide infra) as shown in Scheme 3. For a leading reference on dyotropic shifts see: Fernández, I.; Cossio, F. P.; Sierra, M. A., Chem. Rev. 2009, 109, 6687-6711.

Chapter 2 – Nickel-Catalyzed C–H Silylation of Arenes with Vinylsilanes: Rapid and Reversible β-Si Elimination


Chapter 3 – Probing the Influence of Carbene Steric Bulk on Selectivity in Nickel-Catalyzed C–H Bond Functionalization: Conclusions & Future Work

3.1 Introduction

Previous work in nickel-catalyzed C–H bond stannylation demonstrated that the Ni(0) complex [L]Ni(η²-H₂C=CHSnR₃)₂ catalyzes the reaction between C₆F₅H and H₂C=CHSnR₃, but via two possible pathways which lead to the formation of different products: the C–H bond stannylation product C₆F₅SnR₃, or the alkene hydroarylation product C₆F₅CH₂CH₂SnR₃, shown in Scheme 3.1 [(L = 'Pr₃P, [NQA]), (R = Bu, Ph)]. Using SnBu₃ with either 'Pr₃P or the [NQA] ligand resulted in exclusive stannylation product. Using SnPh₃ with 'Pr₃P also resulted in exclusive stannylation, however, reaction with the [NQA] ligand resulted in the alkene hydroarylation product, with trace amounts of stannylation. This formation of two different products can be attributed to a preference
for the three-coordinate nickel intermediate \((L)\text{Ni(COD})_2\) to undergo either direct C–C reductive elimination, or β-Sn elimination along the catalytic pathway (*vide supra*).

**Scheme 3.1.** General reaction of Ni-catalyzed C–H bond stannylation, and Ni-catalyzed alkene hydroarylation, of \(C_6F_5H\).

Similar results for selectivity were observed in the nickel catalyzed C–H bond silylation of \(C_6F_5H\). The reaction of \(H_2C=CHSiMe_3\) and \(C_6F_5H\) with the nickel catalyst [iPr2Im]Ni(η²-H₂C=CHSiMe₃)₂ (1b), gave exclusively the silylation product \(C_6F_5SiMe_3\) ([iPr2Im] = 1,3-di(isopropyl)imidazole-2-ylidene). With the ancillary carbene ligand, IPr, the reaction of \(H_2C=CHSiMe_3\) and \(C_6F_5H\) with the nickel catalyst [IPr]Ni(η²-
H$_2$C=CHSiMe$_3$)$_2$ (1a), yielded exclusively the hydroarylation product, shown in Scheme 3.2 ([IPr] = 1,3-bis([2,6-diisopropylphenyl]-1,3-dihydro-2H-imidazol-2-ylidene).

Scheme 3.2. General reaction scheme showing two analogues of the Ni(0) catalyst [L]Ni(η$^2$-H$_2$C=CHSiMe$_3$)$_2$, where different carbene ligands lead to selective formation of either silylation or hydroarylation products.

This phenomenon of altering carbene steric bulk to influence reactivity along a catalytic cycle is not unheralded. In 2015, Organ et al. reported the Pd-catalyzed selective cross coupling of secondary alkyl zinc reagents to five-membered heterocycles. Similar competition was observed between reductive elimination and β-elimination along the catalytic pathway. They successfully influenced the reactivity towards the reductive elimination step by synthesizing a large N-heterocyclic carbene ligand, PEPPSI-IHept, which led to selective formation of the desired products with little to no indication of migratory insertion byproducts from β-H elimination. While this reaction sought the opposite step along the catalytic pathway (reductive elimination over β-H elimination).

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compared to the previously discussed C–H bond silylation, it effectively supports this finding that the steric bulk on carbene ligands can dramatically alter the reactivity of transition metal complexes along the catalytic pathway. This chapter details the further study of the potential influence of carbene bulk on reactivity of Ni(0) catalysts in C–H bond silylation, stannylation, and germynylation.

3.2 Results and Discussion

3.2.1 Synthesis of Nickel Complexes and Probing Reactivity for Silylation vs. Hydroarylation

The steric parameters of phosphine ligands have traditionally been reported as a cone angle, θ, defined with the metal center at the vertex and the atoms at the perimeter of the cone. Upon the development of more structurally elaborate ligand systems such as biarylphosphines (Buchwald ligands) or N-heterocyclic carbenes (NHC’s), steric parameter calculations with this model proved insufficient. This led to the development of the now conventional steric parameter for NHC’s: percent buried volume (%V_{bur}), defined as the percent of the total volume of a sphere occupied by the ligand. The sphere has a defined radius with the metal center at the core, and the volume represents the space of the coordination sphere around the metal occupied by the ligand. This parameter is calculated using crystallographic data, or computationally. The reported values of %V_{bur} for the carbene ligands used in the following studies are based from a model Au(I) complex.

The IPr carbene ligand is on the large end of the spectrum with a %V_{bur} value of 44.5, while the iPr₂Im carbene is on the smaller end with %V_{bur} value of 27.4. The two carbene ligands have near identical electronic parameters (2050 cm⁻¹), yet provide a
unique selectivity in C–H bond functionalization, indicating that the steric bulk on the carbene has a significant effect. To further investigate this influence of NHC ligand size on the selectivity of C–H silylation or alkene hydroarylation, the carbene ligands IBn and IMes were chosen to be screened because they have \( V_{\text{bur}} \) values of 30.0 and 36.5 respectively, with near identical electronic parameters (2050.3 and 2049.8 cm\(^{-1}\)), as the IPr and \(^4\)Pr\(^2\)Im ligands ([IBn] = 1,3-dibenzyl-1,3-dihydro-2H-imidazol-2-ylidene) ([IMes] = 1,3-bis[2,4,6-trimethylphenyl]-1,3-dihydro-2H-imidazol-2-ylidene). Possible insight into selectivity may be gained if certain carbene ligands facilitate both reactions, leading to a mixture of products.

The carbene ligand IBn is slightly larger than the \(^4\)Pr\(^2\)Im carbene, which provides exclusive silylation. The reaction of Ni(COD)\(_2\) and IBn with 2 equivalents of H\(_2\)C=CHSiMe\(_3\) provided the unwanted bis NHC complex [IBn]\(_2\)Ni(\(\eta^2\)-H\(_2\)C=CHSiMe\(_3\)), as evidenced by integrations in the \(^1\)H NMR spectrum (Section 3.4. Experimental). This resembles the reaction previously observed with the \(^4\)Pr\(^2\)Im carbene, where less bulk allows the coordination of two carbene ligands. To synthesize the bis-vinyl species, 10 equivalents of H\(_2\)C=CHSiMe\(_3\) was added to a solution of Ni(COD)\(_2\) in toluene and stirred for 1 h, followed by a slow addition of a solution of IBn in toluene, affording the desired Ni(0) complex [IBn]Ni(\(\eta^2\)-H\(_2\)C=CHSiMe\(_3\))\(_2\) (1c), shown in Scheme 3.3. To investigate if the slightly larger IBn carbene could provide a mixture of silylation and hydroarylation, C\(_6\)F\(_5\)H and H\(_2\)C=CHSiMe\(_3\) was reacted with a catalytic amount of 1c at 120 °C for 15 h. The crude \(^19\)F\(\{^1\text{H}\}\) NMR showed exclusive conversion to the silylation product C\(_6\)F\(_5\)SiMe\(_3\) with no indication of hydroarylation.
Scheme 3.3. Synthesis of a series of Ni(0) catalysts with varied carbene ligands. Compounds 1a and 1b were previously shown in Chapter 2.

The carbene ligand IMes has a \( V_{\text{bur}} \) value of 36.5, which is slightly larger than IBn, and seemed a more promising candidate to provide a mixture of C–H functionalization products. The reaction of Ni(COD)\(_2\) and IMes with 2 equivalents of \( \text{H}_2\text{C}=	ext{CHSiMe}_3 \) provided the expected nickel complex [IMes]Ni(\( \eta^2 \)-C–H=CHSiMe\(_3\))\(_2\) (1d), shown in Scheme 3.3. Potential selectivity was examined by reacting a catalytic amount of 1d with \( \text{H}_2\text{C}=	ext{CHSiMe}_3 \) and \( \text{C}_6\text{F}_5\text{H} \) at 120 °C for 18 h. The crude \(^{19}\text{F}\{^1\text{H}\} \) NMR showed conversion to both the silylation product \( \text{C}_6\text{F}_5\text{SiMe}_3 \), and hydroarylation product \( \text{C}_6\text{F}_5\text{CH}_2\text{CH}_2\text{SiMe}_3 \) in 60 and 30 % yields respectively. Investigation into early rates of reaction showed that the initial ratio of silylation to hydroarylation is 3:1 respectively at the 1, 2, and 3 h mark, after which the ratio of silylation and hydroarylation decreases to near 2:1. The reaction goes to completion after 6 h, consuming all of the \( \text{H}_2\text{C}=	ext{CHSiMe}_3 \) starting material. The apparent decrease in rate of silylation proved intriguing, and it was thought that perhaps

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ethylene byproduct from the silylation reaction inhibits this pathway, or alternatively, if it increases the rate of hydroarylation. To investigate if this was true, an atmosphere of ethylene was added to a solution of \( \text{H}_2\text{C}=\text{CHSiMe}_3 \) and \( \text{C}_6\text{F}_5\text{H} \) with a catalytic amount of 1d in an NMR tube sealed with a teflon valve. The reaction mixture was heated at 120 °C and tracked hourly, yielding the same results, which indicates that ethylene does not affect the rates of reaction for either silylation or hydroarylation. It was also thought that the rate of hydroarylation was increased by heterogeneous catalysis occurring on the surface of nickel nanoparticles after decomposition of the catalyst. To test the validity of this, 1d was heated above 120 °C to promote decomposition. The solution was filtered to collect the precipitated nickel nanoparticles, which were charged to a separate solution of \( \text{H}_2\text{C}=\text{CHSiMe}_3 \) and \( \text{C}_6\text{F}_5\text{H} \). The solution was heated at 120 °C for 18 h with no observed conversion to the hydroarylation product. This shows that nickel nanoparticles do not facilitate the hydroarylation reaction or attribute to the change in rate.

In the previously discussed nickel catalyzed alkene hydroarylation of \( \text{H}_2\text{C}=\text{CHSnPh}_3 \), it was shown that the reaction of the \( \text{C}_6\text{F}_5\text{SnPh}_3 \) and ethylene with a 10% loading of \( \text{Ni(COD)}_2 \) and the [NQA] ligand forms the carbostannylation product from insertion of ethylene into the Ni–Sn bond, shown in Scheme 3.4. It was considered that the change in product ratios between silylation and hydroarylation observed with 1d is due to ethylene byproduct reacting with the silylation product \( \text{C}_6\text{F}_5\text{SiMe}_3 \), to form the carbosilylation product, \( \text{C}_6\text{F}_5\text{CH}_2\text{CH}_2\text{SiMe}_3 \). However, it was shown that excess ethylene had no effect on the rates of either reaction pathway. Furthermore, after the reaction had gone to completion with silylation and hydroarylation products in a 2:1 ratio, heating the solution at 120 °C for a further 48 h yielded no change in product ratios. This is further
evidence that the change in product ratios cannot be attributed to the silylation product undergoing further reactivity.

![Scheme 3.4](image.png)

**Scheme 3.4.** Ni-catalyzed carbostannylation of C$_6$F$_5$SnPh$_3$.

Finally, the observed change in product ratios could be attributed to changes in the concentrations of the starting materials as the reaction occurs, either increasing or decreasing the barriers for reactivity of either the silylation or hydroarylation reaction pathway. The change in product ratios observed in C–H bond functionalization with 1d may provide insight into the mechanism, and further investigation is needed to rationalize the observed trends. Overall, the results summarized in Scheme 3.5, support the previous observations that smaller carbene ligands facilitate C–H bond silylation selectively, while larger carbenes support hydroarylation.
Scheme 3.5. General reaction scheme for screening of carbene ligands influence on selectivity of silylation vs. hydroarylation.

3.2.2 Investigating Reactivity of Stannylation vs Hydroarylation with Varying Carbenes

In the Ni-catalyzed silylation of C₆F₅H, tuning the steric bulk on the ancillary carbene ligand provides a useful handle for selectively forming either the C–H silylation product, or the alkene hydroarylation product. Previous work in the Ni-catalyzed C–H bond stannylation of fluorinated aromatics also provided a different set of products based on certain conditions. The use of ³Pr₃P or [NQA] and SnBu₃ yields exclusively the stannylation product C₆F₅HSnBu₃, while using [NQA] and SnPh₃ yields near exclusive hydroarylation product C₆F₅HCH₂CH₂SnPh₃. To potentially gain more insight on selectivity in these
catalytic systems, we investigated whether the trends observed on selectivity in C–H bond silylation with carbene supported nickel catalysts could be extended towards C–H bond stannylation.

Catalysis was carried out by generating the nickel species in situ as the isolated compounds resulted in oils which proved inconvenient to work with. A 10 % loading of Ni(COD)\(_2\) and the IPr carbene was reacted with H\(_2\)C=CHSnBu\(_3\) and C\(_6\)F\(_5\)H at 90 °C for 18 h yielded exclusively the stannylation product in excellent yields. Furthermore, the analogous reactions repeated with the IMes and IBn carbene ligands provided identical results. The \(\text{^Pr}_2\text{Im}\) carbene facilitates the C–H bond stannylation reaction at room temperature slowly. This expected reactivity resembles earlier work in C–H bond stannylation, where when R = Bu, the reaction always resulted in the stannylation product. Only by altering the R substituent on the vinyl tin moiety would alkene hydroarylation be observed.

The reaction of Ni(COD)\(_2\) and IPr with two equivalents of H\(_2\)C=CHSnPh\(_3\) yielded the expected product [IPr]Ni(\(\eta^2\)-H\(_2\)C=CHSnPh\(_3\))\(_2\) (2). The reaction of a 10 % loading of 2 with H\(_2\)C=CHSnPh\(_3\) and C\(_6\)F\(_5\)H at 90 °C for 20 h yielded near exclusive stannylation product, C\(_6\)F\(_5\)SnPh\(_3\), with minimal hydroarylation product C\(_6\)F\(_5\)CH\(_2\)CH\(_2\)SnPh\(_3\) being observed. The reaction was monitored by \(^{19}\text{F}\) NMR spectroscopy and showed that the reaction nears completion after 3 h with exclusively stannylation product. After heating for 24 h minimal hydroarylation product is observed. It is likely that the known carbostannylation reaction between the stannylation product C\(_6\)F\(_5\)SnPh\(_3\) and ethylene results in the formation of the hydroarylation product observed. Identical selectivity for
stannylation was shown when reacting a catalytic amount of the IMes or IBn carbene ligands and Ni(COD)\textsubscript{2} with H\textsubscript{2}C=CHSnPh\textsubscript{3} and C\textsubscript{6}F\textsubscript{5}H at 80 °C.

A surprising result was observed when reacting a 10\% loading of Ni(COD)\textsubscript{2} and the \textsuperscript{3}Pr\textsubscript{2}Im carbene with H\textsubscript{2}C=CHSnPh\textsubscript{3} and C\textsubscript{6}F\textsubscript{5}H at 90 °C for 15 h resulted in formation of the hydroarylation product exclusively. This proved to be extremely unexpected as all previous studies carried out with the small \textsuperscript{3}Pr\textsubscript{2}Im carbene provided either exclusive silylation or stannylation. The \textsuperscript{3}Pr\textsubscript{2}Im carbene ligand resembles the reactivity of the [NQA] ligand in these C–H bond functionalization reactions, yielding exclusive stannylation product when using SnBu\textsubscript{3}, and giving a mixture of stannylation and hydroarylation with SnPh\textsubscript{3}. Similarly to the [NQA] ligand, the \textsuperscript{3}Pr\textsubscript{2}Im carbene facilitates the alkene hydroarylation reaction with H\textsubscript{2}C=CHSnPh\textsubscript{3}, and the room temperature stannylation reaction with H\textsubscript{2}C=CHSnBu\textsubscript{3}. The [NQA] supported nickel catalyst was thermally limited as elevated temperatures beyond 40 °C caused rapid decomposition of the catalyst; however, the \textsuperscript{3}Pr\textsubscript{2}Im supported catalyst proved to me more thermally robust, as it carries out the stannylation reaction at 90 °C. To investigate if this catalyst is potentially able to facilitate the C–H bond stannylation reaction of less activated substrates, a catalytic amount of Ni(COD)\textsubscript{2} and \textsuperscript{3}Pr\textsubscript{2}Im was reacted with H\textsubscript{2}C=CHSnBu\textsubscript{3} and benzene at 90 °C for 24 h.

The crude \textsuperscript{119}Sn\{\textsuperscript{1}H\} NMR spectrum showed no indication of the desired stannylation product. Heating the catalyst beyond 100 °C resulted in decomposition of the nickel catalyst, indicated by formation of a black nickel metal precipitate, and the decomposition product Bu\textsubscript{3}Sn–SnBu\textsubscript{3} being observed in the \textsuperscript{119}Sn\{\textsuperscript{1}H\} NMR. The results are summarized in Scheme 3.6.
Scheme 3.6. General reaction scheme for screening of carbene ligands influence on selectivity of stannylation vs. hydroarylation.

3.2.3 Towards C–H Bond Germylation: Studies of Carbene Bulk Influence on Selectivity

The dramatic role that carbene steric bulk plays on the selectivity of C–H bond silylation as opposed to the unwanted alkene hydroarylation reaction has previously been discussed. This phenomenon did not effectively extend into the C–H bond stannylation reactions, as the \( {^1} \text{Pr}_2 \text{Im} \) carbene with \( \text{H}_2 \text{C} = \text{CHSnPh}_3 \) provided hydroarylation product, while all other ligand and stannyl substrate combinations resulted in stannylation product. This can possibly be attributed to the relative ease of β-Sn elimination as opposed to the more difficult β-Si elimination. To potentially gain more insight into the effect carbene

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<td>44.5</td>
<td>Stannylation</td>
<td>Stannylation</td>
</tr>
<tr>
<td>IMes</td>
<td>36.5</td>
<td>Stannylation</td>
<td>Stannylation</td>
</tr>
<tr>
<td>IBn</td>
<td>30.0</td>
<td>Stannylation</td>
<td>Stannylation</td>
</tr>
<tr>
<td>( {^1} \text{Pr}_2 \text{Im} )</td>
<td>27.4</td>
<td>Stannylation</td>
<td>Hydroarylation</td>
</tr>
</tbody>
</table>

References being on page 105
steric bulk has on these systems, it was thought that extension of the reaction to germanium would prove useful. To the best of our knowledge, there is only one other example of transition metal catalyzed C–H bond germylation which was facilitated by a palladium catalyst using a Ge–Ge starting material and required the use of a strong meta-directing substituent.\(^\text{10}\)

The reaction of Ni(COD)\(_2\) and the IPr with 2 equivalents of H\(_2\)C=CHGePh\(_3\) provided the expected nickel complex [IPr]Ni(\(\eta^2\)-H\(_2\)C=CHGePh\(_3\))\(_2\) (3). A catalytic amount of 3 was reacted with H\(_2\)C=CHGePh\(_3\) and C\(_6\)F\(_5\)H at 90 °C for 18 h. The crude \(^{19}\)F NMR featured a majority of hydroarylation product C\(_6\)F\(_5\)CH\(_2\)CH\(_2\)GePh\(_3\), and 4% conversion to the C–H germylation product C\(_6\)F\(_5\)GePh\(_3\).

Because the largest carbene provided trace amounts of C–H germylation product, it seemed likely that a smaller carbene would further improve the favorability of this reaction. The reaction of a catalytic amount of Ni(COD)\(_2\) and IMes with H\(_2\)C=CHGePh\(_3\) and C\(_6\)F\(_5\)H at 90 °C for 18 h resulted in exclusive conversion to the germylation product, with no indication of hydroarylation product being formed. Furthermore, when the analogous reaction was repeated with the IBn and \(^3\)Pr\(_2\)Im carbene ligands, silylation product was again exclusively observed. The results are summarized in Scheme 3.7.
Scheme 3.7. General reaction scheme for screening of carbene ligands influence on selectivity of germylation vs. hydroarylation.

The C–H bond germylation reaction offers an intriguing middle ground between previous stannylation and silylation reactions. While the C–H bond stannylation reaction with H$_2$C=CHSnBu$_3$ can be easily facilitated with all of the screened carbene ligands, only the two smallest carbene ligands provide exclusive C–H silylation product. The two larger carbene ligands IMes and IPr provide a mixture of silylation and hydroarylation, and exclusive hydroarylation, respectively. The results observed in the C–H bond germylation follow the general trend that a carbene with greater steric bulk favors productions of the hydroarylation product, while a smaller carbene favors the carbon–heteroatom bond formation products.
3.3 Conclusions & Future Work

The original goal of this thesis was accomplished. The Ni(0) complex that acts as a catalyst in the C–H bond stannylation of fluorinated aromatics was successfully tuned to provide a route towards the analogous C–H bond silylation reaction. The addition of a carbene ligand in lieu of the previously utilized phosphine resulted in a more thermally robust complex capable of catalysis. The improved stability allowed for the C–H bond silylation reaction to efficiently proceed at elevated temperatures, facilitating the silylation of aryl C–H bonds in fluorinated aromatics containing two ortho fluorine substituents. The steric bulk of the carbene was found to play a key role in the selectivity of the reaction. The larger IPr carbene ligand facilitated the alkene hydroarylation reaction, while the smaller 1Pr2Im carbene ligand provided the C–H silylation product exclusively. Further investigations into the mechanism of these reactions elucidated that the β-Si elimination is rapid and reversible in both systems. This provided key insight into potential rate determining steps of the C–H silylation reaction.

Follow up investigation into the role that carbene steric bulk has on the selectivity in these systems was carried out. The IBn carbene ligand is slightly larger than 1Pr2Im, and provides exclusively silylation product. The IMes carbene ligand falls between the IPr and IBn carbene ligands, and provides a mixture of silylation and hydroarylation products in a near 2:1 ratio respectively. Further studies to investigate the rates of silylation and hydroarylation, as well as tracing the product ratios should be carried out. A screen of carbene ligands with a greater variety of %V_bur should also be explored; specifically, the Me2Im carbene, which is smaller than 1Pr2Im, should be considered to potentially provide a route towards the activation of more difficult substrates. Furthermore, it could provide
interesting to determine if the electronic parameters of N-heterocyclic carbene donor ligands also plays a role in the selectivity of these systems. A screening of carbenes with similar \( V_{\text{bur}} \) but varied electronic parameters would prove effective.

To determine if the influence that carbene steric bulk has on selectivity could be extended to previous C–H stannylation reactions, a similar screening was performed. The reaction of catalytic amounts of Ni(COD)\(_2\) and L (L = IPr, IMes, IBn, \( \text{iPr}_2\text{Im} \)) with \( \text{H}_2\text{C}=\text{CHSnR}_3 \) (R = Bu, Ph) and C\(_6\)F\(_5\)H provided exclusively stannylation in all but one case, which proved to be extremely unexpected. Furthermore, this methodology was extended towards germanium. The reaction of catalytic amounts of Ni(COD)\(_2\) and IPr with \( \text{H}_2\text{C}=\text{CHGePh}_3 \) and C\(_6\)F\(_5\)H provided the hydroarylation product with trace amounts of germanylation. The analogous reaction with the smaller carbenes (IMes, IBn, \( \text{iPr}_2\text{Im} \)) resulted in conversion to the C–H bond germanylation product exclusively. The results are summarized in Table 3.1.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( V_{\text{bur}} )</th>
<th>SiMe(_3)</th>
<th>GePh(_3)</th>
<th>SnBu(_3)</th>
<th>SnPh(_3)</th>
</tr>
</thead>
<tbody>
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<td>IPr</td>
<td>44.5</td>
<td>Hydro</td>
<td>Germyl (4%) + Hydro (96%)</td>
<td>Stanyl</td>
<td>Stanyl</td>
</tr>
<tr>
<td>IMes</td>
<td>36.5</td>
<td>Silyl (60%) + Hydro (30%)</td>
<td>Germyl</td>
<td>Stanyl</td>
<td>Stanyl</td>
</tr>
<tr>
<td>IBn</td>
<td>30.0</td>
<td>Silyl</td>
<td>Germyl</td>
<td>Stanyl</td>
<td>Stanyl</td>
</tr>
<tr>
<td>( \text{iPr}_2\text{Im} )</td>
<td>27.4</td>
<td>Silyl</td>
<td>Germyl</td>
<td>Stanyl</td>
<td>Hydro</td>
</tr>
</tbody>
</table>

**Table 3.1.** Summary of N-heterocyclic carbene screening studies.

Examining the results shows a trend for the influence of carbene steric bulk as the reactions become more difficult: from stannylation to silylation. In the C – H bond stannylation reactions, the size of the ancillary carbene ligand does not have an effect besides the one unexpected result where the small \( \text{iPr}_2\text{Im} \) with SnPh\(_3\) provides...
hydroarylation. This can be attributed to the relative ease of the β-Sn elimination step along the catalytic pathway. For C–H bond germylation reactions, where the β-Ge elimination step is more difficult, the largest carbene ligand, IPr, provides near exclusive hydroarylation with 4% germylation product. Changing to a smaller carbene provides exclusive germylation product. Finally, for C–H bond silylation reaction, where the β-Si elimination step is the most difficult, the two largest carbene ligands, IPr and IMes, both provide hydroarylation products, with IMes providing a mixture of silylation and hydroarylation. Carbene ligands that are smaller are needed to provide exclusive silylation. Overall, these studies support the original posit that carbene steric bulk has a significant influence on selectivity in these catalytic systems. Future studies should compare the rates of stannylation vs. germylation vs. silylation in systems that display similar reactivity and selectivity.
3.4 Experimental

3.4.1 Materials and Methods

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–d₆, and toluene–d₈ 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, ¹³C{¹H}, ¹⁹F{¹H}, ²H, ²⁹Si{¹H}, and ¹¹⁹Sn{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 (C₆D₆, δ 7.15) or (toluene-d₈, δ 2.17) with respect to tetramethylsilane at δ 0.00. ¹³C{¹H} NMR spectra were referenced relative to solvent resonances (C₆D₆, δ 128.26) or (toluene-d₈, δ 21.37). ¹⁹F{¹H} NMR spectra were referenced to an external sample of 80% CCl₃F in CDCl₃ at δ 0.00. Benzene–d₆ and toluene–d₈ was purchased from Cambridge Isotope Laboratory. All reagents were purchased from commercial suppliers. The compounds Ni(COD)₂,¹¹ IMes,¹² IBn,¹³ and were prepared according to literature procedures.

3.4.2 Synthesis, Characterizations, and Reactions

Synthesis of [IBn]Ni(n²-H₂C=CHSiMe₃)₂ (1c). Ni(COD)₂ (0.243 g, 0.884 mmol) was dissolved in 5 mL of toluene. The solution was charged with 10 equivalents of trimethyl(vinyl)silane (0.177 g, 1.767 mmol) and stirred for 1 h to ensure all Ni(COD)₂ had dissolved. A solution of IBn (0.270 g, 0.884 mmol) in toluene was added dropwise to the reaction mixture and stirred for 30 min. The solution was filtered through celite and

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volatiles were removed in vacuo affording 0.262 g of a thick yellow oil (87% yield). Major
isomer: $^1$H NMR (C$_6$D$_6$, 25 °C, 500.129 MHz): δ 0.18 (s, 18H, Si(CH$_3$)$_3$); 2.52 (broad
multiplet, 2H, vinyl–H); 2.78 (d, 2H, vinyl–H, $^2$J$_{HH}$ = 15.48 Hz); 2.92 (d, 2H, vinyl–H,
$^2$J$_{HH}$ = 12.25 Hz); 4.77 (d, 2H, CH$_2$–Ph, $^2$J$_{HH}$ = 15.05 Hz); 4.81 (d, 2H, CH$_2$–Ph, $^2$J$_{HH}$ =
16.68 Hz); 6.22 (s, 2H, H$_2$C=CH$_2$); 6.98 (m, 8H, 2,6–Ph–H); 7.00 (m, 12H, 3,4,5–Ph–H).
$^{13}$C{${^1}$H} NMR (C$_6$D$_6$, 23°C, 75.47 MHz): δ 1.1 (s, 6C, Si(CH$_3$)$_3$); 28.3 (s, vinyl–C); 30.8
(s, vinyl–C); 51.2 (s, 2C, CH$_2$–Ph); 52.1 (s, 2C, CH$_2$–Ph); 120.9 (s, Ph–C); 127.5 (s, Ph–
C); 128.9 (s, H$_2$C=CH$_2$); 137.4 (s, Ph–C); 137.6 (s, Ph–C); 204.4 (s, Ni–C). $^{29}$Si{${^1}$H} NMR
(C$_6$D$_6$, 27 °C, 59.64 MHz): -4.1 (s, 2Si, SiMe$_3$). Minor isomer: $^1$H NMR (C$_6$D$_6$, 25 °C,
500.129 MHz): δ 0.15 (s, 18H, Si(CH$_3$)$_3$); 2.26 (dd, 2H, vinyl–H, $^2$J$_{HH}$ = 12.54 Hz,
$^2$J$_{HH}$ = 15.86 Hz); 2.78 (d, 2H, vinyl–H, $^2$J$_{HH}$ = 15.86 Hz, $^2$J$_{HH}$ = 1.01 Hz); 2.92 (d, 2H, vinyl–H,
$^2$J$_{HH}$ = 12.54 Hz, $^2$J$_{HH}$ = 1.01 Hz); 4.95 (d, 2H, CH$_2$–Ph, $^2$J$_{HH}$ = 14.85 Hz); 5.00 (d, 2H,
CH$_2$–Ph, $^2$J$_{HH}$ = 8.81 Hz); 6.17 (s, 2H, H$_2$C=CH$_2$); 6.95 (m, 8H, 2,6–Ph–H); 7.08 (m, 12H,
3,4,5–Ph–H). $^{13}$C{${^1}$H} NMR (C$_6$D$_6$, 23°C, 75.47 MHz): δ 0.8 (s, 6C, Si(CH$_3$)$_3$); 24.9 (s,
v vinyl–C); 29.7 (s, vinyl–C); 53.7 (s, 2C, CH$_2$–Ph); 54.4 (s, 2C, CH$_2$–Ph); 120.9 (s, Ph–C);
127.5 (s, Ph–C); 128.9 (s, H$_2$C=CH$_2$); 137.4 (s, Ph–C); 137.6 (s, Ph–C); 203.9 (s, Ni–C).
$^{29}$Si{${^1}$H} NMR (C$_6$D$_6$, 27 °C, 59.64 MHz): -4.3 (s, 2Si, SiMe$_3$).

Synthesis of [IMes]Ni(η$^2$-H$_2$C=CHSiMe$_3$)$_2$ (1d). A solution of Ni(COD)$_2$ (0.243 g, 0.884
mmol), trimethyl(vinyl)silane (0.177 g, 1.767 mmol) and IMes (0.270 g, 0.884 mmol) in
10 mL of pentane was stirred for 30 minutes. The solution was filtered through celite and
evaporated in vacuo to afford 0.420 g (85% yield) of a yellow oil. Compound was
recrystallized by slow evaporation from minimal pentane. $^1$H NMR (C$_6$D$_6$, 25 °C, 500.129
MHz): δ -0.05 (s, 18H, Si(CH$_3$)$_3$); 2.08 (s, 6H, Ar–CH$_3$); 2.09 (s, 6H, Ar–CH$_3$); 2.11 (s,
6H, Ar–CH$_3$); 2.54 (dd, 2H, vinyl–H, $^2J_{HH} = 0.64$ Hz, $^2J_{HH} = 14.53$ Hz); 2.62 (dd, 2H, vinyl–H, $^2J_{HH} = 12.65$ Hz, $^2J_{HH} = 0.64$ Hz); 2.69 (dd, 2H, vinyl–H, $^2J_{HH} = 12.65$ Hz, $^2J_{HH} = 14.53$ Hz); 6.25 (s, 2H, H=CH); 6.70 (s, 2H, Ar–H); 6.72 (s, 2H, Ar–H). $^{13}$C{$_1^H$} NMR (C$_6$D$_6$, 23 °C, 75.47 MHz): δ 1.3 (s, 6C, Si(C$_3$H$_3$)$_3$); 18.5 (s, 2C, Ar–CH$_3$); 18.7 (s, 2C, Ar–CH$_3$); 21.1 (s, 2C, Ar–CH$_3$); 51.2 (s, vinyl–C); 53.1 (s, vinyl–C); 129.0 (s, H$_2$C=CH$_2$); 129.5 (s, Ph–C); 129.7 (s, Ph–C); 135.6 (s, Ph–C); 135.9 (s, Ph–C); 137.9 (s, Ph–C); 138.4 (s, Ph–C); 203.9 (s, Ni–C). $^{29}$Si{$_1^H$} NMR (C$_6$D$_6$, 27 °C, 59.64 MHz): -5.0 (s, 2Si, SiMe$_3$).

**Synthesis of [IBn]$_2$Ni(η$_2$-H$_2$C=CHSiMe$_3$).** A solution of Ni(COD)$_2$ (0.243 g, 0.884 mmol), trimethyl(vinyl)silane (0.177 g, 1.767 mmol) and IBn (0.270 g, 0.884 mmol) in 10 mL of pentane was stirred for 30 min. The solution was filtered affording 0.096 g of a dark yellow precipitate (64 % yield). $^1$H NMR (C$_6$D$_6$, 25 °C, 500.129 MHz): δ -0.05 (s, 9H, Si(C$_3$H$_3$)$_3$); 1.62 (dd, 1H, vinyl–H, $^2J_{HH} = 12.48$ Hz, $^2J_{HH} = 14.04$ Hz); 1.88 (dd, 1H, vinyl–H, $^2J_{HH} = 14.04$ Hz, $^2J_{HH} = 2.54$ Hz); 2.33 (dd, 1H, vinyl–H, $^2J_{HH} = 12.48$ Hz, $^2J_{HH} = 2.54$ Hz); 5.08 (d, 2H, CH$_2$–Ph, $^2J_{HH} = 15.08$ Hz); 5.12 (d, 2H, CH$_2$–Ph, $^2J_{HH} = 15.42$ Hz); 5.52 (d, 2H, CH$_2$–Ph, $^2J_{HH} = 14.85$ Hz); 5.68 (d, 2H, CH$_2$–Ph, $^2J_{HH} = 14.40$ Hz); 6.16 (s, 2H, H=CH); 6.23 (s, 2H, H=CH); 6.94 (m, 8H, 2,6–Ph–H); 7.00 (m, 12H, 3,4,5–Ph–H). $^{13}$C{$_1^H$} NMR (C$_6$D$_6$, 23 °C, 75.47 MHz): δ 1.7 (s, 3C, Si(CH$_3$)$_3$); 30.2 (s, vinyl–C); 31.5 (s, vinyl–C); 53.8 (s, 2C, CH$_2$–Ph); 54.1 (s, 2C, CH$_2$–Ph); 119.3 (s, Ph–C); 127.4 (s, Ph–C); 128.6 (s, H$_2$C=CH$_2$); 138.5 (s, Ph–C); 138.7 (s, Ph–C); 205.8 (s, Ni–C); 206.5 (s, Ni–C). $^{29}$Si{$_1^H$} NMR (C$_6$D$_6$, 27 °C, 59.64 MHz): -6.8 (s, 1Si, SiMe$_3$).

**Synthesis of (IPr)Ni(η$_2$-CH$_2$=CHSnPh$_3$)$_2$ (2).** A solution of Ni(COD)$_2$ (0.056 g, 0.206 mmol) IPr (0.080 g, 0.206 mmol) and triphenyl(vinyl) tin (0.150 g, 0.398 mmol) in 10 mL of pentane was stirred for 30 min. The solution was filtered affording 0.182 g of a yellow
solid. (73% yield). $^1$H NMR (C$_6$D$_6$, 21°C, 500.133 MHz): $\delta$ 0.71 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.7 Hz); 0.87 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.7 Hz); 1.17 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.7 Hz); 1.35 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.7 Hz); 2.80 (d, 2H, vinyl–H, $^3$J$_{HH}$ = 14.8 Hz); 2.93 (d, 2H, vinyl–H, $^3$J$_{HH}$ = 11.7 Hz); 3.01 (d, 2H, vinyl–H, $^3$J$_{HH}$ = 11.7 Hz); 3.15 (septet, 4H, CH$_2$(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.7 Hz); 6.65 (s, 2H, H$_2$C=CH$_2$); 6.86 (m, 6H, 2,6–Ar–H); 7.44 (m, 9H 3,4,5–Ar–H).

$^{13}$C{$^1$H} NMR (C$_6$D$_6$, 23°C, 75.47 MHz): $\delta$ 21.9 (s, isopropyl–(CH$_3$)$_2$); 22.3 (s, isopropyl–(CH$_3$)$_2$); 26.4 (s, isopropyl–(CH$_3$)$_2$); 26.7 (s, isopropyl–(CH$_3$)$_2$); 28.8 (s, isopropyl–CH); 28.9 (s, isopropyl–CH); 51.9 (s, vinyl–C); 57.2 (s, vinyl–C); 123.8 (s, Ar–C); 124.4 (s, Ar–C); 124.7 (s, Ar–C); 129.6 (s, Ar–C); 137.4 (s, 1–Ph–C); 138.0 (s with Sn satellites, 2,6–Ph–C, $^2$J$_{CSn}$ = 34.5 Hz); 141.5 (s, 3,5–Ph–C); 146.1 (s, 4–Ph–C); 204.9 (s, Ni–C).$^{19}$Sn{$^1$H} NMR (C$_6$D$_6$, 20.6°C, 186.50 MHz): $\delta$ −110.3 (s, 2Sn, SnPh$_3$).

**Synthesis of (IPr)Ni(η$^2$-CH$_2$=CHGePh)$_2$ (3).** A solution of Ni(COD)$_2$ (0.062 g, 0.023 mmol), IPr (0.088 g, 0.023 mmol) and triphenyl(vinyl) germane (0.150 g, 0.046 mmol) in 10 mL of pentane was stirred for 30 min. The solution was filtered affording 0.160 g of a yellow solid. (64% yield). $^1$H NMR (C$_6$D$_6$, 21°C, 500.133 MHz): $\delta$ 0.52 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.8 Hz); 0.84 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.8 Hz); 1.05 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.8 Hz); 1.48 (d, 6H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.8 Hz); 2.89 (septet, 2H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.8 Hz); 2.93 (d, 2H, vinyl–H, $^3$J$_{HH}$ = 14.5 Hz); 3.00 (d, 2H, vinyl–H, $^3$J$_{HH}$ = 12.3 Hz); 3.12 (septet, 2H, CH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.8 Hz); 3.19 (d, 2H, vinyl–H, $^3$J$_{HH}$ = 12.3 Hz, $^3$J$_{HH}$ = 14.5 Hz); 7.05 (m, 6H, 2,6–Ar–H); 7.25 (m, 9H 3,4,5–Ar–H). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 23°C, 75.47 MHz): $\delta$ 21.3 (s, isopropyl–(CH$_3$)$_2$); 22.4 (s, isopropyl–(CH$_3$)$_2$); 26.1 (s, isopropyl–(CH$_3$)$_2$); 26.9 (s, isopropyl–(CH$_3$)$_2$); 28.7 (s, isopropyl–CH); 29.0 (s, isopropyl–CH); 51.2

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(s, vinyl–C); 57.5 (s, vinyl–C); 123.9 (s, Ar–C); 124.4 (s, Ar–C); 124.8 (s, Ar–C); 129.3 (s, Ar–C); 135.7 (s, Ph–C); 137.7 (s, Ph–C); 140.0 (s, Ph–C); 146.3 (s, Ph–C); 202.3 (s, Ni–C).

**Synthesis of triphenyl(vinyl) germane.** Triphenylgermanium chloride (3.0 g, 8.8 mmol) was dissolved in 20 mL of THF. Vinylmagnesium chloride (8.3 mL, 13.2 mmol) was added dropwise to solution while stirring. The reaction was left to stir for 4 hours. Degassed water was added to quench the reaction, after which the solution separated into two layers. The THF layer was extracted and dried in vacuo to give a white solid. The solid was dissolved in hot ethanol and filtered while hot through a pad of Celite. Solution was placed in the freezer and afforded 1.5 g of white crystals (50 % yield). $^1$H NMR (C$_6$D$_6$, 21°C, 500.133 MHz): δ 5.78 (dd, 1H, vinyl–CH, $^2J = 3.0$ Hz, $^2J = 20.0$ Hz); 6.14 (dd, 1H, vinyl–CH, $^2J = 3.0$ Hz, $^2J = 13.5$ Hz); 6.65 (dd, vinyl–CH, $^2J = 13.5$ Hz, $^2J = 20.0$ Hz); 7.13 (2nd order m, 9H, 3,4,5–Ph–H); 7.55 (2nd order m, 6H, 3,6–Ph–H). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 23°C, 125.77 MHz): δ 128.5 (s, Ph); 129.2 (s Ph); 134.3 (s, CH=CH$_2$); 134.6 (s, CH=CH$_2$); 135.4 (s, Ph); 136.5 (s, Ph).

**Synthesis of C$_6$F$_5$CH$_2$CH$_2$GePh$_3$.** A solution of pentafluorobenzene (0.025 g, 0.151 mmol) and triphenyl(vinyl)germane (0.050 g, 0.151 mmol) in 0.6 g of toluene was added to a vial charged with 3 (0.016 g, 0.015 mmol, 10 mol %) and FSiPh$_3$ (0.017 g, 0.061 mmol) which was used as an internal standard. The solution was heated at 90 °C for 18 h. The crude $^{19}$F NMR showed a mixture of alkene hydroarylation and C – H germylation products. (65 and 3 % NMR yields respectively). $^1$H NMR (C$_6$D$_6$, 21°C, 500.133 MHz): δ 1.55 (second order m, 2H, CH$_2$Ge); 2.63 (second order m, 2H, CH$_2$CH$_2$Ge); 7.15 (m, 9H, References being on page 105
3,4,5–Ph–H); 7.50 (m, 6H, 2,6–Ph–H). $^{19}$F {1H} NMR (C$_6$D$_6$, 21°C, 470.54 MHz): $\delta$ -145.3 (AA′MM′ second order m, 2F, 2,6–Ar–F); -159.0 (t, 1F, 4–Ar–F, $\textit{J}_{FF} = 21.3$ Hz); -163.4 (AA′MM′X second order m, 2F, 3,5–Ar–F). $^{13}$C{1H} NMR (C$_6$D$_6$, 23°C, 125.77 MHz): $\delta$ 18.5 (s, SnCH$_2$); 22.7 (s, SnCH$_2$CH$_2$); 128.7 (s, Ar–C); 129.5 (s, Ar–C); 135.1 (s, Ar–C); 135.5 (s, Ar–C); 136.4 (s, Ar$^F$–C); 138.7 (dm, Ar$^F$–C); 144.3 (dm, Ar$^F$–C); 150.6 (dm, Ar$^F$–C).

**Synthesis of triphenyl(2,3,5,6-tetrafluorophenyl)germane.** A solution of pentafluorobenzene (0.005 g, 0.030 mmol) and triphenyl(vinyl)germane (0.010 g, 0.030 mmol) in 0.6 g of toluene was added to a vial charged Ni(COD)$_2$ (0.001 g, 0.003 mmol, 10 mol %), iPr$_2$Im (0.001 g, 0.003 mmol, 10 mol %), and FSiPh$_3$ (0.002 g, 0.007 mmol), which was used as an internal standard. The solution was heated at 90 °C for 18 h. (68 % NMR yield). $^1$H NMR (C$_6$D$_6$, 21°C, 500.133 MHz): $\delta$ 7.55 (m, 9H, 3,4,5–Ph–H); 7.62 (m, 6H, 2,6–Ph–H). $^{19}$F {1H} NMR (C$_6$D$_6$, 21°C, 470.54 MHz): $\delta$ -122.2 (AA′MM′N second order m, 2F, 2,6–Ar–F); -150.5 (t, 1F, 4–Ar–F, $\textit{J}_{FF} = 21.3$ Hz); -160.1 (AA′MM′N second order m, 2F, 3,5–Ar–F). $^{13}$C{1H} NMR (C$_6$D$_6$, 23°C, 125.77 MHz): $\delta$ 128.6 (s, Ar–C); 129.3 (s, Ar–C); 134.9 (s, Ar–C); 135.5 (s, Ar–C); 135.8 (s, Ar$^F$–C); 137.3 (dm, Ar$^F$–C); 142.1 (dm, Ar$^F$–C); 147.4 (dm, Ar$^F$–C).

**Alternate Synthesis of triphenyl(2,3,5,6-tetrafluorophenyl)germane.** A solution of pentafluorobenzene (0.005 g, 0.030 mmol) and triphenyl(vinyl)germane (0.010 g, 0.030 mmol) in 0.6 g of toluene was added to a vial charged Ni(COD)$_2$ (0.001 g, 0.003 mmol, 10 mol %), IBn (0.001 g, 0.003 mmol, 10 mol %), and FSiPh$_3$ (0.002 g, 0.007 mmol), which was used as an internal standard. The solution was heated at 90 °C for 18 h. (60 % NMR yield).
Alternate Synthesis of triphenyl(2,3,5,6-tetrafluorophenyl)germane. A solution of pentafluorobenzene (0.005 g, 0.030 mmol) and triphenyl(vinyl)germane (0.010 g, 0.030 mmol) in 0.6 g of toluene was added to a vial charged with Ni(COD)$_2$ (0.001 g, 0.003 mmol, 10 mol %), $^{t}$Pr$_2$Im (0.001 g, 0.003 mmol, 10 mol %), and FSiPh$_3$ (0.002 g, 0.007 mmol), which was used as an internal standard.

**Reaction of C$_6$F$_5$H and H$_2$C=CHSiMe$_3$ with 5\% (1c).** A solution of pentafluorobenzene (0.083 g, 0.498 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.6 g of toluene was added to a vial charged with 1c (0.012 g, 0.025 mmol, 5 mol %) and FSiPh$_3$ (0.017 g, 0.061 mmol) which was used as an internal standard. The solution was heated at 120 °C for 12 h and the crude $^{19}$F NMR showed exclusive conversion to the known C–H silylation product C$_6$F$_5$SiMe$_3$.\(^2\)

**Reaction of C$_6$F$_5$H and H$_2$C=CHSiMe$_3$ with 5\% (1d).** A solution of pentafluorobenzene (0.083 g, 0.498 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.6 g of toluene was added to a vial charged with 1d (0.007 g, 0.025 mmol, 5 mol %) and FSiPh$_3$ (0.017 g, 0.061 mmol), which was used as an internal standard. The solution was heated at 120 °C for 24 h and the crude $^{19}$F NMR showed conversion a mixture of the known C–H silylation product C$_6$F$_5$SiMe$_3$, and alkene hydroarylation product C$_6$F$_5$CH$_2$CH$_2$SiMe$_3$ approximately 60 and 30 % yields respectively.\(^2\) The reaction was monitored via $^{19}$F NMR to track initial rations of silylation to hydroarylation. The initial ratio of silylation to hydroarylation is approximately 3:1. As the reaction nears completion after 5 h the ratio decreases to 2:1. The results are shown in Chart 3.1, and product conversions in mol are shown in Table 3.1.
Chart 3.1. Plot of product conversion (mol) vs. time (h) for C–H silylation product vs. hydroarylation product.

Table 3.2. Amount of mol of silylation and hydroarylation product conversion, product ratio, and overall percent conversion of reaction.

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<tr>
<th>time</th>
<th>silyl(mol)</th>
<th>alkyl(mol)</th>
<th>ratio</th>
<th>% conversion</th>
</tr>
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</tr>
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<td>0.00009825</td>
<td>1.602035623</td>
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</table>
Reaction of C₆F₅H and H₂C=CHSiMe₃ with 5% (1d) under 1 atm C₂H₄. An NMR tube with a teflon valve was put under 1 atm of ethylene (2 mL, 1 atm, 0.082 mmol). The ethylene was charged via a transfer bridge under static vacuum to a separate NMR tube with a teflon valve charged with a solution of pentafluorobenzene (0.083 g, 0.498 mmol), trimethyl(vinyl)silane (0.05 g, 0.498 mmol), 1d (0.007 g, 0.025 mmol, 5 mol %), and FSiPh₃ (0.017 g, 0.061 mmol), which was used as an internal standard, in 0.6 g of toluene. The solution was heated at 120 °C and the reaction was monitored via ¹⁹F NMR to track initial ratios of silylation to hydroarylation. The results were identical to the analogous experiment conducted in the absence of ethylene.

Reaction of C₆F₅H and H₂C=CHSiMe₃ with nickel metal. A solution of 1d in 0.6 g of toluene was heated to 140 °C for 16 h to promote decomposition of 1d with nickel metal precipitate. The solution was filtered to collect the nickel metal, which was charged to a solution of pentafluorobenzene (0.083 g, 0.498 mmol) and trimethyl(vinyl)silane (0.05 g, 0.498 mmol) in 0.6 g of toluene. The solution was heated at 120 °C for 20 h and the crude ¹⁹F NMR showed no indication of hydroarylation product.

Reaction of C₆F₅H and H₂C=CHSnBu₃ with 10% Ni(COD)₂ and IPr. A solution of pentafluorobenzene (0.014 g, 0.078 mmol) and tributyl(vinyl)stannane (0.025 g, 0.078 mmol) in 0.6 g of toluene was added to a vial charged Ni(COD)₂ (0.002 g, 0.008 mmol, 10 mol %), IPr (0.003 g, 0.008 mmol, 10 mol %), and FSiPh₃ (0.017 g, 0.061 mmol), which was used as an internal standard. The solution was heated at 90 °C for 18 h and resulted in exclusive conversion to the known C–H stannylation product C₆F₅SnBu₃ (74 % NMR yield).₁b

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**Reaction of C₆F₅H and H₂C=CHSnBu₃ with 10% Ni(COD)₂ and IMes.** A solution of pentafluorobenzene (0.014 g, 0.078 mmol) and tributyl(vinyl)stannane (0.025 g, 0.078 mmol) in 0.6 g of toluene was added to a vial charged Ni(COD)₂ (0.002 g, 0.008 mmol, 10 mol %), IMes (0.002 g, 0.008 mmol, 10 mol %), and FSiPh₃ (0.017 g, 0.061 mmol), which was used as an internal standard. The solution was heated at 90 °C for 18 h and resulted in exclusive conversion to the known C–H stannylation product C₆F₅SnBu₃. (66 % NMR yield).

**Reaction of C₆F₅H and H₂C=CHSnBu₃ with 10% Ni(COD)₂ and IBn.** A solution of pentafluorobenzene (0.014 g, 0.078 mmol) and tributyl(vinyl)stannane (0.025 g, 0.078 mmol) in 0.6 g of toluene was added to a vial charged Ni(COD)₂ (0.002 g, 0.008 mmol, 10 mol %), IBn (0.002 g, 0.008 mmol, 10 mol %), and FSiPh₃ (0.017 g, 0.061 mmol), which was used as an internal standard. The solution was heated at 90 °C for 18 h and resulted in exclusive conversion to the known C–H stannylation product C₆F₅SnBu₃. (68 % NMR yield).

**Reaction of C₆F₅H and H₂C=CHSnBu₃ with 10% Ni(COD)₂ and 1Pr₂Im.** A solution of pentafluorobenzene (0.014 g, 0.078 mmol) and tributyl(vinyl)stannane (0.025 g, 0.078 mmol) in 0.6 g of toluene was added to a vial charged Ni(COD)₂ (0.002 g, 0.008 mmol, 10 mol %), 1Pr₂Im (0.001 g, 0.008 mmol, 10 mol %), and FSiPh₃ (0.017 g, 0.061 mmol), which was used as an internal standard. The solution was heated at 90 °C for 18 h and resulted in exclusive conversion to the known C–H stannylation product C₆F₅SnBu₃. (72 % NMR yield).
Reaction of C₆F₅H and H₂C=CHSnPh₃ with 10% (2). A solution of pentafluorobenzene (0.011 g, 0.066 mmol) and triphenyl(vinyl)stannane (0.025 g, 0.066 mmol) in 0.6 g of toluene was added to a vial charged with 2 (0.007 g, 0.025 mmol, 5 mol %) and FSiPh₃ (0.017 g, 0.061 mmol), which was used as an internal standard. The solution was heated at 90 °C for 20 h and resulted in exclusive conversion to the known C–H stannylation product C₆F₅SnPh₃. (82 % NMR yield).¹a

Reaction of C₆F₅H and H₂C=CHSnPh₃ with 10% Ni(COD)₂ and IMes. A solution of pentafluorobenzene (0.011 g, 0.066 mmol) in 0.6 g of toluene was added to a vial charged with triphenyl(vinyl)stannane (0.025 g, 0.066 mmol), Ni(COD)₂ (0.002 g, 0.007 mmol, 10 mol %), IMes (0.002 g, 0.007 mmol, 10 mol %), and FSiPh₃ (0.017 g, 0.061 mmol), which was used as an internal standard. The solution was heated at 90 °C for 20 h and resulted in exclusive conversion to the known C–H stannylation product C₆F₅SnPh₃. (60 % NMR yield).¹a

Reaction of C₆F₅H and H₂C=CHSnPh₃ with 10% Ni(COD)₂ and IBn. A solution of pentafluorobenzene (0.011 g, 0.066 mmol) in 0.6 g of toluene was added to a vial charged with triphenyl(vinyl)stannane (0.025 g, 0.066 mmol), Ni(COD)₂ (0.002 g, 0.007 mmol, 10 mol %), IBn (0.002 g, 0.007 mmol, 10 mol %), and FSiPh₃ (0.017 g, 0.061 mmol), which was used as an internal standard. The solution was heated at 90 °C for 20 h and resulted in exclusive conversion to the known C–H stannylation product C₆F₅SnPh₃. (67 % NMR yield).¹a

Reaction of C₆F₅H and H₂C=CHSnPh₃ with 10% Ni(COD)₂ and iPr₂Im. A solution of pentafluorobenzene (0.011 g, 0.066 mmol) in 0.6 g of toluene was added to a vial charged
with triphenyl(vinyl)stannane (0.025 g, 0.066 mmol), Ni(COD)$_2$ (0.002 g, 0.007 mmol, 10 mol %), iPr$_2$Im (0.001 g, 0.007 mmol, 10 mol %), and FSiPh$_3$ (0.017 g, 0.061 mmol), which was used as an internal standard. The solution was heated at 90 °C for 20 h and resulted in exclusive conversion to the known alkene hydroarylation product C$_6$F$_5$CH$_2$CH$_2$SnPh$_3$. (54 % NMR yield).\textsuperscript{1c}
Chapter 3 – Probing the Influence of Carbene Steric Bulk on Selectivity in Nickel-Catalyzed C–H Bond Functionalization: Conclusions & Future Work

3.5 References


APPENDIX

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