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Regioselective Allene Hydrosilylation Catalyzed by *N*-Heterocyclic Carbene Complexes of Nickel and Palladium

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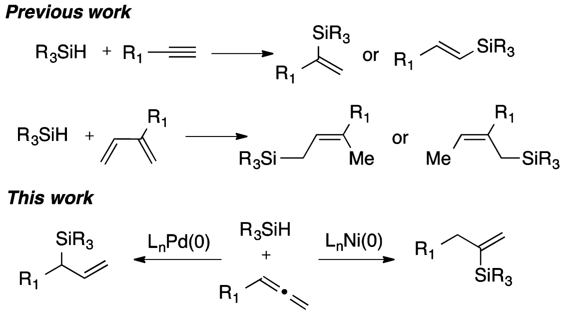
Supporting Information

ABSTRACT: Regioselective methods for allene hydrosilylation have been developed, with regioselectivity being governed primarily by the choice of metal. Alkenylsilanes are produced via nickel catalysis with larger *N*-heterocyclic carbene (NHC) ligands, and allylsilanes are produced via palladium catalysis with smaller NHC ligands. These complementary methods allow either regioisomeric product to be obtained with exceptional regiocontrol.

Alkenylsilanes and allylsilanes are useful reagent classes that are employed in numerous synthetic transformations.[1] For example, the Hiyama cross-coupling[2] and Sakurai-type allylation and crotylation reactions[3] are widely used methods for C−C bond formation. Currently, the most direct and atom-economical routes to vinyl- and allylsilanes proceed via metal-catalyzed hydrosilylations of π-components (Scheme 1). The hydrosilylation of alkynes to afford alkenylsilanes[4] and the hydrosilylation of 1,3-dienes to afford allylsilanes[5] are versatile methods that have been widely employed. In both instances, control of regiochemistry is required with unsymmetrical substrates, and even the most efficient hydrosilylation procedures are often plagued by the lack of complete regioselectivity for a variety of substrates without directing group effects. Compounding these challenges is the difficulty typically seen in the separation of regioisomeric allyl- or vinylsilanes produced by these methods.

In contrast to the significant developments that have been reported in hydrosilylations of alkynes and 1,3-dienes, the hydrosilylation of allenes has rarely been examined.[6] The hydrometalation of allenes presents considerable challenges in selectivity since 1,2- or 2,1-addition to either of the two contiguous π-systems can occur, potentially providing two regioisomeric allylsilanes and two regioisomeric vinylsilanes, in

Scheme 1



Scheme 2

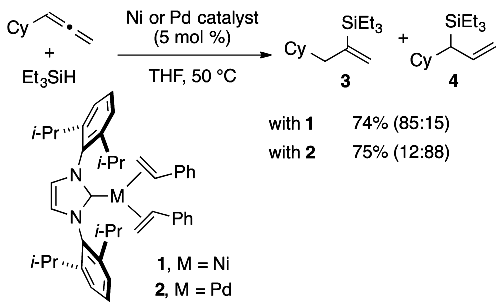
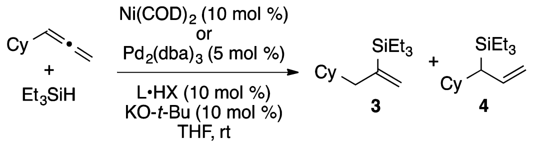
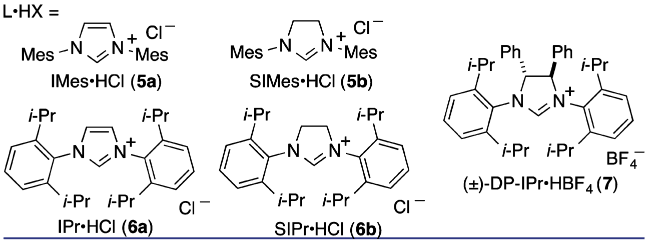


Table 1



entry	precatalyst	L·HX	% yield	regiosel. (**3**:**4**)
1	$Ni(COD)_2$	**5a**	22	33:67
2	$Ni(COD)_2$	**5b**	15	40:60
3	$Ni(COD)_2$	**6a**	58	85:15
4	$Ni(COD)_2$	**6b**	47	81:19
5	$Ni(COD)_2$	**7**	84	>98:<2
6	$Pd_2(dba)_3$	**7**	trace	not determined
7	$Pd_2(dba)_3$	**6b**	56	14:86
8	$Pd_2(dba)_3$	**6a**	75	12:88
9	$Pd_2(dba)_3$	**5b**	74	2:98
10	$Pd_2(dba)_3$	**5a**	80	<2:>98

L•HX =



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Scheme 3

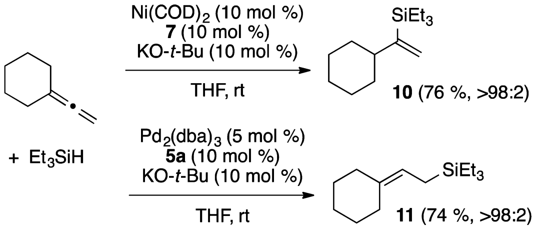
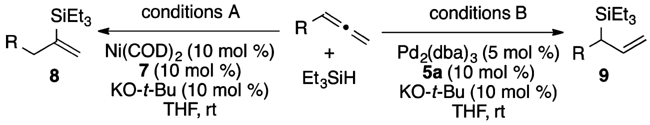
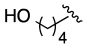
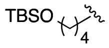
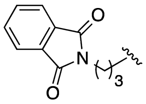


Table 2



entry	R	conditions[a]	product (% yield)	regiosel. (8:9)
1	Cy	A	**3** (84)	>98:2
2		B	**4** (80)	<2:98
3	*n*-Oct	A	**8a** (80)	>98:2
4		B	**9a** (98)	<2:98
5	Ph	A	**8b** (78)	>98:2
6		B	**9b** (94)	<2:98
7	 HO 4	A	**8c** (62)	>98:2
8		B	**9c** (88)	<2:98
9	 TBSO 4	A	**8d** (73)	>98:2
10		B	**9d** (97)	<2:98
11	 O N O 3	A	**8e** (78)	>98:2
12		B	**9e** (97)	<2:98
13	Cy	B[b]	**4** (98)	<2:98
14	Cy	B[c]	**4** (74)	4:96
15	Cy	B[d]	**4** (72)	<2:98

[a] Unless otherwise noted, reactions were conducted on a 0.3 mmol scale. [b] Conducted on 6.0 mmol scale. [c] Conducted with benchtop assembly of the catalyst and ligand followed by three vacuum/purge cycles before allene and silane introduction. [d] Conducted at 2.5 mol % loading of Pd$_2$(dba)$_3$.

some cases as mixtures of alkene stereoisomers. The hydroboration of allenes has been widely developed, but these processes are typically uncatalyzed, thus providing a single allylborane product governed by substrate steric and electronic characteristics.[7,8] Significant advances have appeared in the regioselective bis-metalation of allenes, through catalytic reactions such as diboration[9] and silaboration,[10] but regiodivergent processes in simpler hydrometalations of allenes are lacking. Given the synthetic utility of allyl- and vinylsilanes and the potential to provide regiocontrolled access to both structure classes from a common allene substrate, we report herein our efforts to develop regioselective, catalyst-controlled methods for the hydrosilylation of allenes.

As part of our laboratory's broader interest in the development of regioselective catalytic processes,[11] we initially hoped to develop ligand-controlled regioselectivity reversal in the nickel-catalyzed hydrosilylation of allenes. However, upon screening a broad range of nickel catalysts modified with *N*-heterocyclic carbene or phosphine ligands, combinations that allowed high-yielding and highly regioselective access to both alkenylsilane and allylsilane products were not identified. However, in the course of these exploratory studies, we were attracted to the recent disclosures of well-defined *N*-heterocyclic carbene (NHC) complexes of palladium and nickel.[12] To our surprise, simple modification of the metal, while leaving the ligand and reaction conditions unchanged, provided an encouraging lead toward identifying routes to both product regioisomers. As illustrated in the hydrosilylation of cyclohexylallene with triethylsilane, the use of nickel complex **1** provided the vinylsilane **3** with 85:15 regioselectivity, whereas exactly the same procedure and same ligand, but employing the palladium complex **2** instead, provided the allylsilane **4** with 88:12 regioselectivity (Scheme 2). Reactions involving the presynthesized nickel complex **1** required an elevated temperature, likely due to the need to dissociate styrene to provide the active catalyst form, whereas palladium complex **2** was catalytically active at rt or elevated temperature. This unusual example of regiochemistry reversal with a common ligand scaffold and within a single metal triad presented an unexpected and effective strategy for accessing both allylsilanes and alkenylsilanes from a common allene precursor.

To further boost the regioselectivity of these complementary processes, we examined ligand variation for both nickel- and palladium-catalyzed hydrosilylations. In comparing catalytic

Scheme 4

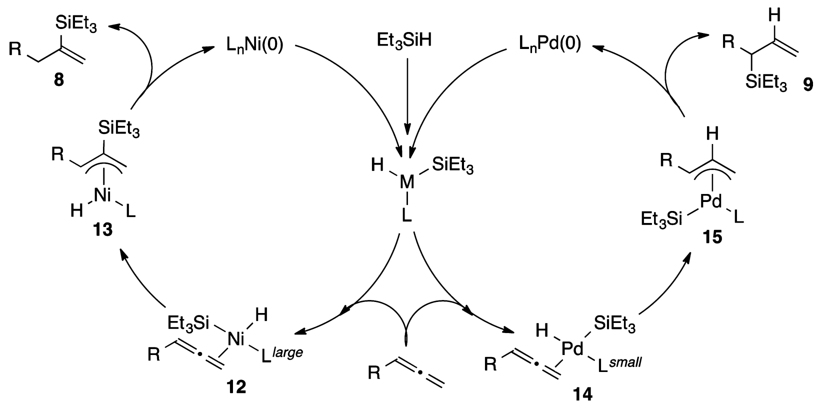
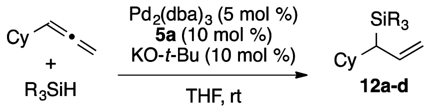


Table 3



entry	silane	product (% yield)	regiosel.
1	$HSiMe_2Ph$	**12a** (91)	>98:2
2	$HSiMe_2Bn$	**12b** (93)	>98:2
3	$HSiMe(OSiMe_3)_2$	**12c** (82)	>98:2
4	$H_2Si(t\text{-}Bu)_2$	**12d** (75)	>98:2

reactions of **1** and **2** with the corresponding complexes prepared *in situ* from $Ni(COD)_2$ or $Pd_2(dba)_3$, the chemical yields are similar and regioselectivities are identical in comparing the catalysts presynthesized or prepared *in situ* (comparing Scheme 2 to Table 1, entries 3 and 8). The use of the presynthesized complexes comes with the advantage of a higher catalyst turnover and ease of accurate weighing on small scale that becomes difficult for the *in situ* protocol. However, to facilitate more rapid screening of a variety of ligands, catalysts for the optimization studies were prepared *in situ* by treatment of $Ni(COD)_2$ or $Pd_2(dba)_3$ with the HCl or HBF_4 salt of the desired NHC ligands.

From the ligand variation studies, an interesting trend emerged that regioselectivities for alkenylsilane products using nickel were enhanced with larger ligands, whereas regioselectivities for allylsilanes using palladium were enhanced with smaller ligands. To illustrate this trend using $Ni(COD)_2$ as the precatalyst, IMes and SIMes slightly favored allylsilane production (Table 1, entries 1 and 2), IPr and SIPr favored alkenylsilane production with good selectivity (Table 1, entries 3 and 4), and the very bulky ligand DP-IPr afforded the alkenylsilane in 84% isolated yield with >98:2 regioselectivity (Table 1, entry 5). In comparison, using $Pd_2(dba)_3$ as the precatalyst, the use of DP-IPr afforded a low-yielding mixture of regioisomers (Table 1, entry 6), IPr and SIPr favored allylsilane production with good selectivity (Table 1, entries 7 and 8), and IMes and SIMes provided exceptional regioselectivities (Table 1, entries 9 and 10), with IMes providing an 80% isolated yield of the allylsilane with >98:2 regioselectivity.

The above guidelines for the *in situ* generated Ni(0) and Pd(0) hydrosilylation catalysts were utilized in the reactions for a variety of allene substrate classes (Table 2). In addition to the use of cyclohexyl allene (entries 1 and 2), allenes containing less hindered aliphatic groups (Table 2, entries 3 and 4), aromatic groups (Table 2, entries 5 and 6), unprotected hydroxyls (Table 2, entries 7 and 8), and silyloxy groups (Table 2, entries 9 and 10) were successfully hydrosilylated using either $Ni(COD)_2$ with ligand **7** (DP-IPr; conditions A) or $Pd_2(dba)_3$ with ligand **5a** (IMes; conditions B) with consistently excellent regioselectivities (>98:2) and in high chemical yields. In addition, an allene containing a phthalimido moiety underwent smooth hydrosilylation to afford either regioisomeric product (Table 2, entries 11 and 12). To further explore the scaleup and utility in reactions not using glovebox manipulations, the palladium-catalyzed procedure with cyclohexyl allene was optimized on a 6 mmol scale, which proceeded in 98% isolated yield in >98:2 regioselectivity (Table 2, entry 13). Additionally, a procedure conducted with a standard benchtop assembly purged with a nitrogen line proceeds in 74% isolated yield with slightly eroded (96:4) regioselectivity (Table 2, entry 14). Finally, an experiment with a reduced catalyst loading (2.5 mol % $Pd_2(dba)_3$) proceeded in 72% isolated yield (Table 2, entry 15), whereas attempts to lower the catalyst loading further resulted in more significant drops in chemical yield.

In order to evaluate the effects of introducing allene 1,1-disubstitution, we subjected vinylidene cyclohexane to both nickel- and palladium-catalyzed reaction conditions (Scheme 3). The nickel-catalyzed reaction resulted in an outcome consistent with the previous observations for monosubstituted allenes, where the silyl group is installed at the central allenic carbon to afford vinylsilane **10**. Reactions with palladium, however, afforded a new observed allylsilane isomer **11**, with the C−Si bond forming at the least substituted allenic carbon. This observation offers a new entry to a useful allylsilane traditionally accessed via the hydrosilylation of 1,3-dienes.

The palladium-based procedure tolerates variation of the silane structure with minimal change in regioselectivity and yield. For example, additions to cyclohexyl allene cleanly proceed with a range of synthetically versatile silane structures (Table 3).[13] Alternatively, the nickel-based procedure is currently more limited with silane variation leading to a drop in yield and erosion of regioselectivy.

While the origin of regiocontrol is at present uncertain, we propose that a likely mechanism involves a change from a silylmetalation pathway with nickel to a hydrometalation pathway with palladium (Scheme 4). Migratory insertions to allenes typically favor addition to the central allene carbon with the formation of a metal π-allyl complex.[9g,10g] Through this common mechanistic feature, silylmetalation of nickel allene complex **12** to generate π-allyl intermediate **13**, followed by C−H reductive elimination, would afford vinylsilane product **8**. Alternatively, hydrometalation of palladium allene complex **14** to generate π-allyl intermediate **15**, followed by C−Si reductive elimination, would afford allylsilane product **9**. By utilizing a large ligand with nickel, disposition of the silyl group trans to the ligand in intermediate **12** reinforces the preference for silylmetalation. However, by utilizing a small ligand with palladium, disposition of the silyl group cis to the ligand in **14** reinforces the preference for hydrometalation. Detailed studies from Morken and Suginome in diborations and silaborations of allenes provide significant insight into the factors that control regiochemistry in these related processes, and the mechanistic model described in Scheme 4 draws from the insights of those studies.[9g,10g] Future work will be devoted to evaluating the intriguing mechanistic basis of these regiodivergent hydrosilylation processes.

In summary, the complementary use of metals (Ni vs Pd) results in regiochemical reversals in allene hydrosilylations. Alterations in NHC ligand structure can further improve the regioselectivities to provide regiodivergent access to a wide range of alkenylsilanes or allylsilanes in high yields and with exceptional regiocontrol. The above study demonstrates the special role that metal identity can play in governing regioselective catalytic reactions. Future studies will explore these effects in other classes of catalytic reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and analytical data. 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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