

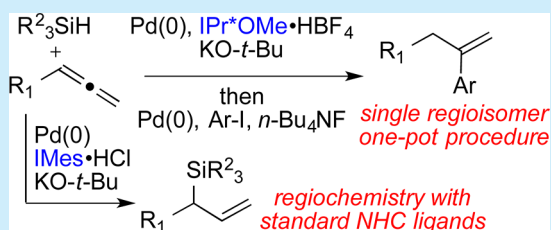
Regioselective Allene Hydroarylation via One-Pot Allene Hydrosilylation/Pd-Catalyzed Cross-Coupling

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Supporting Information

ABSTRACT: Advances in hydroarylation have been achieved by the development of a one-pot regioselective allene hydrosilylation/Pd(0)-catalyzed cross-coupling protocol. The regioselectivity is primarily governed by *N*-heterocyclic carbene (NHC) ligand identity in the hydrosilylation step and is preserved in the subsequent cross-coupling reaction. This methodology affords streamlined access to functionalized 1,1-disubstituted alkenes with excellent regiocontrol.



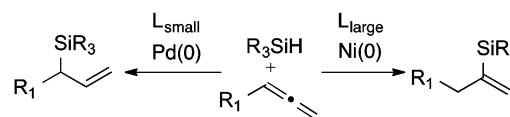
Alkenylsilanes are versatile nucleophiles in metal-catalyzed cross-coupling reactions. Numerous carbon–carbon bond-forming reactions with alkenylsilanes have been well developed,¹ including the powerful cross-coupling methodology extensively developed by Hiyama and Denmark.^{2–4} Currently, the most direct routes to alkenylsilanes are via metal-catalyzed hydrosilylations of alkynes.⁵ However, subtle alterations in the π -component, silane coupling partner, and metal catalyst often have substantial effects on the reaction outcome, leading to challenges in regiocontrol.^{1a} Significant progress has been made in accessing alkenylsilane structures through the development of alternative methods, including reactions that introduce the silane moiety through carbon framework rearrangements,^{6a,b} Heck^{6c} and silyl-Heck reactions,^{6d,e} or by nucleophilic additions to electrophilic halosilanes.^{6f} However, the regio- and stereo-selective addition of silanes to simple π -components remains an especially attractive point of entry to this structure class.

As a part of our laboratory's interests in developing regioselective catalytic processes,⁷ we set out to explore catalytic allene hydrosilylation with the goal to discover conditions that would provide highly selective access to either allylsilanes or alkenylsilanes depending on the metal–ligand combination employed. Our previous work in regioselective allene hydrosilylations demonstrated that the selection of metal is an effective tool for gaining access to either allylsilanes with palladium NHC complexes or alkenylsilanes with nickel NHC complexes (Scheme 1).^{7e} While the nickel-based procedure provided useful access to alkenylsilanes, the scope was somewhat limited, and access to the classes of alkenylsilanes that are most useful in cross-coupling methodology was not obtained. This inspired us to search for conditions with palladium catalysis where the inherent preference for allylsilane production could be reversed to allow alkenylsilane synthesis by simple alteration of the *N*-heterocyclic carbene ligand employed.

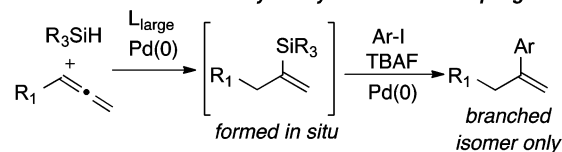
As additional motivation, identification of a palladium-catalyzed entry to alkenyl silanes from allenes would potentially allow a one-pot procedure to be developed involving regioselective allene hydrosilylation followed directly by a Pd-

Scheme 1. Goals of the Current Study

Previous work: Metal-Divergent Regioselective Hydrosilylation



This work: One-Pot Allene Hydrosilylation/ Cross-Coupling



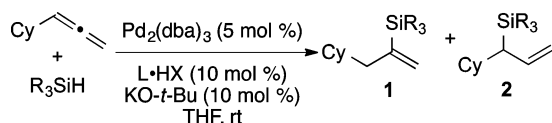
catalyzed cross-coupling event to provide a net hydroarylation process. Although significant progress has been achieved in one-pot alkyne hydroarylations with zinc^{8a–c} and tin,^{8d} one-pot hydroarylations involving hydrosilylation/cross-coupling sequences typically provide 1,2-disubstituted alkenes and often require purification of the alkenyl silane.⁹ To address the above challenges, we report herein a general one-pot hydroarylation procedure that utilizes a catalyst-controlled regioselective allene hydrosilylation reaction in tandem with Pd-catalyzed cross-couplings to provide functionalized 1,1-disubstituted alkenes with exceptional regiocontrol (Scheme 1).

Our efforts to identify the conditions that favor alkenylsilanes in palladium-catalyzed allene hydrosilylation began with an evaluation of the effects of structural modification of NHC ligands on reaction outcome. To facilitate rapid screening, we utilized a protocol where the active catalyst is formed by the deprotonation of the NHC hydrochloride salt with an equivalent of KO-*t*-Bu base and Pd₂dba₃ precatalyst (Table 1). Our preliminary experiments resulted in the observation that methyl substitution of the backbone of *N*-mesityl ligands resulted in a

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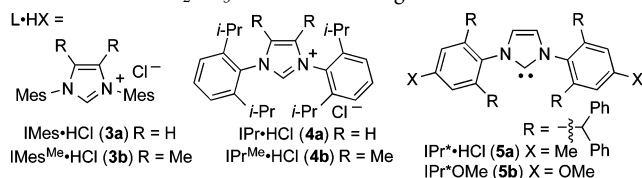
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Table 1. Ligand Effects in Allene Hydrosilylation



entry	silane	L·HX	major product (% yield)	regioselectivity (1:2)
1	Et ₃ SiH	3a	2a (80)	<2:>98
2	Et ₃ SiH	3b	2a (85)	2:98
3	Et ₃ SiH	4a	2a (75)	12:88
4	Et ₃ SiH	4b	1a (83)	>98:2
5	Et ₃ SiH	5a	1a (50)	>98:2
6	Et ₃ SiH	5b ^a	1a (90)	>98:2
7	BnMe ₂ SiH	4a	2b (77)	3:97
8	BnMe ₂ SiH	4b	1b (73)	75:25 ^b
9	BnMe ₂ SiH	5a	1b (62)	81:19
10	BnMe ₂ SiH	5b ^a	1b (79)	95:5

^aReaction conducted in the absence of KO-*t*-Bu. ^bReaction conducted with 2.5 mol % Pd₂dba₃ and 5.0 mol % ligand.



slight erosion of regioselectivity, with allylsilanes strongly preferred in analogy with our prior findings.^{7c} For example, the hydrosilylation of cyclohexylallene with triethylsilane using IMes (3a) as a ligand resulted in excellent regioselectivities (>98:2) favoring allylsilane 2, while use of IMes^{Me} (3b) as a ligand proceeded with slightly decreased regioselectivity (98:2) in an excellent chemical yield of 85% (Table 1, entries 1 and 2).

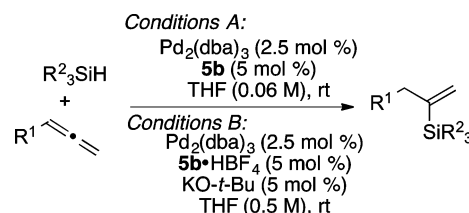
The effects of NHC ligand variation were further explored with bulkier ligands (Table 1, entries 3–5). The reaction with the comparatively large IPr (4a) as the ligand still resulted in the allylsilane 2 as the major product with triethylsilane in 88:12 regioselectivity (Table 1, entry 3). However, use of IPr^{Me} (4b) as the ligand, modified from its IPr variant by simple dimethyl substitution of the backbone, afforded alkenylsilane 1 with triethylsilane in >98:2 regioselectivity in 83% yield. While the steric differences of IPr and IPr^{Me} have been previously recognized including a description of %V_{bur} for silver and gold complexes,^{10a} this dramatic regiochemical reversal is nonetheless surprising.^{10b} Additionally, variation of *N*-aryl rather than the backbone substituent also allows alkenyl silanes to be produced with exceptional regiocontrol. Specifically, the use of commercially available NHC carbene ligand IPr* (5a) or IPr*OMe (5b)¹¹ also provided a highly selective entry to alkenyl silanes, with product 1 being obtained again in >98:2 regioselectivity in both instances.

Given that an important objective of the current study is the utilization of organosilicon structures that perform well in cross-couplings, related hydrosilylations using BnMe₂SiH were next examined (Table 1, entries 6–8). The comparison of IPr (4a), IPr^{Me} (4b), IPr* (5a), and IPr*OMe (5b) exhibited similar trends, with ligand 4a providing allylsilane 2 with 97:3 regioselectivity, ligand 4b providing a 75:25 mixture favoring alkenylsilane 1, ligand 5a favoring alkenylsilane 1 with 81:19 selectivity, and ligand 5b favoring alkenylsilane 1 with optimum 95:5 regiocontrol. The 5a:5b comparison illustrates that both the steric and electronic environment play an important role in

regioselectivity. Given the superior regioselection of alkenylsilane production with IPr*OMe (5b) across the two different silane structures, this procedure was adopted as the standard procedure for alkenylsilane synthesis for the remainder of this study.

Variations in the silane coupling partner and allene substitution were then explored with the optimized procedure using ligand IPr*OMe (5b) as the free carbene (conditions A). Hydrosilylations occurred in 1–2 h at rt with palladium catalysis to afford a range of alkenylsilanes with a high degree of regiocontrol (Table 2). With the allene variations depicted,

Table 2. Silane and Allene Variation



entry	R ¹	conditions	silane	product (% yield)	regioselectivity (1:2)
1	Cy	A	Me ₂ PhSiH	1c (90)	>98:2
2	Cy	A	Me ₂ EtOSiH	1d (81)	96:4
3	Ph	A	Me ₂ PhSiH	6a (83)	>98:2
4	Ph	A	Me ₂ EtOSiH	6b (88)	>98:2
5	Ph	A	BnMe ₂ SiH	6c (90)	>98:2
6	BnO	A	Me ₂ PhSiH	7a (95) ^a	>98:2
7	BnO	A	Me ₂ EtOSiH	7b (84)	>98:2
8	BnO	A	BnMe ₂ SiH	7c (85)	>98:2
9	<i>n</i> -Oct	A	Me ₂ PhSiH	8a (83)	98:2
10	<i>n</i> -Oct	A	Me ₂ EtOSiH	8b (87)	96:4
11	<i>n</i> -Oct	A	BnMe ₂ SiH	8c (91)	93:7
12	Cy	B	BnMe ₂ SiH	1b (94)	98:2
13	Cy	B	Me ₂ EtOSiH	1d (99)	98:2
14	Ph	B	Me ₂ EtOSiH	6b (94)	>98:2
15	Ph	B	BnMe ₂ SiH	6c (92)	>98:2

^aReaction was conducted on a 6.8 mmol scale.

Me₂PhSiH^{12a} and BnMe₂SiH^{12b} were explored due to their previous applications in cross-couplings, and Me₂EtOSiH was also examined, as recent studies have demonstrated that this motif is effective in both fluoride-promoted and fluoride-free cross-couplings.^{12c} The hydrosilylation of cyclohexylallene with Me₂PhSiH afforded product 1c in 90% yield with Me₂PhSiH (Table 2, entry 1) while the reaction with Me₂EtOSiH afforded alkenylsilane 1d in 81% yield with high regioselectivity (96:4) (Table 2, entry 2). Aromatic allene substituents were well-tolerated with high regioselectivity (>98:<2) for each of the three silanes to afford 6a–6c in excellent yields (Table 2, entries 3–5). Similarly, a benzyloxy-substituted allene was also well-tolerated with each of the silanes screened to yield alkenylsilanes 7a–7c in excellent yields and regioselectivities (Table 2, entries 6–8). The ease of scale-up was examined for product 7a, which was afforded in 95% yield in 6.8 mmol scale (Table 2, entry 6). Simple unhindered aliphatics were also well-tolerated with a slight erosion of regioselectivity to form products 8a–8c with excellent yields and regioselectivities (Table 2, entries 9–11).

Improved reaction conditions were optimized to include standard benchtop assembly, without the use of air-free technology such as use of a glovebox (conditions B, Table 2). This protocol employs IPr*OMe·HBF₄ salt 5b, KO-*t*-Bu base,

Pd_2dba_3 precatalyst, and more concentrated reaction conditions (0.5 M in THF). Reactions performed under these conditions were faster and higher yielding than with conditions A (Table 2). For example, four cases examined resulted in higher yields and improved regioselectivities compared with the analogous condition A experiments (Table 2, entries 12–15).

In parallel with our goal to develop a user-friendly hydroarylation protocol, we explored the use of optimum reaction conditions B in tandem with a cross-coupling reaction with electrophilic iodides (Table 3). In this procedure, the hydro-

Table 3. Regioselective Allene Hydroarylations

entry	R ₁	silane	Ar-I	major product (% yield)
1	Cy	Me ₂ EtOSiH	Ph	9 (95)
2	Cy	BnMe ₂ SiH	Ph	9 (85)
3	Cy	Me ₂ EtOSiH	<i>p</i> -NO ₂ Ph	10 (77)
4	Cy	Me ₂ EtOSiH	<i>p</i> -MeCOPh	11 (90)
5	Cy	Me ₂ EtOSiH	<i>p</i> -MeOPh	12 (74)
6	Cy	Me ₂ EtOSiH		13 (81)
7	Cy	Me ₂ EtOSiH		14 (77)
8	<i>n</i> -Oct	Me ₂ EtOSiH	<i>o</i> -tolyl	15 (92)
9	Ph	Me ₂ EtOSiH	Ph	16 (76)
10	Ph	Me ₂ EtOSiH		17 (83)
11	BnO	Me ₂ EtOSiH	Ph	18 (89)
12		Me ₂ EtOSiH		19 (89)
13	<i>n</i> -Oct	Me ₂ EtOSiH	Ph	20 (88) ^a

^aReaction was conducted on a 4.5 mmol scale without the second charge of $\text{Pd}_2(\text{dba})_3$.

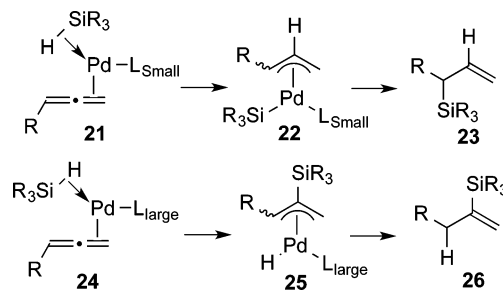
silylation reaction is monitored, and upon complete consumption of allene, tetra-*n*-butylammonium fluoride (TBAF), an iodide electrophile, and an additional 2.5 mol % Pd_2dba_3 precatalyst are added to the reaction mixture. The subsequent cross-coupling reaction occurs within 30 min, affording hydroarylation products **9–18** without detection of alkene isomers (Table 3). Although in very few cases there is slight formation of regioisomeric allylsilanes, these isomers do not afford cross-coupled minor isomers in the hydroarylation manifold likely due to competing protodesilylation.

The scope of the one-pot hydroarylation reaction is general and provides access to a variety of 1,1-disubstituted alkenes. This method tolerates variation in silane structure, as BnMe_2SiH and Me_2EtOSiH were successfully coupled with PhI in high yields of 95% and 85% respectively (Table 3, entries 1 and 2). Aryl iodides with electron-withdrawing substituents (Table 3, entries 3 and 4) and electron-rich groups (Table 3, entry 5) were successfully

coupled in excellent yields. In addition, a variety of heterocyclic-containing iodides functioned under the reaction conditions, as reactions with uracil-containing (Table 3, entry 6) and thienyl-containing (Table 3, entry 7) iodides were tolerated with excellent yields. More hindered substrates such as 2-iodotoluene provided the expected product **15** in excellent yield (Table 3, entry 8). Alterations in allene substitution had insignificant impact on the outcome of the reaction, as aromatic allenes were coupled with PhI (Table 3, entry 9, **16**) and oxacyclic moieties (Table 3, entry 10, **17**) in excellent yields of 76% and 83%. Additionally, a benzyloxy-substituted allene was successfully coupled with PhI in high yield (Table 3, entry 11, **18**). A phthalimido-containing allene was coupled with pyrrole-containing iodide to furnish hydroarylation product **19** in an excellent yield of 89% (Table 3, entry 12). While yields were typically optimum with an additional charge of palladium prior to the cross-coupling step, this was not required in a larger scale illustration using undeca-1,2-diene and phenyl iodide (Table 3, entry 13).

The mechanism and origin of regiochemistry reversal likely derives from changing from a hydrometalation to a silylmatalation pathway (Scheme 2). Our prior studies illustrated that the

Scheme 2. Origin of Regioselectivity Governed by Ligand Size



typical mode of addition in Pd-catalyzed hydrosilylations of allenes favors allylsilane production, consistent with delivery of the metal hydride to the allene central carbon. Typical NHC ligands such as IMes (**3a**) and IPr (**4a**) favor the production of allylsilanes by this route (**21** to **23**). In contrast, less common bulkier ligands such as IPr^{Me} (**4b**) or IPr^*OMe (**5b**) more effectively introduce steric repulsion between the organosilane and ligand and reverse the pathway to favor alkenylsilane production through silyl addition to the central allene carbon (**24** to **26**). Significant insights in the mechanism and regiochemistry of related catalyzed additions to allenes come from the work of Morken and Sugimoto involving additions of diboranes or silylboranes.¹³ A recent computational study of allene hydrosilylations proposed that cleavage of the Si–H bond and addition to the allene central carbon proceed in a single step.¹⁴

In summary, careful selection of NHC ligand structure allows excellent regiocontrol in allene hydrosilylations with palladium catalysis, favoring either allylsilane or alkenylsilane products. While common NHC ligands favor allylsilane production, a variety of alkenylsilanes may be produced with the extremely bulky IPr^*OMe ligand. This methodology utilizes standard benchtop assembly and achieves exceptional regiocontrol without the use of directing groups or electronic substrate biases. Highlights of this approach have been applied to the development of a one-pot hydroarylation reaction that combines the regioselective hydrosilylation strategy with a Pd(0)-catalyzed cross-coupling reaction of aryl and heterocyclic iodides. This

hydroarylation method provides streamlined access to branched isomers in excellent yields without the requirement of isolation of alkenylsilane intermediates.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and copies of NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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