C–H Functionalization

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Iridium-Catalyzed, Diastereoselective Dehydrogenative Silylation of Terminal Alkenes with $(TMSO)_2MeSiH$**

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Vinylsilanes and vinylboranes are versatile synthetic intermediates that can be constructed through catalytic functionalization of C–H bonds with boron and silicon reagents.[1,2] The majority of borylations of alkenes to form vinylboronates as the major product require cyclic alkenes, vinylarenes, or specific substituted alkenes (vinyl ethers and allyltrimethylsilane);[3] therefore methods for the alternative dehydrogenative silylation of terminal alkenyl C–H bonds are desirable. Current methods for the preparation of vinylsilanes include the silyl-Heck reaction,[4] alkyne hydrosilylation,[5] direct dehydrogenative silylation of alkenes,[6] and manipulation of compounds with existing C–Si bonds;[7] each of these methods suffers from a number of drawbacks, including the requirement of an excess of the alkene, limitation to vinylarenes, or the production of the more readily-accessible *E* vinylsilane as the major product.

Recently, Lu and Falck reported the *Z*-selective silylation of terminal alkenes with Et_3SiH in the presence of the iridium/di-*tert*-butylbipyridine catalyst developed by our group for the borylation of arenes.[8] However, the lack of electronegative atoms attached to the silicon atom prevents the products from being substrates for the Tamao oxidation or Hiyama–Denmark coupling reactions.[9] Unfortunately, silylation reactions often occur in lower yields with silanes, such as alkoxysilanes, bearing electronegative atoms than with trialkylsilanes. Because the alkoxysilyl group is electron withdrawing, the hydride is less hydridic.[10] In addition, the rates of side reactions, such as hydrosilylation, silane dehydrocoupling, and silane redistribution, are affected by the identity of the substituents on the silanes.[6b,11] Therefore, reactions with a silane containing a silicon–heteroatom bond are unlikely to parallel directly the reactions of trialkylsilanes. We hypothesized that the dehydrogenative silylation could be made more practical by conducting the reactions with a tertiary hydrosilane containing bulky siloxy groups and that the catalysts we recently developed for the silylation of aliphatic C–H bonds[2f] could make the dehydrogenative silylation faster than the redistribution reactions of a hydrosilane containing one or more electronegative groups.

We report herein the dehydrogenative silylation of terminal alkenes with $(TMSO)_2MeSiH$, a silane that is commercially available in bulk quantities, catalyzed by iridium complexes of 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4Phen), together with subsequent cross-coupling and oxidation of the vinylsilane products. The reaction is highly selective for the *Z* vinylsilane. Isotope labeling suggests that the reaction occurs by insertion of the alkene, rather than direct C–H activation, and the stereoselectivity of the process can be reversed by conducting the reaction with a hindered, chelating nitrogen ligand.

To begin to develop the dehydrogenative silylation with a silane suitable for synthetic purposes, we surveyed the reactions of allylcyclohexane (**4a**) with several inexpensive and readily available siloxysilanes, such as trisiloxane $(TMSO)_2MeSiH$,[12] in the presence of norbornene (nbe) as hydrogen acceptor and a series of catalysts. The reaction of this silane with **4a** catalyzed by $[\{Ir(cod)OMe\}_2]$ and Me_4Phen formed the *Z* vinylsilane **4b** in 82% yield with a *Z*/*E* isomer ratio of 90:10 (Table 1, entry 6). The alkene geometry was assigned based on the *J*-coupling value of the vinylic protons (14.3 Hz for **4b** versus 18.6 Hz for the independently prepared *E* isomer **4c**, see below). Reaction with the more sterically-hindered silane $(TMSO)_3SiH$ occurred with slightly higher diastereoselectivity but required a higher temperature (100°C; Table 1, entry 7) and longer time, whereas reactions with smaller silanes, such as $(TMSO)Me_2SiH$ or Et_3SiH, exhibited higher turnover rates but lower diastereoselectivity (Table 1, entries 8 and 9).

Among the ligands examined, 3,4,7,8-tetramethyl-1,10-phenathroline (Me_4Phen) generated the catalyst that reacted with the highest activity and diastereoselectivity.[13] Reactions conducted with phosphine- or nitrogen-based ligands, other than phenanthroline or bipyridine derivatives, resulted in poor yields of the vinylsilane (see the Supporting Information). Reactions conducted with the hydroxy-bridged binuclear dimer $[\{Ir(coe)_2OH\}_2]$[14] as the catalyst precursor (Table 1, entry 14) occurred faster than those conducted with the related complexes $[\{Ir(coe)_2Cl\}_2]$ (Table 1, entry 13) and $[\{Ir(cod)OMe\}_2]$ (Table 1, entry 6), presumably because of the lack of strongly coordinating ligands and thus faster generation of the catalytically active species.[15] Furthermore, the choice of solvent influenced the yield, but not the diastereoselectivity (Table 1, entries 10–12 and the Supporting Information). Finally, the same reaction conducted without the sacrificial hydrogen acceptor nbe gave the vinylsilane product in 49% yield, along with 50% propylcyclohexane (Table 1, entry 15), showing that nbe is critical for inhibiting substrate hydrogenation (see below).

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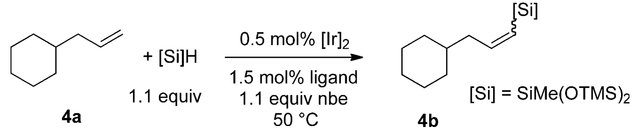
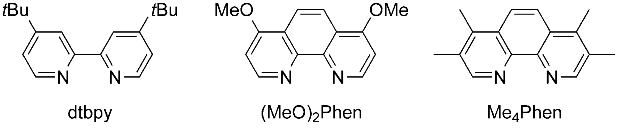
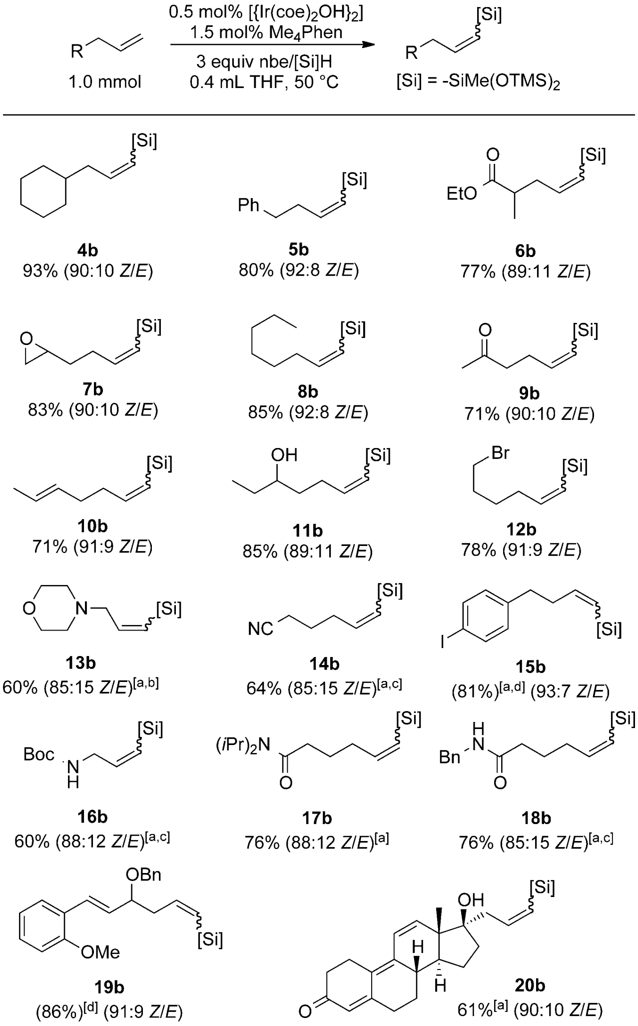
Table 1: Survey of conditions for terminal alkene silylation.[a]



Entry	Ligand	[Ir]	Solvent	Silane	Yield [%][b]	*Z*/*E*[b]
1	Phen	**1**[c]	THF	(TMSO)$_2$MeSiH	58	85:15
2	bpy	**1**	THF	(TMSO)$_2$MeSiH	–	–
3	dtbpy[d]	**1**	THF	(TMSO)$_2$MeSiH	78	85:15
4	(MeO)$_2$Phen[e]	**1**	THF	(TMSO)$_2$MeSiH	19	83:17
5	4-MePhen	**1**	THF	(TMSO)$_2$MeSiH	82	86:14
6	Me$_4$Phen[f]	**1**	THF	(TMSO)$_2$MeSiH	82	90:10
7[g]	Me$_4$Phen	**1**	THF	(TMSO)$_3$SiH	83	92:8
8	Me$_4$Phen	**1**	THF	(TMSO)Me$_2$SiH	75	82:18
9	Me$_4$Phen	**1**	THF	Et$_3$SiH	85	79:21
10	Me$_4$Phen	**1**	heptane	(TMSO)$_2$MeSiH	86	86:14
11	Me$_4$Phen	**1**	MeTHF	(TMSO)$_2$MeSiH	74	90:10
12	Me$_4$Phen	**1**	CH$_2$Cl$_2$	(TMSO)$_2$MeSiH	19	91:9
13	Me$_4$Phen	**2**[h]	THF	(TMSO)$_2$MeSiH	77	88:12
14[i]	Me$_4$Phen	**3**[j]	THF	(TMSO)$_2$MeSiH	83	90:10
15[k]	Me$_4$Phen	**1**	THF	(TMSO)$_2$MeSiH	49	82:18

[a] For detailed reaction conditions, see the Supporting Information. [b] Determined by GC. [c] [{Ir(cod)OMe}$_2$]. [d] 4,4′-di-*tert*-butyl-2,2′-bipyridine. [e] 4,7-dimethoxy-1,10-phenanthroline. [f] 3,4,7,8-tetramethyl-1,10-phenanthroline. [g] Reaction conducted at 100 °C for 7 days. Reaction at 50 °C gave no product. [h] [{Ir(coe)$_2$Cl}$_2$]. [i] Reaction run for 8 h. [j] [{Ir(coe)$_2$OH}$_2$]. [k] No nbe was added. bpy = 4,4′-bipyridine, Phen = 1,10-phenanthroline, TMS = trimethylsilyl.





Scheme 1. Scope of alkene silylation with (TMSO)$_2$MeSiH. Yields are of the isolated products. *Z*/*E* ratios were determined by NMR spectroscopy. [a] 1 mol% of [{Ir(coe)$_2$OH}$_2$] and 3 mol% of ligand were used. [b] Reaction was heated at 65 °C. [c] 4-MePhen was used instead of Me$_4$Phen as ligand. [d] Yield determined by GC. The crude product was directly subjected to oxidation (see below). coe = cyclooctene.

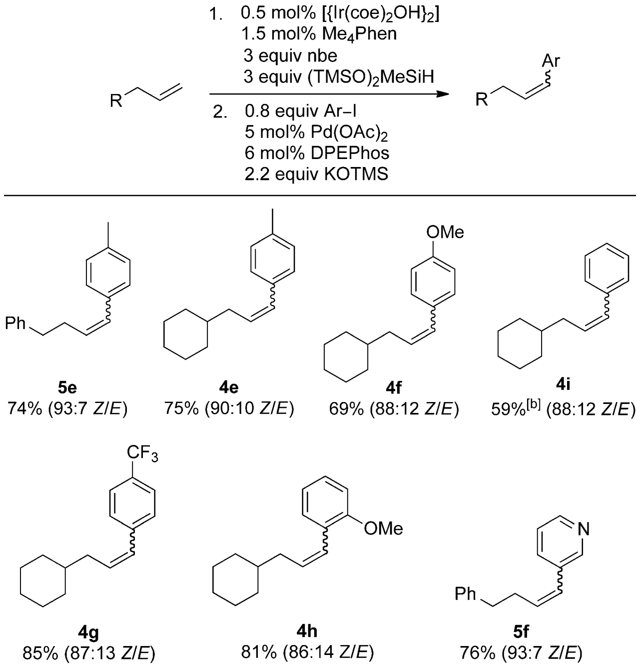
With certain alkenes, the reactions in the presence of 1.1 equiv of silane and nbe led to substantial substrate hydrogenation that lowered the yields of the desired vinylsilane products. One substrate especially prone to hydrogenation is 4-phenyl-1-butene (**5a**). At full conversion, the desired product **5b** was produced in only 68% yield (see the Supporting Information, Table S2, entry 1). However, when the reaction was conducted at higher concentration of nbe (3 equiv) hydrogenation of the starting alkene was greatly reduced, and the yield of the vinylsilane product was increased to 84% (see the Supporting Information, Table S2, entry 5).

Under the conditions developed for the reaction of **5a** (see the Supporting Information, Table S2, entry 5), reactions with various terminal alkenes afforded the corresponding vinylsilanes in good yields with high diastereoselectivity favoring the *Z* product (Scheme 1). A variety of functional groups were tolerated, such as epoxide (**7b**), ketone (**9b**), ester (**6b**), amide (**17b** and **18b**), alcohol (**11b**), aryl iodide (**15b**), and internal alkene (**10b**). Higher catalyst loading or a higher temperature was needed for substrates containing coordinating groups, such as a tertiary amine or nitrile, but the corresponding vinylsilanes were obtained in good yields. This reaction system does not lead to the conversion of internal alkenes, 1,1-disubstituted alkenes, or terminal alkenes with substituents on the α carbon, such as 2-methyl-1-pentene or 3-methyl-1-pentene. This limitation in scope is likely due to the steric demand at the metal center.

Cross-coupling reactions of aryl electrophiles with vinylsilanes in which the silyl group is SiMe(OTMS)$_2$ have only been reported once with TBAF as the activator.[5g] However, the presence of two heteroatoms on the silicon atom made it possible for these materials to undergo Hiyama–Denmark cross-coupling in the absence of a fluoride activator.[9c] Indeed, we found that reactions conducted with catalytic amounts of Pd(OAc)$_2$ and chelating phosphine ligand DPE-Phos and KOTMS as activator in THF gave vinylarene products in good yields with retention of the diastereomeric ratio. Although vinylarenes can be accessed from terminal alkenes through the Heck reaction[16] or direct arene vinylation,[17] the method we report here produces the *Z* isomer as the major product, whereas the Heck reaction produces the *E* isomer. Alternative routes by Suzuki coupling require the

Z vinylhalide or vinylboronate, which are difficult to access.[16e]

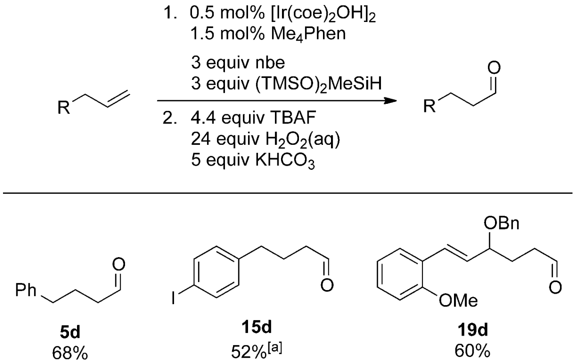
As shown in Scheme 2, the Ir-catalyzed silylation of terminal alkenes with (TMSO)$_2$MeSiH provides an alternative method for the arylation of vinyl C–H bonds by a one-pot procedure involving silylation and coupling. Under these conditions, various aryl iodides and an aryl bromide are all suitable electrophilic coupling partners.



Scheme 2. One-pot synthesis of vinylarenes from alkenes. Yields are of the isolated products based on 0.8 equiv of Ar–I. E/Z ratios were determined by GC or NMR spectroscopy. [a] Bromobenzene (1.1 equiv) was used instead of an aryl iodide. Yield is based on the starting alkene. DPEPhos = bis(2-diphenylphosphinophenyl)ether.

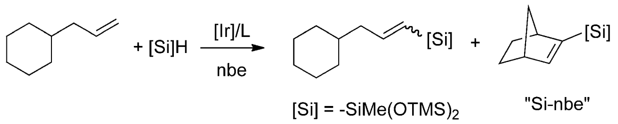
In addition to the cross-coupling with aryl iodide electrophiles, we developed conditions for the oxidation of the vinylsilanes in the presence of aqueous H_2O_2 and 4.4 equivalents of TBAF in a mixture of THF and methanol to give the corresponding aldehydes. The reaction requires 4 equivalents of TBAF, presumably because of the presence of 4 Si–O bonds in the starting material.[18] Scheme 3 shows a series of aldehydes prepared through a one-pot silylation and oxidation sequence starting with terminal alkenes. This protocol leads to the formation of aldehyde products with regioselectivity complementing the Wacker oxidation of alkenes and avoids the need for two oxidation steps to convert an alkylborane into the aldehyde.

While studying the effects of ligands on the diastereoselectivity of alkene silylation, we discovered that the reaction conducted with 2-methyl-1,10-phenanthroline[19] (2-MePhen) as the ligand gave the E vinylsilane as the major product (Z/E = 7:93; Table 2, entry 1). The yield of the E vinylsilane was lower than the yield of the Z vinylsilane obtained from reactions with Me$_4$Phen as ligand; the major side products are hydrogenated starting material and silylated nbe (“Si-nbe”; Scheme 4, $m/z = 299.1$, $M-CH_3$). However, the yields and the selectivity for the E isomer were high. Reactions conducted with other 2-substituted phenanthrolines (Table 2) in which the substituents are larger than a methyl group occurred more



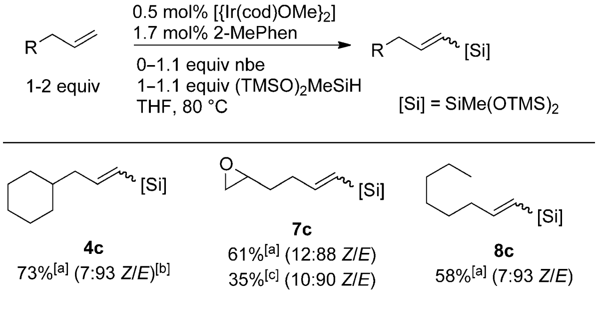
Scheme 3. One-pot aldehyde synthesis from alkenes. Yields are over two steps and are of the isolated products. [a] 1 mol% of [{Ir(coe)$_2$OH}$_2$] and 3 mol% of ligand were used for the silylation. TBAF = tetra-n-butylammonium fluoride.

Table 2: Surveying conditions for the E-selective alkene silylation.[a]



Entry	Ligand	Equiv of nbe	Equiv of Silane	Yield [%][b]	Z/E[b]
1	2-MePhen	1.1	1.1	70	7:93
2	2-EtPhen	1.1	1.1	27	11:89
3	2-MeOPhen	1.1	1.1	nd	nd
4	2-PhPhen	1.1	1.1	5	nd
5	2-ClPhen	1.1	1.1	15	82:18
6	2,9-Me$_2$Phen	1.1	1.1	11	89:11
7	2-MePhen	2.0	2.0	64	9:91
8	2-MePhen	3.8	3.8	54	12:88

[a] For reaction conditions see the Supporting Infomation. [b] Determined by GC. nd = not determined.

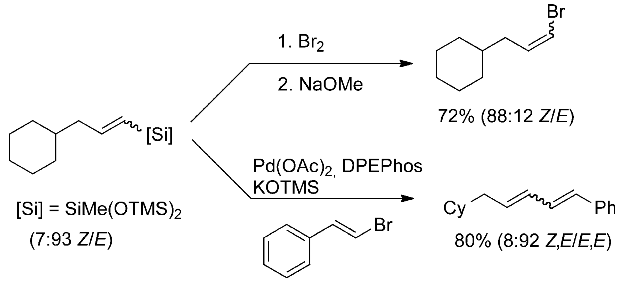


Scheme 4. Scope of the E-selective alkene silylation. Reaction conditions: Method A: [{Ir(cod)OMe}$_2$] (0.5 mol%), 2-MePhen (1.7 mol%), alkene (2.0 mmol), and silane (1.0 mmol) in 0.4 mL THF. Method B: [{Ir(cod)OMe}$_2$] (0.5 mol%), 2-MePhen (1.7 mol%), alkene (1.0 mmol), nbe (1.1 mmol), and silane (1.1 mmol) in 0.4 mL THF. [a] Yield of the isolated product from method A based on silane. [b] Z/E ratios were determined by NMR spectroscopy. [c] Yield of the isolated product from method B based on alkene.

slowly (Table 2, entries 2 and 4) than those with 2-MePhen, whereas reactions conducted with 2,9-dialkyl-1,10-phenanthrolines gave predominantly the *Z* vinylsilane in poor yields (Table 2, entry 6 and the Supporting Information). Reactions run with higher concentrations of nbe led to increased production of Si–nbe, but the yields of the desired product did not increase (Table 2, entries 7 and 8).

The reactions of several alkenes to form *E* vinylsilanes with high diastereoselectivity are summarized in Scheme 4. For the reactions of nonpolar alkenes (**4** and **8**), 2 equivalents of alkenes were used. One equivalent of the alkene serves as the hydrogen acceptor under these conditions to facilitate product purification.[20] High ratios of *E* to *Z* isomers were observed, and the reaction tolerated electrophilic functionality.

The resulting *E* vinylsilanes can be transformed to *Z* vinylbromides (Scheme 5). Addition of bromine to the alkene forms the 1,2-dibromoalkylsilane; reaction of the dibromide generated in situ with base gives the *Z* vinylbromide.



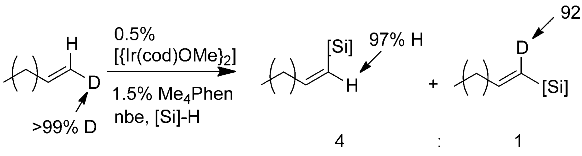
Scheme 5. Transformation of *E* vinylsilanes.

The vinylsilanes also can be converted to stereochemically defined dienes. We studied the *E* vinylsilane to identify conditions for the conversion of the C–H functionalization product to dienes. Reaction of an *E* vinylsilane with an *E* vinylbromide in the presence of $Pd(OAc)_2$ and DPEphos with KOTMS as base generated the diene stereospecifically. Analogous procedures are suitable for the conversion of *Z* vinylsilanes to *Z*,*E* -dienes.[21] Such dienes that lack steric or electronic deactivation of one of the two alkenes are difficult to produce by cross metathesis.[22,23]

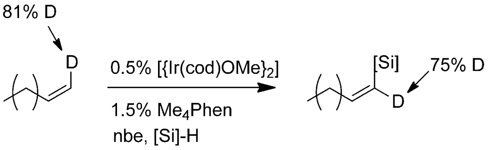
Mechanistic studies suggest that the dehydrogenative silylation of alkenes occurs by a pathway distinct from arene silylation and does not occur by direct insertion of iridium into the vinyl C–H bond. First, the reactions that give predominately the *Z* vinylsilane proceed without nbe as the acceptor (Table 1, entry 15), whereas the reaction with 2-MePhen as ligand strongly favors the *E* vinylsilane product even in the presence of nbe (Table 2, entry). This observation contrasts with published results of reactions involving triethylsilane; in these cases no catalytic reaction was observed in the absence of nbe, and nbe was proposed to promote the selectivity for the *Z* isomer.[8,24] Our data suggest that the diastereoselectivity of the reactions with the siloxysilane is influenced more by the ligand than by the hydrogen acceptor.

Second, the ratios of the rates for separate reactions of 1-octene and [1,1-D_2]oct-1-ene conducted with Me_4Phen or 2-MePhen as ligand are 1.7 and 1.5, respectively. This small kinetic isotope effect suggests that the reaction does not occur by initial, irreversible oxidative addition of the vinyl C–H bond and that the C–H bond cleavage step is similar for reactions catalyzed by the two systems.

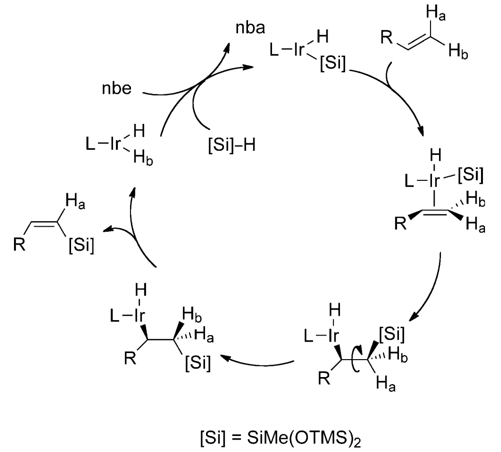
Finally, and most definitively, the reaction of *trans*-[1-D]oct-1-ene under the conditions that favor formation of the *Z* vinylsilane gave the major *Z* product containing hydrogen at the vinylic position [Eq. (1)]. Similarly, the reaction of *cis*-[1-D]oct-1-ene led to the vinylsilane product containing deuterium at the *trans* position [Eq. (2)]. These labeling studies support a mechanism involving syn insertion of the alkene into the iridium–silyl bond, followed by β-hydrogen elimination from a syn coplanar conformation of the silylalkyl intermediate (Scheme 6).



(1)



(2)



Scheme 6. Proposed catalytic cycle for the dehydrogenative silylation.

In summary, we have discovered a diastereoselective intermolecular silylation of terminal alkenes with a siloxysilane to give either *E* or *Z* vinylsilanes depending on the ligand employed. These vinylsilane products are suitable for further functionalization, including cross-coupling and oxidation. The one-pot silylation and Hiyama coupling sequence provides an alternative strategy to the Wittig olefination and Heck reaction for the synthesis of *cis*-1,2-substituted alkenes, whereas the silylation/oxidation sequence complements the regioselectivity of the Wacker process and is shorter than the combination of hydroboration, oxidation to the alcohol, and further oxidation to the aldehyde. The nature of the active silylating species and the origin of difference in diastereoselectivity between 2-MePhen and Me$_4$Phen ligands are currently under investigation.

Experimental Section

A representative procedure for silylation of **4a**: In a nitrogen-atmosphere glovebox, THF (0.4 mL) was added to a 4 mL vial containing $[\{Ir(coe)_2OH\}_2]$ (4.3 mg, 0.005 mmol) and Me$_4$Phen (3.5 mg, 0.015 mmol), and the mixture was stirred at room temperature for 5 min. $(TMSO)_2MeSiH$ (668 mg, 3.0 mmol) was added to the dark brown suspension, and the solution was stirred at room temperature for 5 min. Norbornene (282 mg, 3.0 mmol) and **4a** (124 mg, 1.0 mmol) were added subsequently, the vial was sealed, and the solution was stirred at room temperature for 30 min and then heated at 50 °C for 20 h. The volatiles were removed in vacuo, and the residue was purified by flash column chromatography (hexanes) to give **4b** as colorless oil (320 mg, 93 % yield, $Z/E = 90{:}10$). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 6.35$–6.27 (m, 1H), 5.35 (d, $J = 14.3$ Hz, 1H), 2.11 (t, $J = 7.1$ Hz, 2H), 1.76–1.62 (m, 6H), 1.38–1.28 (m, 1H), 1.28–1.09 (m, 3H), 0.98–0.84 (m, 2H), 0.14–0.07 ppm (m, 21H). ^{13}C NMR (126 MHz, CDCl$_3$): $\delta = 149.14$ (s), 127.74 (s), 41.10 (s), 38.37 (s), 33.38 (s), 26.76 (s), 26.55 (s), 2.25 (s), 2.05 ppm (s). HRMS (EI +) calcd for $[C_{15}H_{33}O_2Si_3]^+$ ($M-CH_3$): 329.1788, found: 329.1793.

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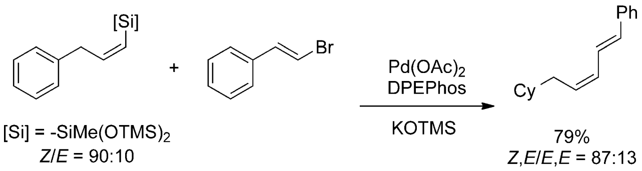
[21] For example, reaction of **4b** with (*E*)-β-bromostyrene gives the coupled product in high yield with retention of the *Z* geometry (see the Supporting Information for details):



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[24] We found that reaction of oct-1-ene with Et_3SiH catalyzed by 0.5 % $[\{Ir(cod)OMe\}_2]$ and 1.5 % Me_4Phen in the absence of nbe gave an equimolar mixture of triethyl-1-octenyl-silane and octane at complete conversion.