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Metal-catalyzed silylation of sp^3C–H bonds†‡

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Metal-catalyzed activations of inert sp^2C–H and sp^3C–H bonds have recently brought about 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 in the formed sp^3C–SiR_3 silanes, a stable organometallic species, for carrying out further functionalizations that cannot be directly achieved using sp^3C–H bonds. 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 high reactivity of the sp^3C–SiR_3 group. 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 using various Ru, Rh, and Ir catalysts and then directed by an amide type function using a Pd(II) catalyst and R_3Si–SiR_3 reagent. The catalytic intramolecular silylations of sp^3C–H bonds can be performed after the 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 using 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 the allylic moiety CH_3–C(R)=CH_2 into its 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 a P(III) atom, will be presented.

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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 functionally useful molecules and molecular materials, often *via* cross-coupling of C–C bonds with better atom economy.[1–13] Due to the high reactivity of C–SiR_3 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 which are difficult to achieve directly from C–H bonds. In addition, C–Si bonds are rather stable, and thus the formed silanes can tolerate different 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 were first developed and several reviews have already illustrated the success of the catalyzed silylation of sp^2C–H bonds and the usefulness of this approach. Chatani in 2003[14] and Goldman in 2011[15] discussed early examples of silylation of sp^2C–H bonds using ruthenium and iridium catalysts. Marciniec in 2005[16] collected the catalyzed silylations of alkene C–H bonds and in 2012[17] Hartwig 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. Hartwig,[18] U. Sharma,[19] C. Wang,[20] and Z. Xu,[21] and the first three of them[18–20] included

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the first examples of catalyzed sp^3C–H bond silylations. Shang and Liu[22] collected in 2016 the silylations of sp^2C–H bonds *via* radical processes. It is noteworthy that in 2017 M. Oestreich presented 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 of the synthesis of reactive sp^3C–Si bonds[25] their catalytic formation directly from sp^3C–H bonds has been much less developed than from sp^2C–H bonds. However, sp^3C–SiR_3 groups undergo easy transformation by oxidation into alcohols[26,27] or into carboxylates directly from CO_2.[28] They also give cross-coupling reactions with suitable electrophiles,[29,30] amination[31,32] or halogenation[33,34] including fluorination.[35,36] In addition, the direct catalytic formation of a reactive sp^3C–Si bond directly from an sp^3C–H bond offers a greener alternative to produce reactive silanes rather than from silylhalides, from lithium or Grignard reagents or from hydrosilanes with alkylchorides.[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 earlier have been presented in the early 2015 reviews by J. F. Hartwig,[18] U. Sharma,[19] and C. Wang.[20] After highlighting these first examples, this review will discuss all examples of metal-catalyzed sp^3C–H bond silylations since 2015 in more detail. 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, and 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 the 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–SiR_2H groups with Ir(I) catalyst and a hydrogen acceptor and (iii) the intramolecular silylations of unactivated sp^3C–H bonds but in proximity to Si–H bonds of arylsilanes and alkylsilanes using an Ir(I) catalyst.

– The intermolecular catalyzed sp^3C–H bond silylations of X–CH_3 groups into X–CH_2SiR_3 groups (X = B, Si, O, N, Ge, S), will then be discussed. They are mostly promoted by Ru(II) and Ir(I) catalysts in the presence of alkenes, with the exception of an yttrium catalyst for SCH_3 group silylation and copper catalysts for alkylsulfonamide silylation. Finally, formal silylations of allylic C–H bonds and the unique and promising example of a catalyzed methyl sp^3C–H bond silylation reaction directed by phosphine will be presented.

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

The first examples of the catalytic silylation of a sp^3 C–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

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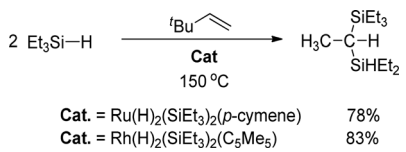
Pierre H. Dixneuf is Emeritus, Research Professor in Rennes, Bretagne, France. He created a Homogeneous Catalysis Center in Rennes in 1985: Ruthenium(II) in catalysis, C–C bond formation from alkynes, vinylidenes, cumulenes, enantioselective formation of amines, and alkene metathesis with indenylidene-ruthenium catalysts. He has pursued his current topic of C–H bond functionalisation since 2008, using ruthenium(II)-carboxylate catalysts for (hetero)-arylations and alkenylations, including in water, and Rh(I) catalysts for modification of phosphines to improve catalyst systems. He has received international awards for research including: IUFrance member 2000, IFP-Academy of sciences 2006, Germany (A. v. Humbold, Wittig), Italy (Sacconi), Spain (Catalan), Chinese Chem. Soc. (1st prize to French Chemist in 2014), Academy of Sciences member: European EASA 2014, Portugal 2017, Indian, NASI 2020.

and observed the activation/cleavage of benzene sp^2C–H and mesitylene sp^3C–H bonds to form related C–Si bonds (Scheme 1).

When benzo-1,2-disilacyclobutene with a $Ni(PEt_3)_4$ catalyst was refluxed in benzene, it led to the cleavage of one benzene sp^2C–H bond and the formation of one Si–C(sp^2) and one Si–H bond (Scheme 1a). The same reaction performed in deuterated benzene led to the disilyl product with Si–C_6D_5 and Si–D bond formation (Scheme 1b). In contrast, the use of mesitylene as the solvent led to one methyl sp^3C–H bond activation and then silylation with the formation of sp^3C–Si and Si–H bonds (Scheme 1c). The catalytic functionalization of C–H and C–D bonds is explained *via* their oxidative addition to the disilylnickel intermediate followed by the formation of Si–C and Si–H bonds (Scheme 1d).

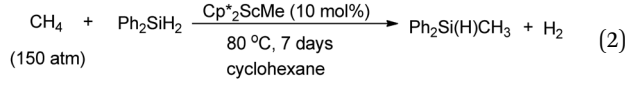
In 1994 an example of sp^3C–H bond silylation of an ethyl group was observed by Berry *et al.*[38] in their study of the hydrosilylation of an alkene ^{t}BuCH=CH_2 with Et_3SiH in the presence of Ru and Rh catalysts at 150 °C. Actually, besides the low production of silylated alkene, they observed a high yield of dihydrogenative dimerization of Et_3SiH into $CH_3CH(SiEt_3)(SiHEt_2)$ with a new sp^3C–Si bond (eqn (1)).



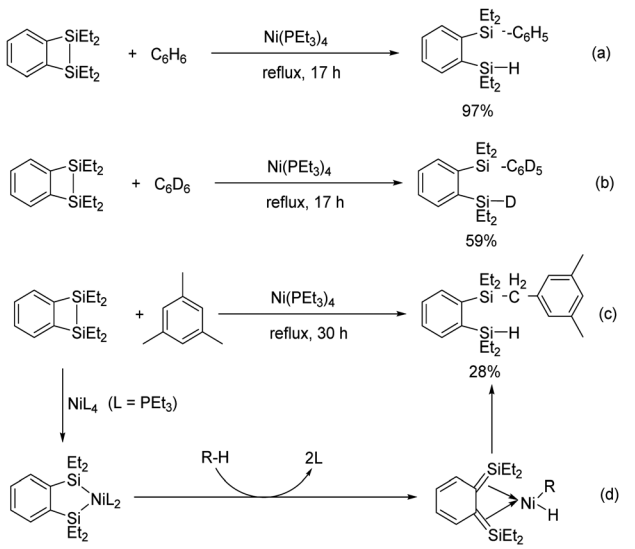
(1)

Cat. = $Ru(H)_2(SiEt_3)_2$(*p*-cymene) 78%
Cat. = $Rh(H)_2(SiEt_3)_2(C_5Me_5)$ 83%

Another unique non-directed silylation of sp^3C–H bonds was observed by Tilley[39] in 2003 during the reaction of methane (150 atm) with H_2SiPh_2 at 80 °C using the scandium catalyst Cp^*_2ScMe (eqn (2)).

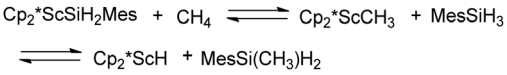


(2)



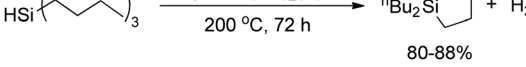
Scheme 1 Ni(0)-Catalyzed silylation of sp^3C–H bonds with benzo-1,2-disilacyclobutene.

$Cp^*_2ScSiH_2Mes$ has been shown to react with CH_4 to give $Cp^*_2SiCH_3$ and $MesSiH_3$ and then Cp^*_2ScH and $MesSi(CH_3)H_2$ (eqn (3)) but it is not clear yet as to which species $Cp^*_2ScSiH_2Mes$ or Cp^*_2Sc–H activates the methane C–H bond before silylation.



(3)

In 2005 Hartwig developed the first intramolecular dehydrogenative regioselective coupling of a silane Si–H bond with the aliphatic δ-C–H bond to generate the 5-membered cyclic organosilane in 80–88% yield by using $Tp^{Me2}PtMe_2H$ (Tp^{Me2} = hydrido tris(3,5-dimethylpyrazolyl)borate) as the catalyst (eqn (4)).[40]



(4)

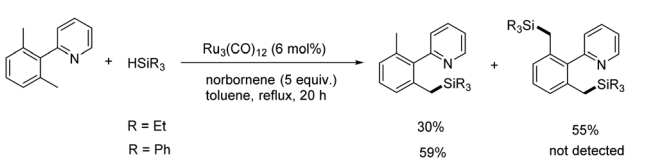
This was the first observation of a three-step process: the initial formation of a Si–metal bond from a Si–H bond, activation by the metal site of one sp^3C–H bond coming at its proximity, followed by Si–C bond formation.

3. Metal-catalyzed intermolecular silylations of sp^3C–H bonds directed by N-containing heterocycles

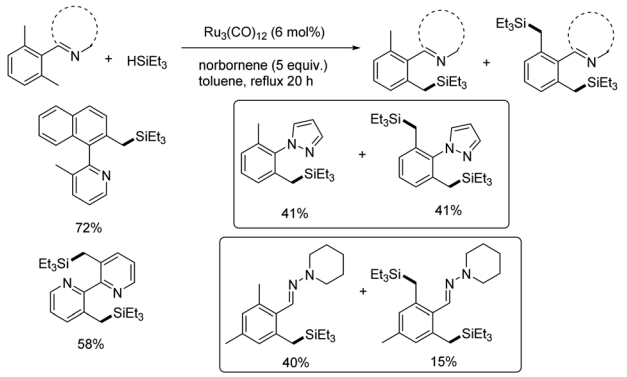
An early example of catalytic sp^3C–H bond silylation directed by pyridine was reported by Kakiuchi in 2004.[41] $Ru_3(CO)_{12}$ was shown to catalyze benzylic silylation with triethylsilane of 2-arylpyridines containing a methyl group at the aryl *ortho* position only, not at the *para* position, thus showing the directing role of the 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]

However, the silylation of an aryl *ortho* sp^2C–H bond is faster than that of an *ortho* methyl sp^3C–H bond with $HSiEt_3$ 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]

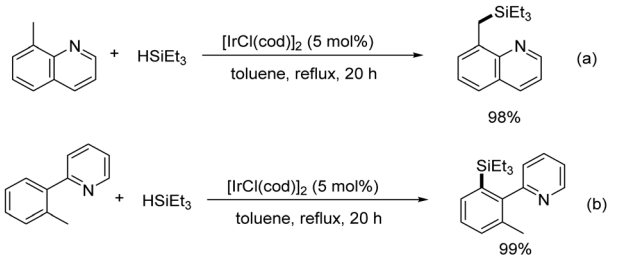
In 2012 Sato *et al.*[42] showed that $[IrCl(cod)]_2$ could catalyze the regioselective silylation of sp^3C–H bonds of arene methyl groups directed by quinolone, but this time without the presence of the hydrogen trap norbornene (Scheme 4(a)).[42] $Ru_3(CO)_{12}$ catalysts led to the same product in 93% under similar conditions but in the presence of norbornene. It is



Scheme 2 Ru(0) catalyzed silylation of sp^3C–H bonds directed by pyridine.



Scheme 3 Ru(0) catalyzed silylation of sp^3C–H bonds directed by N-heterocycles.

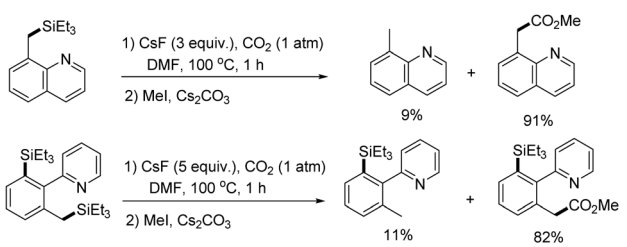


Scheme 4 Catalytic benzylic C(sp^3)–H silylation using an Ir(I) catalyst directed by the pyridine group.

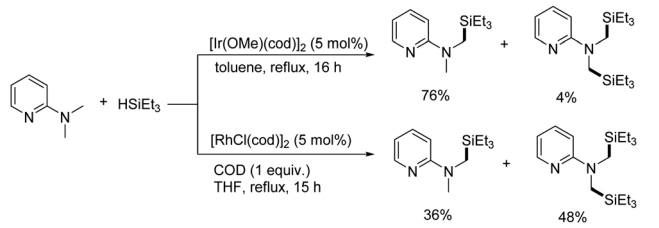
shown that with this Ir(I) catalyst the *ortho* aryl sp^2C–H bond silylation is faster than that of a sp^3C–H bond when it is directed by pyridine, likely because of a more easily generated 5-membered metallacycle intermediate with respect to the 6-membered intermediate required for *ortho* methyl activation (Scheme 4(b)).[42]

The importance of the sp^3C–H benzylic silylation was shown by Sato[42] for the direct access to carboxylates from the silylated products by action of CO_2 in the presence of fluoride, whereas the sp^2C–Si bond is inert toward carboxylation (Scheme 5).[42] This reaction motivates the search for benzylic silylation when the direct carboxylation of sp^3C–H bonds is not easily performed.

Sato has also shown that, in the presence of $HSiEt_3$, the Ir(I) and Rh(I) catalysts $[Ir(OMe)(cod)]_2$ and $[RhCl(COD)]_2$ were able to silylate a sp^3C–H bond of a methyl group bonded to the nitrogen atom of 2-dimethylaminopyridine, thus directed by



Scheme 5 Carboxylations of silylated benzyl groups with CO_2.



Scheme 6 Ir(I) and Rh(I) catalyzed silylation of C(sp^3)–H bonds adjacent to a nitrogen atom and directed by pyridine.

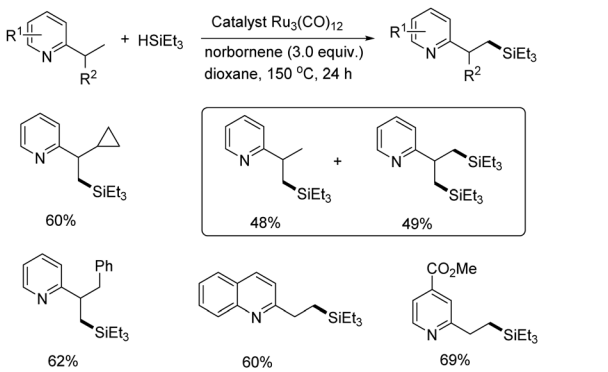
pyridine nitrogen itself (Scheme 6).[43] The Rh(I) catalyst operates only in the presence of the additive cyclooctoadiene COD (1 equiv.) to eliminate the formed hydrogen whereas the latter is not needed for the Ir(I) catalyst which is then not deactivated by *in situ* generated hydrogen.

However, the Rh(I) catalyst is more active for the silylation of the N–H bond compared to the NCH_3 C–H bond of 2-methylaminopyridine.[43] The resulting N–CH_2SiEt_3 groups can also be transformed into the carboxylate group N–CH_2CO_2Me upon reaction with CO_2 and CsF followed by the reaction of MeI and Cs_2CO_3.[43]

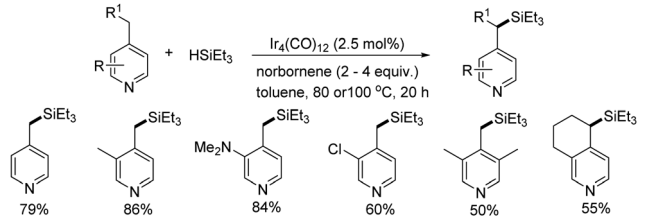
Sato also showed that the same catalyst $[Ir(OMe)(cod)]_2$ could promote the silylation with $HSiEt_3$ of the alkyl group at the beta carbon of 2-ethyl and 2-isopropyl pyridine but with low yields of 20 and 34% respectively.[43]

In contrast, using the $Ru_3(CO)_{12}$ catalyst, Jingsong You in 2016[44] achieved the successful activation and silylation of the sp^3C–H bonds of the alkyl group of 2-alkyl pyridines at the beta carbon in the presence of 3 equiv. of norbornene as the hydrogen trap (Scheme 7).[44] The reaction shows that the silylation is favoured at the alkyl beta carbon position and tolerates functional groups on the pyridine ring (OMe, CO_2R, Ph). Mechanism studies reveal that sp^3CH bond cleavage is reversible and not the rate-determining step.[44] However, this catalytic system was not operative for the sp^3CH silylation of 2-(dimethylamino)pyridine as previously described with a Rh(I) catalyst (Scheme 6).[43]

Fukumoto in 2017[45] succeeded in the silylation of the sp^3C–H bonds of methyl groups at the *para* position of pyridine derivatives. $Ir_4(CO)_{12}$ was used as the catalyst precursor with $HSiEt_3$ in



Scheme 7 Ruthenium-catalyzed intermolecular silylation of C(sp^3)–H bonds at the 2-alkyl group of pyridine.



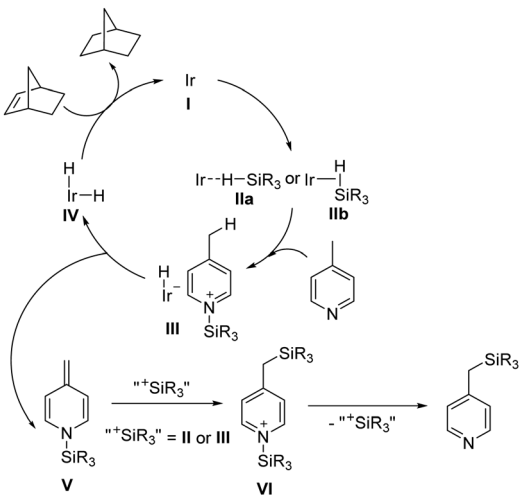
Scheme 8 $Ir_4(CO)_{12}$ catalyzed silylation of the alkyl group of 4-alkyl pyridines at the α-carbon.

the presence of norbornene in toluene at 80–100 °C (Scheme 8).[45] The reaction does not involve the silylation of the methyl group at the 3-position. It tolerates –NMe_2, –Cl, –Br, and –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, 48 h) to produce 12% of the silylated product at the 4-methyl group. Pyridine does not play the directing group role in this case but favours 4-alkyl sp^3C–H bond activation by deprotonation as shown in the mechanism in Scheme 9.[45]

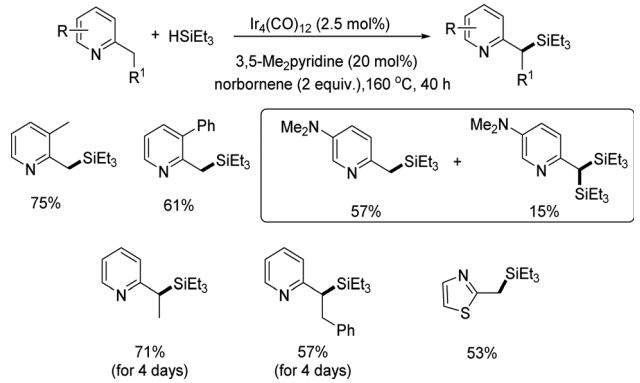
As well as $Ir_4(CO)_{12}$, Ir(acac)$(CO)_2$ is also active at 80 °C (20 h) for the same reaction to produce 74% of 4-triethylsilylmethylpyridine with 15% of the disilylated compound. $[Ir(OMe)(cod)]_2$ is also operative but under one atmosphere of carbon monoxide.

The proposed mechanism by Fukumoto (Scheme 9)[45] is based on deuteriation studies with $DSiEt_3$. It suggests the initial oxidative addition of the H–Si bond to the Ir(0) species **I** derivative of $Ir_4(CO)_{12}$ which leads to the formation of 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 IrH_2 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]

In contrast, Fukumoto recently described the catalytic sp^3CH bond regioselective silylation at the benzylic position



Scheme 9 Proposed mechanism for $Ir_4(CO)_{12}$ catalyzed silylation of 4-alkyl pyridines.



Scheme 10 $Ir_4(CO)_{12}$ catalyzed benzylic sp^3C–H bond silylation of 2-alkylpyridine.

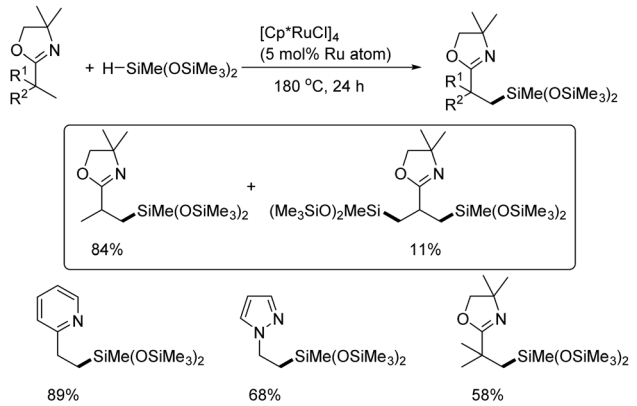
of 2-alkylpyridines leading only to 2-(1-silylalkyl)pyridines. The silylation is performed using $HSiEt_3$ and $Ir_4(CO)_{12}$ as the catalyst in the presence of norbornene as the hydrogen trap but in the presence of a 3,5-dimethylpyridine ligand (Scheme 10).[46] Thus the 3,5-dimethylpyridine modifies strongly by coordination the Ir(0) catalyst which without this ligand favours silylation at 4-methyl pyridine (see Scheme 8).[45]

A mechanism similar to that described in Scheme 9 is proposed for this reaction and based on the initial formation of $[Ir–H]^-$ and the (pyridine)N–$SiEt_3^+$ cation, then upon the deprotonation of 2-methylpyridine methyl group and silylation of the resulting methylene group.

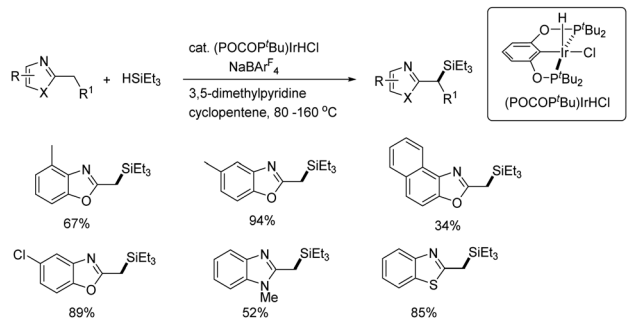
Several other catalytic dehydrogenative silylations of sp^3C–H bonds have been directed by the nitrogen atom of heterocycles such as oxazolines, azoles and quinolines with Ru(II), Ir(III) and Ru(III) respectively, for which the nature of key ligands on the metal catalysts play a crucial role.[47–49]

An excellent example was described by Murata[47] in 2016 who showed that the oxazoline nitrogen atom could direct the silylation of the sp^3C–H bond of the 2-alkyl group but regioselectively at the β-carbon atom. The reaction is performed only efficiently with $HSiMe(OSiMe_3)_2$ in the presence of a Ru(II) catalyst $[Cp^*RuCl]_4$ at 180 °C in cyclohexane. The Ru(III) derivatives $[Cp^*RuCl_2]_2$ and $RuCl_3{\cdot}nH_2O$ 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 $HSiMe_2(OMe)$ 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 H_2O_2/KHF_2 which produced the corresponding alcohol $PyCH_2CH_2OH$.

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 a H–Ru–N(heterocycle) intermediate to eliminate H_2 and to form a Ru(II)-cyclometalate. In 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 kcal mol^{-1}).



Scheme 11 Ru(II)-Catalyzed sp^3C–H silylation at the β-carbon of 2-alkyloxazolines.

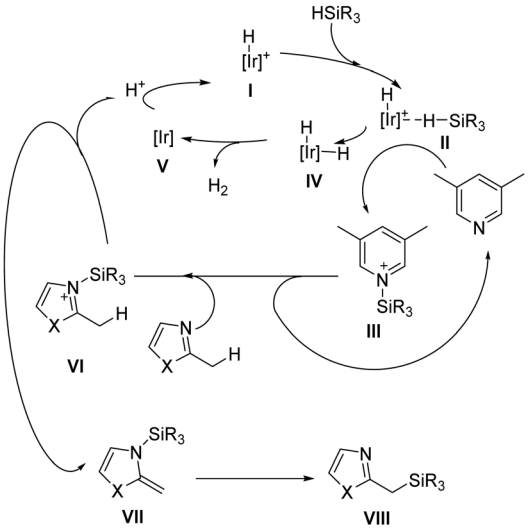


Scheme 12 Pincer hydride-Ir(III)-catalyzed silylation of 2-alkyl azoles at alkyl α-carbon.

In contrast, Fukumoto in 2018[48] using a pincer H–Ir(III) catalyst showed that the α-sp^3C–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 $NaB(C_6F_5)_4$ or $NaB(C_6H_3(CF_3)_2)_4$ containing non-coordinating anion (Scheme 12).[48] The silylation is performed with $HSiEt_3$. In 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.

The plausible mechanism in the absence of the hydrogen trap is shown in Scheme 13.[48] The $[Ir–H]^+$ species arising from chloride displacement of the pincer Ir(III) complex in the presence of a bulky conteranion is expected to trap the silane hydride to give the $(H)_2$Ir(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 the H_2 trap a similar mechanism takes places but alkene inserts into one Ir–H bond of **IV** to give the alkyl-Ir–H intermediate which after reductive elimination offers cycloalkane and Ir(I) **V** more easily.

Finally, during the evaluation of sp^2C–H silylation of 2-aryl N-heterocycles with $HSiEt_3$ in the presence of norbornylene,



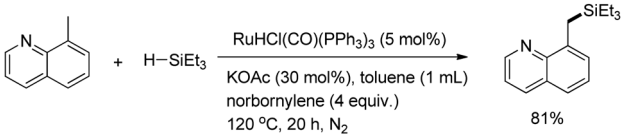
Scheme 13 A plausible reaction mechanism in the absence of alkene as a hydrogen acceptor.

as the hydrogen acceptor, and using the efficient Ru(II) catalyst $RuH(Cl)(CO)(PPh_3)_3$/KOAc, Bin Li[49–51] showed in 2019 that the silylation conditions applied to 8-methylquinoline preferentially led to the sp^3C–H bond silylation of the 8-methyl group (Scheme 14).[49] In this reaction the role of KOAc is crucial to generate a Ru(H)(OAc) intermediate on which oxidative addition of a H–SiR_3 bond is possible.

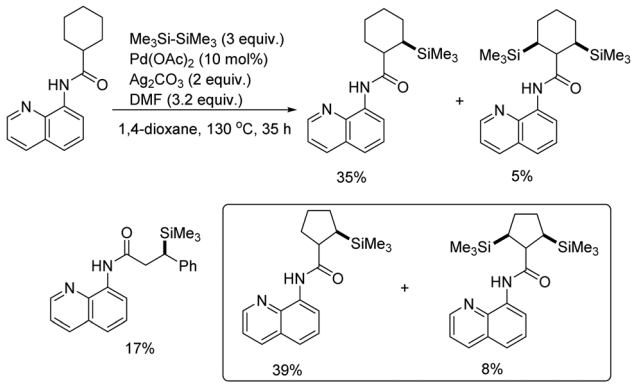
4. Palladium(II) catalyzed intermolecular silylations of sp^3C–H bonds with amide type directing groups

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 *t*BuMgCl/dtbpy will also be presented but it involves a [1,5]-hydrogen transfer.

Kuninobu and Kanai[52] 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



Scheme 14 sp^3C–H bond silylation with H–$SiEt_3$ of 8-methylquinoline with a Ru(II) catalyst.



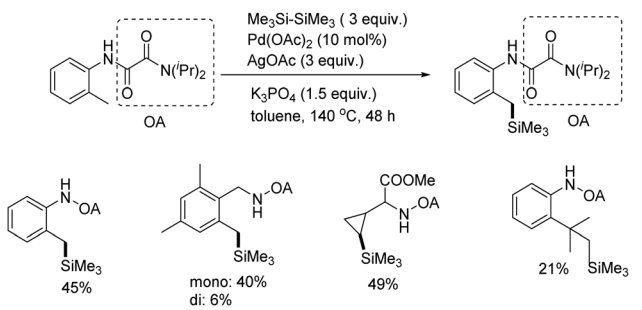
Scheme 15 $Pd(OAc)_2$ catalyzed sp^3C–H silylation of carboxamide alkyl groups with hexamethyldisilane.

(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 the β-carbon of the carbonyl function.

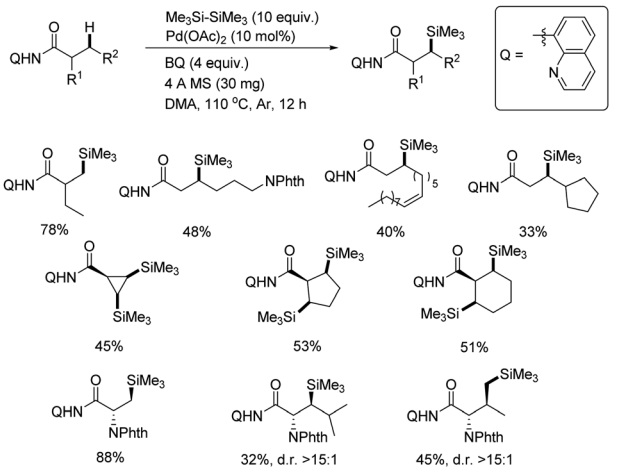
Just after, Y. Zhao[53] reported in 2015 that the oxalyl amide group could favour the sp^3C–H bond silylation, with Me_3Si–$SiMe_3$ and $Pd(OAc)_2$ catalyst of alkylanilines in the presence of 3 equiv. AgOAc and K_3PO_4 at 140 °C (Scheme 16).[53] The oxalyl amide group thus directs sp^3C–H bond activation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

S.-Y. Zhang in 2016 succeeded in the silylation with hexamethyldisilane of remote sp^3C–H bonds at the 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.

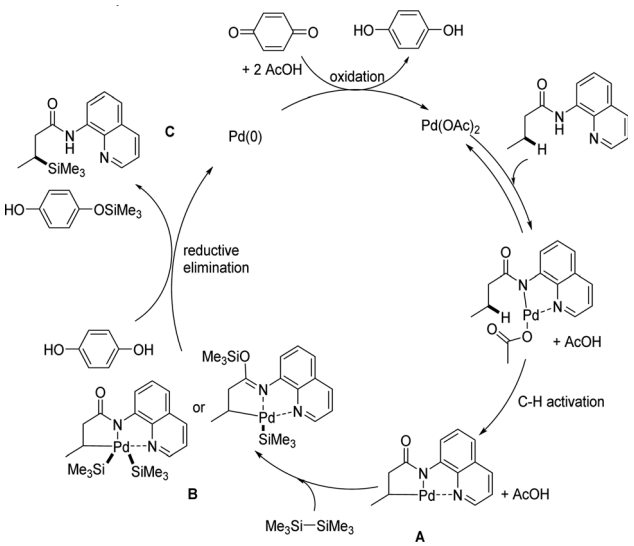
The proposed mechanism is shown in Scheme 18,[54] and involves the bicyclometalate **A** formation by N–H and C_β–H deprotonation, and its disilylation at O and Pd atoms or at the Pd site only in intermediate **B**. After reductive elimination with C–Si bond formation to give product **C**, the Pd(0)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



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



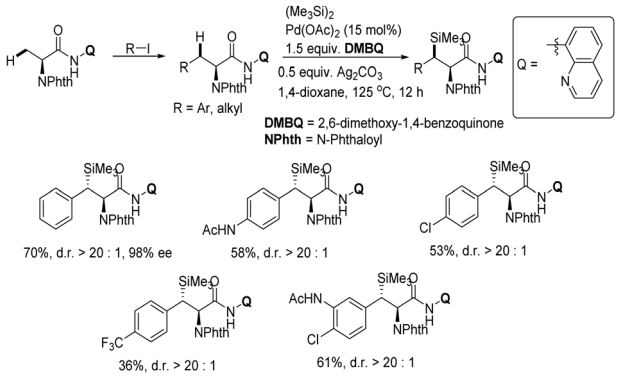
Scheme 17 sp^3 C–H bond silylation at the β-carbon of carboxamides derived from 8-amino quinoline.



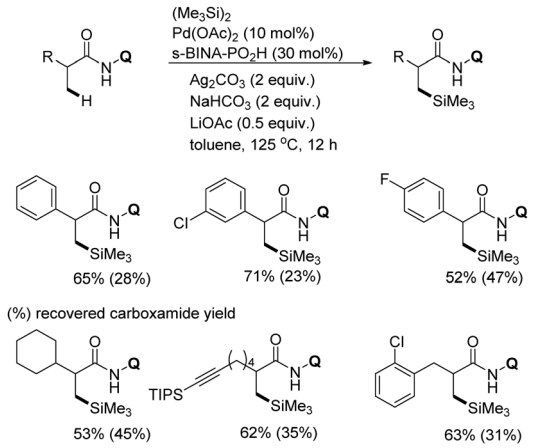
Scheme 18 Proposed mechanism for silylation of the β-carbon of carboxamides.

Bing-Feng Shi *et al.* 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 dimethoxyl-1,4-benzoquinone as the oxidant to regenerate the Pd(II) catalyst (Scheme 19).[55]

2-Aryl propionic acids were treated by Bing-Feng Shi under slightly different conditions using the $Pd(OAc)_2$ catalyst but with *S*-$BINAPO_2H$ (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



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

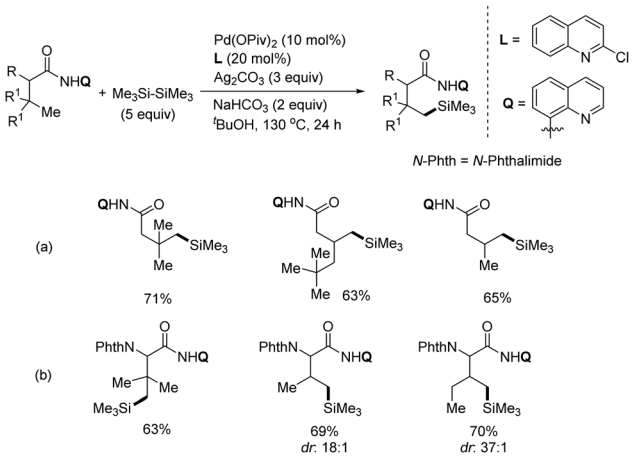


Scheme 20 Pd(II)-Catalyzed silylation of primary C–H bonds of 2-aryl propionic acids.

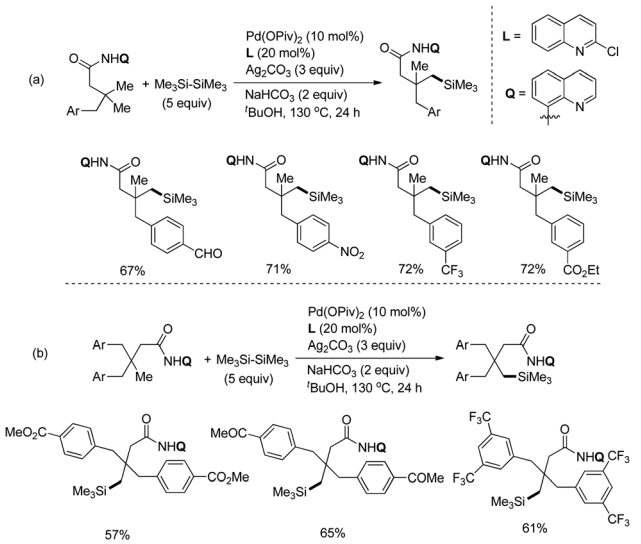
thermodynamically more stable than the *N*,*N* cyclometalate arising from the deprotonation of the NH group only. Importantly, for this silylation the sp^3C–H silylation of alkyl group is favoured over the *ortho* sp^2C–H bond silylation of the aryl group.

Debrabata Maiti succeeded in 2017[56] to perform the regioselective γ-silylation with hexamethyldisilane of amide derivatives of amino acids and 8-aminoquinoline (Scheme 21a).[56] $Pd(OPiv)_2$ 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]

The same reaction applied to γ-arylated amides, derivatives of 8-aminoquinolones, using the $Pd(OPiv)_2$ catalyst and associated with the ligand 2-chloroquinoline furnishes only the sp^3C–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 Me_3Ge–$GeMe_3$ of the same amino acid derivatives was also successfully performed.[56]



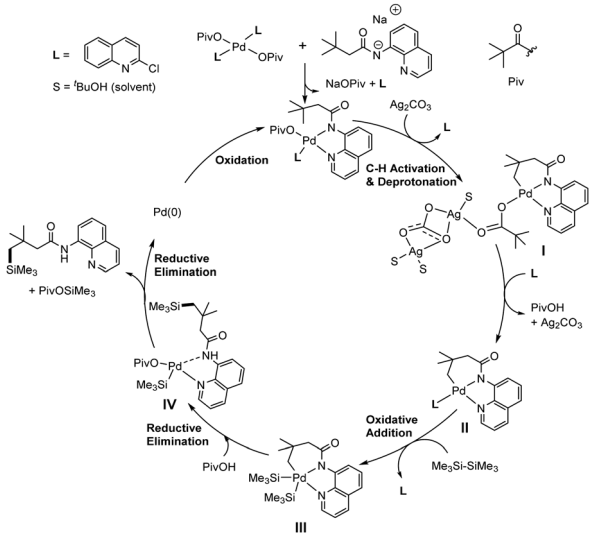
Scheme 21 Aliphatic γ-sp^3C–H bond silylation of 8-aminoquinoline derivatives of amino acids.



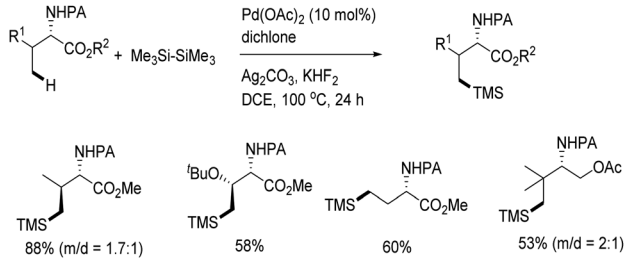
Scheme 22 γ-sp^3C–H silylation of γ-mono and diarylated quinolamides.

The plausible mechanism of the reaction is presented in Scheme 23.[56] It is based on H/D kinetic studies and is assisted by computational studies. It involves γ-C–H methyl activation *via* a deprotonation step first and the initial formation of the 6-membered cyclometalates **I** and **II**. The oxidative addition of Me_3Si–$SiMe_3$ to the Pd(II) intermediate gives **III**. Then the reductive elimination to give the C(γ)–$SiMe_3$ 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^+.

Recently, in 2019, Bing-Feng Shi succeeded in performing the γ-sp^3C–H bond silylation of peptides and α-aminoacids, using the 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 such as valine, leucine-2-aminobutyric acid and to amino alcohol derivatives (NHPA: –NHCO(2-pyridine)) (Scheme 24).[57] The reaction requires the



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



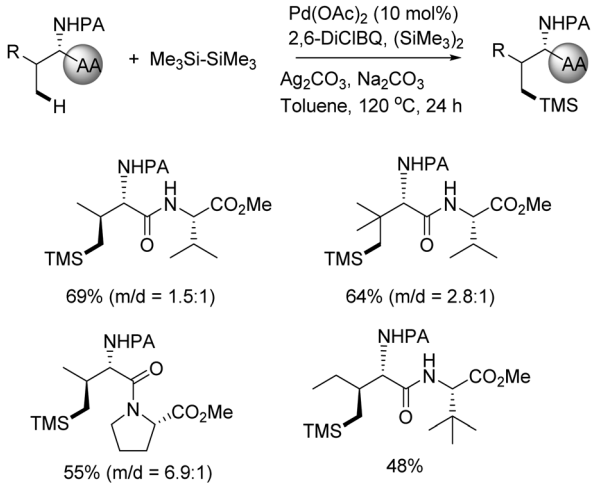
Scheme 24 γ-Methyl silylation of α-amino acids and α-amino alcohols.

presence of Ag_2CO_3 and KHF_2 and is improved by the presence of benzoquinone derivatives such as dichlone as the oxidant to regenerate the Pd(II) catalyst. The picolinamide group is easily removed after silylation upon reaction with Zn/HCl.

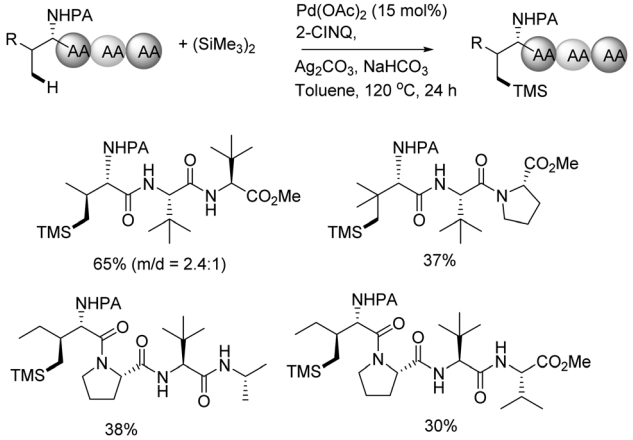
Under closely related conditions the reaction can be applied to the γ-silylation of 15 various dipeptides; in this case the preferable oxidant is 2,6-dichloro-1,4-benzoquinone (2,6-DiClBQ) with the picolinamide directing group (NHPA: –NHCO(2-pyridine)) (Scheme 25).[57]

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

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 the directing group for C–H bond activation by metal catalysts as previously thought. They succeeded in preparing α-silabenzamides *via* sp^3C–H bond silylation but involving a [1,5]-hydrogen transfer to the benzamide *ortho* C–F bond, not a catalytic sp^3C–H bond silylation. The reaction shown in Scheme 27 is



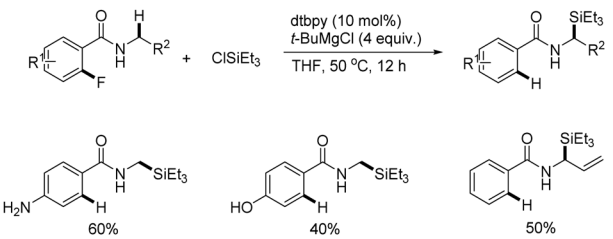
Scheme 25 Pd(II)-Catalyzed sp^3C–H bond γ-silylation of dipeptides.



Scheme 26 Pd(II)-Catalyzed sp^3C–H bond γ-silylation of tripeptides and tetrapeptides.

performed with $ClSiEt_3$, or other trialkyl silyl chlorides, on reaction with *t*BuMgCl and 4,4′-di-tertbutylbipyridine (dtbpy) at only 50 °C. The [1,5] hydrogen transfer is demonstrated to occur *via* the study of a N-CD_3 labelled benzamide derivative.

Kinetic studies suggest that the α-sp^3C–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 upon reaction of the C–Si bond to give a variety of



Scheme 27 Metal-catalyst free, site-selective silylation of aliphatic C–H bonds at the α-position through [1,5]-hydrogen transfer.

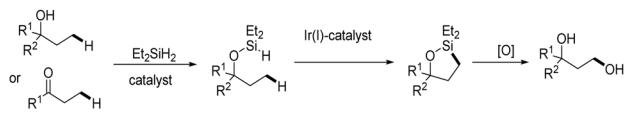
N-formyl (PhCONHCHO), β-hydroxyl (PhCONHCH$_2$CHOHR) or β-amino (PhCONHCH$_2$CH(NHR)Ph) benzamide derivatives.[58]

5. Metal-catalyzed intramolecular silylations of sp^{3}C–H bonds directed by hydrosilylated hydroxy and ketone groups

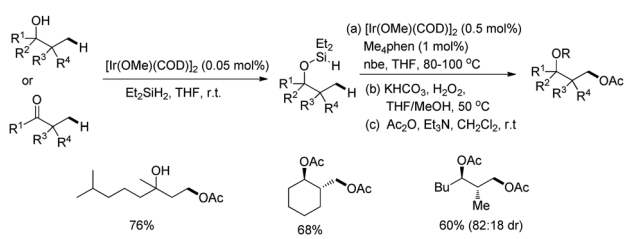
As early as 2012 Hartwig[59] showed that O–SiH(alkyl)$_2$ groups, arising from catalyzed dehydrosilylation with silane alkyl$_2$SiH$_2$ of the hydroxy group or by hydrosilylation of the ketone carbonyl group, could lead to regioselective intramolecular silylation of the γ-sp^{3}C–H bond and hydrogen elimination to form 5-membered oxasiloxane. This was the first example of intramolecular sp^{3}C–H bond silylation without a directing group but by proximity of Si–H and C–H (see also eqn (4)).[40] 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 easy oxidation of the formed oxasiloxanes, with H_2O_2, to generate 1,3-diols, or leads to the corresponding 1,3-acetates upon further treatment with Ac_2O (Scheme 28).

Thus, the hydroxy and ketone groups were first dehydrosilylated and hydrosilylated respectively with alkyl$_2$SiH$_2$ in the presence of the catalyst [Ir(OMe)(cod)]$_2$ in THF. Then the intramolecular dehydrosilylation was performed using the same Ir(I) catalyst but in the presence of 3,4,7,8-tetramethylphenanthroline. The addition of norbornene allowed trapping of the generated hydrogen before the C–Si bond formation to form the cyclic oxasiloxanes (Schemes 28 and 29). The *in situ* treatment of the formed oxasiloxane with hydrogen peroxide leads to 1,3-diol which upon reaction with Ac_2O affords the 1,3-diacetate at room temperature (Scheme 29).[59]

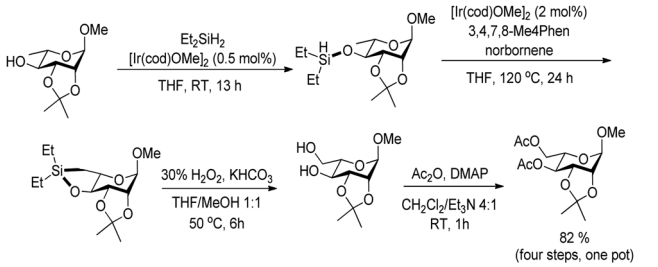
The same year, using the Hartwig procedure, Pedersen and Bols[60] developed a one-pot sequence process to synthesize fully protected L-mannoside in 82% yield only using 4 steps from a methyl glycoside derivative, including Si–H/O–H cross-coupling



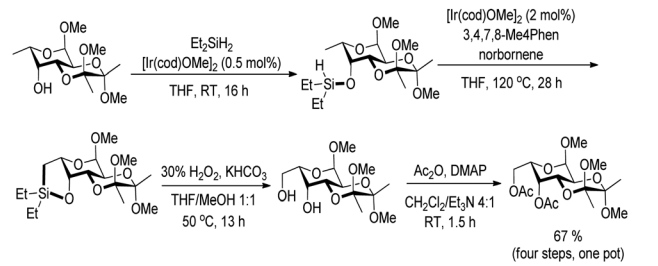
Scheme 28 Silylation of the alkyl sp^{3}C–H bond directed by a silylated hydroxy group or ketone.



Scheme 29 Iridium(I) catalyzed silylation of alcohol and ketone followed by intramolecular γ-sp^{3}C–H bond silylation.



Scheme 30 One-pot sequence for the synthesis of fully protected L-mannoside involving intramolecular γ-sp^{3}C–H bond silylation.

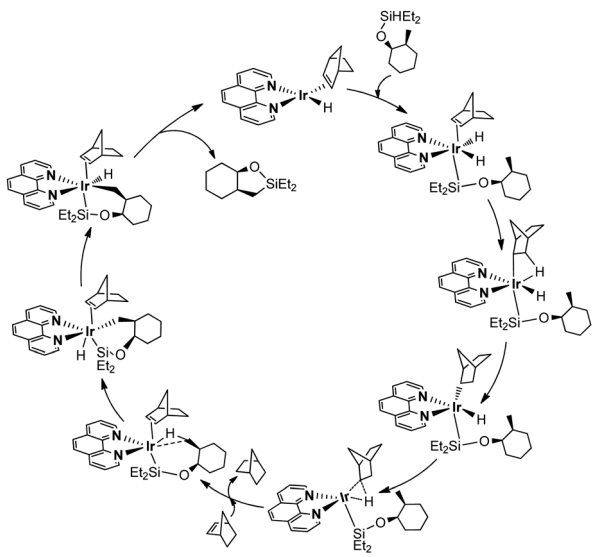


Scheme 31 One-pot synthesis of fully protected L-galactoside through C–H silylation and oxidation.

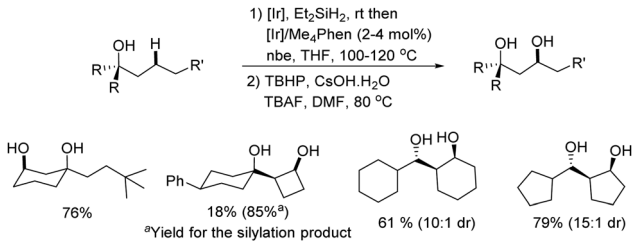
reaction, intramolecular sp^{3}C–H silylation, Fleming–Tamao-type oxidation, and acetylation (Scheme 30).

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

The mechanism of Ir(I)/phenanthroline catalyzed silylation of the γ-sp^{3}C–H bond of 2-methyl cyclohexanol was studied by Sunoj *et al.*[61] using DFT calculations. The proposed mechanism is presented in Scheme 32. It is shown that in the presence of



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



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

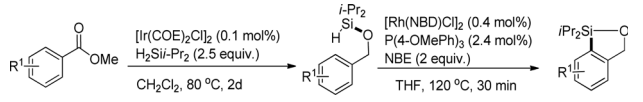
SiH_2Et_2 the $[Ir(OMe)(cod)]_2$ catalyst alone first performs the silylation of the alcohol. Then the Ir–H(Phen) complex can coordinate norbornene before allowing the Si–H oxidative addition. The alkene allows insertion into the Ir–H bond and reductive elimination of alkane. Then the C–H bond oxidative addition of the γ-sp^3C–H bond takes place followed by reductive elimination with C–Si bond formation. The last step of the reductive elimination to form the C–Si bond is the rate-determining step of the reaction (TS: 14.6 kcal mol^{-1}) whereas the C–H bond activation needs lower energy (TS: 9 kcal mol^{-1}).

Hartwig[62] then applied his strategy to generate the oxasilane O–$SiEt_2H$ group, from the hydroxy group or the corresponding ketone, and to direct the intramolecular regioselective γ-sp^3C–H bond dehydrosilylation of intermediate $(R_2C(OSiEt_2H))$–$CH_2CH_2CH_2R'$ to form the oxasilolanes *in situ*. The latter can then be *in situ* oxidized into 1,3-diols with TBHP peroxide (Scheme 33). This dehydrosilylation reaction catalyzed by $[Ir(OMe)(cod)]_2$/Me_4Phen allows the diastereoselective synthesis of a variety of 1,3-diols.

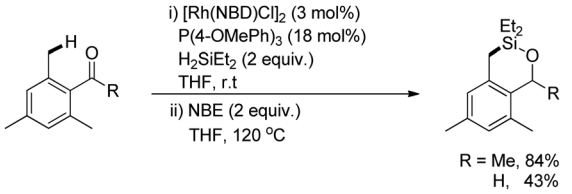
The primary K_H/K_D KIE = 2 indicates that the C–H bond cleavage is the rate-limiting step for this directed intramolecular sp^3C–H bond silylation. The catalytic dehydrosilylation of the derivatives $R_2C(OSiEt_2H)CH_2CH_3$ and $R_2C(OSiEt_2H)CH_2CH_2CH_3$ show that the silylation of the γ-CH_3 group is 49 times faster than that of the γ-methylene group, thus faster at the primary than at the secondary γ-C–H bond.

In 2015 Jeon *et al.*[63] developed a method for the initial hydrosilylation of ester, ketone and aldehyde carbonyl groups followed by sp^2C–H bond *ortho* silylation of aromatic systems. The first hydrosilylation of the carbonyl group is performed using the $[IrCl(COE)]_2$ catalyst with H_2SiEt_2. The following intramolecular silylation was catalyzed by $[RhCl(NBD)]_2$/$P(C_6H_4OMe)_3$ in the presence of norbornene (Scheme 34). The same reaction could be applied to aromatic ketones and aldehydes using the Rh(I) catalytic system only.

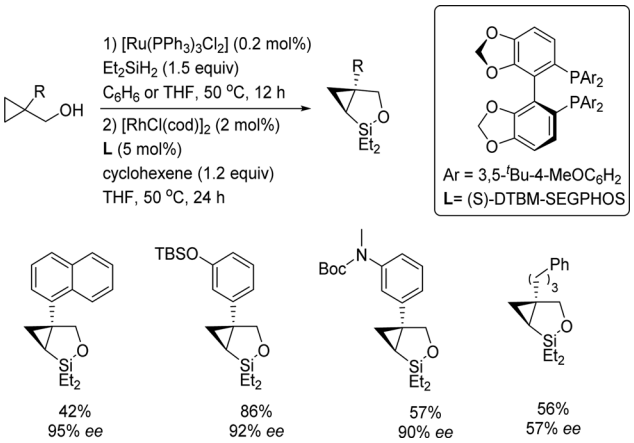
Interestingly, when the reaction was applied to an aromatic ester containing an *ortho* methyl group, similar successive Ir(I)



Scheme 34 Sequential reductive carbonyl and arene *o*-CH silylations with both Ir(I) and Rh(I) catalysts.



Scheme 35 Sequential reductive benzylic sp^3C–H silylation of aromatic esters, ketones and aldehydes with Rh(I) catalysts.

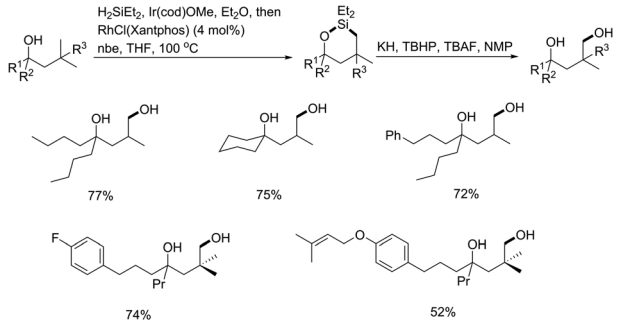


Scheme 36 Rh catalyzed enantioselective silylation of cyclopropyl sp^3C–H bonds.

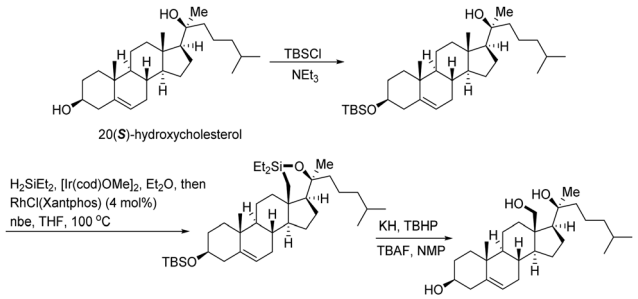
and then Rh(I) reactions led to the reduction of the carbonyl group first and then to the sp^3C–H benzylic bond intramolecular hydrosilylation to afford the benzoxaline derivative. From aromatic ketones and aldehydes containing arene *ortho* methyl groups only a Rh(I)/phosphine catalyst led to their carbonyl hydrosilylation, and then after NBE addition the intramolecular dehydrosilylation took place and the benzoxaline derivative was formed (Scheme 35).

Later on, Hartwig developed the first chiral-rhodium(III) catalyzed highly enantioselective C–H bond silylation of the 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 $[Ru(PPh_3)Cl_2]$/$EtSiH_2$ catalytic system followed by the $[RhCl(cod)]_2$/(*S*)-DTBM-SEGPHOS/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.

Subsequently, the Hartwig group[65] developed a rhodium-catalyzed site selective silylation of alkyl δ-C–H bonds, when no C–H bond was present at the γ-carbon atom, to form six-membered oxasilolanes with the hydroxyl group as the initial directing group. The catalytic reaction takes place in the presence of the [Rh(Xantphos)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 (Xantphos)Rh($SiEt_2OR$)(nbe) is the key complex for



Scheme 37 RhCl(Xantphos) catalyzed alcohol-directed δ-C–H silylation and 1,4-diol synthesis.



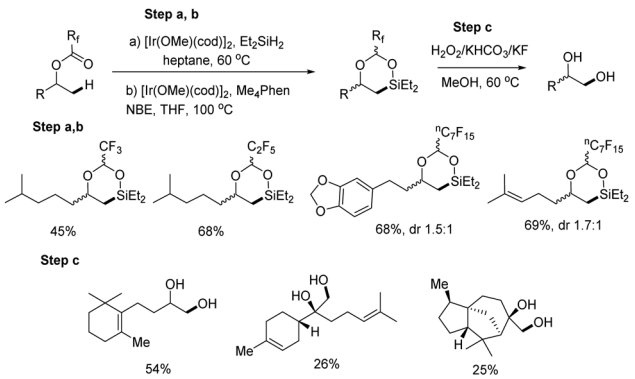
Scheme 38 RhCl(Xantphos) catalyzed δ-C–H silylation of oxysterol.

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-sp^{3}C–H bond silylation followed by the Fleming–Tamao oxidation (Scheme 38).[65]

Hartwig[66] in 2018 applied his method for intramolecular silylation of sp^{3}C–H bonds observed with a Rh(I) catalyst, for regioselective dehydrosilylation of the alkyl β-C–H bond directed by a perfluorinated ester group, which was successful with the Ir(I) catalyst. First, tertiary alcohols were esterified into perfluorinated esters which were treated with Et_2SiH_2 with the catalyst $[Ir(OMe)(cod)]_2$ to afford quantitatively the carbonyl hydrosilylation product containing the O–$SiEt_2H$ group. Then the addition of the $[Ir(OMe)(cod)]_2$/Me_4Phen catalyst allowed the regioselective β-C–H bond silylation with dehydrogenation in the presence of norbornene to form the 6-membered dioxasililanes (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 H_2O_2 according to the Tamao–Fleming reaction.

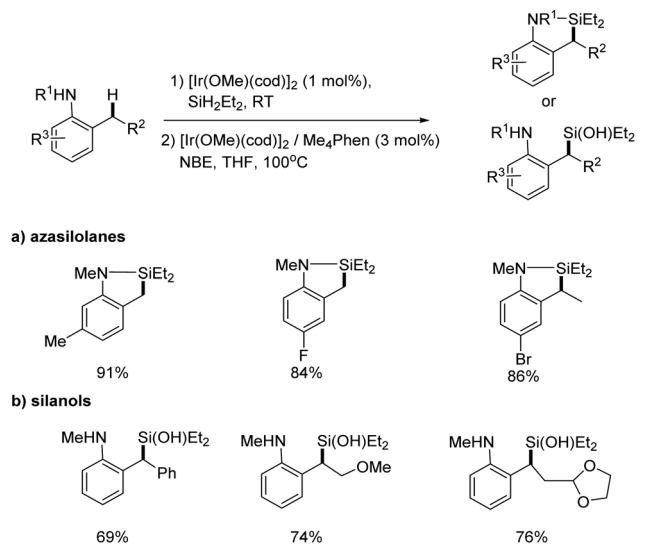


Scheme 39 Hydrosilylation of fluorinated esters, intramolecular sp^{3}C–H bond silylation and oxidation.

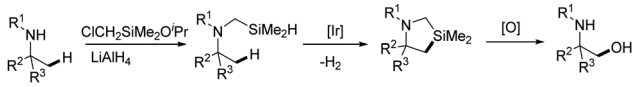
6. Catalyzed regioselective intramolecular sp^{3}C–H bond dehydrosilylation of silylated amine NH bonds

In 2014 Hartwig showed that secondary aromatic amines could direct the silylation with H_2SiEt_2 of N–H bonds first with the $[Ir(OMe)(cod)]_2$ catalyst alone, followed by the intramolecular silylation of the aryl *ortho* sp^{2}C–H bond using the same catalyst, but with an additional phenanthroline ligand $[Ir(OMe)(cod)]_2$/Me_4Phen catalyst and in 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 the initial Ar(R)N–H transformation into (hydro)silylamines $Ar(R)NSiHEt_3$ first and then to the intramolecular alkyl sp^{3}C–H bond silylation of *ortho* methyl groups and of the secondary benzylic sp^{3}C–H bond at the γ-position of the $N(SiHEt_2)$ group to produce a variety of azasilolanes (Scheme 40a).

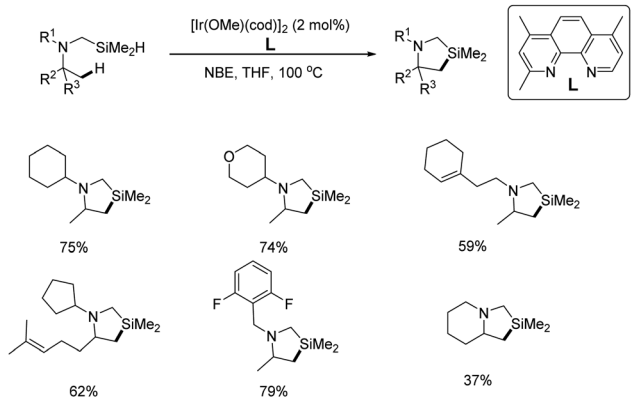
The latter azasilolanes were opened during chromatography to produce the corresponding silanols (Scheme 40b). The reaction successively used the same two iridium(I) catalyst systems which tolerated many functional groups (Br, MeO,



Scheme 40 sp^{3}C–H silylation of *N*-2-alkylanilines and formation of azasilolanes and silanols.



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



Scheme 42 Intramolecular sp^3C–H silylation of aliphatic amines into silapyrrolidines.

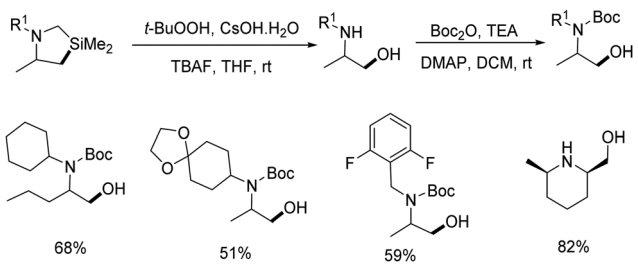
$OSiR_3$, OAc). The silanols can be oxidized easily with H_2O_2 to form aromatic secondary amines with γ-hydroxy groups.

Hartwig recently reported the intramolecular β-selective silylation of unactivated sp^3C–H bonds of alkylamines.[68] The reaction requires the initial formation of the N–CH_2–$SiHMe_2$ group by reaction of a secondary alkyl amine with $ClCH_2SiHMe_2$. Then intramolecular alkyl silylation affords a cyclic silane which can be oxidized into 1,2-aminoalcohol (Scheme 41).

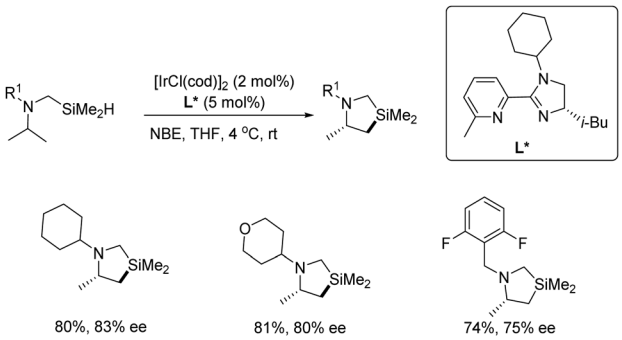
The β-selective intramolecular silylation of amines is performed with $[Ir(OMe)(cod)]_2$ and a trimethyl phenanthroline ligand **L** in the presence of an hydrogen acceptor (NBE) (Scheme 42).[68] Many functional groups are tolerated such as alkenes, C–F bonds or ether groups.

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 Boc_2O (Scheme 43).

Hartwig also performed enantioselective intramolecular dehydrosilylation of silylamines.[68] The silylation reaction has been carried out using an $[Ir(OMe)(cod)]_2$ catalyst but with a



Scheme 43 Synthesis of 1,2-amino alcohols, derived from sp^3C–H silylation, and of their *N*-protected carbamates.



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

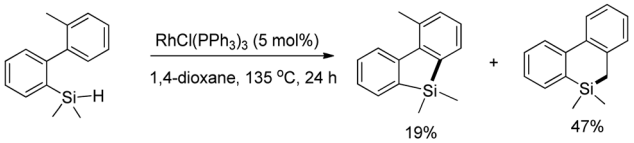
chiral pyridylimidazoline ligand **L***. The chiral ligand **L*** containing an *N*-alkyl imidazoline has led to good enantioselectivities (Scheme 44).[68]

7. Intramolecular silylations of sp^3C–H bonds in proximity to Si–H bonds

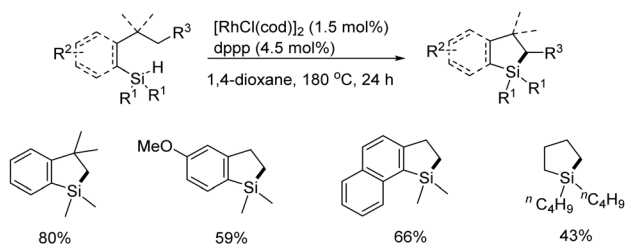
7.1 From arylsilanes

The intramolecular silylation of sp^3C–H bonds of arysilanes without a directing group was observed by Kuninobu and Takai with a Rh(I) catalyst $RhCl(PPh_3)_3$ in 2013 upon reaction of the diphenylhydrosilane containing an *ortho* methyl group (Scheme 45).[69] Thus the sp^3C–H intramolecular silylation appeared to be easier than the expected aryl sp^2C–H silylation.

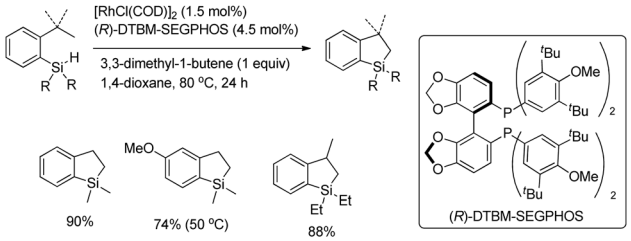
This first example led this group to discover a general intramolecular sp^3C–H bond silylation of arylsilanes containing an *ortho* alkyl group, to form a 5-membered cyclic silane, with a catalytic system based on $[RhCl(cod)]_2$ and diphosphine $Ph_2P(CH_2)_3PPh_2$ (dppp) (Scheme 46).[69] The proposed reaction mechanism suggested the initial insertion of the Rh(I) species



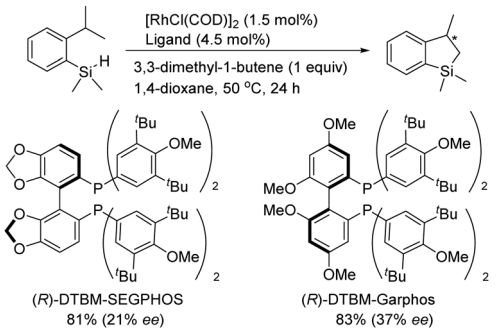
Scheme 45 Rhodium(I)-catalyzed silylation of aromatic sp^2C–H and benzylic sp^3C–H bonds.



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



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



Scheme 48 Rhodium-catalyzed enantioselective sp^{3}C–H bond silylation with chiral diphosphines.

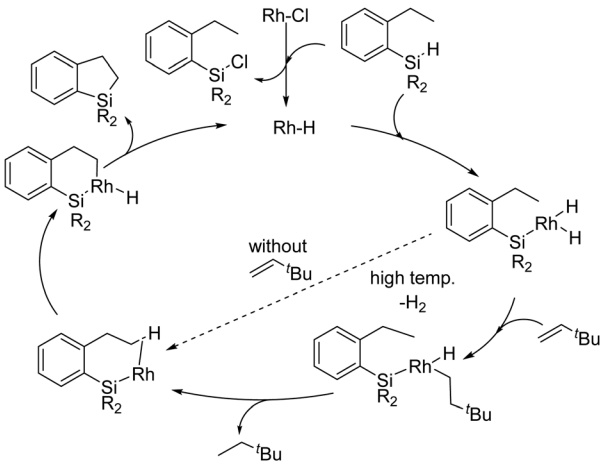
into the Si–H bond followed by the oxidative addition of the proximal alkyl sp^{3}C–H bond to the Rh species followed by the dehydrogenation and formation of the sp^{3}C–Si bond.[69] Further studies led the same group to propose the catalytic mechanism presented later in Scheme 49. This regioselective reaction can also be performed without an aromatic ring such as from H–Si(^{n}Bu)$_3$ by silylation of an alkyl sp^{3}C–H bond,[69] as was also observed using a platinum catalyst (see eqn (4)).[40]

Later, the same Kuninobu–Takai group[70] 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 the β-sp^{3}C–H bond of the alkyl group as shown in Scheme 47.

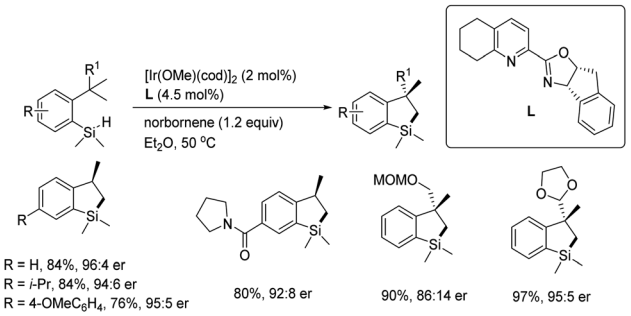
More importantly, the use of chiral SEGPHOS or GARPHOS diphosphine allowed the enantioselective intramolecular methyl silylation of 2-isopropyl phenylsilane although in modest enantiomeric excess (Scheme 48).[70]

The proposed mechanism of the reaction involves first the initial transformation of the Rh–Cl into the Rh–H bond *via* reaction with silane followed by the 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 the 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]

More recently Hartwig *et al.*[71] applied this reaction for the very efficient enantioselective intramolecular silylation of the β-C–H bond of an alkyl group at the *ortho* position of arylsilanes



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

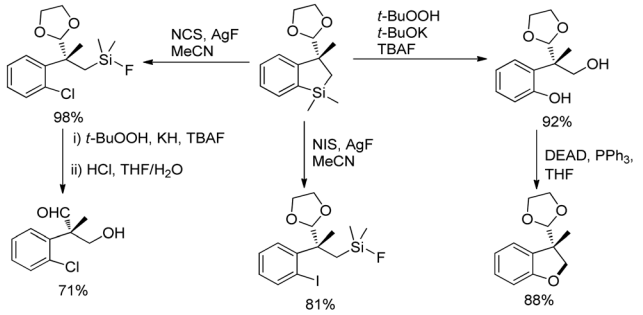


Scheme 50 Enantioselective intramolecular silylation of sp^{3}C–H bonds using the chiral Ir(I) catalyst.

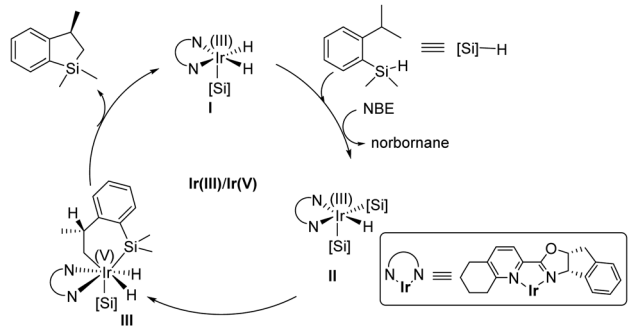
using the [Ir(OMe)(cod)]$_2$ catalyst with the optically active N^N bidentate ligand **L** (Scheme 50).

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 a hydrogen trap. The reaction can be performed at the gram scale. The kinetic isotopic effect KIE of K_H/K_D = 1.9 for intramolecular silylation with the CH(CH$_3$)$_2$/CH(CD$_3$)$_2$ *ortho* alkyl groups suggest 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]

Recently the Genping Huang group[72] studied the mechanism of Hartwig's reaction[71] on intramolecular silylation of the sp^{3}C–H bond in *ortho*-alkyl silyl arenes with the help of DFT calculations. First they showed that the [Ir(OMe)(cod)]$_2$ precursor upon reaction with the chiral N^N ligand and silane (*o*-alkyl)ArSiMe$_2$H led to the Ir(III) (N^N)Ir(H)$_2$[Si] catalytic active species **I** (Scheme 52). The coordination of the norbornene C=C bond allows its insertion into the Ir–H bond and the resulting alkyl group interacts with the remaining Si–H bond to eliminate the norbornane and to form the Ir–SiMe$_2$(aryl) intermediate **II**. The next key step involves the alkyl C–H bond interaction with the Ir(III) center,



Scheme 51 Transformations of the enantioenriched dihydrobenzosiloles.



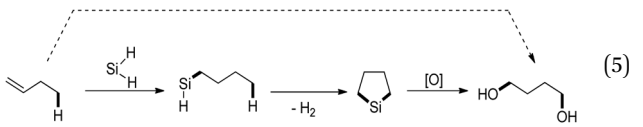
Scheme 52 Catalytic cycle based on DFT calculations of intramolecular silylation of the sp^3C–H bond.

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 the initial Ir-hydride silyl group Ir–H···[Si] interaction. The DFT calculations show that both electronic and steric effects contribute to create the enantioselectivity.

Another recent example of intramolecular silylation of azylsilanes using Ru(ii) catalysts will be described later (Scheme 60).

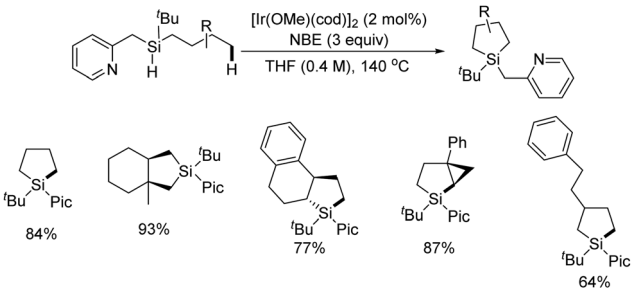
7.2 From alkylsilanes arising from *in situ* hydrosilylation of C=C bonds

Gevorgyan *et al.*[73] 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 (eqn (5)).

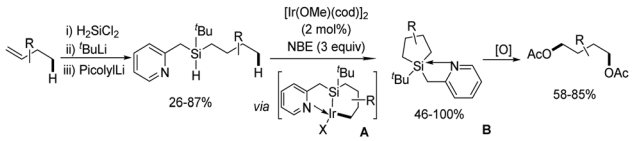


(5)

Silylation reactions are promoted by $[Ir(OMe)(cod)]_2$ as the catalyst. The success firstly required the introduction of a picolyl directing group at the silicon atom to allow the oxidative addition of the neighbouring 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 1,4-diol or diacetate (eqn (6)).



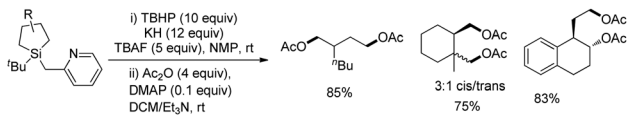
Scheme 53 Ir(i)-Catalyzed δ-C–H dehydrogenative silylation reaction and the formation of silolanes.



(6)

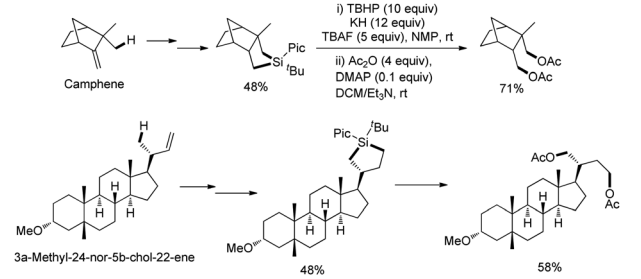
Thus a variety of silolanes have been produced from the silane containing the H–$SiCH_2CH_2CH_2CH_3$ arrangement and the picolyl (Pic) directing group. The presence of the ^{t}Bu group linked to silicon generated stability in the silane. The activation of primary δ-CH_3 is favoured *versus* that of δ-CH_2Ar and the silylation of the δ-C–H bond of a cyclopropyl group is possible. The reaction tolerates many functional groups such as Ar–X: Cl, Br, and CF_3 groups (Scheme 53).

The oxidation of the silolanes by TBHP/KH and then the treatment with Ac_2O allow the selective formation of 1,4-diacetates (eqn (7)).[73]



(7)

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 bonds 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) have been performed, either directed by a functional group or without. The resulting products of type X–CH_2–SiR_3 thus allow a variety of functionalizations into X–CH_2–FG derivatives which cannot be achieved directly using the X–CH_3 group. This section will outline such X–CH_3 silylations and some of the related functionalizations.

8.1 Directed silylation of the B–CH_3 group

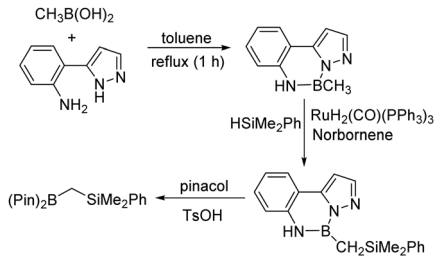
Directed silylation of the B–CH_3 group was performed by Suginome as early as in 2011.[74] He first succeeded in the silylation of the methyl group linked to the boron in boronic acid $CH_3B(OH)_2$ with a ruthenium catalyst but by using 2-(1*H*-pyrazol-3yl)aniline (PZA) as a removable *ortho* directing group. Thus the resulting methyl boronic derivative reacts with a variety of trialkylsilanes, promoted by $RuH_2(CO)(PPh_3)_3$ catalysts which easily affords a classical Ru(0) species *via* dehydrogenation. The reaction takes place in the presence of norbornene as a hydrogen scavenger to give the α-silylated product (Scheme 55).

Analogous efficient directing groups can be used from 2-(1*H*-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]

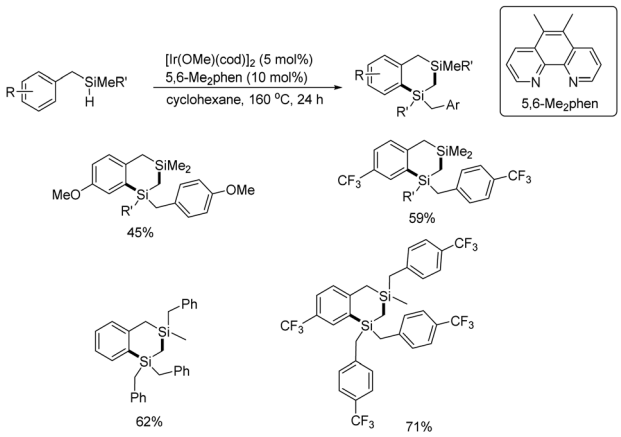
Under similar conditions the silylation of the PZA derivative of ethylboronic acid led to α- and β-silylation of the ethyl group in similar yield. It is noteworthy that these pinacol esters derived from α-silylmethyl boronic acid $(Pin)_2B$–CH_2SiMe_2Ph are good reagents for the Suzuki–Miyaura C–C cross-coupling reactions with arylbromides using a 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 Takai[75] who 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 then the 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).

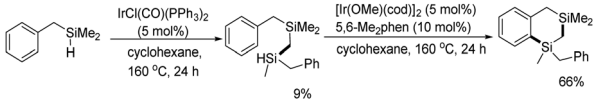


Scheme 55 α-Functionalization of methylboronic acid *via* introduction of a N^N directing group using a ruthenium catalyst.



Scheme 56 Ir-Catalyzed dehydrogenative dimerization of benzylmethylsilane.

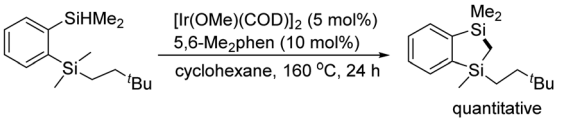
It was shown that when the Vaska complex $IrCl(CO)(PPh_3)_2$ was used as the catalyst the silylation of one Si–CH_3 group was observed first and the resulting product in the presence of $[Ir(OMe)(cod)]_2$/Me_2Phen catalyst gave the disilyne derivative (eqn (8)). This shows the ease of silylation of the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



(8)

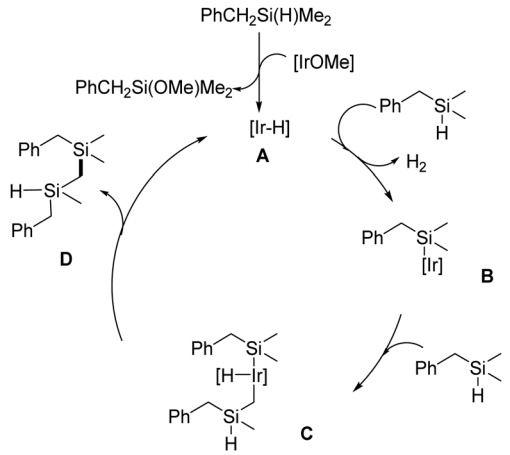
The proposed mechanism firstly involves the formation of Ir–H species **A** from the Ir–X(Ln) catalyst and silane to give the formation of Ir^I–$SiMe_2CH_2Ph$ moiety **B** on elimination of H_2. Then the oxidative addition of the H–C(methyl) bond of $HSiMe_2CH_2Ph$ to $Ir^ISiMe_2CH_2Ph$ is expected to occur 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 the 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 56).

The same catalyst $[Ir(OMe)(cod)]_2$/5,6-Me_2Phen could be used by Takai[75] to perform the intramolecular sp^3C–H bond silylation of a Si–Me group with dehydrogenation as described in eqn (9).



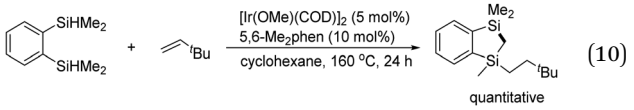
(9)

The intramolecular sp^3C–H bond silylation of one methyl of 1,2-bis(dimethyl silyl)benzene with the same Ir(I)/5,6-Me_2Phen



Scheme 57 Proposed mechanism for the dehydrogenative dimerization of benzylmethylsilane.

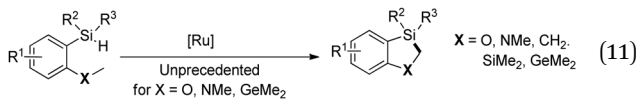
catalytic system in the presence of 3,3-dimethyl butene could also be performed quantitatively (eqn (10)).[75]



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 (eqn (10)) the OCH_3 and NCH_3 group are not silylated.[75]

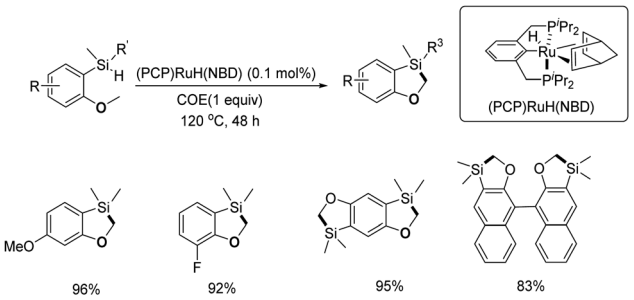
8.3 Silylation of the O–CH_3, N–CH_3, Si–CH_3 and Ge–CH_3 groups using the pincer Ru(II) catalyst

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

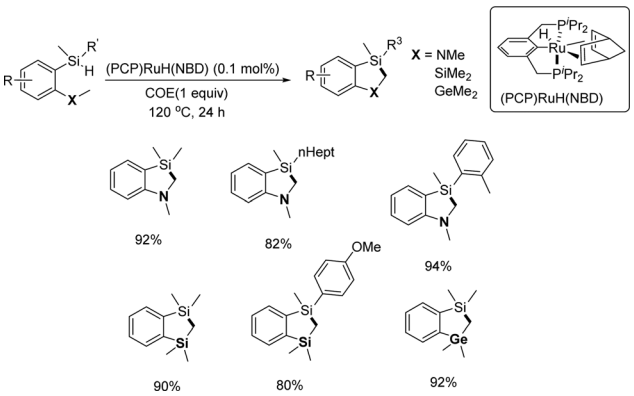


As shown in Scheme 58 a low loading of the pincer Ru(II) complex (PCP)RuH(NBD) (0.1 mol%) allows intramolecular sp^3C–H bond silylation and formation of various [1,3]-oxasilolanes. The reaction takes place with the hydrogen acceptor cyclooctene (COE) at 120 °C. Other selected catalysts based on the pincer Ir(III) complex offer low yield for silylation. This reaction could produce 7.6 g of simple [1,3]-oxasilolane in one step which can easily lead to cross-coupling reactions with ArI and Pd(0) catalysts.[76]

Previously the silylation of NCH_3 groups was reported by Sato[43] but the C–H bond activation was assisted by pyridine as the directing group (Scheme 6). The intramolecular silylation of



Scheme 58 Pincer-Ru(II)-catalyzed intramolecular silylation of sp^3C–H bonds α to the O atoms.

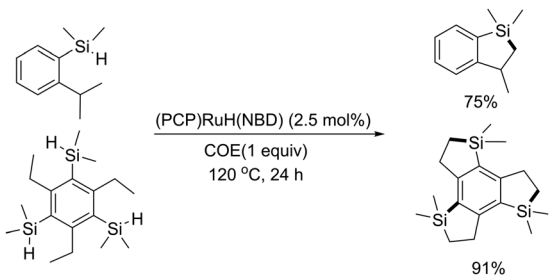


Scheme 59 Pincer Ru-catalyzed intramolecular silylation of sp^3C–H bonds α to the N-, Si-, or Ge-atoms.

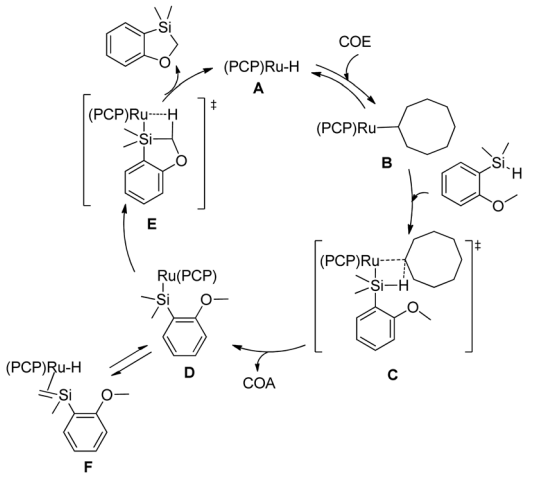
methyl sp^3C–H bonds of $-NRCH_3$, $-Si(CH_3)_3$ and even $-Ge(CH_3)_3$ groups was performed without assistance of a directing group, with the same pincer-Ru/COE catalyst by Zheng Huang.[76] However the loading of the catalyst had to be increased for $Si(CH_3)_3$ (5 mol%) and for $Ge(CH_3)_3$ (10 mol%) to achieve good yields with COE (1 equiv.) at 120 °C for 24 h (Scheme 59).

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

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

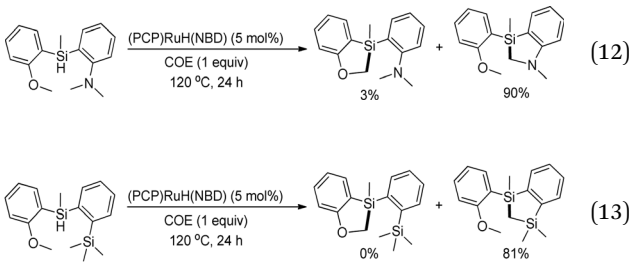


Scheme 60 Ru(II)-Catalyzed intramolecular silylation of sp^3C–H bonds at the *ortho* alkyl β-C-atom of arylsilanes.



Scheme 61 Proposed mechanism for the intramolecular sp^3C–H silylation of *ortho* O–CH_3 groups.

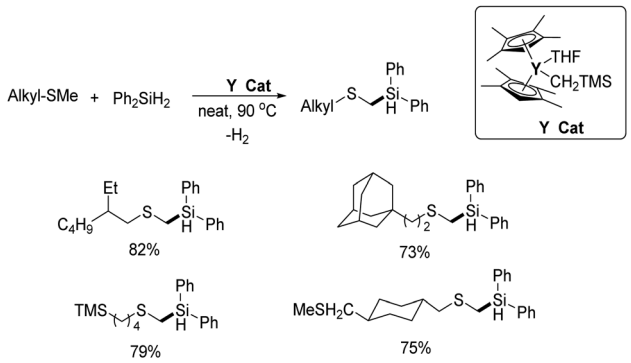
complex (5 mol%) with COE (1 equiv.) at 120 °C for 24 h and show that intramolecular silylation is faster with the NMe_2 compared to the OMe group (eqn (12)) and faster with the $SiCH_3$ compared to OCH_3 (eqn (13)), and faster with the NMe_2 compared to the SiMe group.[76]



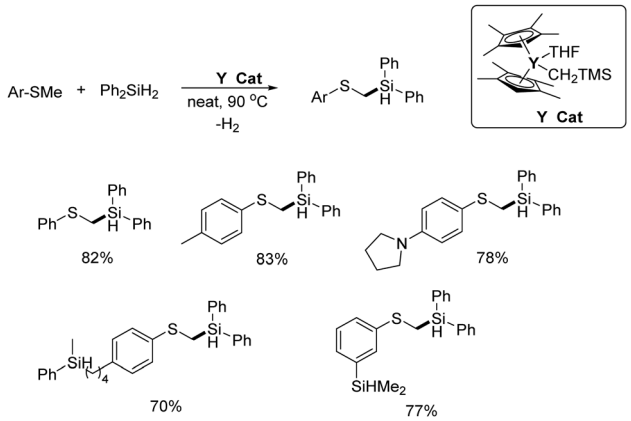
The observed K_H/K_D KIE of 3.9 suggests that the C–H bond cleavage is the rate determining step. The proposed mechanism based on exchange experiments is presented in Scheme 61.[76] The formed cyclooctyl group from **B** assists in **C** H–$SiMe_2$Aryl hydride elimination to give cyclooctane and **D.** Then the intramolecular interaction of the (CH_3O)C–H bond with the Ru–Si bond in **E** leads to C–H bond activation and Si–CH_2O bond formation to release the Ru–H catalyst species **A.**

8.4 Silylation of the S–CH_3 group with an yttrium catalyst

Directed silylation of the S–CH_3 group was observed in 2018 for the first time by Zhaomin Hou *et al.*[77] The catalytic silylation of a sp^3C–H bond of methyl sulfides $RSCH_3$ with H–SiR'_3 to produce $RSCH_2SiR'_3$ derivatives has been performed intermolecularly by using metallocene yttrium catalyst $(C_5HMe_4)_2Y(CH_2SiMe_3)(THF)$ which appeared to be the best catalyst precursor for this *S*-methyl C–H silylation. The catalyst precursor *in situ* gives in the presence of H_2SiR_2 the binuclear complex $(C_5HMe_4)_2Y(\mu H)_2Y(C_5HMe_4)_2$ as revealed for *n*-$C_5H_{11}SCH_3$ methyl silylation with $PhMeSiH_2$.[77] The same catalyst was the most efficient for the silylation of alkyl-SCH_3 sulfides without alkene as the H_2 acceptor (Scheme 62).



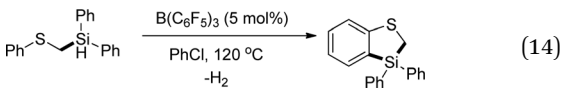
Scheme 62 Silylation of alkyl methyl sulfides with diphenylsilane and an yttrium catalyst.



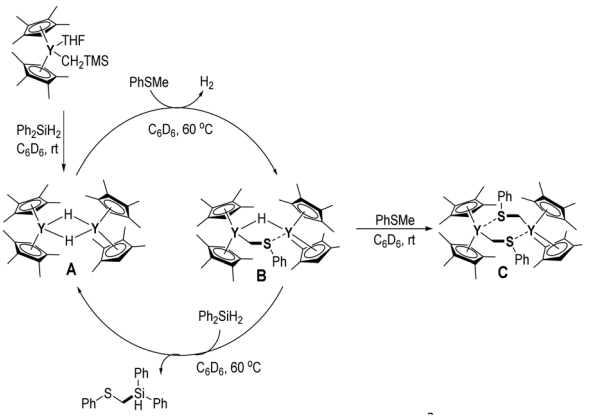
Scheme 63 Silylation of aryl methyl sulfides with diphenylsilane using the metallocene yttrium catalyst.

The same reaction with yttrium catalysts 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]

The prepared silylmethyl sulfides can be used for further intramolecular silylation of the *ortho* aryl sp^2C–H bond to generate 5-membered annulated products in the presence of the Lewis acid $B(C_6F_5)_3$ (eqn (14)).[77]



The proposed mechanism (Scheme 64) is based on stoichiometric reactions with silane with the catalyst precursor. With an excess of Ph_2SiH_2 at room temperature the formation of bimetallocene **A** containing bridged hydrides is observed. Complex **A** reacts at 60 °C with $PhSCH_3$ to give the characterized intermediate **B** with a Y–CH_2S(Ph)–Y bridge. The intermediate **B** can further lead to **C** with two identical –CH_2S(Ph)-bridges. Both **B** and **C** react with 5 equiv. of Ph_2SiH_2 at 60 °C to give the $PhSCH_2SiHPh_2$ silane and to regenerate **A.**



Scheme 64 Mechanism for silylation of the sp^3C–H bond of phenyl methyl sulfide with an yttrium catalyst.

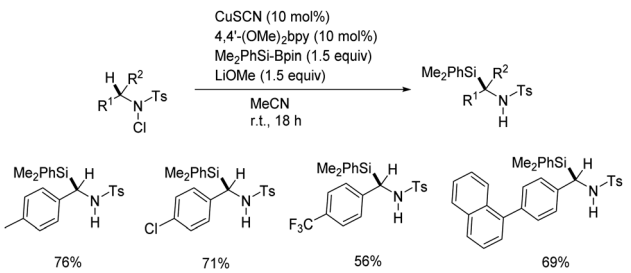
8.5 Directed silylation of the α-C–H bond of (sulfonamide)XN–CHR_2

Recently Oestreich[78] has demonstrated the silylation of the sp^3C–H bond adjacent to amide nitrogen atoms with R_3Si-Bpin/alkoxide. The reaction is catalyzed by CuSCN/4,4′-$(OMe)_2$bpy (10 mol%). The silylation occurred easily with *N*-chloro sulfonamides and with $MePh_2$Si-Bpin (Scheme 65). The yields are in the range 50–76% with aryl as the R^1 group but drop at 29–35% when R^1 is an alkyl group.

Although the reaction presented here corresponds to the formation of an sp^3C–Si bond, it does not involve the formal silylation of an 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/$(MeO)_2$bpy. 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* the initial formation of the radical $PhCH_2N^{\bullet}Ts$, by action of Cu(I), rearranging into $PhC^{\bullet}HNHT$ radicals which can give, by action of Cu(II), the cation intermediate $PhCH^{+}NHTs$ leading to the imine upon deprotonation (eqn (15)).

$$\mathrm{PhCH_2N(Cl)Ts} \xrightarrow[-\mathrm{Cl^-}]{\mathrm{Cu(I)}} \mathrm{PhCH_2N^{\bullet}Ts} \xrightarrow{\text{1,2-H Shift}} \mathrm{PhC^{\bullet}(H)NHTs}$$
$$\xrightarrow{\mathrm{Cu(II)}} \mathrm{PhC^{+}(H)NHTs} \xrightarrow{\mathrm{Base}} \mathrm{PhCH{=}NTs} \qquad (15)$$



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

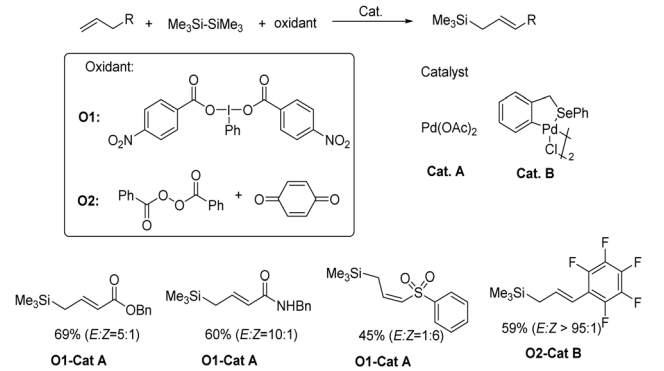
9. Silylation of allylic and alkane C–H bonds producing a terminal CH_2–SiR_3 function

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 Szabó,[79] Peng-Fei Xu[80] and Zheng Huang[81] 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 bonds[80] and the third presents the dehydrogenation of alkanes followed by isomerization and hydrosilylation of resulting alkenes.[81]

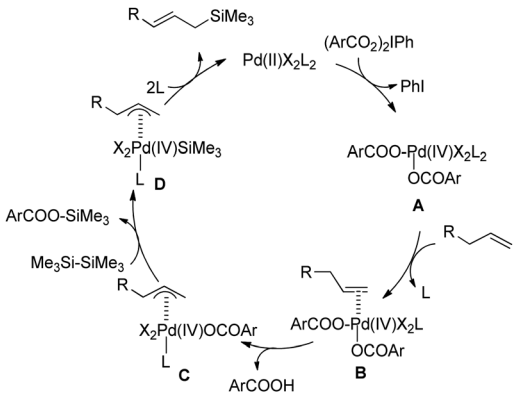
In 2011 Szabó described the catalytic silylation with Me_3Si–$SiMe_3$ of a functional allylic group with sp^3C–Si bond formation.[79] The reaction was catalyzed by $Pd(OAc)_2$ or a Pd(II)-cyclometalate complex but the reaction needed a strong oxidant such as hypervalent iodine reagent $(ArCO_2)_2$IPh, 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).

The proposed mechanism (Scheme 67) suggests the initial formation of a Pd(IV) intermediate **A** upon oxidation of Pd(II) with $(ArCO_2)_2$IPh. Coordination of the allyl double bond in **B** is followed by π-allyl ligand formation in **C** upon C–H bond deprotonation with a carboxylate. Then transmetalation with Me_3Si–$SiMe_3$ leads to the intermediate **D** which is subjected 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).

Photocatalysts have been successfully used for the selective functionalization of C–H bonds, but mostly until now of sp^2 C–H bonds.[82] However, recently Peng-Fei Xu *et al.*[80] reported a new method to generate substituted allylsilanes *via* dehydrogenative silylation of alkenes with H–SiR_3. The silylation does



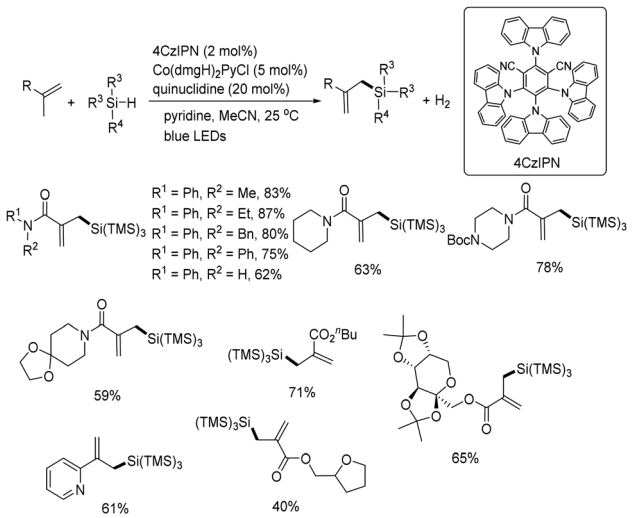
Scheme 66 Synthesis of allylsilanes by catalytic C–H silylation.



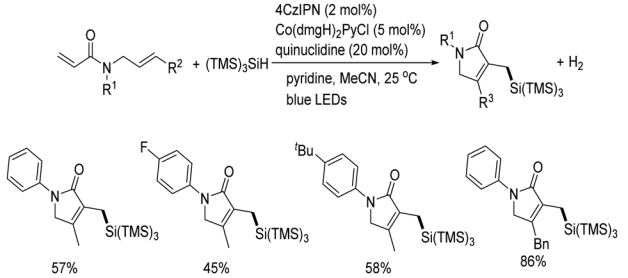
Scheme 67 Proposed catalytic cycle for silylation of the functional allyl group.

not involve the functionalization of the C–H bond but regioselectively takes place by addition of a silyl radical at the terminal carbon of the allyl C=C bond of $RC(CH_3)=CH_2$ to form a terminal CH_2–SiR_3 bond in $R(=CH_2)CH_2SiMe_3$. The reaction involves the initial generation of a $R_3Si^{\bullet}$ 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 a 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 acrylate derivatives (Scheme 68).

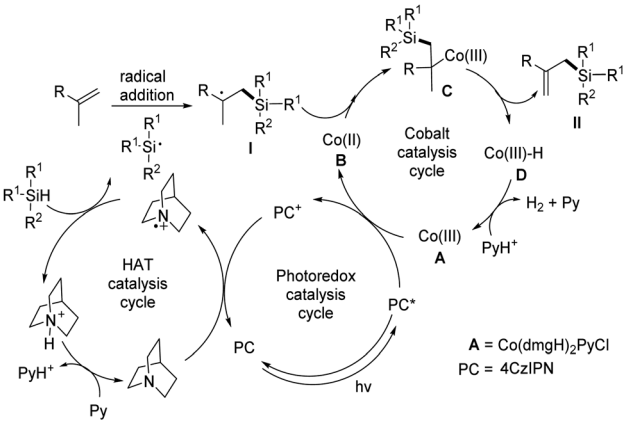
This tricatalytic system was applied to *N*-allyl-*N*-arylacrylamides to produce related cyclic silylated products with a terminal CH_2SiR_3 group: 5-membered α,β-unsaturated γ-lactams *via* 5-*exo*-trig cyclization (Scheme 69). This general transformation was also



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



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



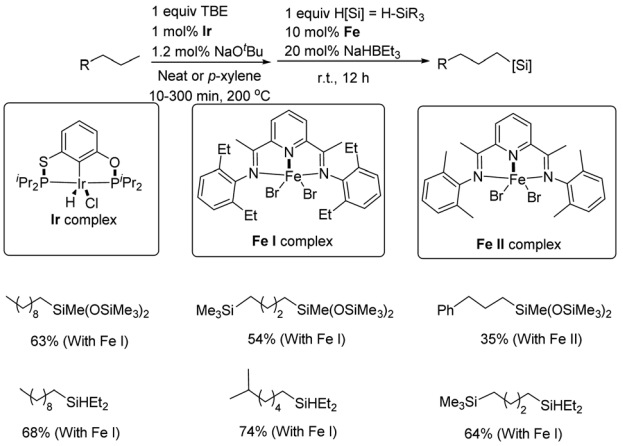
Scheme 70 A proposed mechanism for dehydrogenative silylation of alkenes into allyl silanes.

performed at the gram scale. However, the reaction could not be applied to non-conjugated *N*-benzyl and *N*-cyclohexyl acrylamides.

This transformation involves the formation of radical intermediates as it is inhibited *via* a radical trap TEMPO. The proposed mechanism is shown in Scheme 70.[80] The reaction requires the presence of a photocatalyst **PC** (4CzIPN) which upon excitation with blue LED generates the excited **PC*** which is oxidized by Co(III) species **A** giving $\mathbf{PC}^+$ cations and Co(II) species **B**. ($E_{1/2}^{red}$ Co(III)/Co(II) = −0.68 V *vs.* SCE). Then the $\mathbf{PC}^+$ = $4CzIPN^+$ species ($E_{1/2}^{red}$ P^+/P = +152 V *vs.* SCE) oxidizes the HAT catalyst quinuclidine **Q** ($E_{1/2}^{red}$ = +1.10 V) to give $\mathbf{Q}^{\bullet+}$ and initial photocatalyst **PC**. The radical cation $\mathbf{Q}^{\bullet+}$ is able to trap the hydrogen atom from H–SiR_3 to generate the radical $R_3Si^{\bullet}$.

Subsequent addition of the $R_3Si^{\bullet}$ 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 latter *via* classical beta elimination generates the new alkene with an allyl silyl group **II**. The resulting Co(III)–H species **D** upon 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–$CH(R')=CH_2$, which does not involve a direct C–H bond functionalization, but the formation of a silyl radical, has strong potential to produce regioselectively functional allylsilanes and to open new selective silylations.



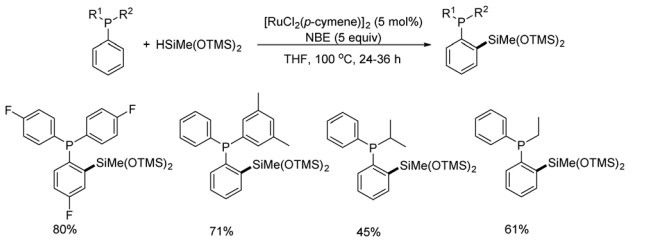
Scheme 71 Catalytic silylation of various alkanes *via* catalytic alkane dehydrogenation and isomerization–hydrosilylation.

Linear alkylsilanes are one of the most important compounds having wide applications in the preparation of 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 has been seldom reported in spite of their importance. However, Zheng Huang *et al.* in 2015[81] reported a new method to produce linear alkylsilanes *via* a dual-catalyst system, and one pot and three-step alkane silylation. These catalytic systems involve a pincer-ligated Ir(III)-catalyzed alkane dehydrogenation to generate an internal olefin and Fe catalyzed successive regioselective olefin isomerization and hydrosilylation (Scheme 71).[81] The (PNN)$FeBr_2$ 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.

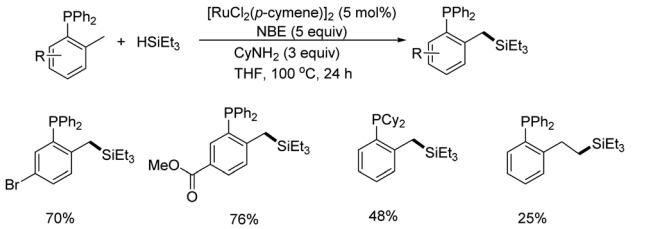
10. Catalyzed sp^3C–H bond silylation directed by phosphine P(III) atoms

Quite recently Zhuangzhi Shi[83] explored the possiblity of silylating the aryl sp^2C–H bond of P(aryl)R_2 phosphines, using H–$SiEt_3$ or $HSiMe(OTMS)_2$ and a Ru(II) catalyst precursor $[RuCl_2(p\text{-cymene})]_2$. In spite of the difficulty of 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 occurred efficiently in the presence of norbornene as the hydrogen acceptor at 100 °C at the *ortho* position of the phosphorous atom (Scheme 72).

More importantly, when an *ortho* methyl group was present on the aryl group of the phosphine, the ruthenium(II) catalyzed dehydrosilylation of the methyl sp^3C–H bond with H–$SiEt_3$ took place easily at 100 °C in THF but with the addition of $CyNH_2$ as



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



Scheme 73 Ru-Catalyzed sp^3C–H silylation of *ortho* methyl groups in arylphosphines.

a base (Scheme 73).[83] The observed silylation shows that the mono silylation of sp^3C–H bonds at *ortho* methyl groups 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, CO_2Me). When an *ortho* ethyl group is present instead of a methyl group, the silylation takes place at the primary C–H bond (Me) rather than at the secondary (CH_2) C–H bond.

The transformation of the *ortho*-CH_2SiEt_3 group, of the triaryl phosphines prepared as shown in Scheme 73, into a $CH_2CH(OH)Ph$ group can be easily performed upon reaction with PhCHO in the presence of the salt $N(^nBu)_4^+F^-$ at 60 °C.[83]

This mild condition, intermolecular silylation of the alkyl group of phosphine ligands likely takes place *via* deprotonation by $CyNH_2$ of the methyl or ethyl sp^3CH bond upon interaction with the Ru(II) center to form a 5-membered cyclometalate, or 6-membered cyclometalate from the ethyl group, as deprotonation assisted by a Ru(II) site requires low energy.[84,85] This simple silylation has the potential to modify many useful phosphorous ligands already used in metal-catalyzed reactions.[86]

11. Conclusions and outlook

Several methods for the metal-catalyzed activation of sp^3C–H bonds synchronized with silylation of this sp^3 carbon to produce sp^3C–SiR_3 bonds are now efficient in the modification of functional molecules, ligands to build catalysts or molecular materials, and to offer functionalization 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 the addition of an alkene as a hydrogen trap. This regioselective formation of CH_2SiR_3 groups allows their easy transformation such as *via* oxidation and carboxylation. Intramolecular sp^3C–H bond silylation with $R_3Si–SiR_3$ can be directed by an amide type function in the presence of Pd(II) catalysts which involves first 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 steroselective sp^3C–H bond silylation of aminoacids and peptides.

The intramolecular silylation of sp^3C–H bonds can be performed, after the initial formation of a $R'CH_2O–SiR_2(H)$ group, by catalytic dehydrohydrosilylation of alcohols or hydrosilylation of ketones with H_2SiR_2. The $R'CH_2O–SiR_2(H)$ 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 the γ or δ position. A similar initial silylation of amine NH bonds into $N–SiR_2H$ groups allows further intramolecular silylation of the neighbouring sp^3C–H bond using Ir(I) catalysts with alkenes as the H_2 trap. Both catalytic silylation steps can be performed in one pot using the same Ir(I) catalyst but with the addition of alkene for the second intramolecular step. The sp^3C–H silylation step can be controlled, upon addition of chiral diphosphine, to reach good enantioselectivities especially in the functionalization of cyclopropyl derivatives.

Silanes containing a $C–SiR_2H$ group at the proximity of a CH_2R group, such as in *ortho* alkyl arylsilanes can lead to an intramolecular catalytic silylation of one sp^3C–H bond with the formation of 5-membered silanes using Rh(I) or Ir(I) catalysts 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 also lead to intramolecular silylation into 5-membered cyclic silanes. This reaction upon oxidation offers new access to 1,4-diols.

Intermolecular and intramolecular sp^3C–H bond silylation of $X–CH_3$ into the $X–CH_2SiR_3$ group can be performed for a variety of heteroatoms X (X = B, Si, O, N, Ge, S). $B–CH_3$ groups are silylated after the addition of a dinitrogen bidentate ligand to boronic acid, with the help of a Ru(0) catalyst precursor. Intermolecular silylation of the $SiCH_3$ bond using Ir(I)/phenanthroline catalysts can be directed for the production of 5- and 6-membered 1,3-disilanes. In contrast, the pincer-Ru(II)–H catalyst allows the intramolecular silylation of the C–H bonds of XCH_3 groups (OCH_3, NCH_3, $Si–CH_3$ and $Ge–CH_3$) to produce 5-membered cycles with the $X–CH_2–Si$ arrangement. The intermolecular silylation of $alkylSCH_3$ and $arylSCH_3$ can now be easily achieved using an yttrium metallocene catalyst.

Formal silylation of the allyl group $CH_3–C(R)=CH_2$ into the reactive group $CH_2=C(R)–CH_2SiR_3$ can be performed in several ways although they do not involve direct sp^3C–H bond silylation. (1) Pd(II) catalysts with an oxidant are used for the silylation with $Me_3Si–SiMe_3$ of the allyl group, *via* an allyl-Pd(IV) intermediate. (2) A photocatalyst associated with 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 $CH_2=C(R)–CH_2SiR_3$ derivatives. (3) A 3-step alkane silylation into a terminal linear alkyl silane alkyl-CH_2SiR_3 can be performed using an Ir(III) catalyst to dehydrogenate the alkane into alkenes and an 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 an sp^3C–H bond has just been performed *via* the silylation directed by a (phosphine)P(III) atom for the regioselective silylation of an *ortho* methyl group of arylphosphine, with a Ru(II) catalyst in the presence of alkene. This new reaction should allow fast modification by sp^3C–H bond silylation of a variety of phosphine or diphosphine ligands containing alkyl groups.

These successful examples show that classical noble metal catalysts which are mostly derivatives of Ru, Rh, Ir and Pd metals are required for both the sp^3C–H bond activation and the Si–H or Si–Si bond activation, for sp^3C–Si bond formation. Recently, many examples of sp^3C–H bond activation to make sp^3C–C bond cross-couplings have been discovered with first row metal catalysts (Mn, Fe, Co),[87–90] and thus we can expect that these cheap and less toxic metal catalysts will also inspire chemists to perform sp^3C–H bond catalytic silylations with them.

The first evidence for direct catalytic silylation of a methyl group linked to an aryl group of phosphine into a aryl-CH_2SiR_3 group suggests that in the near future useful phosphines or diphosphines, even chiral ones, could be modified by the introduction of a sterically hindered group such as CH_2SiR_3 or could be transformed into new functional products quickly leading to new functional ligands and their metal catalysts as has already been shown for phosphine sp^2C–H bond functionalization.[83,86,91,92]

This easy transformation of sp^3C–H bonds into CH_2SiR_3 groups has already allowed 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 will also modify monomers in one pot reactions 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 catalytic sp^3C–H bond silylation will 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.

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