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# Influence of N-Heterocyclic Carbene Steric Bulk on Selectivity in Nickel Catalyzed C-H Bond Silylation, Germylation, and **Stannylation**

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**Supporting Information** 

ABSTRACT: A series of Ni(0) compounds supported by electronically similar N-heterocyclic carbene (NHC) ancillary ligands with a range of  $%V_{\rm bur}$  were used as catalysts for aryl C-H bond silvlation, germylation, and stannylation. The NHC steric bulk strongly influenced the selectivity of C-H functionalization to give new carbon-heteroatom bonds versus alkene hydroarylation, despite little structural change in the resting state of the catalysts. Studies were performed by reacting  $C_6F_5H$  and  $H_2C$ =CHER<sub>3</sub> (ER<sub>3</sub> = SnBu<sub>3</sub>, GePh<sub>3</sub>, SiMe<sub>3</sub>) using catalytic amounts of Ni(COD)<sub>2</sub> and NHC ligands IPr, IMes, IBn, and <sup>i</sup>Pr<sub>2</sub>Im. Catalytic C-H stannylation to give C<sub>6</sub>F<sub>5</sub>SnBu<sub>3</sub> was facile with all ligands. The catalytic C-H germylation reaction was more difficult than stannylation but was



demonstrated using H<sub>2</sub>C=CHGePh<sub>3</sub> to give C<sub>6</sub>F<sub>5</sub>GePh<sub>3</sub> for all but the largest NHC. The bulkiest NHC, IPr, gave a 96:4 ratio of the hydroarylation product  $C_6F_5CH_2CH_2GPh_3$  versus  $C_6F_5GePh_3$ . The C-H silvlation reactions required the highest temperatures and gave selective silvlation product  $C_6F_5SiMe_3$  only for the smallest IBn and  $Pr_2Im$  NHC ligands. Using the larger IMes carbene resulted in a 66:34 mixture of silvlation and hydroarylation products, and the largest NHC, IPr, gave exclusive conversion to the hydroarylation product, C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub>. DFT calculations are provided that give insight into the mechanism and key reaction steps, such as the relative difficulty of the critical  $\beta$ -Sn, Ge, and Si elimination steps.

# ■ INTRODUCTION

Transition metal catalyzed reactions of C-H bonds are a powerful technique for introducing functional groups to aromatic rings by generating new C-C or C-heteroatom bonds.<sup>1</sup> Ligand to ligand hydrogen transfer (LLHT) is a distinct mechanistic pathway through which C-H bond activation may occur<sup>2</sup> and offers a unique catalytic cycle with the potential to selectively form different products.<sup>3</sup> For Ni(0)complexes, it has been shown that LLHT frequently avoids the less thermodynamically favorable direct oxidative addition of C-H bonds by coupling them with an insertion step.<sup>4</sup> Nakao and co-workers first reported this in the hydroarylation of alkynes with Ni(0) monophosphine catalysts.<sup>5</sup> Hartwig and coworkers showed that the bulky NHC ancillary ligand IPr supported the Ni(0) catalyzed hydroarylation of alkenes to afford a mixture of linear and branched alkylarenes ([IPr] =1,3-bis[2,6-diisopropylphenyl]-1,3-dihydro-2H-imidazol-2-ylidene).<sup>6</sup> Both of these reactions undergo LLHT during the C-H activation step and afford new C-C bonded products.

We have previously shown that both <sup>i</sup>Pr<sub>3</sub>P and [NQA]  $([NQA] = MeNC_5H_4N^{i}Pr)$  supported Ni(0) complexes catalyze the reaction of C-H bonds to give new C-Sn bonds,<sup>3e</sup> as summarized in Scheme 1. The hard nitrogen donor [NQA] and Ni(COD)<sub>2</sub> catalyzed stannylation reaction between C<sub>6</sub>F<sub>5</sub>H and H<sub>2</sub>C=CHSnBu<sub>3</sub> occurs instantly at room temperature to produce C<sub>6</sub>F<sub>5</sub>SnBu<sub>3</sub> and liberate ethylene, but the catalyst decomposes above 50 °C. The same reaction using <sup>i</sup>Pr<sub>3</sub>P as the ancillary ligand occurs at higher temperatures, but the catalyst is robust up to 80 °C, which allows for a broader scope of fluorinated aromatic substrates. Attempts at catalytic silvlation using <sup>i</sup>Pr<sub>3</sub>P and  $Ni(COD)_2$  as catalyst precursors gave only trace silvlation products; however, Ni(0) complexes supported by an NHC ligand catalyzed the reaction of  $C_6F_5H$  with  $H_2C=CHSiMe_3$ to give the C-H silvlation product  $C_6F_5SiMe_3$  at temperatures up to 120 °C. These reactions are proposed to proceed through a mechanism shown in Scheme 1.<sup>3a</sup> In step A, the resting state of the catalyst,  $LNi(\eta^2-H_2C=CHER_3)_2$  (1), undergoes reversible dissociation of a vinyl moiety and the

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Scheme 1. Previous Work on Ni-Catalyzed C–H Stannylation Using <sup>i</sup>Pr<sub>3</sub>P and [NQA] as Ancillary Ligands and Ni Catalyzed C–H Silylation Using the IPr and <sup>i</sup>Pr<sub>2</sub>Im Ancillary Ligands<sup>a</sup>



<sup>*a*</sup>(a) Net reaction showing C–H silylation/stannylation products and alkene hydroarylation products; ethylene is also produced in the silylation and stannylation reaction. (b) Previously proposed catalytic pathway.

coordination of  $C_6F_5H$  to give  $LNi(\eta^2-H_2C=CHER_3)(\eta^2-C_6F_5H)$  (int1). This is followed by the C-H activation step **B**, which proceeds through a LLHT transition state (tsB).  $\beta$ -Agostic Ni intermediate int2 can undergo two potential reaction pathways which form different products. Step **C** shows C-C reductive elimination from int2, which provides the hydroarylation product  $C_6F_5CH_2CH_2ER_3$ . Alternatively, int2 can react by  $\beta$ -ER<sub>3</sub> elimination to give int5, shown as step **D**. In step **E**, C-E reductive elimination provides  $C_6F_5ER_3$ . It is unclear experimentally if ethylene remains bound prior to the C-heteroatom bond forming step.

The choice of ancillary *N*-heterocyclic carbene (NHC) ligand plays a dramatic role in the selectivity of the reaction. The reaction of  $H_2C=CHSiMe_3$  and  $C_6F_5H$  with the nickel catalyst  $[^iPr_2Im]Ni(\eta^2-H_2C=CHSiMe_3)_2(\mathbf{1d}-\mathbf{SiMe}_3)$ , gave exclusively the silylation product  $C_6F_5SiMe_3([^iPr_2Im] = 1,3-$ di(isopropyl)imidazole-2-ylidene). With the larger ancillary carbene ligand, IPr, the reaction of  $H_2C=CHSiMe_3$  and  $C_6F_5H$  with the nickel catalyst  $[IPr]Ni(\eta^2-H_2C=CHSiMe_3)_2$ 

(1a-SiMe<sub>3</sub>), yielded exclusively the hydroarylation product,  $C_6F_5CH_2CH_2SiMe_3$ .

Similar selectivity was observed in previous work on nickelcatalyzed C–H bond stannylation, where the choice of ancillary ligand L and substituent R on the SnR<sub>3</sub> fragment influenced the selectivity in the formation of the C–H bond stannylation product  $C_6F_5SnR_3$  versus the alkene hydroarylation product  $C_6F_5CH_2CH_2SnR_3$  (L =  ${}^{i}Pr_3P$  or [NQA], drawn in Scheme 1, and R = Bu, Bn, or Ph).<sup>3c-e</sup> For the SnBu<sub>3</sub> substituent and either  ${}^{i}Pr_3P$  or the [NQA] ancillary ligand exclusively stannylation was observed. Using SnPh<sub>3</sub> with  ${}^{i}Pr_3P$ also resulted in exclusive stannylation; however, reaction with the [NQA] ligand resulted in the alkene hydroarylation product, with trace amounts of stannylation.

The influence of NHC steric bulk on selectivity in a catalytic cycle is not unheralded.<sup>7</sup> For example, the bulky NHC ligand PEPPSI-IHept<sup>Cl</sup> has been used to avoid competitive  $\beta$ -H elimination prior to reductive elimination in selective catalysis.<sup>8</sup> In the silvlation, germylation, and stannylation reactions discussed here, reductive elimination is still a step in the catalytic cycle, but needs to occur after  $\beta$ -ER<sub>3</sub> elimination. Our previous work on C-H bond silylation led us to hypothesize that the steric bulk on carbene ligands could be determining the reactivity of transition metal complexes along a catalytic pathway. This work details the study of the potential influence of carbene steric bulk on the reactivity of Ni(0) catalysts in C-H bond functionalization, as well as an opportunity to determine the relative difficulty of C-H silvlation, stannylation, and newly reported germylation reactions.

# RESULTS

Nickel Silylation Catalyst Syntheses. An alternative to the steric description given by Tolman's cone angle,<sup>9</sup> percent buried volume ( $%V_{bur}$ ), has been shown to be a valid measure of the steric influence of N-heterocyclic carbene ligands.<sup>10</sup> The NHC ancillary ligands used in this study and their  $%V_{bur}$  are given in Scheme 2.

Scheme 2. NHC Ligands Used in This Study and Their %  $V_{\rm bur}.$ 



The IPr (a) and <sup>*i*</sup>Pr<sub>2</sub>Im carbene (d) ligands previously used in C–H silylation have vastly different  $%V_{bur}$  values of 44.5 and 27.4, respectively. To further investigate this influence of NHC ligand size on the selective formation of either C–H silylation or alkene hydroarylation products, the NHC ligands IBn (c) and IMes (b) were screened because they possess near identical electronic parameters as the IPr and <sup>*i*</sup>Pr<sub>2</sub>Im ligands, yet feature intermediate  $%V_{bur}$  values ([IBn] = 1,3-dibenzyl1,3-dihydro-2*H*-imidazol-2-ylidene) ([IMes] = 1,3-bis[2,4,6-trimethylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene).<sup>11</sup>

The active catalysts [NHC]Ni( $\eta^2$ -H<sub>2</sub>C=CHER<sub>3</sub>)<sub>2</sub> are easily prepared *in situ* by the addition of the appropriate NHC **a**-**d** to a solution of Ni(COD)<sub>2</sub> and H<sub>2</sub>C=CHER<sub>3</sub>. The catalysts [IPr]Ni( $\eta^2$ -H<sub>2</sub>C=CHSiMe<sub>3</sub>)<sub>2</sub> (1a-SiMe<sub>3</sub>) and [<sup>i</sup>Pr<sub>2</sub>Im]Ni( $\eta^2$ - $H_2C = CHSiMe_3)_2$  (1d-SiMe<sub>3</sub>) have been previously prepared and structurally characterized by X-ray diffraction.<sup>3a</sup> The synthesis of 1d-SiMe<sub>3</sub> requires the slow addition of <sup>i</sup>Pr<sub>2</sub>Im to a solution of Ni(COD)<sub>2</sub> with a large excess of  $H_2C=$ CHSiMe<sub>3</sub>, to avoid the production of the catalytically inactive di-[<sup>*i*</sup>Pr<sub>2</sub>Im] species, [<sup>*i*</sup>Pr<sub>2</sub>Im]<sub>2</sub>Ni( $\eta^2$ -H<sub>2</sub>C=CHSiMe<sub>3</sub>) (2d-SiMe<sub>3</sub>).<sup>3a</sup> The newly prepared IBn carbene complexes provided similar problems in the synthesis of [IBn]Ni( $\eta^2$ - $H_2C$ =CHSiMe<sub>3</sub>)<sub>2</sub> (1c-SiMe<sub>3</sub>). The reaction of Ni(COD)<sub>2</sub> and IBn with 2 equivalents of H<sub>2</sub>C=CHSiMe<sub>3</sub> provided the unwanted di-NHC complex  $[IBn]_2Ni(\eta^2-H_2C=CHSiMe_3)$  $(2c-SiMe_3)$ , as evidenced by integrations in the <sup>1</sup>H NMR spectrum (see the Supporting Information). To improve selectivity toward the bis-vinyl species [IBn]Ni( $\eta^2$ -H<sub>2</sub>C=  $CHSiMe_3)_{21}$  10 equiv of  $H_2C=CHSiMe_3$  were added to a solution of  $Ni(COD)_2$  in toluene, followed by the slow addition of a solution of IBn, shown in Scheme 3. The IMes carbene generated [IMes]Ni( $\eta^2$ -H<sub>2</sub>C=CHSiMe<sub>3</sub>)<sub>2</sub> (1b-SiMe<sub>3</sub>) without the formation of any di-NHC impurity (Figure 1).

Scheme 3. Synthesis of Catalysts of Type 1a-d-SiMe<sub>3</sub>, [NHC]Ni(H<sub>2</sub>C=CHSiMe<sub>3</sub>)<sub>2</sub>, and Unwanted Catalytically Inactive 2c and 2d

Ν	li(COD) <sub>2</sub>	N equiv/Si	Me <sub>3</sub>	[NHC]Ni(H <sub>2</sub> C=C	HSiMe <sub>3</sub> ) <sub>2</sub> 1	
	NHC	toluene, r.t.	-	[NHC] <sub>2</sub> Ni(H <sub>2</sub> C=0	CHSiMe <sub>3</sub> ) <b>2</b>	
	Compound	NHC	N equiv	v Yield	Ì	
	1a-SiMe₃	IPr ( <b>a</b> )	2	60% <sup>a</sup>		
	1b-SiMe <sub>3</sub>	IMes (b)	2	85% <sup>d</sup>		
	1c-SiMe <sub>3</sub>	IBn ( <b>c</b> )	10 <sup>c</sup>	87% <sup>b</sup>		
	1d-SiMe <sub>3</sub>	<sup>i</sup> Pr <sub>2</sub> Im ( <b>d</b> )	10	77% <sup>a</sup>		
	2c-SiMe₃	IBn ( <b>c</b> )	2	64% <sup>d</sup>		
	2d-SiMe <sub>3</sub>	<sup>i</sup> Pr <sub>2</sub> Im ( <b>d</b> )	2 <sup>c</sup>	95% <sup>a</sup>		

<sup>*a*</sup>Previously reported.<sup>3a</sup> <sup>*b*</sup>Isolated as an oil with multiple isomers observed by NMR. <sup>*c*</sup>NHC added slowly at -40 °C. <sup>*d*</sup>Synthesis performed in *n*-pentane.

**Germylation Catalyst Syntheses.** Nickel-catalyzed C–H bond germylation has not been previously investigated. To allow a comparison of the Ge species to the chemistry previously observed with Sn and Si, the vinyl complex H<sub>2</sub>C= CHGePh<sub>3</sub> was prepared from commercially available GePh<sub>3</sub>Cl. Although the phosphine supported (<sup>i</sup>Pr<sub>3</sub>P)Ni( $\eta^2$ -H<sub>2</sub>C= CHSnPh<sub>3</sub>)<sub>2</sub> was previously shown to be an effective catalyst for stannylation at temperatures up to 80 °C, (<sup>i</sup>Pr<sub>3</sub>P)Ni( $\eta^2$ -H<sub>2</sub>C=CHSiMe<sub>3</sub>)<sub>2</sub> provided only a single turnover in the C–H bond silvlation of pentafluorobenzene prior to catalyst decomposition. The <sup>i</sup>Pr<sub>3</sub>P-supported Ge species (<sup>i</sup>Pr<sub>3</sub>P)Ni-( $\eta^2$ -H<sub>2</sub>C=CHGePh<sub>3</sub>)<sub>2</sub> (**1e-GePh**<sub>3</sub>) was prepared by the reaction of Ni(COD)<sub>2</sub> with <sup>i</sup>Pr<sub>3</sub>P and 2 equiv of H<sub>2</sub>C= CHGePh<sub>3</sub>. Both the solid-state structure obtained from X-ray crystallography and NMR data are representative of a pseudo $C_2$  symmetric complex. The IPr carbene supported [IPr]Ni( $\eta^2$ -H<sub>2</sub>C=CHGePh<sub>3</sub>)<sub>2</sub> complex (**1a-GePh**<sub>3</sub>) was isolated and characterized by NMR spectroscopy and single-crystal X-ray crystallography, as drawn in Figure 2. The remaining carbene supported Ge-containing catalysts were prepared *in situ* prior to catalysis, as shown in Scheme 4.

**Stannylation Catalyst Analogue Syntheses.** The complexes  $[NQA]Ni(\eta^2-H_2C=CHSnPh_3)_2$  and  $[^iPr_3P]Ni-(\eta^2-H_2C=CHSnPh_3)_2$  have both been structurally characterized in the past.<sup>3b,c</sup> To provide a comparison to NHC ligands, the  $C_2$  symmetric complex  $[IPr]Ni(\eta^2-H_2C=CHSnPh_3)_2$  (1a-SnPh\_3) was synthesized by reacting Ni-(COD)<sub>2</sub> and IPr with 2 equiv of  $H_2C=CHSnPh_3$  as shown in Scheme 5. The compound was isolated and characterized by NMR spectroscopy and X-ray crystallography as drawn in Figure 3. Catalytic stannylation was performed with the ubiquitous and commercially available  $H_2C=CHSnBu_3$ . The Bu substituents render all of the Ni complexes as oils, and thus the stannylation catalysts 1a–d-SnBu<sub>3</sub> were prepared *in situ* under catalytic conditions.

Structural Comparisons. The range of structures obtained for the prospective catalysts of the type  $LNi(\eta^2$ - $H_2C = CHER_3)_2$  provides an opportunity to look for possible differences in bonding based on either the nature of donor L, the heteroatom E (Si, Ge, Sn), or NHC steric bulk (Table 1). Remarkably, these factors do not seem to have a strong influence on any structural parameter in these complexes. The previously reported structures for nitrogen donor complex  $[NQA]Ni(\eta^2-H_2C=CHSnPh_3)_2$  and phosphine donor  $[^{i}Pr_{3}P]Ni(\eta^{2}-H_{2}C=CHSnPh_{3})_{2}$  feature nearly identical bonding parameters at Ni to the structure of [IPr]Ni( $\eta^2$ -H<sub>2</sub>C= CHSnPh<sub>3</sub>)<sub>2</sub> (1a-SnPh<sub>3</sub>). Similarly, the structures of [IPr]Ni- $(\eta^2$ -H<sub>2</sub>C=CHSiMe<sub>3</sub>)<sub>2</sub> (1a-SiMe<sub>3</sub>), [IPr]Ni( $\eta^2$ -H<sub>2</sub>C= CHGePh<sub>3</sub>)<sub>2</sub> (1a-GePh<sub>3</sub>), and [IPr]Ni( $\eta^2$ -H<sub>2</sub>C=CHSnPh<sub>3</sub>)<sub>2</sub> (1a-SnPh<sub>3</sub>) feature no obvious trend resulting from the heteroatom Si, Ge, or Sn. Changes in NHC bulk also had limited structural effects in the comparison of the slightly less bulky [IMes]Ni( $\eta^2$ -H<sub>2</sub>C=CHSiMe<sub>3</sub>)<sub>2</sub> (1b-SiMe<sub>3</sub>) to [IPr]- $Ni(\eta^2-H_2C=CHSiMe_3)_2$  (1a-SiMe<sub>3</sub>). The largest structural differences appear to occur in the complexes with the smallest NHC donors, [IBn]Ni( $\eta^2$ -H<sub>2</sub>C=CHSiMe<sub>3</sub>)<sub>2</sub> (1c-SiMe<sub>3</sub>) and  $[^{i}Pr_{2}Im]Ni(\eta^{2}-H_{2}C=CHSiMe_{3})_{2}$  (1d-SiMe<sub>3</sub>). Although 1c-SiMe<sub>3</sub> was not structurally characterized, NMR data confirmed that it behaves like  $1d-SiMe_3$ , where the  $C_2$  symmetric structure is no longer the most energetically favored, and isomers from either rotation around the Ni-vinyl moiety or the binding of the opposite face of the alkene are all observed in solution.<sup>3a</sup> The main structural difference with the larger NHC donors is a favoring of the  $C_2$  symmetric structures, where the two SiMe<sub>3</sub> moieties are as far from the NHC donors as possible, while also remaining spatially separated from each other.

Catalytic Silylation versus Hydroarylation with NHCs of Varying %V<sub>bur</sub>. The influence of NHC bulk on C–H silylation is summarized in Scheme 6. The reaction of  $C_6F_5H$ and  $H_2C$ =CHSiMe<sub>3</sub> has been previously shown to produce the silylation product  $C_6F_5SiMe_3$  selectively using the least bulky catalyst, 1d-SiMe<sub>3</sub>. In contrast, the bulkiest catalyst, 1a-SiMe<sub>3</sub>, gave exclusively the hydroarylation product,  $C_6F_5CH_2CH_2SiMe_3$ . Catalyst 1c-SiMe<sub>3</sub> gives the same selectivity as 1d-SiMe<sub>3</sub>, and provided exclusively silylation but with a slightly slower reaction. Catalyst 1b-SiMe<sub>3</sub>, which is intermediate in size between hydroarylation catalyst 1a-SiMe<sub>3</sub>







Figure 2. Solid-state molecular structures of 1a-GePh<sub>3</sub> and 1e-GePh<sub>3</sub> drawn with 50% probability ellipsoid. Hydrogen atoms are omitted for clarity.

Scheme 4. Syn	thesis of	Cataly	sts of	Type	1-GePh	13
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Ni(COD) <sub>2</sub> N + — NHC	equiv/ toluene, r.t.	ĢePh₃ ───≻ [L]N	li(H <sub>2</sub> C=CHGe 1	Ph <sub>3</sub> ) <sub>2</sub>
Compound	NHC	N equiv	Yield	]
1a-GePh₃	IPr ( <b>a</b> )	2	64% <sup>b</sup>	
1b-GePh₃	IMes (b)	а	а	
1c-GePh₃	IBn ( <b>c</b> )	а	а	
1d-GePh₃	<sup>i</sup> Pr <sub>2</sub> Im ( <b>d</b> )	а	а	
1e-GePh <sub>3</sub>	<sup>i</sup> Pr <sub>3</sub> P ( <b>e</b> )	2	89%	

<sup>a</sup>Complexes prepared *in situ* under catalytic conditions (*vide infra*). <sup>b</sup>Synthesis performed in *n*-pentane.

and silvlation catalyst **1c-SiMe**<sub>3</sub>, gives a mixture of these two products. The crude <sup>19</sup>F{<sup>1</sup>H} NMR showed conversion to both the silvlation product  $C_6F_5SiMe_3$  and hydroarylation product  $C_6F_5CH_2CH_2SiMe_3$  in an approximate 2:1 ratio. The observed selectivity is modestly affected by temperature. Monitoring the reaction using catalytic **1b-SiMe**<sub>3</sub> as it was slowly warmed revealed an initial ratio of  $C_6F_5SiMe_3$  to  $C_6F_5CH_2CH_2SiMe_3$  of

Scheme 5. Synthesis of Catalysts of Type 1-SnBu<sub>3</sub> Prepared *in Situ* under Catalytic Conditions

Ni(COD + NHC	)) <sub>2</sub> <u>N</u> equiv = toluene	SnBu <sub>3</sub>	1C]Ni(H <sub>2</sub> C= 1	∈CHSnBu <sub>3</sub> ) <sub>2</sub>
	Compound	NHC	N equiv	
	1a-SnBu₃	IPr ( <b>a</b> )	2	
	1b-SnBu₃	IMes ( <b>b</b> )	2	
	1c-SnBu₃	IBn ( <b>c</b> )	2	
	1d-SnBu <sub>3</sub>	<sup>i</sup> Pr <sub>2</sub> Im ( <b>d</b> )	2	

3:1 at the lowest temperatures at which the products could be detected by  $^{19}\mathrm{F}\{^{1}\mathrm{H}\}$  NMR spectroscopy.

In general, the silvlation reactions required temperatures of 120 °C for reasonable reaction rates, near the highest temperatures these catalysts can sustain over the reactions time required (7–20 h). For hydroarylation catalyst 1a-SiMe<sub>3</sub>, which bears the largest NHC, a similar reaction rate was observed at the lower temperature of 90 °C. The larger NHC significantly lowers the barrier for hydroarylation, and in particular for the reductive elimination step C in Scheme 1. The use of the isolated catalysts versus *in situ* generated

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Figure 3. Solid-state molecular structures of 1a-SnPh<sub>3</sub> drawn with 50% probability ellipsoid. Hydrogen atoms are omitted for clarity.

catalysts, prepared by the slow addition of the appropriate NHC **a**-**d** to a solution of Ni(COD)<sub>2</sub> containing excess H<sub>2</sub>C=CHSiMe<sub>3</sub>, provided identical catalytic activity. Di-[NHC] species **2c-SiMe<sub>3</sub>** and **2d-SiMe<sub>3</sub>** showed no catalytic activity.

Catalytic C-H Bond Germylation. To the best of our knowledge, the only reported transition metal catalyzed C-H bond germylation reactions include a single intramolecular dehydrogenative bond formation using Rh,<sup>12</sup> and a series of palladium<sup>13</sup> catalyzed reactions of Me<sub>3</sub>Ge-GeMe<sub>3</sub> with substituent activated C-H bonds. Catalytic C-H bond germylation has not been previously observed in Ni catalyzed systems, but it would be logical to hypothesize that these reactions would be of intermediate difficulty to the silvlation reactions, which require NHC donors and temperatures of 120 °C, and the stannylation reactions, which are effectively catalyzed by [NQA] and phosphine-supported Ni catalysts at temperatures from 20 to 80 °C. Attempts at the catalytic reaction of H<sub>2</sub>C=CHGePh<sub>3</sub> with C<sub>6</sub>F<sub>5</sub>H and <sup>i</sup>Pr<sub>3</sub>P supported 1e-GePh<sub>3</sub> catalyst led to catalyst decomposition upon heating above 80 °C, similar as observed in silylation, with only trace amounts of the desired germylation product observed in the <sup>19</sup>F{<sup>1</sup>H} NMR spectrum. Mechanistic studies using C<sub>6</sub>F<sub>5</sub>D and H<sub>2</sub>C=CHGePh<sub>3</sub> and catalytic **1e-GePh<sub>3</sub>** show the generation of the H/D exchange product C<sub>6</sub>F<sub>5</sub>H from deuterium scrambling into H<sub>2</sub>C=CHGePh<sub>3</sub> at temperatures of only 70 °C, which indicates that the C–H bond activation (step B in Scheme 1) is reversible. This is different from the analogous stannylation reaction between C<sub>6</sub>F<sub>5</sub>D and H<sub>2</sub>C=CHSnBu<sub>3</sub>, where no scrambling was observed because C-H activation was irreversible and rate-determining. This confirms that  $\beta$ -GePh<sub>3</sub> elimination step is more difficult than  $\beta$ -SnBu<sub>3</sub> elimination, shown as step D in Scheme 1.



<sup>a</sup>NMR yields with respect to internal standard FSiPh<sub>3</sub>.

The influence of NHC bulk on C–H germylation are summarized in Scheme 7.The reaction of  $C_6F_5H$  and  $H_2C=$ 





<sup>a</sup>NMR yield with respect to internal standard FSiPh<sub>3</sub>.

CHGePh<sub>3</sub> to give  $C_6F_5GePh_3$  proceeds cleanly with catalysts **1b-GePh<sub>3</sub>**, **1c-GePh<sub>3</sub>**, and**1d-GePh<sub>3</sub>**, whereas bulkier catalyst **1a-GePh<sub>3</sub>** gave nearly selective conversion to the hydroarylation product  $C_6F_5CH_2CH_2GePh_3$  (96%), with a trace amount of the germylation product  $C_6F_5GePh_3$  (4%). In comparison to the silylation chemistry, it appears that germylation is successful with a larger range of NHC ligands. The conditions for reaction are also milder. Catalytic reactivity

Table 1. Selected Bond Lengths [Å] and Angles [°] of 1b-SiMe<sub>3</sub>, 1a-GePh<sub>3</sub>, 1a-SnPh<sub>3</sub>, 2c-SiMe<sub>3</sub>, and 1e-GePh<sub>3</sub>

	1b-SiMe <sub>3</sub>	1a-GePh <sub>3</sub>	$1a$ -SnPh $_3$		2c-SiMe <sub>3</sub>	1e-GeP	n <sub>3</sub>
C(1) - Ni(1)	2.040(6)	2.017(14)	2.002(1)	C(1)-Ni(1)	1.965(4)	Ni(1) - P(1)	2.201(13)
C(2) - Ni(1)	2.062(5)	1.991(15)	1.990(1)	C(2) - Ni(1)	1.938(4)	C(2)-Ni(1)	1.997(3)
C(3) - Ni(1)	1.939(8)	1.920(19)	1.997(2)	C(3) - Ni(1)	1.896(3)	C(3) - Ni(1)	2.003(3)
C(4)-Ni(1)	1.980(5)		1.987(1)	C(4)-Ni(1)	1.886(4)	C(2) - C(3)	1.392(4)
C(5)-Ni(1)	1.917(4)		1.929(2)	C(1) - C(2)	1.426(6)		
C(1) - C(2)	1.408(8)	1.398(2)	1.399(3)				
C(3) - C(4)	1.40(1)		1.402(2)				
C(1)-Ni(1)-C(2)	40.14(2)	40.87(7)	41.01(7)	C(3)-Ni(1)-C(4)	115.43(1)	C(2)-Ni(1)-C(3)	40.74(12)
C(3)-Ni(1)-C(4)	41.79(3)		41.20(7)	C(1)-Ni(1)-C(2)	42.87(1)		

was observed by  ${}^{19}F{}^{1}H$  NMR at 80 °C, and all the reactions went to completion within 18 h at 90 °C. It should be noted that although the Ph substituted Ge species was chosen to minimize toxicity previous work shows that the heteroatom substituents like *n*-Bu versus Ph have only a minor role in reaction rate and selectivity.<sup>14</sup>

**Catalytic C–H Bond Stannylation.** Catalytic stannylation was examined with the commercially available reagent  $H_2C=$  CHSnBu<sub>3</sub>, and the results are summarized in Scheme 8. All

Scheme 8. Selectivity of Catalytic Stannylation versus Hydroarylation with NHCs of Varying  $%V_{bur}$  for H<sub>2</sub>C= CHSnBu<sub>3</sub>



<sup>*a*</sup>Reaction conditions: 90 °C, 18–20 h. NMR yield with respect to internal standard FSiPh<sub>3</sub>.

reactions with H<sub>2</sub>C=CHSnBu<sub>3</sub> as the stannane source were carried out by generating the catalytic nickel species in situ, because attempts to isolate these catalysts only gave viscous oils which proved difficult to transfer. The reaction of  $C_6F_5H$ with H<sub>2</sub>C=CHSnBu<sub>3</sub> gave exclusively the stannylation product C<sub>6</sub>F<sub>5</sub>SnBu<sub>3</sub> for all the catalysts studied, with no evidence of hydroarylation even with bulkiest catalyst la-SnBu<sub>3</sub>. In general, catalytic stannylation was observed at 80 °C, although complex 1d-SnBu<sub>3</sub> was observed to give slow catalysis even at room temperature, reminiscent of the [NQA] supported Ni(0) catalysts.<sup>3b,e</sup> Heating up to 90 °C gave complete reaction in a reasonable time without significant catalyst decomposition. By monitoring the reaction with the bulkiest complex tested, 1a-SnBu<sub>3</sub> and heating at 90 °C, complete conversion to C<sub>6</sub>F<sub>5</sub>SnBu<sub>3</sub> was observed within 3 h. Continued heating for 20 h gave less than 5% of C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>SnBu<sub>3</sub>, which appears to arise from the Nicatalyzed reaction of C<sub>6</sub>F<sub>5</sub>SnBu<sub>3</sub> with ethylene to give the alkene carbostannylation, a reaction that has been observed before with the [NQA] ancillary ligand.<sup>3b</sup> The stannylation systems proved more temperature-sensitive than silvlation and germylation systems, and heating over 100 °C led to catalyst decomposition and the precipitation of Ni black. The <sup>119</sup>Sn-<sup>{1</sup>H} NMR spectra showed the formation of Bu<sub>3</sub>SnSnBu<sub>3</sub> as a byproduct under these conditions. The reaction of C<sub>6</sub>F<sub>5</sub>H with  $H_2C$ =CHSnBu<sub>3</sub> to give the stannylation product  $C_6F_5SnBu_3$ with all the NHC ligands a-d tested is consistent with an increasing ease for the C-heteroatom bond formation catalytic cycle with the heavier heteroatom, Sn. The previously reported use of  ${}^{i}Pr_{3}P$  (% $V_{bur}$  = 31.8 in the species ( ${}^{i}Pr_{3}P$ )Ni $(CH_2CHSnPh_3)_{2r}^{3c}$  and  $[NQA] (\%V_{bur} = 30.1$  in the species  $[NQA]Ni(CH_2CHSnPh_3)_2)^{3b,c,15}$  as supporting ligands also gave primarily stannylation.

**DFT Calculations of Silylation, Germylation, and Stannylation versus Hydroarylation.** To gain more insight into the importance of the heteroatom in fundamental reaction steps, DFT calculations were performed on the key reaction steps. For simplicity the studies were done on the SiMe<sub>3</sub>, GeMe<sub>3</sub>, and SnMe<sub>3</sub> substituted catalysts and substrates, as shown in Scheme 9. The Gibbs free energies were calculated at the temperatures at which reactivity was observed experimentally.





**C–H Bond Activation Step.** The C–H bond activation step was calculated to be only modestly influenced by heteroatom E, as shown in Scheme 10. The highest relative

Scheme 10. Energetics for the C-H Activation.



energy for tsB for E = Sn of 18.6 kcal·mol<sup>-1,</sup> and the lowest energy barrier for E = Si of 16.1 kcal·mol<sup>-1</sup> differ by only 2.5 kcal·mol<sup>-1</sup>, with E = Ge having an intermediate value of 17.5 kcal·mol<sup>-1</sup>. Most of the energy difference in this step likely comes from the relative energy of int1, which has a similar range of energies; this can be attributed to a difference in the energy needed to dissociate a vinyl moiety and generate int1 for E = Si, Ge and Sn. The energies of the  $\beta$ -H agostic products of C-H activation, int2, are only between 2.2 and 4.6 kcalmol<sup>-1</sup> higher energy than the initial catalytic resting state of 1d-ER<sub>3</sub>. For E = Sn only, the C-H activation step is found to be irreversible. For Ge and Si this step is predicted to be reversible. The computations show that the ligand-to-ligand hydrogen transfer is more favorable than C-H oxidative addition. Further details regarding the higher energy direct oxidative addition pathway are provided in the Supporting Information.

**General Mechanism.** Figures 4, 5, and 6 show the reaction profiles for E = Si, Ge, and Sn, respectively. The profiles show the hydroarylation manifold in blue to the left, and the C–



**Figure 4.** Calculated energy profile of hydroarylation and C-H silylation from int2-Si in the reaction of  $C_6F_5H$  with  $H_2C$ =CHSiMe<sub>3</sub> catalyzed by 1d-SiMe<sub>3</sub>, where  $L^1$  is the smaller <sup>i</sup>Pr<sub>2</sub>Im NHC. Hydroarylation pathway is shown in blue, and C-H silylation is shown in red.

heteroatom forming silylation, germylation and stannylation reaction pathways to the right in red. Both start from int2-E. Two pathways were modeled for the C-heteroatom bond forming reductive elimination step. The first is via tsE, before ethylene dissociation. In the second pathway, reductive elimination of the C-E bond occurs via tsE'' after the loss of ethylene via tsE'. The second pathway is shown with a dashed red line. The lowest calculated energy pathway depends on the nature of E. Details for Si, Ge, and Sn are given separately below.

**Silylation.** Upon formation of intermediate **int2-Si** from **1d-SiMe**<sub>3</sub>, there are two possible products, as shown in Figure 4. The hydroarylation product  $C_6F_5CH_2CH_2SiMe_3$  is obtained from C-C reductive elimination via **tsC-Si**. The silylation product  $C_6F_5SiMe_3$  can be obtained from  $\beta$ -Si elimination via **tsD-Si** followed by C-Si reductive elimination by **tsE-Si** or **tsE''-Si**. These calculated key transition states are shown on the bottom of Figure 4 along with selected bond lengths. The calculations show that the C-C reductive elimination via **tsC-Si** to give **int4-Si** and ultimately hydroarylation has a barrier of 27.0 kcal·mol<sup>-1</sup>; this is 2.5 kcal·mol<sup>-1</sup> higher than the **tsE-Si** barrier for silylation, so the hydroarylation product is

kinetically disfavored. The hydroarylation product is thermodynamically favored with a net reaction Gibbs free energy of -9.0 versus only -2.2 kcal·mol<sup>-1</sup> for the silylation reaction.

For the C–H silvlation pathway, int2-Si can undergo  $\beta$ -Si elimination via transition state tsD-Si to give intermediate int5-Si. The lowest energy route to the subsequent C-Si bond formation was found to be direct reductive elimination from int5-Si by tsE-Si to give int6-Si, with a barrier of 24.5 kcalmol<sup>-1</sup>. Intermediate int6-Si undergoes a ligand exchange step with H<sub>2</sub>C=CHSiMe<sub>3</sub> to release C-H silvlation product C<sub>6</sub>F<sub>5</sub>SiMe<sub>3</sub> and regenerate 1d-SiMe<sub>3</sub>. Alternatively, ethylene loss prior to the C-Si reductive elimination was also considered and was found to take place through transition state tsE'-Si. The resulting intermediate, int5'-Si, then undergoes C-Si reductive elimination via transition state tsE''-Si. The results show that this latter pathway is only barely higher in energy compared to the direct C-Si reductive elimination from int5-Si. Counterintuitively, it is the barrier to ethylene loss from Ni(II) of 25.2 kcal·mol<sup>-1</sup>, tsE'-Si, that renders this pathway higher energy; the barrier to the subsequent reductive elimination step tsE"-Si is actually lowered after ethylene dissociation to 22.4 kcal·mol<sup>-1</sup>.



Figure 5. Calculated energy profile of hydroarylation and C-H germylation from int2-Ge, where  $L^1$  is the smaller 'Pr<sub>2</sub>Im NHC.



Figure 6. Calculated energy profile of hydroarylation and C-H stannylation from int2-Sn, where L<sup>1</sup> is the smaller <sup>i</sup>Pr<sub>2</sub>Im NHC.

The calculations show that the selectivity is determined by the competition between the C–C reductive elimination and the direct C–Si reductive elimination. The calculated energy difference of 2.5 kcal·mol<sup>-1</sup>(27.0 kcal·mol<sup>-1</sup> for tsC versus 24.5 kcal·mol<sup>-1</sup> for tsE) is in good agreement with the experimental results that the C–H silylation product C<sub>6</sub>F<sub>s</sub>SiMe<sub>3</sub> was observed exclusively for the reaction catalyzed by 1d-SiMe<sub>3</sub>. Moreover, the results show that the  $\beta$ -Si elimination is reversible and the C–Si reductive elimination occurs without the prior loss of ethylene, which are consistent with both the previously reported <sup>13</sup>C-isotope labeling studies<sup>3a</sup> and a recent computational study on this system.<sup>16</sup> **Germylation.** With catalyst **1d-GeMe**<sub>3</sub>, the hydroarylation of H<sub>2</sub>C=CHGeMe<sub>3</sub> through the C-C reductive elimination (via **tsC-Ge**) is also kinetically disfavored, with a reaction barrier of 27.0 kcal·mol<sup>-1</sup> compared to 19.8 kcal·mol<sup>-1</sup> for the germylation reaction (Figure 5). The  $\beta$ -Ge elimination was found to proceed through transition state **tsD-Ge**, with an energy barrier of 14.8 kcal·mol<sup>-1</sup>. From **int5-Ge**, ethylene loss via **tsE'-Ge** and reductive elimination from three-coordinate **int5'-Ge** was calculated to be slightly lower energy than the direct C-Ge reductive elimination via **tsE-Ge**, though these two pathways should both be accessible. Similar to silylation,

Article



Figure 7. Calculated energy profile of hydroarylation and C-H silylation from int2-Si\*, where L<sup>2</sup> is the bulky IPr NHC.

the C–Ge reductive elimination constitutes the rate-determining step of the reaction.

Stannylation. From intermediate int2-Sn, C-C reductive elimination via transition state tsC-Sn to give hydroarylation product C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>SnMe<sub>3</sub> was calculated to be much higher in energy than the pathway leading to the stannylation product  $C_6F_5SnMe_3$ , which is in good agreement with the experimental results (Figure 6). For the C-H stannylation, the calculations show that the  $\beta$ -Sn elimination via transition state tsD-Sn has an energy barrier of only 10 kcal·mol<sup>-1</sup>, which leads to intermediate int5-Sn. The subsequent direct C-Sn reductive elimination was found to take place through transition state tsE-Sn. The resulting intermediate, int6-Sn, undergoes a ligand exchange step with H<sub>2</sub>C=CHSnMe<sub>3</sub> to release C-H stannylation product C<sub>6</sub>F<sub>5</sub>SnMe<sub>3</sub> and regenerate 1d-SnMe<sub>3</sub>. Ethylene loss prior to the C-Sn reductive elimination was found to take place through transition state tsE'-Sn. The resulting intermediate int5'-Sn could then undergo C-Sn reductive elimination via transition state tsE''-Sn. The results

show that the direct C-Sn reductive elimination from int5-Sn is slightly more favored than the reductive elimination from three-coordinate int5'-Sn, with barriers of 13.4 kcal·mol<sup>-1</sup> for tsE-Sn versus 14.6 kcal·mol<sup>-1</sup> for tsE'-Sn. However, the ethylene loss via transition state tsE' was calculated to have rather similar energy compared with the direct C-Sn reductive elimination (13.2 kcal·mol<sup>-1</sup> of tsE-Sn versus 13.4 kcal·mol<sup>-1</sup> of tsE'-Sn), which indicates that the relatively stable intermediate, int5'-Sn, could be formed in the reaction. The direct C-Sn reductive elimination constitutes the ratedetermining step of the reaction, and the overall energy barrier of the reaction is 21.0 kcal·mol<sup>-1</sup> relative to int5'-Sn. In previous work with the nitrogen donor [NQA] ligand, related species  $[NQA]_2Ni(C_6F_5)(SnPh_3)$  was identified as one of the catalyst resting states, with a fluxional ligand exchange process facilitated by three-coordinate  $[NQA]Ni(C_6F_5)(SnPh_3)$ ; this supports the possibility of low-energy species int5'-Sn, although no related species was observed experimentally in the species supported by 'Pr<sub>2</sub>Im under catalytic conditions.

# Table 2

	Step C: 0	C-C reducti	ve eliminati	on		
catalyst	int2	tsC	int4	$\Delta \mathbf{G^{\ddagger}}$ from int2	$\Delta G_{step}$	
1a-SiMe <sub>3</sub>	3.2	21.1	0.5	17.9	-2.7	
1d-SiMe <sub>3</sub>	2.2	27.0	4.2	24.8	2.0	
1d-GeMe <sub>3</sub>	2.8	27.0	8.0	24.2	5.2	
1d-SnMe <sub>3</sub>	4.6	28.9	9.5	24.3	4.9	
	Step D: β	3-E eliminat	tion			
catalyst	int2	tsD	int5	$\Delta \mathbf{G}^{\ddagger}$ from int2	$\Delta \mathbf{G}_{step}$	
1a-SiMe <sub>3</sub>	3.2	24.8	20.0	21.6	16.8	
1d-SiMe <sub>3</sub>	2.2	22.0	17.2	介 19.8 介	15.0 ĵ	ĵ
1d-GeMe <sub>3</sub>	2.8	14.8	7.8	12.0	5.0	∆~20 kcal·mol <sup>-1</sup>
1d-SnMe <sub>3</sub>	4.6	10.0	-0.3	5.4	-4.9	
	Step E:	C-E reduct	tive elimina	tion (4-coordinat	e)	
catalyst	int5	tsE'	int6	$\Delta \mathbf{G^{\ddagger}}$ from int5	$\Delta G_{step}$	
1a-SiMe <sub>3</sub>	20.0	26.4	14.6	6.4	-5.4	
1d-SiMe <sub>3</sub>	17.2	24.5	7.5	7.3	-9.7	
1d-GeMe <sub>3</sub>	7.8	20	5.9	12.2	-1.9	∆~20 kcal mol <sup>-1</sup>
1d-SnMe <sub>3</sub>	-0.3	13.4	11.1	13.7	11.4 .	Ļ
	Step E':	Ethylene o	dissociation			
catalyst	int5	tsE	int5'	$\Delta G^{\ddagger}$ from int5	$\Delta \mathbf{G}_{step}$	
1a-SiMe <sub>3</sub>	20.0	27	3.7	7.0	-16.3	
1d-SiMe <sub>3</sub>	17.2	25.2	3.4	8.0	-13.8	
1d-GeMe <sub>3</sub>	7.8	16.9	-3.0	9.1	-10.8	
1d-SnMe <sub>3</sub>	-0.3	13.2	-7.6	13.5	-7.3	
	Step E":	C-E redu	ctive elimina	ation (3-coordina	ate)	
catalyst	int5'	tsE"	int6'	△G <sup>‡</sup> from int5'	$\Delta \mathbf{G}_{sten}$	
1a-SiMe <sub>3</sub>	3.7	19.1	5.1	15.4	1.4	
1d-SiMe <sub>3</sub>	3.4	22.4	8.6	19	5.2	
1d-GeMe <sub>2</sub>	-3.0	19.8	9.3	22.8	12.3	

**Steric Influence on Selectivity in Silylation.** Similar to the reaction catalyzed by **1d-SiMe**<sub>3</sub>, C–H activation with bulky IPr NHC supported **1a-SiMe**<sub>3</sub> was found to proceed through the more favorable LLHT rather than the C–H oxidative addition. As shown in Scheme 10, the energies of C–H activation step intermediates **int1-Si\*** and **tsB-Si\*** are scarcely any different than those calculated for smaller **1d-SiMe**<sub>3</sub> catalysts, and **int2-Si\*** is only 1 kcal·mol<sup>-1</sup> higher in energy.

1d-SnMe<sub>3</sub>

-7.6

14.6

8

22.2

15.6

Figure 7 shows the pathways for hydroarylation versus silylation starting from int2-Si<sup>\*</sup>. The preference for this bulkier catalyst for hydroarylation is evident given the relatively low barrier of 21.1 kcal·mol<sup>-1</sup> for tsC-Si<sup>\*</sup>, which is 5.9 kcal·mol<sup>-1</sup> lower than the 27.0 kcal·mol<sup>-1</sup> for tsC-Si with the smaller <sup>i</sup>Pr<sub>2</sub>Im NHC previously shown in Figure 4. In contrast, the barrier for C–Si reductive elimination via tsE-Si<sup>\*</sup> is significantly higher at 26.4 kcal·mol<sup>-1</sup>, a value that is actually higher than the tsE-Si barrier of 24.5 kcal·mol<sup>-1</sup> shown in Figure 4. These results support the experimentally found result of exclusive hydroarylation with 1a-SiMe<sub>3</sub>.

**Comparison of Reaction Steps and Intermediates.** The nature of the heteroatom E has an influence in selectivity. The energy of the key intermediates and transition states for the key reaction steps are given in Table 2, along with the  $\Delta G^{\ddagger}$  and  $\Delta G_{\text{step}}$  for these individual steps, to allow a direct comparison. The C–H activation step was already shown to be minimally influenced by heteroatom E. Step C, the C–C reductive elimination that gives the hydroarylation product is barely influenced by heteroatom E, with energies for tsC that are within 2 kcal·mol<sup>-1</sup> for 1d-SiMe<sub>3</sub>, 1d-GeMe<sub>3</sub>, and1d-SnMe<sub>3</sub>. Ligand bulk has a much larger influence on this transition state, and the energy of tsC for 1a-SiMe<sub>3</sub> of 21.1 kcal·mol<sup>-1</sup> is lower than that of 1d-SiMe<sub>3</sub> by almost 6 kcal·mol<sup>-1</sup>. A comparison of the  $\Delta G_{\text{step}}$  for reductive elimination step shows that this reaction is also downhill by -2.7 kcal·mol<sup>-1</sup> for the bulkiest 1a-SiMe<sub>3</sub>, as compared to a  $\Delta G_{\text{step}}$  of 2.0 for 1d-SiMe<sub>3</sub>.

Step D, the  $\beta$ -E elimination step, is dramatically influenced by heteroatom, as would be anticipated given the breaking of a C–E bond and formation of a Ni–E bond in this step. This reaction is easiest with E = Sn, the only heteroatom studied where this reaction step is downhill, with  $\Delta G_{\text{step}} = -4.9$  kcalmol<sup>-1</sup>. For E = Ge and Si, the  $\Delta G_{\text{step}}$  for step D are 5.0 and 15.0 kcal·mol<sup>-1</sup>, respectively; there are differences of ~10.0 kcal·mol<sup>-1</sup> between elements Sn, Ge, and Si for this step. This energy difference shows its effect in the energies of  $\Delta G^{\ddagger}$  for step D, **int5**, and **tsD**. Steric effects have a smaller influence on the  $\beta$ -E elimination step. In bulky **1a-SiMe**<sub>3</sub>, the  $\Delta G_{\text{step}}$  of 16.8 kcal·mol<sup>-1</sup> is only 1.8 kcal·mol<sup>-1</sup> greater than that for **1d-SiMe**<sub>3</sub>.

A similar energy difference between Si, Ge, and Sn would be anticipated for step E, the reductive elimination of a new C–E bond from 4-coordinate **int5** via **tsE**. Indeed, the span of  $\Delta G_{\text{step}}$  for step E is similar to that for step D, with values for Table 3. Influence of Carbene Steric Bulk on Catalytic Selectivity in the Reaction of  $C_6F_5H$  with  $H_2C=CHER_3$  with Catalyst [NHC]Ni( $\eta^2$ -H<sub>2</sub>C=CHER<sub>3</sub>)<sub>2</sub>

Vinyl Substrate					
H <sub>2</sub> C=CHER <sub>3</sub>	IPr (44.5)	IMes (36.5)	IBn (30.0)	<sup>i</sup> Pr <sub>2</sub> Im (27.4)	
H <sub>2</sub> C=CHSnBu <sub>3</sub>	Stannylation	Stannylation	Stannylation	Stannylation	Increased B-FR
H <sub>2</sub> C=CHGePh <sub>3</sub>	96 % Hydroarylation (4%Germylation)	Germylation	Germylation	Germylation	Elimination
H <sub>2</sub> C=CHSiMe <sub>3</sub>	Hydroarylation	66 % Silylation (34 % Hydroarylation)	Silylation	Silylation	

**1d-SnMe<sub>3</sub>**, **1d-GeMe<sub>3</sub>**, and **1d-SiMe<sub>3</sub>** of 11.4, -1.9 and -9.7 kcal·mol<sup>-1</sup> spanning ~ 20.0 kcal·mol<sup>-1</sup>. The energy differences for  $\Delta G^{\ddagger}$  for step E, **int6**, and **tsE** are less dramatic. Unexpectedly, the steric bulk of **1a-SiMe<sub>3</sub>** does not facilitate the reductive elimination of the C–Si bond in Step E, with a  $\Delta G_{\text{step}}$  of -5.4 kcal·mol<sup>-1</sup> that is 4.3 kcal·mol<sup>-1</sup> less favorable than that of **1d-SiMe<sub>3</sub>**; such a result is unanticipated, because steric bulk favors the related C–C reductive elimination step C.

The alternate route to C-E bond formation via step E', ethylene loss, and step E'', reductive elimination of the C-E bond from three coordinate int5' were less dramatically influenced by the nature of heteroatom E. The ethylene loss step featured a  $\Delta G^{\ddagger}$  that correlated to the driving force for the reaction  $\Delta G_{\text{step}}$ , which ranges from -7.3 kcal·mol<sup>-1</sup> for 1d-SnMe<sub>3</sub> to -13.8 kcal·mol<sup>-1</sup> for 1d-SiMe<sub>3</sub>. Ethylene loss is favorable in all cases, consistent with the poor binding of alkene to neutral Ni(II) complexes, and most favorable for Si. The steric bulk of 1a-SiMe<sub>3</sub> both favors ethylene dissociation and slightly decreases the  $\Delta G^{\ddagger}$  for step E' starting from int5. Step E'', reductive elimination of the C-E bond via threecoordinate int5' has the expected trend where the  $\Delta G_{\text{step}}$  is least favorable for 1d-SnMe<sub>3</sub> (15.6 kcal·mol<sup>-1</sup>), and most favorable with Si, with values of 5.2 kcal·mol<sup>-1</sup> for 1d-SiMe<sub>3</sub> and 1.4 kcal·mol<sup>-1</sup> for the bulkier 1a-SiMe<sub>3</sub>. The 10.4 kcal· mol<sup>-1</sup> range of  $\Delta G_{\text{step}}$  values for C–E reductive elimination from **1a-SnMe<sub>3</sub> 1a-GeMe<sub>3</sub>** and **1a-SiMe<sub>3</sub>** of half that of the ~20.0 kcal mol<sup>-1</sup> calculated for the alternate C–E reductive elimination pathway via step E. Also unlike step E, the  $\Delta G^{\ddagger}$  for step E'' starting from int5' are nearly identical for 1d-SnMe<sub>3</sub> and 1d-GeMe<sub>3</sub>, with values of 22.2 and 22.8 kcal·mol<sup>-1</sup>, with a modest drop to 19.0 kcal·mol<sup>-1</sup> for 1d-SiMe<sub>3</sub>.

Another notable difference between these reactions for Si, Ge, and Sn is the overall thermodynamic driving force. In all three cases, the hydroarylation product is thermodynamically favored, with a small range for  $\Delta G$  of -9.0 to -10.1 kcal·mol<sup>-1</sup>. In contrast, the  $\Delta G$  for stannylation, germylation and silylation are -7.2, -4.0, and -2.2 kcal·mol<sup>-1</sup>, respectively; with a minor temperature dependence. This increased driving force for stannylation may explain the relatively large scope for the stannylation reaction, where fluorobenzene will undergo catalytic turnovers, whereas for silylation only the most reactive fluorinated aromatics undergo catalysis.

# CONCLUSIONS

NHCs with similar electronic properties but varied  $%V_{bur}$  were screened to examine the effect in C–H silylation, germylation, and stannylation. The C–H bond germylation reaction offers an insightful middle ground between previous stannylation and silylation reactions, and a summary is shown in Table 3. The results show that the influence of carbene steric bulk becomes

more prominent as the reaction become more difficult. Catalytic C-H bond stannylation with SnBu<sub>3</sub> is facile with all carbene ligands regardless of size. This can be partly attributed to the relative ease of the  $\beta$ -Sn elimination step along the catalytic pathway. For C-H bond germylation reactions, where the  $\hat{\beta}$ -Ge elimination step is more difficult and higher temperatures are needed, the largest NHC, IPr, provides 96% hydroarylation with 4% germylation product. Subsequent smaller carbenes IMes, IBn, and <sup>i</sup>Pr<sub>2</sub>Im provide exclusive germylation product. Finally, for C-H bond silvlation reaction, where the  $\beta$ -Si elimination step is the most difficult, the largest carbene IPr provides exclusive conversion to the hydroarylation product. Using the slightly smaller IMes provided a mixture of silvlation and hydroarylation products of 66 and 34% conversions, respectively. The smallest IBn and <sup>i</sup>Pr<sub>2</sub>Im carbenes provide exclusive conversion to the silvlation product. Computational studies provide support for the experimental work. The observed trends show the influence of the heteroatom in any step where a C-E bond is made or broken. These  $\beta$ -E elimination steps for E = Si, Ge, and Sn are not common in catalysis, but provide a pathway as powerful as  $\beta$ -H elimination for the rearrangement of functional groups.

#### EXPERIMENTAL SECTION

Unless otherwise stated, all reactions were carried out under an atmosphere of dry oxygen free dinitrogen by means of standard Schlenk or glovebox techniques. Benzene- $d_6$  and toluene- $d_8$  were degassed by three freeze-pump-thaw cycles and subsequently dried by running through a column of activated alumina. Toluene, THF, and *n*-pentane were purchased anhydrous from Aldrich or Alfa Aesar and used without further purification. <sup>1</sup>H,  $^{13}C{^{1}H}$ ,  $^{19}F{^{1}H}$ ,  $^{29}Si{^{1}H}$ ,  $^{31}P{^{1}H}$ , and  $^{119}Sn{^{1}H}$  NMR spectra were recorded on a Bruker AMX Spectrometer operating at either 300 or 500 MHz with respect to proton nuclei. <sup>1</sup>H NMR spectra were referenced to residual protons (C<sub>6</sub>D<sub>6</sub>,  $\delta$  7.16) or (toluene-d<sub>8</sub>,  $\delta$  2.08) with respect to tetramethylsilane at  $\delta$  0.00. <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced relative to solvent resonances (C<sub>6</sub>D<sub>6</sub>,  $\delta$  128.06) or (toluene-d<sub>8</sub>,  $\delta$ 20.43). <sup>19</sup>F {<sup>1</sup>H} NMR spectra were referenced to an external sample of 80% CCl<sub>3</sub>F in CDCl<sub>3</sub> at  $\delta$  0.00. <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were referenced to an external sample of tetramethylsilane at  $\delta$  0.00. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced to an external sample of 80%  $H_3PO_4$  at  $\delta$  0.00. <sup>119</sup>Sn{<sup>1</sup>H} NMR spectra were referenced to an external sample of Me<sub>4</sub>Sn in C<sub>6</sub>D<sub>6</sub> at  $\delta$  0.00. Benzene-d<sub>6</sub> and toluened<sub>8</sub> was purchased from Cambridge Isotope Laboratory. All reagents were purchased from commercial suppliers. The compounds Ni- $(COD)_{2}$ ,<sup>17</sup> IPr,<sup>18</sup> IMes,<sup>18</sup> <sup>*i*</sup>Pr<sub>2</sub>Im,<sup>19</sup> and IBn<sup>20</sup> were prepared according to literature procedures. Complexes 1a-SiMe<sub>3</sub> and 1d-SiMe<sub>3</sub> were prepared as previously reported.<sup>3a</sup>

**Computational Details.** All calculations were performed at the B3LYP<sup>21</sup> level of theory using the Gaussian 09 package.<sup>22</sup> Geometry optimizations were carried out with a mixed basis set of LANL2DZ<sup>23</sup> for Ni, Sn, and Ge and 6-31G(d) for other atoms. Vibrational frequencies were computed analytically at the same level of theory to

confirm whether the structures are minima (no imaginary frequencies) or transition states (only one imaginary frequency). Solvation effects (toluene,  $\varepsilon = 2.3741$ ) were taken into account by performing single-point calculations using the SMD model.<sup>24</sup> To obtain better accuracy, single-point energies for the optimized geometries were recalculated with a larger basis set, which is SDD<sup>25</sup> for Ni, Sn, and Ge and 6-311+G(d,p) for other atoms. The final free energies reported in the article are the large basis set single-point energies with gas-phase Gibbs free energy correction (at reaction temperature, see Scheme 9), solvation correction, and dispersion correction using the DFT-D3(BJ) method developed by Grimme and co-workers.<sup>26</sup>

# SYNTHESIS, CHARACTERIZATION, AND REACTIONS

Synthesis of [IMes]Ni( $\eta^2$ -H<sub>2</sub>C=CHSiMe<sub>3</sub>)<sub>2</sub> (1b-SiMe<sub>3</sub>). A solution of Ni(COD)<sub>2</sub> (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 min. The solution was filtered through Celite and evaporated in vacuo to afford 0.420 g (85% yield) of a yellow oil. The product was recrystallized from pentane at -35 °C. NMR data is consistent with the C<sub>2</sub> symmetric structure. <sup>1</sup>H NMR  $(C_6D_6, 25 \text{ °C}, 500.13 \text{ MHz}): \delta -0.05 \text{ (s, 18H, Si}(CH_3)_3); 2.08 \text{ (s, })$ 6H, Ar-CH<sub>3</sub>); 2.09 (s, 6H, Ar-CH<sub>3</sub>); 2.11 (s, 6H, Ar-CH<sub>3</sub>); 2.54 (dd, 2H, vinyl-H,  ${}^{2}J_{HH} = 0.6$  Hz,  ${}^{3}J_{HH} = 14.5$  Hz); 2.62 (dd, 2H, vinyl-H,  ${}^{3}J_{HH}$  = 12.7 Hz,  ${}^{2}J_{HH}$  = 0.64 Hz); 2.69 (dd, 2H, vinyl-H,  ${}^{3}J_{\text{HH}} = 12.7 \text{ Hz}, {}^{3}J_{\text{HH}} = 14.5 \text{ Hz}$ ; 6.25 (s, 2H, HC=CH); 6.70 (m, 2H, Ar–H,  ${}^{4}J_{HH}$  < 1.0 Hz); 6.72 (m, 2H, Ar–H,  ${}^{4}J_{HH}$  < 1.0 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 23 °C, 75.47 MHz):  $\delta$  1.13 (s, 6C, Si( $CH_3$ )<sub>3</sub>); 18.4 (s, 2C, Ar-CH<sub>3</sub>); 18.6 (s, 2C, Ar-CH<sub>3</sub>); 21.0 (s, 2C, Ar-CH<sub>3</sub>); 51.1 (s, vinyl-C); 53.0 (s, vinyl-C); 126.0 (s,  $H_2C=H_2$ ); 129.3 (s, meta-Ph-C); 129.5 (s, meta-Ph-C); 135.5 (s, ortho-Ph-C); 135.7 (s, ortho-Ph-C); 137.8 (s, para-Ph-C); 138.3 (s, ipso-Ph-C-N); 203.8 (s, Ni–C). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 27 °C, 59.64 MHz): -5.0 (s, 2Si, SiMe<sub>3</sub>). Repeated elemental analyses gave variable but consistently low values for C, possibly due to Ni-carbide formation; this was also observed in previous work with 1a-SiMe<sub>3</sub> and 1d-SiMe<sub>3</sub>.

Synthesis of [IBn]Ni( $\eta^2$ -H<sub>2</sub>C=CHSiMe<sub>3</sub>)<sub>2</sub> (1c-SiMe<sub>3</sub>). Ni-(COD)<sub>2</sub> (0.243 g, 0.884 mmol) was dissolved in 5 mL of toluene. The solution was charged with 10 equiv 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 at -40 °C and stirred for 30 min. The solution was filtered through Celite, and volatiles were removed in vacuo affording 0.262 g of a thick yellow oil (87% yield). Major isomer: <sup>1</sup>H NMR ( $C_6D_{61}$  25 °C, 300.129 MHz):  $\delta$  0.18 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>); 2.52 (broad multiplet, 2H, vinyl-H); 2.78 (d, 2H, vinyl-*H*,  ${}^{3}J_{HH} = 15.48$  Hz); 2.92 (d, 2H, vinyl-*H*,  ${}^{3}J_{HH} = 12.25$  Hz); 4.77 (d, 2H,  $CH_2$ –Ph,  ${}^2J_{HH}$  = 15.05 Hz); 4.97 (d, 2H,  $CH_2$ –Ph,  ${}^2J_{HH}$ = 16.23 Hz); 6.23 (s, 2H,  $H_2C=CH_2$ ); 6.98 (m, 8H, 2,6-Ph-H); 7.00 (m, 12H, 3,4,5-Ph-H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 23 °C, 75.47 MHz):  $\delta$  1.2 (s, 6C, Si(CH<sub>3</sub>)<sub>3</sub>); 49.9 (fluctional s, vinyl-C); 53.1 (fluctional s, vinyl–*C*); 53.9 (s, 2C, CH<sub>2</sub>–Ph); 120.9 (s, H<sub>2</sub>C=CH<sub>2</sub>); 128.9 (s, meta-Ph-C); 137.4 (s, ipso-Ph-C); ortho- and para-Ph-C are obscured by solvent  $C_6D_6$  peak P204.4 (s, Ni-C). <sup>29</sup>Si{<sup>1</sup>H} NMR  $(C_6D_6, 27 \ ^{\circ}C, 59.64 \text{ MHz}): -4.1 \text{ (s, 2Si, SiMe}_3)$ . Minor isomer: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 300.129 MHz): δ 0.15 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>); 2.26 (dd, 2H, vinyl-H,  ${}^{3}J_{HH}$  = 12.5 Hz,  ${}^{3}J_{HH}$  = 15.9 Hz); 2.78 (d, 2H, vinyl-H,  ${}^{3}J_{\text{HH}} = 15.9 \text{ Hz}, {}^{2}J_{\text{HH}} = 1.0 \text{ Hz}); 2.92 \text{ (d, 2H, vinyl-H, }^{3}J_{\text{HH}}$ = 12.5 Hz,  ${}^{2}J_{HH}$  = 1.0 Hz); 4.83 (fluctional s, 2H, CH<sub>2</sub>-Ph,  ${}^{2}J_{HH}$  = 16.2 Hz); 5.00 (fluctional s, 2H,  $CH_2$ -Ph,  ${}^2J_{HH}$  = 7.3 Hz); 6.21 (fluctional s, 2H, H<sub>2</sub>C=CH<sub>2</sub>); 6.95 (m, 8H, 2,6-Ph-H); 7.04 (m, 12H, 3,4,5–Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 23 °C, 75.47 MHz):  $\delta$  0.9 (s, 6C, Si(CH<sub>3</sub>)<sub>3</sub>); 51.3 (s, vinyl-C); 52.2 (s, vinyl-C); 53.7 (s, 1C,  $CH_2$ -Ph); 54.4 (s, 1C,  $CH_2$ -Ph); 120.8 (s,  $H_2C = CH_2$ ); 121.2 (s,  $H_2C = CH_2$ ; 128.9 (s, meta-Ph-C); 137.6 (s, ipso-Ph-C); ortho and para Ph-C are obscured by solvent C<sub>6</sub>D<sub>6</sub> peak. 203.9 (s, Ni-C). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 27 °C, 59.64 MHz): -4.3 (s, 2Si, SiMe<sub>3</sub>).

Synthesis of  $[IBn]_2Ni(\eta^2-H_2C=CHSiMe_3)$  (2c-SiMe<sub>3</sub>). A solution of Ni(COD)<sub>2</sub> (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). <sup>1</sup>H NMR ( $C_6D_6$ , 25 °C, 500.129 MHz):  $\delta$  0.34 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>); 1.62 (dd, 1H, vinyl-H,  ${}^{3}J_{\text{HH}}$  = 12.5 Hz,  ${}^{3}J_{\text{HH}}$  = 14.0 Hz); 1.88 (dd, 1H, vinyl-H,  ${}^{3}J_{\text{HH}}$  = 14.0 Hz,  ${}^{2}J_{HH} = 2.5$  Hz); 2.33 (dd, 1H, vinyl-H,  ${}^{3}J_{HH} = 12.5$  Hz,  ${}^{2}J_{HH} = 2.5$  Hz); 5.08 (d, 2H,  $CH_{2}$ -Ph,  ${}^{2}J_{HH} = 15.1$  Hz); 5.12 (d, 2H,  $CH_{2}$ -Ph,  ${}^{2}J_{HH} = 15.4$  Hz); 5.52 (d, 2H,  $CH_{2}$ -Ph,  ${}^{2}J_{HH} = 14.9$  Hz); 5.68 (d, 2H,  $CH_2$ -Ph,  ${}^2J_{HH}$  = 14.4 Hz); 6.18 (s, 2H, HC=CH); 6.25 (s, 2H, HC=CH; 6.94–7.04(m, 20H, Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 24 °C, 125.76 MHz):  $\delta$  1.7 (s, 3C, Si(CH<sub>3</sub>)<sub>3</sub>); 30.3 (s, vinyl-C); 31.5 (s, vinyl-C); 53.8 (s, 2C, CH<sub>2</sub>-Ph); 54.2 (s, 2C, CH<sub>2</sub>-Ph); 119.3 (s, 4C, H<sub>2</sub>C=CH<sub>2</sub>); 127.5 (s, para-Ph-C); 127.5 (s, para-Ph-C); 128.0 (s, ortho-Ph-C); 128.2 (s, ortho-Ph-C); 128.7 (s, meta-Ph-C); 128.7 (s, meta-Ph-C); 138.5 (s, ipso-Ph-C); 138.7 (s, ipso-Ph-C); 205.8 (s, Ni-C); 206.6 (s, Ni-C). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 27 °C, 59.64 MHz): -6.8 (s, 1Si, SiMe<sub>3</sub>). Anal. Calcd for C<sub>39</sub>H<sub>44</sub>N<sub>4</sub>NiSi: C, 71.45; H, 6.77; N, 8.55. Found: C, 71.72; H, 6.76; N, 8.21.

Synthesis of H<sub>2</sub>C=CHGePh<sub>3</sub>. Vinyl triphenyl germane was prepared according to a modified procedure that was previously reported.<sup>27</sup> Triphenylgermanium chloride (3.0 g, 8.8 mmol) was dissolved in 20 mL of THF. Vinylmagnesium chloride in THF (8.3 mL, 13.2 mmol, 1.5 equiv) was added dropwise to solution while stirring. The reaction was left to stir for 4 h. 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 Celite. The solution was cooled to -40 °C and afforded 1.5 g of white crystals (50% yield). <sup>1</sup>H NMR ( $C_6D_6$ , 25 °C, 500.13 MHz):  $\delta$  5.78 (dd, 1H, vinyl-CH, <sup>2</sup>J = 3.0 Hz, <sup>3</sup>J = 20.0 Hz); 6.14  $(dd, 1H, vinyl-CH, {}^{2}J = 3.0 Hz, {}^{3}J = 13.5 Hz); 6.65 (dd, vinyl-CH, )$  ${}^{3}J = 13.5$  Hz,  ${}^{2}J = 20.0$  Hz); 7.13 (second order m, 9H, ortho- and para-H); 7.55 (m, 6H, para-H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 125.76 MHz):  $\delta$  128.6 (s, ortho-Ph-C); 129.2 (s, para-Ph-C); 134.4 (s,  $CH=CH_2$ ; 134.7 (s,  $CH=CH_2$ ); 135.4 (s, meta-Ph-C); 136.5 (s, ivso-Ph-C)

Synthesis of (IPr)Ni( $\eta^2$ -CH<sub>2</sub>=CHGePh<sub>3</sub>)<sub>2</sub> (1a-GePh<sub>3</sub>). A solution ofNi(COD)<sub>2</sub> (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).  $^1\!\mathrm{H}$  NMR (C\_6D\_6, 25 °C, 500.133 MHz):  $\delta$  0.52 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{\text{HH}} = 6.8$  Hz); 0.84 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{HH} = 6.8$  Hz); 1.05 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{HH} =$ 6.8 Hz); 1.48 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{HH} = 6.8$  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,  ${}^{3}J_{HH} = 12.3 \text{ Hz}$ ); 3.12 (septet, 2H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{\text{HH}} = 6.8 \text{ Hz}$ ; 3.19 (dd, 2H, vinyl-H,  ${}^{3}J_{\text{HH}} = 12.3 \text{ Hz}$ ,  ${}^{3}J_{\text{HH}} = 14.5$ Hz); 6.64 (s, 2H, CH=CH); 7.00-7.05 (m, 14H, 2,6-Ph-H, 4- $(2,6^{-i}Pr_2Ph)-H);$  7.06–7.1 (m, 10H 4-Ar–H, 3,5- $(2,6^{-i}Pr_2Ph)-H);$ 7.2-7.3 (m, 12H 3,5-Ar-H).  ${}^{13}C{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 23  ${}^{\circ}C$ , 75.47 MHz):  $\delta$  21.0 (s, isopropyl-(CH<sub>3</sub>)<sub>2</sub>); 22.1 (s, isopropyl-(CH<sub>3</sub>)<sub>2</sub>); 25.8 (s, isopropyl- $(CH_3)_2$ ); 26.6 (s, isopropyl- $(CH_3)_2$ ); 28.4 (s, isopropyl-CH); 28.7 (s, isopropyl-CH); 51.0 (s, vinyl-C); 57.3 (s, vinyl-C); 123.6 (s,CH=CH); 124.2 (s, meta-(2,6-iPr<sub>2</sub>Ph)-C); 124.5  $(s, 4-(2,6-Pr_2Ph)-C); 129.6 (s, para-Ph-C); 135.9 (s, ortho, meta-$ Ph-C);137.4 (s, ipso-Ph-C-N); 139.8 (s, ipso-Ph-C); 146.0 (s, ortho- $(2,6-iPr_2)Ph-C$ ; 146.1 (s, ortho- $(2,6-iPr_2)Ph-C$ ); 204.0. (s, Ni–C). Anal. Calcd For C<sub>67</sub>H<sub>72</sub>Ge<sub>2</sub>N<sub>2</sub>Ni: C, 72.55; H, 6.54; N, 2.53. Found: C, 72.52; H, 6.76; N, 2.37.

**Synthesis of (<sup>†</sup>Pr<sub>3</sub>P)Ni(\eta^2-CH<sub>2</sub>=CHGePh<sub>3</sub>)<sub>2</sub>.** Ni(COD)<sub>2</sub> (0.209 g, 0.76 mmol, 1 equiv) was dissolved in 10 mL of toluene. Triisopropylphosphine (0.120 g, 0.76 mmol, 1 equiv) and triphenyl-(vinyl)germane (0.500 g, 1.51 mmol, 2 equiv) were added, and the solution was stirred for 1 h. The yellow solution was evaporated in vacuo leaving a red/yellow solid. Extraction into pentane, crystallization at -40 °C, and filtration gave 0.601 g of yellow solid (89% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 500.133 MHz): δ 0.56 (dd, 9H, CH<sub>3</sub>CHP, <sup>3</sup>J<sub>HH</sub> = 7.25 Hz, <sup>3</sup>J<sub>HP</sub> = 12.2 Hz); 0.83 (dd, 9H, CH<sub>3</sub>CHP,

<sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, <sup>3</sup>*J*<sub>HP</sub> = 12.2 Hz); 1.92 (d of septets, 3H, CHP, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz); 2.93 (dd, 2H, vinyl–CH, <sup>2</sup>*J*<sub>HH</sub> = 5.1 Hz, <sup>3</sup>*J*<sub>HH</sub> = 11.5 Hz); 3.01 (dd, 2H, vinyl–CH, <sup>2</sup>*J*<sub>HH</sub> = 5.1 Hz, <sup>3</sup>*J*<sub>HH</sub> = 14.8 Hz); 4.04 (ddd, 2H, vinyl–CH, <sup>3</sup>*J*<sub>HP</sub> = 3.1 Hz, <sup>3</sup>*J*<sub>HH</sub> = 11.5 Hz, <sup>3</sup>*J*<sub>HH</sub> = 14.8 Hz); 7.14 (second-order m, 18H, 2,4,6-phenyl H); 7.58 (second-order m, 12H, 3.5-phenyl–H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 125.77 MHz): δ 19.2 (s, CH<sub>3</sub>); 19.7 (s, CH<sub>3</sub>); 25.4 (d, CH(CH<sub>3</sub>)<sub>2</sub>, *J*<sub>CP</sub> = 15.4 Hz); 54.4 (d, CH=CH<sub>2</sub>, *J*<sub>CP</sub> = 10.3 Hz); 57.5 (d, CH=CH<sub>2</sub>, *J*<sub>CP</sub> = 4.5 Hz); 128.2 (s, *ortho*-Ph-C); 128.7 (s, *para*-Ph–C); 136.1 (s, *meta*-Ph–C); 139.2 (s, 1P). Repeated elemental analyses gave variable but consistently low values for C, possibly due to Ni–carbide formation

Synthesis of (IPr)Ni( $\eta^2$ -CH<sub>2</sub>=CHSnPh<sub>3</sub>)<sub>2</sub> (1a-SnPh<sub>3</sub>). 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). <sup>1</sup>H NMR ( $C_6D_6$ , 21 °C, 500.133 MHz):  $\delta$  0.72 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{\rm HH} = 6.7$  Hz); 0.88 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{HH} = 6.7$  Hz); 1.03 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{HH} = 6.7$ Hz); 1.35 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{HH} = 6.7$  Hz); 2.80 (d, 2H, vinyl-H,  ${}^{3}J_{\text{HH}} = 14.8 \text{ Hz}$ ; 2.93 (septet, 2H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{\text{HH}} = 6.7 \text{ Hz}$ ); 3.01 (d, 2H, vinyl-H,  ${}^{3}J_{HH}$  = 11.7 Hz); 3.12 (septet, 2H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{HH}$ = 6.7 Hz); 3.18 (d, 2H, vinyl-H,  ${}^{3}J_{HH}$  = 11.7 Hz,  ${}^{3}J_{HH}$  = 14.8 Hz); 6.65 (s, 2H, H<sub>2</sub>C=CH<sub>2</sub>); 6.86 (dd, 2H, 4-Ar-H); 7.08 (m, 18H, 2,4,6-Ph-H); 7.17 (m, 4H, 3,5-Ar-H); 7.33 (m, 12H, 3,5-Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 23 °C, 75.47 MHz):  $\delta$  21.9 (s, isopropyl-(CH<sub>3</sub>)<sub>2</sub>); 22.3 (s, isopropyl-(CH<sub>3</sub>)<sub>2</sub>); 26.4 (s, isopropyl-(CH<sub>3</sub>)<sub>2</sub>); 26.7 (s, isopropyl-(CH<sub>3</sub>)<sub>2</sub>); 28.8 (s, isopropyl-CH); 28.9 (s, isopropyl-CH); 51.9 (s, vinyl-C); 57.2 (s, vinyl-C); 123.8 (s,CH=CH); 124.5  $(s, meta-(2,6-iPr_2Ph)-C);$  124.8 (s, 4-CH) $(2,6^{-i}Pr_2Ph)-C)$ ; 129.9 (s, para-Ph-C); 137.4 (s, ipso-Ph-C-N); 138.0 (s, ortho, meta-Ph-C); 141.6 (s, ipso-Ph-C); 146.1 (s, ortho- $(2,6^{-i}Pr_2)Ph-C)$ ; 146.2 (s, ortho- $(2,6^{-i}Pr_2)Ph-C)$ ; 204.9 (s, Ni-C).  $^{119}\text{Sn}\{^{1}\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 20.6 °C, 186.50 MHz):  $\delta$  –110.3 (s, 2Sn, SnPh<sub>3</sub>). Repeated elemental analyses gave variable but consistently low values for C, possibly due to Ni-carbide formation.

Synthesis of C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>GePh<sub>3</sub>. 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 1a-GePh<sub>3</sub> (0.016 g, 0.015 mmol, 10 mol %) and FSiPh<sub>3</sub> (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 <sup>19</sup>F NMR showed a mixture of alkene hydroarylation and C-H germylation products. (65 and 3% NMR yields respectively). <sup>1</sup>H NMR ( $C_6D_6$ , 21 °C, 500.133 MHz):  $\delta$ 1.55 (second order m, 2H, CH2Ge); 2.63 (second order m, 2H, CH<sub>2</sub>CH<sub>2</sub>Ge); 7.15 (m, 9H, 3,4,5-Ph-H); 7.50 (m, 6H, 2,6-Ph-H). <sup>19</sup>F {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 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,  ${}^{3}J_{FF} = 21.3$  Hz); –163.4 (AA'MM'X second-order m, 2F, 3,5-Ar–F).  ${}^{13}C{}^{1}H$ NMR (C<sub>6</sub>D<sub>6</sub>, 23 °C, 125.77 MHz): δ 18.1 (s, GeCH<sub>2</sub>); 21.0 (s, GeCH<sub>2</sub>CH<sub>2</sub>); 117.5. (dt, Ar<sup>F</sup>-C,  ${}^{2}J_{CF} = 23$  Hz,  ${}^{3}J_{CF} = 3$  Hz)); 128.4 (s, ortho-Ar-C); 128.9 (s, para-Ar-C); 134.8 (s, meta-Ar-C); 136.1 (s, ipso-Ar–C); 138.9 (dm, ortho-Ar<sup>F</sup>–C,  $J_{CF} = 250$  Hz); 142.9 (dm, para-Ar<sup>F</sup>-C,  $J_{CF} = 253$  Hz); 146.2. (dm, meta-Ar<sup>F</sup>-C,  $J_{CF} = 251$  Hz). The reaction gave both C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>GePh<sub>3</sub> and residual C<sub>6</sub>F<sub>5</sub>GePh<sub>3</sub> as products, which are very similar in terms of their solubility and polarity. Purification by multiple chromatographic and recrystallization attempts were unsuccessful. The spectra of C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>GePh<sub>3</sub> are nearly identical to the previously characterized C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>SnPh<sub>3</sub>.<sup>3</sup>

Synthesis of Triphenyl(pentafluorophenyl)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)<sub>2</sub> (0.001 g, 0.003 mmol, 10 mol %), <sup>i</sup>Pr<sub>2</sub>Im (0.001 g, 0.003 mmol, 10 mol %), and FSiPh<sub>3</sub> (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). The <sup>19</sup>F {<sup>1</sup>H} NMR spectrum was in good agreement with previously reported data.<sup>28</sup>

Synthesis of Trimethyl(pentafluorophenyl)silane with 5 mol % 1c-SiMe<sub>3</sub>. 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-SiMe<sub>3</sub> (0.012 g, 0.025 mmol, 5 mol %) and FSiPh<sub>3</sub> (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 <sup>19</sup>F NMR showed exclusive conversion to the known C–H silylation product  $C_6F_5SiMe_3$ .<sup>3a</sup>

Synthesis of Trimethyl(pentafluorophenyl)silane with 5 mol % 1d-SiMe<sub>3</sub> under 1 atm  $C_2H_4$ . 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-SiMe<sub>3</sub> (0.007 g, 0.025 mmol, 5 mol %), and FSiPh<sub>3</sub> (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 <sup>19</sup>F NMR to track initial rations of silylation to hydroarylation. The results were identical to the analogous experiment conducted in the absence of ethylene.

Synthesis of Trimethyl(pentafluorophenyl)silane with Nickel Metal. A solution of 1d-SiMe<sub>3</sub> in 0.6 g of toluene was heated to 140 °C for 16 h to promote decomposition of 1d-SiMe<sub>3</sub> into 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 <sup>19</sup>F NMR showed no indication of hydroarylation product.

Synthesis of Tributyl(pentafluorophenyl)tin with 5 mol % Ni(COD)<sub>2</sub> 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 with Ni(COD)<sub>2</sub> (0.001 g, 0.004 mmol, 5 mol %), IPr (0.0015 g, 0.004 mmol, 4 mol %), and FSiPh<sub>3</sub> (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  $C_6F_5SnBu_3$  (74% NMR yield).<sup>3e</sup>

Synthesis of Tributyl(pentafluorophenyl)tin with 5 mol %  $Ni(COD)_2$  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 with  $Ni(COD)_2$  (0.001 g, 0.004 mmol, 5 mol %), IMes (0.001 g, 0.004 mmol, 5 mol %), and FSiPh<sub>3</sub> (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  $C_6F_5SnBu_3$  (66% NMR yield).<sup>3e</sup>

Synthesis of Tributyl(pentafluorophenyl)tin with 5 mol %  $Ni(COD)_2$  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 with  $Ni(COD)_2$  (0.001 g, 0.004 mmol, 5 mol %), IBn (0.001 g, 0.004 mmol, 5 mol %), and FSiPh<sub>3</sub> (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  $C_6F_3SnBu_3$  (68% NMR yield).<sup>3e</sup>

Synthesis of Tributyl(pentafluorophenyl)tin with 5 mol %  $Ni(COD)_2$  and  $Pr_2lm$ . 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 with  $Ni(COD)_2$  (0.001 g, 0.004 mmol, 5 mol %),  $Pr_2Im$  (0.0005 g, 0.004 mmol, 5 mol %), and FSiPh<sub>3</sub> (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  $C_6F_5SnBu_3$  (72% NMR yield).<sup>3e</sup>

#### ASSOCIATED CONTENT

# **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00786.

# Accession Codes

CCDC 1875646–1875651 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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barriers in the [NQA] supported system, irrespective of heteroatom substituent. The heteroatom substituent effect is a minor perturbation compared to the control of selectivity imparted by the supporting ligand and nature of the heteroatom.

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