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

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University of Michigan

Montgomery, J. *et al.*
J. Am. Chem. Soc. **2013**, *135*, 15282.

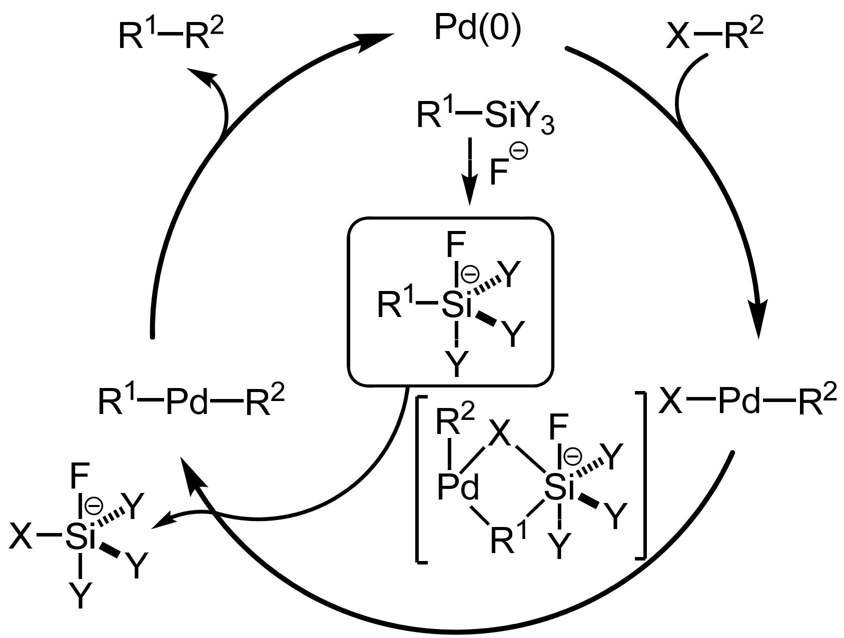
Contents

Introduction

Hiyama Cross-coupling

$$R^1{-}SiY_3 \;+\; X{-}R^2 \xrightarrow{\text{Pd cat., } F^{\ominus}} R^1{-}R^2 \;+\; Y_3Si{-}X$$

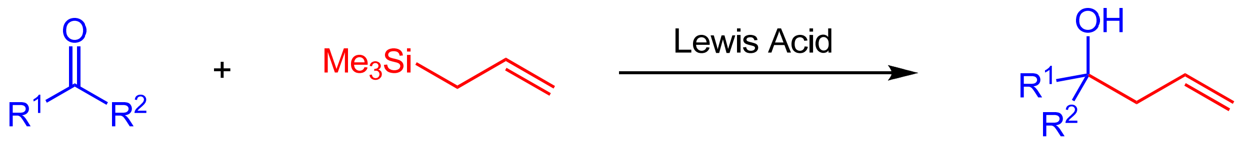
R^1 = Alkenyl, Allyl, Aryl; Y = F, Cl, Alkyl
X = Cl, Br, I, OTf; R^2 = Aryl, Alkyl, Alkenyl, Alkynyl

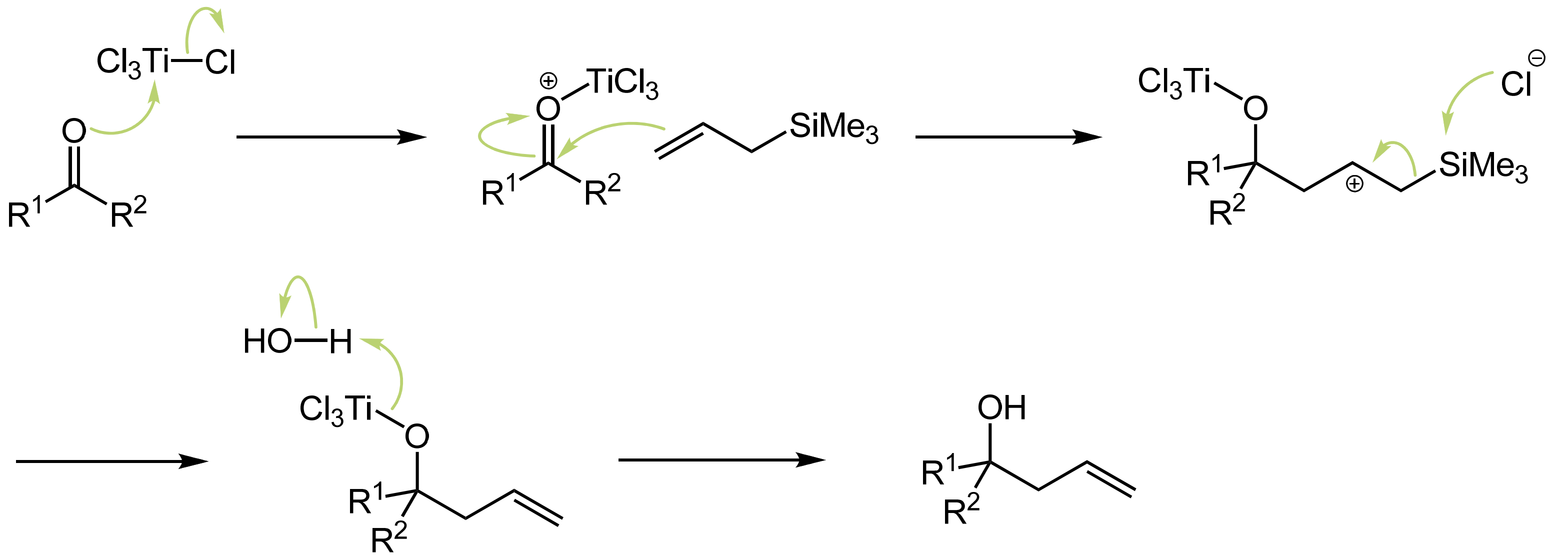


Hiyama, T. *et al. Chem. Soc. Rev.* **2011**, *40*, 4893.

Introduction

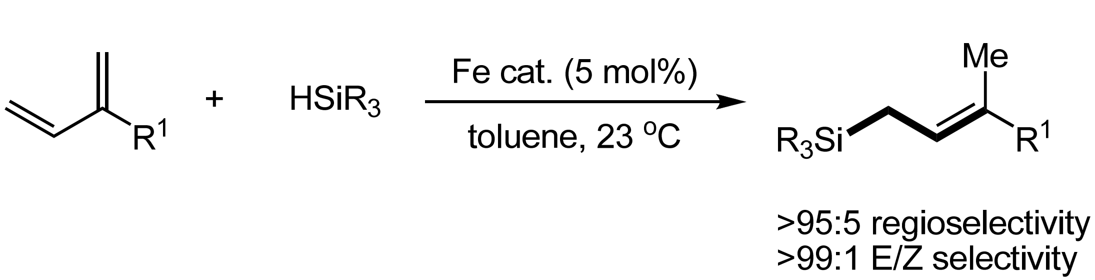
Hosomi-Sakurai Reaction

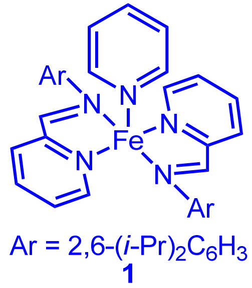




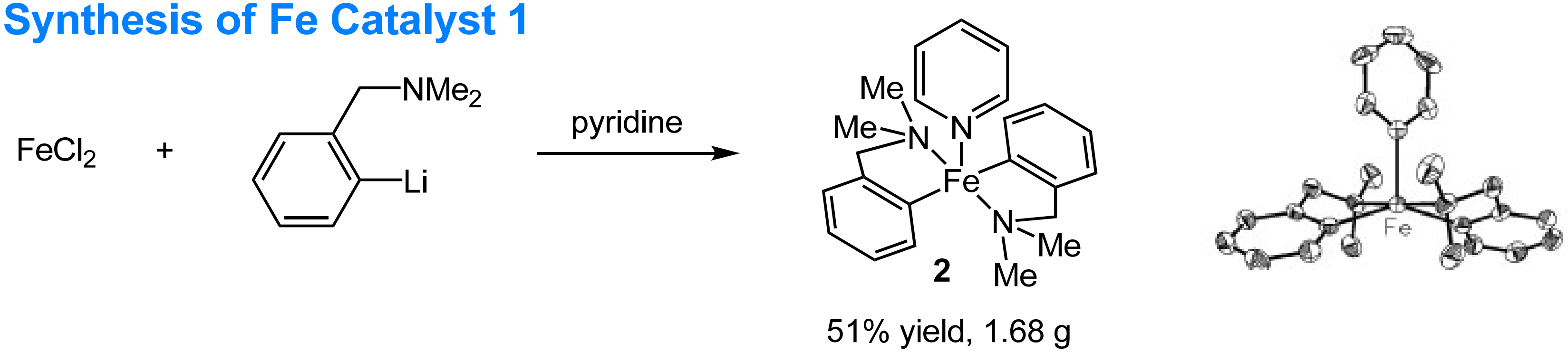
Hosomi, A. *et al. Chem. Lett.* **1976**, 941.

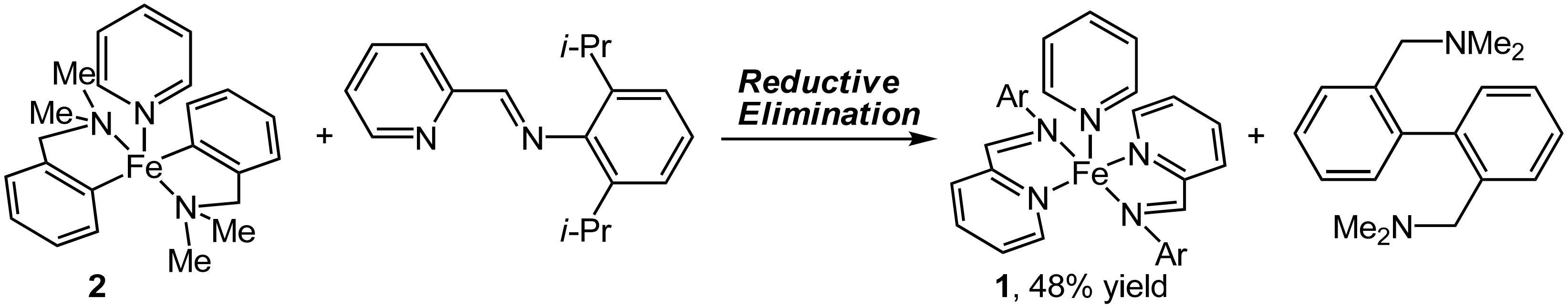
Diene Hydrosilylation





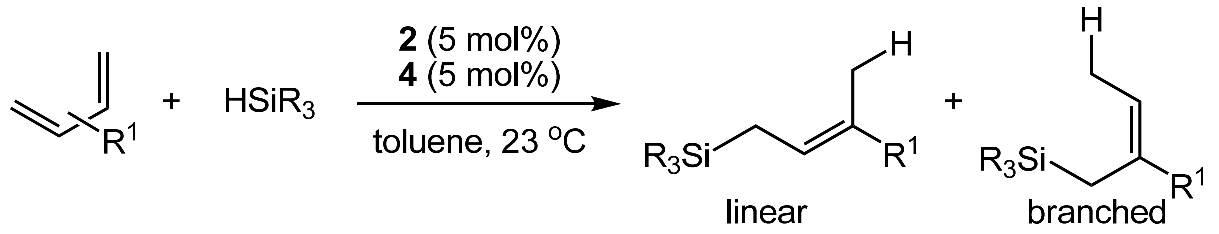
Synthesis of Fe Catalyst 1

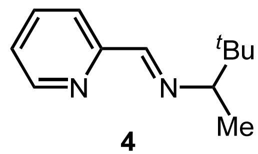




Ritter, T. *et al. J. Am. Chem. Soc.* **2010**, *132*, 13214.

Diene Hydrosilylation





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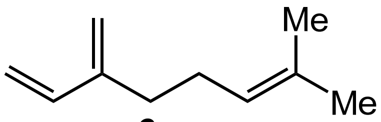

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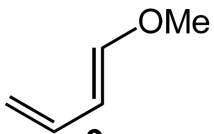

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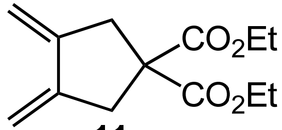

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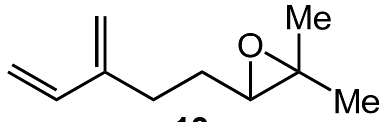

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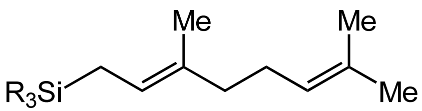
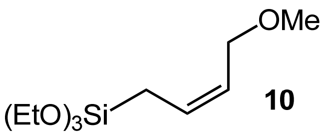
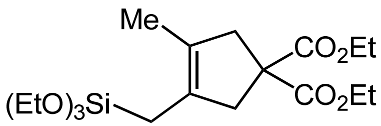
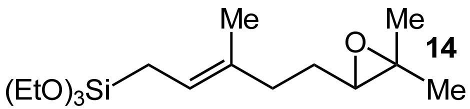
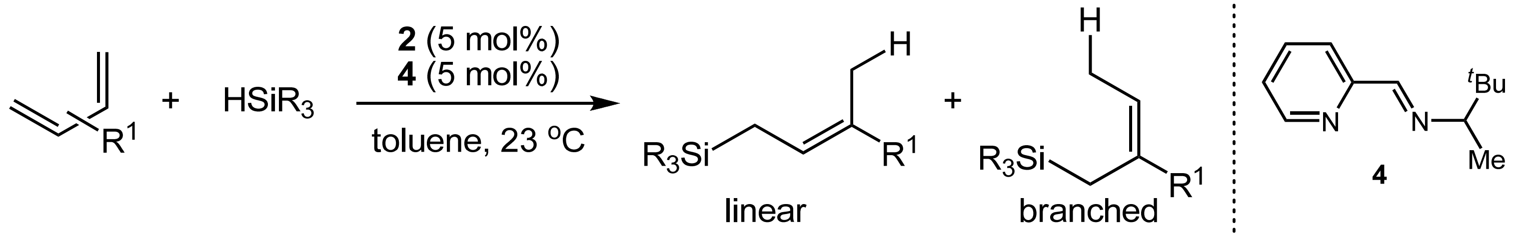
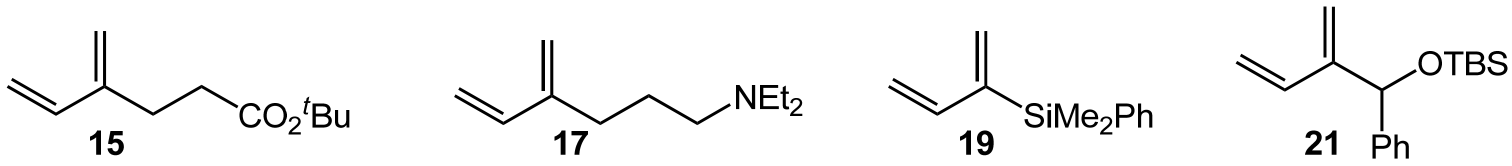
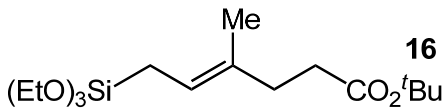
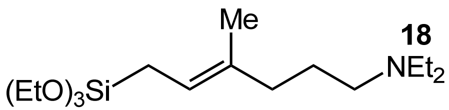
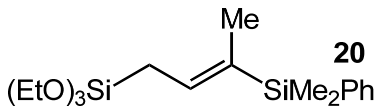
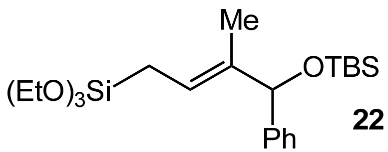
Diene	Linear Product	Linear:Branched	E:Z	Yield (%)
6	 R_3 = $(OEt)_3$ (**7**); $Me(OEt)_2$ (**8**)	95: 5 (**7**)	>99:1	91
		93: 7 (**8**)	>99:1	91
9	 **10**	>99:1	<1:99	89
11	 **12**	--	>99:1	66
13	 **14**	97:3	>99:1	86

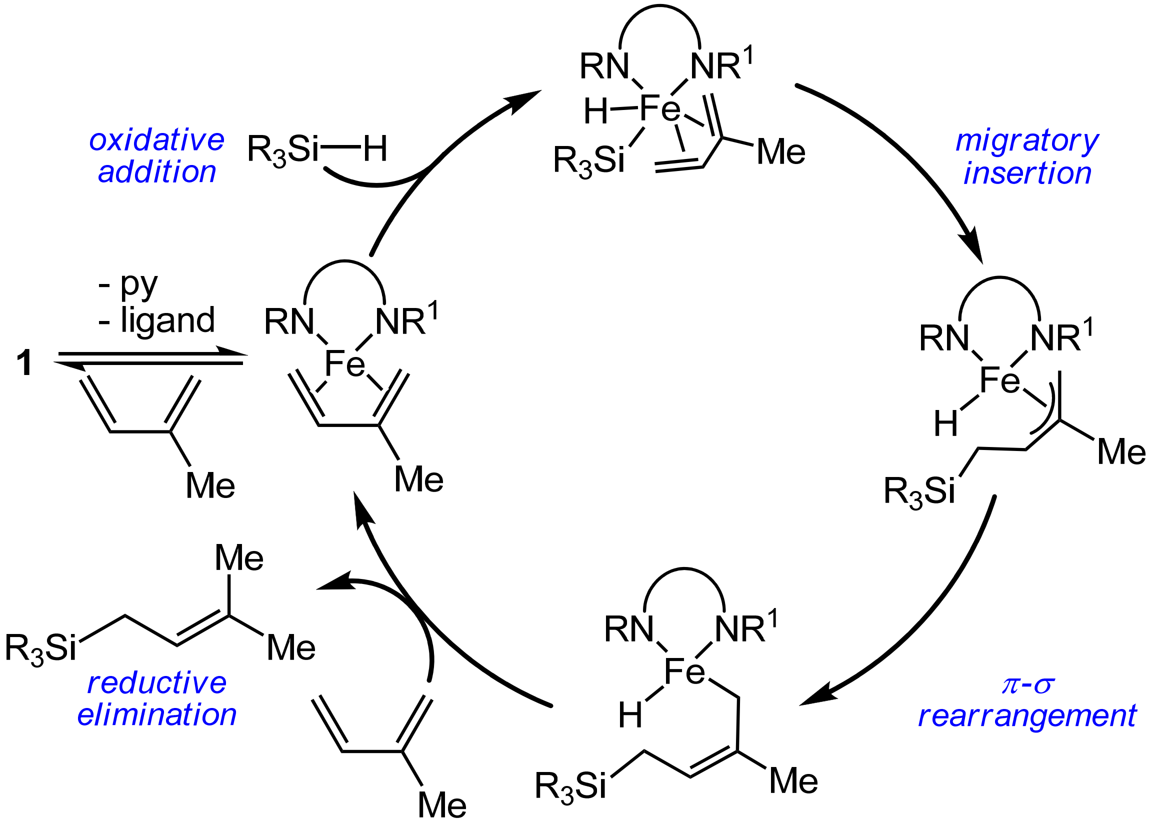
Diene Hydrosilylation



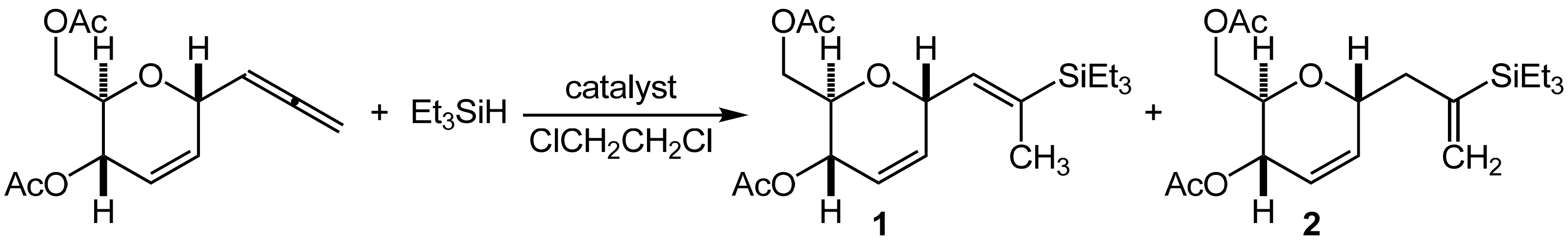


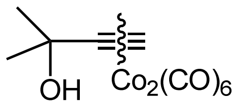
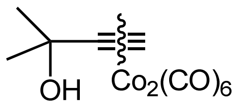
Diene	Linear Product	Linear:Branched	E:Z	Yield (%)
15		94:6	>99:1	76
17		94:6	>99:1	83
19		99:1	>99:1	89
21		99:1	>99:1	80

Diene Hydrosilylation



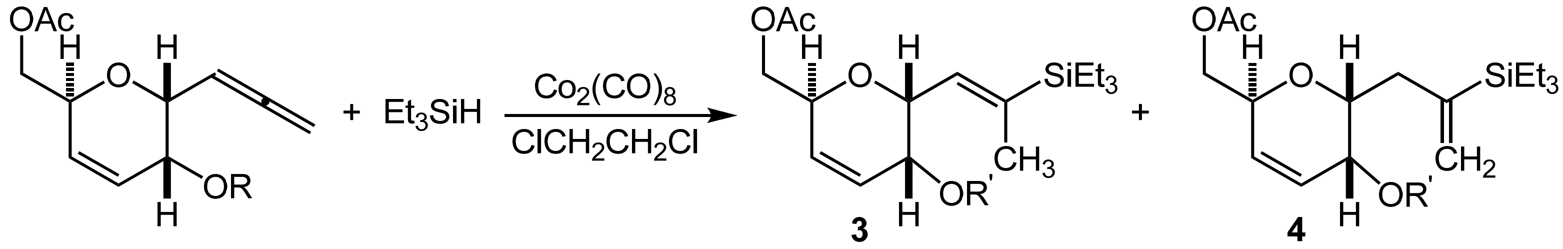
Allene Hydrosilylation



Entry	Catalyst	Mol %	Time (min)	Tem (ºC)	Yield (%)	Ratio **1**:**2**
1		3	300	60	0	-
2		100	240	60	60	2:1
3	$Co_2(CO)_8$	100	60	60	72	2:1
4	$Co_2(CO)_8$	150	60	60	69	2:1
5	**$Co_2(CO)_8$**	**250**	**100**	**25**	**82**	**2:1**

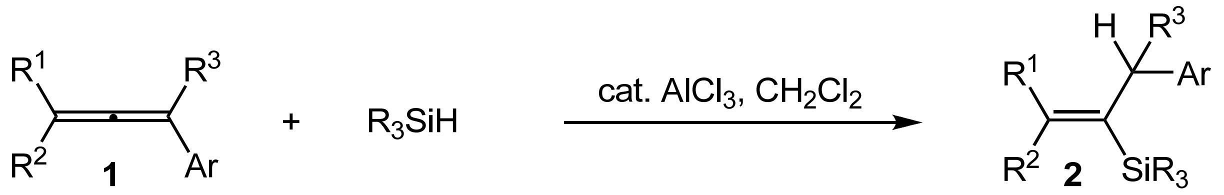
Isobe, M. *et al. Tetrahedron* **2001**, *57*, 10241.

Allene Hydrosilylation



Entry	R	R'	Yield (%)	Ratio **3**:**4**
1	H	$SiEt_3$	51	3:1
2	Ac	Ac	50	4:1
3	**Piv**	**Piv**	**67**	**10:1**

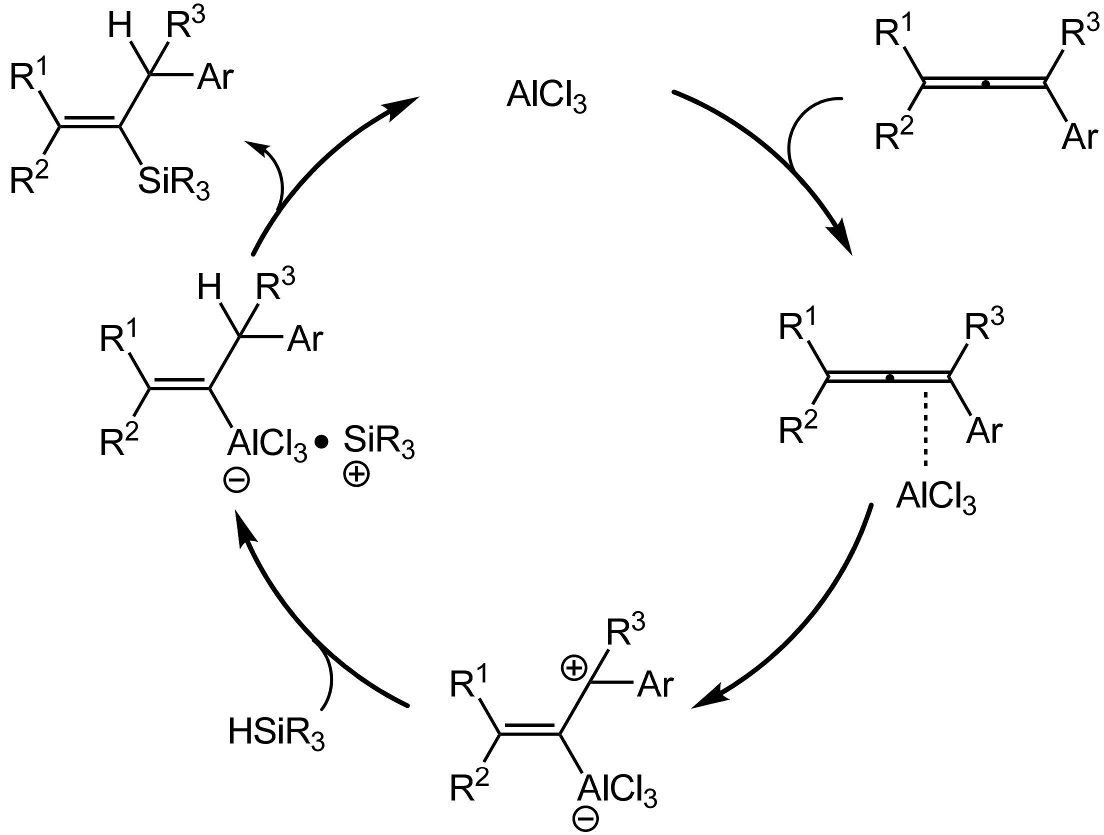
Allene Hydrosilylation



Entry	1				HSiR$_3$	Product (yield %)
	R^1	R^2	R^3	Ar		
1	H	H	H	C_6H_5	HSiMe$_2$Et	**2a** (76)
2	H	H	H	*p*-Me-C_6H_4	HSiMe$_2$Et	**2b** (78)
3	H	H	H	*p*-F-C_6H_4	HSiMe$_2$Et	**2c** (96)
4	H	H	H	*p*-CF_3-C_6H_4	HSiMe$_2$Et	- (0)
5	Me	H	H	*p*-Me-C_6H_4	HSiMe$_3$	**2e** (60)
6	Me	H	H	C_6H_5	HSiMe$_3$	**2f** (66)
7	Me	H	H	*p*-F-C_6H_4	HSiMe$_3$	**2g** (72)
8	Me	Me	H	*p*-F-C_6H_4	HSiMe$_3$	**2h** (58)
9	H	H	Me	*p*-F-C_6H_4	HSiMe$_3$	**2i** (46)

Yamamoto, Y. *et al. J. Org. Chem.* **1999**, *64*, 2494.

Allene Hydrosilylation



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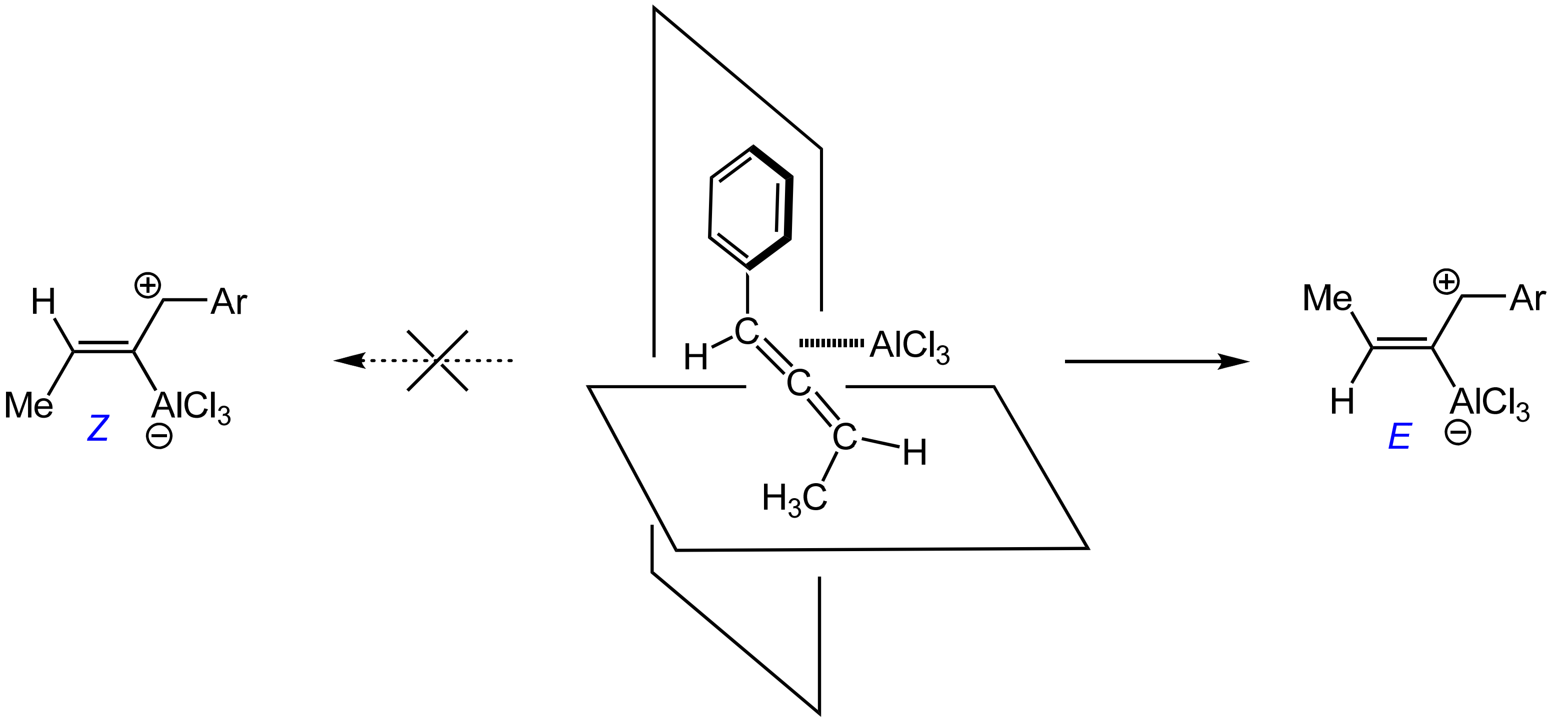

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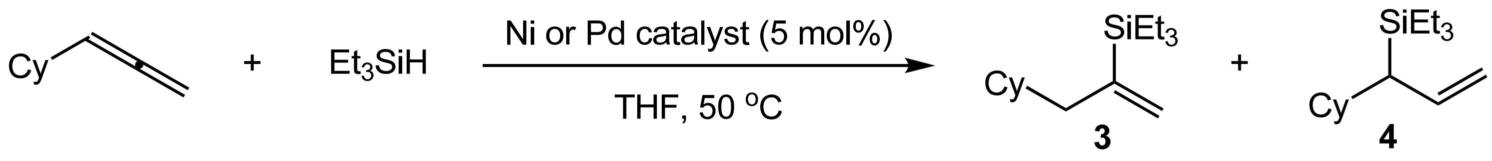
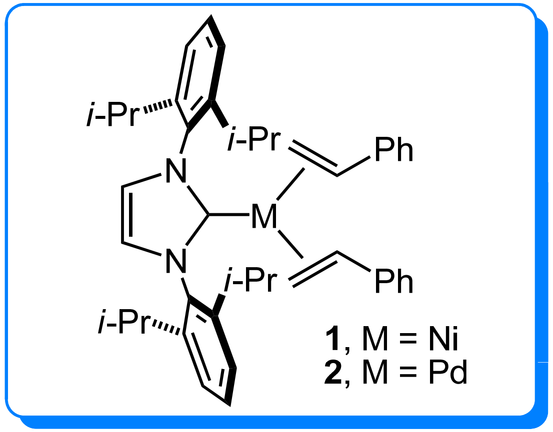
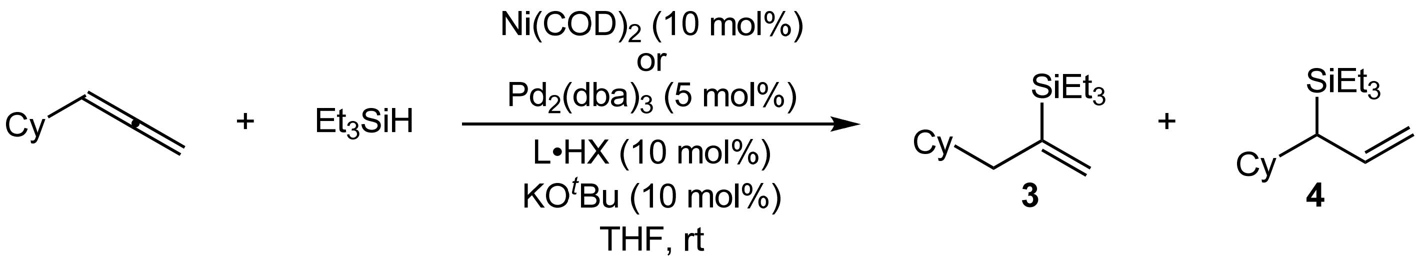


	3:4
with **1**	74% (85:15)
with **2**	75% (12:88)



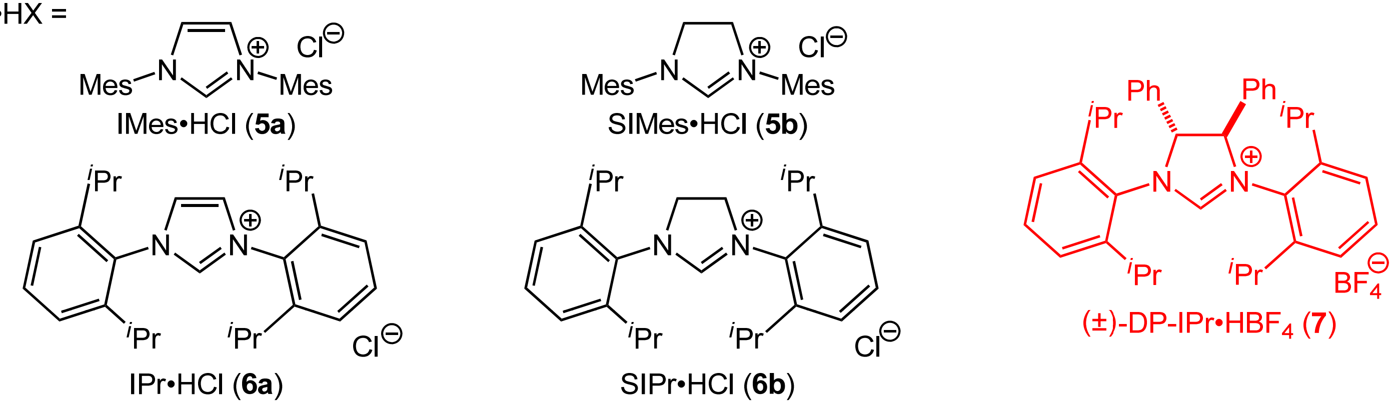
Montgomery, J. *et al. J. Am. Chem. Soc*. **2013**, *135*, 15282.

Allene Hydrosilylation

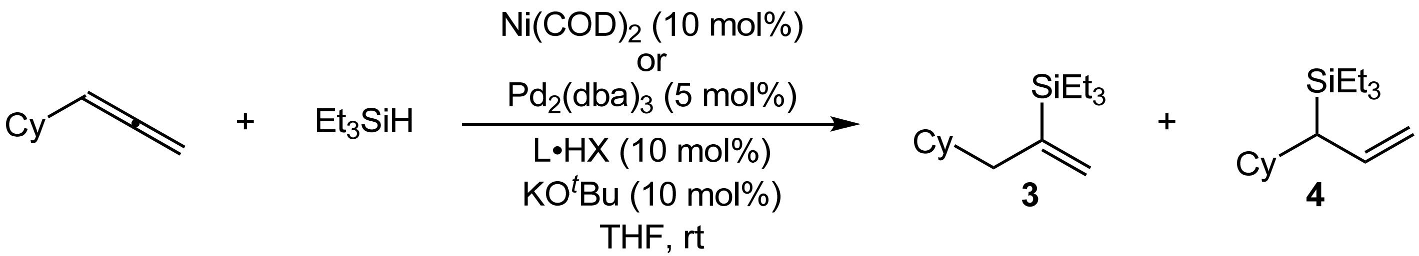


Entry	Precatalyst	L·HX	Yield (%)	Regiosel. (**3**:**4**)
1	$Ni(COD)_2$	**5a**	22	33:67
2	$Ni(COD)_2$	**5b**	15	40:60
3	$Ni(COD)_2$	**6a**	58	85:15
4	$Ni(COD)_2$	**6b**	47	81:19
5	$Ni(COD)_2$	**7**	84	>98:2

L•HX =

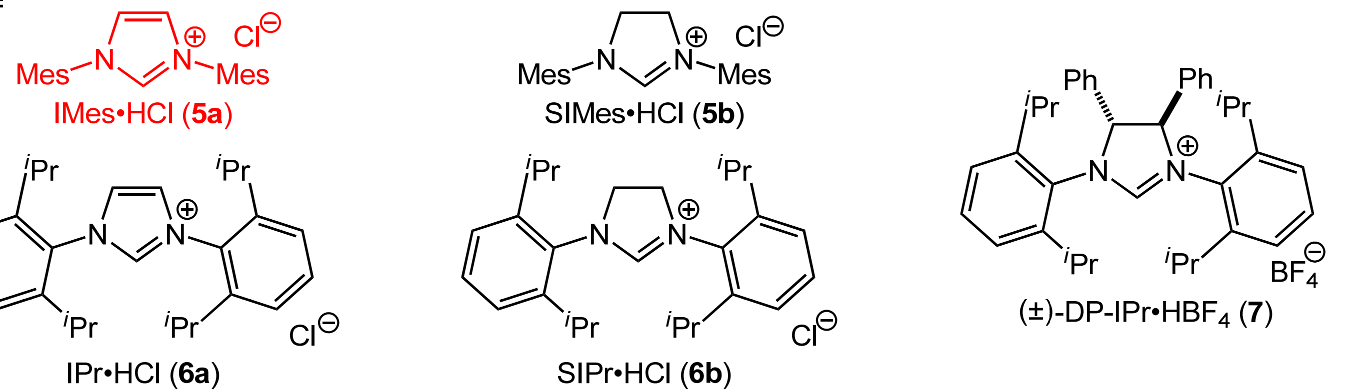


Allene Hydrosilylation

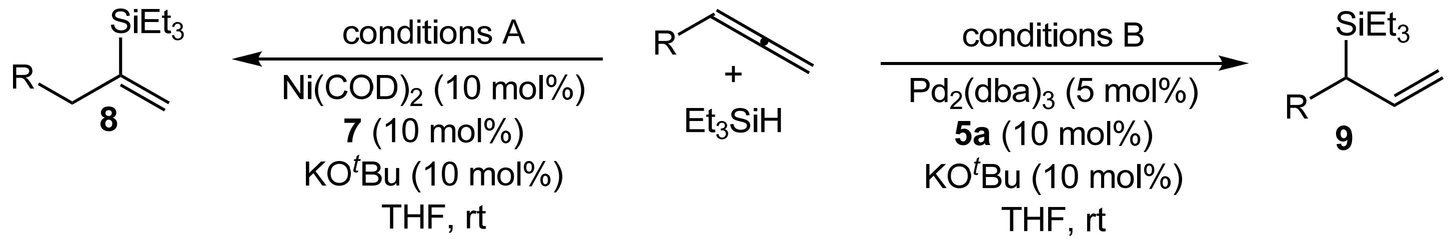


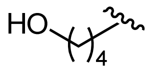
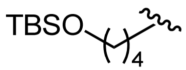
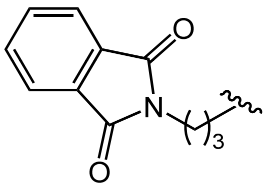
Entry	Precatalyst	L·HX	Yield (%)	Regiosel. (**3**:**4**)
6	$Pd_2(dba)_3$	**5a**	80	<2:98
7	$Pd_2(dba)_3$	**5b**	74	2:98
8	$Pd_2(dba)_3$	**6a**	75	12:88
9	$Pd_2(dba)_3$	**6b**	56	14:86
10	$Pd_2(dba)_3$	**7**	trace	not determined

L•HX =

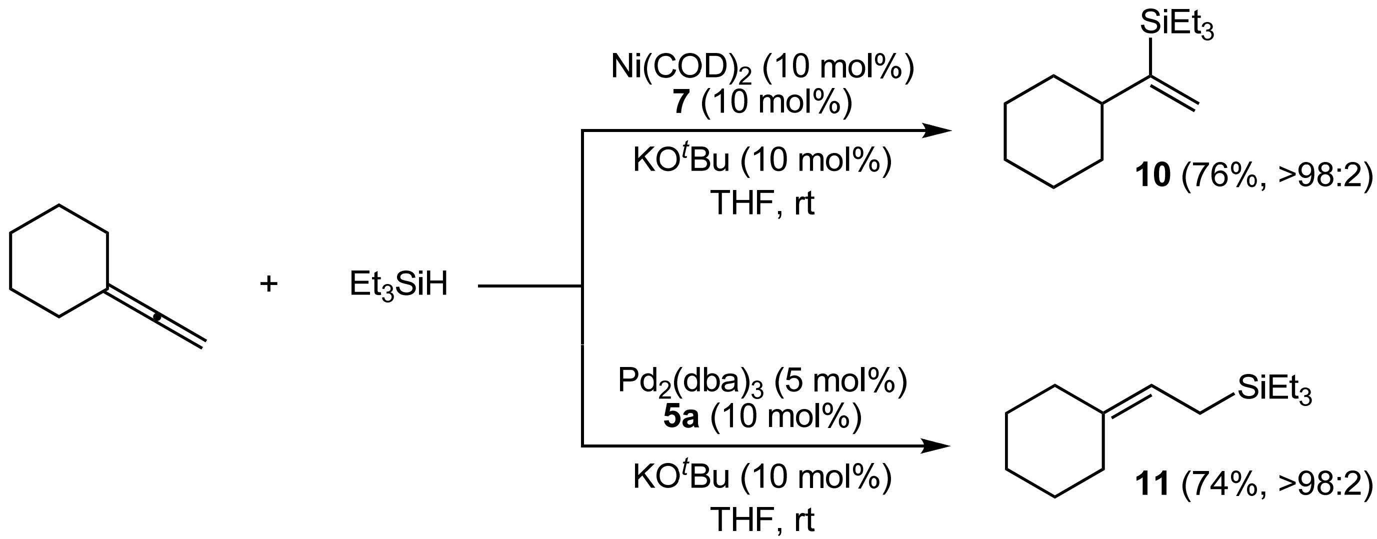


Allene Hydrosilylation

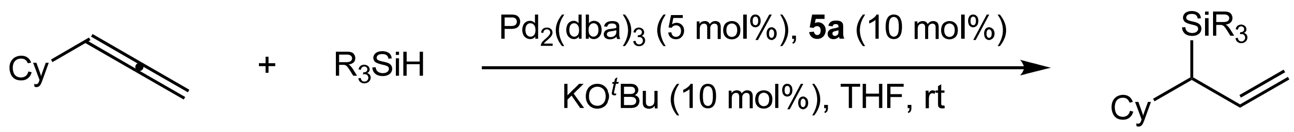


Entry	R	Conditions	Product (yield %)	Regiosel. (**3**:**4**)
1	Cy	A	**3** (84)	>98:2
2		B	**4** (80)	<2:98
3	^{n}Oct	A	**8a** (80)	>98:2
4		B	**9a** (98)	<2:98
5	Ph	A	**8b** (78)	>98:2
6		B	**9b** (94)	<2:98
7		A	**8c** (62)	>98:2
8		B	**9c** (88)	<2:98
9		A	**8d** (73)	>98:2
10		B	**9d** (97)	<2:98
11		A	**8e** (78)	>98:2
12		B	**9e** (97)	<2:98

Allene Hydrosilylation



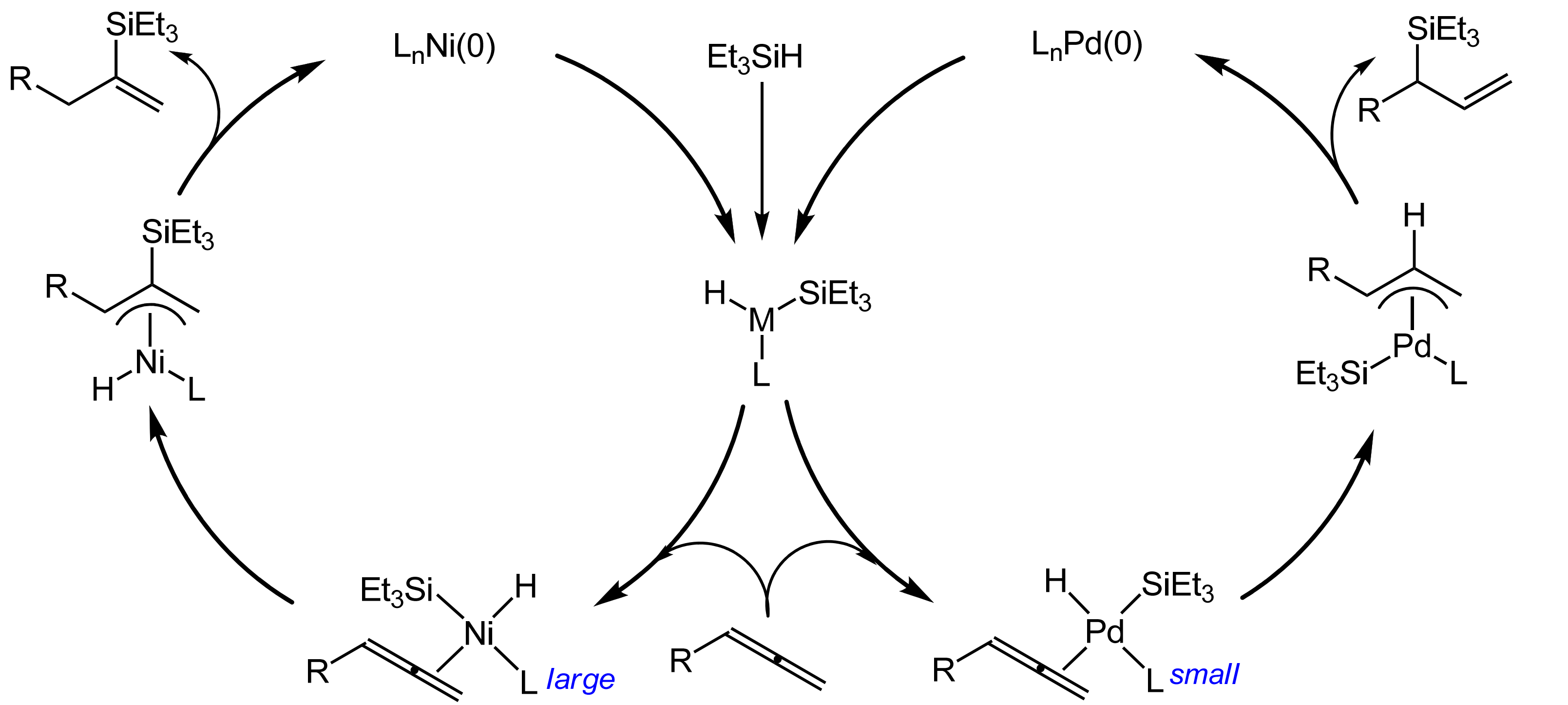
Allene Hydrosilylation



12a-d

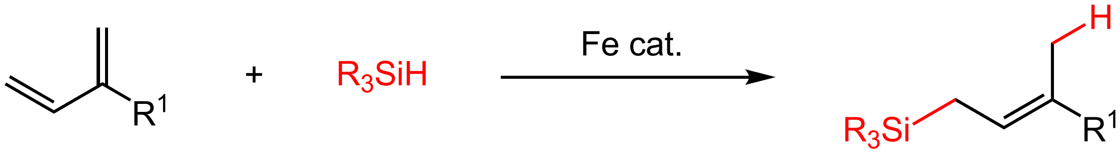
Entry	Silane	Product (yield %)	Regiosel.
1	$HSiMe_2Ph$	**12a** (91)	>98:2
2	$HSiMe_2Bn$	**12b** (93)	>98:2
3	$HSiMe(OSiMe_3)_2$	**12c** (82)	>98:2
4	$H_2Si(^tBu)_2$	**12d** (75)	>98:2

Allene Hydrosilylation



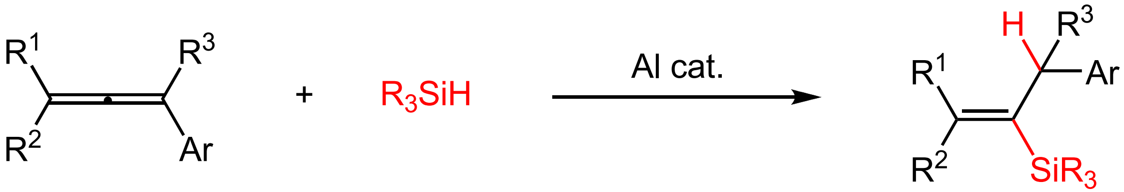
Summary

Diene Hydrosilylation

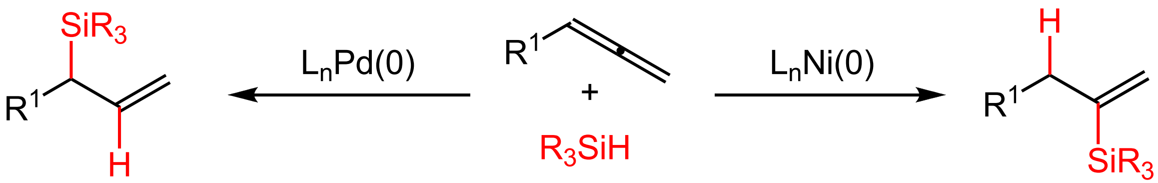


Ritter

Allene Hydrosilylation



Yamamoto



Montgomery

Alkenylsilanes and allylsilanes are useful reagent classes that are employed in numerous synthetic transformations. For example, the Hiyama cross-coupling and Sakurai-type allylation and crotylation reactions 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. The hydrosilylation of alkynes to afford alkenylsilanes and the hydrosilylation of 1,3-dienes to afford allylsilanes 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 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.