

Inorganometallics (Transition Metal–Metalloid Complexes) and Catalysis

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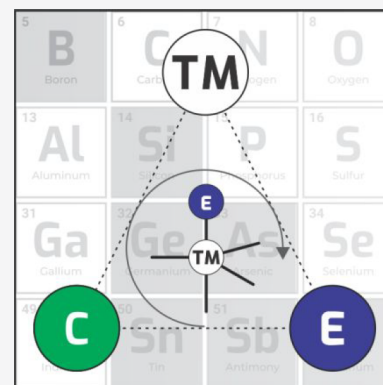
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ABSTRACT: While the formation and breaking of transition metal (TM)–carbon bonds plays a pivotal role in the catalysis of organic compounds, the reactivity of inorganometallic species, that is, those involving the transition metal (TM)–metalloid (E) bond, is of key importance in most conversions of metalloid derivatives catalyzed by TM complexes. This Review presents the background of inorganometallic catalysis and its development over the last 15 years. The results of mechanistic studies presented in the Review are related to the occurrence of TM–E and TM–H compounds as reactive intermediates in the catalytic transformations of selected metalloids (E = B, Si, Ge, Sn, As, Sb, or Te). The Review illustrates the significance of inorganometallics in catalysis of the following processes: addition of metalloid–hydrogen and metalloid–metalloid bonds to unsaturated compounds; activation and functionalization of C–H bonds and C–X bonds with hydrometalloids and bismetalloids; activation and functionalization of C–H bonds with vinylmetaloids, metalloid halides, and sulfonates; and dehydrocoupling of hydrometalloids. This first Review on inorganometallic catalysis sums up the developments in the catalytic methods for the synthesis of organometalloid compounds and their applications in advanced organic synthesis as a part of tandem reactions.



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INTRODUCTION: INORGANOMETALLIC VERSUS ORGANOMETALLIC CHEMISTRY AND CATALYSIS: GENERAL GUIDELINES

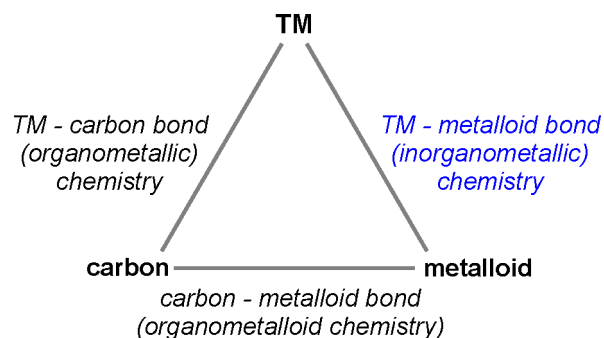
According to the commonly accepted definition, organometallics are compounds that contain at least one chemical bond between a carbon atom of an organic group or molecule and a metal atom or atoms (a main group element, a transition metal (TM) or a lanthanide or actinide). The importance of organometallics in catalysis results from the reactivity of TM–C intermediates, which are active in the crucial steps of important organic synthesis processes (e.g., olefin oxidation, hydroformylation, carbonylation, hydrogenation, olefin metathesis) and the preparation of polymers (Ziegler–Natta polymerization, oligomerization of olefins).

Elements such as boron, silicon, germanium, tin, arsenic, antimony, and tellurium, known in the literature as metalloids,

can form chemical bonds with carbon, and the resulting compounds are also classified as organometallic compounds. However, if metalloids form at least one chemical bond with a metal atom or atoms, the resulting species may be called inorganometallics. Such compounds are investigated in a new field of science called inorganometallic chemistry.¹ Therefore, although distinctly different from organometallics, the compounds that contain TM–metalloid bonds also act as active intermediates, particularly in the transformations of *p*-block compounds, such as those with silicon, boron, germanium, tin, arsenic, antimony, and tellurium.

Advances in organometallic chemistry, including the results of intensive research on the organometallic chemistry of boron, silicon, and other metalloid compounds, have clearly shown that the chemical properties of compounds containing a metal–metalloid bond, particularly when the metal is a TM, significantly differ from those having a metal–heteroatom (O, S, N, P) bond. The interrelation between organometallic, organometalloid, and inorganometallic chemistry is illustrated by the triangular Scheme 1.^{2,3}

Scheme 1. Concept of Inorganometallic Chemistry and its Relationship with Organometallic and Organometalloid Chemistry



According to a number of findings, the reactivity of inorganometallic species, particularly those having a TM–metalloid bond, is of key importance in most conversions of metalloid derivatives catalyzed by TM complexes.

Our review “*Inorganometallic Chemistry*”, published in 2007, focused on the synthesis, structure, and reactivity of inorganometallic compounds containing a bond between a TM and elements of main groups 13–16 (excluding C, N, P, O, and S).² The review discussed the key role of TM–metalloid bonds (inorganometallics) in catalytic transformations as well as their use in materials chemistry.

The purpose of the current Review is to discuss the scientific literature published since 2006 on the catalytic transformations of compounds of selected metalloids (B, Si, Ge, Sn, As, Sb, Te) catalyzed by TM complexes and to present and systematize the most important achievements of inorganometallic catalysis. By way of exception, we will consider tin as well because its electronegativity and first ionization potential values meet the criteria of metalloids and the reactivity of tin compounds in catalytic processes is similar to that of germanium and silicon derivatives. We intend to show the great potential of such inorganometallic compounds in chemical synthesis, thereby drawing special attention to reaction mechanisms and illustrating the role of inorganometallics in catalysis.

The following processes are discussed in this Review:

1. addition of metalloid–hydrogen bonds to unsaturated compounds
2. addition of metalloid–metalloid bonds to unsaturated compounds
3. activation (and functionalization) of C–H bonds with hydrometalloids and bismetalloids
4. activation (and functionalization) of C–X bonds with hydrometalloids and bismetalloids
5. dehydrocoupling of hydrometalloids
6. activation (and functionalization) of C–H bonds with vinylmetalloids
7. activation (and functionalization) of C–H bonds with metalloid halides and sulfonates
8. applications in organic synthesis

Most of the above processes that involve the reactivity of organometalloids in addition and coupling reactions in the presence of TM complexes have been addressed in several reviews and books that will be cited in the discussion of individual reactions. Most of them are written in a similar way and focus mostly on catalyst reactivity and efficiency of synthesis, while the role of inorganometallic compounds as key intermediates has not been given the attention it deserves. In this Review, we address the background of inorganometallic catalysis and present its development over the past 15 years. We also discuss our personal perspectives on the future trends and directions that could make inorganometallic catalysis the new benchmark in homogeneous catalysis. Consequently, the aim of this work is to present an overview of the main achievements in a variety of the above-mentioned reactions of *p*-block element compounds catalyzed by TM complexes leading to organometalloid products. In their transformations, inorganometallics are actually catalysts, but they simultaneously yield products that contain carbon–metalloid and metalloid–metalloid bonds.

Finally, it is noted that the above-mentioned processes may be incorporated in the tandem (sequential) reactions that play an important role in advanced organic synthesis.

TRANSFORMATIONS OF METALLOID COMPOUNDS CATALYZED BY TM COMPLEXES: MECHANISTIC ASPECTS OF CATALYSIS

The aim of this paper is to present an overview of the main achievements in a variety of reactions of metalloid compounds of groups 13, 14, 15, and 16 catalyzed by TM complexes. In these transformations, TM–metalloid complexes (inorganometallics) are the actual catalysts, and the E derivatives do not act as ancillary ligands but undergo transformations leading to products containing carbon–metalloid or metalloid–metalloid bonds.

TM-catalyzed carbon–carbon bond formation developed in the 1970s was a milestone in synthetic organic chemistry, and this type of catalysis has been successfully applied in the selective syntheses of a variety of molecular and macromolecular organometallic compounds.^{4–9} However, TM complexes have been recognized as very efficient catalysts in the transformations in which the molecular and macromolecular compounds that contain carbon–metalloid or metalloid–metalloid bonds can be synthesized. The results of mechanistic studies published since 2006 indicate that such processes occur in the presence of catalytic species that contain initially or in situ generated TM–H and TM–E bonds. Therefore, in this paper, we discuss the important role

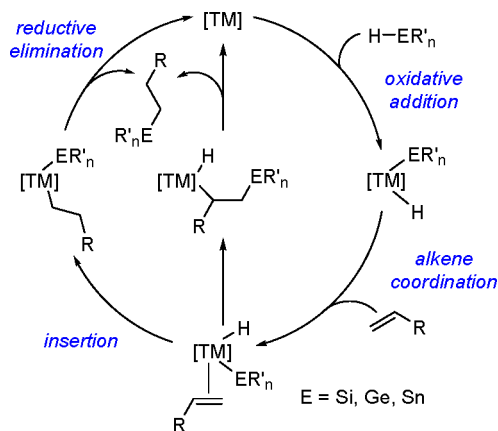
of inorganometallics (transition metal–metalloid complexes) as reactive intermediates in the catalytic transformations.

1. ADDITION OF METALLOID–HYDROGEN BONDS TO UNSATURATED COMPOUNDS

The most widely used methods for forming E–C bonds in the presence of a TM include the addition reactions of hydrides of group 14 elements to carbon–carbon double and triple bonds (hydrosilylation, hydrostannylation, and hydrogermylation) and of group 13 (hydroboration). The knowledge on hydrometalation with group 14 and group 13 elements was discussed in the first edition of *Comprehensive Organic Synthesis II* in 2014.^{10,11}

The general mechanism presented in Scheme 2 for the addition of R_nE–H (where E is Si, Ge, or Sn) to alkenes

Scheme 2. General Mechanism of the Hydrometalation (E = Si, Ge, Sn) of Alkenes by TM Complexes



catalyzed by late TM complexes, provided by Chalk and Harrod in 1965, is based on hydrosilylation¹² catalyzed by Pt complexes.

Intermediates with metal–silicon bonds (i.e., silicometallics) or other inorganometallics versus organometallics play a decisive role in the mechanisms of all catalytic reactions of substrates that contain silicon (or other metalloids).^{2,13}

The mechanism includes a conventional oxidative addition of Si–H (Ge–H, Sn–H) to a metal–alkene complex configuration (usually d^8 – d^{10}), followed by alkene insertion into the TM–H bond. The resulting metal–inorganometallic alkyl complex undergoes reductive elimination by E–C bond formation and regeneration of the TM catalyst. However, a modified version of the mechanism has also been proposed, which involves alkene insertion into the metal–metalloid bond followed by reductive elimination.¹⁴

TM complexes with a silyl (or germyl or stannyl) ligand as an anionic X-type ligand have been extensively studied as important intermediates in various catalytic silylation (germylation, stannylation) reactions, such as hydrosilylation and C–H silylation.^{15–18}

1.1. Hydrosilylation of Unsaturated Bonds

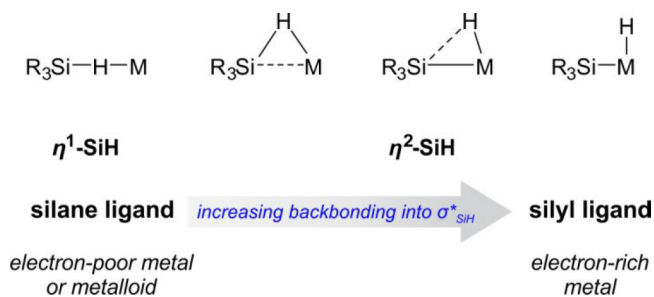
Hydrosilylation (also called hydrosilation) is the most significant hydrometalation in group 14. This process of industrial importance is used primarily to synthesize organofunctional silicon monomers and cross-linked silicone polymers and to prepare other molecules and macromolecules, such as saturated and unsaturated organosilicon compounds

and inorganic materials. Most industrial hydrosilylation processes occur in the presence of H_2PtCl_6 , used as the initial precursor (mostly Speier's catalyst and Karstedt's complex catalyst, $[\text{Pt}_2\{(\text{CH}_2=\text{CHMe}_2\text{Si})_2\text{O}\}_3]$).

Hydrosilylation is a well-documented process in silicon chemistry discussed in detail (including the catalyst selection) in several excellent reviews and books.^{17–32} In our review of 2009,¹⁸ we addressed all the mechanistic aspects of alkene and alkyne hydrosilylation catalyzed by nickel and iron and cobalt group complexes, which follows the anti-Markovnikov rule but under some conditions yields α -adducts or dehydrogenative silylation products that are also attractive for synthesis.¹³ In this Review, we discuss only the new mechanistic aspects of TM-catalyzed hydrosilylation published in the past 12 years.

1.1.1. Homogeneous Catalysis of Alkene and Alkyne Hydrosilylation. TM organosilicon complexes have recently drawn much attention, particularly in view of catalysis and the differences between metal–silicon and metal–carbon bonds. Some reviews^{15,19,30} have shown the special role of silicon in catalytic processes. Silicon is less electronegative than carbon, and many of the mid-to-late TMs act mostly as electrophiles and Lewis acids. Owing to this low electronegativity and a relatively large size, silicon develops a variety of bonds exhibiting secondary interactions, for example, with hydrides. Polarization of the Si–H unit in hydrosilanes combined with the steric effect of H makes the Si–H unit a good electron donor for TM complexes. The electron-richness of a metal formally dictates a variety of structures. For an electron-poor acceptor, the interaction with a hydrosilane occurs via η^1 -coordination (see Scheme 3).³⁰

Scheme 3. Hydrosilane Binding Mode as a Function of Electron Density of the Metal Site

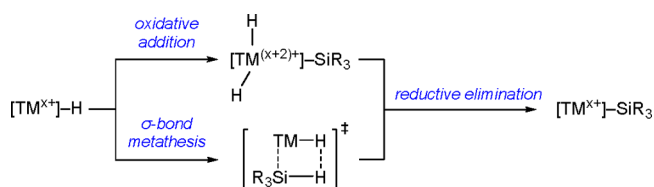


Most TM compounds with hydrosilanes include some M–Si interactions (π -back bonding into $\sigma^*\text{SiH}$) whose ultimate role is to bring about Si–H oxidative addition. However, for an oxidative addition process to occur, a coordinatively unsaturated metal precursor is required, which can be obtained via a reductive elimination process (H_2 or HX). When oxidative addition is not favored (especially for early TMs), another reaction pathway can be used: σ -bond metathesis may provide a low-energy step to a TM–silyl complex (Scheme 4).¹⁵

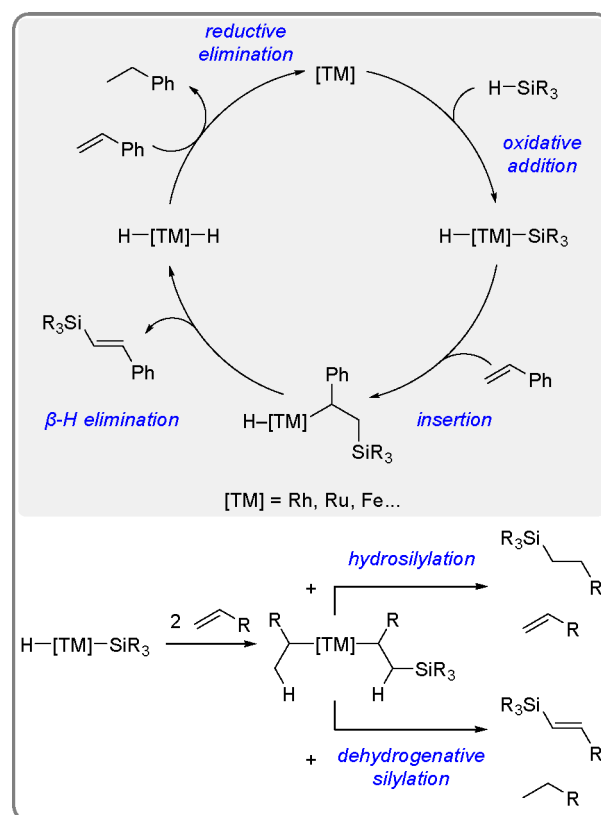
In contrast to the well-established platinum-catalyzed hydrosilylation, dehydrogenative silylation appears to involve iron and cobalt triad complexes, particularly cationic ones, and nickel complexes as its favored catalysts. A general scheme of the dehydrogenative silylation of styrene catalyzed by Rh, Ru, and Fe¹³ complexes is given in Scheme 5.

The key step of the two alternative reactions is a competitive σ -H transfer from two ligands (σ -alkyl and σ -silylalkyl) of the

Scheme 4. Simplified Comparison of the Oxidative Addition Reaction Pathway and σ -Bond Metathesis Pathway



Scheme 5. General Mechanism for the Dehydrogenative Silylation of Styrene Catalyzed by the Fe and Co Triad



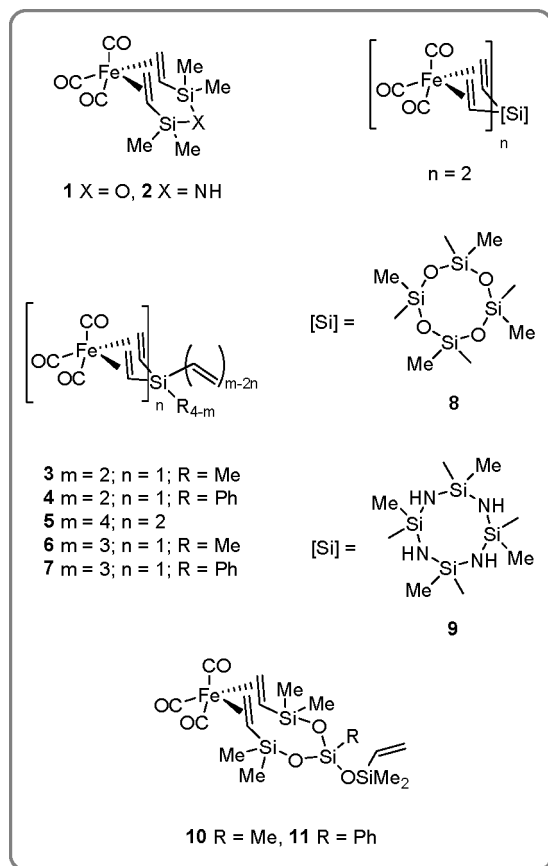
intermediate formed in the reaction. The mechanism of the dehydrogenative silylation of vinyl derivatives in the presence of a nickel equivalent of Karstedt's catalyst, with the first documented insertion of an olefin (styrene) into the Ni–Si bond, has been published.³³

The high cost of Pt-based hydrosilylation catalysts—caused by the low abundance of platinum in the earth's crust, the consumption of Pt-metals in silicone chemistry, and the low abundance of other noble metals (Pd, Ir, Rh) and their toxicity—has recently motivated experts on the catalysis of hydrosilylation to concentrate on earth-abundant TMs, such as iron, cobalt, and nickel complexes, as efficient homogeneous catalysts. Much progress has been recently seen in the investigation of the first-row TMs in the hydrosilylation of multiple bonds (e.g., alkenes, alkynes, $\text{C}=\text{O}$).

Therefore, based on the information from the past decade as cited in numerous reviews and original publications, we concentrate here predominantly on the coordination chemistry of earth-abundant metals (mainly Fe, Co, and Ni) and their role in the catalysis of the hydrosilylation of alkenes and alkynes and other multiple bonds, which can explain their wide application in synthesis and silicone industry. However,

examples of other novel TM–silicon complexes introduced as homogeneous and heterogeneous catalysts for efficient and selective hydrosilylation and dehydrogenative silylation have also been discussed. The studies on the reactivity of iron(0) carbonyl complexes of the 1960s led to the synthesis of many organometallic compounds by the substitution of carbonyl ligands with olefins, dienes, and alkynes.^{21,23,24,34} Diene ligands stabilize $\text{Fe}(\text{CO})_3$ reactive species as hydrosilylation catalysts.¹⁷ We developed a general strategy for the synthesis of new, well-defined iron(0) carbonyl complexes $[\text{Fe}(\text{CO})_3(\text{L})]$ and $[\text{Fe}(\text{CO})_3]_2\text{L}$, stabilized by multivinylsilicon ligands (by analogy to Karstedt's catalyst; see Scheme 6), which appeared

Scheme 6. A New Class of Well-Defined $\text{Fe}(\text{CO})_3$ -Based Complexes Stabilized with Multivinylsilicon Ligands



to be very active catalysts for the hydrosilylation and/or dehydrogenative silylation of alkenes as well as the cross-linking of silicone fluids.^{35–37} The X-ray structures of **1**, **2**, **4**, **5**, and **9** have also been published.

The UV-accelerated reaction of iron(0) carbonyl precursors with various multivinyl-substituted silicon derivatives, as shown in Scheme 7, resulted in a series of well-defined, five-coordinated $\text{Fe}(0)$ complexes in which highly reactive $\text{Fe}(\text{CO})_3$ species were stabilized by two vinyl groups.³⁵ The catalytic activity of all the $\text{Fe}(\text{CO})_3$ surrogates (see Scheme 7) has been examined in transformations in molecular and macromolecular Si–H/olefin systems. Detailed studies of the catalytic processes that occur between the above-mentioned compounds have shown that depending on the type of the olefin used or reaction conditions, two reactions may proceed effectively: hydrosilylation and dehydrogenative silylation.³⁶ Iron disilyl dicarbonyl complexes bearing two weakly

coordinated $\eta^2\text{-Si-H}$ moieties appeared to be good catalysts for the hydrosilylation of olefins and reduction of carbonyl compounds.³⁸

The possibility of replacing expensive platinum by catalytically active but cheaper derivatives of Fe, Co, Ni, and other TMs and novel applications of potent hydrosilylation and dehydrogenative silylation products in the synthesis of fine chemicals in materials science have been shown over the past decade by the research groups of Obligation and Chirik,²⁵ Nakazawa,³⁴ Huang,²⁰ Wiesbrock,²³ Beller,¹⁹ Lu,²⁴ Liu,²⁸ Findlater,²¹ and Nagashima,³⁸ among others.

The traditional study of alkene and alkyne hydrosilylation and dehydrogenative silylation by primary silanes has been extended to include secondary and tertiary silanes and (poly)hydrosiloxanes, as well as the hydrosilylation of dienes, ketones, aldehydes, and imines.

However, the most attractive aspect from the scientific point of view is the introduction of novel TM complexes including not only monodentate and bidentate ligands but also tridentate (pincer) ligands (for recent reviews, see refs 19 and 21). Using a ligand with the desired electronic and steric properties has appeared to be crucial for high catalytic activity and product selectivity and yield. Syntheses of new TM complexes that proved to be specific catalysts for some organosilicon products have often become the starting points for the mechanistic studies of hydrosilylation and dehydrogenative silylation processes.

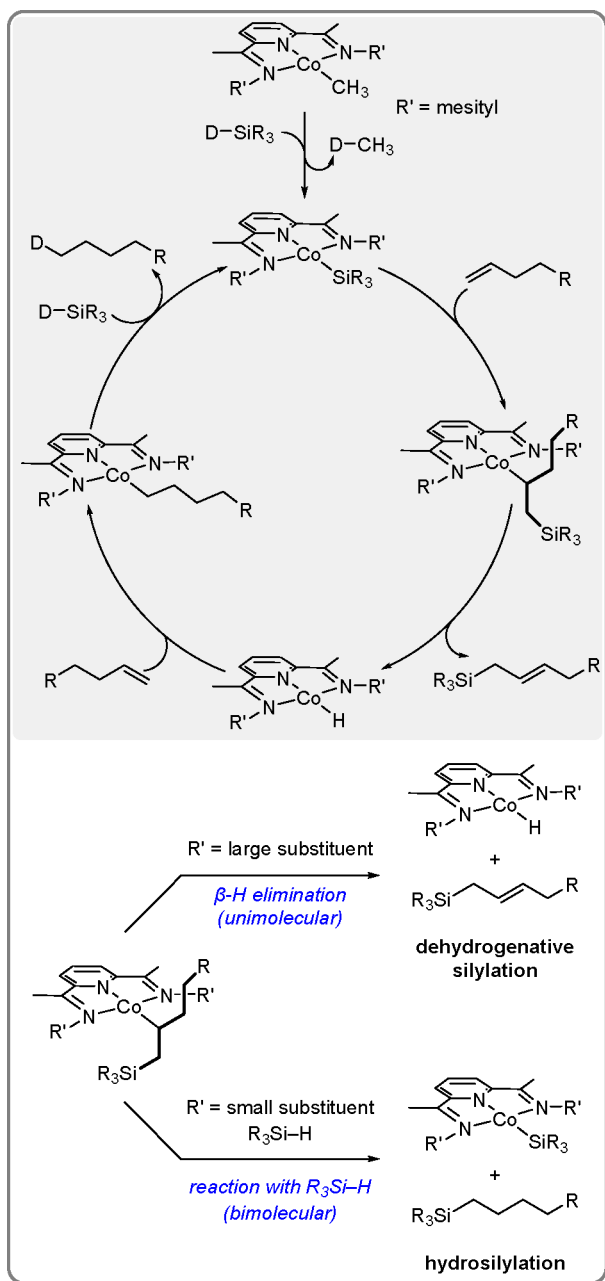
Example iron and cobalt pincer catalysts used in the hydrosilylation of alkenes, alkynes, aldehydes, and ketones are shown in Schemes 7–9 and 13–15 (see the above reviews). Certain examples of the mechanistic implications of these new systems are given below (see Schemes 7 and 9). A recent review by the Obligation and Chirik group²⁵ is a comprehensive report on the application of Fe and Co catalysts in commercially important alkene hydrosilylation, and industrially relevant tertiary silanes are predominantly used. Chirik's experiments using precatalysts in the form of $[(\text{RPDI})\text{Fe}(\text{N}_2)_2]$, where RPDI denotes 2,6-diiminopyridine and R represents substituents at the imine atom (Scheme 7), helped find the conditions for selective anti-Markovnikov alkene hydrosilylation in a very selective synthesis of functionalized silanes and effective cross-linking of silicone fluids. Preliminary treatment of the initial complex with excess silane yielded iron bis(silane) species, proposed as active intermediates in hydrosilylation catalysis.

New iron catalysts for these reactions were developed through experiments continued by other groups (Scheme 8).

The Co–alkyl complex $[(\text{RPDI})\text{Co}(\text{R})]$ (where R is CH_3) promotes the highly selective dehydrogenative silylation of linear olefins to yield allylsilanes.²² The starting alkene acts as the H acceptor to be converted to the corresponding alkane (Scheme 9). Large R' substituents at the imine promote unimolecular dehydrogenative silylation, whereas small substituents promote bimolecular reactions with hydrosilylation.

The proposed mechanism involves initiation of a precatalyst by the silane to yield a Co–silyl intermediate, followed by selective alkene 2,1-insertion and $\beta\text{-H}$ elimination to form a Co–H intermediate and allylsilane. Subsequently, alkene insertion is followed by the reaction of the silane with a Co–alkyl to regenerate the Co–silyl intermediate. The characteristic feature of this mechanism is that there is no need for a formal oxidative addition step of the silane; $1e^-$

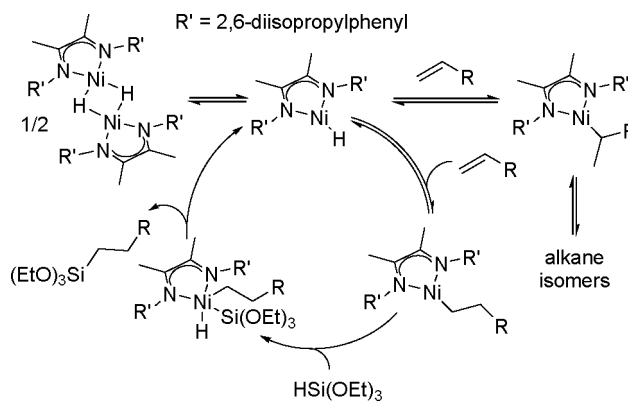
Scheme 9. Pyridine(diamine)Co-Catalyzed Dehydrogenative Silylation of 1-Olefins



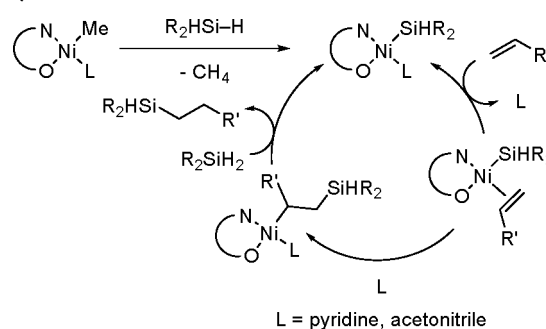
A different mechanism of olefin hydrosilylation by secondary silanes has been suggested by the Shimada and Nakajima group, using highly active and selective salicylaldiminato Ni catalysts³⁹ (Scheme 11). The hydrosilylation occurred at room temperature, but tertiary and primary silanes could not be used. The internal alkenes were also successfully hydrosilylated at 50 °C. ¹H and ²⁹Si NMR spectroscopic studies provided direct evidence that Ni–Si complexes were generated from the initial complexes with Ph₂SiH₂. Therefore, the proposed mechanism involves an active Ni–Si intermediate instead of the Ni–H complex.

The TM-catalyzed hydrosilylation of alkynes is one of the best methods for the synthesis of vinylsilanes, used as valuable starting fine chemicals for organic synthesis. The hydrosilylation process of terminal alkynes can produce three

Scheme 10. Mechanism of Alkene Hydrosilylation Catalyzed by the (α -Diimine)Ni Complex



Scheme 11. Mechanism of Olefin Hydrosilylation by Secondary Silanes Using (Salicylaldiminato)Ni(II) Catalysts



possible isomers: (*E*)- β -, (*Z*)- β -, and α -vinylsilanes. (*E*)- β -isomers are usually thermodynamically favored and therefore generated with high selectivity (for a review, see ref 28.).

The (*Z*)-selective hydrosilylation of terminal alkynes is more challenging than the synthesis of *E*-isomers. In a recent study by the Ge group, sterically congested pyridine-2,6-diimine (Mes PDI) (Co-1) and *i*-PrPDI (Co-2) pincer ligands have been found to be effective in the Co-catalyzed (*Z*)-selective anti-Markovnikov hydrosilylation of many terminal alkynes⁴⁰ (Scheme 12).

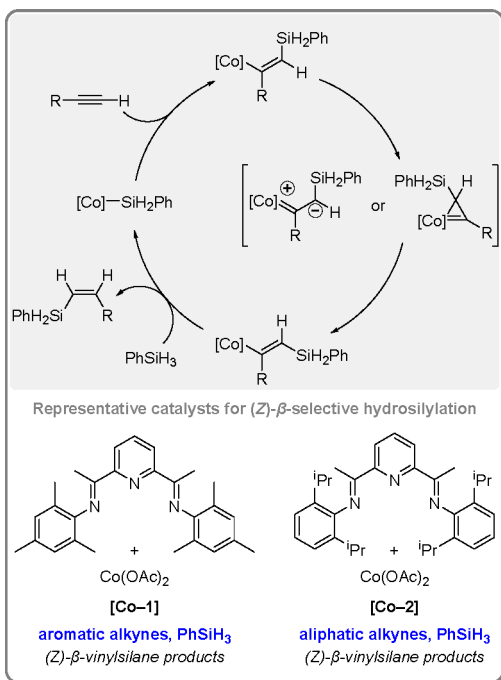
Deuterium labeling and kinetic measurements supported the catalytic cycle starting from a Co(I)–silyl intermediate.

However, the Huang⁴¹ and Lu⁴² groups have independently reported the α -selective hydrosilylation of terminal alkynes by secondary silanes using Co-3 and Co-4 catalysts. The mechanistic scheme (Scheme 13) proposes selective formation of a Co–silyl intermediate, but because of steric effects, selective 1,2 insertion proceeds to form a Co–alkenyl intermediate and to finally eliminate the α -adduct.

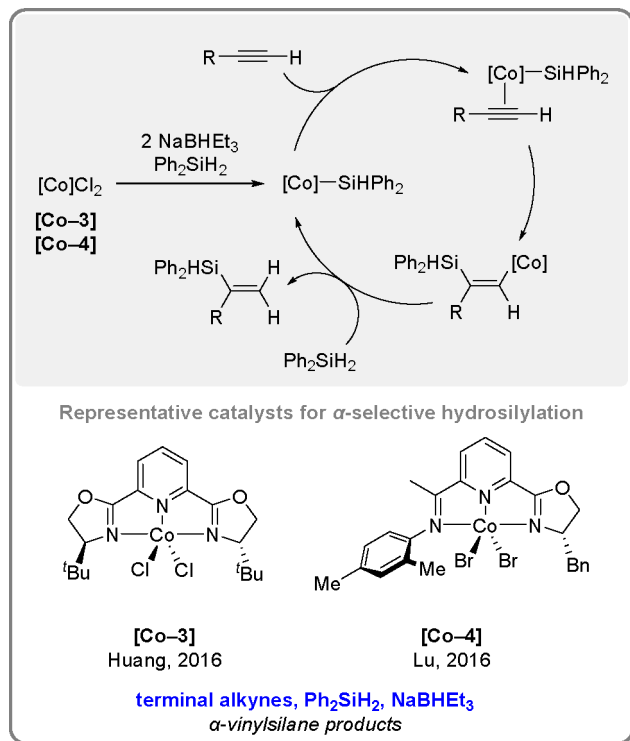
1.1.2. Homogeneous Hydrosilylation of Carbonyl Compounds and Imines. Continuing the review on the new developments in catalysis (by Fe, Co, and Ni complexes) from the previous decade, we also present the hydrosilylation of aldehydes, ketones, esters, and imines (for reviews, see refs 21, 23). The reviews summarize novel noninnocent redox-active ligands and mostly pincer ligands of the above metal triad (see Schemes 14–16).

Some examples of iron pincer complexes as catalysts for the hydrosilylation of ketones and aldehydes have been reported by the Chirik group.⁴³ The number of mechanistic studies is

Scheme 12. Mechanism of the Z-Selective, Anti-Markovnikov Hydrosilylation of Terminal Alkynes by Phenylsilanes



Scheme 13. Postulated Catalytic Cycle for the α-selective Hydrosilylation of Terminal Alkynes by Secondary Silanes Using Co-3 and Co-4 Catalysts



limited, and most studies have not been confirmed. Yet some evidence for the generation of active species, including Fe–H and Co–H bonds, has been reported. In situ activation of the catalysts with NaHBET₃ to generate Co–H bonds has been reported by the Lu⁴⁴ and Findlater^{21,47} groups, but the

activation mechanism proposed by Li's group⁴⁵ using a hydrido-cobalt complex does not require NaHBET₃.²¹

On the other hand, a broad iron-hydride resonance peak detected by the Enders and Gade group⁴⁶ using ¹H NMR provides reliable evidence for the TM–H catalysis of carbonyl hydrosilylation.

Cobalt pincer complexes have been recently applied for enantioselective hydrosilylation of carbonyl moieties (see ref 21). Gade et al. reported catalysis by a cobalt complex with a chiral 1,3-bis(2-pyridylimino)isoindolate ligand (see Scheme 14), which gave high yields and enantioselectivity up to 91% ee.⁴⁸ The combination of CoCl₂ with chiral iminophenyl-azolinylphenylamines (Scheme 14) reported by Chen and Lu⁴⁴ showed excellent activity with enantioselectivity up to 99%.

The Li group used a binuclear imine/nitrogen-bridged nickel catalyst for aldehyde hydrosilylation.⁴⁹ The mechanism they proposed includes preliminary cleavage of the binuclear bond to form a mononuclear species containing the (η²-Si-H)Ni(II) motif. One Si–H bond is cleaved and then an aldehyde molecule is inserted. A second H₂SiPh₂ molecule is involved in the reductive elimination, while the silane–nickel intermediate is recovered in the cycle⁴⁹ (Scheme 15).

Hydrosilylation of imines catalyzed by iron complexes has recently been developed as a reductive method for the synthesis of amines. Carbene ligands and ionic liquids are predominantly used for iron catalysts (see Scheme 16).^{50,51} A mechanistic study by Mandal group⁵¹ showed that the hydrosilylation process occurred according to the Chalk–Harrod mechanism, involving the oxidative addition of Si–H followed by hydride migration in the imine and reductive elimination of the product.

The Findlater group observed general tolerance to substrates having various functional groups when the [(dpp)(BIAN)Fe(η⁶-toluene)] complex was used as a catalyst for aldimine reduction into secondary amines.²¹ Photo- and peroxide-initiated catalysis by metal complexes is another method applied in hydrosilylation.^{13,18}

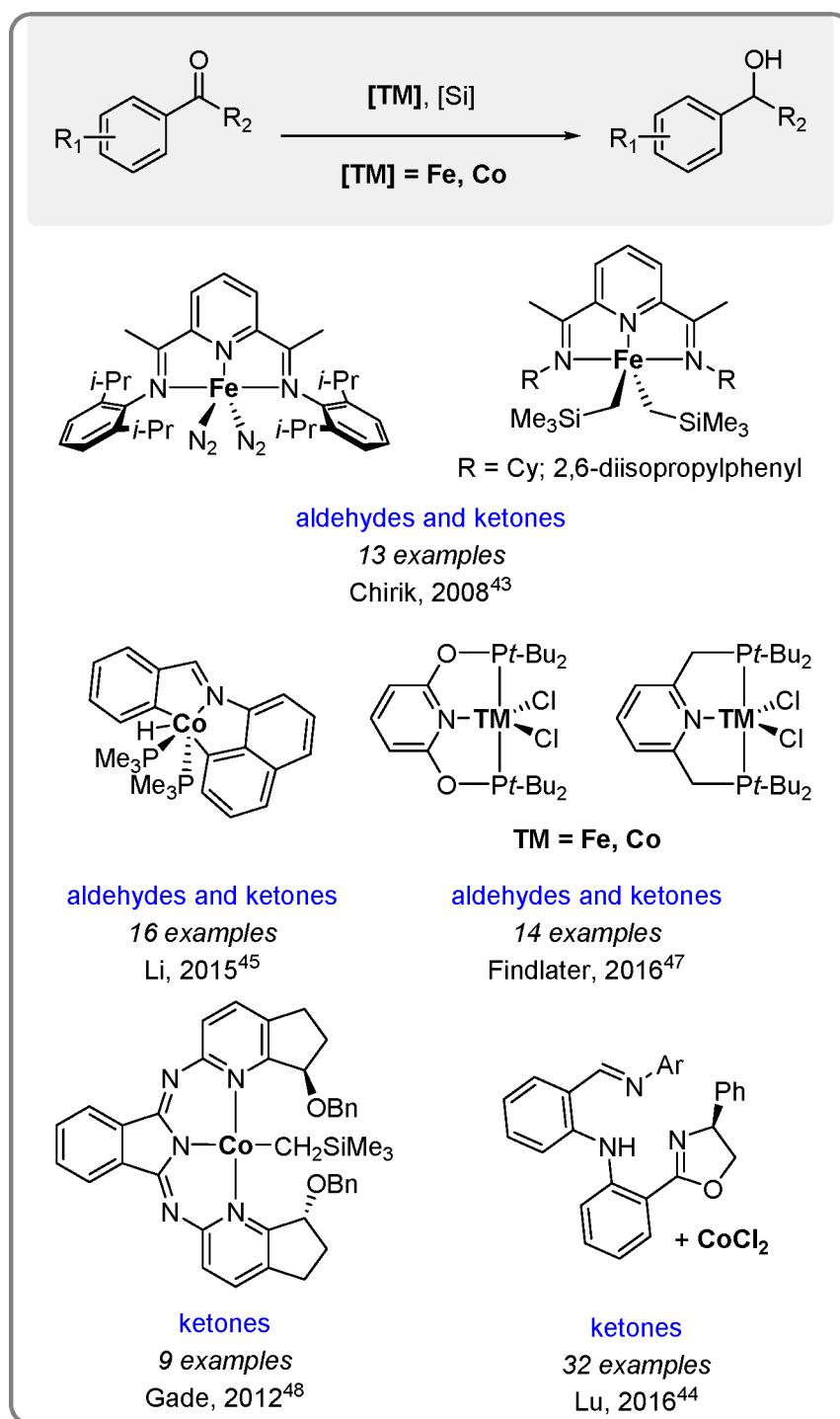
1.1.3. Immobilized TM Complexes as Catalysts.

Although most of the recent reviews address the important developments on cheaper homogeneous complex catalysts, some of the reviews emphasize the need for recyclable heterogeneous catalysts, that is, TM-complexes immobilized on appropriate polymers or inorganic supports such as silica. We reported the synthesis and characterization of a well-defined rhodium–siloxide complex immobilized by the direct reaction of a molecular siloxide precursor with Aerosil⁵² (Scheme 17).

Solid-state NMR results confirmed the presence of a surface siloxide complex (2) identified as a product of the oxidative addition of PhSiMe₂H to the surface siloxide complex (1 → 2). The absence of disiloxane elimination (confirmed by GC-MS) also shows involvement of such a key intermediate in the heterogeneous system, which apparently differs from the intermediate in the homogeneous system. The subsequent alkene coordination to the surface siloxide–Rh complex (2 → 3) is followed by its insertion into a Rh–H bond (3 → 4), with the final elimination of the product and regeneration of the stable surface complex (1). The interaction of the silanol group in 1 is responsible for the high stability of such a single-site rhodium catalyst which can be recycled at least 10–20 times without a decrease in high yield and selectivity.

The simultaneous immobilization of a Rh complex and a tertiary amine on the SiO₂ surface afforded a highly active

Scheme 14. Selected Examples of Iron and Cobalt Pincer Catalysts for the Hydrosilylation of Aldehydes and Ketones



supported catalyst for the hydrosilylation of terminal olefins⁵² (see Scheme 18). The interaction between the Rh complex and tertiary amines is a key factor in the preparation of a highly active catalyst. The TON was close to 1.9×10^5 over 24 h, and a variety of silanes and olefins were shown to be effective substrates.⁵³

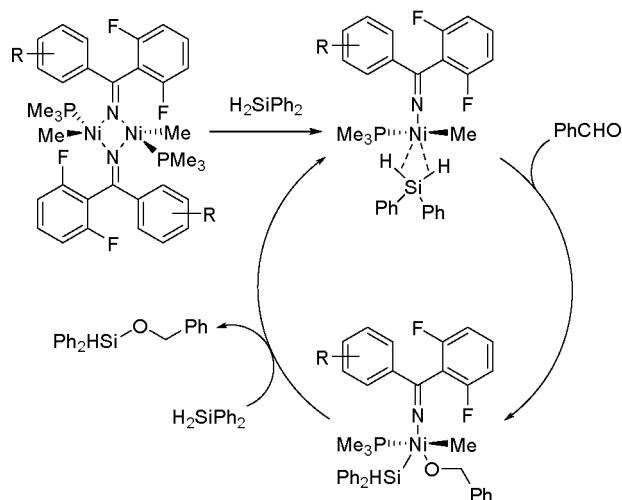
The catalytic mechanism by supported metal complexes is not yet clear. Thus, it is possible that the anchored complex could reversibly detach from the support during the reaction and that after detachment it would act in either a

homogeneous or a heterogeneous manner depending on the system.

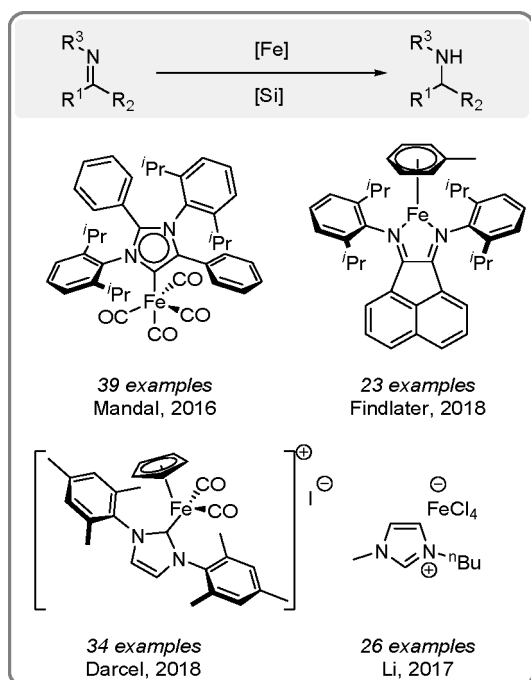
Although several supported Pt nanoparticles (NPs) have been developed for hydrosilylation, in some cases, poor recyclability caused by leaching was observed. Therefore, a new concept for catalytic hydrosilylation, which can be applied in industry and academia, was introduced by the Beller group. They proposed simple atom catalysts (SACs), that is, materials with isolated metal centers stabilized by neighboring salts (for example, impregnation of platinum salts on aluminum oxide nanorods).⁵⁴ These Pt-SACs showed high stability owing to

Scheme 15. Mechanism of the Nickel Complex Catalysis of Aldehyde Hydrosilylation by Secondary Silanes

R = H, p-Me, p-Cl, aryl-R = thienyl



Scheme 16. Hydrosilylation of Imines Catalyzed by Fe Complexes²¹



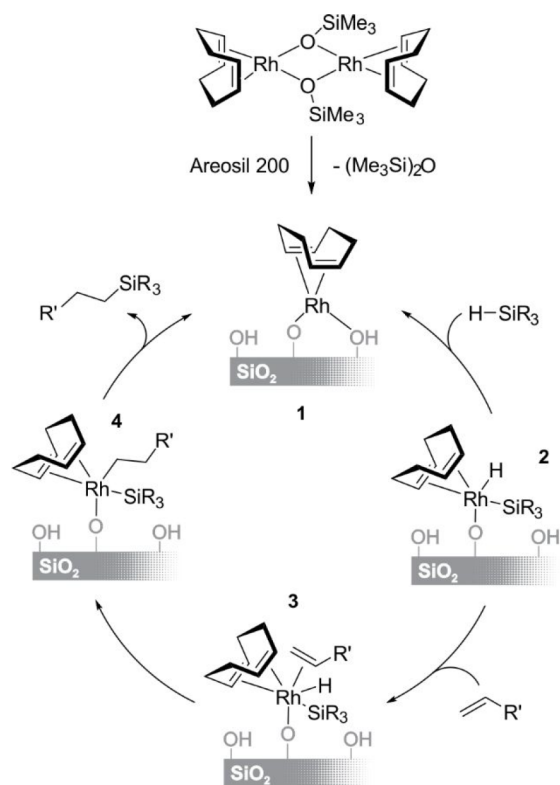
the strong binding of individual Pt atoms with their neighboring oxygen atom; therefore, the single atom-based catalyst shows significantly higher activity compared with related Pt-nanoparticles.¹⁹

However, a detailed mechanistic study on this type of heterogenized systems in view of TM-Si and TM-H activity in catalysis at the molecular level has been only initiated.

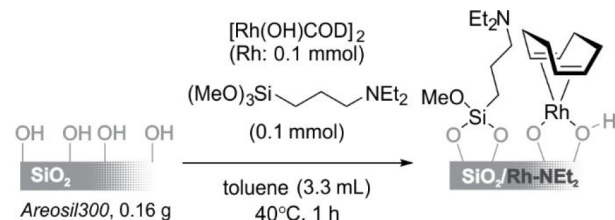
1.2. Hydrostannation of Alkenes and Alkynes

Organostannanes are tremendously useful synthetic building blocks in organic chemistry. The current most frequently used reactions for the synthesis of functionally rich rings and allyl organostannanes are the TM-catalyzed hydrostannation (hydrostannylation) of alkynes, alkenes and allenes, and

Scheme 17. Mechanism of the Heterogeneous Catalysis of Alkene Hydrosilylation by a Surface Rhodium (Diene)siloxide Complex



Scheme 18. Preparation of a SiO₂/Rh-NEt₂ Catalyst

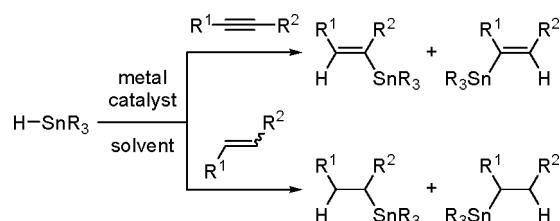


stannylation that affects their protonation.¹⁰ A comprehensive review of metal-catalyzed hydrostannation before the year 2000 was published by Lautens et al.⁵⁵

The general equation for the hydrostannation of the above-mentioned unsaturated compounds is shown in Scheme 19.

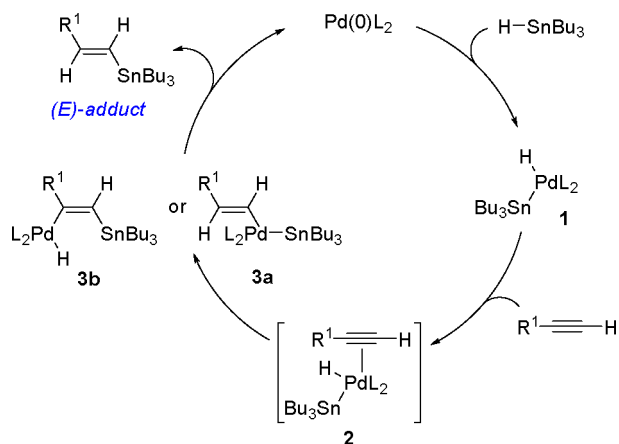
The reaction presented above usually occurs with *cis* stereoselectivity as a consequence of the reaction mechanism. The use of organostannanes is often hampered by their toxicity. Trimethyl and triethyltin compounds are especially poisonous, and their toxicity decreases with increasing alkyl chain length. The most commonly used tributyltin compounds

Scheme 19. Hydrostannation of Alkynes and Alkenes



are moderately toxic, while trioctyltin compounds exhibit almost no toxicity.⁵⁶ The palladium-catalyzed hydrostannylation of alkynes is the most widely used procedure for the synthesis of (*E*)-alkenylstannanes.⁵⁵ The regiochemistry of addition is controlled by many factors, of which the structure of the alkyne substrate is the most critical. The mechanism (Scheme 20)

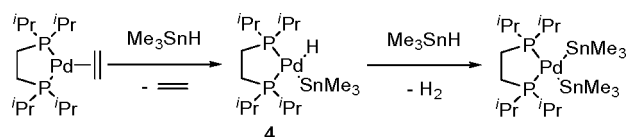
Scheme 20. Proposed Mechanism of the Pd-Catalyzed Hydrostannylation of Alkynes



assumes an oxidative addition of R_3Sn-H to an $L_2Pd(0)$ complex (1), followed by coordination of the alkyne with a vacant orbital on the metal atom and subsequent addition of the coordinated Pd-H bond of 2 into the alkyne π -bond to give complexes 3a and/or 3b via the competing pathway of hydropalladation and stannylpalladation. Finally, however, a β -(*E*)-alkenylstannane is formed, and the Pd(0) catalyst is regenerated.

The proposed formation of an intermediate (1) has been supported by the isolation of a *cis* Pd(II) hydride trialkylstannyl intermediate (4) when bulky bidentate phosphine ligands were added (Scheme 21).⁵⁷ However, numerous subsequent experiments were proposed to test whether hydropalladation or stannylpalladation of specific alkynes occurred.^{58,59}

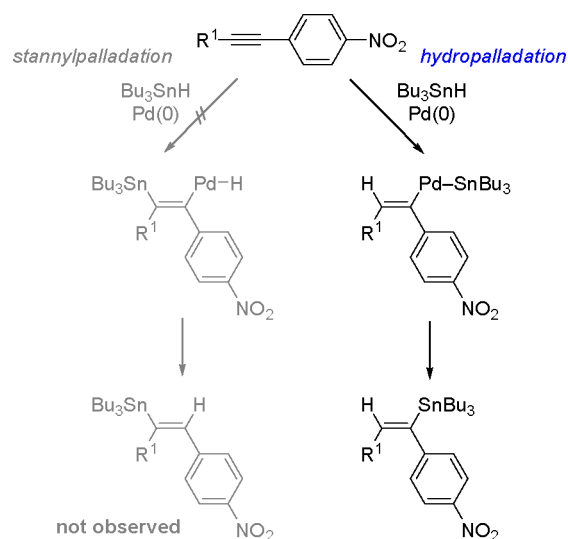
Scheme 21. Isolation of Pd(II) Hydride, Stannyl Intermediate



Scheme 22 presents the Pd-catalyzed hydrostannylation of terminal or internal aromatic alkynes in which the triple bond is significantly polarized because of a nitro group on the aryl ring.⁵⁵ Thus, the results illustrate the electronic effect of the $C\equiv C$ bond on regioselectivity. Besides, Bu_3Sn-H formally acts as a hydride donor.

In addition to the most widely used numerous palladium complexes with various ligands, other metal complexes, such as cobalt, molybdenum, nickel, platinum, rhodium, ruthenium, and tungsten, have been employed in the hydrostannylation of alkynes for the past 10 years.⁵⁷ In particular, in contrast to all the other TM-catalyzed hydrostannylation reactions documented in the literature, the reaction of symmetrical and

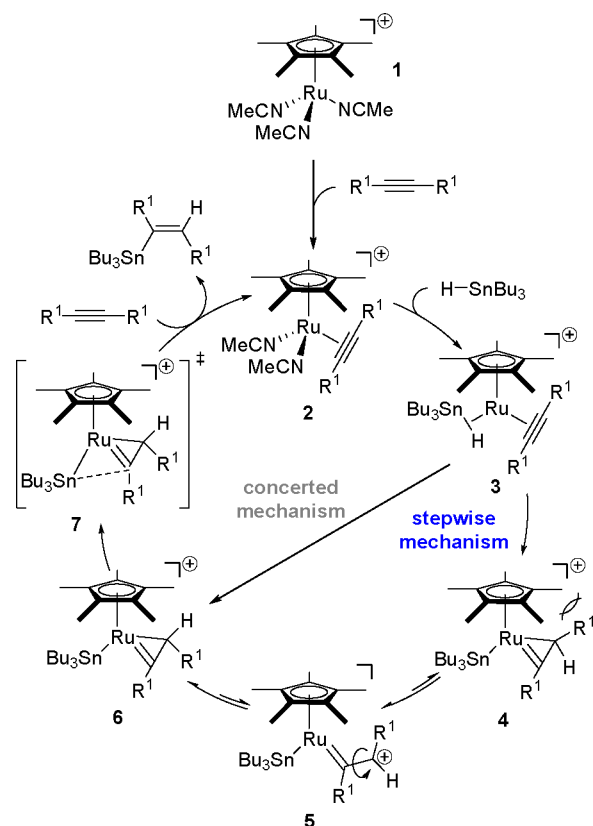
Scheme 22. Pd-Catalyzed Hydrostannylation of *p*-NO₂ Arylalkynes



unsymmetrical internal alkynes in the presence of ruthenium complexes^{60–62} (Scheme 23), originally proposed by the Trost group,⁶³ was discussed in terms of mechanisms by the Fürstner.⁶²

The first step of the reaction is the coordination of the alkyne with the electrophilic metal center of 1 to give intermediate 2, followed by the coordination of Bu_3SnH to provide 3, in which the R^1 group of the alkyne acts as a four-

Scheme 23. Mechanism of the *trans*-Hydrostannylation of Symmetrical and Unsymmetrical Internal Alkynes Using a Ru-Complex



electron donor. Subsequently, after inner-sphere hydride delivery, intermediate **4** is formed, in which the R^1 group is oriented toward the bulky Cp^* ligand. Metallacyclopropene (**4**) may reversibly isomerize into **6** in which the R^1 substituent is farther away from the Cp^* ligand. These steric factors induce *trans*-hydrostannation and final reductive elimination of **6** via **7**, which places Sn in an *anti* position to the hydride and leads to (*E*)-vinylstannane. These considerations cannot exclude a concerted mechanism from **3** to **6**.

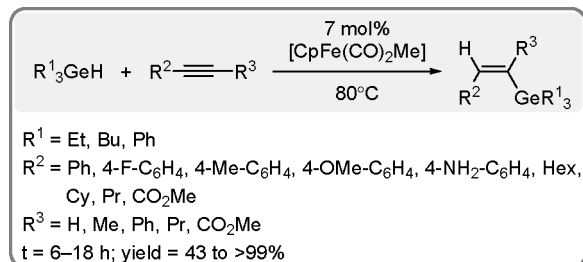
Recently, an experimental and theoretical study by the Fürstner⁶² has extended the above detailed picture to the ruthenium-catalyzed hydrometalation of internal alkynes by R_3M-H (where M is Si, Ge, Sn). Ruthenacyclopropene appeared as a key intermediate in the final *trans*-addition product.

1.3. Hydrogermylation of Alkynes

Like organosilanes, organogermans have recently been found to undergo reactions different from the Stille–Suzuki reactions for Pd-catalyzed cross-coupling (for a review, see ref 64.). Organogermans are synthesized via the TM-catalyzed hydrometalation of alkene and alkyne derivatives by hydrogermanes according to the Chalk–Harrod mechanism presented in Scheme 3.

The catalytic *trans*-selective hydrogermylation of both terminal and internal alkynes has been reported by Nakazawa (Scheme 24).⁶⁵ The crystal structure of the intermediates confirms the mechanistic considerations.

Scheme 24. Iron Complex-Catalyzed Hydrogermylation of Alkynes



Furthermore, the hydrogermylation mechanism of alkynols or alkynes by Et_3GeH catalyzed by rhodium complexes was confirmed by the isolation of a rhodium intermediate (Scheme 25).^{66,67}

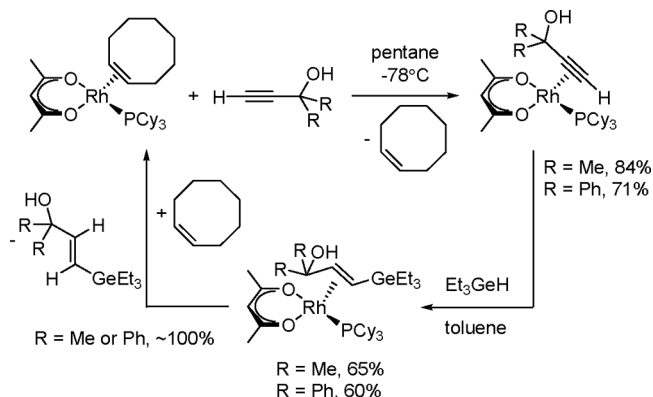
By analogy with the *trans*-hydrogermylation of 1,3-diyne with dihydrogermanes (e.g., Ph_2GeH_2), $[Cp^*Ru(MeCN)_3][PF_6]$ allows the synthesis of 2,5-disubstituted germales. A double addition process was applied to the synthesis of 2,2'-bigermole (Scheme 26).⁶⁸

Hydrogermylation products have several multidisciplinary applications, for example in electronics, germanium nanowires,⁶⁹ and materials science at large.

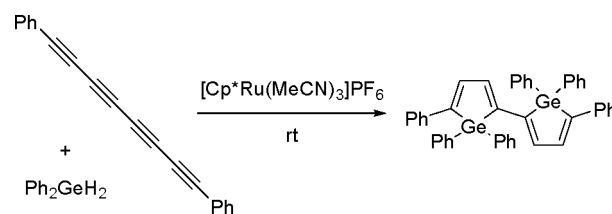
1.4. Silyl(germyl)formylation of Alkynes

A general catalytic cycle for the silylformylation of 1-alkynes catalyzed by rhodium–cobalt clusters has already been presented^{2,13} (see Scheme 27) (for a review, see ref 70). The mechanism involves the selective insertion of a 1-alkyne into the $[M]-Si$ bond of the (hydrido)metal intermediate to form a silyl–vinyl–TM complex, followed by a facile insertion of CO into the vinyl–TM bond. A subsequent hydride shift gives the silylformylation product. The first catalytic

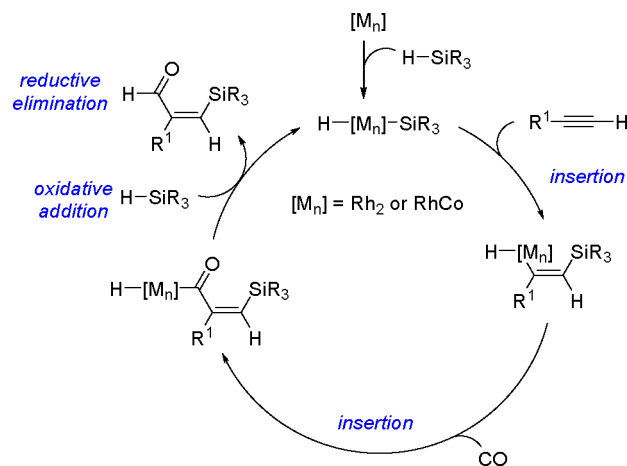
Scheme 25. Hydrogermylation of Alkynes and Alkynols Catalyzed by a Rh-Complex



Scheme 26. Double *trans*-Hydrogermylation Catalyzed by a Ru complex



Scheme 27. Mechanism of the Silylformylation of Alkynes



germylformylation has also been reported, but only for terminal alkynes.⁷⁰

1.5. Hydroboration

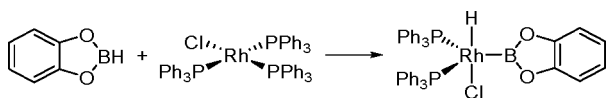
Hydroboration is the second most popular and suitable process for the industrial application of hydrometalation after hydrosilylation. Hydroboration of unsaturated bonds serves as a powerful strategy for the preparation of organoboranes, which are excellent reaction surrogates as they provide important reaction intermediates that could be transformed into a myriad of value-added products. They may have promising applications in the pharmaceutical, petroleum, and fragrance industries.

The borane reagents for originally used hydroboration included highly reactive boranes, such as diborane (B_2H_6), the BH_3-THF complex or $BH_3-S(Me)_2$ and some alkylboranes (mainly 9-borabicyclo[3.3.1]nonane), and they allowed hydro-

boration of alkenes at ambient temperatures without a catalyst. It should be noted, however, that both the borylating reagent and the resulting borylated product require careful handling as they are sensitive to air and moisture, which limits their use in practical synthesis. On the other hand, dialkoxyboranes $\text{HB}(\text{OR})_2$, such as catecholborane (HBcat) and pinacolborane (HBpin), are much easier to handle because of their relative stability, but their reactions usually require elevated temperatures and/or a catalyst because of the diminished electrophilicity of the boron atoms.

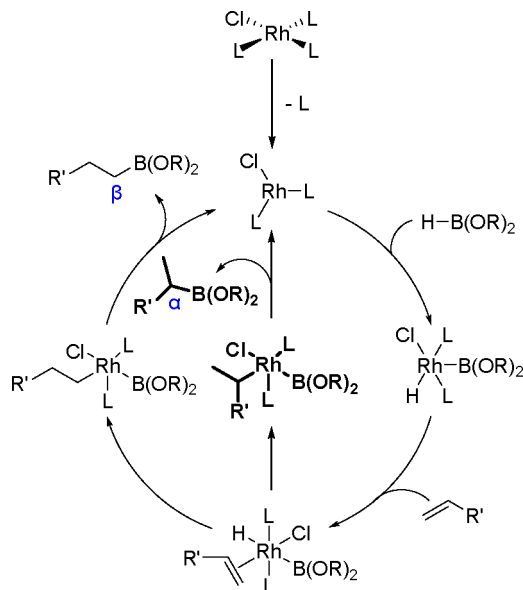
1.5.1. Hydroboration and Dehydrogenative Borylation of Alkenes and Alkynes. Using metal complexes as hydroboration catalysts became possible owing to the work of Kono and Ito who showed that Wilkinson's catalyst in the presence of catecholborane undergoes oxidative addition⁷¹ (Scheme 28).

Scheme 28. A Rhodium Complex Undergoing Oxidative Addition with Catecholborane



Therefore, the first example of the catalytic hydroboration of alkenes was a reaction in the presence of Wilkinson's catalyst, $[\text{RhCl}(\text{PPh}_3)_3]$, reported by Männig and Nöth in 1985.⁷² It initiated intensive research into the catalytic aspects of hydroboration, in particular with rhodium catalysts, which led to the development of the mechanism of this reaction (Scheme 29).

Scheme 29. General Mechanism for the Rhodium-Catalyzed Hydroboration of Alkenes

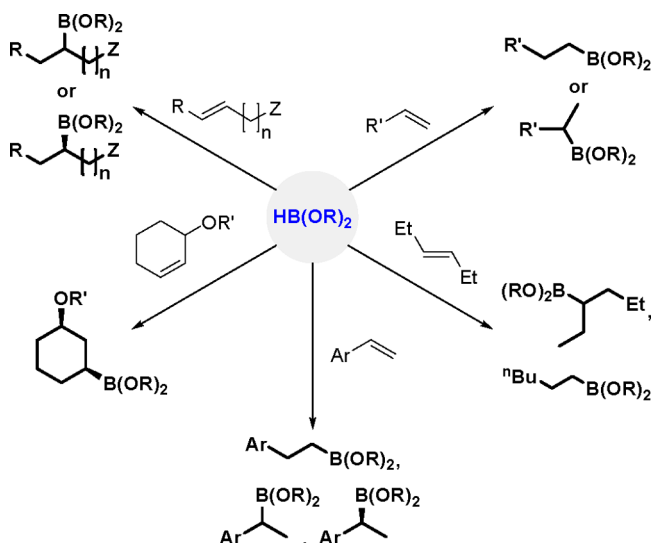


The rhodium-catalyzed hydroboration reaction is thought to be initiated by the dissociation of triphenylphosphine from the $\text{Rh}(\text{I})$ center. The oxidative addition of the $\text{B}-\text{H}$ bond from the borane reagent to this 14e^- species is then followed by coordination of the alkene to the 16e^- $\text{Rh}(\text{III})$ hydride complex. Formation of the oxidative addition product was confirmed a few years later when the $[\text{RhCl}(\text{Pi-Pr}_3)_2(\text{H})-$

(Bcat)] complex was isolated and structurally characterized.⁷³ Subsequent migratory insertion of the alkene into the rhodium–hydride bond can give two regioisomeric alkyl–rhodium(III)–boron complexes. Reductive elimination of the boronate ester regenerates the catalyst. The catalyst prepared and handled under anaerobic conditions reverses the selectivity to favor the secondary boronate ester. Although the reaction mechanism of the TM -catalyzed hydroboration of unsaturated $\text{C}-\text{C}$ bonds has been extensively investigated through labeling experiments and theoretical calculations, there is no consensus on its mechanistic steps or transition states. What has been debated is the coordination of the alkene. In the dissociative mechanism, proposed by Männig and Nöth⁷² and supported by Evans and co-workers,⁷⁴ the coordination is accompanied by a loss of one triphenylphosphine ligand. In the associative mechanism, proposed by Burgess et al.,⁷⁵ the alkene binds *trans* to the chloride without the dissociation of the triphenylphosphine ligand. The mechanism has been studied by computational methods.^{76,77} Dorigo and Schleyer excluded the associative mechanism by an *ab initio* study on the dissociative mechanism,⁷⁸ whereas Morokuma and co-workers supported the associative mechanism.⁷⁹ Theoretical studies also predict alkene insertion into $\text{Rh}-\text{H}$ or $\text{Rh}-\text{B}$ bonds; however, calculations of the possible pathways indicated that the insertion barrier in the $\text{Rh}-\text{H}$ bond is much lower than that in the $\text{Rh}-\text{B}$ bond. On the other hand, the reaction catalyzed by iridium complexes involves alkene insertion into metal–boron bonds.⁸⁰

Since then, there have been many excellent reviews over the past 35 years that addressed various aspects of this reaction and formation of specific products.^{11,24,25,81–85} The chemoselectivity, regioselectivity, and enantioselectivity of the catalytic reactions vary depending on the metal center, ligands, and substrates. Rhodium is usually identified as the metal of choice to promote the efficiency of such reactions. Regioselectivity, which is relevant to a typical hydroboration reaction of terminal alkenes with alkoxyboranes, leads to two resulting forms: linear products (β -isomer, anti-Markovnikov selectivity) and branched products (α -isomer, Markovnikov selectivity)⁷² (see Scheme 30).

Scheme 30. Various Organoboranes Obtained by Hydroboration

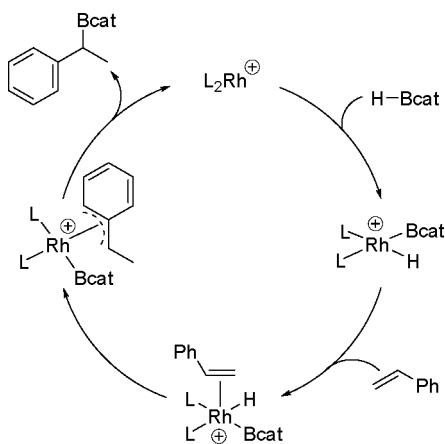


Linear selectivity is more commonly observed in the hydroboration of aliphatic alkenes catalyzed by rhodium complexes, while branched selectivity is observed in the reactions with vinylarenes.^{74,75} This remarkable selectivity has been attributed to a metal-stabilized benzylic intermediate. The results indicate the influence of electronic effects on regioselectivity, which also depends on the reagent and catalyst.

Although high Markovnikov selectivity was observed when cationic rhodium complexes were used in combination with tertiary phosphine ligands, the corresponding primary alkyl boronic esters were produced selectively in the presence of neutral rhodium complexes, such as Wilkinson's complex.

Hayashi and Ito postulate that alkene insertion into the rhodium–hydride bond occurs regioselectively for styrene derivatives to place the rhodium center at the benzylic position, and a stabilized η^3 -benzylrhodium complex forms (see Scheme 31).⁸⁶ Such a process is possible only for the

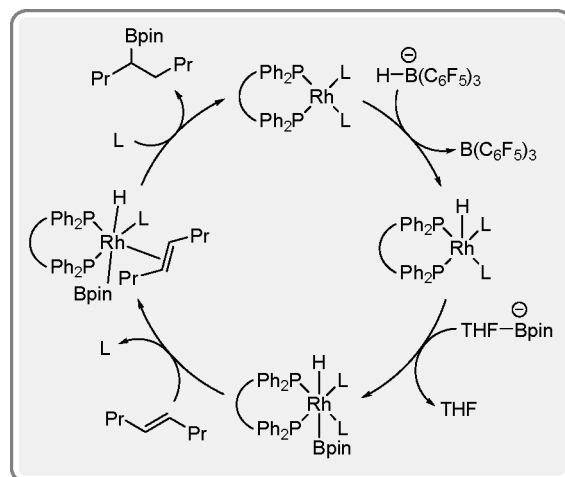
Scheme 31. Mechanistic Rationale for the Cationic Rhodium-Catalyzed Hydroboration of Styrene Derivatives



cationic complex, which has a vacant coordination site that facilitates formation of the η^3 -benzyl complex. The corresponding neutral complex, which lacks such a site, is unable to form this complex, thus leading to anti-Markovnikov selectivity. Quite recently, an excellent review that summarizes the asymmetric methods for the introduction of boronic esters into organic molecules has been published.⁸⁷

Apart from the influence of the type of catalyst on the course of reaction, it may also be changed by other factors. It has been found that the addition of Lewis acids significantly influences the rate, efficiency, and regioselectivity of the Rh-catalyzed hydroboration reaction. For example, the addition of $(C_6F_5)_3B$ to the reaction of vinylarenes (or aliphatic olefins) with HBpin, catalyzed by $[Rh(cod)(dppb)][BF_4] \cdot THF$, facilitates oxidative addition (as shown in Scheme 32), which increases the reaction rate and in some cases makes the reaction possible, which would not take place without the addition of a Lewis acid (for example, a reaction with *cis*-cyclooctene).⁸⁸ The mechanism is based on the formation of $HB(C_6F_5)_3^-$ hydride by hydride transfer from HBpin to $B(C_6F_5)_3$. However, it has been confirmed that it only occurs in the presence of the rhodium complex. Therefore, the transfer and hydride formation is not clear because it does not occur in the absence of the rhodium complex.

Scheme 32. Catalytic Cycle for Tris(pentafluorophenyl)boron-Promoted Hydroboration Catalyzed by a Rh Complex

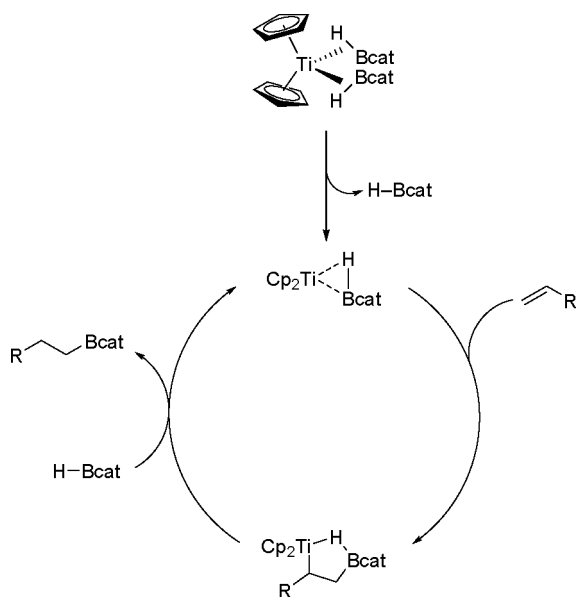


Initially, hydroboration reactions were mostly catalyzed by rhodium complexes, but interest in other metals, particularly first-row TMs, has increased significantly over time.⁸⁹ Unfortunately, these metals often promote the course of side processes, which significantly affects the efficiency of the actual process. In order to limit this phenomenon, it is important to select an appropriate metal–ligand system. Well-designed and properly selected ligands for a given metal make it possible to obtain an efficient and selective catalytic system.⁹⁰ Over the last 5 years, many articles in this field have appeared, and the conducted research has allowed the creation of a database of effective complexes, which are a combination of a metal and a specially designed ligand. A few reviews were published in 2018–2019 in which the general (asymmetric) hydrofunctionalization of alkenes and alkynes catalyzed by earth-abundant metals^{21,24,25,91–98} and lanthanide and actinide complexes⁹⁹ was discussed. An excellent review recently presented complexes of elements from the first row of d-block as catalysts for the formation of a carbon–boron bond.¹⁰⁰ Diverse main group metal catalysts, such as Li,¹⁰¹ K,¹⁰² Mg,¹⁰³ and Al,^{104,105} and other TM catalysts, such as Pd,¹⁰⁶ Ir,¹⁰⁷ Ag,¹⁰⁸ and Zn,¹⁰⁹ were also designed to efficiently and selectively promote the hydroboration of unsaturated bonds.

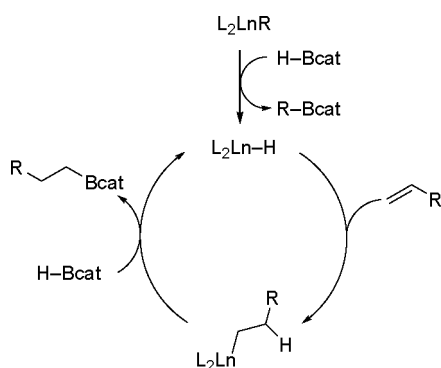
In most cases, the hydroboration of alkenes follows the mechanism proposed for Rh complexes. However, the hydroborating agent sometimes plays an additional role. For example, in the reaction catalyzed by a titanium complex, HBcat is the ligand in the initial state of the catalyst (see Scheme 33). The mechanism has been studied by computational methods. Initial dissociation generates an intermediate that reacts with the olefin to give a five-membered intermediate. In the last step, the addition product is formed by reductive elimination. A less-hindered α -position of the R group to the Cp_2Ti group determines reaction regioselectivity.¹¹⁰

For the reactions catalyzed by lanthanide complexes, Marks and co-workers¹¹¹ have proposed a completely different mechanism (Scheme 34). The entire catalytic cycle takes place without any changes in the oxidation state of the central metal. In the first activation step, protonolysis of the lanthanide alkyl catalyst with HBcat generates a lanthanide hydride (the active species), followed by olefin insertion in an anti-

Scheme 33. Catalytic Cycle for Hydroboration Catalyzed by a Ti Complex



Scheme 34. Proposed Mechanism of Organolanthanide-Catalyzed Olefin Hydroboration



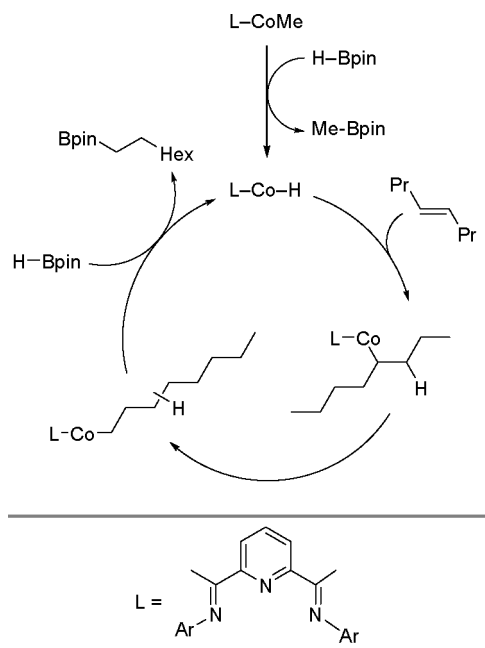
Markovnikov manner to form a complex, which gives the final product with another HBcat molecule.

Since the mechanism is significantly different, it is not surprising that the regioselectivity and scope are also distinct. Unlike the reaction catalyzed by Rh, the reaction with vinylarenes gives predominantly the linear isomer. Most remarkably, trisubstituted olefins can be hydroborated with high yield.

During hydroboration, internal alkenes can isomerize, and internally and terminally functionalized products could be obtained, which was previously possible only in the presence of precious metal catalysts.⁸⁸ Recently, the first-row metal catalysts (especially Fe and Co) have also been reported as catalysts with high activity in isomerization–hydroboration reactions.²⁵ Deuterium-labeling experiments using a Co precatalyst support the mechanism (see Scheme 35), in which an alkene reversibly inserts into the Co–H bond to give a secondary alkyl intermediate. Chain walking occurs through the β -H elimination step, and the two steps can be repeated to furnish a primary alkyl intermediate, which is intercepted by HBpin to yield a terminal alkylboronate ester.¹¹²

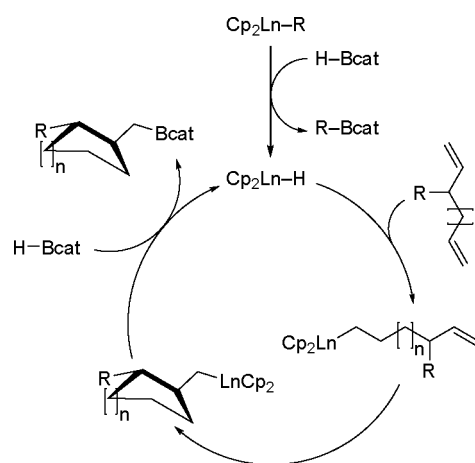
This alkene isomerization–functionalization strategy has been applied in the conversion of internal alkenes into linear α -

Scheme 35. Cobalt-Catalyzed Isomerization-Hydroboration of Alkenes

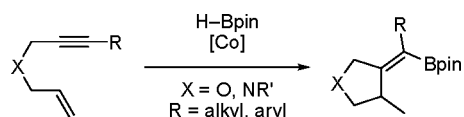


olefins. Hydroboration of monosubstituted cyclic alkenes (i.e., cyclohexenes or cyclooctenes) can proceed in the presence of Rh or Ir complexes in a diastereoselective manner to yield a 1,3-*anti*-isomer,¹¹³ but similarly directed hydroboration can also be effective in the presence of Fe and Co complexes.²⁵ In the reaction with 1,5- or 1,6-dienes, lanthanide complexes catalyze the cyclization/boration reaction (Scheme 36).

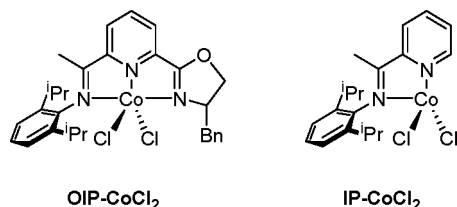
Scheme 36. Proposed Mechanism for Organolanthanide-Catalyzed Cyclization Boration



The first step is the same as in Scheme 34. The lanthanide hydride is then regioselectively inserted into one of the terminal double bonds to give a metal–hydrocarbyl compound. Subsequently, intramolecular cyclization between the metal species and another double bond, followed by reaction with another HBcat molecule, gives the desired cyclic product.¹¹⁴ In 2017, Lu reported the cobalt-catalyzed ligand-controlled regioselective hydroboration/cyclization of 1,6-enynes with HBpin (Scheme 37) that gave cyclic alkenylboronates.¹¹⁵

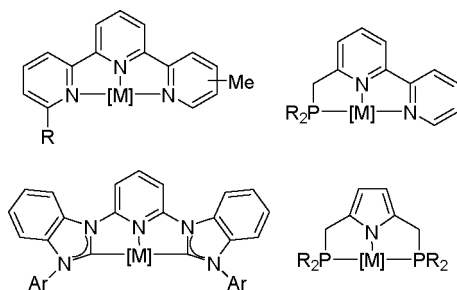
Scheme 37. Hydroboration/Cyclization of 1,6-Enynes in the Presence of a Cobalt Complex

Different reaction products were obtained depending on the type of ligand present in the complex (Scheme 38).

Scheme 38. Two Cobalt Complexes with Different Ligands as Ligand-Controlled Catalysts

When an OIP ligand was used, the product was mainly an alkylboronate. However, when a bidentate IP was used as the ligand, selective formation of alkenylboronate was observed.

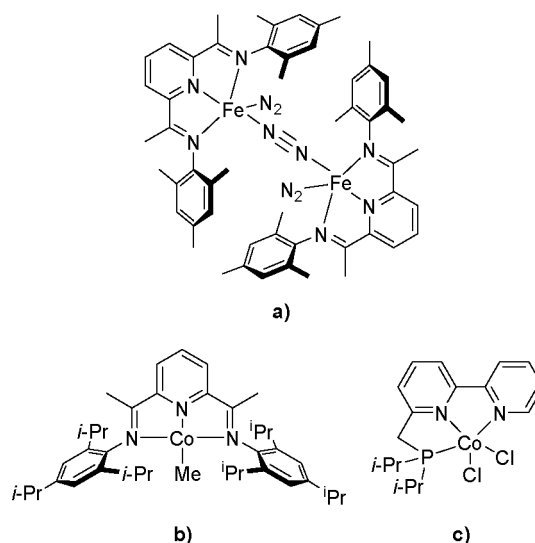
There has recently been a great interest in earth-abundant metals as potential chemo- and regioselective hydroboration catalysts. As in the hydrosilylation processes (see above), complexes containing tridentate ligands are of particular importance. Various complexes with NNN, PNN, CNC, and PNP ligands are known, as shown in Scheme 39.

Scheme 39. Examples of Tridentate Metal Complexes for the Hydrofunctionalization of Olefins

Such ligands may stabilize low-valent metal centers by chelating effects, while leaving vacant coordination sites at the metal center for the bond activation of substrates. These types of complexes have been summarized in excellent review articles.^{28,97,98}

Presently, many examples of these types of complexes are known, mainly Fe, Co, and Cu, and the Chirik and Huang groups have made a large contribution to progress in this field. For example, dinitrogen complexes (Scheme 40a) enabled the chemo- and regioselective hydroboration of monosubstituted, 1,1-disubstituted and 1,2-disubstituted alkenes without the need for an organic solvent, an external activator, or excess alkenes and afforded anti-Markovnikov products in high yield.²⁵

In comparison with the above complex, an analogous cobalt complex (Scheme 40b) was easier to prepare and showed comparable or improved activity in the hydroboration of terminal alkenes and disubstituted internal alkenes.¹¹² In turn,

Scheme 40. Some Types of Tridentate Iron and Cobalt Complexes as Efficient Hydroboration Catalysts

the cobalt complex (see Scheme 40c) catalyzed anti-Markovnikov hydroboration that occurred exclusively for various aryl and aliphatic alkenes.

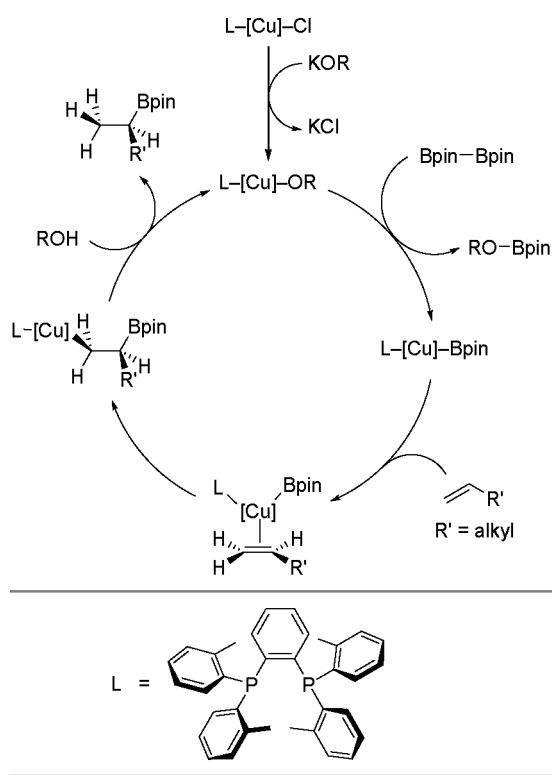
Although several tridentate (pincer) earth-abundant metal complexes have been developed for catalytic alkene hydroboration, only a few of them could provide high selectivity for Markovnikov addition (branched-selective hydroboration).¹¹⁶ As discussed above, the rhodium cationic complex selectively catalyzes Markovnikov addition. However, branched-selective hydroboration is limited to vinylarene substrates (also in the case of earth-abundant metal catalysts), except for several Cu catalysts.^{117–119} The first copper(I)-catalyzed highly branched-selective hydroboration of alkyl-substituted terminal alkenes was achieved by the Ito group.¹¹⁷ In this case, B₂pin₂ instead of HBpin had to be used as the boron source, and alcohol was required for providing the proton (Scheme 41).

In this scheme, a combination of CuCl with a sterically hindered bisphosphine ligand is used to promote the hydroboration of aliphatic terminal alkenes.

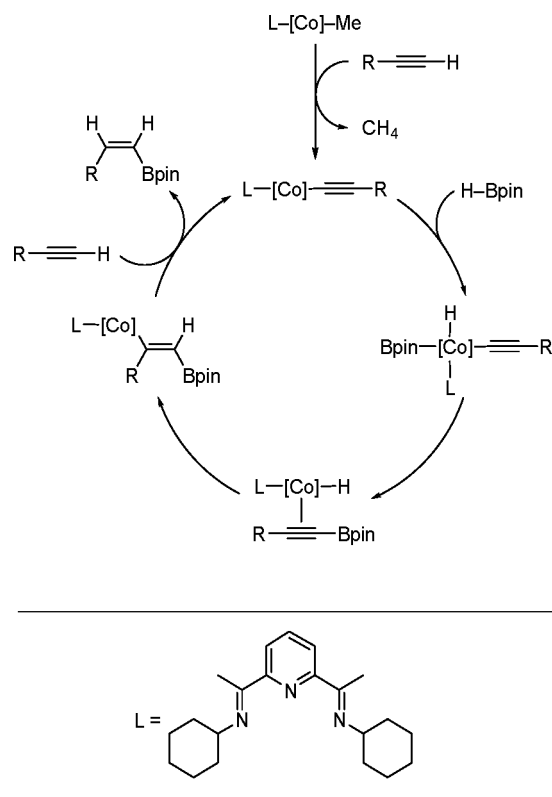
In the hydroboration of alkynes, significant differences in the course of the reaction are found depending on the type of catalyst. Many TM catalysts are known to convert terminal alkynes into (*E*)-vinylboronate esters, perhaps because of the prevalence of metal hydrides and the facile nature of alkyne hydrometalation.¹²⁰ In 2015, Chirik and co-workers¹²¹ developed catalytic hydroboration of terminal alkynes with HBpin, using a cobalt catalyst. This complex can produce (*Z*)-vinylboronates with regio- and stereoselectivity.¹²¹

The process starts with the reaction of a cobalt–methyl complex with an alkyne to form a cobalt acetylide species (see Scheme 42). Following the oxidative addition of HBpin to the cobalt center, reductive elimination occurs to give a cobalt–alkynylboronate complex. Subsequently, *syn*-hydrocobaltation generates a (*Z*)-cobalt–vinyl intermediate, which reacts with alkyne to release the corresponding product and to regenerate the starting complex. In principle, the mechanism can give a single product. The observed (*Z*)-selectivity is proposed to occur through the stereodefined *syn*-hydrometalation of the alkynylboronate—a mechanism distinct from those mediated by precious metal catalysts.

Scheme 41. Plausible Catalytic Cycle of the Copper(I)-Catalyzed Branched-Selective Hydroboration of Aliphatic Alkenes



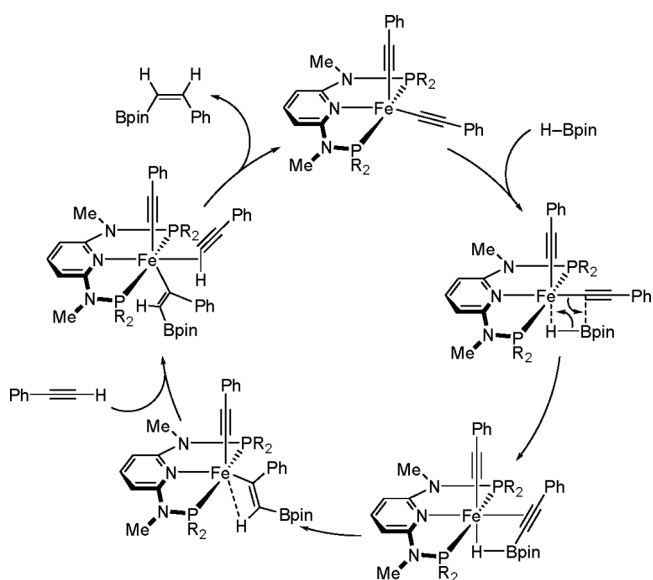
Scheme 42. An NNN-Pincer-Cobalt-Catalyzed Hydroboration of Terminal Alkynes



In a related work, (*Z*)-selective terminal alkyne hydroboration was also observed when [(PNP-pincer)Fe(H)₂(H₂)] precatalysts were used.¹²²

Kirchner and co-workers proposed another reaction mechanism for the *Z*-selective hydroboration of terminal alkynes.¹²³ The pincer complex [Fe(PNP)(C≡CPh)₂] was used as an active catalyst in the hydroboration reaction. In this case, the hydroboration reaction did not involve vinylidene intermediate formation but rather proceeded via a σ -bond metathesis/hydrometalation reaction sequence (Scheme 43).

Scheme 43. Catalytic Cycle for the Hydroboration of Terminal Alkynes Catalyzed by a PNP-Pincer-Iron Complex



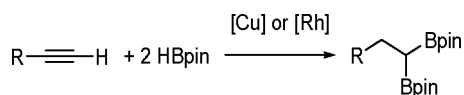
In the first step, the borane closely binds to the catalyst, giving an intermediate with two alkynyl ligands in the *cis* position to each other. The H atom is attached to the iron center acting as an electron donor, while boron is attached to a neighboring acetylide α -carbon acting as an electron acceptor. This initiates C–B bond formation. The B–H bond, which is still present, is cleaved and thus permits alkyne insertion into the iron–hydride bond to finally yield an iron–vinyl intermediate. The elimination of the final product and the recovery of the initial bis(acetylide) complex is accomplished via proton transfer from another alkyne. The mechanism was presented on the basis of experimental results (species and intermediates were trapped and fully characterized spectroscopically) and based on DFT calculations.

The catalytic sequential hydroboration of terminal alkynes is a synthetically useful approach to the generation of 1,1-diboronates. However, sequential and regioselective hydroborations of alkenylboronate intermediates are rare, and most reactions generate a mixture of regioisomers. There are examples of Rh and Cu complexes used as catalysts for the sequential hydroboration of alkynes with HBpin to produce double hydroboration products (Scheme 44).

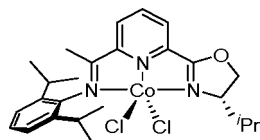
An iminopyridine oxazoline-ligated cobalt complex is one of the most effective catalysts (Scheme 45).

This catalyst offers high conversion and regioselectivity, broad functional group tolerance, and transformation under mild reaction conditions.¹²⁴

Scheme 44. Sequential Hydroboration of Alkynes Catalyzed by Rh or Cu Complexes



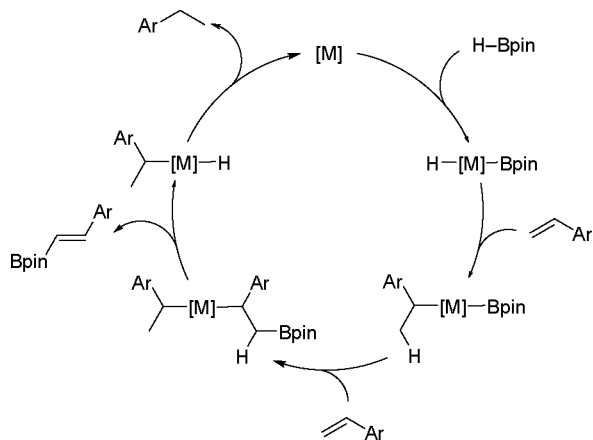
Scheme 45. NNN-Pincer–Cobalt Complex as an Effective Catalyst for the Hydroboration of Alkynes



Although alkenylboronate esters are traditionally prepared by the hydroboration of alkynes, this method can be complicated by regioselectivity issues and gives a mixture of isomers. In some cases, the addition of a second equivalent of borane to the activated alkenylboronates once again leads to a mixture of saturated bisboron-containing alkanes. The dehydrogenative borylation reaction is an alternative method for synthesizing alkenylboronates.¹²⁵ Today, many different TM complexes (i.e., Rh, Pd, Ir, Ru, Fe, Co, Ti) are known to be effective catalysts of this process. This aspect has been thoroughly summarized in ref 85.

The key to the success of this reaction is to use a metal system capable of alkene insertion into an M–B bond (followed by β -hydride elimination) while avoiding metal hydride and dihydrido species that are capable of forming hydroboration and hydrogenation products, respectively (see Scheme 46). This catalytic reaction provides an attractive

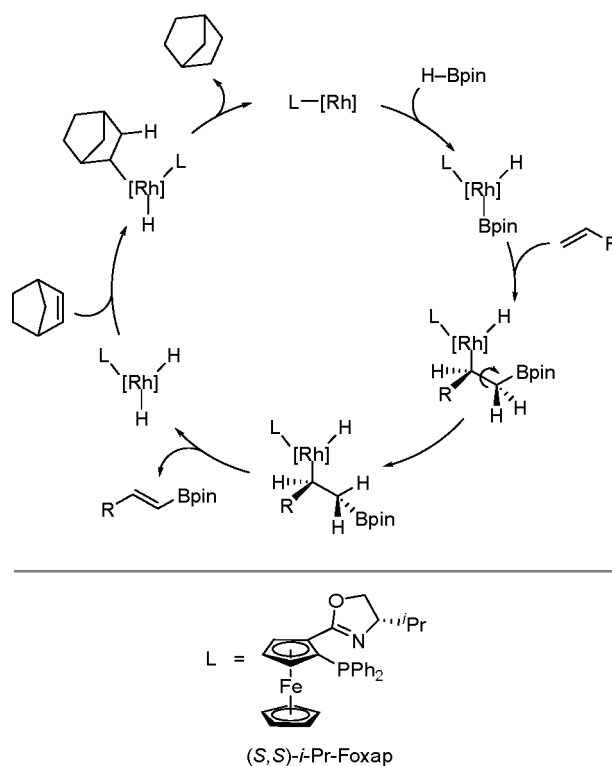
Scheme 46. General Mechanism for Dehydrogenative Borylation



method for generating valuable alkenylboronate esters. The group of Miura and Murakami¹²⁶ reported the first general dehydrogenative borylation of aryl and aliphatic alkenes using $[\text{Rh}(\text{cod})_2][\text{BF}_4]/i\text{-Pr-Foxap}$ as a catalyst (Scheme 47).

Norbornene was used as the H_2 acceptor as it was surmised that its strained structure would be reduced in preference to the alkene substrate. Oxidative addition of B–H onto rhodium(I) affords a boryl(hydrido)rhodium species which undergoes alkene insertion to give an alkyl–rhodium intermediate. This intermediate subsequently rotates around the C–C bond axis to form a conformer, which gives the E-

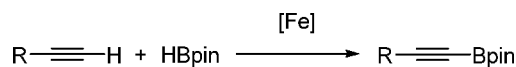
Scheme 47. Plausible Catalytic Cycle for the Rhodium-Catalyzed Dehydrogenative Borylation of Alkenes in the Presence of Norbornene



isomer of the vinylboronate ester after *syn* β -H elimination. The dihydride rhodium species reacts with norbornene to regenerate the rhodium(I) catalyst, together with norbornane.

Recently, a catalytic system based on an iron complex ($\text{Fe}(\text{OTf})_2$ with DABCO) that selectively promotes the dehydrogenative borylation of both aromatic and aliphatic terminal alkynes has been reported (see Scheme 48) to generate alkynylboronate derivatives.¹²⁷

Scheme 48. Dehydrogenative Borylation of Terminal Alkynes Catalyzed by an Iron Complex



This method is applicable to a variety of terminal alkynes. Very recently, iridium complexes with diarylamido/bis-(phosphine) PNP ligands have also been studied using DFT calculations as catalysts for the dehydrogenative borylation of terminal alkynes.¹²⁴

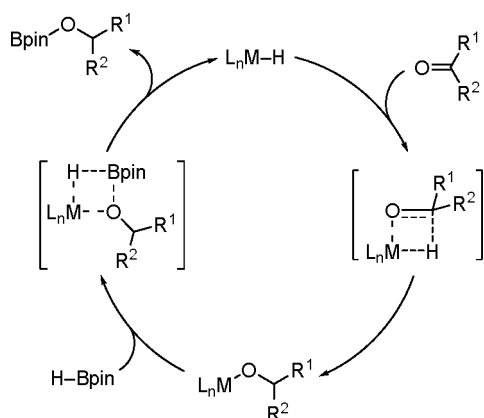
1.5.2. Hydroboration of Carbonyl Compounds.

Hydroboration of carbonyl compounds is an efficient strategy for accessing primary and secondary alcohols. It is especially useful for the preparation of a variety of chiral alcohols that are widely used in organic synthesis, materials science, and pharmaceutical chemistry.^{129,130} The hydroboration of carbonyl compounds using both homogeneous and heterogeneous catalyst systems has been addressed in excellent reviews. Kinjo demonstrated TM-catalyzed hydroboration of unsaturated bonds, such as C=O and C=N, and investigated its mechanism.¹³¹ A recent review by Bose summarizes the developments in the hydroboration of C=O bonds via s- and

p-block elements and TMs (including precious and nonprecious metals and lanthanides) as efficient catalysts, as well as heterogeneous catalyst systems.¹³²

In the majority of the proposed mechanisms, the transformation proceeds via a σ -bond metathesis in reactions catalyzed by TMs or main group metals (Scheme 49).

Scheme 49. General Mechanism for the TM-Catalyzed Hydroboration of Carbonyl Compounds

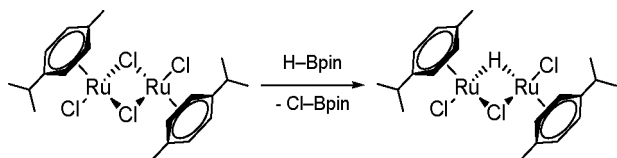


All the studies of this mechanism imply generation of M–H intermediate species, and this might be the key step in the hydroboration of aldehydes and ketones.

In 2015, Gunanathan group reported a ruthenium [$\{\text{Ru}(\text{p-cymene})\text{Cl}_2\}_2$] complex as an efficient catalyst of the hydroboration of various aromatic and aliphatic aldehydes with electron-withdrawing and electron-donating groups.¹³³ The proposed mechanism of this reaction type is different from the one described above.

The reaction of the starting complex with HBpin gave a monohydrido-bridged dinuclear ruthenium complex, [$\{(\eta^6\text{-p-cymene})\text{RuCl}\}_2(\mu\text{-H}-\mu\text{-Cl})$] (Scheme 50). This complex was prepared and spectroscopically characterized.

Scheme 50. Formation of a Monohydrido-Bridged Dinuclear Ruthenium Complex

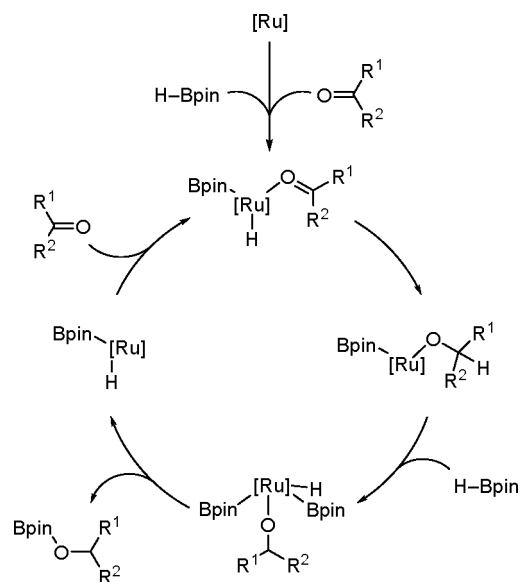


This complex leads to the formation of an active intermediate in a reaction with the next HBpin molecule in the presence of a carbonyl, according to Scheme 51.

In the first step, the hydride is transferred from the metal to the carbonyl group, followed by the oxidative addition of HBpin, which increases the oxidation state and the coordination number of ruthenium. In the final stage, the product is reductively eliminated, and the starting catalyst is reconstituted in the presence of the raw material.

1.5.3. Double Hydroboration of Carbon–Nitrogen Triple Bonds. Borylamines have been reported to show unique reactivity as iminium ion generators. Hydroboration of the $\text{C}\equiv\text{N}$ bond is also one of the effective methods for reducing organonitriles. However, the reaction does not occur under typical hydroborylation conditions because of the high

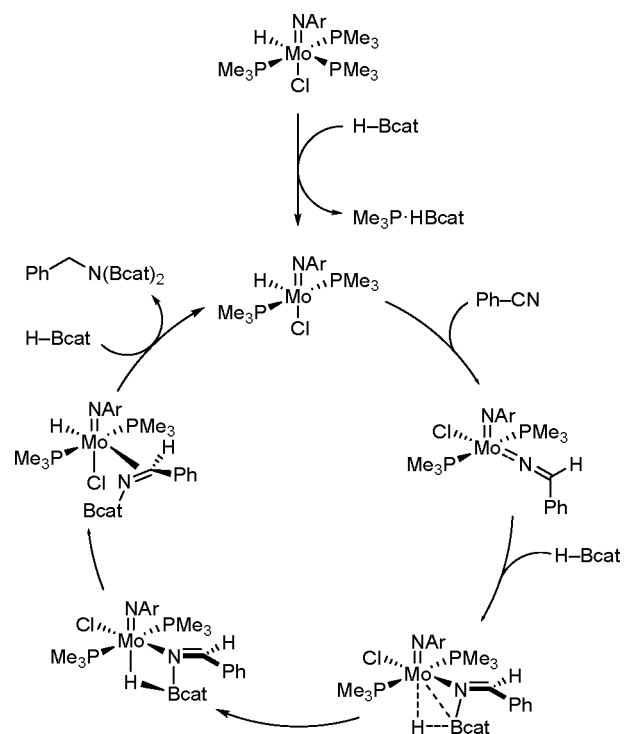
Scheme 51. Catalytic Cycle for the Ruthenium-Catalyzed Hydroboration of Ketones



dissociation energy of the strong $\text{C}\equiv\text{N}$ bond. At present, only a few examples of the catalytic hydroboration of carbon–nitrogen triple bonds are known (presented in ref 134). The imido–hydrido Mo(IV) complex was one of the first examples of an active double hydroboration catalyst, presented by Nikonov and Khalimon groups (see Scheme 52).¹³⁵

As a result of the elimination of the phosphine molecule with HBcat, the Mo(IV) complex is formed, which initiates the catalytic cycle. The addition of benzonitrile followed by HBcat

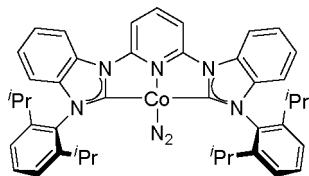
Scheme 52. Reaction Pathway of the Double Hydroboration of Nitriles Catalyzed by an Imido–Hydrido Mo(IV) Complex



produces an amido-borane adduct is formed, which is finally converted to a borylimine complex. In the final stage, reductive elimination of diborylamine occurs and the active Mo(IV) complex is restored.

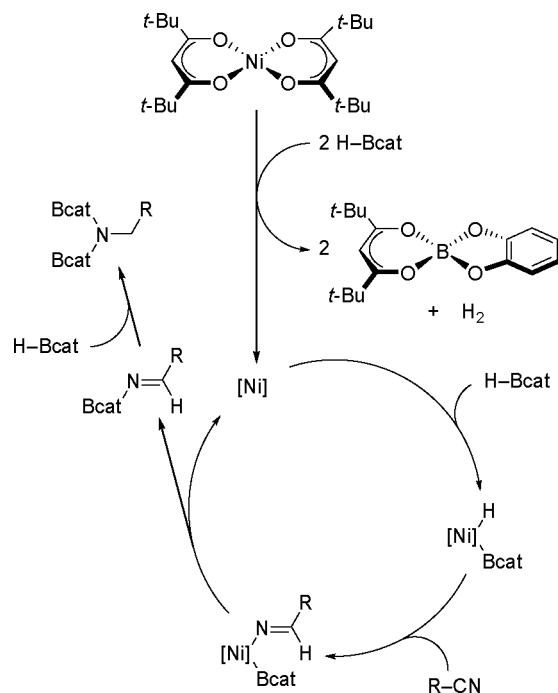
In 2017, the Fout group reported the double hydroboration of organonitriles catalyzed by a Co(I) complex¹³⁶ (Scheme 53).

Scheme 53. Cobalt(I) Complex as a Catalyst of the Double Hydroboration of Nitriles



An interesting example of using a simple nickel salt (a nickel–acetylacetonate derivative) as an active double hydroboration catalyst has been presented by Nakajima and Shimada groups.¹³⁷ (see Scheme 54).

Scheme 54. Proposed Mechanism for the Ni-Catalyzed Double Hydroboration of Nitriles



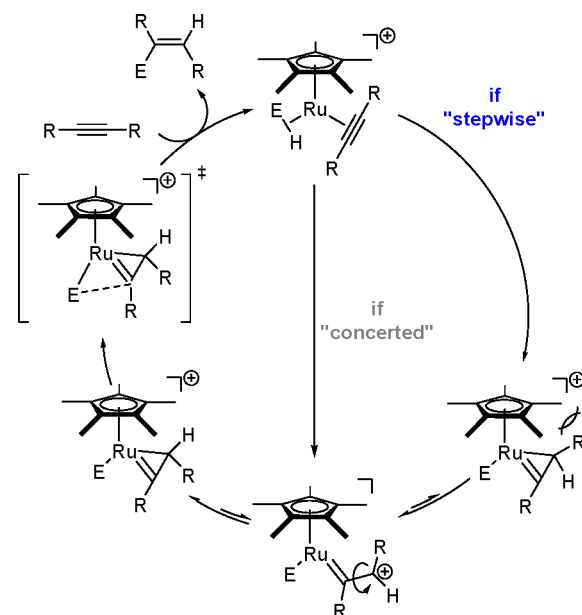
Reduction of the starting complex by 2 equiv of HBcat produces an active Ni(0) species. The elimination product was confirmed by NMR spectroscopy as well as by single crystal X-ray diffraction analysis. Oxidative addition of HBcat to the Ni(0) center gives a boryl–hydrido intermediate. The nitrile insertion into the Ni–H bond, followed by the subsequent reductive elimination of borylimine, regenerates the active catalyst. The resulting borylimine further reacts with HBcat to give *N,N*-diborylamine. The proposed mechanism of this reaction is a typical hydroboration reaction mechanism. The distinguishing feature of this reaction, however, is the use of a very cheap commercially available catalyst that can successfully replace precious metal complexes.

Several other effective catalytic systems based on other metals, such as Ru, Mg, Co, and Fe, are currently known,¹³⁴ which demonstrates the great interest in the possibility of selective double hydroboration. A titanium(IV) complex $[\{\text{Ph}_2\text{P}(\text{BH}_3)\text{-N}\}_2\text{C}_6\text{H}_4\text{Ti}(\text{NMe}_2)_2]$ is one of the latest examples of this reaction type and it enables chemoselective hydroboration of organic nitriles to obtain *N,N*-diborylamines with a wide substrate range, containing both aliphatic and aromatic nitriles.¹³⁸

1.6. General Mechanism for Hydrometalation

On the basis of a comprehensive study by Fürstner of the catalysis of hydrometalation with ruthenium complexes, a general mechanism of the *trans* addition of E–H bonds to triple bonds has been presented¹³⁹ (see Scheme 55). Thus, the mechanistic scheme above may provide excellent preliminary evidence for the general role of the TM–metalloid catalytic system in inorganometallic chemistry.

Scheme 55. Putative Mechanism of the Hydrometallation of Alkynes (E = H, (RO)₂B, R₃Si, R₃Ge, R₃Sn)



2. ADDITION OF METALLOID–METALLOID BONDS TO CARBON–CARBON MULTIPLE BONDS

2.1. Mechanistic Aspects of Bis-Metalations

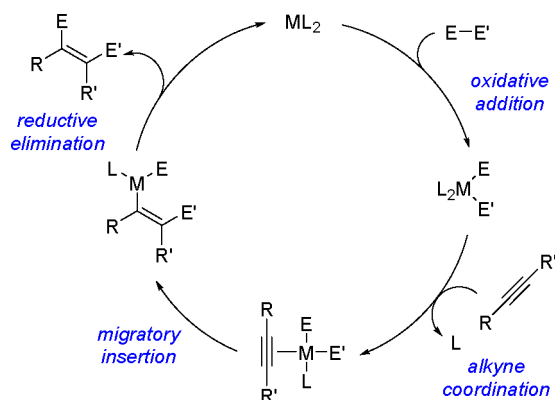
Since the early 1990s, the TM-catalyzed insertion of a bond between two elements of the *p*-block (Si–Si, Si–Sn, Sn–Sn, B–B, Si–B, etc.) into carbon–carbon multiple bonds (alkenes, alkynes, and allenes) has drawn significant attention because these additions provide promising methods for the introduction of metalloids into organic molecules in a regio- and stereoselective manner.^{56,140–145} Significant progress in this area in the past two decades has been made possible by the application of new effective catalysts, deeper understanding of the reaction mechanisms, and introduction of selective chiral ligands so that bis-metalation chemistry can be used for enantioselective synthesis.¹⁴⁶

A variety of *p*-block element σ -bonds can be added to unsaturated organic molecules owing to TM catalysts, mostly group 10 TM complexes (commonly phosphine Pd(0) and

Pt(0) complexes); however, other complexes containing rhodium or ruthenium could also be employed as bis-metalation catalysts. On the other hand there has been much interest in the promising catalysis of base (Fe, Co, Ni) and coinage (Cu, Au) metals for the bis-metalation of C–C multiple bonds.

It is widely accepted that inorganometallic complexes containing TM–metalloid (TM–E) bonds are the key intermediates of catalytic bis-metalation. The general mechanism of bis-metalation involves oxidative addition of the E–E σ -bond into the TM complex, which gives a bis-metalated TM complex, insertion of the C–C multiple bond into the TM–E bond and reductive elimination of the bis-metalated compound with regeneration of the catalyst (Scheme 56). The

Scheme 56. General Mechanism of Alkyne Bis-Metalation

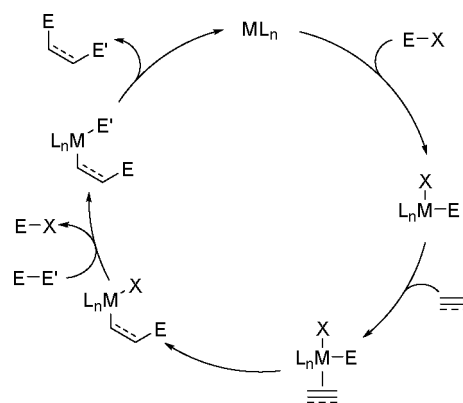


regioselectivity of the E–E addition is usually defined by the insertion of the alkyne (alkene), and the determining factors include the energy of the bonds broken versus that of the bonds formed, steric effects of the system, and electronic stabilization effects within the resulting intermediates. However, experimental studies suggest that the insertion is often the rate-limiting step in these reaction pathways.¹⁴⁶

Alternatively, bis-metalation may occur without oxidative addition of the E–E reagent. As already determined for a palladium-catalyzed allene bis-boration and silaboration (see below) these reactions can be initiated by the oxidative addition of a metalloid halide (E–X) to a TM complex. Allene insertion is followed by transmetalation with the E–E-bonded reagent. This step regenerates the metalloid halide and provides an intermediate for product release (Scheme 57). Thus, phosphine-free palladium complexes together with alkenyl or aryl iodides are very efficient catalysts for the 1,2-diboration of allenes. This Pd-catalyzed reaction proceeds via a mechanism involving the oxidative addition of an I–B bond to the palladium center instead of the oxidative addition of a B–B bond to a metal.¹⁴⁷ A similar mechanistic pathway involving a palladium-catalyzed three-component assembling reaction of iodosilane, allene, and borylsilane has been proposed to account for the silaboration reaction.¹⁴⁸

The mechanistic implications of the bis-metalation processes have been explored mostly for platinum and palladium complexes in alkyne bis-silylation, bis-boration, and silaboration (silylborylation) reactions. Therefore, we will focus mainly on alkyne bis-metalation reactions in this section, as proven by stoichiometric or computational studies.

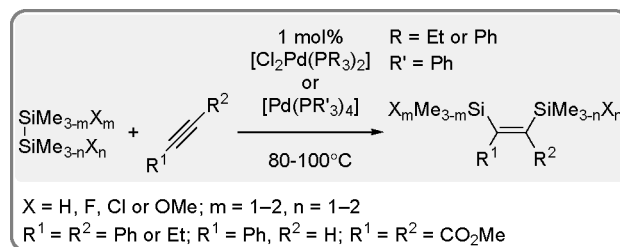
Scheme 57. Alternative Mechanism of Three-Component Bis-Boration and Silaboration



2.2. Addition of Homoelement–Element Linkages to Unsaturated Substrates

The catalytic addition of the Si–Si bond to alkynes (the first example of element–element additions to unsaturated compounds) has been developed since the 1970s.^{149,150} The addition of disilanes to terminal as well as internal alkynes catalyzed by TM complexes occurs with high *syn*-selectivity (Scheme 58). When the disilane reagents are nonsymmetric,

Scheme 58. Bis-Silylation of Alkynes in the Presence of Palladium Catalysts



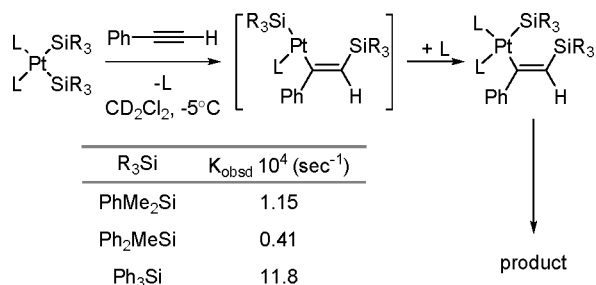
the more electron-deficient silicon atom tends to be added to the internal position of alkynes.¹⁵¹ The majority of bis-silylation reactions are catalyzed by palladium complexes but also other types of catalysts based on platinum, rhodium, and nickel are able to catalyze the addition of disilanes to alkynes.

Since the Si–Si bond energy (74–80 kcal mol^{−1}) is similar to that of the Si–H bond (88–92 kcal mol^{−1}), it is reasonable to assume that the oxidative addition of a Si–Si bond would also be a facile process and would offer the potential for the formation of bis(silyl) TM complexes. An *ab initio* MO/MP4 study of the oxidative addition of SiH₄ and H₃Si–SiH₃ to a [Pt(PPh₃)₂] complex showed that the addition of a Si–Si bond is more exothermic than that of a Si–H bond (46.4 and 25.8 kcal/mol, respectively), but the activation barrier is higher for bis-silylation (17.4 and 0.7 kcal/mol for Si–Si and Si–H, respectively).¹⁵² Therefore, the two reaction types can compete with the compounds that contain both types of bonds, with the actual result being dependent on the structure of the reagents and reaction conditions. It has been shown that the oxidative addition of H₃Si–SiH₃ to Pd(0) is less exothermic than that to Pt(0), although the former process has a slightly lower activation energy.¹⁵³ Successful synthesis and isolation of bis(silyl)palladium,¹⁵⁴ platinum,¹⁵⁵ and

nickel¹⁵⁶ complexes via oxidative addition of the Si–Si bond have been reported.

The insertion of acetylenes into the Pt–Si bond has been studied by Ozawa and Hikida¹⁵⁷ In the presence of excess phenylacetylene, pseudo-first-order rate constants (k_{obsd}) were measured for the insertion of $[\text{Pt}(\text{PMe}_2\text{Ph})_2(\text{SiR}_3)_2]$ compounds into the Pt–Si bond (Scheme 59). However, the rate

Scheme 59. Insertion of Phenylacetylene into Pt–Si Bonds in Pt(II) Disilyl Complexes



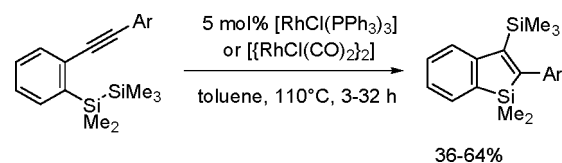
constants for the insertion of phenylacetylene into Pt–Si bonds in Pt(II)–disilyl complexes revealed a reactivity order that was inconsistent with the steric and electronic nature of the silyl substituents. A detailed kinetic investigation has shown that the first step is the dissociation of one of the phosphine (L) ligands to form an unsaturated complex which undergoes rate-determining migratory insertion via the prior coordination of acetylene to the vacant site.

The use of disilanes with electron-withdrawing substituents or strained cyclic disilanes is crucial for the formation of bis(silyl) TM complexes. However, there are two catalytic systems that allow bis-silylation with unreactive hexaalkyldisilanes. Ito et al. employed an efficient catalyst comprising $\text{Pd}(\text{OAc})_2/1,1,3,3$ -tetramethylbutyl isocyanide,¹⁵⁸ widely used for the intramolecular bis-silylation of disilanyl propargyl ethers. Tanaka and Yamashita discovered a catalytic system based on a combination of $[\text{Pd}(\text{dba})_2]$ with a bicyclic phosphate: $\text{P}(\text{OCH}_2)_3\text{CEt}$ (4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane), applied in the synthesis of silicon-containing polymers and oligomers.¹⁵⁹ More recently, the application of nonactivated hexamethyldisilane as a silylating agent using the $[\text{Pd}(\text{ITMe})_2(\text{SiMe}_3)_2]$ complex as a catalyst (ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene) has been demonstrated.¹⁶⁰ A *cis*- $[(\text{ITMe})_2\text{Pd}(\text{SiMe}_3)_2]$ complex as a result of the oxidative cleavage of $\text{Me}_3\text{Si}-\text{SiMe}_3$ with a $[(\text{ITMe})\text{Pd}(\text{methallyl})\text{Cl}]$ precursor was isolated, which supported the catalytic studies.

Furthermore, the rhodium(I)-catalyzed intramolecular bis-silylation of disilanyl propargyl ethers or (2-alkynylphenyl)-disilanes proceeded with a stereoselectivity opposite to that of the analogous palladium-catalyzed addition, and 4-silyl-2,5-dihydro-1,2-oxasilole or 3-silyl-1-benzosilole derivatives were obtained (Scheme 60).¹⁶¹

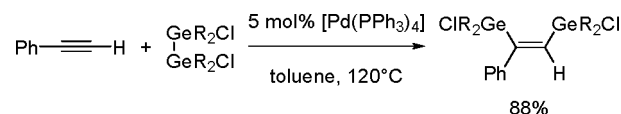
Alkene bis-silylation reactions seem to be less important because the use of bis(silyl)alkane products is limited. They are mainly carried out in the presence of platinum and palladium complexes. $\text{Me}_3\text{Si}-\text{SiF}_2\text{Ph}$ has been found to undergo oxidative addition with an $\text{L}_2\text{Pd}(\text{styrene})$ complex furnishing a *trans*- $[\text{Pd}(\text{SiMe}_3)(\text{SiF}_2\text{Ph})\text{L}_2]$ complex (L = PMe_3 , PMe_2Ph), which supports the classical oxidative addition/reductive elimination mechanism.¹⁶²

Scheme 60. Rhodium(I)-Catalyzed Intramolecular Bis-Silylation of (2-Alkynylphenyl)-disilanes



In contrast to the insertion of alkynes into Si–Si and B–B bonds, the insertion of alkynes into Ge–Ge bonds has been investigated to a much lesser extent. The first additions of Ge–Ge bonds to triple bonds were reported by Ando and Tsumuraya who used a strained cyclic digermirane in the reaction with acetylene and dimethyl acetylene dicarboxylate in the presence of $[\text{Pd}(\text{PPh}_3)_4]$, with moderate yields (20%–51%).¹⁶³ Linear nonstrained dichlorotetramethyldigermene underwent effective double germylation with terminal alkynes in the presence of the $[\text{Pd}(\text{PPh}_3)_4]$ or $[\text{Pd}(\text{dba})_2]/\text{P}(\text{OCH}_2)_3\text{CEt}$ catalytic system (Scheme 61),¹⁶⁴ whereas the

Scheme 61. Bis-Germylation of Phenylacetylene with Dichlorotetraorganodigermene



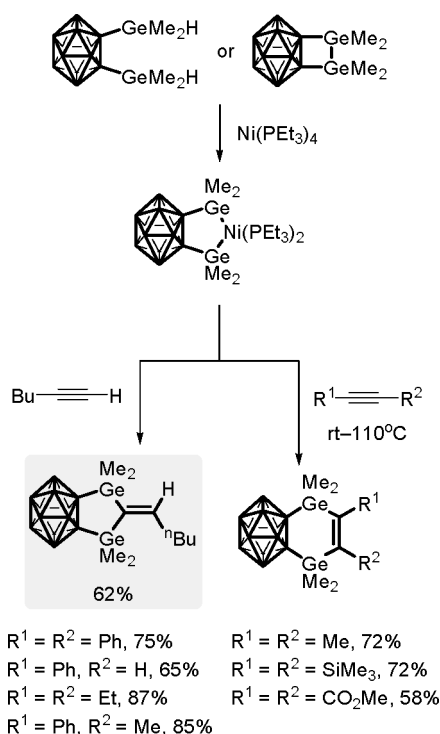
more challenging hexamethyldigermene required a $[\text{Pt}(\text{acac})_2]$ catalyst.¹⁶⁵ However, a wide variety of aromatic and aliphatic terminal alkynes reacted quantitatively with nonactivated hexamethyldigermene in the presence of a heterogeneous catalyst (Au/TiO_2) to form exclusively *cis*-1,2-digermylated alkenes with high yields (76–96%).¹⁶⁶ As in the case of homogeneous catalysis, inorganometallic complexes containing Au–Ge bonds are postulated as key intermediates in this process.

A stoichiometric study of alkyne bis-germylation has been performed using 1,2-digermylcarborane and a nickel(0) complex. A digermyl–nickel(II) complex, generated by the oxidative addition of 3,4-carboranyl-1,1,2,2-tetramethyl-1,2-digermacyclobutane to tetrakis(triethylphosphine)nickel(0) reacted with internal alkynes to give *cis*-addition products. In contrast, the stoichiometric reaction of the digermyl–nickel(II) complex with 1-hexyne provided vinylidenedigermacyclopentane as the major product (Scheme 62).¹⁶⁷

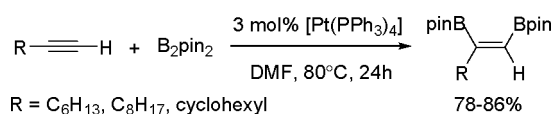
The catalytic addition of diboranes to internal and terminal alkynes in the presence of a platinum catalyst to form *cis*-diboration products was discovered by Miyaura and co-workers in 1993 (Scheme 63). In the original report, NMR data showed that the oxidative addition of B_2pin_2 to $[\text{Pt}(\text{PPh}_3)_4]$ followed the generally accepted oxidative addition/reductive elimination mechanism.¹⁶⁸

In the following years, Pt(0) complexes were proved to be the most effective catalysts for diboration reactions, for example $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)_2]$ ¹⁶⁹ and $[\text{Pt}(\text{dba})_2]/[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_3\text{P}$.¹⁷⁰ Platinum(0) monophosphine complexes containing PCy_3 or $\text{PPh}_2(o\text{-Tol})$ ligands generated in situ from $[\text{Pt}(\text{nbe})_3]$ (nbe–norbornene) as well as isolated platinum(0) complex $[\text{Pt}(\text{PCy}_3)(\eta^2\text{-C}_2\text{H}_4)_2]$ provide high catalytic activity for terminal and internal alkyne diboration at room temperature.¹⁷¹ However, nanoporous gold¹⁷² and platinum nanoparticles¹⁷³ were also found to be effective catalysts for the

Scheme 62. Stoichiometric Reaction of Alkynes with 1,2-Digermylcarborane and a Nickel(0) Complex



Scheme 63. Bis-Boration of Terminal Alkynes with Bis(pinacolato)diboron

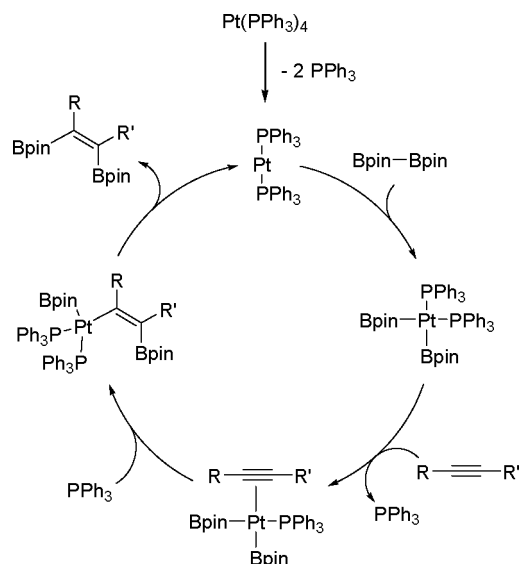


diboration of internal alkynes with B_2pin_2 . Most Pt-catalyzed diboration reactions employ symmetrical diboranes, such as bis(pinacolato)diboron (B_2pin_2) and bis(catecholato)diboron (B_2cat_2), with the latter being more active. The application of a diborane with two different boryl groups, (pin)B–B(dan) (dan = naphthalene-1,8-diaminato), provides access to unsymmetrically substituted bis-borated alkenes, with the B(dan) group occupying the terminal carbon position.¹⁷⁰ Platinum-catalyzed diboration of alkynes is proposed to proceed via the oxidative addition of B–B bonds to Pt(0), insertion of C–C multiple bonds into Pt–B bonds and reductive elimination of C–B bonds with regeneration of the catalytically active Pt(0) species (Scheme 64).

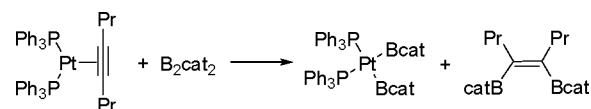
Experimental evidence has been found for each step of the catalytic cycle.¹⁷⁴ The groups of Marder¹⁶⁹ and Smith¹⁷⁵ reported the isolation and characterization of $[\text{Pt}(\text{PR}_3)_2(\text{B}(\text{OR})_2)_2]$ complexes, which proved to be highly active in the diboration of alkynes (Scheme 65). On the basis of studies with monodentate and chelating phosphine ligands, the authors concluded that phosphine dissociation was a key step in the diboration reaction mechanism.

The results obtained by the Braunschweig¹⁷⁶ and Marder¹⁷⁷ groups on the reversible oxidative addition/reductive elimination of diboranes in Pt(II) complexes show a more complicated reaction mechanism. The oxidative addition of B_2cat_2 to rhodium(I) and iridium(I) complexes^{178,179} as well as to cobalt(0) precursors,¹⁸⁰ further supported by studies on

Scheme 64. General Mechanism of the Platinum-Catalyzed Bis-Boration of Alkynes



Scheme 65. Synthesis of a Bis(boryl)–Platinum(II) Complex

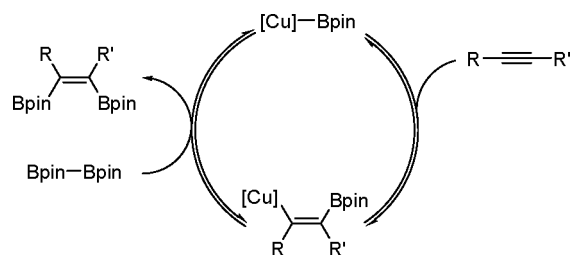


alkene insertions into TM–boron bonds, suggested that diborations using other TM catalysts could occur through a similar reaction mechanism. However, it is noted that dehydrogenative borylation products of rhodium catalysis could also be detected as a result of a competitive β -hydride elimination process. Pt(0) complexes are generally more effective in alkyne diboration than Rh(I) and Pd(0) complexes since the increased d-electron energy of Pt(0) facilitates oxidative addition more than Pd(0) and Rh(I). However, $[\text{Pd}(\text{ITMe})_2(\text{PhC}\equiv\text{CPh})]$ complex (ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene) has been found to be a highly reactive precatalyst in the diboration of sterically and electronically demanding alkynes under mild reaction conditions. DFT calculations suggest a reaction pathway similar to that proposed for platinum phosphine analogues. According to the results of the computational study, dissociation of one NHC ligand is a crucial part of the reaction mechanism. Destabilization of the $[(\text{BR}_2)_2\text{Pd}(0)(\text{ITMe})_2]$ complex by the NHC ligand has been shown to facilitate oxidative addition of the B–B bond.¹⁸¹

Yoshida and co-workers disclosed general *syn*-diboration with bis(pinacolato)diboron using a $\text{Cu}(\text{OAc})_2/\text{PCy}_3$ catalytic system,¹⁸² which was equally effective as platinum catalysts. The reaction proceeds through a boryl-substituted alkenyl–copper intermediate (formed by alkyne insertion into a Cu–B bond), which reacts with a diborane to give a bis-boration product, thereby regenerating the boryl–copper complex (Scheme 66).

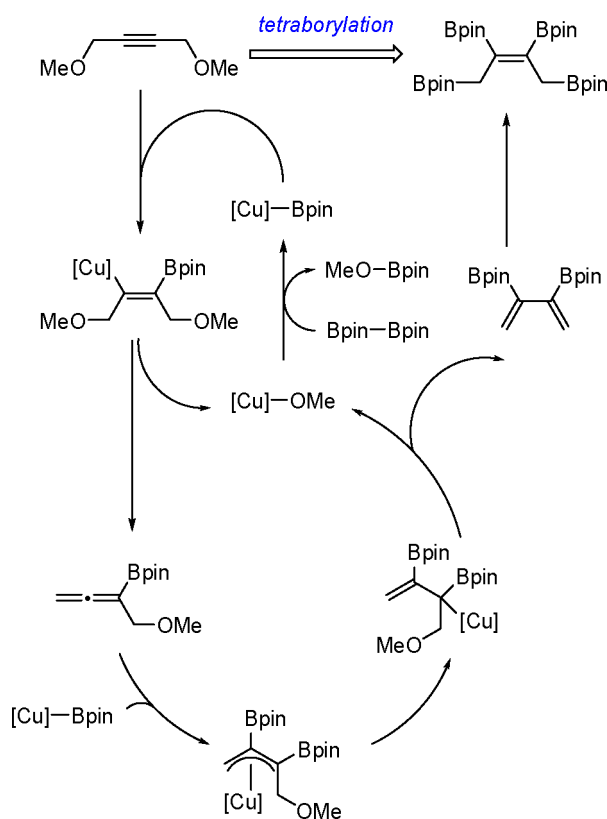
This catalytic system has been explored using 1,4-dimethoxy-2-butyne converted into a tetraborylated product, in which the MeO groups were also substituted by B(pin) groups.¹⁸² This unique tetraborylation reaction involves the formation of boryllene (by the elimination of copper(I)

Scheme 66. Insertion of Alkyne into the Cu–B Bond



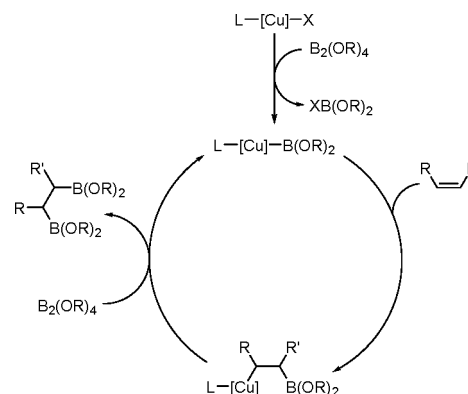
methoxide from the alkenyl–copper intermediate) and 2,3-diboryl-1,3-butadiene (boryllallene insertion into a Cu–B complex) as key intermediates. In the final step, 2,3-diboryl-1,3-butadiene underwent copper(I)-catalyzed 1,4-diboration to give tetraborylethylene (Scheme 67).

Scheme 67. Mechanism of Copper-Catalyzed Alkyne Tetraboration



The high catalytic activity of copper(I) complexes in alkene diboration reactions prompted the search for a new mechanism based on a series of σ -bond metathesis steps, resulting in the overall transfer of both boryl groups to the substrate.¹⁸³ Computational studies have shown that in contrast to the catalytic cycle proposed for platinum(0) complexes, the catalytic cycle of copper catalysts is believed to operate through the transmetalation pathway. The reaction occurred via the formation of a monoborylcopper(I) complex. Insertion of an alkene into the Cu–B bond formed an alkyl–copper(I) complex, which subsequently reacted with diborane to produce the bis-boration product with regeneration of the boryl–copper complex (Scheme 68). Detailed DFT studies by Marder, Lin, and co-workers showed the mechanism and

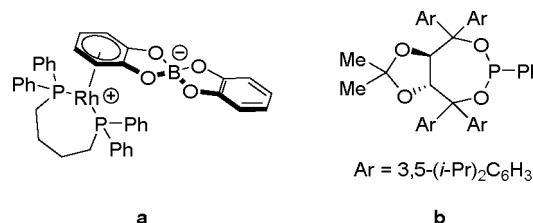
Scheme 68. Mechanism of Copper-Catalyzed Alkene Bis-Boration



confirmed differences in the reactivity of B_2cat_2 and B_2pin_2 .¹⁸⁴ Further support for the stepwise transfer of boryl groups was provided by Fernández and co-workers who generated mixed bis-borylalkanes using two different diboranes.¹⁸⁵

Stoichiometric σ -bond metathesis reactions of nickel(II) and cobalt(II) *tert*-butoxide complexes with B_2cat_2 or B_2pin_2 to generate TM–boryl species and to support the transmetalation mechanism of diboration have been also demonstrated.¹⁸⁶

The catalytic diboration of alkenes was first reported in 1995 and employed bis(catecholato)diboron in the presence of Rh or Au catalysts.¹⁸⁷ Catalysis with the $[RhCl(PPh_3)_3]$ rhodium complex was based on an earlier report on the oxidative addition of B_2cat_2 with Rh(I) to give bis(boryl)Rh complexes and on another report showing that bis(boryl)rhodium complexes reacted with alkenes to give alkene 1,2-diborylation.¹⁸⁸ β -Hydrogen elimination, which generates vinyl boronates, often competes with the reaction pathway in the presence of rhodium catalysts. However, the formation of byproducts arising from β -hydride elimination can be significantly diminished by using a zwitterionic η^6 -(arene) rhodium catalyst with a diphenylphosphinomethane ligand (dppm) (Scheme 69a).¹⁸⁹ The synthetic utility of rhodium-

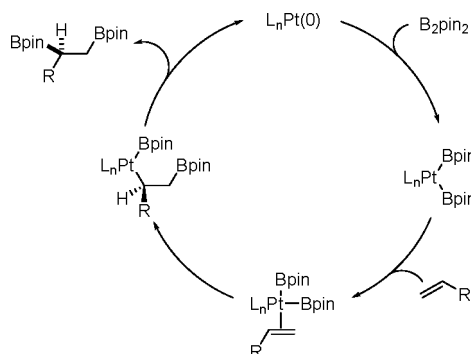
Scheme 69. (a) Zwitterionic η^6 -(Arene)Rhodium Complex and (b) TADDOL Ligand Structure

catalyzed diboration has been considerably expanded by the development of its enantioselective variant in the presence of an (*S*)-QUINAP/ $[(nbd)Rh(acac)]$ catalytic system ((*S*)-QUINAP is (*S*)-1-(2-diphenylphosphino-1-naphthyl)-isoquinoline).¹⁹⁰

Successful catalytic bis-boration of aliphatic alkenes with B_2pin_2 ¹⁹¹ and B_2cat_2 ¹⁹² using nonphosphine platinum(0) catalysts bearing π -ligands (dibenzylideneacetone (dba), norbornene (nbe) or cyclooctadiene (cod)) has been disclosed. An experimental and computational study of enantioselective $[Pt(dba)_3]$ -catalyzed terminal alkene bis-boration in the presence of chiral phosphonite ligands

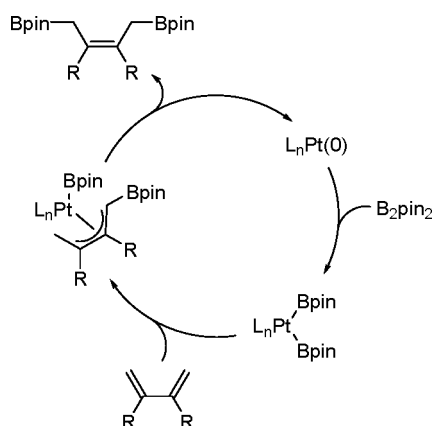
(TADDOL-derivatives, Scheme 69b) was published by Morken and co-workers.¹⁹³ A DFT study combined with other experimental data suggests olefin migratory insertion into a Pt–B bond to give an internal C–Pt intermediate as the rate-limiting and stereocontrolling step of the reaction (Scheme 70).

Scheme 70. Mechanism of Enantioselective Pt(0)-Catalyzed Terminal Alkene Bis-Boration



Catalytic bis-boration of conjugated 1,3-dienes proceeded in the presence of platinum(0) catalysts (Scheme 71). Depending

Scheme 71. Mechanism of Pt(0)-Catalyzed Bis-Boration of Conjugated 1,3-Dienes

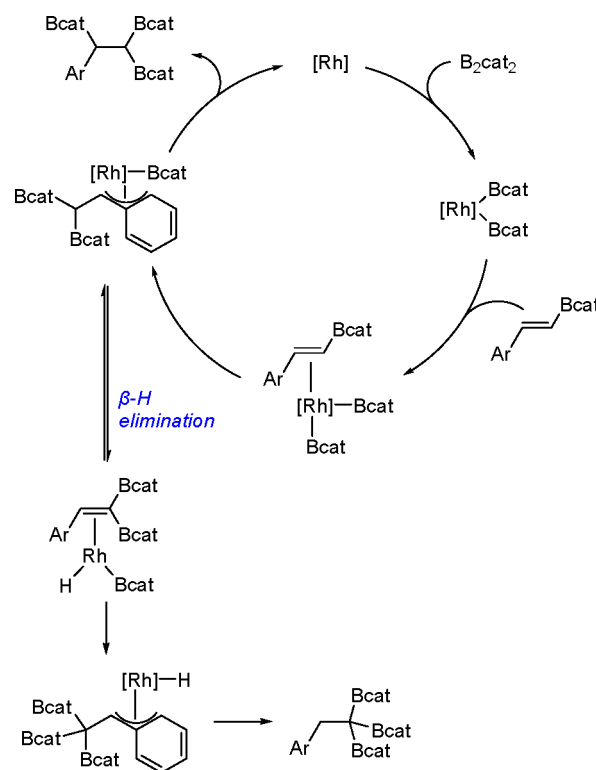


on the structure of the substrate and catalysts, the reaction leads either to 1,4-diboration products—as in the presence of $[\text{Pt}(\text{PPh}_3)_4]$ ¹⁹⁴—or to 1,2-diboration products when the reaction is mediated by $[\text{Pt}(\text{dba})_2]$.¹⁹¹

The Rh(I)-catalyzed bis-boration of (*E*)-styrylboronate esters gave predominantly 1,1,1-triboryl-2-arylethane in the presence of Wilkinson's catalyst, but isomeric 1,1,2-triboryl-2-arylethanes were formed with the $[\{\text{Rh}(\text{coe})_2(\mu\text{-Cl})\}_2]$ complex.¹⁹⁵ The formation of untypical 1,1,1-triboryl-2-arylethanes involves the regioselective insertion of vinylboronates into a Rh–B bond followed by β -hydride elimination and the second insertion of 2,2-vinyl bis(boronate) into the remaining Rh–B bond and C–H reductive elimination, leading to 2,2-diboration and a 2,1-hydrogen shift (Scheme 72).

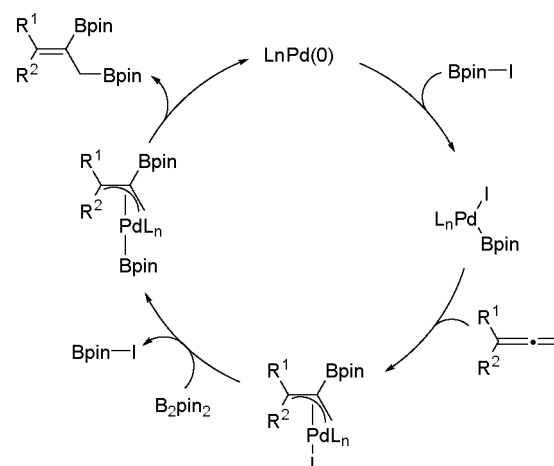
A new mechanism has been discovered in the study of the palladium-catalyzed bis-boration of allenes in the presence of alkenyl- or aryl iodide as a cocatalyst. This three-component coupling of iodoborane, diborane, and allene proceeds through

Scheme 72. Mechanism of the Rh(I)-Catalyzed Bis-Boration of (*E*)-Styrylboronate Esters



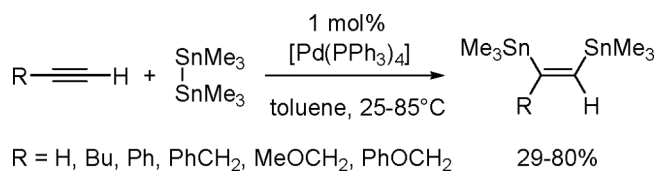
the oxidative addition of the boron–iodine bond instead of the boron–boron bond, and the terminal double bond of the allene is then inserted into the palladium–boron bond. The transmetalation with diborane results in the elimination of the diboration product and regeneration of the palladium–boryl–iodide complex (Scheme 73).¹⁴⁸

Scheme 73. Mechanism of the Pd(0)-Catalyzed Three-Component Coupling of Iodoborane, Diborane, and Allene

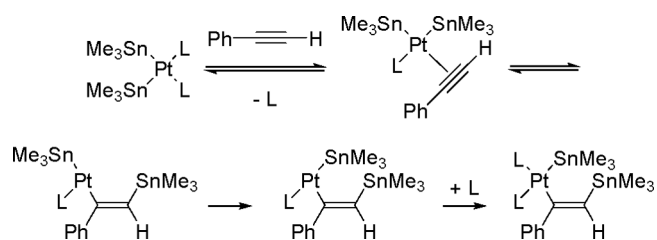


Bis-stannylation (bis-stannylation) of functionalized terminal alkynes with hexamethyldistannane catalyzed by $[\text{Pd}(\text{PPh}_3)_4]$ has been reported for the first time in good yields by Mitchell and co-workers (Scheme 74).¹⁹⁶

As for the other bis-metalations, it is believed that reactions of alkynes with distannanes proceed via *syn*-addition according

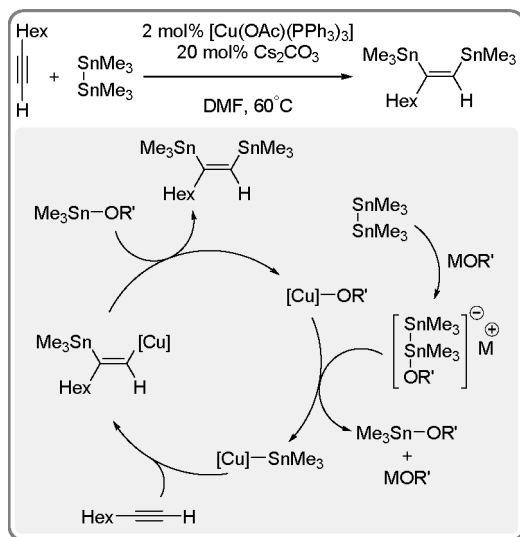
Scheme 74. Bis-Stannylation of Terminal Alkynes with Hexamethyldistannane

to the oxidative addition/reductive elimination mechanism. A detailed experimental study of the insertion of phenylacetylene into Pt–Sn bonds was reported by Ozawa and co-workers (Scheme 75).¹⁹⁷

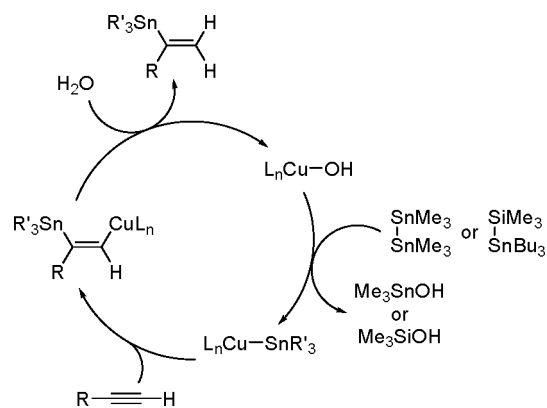
Scheme 75. Insertion of Phenylacetylene into Pt–Sn Bonds

Catalysts other than platinum and palladium complexes are rarely used in bis-stannylation reactions. However, similarly to bis-boration, addition of Sn–Sn bonds can be achieved with copper catalysts. Yoshida and co-workers reported catalytic bis-stannylation of alkynes with Me₃Sn–SnMe₃ using a copper catalyst, [Cu(OAc)(PPh₃)₃], in the presence of Cs₂CO₃. The proposed key intermediate in this process is an inorganometallic complex containing a Cu–Sn bond derived from an alkoxycopper complex and a base-activated distannane (Scheme 76).¹⁹⁸

Stannyl-substituted alkenylcopper species were also found to serve as key intermediates in the α -selective hydrostannylation of terminal alkynes using Me₃Sn–SnMe₃ or Me₃Si–SnBu₃ as a stannylating agent and water as a hydrogen source.¹⁹⁹ Formation of the Cu–Sn complex proceeds through σ -bond

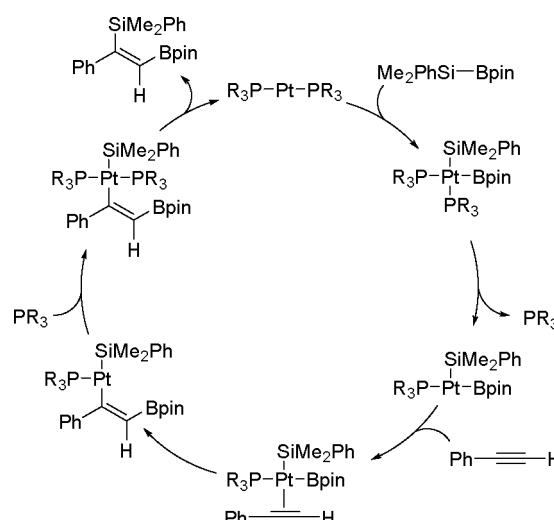
Scheme 76. Mechanism of the Bis-Stannylation of Alkynes with Hexamethyldistannane Using a Cu(I) Catalyst

metathesis between a hexamethyldistannane (or trimethylsilyl-tributylstannane) and Cu–OH complex that is formed in the reaction mixture in the presence of water. The resulting stannylcopper species is inserted into the carbon–carbon triple bond (stannylcupration), which induces the formation of β -stannylvinylcopper species. Finally, the latter is transformed into a hydrostannylation product through protonation with water followed by regeneration of copper hydroxyl intermediate (Scheme 77).

Scheme 77. Mechanism of the Markovnikov Hydrostannylation of Terminal Alkynes with Distannanes

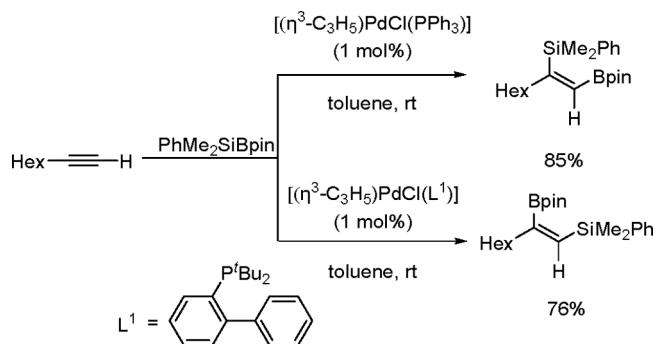
2.3. Addition of Heterolement–Element Linkages to Unsaturated Substrates

Silaboration (silylboration or silylborylation) of alkynes and silaborative carbocyclization of diynes and enynes have first been reported by Ito²⁰⁰ and Tanaka groups.²⁰¹ As for homolement–element linkages, the proposed catalytic cycle for silaboration using Pt group catalysts involves an initial oxidative addition resulting in the formation of a *cis*-[Pt(L)₂(SiR₃)(BR₂)] complex. The alkyne then undergoes migratory insertion into the M–B bond to form the corresponding [Pt(L)₂(SiR₃)(CH=CHBR₂)] species, followed by reductive elimination to form 1-silyl-2-borylalkene (Scheme 78).²⁰²

Scheme 78. Mechanism of Pt(0)-Catalyzed Alkyne Silaboration

The catalytic addition of Si–B bonds to alkynes is highly regio- and stereoselective since the boryl group is usually linked to the terminal carbon atom, whereas the silyl group is connected to the internal carbon atom. However, the application of palladium complexes and bulky phosphine ligands reverses the regioselectivity, yielding products that contain terminal silyl groups.²⁰³ Thus, the silaboration of alkynes with silylboronic esters proceeds with normal regioselectivity in the presence of $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\text{PPh}_3)\text{Cl}]$ to give 1-boryl-2-silyl-1-alkenes, but 2-boryl-1-silyl-1-alkenes are formed selectively when a palladium catalyst bearing $\text{P}(t\text{-Bu})_2$ (biphenyl-2-yl) is applied (Scheme 79). Quantum-

Scheme 79. Regiodivergent Oct-1-yne Silaboration in the Presence of Palladium Complexes



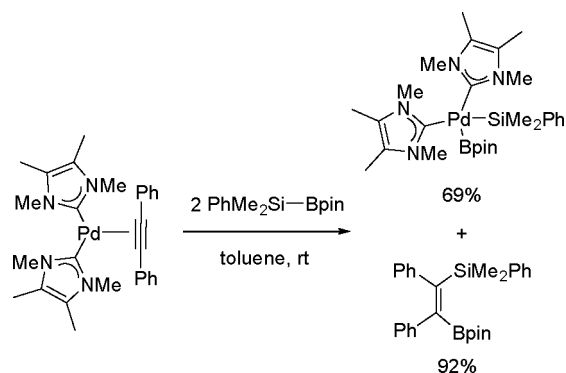
chemical calculations suggest that ligand-controlled regioselective alkyne insertion into the Pd–B bond followed by reductive elimination is responsible for the observed switch in regioselectivity.²⁰³

Isolation of the oxidative addition products of Pt complexes is extremely rarely reported because of their low stability. However, Ozawa and co-workers have demonstrated that all the elementary processes presumed for the catalytic silaboration of phenylacetylene with $\text{PhMe}_2\text{SiBpin}$ can be examined stepwise using platinum complexes with phosphine ligands.²⁰⁴ Thus, silyl(boryl)platinum(II) complexes prepared by the oxidative addition of silylborane to platinum(0) complexes of the formula $\text{cis-}[\text{Pt}(\text{SiMe}_2\text{Ph})(\text{Bpin}_2)\text{L}_2]$ ($\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PEt}_3$) undergo selective insertion of phenylacetylene into the Pt–B bond to give $\text{cis-}[\text{Pt}\{\text{C}(\text{Ph})=\text{CH}(\text{Bpin})\}(\text{SiMe}_2\text{Ph})\text{L}_2]$. The insertion complexes undergo C–Si reductive elimination to give (*Z*)- α -silyl- β -borylstyrene.

More recently, a $\text{cis-}[\text{Pd}(\text{ITMe})_2(\text{SiMe}_2\text{Ph})(\text{Bpin})]$ ($\text{ITMe} = 1,3,4,5\text{-tetramethylimidazol-2-ylidene}$) complex was synthesized by the oxidative addition of $\text{PhMe}_2\text{SiBpin}$ to a $[\text{Pd}(\text{ITMe})_2(\text{PhCCPh})]$ precursor. This was a very rare example of a (silyl)(boryl)palladium(II) complex isolated from the oxidative addition of a Si–B reagent to a Pd(0) center (Scheme 80).²⁰⁵ On the basis of stoichiometric studies, the authors proposed a catalytic cycle of alkyne silaboration in the presence of a $(\text{NHC})_2\text{-Pd}(0)$ complex.²⁰⁵

Supported gold nanoparticles (Au/TiO_2) have been found to catalyze the easily *syn*-selective silylboration of alkynes, giving vicinal boryl(silyl)alkenes.²⁰⁶ The regioselective silaboration could be used for aliphatic, aromatic, and propargyl-functionalized terminal alkynes and led to the preferential incorporation of the boryl moiety into the internal carbon. Similarly to homogeneous catalysis, oxidative addition of a silylborane and insertion of an alkyne into $[\text{Au}]\text{-B}(\text{pin})$ have been proposed to be the key steps of silylboration. The

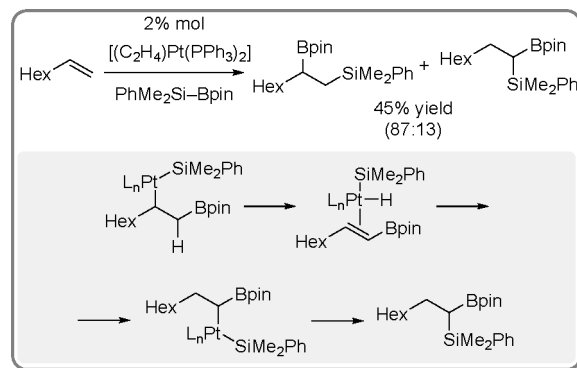
Scheme 80. Synthesis of a (Silyl)(boryl)palladium(II) Complex



observed regioselectivity may be attributable to steric repulsion between $[\text{Au}]$ and a substituent of the alkyne in the insertion step.

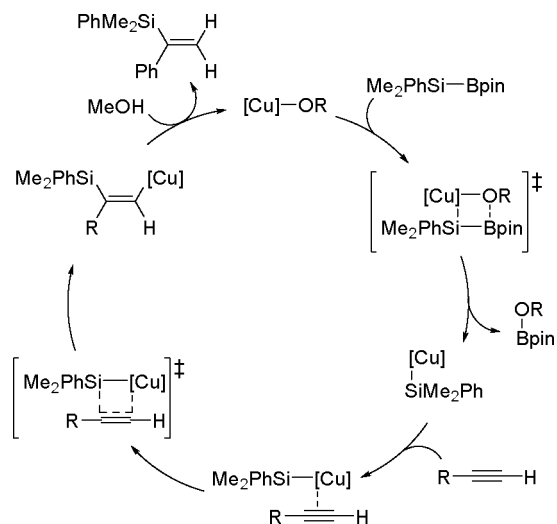
In contrast to the regioselectivity observed in alkyne silaboration, the platinum(0)-catalyzed (e.g., $[(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)]$ or $[\text{Pt}(\text{PPh}_3)_4]$) addition of silylboranes across terminal C=C double bonds resulted in 1,2-difunctionalized alkanes with the silyl group attached to the terminal carbon atom (2-boryl-1-silylalkanes). However, minor amounts of 1,1-silaboration products could also be formed in this process as a result of a competitive β -hydrogen elimination/hydrometalation pathway (Scheme 81).²⁰⁷

Scheme 81. Platinum(0)-Catalyzed Addition of Silylboranes to Terminal Alkenes

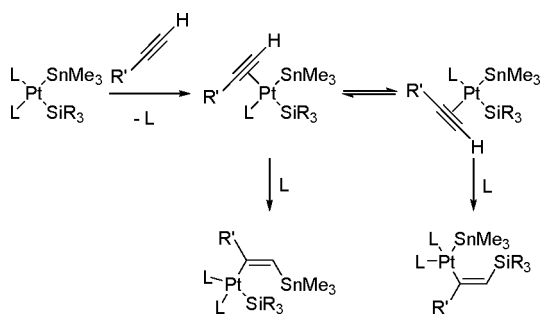


In addition to their involvement in classical bis-metalation, silylboranes can also act as silylating reagents. Several examples of the selective preparation of linear or branched vinylsilanes from alkynes, mainly in the presence of copper salts, have been reported in the literature.²⁰⁸ The mechanism of this process is similar to copper(I)-catalyzed Markovnikov borylation¹¹⁷ with diboranes (Scheme 41) and does not assume the oxidative addition of silylborane to copper, but the formation of the inorganometallic Cu–Si complex via the reaction of alkoxycopper with silylborane, into which an alkyne is inserted, is of key importance (Scheme 82).

Palladium-catalyzed addition of Si–Sn bonds to terminal alkynes proceeds in a highly regioselective manner with a stannyl group attached to the more substituted carbon atom.²⁰⁹ A detailed mechanistic study of alkyne insertion into *cis*-silyl(stannyl)platinum(II) complexes has been reported by Ozawa and co-workers²¹⁰ Competitive insertion of alkyne

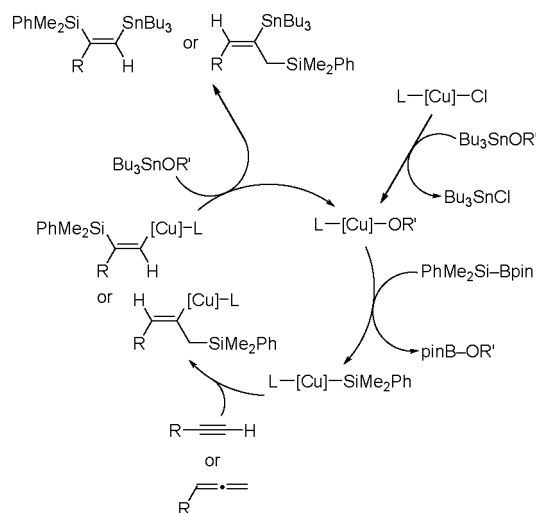
Scheme 82. Mechanism of the Markovnikov Silylation of Alkynes Using Silylboranes

into Pt–Si and Pt–Sn bonds has been considered, with the ratio of the two product types being dependent on the substituents on the silyl and phosphine ligands (*cis*-[Pt{C(R')=CHSnMe₃}(SiR₃)L₂] and *cis*-[Pt(SnMe₃){C(R')=CHSiR₃}-L₂], respectively) (Scheme 83).

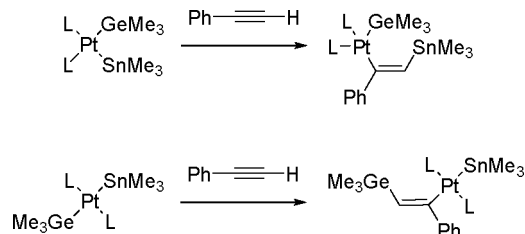
Scheme 83. Competitive Alkyne Insertion into Pt–Si and Pt–Sn Bonds

A theoretical study of the alkyne silylstannylation mechanism with a palladium catalyst suggested that alkyne insertion into the Pd–Sn bond, with Sn attack at the terminal position, is favored over Pd–Si insertion.²¹¹ Inverse regioselectivity in the silylstannylation reaction can be achieved using a copper catalyst in the three-component variant of this process, with terminal alkynes, a silylborane (PhMe₂SiBpin), and a tin alkoxide (*n*-Bu₃SnOt-Bu) in the presence of the [Cu(Cl)P(*t*-Bu)₃] catalyst. In this case, the silylcopper species, Cu–SiMe₂Ph (formed via σ -bond metathesis between the copper alkoxide and silylborane), played a key role in the catalytic cycle to enable alkyne insertion into the Cu–Si bond and give a β -silylalkenylcopper intermediate, which in the reaction with the tin alkoxide produced the addition product and regenerated the copper alkoxide (Scheme 84).²¹²

Studies of the addition of germastannanes to alkynes are limited to arylacetylenes²¹³ and propargylic esters²¹⁴ in the presence of the [Pd(dba)₂/P(OCH₂)₃CET] or the [Pd-(PPh₃)₄] catalytic system, respectively. In contrast to other *bis*-metalation products, germylstannylation products are usually formed with poor stereo- and regioselectivity. A

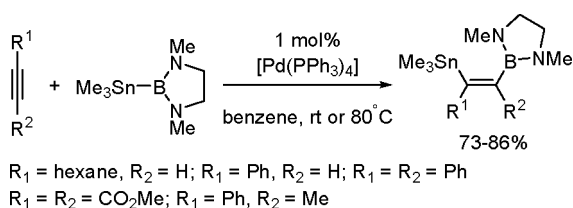
Scheme 84. Mechanism of the Cu(I)-Catalyzed Three-Component Silastannylation of Terminal Alkynes

study of the insertion of phenylacetylene into a mixture of *cis*-*trans* isomers of [Pt(GeMe₃)(SnMe₃)(PMe₂Ph)₂], obtained by the oxidative addition of Me₃Ge–SnMe₃ with a Pt(0) complex, supported the classical *bis*-metalation mechanism.²¹⁵ The isomeric germyl(stannyl)platinum complexes underwent competitive insertion of phenylacetylene into Pt–Sn and Pt–Ge bonds to give a mixture of *cis*-[Pt(GeMe₃){C(Ph)=CH(SnMe₃)}(PMe₂Ph)₂] and *cis*-[Pt{C(Ph)=CH(GeMe₃)}(SnMe₃)(PMe₂Ph)₂] complexes in the 8:2 ratio (Scheme 85).²¹⁵

Scheme 85. Competitive Insertion of Phenylacetylene into Pt–Sn and Pt–Ge Bonds

The borastannylation (borylstannylation) of terminal and internal alkynes was discovered by Tanaka and co-workers in 1996. Sterically hindered borylstannanes are usually employed, for example, 1,3-dimethyl-2-(trimethylstannyl)-2-bora-1,3-diazacyclopentane (Me₃SnB[NMe{CH₂CH₂}NMe]) or 1,3-di-*tert*-butyl-2-(trimethylstannyl)-2-bora-1,3-diaza-cyclopentane (Me₃SnB[N*t*-Bu{CH₂CH₂}N*t*-Bu]), in the presence of the [Pd(PPh₃)₄] catalyst to yield *cis*-1-boryl-2-stannyl-1-alkenes as predominant products (Scheme 86).^{216,217} The results are in agreement with the accepted mechanism, with the alkyne being inserted into the Pd–B bond. Application of Tanaka's methodology to 1,3-enynes led to the formation of *cis*-1-boryl-2-stannyl-1,3-dienes in a regio- and stereoselective manner.²¹⁸

Regio- and stereoselective installation of boryl and stannyl moieties into the carbon–carbon triple bonds of various alkynes has also been achieved using three-component coupling with a *bis*(pinacolato)diborane and a tin alkoxide, Bu₃SnOMe, with the aid of a Cu(OAc)₂/PCy₃ catalytic

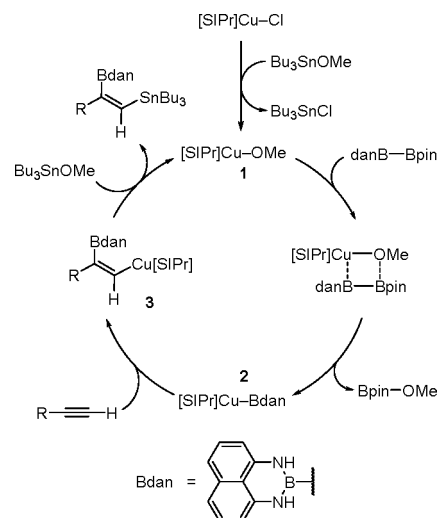
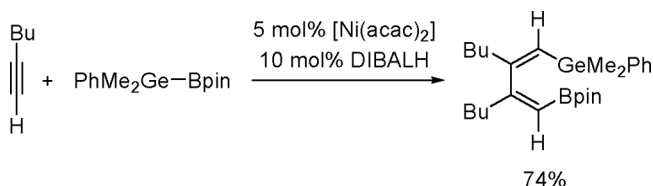
Scheme 86. Pd(0)-Catalyzed Borylstannylation of Terminal and Internal Alkynes


system, and vicinal boryl(stannyl)alkenes were obtained in a straightforward manner.²¹⁹ In this variant of *cis*-borylstannylation, a stannyl alkoxide acted as the electrophile for capturing catalytically generated organocopper species. The stannyl group was found to be exclusively attached to the α -position of an aryl substituent in the reaction with alkyl(aryl)alkynes, whereas the reaction of terminal alkynes led to products with a stannyl moiety at the internal carbon.

A copper complex, [(IMes)CuCl] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), has been found to catalyze the borylstannylation of alkenes and allenes through three-component coupling with a diborane and a tin alkoxide, yielding structurally diverse *vic*-boryl(stannyl)alkanes (or alkenylstannanes with boryl moieties in the case of allenes) in a regio- and stereoselective manner.²²⁰ Copper-catalyzed asymmetric three-component borylstannylation of aryl-substituted alkenes with B₂pin₂ and Bu₃SnOMe, leading to the enantioselective formation of α -aryl- β -borylstannane compounds, has also been reported with chiral sulfanylphosphine ligands.²²¹

A *N*-heterocyclic carbene copper complex [(SIPr)CuCl] (SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene) is used as a catalyst in the borylstannylation of terminal alkynes with a (pin)B–B(dan) unsymmetrical diborane of inverse regioselectivity to produce compounds with a stannyl moiety at the terminal carbon.²²² The reaction is initiated by the formation of a catalytically active Cu–OMe complex (1), which subsequently reacts with diborane to form a boryl complex (2). Insertion of an alkyne into a Cu–B bond generates complex (3), which is then captured by tin methoxide to furnish a *cis*-boryl(stannyl)alkene (Scheme 87). A rational explanation of the formation of Cu–B(dan) vs Cu–B(pin) is based on assumption of a selective interaction between the Lewis acidic B(pin) moiety of unsymmetrical diborane and the methoxy moiety of copper methoxide species, which may lead to selective introduction of the boryl group into the triple bond of the alkynes. The regiochemical outcome of the borylstannylation and positioning of the B(dan) moiety at the internal carbon of the terminal alkynes follows from the orientation of the Cu–B species in the borylcupration step.

The products obtained in the germaboration (germylborylation) of alkynes are highly dependent on the metal catalyst used. Classical *cis*-addition products can be obtained in the presence of the [Pt(PPh₃)₂(C₂H₄)] catalyst; however, with the [Ni(acac)₂]/DIBALH catalytic system, the reaction of germylboranates with alkynes led to 1-germyl-4-borylbuta-1,3-diene derivatives in a regio- and stereoselective manner (Scheme 88).²²³

Scheme 87. Cu(I)-Catalyzed Three-Component Borylstannylation of Terminal Alkynes

Scheme 88. Germaborative Dimerization of Hex-1-yne in the Presence of a Ni(II) Catalyst


3. ACTIVATION (AND FUNCTIONALIZATION) OF C–H BONDS WITH HYDROMETALLOIDS AND BISMETALLOIDS

3.1. Dehydrogenative Borylation of C–H Bonds

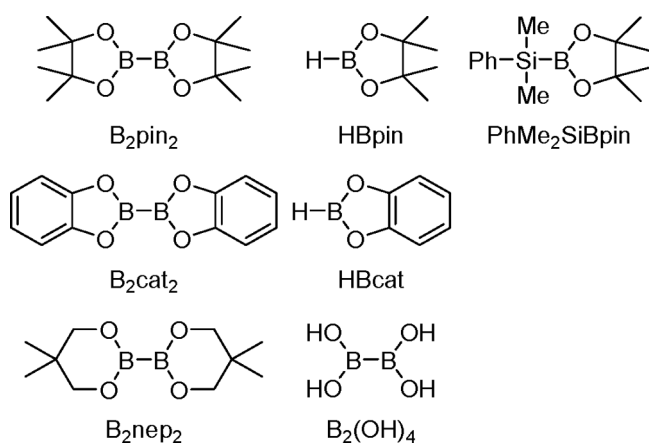
Direct borylation of C–H bonds is currently one of the best developed types of metal-catalyzed C–H bond functionalization. The reaction is catalyzed by metal salts and complexes of Ir, Zn, Pd, Co, Cu, Fe, and Ag. Procedures for the borylation of C–H bonds in alkanes, alkenes, arenes, and alkynes that ensure high yields and high selectivities have been described. The reaction permits the synthesis of several useful building blocks of wide applicability in organic synthesis. The state of knowledge of the reaction has been presented in many reviews.^{100,224–230} Scheme 89 illustrates the borylating agents that are most frequently used in C–H and C–X borylation.

3.1.1. Dehydrogenative Borylation of C(sp)–H Bonds.

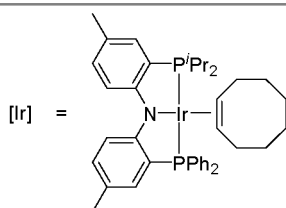
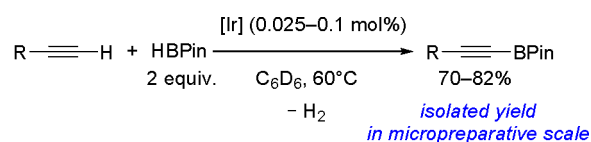
Dehydrogenative borylation of C(sp)–H bonds in terminal alkynes greatly expands the access to alkynylboronates that act as versatile reagents in organic synthesis.²³¹ This has recently been briefly summarized.²³² The first efficient examples of the reactions were discovered by Ozerov and co-workers who reported the activity of iridium complexes featuring a silyl-amido-quinoline tridentate SiNN-pincer ligand in the selective and efficient reaction of a variety of terminal alkynes with pinacolborane to form alkynylboronates.²³³ The most promising results were obtained using iridium–diarylamido/bis(phosphine) pincer complexes (Scheme 90).²³⁴ Selective and high-yield borylation of a variety of alkynes was possible in the presence of small amounts of catalysts.

On the basis of experimental studies, including detailed kinetic studies, as well as computational analysis in the

Scheme 89. Commonly Used Borylating Agents

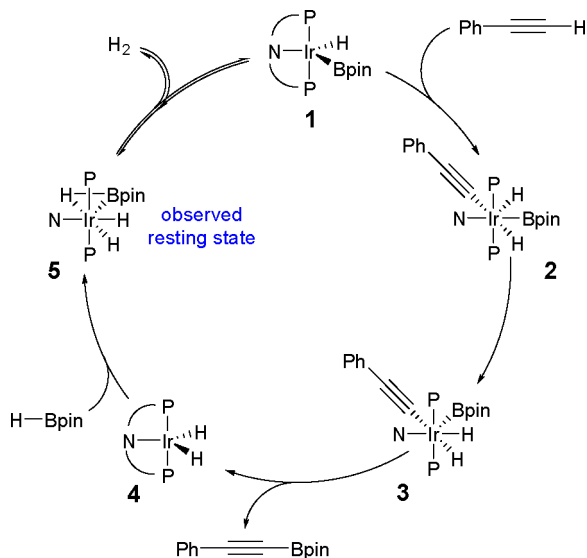


Scheme 90. Dehydrogenative Borylation of Acetylenes with Pinacolborane



presence of optimized PNP–pincer iridium complexes, the mechanism of the process was suggested (Scheme 91).¹²⁸

According to the proposed mechanism, the iridium(III) monoboryl monohydride complex (1) was assumed to be the

Scheme 91. Mechanism of C(sp)–H Borylation in the Presence of an Ir-PNP-Pincer Complex^a (P = P(*i*-Pr)₂)¹²⁸

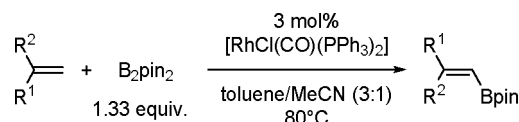
^aFor clarity, the structure of the diarylamidobis(phosphine) pincer ligand is not shown in complexes 2, 3 and 5.

active form of the catalyst. Complex 1 is in equilibrium with the dihydrido(σ -pinacolborane)iridium(III) complex (5), which is the resting state of the catalyst. Oxidative addition of phenylacetylene to 1 leads to the formation of 2. Subsequently, to displace the alkynyl group next to the boron molecule and allow the reductive elimination of the C–B bond, rotation of the B–H unit and formation of complex 3 is needed. In DFT calculations, this process has been found to be the rate-limiting step. Subsequently, reductive elimination of alkynylboronate from 3 produces dihydrido–iridium complex 4. The catalytic cycle is completed by the oxidative addition of HBpin and reductive elimination of dihydrogen.

3.1.2. Dehydrogenative Borylation of Olefinic C(sp²)–H Bonds. Vinylboronate esters are useful intermediates in organic synthesis. Catalytic methods for their formation include hydroboration of alkynes, palladium-catalyzed borylation of alkenyl halides, hydrogenation of 1-borylalkynes, cross-metathesis of terminal olefins with vinylboronate, and diboration of alkynes with diboron compounds. Borylation of olefins has recently been briefly reviewed.¹²⁵ Dehydrogenative borylation of olefins with HBR₂ is discussed in Section 1.5.1. Herein, dehydrogenative borylation of olefins with diboron derivatives is described.

Borylation of vinylarenes and 1,1-disubstituted alkenes with bis(pinacolato)diboron (B_2pin_2) in the presence of a rhodium catalyst, leading to corresponding vinylboronate esters, has first been reported by Marder (Scheme 92).²³⁵ The method does not suffer from significant formation of hydroboration and/or hydrogenation byproducts, seen when H-BR₂ is used as the borylating agent.

Scheme 92. Dehydrogenative Borylation of Olefin with Bis(pinacolato)diboron

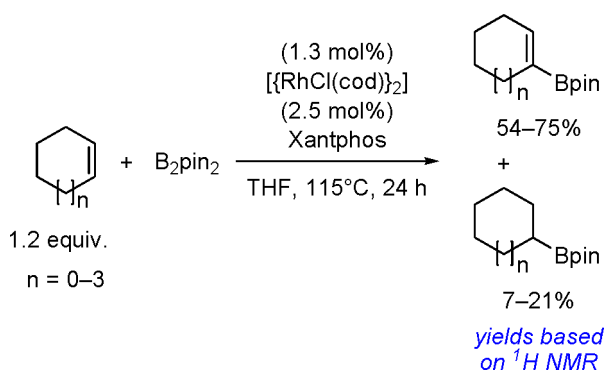


The use of double excess B_2pin_2 and a higher catalyst concentration (5 mol %) afforded a 1,1-disubstituted derivative that could not be synthesized by alkyne hydroboration. In a separate paper, the same authors reported the conditions resulting in higher yields and selectivities. The reaction time could be shortened to 60 min by using microwave reactors.²³⁶ The rhodium complexes also show activity in the borylation of cycloolefins, but in this case, saturated products also form in the reaction (Scheme 93).²³⁷

Allylsilanes and some vinyl substrates such as methyl acrylate or vinyl methyl ketone undergo borylation with B_2pin_2 in the presence of $[IrCl(cod)]_2$.^{238,239} A similar $[Ir(OMe)(cod)]_2$ complex and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy) have been used in the borylation of cyclic vinyl ethers.²⁴⁰ Optimized conditions for the iridium-catalyzed borylation of α,β -unsaturated esters with B_2pin_2 involve $[IrCl(cod)]_2$ or $[Ir(OMe)(cod)]_2$ and $AsPh_3$ as the ligand of choice. Such reaction conditions give borylated esters with isolated yields of 29–56%.²⁴¹

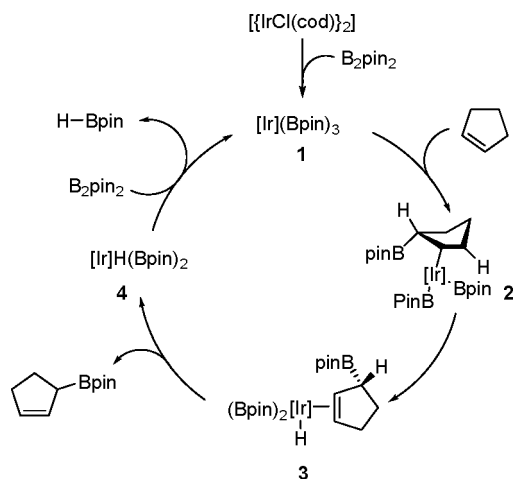
Although the literature does not provide the mechanism of olefin borylation supported by unquestionable evidence, the results strongly indicate that the mechanism involves olefin insertion into the M–B bond, followed by product formation and activation of the C–H bond via β -H elimination. The

Scheme 93. Undirected Dehydrogenative Borylation of Cycloolefins with B₂pin₂



mechanism for the iridium-based catalytic system has been proposed by Szabo on the basis of earlier literature data²³⁰ and results of labeling and kinetic studies (Scheme 94).²³⁹

Scheme 94. Mechanism of the Ir-Catalyzed Dehydrogenative Borylation of Cyclic Olefins. Adapted with Permission from Ref 239. Copyright 2009 American Chemical Society

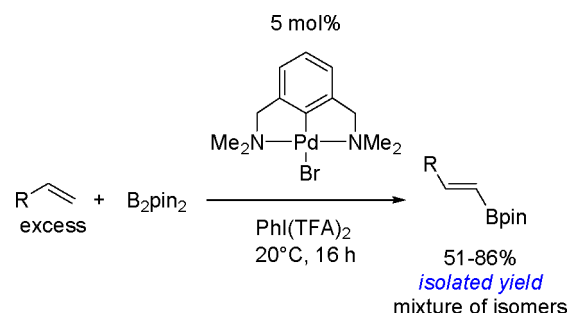


According to this mechanism, the starting iridium(I) complex $[\{\text{IrCl}(\text{cod})\}_2]$ reacts with an excess of B₂pin₂, providing an active triboronate catalyst (1). Association of the cycloalkene and its migratory insertion into the iridium–boron bond produces 2, which subsequently undergoes β -H elimination to give 3. Subsequently, the allylic product dissociates, and the iridium–hydride complex (4) reacts with the diboronate, thus regenerating the active catalyst and producing pinacolborane. The formation of the allyl derivative instead of the expected vinylboronate is a consequence of the stereochemistry of the β -H-elimination of hydrogen.²³⁹ Dehydrogenative borylation of acyclic olefins proceeds via an analogous mechanism.²³⁹ Similar mechanisms have been proposed for rhodium complexes²³⁵ and palladium–pincer complexes.²⁴² However, it should be noted that an alternative mechanism has been proposed in the literature, which assumes oxidative addition of the olefinic C–H bond to the metal center.²⁴¹

Efficient palladium-catalyzed olefin borylation has first been described by Szabo and co-workers.²⁴³ Cycloolefins, allyltrimethylsilane, and vinylboronic acid pinacol ester undergo

efficient borylation with B₂pin₂ in the presence of a palladium pincer complex and [bis(trifluoroacetoxy)iodo]benzene as oxidant (Scheme 95). Cycloolefin borylation leads to a mixture of the target product and an allyl isomer, while the ratio of isomers depends on the size of the cycloolefin ring.

Scheme 95. Dehydrogenative Borylation of Olefins with Bis(pinacolato)diboron Catalyzed by a Palladium NCN-Pincer Complex



Borylation of allyl derivatives of the general formula R¹R²CHCH=CH₂ in a catalytic system containing selectfluor as an oxidant enables efficient synthesis of allylboronates.²⁴⁴

The proposed reaction mechanism involves the formation of a palladium(IV) complex which undergoes transmetalation with diboronate, olefin insertion into the palladium–boron bond, and finally reductive elimination.

Another monoborylpalladium complex with an anionic PSiP-pincer ligand was used by Iwasawa.²⁴² The reaction leads to the selective synthesis of 1,1-diboryl- or monoborylalkenes depending on the amount of diborane used without sacrificial hydroboration. Contrary to the system described by Szabo, the reaction proceeds in oxidant-free conditions through a monoborylpalladium complex bearing an anionic PSiP-pincer ligand as the key intermediate.

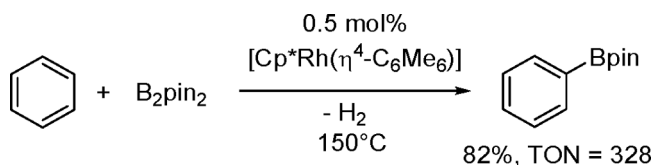
Finally, *N*-heterocyclic carbene copper complexes $[(\text{NHC})\text{-Cu}(\text{O}t\text{-Bu})]$, where NHC = IPr = (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) or NHC = 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) were found to be catalytically active in the borylation of styrenes.²⁴⁵ The method provides access to trisubstituted vinylboronates. The protocol involves addition of a ketone which is to react with the hydride complex and enables reformation of the boronate complex, the proposed key intermediate. The type of catalyst used, the ketone, and the pattern of substituents at the double bond affect the reaction yield.

A copper salt (CuSCN, 10 mol %), with a specific phosphine (CyJohnPhos or Xantphos (22 mol %)) and TEMPO as a mild oxidant, has been reported to catalyze the borylation of terminal aryl and aliphatic alkenes with B₂pin₂.²⁴⁶ This approach enables direct functionalization of both aryl- and alkyl-substituted terminal alkenes. Mechanistic studies indicate a radical pathway of the reaction.

3.1.3. Dehydrogenative Borylation of Arene C(sp²)–H Bonds. Borylation of the arene C(sp²)–H bond—a method that has been greatly developed over the past two decades—provides a rapid and versatile route to synthetically useful (hetero)arylboronic esters. A series of catalytic systems are available that permit effective undirected, directed, and intramolecular borylation of arenes. The complexes of many TMs (iridium, rhodium, ruthenium, palladium, platinum,

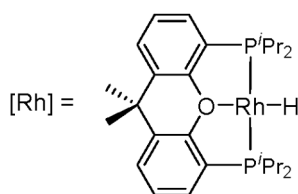
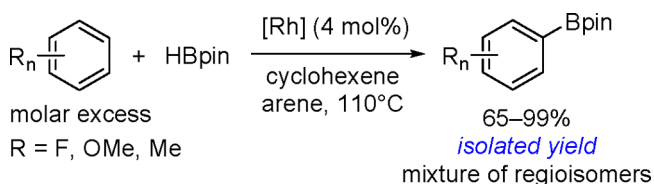
manganese, iron, cobalt, and nickel) and rare-earth metals have been demonstrated to exhibit catalytic activity in this process. The research on the process has been described in excellent review papers.^{224,230,247} The success story of arene borylation begins with the observation that photochemically activated $[\text{FeCp}(\text{CO})_2\text{Bcat}]$ (cat = catecholate) reacts with benzene to form PhBcat.²⁴⁸ The first thermally activated catalytic borylation was reaction of benzene solvent with B_2pin_2 in the presence of $[\text{Cp}^*\text{Rh}(\eta^4\text{-C}_6\text{Me}_6)]$, leading to the formation of PhBpin with TON > 300 (Scheme 96).²⁴⁹

Scheme 96. Rhodium-Catalyzed Undirected Dehydrogenative Borylation of Arene with B_2pin_2



Currently, rhodium catalysts have been less used as catalysts of the C–H bond borylation of arenes. Since 2006, rhodium complexes have been used in the *ortho*-borylation of arylphosphines,²⁵⁰ SCF_3 -functionalized arenes,²⁵¹ pyridylarenes,²⁵² and *N*-(2-pyridyl)-2-pyridone.²⁵³ Sawamura reported silica-supported bridgehead phosphine–Rh systems for the C–H borylation of a large variety of arenes assisted by nitrogen-based directing groups.²⁵⁴ A POP-pincer rhodium hydride $[\text{RhHL}]$ (Scheme 97) was found to catalyze the borylation of

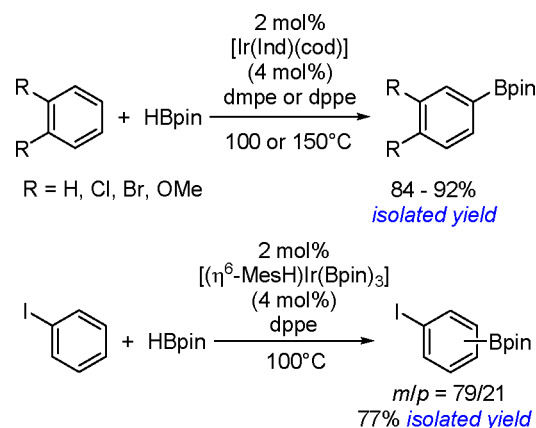
Scheme 97. Arene Borylation with HBpin Catalyzed by a Rhodium POP-Pincer Monohydrido Complex



methyl-, methoxy-, and fluoro-substituted arenes. This complex serves as a model for studying the stoichiometric steps of arene borylation with HBpin and permits isolation of the key intermediates.²⁵⁵

Presently, the most successful group of arene borylation catalysts are those based on iridium. The catalytic activity of iridium complexes was shown by Smith who reported indirect borylation of benzene²⁵⁶ and aryl derivatives²⁵⁷ with pinacolborane in the presence of $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{H})(\text{Ph})]$. Initial results were soon improved using a system consisting of $[(\text{Ind})\text{Ir}(\text{cod})]$ and a bulkier and more stable bidentate phosphine, that is, 1,2-bis(diphenylphosphino)ethane (dppe) or 1,2-bis(dimethylphosphino)ethane (dmpe) (Scheme 98).²⁵⁸ The system enables borylation of benzene and selected mono- and disubstituted aryl compounds with pinacolborane

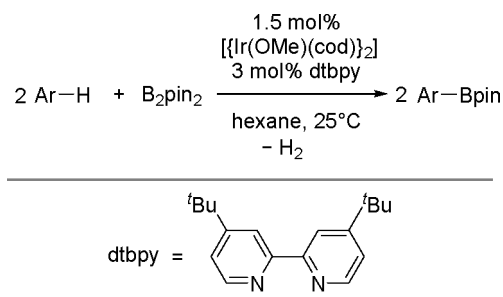
Scheme 98. Iridium-Catalyzed Undirected Dehydrogenative Borylation of Arenes with HBpin



(HBpin), leading to the highly efficient and selective formation of corresponding arylboronates.

Subsequently, Ishiyama and Miyaura and Hartwig described an analogous system of $[\{\text{Ir}(\text{OME})(\text{cod})\}_2]$ and dtbpy (dtbpy = 4,4'-di(*tert*-butyl)-2,2'-bipyridine) for the borylation of benzene and aryl derivatives with B_2pin_2 at room temperature.²⁵⁹ Currently, $[\{\text{Ir}(\text{OME})(\text{cod})\}_2]$ is the most common catalyst for the borylation of arenes with B_2pin_2 in combination with dtbpy developed by Ishiyama, Miyaura, and Hartwig.^{260,261} This complex ensures high yields of arylboronates already at room temperature and tolerates the presence of several functional groups in the reagents (Scheme 99).

Scheme 99. Undirected Dehydrogenative Borylation of Arenes with Pinacolborane

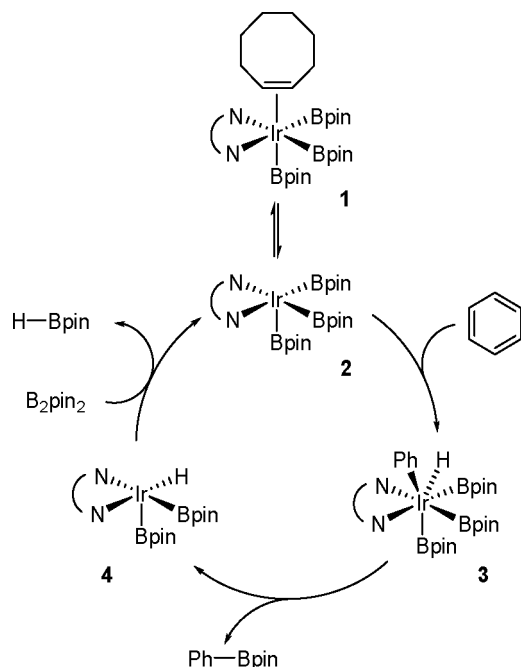


Recently, a combination of $[\{\text{Ir}(\text{OME})(\text{cod})\}_2]$ and Me_4phen (3,4,7,8-tetramethyl-1,10-phenanthroline) has been shown to exhibit increased reactivity in the borylation of alkanes and some arenes.²⁶² The proper choice of the chelating ligand may be crucial for obtaining high yields and site selectivity of C–H borylation.²⁶³ Krska, Maleczka, Smith, and co-workers published a tutorial on the practical applications of iridium-based arene borylation.²⁶²

The mechanism of the process with the involvement of iridium catalysts has been proposed by Hartwig (Scheme 100).²⁶⁴ The mechanism assumes that the iridium(III)–tri(boronate) complex, $[\text{Ir}(\text{Bpin})_3(\text{bpy})]$, (2) is the active catalyst. The C–H bond is activated as a result of oxidative addition to the iridium(III) complex, with the formation of a seven-coordinate iridium(V) complex (3), which then undergoes reductive elimination to form 4.

Bis(pinacolato)diboron (when present in excess) readily oxidatively adds to 4, and the subsequent reductive elimination

Scheme 100. Mechanism of the Ir-Catalyzed Dehydrogenative Borylation of Arene C–H Bonds with B₂pin₂. Adapted with Permission from Ref 264. Copyright 2005 American Chemical Society



of HBpin regenerates complex **2**. Results of DFT calculations confirmed the proposed mechanism, in particular the potential oxidative addition of the C_{aryl}–H bond to the iridium(III) complex with formation of an iridium(V) complex (**3**), and the pathway from the [$\{\text{IrCl}(\text{cod})\}_2$] precursor to the active complex (**2**).²⁶⁵ Complex **1**, which is an olefin-stabilized catalyst in the process, has been synthesized and characterized by spectroscopic and X-ray diffraction methods.²⁵⁹ Complex **1** has also been used in kinetic studies whose results, together with those of DFT calculations, have proved that the reaction rate is determined by the oxidative addition of arene and the reductive elimination of arylborane. The heteroarene borylation reaction proceeds according to a similar mechanism. However, heteroarenes could be associated with a catalyst and their binding strength determines the resting state.²⁶⁶

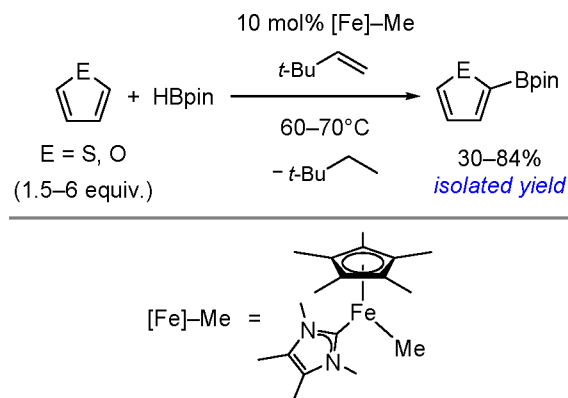
The selectivity of undirected arene C–H borylation is determined by steric effects; that is, borylation occurs at the least sterically crowded position. In contrast, the regioselectivity of heteroarene borylation is controlled mainly by electronic effects.²²⁸ Regioselectivity of C–H functionalization remains a challenge in synthetic chemistry. A number of procedures for the selective functionalization of arenes in the *ortho*-position have been described. The use of directing groups in C–H borylation has recently been summarized.^{225,267} Meta and para C–H borylation remains more challenging.^{268,269} Palladium complexes have been used in the directing group-assisted *ortho*-borylation of acetanilides, *N*-arylanilides, 2-(thiomethyl)phenyl, and 2-pyridyl ferrocenyl rings.

Ruthenium catalysts have been used in the directing group-assisted *ortho*-selective borylation of arenes. N-Donor groups, that is, pyridyl,^{270,271} pyrazolyl,²⁷² and imine groups,²⁷³ were most frequently used. In addition, the Ru-catalyzed directed *ortho*-borylation of arylphosphines,²⁷⁴ arylphosphinites and phosphites,²⁷⁵ and arylimides²⁷⁶ was described. Moreover, Murata and co-workers reported undirected borylation of

arenes with pinacolborane in the presence of a ruthenium complex prepared *in situ* from [$\{\text{RuCl}_2(\text{p-cymene})\}_2$] and TpMe₂K (TpMe₂ = hydrotris(3,5-dimethylpyrazolyl)-borate).²⁷⁷

The first iron-catalyzed C–H borylation of heteroarenes with HBpin was reported in 2010 (Scheme 101).²⁷⁸ A half-sandwich iron *N*-heterocyclic carbene (NHC) complex was found to be catalytically active in the C–H bond borylation of furans and thiophenes with pinacolborane.

Scheme 101. Iron-Catalyzed Dehydrogenative Borylation of Heteroarenes in the Presence of Pinacolborane, with 3,3-Dimethylbut-1-ene Acting as a Hydrogen Acceptor

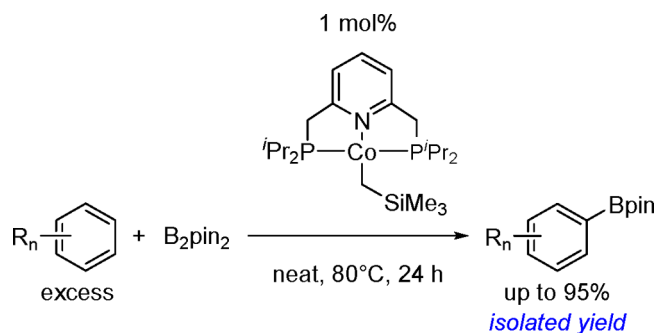


[FeMe₂(dmpe)₂] used under UV irradiation (350 nm) was the first iron-based catalyst of arene borylation.²⁷⁹ Various substituted arenes can undergo undirected borylation at ambient temperatures with isolated yields of 25–73%. The [Fe(H)(Bpin)(dmpe)₂] hydrido(boryl)iron complex has been isolated and shown to be a competent catalyst of the process. FeBr₃ has been found to catalyze the directed *ortho*-borylation of pyridylarenes with a 9-borabicyclo[3.3.1]nonane dimer (9-BBN dimer).²⁸⁰ Borylated products were obtained in 50%–74% yield with good functional group tolerance. A plausible mechanism operating via the Lewis acid–base interaction of 2-phenylpyridines **1** and 9-BBN and iron-catalyzed C–H bond activation has been proposed.

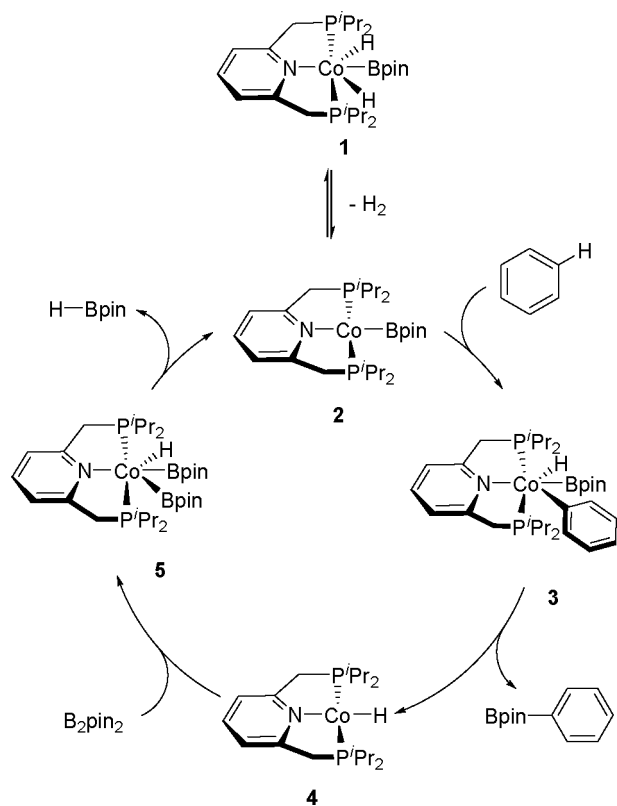
Mankad, Keith and co-workers have elucidated the mechanism of the photochemical C–H borylation in the presence of heterobimetallic Cu–Fe catalysts.²⁸¹ A Ni-based catalytic system ([Ni(cod)₂]/[ICyH]⁺Cl[−]/NaO(*t*-Bu)) (ICy = 1,3-dicyclohexylimidazol-2-ylidene) catalyzes the borylation of arenes and indoles with HBpin at 100 °C.²⁸² Preliminary investigation of the reaction mechanism suggests that heterogeneous nickel species are likely to be the catalytically active forms.

PNP-pincer cobalt(I) complexes developed by Milstein have been found to be active in the catalytic borylation of aryl C–H bonds. Chirik group reported the high catalytic activity of these complexes in the borylation of variously substituted arenes and heteroarenes with HBpin or B₂pin₂ (Scheme 102).²⁸³

As with other undirected functionalization reactions, regioselectivity depends on the arene substitution pattern. In subsequent papers,^{284–286} the catalytic studies were supplemented with mechanistic research on the isolation of catalytic intermediates, stoichiometric experiments, and kinetic measurements. On the basis of the results, a mechanism of arene borylation in the presence of a cobalt bis(phosphine)pyridine

Scheme 102. Undirected Arene Borylation with B₂pin₂ Catalyzed by a Cobalt–PNP–Pincer Complex


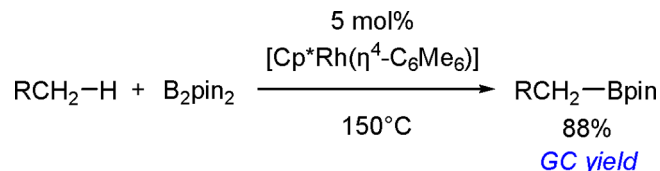
pincer complex was proposed. Borylation of the benzene C–H bond with B₂pin₂ catalyzed by cobalt–pincer complexes was also included in DFT calculations.²⁸⁶ The suggested mechanism (Scheme 103) involved three distinct steps:

Scheme 103. Mechanism of the Co-Catalyzed Dehydrogenative Borylation of Arenes with B₂pin₂²⁸⁶


oxidative addition of C₆H₆, reductive elimination of PhBpin, and regeneration of the catalytically active Co(I)–boronate complex. The *trans*-[(PNP)CoH₂(Bpin)] complex was experimentally observed as the resting state in the borylation of five-membered ring heteroarenes. The active catalyst of this complex can be generated by reductive dihydrogen elimination, preceded by the rearrangement of the complex into a *cis*-isomer. A boronate complex is proposed as the active catalyst (2). Oxidative addition of the benzene C–H bond to 2 forms a six-coordinate cobalt(III) complex (3) which subsequently undergoes reductive elimination of PhBpin (4). Finally, the sequence of the oxidative addition of B₂pin₂ and

the reductive elimination of HBpin results in the regeneration of the active species (2).²⁸⁶

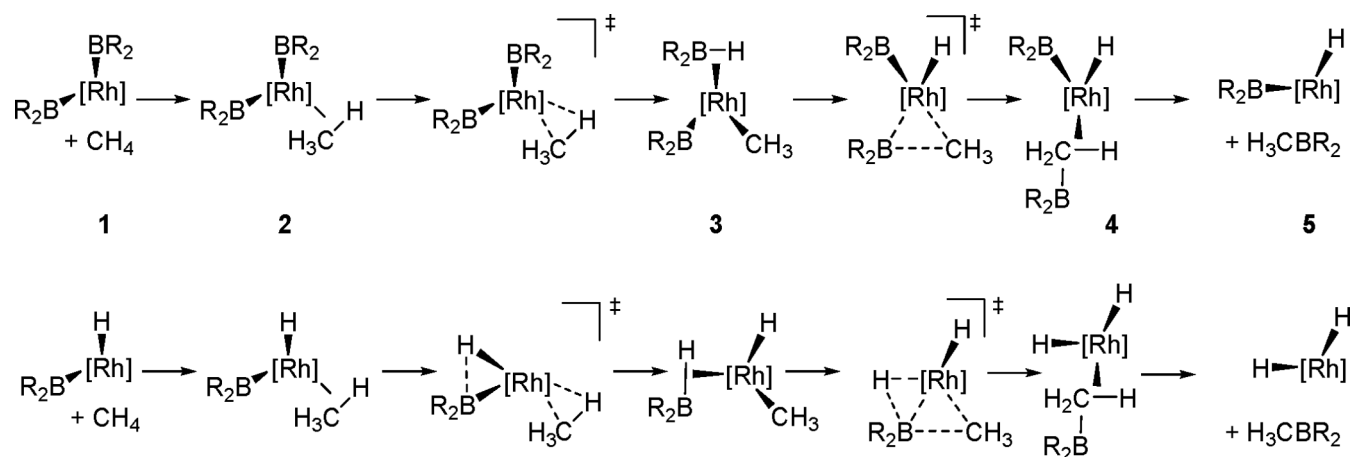
3.1.4. Dehydrogenative Borylation of C(sp³)–H Bonds. Activation and functionalization of the C(sp³)–H bond, especially a site-selective process, remains a challenge in catalysis.²⁸⁷ In 1999, the Hartwig group reported the catalytic functionalization of alkanes at primary C–H bonds in the presence of a rhenium complex [Cp*Re(CO)₃] under photochemical activation²⁸⁸ and the first regioselective catalytic borylation of linear alkanes under thermal conditions (Scheme 104).²⁴⁹

Scheme 104. Dehydrogenative Borylation of Linear Alkanes


Selective borylation of the least congested terminal methyl groups of linear and branched alkanes, alkyl ethers, linear and cyclic tertiary amines, and partially fluorinated alkanes with bis(pinacolato)diboron or pinacolborane has been achieved in the presence of [Cp*Rh(C₂H₄)₂] and [Cp*Rh(η⁴-C₆Me₆)]. Other rhodium complexes, such as [Cp*Rh(η⁴-C₆Me₆)], [Cp*Rh(H)₂(SiEt₃)₂], and [Cp*Rh(C₂H₃SiMe₃)₂], also showed catalytic activity in the borylation of octane with B₂pin₂. In contrast, the tested iridium complexes, [Cp*IrH₄] and [Cp*Ir(C₂H₄)₂], showed much lower catalytic activity. [Cp*Rh(η⁴-C₆Me₆)] gave the highest yield of octane borylation of 88% (Scheme 109). According to the proposed reaction mechanism, the catalytically active species [Cp*Rh-(H)_x(Bpin)_{4-x}] was generated by the dissociation of hexamethylbenzene and the addition of a combination of HBpin and B₂pin₂. It was possible to isolate [Cp*Rh-(H)₂(Bpin)₂] from the reaction of the starting [Cp*Rh(η⁴-C₆Me₆)] with HBpin under photochemical conditions. Moreover, [Cp*Rh(H)(Bpin)₃] was isolated from the reaction of [Cp*Rh(H)₂(Bpin)₂] with HBpin. Both complexes reacted with octane to yield octylBpin. The yields and reaction rates imply that [Cp*Rh(H)₂(Bpin)₂] and [Cp*Rh(H)(Bpin)₃] are chemically and kinetically competent to be intermediates in the borylation of alkanes. Energetic profiles of methane borylation with diboron bispinacolate have been calculated by DFT. In line with the DFT calculations, the dissociation of HBpin from complexes 2 and 3 is faster than the dissociation of H₂ or B₂pin₂ from these complexes. On the basis of the calculation results, the mechanism of activation of the methane C–H bond in the presence of boryl–rhodium complexes as well as the mechanism of the reductive elimination of methylborane were proposed (Scheme 105).²⁸⁹

The reaction of a diborate complex (1) with methane occurs via the coordination of an alkane to the boryl complex to form a σ-alkane complex (2), followed by its transformation into a σ-pinacolborane complex (3). Subsequently, the methyl group undergoes bond formation with the second boryl group to form MeBpin. An analogous reaction of methane with pinacolborane proceeds via a similar mechanism involving formation of the σ-alkane complex and breaking of the C(sp³)–H bond with the simultaneous formation of the σ-borane complex. Product formation proceeds through a

Scheme 105. Mechanism of C–H Activation and C–B Formation according to the Results of DFT Calculations for $[\text{CpRhH}(\text{BR}_2)]$ (a) and $[\text{CpRh}(\text{BR}_2)_2]$ (b) Complexes ($\text{BR}_2 = 1,3\text{-Dioxaborolane}$). Reprinted with Permission from Ref 289. Copyright 2005 American Chemical Society



multicenter transition state. DFT calculations suggest that the processes of C–H bond cleavage and B–C bond formation run via a metal-assisted σ -bond metathesis mechanism. The calculations have shown a specific role of boron in the activation of C–H bonds in alkanes and arenes. According to Hartwig and Hall,²⁸⁹ the presence of an unoccupied p orbital in boron and the interaction of the boryl ligand with the hydride located *cis* to it is crucial for the activation of the C–H bond in alkenes. The thermodynamic driving force of the reaction is the formation of the B–C bond, while the unoccupied orbital in boron reduces the energy barrier for C–H bond activation and formation of the borylated product.

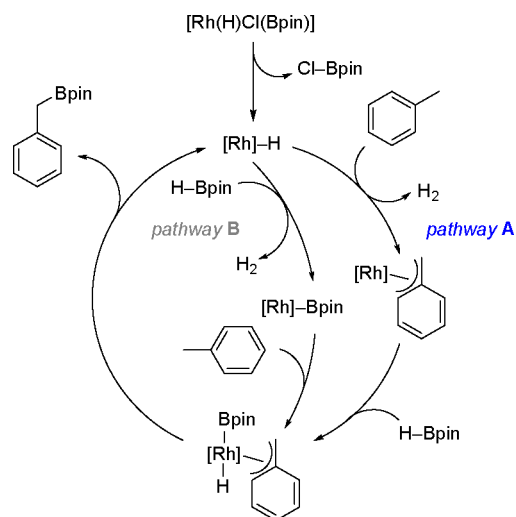
Efficient borylation of the benzylic C–H bond has first been reported by Marder and co-workers.²⁹⁰ In the presence of $[\text{RhCl}(\text{P}(i\text{-Pr})_3)_2(\text{N}_2)]$, toluene, *p*-xylene, and mesitylene have been shown to react with HBpin. Benzylic monoborylation was accompanied by diboration and aromatic borylation. Highly selective borylation at the benzylic position compared with the aryl position was observed in the reaction with *para*-xylene. On the basis of the investigation of stoichiometric reactions, a mechanism of the process was proposed, assuming the $[\text{Rh}(\text{H})\{\text{P}(i\text{-Pr})_3\}_2]$ rhodium hydride as the active catalyst. Scheme 106 presents two proposed mechanistic pathways.

DFT calculations by Lin and Marder for a slightly simplified model indicate that the activation of the benzylic C–H bond is the rate-limiting step and that it occurs more favorably in the coordination sphere of $[\text{L}_2\text{Rh}(\text{H})]$ (pathway A, Scheme 106).²⁹¹ Secondary benzylic C–H bonds were selectively borylated in the presence of a hydrosilyl directing group and an iridium complex (Scheme 107).²⁹²

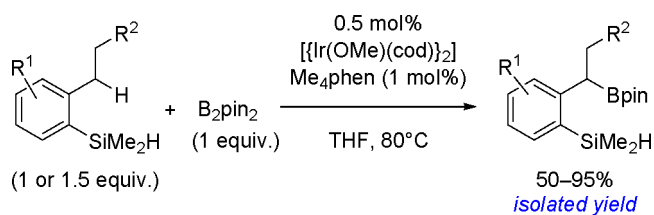
Hartwig and co-workers reported selective borylation of the benzylic C–H bonds of methylarenes with Et_3SiBpin as the borylating agent in the presence of an iridium complex bearing an optimized phenanthroline ligand (Scheme 108).²⁹³ The reaction suffered from competitive arene C–H borylation. However, optimization of the phenanthroline ligand achieved high chemoselectivity because of the high sensitivity of aryl C–H borylation to the electronic properties of the catalyst. Reactions of toluene and *meta*-substituted methylarenes resulted in the formation of benzylic boronates with moderate yields and good to excellent selectivity.

The resting state of the $[\text{L}(\text{Ir}(\text{Bpin})_2(\text{SiEt}_3))]$ catalyst (1) has been identified, isolated, and characterized (Scheme 110) and

Scheme 106. Mechanism for the Rh-Catalyzed Borylation of the Benzylic C–H Bond with HBpin²⁹⁰

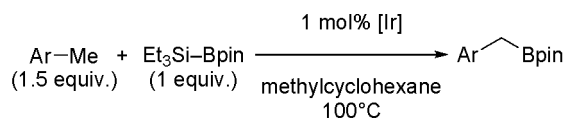


Scheme 107. Silyl-Directed Dehydrogenative Borylation of Secondary Benzylic C–H Bonds

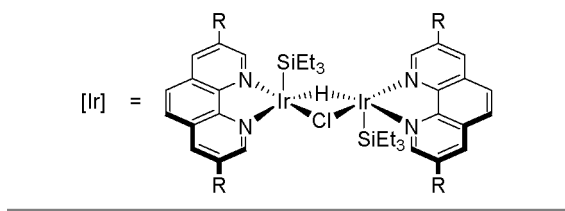


has been found to be kinetically competent to act as an intermediate in the reaction. The iridium–diborylsilyl complex has been demonstrated to be more electron-deficient than the trisboryl complexes used for C–H borylation. It has been shown that a reduction in the electron density in the metal leads to a decrease in the borylation rate of the aryl C–H bond that is much greater than the decrease in the borylation rate at the benzylic position, which enhances reaction selectivity. On the basis of the isolation of the resting state of the catalyst, analysis of stoichiometric reactions, kinetic studies, and DFT calculations, a reaction mechanism has been proposed

Scheme 108. Undirected Dehydrogenative Borylation of Primary Benzylic C–H Bonds

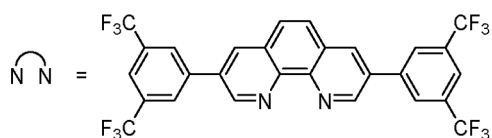
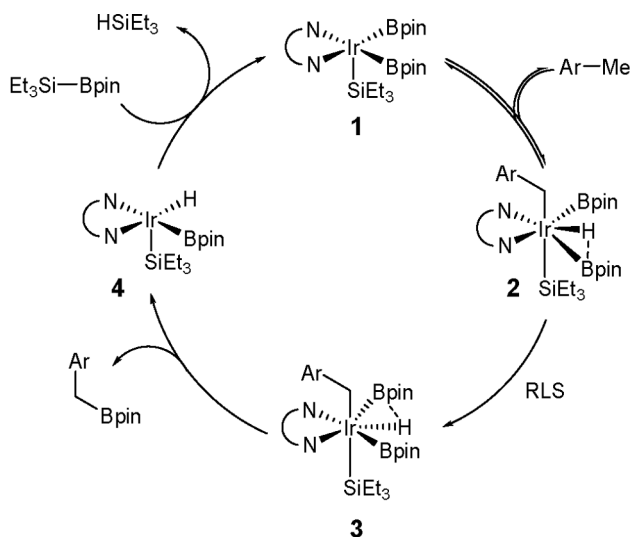


Ar = arene, heteroarene
R = C₆H₃(CF₃)₂-3,5



involving reversible oxidative addition of the benzylic C–H bond to [Lr(Bpin)₂(SiEt₃)], rate-limiting isomerization, and reductive elimination of the benzylic boronate ester (Scheme 109). The reaction of **4** with Et₃SiBpin regenerates the catalyst and HSiEt₃ forms.

Scheme 109. Mechanism of the Ir-Catalyzed Borylation of Benzylic C(sp³)–H Bonds with Et₃SiBpin. Adapted with Permission from Ref 293. Copyright 2015 American Chemical Society



Mono- and polyborylation of benzylic C–H bond(s) with B₂pin₂ has also been reported in the presence of cobalt–diamine complexes by the Chirik group.²⁹⁴

3.2. Dehydrogenative Silylation of C–H Bonds

Direct silylation of C–H bonds is a well-explored class of metal-catalyzed C–H bond functionalizations. Efficient procedures have been developed for the silylation of C–H bonds in alkanes, alkenes, arenes, and alkynes. The reaction

permits the synthesis of useful building blocks with a wide range of applications in organic synthesis. The current knowledge of the reaction has been presented in several review papers.^{227,295–300}

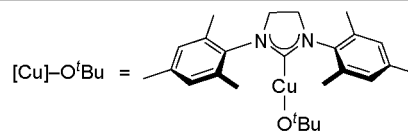
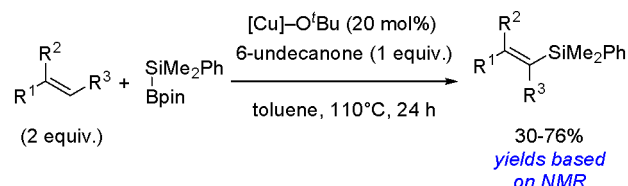
3.2.1. Dehydrogenative Silylation of C(sp)–H Bonds.

Alkynylsilanes are important structural motifs in organic chemistry. The silyl group not only acts as a protecting group for the reactive C(sp)–H bond but also modifies the steric and electronic properties of the triple bond. Alkynylsilanes are convenient reagents for the formation of carbon–carbon and carbon–heteroatom bonds.³⁰¹ The first selective C(sp)–H silylation of terminal alkynes with hydrosilanes was reported by Voronkov in 1980, using a combination of H₂PtCl₆·6H₂O and LiI (100 equiv) as a catalytic system.^{302,303} The literature provides a few other examples of the dehydrogenative silylation of acetylenes with trisubstituted silanes (HSiR₃) catalyzed by TM complexes. Although the mechanisms of ethynylsilane formation have been proposed (e.g., ref 304), no detailed mechanistic studies have been carried out so far.

3.2.2. Dehydrogenative Silylation of Olefinic C(sp²)–H Bonds.

Dehydrogenative silylation with HSiR₃ as the silylating agent was discussed in Section 1.1.1. Metal-catalyzed silylation of olefinic C(sp²)–H bonds with disilanes is in the early stage of development, and as yet no mechanism has been proposed. Recently, Mankand has described dehydrogenative silylation in the presence of a *N*-heterocyclic carbene–copper complex and commercially available PhMe₂SiBpin as the silylating agent (Scheme 110).²⁴⁵

Scheme 110. Dehydrogenative Silylation of Olefinic C(sp²)–H Bonds with PhMe₂SiBpin Catalyzed by the NHC Copper Complex

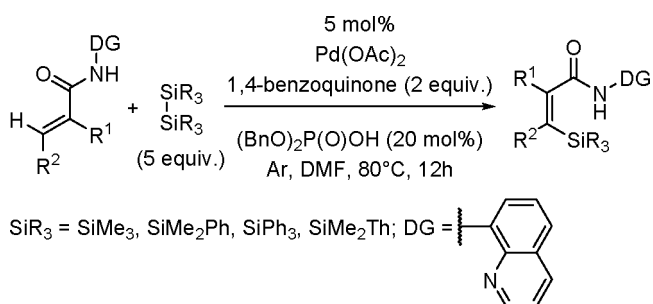


Another publication described the activity of a palladium-based catalyst in the selective synthesis of (*Z*)-vinylsilanes via olefinic C–H silylation with disilanes (Scheme 111).³⁰⁵

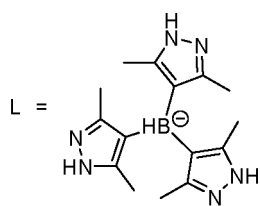
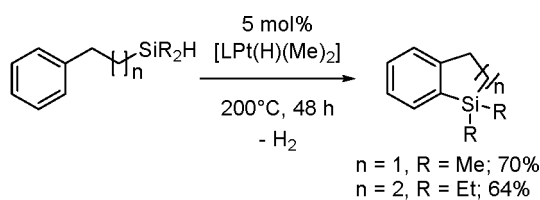
3.2.3. Dehydrogenative Silylation of Arene C(sp²)–H Bonds.

The silylation of aryl C–H bonds is a suitable method for the synthesis of arylsilanes that are valuable synthetic intermediates. The known examples of the reaction can be divided into three classes: (i) intramolecular, (ii) directed intermolecular, and (iii) undirected intermolecular silylations of aryl C–H bonds.

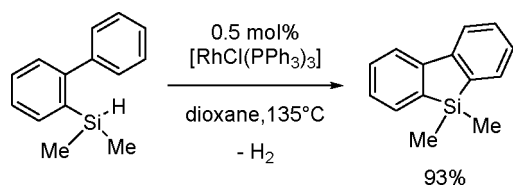
Intramolecular arene silylation leads to the formation of silacyclic compounds and it is catalyzed mainly by Rh and Ir complexes but also by Pt and Ru complexes. In 2005, Hartwig group reported the first examples of the intramolecular dehydrogenative coupling of silanes, leading to the efficient formation of both five- and six-membered organosilicon

Scheme 111. Directed Dehydrogenative Silylation of Olefins

products in the presence of a platinum complex (Scheme 112).³⁰⁶

Scheme 112. Intramolecular Silylation of Arenes

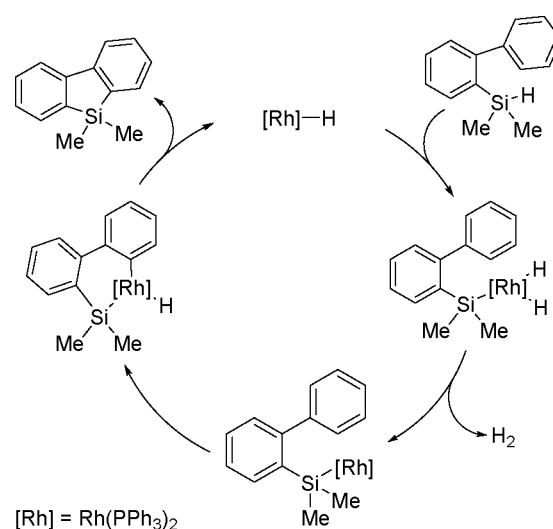
Kuninobu, Takai, and co-workers demonstrated the synthesis of silafluorene derivatives (Scheme 113) via the

Scheme 113. Intramolecular Silylation of 2-(Silyl)-substituted Biarene in the Presence of Wilkinson's Catalyst

intramolecular silylation of [1,1'-biphenyl]-2-yl-dimethylsilanes in the presence of Wilkinson's catalyst.³⁰⁷ The presence of electron-withdrawing substituents in the aromatic ring achieved a highly efficient reaction without the need for a hydrogen acceptor in the reaction system.

The reaction tolerates halides, methoxy and trifluoromethyl groups, and thiophene rings. Further research on this reaction permitted optimization of the catalytic system ([{RhCl(cod)}₂]/6 PPh₃) and use of milder reaction conditions.³⁰⁸

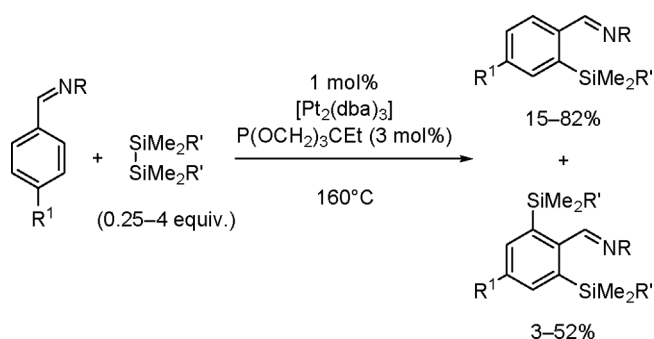
In the presence of an analogous iridium complex, a much lower yield was obtained. On the basis of a combined experimental and computational mechanistic study, Murai and Takai proposed the reaction mechanism (Scheme 114). The authors demonstrated that intramolecular dehydrogenative silylation can proceed efficiently, even without hydrogen acceptors.³⁰⁸ The reaction in the presence of a hydrogen acceptor (3,3-

Scheme 114. Mechanism of the Rh-Catalyzed Intramolecular Dehydrogenative Silylation of Arene C–H Bonds³⁰⁸

dimethyl-1-butene) was proved by calculations to increase the free enthalpy of the process.

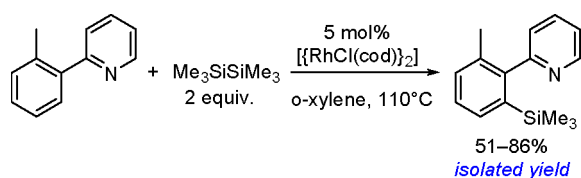
The mechanism is essentially the same as that proposed by Hartwig and Cheng for undirected intermolecular silylation.³⁰⁹

Directed intermolecular silylation of the arene C(sp²)–H bond is assisted by a directing group and occurs with high regioselectivity, generally in the *ortho* position to the directing group. The first directed silylation of aryl C–H bonds catalyzed by [Pt₂(dba)₃] accompanied by P(OCH₂)₃CET has been reported by Tanaka who described the *ortho*-silylation of benzyldeneamines (Scheme 115).³¹⁰

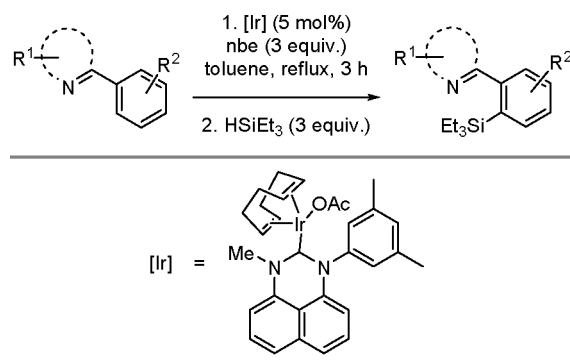
Scheme 115. Directed Intermolecular Silylation of Arenes with Disilanes

A great contribution has been made by Murai who described the ruthenium-catalyzed directed silylation of five-membered ring heteroarenes with vinylsilanes, followed by silylation of the aryl C–H bond with tertiary silanes (HSiR₃), applicable to a great variety of directing groups.^{311,312} Tobisu and Chatani designed the Rh-catalyzed, pyridine-directed *ortho*-silylation of aryl C–H bonds with hexamethyldisilane using a pyridyl directing group (Scheme 116).³¹³

Further progress was made by Suginoe,³¹⁴ Murata,³¹⁵ as well as Kuninobu and Kanai.³¹⁶ Efficient silylation of heteroarenes was reported by Mashima and co-workers.³¹⁷ The reaction occurred in the presence of an iridium complex, [Ir(NHC)(OAc)(cod)], bearing a hemilabile carbene ligand.

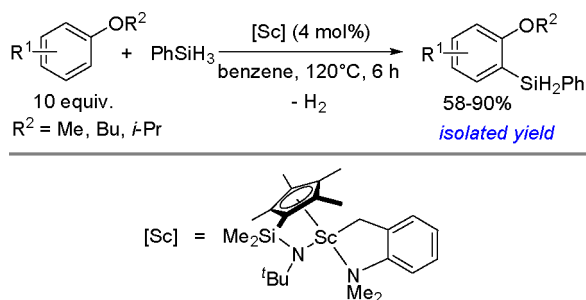
Scheme 116. Rhodium-Catalyzed Directed Intermolecular Silylation of Arenes with Disilanes


By using a 3-fold molar excess of triethylsilane and norbornene as a hydrogen acceptor (Scheme 117), a mono-*ortho*-silylation

Scheme 117. Iridium-Catalyzed Directed Intermolecular Silylation of Arenes with Tertiary Silanes


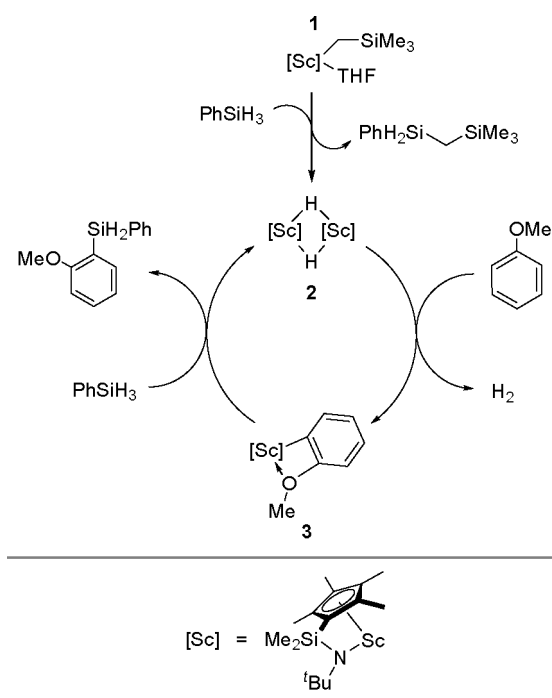
product was obtained in good to excellent yields. In addition, excellent research has been conducted to determine the mechanism of the Ir-based directed silylation of 2-phenylpyridine in the presence of hemilabile ligands.

Half-sandwich scandium σ -alkyl complexes have been reported to catalyze the *ortho*-selective C–H silylation of alkoxy-substituted benzene derivatives with a primary silane (H_3SiPh) without the need for a hydrogen acceptor (Scheme 118).³¹⁸

Scheme 118. Alkoxy-Directed *ortho*-Silylation of Arenes in the Presence of a Scandium Complex


An efficient course of the reaction is observed with PhSiH_3 as the silylating agent. The reaction tolerates functional groups such as Cl, Br, I, SMe, and NMe_2 in the aromatic ring. The proposed mechanism of the Sc-catalyzed directed silylation of anisole is shown in Scheme 119.³¹⁸

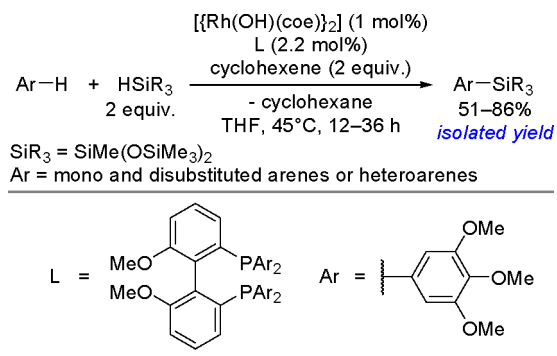
The precatalyst (1) undergoes σ -bond metathesis with H_3SiPh to generate a dimeric Sc(II) complex (2) and $\text{PhSiH}_2\text{CH}_2\text{SiMe}_3$. Complex 2 then undergoes σ -bond metathesis with the arene substrate to form 3. Complex 3 undergoes σ -bond metathesis with H_3SiPh to generate the

Scheme 119. Mechanism of the Sc-Catalyzed Directed Dehydrogenative Silylation of Arene C–H Bonds with PhSiH_3 ³¹⁸


silylarene product and regenerate the Sc dimer (2). The key intermediates (2 and 3) were synthesized independently, characterized by X-ray diffraction, and tested for their kinetic relevance. Nuncatalytic reactions of 2 with anisole yielded 3, accompanied by the release of hydrogen. The reaction of 3 with H_3SiPh at 40 °C in the absence of an arene afforded complex 2 in a quantitative yield. Additional experiments suggested that the rate-limiting step was substrate coordination to the metal center and not the cleavage of the C–H bond.

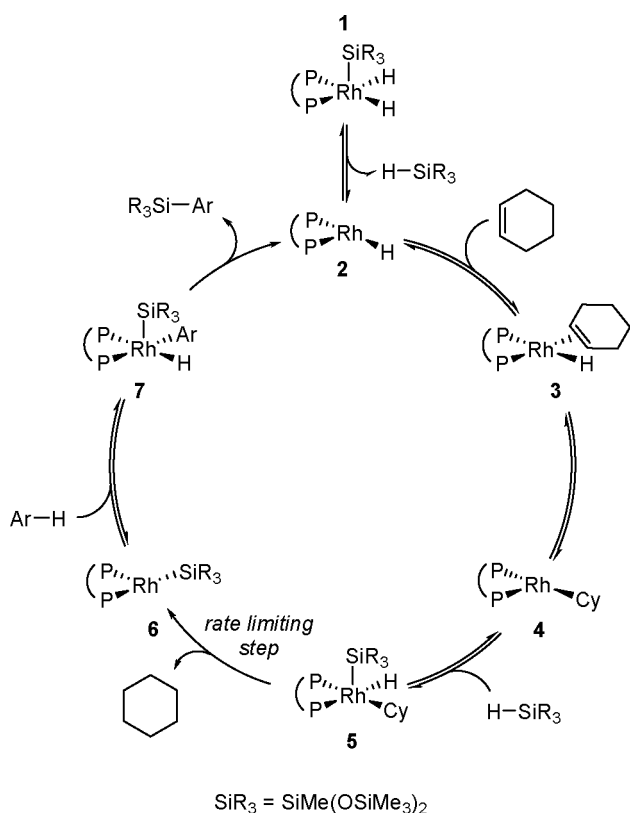
Undirected intermolecular silylation of the aryl $\text{C}(\text{sp}^2)$ –H bond started with the seminal work of Curtis who reported the silylation of benzene (used as a solvent) in the presence of Vaska's complex, $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$.³¹⁹ Significant progress was made by Ishiyama and Miyaura who described effective silylation of arenes using $t\text{-BuF}_2\text{SiSiF}_2t\text{-Bu}$ in the presence of $[\{\text{Ir}(\text{OMe})(\text{cod})\}_2]/\text{dtbpy}$ ($\text{dtbpy} = 4,4'$ -di-*tert*-butyl)-2,2'-bipyridine)^{320,321} and arene silylation with 1-hydrosilatane in the presence of $[\{\text{Ir}(\text{OMe})(\text{cod})\}_2]/\text{dmphen}$ ($\text{dmphen} = 2,9$ -dimethyl-1,10-phenanthroline).³²² Hartwig, who reported the activity of $[\text{Tp}^{\text{Me}_2}\text{PtRR}'\text{H}]$ ($\text{Tp}^{\text{Me}_2} = \text{hydridotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$; $\text{R}, \text{R}' = \text{H}, \text{Me}, \text{or Ph}$) in the silylation of benzene with triethylsilane,²⁹⁶ and Murata, who described the activity of $\text{PtCl}_2/\text{Tp}^{\text{Me}_2}\text{K}$ in the C–H silylation of arenes with $\text{HSiMe}(\text{OSiMe}_3)_2$,³²³ greatly contributed to the field. Unfortunately, all these methods suffered from the need for the high excess of the arene reacting partner and harsh reaction conditions. Currently, the most commonly used rhodium-based catalytic system for arene C–H silylation is the one proposed by Hartwig (Scheme 120).³²⁴ The system enables efficient silylation of the arene as the limiting reagent under mild conditions. Moreover, the reaction exhibits high sterically derived regioselectivity and tolerates several functional groups, such as halides, alkyl, alkoxy, CF_3 , and secondary amine and amide.

Scheme 120. Undirected Dehydrogenative Silylation of Arenes with Tertiary Silanes



The mechanism of the process was proposed on the basis of kinetic studies, deuterium-labeling experiments, and stoichiometric reactions of isolated complexes.³⁰⁹ The proposed mechanism of the Rh-catalyzed intermolecular silylation of aryl C–H bonds shown in Scheme 121 comprises two

Scheme 121. Mechanism of the Rh-Catalyzed Silylation of Aryl C–H Bonds in the Presence of HSiR₃ with Cyclohexene as a Hydrogen Acceptor. Adapted with Permission from Ref 309. Copyright 2014 American Chemical Society

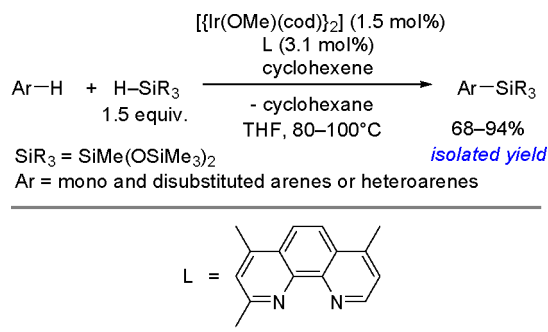


processes: hydrogenation of the hydrogen acceptor (cyclohexene) and arene C–H silylation. The presence of the hydrogen acceptor is necessary for the reaction to proceed. The identified rate-limiting step of the mechanism is the reductive elimination of cyclohexane from an alkyrhodium(III)–hydride complex (5). Moreover, it has been found that the oxidative addition step is reversible. The phosphine-ligated

rhodium(III)–silyldihydride complex (1), postulated to be the resting state of the catalyst, has been synthesized and characterized by X-ray crystallography.

The $[\{\text{Ir}(\text{cod})(\text{OMe})_2\}_2]$ iridium complex, with an excess phenanthroline-based ligand enables efficient undirected silylation of arenes with $\text{HSiMe(OSiMe}_3)_2$ (Scheme 122).³²⁵ The ligand structure has been found to strongly influence catalytic activity. The highest yields were obtained using 2,4,7-trimethyl-1,10-phenanthroline.

Scheme 122. Iridium-Catalyzed Undirected Silylation of Arenes in the Presence of HSiMe(OSiMe₃)₂ with Cyclohexene Acting as a Hydrogen Acceptor



The reaction occurs with arene as the limiting reagent and is highly regioselective. The catalyst enables efficient silylation of the C–H bond of both electron-rich and electron-poor arenes and heteroarenes. The use of 2,9-dimethylphenanthroline provides good yields (66%–94%) in the silylation of more challenging electron-rich arenes.³²⁶ Through a combination of experimental and computational studies, the catalytic cycle for the iridium-catalyzed silylation of aromatic C–H bonds was proposed (Scheme 123).³²⁷ The mechanisms involve sequences of oxidative addition of aromatic C–H bonds and reductive elimination of arylsilanes. The results indicate that the reactions involving electron-rich and electron-poor C–H bonds may be described by the same mechanistic scheme, but they differ in the rate-limiting step and the resting state of the catalyst.

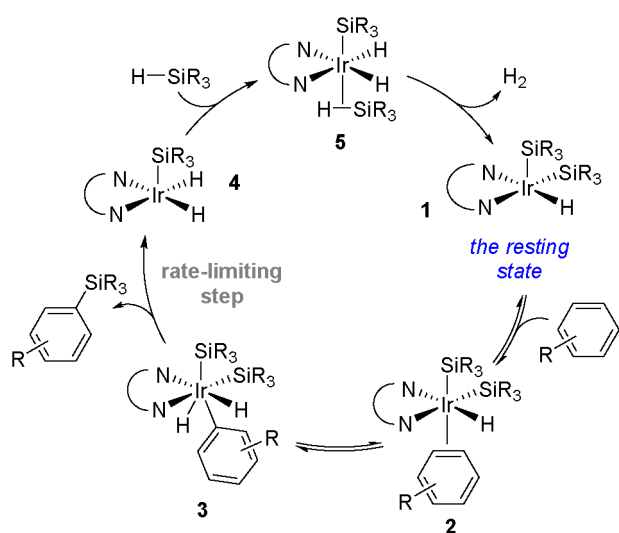
Another attractive iridium-based catalytic system is $[\text{Ir}(\text{H})_2(\text{IPr})(\text{py})_3][\text{BF}_4]$, containing the *N*-heterocyclic carbene ligand, described by Iglesias, Oro, and co-workers (Scheme 124).³²⁸ The reaction enables both directed and undirected silylation of C–H bonds with the arene as the limiting reagent. However, most of the research on the reaction mechanism concerns the silylation of arylpyridines. A variety of hydrosilanes, including Et_3SiH , Ph_2MeSiH , PhMe_2SiH , Ph_3SiH , and $(\text{EtO})_3\text{SiH}$, can be used here as reacting partners.

DFT calculations have been conducted for a system consisting of an iridium–carbene complex (1) (Scheme 124), 2-phenylpyridine, HSiMe_3 as a model hydrosilane, and norbornene as the hydrogen acceptor. Scheme 125 sums up the results of the calculations which indicate that complex 6 is the resting state of the catalyst. Transfer of the silyl group from the coordinated silane to phenylpyridine has been proposed to be the rate-limiting step, and it proceeds via σ -metathesis. The energy profile calculated for a system without a hydrogen acceptor shows a higher energy barrier.

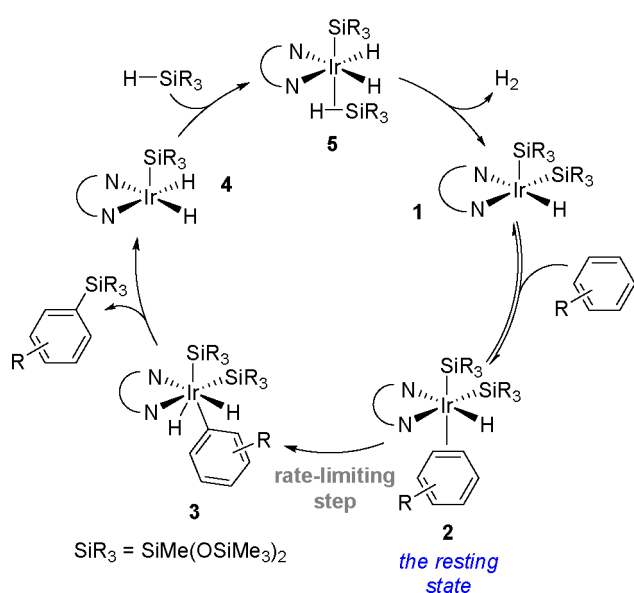
The cyclometalated complexes corresponding to the calculated resting state of the catalyst have been synthesized,

Scheme 123. Catalytic Cycles for the Silylation of Electron-Poor (a) and Electron-Rich (b) Aromatic C–H Bonds. Adapted with Permission from Ref 327. Copyright 2020 American Chemical Society

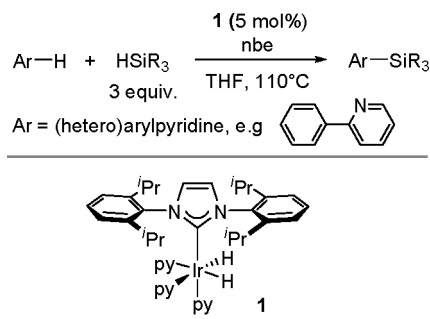
a) silylation of electron-poor aromatic C–H bonds



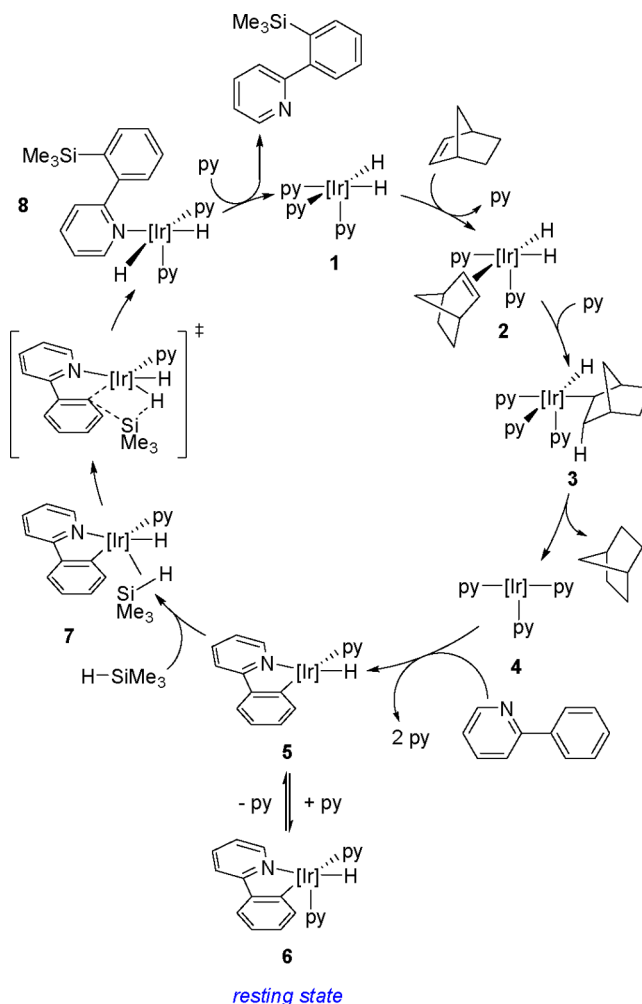
b) silylation of electron-rich aromatic C–H bonds



Scheme 124. Iridium-Catalyzed Dehydrogenative Silylation of Arenes with Tertiary Silanes



Scheme 125. Mechanism for the Ir-Catalyzed Directed Dehydrogenative Silylation of Arene C–H Bonds with Norbornene as a Hydrogen Acceptor



characterized, and demonstrated to be catalytically competent in arene C–H silylation.³²⁸

3.2.4. Dehydrogenative Silylation of C(sp³)–H Bonds.

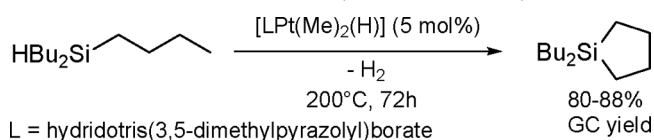
Silylation of C(sp³)–H bonds was originally observed as a side reaction in the studies of other processes.^{329–332} The reaction has recently been described in a comprehensive review.³³³ As for arene silylation, the silylation of alkyl C(sp³)–H bonds can be divided into three classes: (i) intramolecular, (ii) directed intermolecular, and (iii) undirected intermolecular silylation of C(sp³)–H bonds. Complexes of Ru, Rh, Pd, Ir, and Pt have been shown to be active in the functionalization of C(sp³)–H bonds.

Presently, only the intramolecular mode of alkyl C–H silylation has gained importance in organic synthesis. The catalytic activity of Pt, Ir, Rh, and Ru complexes in the intramolecular silylation of C(sp³)–H bonds has been described. Most of the published examples concern reactions of the activated C–H bond, that is, the benzylic C(sp³)–H bond or the one located α to a heteroatom (N, O, Ge, Si). Moreover, in most examples, the presence of a directing group is needed. As dihydrogen is formed in the reaction, an olefin is used as a hydrogen acceptor (usually norbornene) in many reaction systems. Cyclizations can be classified as (i) reactions of an isolated silane substrate and (ii) cyclizations of an *in situ*

generated silane substrate. A silyl group can be incorporated by the silylation of an O–H or N–H bond or by the hydrosilylation of an unsaturated carbon–carbon or carbon–heteroatom bond.

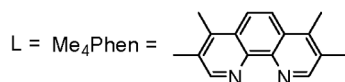
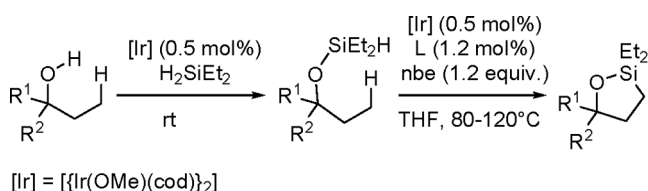
The first example of the intramolecular silylation of a C(sp³)–H bond has been reported by Hartwig. In the presence of a platinum complex, tributylsilane was selectively converted into a 5-membered cyclic organosilane (Scheme 126).³⁰⁶

Scheme 126. Intramolecular Cyclization of Alkylsilanes



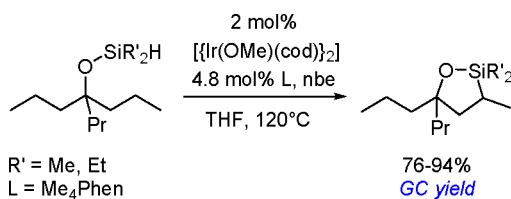
Silylation of the inactivated primary alkyl C–H bond by the *in situ* installation of a silyl group and the subsequent selective intramolecular activation of the primary C–H bond have been proposed by the Hartwig group (Scheme 127).³³⁴

Scheme 127. Sequential OH Silylation and Intramolecular Dehydrogenative Silylation of C(sp³)–H Bonds



Five-membered cyclic silyl ethers can be obtained through the activation of secondary C–H bonds in the presence of iridium complexes (Scheme 128).³³⁵

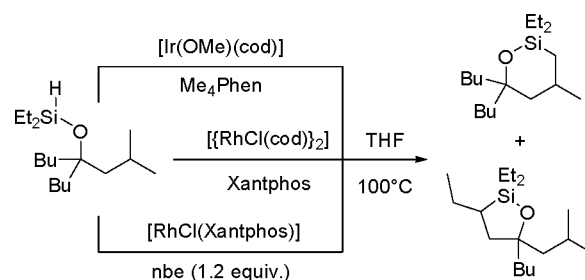
Scheme 128. Intramolecular Dehydrogenative Silylation of Secondary C(sp³)–H Bonds



For the reagents with available C–H bonds at the γ and δ positions, a mixture of products is formed (Scheme 129).³³⁶

In the presence of the [Ir(OMe)(cod)] iridium complex with Me₄Phen, a very high yield (94%) of a mixture of isomers was obtained, with significant prevalence of a five-membered product formed as a result of secondary C(γ)–H activation, which suggests that the size of the formed ring has a greater effect on selectivity than the degree of substitution at the C–H bond. The reaction is also effective in the presence of [RhCl(cod)]₂ used along with an appropriate diphosphine. Selectivity and yield of the reaction depend significantly on the diphosphine used; the highest yield and selectivity of the

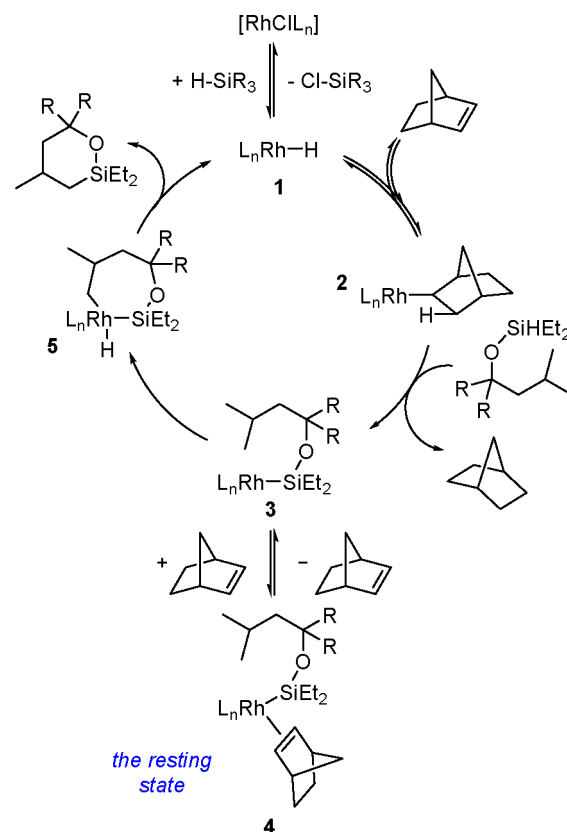
Scheme 129. Intramolecular Silylation of C(sp³)–H Bonds at the γ and δ Positions



C(δ)–H silylation product were obtained for [RhCl(Xantphos)]. In contrast, [RhCl(Segphos)] afforded the same products with prevalent C(γ)–H silylation. Mechanistic studies identified [(Xantphos)Rh(SiR₃)(nbe)] as the resting state of the catalyst. An analogue of the proposed resting state with a modified SiR₃ group was synthesized and characterized by X-ray diffraction studies. The rate-limiting step of the process was demonstrated to be the oxidative addition of the C(δ)–H bond to Rh. The proposed mechanism of the reaction is illustrated in Scheme 130.³³⁶

The active catalyst has been proposed to form via the oxidative addition of a silane to [RhCl(cod)]₂ and the subsequent reductive elimination of chlorosilane. Rhodium(I) hydride (1), formed in the first step of the catalytic cycle,

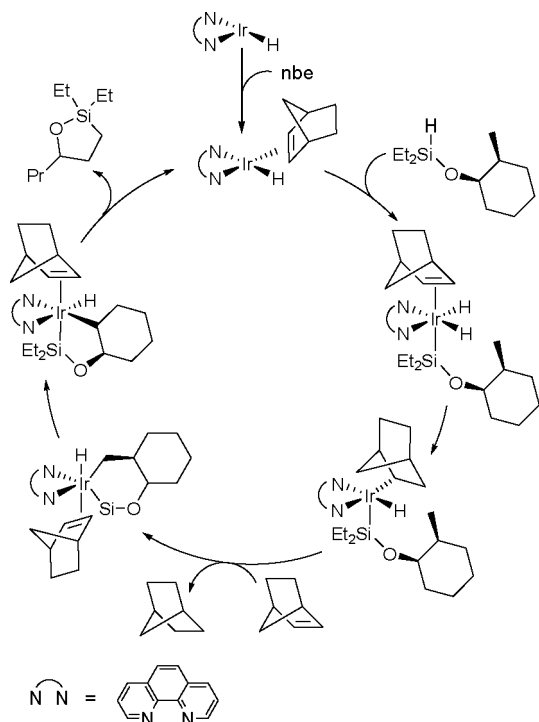
Scheme 130. Mechanism of the Rh-Catalyzed Intramolecular Silylation of Alkyl C–H Bonds, with Norbornene as a Hydrogen Acceptor. Adapted with Permission from Ref 336. Copyright 2018 American Chemical Society



undergoes migratory insertion of norbornene to form **2**. Subsequent oxidative addition of a silyl hydride and reductive elimination of norbornane produces the 14-electron Rh(I) silyl complex (**3**). Association of norbornene to complex **3** produces the resting state (**4**), which arrests the catalytic cycle. Oxidative addition of the C–H bond to the rhodium center in **3** forms the metallacycle (**5**). Finally, reductive elimination of a six-membered cyclic silyl ether leads to the regeneration of the Rh(I) hydride complex (**1**). Kinetic studies show that C–H bond cleavage is irreversible and rate limiting. Computational studies have demonstrated that the selectivity for the silylation of a C(δ)–H bond over a C(γ)–H bond in the presence of the Rh–Xantphos catalyst results from a higher barrier of reductive elimination from the six-membered metallacyclic complex than from the seven-membered complex.

Sunoj examined the Ir-catalyzed γ -functionalization of a primary C(sp^3)–H bond in 2-methyl cyclohexanol using DFT calculations.³³⁷ The [IrH(nbe)(phen)] complex was identified as the active catalyst. The proposed mechanism assumed a catalytic cycle with activities of Ir(I) and Ir(III) complexes (Scheme 131).

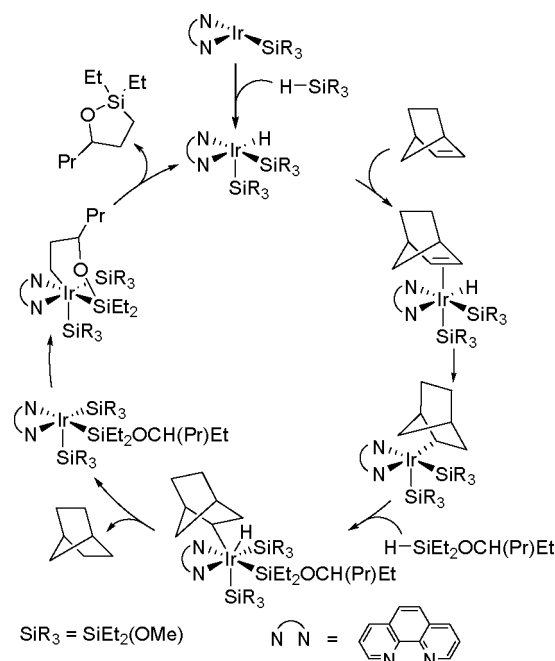
Scheme 131. Intramolecular Silylation of Primary C(sp^3)–H Bonds in 2-(Methyl)cyclohexanol Proposed by Sunoj³³⁷



In contrast, the calculations performed by Li³³⁸ for the reaction presented in Scheme 132 indicate that the Ir(III)/Ir(V) mechanism is more feasible than the one proposed by Sunoj.³³⁷

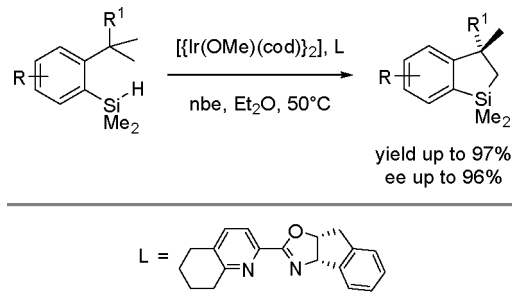
Formation of [Ir(Me₄phen){Si(OR)Et₂}] as the catalyst precursor was postulated to be more probable than the formation of [IrH(Me₄phen)(nbe)] as proposed by Sunoj. The intramolecular oxidative addition of the C(sp^3)–H bond was proposed to occur in the [(Me₄Phen)Ir{SiEt₂(OR)}₃] iridium(III) complex. This step was calculated to be rate limiting.

Scheme 132. Intramolecular Silylation of Primary C(sp^3)–H Bonds in 2-(Methyl)cyclohexanol Proposed by Li³³⁸



The first example of the asymmetric intramolecular silylation of inactivated C(sp^3)–H bonds was reported by Murai, Takai, and co-workers.³³⁹ Hartwig developed a highly enantioselective intramolecular silylation of inactivated C(sp^3)–H bonds under relatively mild reaction conditions (Scheme 133).³⁴⁰ It

Scheme 133. Asymmetric Intramolecular Silylation of Inactivated C(sp^3)–H Bonds

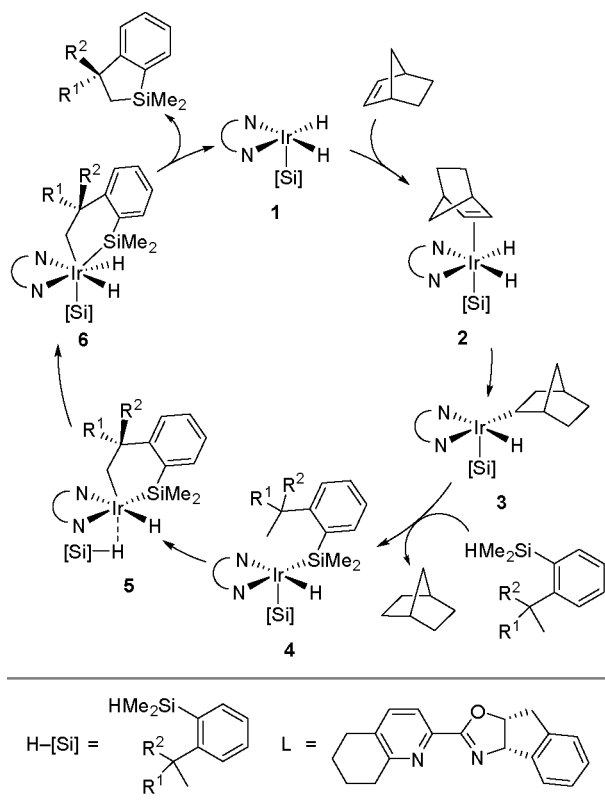


was found that in the presence of a combination of [Ir(OMe)(cod)]₂, a chiral pyridyl oxazoline ligand (L) and norbornene (nbe) as the hydrogen acceptor, dimethylarylsilanes (**1**) underwent selective silylation at one of the two prochiral methyl groups to afford **2** in high yields and with excellent enantioselectivity.

Kinetic studies suggest that C–H bond cleavage is the turnover-limiting step of the catalytic cycle.³³⁵ In 2019, Huang and co-workers presented results of density functional theory calculations for the mechanism of the iridium(I)-catalyzed intramolecular silylation of inactivated C(sp^3)–H bonds, and a reasonable reaction mechanism was proposed with the origin of enantioselectivity explained (Scheme 133).³⁴¹ Dimethylarylsilane was selected as the model substrate in these calculations. Formation of the [Ir(OMe)L(nbe)] complex from [Ir(OMe)(cod)]₂, L and norbornene as the hydrogen acceptor was calculated to be the most exergonic. The

subsequent reactions of the complex with two silane molecules produced the $[\text{IrLH}_2\text{Si}]$ iridium(III) complex (**1**), proposed to be the active catalyst of the reaction. According to the mechanism (Scheme 134), the coordination of nbe to complex

Scheme 134. Mechanism of the Ir-Catalyzed Intramolecular Silylation of Alkyl C–H Bonds, with Norbornene as the Hydrogen Acceptor³⁴¹



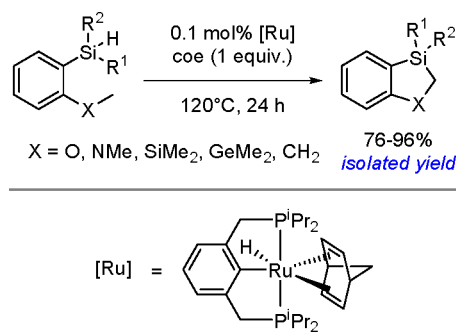
1 produces intermediate **2**. Subsequently, **2** undergoes migratory insertion of a C=C double bond of norbornene into the Ir–H bond. The resultant intermediate (**3**) has been found to interact with silane to give an iridium(III) disilyl hydride species (**4**) and release norbornene. Further steps of the mechanism occur through the Ir(III)/Ir(V) catalytic cycle and involve the oxidative addition of the $\text{C}(\text{sp}^3)\text{-H}$ bond to the metal center and subsequent reductive elimination. Oxidative addition may lead to the formation of two enantiomeric complexes, S-**5** or R-**5**, and consequently to an enantiomeric product. The calculated energy profile shows that $\text{C}(\text{sp}^3)\text{-H}$ oxidative addition constitutes the rate-limiting and enantioselectivity-determining step.

On the basis of the optimized geometric structures of the respective transition states, the origin of enantioselectivity was suggested as a combination of steric and electronic effects.

Finally, Huang reported that a ruthenium–pincer complex was capable of the silylation of activated and inactivated primary $\text{C}(\text{sp}^3)\text{-H}$ bonds to form sila(hetero)cyclic products (Scheme 135).³⁴²

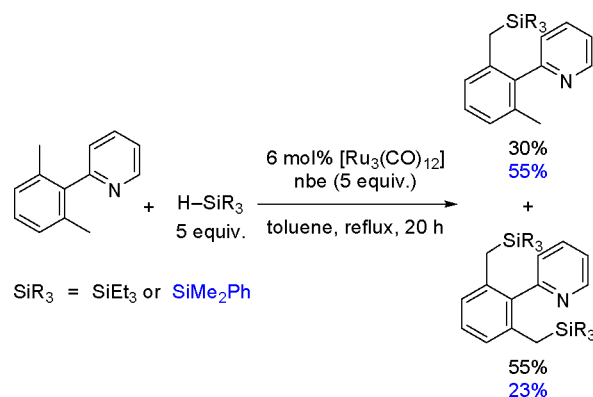
Directed intermolecular silylation of alkyl C–H bonds has been demonstrated for substrates with activated C–H bonds, such as those located in the benzylic position or α to a heteroatom (e.g., N, O or Ge). Only a few examples of the directed silylation of inactivated C–H bonds are known. The first intermolecular silylation of benzylic C–H bonds has been

Scheme 135. Intramolecular Silylation of Primary $\text{C}(\text{sp}^3)\text{-H}$ Bonds Catalyzed by a Ruthenium–Pincer Complex



reported by Kakiuchi and co-workers (Scheme 136)³⁴³ who described several examples using a pyridyl or a pyrazolyl directing group.

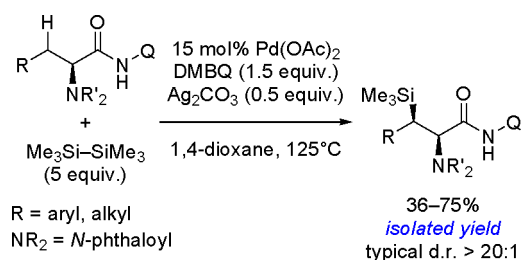
Scheme 136. Directed Intermolecular Silylation with Tertiary Silanes



Mita and Sato have reported analogous silylation to occur in the presence of the iridium complex $[\{\text{Ir}(\text{cod})\text{Cl}\}_2]$ and pyrimidine, pyrazine, and oxazole directing groups. The Ir-catalyzed reaction does not require a hydrogen acceptor to proceed efficiently.³⁴⁴ Stereoselective silylation of inactivated primary or secondary $\text{C}(\text{sp}^3)\text{-H}$ bonds of α -amino acids in the β position to oxygen has been reported by Shi.³⁴⁵ The reaction runs in the presence of palladium complexes and uses hexamethyldisilane as the silylating agent (Scheme 137). A directing-group-assisted approach was used, as proposed for carboxylic acid derivatives by Kuninobu and Kanai.³¹⁶

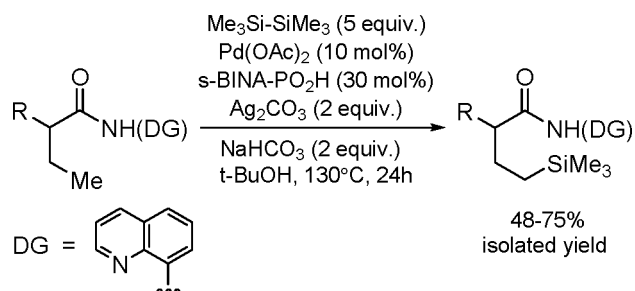
The yields were 31%–71% and 36%–75% in the silylation of primary and secondary C–H bonds, respectively. When the

Scheme 137. Directed Intramolecular Silylation of Secondary $\text{C}(\text{sp}^3)\text{-H}$ Bonds with Disilane



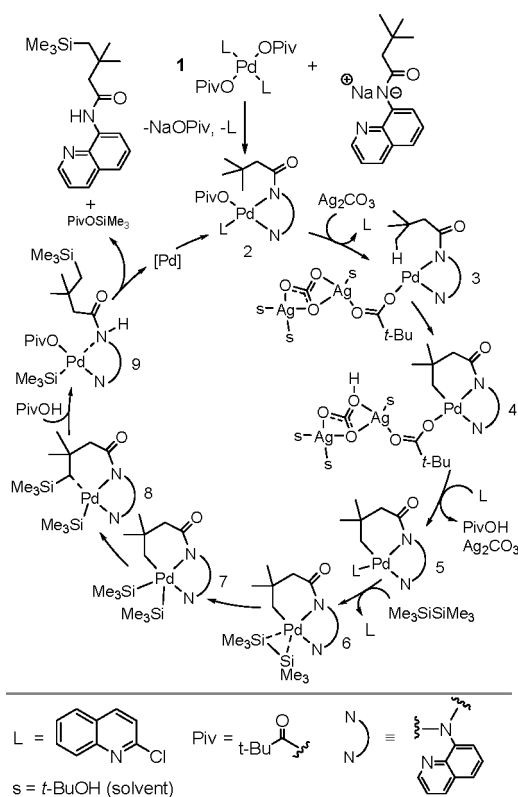
mechanism of this process was investigated, palladacyclic intermediates were isolated, shown to form silylation products in a stoichiometric reaction with disilane and being catalytically active intermediates in primary and secondary C(sp³)-H silylation. The palladium-catalyzed silylation of γ C(sp³)-H bonds in a series of aliphatic carboxamides with hexamethyldisilane has been described by Sunoj and Maiti (Scheme 138).³⁴⁶

Scheme 138. Directed Intramolecular Silylation with Disilanes



A reaction mechanism has been proposed on the basis of preliminary kinetic studies and DFT calculations (Scheme 139). [Pd(OPiv)₂L₂] (L = 2-chloroquinoline) (**1**) has been found to be energetically the most favorable active species. Association of the substrate as a sodium amidate to complex (**1**) forms a catalyst-substrate chelate complex (**2**), proposed to be the starting point of the catalytic cycle. Activation of the

Scheme 139. Mechanism of the Pd-Catalyzed γ -Silylation (or Germylation) of Alkyl C-H Bonds. Adapted with Permission from Ref 346. Copyright 2017 American Chemical Society

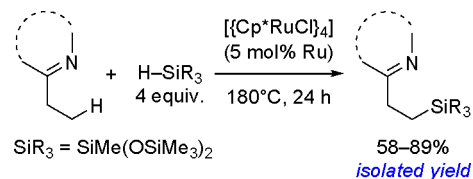


C-H bond occurs via concerted metalation-deprotonation to form palladacycle (**4**). Calculations show that the carbonate ligand is involved in C-H activation. Subsequently, 2-chloroquinoline replaces the labile pivalic acid and silver carbonate (formed by combining silver pivalate and silver bicarbonate) to give **5**. A model of **5** has been successfully synthesized and characterized by X-ray diffraction studies. In the next step, disilane displaces ligand L to form intermediate **6**, which subsequently undergoes oxidative addition to form a palladium(IV) complex (**7**). This step was calculated to be rate-limiting. The subsequent stage is the formation of a C-Si bond as a result of reductive elimination. The PivOH formed in the C-H activation step then interacts with intermediate **8** by proton transfer to the amidate nitrogen to form a product-catalyst complex (**9**). Subsequently, product dissociation, reductive elimination of silyl pivalate, and oxidation of the formed palladium(0) complex occur. Silver carbonate is used as an oxidant. The C(sp³)-H bond activation step is proposed to be reversible.

DFT calculations were also performed for the analogous process of germylation.³⁴⁶ The potential energy profiles for the silylation and germylation reactions are slightly different. For both processes, the highest-energy points are the transition states for the oxidative addition of Si-Si (or Ge-Ge) bonds to the palladium(II) complex and for reductive elimination. Analysis of the energy profiles shows that the oxidative addition of disilane is the rate-limiting step of silylation, whereas reductive elimination is the rate-limiting step of germylation.

The silylation of the C(sp³)-H bond in 2-alkyloxazolines and 2-alkylpyridines occurs in the presence of the [{Cp*₂RuCl}₄] ruthenium tetramer (Scheme 140).³⁴⁷ The

Scheme 140. Directed Intramolecular Silylation with HSiMe(OSiMe₃)₂



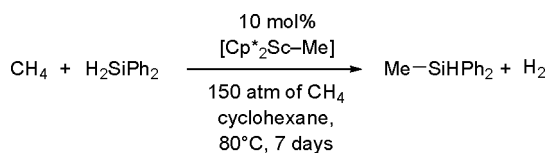
reaction is site-selective and proceeds at the inactivated primary C-H bond in the γ -position to nitrogen. The reaction is effective only in the presence of HSiMe(OSiMe₃)₂. It requires high temperature to run efficiently and is accompanied by efficient silane dehydrocoupling.

Labeling studies and DFT calculations show that the reductive elimination of the C-Si bond limits the reaction rate.

Undirected silylation of the C(sp³)-H bond is the least developed silylation of C-H bonds. In 2003, Tilley reported the intermolecular silylation of methane in the presence of the [Cp*₂ScMe] scandium complex.^{348,349} On the basis of DFT calculations, the reaction was proposed to involve Si-Me bond formation via σ -bond metathesis between the Sc-Me and Si-H bonds (Scheme 141).

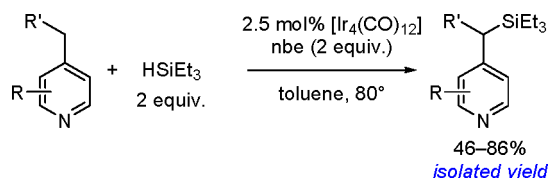
The reaction has not gained practical importance. However, reports on the reaction opened up new opportunities for catalysis as the productive functionalization of methane by σ -bond metathesis had not been described.

Scheme 141. Dehydrogenative Silylation of Methane



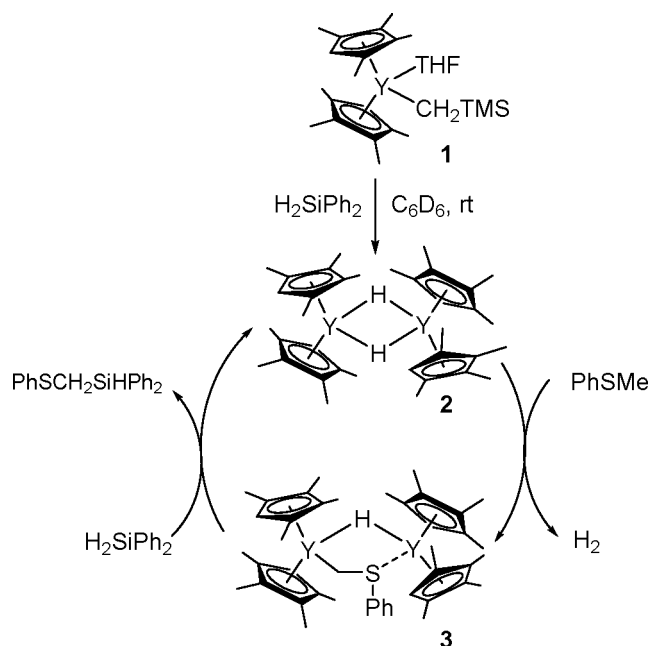
Fukumoto has revealed the silylation of C(sp³)-H bonds at the benzylic position in 4-alkylpyridines³⁵⁰ and 2-alkylpyridines³⁵¹ with hydrosilanes (Scheme 142).

Scheme 142. Undirected Silylation at the Benzylic Position of 4-Alkylpyridines



The reaction takes place in the presence of [Ir₄(CO)₁₂]. The yield is strongly improved when 3,5-dimethylpyridine is added. The proposed mechanism includes an electrophilic silicon species as the key intermediate. Product formation is proposed to occur by the silylation of a *N*-silylated enamine with electrophilic silicon species and subsequent elimination of the silyl group. However, several details of the mechanism remain unclear. Finally, Hou and co-workers reported the regioselective α -C-H silylation of methyl sulfides with hydrosilanes catalyzed by yttrium complexes.³⁵² The catalytic cycle has been proposed on the basis of stoichiometric reactions and isolation of key intermediates (Scheme 143).

Scheme 143. Mechanism of the Y-Catalyzed Intramolecular Silylation of Alkyl C-H Bonds. Adapted with Permission from Ref 352. Copyright 2018 American Chemical Society

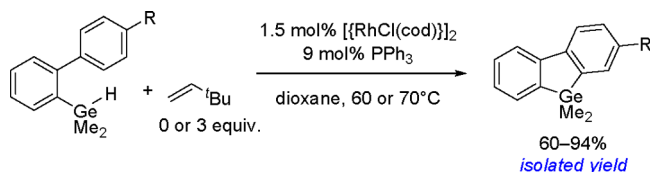


3.3. Dehydrogenative Germylation of C-H Bonds

Direct germylation of organic molecules is still at the early stage of development. The interest in the germylation of arene C(sp²)-H and C(sp³)-H bonds has grown in the past decade.

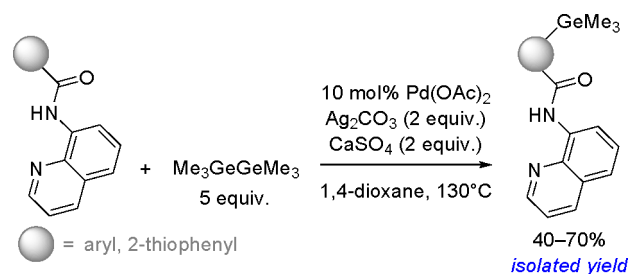
3.3.1. Dehydrogenative Germylation of Arene C(sp²)-H Bonds. Murai and Takai have reported rhodium-catalyzed intramolecular germylation leading to 9-germafluorene and germylene-bridged π -conjugated systems (Scheme 144).^{308,353}

Scheme 144. Intramolecular Dehydrogenative Germylation of Arene C-H Bond



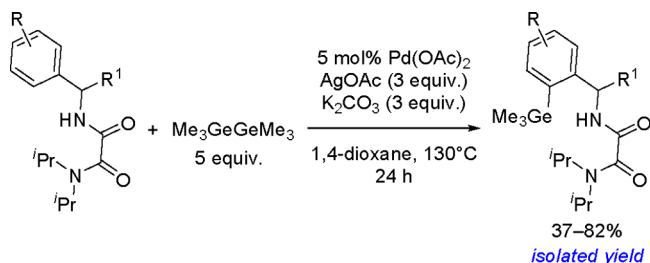
Directed germylation of arenes has been reported by Kuninobu and Kanai. Benzamides and carboxamides undergo germylation with Me₃GeGeMe₃ in the presence of a palladium catalyst (Scheme 145).³¹⁶

Scheme 145. Directed Germylation of Arenes with Digermanes



An analogous palladium-catalyzed directed germylation of modified benzylamines has been reported by Wen and Zhao (Scheme 146).³⁵⁴

Scheme 146. Directed Germylation of Arenes with Digermanes

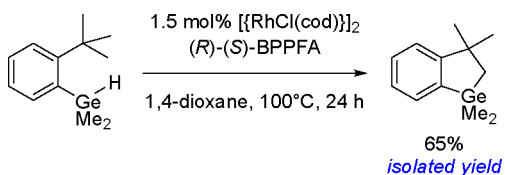


Finally, Maiti and co-workers demonstrated the directed *meta*-selective germylation of the arene C-H bond.³⁵⁵ The procedure of arene germylation with HGeEt₃ in the presence of a palladium phosphine dimer via formation and functionalization of a tetrafluorothianthrenium salt has been reported by Schoenebeck.³⁵⁶ The reaction proceeds in mild conditions and enables germylation of nonactivated and directing group-free arenes. The transformation tolerates a variety of functional

groups (i.e., phenoxy, carbonyl, amide, nitro, nitrile, and chloride).

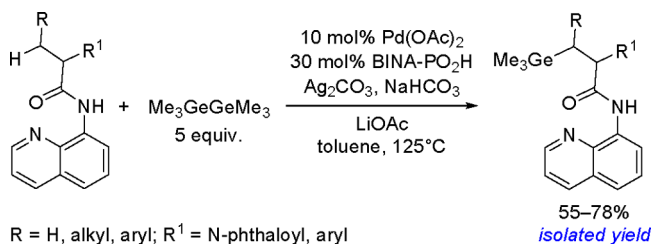
3.3.2. Dehydrogenative Germylation of C(sp³)-H Bonds. Murai and Takai have described the rhodium-catalyzed intramolecular germylation of the primary C(sp³)-H bond leading to the synthesis of 2,3-dihydrobenzo[*b*]germole (Scheme 147).³³⁹

Scheme 147. Rhodium-Catalyzed Intramolecular Germylation



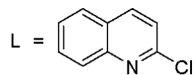
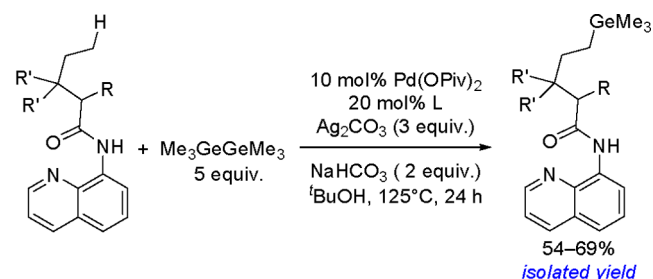
Palladium-catalyzed germylation of primary and secondary alkyl C(sp³)-H bonds enables the synthesis of β -germyl- α -amino amides and β -germyl-modified α -amino acids after deprotection of the amine group (Scheme 148).³⁵⁷

Scheme 148. Directed Germylation of Primary and Secondary Alkyl C(sp³)-H Bonds



Directed γ -C(sp³)-H germylation of aliphatic carboxamides has been successfully performed by Maiti (Scheme 149).³⁴⁶

Scheme 149. Directed Dehydrogenative Germylation of γ -C(sp³)-H Bonds



4. ACTIVATION (AND FUNCTIONALIZATION) OF C-X BONDS WITH HYDROMETALLOIDS AND BISMETALLOIDS

This section covers the activation of the C-X bond, where X is a halide or sulfonate, and its functionalization leading to the formation of the carbon-metalloid bond. The activation and

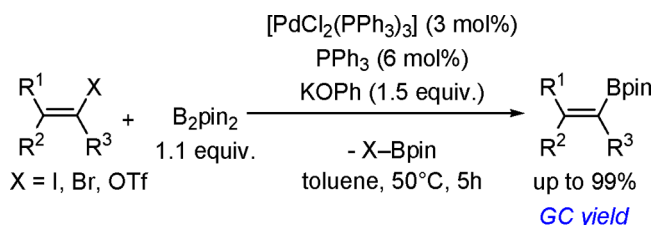
functionalization of C-C, C-O, C-N, and C-S bonds in cross-coupling processes is beyond the scope of this Review.

4.1. Borylation of C-X Bonds

The reaction offers an alternative to the classical method of C-B bond synthesis, including the treatment of trialkyl borates with magnesium or lithium alkyl reagents, followed by hydrolysis or transesterification. Unlike the catalytic C-H borylation reaction, this reaction does not suffer from a lack of site selectivity. This section also discusses the activation and functionalization of the C-F bond.

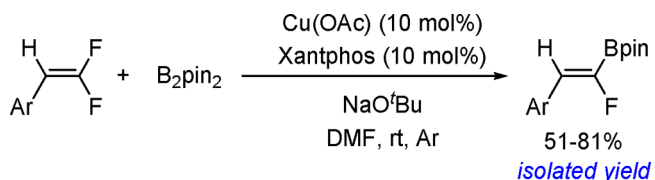
4.1.1. Borylation of Olefinic C(sp²)-X Bonds. Miyaura has shown that 1-alkenyl iodides, bromides, and triflates can be borylated with B₂pin₂ in the presence of a palladium complex and potassium phenoxide (Scheme 150).^{358,359} The reaction is highly efficient and proceeds with complete retention of the double bond configurations.

Scheme 150. Borylation of Olefins



Buchwald has reported that vinyl chloride can be successfully converted into the corresponding pinacol boronate ester by borylation with HBpin in the presence of [PdCl₂(CH₃CN)₂] and SPhos.³⁶⁰ The first example of olefin defluoroborylation has been described by Braun.³⁶¹ The [RhH(PEt₃)₃] rhodium complex was shown to catalyze the C-F bond borylation of hexafluoropropene with HBpin at room temperature in quantitative yields. The sequence of catalytic transformations involves consecutive hydroboration, hydrogenation, and/or dehydrogenative borylation. Cao and co-workers reported the Cu-catalyzed stereoselective monoborylation of gem-difluoroalkenes with B₂pin₂ (Scheme 151).³⁶² In the presence of CuOAc, NaOt-Bu, and Xantphos,

Scheme 151. Borylation of Fluoroolefins

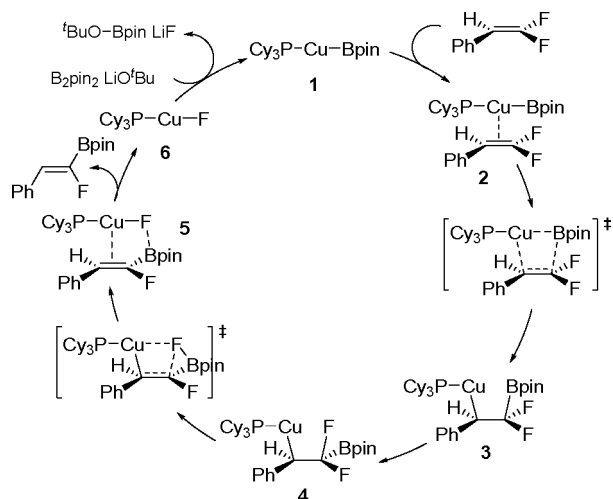


a variety of (*Z*)-fluorinated alkenylboronic acid pinacol esters were obtained with moderate to good yields at room temperature. Involvement of the phosphine-coordinated copper-boryl complex in the reaction mechanism was proposed.

[CuCl(PCy₃)₂], another copper complex, catalyzes regioselective monodefboroborylation of polyfluoroalkenes.³⁶³ The reaction takes place under mild conditions in the presence of a base. The choice of the boron source has been found to be important for the efficient transformation of gem-(difluorovinyl)arenes. While B₂pin₂ was suitable for substrates with an electron-deficient aryl group, B₂nep₂ performed better

with reagents bearing an electron-rich aryl group. By examining an analogous stereoselective borylation of gem-difluoroalkenes, Ito³⁶⁴ and Gao and Wang³⁶⁵ independently proposed a reaction mechanism based on DFT calculations (Scheme 152). The identified active catalyst of the process is the

Scheme 152. Mechanism of the Cu-Catalyzed Defluorinative Borylation of gem-Difluoroalkenes



[Cu(Bpin)(PCy₃)] complex (1). The olefin associates to the complex and undergoes regioselective insertion into the Cu–B bond, resulting in the formation of complex 3 in which boron is bound to the gem-difluoromethylene unit. Subsequently, after rotation of the C–C bond, syn-planar β-F elimination occurs, and 5 is formed. The interaction of the fluorine atom with the empty p orbital of boron contributes to the weakening of the C–F bond. Reductive elimination of vinylboronate and subsequent transmetalation result in the regeneration of complex 1. The possibility of inserting olefins into the Cu–B bond was previously demonstrated experimentally by Sadighi³⁶⁶ and as a result of DFT calculations by Lin and Marder groups.³⁶⁷

4.1.2. Borylation of Aryl C(sp²)–X Bonds. The first borylation of aryl halides was reported in 1995 by the Miyaura group (Scheme 153).³⁶⁸ Cross-coupling of aryl iodides or

Scheme 153. Borylation of Bromoarenes with B₂pin₂



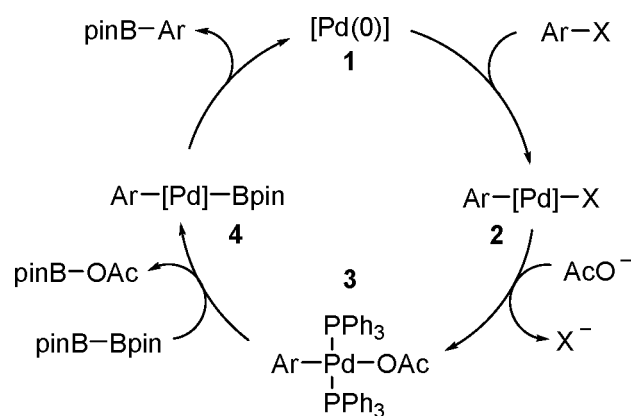
bromides with a pinacol ester of diboronic acid (B₂pin₂) in the presence of [PdCl₂(dppf)] and KOAc as a base gave bromoarenes with high selectivities and yields. The use of KOAc is crucial for the selective synthesis of the arylboronic acid pinacol ester, as competing Suzuki–Miyaura cross-coupling may occur in the presence of stronger bases. The process is known as Miyaura borylation.

Borylation of chloroarenes has been found to proceed in the presence of [Pd(dba)₂]/PCy₃ and KOAc (1.5 equiv). This catalyst also permitted the borylation of aryl bromides and triflates and tolerated the presence of ester, ketone, and nitrile functionalities.³⁶⁹ Procedures for the effective borylation of

(hetero)aryl halides (electron-rich or -poor) and procedures for the borylation of sterically crowded aryl halides have been described.^{370–372} This important reaction feature has been achieved using bulky ligands. Besides, the activation and functionalization of C–X bonds (X = I, Br, Cl, OTf, OTs, OMs) is possible. Another important property of the reaction is functional group compatibility. The reaction can run effectively with a broad spectrum of functional groups. The metals Mn, Fe, Co, Ni, Cu, and Zn are known to show catalytic activity in Miyaura borylation. Examples of photoinduced and photocatalyzed reactions have been reported.^{373–375} Advances in the TM-catalyzed borylation of aryl halides have been reviewed (e.g., refs 100, 376, and 377).

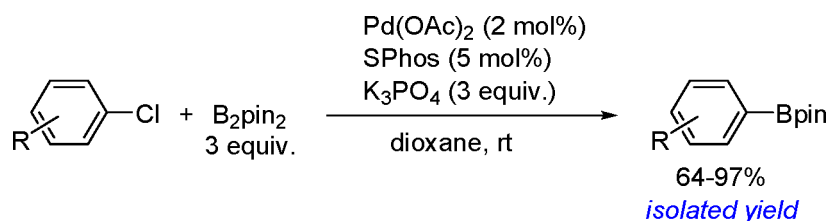
The reaction mechanism has been proposed in Miyaura's seminal paper³⁶⁸ on the basis of the isolation and characterization of the *trans*-[Pd(OAc)Ph(PPh₃)₂] intermediate and a study of its stoichiometric reactivity with bis(pinacolato)-diboron (Scheme 154).

Scheme 154. Mechanism of Aryl Halide Borylation with B₂pin₂ Proposed by the Miyaura Group³⁵⁷



The transmetalation step in a simplified reaction model has been investigated by DFT.³⁷⁸ The results showed the importance of the type of base used for the energy profile of the process. When a hydroxide or a fluoride is used as an anionic ligand in the palladium complex, the formation of strong X–B bonds weakens the Pd–X and B–B bonds and accelerates both the transmetalation and the cleavage of B–B bonds. According to DFT calculations, corroborated by experimental results, the energy barrier for the transmetalation of palladium chloride is high. Moreover, the calculations imply that the associative mechanism of transmetalation takes place more easily than the dissociative mechanism, while the reductive elimination of an arylboronic ester from the bisphosphinic complex occurs with no significant energy barrier.

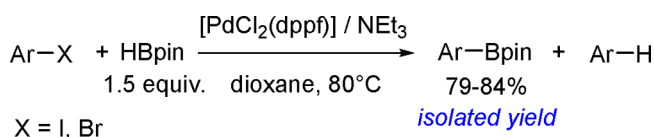
A recently reported convenient reaction procedure involves the use of lipophilic bases such as potassium 2-(ethyl)-hexanoate; the reaction proceeds under low palladium catalyst loading (0.5 mol %) in mild conditions.³⁷⁹ A preliminary mechanistic study showed an inhibitory effect exerted by the carboxylate anion on the catalytic cycle.³⁷⁹ On the basis of the results, a modification of the reaction mechanism was proposed to include the formation of an inactive diacetate anionic complex. Moreover, a dissociative mechanism of phosphine substitution by a borylating agent prior to transmetalation was suggested. Buchwald has shown that

Scheme 155. Borylation of Aryl Chlorides with B₂pin₂

catalysts composed of Pd and bulky biarylmonophosphine such as XPhos or SPhos are highly stable and active for the borylation of aryl chlorides (Scheme 155).³⁷⁰

In 1997, the borylation of aryl halides using HBpin was described by Masuda and co-workers (Scheme 156).³⁸⁰ The

Scheme 156. Arene Borylation with Pinacolborane

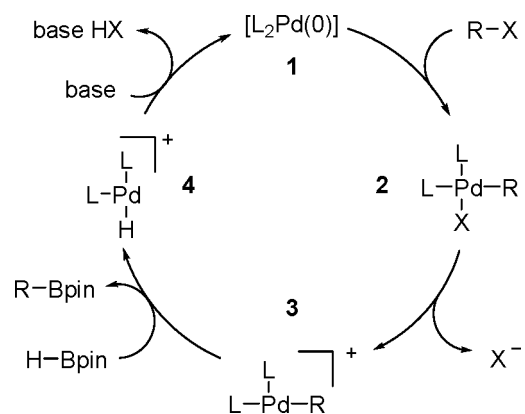


reaction occurs in the presence of [PdCl₂(dppf)] (dppf = 1,1'-bis(diphenylphosphino)ferrocene) as a precatalyst, requires the presence of triethylamine, and affords arylboronic esters in yields higher than 80%. Compared with Miyaura borylation, the reaction shows higher atom efficiency and uses a cheaper and more available borylating agent. The drawback of the process is side hydrodehalogenation which can partly be eliminated with the right choice of the base. The reaction was briefly reviewed in 2012.³⁸¹

Similar yields have been reported for aryl halides containing either electron-donating or electron-accepting substituents. A combination of [Pd(dba)₂] and bis(2-di-*tert*-butylphosphino-phenyl) ether was found to be active in the efficient borylation of electron-rich and electron-deficient aryl bromides and electron-rich aryl chlorides with pinacolborane.³⁸² The system permitted efficient borylation of bulky aryl bromides. Buchwald has shown that [PdCl₂(CH₃CN)₂] and bulky SPhos used as the supporting ligands achieve effective borylation of several aryl bromides and chlorides.³⁶⁰

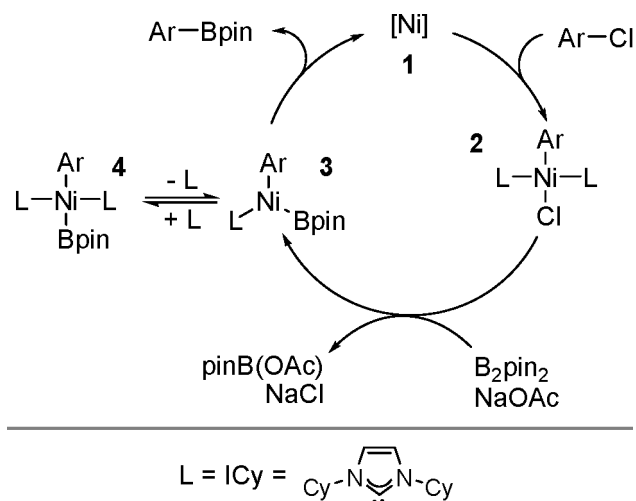
On the basis of DFT computations, the mechanism of the process proposed by Masuda³⁸³ was corrected by Marder and Lin.³⁸⁴ The results of the calculations indicated that the formation of an ammonium/boride ion pair, [Et₃NH]⁺[Bpin]⁻, is energetically unfavored. The same authors examined the mechanism involving the participation of neutral and cationic palladium complexes using DFT methods. The calculations showed that the cationic pathway was favored over the neutral one. The proposed mechanism (Scheme 157) involves the oxidative addition of an aryl halide to a palladium(0) complex (1) leading to compound (2). Subsequently, as a result of the NEt₃-assisted dissociation of the iodide anion, a cationic, coordinatively unsaturated 14-electron complex (3), *cis*-[Pd(Ph)(NMe₃)(η²-dhpp)]⁺ (dhpp = PH₂CH₂CH₂CH₂PH₂), is formed. Cation 3 reacts with HBpin via σ-bond metathesis to generate an arylboronic ester and cationic palladium hydride (4). Finally, base-assisted deprotonation of 4 leads to the regeneration of the active complex (1).

Complexes of the first-row transition metals may be an attractive alternative to palladium complexes because of their

Scheme 157. Mechanism of Masuda Borylation³⁸⁴

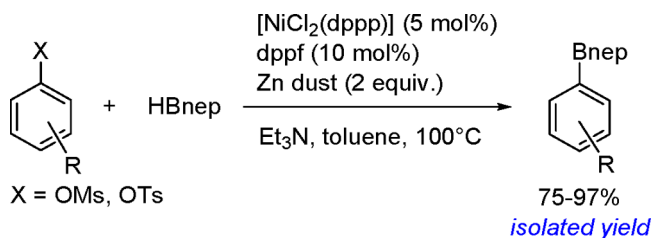
lower cost and toxicity. Of the 3d group metals, nickel is the most important in catalysis. The [NiCl₂(PMe₃)₂] complex has been found to be active in the borylation of aryl chlorides with bis(pinacolato)diboron in the presence of a metal 2,2,2-trifluoroethoxide as a base.³⁸⁵ A variety of functional groups are tolerated. The reaction achieves effective conversion of derivatives with strong steric hindrance. Molander has extended these methods to include the borylation of aryl and heteroaryl halides and pseudohalides using tetrahydroxydiboron.³⁸⁶ The reactions are catalyzed by a combination of [NiCl₂(dppp)], PPh₃, and diisopropylethylamine. An important feature of the reaction is its functional group compatibility and applicability to several heterocyclic systems. Recently, Marder and Radius have reported the activation and borylation of aryl chlorides using *N*-heterocyclic carbene (NHC) ligated nickel(0) complexes [Ni₂(ICy)₄(μ-(η²:η²)-cod)] (ICy = 1,3-dicyclohexylimidazol-2-ylidene) or [Ni₂(IPr)₄(μ-(η²:η²)-cod)], with NaOAc as the base and B₂pin₂ as the boron source.³⁸⁷ On the basis of the examination of stoichiometric reactions and the isolation of complexes of the *trans*-[Ni(ICy)₂(Cl)(Ar)] type, formed in the reaction of [Ni₂(ICy)₄(μ-(η²:η²)-cod)] with different aryl chlorides at room temperature, a reaction mechanism has been proposed (Scheme 158).

The proposed mechanism involves the oxidative addition of an aryl chloride to [Ni(ICy)₂] (1), transmetalation and reductive elimination. The diboron compound undergoes transmetalation, possibly in the form of an adduct, with an acetate anion (Na[B₂pin₂(OAc)]). The final reductive elimination step occurs from a three-coordinate species (3) to produce the borylated product and to regenerate [Ni(ICy)₂]. The deduced rate-limiting step is the formation of the boryl complex. The mechanism requires further in-depth experimental and computational research. In 2020, Guo, Radius, and Marder described the visible light-induced Ni-catalyzed radical borylation of chloroarenes with B₂pin₂.³⁷⁵

Scheme 158. Mechanism of the Ni-Catalyzed Borylation of Aryl Chlorides³⁸⁷

A mixed-ligand system consisting of $[\text{NiCl}_2(\text{dppf})]/\text{dppf}$ permits the borylation of aryl halides with pinacolborane and neopentylglycolborane as borylating agents.^{388,389} This catalytic system combined with Zn strongly increases the reaction rate and yield of aryl neopentylglycolboronates. Diverse electron-rich and electron-deficient aryl iodides, bromides, and chlorides have been efficiently borylated.³⁹⁰ Aryl mesylates and tosylates undergo borylation in the presence of a nickel-based catalytic system, using two different phosphine ligands and a zinc additive (Scheme 159).³⁹¹

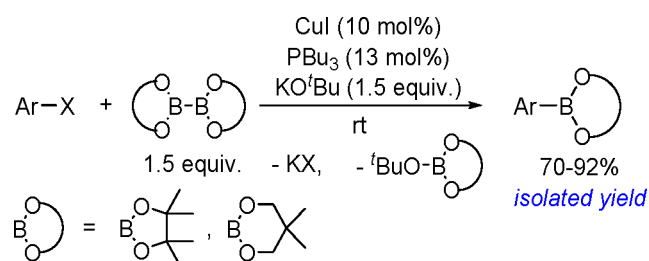
Scheme 159. Borylation of Aryl Sulfonates with Neopentylglycolborane Pinacolborane



Copper complexes were found to efficiently catalyze the borylation of aryl iodides and electron-rich aryl bromides under mild conditions in the presence of CuI, PBu_3 , or $\text{KO}t\text{-Bu}$ as a base (Scheme 160).³⁹²

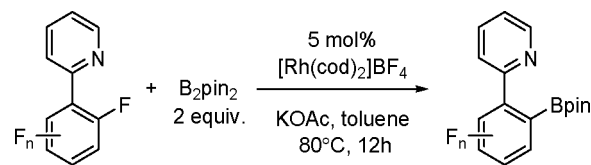
The catalytic cycle of copper-catalyzed borylation proposed on the basis of experimental observations and DFT calculations involves the formation and the key role of Cu-

Scheme 160. Copper-Catalyzed Borylation of Aryl Bromides



B intermediate. DFT calculations suggest its formation by σ -bond metathesis.³⁹²

Further research established procedures for the efficient borylation of aryl chlorides with different electronic and steric properties.³⁹³ NHC copper complexes afford isolation yields of 37%–80% in the presence of $\text{KO}t\text{-Bu}$. The reaction shows a broad functional group tolerance. In the presence of copper iodide and NaH, aryl iodides undergo borylation with pinacolborane (HBpin) as a borylating agent. The reaction is effective already at room temperature and leads to the corresponding aryloboronates in yields of 61%–83%.³⁹⁴ Cobalt³⁹⁵ and iron complexes^{396,397} have also been found to be active in aryl halide borylation. As in palladium catalysis the formation of a metal-boryl complex is of key importance for catalysis with Ni, Cu, Fe, and Co complexes. Recently, the borylation of aryl iodides with B_2pin_2 has been reported to proceed in the presence of the rhodium complex $[\{\text{RhCl}(\text{cod})\}_2]$ and KOAc as a base.³⁹⁸ In 2015, Zhang described the directing-group-assisted *ortho*-selective defluoroborylation of polyfluoroarenes with B_2pin_2 (Scheme 161).³⁹⁹ Several di-, tri-, tetra-, and pentasubstituted fluoroarenes were transformed with different isolation yields, typically exceeding 70%.

Scheme 161. Directed *ortho*-Defluoroborylation of Polyfluoroarenes

On the basis of preliminary studies of the reaction mechanism, a Rh(III)/Rh(V) catalytic cycle was suggested as involved in the reaction. Nonactivated fluoroarene was borylated with B_2nep_2 in the presence of a nickel catalyst.⁴⁰⁰ On the basis of results of preliminary studies, a mechanism was proposed, involving the oxidative addition of an aromatic C–F bond to a Ni(0) complex followed by boryl transfer and C–B bond formation via reductive elimination. The nickel complex was reported to catalyze fluoroarenes with B_2pin_2 when used in the presence of a copper(I) salt.⁴⁰¹ However, examination of this reaction suggested that the Ni(I) complex was involved in the activation of the C–F bond. Marder and Radius used the $[\text{Ni}(\text{IMes})_2]$ N-heterocyclic carbene nickel complex in the borylation of multifluorinated arenes with B_2pin_2 .⁴⁰² Several partially fluorinated arenes were converted into their corresponding boronate esters. It was demonstrated that the formation of monoborylation and diborylation products as the main product can be controlled by the fluoroarene to B_2pin_2 ratio.

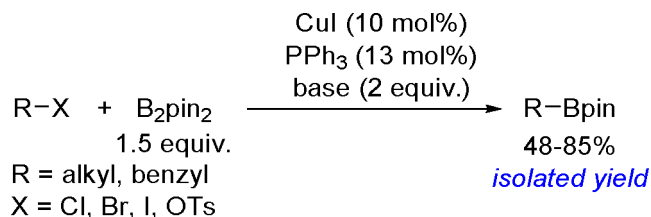
Copper complexes have been found to catalyze the C–F borylation of mono-, di-, and trifluoroarenes.⁴⁰³ Mechanistic studies suggest that the reaction occurs via an SRN1 mechanism⁴⁰⁴ involving a single-electron transfer process. In the presence of lithium bis(silyl)amide (LiHMDS) as a base, both palladium complexes ($[\text{Pd}_2\text{dba}_3]$) and iron salts (FeCl_2) exhibit catalytic activity in the borylation of an aryl fluoride with B_2pin_2 .⁴⁰⁵ The proposed mechanism comprised oxidative addition, base-assisted transmetalation, and reductive elimination of aryl boronate. LiHMDS was proposed to play a

role in the activation of the B–B bond and in the transmetalation step.

Guo, Radius, Marder, and co-workers described the selective photocatalytic C–F borylation of polyfluoroaromatics with B_2pin_2 in the presence of an NHC nickel catalyst.⁴⁰⁶ The protocol employed a rhodium–biphenyl complex as a triplet sensitizer. Finally, Shi reported the copper-catalyzed multi-borylation of *gem*-difluoroalkenes.⁴⁰⁷

4.1.3. Borylation of $C(sp^3)$ –X Bonds. The reaction is an alternative synthetic method for the Csp^3 –B bond. The most important information on this reaction has been published in a recent review.³⁷⁶ Catalytic activity in this reaction has been observed for the salts or complexes of several TMs, including Co, Cu, Fe, Mn, Ni, and Pd; most papers concern copper-based catalysis. Advances in Cu-catalyzed $C(sp^3)$ –B bond formation have recently been reviewed.⁴⁰⁸ The first reported example of the reaction was the borylation of activated allyl chlorides with bis(pinacolato)diboron, and stoichiometric amounts of a copper(I) salt had to be used.⁴⁰⁹ Inactivated alkyl halides were found to undergo borylation in the presence of 10 mol % copper(I) iodide, PPh_3 , and a base (Scheme 162).⁴¹⁰ The reaction provides primary and secondary alkylboronic esters with diverse structures and a variety of functional groups.

Scheme 162. Copper-Catalyzed Borylation of Inactivated Alkyl Halides



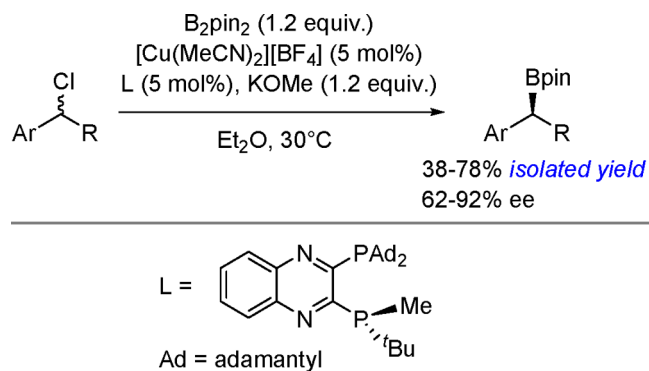
Subsequent results expanded the scope of the reaction. In the presence of copper(I)/Xantphos, primary and secondary alkyl chlorides, bromides, and iodides undergo efficient borylation with B_2pin_2 .⁴¹¹ A radical mechanism was postulated on the basis of a reaction with cyclopropylmethyl bromide, which resulted in the formation of ring-opening products. Recently, Ito has reported the first copper(I)-catalyzed enantioconvergent borylation of racemic benzyl chlorides (Scheme 163).⁴¹² Benzyl boronates were obtained with high enantioselectivity (up to 92% ee) and isolation yields, depending on the substrate and reaching 78%.

Although the detailed mechanism of the process is not known and further experimental and computational research is necessary, Ito has proposed a reasonable reaction mechanism (Scheme 164).³⁷⁶

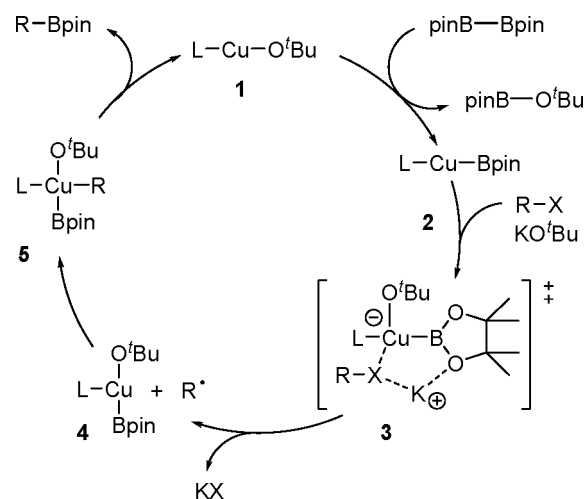
According to the mechanism, a copper(I) boryl complex is generated when a copper(I) alkoxide (1) reacts with a diboron compound. The proposed oxidative addition takes place in the presence of a base and leads, in the first stage, to a copper(II) complex (4) and an alkyl radical as a result of single-electron transfer between the alkyl halide and copper(I). The association of the radical in the second stage generates a copper(III) complex (5). Subsequent reductive elimination gives the borylation product and leads to the regeneration of copper(I) alkoxide (1).

Copper(II) salts in the presence of NHC (IMes, IPr) were proved to be catalytically active in the borylation of primary,

Scheme 163. Enantioconvergent Borylation of Racemic Benzyl Chlorides

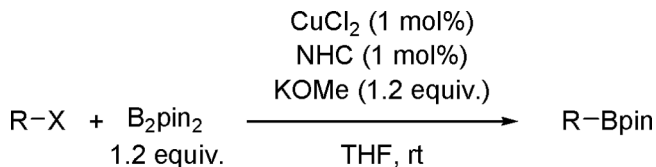


Scheme 164. Mechanism of Alkyl Halide Borylation in the Presence of a Copper Complex



secondary, and tertiary alkyl halides with B_2pin_2 (Scheme 165).⁴¹³

Scheme 165. Copper-Catalyzed Borylation of Alkyl Halides



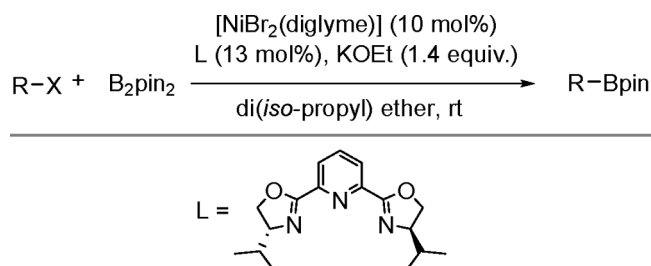
The procedure enables the borylation of a wide range of primary, secondary, and some tertiary alkyl halides to give corresponding alkyl boronates in good yields. Allyl and benzyl bromides can be converted into the desired products in moderate to good yields. The reaction tolerates a range of functional groups, such as ethers, ketals, esters, alcohols, and nitriles. Preliminary mechanistic studies suggest that the reaction mechanism involves the formation of an alkyl radical. The advances and perspectives of Cu-catalyzed $C(sp^3)$ –B bond formation have recently been discussed.⁴⁰⁸

Allyl chlorides undergo borylation with bis(pinacolato)diboron in the presence of $PdCl_2$ or $[Pd_2(dba)_3]$.⁴¹⁴ $[Pd_2(dba)_3]$ used with $P(t-Bu)_2Me \cdot HBF_4$ is active in the borylation of primary alkyl bromides.⁴¹⁵ The process enables

the synthesis of primary alkyl boronate esters with various skeletons and functional groups.

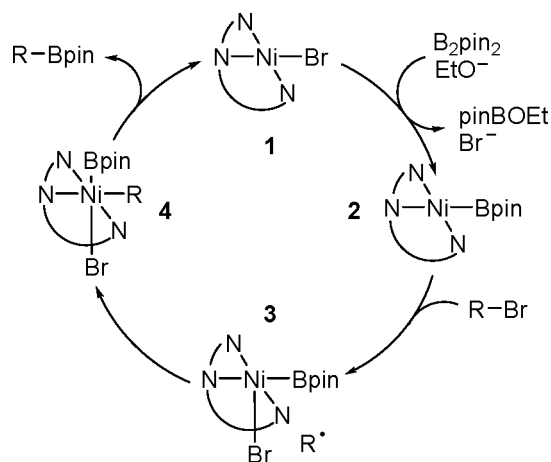
Fu group has reported borylations of inactivated primary, secondary, and tertiary alkyl halides (iodides, bromides, and chlorides) in the presence of nickel complexes (Scheme 166).⁴¹⁶ The method enables highly efficient and regioselective synthesis of a large variety of alkyl boronates.

Scheme 166. Nickel-Catalyzed Borylation of Alkyl Halides



The observed reactivity trend for primary, secondary, and tertiary halides (more substituted electrophiles are more reactive) and stereochemical probes⁴¹⁷ suggest the involvement of an organic radical in the mechanism (Scheme 167).⁴¹⁶

Scheme 167. Mechanism of the Nickel-Catalyzed Borylation of Alkyl Halides



The proposed mechanism is supported by the results of DFT calculations.⁴¹⁸ The calculated energy diagram indicates that the transfer of a halogen atom to the metal is the rate-limiting step. According to the calculation results, the barrier to atom transfer increases with a decreasing substitution degree of the alkyl bromides, which explains the experimentally observed reactivity trend.⁴¹⁶ Involvement of organic radicals in the reaction mechanism of alkyl halide borylations catalyzed by Mn,⁴¹⁹ Fe,⁴²⁰ or Co⁴²¹ has also been postulated.

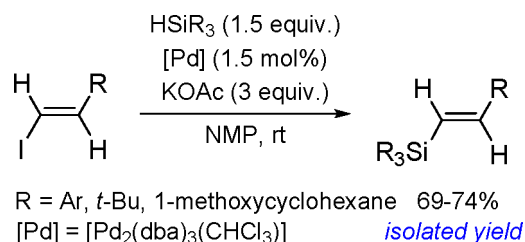
4.2. Silylation of C–X Bonds

Catalytic silylation of the C–X bond is a versatile method for synthesizing silyl-substituted organic derivatives. Disilanes, tertiary silanes (HSiR₃), and silyboranes (PhMe₂Si–Bpin) can be used as silylating agents. The reaction is typically used in the synthesis of silylarenes characterized by high site selectivity.

4.2.1. Silylation of Olefinic C(sp²)–X Bonds. In 1978, Nagai demonstrated the synthesis of vinylsilanes and bis-

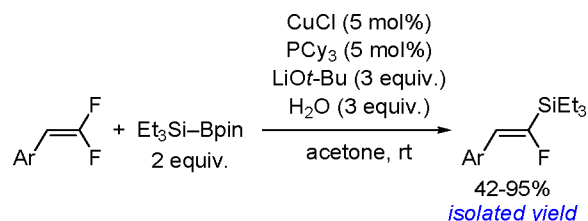
(silyl)ethenes via the coupling of vinyl chloride or *trans*-1,2-dichloroethylene with disilane in the presence of [Pd(PPh₃)₄].⁴²² The palladium(0)-catalyzed silylation of vinyl iodides with HSiR₃ has been reported by the Masuda group.⁴²³ The reaction permits the synthesis of alkenylsilanes with yields of up to approximately 70%. Reaction selectivity depends on the nature of reagents (both tertiary silanes and olefins), and for some systems, alkylsilane is observed as a byproduct (Scheme 168).

Scheme 168. Palladium-Catalyzed Silylation of Vinyl Iodides with Tertiary Silanes



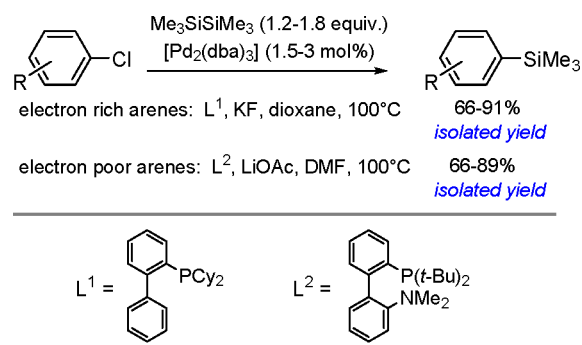
gem-Difluoroalkenes undergo stereoselective defluorosilylation with Et₃SiBpin in the presence of copper(I) chloride and PCy₃ (Scheme 169).³⁶⁵ The reaction leads exclusively to *Z*-monofluoroalkenylsilanes.

Scheme 169. Copper-Catalyzed Defluorosilylation of *gem*-Difluoroalkenes with Silaboronate



4.2.2. Silylation of Aryl C(sp²)–X Bonds. Silylation of aryl halides with disilanes was reported already in 1975 by Matsumoto and co-workers who described the catalytic activity of [Pd(PPh₃)₄] in the silylation of aryl bromides and certain chlorides with hexamethyldisilane.⁴²⁴ Eaborn extended the scope of the reaction by demonstrating the germylation and stannylation of aryl bromides with digermane and distannane, respectively.⁴²⁵ Tsuji⁴²⁶ and Buchwald (Scheme 170)⁴²⁷ reported catalytic systems active in the silylation of aryl

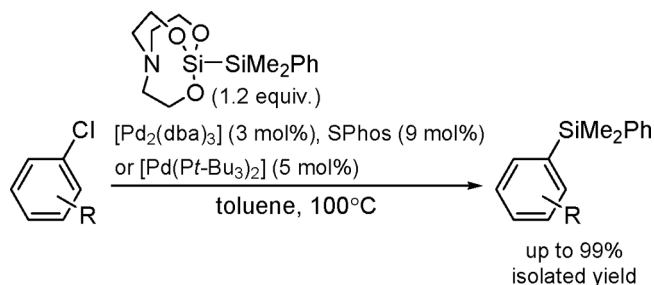
Scheme 170. Palladium-Catalyzed Silylation of Aryl Chlorides with Disilane



chlorides so that the reaction provided access to a wide variety of arylsilanes from commercially available aryl chlorides. The method produced the desired silylarennes in good yields and tolerated a variety of functional groups.

The Denmark group has described the palladium-catalyzed coupling of a variety of aryl bromides with 1,2-diethoxy-1,1,2,2-tetramethyldisilane (EtO)₂Me₂Si-SiMe₂(OEt) for the synthesis of dimethylalkoxyarylsilanes that are active reagents in Hiyama–Denmark coupling.⁴²⁸ An analogous process using aryl chlorides has also been described.⁴²⁹ The palladium-catalyzed silylation of aryl chlorides with silylsilatrane proceeds under external base-free conditions (Scheme 171).⁴³⁰ Experimental and computational studies show that

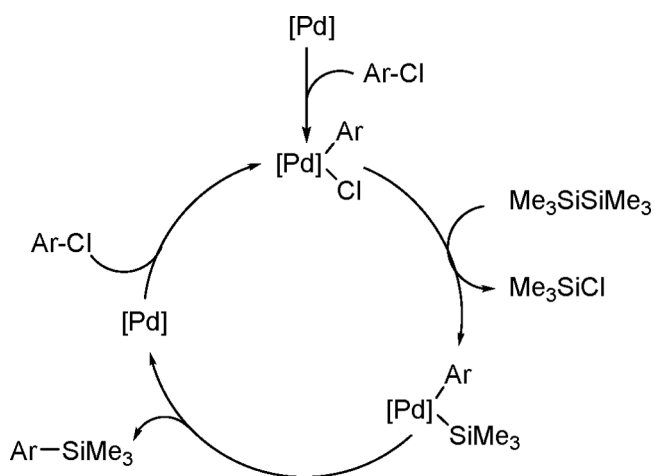
Scheme 171. Silylsilatrane as a Silylating Agent



smooth transmetalation from a silylsilatrane to arylpalladium chloride is facilitated by a strong interaction between the Lewis acidic silicon and the chloride.

The reaction mechanism has been presented first by Matsumoto et al. (Scheme 172);⁴³¹ however, it should be modified to take into account the beneficial effect of a base, in particular KOAc.

Scheme 172. Mechanism of the Silylation of Aryl Halides with Disilanes⁴³¹

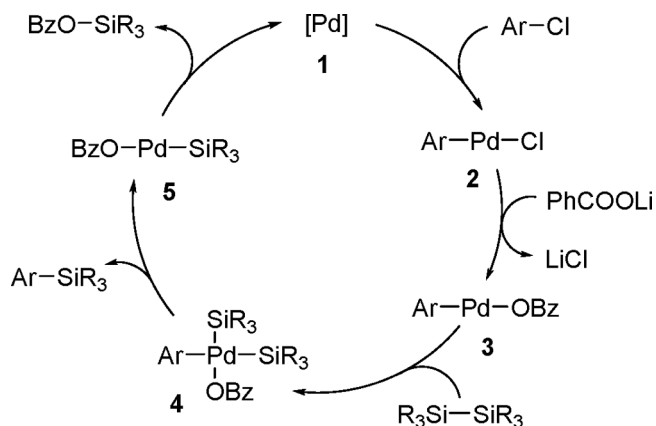


Shimokawa proposed possible involvement of palladium(IV) complexes in the reaction mechanism (Scheme 173).⁴²⁹

However, it may be the case that disilane undergoes transmetalation with a Pd(II) carboxylate to give silyl benzoate and an Ar–Pd(II)–SiMe₂(O*t*-Bu) species, which would then form the arylsilyl ether via reductive elimination and regenerate the Pd(0) complex.⁴²⁹

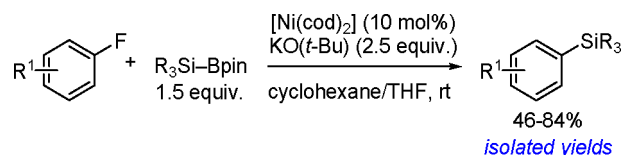
In 1998, the Murai group reported the functional group-directed defluorosilylation of aryl fluorides, fluoroacetophen-

Scheme 173. Mechanism of the Pd-Catalyzed Silylation of Aryl Chlorides with Disilanes



ones and (fluorophenyl)oxazolines with hexamethyldisilane in the presence of [Rh(cod)₂][BF₄].⁴³² Recently, Shibata presented an efficient Ni-catalyzed defluorosilylation of fluoroarenes with the R₃SiBpin silylborane, providing arylsilanes in good to high yields. In the presence of [Ni(cod)], KO*t*-Bu and without an additional ligand, the activation and functionalization of the C–F bond occurs at room temperature (Scheme 174).⁴³³

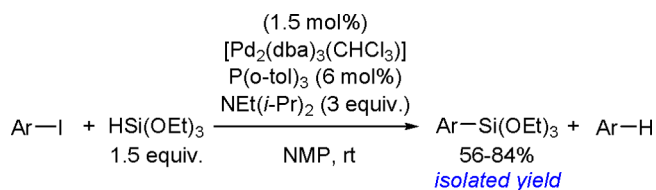
Scheme 174. Silylation of Aryl Fluorides with Silaborane



Benzyl and alkyl fluorides are silylated at room temperature in the absence of a nickel complex. Results of experimental studies (free radical clock, effect of radical scavengers) suggest that the mechanism of defluorosilylation does not involve free radical intermediates. The reaction mechanism has been proposed, but further studies are needed for corroboration.

Silylation with tertiary silanes (HSiR₃) carries the risk of the competing hydrodehalogenation reaction. However, a few catalytic systems for this reaction have been described, showing high selectivity for the formation of arylsilanes. The advantages, drawbacks, and the scope of the reaction have been reviewed.³⁰⁰ In 1997, Masuda's group described the first example of the palladium-catalyzed silylation of para-substituted aryl iodides with triethoxysilane leading to arylsilanes (Scheme 175).⁴³⁴ The use of [Pd₂(dba)₃(CHCl₃)], P(*o*-tol)₃, and NEt(*i*-Pr)₂ permitted high silylation yields for electron-rich (hetero)aryl iodides. The presence of electron-

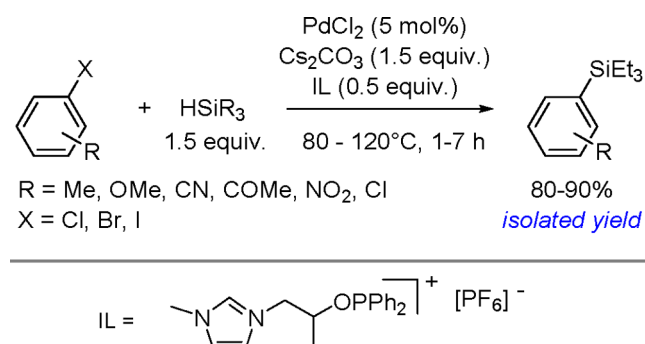
Scheme 175. Silylation of Aryl Iodides with HSi(OEt)₃



accepting substituents in the aryl ring has significantly increased the yield.

Different substituted tertiary silanes, for example, tri(furan-2-yl)silane, tri(thiophen-2-yl)silane, Ph_3SiH , and Ph_2MeSiH , have been successfully used as silylating agents in the presence of $[\text{Pd}(\text{dba})_3(\text{CHCl}_3)]/\text{P}(o\text{-tol})_3/\text{NEt}(i\text{-Pr})_2$ in mild conditions.⁴³⁵ Efficient silylation of aryl chlorides (as well as iodides and bromides) with triethylsilane has been observed in a system containing PdCl_2 , imidazolium-based phosphinite ionic liquid, and cesium carbonate as a base (Scheme 176).⁴³⁶ Silylation in this system occurs with a minor contribution of hydrodehalogenation.

Scheme 176. Palladium-Catalyzed Silylation of Aryl Halides with HSiEt_3

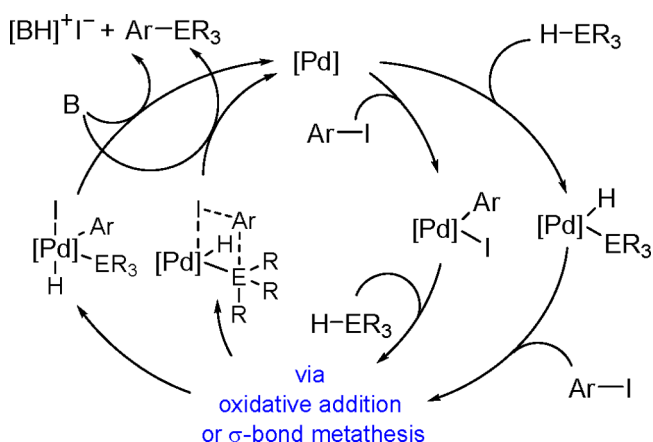


Presently, the reaction achieves effective silylation of aryl iodides, bromides, and chlorides with a variety of tertiary and some secondary silanes. The reaction proceeds more readily for electron-rich arenes and at less sterically crowded positions (e.g., para and meta positions in the aromatic ring). The reaction also permits the syntheses of optically active tertiary silanes via the enantioselective arylation of secondary silanes.⁴³⁷

No mechanism supported by convincing experimental evidence and quantum-chemical calculations has been proposed so far for the silylation of aryl halides with tertiary silanes. The present knowledge of the reaction mechanism is illustrated in Scheme 177.

Results of DFT calculations⁴³⁸ suggest that the preferred mechanism depends on the reaction conditions, composition

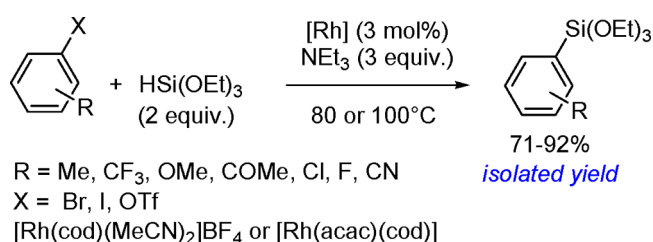
Scheme 177. Current Mechanistic Understanding of the Silylation of Aryl Halides with Tertiary Silanes (HSiR_3)



of the reaction system, and stereoelectronic properties of the catalyst. The suggested first step is the oxidative addition of an aryl iodide to a $\text{Pd}(0)$ complex. Subsequently, a silylation product or a hydrodehalogenation product may form by σ -bond metathesis. A cycle involving palladium(IV) complex formation and its further conversion by reductive elimination cannot be ruled out. Further research is needed to clarify the ambiguities of the reaction mechanism.

In addition to palladium-based systems, the reaction is catalyzed by rhodium complexes. In each case, competition between silylation and reduction of the aromatic ring has been observed. The first selective silylation of aryl iodides and bromides with triethoxysilane $(\text{EtO})_3\text{SiH}$ in the presence of catalytic amounts of $[\text{Rh}(\text{cod})(\text{MeCN})_2][\text{BF}_4]$ and NEt_3 has been described by Murata and Masuda.⁴³⁹ The Rh-catalyzed silylation process leads to the general and efficient silylation of aryl halides with triethoxysilane in the presence of a rhodium catalyst (Scheme 178).⁴⁴⁰ Aryl iodide, bromide, and

Scheme 178. Rhodium-Catalyzed Silylation of Aryl Halides with $\text{HSi}(\text{OEt})_3$

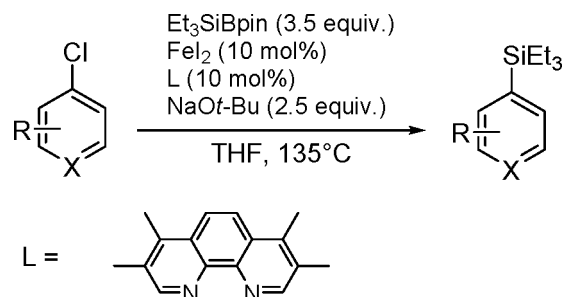


trifluoromethylsulfonate are efficiently silylated with $\text{HSi}(\text{OEt})_3$ in the presence of $[\text{Rh}(\text{cod})(\text{MeCN})_2][\text{BF}_4]$ or $[\text{Rh}(\text{acac})(\text{cod})]$. The substrate scope includes electron-rich and -deficient aryl halides with different substitution patterns. Rhodium catalysts ensure efficient silylation at sterically crowded positions (e.g., in *ortho*-substituted aryl halides).

A variety of aryltriethylsilanes have been synthesized in the presence of a rhodium-based catalytic system consisting of $[\text{Rh}(\text{cod})_2][\text{BF}_4]$ or $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$, K_3PO_4 and *N*-methylpyrrolidinone (NMP) as a solvent.⁴⁴¹ The catalytic system is active already at room temperature and is highly tolerant to various sensitive functional groups on the substrates.

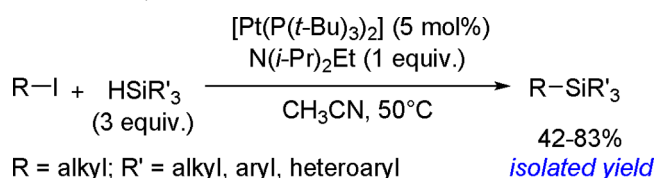
Recently, an iron-catalyzed method for the silylation of (hetero)aromatic chlorides has been reported (Scheme 179). The protocol offers high efficiency, a broad substrate scope, and good functional group compatibility.⁴⁴²

Scheme 179. Iron-Catalyzed Silylation of Aryl Halides with $\text{HSi}(\text{OEt})_3$



4.2.3. Silylation of C(sp³)-X Bonds. Palladium, platinum, iron, cobalt, nickel, and copper salts or complexes have been proved to have catalytic activity in the silylation of alkyl halides or sulfonates. Whereas palladium and platinum complexes are able to catalyze silylation with disilanes (Pd) or tertiary silanes (Pt), the first-row transition metals are active in the presence of silylborane or silyl-derivatives of organozinc and organomagnesium compounds. Copper-catalyzed C(sp³)-Si bond-forming reactions have recently been reviewed.⁴⁰⁸ As early as in 1983, Nagai reported that benzyl chlorides were silylated with Cl₂MeSiSiMeCl₂ in the presence of [Pd(PPh₃)₄]. The corresponding benzyldichloromethylsilanes were obtained in high GLC yields (up to 98%).⁴⁴³ Nonactivated alkyl iodides react in the presence of [Pt(P(*t*-Bu)₃)₂]/N(*i*-Pr)₂Et with tertiary silanes to give alkylsilanes in moderate to good isolation yields (Scheme 180).⁴⁴⁴

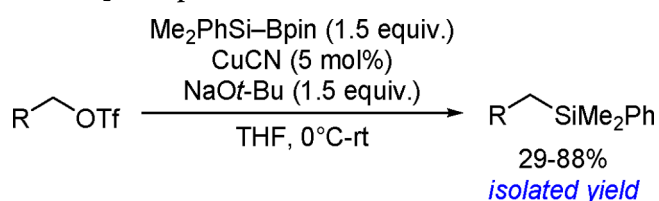
Scheme 180. Platinum-Catalyzed Silylation of Alkyl Iodides with Tertiary Silanes



More recent procedures for C-Si bond formation use nucleophilic silylating agents, for example, Me₂PhSiBpin (Suginome's reagent). The methods based on silylborane reagents have recently gained importance in organic synthesis.^{202,445} Primary and secondary benzyl halides undergo silylation with Me₂PhSiBpin in the presence of only 2 mol % of the [Pd(PPh₃)₄]/Ag₂O palladium catalyst at room temperature.⁴⁴⁶ The reaction permits synthesis of differently substituted benzylphenyldimethylsilanes with yields of 49%–95%.

Primary alkyl triflates undergo silylation with Me₂PhSiBpin in the presence of copper(I) cyanide (Scheme 181).⁴⁴⁷

Scheme 181. Copper-Catalyzed Silylation of Alkyl Triflates with Me₂PhSiBpin



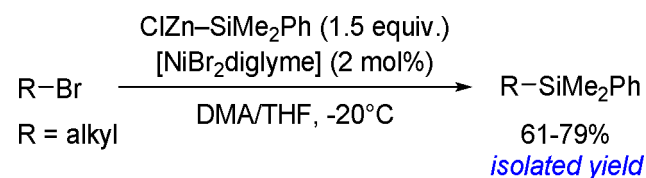
The first metal-catalyzed cross-coupling reactions of inactivated secondary and tertiary alkyl electrophiles to form C-Si bonds were carried out using a nickel-based catalyst and ClZn-SiMe₂Ph as a silylating agent (Scheme 182).⁴⁴⁸ The reaction proceeded efficiently under very mild conditions and tolerated a variety of functional groups.

Iron and cobalt salts are active in the silylation of primary, secondary, and tertiary alkyl bromides with silyl Grignard reagents of the R₃SiMgX type (Scheme 183).⁴⁴⁹

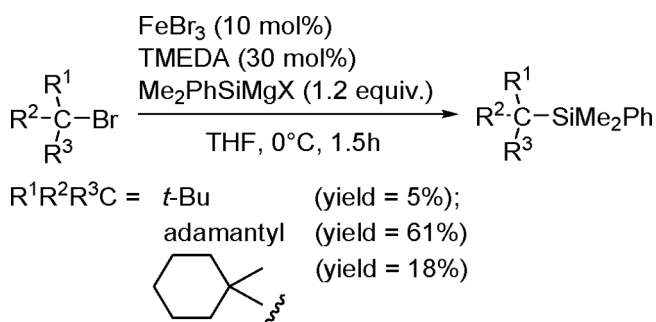
4.3. Germylation of C-X Bonds

Germylation of olefins was attempted first by Tanaka and co-workers.⁴⁵⁰ Palladium-catalyzed germylation of (*E*)-(2-

Scheme 182. Silylation of Inactivated Secondary and Tertiary Alkyl Halides



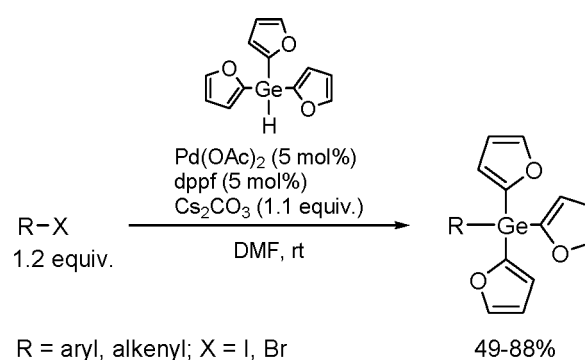
Scheme 183. Fe-Catalyzed Silylation of Tertiary Alkyl Bromides with a Silyl Grignard Reagent



bromovinyl)benzene and (*E*)-1,2-dichloroethene with ClMe₂GeGeMe₂Cl gave yields close to 30%. The first germylation of aryl bromides with Et₃GeGeEt₃ was reported by Eaborn.⁴²⁵ PhGeEt₃ and 4-Me-C₆H₄GeEt₃ were synthesized with yields of 28% and 35%, respectively. Tanaka used similar conditions and employed ClMe₂GeGeMe₂Cl; however, the reaction was nonselective, and the yields did not improve.⁴⁵⁰ In 2018, Yoshino and Matsunaga described the germylation of aryl bromides and aryl triflates using commercially available hexamethyldigermane.⁴⁵¹ In optimized reaction conditions (typically, Pd(OAc)₂, 2-(diphenylphosphanyl)phenol, Cs₂CO₃, Et₄NBr, toluene, 120 °C, 24 h), moderate to good yields (up to 87%) of the corresponding aryltrimethylgermanes were obtained. Tri(furan-2-yl)germane readily reacts with aryl iodide, α- and β-bromostyrene, 1- and 2-bromopropene and 2-bromopyridine in the presence of palladium(II) acetate, 1,1'-bis(diphenylphosphino)ferrocene (dppf) and cesium carbonate (Scheme 184).⁴⁵² Aryltri(2-furyl)germane (formed directly before the reaction) can be used as a reacting partner in palladium-catalyzed coupling with aryl iodide or bromide.

Monoarylation of tertiary germanes, diarylation of secondary germanes and stepwise arylation of secondary and primary germanes with aryl iodides were tested in the presence of

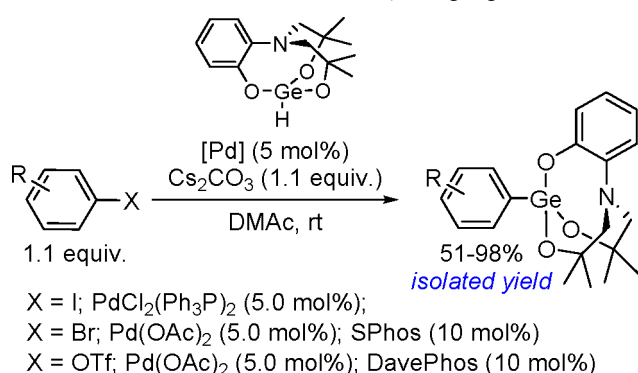
Scheme 184. Germylation of Aryl Halides with Tri(2-furyl)germanes



[Pd{P(*t*-Bu)₃]₂] and a base in THF under mild conditions.⁴⁵³ Depending on the reacting partners, the yields varied in the range of 20%–63%. However, the reaction suffered from the lack of selectivity.

Pd-catalyzed germatrization was shown to be an efficient method for the formation of arylgermatranes (Scheme 185).⁴⁵⁴

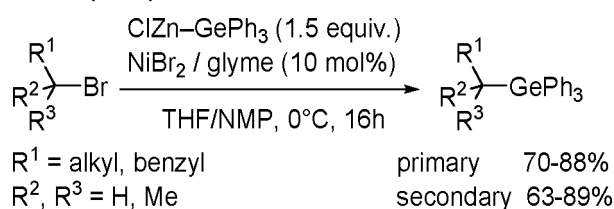
Scheme 185. Germatranes as Germylating Agents



Arylgermatranes can be subsequently used for palladium-catalyzed cross-coupling with aryl halides.

Recently, Oestreich and co-workers have reported methods for the synthesis of C(sp³)–Ge bonds from alkyl electrophiles and germanium nucleophiles.⁴⁵⁵ A germanium Grignard reagent was synthesized and shown to be active in reactions with primary and secondary alkyl bromides. The corresponding germanium zinc reagent (Ph₃GeZnCl) undergoes a nickel-catalyzed reaction with primary, secondary, and, less successfully, tertiary alkyl bromides (Scheme 186).

Scheme 186. Nickel-Catalyzed Germylation of Primary and Secondary Alkyl Bromides



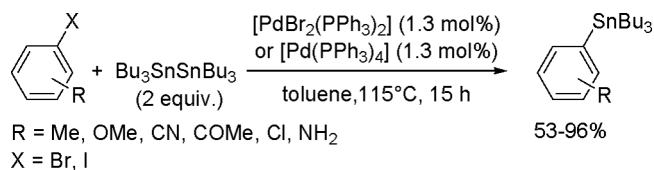
Silylation of tertiary alkyl bromides proceeds less efficiently and is accompanied by C–H bond activation and borylation. Mechanistic studies, in particular the ring opening observed in a radical-probe experiment using (bromomethyl)cyclopropane, the loss of the stereochemical information in the C(sp³)–Ge coupling of an enantioenriched secondary alkyl bromide, and the observed order of reactivity of alkyl bromides (tertiary > secondary > primary) strongly support the involvement of alkyl radical intermediates in the reaction mechanism.

4.4. Stannylation of C–X Bonds

The first examples of the stannylation of aryl halides with distannanes have been reported by Eaborn.⁴²⁵ In the presence of [Pd(PPh₃)₄] at 120 °C in toluene, 1-bromo-4-methoxybenzene reacts with hexamethyldistannane or hexabutyldistannane to give corresponding arylstannanes. The reaction was accompanied by the competitive formation of biaryls. As a result of further studies, the activity of aryl iodides and bromides containing several functional groups—such as OMe,

Cl, CN, COCH₃, NO₂, and bromide and chloride allyl and benzyl derivatives—in the reaction was proved (Scheme 187).⁴⁵⁶ The achievements in the palladium-catalyzed synthesis of stannanes from corresponding organic halides by 2000 were summarized by Marshall.⁴⁵⁷

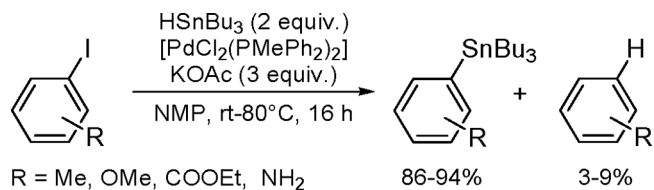
Scheme 187. Stannylation of Aryl Halides with Distannanes



After 2005, the search for new efficient stannylation procedures has been reported rarely. Hanson showed high catalytic activity of [PdCl₂(PhCN)₂]/PCy₃ and [Pd₂dba₃]/PCy₃ in the stannylation of 5- and 6-bromoindoles with Sn₂Bu₆.⁴⁵⁸ Moderate to high yields of stannylation products in reactions of allyl chlorides,⁴⁵⁹ heteroaryl bromides, or iodides have been described.^{460,461} A variety of variously substituted aryl halides have been stannylated with Sn₂Bu₆ at 120 °C in the presence of Pd(OAc)₂/PCy₃.⁴⁶²

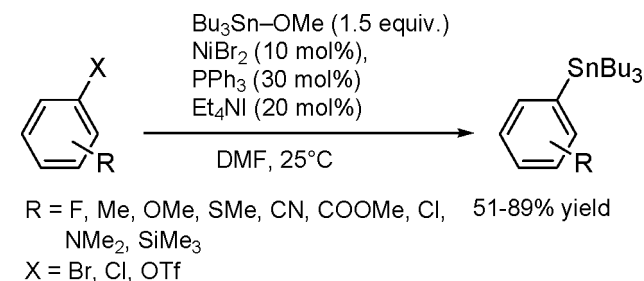
Masuda has demonstrated that HSnBu₃ can be used as a stannylation agent (Scheme 188).⁴⁶³ In the presence of a catalytic amount of [PdCl₂(PMePh₂)₂] and KOAc, aryl iodides undergo coupling with tributyltin hydride to afford the corresponding arylstannanes.

Scheme 188. Stannylation of Aryl Halides with Tributylstannane



It has been established that Sn₂Bu₆ is the actual tin source, formed by the dehydrocoupling of HSnBu₃ under the reaction conditions used. Komeyama and co-workers have reported the nickel-catalyzed stannylation of aryl and alkenyl halides using Bu₃SnOMe as a stannylation agent to afford aryl- and vinylstannanes, respectively (Scheme 189).⁴⁶⁴

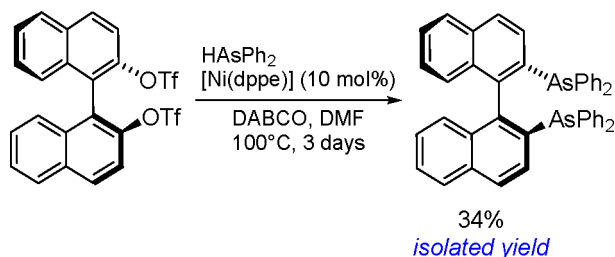
Scheme 189. Stannylation of Aryl Halides with Tributylmethoxystannane



4.5. Arsination, Stibination, and Telluration of C–X Bonds

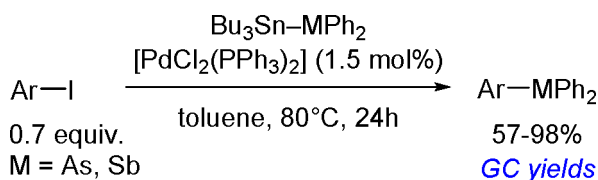
In 1997, Shibasaki described the synthesis of 2,2'-bis-(diphenylarsino)-1,1'-binaphthyl (BINA), the arsine analogue of BINAP (Scheme 190).⁴⁶⁵

Scheme 190. Nickel-Catalyzed Arsination of Aryl Triflates



Rossi and Martín have developed a method leading to functionalized triarylarisines and triarylstibines by the palladium-catalyzed coupling of aryl iodides with reagents containing Sn–As or Sn–Sb (Scheme 191) bonds.⁴⁶⁶

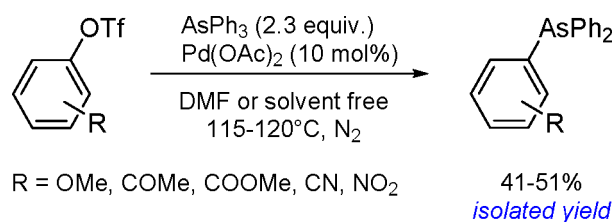
Scheme 191. Palladium-Catalyzed Arsination or Stibination of Aryl Iodides



The scope of the reaction has been extended to *ortho*-substituted aryl iodides containing a variety of functional groups (Br, Cl, NH₂, COOMe), perfluoroalkyl iodides⁴⁶⁷ and naphthyl triflates.⁴⁶⁸ The method has been used for the synthesis of a chiral bis(arsine) ligand.⁴⁴⁸ Mechanistic studies by DFT calculations show that the reaction proceeds according to the typical Stille mechanism, involving oxidative addition, transmetalation, and reductive elimination.⁴⁶⁹ The transmetalation step has been found to be rate-limiting. The lack of reactivity of aryl chlorides in the analogous Stille coupling is a consequence of the high energy barrier for the oxidative addition of aryl halides. The syntheses and applications of organostannanes bonded to group 14, 15, and 16 elements have been reviewed.⁴⁷⁰

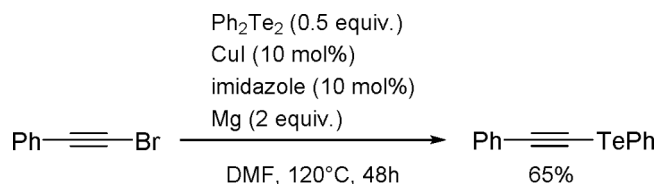
Another method for the synthesis of aryl arsines uses the palladium-catalyzed arsination of aryl triflates with commercially available, air-stable and inexpensive triphenylarsine as the arsinating agent (Scheme 192).⁴⁷¹ The reaction is highly functional group-compatible, but it permits only moderate yields of functionalized aryl arsines.

Scheme 192. Arsination of Aryl Triflates with AsPh₃



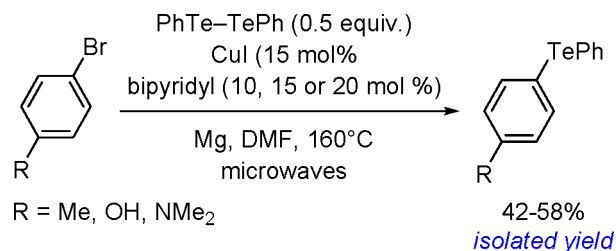
Sharma and Braga have reported a single example of the copper-catalyzed synthesis of alkynyltelluride from alkynyl bromides and diaryl ditellurides (Scheme 193).⁴⁷²

Scheme 193. Telluration of Alkynyl Bromides with Ditellurides



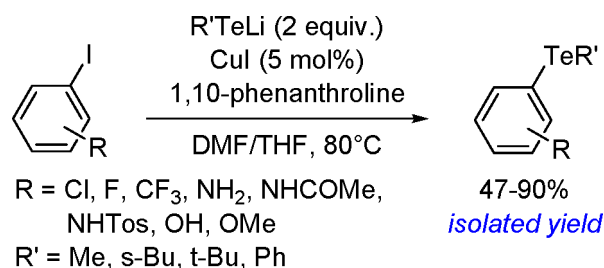
CuI used with bipyridyl has been found to show catalytic activity in the coupling of aryl iodides with diaryl ditellurides (Scheme 194).⁴⁷³ A highly efficient reaction has also been observed for 3-bromopyridine and 1-bromonaphthalene.

Scheme 194. Telluration of Aryl Bromides with Ditellurides



Synthesis of arylmethyltellurides is possible through the copper-catalyzed coupling of aryl iodides with lithium tellurolates (R'TeLi) (Scheme 195).⁴⁷⁴ The tellurating agent is prepared directly before the reaction. The scope of the coupling includes a variety of substituted aryl iodides.

Scheme 195. Copper-Catalyzed Telluration of Aryl Bromides with Lithium Tellurides



5. DEHYDROCOUPLING OF HYDROMETALLOIDS

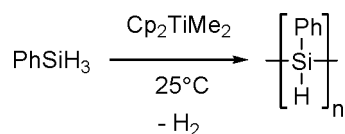
While TM-catalyzed carbon–carbon bond-forming reactions are an extremely important part of modern organic synthesis, the catalytic formation of main group element–element bonds represents a comparatively less studied area.^{475–477} In this section, we focus on the dehydrocoupling reactions of hydrometalloids, but we do not discuss the heterodehydrocoupling reactions of hydrometalloids with compounds containing nonmetal–hydrogen bonds. Macromolecular compounds with metalloid–metalloid bonds show a wide range of applications (e.g., in high-performance elastomers, emissive and preceramic materials, thin films' precursors),⁴⁷⁸ which stimulates the development of their synthesis methods, of the which catalytic

dehydrocoupling of hydrometalloids is the most benign and atom-economical process.

Catalytic formation of metalloid–metalloid bonds via the dehydrogenative coupling of hydrometalloids was first reported by Sneddon and Corcoran in 1984 for the coupling of polyhedral boron cages using PtBr_2 as a catalyst.⁴⁷⁹ The development of methods for coupling boronate esters was much more important as diborane esters are valuable reagents in catalytic borylation and bis-boration processes. Catalytic dehydrocoupling of pinacolborane and catecholborane has been discovered using palladium(II) and platinum(II) complexes with bidentate phosphine ligands as well as heterogeneous systems involving palladium, rhodium, and platinum on alumina, of which the last one seems to be most effective (with TONs of up to 11 600).^{480,481} In addition, the rhodium(I)-mediated homocoupling of amine-borane ($\text{H}_3\text{B-NMe}_3$), which gives a diborane coordinated to a Rh(I) center,⁴⁸² and the rhodium(I)-catalyzed homocoupling of guanidine bases containing B–H bonds have been reported.⁴⁸³ The dehydrocoupling of the bulky $\text{H}_2\text{B}(\text{dur})$ aryldihydroborane (dur = 2,3,5,6-tetramethylphenyl) with equimolar amounts of $[\text{Pt}(\text{PCy}_3)_2]$ leads to electron-precise boron networks with bridging diborene and diborane(3) ligands and a platinum complex with both borylene and borane ligands.⁴⁸⁴ More recently, the dehydrocoupling of the electron-poor 3,5-(CF_3)₂ $\text{C}_6\text{H}_3\text{BH}_2$ aryldihydroborane mediated by a $[(\text{Cp}^*\text{Ru})_2(\mu\text{-H})_4]$ diruthenium–tetrahydrido complex has been reported, which yields an anionic ruthenium complex bearing a tetraarylated chain of four boron atoms.⁴⁸⁵ Longer chains of boronated molecules are practically nonexistent. Computational studies of B_nH_{n+2} homologues have shown that in the absence of electronic or steric perturbations, the stability of linear B–B chains quickly diminishes relative to cluster structures as n increases.⁴⁸⁶

The dehydrocoupling of organosilanes is an efficient method for producing polysilanes known as polymers with interesting electronic and optical properties resulting from the strong delocalization of σ electrons along the main silicon chain. Development of the dehydrocoupling of primary silanes to produce Si–Si bonds began with the discovery by Harrod and co-workers that the $[\text{Cp}_2\text{TiMe}_2]$ complex initiated the polycondensation of PhSiH_3 with the evolution of molecular hydrogen to produce phenylsilane oligomers (with DPs of around 10–20) (Scheme 196).⁴⁸⁷

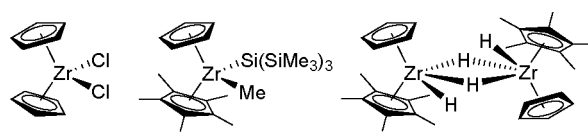
Scheme 196. Dehydrocoupling of Primary Silanes in the Presence of Cp_2TiMe_2



Tilley and Corey as well as Harrod and Tanaka groups developed other active catalytic systems (Scheme 197) leading to polysilanes, mainly group 4 metallocenes of the R_2MX_2 type (where M is Zr or Ti, R is Cp or Cp^* , and X is usually halide or alkyl) for mechanistic and synthetic studies (e.g., $\text{Cp}_2\text{ZrCl}_2/2n\text{-BuLi}$, $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$, $[\text{CpCp}^*\text{ZrH}_2]_2$, Cp_2ZrMe_2 , $\text{Cp}^*_2\text{NdCH}(\text{SiMe}_3)_2$).^{488,489}

The condensation of secondary silanes usually requires more rigorous conditions, and as yet no universal catalyst has been reported to efficiently couple tertiary silanes, with the

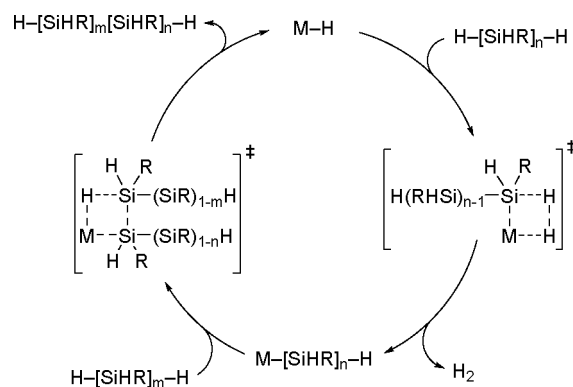
Scheme 197. Zirconium Metallocene Catalysts for the Dehydrocoupling Reactions of Silanes



exception of structurally complex substrates (e.g., Si–H-functionalized dithienophosphole in the presence of Karstedt's catalyst).⁴⁹⁰

Detailed mechanistic studies of the early TM-catalyzed dehydrocoupling of silanes have revealed σ -bond metathesis via four-membered metallacyclic transition states. In most cases, the active catalyst is considered to be a coordinatively unsaturated metal hydride. The coupling is essentially concerted $2\sigma + 2\sigma$ cycloaddition and passes through two 4-center transition states, resulting in chain elongation by step growth (Scheme 198).⁴⁹¹

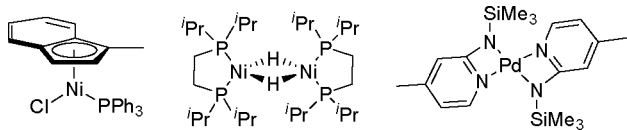
Scheme 198. Mechanism of the Early TM-Catalyzed Dehydrocoupling of Silanes



Platinum group metal complexes have also been applied as catalysts in the dehydrocoupling of silanes, with activities comparable to those of early metal complexes; however, these reactions usually show low selectivity and produce a mixture of short-chain linear and cyclic oligomers. However, there are some exceptions of increased selectivity. $[\text{Pt}(\text{cod})_2]$ has been found to be a good catalyst for the dehydropolymerization of secondary aliphatic silanes (with yields of 76–92%) and silafluorene to produce linear polymers.⁴⁹² Rosenberg and co-workers reported Wilkinson's catalyst used in the dehydrogenative coupling of primary and secondary silanes and confirmed the presence of rhodium–hydride species as active catalysts.^{493,494} For example, Ph_2SiH_2 was reported to dehydrocouple at room temperature with a $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst to afford selectively $\text{Ph}_2\text{HSiSiHPh}_2$ in a yield of 78%. An aminopyridinato–palladium complex successfully catalyzed the polymerization of $\text{MeH}_2\text{SiSiH}_2\text{Me}$ toward linear poly(methylsilane).⁴⁹⁵ In most cases, the postulated mechanism involves transition metal–silylene complexes as the key intermediates.

The dehydrocoupling of phenylsilane and phenylmethylsilane in the presence of the dimeric hydride-bridged nickel–phosphine complex $[(\text{dippe})\text{Ni}(\mu\text{-H})_2]$ (dippe = 1,2-bis-(diisopropylphosphino)-ethane) has been reported, leading to linear oligosilanes (PhSiH)_n and (PhSiMe)_n ($n = 10\text{--}16$) (Scheme 199). The proposed catalytically active species is a

Scheme 199. Late TM Catalysts for the Dehydrocoupling of Silanes



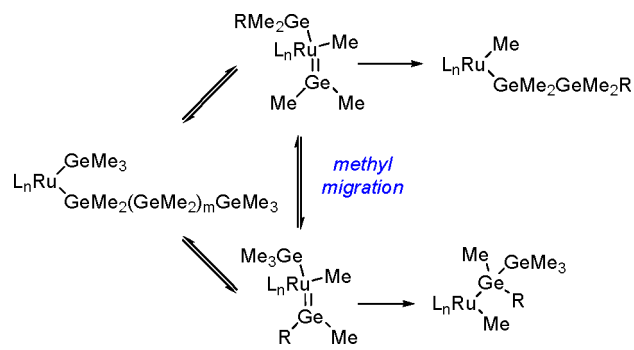
hydrido-silyl-nickel(II) complex formed by dimer cleavage in a reaction with a silane.⁴⁹⁶ On the other hand, the dehydrogenative polymerization of hexylsilane or phenylsilane catalyzed by the $[\text{Ni}(\text{dmpe})_2]$ complex (dmpe = 1,2-bis(dimethylphosphino)ethane) yielded cyclic silanes as predominant products.⁴⁹⁷ The $[\text{Ni}(\text{dmpe})_2]$ complex has also been applied as a catalyst for the dehydrogenative polymerization of silafluorenes.⁴⁹⁸ The nickel(0) complex $[\text{Ni}_2(\text{iPr}_2\text{Im})_4(\text{cod})]$ (iPr_2Im - 1,3-(diisopropyl)imidazol-2-ylidene) has been found an effective catalyst for the acceptorless dehydrogenative coupling of Ph_2SiH_2 to the corresponding disilane $\text{Ph}_2\text{HSi-SiHPh}_2$ and trisilane $\text{Ph}_2\text{HSi-Si}(\text{Ph})_2\text{-SiHPh}_2$, whereas the coupling of PhSiH_3 gives a mixture of cyclic and linear oligomers (with $5 < n < 17$). Nickel silyl complexes, that is, $\text{cis-}[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{HSiPh}_2)_2]$ and $[\{(\text{iPr}_2\text{Im})\text{Ni}(\mu^2\text{-}(\text{HSiPh}_2)_2)\}_2]$, have been identified in the resulting mixture and they are likely to be the intermediates in the catalytic cycle.⁴⁹⁹

Another application of a nickel-based precatalyst for phenylsilane dehydropolymerization involves an indenyl-phosphine-nickel complex, $[(1\text{-MeInd})\text{Ni}(\text{PPh}_3)\text{Cl}]$, known as an alkene polymerization catalyst.⁵⁰⁰ Generally, the mechanism of late TM-catalyzed dehydrogenative polymerization has not yet been fully clarified, and three possible options for Si-Si bond formation are postulated: via repetitive σ -bond metathesis, via disproportionation through a metal-silylene complex, or via oxidative addition/reductive elimination.

The activation of third- and fourth-row main group E-H bonds (E = Ge, As, Sn, Sb, Te) has been less studied since the resulting E-E bonds have generally reduced stability relative to that of the lighter *p*-block elements. Harrod and co-workers have reported that phenylgermane PhGeH_3 reacts in the presence of $[\text{Cp}_2\text{TiMe}_2]$ catalysts by analogy with phenylsilane to afford complex germanium-based polymers as a result of the further intermolecular dehydrocoupling and cross-linking of $(\text{PhGeH})_n$ oligomers.⁵⁰¹ Similar results have been achieved by Tanaka and Choi using $[\text{Cp}_2\text{ZrCl}_2]$ or $[\text{Cp}^*\text{CpZrCl}_2]$ complexes activated by *n*-BuLi.⁵⁰² On the other hand, the $[\text{Ru}(\text{PMe}_3)_4(\text{GeMe}_3)_2]$ -catalyzed coupling of tertiary germane HGeMe_3 led to highly branched polygermanes, as reported by Berry and co-workers.⁵⁰³ This unprecedented demethanative coupling proceeded through sequential α -methyl- and germyleto-germylene migration steps to form ruthenium-germylene intermediates (Scheme 200).

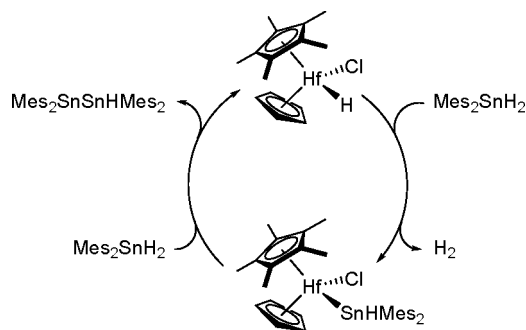
The dehydrocoupling of dialkylstannanes proceeds with catalysts based on zirconium, lanthanides, rhodium, or palladium.⁵⁰⁴ Tilley and co-workers reported the catalytic dehydrocoupling of secondary stannanes mediated by zirconocenes (e.g., $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3\text{Me}]$) to yield a mixture of high-molecular weight polystannanes and cyclic oligomers.⁵⁰⁵ The dehydrogenative dimerization of Mes_2SnH_2 (Mes = mesityl) has been successfully performed with the $[\text{CpCp}^*\text{Hf}(\text{H})\text{Cl}]$ complex.⁵⁰⁶ Isolation of the hafnium-hydrostannyl complex $[\text{CpCp}^*\text{Hf}(\text{SnHMe}_2)\text{Cl}]$ as an inter-

Scheme 200. Mechanism of the Demethanative Coupling of HGeMe_3



mediate supported the concept of the key role of inorganometallic species in catalysis (Scheme 201). The

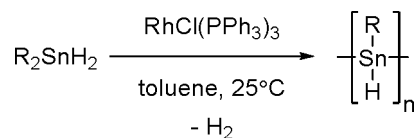
Scheme 201. Mechanism of the Dehydrocoupling of Diarylstannanes in the Presence of a Hafnium Catalyst



dehydrocoupling appears to occur by elimination of a SnMe_2 molecule from $[\text{CpCp}^*\text{Hf}(\text{SnHMe}_2)\text{Cl}]$, with Sn-Sn bond formation proceeding via stannylene insertion into the Sn-H bond.

Wilkinson's catalyst has been reported to yield linear polystannanes using secondary stannanes such as *n*-Bu₂SnH₂ as substrates at room temperature (Scheme 202),^{507,508} whereas the dichlorobis(triphenylphosphine)palladium(II) complex promoted the formation of cyclic oligomers.⁵⁰⁹

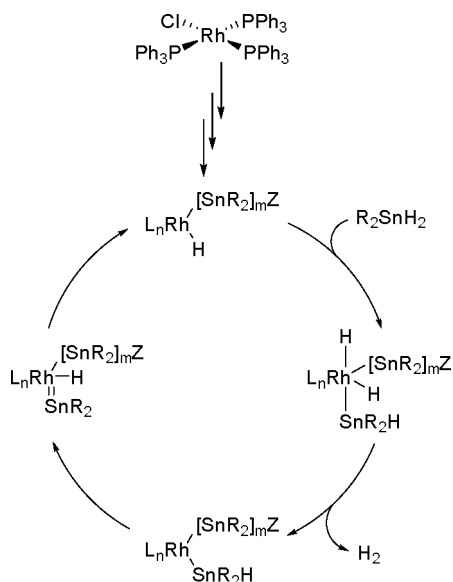
Scheme 202. Dehydrocoupling of Dialkylstannanes in the Presence of Wilkinson's Catalyst



The proposed mechanism for the late TM-catalyzed dehydrocoupling of secondary stannanes involves an oxidative-addition and reductive-elimination sequence followed by α -hydrogen elimination to furnish a stannylene ligand before the subsequent insertion into a growing stannane chain (Scheme 203).

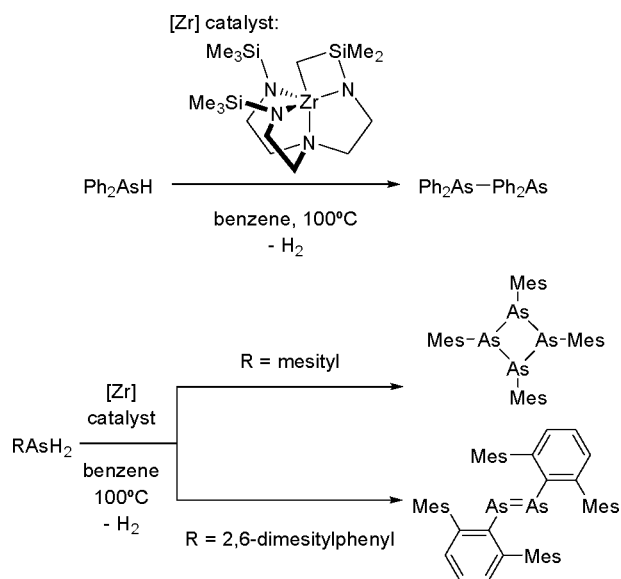
Dehydrocoupling of secondary arsine leads to the formation of dimeric species with As-As bonds in the presence of triamidoamine-supported zirconium complexes, $(\text{N}_3\text{N})\text{ZrX}$ (where N_3N is $\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3^{3-}$ and X is a mono-anionic ligand). Mechanistic studies show that As-As bond formation proceeds via σ -bond metathesis steps similarly to the

Scheme 203. Mechanism of Dialkylstannane Dehydrocoupling in the Presence of Wilkinson's Catalyst



previously reported dehydrocoupling of phosphines by the same catalysts. The reaction of primary arsines bearing bulky ligands (MesAsH_2 or dmpAsH_2 ($\text{dmp} = 2,6\text{-dimesitylphenyl}$)) under similar conditions resulted in the formation of a *trans*-bent diarsene dimer $(\text{dmp})\text{As} = \text{As}(\text{dmp})$ (through the elimination of the arsinidene molecule (dmpAs:) from the arsenido–zirconium intermediate ($(\text{N}_3\text{N})\text{ZrAsH}(\text{dmp})$) or the cyclic Mes_4As_4 tetramer, depending on the level of steric crowding caused by the ligand (Scheme 204).⁵¹⁰

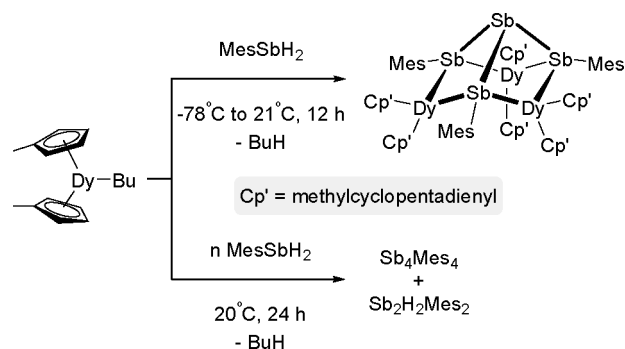
Scheme 204. Dehydrocoupling of Hydroarsines in the Presence of a Zirconium Catalyst



Similar reactivity has been observed for stibine dehydrocoupling. The reaction of the MesSbH_2 primary stibine with group 4 metallocene catalysts (e.g., $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]$, $[\text{CpCp}^*\text{Hf}(\text{H})\text{Cl}]$) proceeds effectively to generate the Sb_4Mes_4 cyclic tetrastibetane.⁵¹¹ It has been confirmed that the reaction occurs through α -hydrogen migration with stibinidene ($:\text{SbR}$)

elimination from the $[\text{CpCp}^*\text{HfCl}\{\text{Sb}(\text{H})\text{Mes}\}]$ intermediate, formed in a stoichiometric reaction between $[\text{CpCp}^*\text{Hf}(\text{H})\text{Cl}]$ and MesSbH_2 . MesSbH_2 dehydrocoupling activated by $n\text{-BuLi}$ in the presence of the $[\text{Cp}'_3\text{Y}]$ ($\text{Cp}' = \text{methylcyclopentadienyl}$) yttrium metallocene complex occurs to give a 1,2-distibane ($\text{Sb}_2\text{H}_2\text{Mes}_2$) and tetrastibetane (Sb_4Mes_4). $[\text{Cp}'_3\text{Dy}]$ used as a precatalyst furnished a more complex product of the *cross*-dehydrocoupling of the former with MesSbH_2 .⁵¹² Such dysprosium compounds that contain the unusual $[\text{Sb}_4\text{Mes}_3]^{3-}$ Zintl-like ligand (e.g., $[(\eta^5\text{-Cp}'_2\text{Dy})_3\{\mu\text{-}(\text{SbMes})_3\text{Sb}\}]$) have been found as promising single-molecule magnets (Scheme 205).

Scheme 205. Cross-Dehydrocoupling of a Dysprosium Metallocene Complex with MesSbH_2



The $[\text{Cp}'_2\text{YSb}(\text{H})\text{Mes}]$ stibinide complex has been proposed as an active catalyst, but the formation of $\text{Sb}_2\text{H}_2\text{Mes}_2$ suggests that the dehydrocoupling does not occur via stibinidene (MesSb:) elimination. In the case of yttrium catalysis, the reaction mechanism involves the formation of a cyclic, four-membered transition state in which a distibine ($\text{Sb}_2\text{H}_2\text{Mes}_2$) and a $[\text{Cp}'_2\text{YH}]$ yttrium–hydride intermediate are generated (Scheme 206).⁵¹² To explain the formation of Sb_4Mes_4 from $\text{Sb}_2\text{H}_2\text{Mes}_2$, the formation of the $\text{MesSb} = \text{SbMes}$ distibene via β -hydride elimination of the distibinide intermediate, $[\text{Cp}'_2\text{Y}\{\text{RSb} - \text{Sb}(\text{H})\text{R}\}]$, has been proposed.

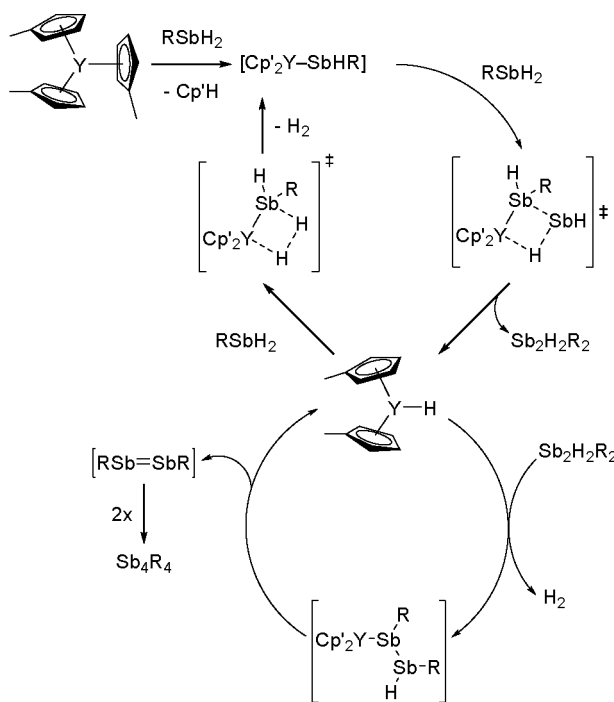
Heterodehydrocoupling reactions require that bonds between different metalloids are formed selectively over competitive homodehydrocoupling, so these are generally more challenging processes. It is worth emphasizing that among this group of processes, the dehydrocoupling of hydroboranes or hydrosilanes with P–H and N–H bonds is of practical importance, and it has been described in other reviews.^{513–515}

The synthesis of silylboranes through the catalytic borylation of Si–H bonds has been reported by Boebel and Hartwig.⁵¹⁶ The reaction of trialkylhydrosilanes with B_2pin_2 catalyzed by the combination of $[\text{Ir}(\text{OMe})\text{cod}]_2$ and 4,4'-di-*tert*-butylbipyridine (*dtbpy*) leads to the formation of trialkylsilyl-(pinacolato)boranes in good yields (Scheme 207).

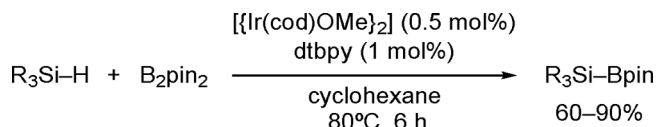
A titanocene catalyst (Cp^*_2TiH) has been used for the preparation of Sn–Te bonds by heterodehydrocoupling (Scheme 208).⁵¹⁷ The reaction of tributylphosphine telluride ($\text{Te} = \text{PBU}_3$) with tributylstannane led to $\text{Bu}_3\text{Sn}-\text{Te}-\text{SnBu}_3$, a potential single-source precursor for the synthesis of tin telluride (SnTe), a small band gap semiconductor.

This reaction is postulated to proceed via $[(\text{Cp}^*_2\text{Ti})_2(\mu\text{-Te})]$ and $[\text{Cp}^*_2\text{Ti}(\text{H})\text{TeSnBu}_3]$ as intermediates (Scheme 209).

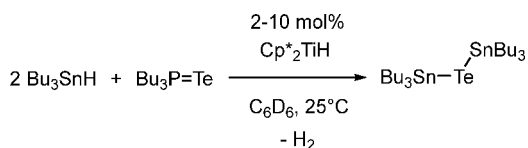
Scheme 206. Dehydrocoupling of Stibines in the Presence of an Yttrium Catalyst



Scheme 207. Iridium-Catalyzed Cross-Dehydrocoupling of Hydrosilanes with Diboranes



Scheme 208. Preparation of Sn–Te Bonds by Heterodehydrocoupling



6. ACTIVATION (AND FUNCTIONALIZATION) OF C–H BONDS WITH VINYLMETALLOIDS

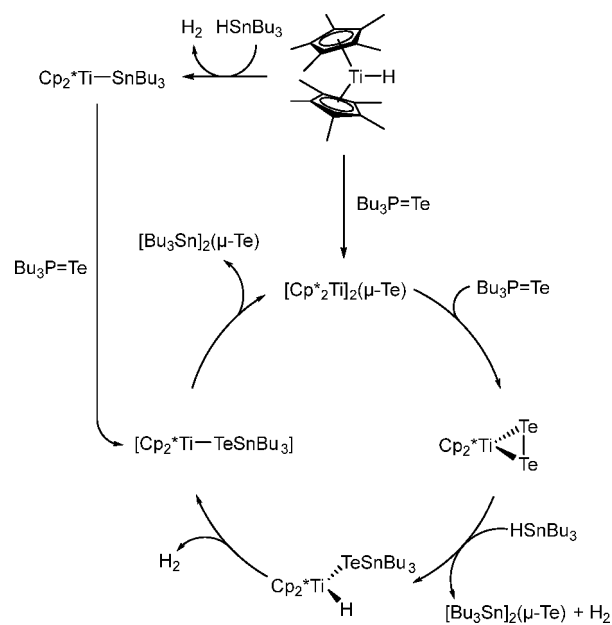
In the systems that contain hydride complexes or enable their generation in situ, vinylmetaloids can be used for TM–E bond formation (Scheme 210).

6.1. Borylation of C–H Bonds

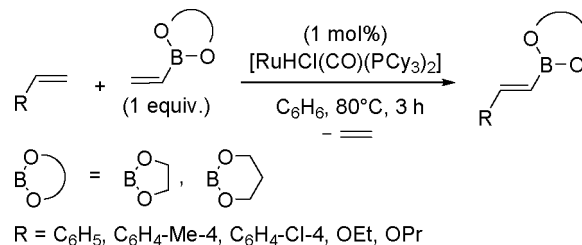
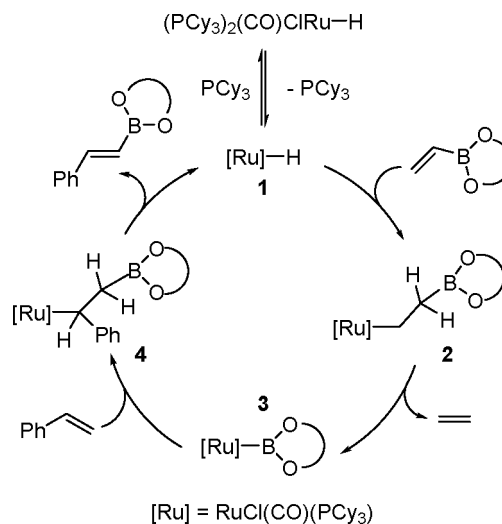
Vinyl-substituted boronates (i.e., vinyl-dioxaborolane and vinyl-dioxaborinane) have been reported to react with olefins in the presence of $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ with formation of functionalized vinylboronic derivatives and evolution of ethene (Scheme 211).⁵¹⁸

Deethenative coupling achieves yields of 80%–95% and full E-stereoselectivity in the borylation of styrenes and vinyl ethers. Investigation of the reaction between the boryl complex $[\text{Ru}(\text{Bcat})\text{Cl}(\text{CO})(\text{PCy}_3)_2]$ and styrene suggested a mechanism of the reaction (Scheme 212). It assumes that the active catalyst species is a monophosphine–chlorohydridocarbonyl–ruthenium complex (1). In the first step of the reaction,

Scheme 209. Mechanism of the Dehydrocoupling of Tributylphosphine Telluride with Tributylstannane

Scheme 210. Formation of TM–E bonds via Sequential Insertion and β -E-Elimination

Scheme 211. Ruthenium-Catalyzed Deethenative Borylation of Olefins

Scheme 212. Mechanism for the Ru-Catalyzed Deethenative Borylation of Olefinic C–H Bonds⁵⁰⁶

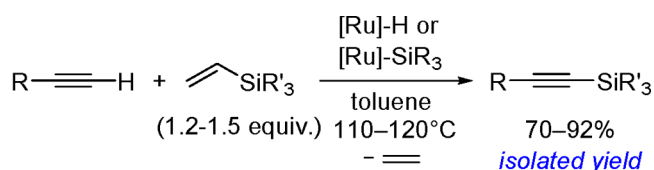
vinylboronate associates to complex **1** and undergoes migratory insertion into the Ru–H bond to produce **2**. Subsequently, a boryl complex (**3**) is formed, and ethylene is eliminated via β -boryl elimination. Styrene then undergoes association and migratory insertion into the ruthenium–boron bond to form **3**. Finally, vinylboronate is formed, and complex **1** is regenerated via β -hydrogen elimination.⁵¹⁸

This mechanism was confirmed by DFT studies of the β -boryl elimination process.⁵¹⁹ The studies conducted for a simplified model layout showed reversibility of deethenative borylations and relatively low energetic barriers for these processes. A relatively small effect of the phosphine nucleophilic character on the energy profile of the process was shown.

6.2. Silylation and Germylation of C–H Bonds

In 2006, the Marciniak group reported a new catalytic method for the synthesis of silylalkynes with vinylsilanes as silylating agents (Scheme 213).⁵²⁰ This deethenative silylation of

Scheme 213. Ruthenium-Catalyzed Deethenative Silylation of Acetylenes



[Ru] = RuClCO(PCy₃)₂ and four other complexes

R = alkyl, cycloalkyl, trialkylsilyl

SiR'₃ = SiMe₂Ph, Si(OEt)₃, SiMe(OSiMe₃)₂

acetylenes was shown to occur in the presence of ruthenium complexes containing [Ru]–H or [Ru]–Si bonds, such as [RuHCl(CO)(PCy₃)₂], [RuHCl(CO)(Pi-Pr₃)₂], [RuH(CO)(MeCN)₂(PCy₃)₂][BF₄], and [Ru(SiMe₃)Cl(CO)(PPh₃)₂], with evolution of ethene and selective formation of silyl-substituted acetylenes with yields in the range of 70%–100%. The reaction is efficient in the presence of a series of vinylsilanes containing a variety of silyl groups, such as SiMe₂Ph, SiMe₂(OSiMe₃), SiMe(OSiMe₃)₂, and Si(OEt)₃, as well as vinylsiloxanes and vinylsilazanes.

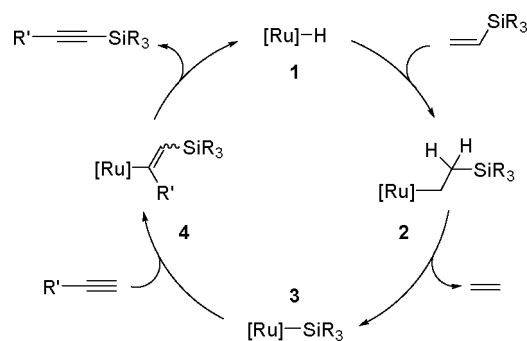
On the basis of an analysis of the literature data on the formation of silyl complexes from ruthenium hydrides^{521,522} and studies of the stoichiometric reaction of silyl complexes with phenylacetylene, a reaction mechanism has been proposed. The mechanism involves vinylsilane insertion into the ruthenium–hydrogen bond followed by β -H elimination to form a ruthenium–silyl complex (**3**). The subsequent step is proposed to be the migratory insertion of terminal acetylene into the ruthenium–silicon bond (Scheme 214). However, the details of the isomerization of complex **4**, necessary for the postulated β -H elimination, require further investigation.⁵²⁰

In subsequent papers, the Marciniak group showed that the reaction can be used for the effective synthesis of germylacetylenes (Scheme 215).⁵²³

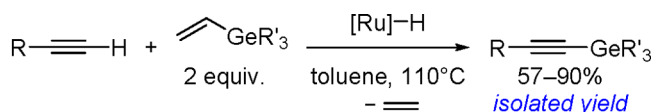
Through the successful isolation of a germyl–ruthenium complex and the investigation of its stoichiometric reactions with acetylenes a mechanism has been proposed, analogous to that presented in Scheme 214.^{523,524}

The deethenative silylation of olefins has first been described by the Marciniak⁵²⁵ and Seki⁵²⁶ groups in the study of

Scheme 214. Mechanism of the Ru-Catalyzed Deethenative Silylation of C(sp)–H Bonds



Scheme 215. Ruthenium-Catalyzed Deethenative Germylation of Acetylenes



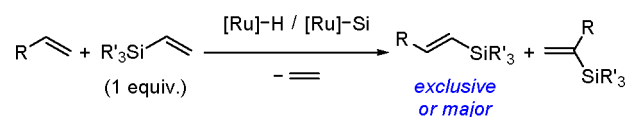
[Ru] = RuClCO(PCy₃)₂ and four other complexes

R = alkyl, cycloalkyl, aryl, silyl, germyl

GeR'₃ = GeEt₃, GeMe₂Ph

hydrosilylation processes in the presence of ruthenium complexes (Scheme 216).

Scheme 216. Deethenative Silylation of Olefins



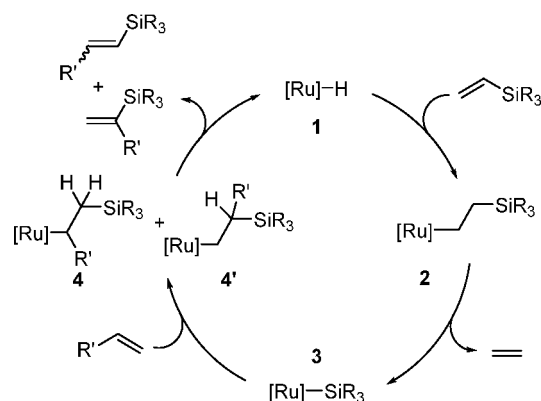
R = alkyl, aryl, silyl, OR"

R' = alkyl, aryl, OR"

The reaction has been addressed in several reviews.^{527–529} The process occurs in the presence of ruthenium, rhodium, cobalt, and iridium complexes. However, the highest yields have been reported for ruthenium-based catalysts, in particular [RuHCl(CO)(PCy₃)₂]. The most important application examples for organic synthesis have been described in ref 530. The catalytic system used tolerates many functional groups, including F, Cl, Br, OR, silyl, thiophenyl, ferrocenyl, carbazolyl, borolanyl, and borinanyl. In the reaction with vinylaromatic compounds, E isomers form exclusively. The applications of the process in synthesis are illustrated by the silylation of dienes,⁵³¹ N-vinylcarbazole,⁵³² vinylferrocene,⁵³³ and vinyl ethers.⁵³⁴ An attractive possibility of using the reaction in the modification of vinylsiloxanes has been demonstrated.⁵³⁵

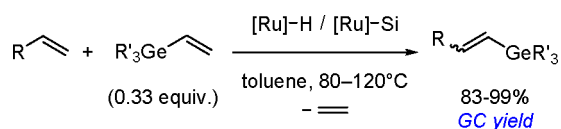
The mechanism of deethenative coupling in the presence of ruthenium complexes has been proposed by Wakatsuki⁵²¹ and Marciniak⁵³⁶ groups on the basis of studies on the reactivity of ruthenium–hydride complexes with vinylsilanes⁵²¹ and silyl complexes with styrenes.^{522,536} In addition, studies were performed with deuterium-labeled reagents.⁵²² According to the mechanism (Scheme 217), hydride and/or silyl complexes are the active catalysts of the reaction.

How easily a silyl complex forms through the sequence of vinylsilane migratory insertion into the Ru–H bond and β -SiR₃ elimination, leading to a silyl complex and ethane, is of

Scheme 217. Mechanism of the Ru-Catalyzed Deethenative Silylation of Olefinic C(sp²)-H Bonds

key importance for the silylation process with vinylsilanes. Removal of ethene from the reaction medium allows the process to run almost quantitatively. In the next step, the olefin undergoes insertion into the Ru–Si bond. Subsequent β -H elimination gives ruthenium hydride and a silylated olefin. Selectivity depends on the nature of the R group in the olefin and the substituents at silicon. The silylation of styrenes and vinylarenes leads almost exclusively to E-isomer formation.

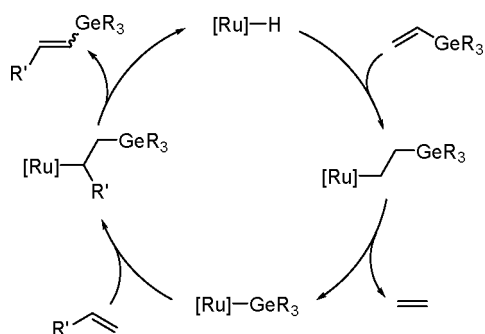
Further studies on the reactivity of vinylmetaloids performed by Marciniak group revealed a similar transformation of vinylgermanes (Scheme 218),⁵²⁴ and a new method of olefin germylation was proposed.

Scheme 218. Deethenative Germylation of Olefins

R' = Me, Et

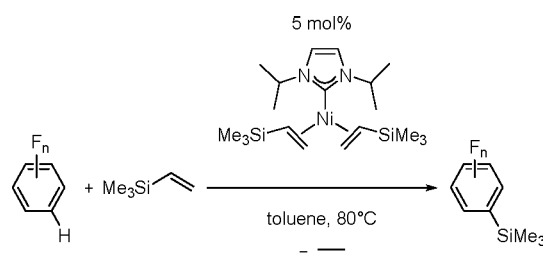
R = aryl, OBU, 9-carbazole, 2-pyrrolidinone, GeEt₃

The germylation of styrenes, 9-vinylcarbazole, 1-vinylpyrrolidin-2-one, and vinyltriethylgermane with H₂C=CHGeEt₃ runs stereoselectively, with the exclusive formation of E-isomers. A mechanism of the process has been proposed on the basis of studies on the reaction of the ruthenium-hydride complex with vinylgermane, isolation and characterization of the ruthenium–germyl complex, and the determination of its reactivity with olefins (Scheme 219). [RuCl-

Scheme 219. Mechanism of the Ru-Catalyzed Deethenative Germylation of Olefinic C(sp²)-H Bonds

(CO)(GeMe₃)(PPh₃)₂] has been proved to be catalytically competent in the reaction. The proposed mechanistic scheme, by analogy with the previous schemes, involves sequential insertion of vinylgermane into the ruthenium–hydride complex followed by β -Ge-elimination and olefin insertion into the ruthenium–germyl complex followed by β -H-elimination.

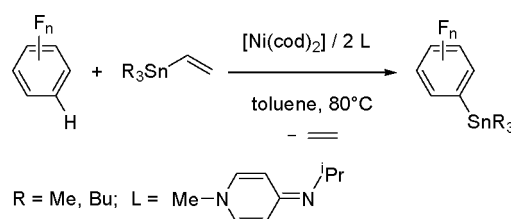
The first example of C–H bond silylation in aromatic compounds with vinylsilanes was provided in 2000 by the Murai group who reported the catalytic activity of [Ru₃(CO)₁₂] in the silylation of heteroarels.³¹¹ In 2017, similar deethenative silylation of the aromatic C–H bond was described in the presence of a nickel complex, [Ni(NHC)(η^2 -H₂C=CHSiMe₃)₂] (where NHC = 1,3-di(iso-propyl)-imidazol-2-ylidene) (Scheme 220).⁵³⁷

Scheme 220. Nickel-Catalyzed Deethenative Silylation of Fluoroarenes

Similar transformations were observed for vinylgermanes.⁵³⁸

6.3. Stannylation of C–H Bonds

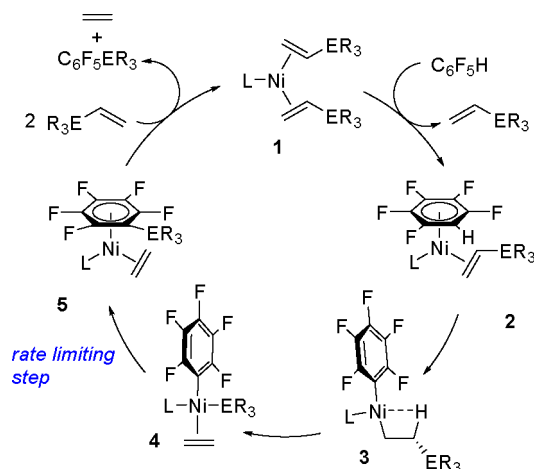
Stannylation of the fluoroarene C–H bond with vinylstannane was reported by Johnson and co-workers (Scheme 221).⁵³⁹

Scheme 221. Nickel-Catalyzed Deethenative Stannylation of Fluoroarenes

R = Me, Bu; L = Me-N-C₆H₄-N-Pr

The scope of arene C–H activation and functionalization with vinylmetaloids is limited to fluorinated aromatics and the trimethylsilyl group. The deethenative stannylation reaction activates one, two, or three C–H bonds in the ring. In the optimum conditions, the yields of stannylated arenes were 90%–99% in most cases.⁵³⁹ Silylation is the most difficult Ni-catalyzed arene metalation process with vinylmetaloids, but the proper choice of the catalyst and high temperature of the process permit high yields of arylsilanes. On the basis of kinetic studies and DFT computations, a mechanism of the deethenative metalation of arenes has been proposed (Scheme 222).⁵³⁸

For all vinylmetaloids, the mechanism involves a similar sequence of steps starting with the oxidative addition of the C–H bond to the π -olefin complex (2), leading to a σ -alkyl stabilized by the interaction of hydrogen at position β with the metal center (3). As a result of β -ER₃ elimination, complex 4 is formed and undergoes reductive elimination of the carbon–

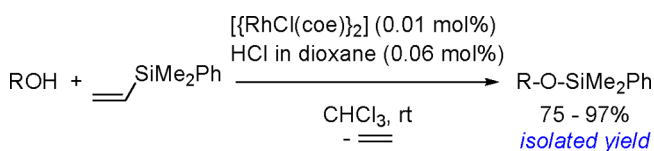
Scheme 222. Mechanism of the Ni-Catalyzed Deethenative Metallation of Aryl C(sp²)-H Bonds⁵³⁸

metalloid bond. The cycle is closed by the dissociation of ethylene and the association of two vinylmetaloid molecules. The reductive elimination is the rate-limiting step. The energies of the key intermediates and the transition states for the key reaction steps differ for derivatives of different metalloids. Particularly for vinylsilanes, high energies of the transition states are observed, corresponding to β -SiMe₃ elimination and reductive elimination of arylsilane. Complex 3, in the presence of silicon as a metalloid and ligand L of high steric hindrance (e.g., IMes), may undergo a competing reductive elimination of the C–C bond and formation of a hydroarylation product. The choice of ligand L of lower steric hindrance (e.g., 1,3-diisopropylimidazol-2-ylidene) permits selective silylation.⁵³⁸

6.4. Functionalization of O–H and N–H Bonds with Vinylmetaloids

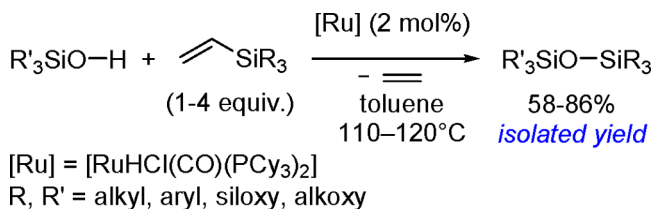
Catalytic alcohol silylation methods involve hydrosilylation of the C=O bond, dehydrocoupling of alcohols with the H–Si bond, and a relatively new silylation with vinylsilanes. The first silylation of alcohols (and phenols) with vinylsilane in the presence of Wilkinson's catalyst ([RhCl(PPh₃)₃]) has been reported by Jun.⁵⁴⁰ The scope of the reaction includes efficient silylation of phenol, pyrocatechol, benzyl alcohol, alkyl alcohols, diol, and triol with vinyltrimethylsilane. Corresponding silyl ethers were formed with high isolation yields (up to 97%). In a subsequent paper, Jun presented optimized reaction conditions and several examples illustrating the reactivities of primary, secondary, and tertiary alcohols (Scheme 223).⁵⁴¹

In the conditions tested, no catalytic activity of ruthenium and platinum complexes was observed. The system ([{IrCl(coe)₂}]₂/HCl) enabled the catalyst loading decreased to 0.5 mol % and reaching a high TON of 5000 for the test reaction. Preliminary mechanistic studies indicate that in the system

Scheme 223. Rhodium-Catalyzed Deethenative Silylation of Alcohols and Phenols

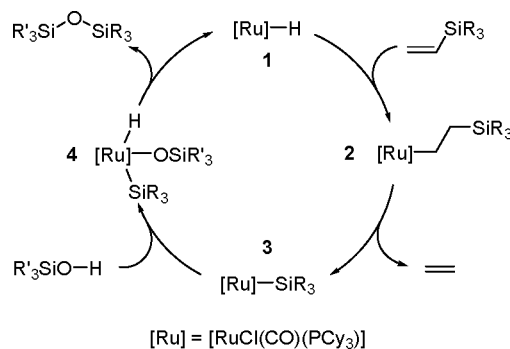
employed and in the presence of HCl, chlorosilane formation occurs, which then reacts with the alcohol.

The Marciniak group has extended the scope of the reaction to silanols (R₃SiOH) and demonstrated the catalytic activity of the ruthenium–hydride complex ([RuHCl(CO)(PCy₃)₂]) (Scheme 224).⁵⁴² The reported reactions proceeded in good

Scheme 224. Ruthenium-Catalyzed Deethenative Silylation of Silanols

yields (up to 99%). In the procedure, as well as the siloxane, being the synthetic target, undesirable 1,2-bis(silyl)ethenes formed. Only with alkoxy-substituted vinylsilanes did the reaction permit selective formation of corresponding siloxanes.

On the basis of literature data⁵²¹ and studies of stoichiometric reactions, a mechanism of the process has been proposed (Scheme 225). It assumes vinylsilane insertion

Scheme 225. Mechanism of the Ru-Catalyzed Deethenative Silylation of Silanols

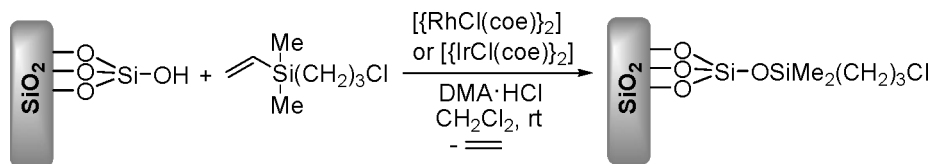
into the Ru–H bond and subsequent β -SiR₃ elimination resulting in the formation of a ruthenium–silyl complex (3). Subsequently, oxidative addition leads to a ruthenium complex (4), followed by reductive elimination of a siloxane. The second part of the mechanism (3 → 4 → 1), supported by the investigation of stoichiometric reactions, needs further experimental and computational verification.

The reaction has been used for the transition metal-catalyzed immobilization of organic functional groups onto solid supports. Jun has reported immobilization of functionalized vinylsilane onto a silica and glass surface (Scheme 226).⁵⁴³

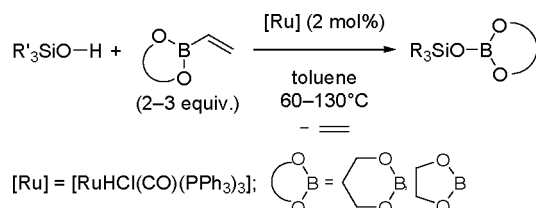
Modification of a silica surface with vinylsilanes, using the catalytic activity of ruthenium complexes, has been proposed by Hreczycho et al.⁵⁴⁴

Hydroxyl group functionalization with other vinylmetaloids was proposed by Marciniak. Both silanols⁵⁴⁵ and alcohols⁵⁴⁶ were demonstrated to react with vinylboronates to form borasiloxanes and boryl ethers, respectively (Schemes 227 and 228). Both reactions were accompanied by the competing deethenative silylation of vinylboronates; however, the less active [RuHCl(CO)(PPh₃)₃] ensured reaction selectivity. The

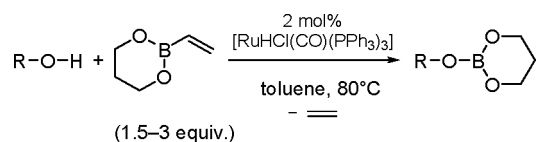
Scheme 226. Immobilization of a Silica Surface via Catalytic Deethenative Silylation



Scheme 227. Ruthenium-Catalyzed Deethenative Borylation of Silanols



Scheme 228. Ruthenium-Catalyzed Deethenative Borylation of Alcohols



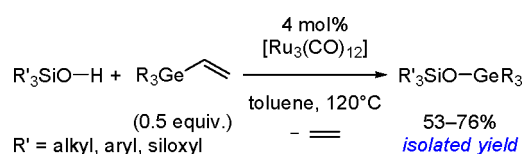
scope of the reaction involves primary alkyl-, aryl-, siloxyl- and alkoxy-substituted silanols as well as primary alcohols including benzyl alcohol. The boron derivatives used were 2-vinyl-1,3,2-dioxaborinane and 2-vinyl-1,3,2-dioxaborolane.

In the presence of $[\text{Ru}_3(\text{CO})_{12}]$, 2-vinyldioxaborinane, 2-vinyldioxaborolane, and vinylboronic acid pinacol ester were transformed nearly quantitatively into corresponding borasiloxanes.⁵⁴⁷ A mechanism of the process was proposed on the basis of NMR monitoring of the $[\text{Ru}_3(\text{CO})_{12}]$ reaction with triethylsilanol and vinylboronate to include oxidative addition of silanol to ruthenium, insertion of vinylborate into the Ru–H bond, formation of a silyl complex as a result of β -SiEt₃-elimination, and product release in reductive elimination. However, the mechanism proposed needs thorough corroboration by further studies.

An analogous reaction of silanols with vinylgermanes in the presence of a ruthenium–carbonyl cluster ($[\text{Ru}_3(\text{CO})_{12}]$) leads to the formation of silagermoxanes (Scheme 229).⁵⁴⁸ Selective transformations of trialkylvinylgermanes and diethyldivinylgermane have been described with moderate isolation yields (53%–76%).

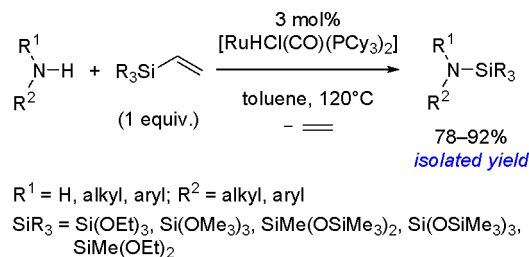
To the best of our knowledge, the only example of amine *N*-silylation with vinylsilane is the one reported by Marciniak and co-workers.⁵⁴⁹ In the presence of the $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ ruthenium hydride, primary and secondary amines undergo silylation by vinylsilanes, bis(silyl)ethene, or 1-alkenylsilanes to yield silylamines. Depending on the silylating agent used, the

Scheme 229. Ruthenium-Catalyzed Deethenative Germylation of Silanols



second product is ethene, terminal olefin, or vinylsilane (Scheme 230).

Scheme 230. Ruthenium-Catalyzed Deethenative Silylation of Primary and Secondary Amines



The scope of amine reagents includes examples of primary and secondary amines and carbazole. The reaction permits high yields of silylated amines (typical isolation yields of 78%–92%). A mechanism of the reaction has been proposed, but it needs to be corroborated by further experimental and computational studies.

7. ACTIVATION (AND FUNCTIONALIZATION) OF C–H BONDS WITH METALLOID HALIDES AND SULFONATES

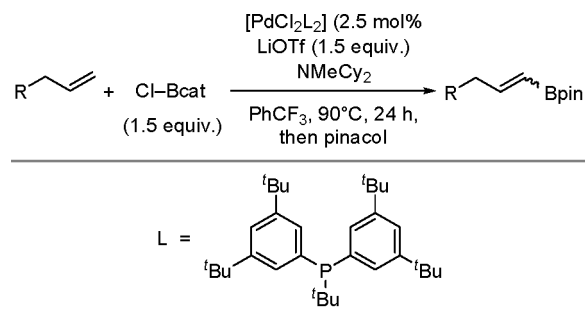
This type of reactivity is possible through activation of the metalloloid-halogen or sulfonate bond by oxidative addition to the transition metal complex.

7.1. Borylation of C–H Bonds

The first examples of the efficient palladium-catalyzed borylation of olefins using chlorocatecholborate as a borylating agent have been reported by Watson and co-workers (Scheme 231).⁵⁵⁰

A Heck-like reaction mechanism has been postulated that starts with the oxidative addition of a B–Cl bond to palladium(0).

Scheme 231. Borylation of Olefins with Chlorocatecholborate: Boryl-Heck Reaction

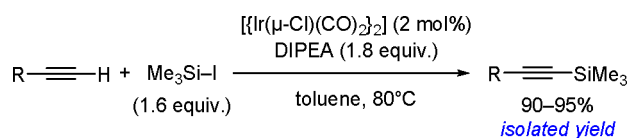


7.2. Silylation and Germylation of C–H Bonds

The oxidative addition of bromosilane to platinum(0) complexes described by Tanaka in 1988 opened up new ways for using metalloid derivatives in synthesis.⁵⁵¹ In subsequent papers, Tanaka⁵⁵² and Murai⁵⁵³ reported the first applications of the process in palladium-catalyzed reactions. Several subsequent studies demonstrated that oxidative addition of a Si–halogen bond to metals such as Pd and Ni was possible. The results obtained by Watson, collected in several recent reviews,^{554–556} clearly show the great potential of halosilanes in catalyzed coupling processes.

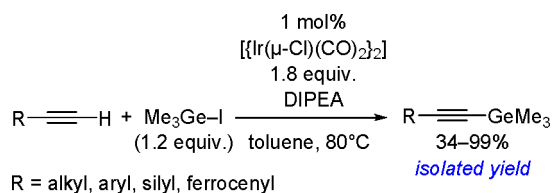
Marciniac has reported that catalyzed treatment of terminal alkynes with iodotrimethylsilane (or iodotrimethylgermane) leads to the efficient synthesis of silylacetylenes and germylacetylenes, respectively. A series of silylacetylenes⁵⁵⁷ (Scheme 232) and germylacetylenes⁵⁵⁸ (Scheme 233) have been obtained in high yields in the presence of $[\{\text{Ir}(\mu\text{-Cl})(\text{CO})_2\}_2]$ and $\text{NEt}(i\text{-Pr})_2$.

Scheme 232. Silylation of Terminal Alkynes with Iodotrimethylsilane



R = alkyl, aryl, silyl, ferrocenyl

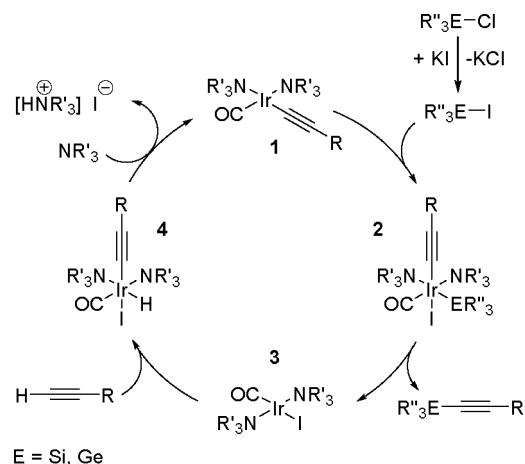
Scheme 233. Germylation of Terminal Alkynes with Iodotrimethylgermane



Further research has shown that cheaper and more readily available chlorosilanes⁵⁵⁹ or chlorogermanes⁵⁶⁰ can be used as reaction partners. The synthetic method consists of an *in situ* generation of iodosilanes in a reaction with NaI or KI. The mechanism of the process has been proposed on the basis of the isolation of a hydridoalkynyl complex, studies of its stoichiometric reactions with reagents and DFT calculations (Scheme 234).

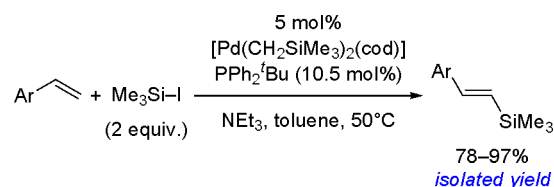
The active catalyst of the process is a square-planar σ -acetylene iridium(I) complex (1). Complex 1 undergoes oxidative addition of iodosilane and subsequent reductive elimination of the organosilicon product. Subsequently, the formed complex (3) undergoes oxidative addition of the C(sp)–H bond of acetylene. Finally, reductive elimination of hydrogen iodide (which is consumed by the reaction with amine) leads to the regeneration of the starting complex (1). An important fact in support of the proposed mechanism was the isolation of the $[\text{IrHCl}(\text{CO})(\text{PhC}\equiv\text{C})\text{py}_2]$ complex (model of complex 4) and its characterization by X-ray diffraction and examination of stoichiometric reactions. DFT computations suggest that the reductive elimination of germylacetylene is the rate-limiting step of germylation.⁵⁶⁰ Still, further studies are needed to account for many details of the mechanism.

Scheme 234. Mechanism of the Silylation (Germylation) of C(sp)–H Bonds with Chlorosilane (Chlorogermane)



The coupling of iodotrimethylsilane with styrenes as olefinic partners proceeds stereoselectively and leads to efficient formation of E-silylstyrenes (Scheme 235).⁵⁶¹ The results were obtained in the presence of the palladium(II) precursor $[\text{Pd}(\text{cod})(\text{CH}_2\text{SiMe}_3)_2]$ and $\text{PPh}_2(t\text{-Bu})$ used as a ligand.

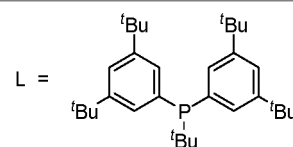
Scheme 235. Silylation of Terminal Olefins with Iodotrimethylsilane



The much cheaper chlorosilane can be used in the reaction in the presence of LiI, which enables the generation of iodosilane *in situ*.⁵⁶¹ Coupling with alkyl-substituted α -olefins yields allylsilanes accompanied by vinylsilanes and the isomerized starting olefin. A strongly donating and bulky phosphine was used to achieve chemo- and stereoselective formation of allylsilanes (Scheme 236).⁵⁶²

The palladium dimer $[\{\text{PdI}_2(\text{Pt-BuAr}_2)\}_2]$ (Ar = 3,5-di-*tert*-butylphenyl) developed by Watson enables efficient and stereoselective silylation of styrenes, selective silylation of terminal olefins to allylsilanes, and use of sterically demanding silyl groups such as SiMe_2Ph , SiMePh_2 , and $\text{SiMe}_2\text{CH}_2\text{Ph}$.⁵⁶³

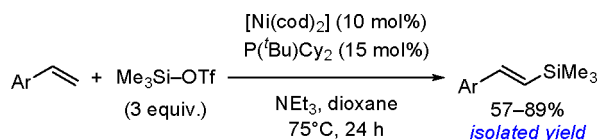
Scheme 236. Stereoselective Silylation of Allyl Derivatives with Iodotrimethylsilane



$[\text{Pd}_2(\text{dba})_3]/\text{PtBuPh}_2$ is an alternative catalytic system useful for the silylation of styrenes, which offers high efficiency and stereoselectivity and allows conversion with silyl bis(triflates). By using silyl bis(triflates) (in the presence of NaI to generate in situ monoiodosilanes), alkoxy-silyl derivatives could be obtained, which can easily undergo further transformations, such as Hiyama–Denmark coupling and Tamao–Fleming oxidation.⁵⁶⁴

A commercially available nickel(0) catalyst precursor, $[\text{Ni}(\text{cod})_2]$, used with the appropriate phosphine ligand enabled oxidative addition of silyl triflates (Scheme 237).⁵⁶⁵

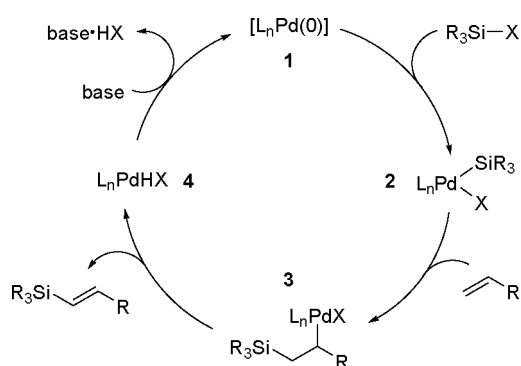
Scheme 237. Olefin Silylation with Trimethylsilyltriflate



Nickel catalysts show good functional group tolerance in the production of vinylsilylans; however, the electron-withdrawing groups present in the aromatic rings significantly reduce conversion. Appropriate selection of the phosphane ligand enabled the conversion of silanes bearing bulkier silyl groups than Me_3Si . Trichlorosilanes, dichlorosilanes, and monochlorosilanes were shown to react with an olefin in the presence of $[\text{Ni}(\text{cod})_2]$, PCy_3 , AlMe_3 , and NEt_3 to yield corresponding alkenylsilylans. The process is the first example of a direct silyl-Heck reaction of chlorosilanes.⁵⁶⁶

In terms of the reaction mechanism (Scheme 238), the key step is the oxidative addition of the Si–X bond (X = halogen)

Scheme 238. Mechanism of the Ni-Catalyzed Silylation of Olefinic C(sp²)–H Bonds with Halosilane (Silyl-Heck Reaction)⁵⁵⁴



to the metal. It has been found that $[\text{Pd}(\text{CH}_2\text{SiMe}_3)_2(\text{cod})]$ undergoes oxidative addition of iodosilane to form $[\text{Pd}(\text{SiMe}_3)\{\text{PAr}_2(t\text{-Bu})\}]$ (Ar = 4-hydroxy-3,5-dimethylphenyl), stabilized by a phosphine ligand. The complex was characterized by spectroscopic and X-ray diffraction methods. The complex was demonstrated to be a competent precatalyst in the reaction of iodosilane with 1-decene.⁵⁶² The further steps in the process were proposed to follow the Heck reaction mechanism. The olefin is inserted into the resulting M–Si bond followed by β -silyl elimination. The last step is the reductive elimination of the hydrogen halide, which is favored when a base is present. However, the proposed mechanism still needs further detailed investigation.

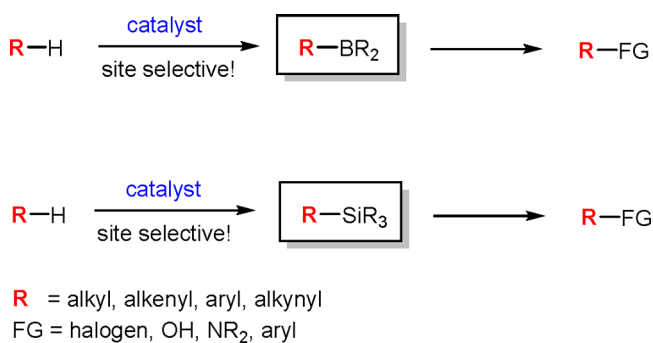
8. APPLICATIONS IN ORGANIC SYNTHESIS

In the past two decades, the catalytic methods for the synthesis of organometalloid compounds have been rapidly developing, as described in detail in sections 1–7 of our Review. Through the in-depth understanding of the reaction mechanisms and the role of inorganometallic intermediates in catalysis, many new addition and coupling reactions involving hydro-, halogen-, vinyl-, and bis-metalloids have been discovered, which opened up new routes to the selective and effective preparation of several metalloid-containing derivatives.

However, it has been known for many years that the unique reactivity of organometalloids can successfully be used in organic synthesis. As a result, new synthetic strategies have been developed using mostly unsaturated or (hetero)aromatic boron and silicon derivatives as precursors for subsequent functionalization reactions to yield a wide variety of organic derivatives from available and inexpensive substrates (alkenes, alkynes, arenes, etc.). The application of tin and germanium compounds, although less spectacular, has also been intensively studied, and interesting applications in organic synthesis followed. The literature also provides some examples of using tellurium and antimony compounds.

Among the organic derivatives of metalloids, organoboron compounds are typically used in organic synthesis. Silicon derivatives are used slightly less commonly. The procedures for the selective and efficient borylation and silylation of C–H bonds allow convenient and selective introduction of a number of functional groups into an organic molecule as a result of further functionalization (Scheme 239).^{227,230,297,567}

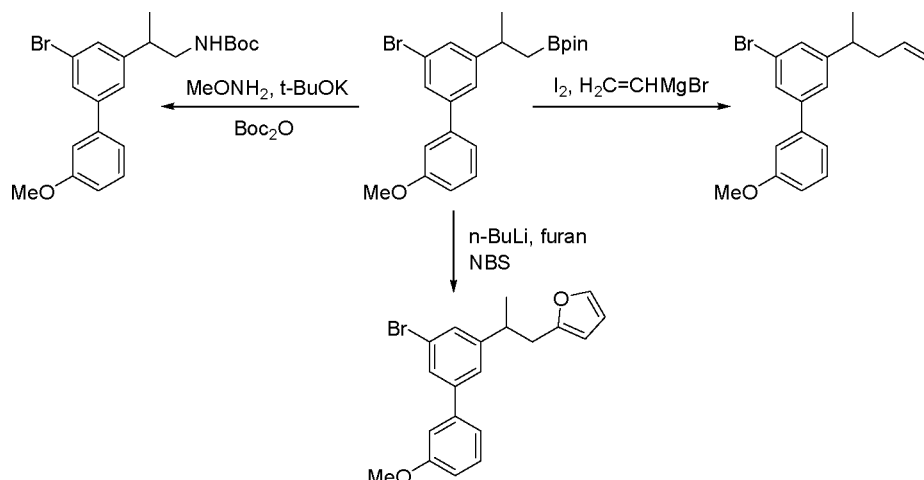
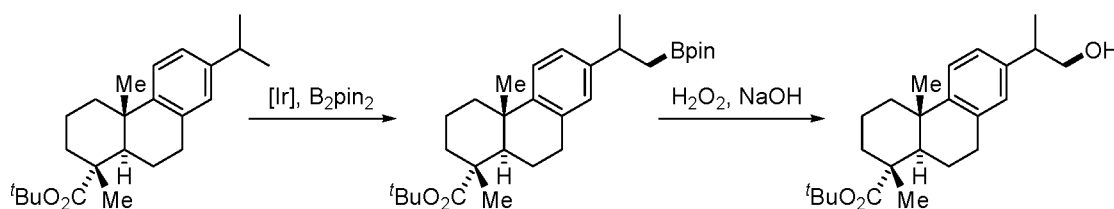
Scheme 239. Functionalization of C–H Bonds via Borylation (Silylation) and Subsequent Derivatization of C–B (C–Si) Bonds



The unique feature of these sequential methodologies is that the metalation step and further functionalization can usually be performed in a one-pot procedure. The selectivity of the overall processes can be controlled during the initial step (which is especially important for addition or aromatic substitution reactions) as the subsequent demetalation usually proceeds with retention of the configuration (*ipso*-substitution) at the carbon atom, and the desired products can be formed.⁵⁶⁸

The high selectivity and high yields of the metal-catalyzed borylation of alkanes enables the synthesis of functionalized materials that are hardly formed selectively by other methods. Owing to the selective borylation of primary C–H bonds or C–H bonds located alpha to heteroatoms or alpha to an aryl ring, alkylborates are widely used in organic synthesis with the borylation-functionalization sequence. A recent procedure reported by Hartwig and co-workers⁵⁶⁷ enables undirected

Scheme 240. Synthetic Application of Alkylboronic Acids and Esters

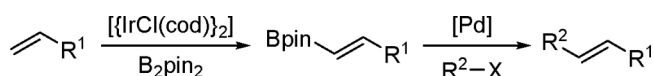
Scheme 241. Borylation and Oxidation of Dehydroabietic Acid *tert*-Butyl Ester

borylation of primary C–H bonds or borylation of strong secondary C–H bonds when primary C–H bonds are absent or blocked. It opens up a range of possibilities for installing a vast variety of carbon–carbon and carbon–heteroatom bonds at previously inaccessible positions of organic molecules (Scheme 240).

As borylation can be carried out with the substrate as the limiting reagent, it enables borylation of multifunctional natural products or medically relevant molecules containing multiple C–H bonds (Scheme 241).⁵⁶⁷

The synthesis and applications of alkenylboronates were summarized in a recent review.⁵⁶⁹ Alkenylboronates are used primarily in Suzuki–Miyaura cross-coupling reactions. Olsson and Szabo demonstrated that a number of allylsilanes and dienes could be synthesized using a sequence of borylation of allylsilane (or selected olefins) and cross-coupling with an aryl or alkenyl halide (Scheme 242).²³⁸

Scheme 242. Synthesis of Allylsilanes and Dienylsilanes by a One-Pot C–H Borylation–Suzuki–Miyaura Coupling Sequence



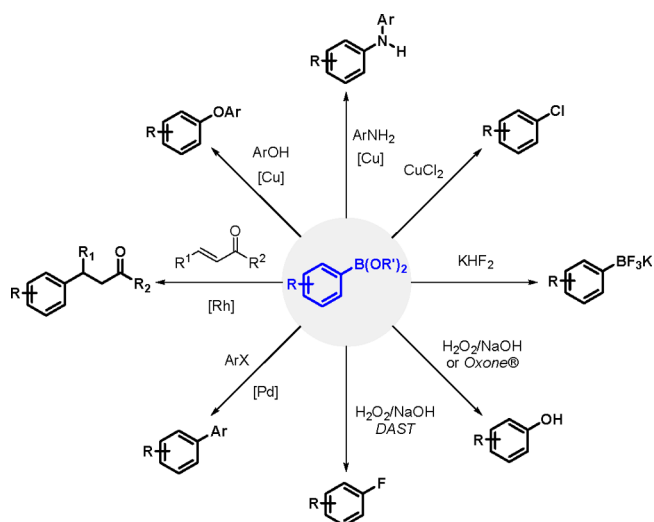
$\text{R}^1 = \text{CH}_2\text{SiMe}_3, \text{CH}(\text{OMe})_2, \text{COOMe}, \text{COMe}, \text{OBu}$;
 $\text{R}^2 = \text{aryl}, \text{alkenyl}, \text{CH}=\text{CHSiMe}_3$; $\text{X} = \text{I}, \text{Br}$

The synthesis and reactivity of alkynyl boron compounds has been described in review articles.^{231,570} Catalytic transformations that occur via the activation of C–B bonds involve halodeboration, syn-alkynylboration of alkynes, and cross-coupling of alkynyl boronic esters with aryl, alkynyl and acyl halides. It has been demonstrated that alkynyl boronates can

also be efficiently transformed into carboxylic acids, esters, and amides.⁵⁷¹

Arylboronic acids and esters, synthesized by the catalytic borylation of C–H bonds with hydro- or diboranes, open up a gateway to a plethora of derivatization methods for the selective installation of complex and valuable functional groups through oxidation, amination, halogenation, arylation, etherification, homologation, and cross-coupling for the selective preparation of functionalized arenes (Scheme 243).²³⁸ The advantage of these synthetic protocols is that the sequences of borylation and deborylative functionalization can be imple-

Scheme 243. Synthetic Applications of Arylboronic Acids and Esters

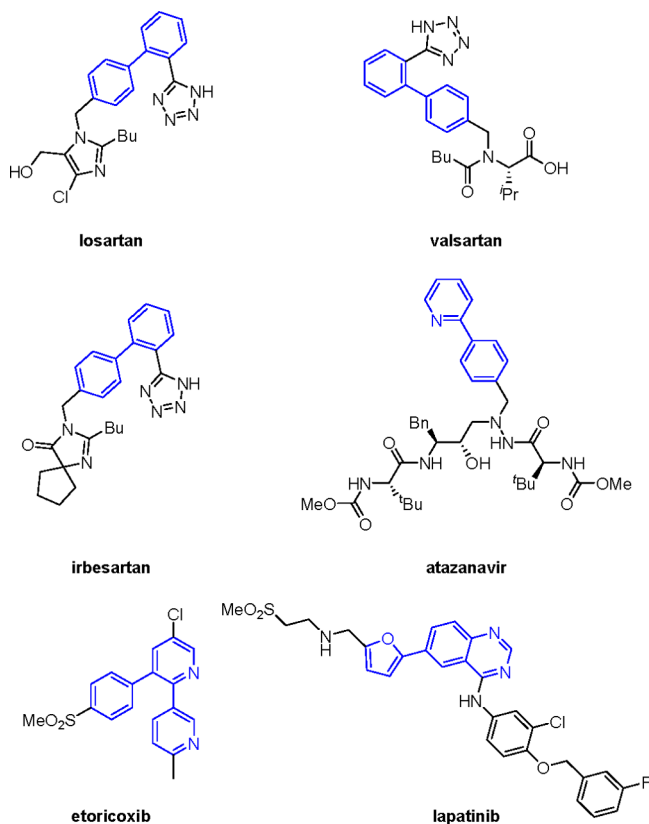


mented as a one-pot procedure without the isolation of organoboron intermediates.

Multiborylated compounds, readily available owing to convenient synthesis protocols (e.g., refs 572–575) are valuable intermediates for the synthesis of multifunctional molecules.^{575,576}

Suzuki–Miyaura coupling, a major application of organoboron compounds, is widely used both in the synthesis of small molecules and as a key step in the overall synthesis of pharmaceuticals and natural products.^{577–582} Its growing popularity in pharmaceutical industry comes from its ability to drive a wide range of C(sp²)–C(sp²) couplings to generate a wide gamut of (hetero)biaryl motifs in a selective manner, while displaying a high level of functional group tolerance.^{583,584} Moreover, palladium-catalyzed coupling reactions, with boronic acids or boronates, ensure considerably shorter routes to corresponding products compared to other approaches, thus minimizing side products and waste. Examples of the approved drugs whose production employs Suzuki–Miyaura coupling to form critical carbon–carbon bonds with aromatic or heteroaromatic groups are presented in Scheme 244.

Scheme 244. Structures of Commercial Drugs Produced with Suzuki–Miyaura Cross-coupling to Form Carbon–Carbon Bonds



As an example, the synthesis of *losartan* (Merck), an angiotensin II receptor antagonist prescribed worldwide for high blood pressure, is shown in Scheme 245. Owing to optimization of the cross-coupling reaction conditions, cost-effective solutions could be applied on a large scale with the Pd(OAc)₂/PPh₃ catalytic system and a mixture of water, THF, and dimethoxymethane as solvent.

Through phase-transfer catalytic conditions for the cross-coupling step, efficient large-scale synthesis of crizotinib could be developed (Scheme 246) as a mesenchymal epithelial transition factor/anaplastic lymphoma kinase inhibitor (about 100 kg via a six-step procedure in 40% yield from chiral (*S*)-1-(2,6-dichloro-3-fluorophenyl)ethanol).⁵⁸⁴

Cross-coupling chemistry has been vital for the rapid assessment of structure–activity relationships in the drug discovery phase to facilitate subsequent selection of drug candidates. A synthetic methodology based on the rhodium-catalyzed asymmetric Suzuki–Miyaura reaction was used for the synthesis of potential drug candidates containing chiral molecules, such as *preclamol* (studied for the treatment of schizophrenia), *niraparib* (ovarian cancer), and a natural alkaloid *isoanabasine* (Scheme 247).⁵⁸³

Suzuki–Miyaura coupling is also widely applied in the synthesis of agrochemicals such as fungicides (e.g., *boscalid*, *bixafen*, *pyrofenone*), insecticides (*bifenazate*) and herbicides (*halauxifen-methyl*).⁵⁸⁵ As an example, the cross-coupling of 4-chlorophenylboronic acid with 1-chloro-2-nitrobenzene mediated by Pd(PPh₃)₄ with the addition of tetrabutylammonium bromide (TBAB) as a phase-transfer catalyst is a key step to produce *boscalid* on a large-scale (>1000 tons per year). Low catalyst loading (0.25 mol % Pd), functional group tolerance and use of cost-effective aryl chlorides make this method one of the largest-known industrial applications of the Suzuki–Miyaura cross-coupling reaction (Scheme 248).

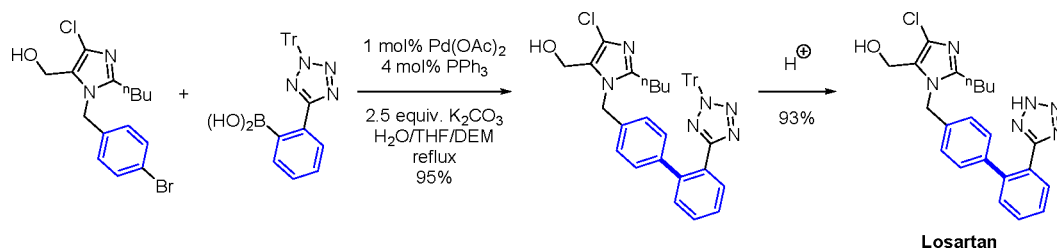
Recently, straightforward silylation of C–H bonds with hydrosilanes catalyzed by Rh, Ir, or Pt complexes has been extensively studied in parallel with similar transformations with boron reagents to achieve much easier access to novel organosilicon and organoboron compounds. Organosilicon compounds are in general superior to other organometalloid compounds in view of their stability, solubility, nontoxicity, and ease of handling.

Arylsilanes, heteroarylsilanes and alkenylsilanes obtained via C–H bond silylation reactions are highly versatile substrates that can be transformed into several compounds with useful functionalities, such as halides, ketones, and esters; they are also valuable precursors for cross-coupling with aryl, alkenyl, and alkyl halides (Scheme 249).^{297,586,587}

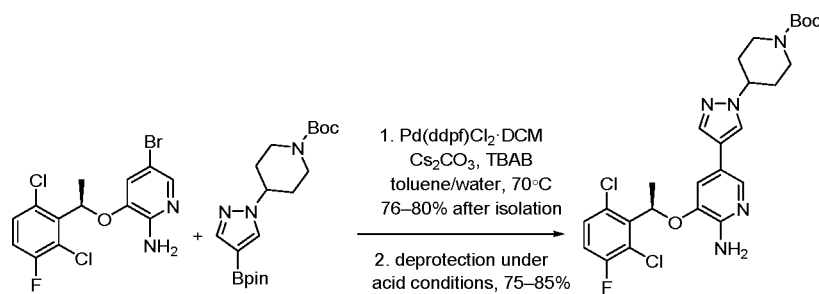
The growing interest in the development of sequential or tandem processes, including intramolecular hydrometalation and bis-metalation as the initial steps, stems from the ability to assemble complex molecules from simple starting materials (functionalized alkenes, dienes, and alkynes) through organometalloid intermediates in a convergent and stereoselective manner. Classical examples involve the use of the platinum-catalyzed intramolecular hydrosilylation/Tamao–Fleming oxidation sequence as a powerful method for the stereoselective synthesis of various structurally diverse alcohols (1,3-diols, 2-alkoxy-1,3-diols, 1,3,5-triols, 2-aminoalcohols) and ketone derivatives (β -hydroxyketones, γ -hydroxyketones, α,β -dihydroxyketones, and α,γ -dihydroxyketones) from simple and readily available substituted allyl- or propargyl alcohols and their homologues (Scheme 250).

Several protocols using a combination of TM-catalyzed hydrosilylation and a palladium-catalyzed cross-coupling (Hiyama–Denmark coupling) sequence leading to stereo-defined π -conjugated alkene derivatives have been successfully developed in the past two decades.^{587,588} Consecutive platinum- or ruthenium-catalyzed intramolecular hydrosilylation of propargyl and homopropargyl alcohols in combination

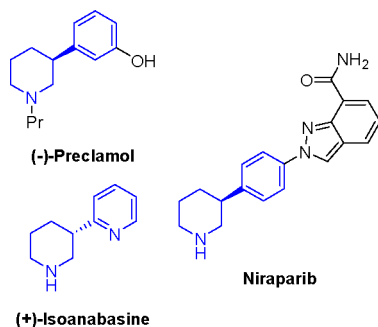
Scheme 245. Application of Suzuki–Miyaura Coupling for the Synthesis of Losartan



Scheme 246. Application of Suzuki–Miyaura Coupling in the Large-Scale Synthesis of Crizotinib



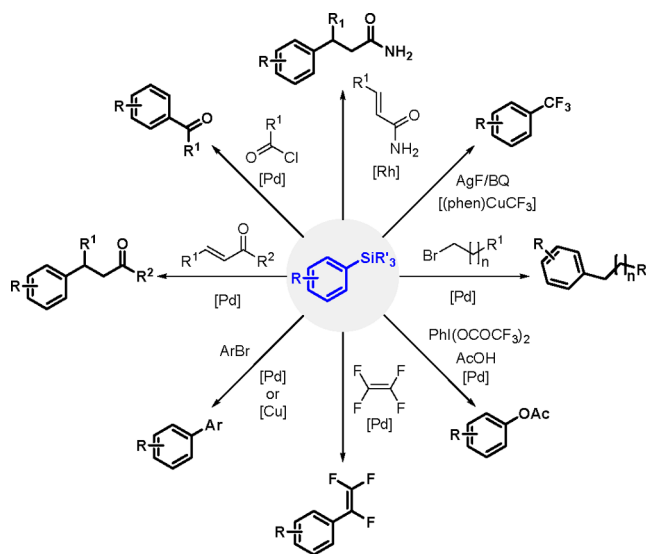
Scheme 247. Examples of Molecules Synthesized via Asymmetric Suzuki–Miyaura Coupling Reactions



with palladium-catalyzed cross-coupling reactions has been shown as a powerful tool in the stereoselective synthesis of a wide variety of aryl-substituted (*E*)- and (*Z*)-allyl and homoallyl alcohols (Scheme 251)^{589,590} and in the synthesis of natural products.^{591,592}

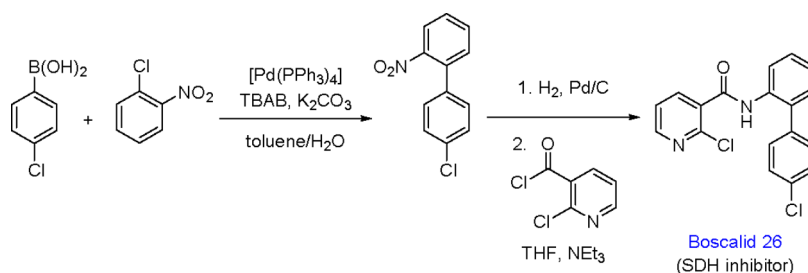
A combination of the intramolecular bis-silylation of protected disilyl homoallylic alcohols in the presence of a palladium catalyst and the oxidation of silacyclic products provides a unique method for diastereoselective alkene dihydroxylation.⁵⁹³ The development of enantioselective bis-boration gave the impetus to the selective synthesis of diols. An example is the bis-boration of terminal alkenes and *trans*-

Scheme 249. Synthetic Utility of Arylsilanes

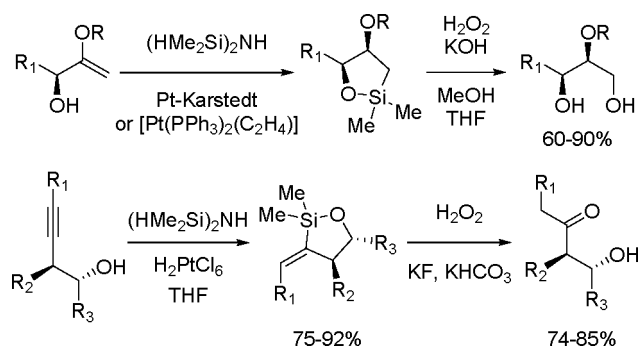


alkenes in the presence of rhodium and an (*S*)-Quinap ligand, followed by oxidation to efficiently give vicinal diols with high enantioselectivity.¹⁹⁰ A combination of the bis-boration of terminal alkenes in the presence of a Pd(0) catalyst and chiral TADDOL-derived phosphonites with subsequent oxidation has been demonstrated to be an effective synthetic route to

Scheme 248. Application of Suzuki–Miyaura Coupling for the Synthesis of Boscalid



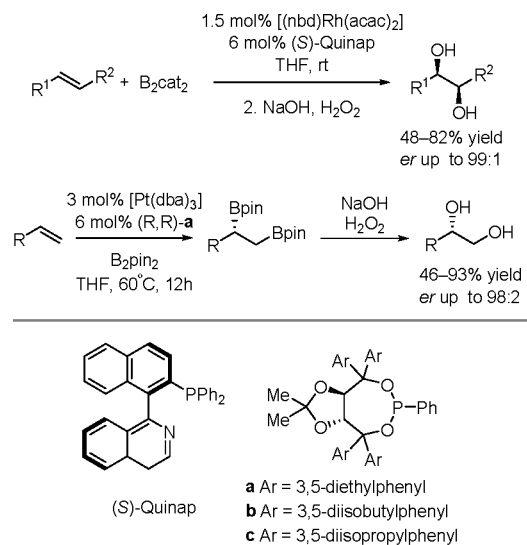
Scheme 250. Synthesis of Alcohols via the Hydrosilylation/Tamao-Fleming Oxidation Sequence



1,2-diols with high enantioselectivity (Scheme 252).⁵⁹⁴ An alternative transformation applicable to 1,2-bis(boryl)alkane intermediates that involves tandem rhodium-catalyzed bis-boration and Suzuki cross-coupling has also been reported.⁵⁹⁵ A similar reaction sequence has been performed for palladium catalysts.⁵⁹⁶

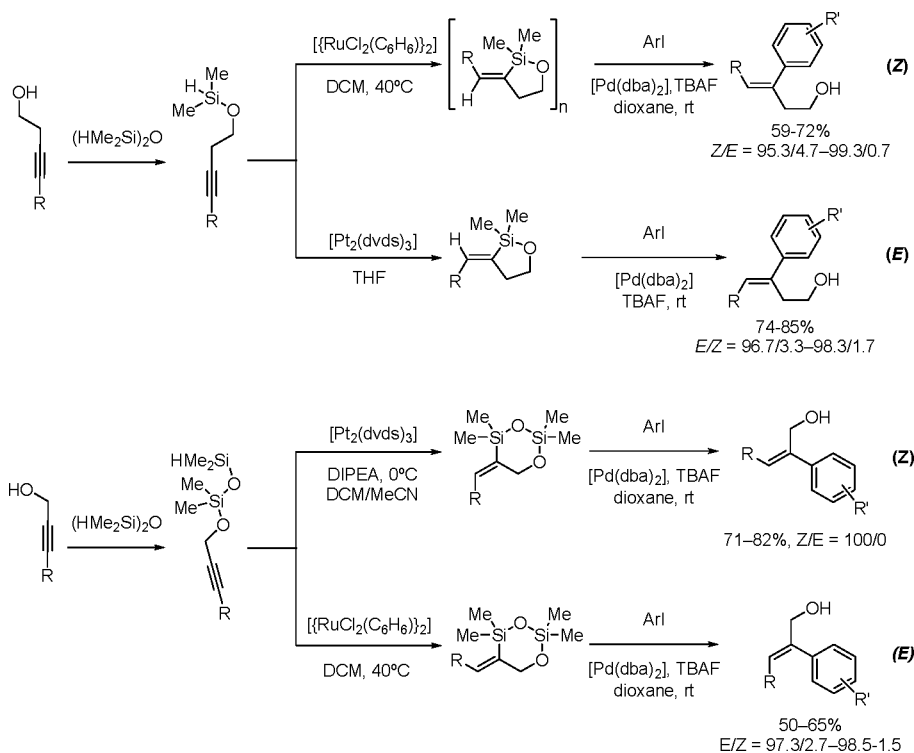
The deethenative silylation of olefins with vinyl-substituted organosilicon compounds catalyzed with ruthenium complexes has been a very attractive and highly efficient method for the synthesis of (*E*)-alkenylsilanes and bis(silyl)alkenes. These products have been used as effective platforms for further transformations, including palladium-catalyzed cross-coupling with aryl or alkenyl halides or electrophilic substitution.^{529,597} The combination of deethenative silylation and Hiyama–Denmark coupling has been used for the stereoselective synthesis of (*E*)-stilbenes, (*E*)-styrylarenes and arylene-vinylene oligomers (Scheme 253).

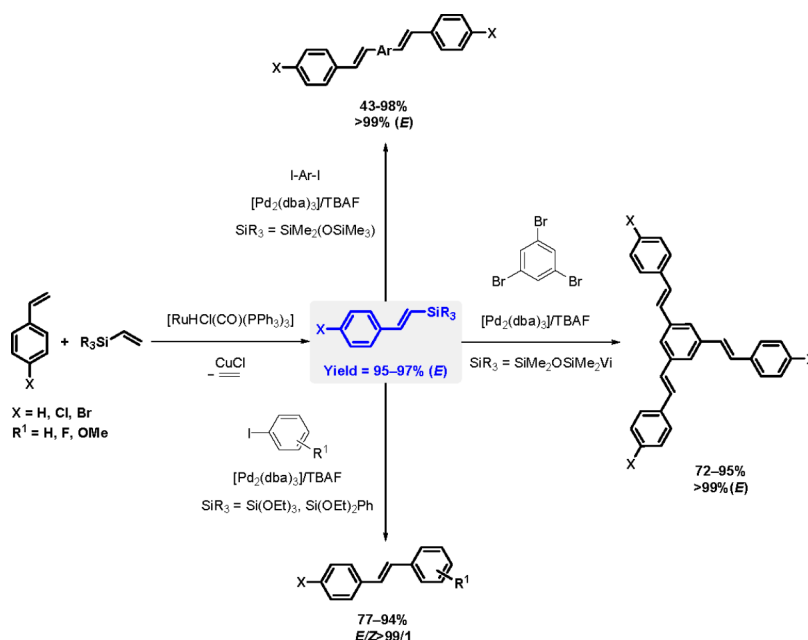
Scheme 252. Enantioselective Bis-boration in the Synthesis of 1,2-Diols



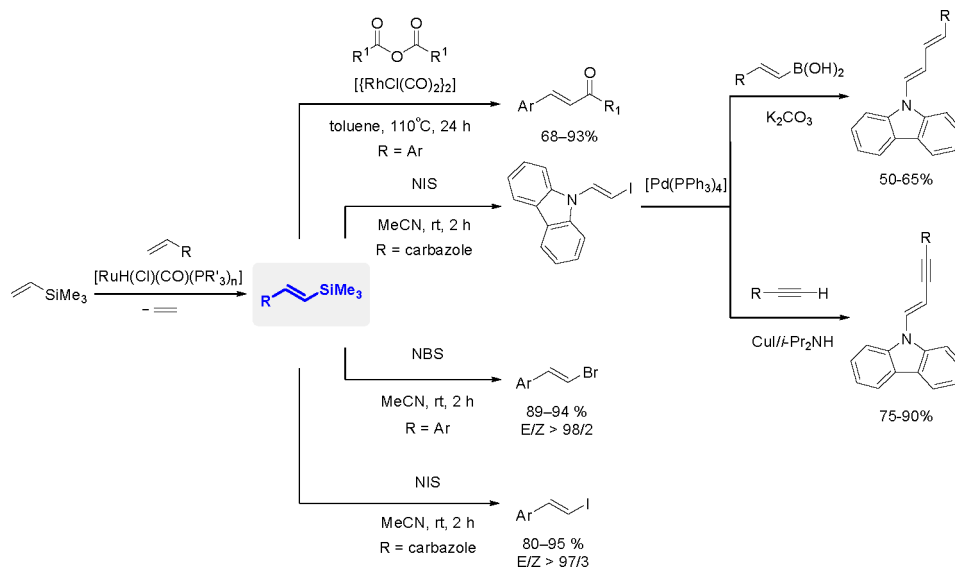
However, a combination of deethenative silylation with the electrophilic halodesilylation reaction has been applied in the selective one-pot preparation of synthetically useful alkenyl halides (e.g., (*E*)-styryl halides, (*E*)-*N*-2-iodovinylcarbazole, (*E*)-*N*-2-iodovinylamides). These halides are versatile coupling partners in palladium-catalyzed Suzuki and Sonogashira couplings, leading to a wide variety of stereodefined β -substituted (*E*)-enimides, (*E,E*)-dienimides, and (*E*)-enynimides as well as related π -conjugated *N*-substituted carbazole derivatives. The discovery of sequential deethenative silylation and rhodium- or iridium-catalyzed acylation is

Scheme 251. Synthesis of Aryl-Substituted Allyl and Homoallyl Alcohols by Sequential Hydrosilylation/Hiyama–Denmark Cross-coupling



Scheme 253. Sequential Deethenative Silylation/Hiyama–Denmark Cross-coupling in the Synthesis of π -Conjugated Derivatives

Scheme 254. Deethenative Silylation of Olefins with Vinylsilanes in the Synthesis of Functionalized Organic Compounds



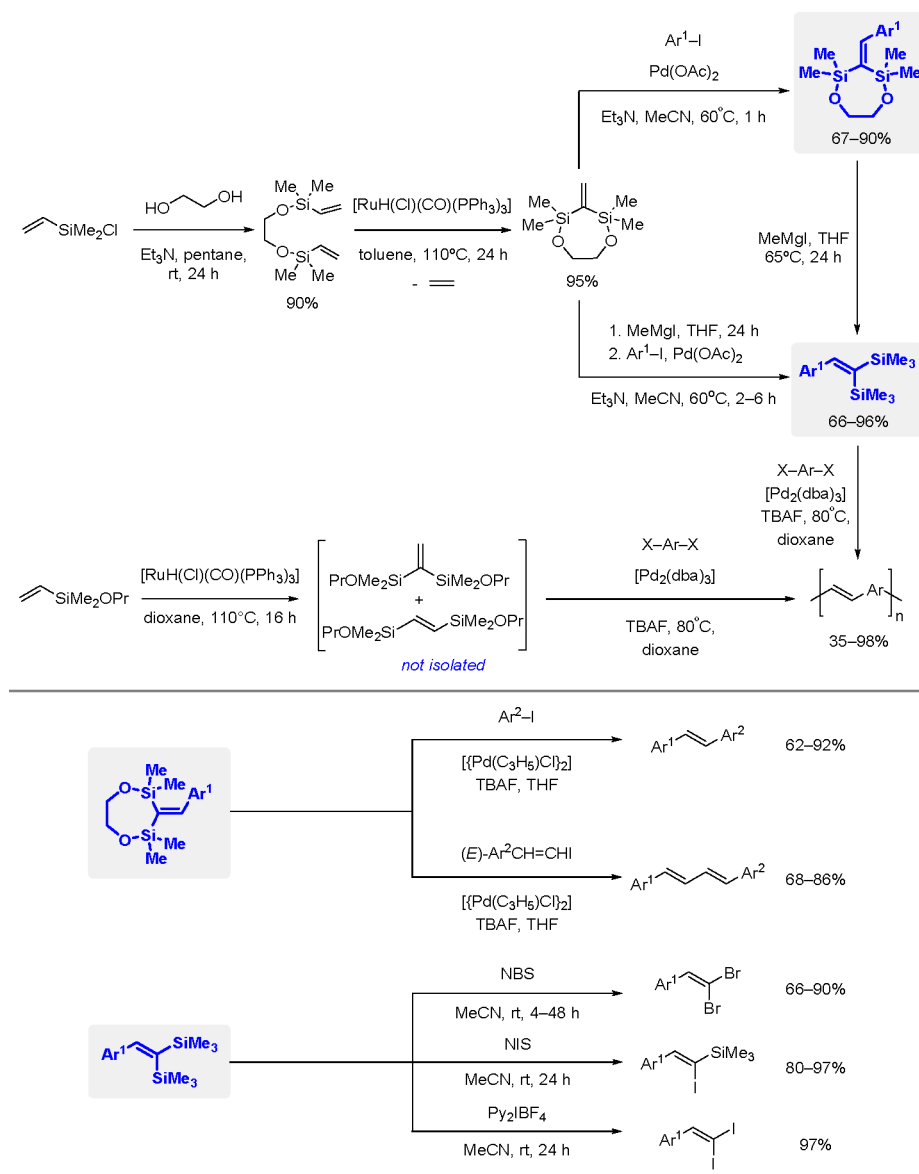
important for the synthesis of (*E*)- α,β -unsaturated ketones (Scheme 254).

Isomeric bis(silyl)alkenes, easily obtained via the ruthenium-catalyzed deethenative silylation of divinyl-substituted organosilicon compounds or silylative homocoupling of vinylsilanes, are particularly attractive scaffolds for further transformations including palladium-catalyzed cross-coupling with organic halides or substitution with organic and inorganic electrophiles (Scheme 255).

Alkynylsilanes obtained through the catalytic silylation of terminal alkynes with hydro-, vinyl-, or halosilanes can act as versatile building blocks in the synthesis of π -conjugated derivatives with triple and double bonds.³⁰¹ Selected examples of alkynylsilane transformations in desilylative substitution, cycloaddition, and cross-coupling reactions are presented in Scheme 256.

Germanium, despite its position in group 14 of the periodic table between silicon and tin, which causes organogermanium compounds to exhibit properties between those of organosilicon and organotin compounds, has not received significant interest from synthetic organic chemists. The state of the art on the use of germanium compounds in organic synthesis up to the early 2000s has been reviewed.⁵⁹⁸ The first application of organogermane derivatives in catalytic coupling was reported in 1996 by Kosugi and co-workers.⁵⁹⁹ It has been shown that variously substituted germatranes undergo coupling with tolyl (or phenyl) bromide in the presence of a palladium catalyst, $[\text{Pd}_2(\text{dba})_3\text{CHCl}_3]/\text{PPh}_3$ or $\text{P}(o\text{-tol})_3$. In 2002, Oshima and co-workers described the Pd-catalyzed coupling of aryl iodides or bromides with aryltri(2-furyl)germane.⁴⁵² Subsequent studies included proposals for efficient and selective cross-coupling reactions for organogermanes with

Scheme 255. Application of Bis(silyl)alkenes in the Synthesis of Functionalized Organic Compounds



organic halides and some other derivatives. Recently, dynamic progress in the application of trialkylarylgermanes has been made in the work of Schoenebeck and Fricke, as discussed in an excellent account.⁶⁰⁰ Schoenebeck has shown that organogermanium derivatives can be characterized by complementary reactivity in relation to that of other coupling agents. For example, it has been shown that aryltriethylgermanes exhibit efficient coupling with aryl halides in the presence of Pd nanoparticles as opposed to corresponding boronic acids or their esters. The reactivity series is reversed in a homogeneous system with palladium(0) and palladium(II) complexes. A useful property of aryltriethylgermanes is their tolerance to nucleophilic and electrophilic fluorinating agents, which distinguishes them from tin, silicon, and boron compounds.

Alkynyl germanium derivatives have been used in catalytic coupling reactions only in the form of germatranes (Scheme 257).

Vinylgermanes play a limited role in organic synthesis. The literature describes in particular examples of palladium-catalyzed coupling processes (Scheme 258). The catalytic

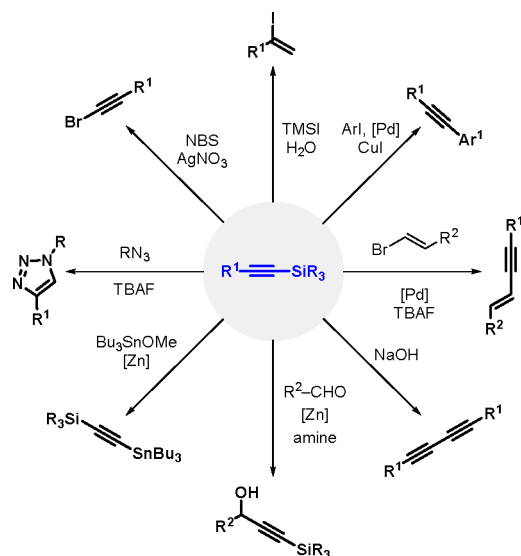
coupling of vinylgermatrane with *p*-bromotoluene by Kosugi and co-workers is the first reported example.⁵⁹⁹

Cross-coupling of *Z*- β -(trialkylgermyl)acrylic acid with 4-iodobenzaldehyde was used in the total synthesis of (*Z*)-tamoxifen.⁶⁰¹ The observation of arylgermanium activity in gold-catalyzed coupling with an aryl C–H bond will hopefully make organogermanes more useful as transmetalation agents (Scheme 259).⁶⁰²

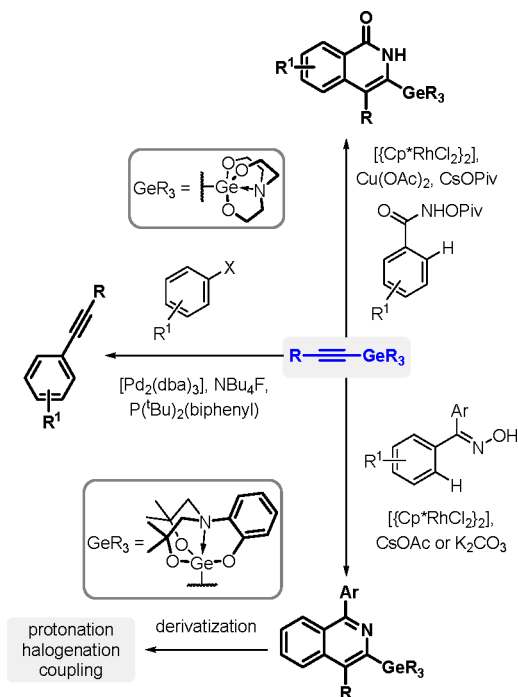
Arylstannanes that are readily synthesized using traditional methods with lithium or magnesium-based organometallic reagents or via TM-catalyzed stannylation of corresponding aryl electrophiles with distannanes or tertiary stannanes (HSnR₃) have gained importance because of their application in Migita–Kosugi–Stille cross-coupling reactions with aryl and alkenyl halides.^{603–606} They are also frequently used in the construction of diverse carbon–heteroatom bonds, such as C–X, C–N, C–S, and C–O bonds (Scheme 260).

Although other alternative Pd-catalyzed cross-coupling reactions have been rapidly developed, Migita–Kosugi–Stille coupling is still an extremely useful and competitive tool in

Scheme 256. Synthetic Utility of Alkynylsilanes



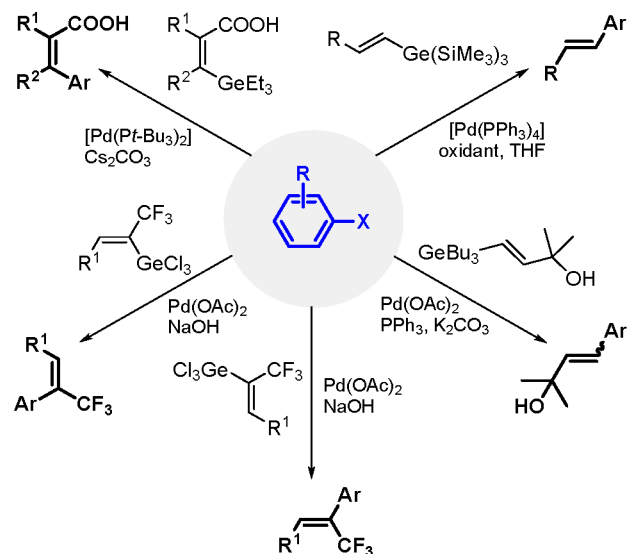
Scheme 257. Alkynylgermanes in Organic Synthesis



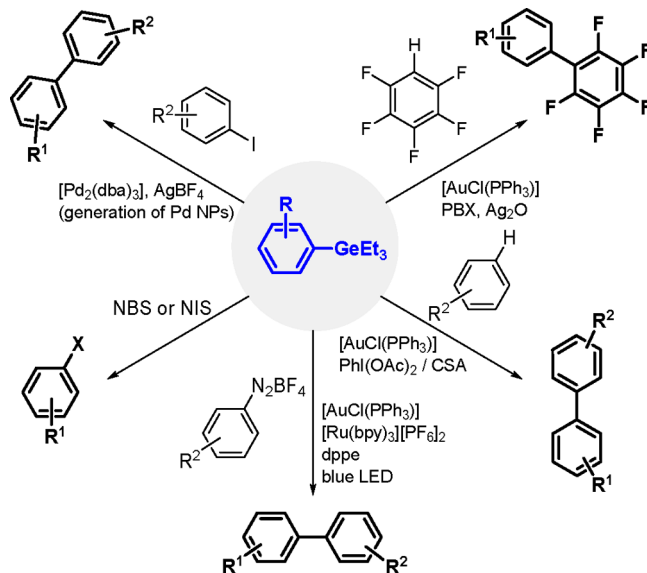
organic synthesis. The synthetic process involves the coupling of organic electrophiles (halides, acyl chlorides, and pseudohalides, such as triflates, sulfonates, and phosphates) with organostannanes in the presence of catalytic amounts of Pd(0) or Pd(II) precatalysts (Scheme 261). The unique features of this cross-coupling reaction are the use of organostannanes (relatively insensitive to moisture and oxygen) and a diversity of organic electrophiles, mild reaction conditions (no requirement for a base), and tolerance to a wide variety of functional groups, which enables synthesis of complex heterocyclic molecules.

Migita–Kosugi–Stille coupling is widely applied for the total synthesis of natural products.^{577,578,603,607} The reaction tolerates air and moisture, and it is compatible with various functional groups.

Scheme 258. Catalyzed Cross-coupling of Vinylgermanes



Scheme 259. Synthetic Utility of Arylgermanes

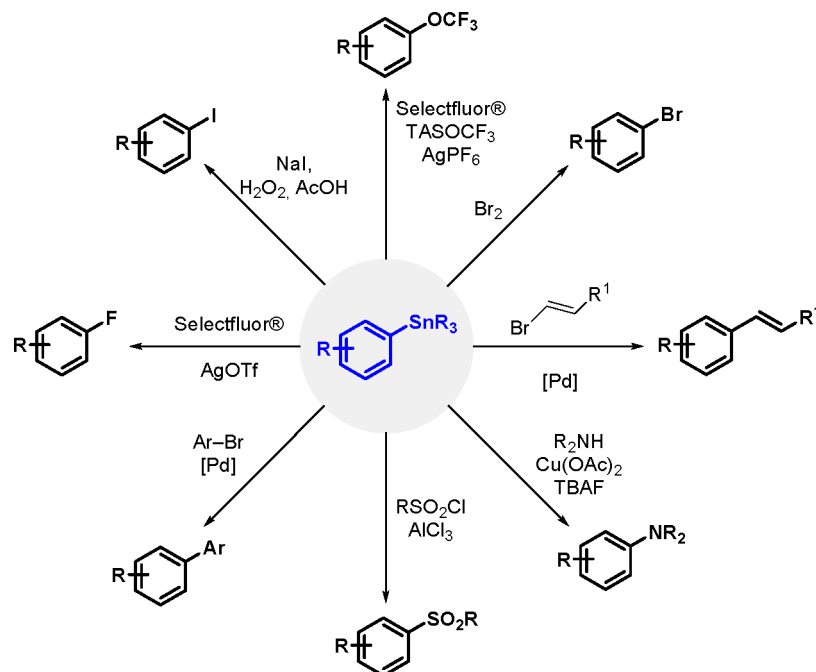


Alkenylstannanes, which can be easily and selectively prepared via hydrostannylation of acetylenes or via palladium-catalyzed stereospecific cross-coupling of alkenyl halides or triflates with distannanes, are versatile precursors for disubstituted olefins (Scheme 262). Their most synthetically useful TM-catalyzed transformation is Stille coupling with a variety of organic electrophiles.

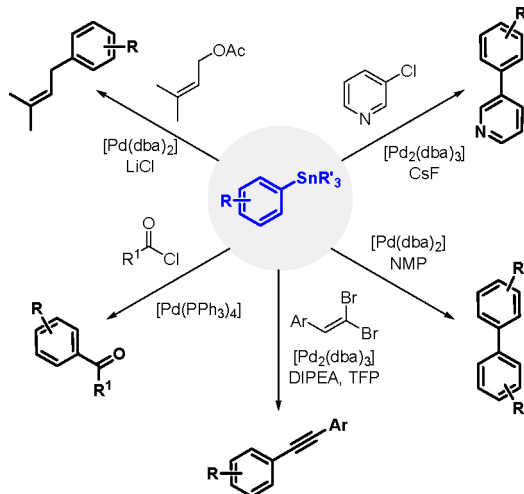
Alkynylstannanes are formed either directly from terminal alkynes or through their metal derivatives. The activity of alkynylstannanes in cross-coupling is generally lower than that of other alkynylmetals. However, their stability and tolerance to a wide range of functionalities make them convenient coupling agents (Scheme 263).

Organostannanes have been found to be good coupling partners in the synthesis of complex heterocyclic systems. As an example, Migita–Kosugi–Stille cross-coupling has been applied in the large-scale preparation of an imidazole–thienopyridine VEGFR kinase inhibitor for pharmaceutical purposes (Scheme 264).

Scheme 260. Synthetic Application of Arylstannanes



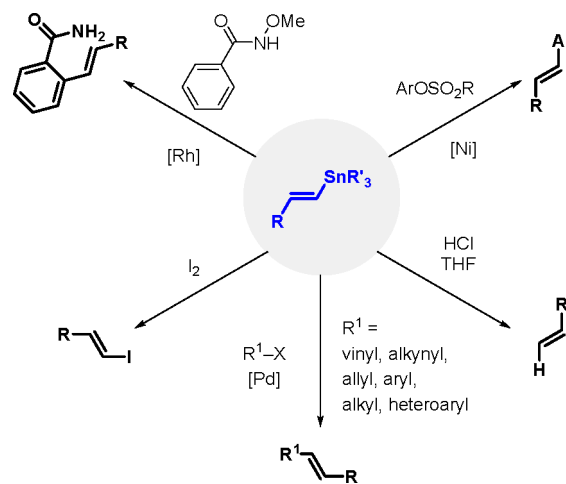
Scheme 261. Application of Arylstannanes in Cross-coupling Reactions



Likewise, catalytic vinylation of haloarenes is most efficient with vinylstannanes, as illustrated by the *pinoxaden* manufacturing method (Scheme 265). This is a selective post-emergence herbicide for the control of annual grass weeds in cereal crops. However, the use of tin reagents in other industrial scale carbon–carbon bond formation reactions has been hampered by residue toxicity and purification costs.

Early studies on the application of stibanes in catalytic organic synthesis confirmed that these compounds can be used in coupling reactions. The state of the art on the application of organoantimony compounds in organic synthesis, including the achievements up to the early 2000s, has been summarized.^{608,609} Although effective procedures for the catalytic formation of C–C bonds using tellurium compounds have recently been proposed, the related chemistry is still underdeveloped. Organoantimony(III) derivatives need to be oxidized to be active in Pd-catalyzed coupling. Triarylantimony

Scheme 262. Synthetic Applications of Vinylstannanes

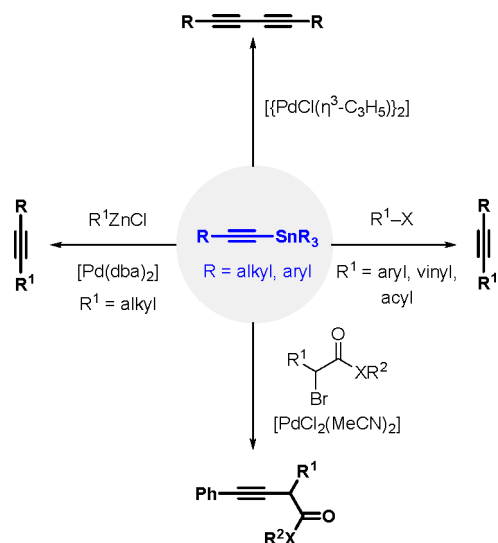


dicarboxylates have been reported to be effective in TM-catalyzed carbon–carbon bond-forming reactions such as Heck, Suzuki, Stille, and Hiyama cross-couplings (Scheme 266).

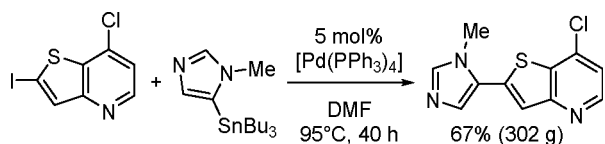
Remarkable enhancement in reactivity has been observed for the reagents exhibiting intramolecular N → Sb interactions. This phenomenon has been used in the design of convenient antimony-based coupling reagents, which are easy to synthesize and readily undergo Suzuki cross-coupling.⁶¹⁰

The TM-catalyzed transformation of organotellurium compounds has remained largely unexplored. However, some progress in the application of tellurium has been observed in the past 20 years because these species have been identified as alternatives to halogens as electrophilic partners in palladium-catalyzed cross-coupling reactions. The application of organotellurium compounds in organic synthesis has been summarized in several reviews.^{611–614} Alkynyltellurides readily undergo ultrasound-assisted homocoupling in the presence of a

Scheme 263. Alkynylstannanes in Organic Synthesis



Scheme 264. Synthetic Applications of Migita–Kosugi–Stille Coupling in the Synthesis of the VEGFR Kinase Inhibitor



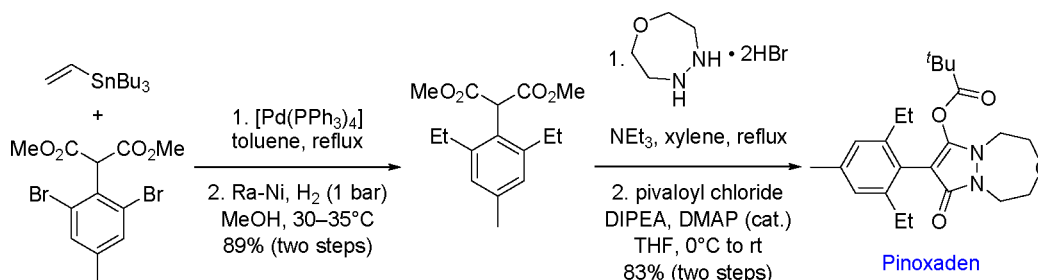
palladium catalyst or may undergo Kumada coupling with a Grignard reagent in the presence of manganese(II) chloride and copper(I) iodide as catalysts (Scheme 267).

Vinyltellurium derivatives undergo several palladium-catalyzed cross-coupling reactions (Scheme 268).

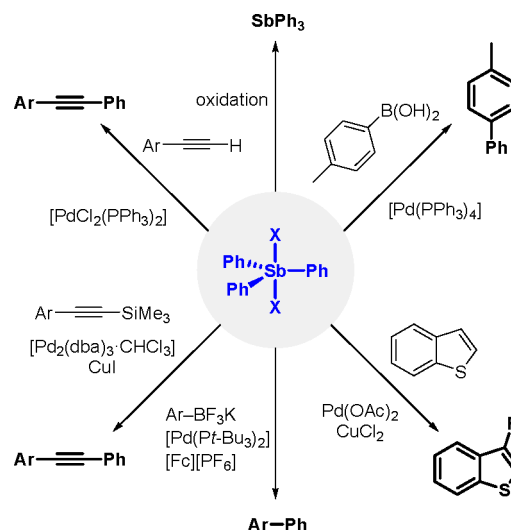
Perspectives of Inorganometallic Catalysis

It can be concluded on the basis of this Review that inorganometallic compounds containing direct metal–metalloid bonds play a crucial role in catalysis. We considered only the compounds containing bonds between metals, mainly TMs, and seven other elements, typically metalloids (E) (E = B, Si, Ge, Sn, As, Sb, Te) in our Review. In terms of catalysis, all these bonds are important and are often found in intermediates that are essential parts of the catalytic cycles of many processes that furnish new or well-known organometalloid compounds. In most cases, they are derivatives that contain C–E but also O–E or N–E bonds. Through catalytic transformations involving such derivatives, a process can have

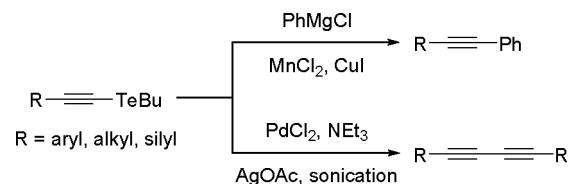
Scheme 265. Synthesis of Pinoxaden



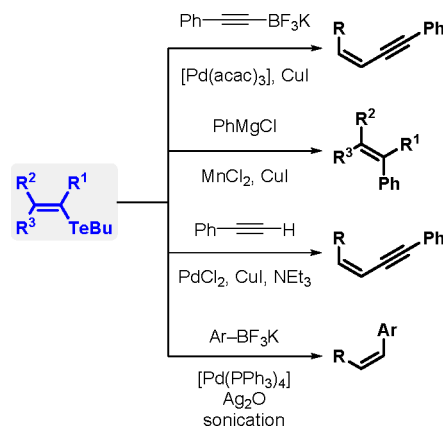
Scheme 266. Triarylantimony Dicarboxylates in Catalytic Organic Synthesis



Scheme 267. Synthetic Applications of Alkynyltellurides



Scheme 268. Applications of Vinyltellurides in Cross-coupling



certain regio-, chemo-, and stereoselectivity to produce compounds not available by other synthetic methods.

Analysis of the recent literature reports shows some specific trends in the catalytic processes that use inorganometallic compounds. First of all, interest in the first row TMs, in particular earth-abundant metals, has grown significantly. This is of course associated with much higher abundance, lower toxicity and, especially, price that is lower than that of the platinum group metals, which have long dominated this type of catalytic processes. The use of these TMs to form bonds with metalloids as effective catalysts has increased the interest in multidentate, and especially tridentate, ligands. These tridentate ligands in particular enable the formation of pincer complexes, which are highly active, selective, and, above all, stable.

However, the processes involving complexes that contain a double bond between a TM and a metalloid are also gaining importance. The associations of this type have not been addressed in our review, but there are many interesting articles on this topic.³⁰ In particular, numerous studies by the Tilley group (for example, see ref 615) on metal–silylene complexes and the studies by Braunschweig^{616,617} and Ghosh⁶¹⁸ groups on metal–borylene complexes are extremely interesting and provide plenty of valuable information.

Despite the extremely rapid evolution of this field, there are still a few areas that will surely be developed in the near future. Hydrofunctionalization of alkenes and alkynes catalyzed by earth-abundant metal complexes with tridentate ligands has not yet found any large-scale industrial application. The formation of low-oxidation metal species is necessary to activate hydrogen-heteroatom bonds, but it is very sensitive to oxygen and moisture, which is a major obstacle to their industrial application. Consequently, to scale up the process for industrial applications, the issue of sensitivity must be addressed without compromising their catalytic performance. The development of highly efficient and easy-to-handle catalysts that can be used in the large-scale synthesis of commercially important products is certainly an investigation area for the near future. On the other hand, transition metal-free catalysts for alkyne hydroelementation using Si, B, Sn, and Ge hydrides, intensively reported over the past decade, seem to be an interesting alternative to the conventional catalytic regimes based on transition metal complexes.⁶¹⁹

Some reviews emphasize the need for TM-complexes immobilized on inorganic or polymeric supports^{18,19} as recyclable heterogeneous catalysts. Although heterogeneous catalysts are not discussed in the review, their connections with well-defined surface-immobilized TM complexes illustrate the general strategy for this type of heterogeneous catalysis. The reported examples, particularly in the catalysis of hydro-silylation^{50–52} as well as Beller's concept of SACs as materials with isolated TM centers stabilized by neighboring salts,^{19,51} have been convincing arguments for the initiation of extensive studies which can be applied in academia and industry.

In view of the known activity of metal nanoparticles in catalytic processes^{620,621} in some reactions described in this Review, metal clusters and/or metal nanoparticles can be considered as active intermediates. The activity of stabilized or immobilized metal nanoparticles has been well described for the formation of C–B bonds as a result of hydroboration (Ir, Fe), diboration (Au, Pd, Pt) silaboration (Pt) or borylation of C–H (Pd, Ir) and C–X bonds (Cu, Pd) [for review see ref 622, 623.]. Recently, Mandal reported arene C–H borylation with HBpin catalyzed by Ni nanoparticles generated in situ from abnormal *N*-heterocyclic carbene Ni(II) complex.⁶²⁴

Bose revealed catalytic activity of presynthesized copper nanoparticles in hydroboration of alkenes and β -borylation of α , β -enones with B₂pin₂⁶²⁵ as well as borylation of alkyl chlorides and bromides.⁶²⁶ On the other hand, Kleeberg's works show that copper boron complexes recognized as key intermediates in copper catalyzed borylation may decompose under catalytic reaction conditions to form low valent copper clusters,⁶²⁷ which as sources of boron nucleophiles, have to be considered as potential reactive intermediates in borylation reactions.⁶²⁸ In the future research, this aspect of catalysis with transition metal complexes should be taken into greater consideration.

TM-catalyzed bis-metalations of C–C multiple bonds have received considerable attention during the past two decades because they provide a convenient and direct method for regio- and diastereodivergent as well as regio- and stereoselective access to difunctional building blocks. Significant progress in this area has been made by the application of new effective catalysts, deeper understanding of the reaction mechanisms, and introduction of selective chiral ligands so that bis-metalation chemistry can be applied in enantioselective synthesis. The developments over the past decade have made it possible to employ simple copper catalysts instead of the traditionally used platinum and palladium complexes and revealed many new variants of bis-metalation processes (also enantioselective) based on the three-component coupling of alkynes or alkenes with bis-metalloids and metalloid alkoxides. Special attention has been paid to the development of bis-metalations with heterodimetallid compounds, among which silaboration plays a particularly important role as the resulting products can undergo chemoselective cross-coupling reactions with a high regiocontrol level to give biologically and pharmaceutically active molecules.

Arene C–H borylation in the presence of the most active catalysts proceeds effectively under mild conditions (rt) with a 1:1 ratio of the boron unit and arene, with functional group tolerance. The reaction offers a convenient method for arylboronic ester synthesis. Recent achievements from the Hartwig laboratory demonstrate selective procedures for the undirected borylation of primary C–H bonds (or secondary bonds if the primary C–H bonds are absent or blocked).⁵⁶⁷ The protocol enables the introduction of a range of functional groups at the strongest alkyl C–H bonds in organic molecules. More research will certainly be carried out on this system and other methods for the borylation of Csp³–H bonds. A further increase in the importance of boron compounds should be anticipated.

Silylation of arene C–H bonds is much less developed than the borylation. Catalysts have been developed for reactions with an arene as a limiting reagent. Further progress should be made for finding new more active catalysts for the process. Undirected intermolecular silylation of unactivated Csp³–H bonds is currently in the initial stage of research. The reaction, including the challenging methane silylation, is expected to be the subject of intensive research in the near future.

Methods for the borylation of C–X bonds (X = halogen, sulfonate) are well developed and represent an attractive alternative for the formation of metal–metalloid bonds. For example, they enable the synthesis of C–As or C–Te bonds. Progress in research on processes involving the activation of C–F bonds can be expected. Research on the functionalization of C–C and C–Het bonds will continue.

The asymmetric synthesis of secondary and tertiary boronic esters remains an area with great potential for the development of new methodologies. The versatility of alkylboronic esters and their importance in the synthesis of complex molecules mean that the challenge of introducing a carbon–boron bond in a stereodefined and site-selective manner will continue to be of great interest to many research groups. Enantioselective intermolecular borylation of Csp^2 –H and Csp^3 –H bonds is still underdeveloped. As it remains an area with great potential for the development of new methodologies, steady progress in this field can be expected.

The dehydrocoupling of hydrometalloids remains the most benign and atom-economical process for producing macromolecular compounds with metalloid–metalloid bonds with interesting electronic and optical properties. According to the general trend observed in inorganometallic catalysis, traditionally used d^0 metallocene complexes and noble metal complexes are slowly being replaced by earth-abundant metal catalysts (e.g., Cr, Fe, and Ni complexes). However, the reported catalytic systems often suffer from catalyst sensitivity toward moisture and oxygen, complexity, and the high cost of the ligand used. High expectations are also related to the development of modern homo- and heterodehydrocoupling reactions leading to molecular bis-metalloids (e.g., diboranes or silyboranes), which are commonly used as reagents in bis-metallation and C–H metalation processes.

Metalloid vinyl derivatives react with presynthesized transition metal hydride complexes, which leads to a nearly quantitative formation of TM–E (E = B, Si, Ge) and ethylene bonding. They can be used as convenient sources of metalloids. Therefore, they can participate in reactions in which TM–H bonds are formed (e.g., as a result of the oxidative addition of CH, EH, or Het–H bonds to Ru, Ni transition metals), which ultimately leads to the formation of C–E, E–E, or Het–E bonds. The reaction potential has not been fully exploited, and further research is to be expected.

All the previously discussed catalytic processes show the importance of the TM–E bond, which was generally generated *in situ*. Therefore, a recent challenging problem is to prepare TM–E bond-containing complexes that can later be used as catalysts. In particular, it will be important to select a ligand for the metal and use it to activate nonreactive chemical bonds and molecules based on rational design of the ligand structure. This topic has been very well presented in Takaya's review article.¹⁶

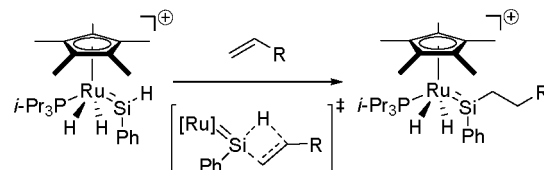
An important challenge for the future is to implement new and synthetically valuable molecular transformations that are not easy to achieve with standard transition metal catalysts, using the characteristic reactivity of TM–E complexes from the point of view of synthetic chemistry.

The best argument for the essentially different role of organometallic (TM–C) and inorganometallic (TM–E) complexes in catalysis is provided in a very recent review by the Whited and Taylor group,³⁰ and it focuses on considerations for catalysis and similarities and differences between TM–C and TM–Si chemistry. The latter is the best representative of inorganometallics (TM–E complexes).³⁰ Most reactions of TM–Si complexes can be predicted on the basis of several principles important in catalytic systems, such as electronegativity that is lower than that of carbon (and also of hydrogen and many TMs). However, the relatively large size of the silicon atom enables the formation of a variety of bonds at the metalloid (e.g., secondary interactions with

hydride and other X-type ligands). Finally, the above features are quite powerful and allow silicon to behave in many instances more as a second TM than as an organometallic ligand.

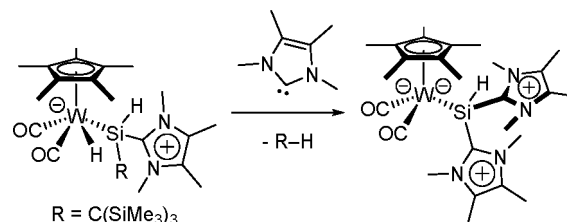
The concerted insertions of alkenes into Si–H bonds (in the Glaser–Tilley mechanism of hydrosilylation (Scheme 269)

Scheme 269. Insertion of Unsaturated Substrates into Si–H Bonds of Silylenes



and the breaking of strong silicon–carbon bonds with 1,2-alkane elimination (Scheme 270)⁶²⁹ provide convincing

Scheme 270. NHC-Promoted 1,2-Alkane Elimination from a W–Si Complex. Adapted from Ref 629. Copyright 2015 American Chemical Society



evidence that the TM–Si complex may behave like a bimetallic system to develop cooperative catalysis, which has been demonstrated primarily for TM–boron systems.³⁰

The examples show that the reaction pathways of TM and silicon share some features (e.g., flexible coordination environment and kinetically labile bonds) and can therefore be quite complementary.

As well as silicon compounds, boron compounds play the most important role among organometalloids. Direct borylation is a powerful synthetic methodology to generate organo-boron compounds. However, there are also many areas for improvement and further development on this topic. One of these is the limitation of the substrates. Increasing efforts have been made to use sustainable aliphatic feedstocks for syntheses of alkylboronates. Moreover, the borylation of simple raw materials using nonactivated OH, SH, NH₂, and COOH as the leaving groups is still a huge challenge due to the kinetic and thermodynamic stability of these chemical bonds. The functionalization of internal alkenes without isomerization also requires further improvement. In Markovnikov hydroboration, the regioselectivity control of aliphatic alkenes is far from ideal. Outstanding regioselectivity control in the hydroboration of unsymmetrical 1,2-disubstituted alkenes remains a challenge. Overcoming this will likely require more modular ligand platforms for the accelerated evaluation of metal–ligand combinations to find a more preferred precatalyst system. The versatility of alkylboronic esters and their resulting importance in the synthesis of complex molecules means that the challenge of introducing a carbon–boron bond in a stereodefined and site-selective manner will continue to be of great interest to many research groups. Certainly, research will

be carried out on the further improvement of selectivity in the late stage of modification of complex functional molecules as well as on the development of asymmetric transformations.

Catalytic hydrometalation processes—and above all, C–H bond activation reactions with hydro- and bis-metalloids, which have been intensively developed in recent years—have revolutionized modern synthetic organic chemistry ensuring straightforward access to a wide variety of organometalloids. Boronate esters, organosilanes, and organostannanes represent the most popular organometalloid nucleophiles that offer beneficial robustness and reactivity in cross-coupling reactions, and these have been applied in numerous sequential (tandem) processes of alkene, alkyne, and arene functionalization. The experimental advances in the reactivity of new organometalloid reagents (e.g., organogermanium and organoantimony derivatives) in C–C- and C–X-bond-forming transformations as well as the application of novel catalysts (based on gold but also coinage metal complexes) open up new routes for the intensive development of cross-coupling methods. The growing needs of organic synthesis will certainly stimulate the development of further synthesis methods of organometalloids, for which inorganometallic catalysis is an invaluable tool.

From the catalytic point of view, all transformations involving the TM–E bond are important, but when it comes to the production of materials, the silicon derivatives are of the greatest importance, as all other derivatives are in most cases raw materials for the production of new organometalloid compounds. Formation of the TM–Si bond is a key step in the catalytic process of hydrosilylation. It is concluded that hydrosilylation processes are commonly used in the production of silane coupling agents, in the cross-linking of silicones, and in the production of hybrid and preceramic materials. They are also used in the synthesis of nanoparticles with a strictly defined spatial structure (silsesquioxanes and dendrimers) and in the production of nanocomposites containing nanoparticles.⁶³⁰ The methods for synthesizing polysilanes (crucial raw materials for the production of sensors, LEDs, photovoltaic devices, and nonlinear optics) are also continuously developed, using new catalytic systems. Silicone materials and production technologies have steadily improved since the turn of the 21st century, with the majority of advances driven by new application needs, which have been met primarily by new products developed by established silicone manufacturers or specialty formulators.

Boron compounds also play an increasingly important role in applications such as small-molecule activation for fuel synthesis, organic light-emitting diodes (OLEDs), hydrogen production and storage, and electrolyte materials.^{630–632} The widespread use of boron-containing compounds is closely related to the unique properties of the element itself. Because of the electron deficiency of boron, its compounds may act as electrophiles under certain conditions, while under other conditions, they will act as nucleophiles. As a result, boron can form a variety of compounds whose properties can be tailored to specific applications.

It can be concluded on the basis of this Review that inorganometallic compounds containing direct transition metal–metalloid bonds play a crucial role in catalysis as well as in the synthesis and functionalization of many organic and inorganic derivatives. Such catalytic transformations produce compounds that cannot be obtained by other methods or permit running a process with certain regio-, chemo-, and

stereoselectivity. The deep insight into the catalytic activity of TM–Si and TM–B complexes can be extended to other TM–E complexes, particularly when E is Ge or Sn, and a variety of supporting coligands at the TM complex. Based on the comprehensive information collected here, new catalysts of the known reactions could be designed and, at the same time, novel strategies for the development of new processes will be proposed.

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Notes

The authors declare no competing financial interest.

Biographies

Professor Bogdan Marciniak received M.Sc. (1963), Ph.D. (1970) and D.Sc. (1975) from the Adam Mickiewicz University, Poznań (Poland). He is a member of the Polish Academy of Sciences (1994), member of European Academy of Arts, Sciences and Humanities (2009); doctor honoris causa of the Technical University in Łódź (Poland). Dean of Faculty of Chemistry (1985–1988) and President of the Adam Mickiewicz University (1988/1990). He was a postdoctoral associate with Professor R.C. Schowen, Kansas University (1970/1971) and he founded (the first in Poland) Poznań Science and Technology Park (Director 1995–2015).

His research activity is focused on the organosilicon chemistry and catalysis by organometallic and inorganometallic compounds. Synthesis and reactivity of organic derivatives of silicon but also containing B, Ge, Sn, and other metalloids mainly in the presence of transition metal complexes are of particular interest. Properties and application of organosilicon compounds are widely studied.

Professor Marciniak supervised 40 Ph.D. Thesis and is an author or coauthor of over 450 publications (cited over 6000 times with h-index 35), 200 patents, 11 licenses, and 42 technologies as well as 22 book chapters (e.g., *Handbook of Metathesis* (Wiley-VCH, 2003), *Encyclopedia of Catalysis*, (J.Wiley & Sons, Inc. N.Y., 2003 and new on-line edition, 2010), *Applied Homogeneous Catalysis with Organometallic Compounds* (Wiley-VCH, 2002). He is also editor and coauthor 15 books, including “*Comprehensive Handbook on Hydrosilylation*” (Pergamon Press, 1992).

His group has cooperated with large international corporations producing silicones and silanes, including Degussa-Hüls (1992-1995), General Electric Silicones (1998-2005), Momentive Performance Materials (2006), and Dow Corning (2007-2010) in the area of developing new catalytic systems used for silicone curing via hydrosilylation.

Cezary Pietraszuk received M.Sc. (1988) and Ph.D. (1995) from the Adam Mickiewicz University, Poznań under the supervision of Professor Bogdan Marciniak. In the years 1998-2000 he completed a postdoctoral fellowship in the group of Professor Helmut Fischer at the University of Konstanz as a scholarship holder of the Alexander von Humboldt Foundation. He received habilitation in 2006. Since 2016, he has been a professor at the Adam Mickiewicz University and since 2011, a head of the Department of Organometallic Chemistry. He is the coauthor of over 100 scientific publications, book chapters and patents. His research interests include organometallic chemistry and catalysis with transition metal complexes.

Piotr Pawluć is employed at the Faculty of Chemistry, Adam Mickiewicz University, Poznań. He is a student of Professor Bogdan Marciniak (Ph.D. 2004, habilitation in 2012). In the years 2008-2009, he completed a postdoctoral research internship at the University of Lille in the group of Professor Andre Mortreux. Since 2021, he has been a professor at the Adam Mickiewicz University. His research interests deal with the synthesis and reactivity of organometallic compounds in addition and coupling reactions catalyzed by transition metal complexes and recently also in the presence of p-block element compounds. His research also focuses on the use of organometallic compounds in selective organic synthesis. Scientific achievements of professor Piotr Pawluć include the coauthorship of over 70 scientific publications, book chapters, and patents.

Hieronim Maciejewski – Professor of chemistry, graduated from the Faculty of Chemistry, Poznan University of Technology (1986). In 1995, he received a Ph.D. degree in chemistry at the Faculty of Chemistry, Adam Mickiewicz University, Poznań. He received Habilitation in 2005. Since 2014, he has been a professor of chemistry at Adam Mickiewicz University. He is a coauthor of 45 technologies for silicon compounds syntheses, an author or coauthor of 196 publications in international specialized journals, 98 patents and patent applications, a coauthor of 1 book and 12 chapters in English concerning hydrosilylation. Currently, he is the head of the Department of Chemistry and Technology of Silicon Compounds at the Faculty of Chemistry, Adam Mickiewicz University, Poznań. He is also the director at Poznan Science and Technology Park, Adam Mickiewicz University Foundation, and the president of the Board of AMU Foundation.

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