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Metal-catalyzed activations of inert sp^2C-H and sp^3C-H bonds have recently brought a revolution in the synthesis of useful molecules and molecular materials. Among them the catalytic silylation of sp^3C-H bonds has been developed due to the interest of the formed sp^3C-SiR_3 silanes, stable organometallic species, for further functionalizations that sp^3C-H bonds cannot reach directly. Besides many examples of sp^2C-H bond catalytic silylations, metal-catalyzed silylations of sp^3C-H bonds have been mostly discovered during the last decade in spite of the sp^3C-SiR_3 group high reactivity. This review will present all the methods of metal-catalyzed silylations of sp^3C-H bonds into sp^3C-SiR_3 functions, discuss the catalytic mechanisms according to various metal-catalysts, and illustrate their applications in synthesis. The review describes successively the intermolecular sp^3C-H bond silylations directed first by N-containing heterocycles with silanes with various Ru, Rh, and Ir catalysts and then directed by an amide type function with Pd(II) catalyst and $R_3Si-SiR_3$ reagent. The catalytic intramolecular silylations of sp^3C-H bonds can be performed after catalytic formation of $CH-OSiR_2H$ or $CH-N(R)SiR_2H$ groups from alcohols, ketones, esters, or amine NH bonds by catalytic hydrosilylation with R_2SiH_2 . Both catalytic processes can be performed with Ir(I) and Rh(I) catalysts with an alkene to capture the formed H_2 . This reaction with Rh(I) and Ir(I) catalysts can be applied to the formation of 5-membered cyclic silanes from aryl silanes and from alkyl silanes arising from hydrosilylated terminal $C=C$ bonds of alkenes. Oxidation of the cyclic silane derivatives easily leads to 1,3- and 1,4-diols, from alcohol or ketone precursors and to 1,2-amino alcohols from amines. Several methods show how to transform various heteroatom-methyl groups $X-CH_3$: B- CH_3 , O- CH_3 , Si- CH_3 , N- CH_3 , Ge- CH_3 and S- CH_3 into their reactive functionalized $X-CH_2SiR_3$ group, using various Ru(0), Ir(I), pincer-Ru(II), or Y catalysts. Examples are shown of catalytic transformations of allylic moiety $CH_3-C(R)=CH_2$ into their silylated $CH_2=C(R)-CH_2SiR_3$ form via i) Pd(II) allyl activation, ii) silyl radical generation with photocatalyst and iii) dual Ir(I) and Fe(II) catalysts for hydrosilylation of alkanes, via alkene formation, isomerization and hydrosilylation. Finally a Ru(II)-catalyzed sp^3C-H silylation of a methyl group of arylphosphine, directed by P(III) atom, will be presented.

1. Introduction

During the last two decades metal-catalyzed activation and functionalization of C-H bonds have tremendously improved the syntheses of a variety of functional useful molecules and molecular materials, often via cross-couplings of C-C bonds with better atom economy.¹⁻¹³ Due to the high reactivity of C-SiR₃ bonds efforts have been recently made to regioselectively transform C-H bonds into more reactive and versatile C-Si bonds via successive metal-catalyzed C-H bond activation and silylation. The C-Si bonds are used as temporary functional groups to further promote transformations leading to molecules difficult to reach directly from C-H bonds. In addition C-Si bonds are rather stable thus the formed silanes can tolerate functional groups and be handled more easily than many reactive organometallic derivatives containing a more polar C-M bond.

The regioselective catalyzed silylations of sp^2C-H bonds into sp^2C-SiR_3 groups has been first developed and several reviews already

illustrate the successes of catalyzed silylation of sp^2C-H bonds and the usefulness of this approach. Chatani in 2003¹⁴ and Goldman in 2011¹⁵ have discussed early examples of silylation of sp^2C-H bonds with ruthenium and iridium catalysts. Marciniec in 2005¹⁶ has gathered the catalyzed silylations of alkene C-H bonds and in 2012¹⁷ Hartwig has compared borylations and silylations of sp^2C-H bonds. In 2015 several reviews on catalytic silylation of sp^2C-H bonds were presented by J. F. Hartwig¹⁸, U. Sharma¹⁹, C. Wang²⁰, and Z. Xu²¹, and the three first of them¹⁸⁻²⁰ included the first examples of catalyzed sp^3C-H bond silylations. Shang and Liu²² gathered in 2016 the silylations of sp^2C-H bonds via radical processes. Noteworthy M. Oestreich has presented in 2017 all the Friedel-Crafts sp^2C-H bond silylations,²³ and recently he reviewed the various emerging strategies for C-H bond silylations, and briefly discussed the sp^3C-H bond silylations.²⁴

In spite of the usefulness in synthesis of reactive sp^3C-Si bonds²⁵ their catalytic formations directly from sp^3C-H bonds has been much less developed than from sp^2C-H bonds. However sp^3C-SiR_3 groups allow their easy transformation by oxidation into alcohols²⁶⁻²⁷ or into carboxylates directly from CO_2 ²⁸. They also give cross-coupling reactions with suitable electrophiles²⁹⁻³⁰, amination³¹⁻³² or halogenation³³⁻³⁴ including fluorination.³⁵⁻³⁶ In addition the direct catalytic formation of a reactive sp^3C-Si bond directly from a sp^3C-H bond offers a greener alternative to produce reactive silanes rather

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than from silylhalides, from lithium or grignard reagents or from hydrosilanes with alkylchlorides.²⁵

This review will present the known metal-catalyzed sp^3C-H bond silylations, discuss the catalytic mechanisms, and show the usefulness of the produced silane derivatives. Some early examples obtained in 2014 and before have been presented in the early 2015 reviews by J. F. Hartwig¹⁸, U. Sharma¹⁹, C. Wang²⁰. After pointing out these first examples this review will discuss in more details all recent examples of metal-catalyzed sp^3C-H bond silylations since 2015. The following sequence will be used to present the successful examples and will focus on the recent updates.

-After a few early and non directed examples of sp^3C-H bond silylations, the metal-catalyzed *intermolecular* silylations of sp^3C-H bonds with silane directed by N-containing heterocycles, which take place mostly with Ir, Rh, Ru catalysts, and the metal-catalyzed *intermolecular* silylations of sp^3C-H bonds directed by amide type groups with Pd(II) catalysts, will be described first.

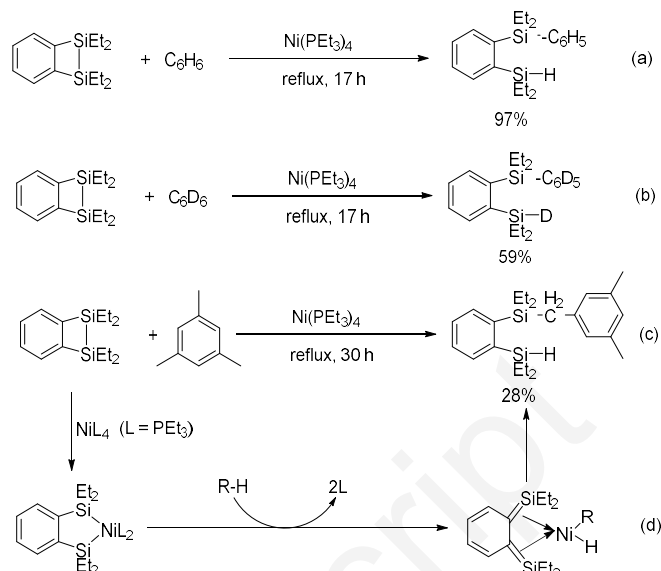
-Then will be presented successively i) the catalyzed *intramolecular* silylations of sp^3C-H bonds directed by silylated hydroxy group, resulting from dehydrosilylation of alcohols, or hydrosilylation of ketones, with Ir(I) or Rh(I) catalysts, ii) the catalyzed *intramolecular* sp^3C-H bond dehydrosilylation directed by N-SiR₂H groups with Ir(I) catalyst and hydrogen acceptor and iii) the *intramolecular* silylations of unactivated sp^3C-H bonds but in proximity with Si-H bonds of arylsilanes and alkylsilanes with Ir(I) catalyst.

-The *intermolecular* catalyzed sp^3C-H bond silylations of X-CH₃ groups into X-CH₂SiR₃ groups (X = B, Si, O, N, Ge, S), will be then discussed. They are mostly promoted by Ru(II) and Ir(I) catalysts in the presence of alkene, with the exception of Yttrium catalyst for SCH₃ group silylation and Copper catalysts for alkylsulfonamide silylation. Finally formal silylations of allylic C-H bonds and the unique and promising example of catalyzed methyl sp^3C-H bond silylation directed by phosphine will be presented.

2. The first steps in non directed catalytic silylations of sp^3C-H bonds

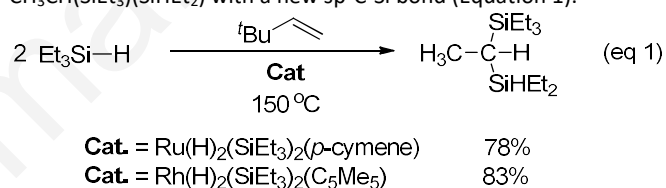
The first examples of catalytic silylation of a sp^3C-H bond were observed without the assistance of a directing group, but with modest efficiency. As early as 1992 Ishikawa *et al.*³⁷ studied the Ni(0)-catalyzed transformation of benzo-1,2-disilacyclobutene and observed the activation/cleavage of benzene sp^2C-H and mesitylene sp^3C-H bonds to form related C-Si bonds (Scheme 1).

The benzo-1,2-disilacyclobutene with Ni(PEt₃)₄ catalyst in refluxing benzene led to the cleavage of one benzene sp^2C-H bond and to the formation of one Si-C(sp^2) and one Si-H bonds (Scheme 1a). The same reaction performed in deuterated benzene led to the disilyl product with Si-C₆D₅ and Si-D bond formation (Scheme 1b). By contrast the use of mesitylene as solvent led to one methyl sp^3C-H bond activation and then silylation with formation of Si-C(sp^3) and Si-H (Scheme 1c). The catalytic functionalization of C-H and C-D bonds are explained via their oxidative addition to disilyl-Nickel intermediate followed by formation Si-C and Si-H bonds (Scheme 1d).

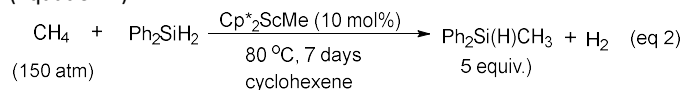


Scheme 1. Ni(0)-catalyzed silylation of sp^3C-H bond with benzo-1,2-disilacyclobutene.

In 1994 an example of sp^3C-H bond silylation was observed by Berry *et al.*,³⁸ in their study of hydrosilylation of an alkene ^tBuCH=CH₂ with Et₃SiH in the presence of Ru and Rh catalyst at 150 °C. Actually they observed besides the low production of silylated alkene, the high yield of dihydrogenative dimerization of 2 Et₃SiH into CH₃CH(SiEt₃)(SiH₂Et₂) with a new sp^3C-Si bond (Equation 1).



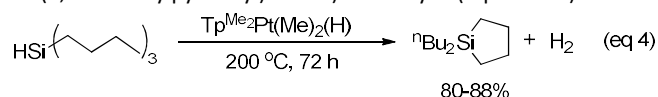
Another unique non directed silylation of sp^3C-H bond was observed by Don Tilley³⁹ in 2003 during the reaction of methane (150 atm) with H₂SiPh₂ at 80 °C with Scandium catalyst Cp*₂ScMe (Equation 2).



Cp*₂ScSiH₂Mes has been shown to react with CH₄ to give Cp*₂SiCH₃ and MesSiH₃ and then Cp*₂ScH and MesSi(CH₃)H₂ (Equation 3) but it is not clear yet which species Cp*₂ScSiH₂Mes or Cp*₂Sc-H activates the methane C-H bond before silylation.



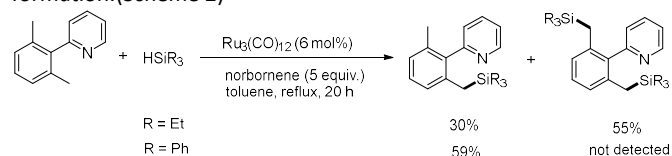
Hartwig in 2005 developed the first *intramolecular* dehydrogenative regioselective coupling of a silane Si-H bond with aliphatic δ -C-H bond to generate the 5-membered cyclic organosilane in 80-88% yield by using Tp^{Me2}PtMe₂H (Tp^{Me2} = hydrido tris(3,5-dimethylpyrazolyl)borate) as catalyst. (Equation 4)⁴⁰



It was the first observation of a three step process: initial formation of a Si-Metal bond from Si-H bond, activation by the Metal site of one sp^3C-H bond coming at its proximity followed by Si-C bond formation.

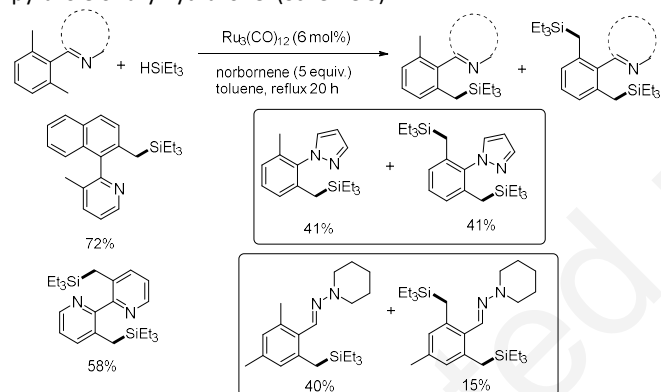
3. Metal-catalyzed intermolecular silylations of sp³C-H bonds directed by N-containing heterocycles.

An early example of catalytic sp³C-H bond silylation directed by pyridine was reported by Chatani in 2004.⁴¹ Ru₃(CO)₁₂ was shown to catalyze benzylic silylation with triethylsilane of 2-arylpyridines containing a methyl group at aryl *ortho* position only, not at *para* position, thus showing the directing role of pyridine nitrogen atom. The reaction took place in toluene at reflux in the presence of norbornene for hydrogen capture with norbornane formation. (Scheme 2)⁴¹



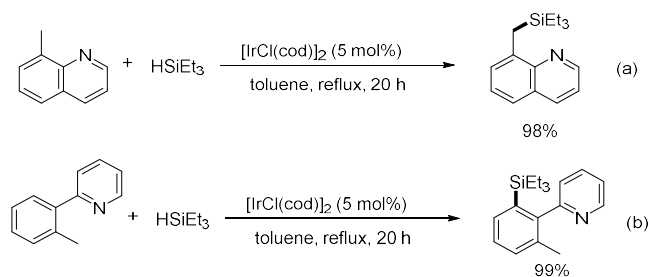
Scheme 2. Ru(0) catalyzed silylation of sp³C-H bond directed by pyridine.

However the silylation of an aryl *ortho* sp²C-H bond is faster than that of an *ortho* methyl sp³C-H bond with HSiEt₃ and the silylation of an *ortho* ethyl group of arene does not take place. Under similar conditions the silylation of *ortho* methyl groups of arenes can be directed by other N-containing heterocycles such as quinoline, pyrazole or arylhydrazone. (Scheme 3)⁴¹



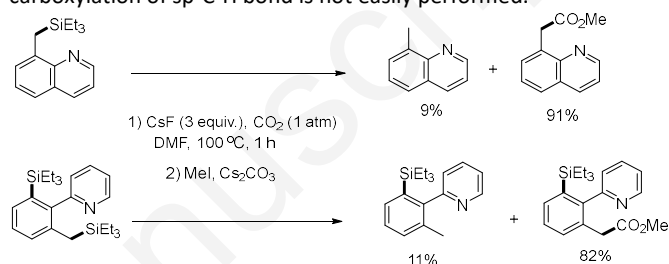
Scheme 3. Ru(0) catalyzed silylation of sp³C-H bonds directed by N-heterocycles.

In 2012 Sato *et al.*⁴² showed that [IrCl(COD)]₂ could catalyze the regioselective silylation of sp³C-H bonds of arene methyl groups directed by quinolone but this time without the presence of the hydrogen trap norbornene (Scheme 4 (a)).⁴² Ru₃(CO)₁₂ catalyst led to the same product in 93% under similar conditions but in the presence of norbornene. It is shown that with this Ir(I) catalyst the *ortho* aryl sp²C-H bond silylation is faster than that of a sp³C-H bond when it is directed by pyridine, likely because of a more easily generated 5-membered metallacycle intermediate with respect to the 6-membered intermediate required for *ortho* methyl activation (Scheme 4 (b)).⁴²



Scheme 4. Catalytic benzylic C(sp³)-H silylation with Ir(I) catalyst directed by pyridine group.

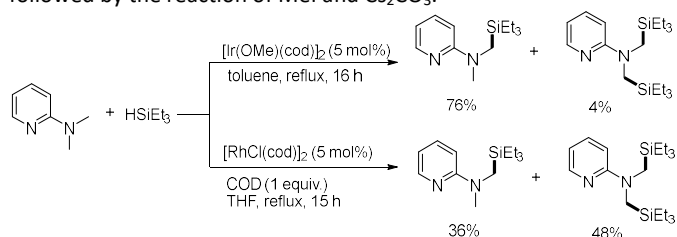
The importance of the sp³C-H benzylic silylation was shown by Sato⁴² for the direct access to carboxylates from the silylated products by action of CO₂ in the presence of fluoride, whereas the sp²C-Si bond is inert toward carboxylation (Scheme 5).⁴² This reaction motivates the search for benzylic silylation when the direct carboxylation of sp³C-H bond is not easily performed.



Scheme 5. Carboxylations of silylated benzyl groups with CO₂.

Sato has also shown that Ir(I) and Rh(I) catalysts [Ir(OMe)(COD)]₂ and [RhCl(COD)]₂ were able in the presence of HSiEt₃ to silylate a sp³C-H bond of a methyl group bonded to the nitrogen atom of 2-dimethylaminopyridine, thus directed by pyridine nitrogen itself (Scheme 6).⁴³ The Rh(I) catalyst operates only in the presence of the additive cyclooctadiene COD (1 equiv.) to eliminate the formed hydrogen whereas the later is not needed with the Ir(I) catalyst which is then not deactivated by in situ generated hydrogen.

However, the Rh(I) catalyst is more active for the silylation of N-H bond than of NCH₃ C-H bond of 2-methylaminopyridine.⁴³ The resulting N-CH₂SiEt₃ groups can also be transformed into the carboxylate group N-CH₂CO₂Me on reaction with CO₂ and CsF followed by the reaction of MeI and Cs₂CO₃.⁴³

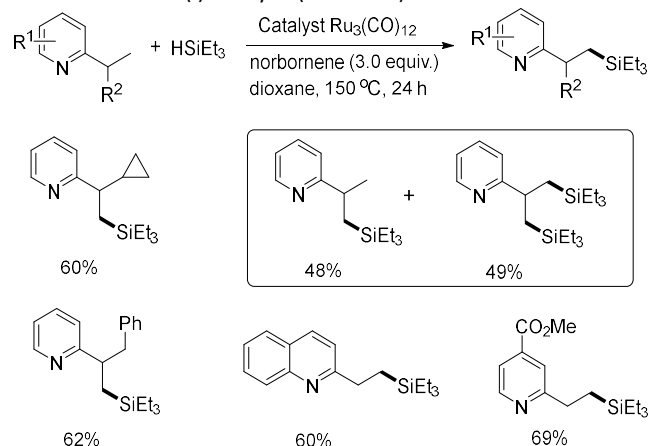


Scheme 6. Ir(I) and Rh(I) catalyzed silylation of C(sp³)-H bonds adjacent to a nitrogen atom and directed by pyridine.

Sato also showed that the same catalyst [Ir(OMe)(COD)]₂ could promote the silylation with HSiEt₃ of the alkyl group at *beta* carbon of 2-ethyl and 2-isopropyl pyridine but with low yield, 20 and 34 % respectively.⁴³

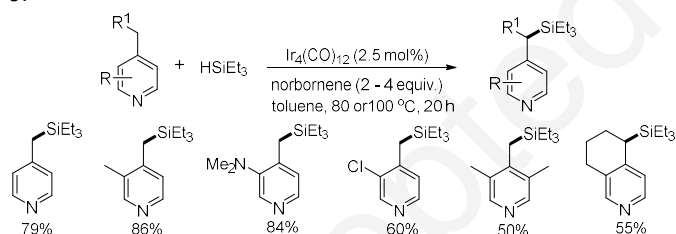
By contrast using the Ru₃(CO)₁₂ catalyst Jingsong You in 2016⁴⁴ succeeded to activate and silylate sp³C-H bonds of the alkyl group of 2-alkyl pyridines at the *beta* carbon in the presence of 3 equiv. of norbornene as hydrogen trap (Scheme 7).⁴⁴ The reaction shows that the silylation is favoured at alkyl *beta* carbon position and tolerates

functional groups on the pyridine ring (OMe, CO₂R, Ph). Mechanism studies reveal that sp³CH bond cleavage is reversible and not the rate-determining step⁴⁴. However this catalytic system was not operative for the sp³CH silylation of 2-dimethylaniline as previously described with Rh(I) catalyst. (Scheme 6)⁴³



Scheme 7. Ruthenium-catalyzed intermolecular silylation of C(sp³)-H bonds at 2-alkyl group of pyridine.

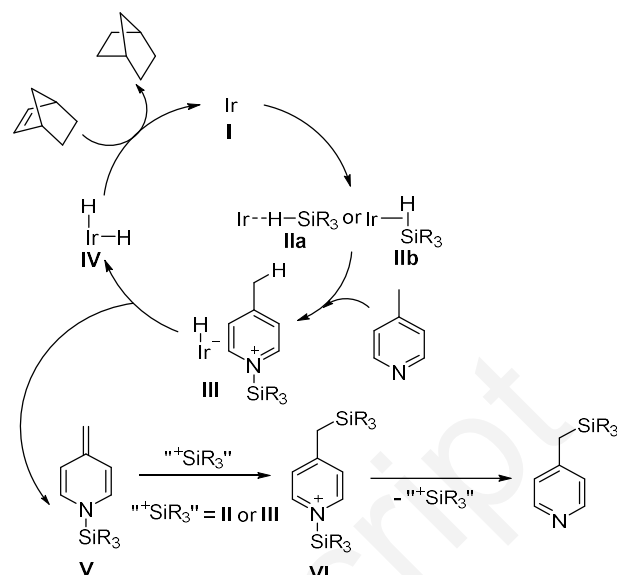
Chatani in 2017⁴⁵ has succeeded to silylate the sp³CH bond of methyl groups at the *para* position of pyridine derivatives. Ir₄(CO)₁₂ was used as catalyst precursor with HSiEt₃ and in the presence of norbornene in toluene at 80-100 °C (Scheme 8).⁴⁵ The reaction does not involve silylation of methyl at 3-position. It tolerates -NMe₂, -Cl, -Br, -OMe groups on the pyridine and is regioselective at the *alpha* carbon of the alkyl chain. The silylation of 2,4-dimethyl pyridine requires more drastic conditions (120 °C, 48h) to produce 12% of silylated product at 4-Methyl group. Pyridine does not play the directing group role in that case but favours the 4-alkyl sp³C-H bond activation by deprotonation as shown in the mechanism on scheme 9.⁴⁵



Scheme 8. Ir₄(CO)₁₂ catalyzed silylation of alkyl group of 4-alkyl pyridines at α -carbon.

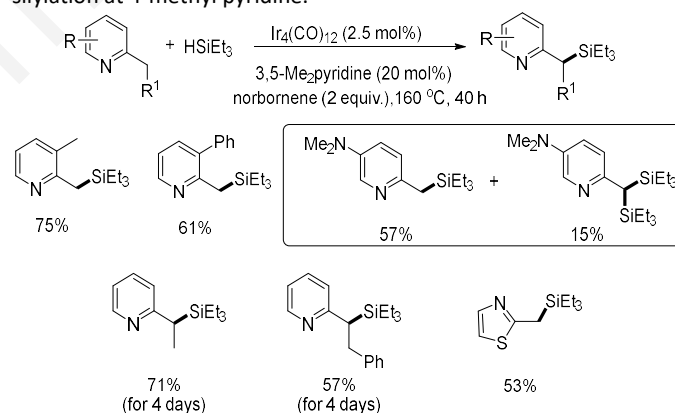
Beside Ir₄(CO)₁₂, Ir(acac)(CO)₂ is also active at 80 °C (20h) for the same reaction to produce 74% of 4-triethylsilylmethylpyridine with 15% of disilylated compound. [Ir(OMe)(COD)]₂ is also operative but under one atmosphere of carbon monoxide.

The proposed mechanism by Chatani (Scheme 9)⁴⁵ is based on deuteration studies with DSiEt₃. It suggests initial oxidative addition of the H-Si bond to the Ir(0) species **I** derivative of Ir₄(CO)₁₂ which leads to a [Ir-H]⁻ species and silylation of the pyridine nitrogen **III**. The [Ir-H]⁻ hydride deprotonates the 4-methyl group to give the enamine **V** which is silylated to give the intermediate **VI** which then affords the 4-silylmethyl pyridine. The *in situ* formation of IrH₂ species **IV** allows the insertion of the norbornene double bond and reductive elimination to produce norbornane and to regenerate the Ir(0) catalytic species.⁴⁵



Scheme 9. Proposed mechanism for Ir₄(CO)₁₂ catalyzed silylation of 4-alkyl pyridines.

By contrast Chatani recently described the catalytic sp³CH bond regioselective silylation at the benzylic position of 2-alkylpyridines leading only to 2-(1-silylalkyl)pyridines. The silylation is performed with HSiEt₃ and Ir₄(CO)₁₂ as catalyst in the presence of norbornene as hydrogen trap but in the presence of 3,5-dimethylpyridine ligand (Scheme 10).⁴⁶ Thus the 3,5-dimethylpyridine modifies strongly by coordination the Ir(0) catalyst which without this ligand favours silylation at 4-methyl pyridine.⁴⁵



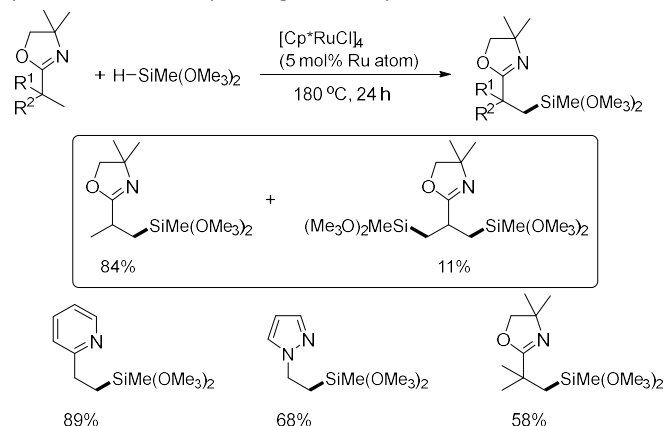
Scheme 10. Ir₄(CO)₁₂ catalyzed benzylic sp³C-H bond silylation of 2-alkylpyridine.

A mechanism similar to that described in Scheme 9 is proposed for this reaction and based on the initial formation of [Ir-H]⁻ and (pyridine)N-SiEt₃⁺ cation, then on the deprotonation of 2-methylpyridine methyl group and silylation of the resulting methylene group.

Several other catalytic dehydrogenative silylations of sp³C-H bonds have been directed by the nitrogen atom of heterocycles such as oxazolines, azoles and quinolines with Ru(II), Ir(III) and Ru(III) respectively, for which the nature of key ligands on the metal catalysts play a crucial role.⁴⁷⁻⁴⁹

An excellent example was described by Murata⁴⁷ in 2016 who showed that the oxazoline nitrogen atom could direct the silylation of sp³C-H bond of the 2-alkyl group but regioselectively at the β -

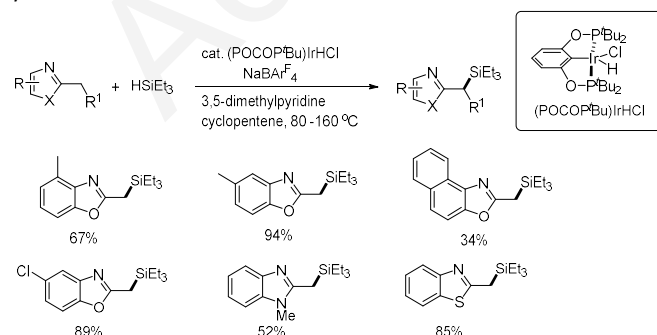
carbon atom. The reaction is performed only efficiently with $\text{HSiMe}(\text{OSiMe}_3)_2$ in the presence of a Ru(II) catalyst $[\text{Cp}^*\text{RuCl}]_4$ at 180 °C in cyclohexane. The Ru(III) derivatives $[\text{Cp}^*\text{RuCl}_2]_2$ and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ also display a rather good catalytic activity for this reaction which also allows disilylation at the alkyl β -carbon atoms. (Scheme 11)⁴⁷ However the nature of the silane is crucial as HSiEt_3 and $\text{HSiMe}_2(\text{OMe})$ are not efficient for this reaction. The silylation can be extended efficiently to 2-ethylpyridine (89%) and 1-ethylpyrazole (68%). The interest of the β -silylated 2-ethylpyridine is demonstrated using the Fleming-Tamao oxidation reaction with $\text{H}_2\text{O}_2/\text{KHF}_2$ which produced the corresponding alcohol $\text{PyCH}_2\text{CH}_2\text{OH}$.



Scheme 11. Ru(II)-catalyzed $\text{sp}^3\text{C-H}$ silylation at β -carbon of 2-alkyloxazolines.

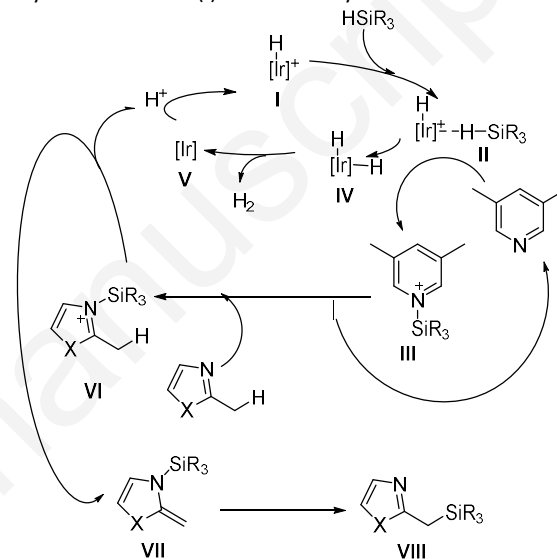
To understand the mechanism DFT calculations were made using HSiMe_3 and Ru-H as the initial reagents.⁴⁷ They showed the easy interaction of one β -C-H bond with H-Ru-N(heterocycle) intermediate to eliminate H_2 and to form a Ru(II)-cyclometalate. By contrast the oxidative addition of the H-Si bond to the (cyclometalate)Ru species and β -Carbon silylation require higher energy ($\Delta G^\ddagger = 35.9 \text{ kcal. Mol}^{-1}$).

By contrast Fukumoto and Chatani in 2018 using a pincer H-Ir(III) catalyst showed that the α - $\text{sp}^3\text{C-H}$ bond silylation of 2-alkyl-1,3-azoles was readily performed in the presence of cyclopentene, 3,5-dimethylpyridine ligand, but also of the salt $\text{NaB}(\text{C}_6\text{F}_5)_4$ or $\text{NaB}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4$ containing non coordinating anion (Scheme 12).⁴⁸ The silylation is performed with HSiEt_3 . By contrast when HSiEt_2Me or HSiEtMe_2 are used the disilylation of the α carbon is favored. It is observed that when the azole nitrogen is sterically hindered the yields are lower.



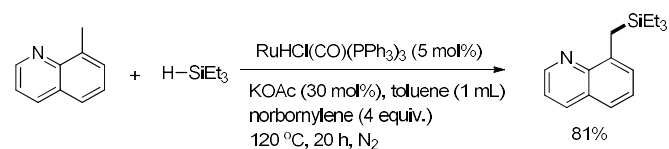
Scheme 12. Pincer hydride-Ir(III)-catalyzed silylation of 2-alkyl azoles at alkyl α -carbon.

The plausible mechanism in the absence of hydrogen trap is shown on scheme 13.⁴⁸ The $[\text{Ir-H}]^+$ species arising from chloride displacement of the pincer Ir(III) complex in the presence of a bulky coneranion is expected to trap the silane hydride to give the $(\text{H})_2\text{Ir}(\text{III})$ intermediate (IV) and the N-silylated 3,5-dimethylpyridine cation III can transfer the R_3Si^+ cation to the azole nitrogen forming (VI) thus favoring the methyl deprotonation to give VII. The migration of the silyl group to the methylene carbon affords the silylated product VIII. The catalytic species I is regenerated by protonation of Ir(I) intermediate V with the cationic compound VI. In the presence of alkene (cyclopentene) as H_2 trap a similar mechanism takes places but alkene inserts into one Ir-H bond of IV to give alkyl-Ir-H intermediate which after reductive elimination offers cycloalkane and Ir(I) V more easily.



Scheme 13. A plausible reaction mechanism in the absence of alkene as a hydrogen acceptor.

Finally during the evaluation of $\text{sp}^2\text{C-H}$ silylation of 2-aryl *N*-heterocycles with HSiEt_3 in the presence of norbornylene, as hydrogen acceptor, and with the efficient Ru(II) catalyst $\text{RuH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3/\text{KOAc}$, Bin Li⁴⁹⁻⁵¹ showed in 2019 that the silylation conditions applied to 8-methylquinoline preferentially led to the $\text{sp}^3\text{C-H}$ bond silylation of the 8-methyl group (Scheme 14).⁴⁹ For this reaction the role of KOAc is crucial to generate a Ru(H)(OAc) intermediate on which oxidative addition of H-SiR₃ bond is possible.

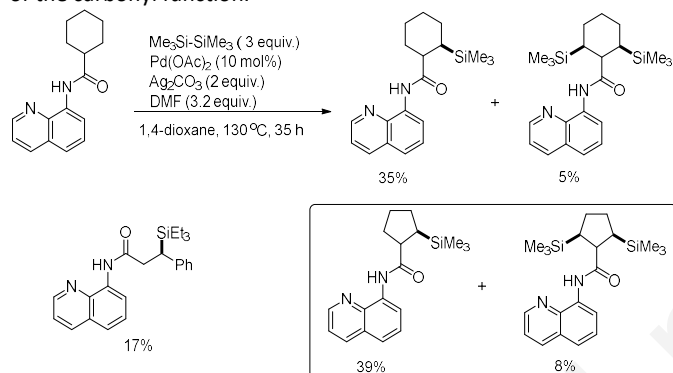


Scheme 14. $\text{sp}^3\text{C-H}$ bond silylation with H-SiEt₃ of 8-methylquinoline with a Ru(II) catalyst.

4. Palladium(II) catalyzed intermolecular silylations of sp^3C-H bonds with amide type directing groups.

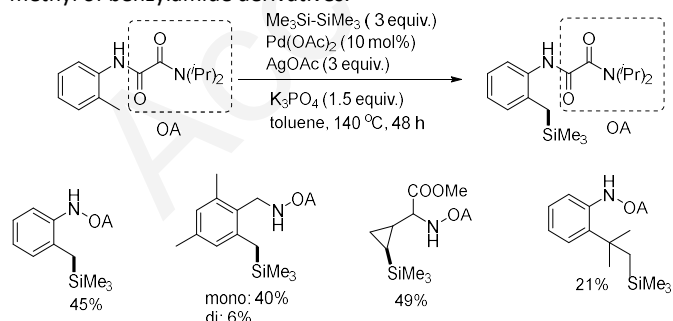
Since 2014 several reports gave evidence that amide functions $RNHCO-alkyl$, $R_2NCOCONH-alkyl$ or $ArCONH-alkyl$ could direct metal catalyzed silylations via directed alkyl sp^3C-H bond activation and *intermolecular* silylation with $R_3Si-SiR_3$. The metal catalysts are based mostly on Palladium(II) catalysts $Pd(OAc)_2$ or $Pd(OPiv)_2$. One rare example of α -silylation of benzamides with $tBuMgCl/dtbpv$ will be also presented but it involves a [1,5]-hydrogen transfer.

Kuninobu and Kana⁵² were the first to report in 2014 that the simple $Pd(OAc)_2$ catalyst could promote the silylation of aryl sp^2C-H bonds of $RNHCO-aryl$ with $R_3Si-SiR_3$. At the same time they showed a few examples of alkyl sp^3C-H bond silylation with $Me_3Si-SiMe_3$ of carboxamides directed by 8-aminoquinoline in (heteroaryl) $NHCO-alkyl$ derivatives with $Pd(OAc)_2$ catalyst and Ag_2CO_3 in DMF (Scheme 15)⁵² These 8-aminoquinoline derivatives were able to direct sp^3C-H bond activation and functionalization of the alkyl group at β -carbon of the carbonyl function.



Scheme 15. $Pd(OAc)_2$ catalyzed sp^3C-H silylation of carboxamide alkyl groups with hexamethyldisilane.

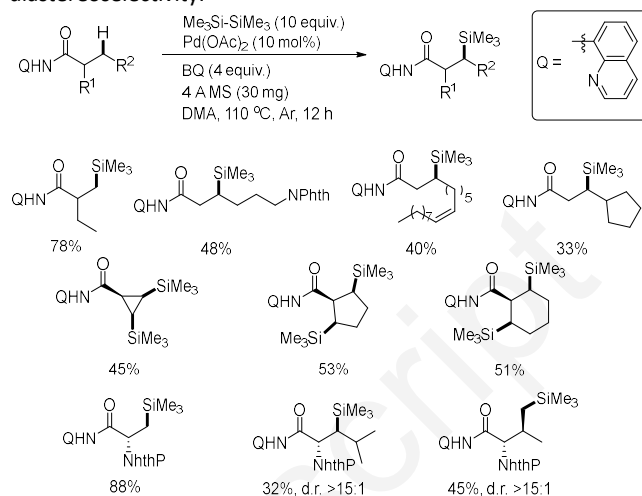
Just after, Y. Zhao⁵³ reported in 2015 that the oxalyl amide group could favour the sp^3C-H bond silylation, with $Me_3Si-SiMe_3$ and $Pd(OAc)_2$ catalyst of alkyylanilines in the presence of 3 equiv. $AgOAc$ and K_3PO_4 at 140 °C (Scheme 16).⁵³ The oxalyl amide group thus directs sp^3C-H bond activation with $Pd(OAc)_2$. The silylation takes place at the *ortho* methyl group of *ortho* methylaniline derivatives or of the cyclopropyl group of amide ester group. The δ -silylation takes place when no hydrogen is present at γ -position or at the *ortho* methyl of benzylamide derivatives.



Scheme 16. Palladium catalyzed sp^3C-H silylation with oxalyl amide directing groups.

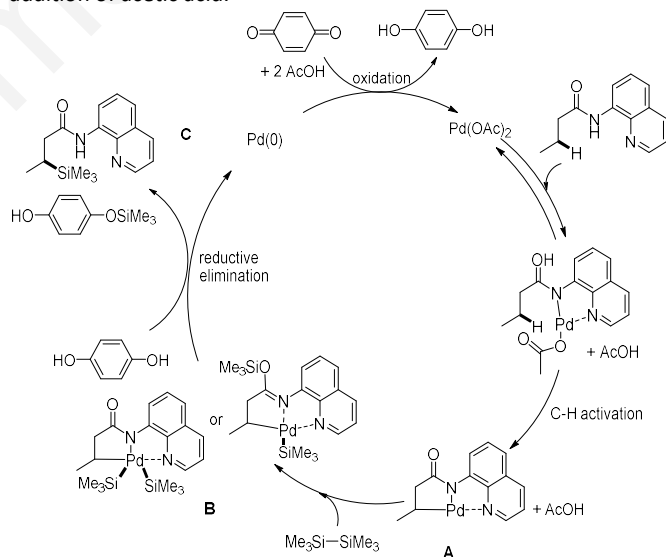
S.-Y. Zhang in 2016 succeeded to silylate with hexamethyldisilane remote sp^3C-H bonds at β -carbon of 8-aminoquinoline amide

derivatives as directing groups. The reaction catalyzed by $Pd(OAc)_2$ needs an oxidant such as benzoquinone (BQ) at 110 °C in DMA (Scheme 17).⁵⁴ This silylation can be applied to *N*-Phthalimide (Phth) protected chiral amino acid derivatives with good diastereoselectivity.



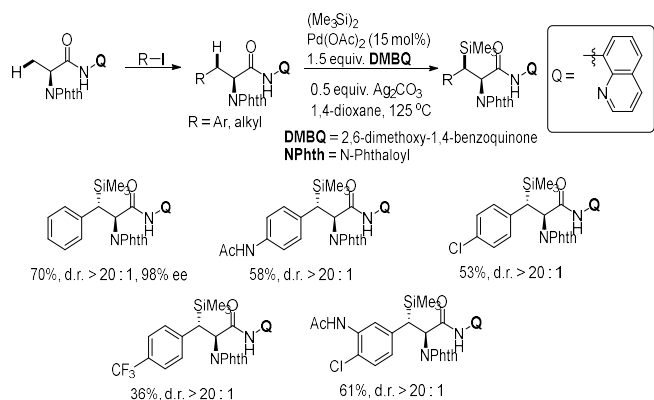
Scheme 17. $sp^3 C-H$ bond silylation at β -carbon of carboxamides derived from 8-amino quinoline.

The proposed mechanism is shown on scheme 18,⁵⁴ and involves the bicyclopalladate **A** formation by $N-H$ and $C_\beta-H$ deprotonation, and its disilylation at O and Pd atoms or at Pd site only in intermediate **B**. After reductive elimination with $C-Si$ bond formation to give product **C** the $Pd(0)$ is reoxidized into $Pd(OAc)_2$ with benzoquinone and addition of acetic acid.



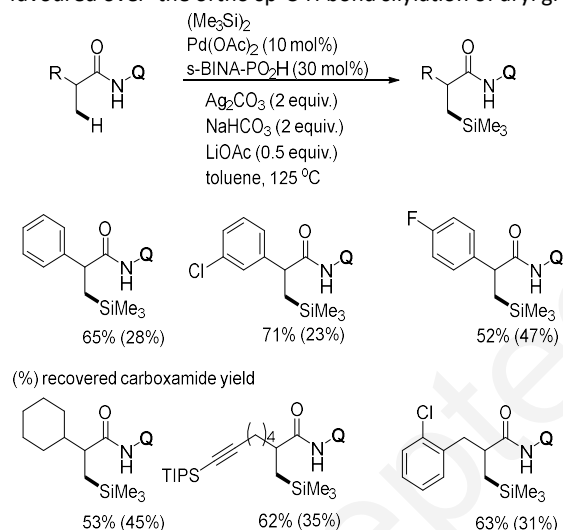
Scheme 18. Proposed mechanism for silylation of β -carbon of carboxamides.

Bing-Feng Shi et al. have found in 2016 the Pd -catalyzed intermolecular silylation of unactivated primary and secondary sp^3C-H bonds of *N*-Phthaloyl (PhTh) protected α -amino acids but containing the directing group 8-aminoquinoline (AQ), which is easy to be removed by action of $BF_3 \cdot Et_2O$ in MeOH. A variety of chiral β -silylamino acids can be prepared with retention of configuration and high *diastereoselectivity* using $Me_3SiSiMe_3$, $Pd(OAc)_2$ catalyst Ag_2CO_3 (0.5 equiv.) and DMBQ = 2,6 dimethoxy-1,4-benzoquinone as oxidant to regenerate the $Pd(II)$ catalyst (Scheme 19).⁵⁵



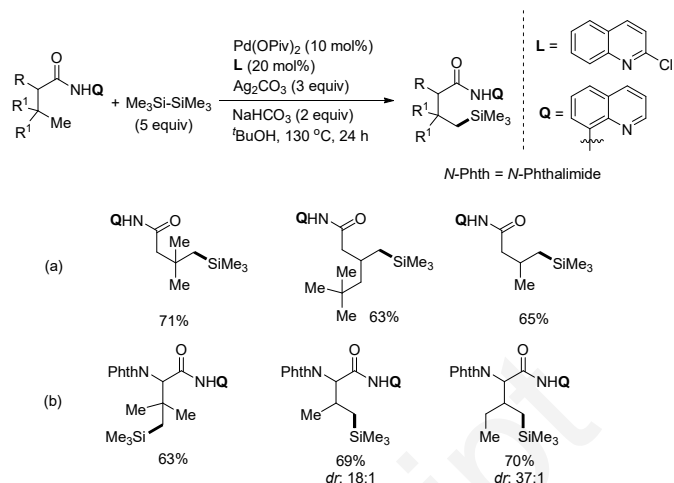
Scheme 19. Synthesis of chiral TMS-amino acid derivatives via Pd(II) catalyzed silylation.

2-Aryl propionic acids were treated by Bing-Feng Shi under slightly different conditions using $\text{Pd}(\text{OAc})_2$ catalyst but with *S*-BINAPO₂H (30 mol%) and Ag_2CO_3 (2 equiv.) and silylation occurred at the β -methyl group (Scheme 20).⁵⁵ Stoichiometric reactions show that the isolated bicyclic cyclometalate arising from deprotonation of NH and one methyl C-H bond is thermodynamically more stable than the N,N cyclometalate arising from deprotonation of NH group only. Importantly for this silylation the $\text{sp}^3\text{C-H}$ silylation of alkyl group is favoured over the ortho $\text{sp}^2\text{C-H}$ bond silylation of aryl group.



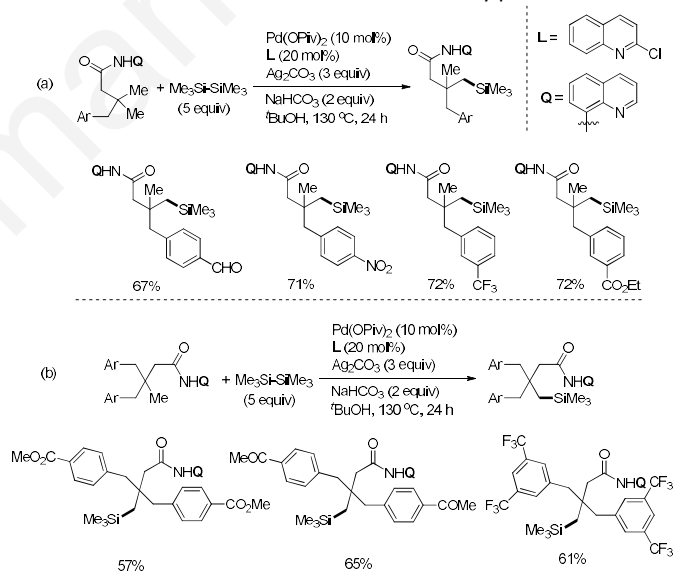
Scheme 20. Pd(II)-catalyzed silylation of primary C-H bonds of 2-aryl propionic acids.

Debrabata Maiti has succeeded in 2017⁵⁶ to perform the regioselective γ -silylation with hexamethyldisilane of amide derivatives of amino acids and 8-aminoquinoline (Scheme 21a).⁵⁶ $\text{Pd}(\text{OPiv})_2$ appears to be the best catalyst partner when associated to the ligand 2-chloroquinoline L in the presence of Ag_2CO_3 and NaHCO_3 . Several *N*-Phthalimide protected natural α -amino acid derivatives were also γ -silylated under similar conditions such as the derivatives of L-valine, L-isoleucine and *tert*-butyl leucine (Scheme 21b).⁵⁶



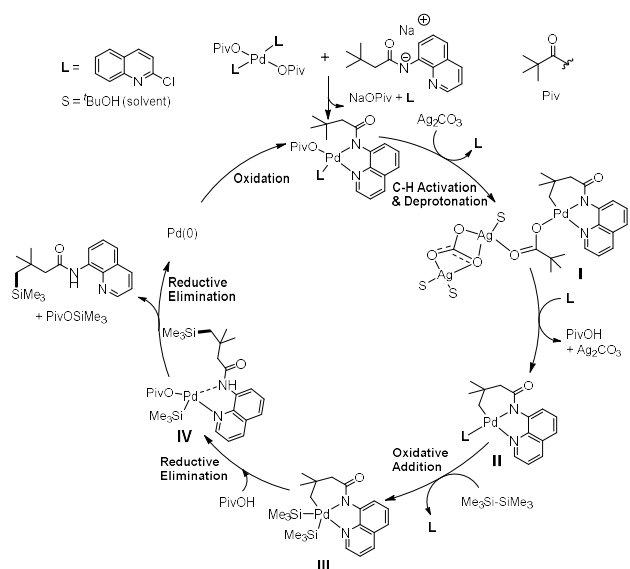
Scheme 21. Aliphatic γ - $\text{sp}^3\text{C-H}$ bond silylation of 8-aminoquinoline derivatives of amino acids.

The same reaction applied to γ -arylated amides, derivatives of 8-amino quinolones, with $\text{Pd}(\text{OPiv})_2$ catalyst and associated to the ligand 2-chloroquinoline furnishes only the $\text{sp}^3\text{C-H}$ bond γ -silylated products (Scheme 22a).⁵⁶ The similar γ -diarylated products under the same conditions only lead to the γ -silylation of the remaining methyl group (Scheme 22b).⁵⁶ The germylation with $\text{Me}_3\text{Ge-GeMe}_3$ of the same amino acid derivatives was also successfully performed.⁵⁶



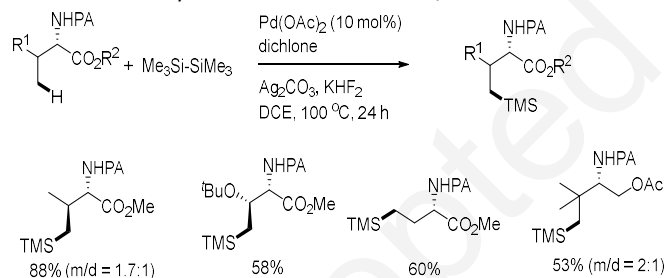
Scheme 22. γ - $\text{sp}^3\text{C-H}$ silylation of γ -mono and diarylated quinolamides.

The plausible mechanism of the reaction is presented on Scheme 23.⁵⁶ It is based on H/D kinetic studies and assisted by computational studies. It involves the γ -C-H methyl activation via deprotonation step first and the initial formation of the 6-membered cyclometalates I and II. The oxidative addition of $\text{Me}_3\text{Si-SiMe}_3$ to the Pd(II) intermediate gives III. Then the reductive elimination to give the C(γ)-SiMe₃ bond leads to IV, and the reductive elimination leading to the γ -silylated product releases PivOSiMe_3 and Pd(0) species which needs to be reoxidized by Ag^+ .



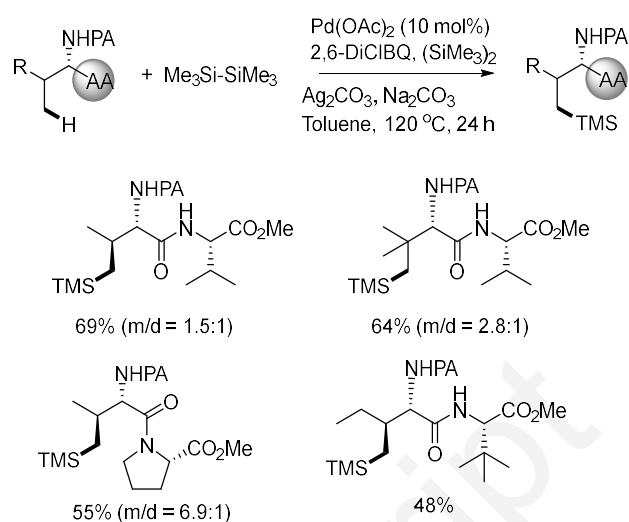
Scheme 23. Mechanistic cycle for palladium-catalyzed α -silylation of quinolamide derivatives.

Recently in 2019 Bing-Feng Shi has succeeded to perform the α - sp^3C -H bond silylation of peptides and α -amino acids, with $Me_3Si-SiMe_3$ and $Pd(OAc)_2$ catalyst, but assisted by a picolinamide (PA) directing group. This silylation has been applied to various amino acids valine, leucine-2-aminobutyric acid and to amino alcohol derivatives (NHPA : $-NCO(2-Pyridine)$) (Scheme 24).⁵⁷ The reaction requires the presence of Ag_2CO_3 and KHF_2 and is improved by the presence of benzoquinone derivative such as dichlone as oxidant to regenerate the $Pd(II)$ catalyst. The picolinamide group is easily removed after silylation on reaction with Zn/HCl .



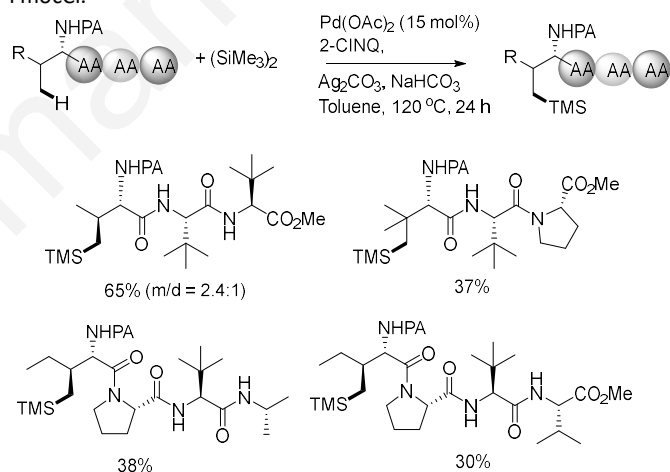
Scheme 24. α -methyl silylation of α -amino acids and α -amino alcohols.

Under closely related conditions the reaction can be applied to the α -silylation of 15 various dipeptides, in this case the preferable oxidant is 2,6-dichloro-1,4-benzoquinone (2,6-DiCIBQ) with picolinamide directing group (NHPA : $-NCO(2-Py)$). (Scheme 25).⁵⁷



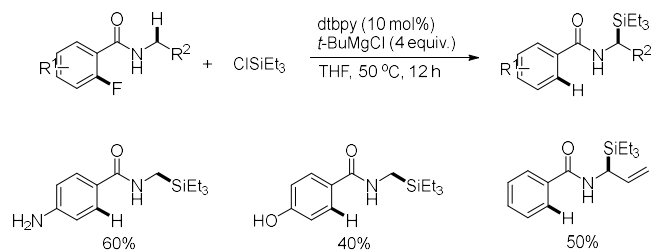
Scheme 25. $Pd(II)$ -catalyzed sp^3C -H bond α -silylation of dipeptides.

Bing-Feng Shi showed that this α -silylation can also be extended to tripeptides and tetrapeptides under similar conditions with $Pd(OAc)_2$ catalyst, but rather using 2-chloro-1,4-napthoquinone (2-CINQ) as oxidant (Scheme 26).⁵⁷ The picolinamide directing group in these peptides is shown to be removed easily by action of Zn/HCl in THF and replaced by useful protecting Fmoc group on reaction with FmocCl.



Scheme 26. $Pd(II)$ -catalyzed sp^3C -H bond α -silylation of tripeptides and tetrapeptides.

Another quite different intermolecular sp^3C -H bond silylation process of amides was discovered in 2016 by Xiaoming Zeng *et al.*⁵⁸ for the functionalization of benzamides in which the amide does not play the role of directing group for C-H bond activation by metal catalyst as previously. They succeeded to prepare α -silylamides *via* sp^3C -H bond silylation but involving a [1,5]-hydrogen transfer to the benzamide *ortho* C-F bond. The reaction shown on Scheme 27 is performed with $ClSiEt_3$, or other trialkyl silyl chlorides, on reaction with $tBuMgCl$ and 4,4'-di-tertbutylbipyridine (dtbpy) at only 50 °C. The [1,5] hydrogen transfer is demonstrated to occur by study of a $N-CD_3$ labeled benzamide derivative.

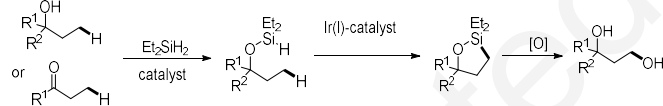


Scheme 27. Site-selective silylation of aliphatic C-H bonds at the α -position through [1,5]-hydrogen transfer.

Kinetic studies suggest that the α -sp³C-H bond cleavage is the rate determining step and that the *ortho* C-F bond is not cleaved in the absence of chlorosilane. To show the advantage of this regioselective silylation the prepared α -silabenzamides were easily functionalized on reaction of the C-Si bond to give a variety of *N*-formyl (PhCONHCHO), β -hydroxyl (PhCONHCH₂CHOHR) or β -amino (PhCONHCH₂CH(NHR)Ph) benzamide derivatives.⁵⁸

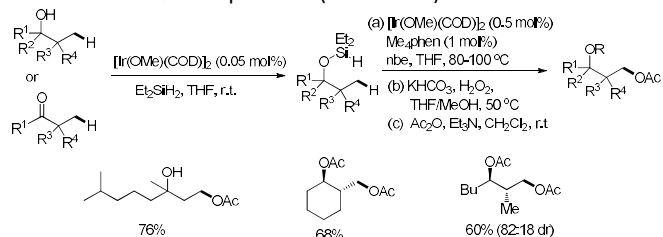
5. Metal-catalyzed intramolecular silylations of sp³C-H bonds directed by hydrosilylated hydroxy and ketone groups

As early as 2012 Hartwig⁵⁹ showed that O-SiH(alkyl)₂ groups, arising from catalyzed dehydrosilylation with silane alkyl₂SiH₂ of hydroxy group or by hydrosilylation of ketone carbonyl group, could lead to regioselective *intramolecular* silylation of γ -sp³C-H bond and hydrogen elimination to form 5-membered oxasiloxane. The efficient catalyst was based on Iridium(I) in the presence of a bulky phenanthroline ligand. One major advantage of this regioselective silylation is that it offers the easy oxidation of the formed oxasiloxanes, with H₂O₂, to generate 1,3-diols, or lead to the corresponding 1,3-acetates on further treatment with Ac₂O. (Scheme 28).



Scheme 28. Silylation of alkyl sp³C-H bond directed by silylated hydroxy group or ketone.

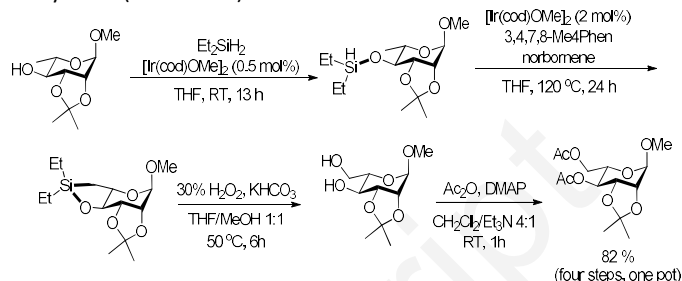
Thus the hydroxy and ketone groups were first dehydrosilylated and hydrosilylated respectively with alkyl₂SiH₂ in the presence of the catalyst [Ir(OMe)(COD)]₂ in THF. Then the intramolecular dehydrosilylation was performed with the same Ir(I) catalyst but in the presence of 3,4,7,8-tetramethylphenanthroline. The addition of norbornene allowed to trap the generated hydrogen before the C-Si bond formation to form the cyclic oxasiloxanes (Schemes 28, 29). The in situ treatment of the formed oxasiloxane with hydrogen peroxide leads to 1,3-diol which on reaction with Ac₂O affords the 1,3-diacetate at room temperature (Scheme 29).⁵⁹



Scheme 29. Iridium(I) catalyzed silylation of alcohol and ketone

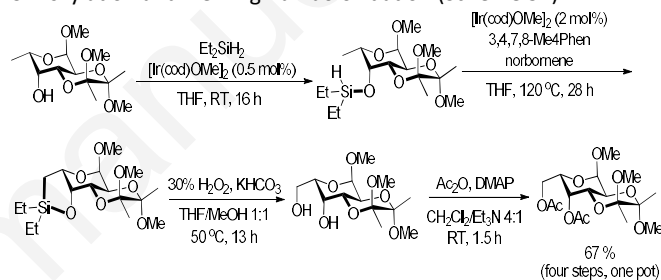
followed by intramolecular γ -sp³C-H bond silylation.

The same year, with the Hartwig procedure, Pedersen and Bols⁶⁰ developed a one-pot sequence process to synthesize fully protected L-mannoside in 82% yield only using 4 steps from methyl glycoside derivative, including Si-H/O-H cross-coupling reaction, intramolecular sp³C-H silylation, Fleming-Tamao-type oxidation, and acetylation (Scheme 30).



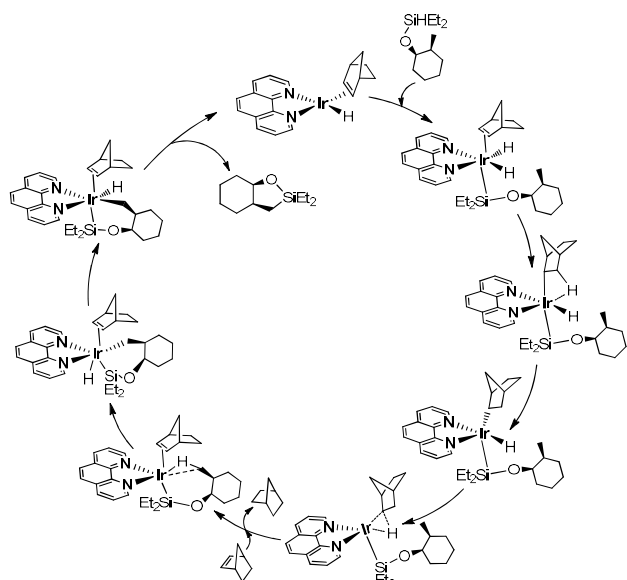
Scheme 30. One-pot sequence for the synthesis of fully protected L-mannoside involving an intramolecular γ -sp³C-H bond silylation.

Furthermore, this method could be also applied to synthesize fully protected L-galactosides from the corresponding L-fucoside through C-H silylation and Fleming-Tamao oxidation (Scheme 31).⁶⁰



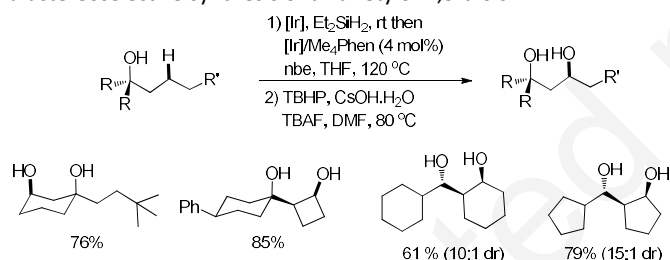
Scheme 31. One-pot synthesis of fully protected L-galactoside through C-H silylation and oxidation.

The mechanism of Ir(I)/phenanthroline catalyzed silylation of γ -sp³C-H bond of 2-methyl cyclohexanol was studied by Sunoj *et al*⁶¹ using DFT calculations. The proposed mechanism is presented on scheme 32. It is shown that in the presence of SiH₂Et₂ the [Ir(OMe)(COD)]₂ catalyst alone first performs the silylation of the alcohol. Then the Ir-H(Phen) complex can coordinate norbornene before allowing the Si-H oxidative addition. The alkene allows insertion into Ir-H bond and reductive elimination of alkane. Then C-H bond oxidative addition of the γ -sp³C-H bond takes place followed by reductive elimination with C-Si bond formation. The last step of the reductive elimination to form C-Si bond is the rate-determining step of the reaction (TS: 14.6 kcal/mol) whereas the C-H bond activation needs lower energy (TS: 9 kcal/mol).



Scheme 32. Mechanism of conversion of (hydrido)silyl ether to oxasilolane catalyzed by neutral $[\text{IrH}(\text{nbe})(\text{phen})]$.

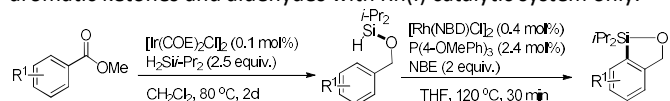
Hartwig⁶² has then applied his strategy to generate oxasilane $\text{O-SiEt}_2\text{H}$ group, from hydroxy group or corresponding ketone, and to direct the intramolecular regioselective γ - $\text{sp}^3\text{C-H}$ bond dehydrosilylation of intermediate $\text{R}_2\text{C}(\text{OSiEt}_2\text{H})-\text{CH}_2\text{CH}_2\text{CH}_2\text{R}'$ to *in situ* form the oxasilolanes. The later can then be *in situ* oxidized into 1,3-diols with TBHP peroxide (Scheme 33). This dehydrosilylation reaction catalyzed by $[\text{Ir}(\text{OME})(\text{COD})]_2/\text{Me}_4\text{Phen}$ allows the *diastereoselective* synthesis of a variety of 1,3-diols.



Scheme 33. Intramolecular dehydrosilylation of secondary C-H bonds and synthesis of 1,3-diols.

The primary C-D/C-H KIE=2 indicates that the C-H bond cleavage is the rate-limiting step for this directed intramolecular $\text{sp}^3\text{C-H}$ bond silylation. The catalytic dehydrosilylation of the derivatives $\text{R}_2\text{C}(\text{OSiEt}_2\text{H})\text{CH}_2\text{CH}_3$ and of $\text{R}_2\text{C}(\text{OSiEt}_2\text{H})\text{CH}_2\text{CH}_2\text{CH}_3$ show that the silylation of the γ - CH_3 group is 49 times faster than that of the γ -methylene group, thus faster at the primary than at secondary γ -C-H bond.

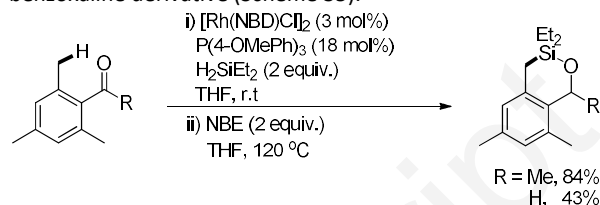
In 2015 Jeon *et al.*⁶³ have developed a method for initial hydrosilylation of ester, ketone and aldehyde carbonyl groups followed by $\text{sp}^2\text{C-H}$ bond *ortho* silylation of aromatic systems. The first hydrosilylation of carbonyl group is performed with $[\text{IrCl}(\text{COE})]_2$ catalyst with H_2SiEt_2 . The following intramolecular silylation was catalyzed by $[\text{RhCl}(\text{NBD})]_2/\text{P}(\text{C}_6\text{H}_4\text{OMe})_3$ in the presence of norbornene (Scheme 34). The same reaction could be applied to aromatic ketones and aldehydes with Rh(I) catalytic system only.



Scheme 34. Sequential reductive carbonyl and arene *o*-CH silylations

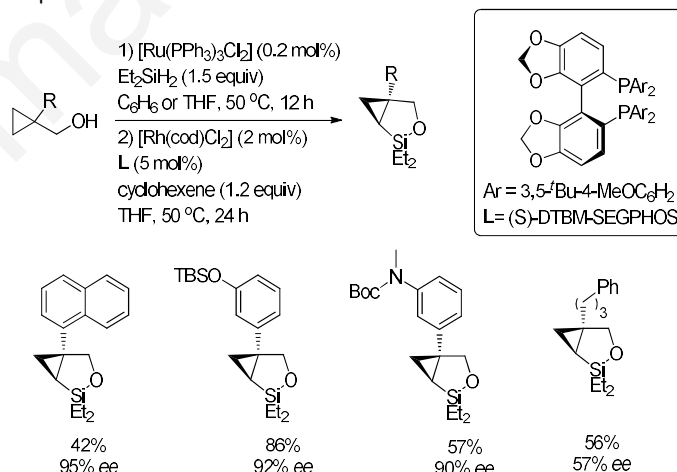
with both Ir(I) and Rh(I) catalysts.

Interestingly, when the reaction was applied to an aromatic ester containing an *ortho* methyl group, the similar successive Ir(I) and then Rh(I) reaction led to the reduction of carbonyl group first and then to the $\text{sp}^3\text{C-H}$ benzylic bond intramolecular hydrosilylation to afford the benzoxaline derivative. From aromatic ketone and aldehyde containing an arene *ortho* methyl group only the Rh(I)/Phosphine catalyst led to both carbonyl hydrosilylation and then in the presence of NBE intramolecular dehydrosilylation to form the benzoxaline derivative (Scheme 35).



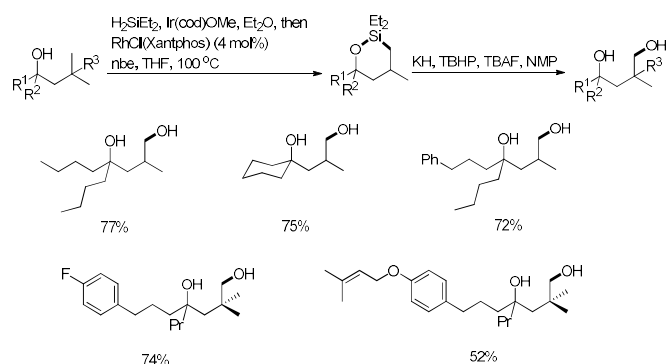
Scheme 35. Sequential reductive benzylic $\text{sp}^3\text{C-H}$ silylation of aromatic esters, ketones and aldehydes with Rh(I) catalyst.

Later on, Hartwig developed the first chiral-rhodium(III) catalyzed highly enantioselective C-H bond silylation of cyclopropyl C-H bond to form a five-membered ring oxasilolane. Up to 89% isolated yield and 95% *ee* of oxasilolane were obtained by using a sequence of $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]/\text{Et}_2\text{SiH}_2$ catalytic system followed by $[\text{Rh}(\text{cod})\text{Cl}_2]/(\text{S})\text{-DTBM-SEGPHOS}/\text{cyclohexene}/\text{cyclohexene}$ catalytic system (Scheme 36).⁶⁴ The H/D KIE value is 2.1 which indicates that the Rh catalyzed C-H bond cleavage is the turnover-limiting and enantioselectivity-determining step.

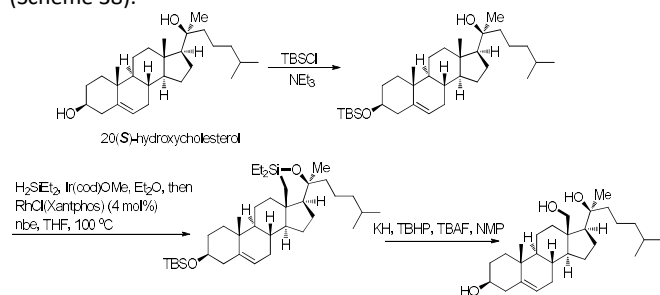


Scheme 36. Rh catalyzed enantioselective silylation of cyclopropyl $\text{sp}^3\text{C-H}$ bonds.

Then the Hartwig group⁶⁵ developed a rhodium-catalyzed site selective silylation of alkyl δ -C-H bonds, when no C-H bond is present at γ -carbon atom, to form six-membered oxasilolanes with hydroxyl group as the initial directing group. The catalytic reaction takes place in the presence of $[\text{Rh}(\text{Xantphos})\text{Cl}]$ catalyst with norbornene as the hydrogen acceptor (Scheme 37).⁶⁵ The oxidation of the resulting six-membered oxasilolanes led to 1,4-diols in high yields with tolerance of many functional groups. The mechanistic studies show that the $(\text{Xantphos})\text{Rh}(\text{SiEt}_2\text{OR})(\text{nbe})$ is the key complex for the rate-resting state and that the oxidative addition of the δ C-H bond to Rh(I) is the rate-limiting step of the process.



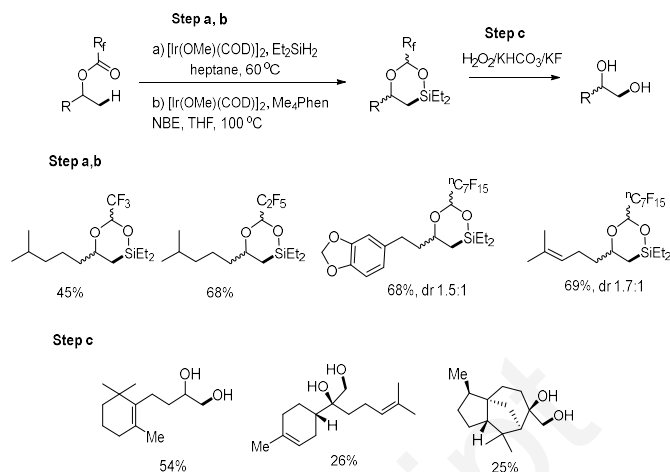
This method could be applied to functionalize the natural oxysterol compound 20(S)-hydroxycholesterol with alcohol-directed oxygenation at the C18 position *via* the [Rh(Xantphos)Cl] catalyzed δ -sp³C-H bond silylation followed by the Fleming-Tamao oxidation (Scheme 38).⁶⁵



Scheme 38. Rh(Xantphos)Cl catalyzed δ -C-H silylation of oxysterol.

Hartwig⁶⁶ in 2018 has applied his method for intramolecular silylation of sp³C-H bonds observed with the Rh(I) catalyst, for regioselective dehydrosilylation of alkyl β -C-H bond directed by a perfluorinated ester group, which was successful with Ir(I) catalyst. First tertiary alcohols were first esterified into perfluorinated esters which were treated with Et₂SiH₂ with catalyst [Ir(OMe)(COD)]₂ to afford quantitatively the carbonyl hydrosilylation product containing the O-SiEt₂H group. Then the addition of [Ir(OMe)(COD)]₂/Me₄Phen catalyst allowed the regioselective β -C-H bond silylation with dehydrogenation in the presence of norbornene to form the 6-membered dioxasilanes (Scheme 39).

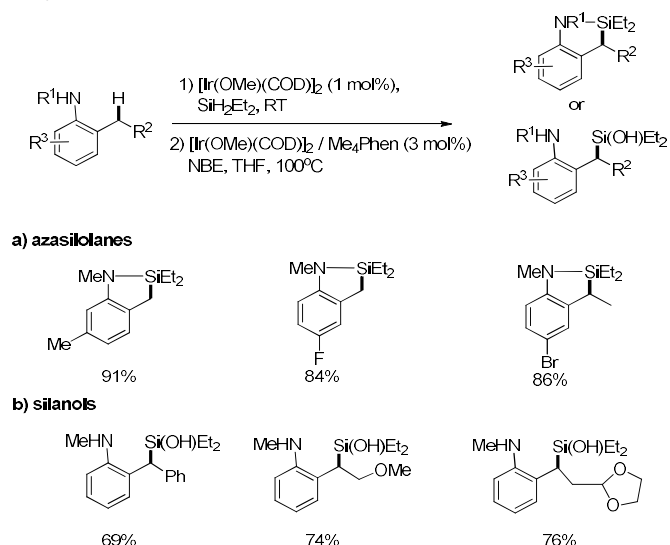
These perfluorinated esters can be used as starting substrates to produce a variety of natural 1,2-diols,⁶⁶ by successive Ir(I) catalyzed β -C-H bond silylation and then oxidation with H₂O₂ according to the Tamao-Fleming reaction.



Scheme 39. Hydrosilylation of fluorinated esters, intramolecular sp³C-H bond silylation and oxidation.

6. Catalyzed regioselective intramolecular sp³C-H bond dehydrosilylation of silylated amine NH Bonds

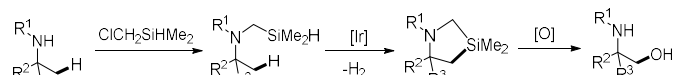
Hartwig has shown in 2014 that secondary aromatic amines could direct the silylation with H₂SiEt₂ of N-H bond first with [Ir(OMe)(COD)]₂ catalyst alone, followed by the *intramolecular* silylation of aryl *ortho* sp²C-H bond using the same catalyst, but with an additional phenanthroline ligand [Ir(OMe)(COD)]₂/Me₄Phen catalyst and with the presence of norbornene to eliminate the hydrogen.⁶⁷ This principle was then applied to secondary aryl amines containing an *ortho* alkyl group which led to initial Ar(R)N-H transformation into (hydro)silylamines Ar(R)NSiH₂Et first and then to the intramolecular alkyl sp³C-H bond silylation of *ortho* methyl groups and of secondary benzylic sp³C-H bond at the γ -position of the N(SiH₂Et) group to produce a variety of azasilolanes (Scheme 40a).



Scheme 40. sp³C-H silylation of N-2-alkylanilines and formation of azasilolanes and silanols.

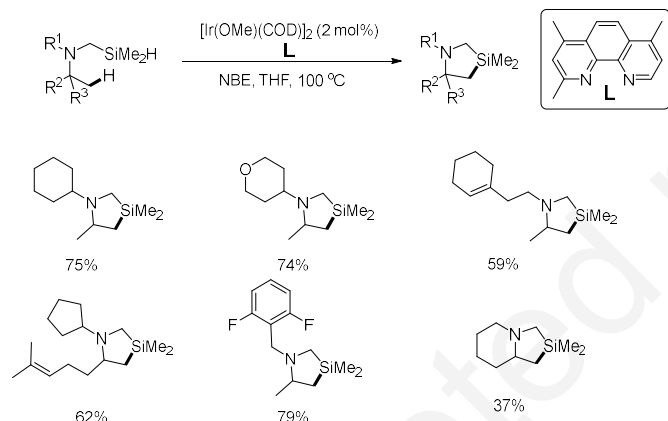
The later azasilolanes during chromatography were opened to produce the corresponding silanols (Scheme 40b). The reaction used successively the same two iridium(I) catalyst systems which tolerated many functional groups (Br, MeO, OSiR₃, OAc). The silanols can be oxidized easily with H₂O₂ to form aromatic secondary amines with γ -hydroxy group.

Hartwig has recently reported the intramolecular β -selective silylation of unactivated sp³C-H bonds of alkylamines.⁶⁸ The reaction requires the initial formation of the N-CH₂-SiHMe₂ group by reaction of secondary alkyl amine with ClCH₂SiHMe₂. Then intramolecular alkyl silylation affords a cyclic silane which can be oxidized into 1,2-aminoalcohol. (Scheme 41)



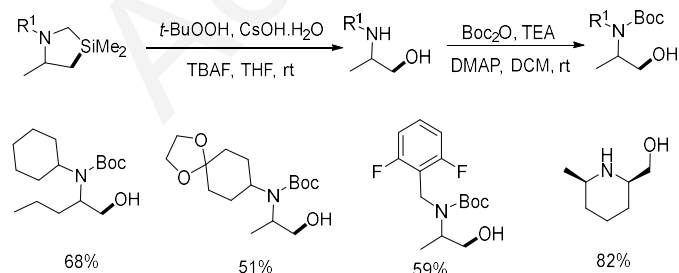
Scheme 41. Selective C-H silylation of aliphatic amines and oxidation into 1,2-amino alcohols.

The β -selective intramolecular silylation of amines is performed with [Ir(OMe)(COD)]₂ and a trimethyl phenanthroline ligand **L** in the presence of an hydrogen acceptor (NBE) (Scheme 42)⁶⁸. Many functional groups are tolerated such as alkene, C-F bond or other groups.



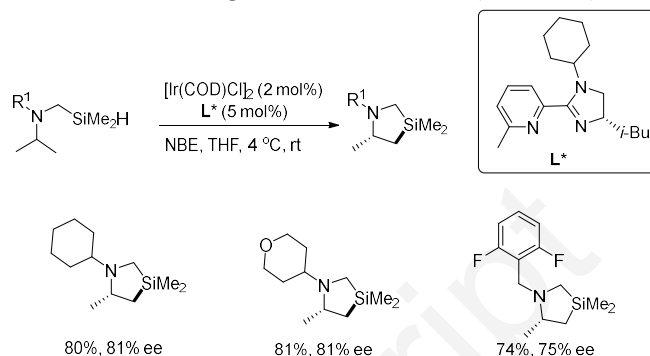
Scheme 42. Intramolecular sp³C-H silylation of aliphatic amines into silapyrrolidines.

The formed silapyrrolidines can be oxidized easily with *t*-BuOOH to produce 1,2-amino alcohols (Scheme 43). These 1,2-amino alcohols are easily transformed into *N*-protected carbamates by treatment with Boc₂O (Scheme 43).



Scheme 43. Synthesis of 1,2-amino alcohols, derived from sp³C-H silylation, and of their *N*-protected carbamates.

Hartwig also performed enantioselective intramolecular dehydrosilylation of silylamines.⁶⁸ The silylation reaction has been carried out with [Ir(OMe)(COD)]₂ catalyst but with a chiral pyridylimidazoline ligand **L***. The chiral ligand **L*** containing a *N*-alkyl imidazoline has led to good enantioselectivities (Scheme 44).⁶⁸

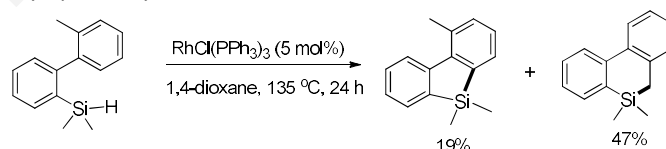


Scheme 44. Enantioselective intramolecular C-H silylation of aliphatic amines.

7. Intramolecular silylations of sp³C-H bonds in proximity with Si-H bonds.

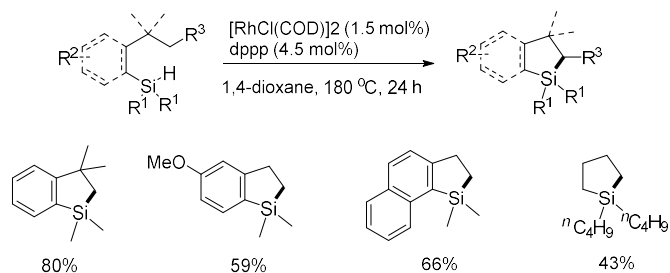
7.1 From arylsilanes

The first example of *intramolecular* silylation of sp³C-H bond *without directing group* was observed by Kuninobu and Takai with a Rh(I) catalyst RhCl(PPh₃)₃ in 2013 on reaction of the diphenylhydrosilane containing an *ortho* methyl group (Scheme 45)⁶⁹. Thus the sp³C-H intramolecular silylation appeared to be easier than the expected aryl sp²C-H silylation.



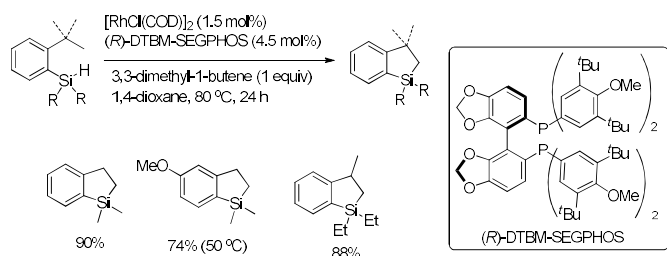
Scheme 45. Rhodium(I)-catalyzed silylation of aromatic sp²C-H and benzylic sp³C-H bonds.

This first example led this group to discover a general intramolecular sp³C-H bond silylation of arylsilanes containing an *ortho* alkyl group, to form a 5-membered cyclic silane, with a catalytic system based on [RhCl(COD)]₂ and diphosphine Ph₂P(CH₂)₂PPh₂ (dppp) (Scheme 46).⁶⁷ The proposed reaction mechanism suggested the initial insertion of the Rh(I) species into the Si-H bond followed by oxidative addition of the proximal alkyl sp³C-H bond to the Rh species followed by dehydrogenation and formation of the sp³C-Si bond.⁶⁹ Further studies led the same group to propose the catalytic mechanism presented later in Scheme 49. This regioselective reaction can also be performed without aromatic ring such as from H-Si(^{*n*}Bu)₃ by silylation of alkyl sp³C-H bond,⁶⁹ as it was also observed with a platinum catalyst (see Equation 4).⁴⁰



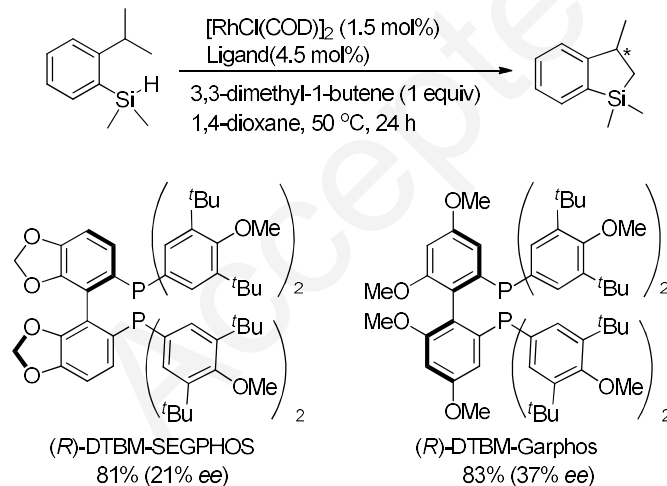
Scheme 46. Rhodium-catalyzed intramolecular silylation of unactivated sp^3C-H Bonds.

Later the same Kuninobu-Takai group⁷⁰ showed the strong influence of the phosphine ligand on the efficiency of the $[RhCl(COD)]_2$ catalyst as well as the required presence of an alkene. For instance (*R*)-DTBM-SEGPHOS and 3,3-dimethyl-1-butene appeared to be excellent partners for intramolecular silylation at β - sp^3C-H bond of the alkyl group as shown in scheme 47.



Scheme 47. Rhodium-catalyzed dehydrogenative silylation leading to 2,3-dihydro-1H-benzo[*b*]siloles.

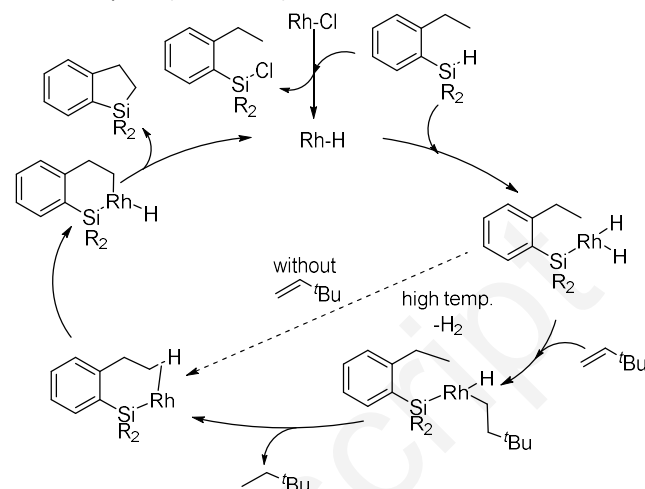
More importantly, the use of chiral SEGPHOS or GARPHOS diphosphine allowed the enantioselective intramolecular methyl silylation of 2-isopropyl phenylsilane although in modest enantiomeric excess. (Scheme 48)⁷⁰



Scheme 48. Rhodium-catalyzed enantioselective sp^3C-H Bond silylation with chiral diphosphines.

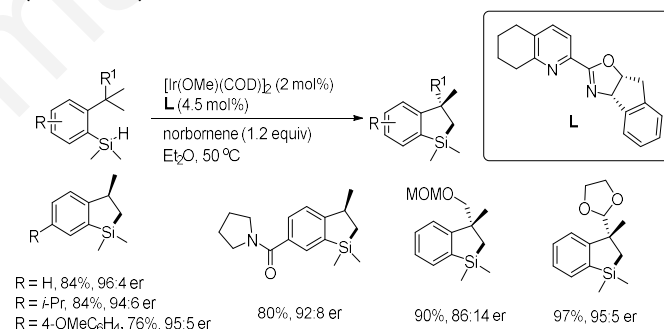
The proposed mechanism of the reaction involves first the initial transformation of the Rh-Cl into the Rh-H bond by reaction with silane followed by oxidative addition of the Si-H bond to the Rh-H moiety. The dehydrogenation with the help of the alkene proceeds

by its insertion into Rh(III)-H bond and alkane elimination. The insertion of the resulting Rh(I) species into the neighbour alkyl β -C-H bond, followed by reductive elimination to form the Si-C bond can then take place (Scheme 49)⁷⁰.



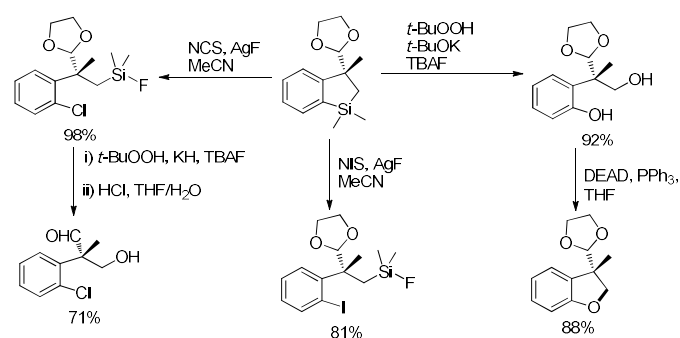
Scheme 49. Proposed reaction mechanism for intramolecular silylation of alkyl group with Rh(I) catalyst.

More recently Hartwig *et al.*⁷¹ have applied this reaction for the very efficient enantioselective intramolecular silylation of β -C-H bond of an alkyl group at *ortho* position of arylsilanes using $[Ir(OMe)(COD)]_2$ catalyst with optically active *N,N* bidentate ligand **L**. (Scheme 50)



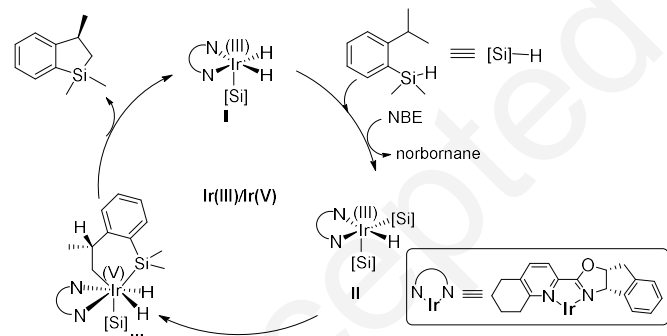
Scheme 50. Enantioselective intramolecular silylation of sp^3C-H bond with chiral Ir(I) catalyst.

The use of the chiral tetrahydroquinoline **L** led to high enantioselectivity (*e.r.* = 92.8 to 98.2) and good yield of the 5-membered cyclic dihydrobenzosiloles at 50° C but in the presence of norbornene as hydrogen trap. The reaction can be performed at a gram scale. The kinetic isotopic effect KIE of $kH/kD = 1.9$ for intramolecular silylation with the $CH(CH_3)_2/CH(CD_3)_2$ *ortho* alkyl groups suggested that the C-H bond cleavage is the rate determining step. The formed chiral dihydrobenzosiloles can be transformed easily by classical reactions of silanes into polyfunctional derivatives as some are illustrated in Scheme 51.⁷¹



Scheme 51. Transformations of the enantioenriched dihydrobenzosiloles.

Recently the Genping Huang group⁷² has studied the mechanism of Hartwig's reaction⁷¹ on intramolecular silylation of sp^3C-H bond in *ortho*-alkyl silyl arenes with the help of DFT calculations. First they showed that the $[Ir(OMe)(COD)]_2$ precursor on reaction with the chiral N^*N^* ligand and silane (*o*-alkyl)ArSiMe₂H led to the Ir(III) (N^*N^*)Ir(H)₂[Si] catalytic active species **I** (Scheme 52). The coordination of norbornene C=C bond allows its insertion into Ir-H bond and the resulting alkyl group interact with the remaining Si-H bond to eliminate the norbornane and to form the Ir-SiMe₂(aryl) intermediate **II**. The next key step involves the alkyl C-H bond interaction with the Ir(III) center, followed by C-H bond oxidative addition to form the Ir(V) intermediate (**III**). The reductive elimination with C-Si bond formation leads to the product and the catalytic species **I**. The reductive elimination from **III** cannot take place directly but occurs after initial Ir-hydride silyl group Ir-H...[Si] interaction. The DFT calculation shows that both electronic and steric effects contribute to create the enantioselectivity.

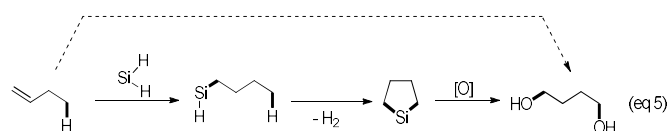


Scheme 52. Catalytic cycle based on DFT calculations of intramolecular silylation of sp^3C-H bond.

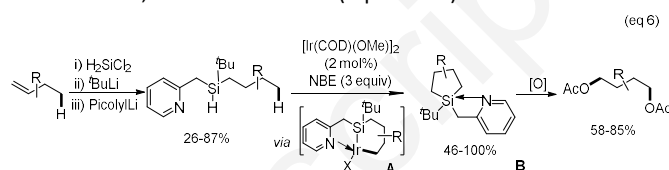
Another recent example of intramolecular silylation of azylsilanes with Ru(II) catalyst will be described later (Scheme 60)

7.2 From alkylsilanes arising from in situ hydrosilylation of C=C bonds

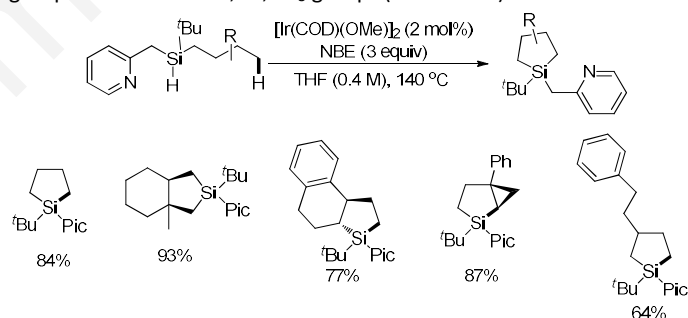
Gevorgyan *et al.*⁷³ have contributed to formally transform an alkene into a 1,4-diol *via* hydrosilylation of the alkene C=C double bond first with R_2SiH_2 , followed by regioselective sp^3C-H bond intramolecular dehydrosilylation at the δ -carbon of the resulting alkylsilane, to form a 5-membered silolane which on oxidation selectively leads to 1,4-diol. (Equation 5)



The silylation reactions are promoted by $[Ir(OMe)(COD)]_2$ as catalyst. The success required first the introduction of a picolyl directing group at the silicon atom to allow the oxidative addition of the neighbour Si-H bond at the picoline coordinated Ir(I) center and then the efficient oxidation. Then the δ sp^3C-H bond activation at the Iridium center is expected to release hydrogen, trapped by norbornene (NBE), to give intermediate **A** followed by C-Si bond formation to give cyclic silolane **B**. Then the oxidation of the silolane leads to the 1,4-diol or diacetate. (Equation 6)

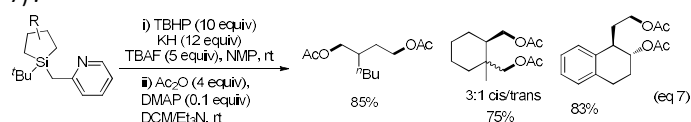


Thus a variety of silolanes have been produced from the silane containing the H-SiCH₂CH₂CH₂CH₃ arrangement and the picolyl (Pic) directing group. The presence of ^tBu group linked to silicon allowed the stability of the silane. The activation of primary δ -CH₃ is favoured versus that of δ -CH₂Ar and the silylation of δ -C-H bond of a cyclopropyl group is possible. The reaction tolerates many functional groups such as Ar-X: Cl, Br, CF₃ groups (Scheme 53).

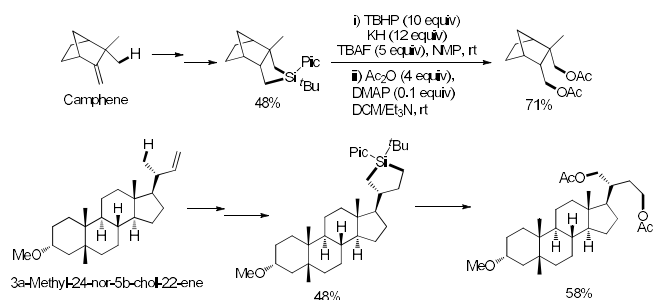


Scheme 53. Ir(I)-catalyzed δ -C-H dehydrogenative silylation reaction and formation of silolanes.

The oxidation of the silolanes by TBHP/KH and then the treatment with Ac₂O allow the selective formation of 1,4-diacetates. (Equation 7).⁷³



Similarly Camphene, 2-methylenebornane and a derivative of lithocholic acid were selectively transformed into their 1,4-diacetate derivatives (Scheme 54).⁷³



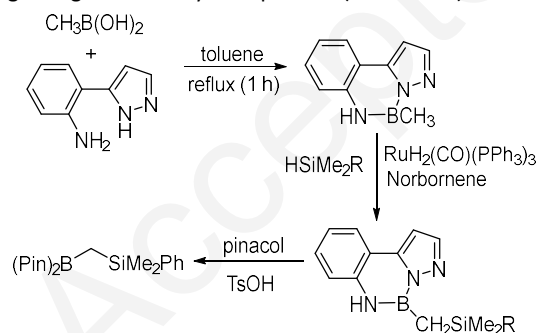
Scheme 54. 1,4-oxygenation of alkene containing natural products via hydrosilylation, silylation of sp^3C-H bond and oxidation.

8. Intermolecular catalyzed sp^3C-H bond silylation of $X-CH_3$ into $X-CH_2SiR_3$ groups ($X = B; Si; O; N; S$)

A variety of sp^3C-H bond silylations of groups of type $X-CH_3$ ($X = B; Si; O; N; S$) has been performed, either directed by a functional group or without. The resulting products of type $X-CH_2SiR_3$ thus allow a variety of functionalizations into $X-CH_2-FG$ derivatives which cannot be reached directly from the $X-CH_3$ group. This part will describe such $X-CH_3$ silylations and some of the related functionalizations.

8.1 Directed silylation of the $B-CH_3$ group

Directed silylation of the $B-CH_3$ group was performed by Sugimoto as soon as 2011⁷⁴. He first succeeded to silylate the methyl group linked to the boron in boronic acid $CH_3B(OH)_2$ with a ruthenium catalyst but using 2-(1H-pyrazol-3-yl)aniline (PZA) as a removable *ortho* directing group. Thus the resulting methyl boronic derivative reacts with a variety of trialkylsilanes, promoted by $RuH_2(CO)(PPh_3)_3$ catalyst which easily affords a classical $Ru(0)$ species via dehydrogenation. The reaction takes place in the presence of norbornene as hydrogen scavenger to give the α -silylated product (Scheme 55).



Scheme 55. α -functionalization of methylboronic acid via introduction of a N^N directing group with Ruthenium catalyst.

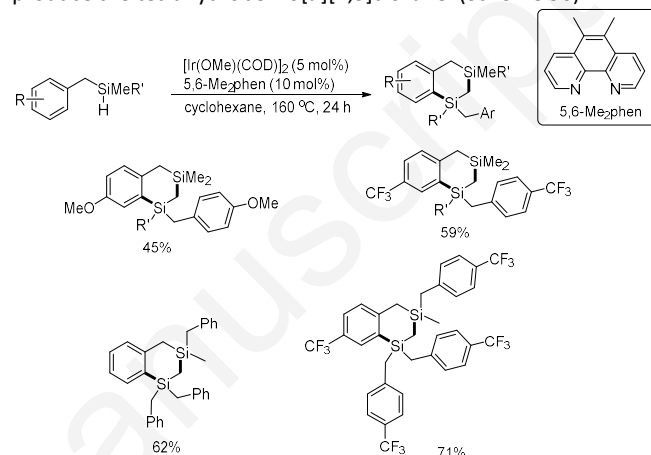
Analogous efficient directing groups can be used from 2-(1H-pyrazol-3-yl)phenol or anthranilamide for this reaction. The formed primary silylation products were treated with pinacol and TsOH to give the corresponding pinacol esters (Scheme 55).⁷⁴

Under similar conditions the silylation of the PZA derivative of ethylboronic acid led to α - and β -silylation of the ethyl group in similar yield. It is noteworthy that these pinacol esters derived from α -silylmethyl boronic acid $(Pin)_2B-CH_2SiMe_2Ph$ are good reagents for

the Suzuki-Miyaura C-C cross-couplings with aryl bromides with $Pd(0)$ catalyst to afford $Aryl-CH_2SiMe_2Ph$ derivatives.

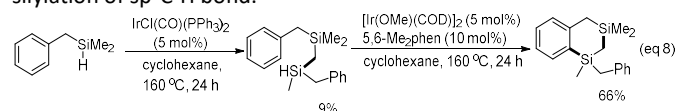
8.2 Silylation of the $Si-CH_3$ group with Ir(I) catalyst

Directed silylation of the $Si-CH_3$ group was recently observed in 2017 by Takai⁷⁵. They performed the novel combination of two molecules of $PhCH_2SiHMe_2$ by intermolecular silylation of a $SiCH_3$ group via initial sp^3C-H bond silylation of one $SiCH_3$ group to produce first the intermediate $PhCH_2(Me)_2Si-CH_2Si(H)(Me)CH_2Ph$ and formation of hydrogen in the presence of $IrCl(CO)(PPh_3)_2$ catalyst. The catalyst $[Ir(OMe)(COD)]_2$ with $Me_2Phenanthroline$ after the formation of $PhCH_2(Me)_2Si-CH_2Si(H)(Me)CH_2Ph$ further promoted the intramolecular silylation of the *ortho* sp^2C-H bond of one phenyl to produce the tetrahydrobenzo[*d*][1,3]disilane. (Scheme 56).

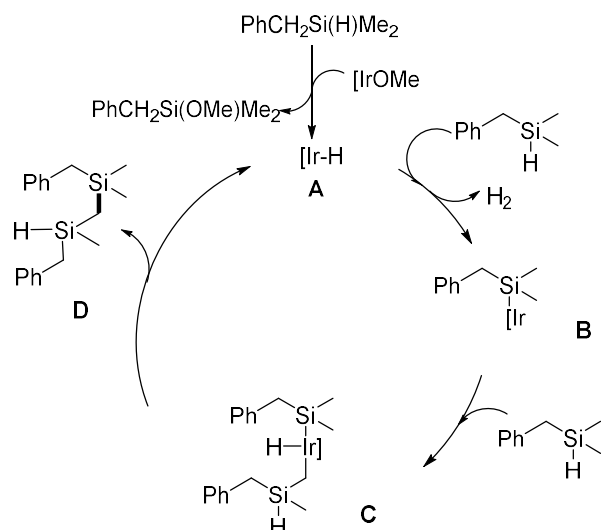


Scheme 56. Ir-catalyzed dehydrogenative dimerization of benzylmethylsilane.

It was shown that when the Vaska complex $IrCl(CO)(PPh_3)_2$ was used as catalyst the silylation of one $Si-CH_3$ group was observed first and the resulting product in the presence of $[Ir(OMe)(COD)]_2/Me_2Phen$ catalyst gave the disilane derivative (Equation 8). This shows the easyness of silylation of the methyl group and the importance of catalyst nature for successive intermolecular silylations of sp^3C-H bond and intramolecular silylation of sp^2C-H bond.⁷⁵

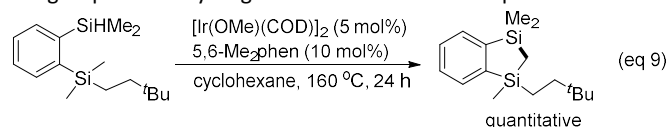


The proposed mechanism involves first the formation of Ir-H species **A** from the $Ir-X(Ln)$ catalyst and silane to give the formation of $Ir^I-SiMe_2CH_2Ph$ moiety **B** on elimination of H_2 . Then the oxidative addition of $H-C$ (methyl) bond of $HSiMe_2CH_2Ph$ to $Ir^I-SiMe_2CH_2Ph$ is expected to form the intermediate **C** which on reductive elimination forms the product **D** and regenerates the catalyst **A** (Scheme 57). Then the insertion of the Ir(I) center of $IrH(Phen)Ln$ into the $Si-H$ bond of **D**, elimination of H_2 and classical *ortho* sp^2C-H bond activation by the $Ir(I)(Phen)$ moiety should lead to sp^2C-Si bond formation by reductive elimination to give the disilane derivative.

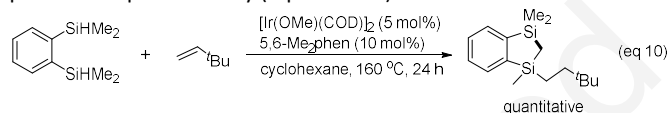


Scheme 57. Proposed mechanism for dehydrogenative dimerization of benzylmethylsilane.

The same catalyst $[\text{Ir}(\text{OMe})(\text{COD})]_2/5,6\text{-Me}_2\text{Phen}$ could be used by Takai⁷⁵ to perform the *intramolecular* $\text{sp}^3\text{C-H}$ bond silylation of a Si-Me group with dehydrogenation as described in equation 9.



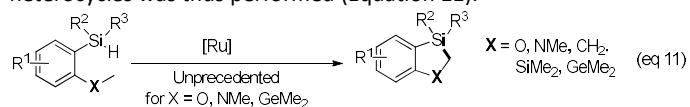
The intramolecular $\text{sp}^3\text{C-H}$ bond silylation of one methyl of 1,2-bis(dimethyl silyl)benzene with the same $\text{Ir}(\text{I})/5,6\text{-Me}_2\text{Phen}$ catalytic system in the presence of 3,3-dimethyl butene could also be performed quantitatively (Equation 10).⁷⁵



It is important to note that the above silylation reactions are efficient only for a SiCH_3 moiety as when one -SiHMe_2 group of 1,2-bis(dimethylsilyl)benzene is replaced by OMe or NMe_2 (Equation 10) the OCH_3 and NCH_3 group are not silylated.⁷⁵

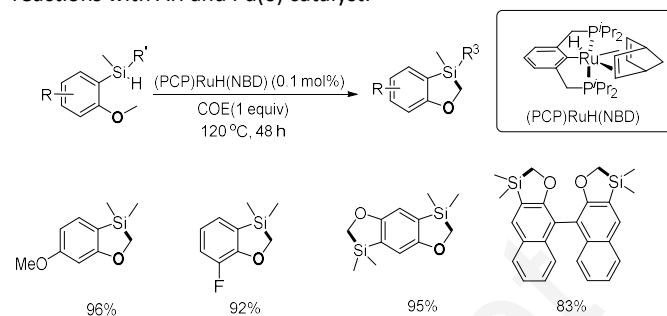
8.3 Silylation of the O-CH_3 , N-CH_3 , Si-CH_3 and Ge-CH_3 groups with Pincer Ru(II) catalyst.

Directed silylation of the O-CH_3 , N-CH_3 , $\text{Si}(\text{CH}_3)_2$ and $\text{Ge}(\text{CH}_3)_2$ groups has recently been solved with a Ru(II) catalyst. The previous problem of absence of intramolecular silylation by a H-SiR_2 *ortho* group of a $\text{sp}^3\text{C-H}$ bond of an *ortho* OMe or NMe_2 group has been solved in 2017 by Zheng Huang who introduced a pincer ruthenium(II) catalyst for catalytic silylations. The fast synthesis of [1,3]-oxasilolanes, azasilolanes, germsilolanes and [1,3]-disilaheterocycles was thus performed (Equation 11).⁷⁶



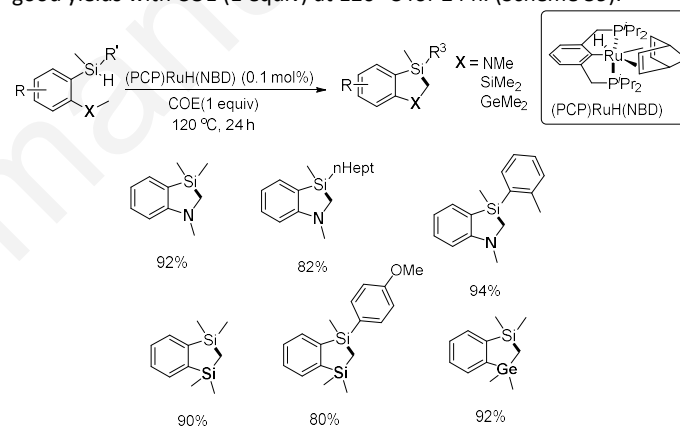
As shown in scheme 58 a low loading of pincer Ru(II) complex $(\text{PCP})\text{RuH}(\text{NBD})$ (0.1 mol%) allows the intramolecular $\text{sp}^3\text{C-H}$ bond silylation and formation of various [1,3]-oxasilolanes. The reaction takes place with hydrogen acceptor cyclooctene (COE) at 120 °C.

Other selected catalysts based on pincer Ir(III) complex offer low yield for silylation. This reaction could produce in one step 7.6 g of simple [1,3]-oxasilolane which can easily lead to cross coupling reactions with ArI and $\text{Pd}(\text{O})$ catalyst.⁷⁶



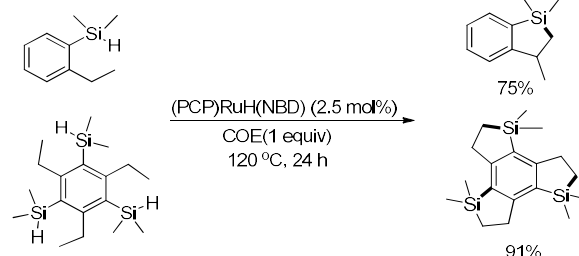
Scheme 58. Pincer-Ru(II)-catalyzed intramolecular silylation of $\text{sp}^3\text{C-H}$ bonds α to O-atom.

Previously the silylation of NCH_3 group was reported by Sato⁴³ but the C-H bond activation was assisted by pyridine as directing group (Scheme 6). The *intramolecular* silylation of methyl $\text{sp}^3\text{C-H}$ bonds of -NRCH_3 , $\text{-Si}(\text{CH}_3)_3$ and even $\text{-Ge}(\text{CH}_3)_3$ groups was performed, without assistance of a directing group, with the same pincer-Ru/COE catalyst by Zheng Huang⁷⁶. However the loading of catalyst had to be increased for $\text{Si}(\text{CH}_3)_3$ (5 mol%) and for $\text{Ge}(\text{CH}_3)_3$ (10 mol%) to reach good yields with COE (1 equiv) at 120 °C for 24 h. (Scheme 59).



Scheme 59. Pincer Ru-catalyzed intramolecular silylation of $\text{sp}^3\text{C-H}$ bonds α to N-, Si-, or Ge-atom.

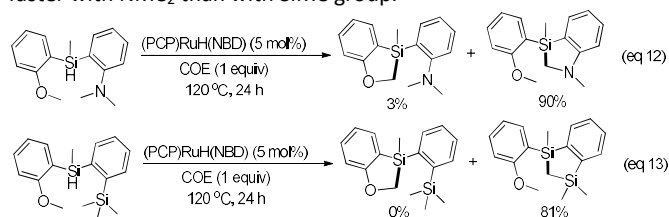
The silylation with pincer-Ru catalyst could also be performed at methyl primary $\text{sp}^3\text{C-H}$ bond of *ortho* alkyl group not attached to a hetero atom element in proximity with the Si-H bond (Scheme 60).⁷⁶ The intramolecular silylation of *ortho* alkyl of 2-alkyl arylsilanes was also observed previously using $\text{Rh}(\text{I})$ catalysts (see Schemes 45,46).⁶⁹



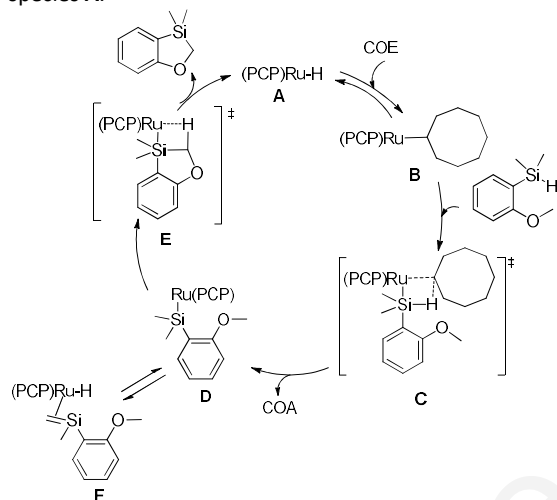
Scheme 60. Ru(II)-catalyzed intramolecular silylation of $\text{sp}^3\text{C-H}$ bonds at *ortho* alkyl $\beta\text{-C}$ -atom of arylsilanes.

To establish the relative reactivity of these (X-CH_3) C-H bonds, experiments were performed with this pincer Ru(II) complex (5

mol%) with COE (1 equiv) at 120 °C for 24 h and show that intramolecular silylation is faster with NMe₂ than OMe group (Equation 12) and faster with SiCH₃ than OCH₃ (Equation 13), and faster with NMe₂ than with SiMe group.⁷⁶



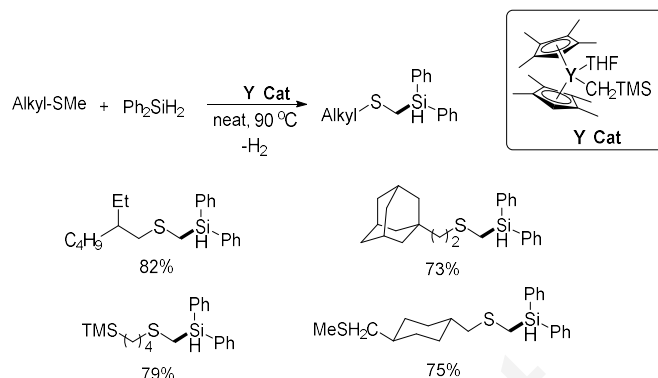
The observed H/D KIE of 3.9 suggests that the C-H bond cleavage is the rate determining step. The proposed mechanism based on exchange experiments is presented in scheme 61.⁷⁶ The formed cyclooctyl group from **B** assists in **C** the H-SiMe₂Aryl hydride elimination to give cyclooctane and **D**. Then the intramolecular interaction of (CH₃O)C-H bond with Ru-Si bond in **E** leads to C-H bond activation and Si-CH₂O bond formation to release the Ru-H catalyst species **A**.



Scheme 61. Proposed mechanism for the intramolecular sp³C-H silylation of *ortho* O-CH₃ group.

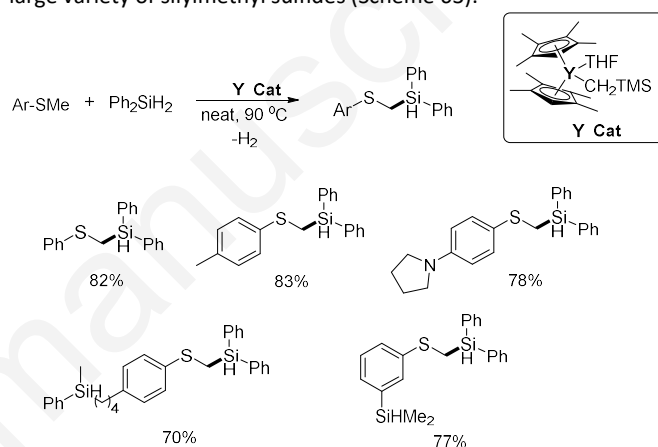
8.4 Silylation of the S-CH₃ group with Yttrium catalyst

Directed silylation of the S-CH₃ group was observed in 2018 for the first time by Zhaomin Hou *et al.*⁷⁷ The catalytic silylation of a sp³C-H bond of methyl sulfides RSCH₃ with H-SiR'₃ to produce RSCH₂SiR'₃ derivatives has been performed *intermolecularly* by using metallocene yttrium catalyst (C₅HMe₄)₂Y(CH₂SiMe₃)(THF) which appeared as the best catalyst precursor for this S-methyl C-H silylation. The catalyst precursor *in situ* gives in the presence of H₂SiR₂ the binuclear complex (C₅HMe₄)₂Y(μH)₂Y(C₅HMe₄)₂ as revealed for *n*-C₅H₁₁SCH₃ methyl silylation with PhMeSiH₂.⁷⁷ The same catalyst was the most efficient for the silylation of alkyl-SCH₃ sulfides *without alkene* as H₂ acceptor (Scheme 62).



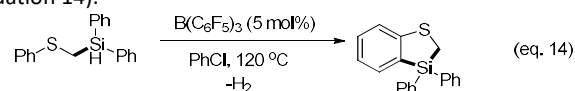
Scheme 62. Silylation of alkyl methyl sulfides with diphenylsilane and yttrium catalyst.

The same reaction with Yttrium catalyst can be applied to aryl methyl sulfides with diarylsilanes to give in neat medium at 90 °C a large variety of silylmethyl sulfides (Scheme 63).⁷⁷

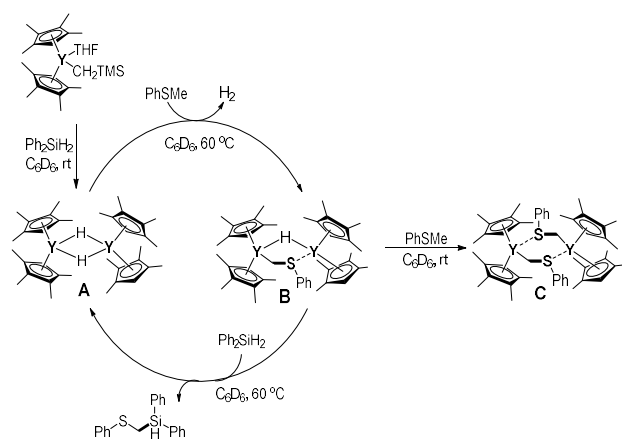


Scheme 63. Silylation of aryl methyl sulfides with diphenylsilane with metallocene yttrium catalyst.

The prepared silylmethyl sulfides can be used for further intramolecular silylation of *ortho* aryl sp²C-H bond to generate 5-membered annulated products in the presence of Lewis acid B(C₆F₅)₃ (Equation 14).⁷⁷



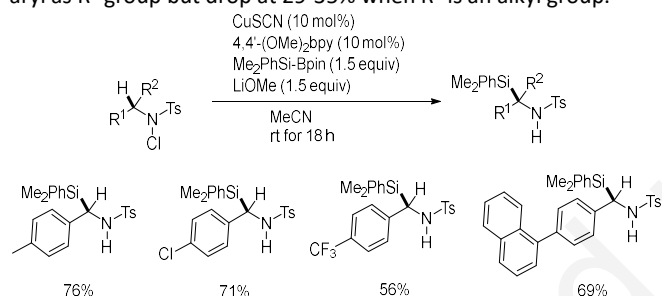
The proposed mechanism (Scheme 64) is based on stoichiometric reactions with silane with the catalyst precursor. With an excess of Ph₂SiH₂ at room temperature the formation of bimetalocene **A** containing bridged hydrides is observed. Complex **A** reacts at 60 °C with PhSCH₃ to give the characterized intermediate **B** with a Y-CH₂S(Ph)-Y bridge. The intermediate **B** can further lead to **C** with two identical -CH₂S(Ph)- bridges. Both **B** and **C** react with 5 equiv of Ph₂SiH₂ at 60 °C to give the PhSCH₂SiHPh₂ silane and to regenerate **A**.



Scheme 64. Mechanism for silylation of sp^3C-H bond of phenyl methyl sulfide with Yttrium catalyst.

8.5 Directed silylation of the $\alpha-C-H$ bond of (sulfonamide)XN-CHR₂.

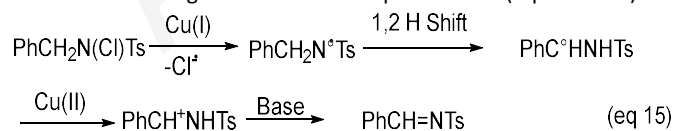
Recently Oestreich⁷⁸ has demonstrated the silylation of sp^3C-H bond adjacent to amide nitrogen atoms with $R_3Si-Bpin/alkoxide$. The reaction is catalyzed by $CuSCN/4,4'-(OMe)_2bpy$ (10 mol%). The silylation occurred easily with *N*-chloro sulfonamides and with $MePh_2Si-Bpin$ (Scheme 65). The yields are in the range 50–76% with aryl as R^1 group but drop at 29–35% when R^1 is an alkyl group.



Scheme 65. Copper-catalyzed silylation of sp^3C-H bonds adjacent to a *N*-chloro sulfonamide *N* atom.

Although the reaction presented here corresponds to the formation of a sp^3C-Si bond, it does not involve the formal silylation of sp^3C-H bond. Control experiments show that the initial step is the formation of the imine $PhCH=NTs$ in the presence of $LiOMe$ and the catalytic system $CuSCN/(MeO)_2bpy$. This imine in the presence of $Me_2PhSi-Bpin$ at room temperature gives the α -silylated product *via* classical Cu -catalyzed 1,2 addition of the silicon nucleophile.

It is possible that the imine formation, usually arising from base mediated β -elimination, is formed *via* initial formation of the radical $PhCH_2N^{\bullet}Ts$, by action of $Cu(I)$, rearranging into $PhCH^{\bullet}NHTs$ radical which can give, by action of $Cu(II)$, the cation intermediate $PhCH^+NHTs$ leading to the imine on deprotonation (Equation 15).

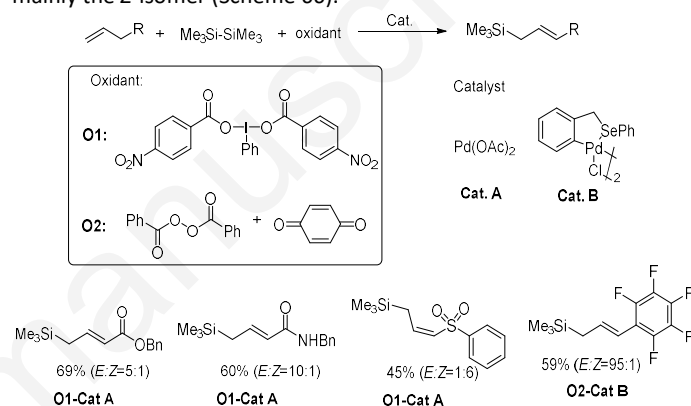


9. Silylation of allylic and alkane C-H bonds producing terminal CH_2-SiR_3 function

Some silylations leading to $sp^3CH_2-SiR_3$ bond formation will be presented here, although they do not involve a real sp^3C-H bond

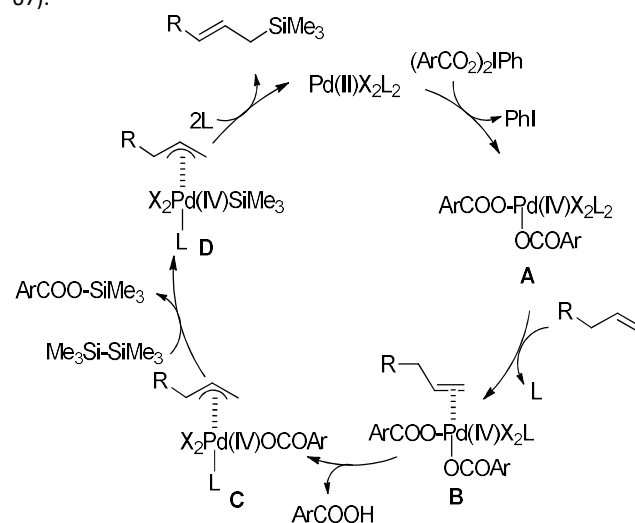
catalytic silylation. Three different examples reported by Swabó,⁷⁹ Peng-Fei Xu⁸⁰ and Zheng Huang⁸¹ will be presented here as they constitute useful approaches to produce reactive $sp^3CH_2-SiR_3$ from allylic compounds and from initial alkane dehydrogenation. The first one involves a classical $Pd(II)/Pd(IV)$ activation of alkene into allyl derivatives,⁷⁹ the second one involves a silyl radical formation able to regioselectively add to allylic $C=C$ bond⁸⁰ and the third presents the dehydrogenation of alkanes followed by isomerization and hydrosilylation of resulting alkenes.⁸¹

In 2011 Swabó described the catalytic silylation with $Me_3Si-SiMe_3$ of a functional allylic group with sp^3C-Si bond formation.⁷⁹ The reaction was catalyzed by $Pd(OAc)_2$ or a $Pd(II)$ -cyclometalate complex but the reaction needed a strong oxidant such as hypervalent iodine reagent $(ArCO_2)_2IPh$, but also $PhOCO-COOPh$ with benzoquinone or 4-nitro benzoic acid. This oxidant prevents the use of a hydrogen acceptor such as an alkene. The reaction at 80 °C for 48 h offers preferably the stereoselective formation of the *E*-isomer, except for the allyl sulfones and the allylsulfonamides which provide mainly the *Z*-isomer (Scheme 66).



Scheme 66. Synthesis of allylsilanes by catalytic C-H silylation.

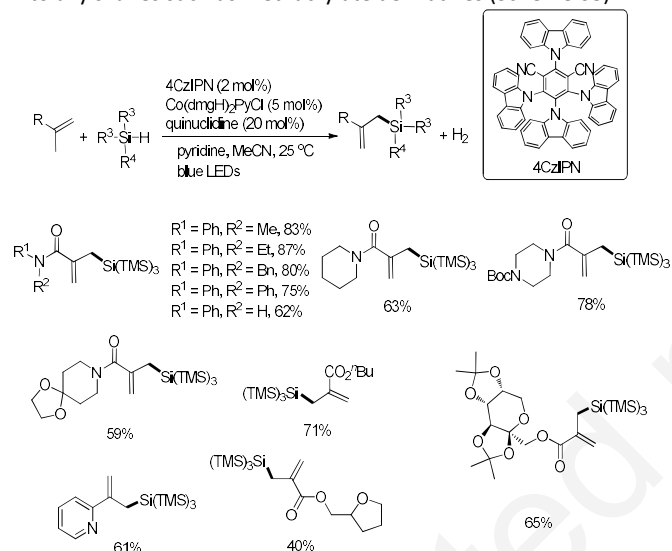
The proposed mechanism (Scheme 67) suggests the initial formation of a $Pd(IV)$ intermediate **A** on oxidation of $Pd(II)$ with $(ArCO_2)_2IPh$. Coordination of the allyl double bond in **B** is followed by π -allyl ligand formation in **C** on C-H bond deprotonation with a carboxylate. Then transmetalation with $Me_3Si-SiMe_3$ leads to the intermediate **D** which is subject to reductive elimination with sp^3C-Si bond formation with the less substituted allylic carbon to generate the silylated functional allyl derivative and $Pd(II)$ catalyst. (Scheme 67).



Scheme 67. Proposed catalytic cycle for silylation of functional allyl

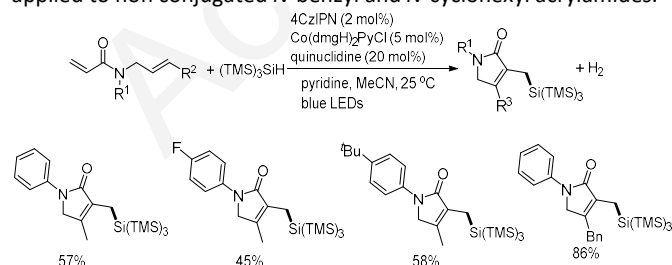
group.

Photocatalysts have been successfully used for the selective functionalization of C-H bonds, but mostly till now of sp^2 C-H bonds.⁸² However recently Peng-Fei Xu *et al.*⁸⁰ have reported a new method to generate substituted allylsilanes by dehydrogenative silylation of alkenes with $H-SiR_3$. The silylation does not involve the functionalization of C-H bond but regioselectively takes place by addition of a silyl radical at the terminal carbon of the allyl C=C bond $RC(CH_3)=CH_2$ to form a terminal CH_2-SiR_3 bond. The reaction involves the initial generation of a $R_3Si\cdot$ radical by hydrogen atom transfer (HAT) catalysis and the reaction is promoted by an organic photocatalyst and a Co(II) catalyst $Co(dmgH)_2Cl(Py)$ (dmg = dimethyl glyoximate) for single electron transfer (SET) (Scheme 68). The dehydrogenative silylation of alkenes was performed with photocatalyst 4CzIPN using blue LEDs with $Co(dmgH)_2(Py)Cl$ for single electron transfer (SET) and quinuclidine as HAT catalyst in the presence of pyridine as a required base. A large variety of functional alkenes were selectively transformed at room temperature in MeCN, into allylsilanes such as methacrylate derivatives (Scheme 68).



Scheme 68. Dehydrogenative radical silylation of alkenes into allylsilanes with multiple catalysis.

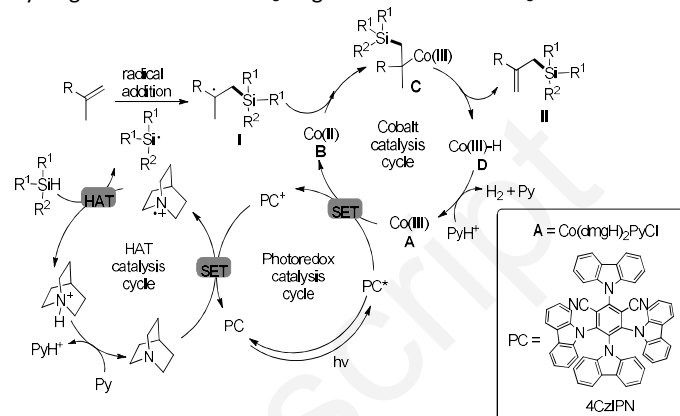
This tricatalytic system was applied to *N*-allyl-*N*-arylacrylamides to produce related cyclic silylated products with a terminal CH_2SiR_3 group: 5-membered α,β -unsaturated γ -lactams *via* 5-exo-trig cyclization (Scheme 69). This general transformation was also performed at the gram scale. However the reaction could not be applied to non conjugated *N*-benzyl and *N*-cyclohexyl acrylamides.



Scheme 69. Dehydrogenative radical silylation of *N*-allyl arylamides and 5-exo-trig cyclization.

This transformation involves the formation of radical intermediates as it is inhibited by radical trap TEMPO. The proposed mechanism is

shown on Scheme 70.⁸⁰ The reaction requires the presence of a photocatalyst **PC** (4CzIPN) which on excitation with blue LED generates the excited **PC*** which is oxidized by Co(III) species **A** giving **PC*** cation and Co(II) species **B**. ($E_{1/2}^{red} Co(III)/Co(II) = -0.68V$ vs SCE). Then the **PC*** = 4CzIPN⁺ species ($E_{1/2}^{red} P^+/P = +152V$ vs SCE) oxidizes the HAT catalyst quinuclidine **Q** ($E_{1/2}^{red} = +1.10V$) to give **Q*** and initial photocatalyst **PC**. The radical cation **Q*** is able to trap the hydrogen atom from $H-SiR_3$ to generate the radical $R_3Si\cdot$.

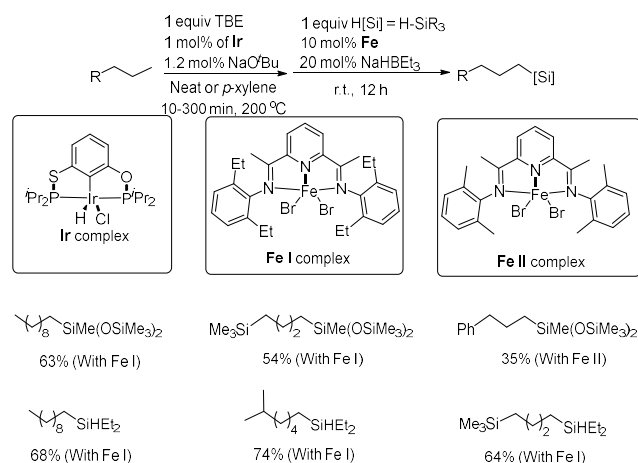


Scheme 70. A proposed mechanism for dehydrogenative silylation of alkenes into allylsilanes.

Subsequent addition of the $R_3Si\cdot$ radical to the terminal carbon atom of the alkene generates the carbon center radical which adds the Co(II) species **B** arising from the reduction of the initial Co(III) species **A** by SET from **PC***, to give **C**. The later *via* classical beta elimination generates the new alkene with an allyl silyl group **II**. The resulting Co(III)-H species **D** on protonation with PyH^+ releases H_2 and the initial Co(III) catalyst **A**.

This new synergetic catalytic reaction to form $CH_2=CH(R')-CH_2SiR_3$, from $CH_3-CH(R')=CH_2$, does not involve a direct C-H bond functionalization, but the formation of silyl radical, has a strong potential to produce regioselectively functional allylsilanes and to open new selective silylations.

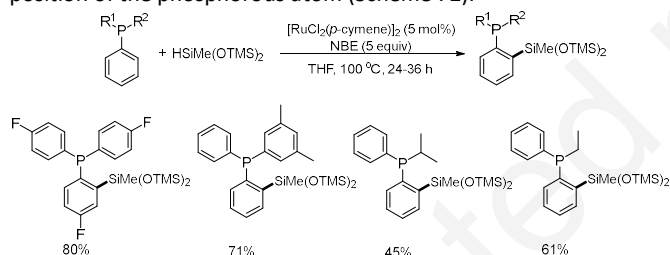
Linear alkylsilanes are one of the most important compounds for the wide applications to lead to coatings, silicone rubbers and moulding products. Hydrosilylation of terminal olefins is the most efficient method for the synthesis of linear alkylsilanes, but the direct and selective functionalization of alkanes at primary C-H bonds into a C-Silyl group have been seldom reported in spite of their importance. However, Zheng Huang *et al.* in 2015⁸¹ reported a new method to produce linear alkylsilanes *via* a dual-catalyst system, one pot and three-step alkane silylation. These catalytic systems involve a pincer-ligated Ir(III)-catalyzed alkane dehydrogenation to generate internal olefin and Fe catalyzed successive regioselective olefin isomerization and hydrosilylation (Scheme 71).⁸¹ The (PNN)FeBr₂ complex is ineffective for the hydrosilylation of internal olefins, but plays two important roles for the catalytic system, i) the fast isomerization of internal olefins, produced by Ir catalyzed alkane dehydrogenation, into the terminal olefin and ii) the catalyzed Markovnikov hydrosilylation of the terminal alkenes to yield terminal alkylsilanes.



Scheme 71. Catalytic silylation of various alkanes via catalytic alkane dehydrogenation and isomerization–hydrosilylation.

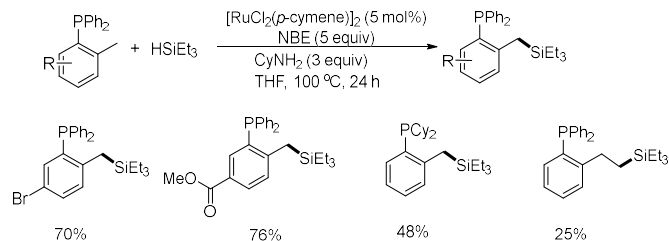
10. Catalyzed sp^3C -H bond silylation directed by phosphine P(III) atom

Quite recently Zhuangzhi Shi⁸³ explored the possibility to silylate aryl sp^2C -H bond of P(Aryl) R_2 phosphines, with H-SiEt₃ or HSiMe(OTMS)₂ and Ru(II) catalyst precursor [RuCl₂(*p*-cymene)]₂. In spite of the difficult formation of a strained 4-membered cyclometalate intermediate, directed by a phosphine phosphorous(III) atom, with P-Ru-C(*ortho*) bond formation and via deprotonation of the *ortho* aryl sp^2C -H bond, the dehydromonosilylation was efficient in the presence of norbornene as hydrogen acceptor at 100 °C at the *ortho* position of the phosphorous atom (Scheme 72).



Scheme 72. Ruthenium(II) catalyzed *ortho* silylation of arylphosphine sp^2C -H bond.

More importantly, when an *ortho* methyl group was present on the aryl group of the phosphine, the ruthenium(II) catalyzed dehydrosilylation of methyl sp^3C -H bond with H-SiEt₃ took place easily at 100 °C in THF but with additional CyNH₂ as a base (Scheme 73).⁸³ The observed silylation shows that the mono silylation of sp^3C -H bond at *ortho* methyl group is easier than at the *ortho* sp^2C -H bond as no *ortho* sp^2C -H arylation was now observed. The *ortho* methyl arylation seems to be favoured by the presence of an electron withdrawing group on the aryl group (Cl, F, Br, CO₂Me). When an *ortho* ethyl group is present instead of a methyl group, the silylation takes place at primary C-H bond (Me) rather than at the secondary (CH₂) C-H bond.



Scheme 73. Ru-catalyzed sp^3C -H silylation of *ortho* methyl group in arylphosphines.

The transformation of the *ortho*-CH₂SiEt₃ group, of the triaryl phosphines prepared as shown in scheme 73, into a CH₂CH(OH)Ph group can be easily performed on reaction with PhCHO in the presence of the salt N(^tBu)₄⁺F⁻ at 60 °C.⁸³

This mild condition, intermolecular silylation of alkyl group of phosphine ligands likely takes place via deprotonation by CyNH₂ of the methyl or ethyl sp^3CH bond on interaction with the Ru(II) center to form a 5-membered cyclometalate, or 6-membered cyclometalate from ethyl group, as deprotonation assisted by Ru(II) site requires low energy.⁸⁴⁻⁸⁵ This simple silylation has potential to modify many useful phosphorous ligands already used in metal-catalyzed reactions.⁸⁶

Conclusions and Outlook

Several methods of metal-catalyzed activation of sp^3C -H bonds synchronized with silylation of this sp^3C carbon to produce sp^3C -SiR₃ bonds are now efficient to modify functional molecules, ligands to build catalysts or molecular materials, and to offer functionalizations of silicon containing products. *Intermolecular* silylations of a variety of sp^3C -H bonds can be directed by a N-containing heterocycle in the presence of silane and of various catalysts based on Ru(0), Ru(II), Rh(I), Ir(I) and Ir(III) metal complexes. The transformation is based on heterocycle directed sp^3C -H bond metal activation and Si-H bond metal activation with hydrogen elimination which can be solved with addition of an alkene as hydrogen trap. This regioselective formation of CH₂SiR₃ groups allows their easy transformations such as via oxidation and carboxylation. *Intramolecular* sp^3C -H bond silylation with R₃Si-SiR₃ can be directed by an amide type function in the presence of Pd(II) catalyst which involves first a sp^3C -H bond deprotonation and palladacycle formation usually followed by oxidative addition of the silane Si-Si bond and formation of the C-Si bond. This method can be successfully applied to the stereoselective sp^3C -H bond silylation of aminoacids and peptides.

The *intramolecular* silylation of sp^3C -H bonds can be performed, after initial formation of a R'CH₂O-SiR₂(H) group, by catalytic dehydrohydrosilylation of alcohols or hydrosilylation of ketones with H₂SiR₂. The R'CH₂O-SiR₂(H) groups lead to 5- or 6-membered oxasiloxanes in the presence of Ir(I) or Rh(I) with an alkene for hydrogen capture. This silylation is currently used for the access to 1,3- and 1,4- diols from alcohols with a sp^3C -H bond at γ or δ position. Similarly initial silylation of amine NH bonds into N-SiR₂H group allows further *intramolecular* silylation of neighbour sp^3C -H bond with Ir(I) catalyst with H₂ trap alkene. Both catalytic silylation steps can be performed in one pot with the same Ir(I) catalyst but on addition of alkene for the second intramolecular step. The sp^3C -H silylation step can be controlled, on addition of chiral diphosphine, to reach good enantioselectivities especially in the functionalization of cyclopropyl derivatives.

Silanes containing a C-SiR₂H group at the proximity of a CH₂R group, such as in ortho alkyl arylsilanes can lead to an intramolecular catalytic silylation of one sp³C-H bond with formation of 5-membered silanes with Rh(I) or Ir(I) catalyst mostly in the presence of an alkene. The addition of chiral dinitrogen ligand to the Ir(I) catalyst can lead to excellent enantioselectivities. Alkyl silanes arising from initial catalytic hydrosilylation of terminal alkenes leads also to intramolecular silylation into 5-membered cyclic silanes. This reaction on oxidation offers new access to 1,4-diols.

Intermolecular and intramolecular sp³C-H bond silylation of X-CH₃ into X-CH₂SiR₃ group can be performed with a variety of heteroatoms X (X = B, Si, O, N, Ge, S). B-CH₃ groups are silylated after addition of a dinitrogen bidentate ligand to boronic acid, with the help of Ru(0) catalyst precursor. Intermolecular silylation of SiCH₃ bond with Ir(I)/Phenanthroline catalyst can be directed for the production of 5- and 6- membered 1,3-disilanes. By contrast pincer-Ru(II)-H catalyst allows the intramolecular silylation of XCH₃ groups (OCH₃, NCH₃, Si-CH₃ and Ge-CH₃) C-H bonds to produce 5-membered cycles with X-CH₂-Si arrangement. The intermolecular silylation of alkylSCH₃ and arylSCH₃ can now be easily achieved using an yttrium metallocene catalyst.

Formal silylation of allyl group CH₃-C(R)=CH₂ into useful function CH₂=C(R)-CH₂SiR₃ can be performed in several ways although they do not involve direct sp³C-H bond silylation. 1) Pd(II) catalysts with an oxidant are used for the silylation with Me₃Si-SiMe₃ of allyl group, via allyl-Pd(IV) intermediate. 2) A photocatalyst associated to a cobalt(III) catalyst has been used to generate a silyl radical from silane, via hydrogen atom transfer (HAT), which can add to the allyl C=C bond to further produce CH₂=C(R)-CH₂SiR₃ derivatives. 3) A 3-step alkane silylation into terminal linear alkyl silane alkyl-CH₂SiR₃ can be performed using a Ir(III) catalyst to dehydrogenate the alkane into alkenes and a Fe(II) catalyst to isomerize the produced internal alkenes into a terminal alkene and to hydrosilylate this terminal alkene into linear alkylsilane.

Finally a new useful orientation for the silylation of a sp³C-H bond has just been performed via the silylation directed by a (phosphine)P(III) atom for the regioselective silylation of an *ortho* methyl of arylphosphine, with a Ru(II) catalyst in the presence of alkene. This new reaction should allow fast modification by sp³C-H bond silylation of a variety of phosphine or diphosphine ligands containing alkyl groups.

These successful examples show that classical noble metal catalysts mostly derivatives of Ru, Rh, Ir and Pd metals are required for both the sp³C-H bond activation and the Si-H or Si-Si bond activation, for sp³C-Si bond formation. Recently many examples of sp³C-H bond activation to make sp³C-C bond cross-couplings have been discovered with first row metal catalysts (Mn, Fe, Co),⁸⁷⁻⁹⁰ thus we can expect that these cheap and less toxic metal catalysts will also inspire chemists to perform with them sp³C-H bond catalytic silylations.

The first evidence for direct catalytic silylation of a methyl group graphed on an aryl group of phosphine into a aryl-CH₂SiR₃ group suggests that in the near future useful phosphines or diphosphines, even chiral ones, can be modified by the introduction of a steric hindered group CH₂SiR₃ or which can be transformed into a new function to quickly reach new functional ligand and their metal catalysts as it is already shown for phosphine sp²C-H bond functionalization.^{86, 91-92}

This easy transformation of sp³C-H bond into CH₂SiR₃ group has already allowed the direct access to carboxylates, alcohols, diols, esters, or aminoalcohols, sometimes with excellent enantioselectivity. Thus these reactions should allow new

functionalizations leading to natural products but also to modify in one pot reaction monomers for further polymerization or polymers themselves,⁹³⁻⁹⁴ or the physical properties of molecular materials,⁹⁵ including luminescence properties.⁹⁶⁻⁹⁷ One can even expect that in the near future that catalytic sp³C-H bond silylation can be applied to directly modify metal-complexes and their optical properties,⁹⁸ or to produce more efficient catalysts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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