

General Introduction

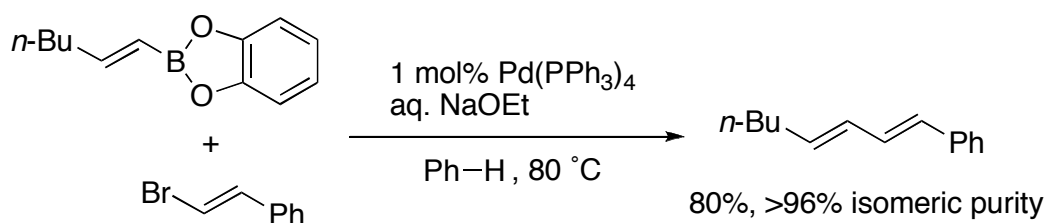
1. Organoborons under Nickel Catalysis

Organoboron compounds were first synthesized in the mid-19th century by Frankland¹ from boronic acid esters and organozinc reagents. Subsequently, analogous procedures were developed with other organometallic compounds.² On the other hand, Stock³ and Hurd⁴ reported reactions of diborane (B_2H_6) with alkynes and alkenes in 1923 and 1948, respectively. Although the reactions were the breakthrough of hydroboration chemistry, these were not synthetically useful due to low yields. In 1956, Brown discovered that alkenes reacted with diborane very smoothly in ethereal solvent at low temperature to give the corresponding alkylboron derivatives in quantitative yields.⁵ Since then, hydroboration chemistry has been widely explored involving the development of new hydroboration agents and provided the facile and practical access to organoborons from readily available unsaturated molecules.⁶

The unique properties of organoborons are fundamentally based on their high electron deficiency caused by the vacant *p*-orbital on the boron atom. Indeed, carbon-boron bonds are easily converted to the corresponding carbon-oxygen⁷ and carbon-nitrogen⁸ bonds through the nucleophilic attack of peroxides and hydroxyamines to the boron center followed by 1,2-migration of the organic groups on boron. On the other hand, the transformation of carbon-boron bonds to carbon-carbon bonds was believed to be generally difficult because organoborons are highly electrophilic and have barely polarized carbon-boron bonds. For instance, unlike Grignard reagents and organolithium compounds, organoborons do not react with carbonyl compounds such as aldehyde and ketone (except for allylborane reagents⁹). However, in 1979, Suzuki and Miyaura opened the door to the carbon-carbon bond formation with organoboron compounds with the aid of transition metal catalysts and suitable bases (Scheme 1).¹⁰ It was the discovery of so-called “Suzuki–Miyaura cross-coupling reaction”. They activated vinylboronates through the coordination of negatively charged base to the boron atom

and succeeded in the transfer of the vinyl groups from boron to palladium. The coupling products were obtained with high isomeric purities in good yields.

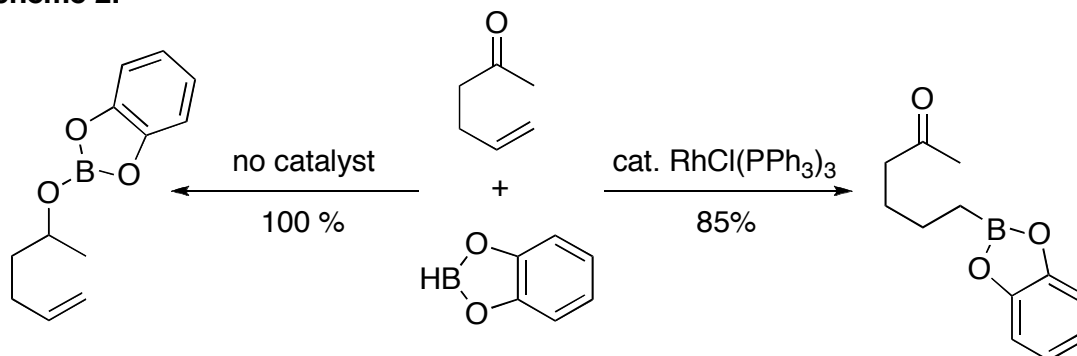
Scheme 1.



At that time, many organometallic reagents such as lithium,¹¹ magnesium,¹² aluminum,¹³ zinc,¹⁴ zirconium,¹⁵ and tin¹⁶ were known to undergo similar cross-coupling reactions in the presence of nickel or palladium catalysts. However, significant attention have been focused on the use of organoboronates since they were more stable to water and oxygen and easier to handle without any special precautions. Moreover, the functional group compatibility of the Suzuki-Miyaura coupling was generally superior to that of cross-coupling reactions using other organometallic reagents. These advantages enabled Suzuki–Miyaura cross-coupling reaction to spread widely over various fields of organic synthesis.¹⁷ With the recent development of new ligands for transition metal catalysts,¹⁸ it is now among the most reliable and promising methods for the carbon-carbon bond formation.

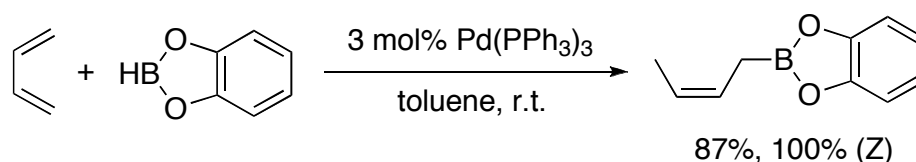
The pioneering work with palladium catalysts by Suzuki and Miyaura promoted the development of hydroboration chemistry using a variety of transition metals. Nöth reported rhodium-catalyzed regio- and chemoselective hydroboration of alkenes with less reactive 1,3,2-benzodioxaborole (catecholborane) (Scheme 2).¹⁹ In the absence of the catalyst, the reduction of carbonyl function was favored to furnish the corresponding alcohol. The preferable insertion of the olefin moiety to the rhodium-hydride bond of the borylrhodium hydride species formed in situ would lead to the selective formation of organoboron compound. Later efforts for the development of chiral catalyst system $[\text{Rh}(\text{cod})_2]^+\text{BF}_4^-/(\text{R})\text{-BINAP}$ ²⁰ made the reaction asymmetric. The combination of the Rh-catalyzed hydroboration process and the subsequent oxidation is formal asymmetric synthesis of chiral alcohols from alkenes.

Scheme 2.



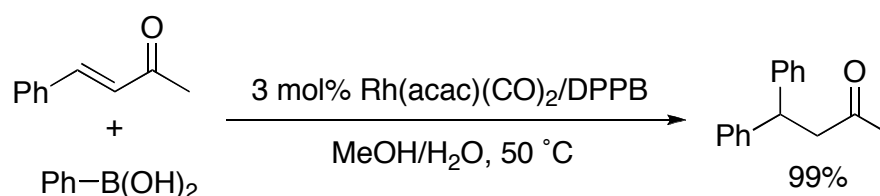
Suzuki and Miyaura themselves presented palladium-catalyzed hydroboration of 1,3-dienes.²¹ The products are synthetically useful allylboronates (Scheme 3).

Scheme 3.



In 1997, Miyaura reported rhodium-catalyzed conjugate addition of aryl- and alkenylboronic acids to α,β -unsaturated ketones (Scheme 4).²² Subsequent improvement of catalyst systems and detailed mechanistic studies broadened the substrate scope and rendered the catalytic reactions asymmetric.²³ The catalytic reactions compensate the low nucleophilicity of organoborons to carbonyl compounds and allow aryl- and alkenylboronic acids to be the promising reagents for arylation and alkenylation of various unsaturated substrates such as aldehydes, enones, and alkynes. Recently, cationic palladium complexes have been also found to catalyze similar reactions at much lower temperature.²⁴

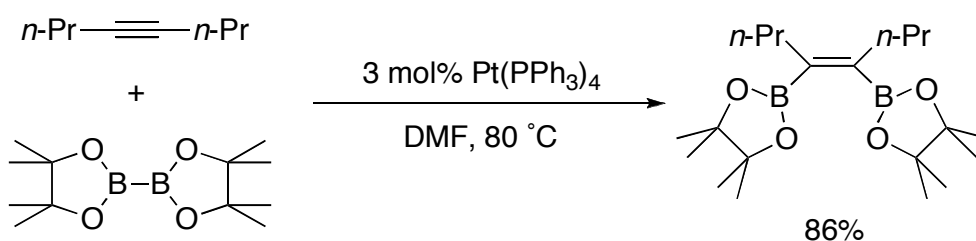
Scheme 4.



During the course of these studies, more efficient and mild preparative procedures for synthesis of organoborons were strongly desired. Such procedures could replace the

conventional methods such as transmetalation between highly reactive organometallic reagents and boronic acid esters and hydroboration reaction. Suzuki and Miyaura described platinum-catalyzed diboration of alkynes with stable and easy-to-handle bis(pinacolato)diboron (Scheme 5).²⁵ Subsequently, they succeeded in palladium-catalyzed cross-coupling reactions of aryl halides or allyl acetates with bis(pinacolato)diboron (Scheme 6).²⁶ The catalytic cycle would involve transmetalation of Pd(II) complexes with diboron. These methods provide a general route to a variety of highly functionalized organoboronates and polyborylated reagents. Furthermore, Hartwig and coworkers discovered direct borations of sp^2C-H and sp^3C-H with diborons under transition metal catalysis. So far, rhenium, ruthenium, rhodium, and iridium complexes are known to catalyze the direct boration of sp^2C-H and sp^3C-H .²⁷ 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (pinacolborane) instead of bis(pinacolato)diboron is often available for use. In particular, iridium catalysts are applicable to the regioselective boration of various aromatic and heterocyclic compounds (Scheme 7).²⁸

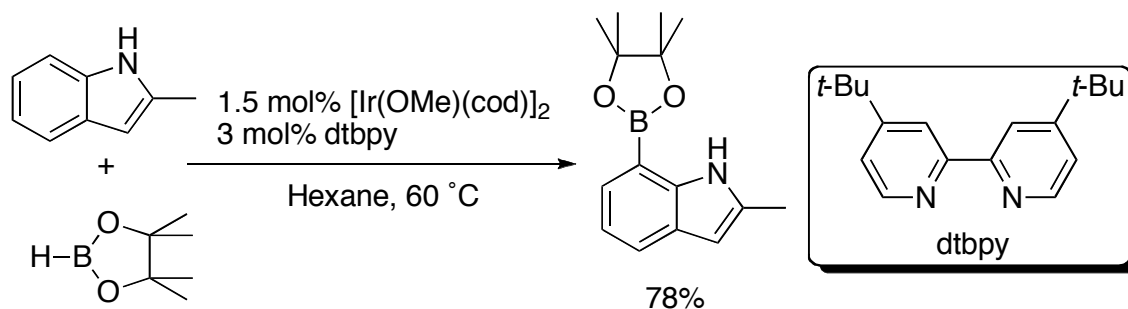
Scheme 5.



Scheme 6.



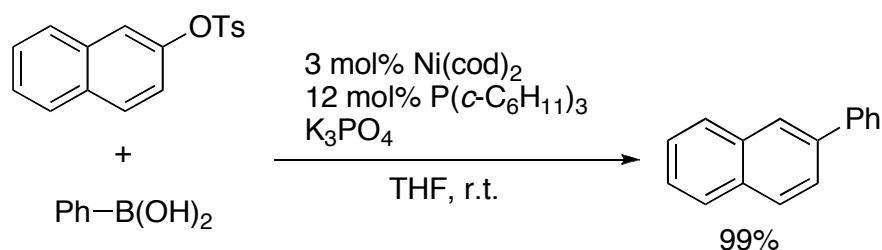
Scheme 7.



Taking account of the important roles of transition metals in the development of organoboron chemistry, it is no wonder many researchers have attempted to exploit nickel-catalyzed reactions with organoboron compounds.

Synthesis of biaryls via cross-coupling reactions has been extensively investigated, and has attracted much attention from the industrial point of view. Recent development of new ligands that possess sterically demanding and strongly σ -donating natures enabled the use of unreactive aryl chlorides for palladium-catalyzed reactions under very mild conditions. In Suzuki–Miyaura cross-coupling reaction of aryl tosylates or mesylates, nickel catalysts compensate palladium ones.²⁹ The reaction often proceeds even at room temperature (Scheme 8). It should be noted that the use of palladium catalysts with the same ligands did not lead to the formation of the cross-coupling products.

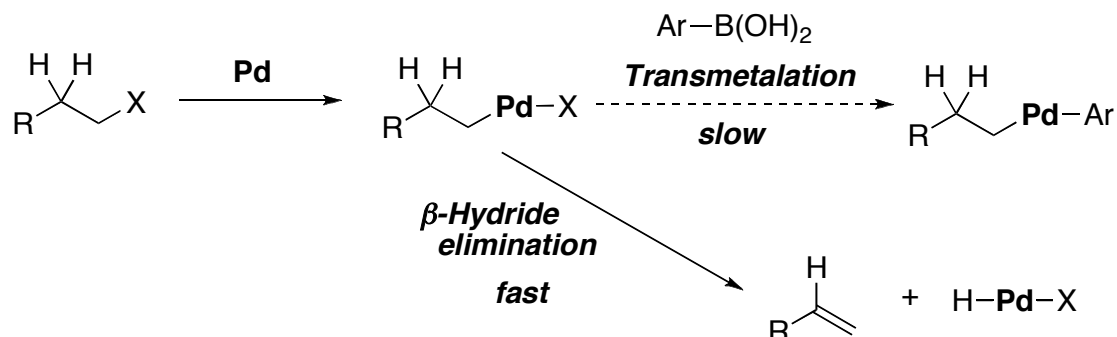
Scheme 8.



The most remarkable advantage of nickel catalyst compared to palladium catalyst is observed in the coupling reactions of alkyl halides. In general, attempts to perform the palladium-catalyzed coupling reaction of alkyl electrophiles with arylboronic acids fail due to the

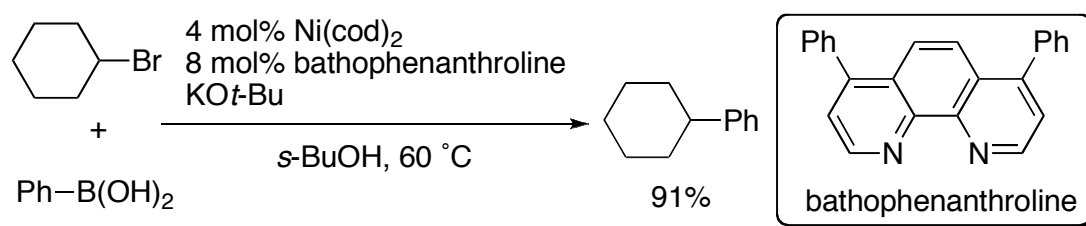
rapid decomposition of alkylpalladium intermediates through β -hydride elimination (Scheme 9).

Scheme 9.



Many efforts by Fu overcame the problem using $\text{Ni}(\text{cod})_2$ /bathophenanthroline catalyst (Scheme 10).³⁰ Further modification of ligands enabled the employment of quite unreactive secondary alkyl chlorides and the alkyl-alkyl coupling with 9-alkyl-9-BBNs.³¹ The catalytic cycle would involve the alkyl radical intermediates generated through a single electron transfer from electron-rich Ni to alkyl halides. Similar catalyst systems are effective for the cross-coupling reactions of alkyl halides with other organometallic reagents such as zinc, tin, and silicon.³²

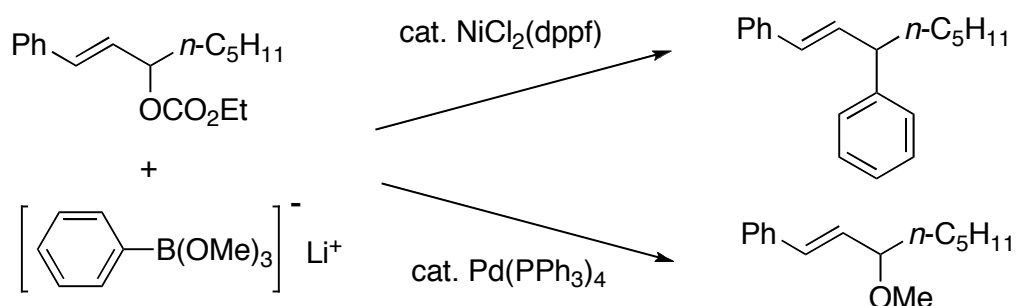
Scheme 10.



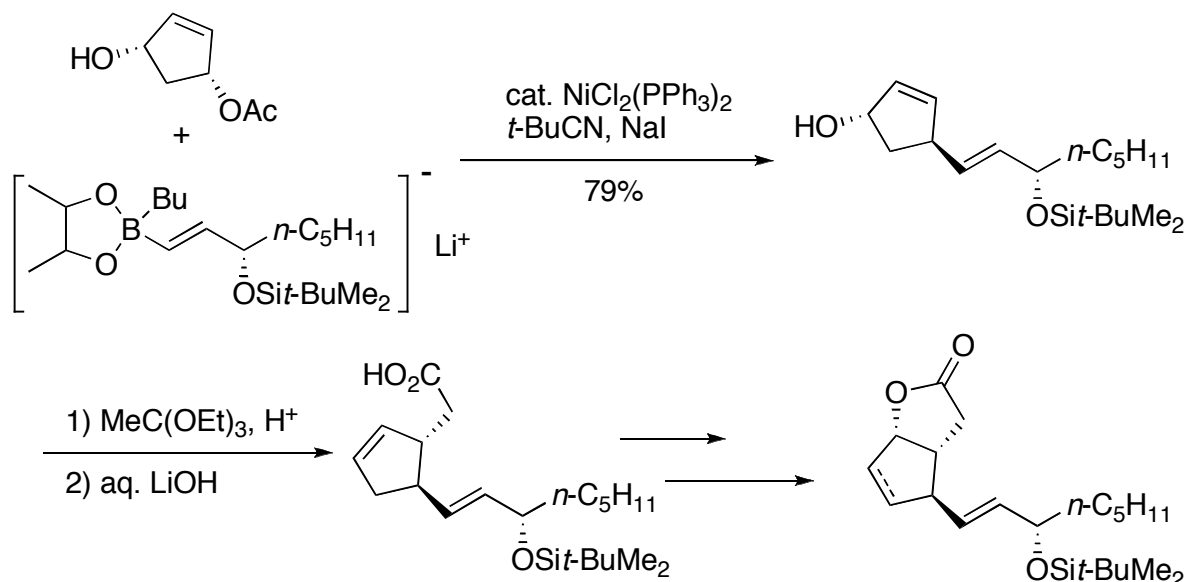
Although nickel-catalyzed allylic substitution of allyl alcohol derivatives has been studied over the past three decades, the nickel catalysts have much less attention than palladium ones. This is probably because nickel-catalyzed reactions with soft nucleophiles generally provided the lower regio- and stereoselectivity and efficiency, compared to palladium-catalyzed systems. However, recent studies have shown unique characters of nickel catalysts, in particular using tetracoordinated organoborates as nucleophiles. Kobayashi reported efficient and regioselective

nickel-catalyzed allylic arylation with lithium aryltrimethoxyborates (Scheme 11). Interestingly, with a catalytic amount of $\text{Pd}(\text{PPh}_3)_4$, the transfer of the methoxy group on the boron preferably occurred to afford the corresponding methyl ethers.³³ Alkenylation and alkynylation were also available in the presence of similar nickel catalysts.³⁴ The use of zinc borates instead of lithium ones enabled the installation of highly functionalized organic groups.³⁵ The reaction with chiral cyclopentenyl acetate under the modified conditions was applicable to the successful short-step synthesis of 11-deoxy PGE_2 and PGA_2 intermediates (Scheme 12).³⁶

Scheme 11.



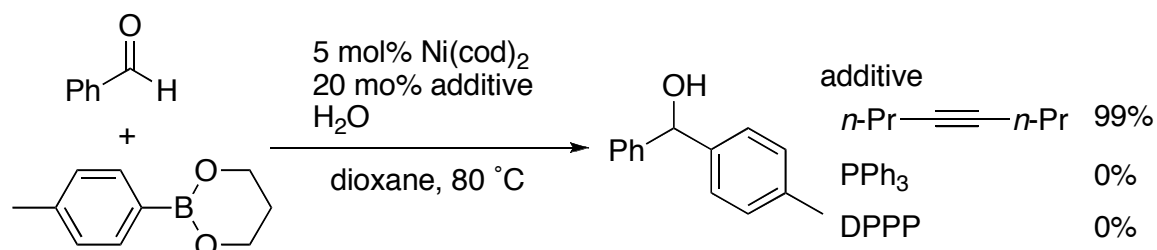
Scheme 12.



Like rhodium and palladium, nickel complexes were known to catalyze addition of organoborons to unsaturated molecules. Shirakawa and coworkers reported nickel-catalyzed

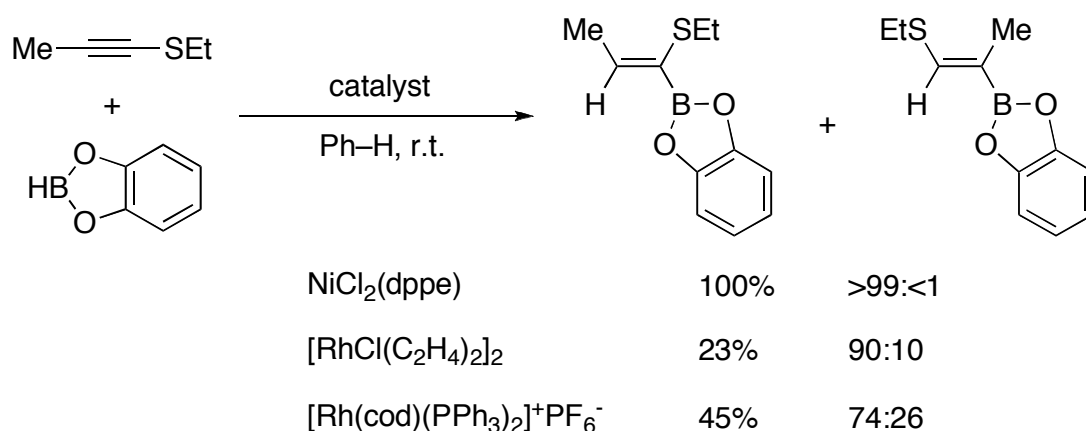
arylation and alkenylation of alkynes,^{37a} allenes,^{37b} aldehydes,^{37c} and enones^{37d} with aryl- and alkenylboronic acid derivatives (Scheme 13). Notably, in the case of aldehydes and enones, a catalytic amount of internal alkyne worked as an activator. The use of phosphine ligands such as PPh₃ and DPPP instead of 4-octyne resulted in no reactions and the starting carbonyls were recovered intact. Very recently, the Ni(cod)₂/(*R,R*)-Et-Duphos system was also found to show similar catalytic activities and the catalytic asymmetric addition was achieved albeit moderate enantiomeric excess.³⁸ η^2 -Coordinated nickel complexes with aldehyde would be the most plausible intermediate.

Scheme 13.



As described above, transition-metal-catalyzed hydroboration with unreactive hydroboranes ranks as one of the practical methods for the preparation of organoboron compounds. In the catalytic hydroboration of alkynyl sulfide, nickel catalysts are superior to rhodium catalysts with respect to their performance and regioselectivity (Scheme 14).³⁹

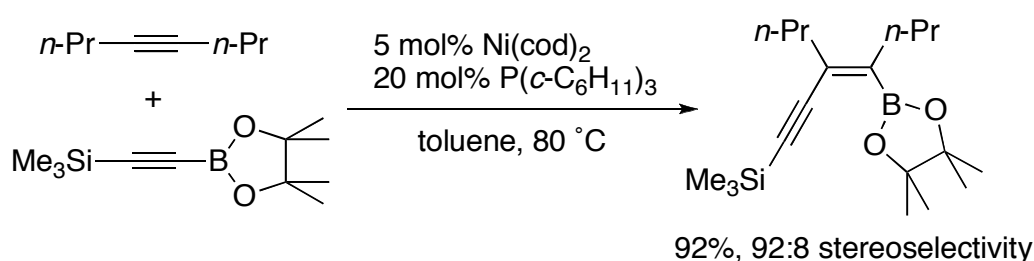
Scheme 14.



Suginome utilized nickel catalysts for boration of alkynes and 1,3-dienes with the

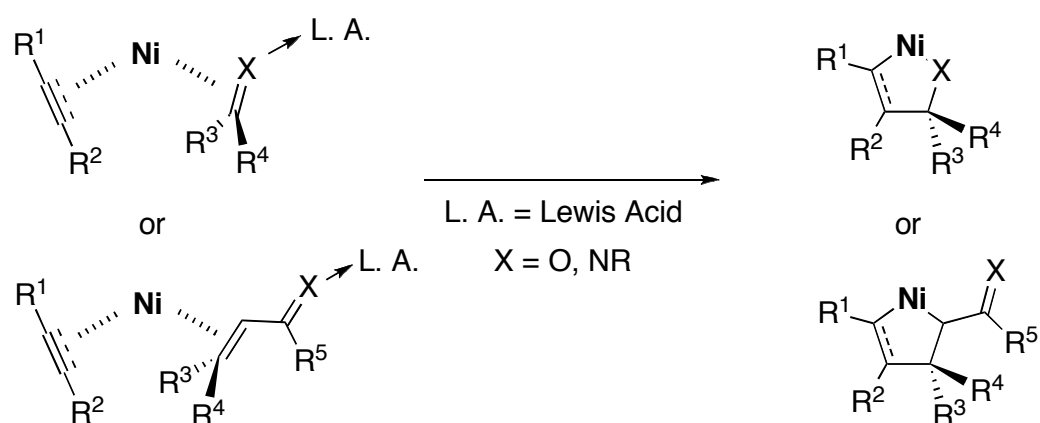
concomitant formations of the carbon-silyl and carbon-cyano bonds using versatile borane reagents such as silylboranes⁴⁰ and cyanoboranes⁴¹ to succeed in the multifunctionalization of unsaturated substrates. Moreover, he demonstrated carboboration of alkynes with alkynylboronates under nickel catalysis, which is an ideal transformation from the viewpoints of atom economy (Scheme 15).⁴² Further carbon-carbon bond formations from the products could be available using Suzuki-Miyaura cross-coupling reaction, thus, these transformations are powerful synthetic tools for the stereoselective construction of multisubstituted alkenes.

Scheme 15.



The Lewis acidity of organometallic reagents accelerates the cyclization of carbon-carbon unsaturated compounds and carbonyl compounds on nickel through the coordination of the carbonyl moiety to the Lewis acidic metal center (Scheme 16).⁴³

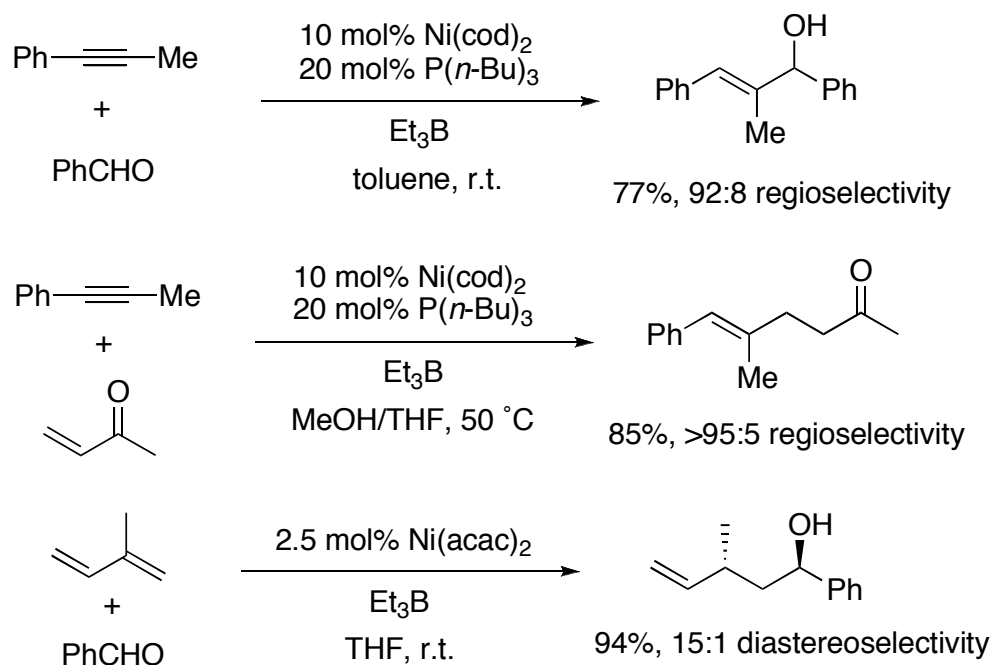
Scheme 16.



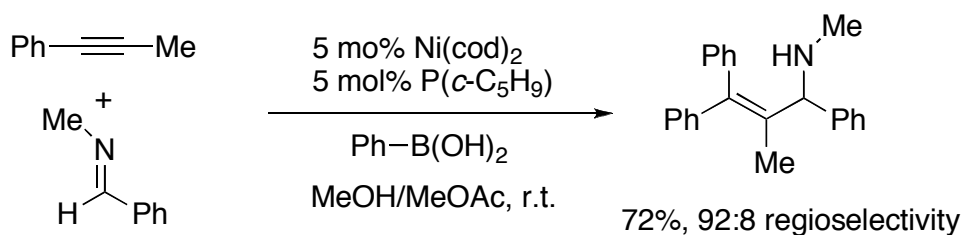
In particular, Et_3B is widely used for a variety of nickel-catalyzed reductive coupling reactions involving the cyclization process mentioned above in the catalytic cycle (Scheme 17).⁴⁴ The catalytic reactions are quite useful in organic synthesis, since two-step sequences were

required for the completion of the type of transformations according to the conventional procedures, i.e., (1) the preparation of vinylmetal reagents from a stoichiometric amount of metal hydrides and C–C unsaturated bonds and (2) addition of the vinylmetals to the carbonyl compounds. Moreover, high regio- and stereoselectivity were generally observed. The coupling reactions in water and alcoholic solvents are also conducted because of the stability of Et₃B. Organoboronic acids often play similar roles to Et₃B. In some cases, the installation of organic groups on boron to the products occurs to realize the three-component coupling reaction (Scheme 18).⁴⁵ Not only electron deficient π systems but also epoxides take part in a similar coupling reaction to furnish the corresponding homoallyl alcohols (Scheme 19). The formation of products proceeds as follows. An initial oxidative addition of epoxide to Ni(0) followed by insertion of alkyne gives the six-membered oxanickelacycle. The subsequent transmetalation with Et₃B, β -hydride elimination, and reductive elimination afford the products.⁴⁶

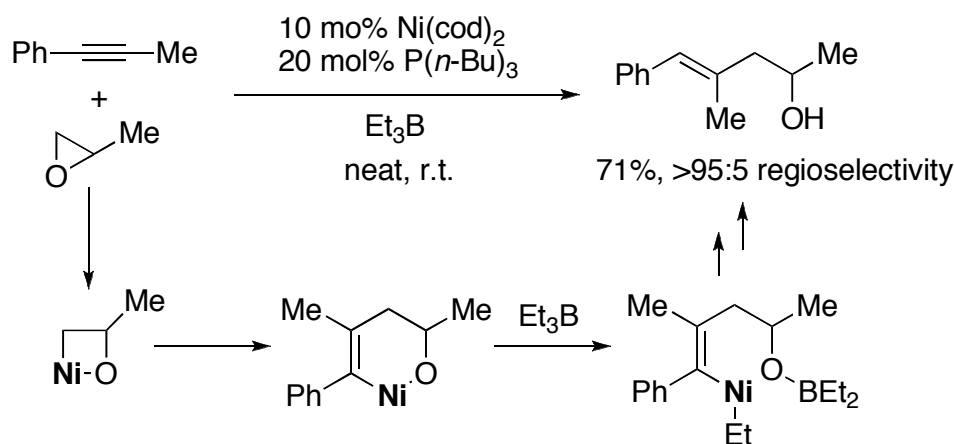
Scheme 17.



Scheme 18.



Scheme 19.

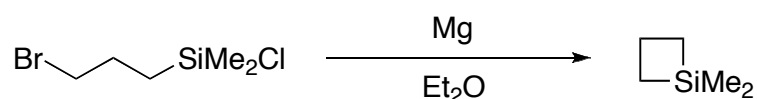


2. Silacyclobutane under Transition Metal Catalysis

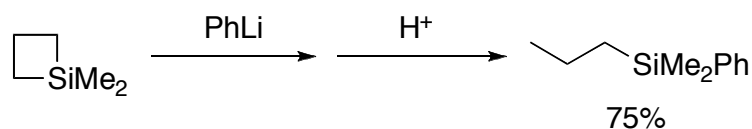
Development of highly selective reactions is one of the most fundamental and important goals in modern organic chemistry. To realize the aim, a variety of organometallic reagents have been prepared and applied to organic synthesis. Among them, organomagnesium and organolithium reagents have been widely studied. However, their high reactivity often causes a problem such as low chemoselectivity. In order to overcome the problem, many chemists have focused on organometallic reagents of group 13 or 14 metals such as boron, aluminum, and tin. With these reagents, many highly selective transformations have been accomplished, and nowadays they are indispensable synthetic reagents.

Organosilicon compounds have generally high thermal and chemical stabilities, compared to other organometallic reagents. Especially, tetraalkylsilanes are quite stable so that they are inert

to water and oxygen. Therefore, their low reactivity often becomes somewhat problematic from the synthetic point of view. However, silacyclobutanes have quite interesting reactivity based on their ring strain and high Lewis acidity.⁴⁷ Silacyclobutanes were first prepared in 1954 by Sommer and Baum via ring closure of 3-bromopropyldimethylchlorosilane with Mg (Scheme 20). To date, this is still the most general approach to silacyclobutanes.⁴⁸

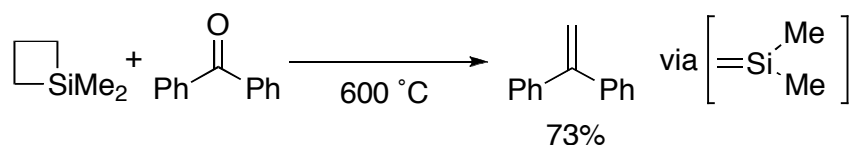
Scheme 20.

Silacyclobutanes easily undergo ring opening reactions in the presence of various nucleophiles. The reactions of 1,1-dimethylsilacyclobutane with acetic acid and water provided Me₂(*n*-Pr)SiOAc and Me₂(*n*-Pr)SiOH, respectively.⁴⁹ In contrast, nitrogen nucleophiles such as diethylamine did not cause a similar ring opening reaction. Treatment with phenyllithium followed by protonolysis afforded Me₂(*n*-Pr)PhSi (Scheme 21).⁵⁰

Scheme 21.

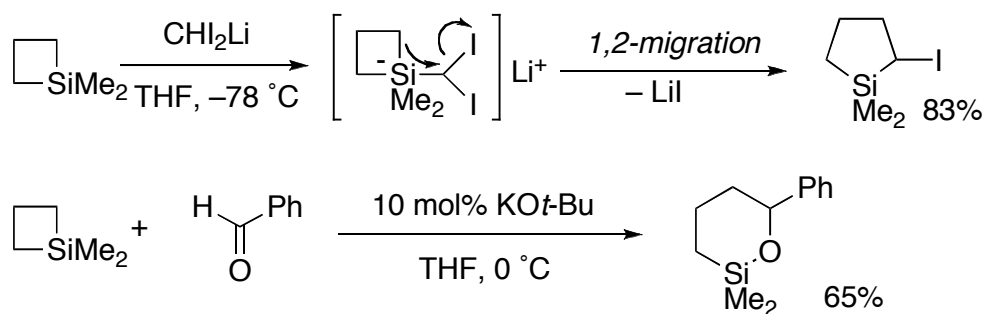
Silacyclobutanes are precursors of silene as well. 1,1-Dimethylsilacyclobutane is pyrolyzed at ca. 600 °C to generate 1,1-dimethylsilene. The highly reactive silene rapidly undergoes dimerization to provide 1,3-disila-1,1,3,3-tetramethylcyclobutane.⁵¹ Carbon–Carbon⁵² and Carbon–Oxygen⁵³ multiple bonds are able to trap the silene. Copyrolysis of 1,1-dimethylsilacyclobutane and propyne furnishes 1,1,3-trimethyl-1-silacyclo-2-butene, although the yield is low. On exposure of benzophenone to the pyrolytic conditions of 1,1-dimethylsilacyclobutane, Wittig-type olefination proceeds to afford 1,1-diphenylethene in good yield (Scheme 22).

Scheme 22.



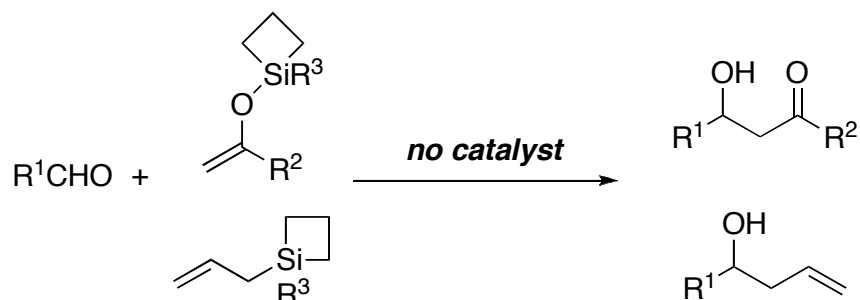
Although the fundamental reactivity of silacyclobutanes was studied as described above, their practical and synthetic utilities were not developed until Oshima and Utimoto applied them to a C_3 building block in the construction of carbon skeletons. They found the ring enlargement of silacyclobutanes with lithium carbenoids^{54a} or $\text{KO}t\text{-Bu}$ ^{54b} (Scheme 23).

Scheme 23.



The impact of the reports promoted further development by other research groups. Myers^{55a} and Denmark^{55b,c} focused on the high Lewis acidity of silacyclobutanes and independently developed aldol-type reaction of (1-alkenyl)oxysilacyclobutanes with carbonyl compounds in the absence of any catalysts. Oshima and Utimoto themselves also presented uncatalyzed allylation of carbonyl compounds with allylsilacyclobutanes (Scheme 24).⁵⁶ The reactions proceed via regulated six-membered transition states to afford the corresponding alcohols with high diastereoselectivity when the substrates have substituents at the terminal position of the olefinic moiety.

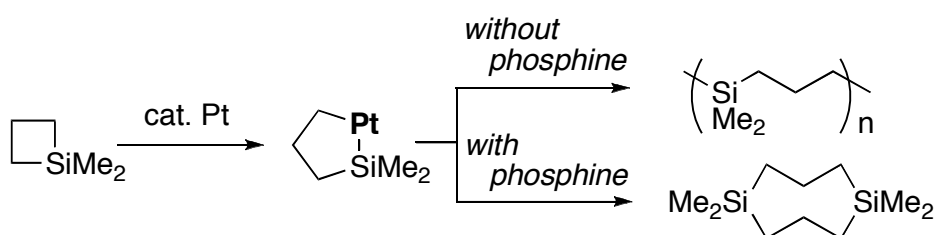
Scheme 24.



In the course of these studies,⁵⁷ silacyclobutanes have proved to be applicable to the transition-metal-catalyzed transformations.

Phosphine-free platinum complexes were found to catalyze ring-opening polymerization of silacyclobutanes in 1960's although the detailed mechanism was not clear.⁵⁸ Recently, Tanaka has succeeded in the isolation of the platinasilacyclopentane formed through the oxidative addition of the C–Si bond of silacyclobutane to Pt(0) and demonstrated that it could catalyze the polymerization of silacyclobutanes (Scheme 25).⁵⁹ This is the first direct evidence for the oxidative addition of silacyclobutane to transition metal. Moreover, he showed that the platinasilacyclopentane having suitable phosphine ligands catalyzed the dimerization but not the polymerization.

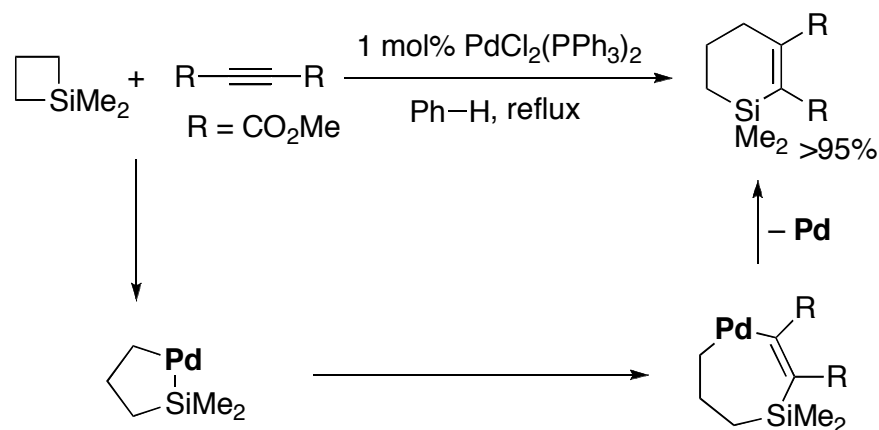
Scheme 25.



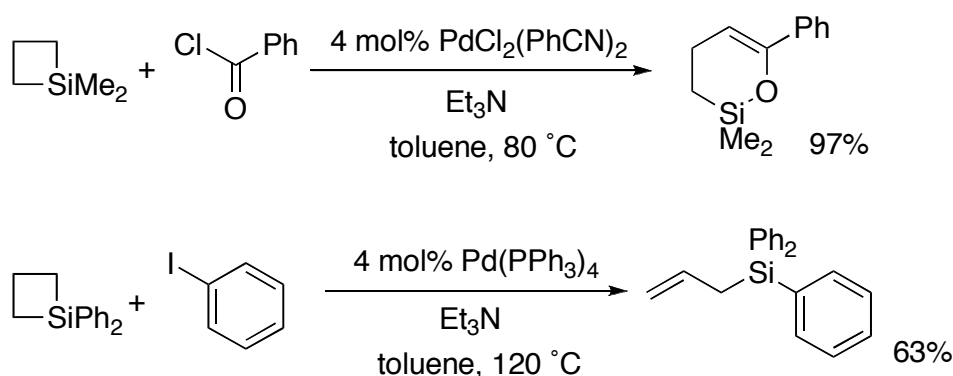
Palladium is the most actively studied transition metal to explore the useful catalytic transformation of silacyclobutanes. $PdCl_2(PPh_3)_2$ catalyzes [4+2] cycloaddition of 1,1-dimethylsilacyclobutane with dimethyl acetylenedicarboxylate to give the corresponding cyclic vinylsilane (Scheme 26).⁶⁰ The formation of the product could proceed as follows. Initial oxidative addition of 1,1-dimethylsilacyclobutane to palladium followed by insertion of the carbon-carbon triple bond of dimethyl acetylenedicarboxylate to the Pd–Si bond provides

seven-membered silapalladacycle. Subsequent reductive elimination furnishes the product and regenerates the palladium complex.

Scheme 26.

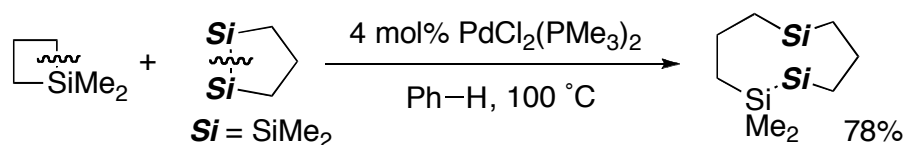


Tanaka circumstantially investigated the behavior of some palladium complexes in the presence of silacyclobutanes. He tested the insertion of acetylene compounds to palladasilacyclopentane, which was isolated from the reaction of silacyclobutane with the palladium complexes. However, the coordination of acetylene caused the reductive elimination of silacyclobutane instead of the expected insertion reaction. While the result was not consistent with the plausible mechanism illustrated in Scheme 26, it provided a new aspect that the oxidative addition of silacyclobutane to Pd(0) would be reversible.⁶¹ During the course of his studies, palladium complexes were also found to catalyze coupling reactions of silacyclobutanes with acid chlorides and aryl iodides in the presence of suitable amines to give the corresponding cyclic silyl enolates^{62a} and allylsilanes⁶³, respectively (Scheme 27). Acid anhydrides^{62b} or combinations of organic halides and carbon monoxide^{62c} are alternatives to acid chlorides. In the case of acid anhydrides, the addition of amine is not necessary for the reaction. A platinum complex, Pt(CH₂=CH₂)(PPh₃)₂, also mediates the reaction, although its performance is inferior to that of palladium complexes.

Scheme 27.

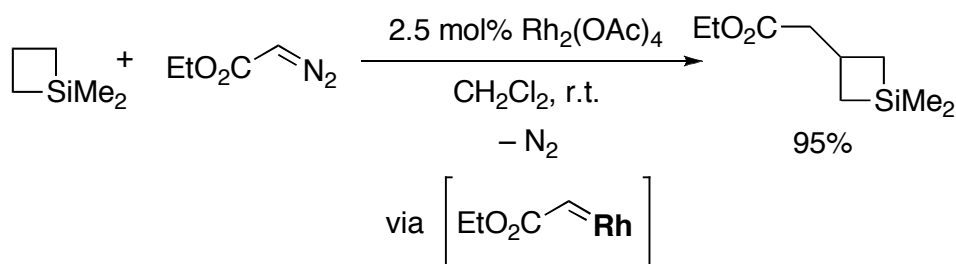
These catalytic reactions would proceed through the reaction between the R-Pd-X generated from Pd(0) and acid chloride or aryl iodide and silacyclobutane but not the oxidative addition of silacyclobutane to Pd(0), indicating that silacyclobutane works as not only an electrophile for low valent transition metal but also a nucleophile.

In addition, Tanaka reported palladium-catalyzed cross-metathesis between the C–Si bond of 1,1-dimethylsilacyclobutane and the Si–Si bond of 1,2-disila-1,1,2,2-tetramethylcyclopentane (Scheme 28).⁶⁴ Although the reaction mechanism was obscure, his group proposed that the oxidative addition of the C–Si bond of silacyclobutane or the Si–Si bond of disilane to the palladium complex initiated the reaction.

Scheme 28.

The reports on the reactions of silacyclobutane catalyzed by transition metals other than group 10 metals are quite rare. Only one precedent is rhodium-catalyzed coupling reaction with diazo compounds (Scheme 29).⁶⁵ The β C–H bond of 1,1-dimethylsilacyclobutane undergoes insertion of an ethoxycarbonyl-substituted rhodium carbenoid in a highly regioselective fashion. The catalytic reaction provides a facile access to functionalized silacyclobutanes.

Scheme 29.



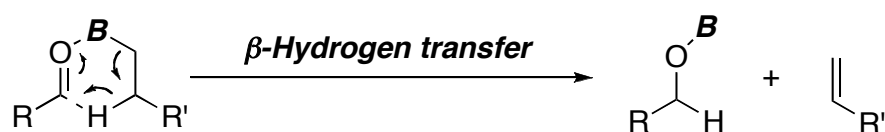
3. Overview of This Thesis

The author focused on the reactivity of low valent nickel complexes and found some new reactions of aldehydes and alkenes with organoborons and silacyclobutanes under nickel catalysis. In Chapters 1–4, nickel-catalyzed additions of organoboron compounds, in particular trialkylboranes, to aldehydes and α,β -unsaturated carbonyl compounds are described. In Chapters 5 and 6, unprecedented silylation reactions of aldehydes and terminal alkenes with silacyclobutanes in the presence of nickel catalysts are disclosed. Overview of this thesis is described below.

3.1. Nickel-Catalyzed Alkylation of Aldehydes with Trialkylboranes (Chapters 1 and 2)

Alkylation of aldehydes with alkylmetals is one of the most fundamental and practical methods for synthesis of secondary alcohols. In general, highly reactive alkylmagnesium and alkyllithium compounds are used to achieve the alkylation. On the other hand, trialkylboranes are known to react with aldehydes to furnish the corresponding reduced products, primary alcohols, not alkylated products, via β -hydrogen transfer reaction (Scheme 30).⁶⁶

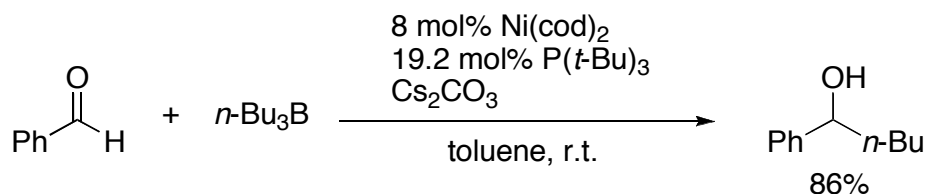
Scheme 30.



In Chapter 1, the author describes the alkylation of various aldehydes with trialkylboranes in

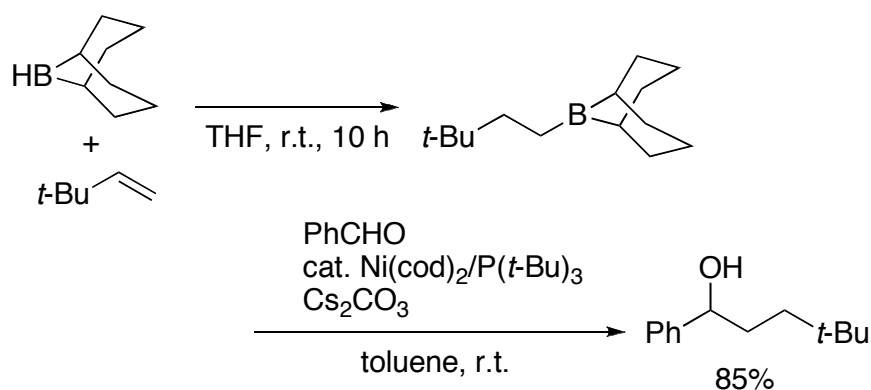
the presence of nickel catalysts and cesium base (Scheme 31). In the catalytic reaction, no undesired reduced products are detected.

Scheme 31.



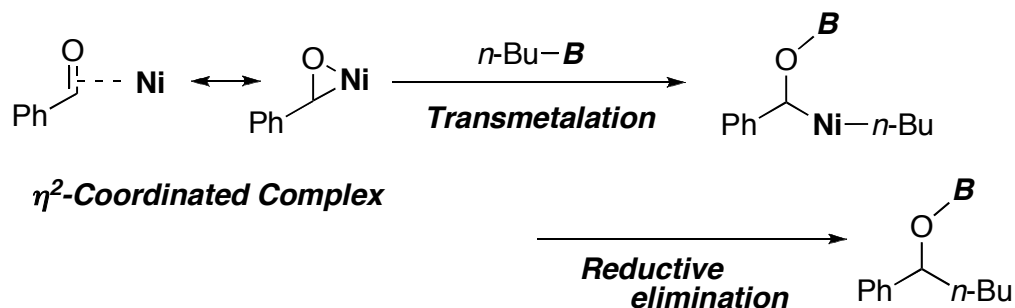
Moreover, hydroboration–alkylation sequences can be achieved (Scheme 32).

Scheme 32.



He hypothesizes η^2 -coordinated nickel complexes with aldehydes as the key intermediate and proposes the reaction mechanism involving transmetalation between the complexes and trialkylboranes followed by reductive elimination (Scheme 33).

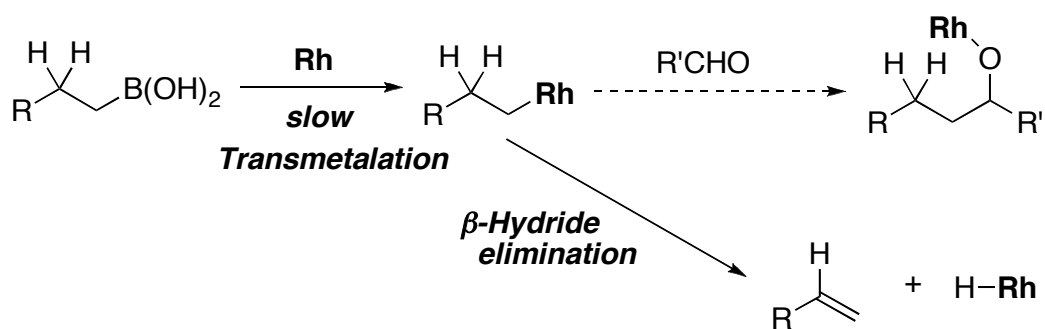
Scheme 33.



In Chapter 2, the author shows nickel-catalyzed alkylation reaction of aldehydes in water. Transition-metal-catalyzed arylation and alkenylation of aldehydes in aqueous media have been

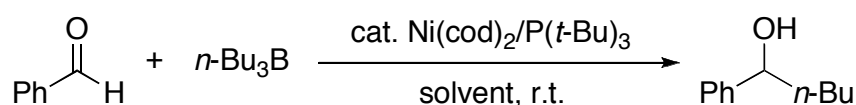
established. On the contrary, the alkylation of aldehydes in water is quite rare. On the basis of the precedent rhodium-catalyzed arylation and alkenylation of aldehydes with aryl- and alkenylboronic acid derivatives in aqueous media,⁶⁷ water-tolerant alkylboronic acid derivatives seem to be suitable alkylating agents. However, the transfer of alkyl groups from boron to rhodium is generally much more difficult than that of aryl and alkenyl ones. Even if the transfer were available, the resulting alkylrhodium species would decompose via rapid β -hydride elimination prior to the reaction with aldehydes (Scheme 34).

Scheme 34.



The reaction systems developed by the authors overcome this problem since the reaction mechanism is quite different from that of the rhodium-catalyzed reaction. In the rhodium-catalyzed reaction, the β -hydride elimination from alkylrhodium species competes the insertion of aldehydes. On the contrary, in the nickel catalyst system, the β -hydride elimination from alkylnickel competes the reductive elimination, and bulky phosphine, $P(t\text{-Bu})_3$, generally accelerates the latter. Furthermore, the unique effect of water is observed. The addition of cesium carbonate, which is essential for the reaction in organic solvents, is not necessary in water. It is no doubt that the role of water not as an additive but as a solvent is important (Scheme 35).

Scheme 35.

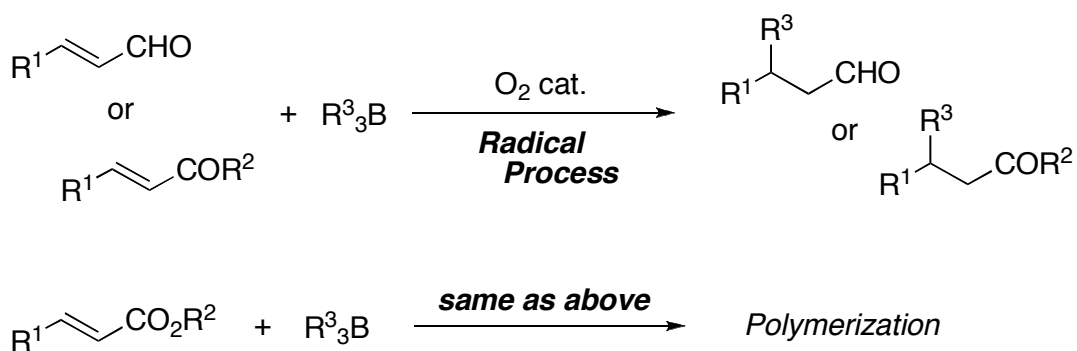


solvent	additive	yield
toluene (10 mL)	none	<2%
toluene (10 mL)	Cs ₂ CO ₃ (3.0 equiv)	88%
toluene (10 mL)	H ₂ O (3.0 equiv)	<2%
H ₂ O (5 mL)	none	33%
H ₂ O (10 mL)	none	63%
H ₂ O (20 mL)	none	90%

3.2. Nickel-Catalyzed 1,4-Addition of Trialkylboranes to α,β -Unsaturated Esters (Chapter 3)

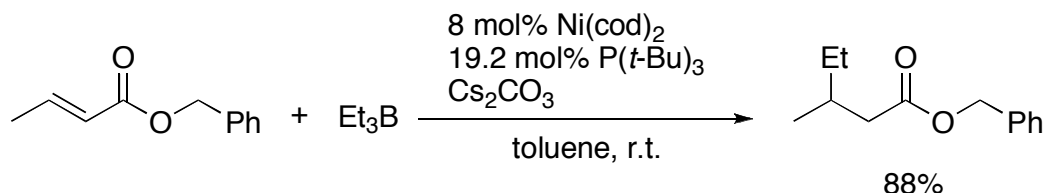
Transition-metal-catalyzed 1,4-addition of alkylmetals is among the most powerful and promising C–C bond formations in organic synthesis. In particular, copper-catalyzed addition of alkylmagnesium, alkylzinc, and alkylaluminum reagents have been widely studied and accomplished the asymmetric induction using a variety of chiral ligands.⁶⁸ On the other hand, the reactions with trialkylboranes have been less explored. There are a few examples of the 1,4-additions of trialkylboranes to α,β -unsaturated aldehydes and ketones under radical conditions. However, the radical conditions are not applicable to the addition to α,β -unsaturated esters due to the rapid radical polymerization (Scheme 36).⁶⁹

Scheme 36.



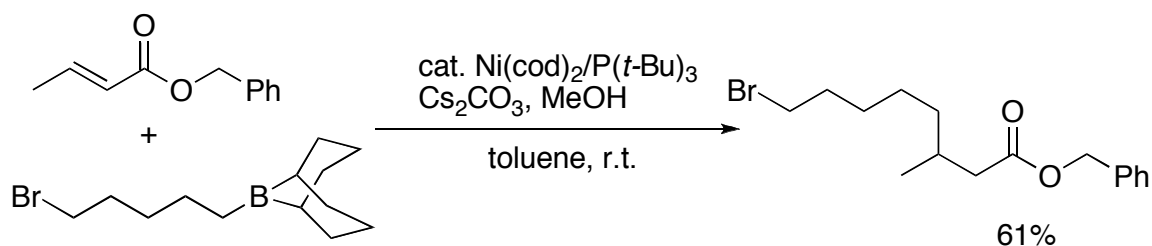
On the basis of results obtained in Chapter 1, the author develops nickel-catalyzed 1,4-addition of trialkylboranes to α,β -unsaturated esters (Scheme 37).

Scheme 37.



The advantage of the catalytic reaction is that the preparation of highly functionalized alkyl groups is possible. For instance, alkylborane having an $\text{sp}^3\text{C}-\text{Br}$ bond, which the corresponding alkylmagnesium halide and dialkylzinc are difficult to prepare, undergoes 1,4-addition smoothly (Scheme 38).

Scheme 38.

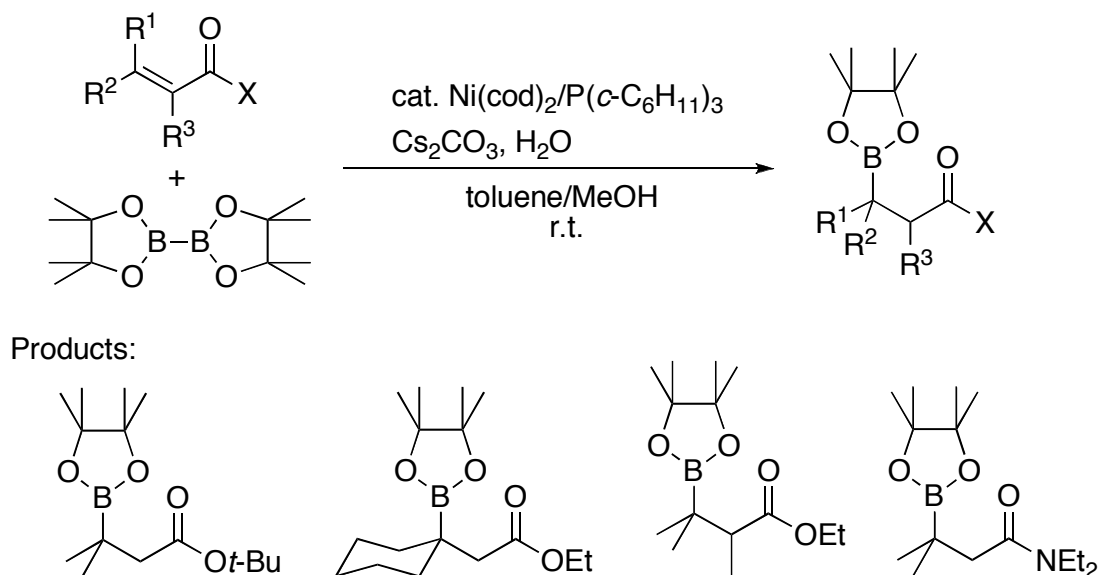


3.3. Nickel-Catalyzed β -Boration of α,β -Unsaturated Esters and Amides with Bis(pinacolato)diboron (Chapter 4)

Organoboron compounds are indispensable synthetic reagents in modern organic synthesis. As described in Section 1, transition-metal-catalyzed boration of unsaturated molecules with diboron reagents is an attractive alternative for the preparation of organoboranes to the conventional methods such as hydroboration. Among them, β -boration of α,β -unsaturated carbonyl compounds ranks as the most important procedure for the synthesis of organoborons having carbonyl functions at the β -position. In Chapter 4, the author shows that the nickel catalyst system developed in Chapter 3 is applicable to the conjugate boration of α,β -unsaturated esters and amides. The reaction provides a facile approach to primary, secondary, and tertiary

alkylboronates bearing carbonyl functions, synthesis of which is often difficult with reported procedures (Scheme 39).⁷⁰

Scheme 39.



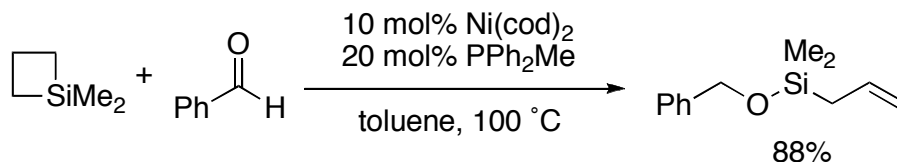
3.4. Nickel-Catalyzed Reactions of Silacyclobutanes with Aldehydes: Ring Opening and Ring Expansion Reaction (Chapter 5)

Silacyclobutanes are an interesting class of compounds that have unique reactivity due to their ring strain and Lewis acidity. Therefore, their synthetic utilities have been widely developed. Among many studies, palladium and platinum complexes are proved to catalyze quite useful transformations such as ring opening polymerization, cycloaddition with alkynes and allenes, and coupling reactions with acid halides. These precedents are summarized in Section 2. In contrast, nickel-catalyzed reactions of silacyclobutanes have not been explored, although nickel belongs to the same group, group 10. In Chapter 5, the author discloses the first transformations of silacyclobutanes under nickel catalysis.

Treatment of 1,1-dimethylsilacyclobutane with benzaldehyde in the presence of 10 mol% of Ni(cod)₂ and 20 mol% of PPh₂Me in toluene at 100 °C for 20 h affords allylbenzyloxydimethylsilane in 88% yield. The reaction is regarded as a hydrosilane-free

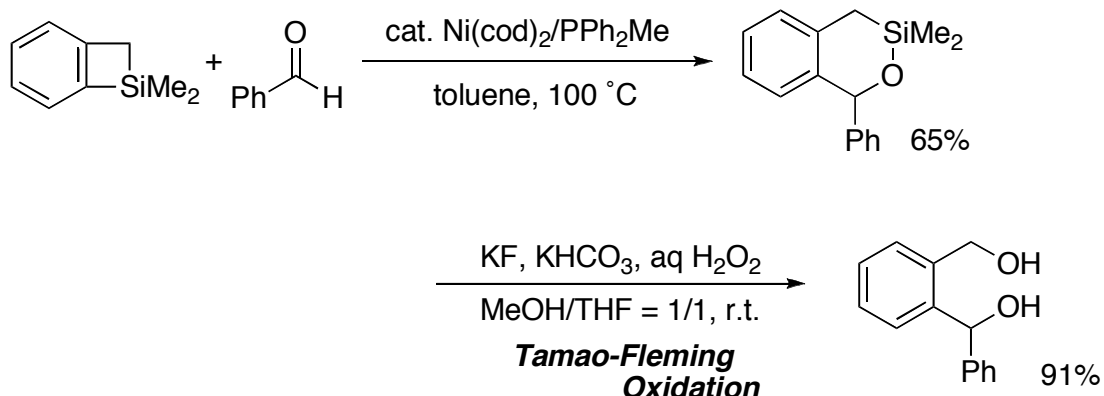
reductive silylation of aldehydes (Scheme 40).

Scheme 40.



Interestingly, with benzene-fused silacyclobutane instead of 1,1-dimethylsilacyclobutane, a ring expansion reaction proceeds to produce the six-membered cyclic silyl ether. The subsequent Tamao-Fleming oxidation could convert the cyclic product to the corresponding diol (Scheme 41).

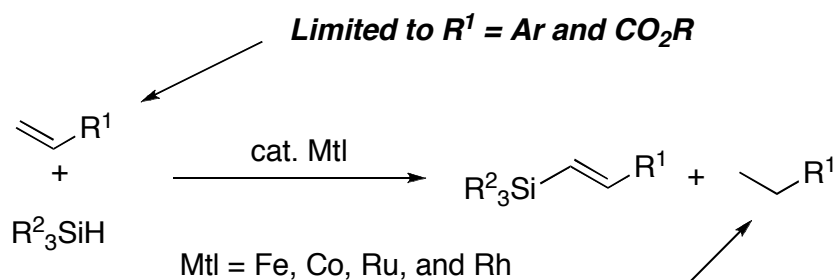
Scheme 41.



3.5. Nickel-Catalyzed Regio- and Stereoselective Silylation of Terminal Alkenes with Silacyclobutanes: Facile Access to Vinylsilanes from Alkenes (Chapter 6)

Vinylsilanes are quite important compounds in organic synthesis and organosilicon chemistry. Transition-metal-catalyzed dehydrogenative silylation with hydrosilanes is useful reaction for the synthesis of vinylsilanes from terminal alkenes.⁷¹ The reaction proceeds in a highly regio- and stereoselective manner, however, the substrates are still limited to activated alkenes such as styrenes and acrylates. Moreover, the process produces the corresponding reduced products, alkanes, as the inevitable byproducts (Scheme 42).

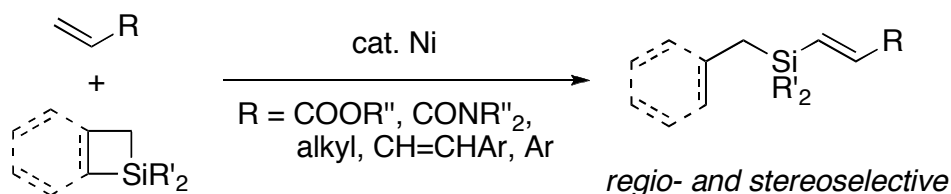
Scheme 42.



Inevitable byproduct since alkenes are hydrogen acceptors as well as substrates to be silylated

During his course of studies on nickel-catalyzed reactions with silacyclobutanes, the author serendipitously finds a facile and straightforward access to vinylsilanes from terminal alkenes with high regio- and stereoselectivity (Scheme 43). The catalytic reaction can be applied to ordinary alkenes as well as activated alkenes, and gives no byproducts such as alkanes.

Scheme 43.



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Chapter 1

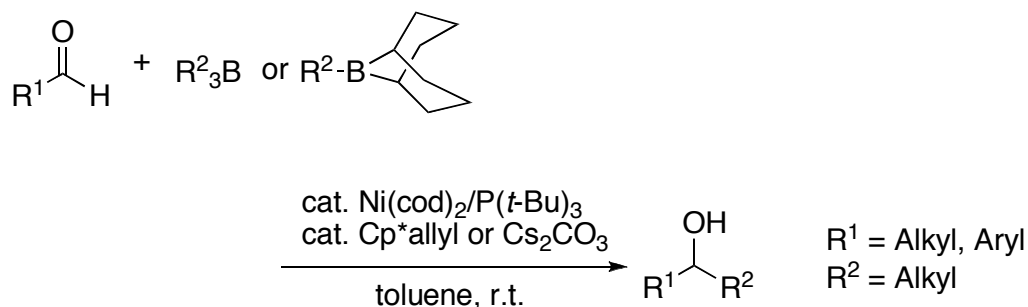
Nickel-Catalyzed Alkylation of Aldehydes with Trialkylboranes

Nickel-catalyzed alkylation of aldehydes with trialkylboranes proceeds smoothly in the presence of a catalytic amount of 5-allyl-1,2,3,4,5-pentamethyl-1,3-cyclopentadiene or an excess of cesium carbonate to afford the corresponding secondary alcohols. The reaction would proceed via η^2 -coordinated nickel complexes with aldehydes as key intermediates.

Introduction

The alkylation of aldehydes with organometallic reagents is one of the most important reactions in organic chemistry. Generally, reactive alkylmetals such as Grignard reagents are utilized to achieve this transformation. Conventional alkylborane reagents do not react with aldehydes. The few exceptional examples require highly reactive alkylborane compounds such as 1-boraadamantane¹ and dialkylhaloboranes.^{2,3} On the other hand, alkylations of aldehydes with dialkylzinc⁴ and trialkylaluminum⁵ reagents under nickel catalysis have been reported. These reactions prompted the author to develop a nickel-catalyzed alkylation reaction with alkylboranes. In this chapter, he describes such a reaction (Scheme 1). To the best of his knowledge, this is the first example of a transition metal-catalyzed 1,2-addition reaction of alkylboranes.⁶

Scheme 1.



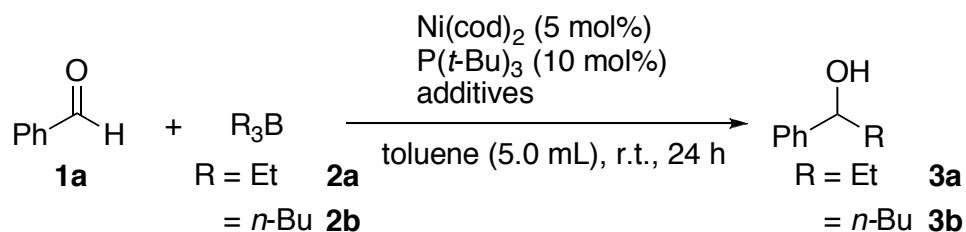
Results and Discussion

Nickel-Catalyzed Alkylation of Aldehydes with Trialkylboranes

Treatment of benzaldehyde (**1a**, 0.5 mmol) with triethylborane (**2a**, 1.0 mmol) in the presence of 5 mol% of Ni(cod)₂ and 10 mol% of P(*t*-Bu)₃ in toluene (5 mL) at room temperature for 24 h afforded 1-phenyl-1-propanol (**3a**) in low yield (45%) (Table 1, entry 1).⁷ Half of the **1a** remained unchanged. In the reaction flask, a black suspension was formed. It is assumed that bulky phosphines dissociated easily from the nickel center, which resulted in the generation of catalytically inactive nickel species. The author then examined the effect of various additives (Table 1). As a result, he found that olefins behaved effectively as stabilizers of active

zerovalent nickel. A monodentate olefin, 3,3-dimethyl-1-butene, was not effective (entry 2) while a bidentate diene, norbornadiene, slightly improved the yield (entry 3). Then, he surveyed conjugated 1,3-dienes, which would be expected to bind nickel more tightly. Fortunately, 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene derivatives proved to be effective stabilizers in this reaction. An addition of 0.1 equiv of 1,2,3,4,5,5-hexamethyl-1,3-cyclopentadiene (Cp*Me) improved the yield to 70% (entry 4). Moreover, 5-allyl-1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (Cp*allyl) drastically enhanced the efficiency of the ethylation (entry 5). Under the optimized conditions (5 mol% of Ni(cod)₂, 10 mol% of P(*t*-Bu)₃, and 0.1 equiv of Cp*allyl in toluene (5.0 mL) at 0 °C for 24 h), the desired alcohol was obtained in excellent yield (entry 6).

Next, the author examined butylation reaction of **1a** with tributylborane (**2b**). To his surprise, the desired product, 1-phenyl-1-pentanol (**3b**), was obtained in only 2% yield even with the aid of Cp*allyl (entry 7). Considering tributylborane has lower reactivity than triethylborane, he screened various bases as an additive to increase the reactivity of tributylborane. Although TBAF, K₂CO₃, and Na₂CO₃ were not effective, CsF (entry 8) and Cs₂CO₃ (entry 9) improved the yield. Additionally, the concentration of nickel catalysts dramatically influenced the reaction (entry 10), and the existence of Cp*allyl was not essential in this case (entry 11). Finally, with 8 mol% of Ni(cod)₂, 19.2 mol% of P(*t*-Bu)₃, and 3.0 equiv of Cs₂CO₃ in toluene (10 mL), butylation of benzaldehyde (**1a**) afforded **3b** in 86% yield (entry 12).

Table 1. Optimization for Ethylation and Butylation of Benzaldehyde (**1a**)

entry	additives (equiv)	R ₃ B (equiv)	% yield (product)
1	none	2a (2.0)	45 (3a)
2	3,3-Dimethyl-1-butene (0.3)	2a (2.0)	46 (3a)
3	Norbornadiene (0.1)	2a (2.0)	48 (3a)
4	Cp*Me (0.1)	2a (2.0)	70 (3a)
5	Cp*allyl (0.1)	2a (2.0)	90 (3a)
6 ^a	Cp*allyl (0.1)	2a (1.2)	93 (3a)
7	Cp*allyl (0.1)	2b (1.2)	2 (3b)
8	Cp*allyl (0.1) and CsF (2.0)	2b (2.0)	12 (3b)
9	Cp*allyl (0.1) and Cs ₂ CO ₃ (2.0)	2b (2.0)	38 (3b)
10 ^b	Cp*allyl (0.1) and Cs ₂ CO ₃ (2.0)	2b (2.0)	64 (3b)
11 ^b	Cs ₂ CO ₃ (2.0)	2b (2.0)	80 (3b)
12 ^{b, c}	Cs ₂ CO ₃ (3.0)	2b (3.0)	86 (3b)

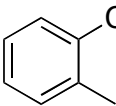
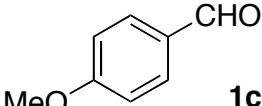
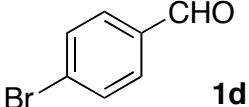
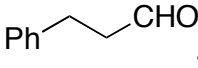
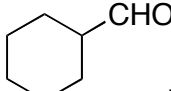
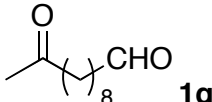
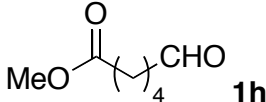
^a At 0 °C. ^b 10 mL of toluene was used.

^c 8 mol% of Ni(cod)₂ and 19.2 mol% of P(*t*-Bu)₃ were used.

By using the optimal cesium-promoted conditions, the author performed ethylation and

butylation of an array of aldehydes (Table 2). Sterically hindered 2-methylbenzaldehyde (**1b**) and electron-rich 4-anisaldehyde (**1c**) underwent alkylation smoothly (entries 1, 2, and 3). Exceptionally, ethylation of electron-deficient 4-bromobenzaldehyde (**1d**) gave **3f** in moderate yield (entry 4).⁸ Aliphatic aldehydes were converted to secondary alcohols without any difficulties. Alkylation of dihydrocinnamaldehyde (**1e**) furnished **3g** and **3h** in 76% and 83% yields, respectively (entries 5 and 6). The reaction of cyclohexanecarbaldehyde (**1f**) also afforded the corresponding alcohols **3i** and **3j** in good yields (entries 7 and 8). Ketone and ester functionalities were compatible under the reaction conditions (entries 9 and 10).

Table 2. Nickel-catalyzed Alkylation of Aldehydes with Trialkylboranes^a

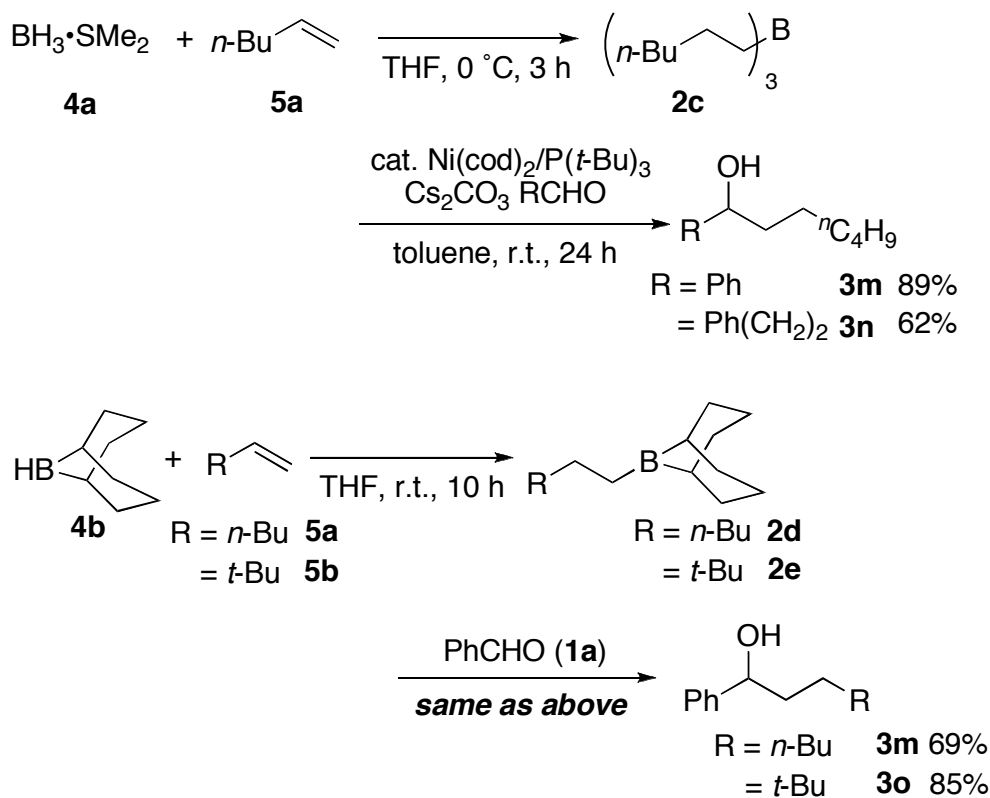
entry	aldehyde	borane	product	yield (%) ^b
1	 1b	2a	3c	83 (100)
2	1b	2b	3d	88
3	 1c	2a	3e	81 (86)
4	 1d	2a	3f	50
5	 1e	2a	3g	76 (83)
6	1e	2b	3h	83
7	 1f	2a	3i	82 (88)
8	1f	2b	3j	66
9	 1g	2a	3k	84
10	 1h	2a	3l	62

^a For ethylation, the reaction was carried out with 2.0 equiv of Et₃B in the presence of 2.0 equiv of Cs₂CO₃ while for butylation, 3.0 equiv of *n*-Bu₃B and 3.0 equiv of Cs₂CO₃.

^b The yields in the presence of 0.1 equiv Cp*allyl instead of Cs₂CO₃ are in parentheses.

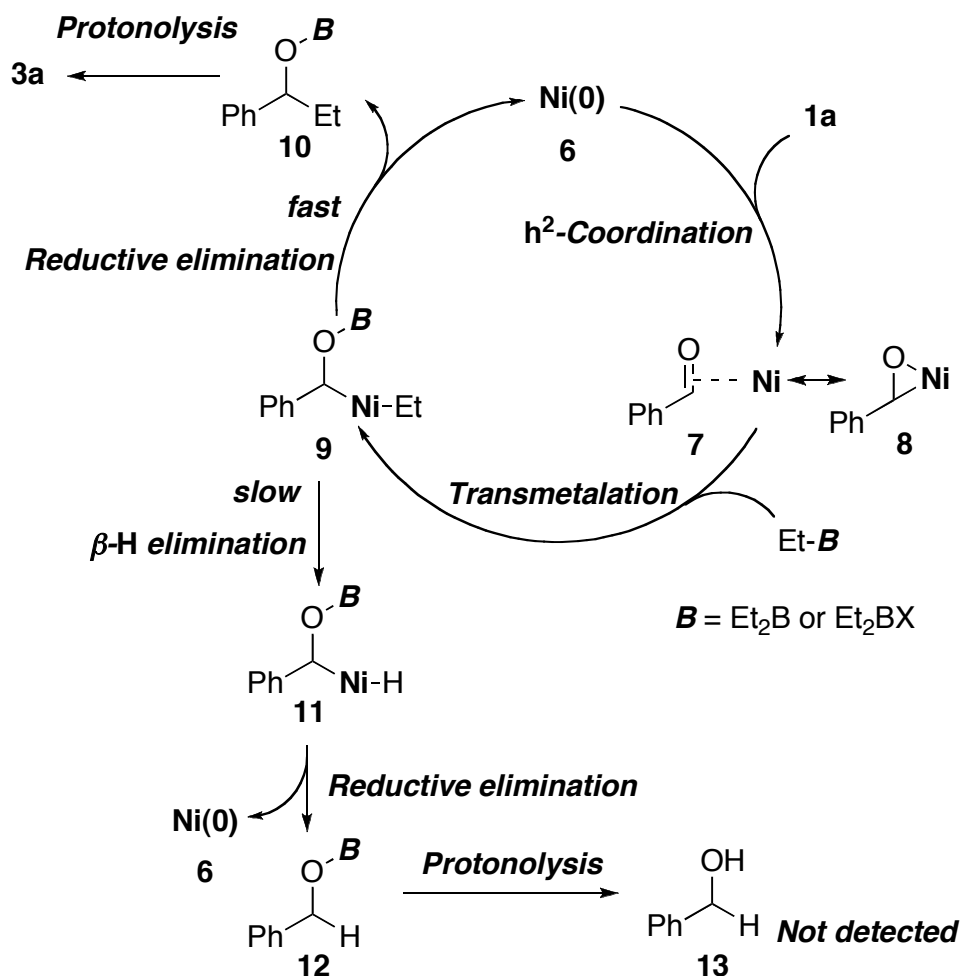
Trialkylboranes prepared from hydroboranes and alkenes via hydroboration can be employed for the reaction (Scheme 2). Trihexylborane (**2c**) was first prepared from borane-dimethyl sulfide complex (**4a**) and 3 equiv of 1-hexene (**5a**). Treatment of benzaldehyde (**1a**) with **2c** in the presence of 8mol % of Ni(cod)₂, 19.2mol % of P(*t*-Bu)₃, and 3.0 equiv of Cs₂CO₃ afforded 1-phenyl-1-heptanol (**3m**) in 89% yield. The hexylation of **1e** also took place to give the corresponding alcohol **3n** in moderate yield. To reduce the amount of alkene employed, the use of 9-borabicyclo[3.3.1]nonane (**4b**, 9-BBN) instead of borane-dimethyl sulfide complex (**4a**) as a hydroboration agent was preferred. With 9-hexyl-9-BBN (**2d**), alkylation of **1a** also proceeded to furnish **3m** in 69% yield. 9-(3,3-Dimethylbutyl)-9-BBN (**2e**) prepared from **4b** and 3,3-dimethyl-1-butene (**5b**) also reacted with **1a** to provide 4,4-dimethyl-1-phenyl-1-pentanol (**3o**) in 85% yield.

Scheme 2.



The author is tempted to assume the following mechanism for the alkylation of aldehyde (Scheme 3). A nickel(0) species **6** initially reacts with **1a** to generate η^2 -coordinated complex **7** or its resonance form **8**.⁹ Subsequent transmetalation with Et_3B or its borate formed by the action of Cs_2CO_3 gives the intermediate **9**. Reductive elimination from **9** provides **10** and regenerates **6**. Finally, protonolysis of **10** upon work up affords alcohol **3a**. If β -H elimination from the intermediate **9** could occur, subsequent reductive elimination from **11** followed by protonolysis of **12** would afford **13**. However, **13** was not detected. This result would indicate that reductive elimination from **9** is more rapid than β -H elimination.¹⁰

Scheme 3.



Conclusion

The author has found the first example of 1,2-addition of trialkylboranes to aldehydes under nickel catalysis. This system allows alkylboranes to serve as promising nucleophilic alkyl sources to aldehydes.

Experimental Section

Instrumentation and Chemicals

^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained in CDCl_3 with tetramethylsilane as an internal standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was dried over slices of sodium and degassed before use. Et_3B , $n\text{-Bu}_3\text{B}$, 9-Borabicyclo[3.3.1]nonane (9-BBN) were purchased from Aldrich. $\text{P}(t\text{-Bu})_3$ was obtained from Wako. Et_3B and $\text{P}(t\text{-Bu})_3$ were diluted to prepare 1.0 M hexane solutions, which were stored strictly under argon. Bis(1,5-cyclooctadiene)nickel was available from Strem.

Typical Procedure for the Nickel-Catalyzed Alkylation of Aldehydes with Trialkylboranes

Synthesis of **3a**

With a glovebox, $\text{Ni}(\text{cod})_2$ (6.9 mg, 0.025 mmol) was placed in a reaction flask. Toluene (3.0 mL), $\text{P}(t\text{-Bu})_3$ (1.0 M hexane solution, 0.050 mL, 0.050 mmol) and a solution of Cp^*allyl (8.8 mg, 0.050 mmol) in toluene (2.0 mL) were added dropwise. The solution was stirred for 10 min at 0 °C. Benzaldehyde (**1a**, 53 mg, 0.50 mmol) and Et_3B (1.0 M hexane solution, 1.0 mL, 1.0 mmol) were then added. After being stirred for 24 h at the same temperature, the resulting mixture was poured into 3.0 M hydrochloric acid (10 mL). Extraction with hexane/ethyl acetate (5:1) followed by silica gel column purification afforded 1-phenyl-1-propanol (**3a**, 63 mg, 0.47 mmol) in 93% yield.

Synthesis of 3b

With a glovebox, Ni(cod)₂ (11 mg, 0.040 mmol) and Cs₂CO₃ (489 mg, 1.5 mmol) were placed in a reaction flask. Toluene (10 ml) and P(*t*-Bu)₃ (1.0 M hexane solution, 0.096 mL, 0.096 mmol) were added. The resulting suspension was stirred for 10 min at 0 °C. Benzaldehyde (**1a**, 53 mg, 0.50 mmol) and *n*-Bu₃B (1.0 M THF solution, 1.5 mL, 1.5 mmol) were then added and the mixture was allowed to warm to room temperature. After being stirred for 24 h at the same temperature, the reaction was quenched with 1.0 M hydrochloric acid (10 mL). Extraction with hexane/ethyl acetate (5:1) and concentration gave the crude product. The crude product obtained was oxidized upon treatment with aqueous H₂O₂ (30%, 0.80 mL) and aqueous NaOH (6.0 M, 0.50 mL) in EtOH/THF (1.2 mL:2.0 mL) at reflux for 1 h. After aqueous sodium thiosulfate was added, extraction and purification provided 1-phenyl-1-pentanol (**3b**, 71 mg, 0.43 mmol) in 86% yield.

Synthesis of 3m

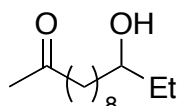
1-Hexene (151 mg, 1.8 mmol) was added to a solution of 9-BBN in THF (1.0 M THF solution, 1.5 mL, 1.5 mmol) and the solution was stirred for 10 h at room temperature to prepare 9-hexyl-9-BBN. On the other hand, with a glovebox filled with argon, Ni(cod)₂ (11 mg, 0.040 mmol) and Cs₂CO₃ (489 mg, 1.50 mmol) were placed in another reaction flask. Degassed toluene (10 mL) and P(*t*-Bu)₃ (1.0 M hexane solution, 0.096 mL, 0.096 mmol) were added dropwise. The solution was stirred for 10 min at 0 °C. Benzaldehyde (53 mg, 0.50 mmol) was then added. Finally, 9-hexyl-9-BBN prepared in advance was transferred to the mixture via a syringe under argon. The resulting mixture was allowed to warm to room temperature. After being stirred for 24 h, the mixture was poured into aqueous HCl (1.0 M, 10 mL) and extraction with hexane/ethyl acetate (5:1) followed by concentration afforded the crude product. The crude product obtained was oxidized with aqueous H₂O₂ (30%, 0.80 mL) and aqueous NaOH (6.0 M, 0.50 mL) in EtOH/THF (1.2 mL:2.0 mL) at reflux for 1 h. After aqueous sodium thiosulfate was added, extraction and silica gel column purification with hexane/ethyl acetate (10:1) as an

eluent provided 1-phenyl-1-heptanol (**3m**, 66 mg, 0.35 mmol) in 69% yield.

Characterization Data

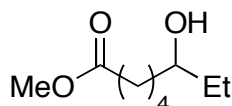
Except for **3k**, **3l**, and **3o**, all compounds are well known.

11-Hydroxy-2-tridecanone (**3k**)



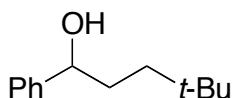
IR (nujol) 3261, 2849, 1672, 1707, 1464, 1364, 1205, 1169, 1132, 1115, 989, 943, 868, 719 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.95 (t, $J = 7.5$ Hz, 3H), 1.30 (bs, 7H), 1.40–1.59 (m, 10H), 2.14 (s, 3H), 2.43 (t, $J = 7.5$ Hz, 2H), 3.51–3.55 (m, 1H); ^{13}C NMR (CDCl_3) δ 9.87, 23.82, 25.60, 29.13, 29.31, 29.40, 29.61, 29.86, 30.14, 36.91, 43.79, 73.32, 209.43. Found: C, 72.71; H, 11.95%. Calcd for $\text{C}_{13}\text{H}_{26}\text{O}_2$: C, 72.84; H, 12.23%. m.p.: 41–43 $^\circ\text{C}$

Methyl 6-hydroxyoctanoate (**3l**)



IR (neat) 3433, 2937, 287, 1740, 1460, 1439, 1366, 1200, 1173, 111, 1097, 968 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.95 (t, $J = 7.0$ Hz, 3H), 1.36–1.55 (m, 7H), 1.62–1.70 (m, 2H), 2.34 (t, $J = 7.5$ Hz, 2H), 3.52–3.57 (m, 1H), 3.68 (s, 3H); ^{13}C NMR (CDCl_3) δ 9.86, 24.88, 25.19, 30.18, 34.00, 36.46, 51.49, 73.00, 174. Found: C, 61.97; H, 10.15%. Calcd for $\text{C}_9\text{H}_{18}\text{O}_3$: C, 62.04; H, 10.41%.

4,4-Dimethyl-1-phenyl-1-pentanol (**3o**)



IR (nujol) 3748, 3674, 2923, 2855, 1451, 1366, 1032, 699 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88 (s,

9H), 1.11 (td, $J = 13.0, 4.5$ Hz, 1H), 1.39 (td, $J = 13.0, 4.5$ Hz, 1H), 1.67–1.74 (m, 1H), 1.75–1.83 (m, 1H), 4.63 (dd, $J = 7.5, 5.5$ Hz, 1H), 7.27–7.39 (m, 5H); ^{13}C NMR (CDCl_3) δ 29.30, 30.08, 34.21, 39.98, 75.53, 125.93, 127.54, 128.46, 144.90. Found: C, 80.94; H, 10.70%. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}$: C, 81.20; H, 10.48%. m.p.: 46–47 °C

References and Notes

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- (3) Additions of trialkylboranes under electrochemical and free radical conditions were reported:
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- (6) Nickel-catalyzed 1,2-addition reactions of aryl- and alkenylboronic ester derivatives have been reported. Takahashi, G.; Shirakawa, E.; Tsuchimoto, T.; Kawakami, Y. *Chem. Commun.* **2005**, 1459–1460.
- (7) NiCl₂ and Ni(acac)₂ did not catalyze the reaction. Other ligands such as PPh₃, P(*n*-Bu)₃, and P(*c*-C₆H₁₁)₃ were ineffective.
- (8) The conversion of **1d** was low and about 40% of the starting material remained unchanged. The conceivable Suzuki-Miyaura coupling product was obtained in less than 2% yield. The reaction of other electron-deficient aromatic aldehydes also resulted in low conversions. For examples, ethylations of 4-trifluoromethylbenzaldehyde and 4-methoxycarbonylbenzaldehyde provided the corresponding adducts in 49% and 29% yields, respectively.
- (9) η^2 -Coordinated nickel complexes with aldehydes have been reported. Ogoshi, S.; Oka, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2004**, *126*, 11802–11803. Although the possibility of a radical pathway cannot be completely excluded, addition of a radical scavenger, TEMPO, gave no effect on yield.

(10) Unfortunately, in the case of alkylboranes having secondary alkyl groups such as ${}^s\text{Bu}_3\text{B}$, the reduced product **13** was mainly obtained, probably due to considerably rapid β -H elimination from the intermediate corresponding to **9**.

Chapter 2

Alkylation of Aldehydes with Trialkylboranes in Water

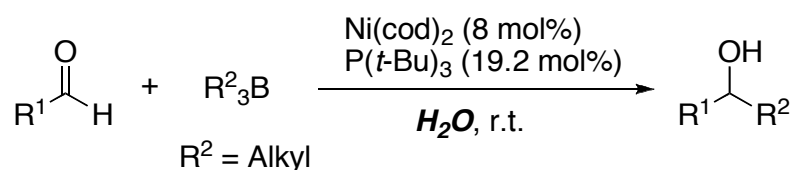
Water enabled alkylation of aldehydes with trialkylboranes under nickel catalysis without an addition of base. Trialkylboranes prepared from borane-dimethyl sulfide and terminal olefins via hydroboration as well as commercially available trialkylboranes could be employed for the reaction. The reaction would proceed via η^2 -coordinated nickel complexes with aldehydes as key intermediates.

Introduction

Water is an interesting solvent in organic synthesis due to its cheap, nontoxic, and nonflammable properties. Therefore, use of water instead of organic solvent has attracted significant attention in the viewpoint of economy and green chemistry. In addition, synthetic reactions that are unique in water have been developed¹ since the extraordinary effect of water as a solvent was observed in pericyclic processes of Diels-Alder reactions² and Claisen rearrangement.³ The additions of organometallic reagents to aldehydes in water have also been widely explored. Allylation with allylmetals⁴ and arylation or alkenylation with organoboronic acid derivatives in the presence of transition metal catalysts⁵ have been established in aqueous media. However, the alkylation of aldehydes in water is not a trivial reaction.⁶ This is probably because organometallic reagents having alkyl groups, which are effective in alkylation of carbonyl compounds, are generally highly reactive and very sensitive to water.⁷ With the aid of transition metal catalysts, water-tolerant organoboranes seem to be good reagents for the alkylation in water. However, alkyl group transfer from boron to transition metals is usually difficult.

In Chapter 1, the author has described nickel-catalyzed addition of trialkylboranes to aldehydes in an organic solvent with cesium carbonate as an activator.⁸ By using this reaction, alkyl group transfer from boron to nickel has become available. This advantage promotes him to develop the alkylation of aldehydes with trialkylboranes by nickel catalysts in water. In Chapter 2, he presents the result of the alkylation in water and the unique effect of water as a solvent in the alkylation reaction (Scheme 1).

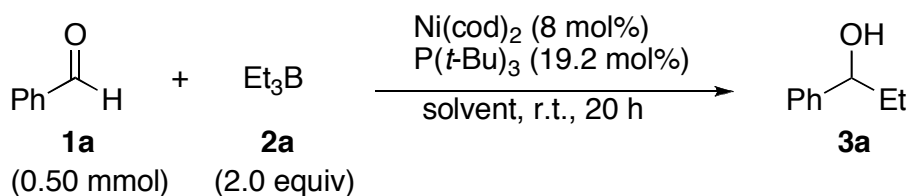
Scheme 1.



Results and Discussion

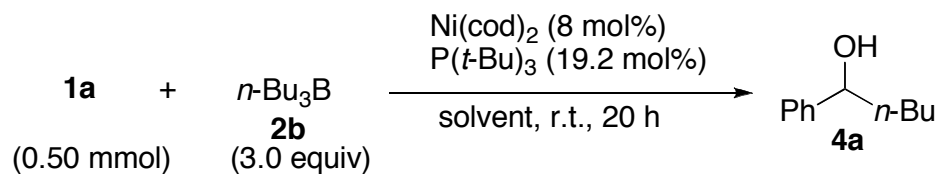
The author first examined ethylation and butylation of benzaldehyde (**1a**) (Scheme 2 and 3). Treatment of **1a** (0.50 mmol) with triethylborane (**2a**, 1.0 mmol) in the presence of 8 mol% of Ni(cod)₂ and 19.2 mol% of P(*t*-Bu)₃ in degassed water (20 mL) at room temperature for 20 h provided the corresponding secondary alcohol **3a** in 81% yield.⁹ It is worth noting that **1a**, **2a**, and the nickel catalyst were completely insoluble in water, and the reaction proceeded in a biphasic system, organic particles in water. On the other hand, **1a** was converted to **3a** in moderate yield in degassed toluene. The addition of an excess amount of cesium carbonate was essential for a satisfactory yield. In the butylation of **1a** with tributylborane (**2b**), the effect of water as a solvent was much more remarkable. The reaction of **1a** in toluene without cesium carbonate resulted in no conversion. Other organic solvents such as THF, DMF, and AcOEt led to the same result. Gratifyingly, use of water (20 mL) as a solvent improved the yield of the desired product **4a** to 90%. The amount of water also dramatically influenced the yield. An addition of 3.0 equiv of water in toluene had no effect. In 5 mL and 10 mL of water, benzaldehyde (**1a**) underwent butylation to give the corresponding alcohol **4a** in 33% and 63% yield, respectively. The results strongly suggest that use of water as a solvent would play an important role in the reaction.

Scheme 2.



solvent	additive	yield of 3a
toluene (10 mL)	none	45%
toluene (10 mL)	Cs ₂ CO ₃ (2.0 equiv)	87%
H ₂ O (20 mL)	none	81%

Scheme 3.



solvent	additive	yield of 4a
toluene (10 mL)	none	<2%
toluene (10 mL)	Cs ₂ CO ₃ (3.0 equiv)	88%
toluene (10 mL)	H ₂ O (3.0 equiv)	<2%
H ₂ O (5 mL)	none	33%
H ₂ O (10 mL)	none	63%
H ₂ O (20 mL)	none	90%

By using optimal conditions, the author performed the ethylation and butylation of an array of various aldehydes in water (Table 1). The reaction of sterically demanding aldehyde **1b** proceeded smoothly to furnish the corresponding alcohol **3b** in 81% yield. Electron-rich aldehyde **1c** was converted to **3c** and **4c** in moderate yields. However, electron-deficient aldehyde **1d** resulted in a low conversion. Aliphatic aldehydes as well as aromatic ones participated in the reaction.¹⁰ Dihydrocinnamaldehyde (**1e**) and cyclohexanecarbaldehyde (**1f**) underwent ethylation without difficulties to afford the alkylated products in good yields.

Table 1. Nickel-Catalyzed Alkylation of Aldehydes with Trialkylboranes in Water

$$\text{R}^1\text{CHO} + \text{R}^2_3\text{B} \xrightarrow[\text{H}_2\text{O (20 mL), r.t., 20 h}]{\text{Ni(cod)}_2 \text{ (8 mol\%)} \\ \text{P}(t\text{-Bu)}_3 \text{ (19.2 mol\%)}} \text{R}^1\text{CH(OH)R}^2$$

1 $\text{R}^2 = \text{Et}$ **2a** (2.0 equiv)
 $= n\text{-Bu}$ **2b** (3.0 equiv)

$\text{R}^2 = \text{Et}$ **3**
 $= n\text{-Bu}$ **4**

entry	aldehyde	borane	product	yield (%)
1		2a	3b	81
2		2a	3c	59
3	1c	2b	4c	27
4		2a	3d	5
5		2a	3e	69
6		2a	3f	60

Trialkylboranes prepared from alkenes via hydroboration can be also employed for the reaction (Table 2). 1-Hexene (**5a**) was added to a solution of borane-dimethyl sulfide in THF and the mixture was stirred for 3 h at 0 °C. Dimethyl sulfide was then removed under vacuum (30 torr) at 0 °C for 1 h. The trihexylborane (**6a**) obtained was transferred under argon to a dispersion of benzaldehyde (**1a**) and the nickel catalyst in water at 0 °C. The mixture was

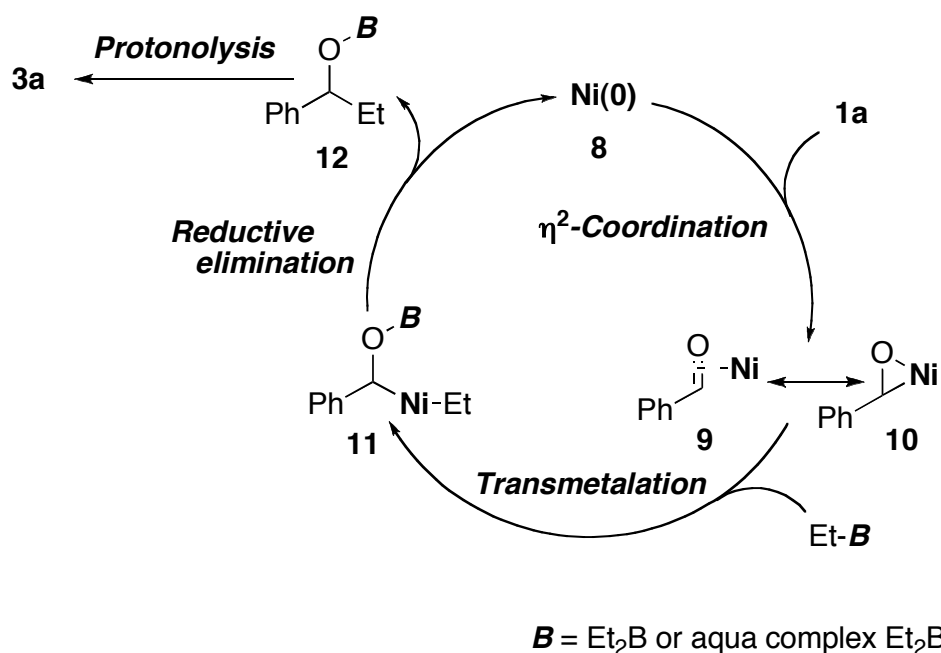
allowed to warm to room temperature and rigorously stirred for 20 h to furnish 1-phenyl-1-heptanol (**7a**) in 74% yield (entry 1). Bulky substituent on the trialkylborane at the β position did not prevent the reaction (entry 2). However, the reaction with tri(4-phenylbutyl)borane (**6c**) resulted in moderate yield (entry 3). Ester functional group was compatible under the reaction conditions albeit the yield was low (entry 4). The reaction with trialkylborane having a silyl ether moiety proceeded smoothly to produce the corresponding alcohol **7e** (entry 5) while a benzyl ether moiety in **6f** decreased the yield (entry 6).

Table 2. One-pot Hydroboration/alkylation

entry	alkene	borane	product	yield (%)
1	5a	6a	7a	74
2	5b	6b	7b	71
3	5c	6c	7c	36
4	5d	6d	7d	17
5	5e	6e	7e	69
6	5f	6f	7f	24

The author is tempted to assume the mechanism for the alkylation of aldehyde to be as follows (Scheme 4). A nickel(0) species **8** initially reacts with **1a** to generate η^2 -coordinated complex **9** or its resonance form **10**.¹¹ Subsequent transmetalation of **10** with Et_3B or its aqua complex $\text{Et}_3\text{B}\cdot\text{OH}_2$ gives intermediate **11** followed by reductive elimination to furnish **12** and to regenerate **8**. Finally, protonolysis of **12** upon work-up affords alcohol **3a**. The effect of water as a reaction medium is not clear at this stage. Water can enhance the η^2 -coordination step and/or the transmetalation step. These steps cause a reduction of the total volume of the organic components, which water would enhance by taking advantage of hydrophobic interaction. Moreover, the aqua complex $\text{Et}_3\text{B}\cdot\text{OH}_2$ can undergo the transmetalation more readily.

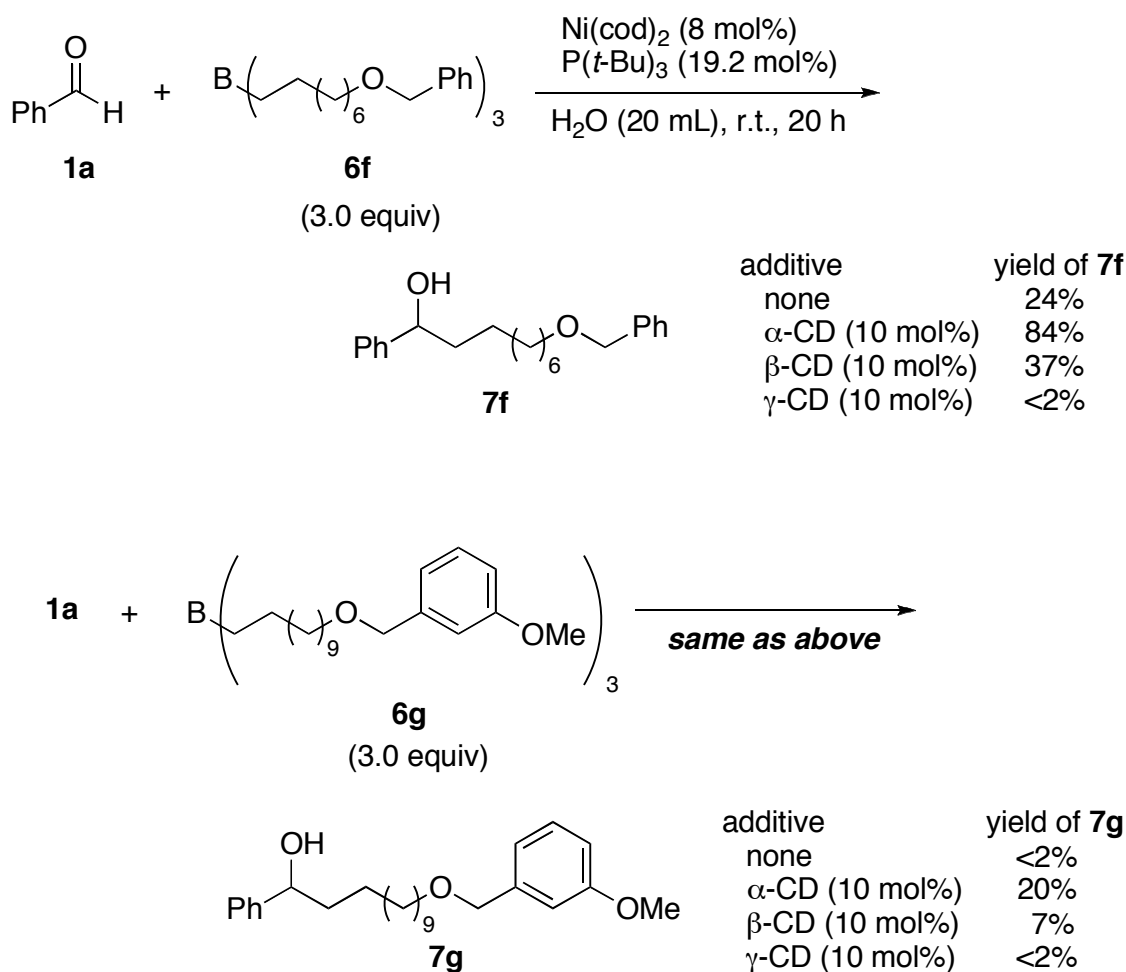
Scheme 4.



To his delight, the addition of 10 mol% of α -cyclodextrin (α -CD) improved the yield of **7f** to 84% compared to Table 2, entry 6 (Scheme 5). Interestingly, additions of β -cyclodextrin (β -CD) and γ -cyclodextrin (γ -CD) showed less efficiency.¹² The effect was also examined in the reaction of benzaldehyde (**1a**) with trialkylborane **6g** having a *meta*-substituted

benzyl ether moiety. In the absence of α -CD, the reaction completely failed to afford the desired product. The addition of 10 mol% of α -CD enabled the conversion of **1a** to the corresponding alcohol **7f** albeit the yield was low.¹³ Unfortunately, additions of β -CD or γ -CD could not improve the yield. The exact role of α -CD is not clear at this stage.^{14,15}

Scheme 5.



Conclusion

The author found an example of the alkylation of aldehydes in water and the unique effect of water as a solvent in the reaction. In addition, an interesting effect of cyclodextrins was observed.

Experimental Procedure

Instrumentation and Chemicals

^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on Varian UNITY INOVA 500 spectrometers and were recorded in CDCl_3 . Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^1H and relative to CDCl_3 at 77.2 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra (EI unless otherwise noted) were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was dried over slices of sodium and degassed before use. Et_3B , $n\text{-Bu}_3\text{B}$, and $\text{BH}_3\cdot\text{SMe}_2$ were purchased from Aldrich. $\text{P}(t\text{-Bu})_3$ was obtained from Wako. Et_3B and $\text{P}(t\text{-Bu})_3$ were diluted to prepare 1.0 M hexane solutions, which were stored strictly under argon. Bis(1,5-cyclooctadiene)nickel was available from Strem.

Typical Procedure for the Alkylation of Aldehydes with Trialkylboranes in Water

Synthesis of **3a**

In a glovebox filled with argon, $\text{Ni}(\text{cod})_2$ (11 mg, 0.040 mmol) was placed in a reaction flask. THF (0.50 mL) and $\text{P}(t\text{-Bu})_3$ (1.0 M hexane solution, 0.096 mL, 0.096 mmol) were added dropwise. The solution was stirred for 10 min at 0 °C. Degassed water (20 mL), benzaldehyde (**1a**, 53 mg, 0.50 mmol), and Et_3B (1.0 M hexane solution, 1.0 mL, 1.0 mmol) were then added. The mixture was allowed to warm to room temperature and stirred for 20 h. The resulting mixture was poured into 3.0 M hydrochloric acid (10 mL). Extraction with hexane/ethyl acetate (5:1) followed by silica gel column purification afforded 1-phenyl-1-propanol (**3a**, 55 mg, 0.41 mmol) in 81% yield.

Synthesis of 4a

In a glovebox filled with argon, Ni(cod)₂ (11 mg, 0.040 mmol) was placed in a reaction flask. THF (0.50 mL) and P(*t*-Bu)₃ (1.0 M hexane solution, 0.096 mL, 0.096 mmol) were added dropwise. The solution was stirred for 10 min at 0 °C. Degassed water (20 mL), benzaldehyde (**1a**, 53 mg, 0.50 mmol), and *n*-Bu₃B (1.0 M THF solution, 1.5 mL, 1.5 mmol) were then added. The mixture was allowed to warm to room temperature and stirred for 20 h. Extraction with hexane/ethyl acetate (5:1) followed by concentration afforded the crude product. The crude product obtained was oxidized with aqueous H₂O₂ (30%, 0.80 mL) and aqueous NaOH (6.0 M, 0.50 mL) in EtOH/THF (1.2 mL:2.0 mL) at reflux for 1 h. After aqueous sodium thiosulfate was added, extraction and purification provided 1-phenyl-1-pentanol (**4a**, 74 mg, 0.45 mmol) in 90% yield.

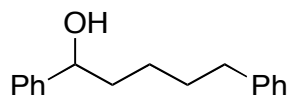
Synthesis of 7a

1-Hexene (**5a**, 379 mg, 4.5 mmol) was added to a solution of borane-dimethyl sulfide (10 M, 0.15 mL, 1.5 mmol) in THF (2.0 mL) and the solution was stirred for 3 h at 0 °C. Dimethyl sulfide was then removed under vacuum (30 torr) at 0 °C for 1 h to prepare trihexylborane (**6a**). At the same time, in a glovebox filled with argon, Ni(cod)₂ (11 mg, 0.040 mmol) was placed in another reaction flask. THF (0.50 mL) and P(*t*-Bu)₃ (1.0 M hexane solution, 0.096 mL, 0.096 mmol) were added dropwise. The solution was stirred for 10 min at 0 °C. Degassed water (20 mL) and benzaldehyde (**1a**, 53 mg, 0.50 mmol) were then added. Finally, the trihexylborane (**6a**) prepared in advance was transferred to the mixture via a syringe under argon. The resulting mixture was allowed to warm to room temperature and stirred for 20 h. Extraction with hexane/ethyl acetate (5:1) followed by concentration afforded the crude product. After the crude product obtained was oxidized under the same conditions for the synthesis of **4a**, extraction and purification provided 1-phenyl-1-heptanol (**7a**, 71 mg, 0.37 mmol) in 74% yield.

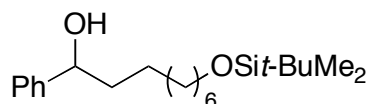
Characterization Data

The compounds shown in Table 1 and **7a** are well known compounds.

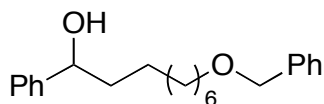
Compound **7b** is found in chapter 1.

1,5-Diphenyl-1-pentanol (7c)

IR (neat) 3354, 3085, 3062, 3026, 3002, 2933, 2857, 1604, 1496, 1453, 1261, 1203, 1055, 1029, 1002, 748, 699 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.31–1.40 (m, 1H), 1.46–1.55 (m, 1H), 1.63–1.70 (m, 2H), 1.72–1.79 (m, 2H), 1.82–1.89 (m, 1H), 2.61 (t, $J = 7.5$ Hz, 2H), 4.68 (dd, $J = 7.5, 5.5$ Hz, 1H), 7.16–7.20 (m, 3H), 7.26–7.31 (m, 3H), 7.33–7.38 (m, 4H); ^{13}C NMR (CDCl_3) δ 25.54, 31.41, 35.84, 38.93, 74.58, 125.64, 125.85, 127.54, 128.25, 128.36, 128.46, 142.55, 144.82. Found: C, 84.40; H, 8.63%. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}$: C, 84.95; H, 8.39%.

9-(*tert*-Butyldimethylsiloxy)-1-phenyl-1-nonanol (7e)

IR (neat) 3344, 2929, 2856, 1464, 1455, 1387, 1361, 1256, 1098, 1006, 836, 814, 774, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.05 (s, 6H), 0.90 (s, 9H), 1.23–1.31 (m, 9H), 1.38–1.45 (m, 1H), 1.47–1.52 (m, 2H), 1.69–1.85 (m, 3H), 3.60 (t, $J = 7.0$ Hz, 2H), 4.68 (dd, $J = 7.5, 6.0$ Hz, 1H), 7.27–7.38 (m, 5H); ^{13}C NMR (CDCl_3) δ -5.27, 18.37, 25.74, 25.81, 25.97, 29.35, 29.45, 29.51, 32.83, 39.10, 63.30, 74.69, 125.87, 127.48, 128.42, 144.90. Found: C, 71.75; H, 11.03%. Calcd for $\text{C}_{21}\text{H}_{38}\text{O}_2\text{Si}$: C, 71.94; H, 10.92%.

9-Benzyloxy-1-phenyl-1-nonanol (7f)

Chapter 2

IR (neat) 3345, 3063, 3029, 2855, 2794, 1496, 1456, 1436, 1363, 1204, 1002, 912, 737, 699 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.24–1.38 (m, 10H), 1.39–1.45 (m, 1H), 1.58–1.64 (m, 2H), 1.68–1.74 (m, 1H), 1.77–1.84 (m, 1H), 3.46 (t, $J = 7.0$ Hz, 2H), 4.51 (s, 1H), 4.67 (dd, $J = 8.0, 6.0$ Hz, 1H), 7.27–7.31 (m, 2H), 7.34–7.37 (m, 8H); ^{13}C NMR (CDCl_3) δ 25.79, 26.13, 29.37, 29.43, 29.45, 29.72, 39.09, 70.46, 72.83, 74.68, 125.86, 127.45, 127.48, 127.60, 128.32, 128.42, 138.66, 144.89. Found: C, 81.11; H, 9.29%. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}_2$: C, 80.94; H, 9.26%.

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- (7) Recently, Woodward has reported alkylation of aldehydes with air-stable trialkylaluminum reagents in organic solvent under nickel catalysis. Biswas, K.; Prieto, O.; Goldsmith, P. J.; Woodward, S. *Angew. Chem. Int. Ed.* **2005**, *44*, 2232–2234.
- (8) Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2005**, *7*, 4689–4691.
- (9) NiCl₂ and Ni(acac)₂ did not catalyze the reaction. Other ligands such as PPh₃, P(*n*-Bu)₃, and P(*c*-C₆H₁₁)₃ were ineffective.
- (10) Similar trend was observed in an organic solvent. See ref 8.
- (11) η²-Coordinated nickel complexes with aldehydes have been reported. (a) Ogoshi, S.; Oka, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2004**, *126*, 11802–11803. The intermediate **9** or **10** was suggested in other nickel-catalyzed reactions. See: ref 7, 8, and (b) Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2006**, *8*, 483–485.
- (12) The cavity volume of α-CD, β-CD, and γ-CD are 174, 262, and 472 mL/mol, respectively. α-CD is known to accommodate a phenyl ring most tightly. See: Hapiot, F.; Tilloy, S.; Monflier, E. *Chem. Rev.* **2006**, *106*, 767–781.
- (13) The author assumed that the substitution at the *meta*-position in **6g** would allow α-CD to dissociate easily from the phenyl ring of **6g** due to the steric factor.
- (14) In the catalytic cycle, transmetalation of the nickel complex **10** with trialkylborane would be a key step. Therefore, we suppose that in the reaction with trialkylborane **6f**, interaction between the oxygen atom of **6f** and the nickel or boron center would suppress the step to result in the low yield (Table 2, entry 6). On the basis of the assumption, the author thus tested an addition of cyclodextrins into the reaction media. Namely, he expected the internal cavity of cyclodextrins would accommodate the aromatic ring of **6f** to block out the unfavorable interaction as described above.
- (15) Cyclodextrin can interact with phosphine or nickel(phosphine) complex to improve the catalytic activity: (a) Monflier, E.; Bricout, H.; Hapiot, F.; Tilloy, S.; Aghmiz, A.; Masdeu-Bultó, A. M. *Adv. Synth. Catal.* **2004**, *346*, 425–431. (b) Binkowski, C.; Cabou, J.; Bricout, H.; Hapiot, F.; Monflier, E. *J. Mol. Catal. A* **2004**, *215*, 23–32.

Chapter 3

Nickel-Catalyzed 1,4-Addition of Trialkylboranes to α,β -Unsaturated Esters: Dramatic Enhancement by Addition of Methanol

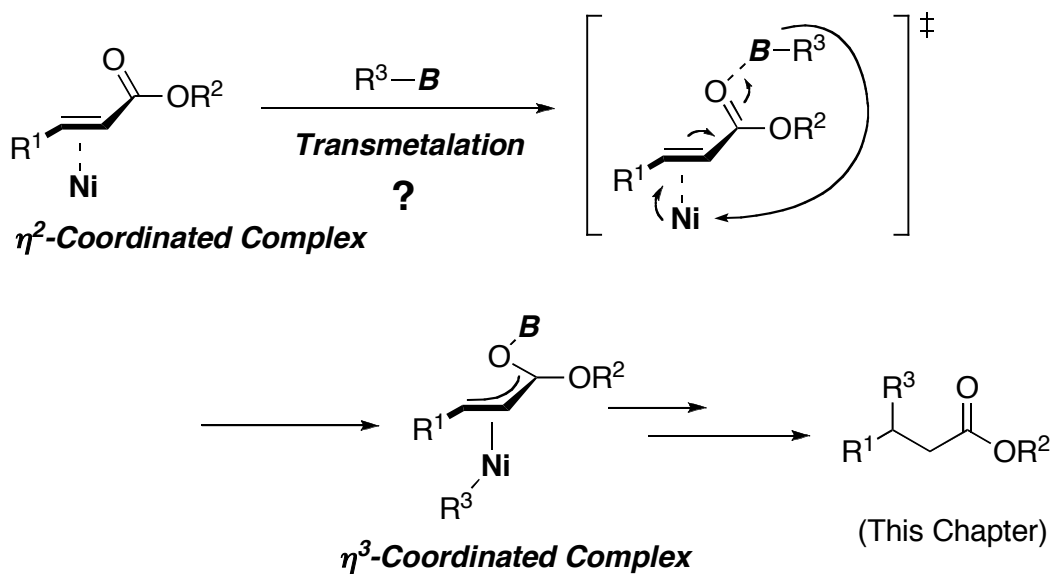
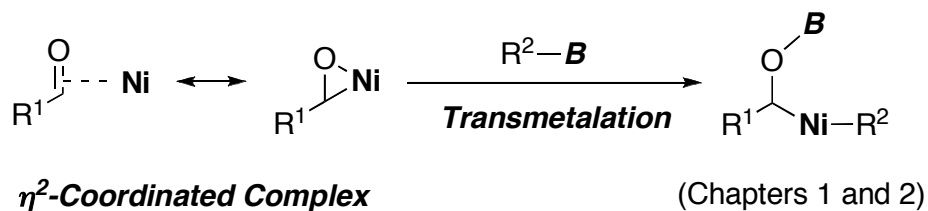
Nickel catalyst systems for 1,4-addition of trialkylboranes to α,β -unsaturated esters have been developed. Addition of methanol was found to be essential for the alkylation reaction with 9-alkyl-9-BBNs. The reaction would proceed through the formation of the η^3 -coordinated nickel complexes with α,β -unsaturated esters starting from the corresponding η^2 -coordinated ones.

Introduction

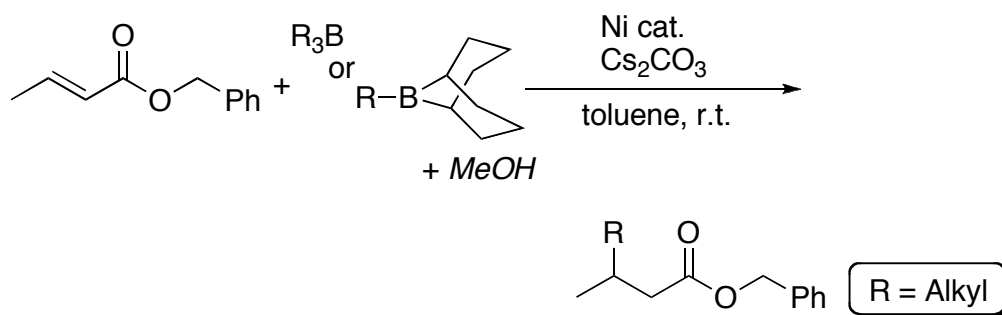
Transition-metal-catalyzed 1,4-addition of alkylmetal reagents to α,β -unsaturated carbonyl compounds is one of the most powerful and promising carbon–carbon bond formations in organic synthesis. In particular, 1,4-addition of alkylmagnesium halides, dialkylzincs, and trialkylaluminums in the presence of copper catalysts has been developed and widely used for alkylation of various unsaturated molecules involving the asymmetric version.¹ In contrast, 1,4-addition of trialkylboranes to α,β -unsaturated carbonyl compounds has been much less explored. 1,4-Addition of trialkylboranes to α,β -unsaturated aldehydes and ketones is a well-established process under radical conditions initiated by molecular oxygen.² However, the radical conditions could not be applicable to the reactions of α,β -unsaturated esters due to rapid radical polymerization.³ Only photo-⁴ and electrochemical⁵ conditions could achieve these transformations. In addition, very recently 1,4-addition of aryl- and alkenylboronic acid derivatives to various unsaturated compounds including α,β -unsaturated esters became available in the presence of transition metal catalysts such as rhodium,⁶ palladium,⁷ and nickel.⁸

In Chapters 1 and 2, the author has described the nickel-catalyzed 1,2-addition of trialkylboranes to aldehydes and proposed the reaction mechanism involving the formation of η^2 -coordinated nickel complexes with aldehydes followed by transmetalation between the complexes and trialkylboranes.⁹ On the basis of these findings, he assumes that a similar type of η^2 -coordinated nickel complexes with α,β -unsaturated esters would react with trialkylboranes to provide the corresponding 1,4-adducts via a formation of η^3 -coordinated nickel complexes (Scheme 1). In Chapter 3, the author presents effective nickel catalyst systems for 1,4-addition of trialkylboranes to α,β -unsaturated esters. Moreover, the dramatic effect of coexisting methanol in the nickel-catalyzed 1,4-addition is also described (Scheme 2).¹⁰

Scheme 1.



Scheme 2.

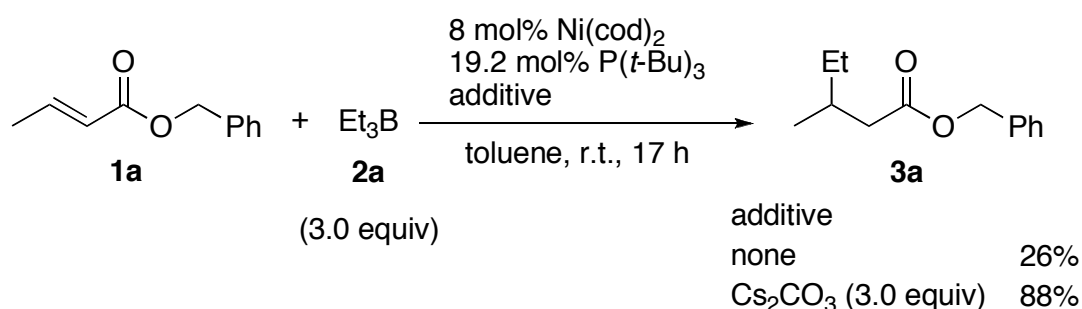


Results and Discussion

Treatment of benzyl (*E*)-crotonate (**1a**) with triethylborane (**2a**) in the presence of 8 mol%

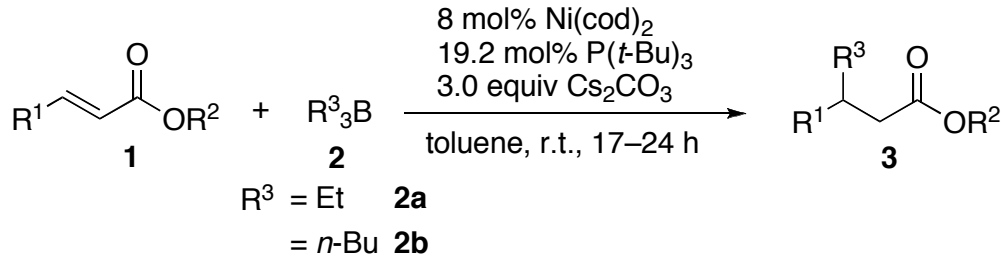
of Ni(cod)₂ and 19.2 mol% of P(*t*-Bu)₃ in toluene at room temperature, which are the optimized conditions in our previous work, for 17 h afforded the 1,4-adduct, benzyl 3-methylpentanoate (**3a**), in 26% yield (Scheme 3).¹¹ Half of the **1a** remained untouched. According to the author's previous observation,⁹ a stoichiometric (to triethylborane) amount of cesium carbonate was added to the reaction mixture as an activator for triethylborane. To his delight, the reaction was completed in 17 h and the desired product was obtained in 88% yield.

Scheme 3.



With the optimized conditions in hand, we examined 1,4-addition of triethylborane to a variety of α,β -unsaturated esters (Table 1). Triethylborane reacted with **1b** smoothly to furnish **3b** in 94% yield. The conceivable Suzuki-Miyaura cross-coupling product was not obtained (entry 2). Not only crotonic acid esters but unsaturated esters having a larger alkyl group at the β position participated in the reaction. Phenylethyl- and cyclohexyl-substituted esters **1c** and **1d** were converted to **3c** and **3d** in 74% and 81% yields, respectively (entries 3 and 4). In contrast, the reaction of cinnamic acid ester **1e** resulted in low conversion and yielded a trace amount of the desired product (entry 5). Interestingly, the substitution of an electron-donating methoxy group on the aromatic ring improved the yield to 57% (entry 6). Tributylborane (**2b**) as well as triethylborane was a suitable alkylation agent. Crotonate ester **1a** underwent the butylation to provide **3g** in 87% yield while the reaction of **1b** afforded **3h** in 35% yield (entries 7 and 8). The butylations of **1c** and **1d** led to moderate conversions and yields probably due to the steric factors (entries 9 and 10).

Table 1. Nickel-catalyzed 1,4-Addition of Triethylborane (**2a**) and Tributylborane (**2b**) to α,β -Unsaturated Esters **1a**^a



8 mol% Ni(cod)₂
19.2 mol% P(*t*-Bu)₃
3.0 equiv Cs₂CO₃
toluene, r.t., 17–24 h

R³ = Et **2a**
= *n*-Bu **2b**

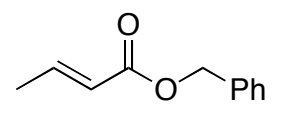
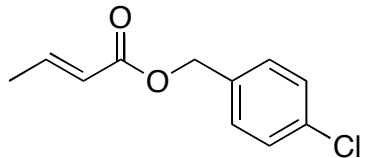
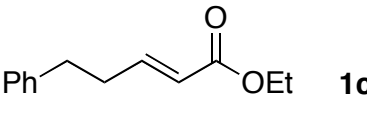
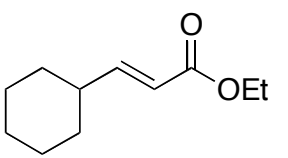
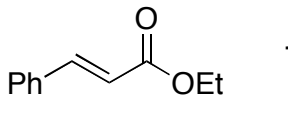
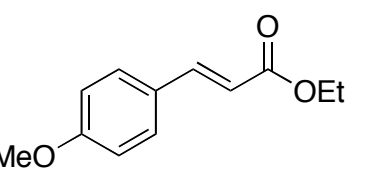
entry	1	2	3, yield (%) ^b
1	 1a	2a	3a , 88
2	 1b	2a	3b , 94
3	 1c	2a	3c , 74
4	 1d	2a	3d , 81 ^c
5	 1e	2a	3e , trace
6	 1f	2a	3f , 57 ^d
7	1a	2b	3g , 87
8	1b	2b	3h , 35

Table 1. (Continued)

entry	1	2	3 , yield (%) ^b
9	1c	2b	3i , 45
10	1d	2b	3j , 52 ^{c, e}

^a A mixture of **1** (0.50 mmol), **2** (3.0 equiv), Ni(cod)₂ (8 mol%), P(*t*-Bu)₃ (19.2 mol%), and Cs₂CO₃ (3.0 equiv) was stirred in toluene (5.0 mL) for 17-24 h at room temperature.

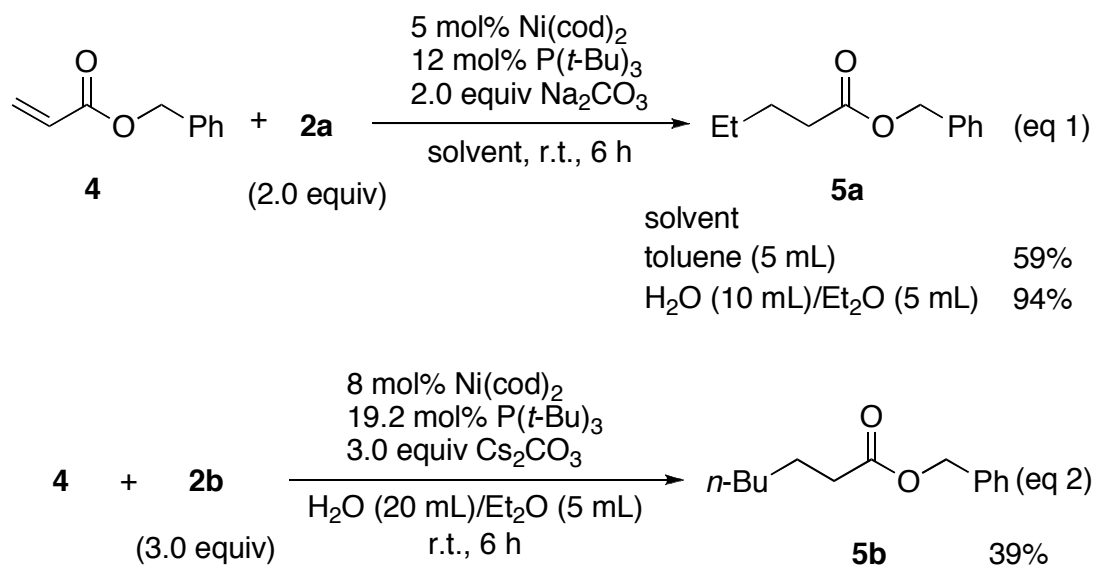
^b Isolated yield. ^c ¹H NMR yield.

^d Reduced product, ethyl 3-(4-methoxyphenyl)propanoate was also obtained in 10% yield.

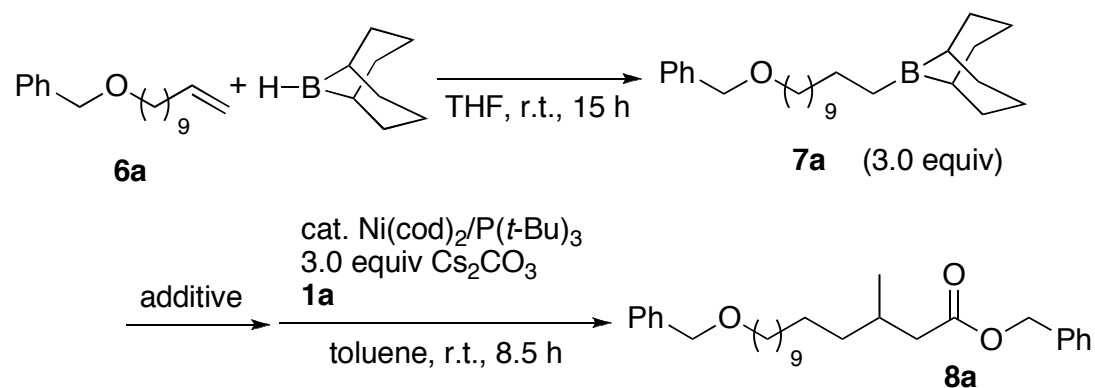
^e Reduced product, ethyl 3-cyclohexylpropanoate was also obtained in 5% yield.

Next, the author performed 1,4-addition of triethylborane (**2a**) to benzyl acrylate (**4**) (Scheme 4, eq 1), which is a challenging substrate since **4** can undergo polymerization much more readily. Under similar conditions for the reaction of β -substituted α,β -unsaturated esters **1**, 1,4-adduct **5a** was obtained in 59% yield.¹² About half of **4** underwent the undesired polymerization. The addition of the initially formed boryl enolate to **4** would cause the side reaction. Given that the smooth protonolysis of the intermediate enolate was essential, we conducted the reaction in an aqueous/organic biphasic system.¹³ Gratifyingly, the desired product **5a** was obtained in 94% yield in H₂O/Et₂O mixed solvent. Unfortunately, in 1,4-addition of tributylborane (**2b**) to **4**, the polymerization was not completely suppressed even in the presence of water (eq 2).

Scheme 4.



Alkylboranes are easily prepared by hydroboration of alkenes. Taking advantage of the facile access to alkylboranes, the author tested one-pot procedure including hydroboration and 1,4-addition. Terminal olefin having a benzyl ether moiety **6a**, 9-borabicyclo[3.3.1]nonane (9-BBN), and benzyl (*E*)-crotonate (**1a**) were chosen as model substrates. Alkylborane **7a** was prepared from **6a** and 9-BBN in advance and transferred to a mixture of the nickel catalyst and cesium carbonate in toluene. Finally, **1a** was added dropwise. However, to his surprise, 1,4-adduct **8a** was not detected (Table 2, entry 1). The starting material **1a** was completely recovered. Thus, further optimization studies were performed to achieve the reaction with 9-alkyl-9-BBN. An addition of water was found to improve the yield of the desired product to 24% (entry 2). Interestingly, a large excess of water completely suppressed the reaction (entry 3). The oxygen atom of water seemed to coordinate to the boron center as a Lewis base and to activate alkylborane **7a**. Hence, various Lewis bases were screened. Fortunately, an addition of 4.0 equiv of methanol dramatically enhanced the reaction to provide **8a** in 96% yield (entry 4). As observed in the case of the addition of water, a large amount of methanol prevented the reaction (entry 5). Other alcohols such as *tert*-butyl alcohol and phenol gave no effect on yield (entries 6 and 7). The use of *N,N*-dimethylacetamide (DMA), which is known to catalyze hydroboration of alkenes with catecholborane,¹⁴ also led to the improvement of the yield, although the yield was lower than that in the presence of methanol (entry 8 vs entry 4). A much stronger Lewis base, pyridine, did not work to promote the reaction (entry 9).

Table 2. Nickel-catalyzed One-pot Hydroboration/1,4-Addition: The Effect of an Additive^a

entry	additive	8a , yield (%) ^b
1	none	0
2	H ₂ O (4.0 equiv)	24
3	H ₂ O (1.0 mL)	0
4	MeOH (4.0 equiv)	96
5	MeOH (1.0 mL)	0
6	<i>t</i> -BuOH (4.0 equiv)	0
7	phenol (4.0 equiv)	0
8	DMA (4.0equiv)	65
9	pyridine (4.0 equiv)	0

^a A mixture of **1a** (0.50 mmol), **7a** (3.0 equiv) prepared in advance from **6a** and 9-BBN, additive, Ni(cod)₂ (8 mol%), P(*t*-Bu)₃ (19.2 mol%), and Cs₂CO₃ (3.0 equiv) was stirred in toluene (5.0 mL) for 8.5 h at room temperature.

^b Isolated yield.

By using the optimal methanol-promoted conditions, the author conducted 1,4-addition of an array of 9-alkyl-9-BBN to benzyl (*E*)-crotonate (**1a**) (Table 3). The 1,4-addition of 9-hexyl-9-BBN (**7b**) and 9-(4-phenylbutyl)-9-BBN (**7c**) to **1a** proceeded to produce **8b** and **8c** in

90% and 85% yields, respectively. Alkylborane **7d** prepared from β,β -disubstituted olefin **6d** took part in the reaction without any difficulties (entry 4) while bulky substituent at the β position on alkylborane decreased the yield (entry 5). The reaction of **6f** provided **8f** in good yield, leaving the silyl moiety untouched (entry 6). Silyl ether and ester functionalities were tolerated under the reaction conditions (entries 7 and 8). It should be noted that alkylborane **7i** having an sp^3C-Br bond, which the corresponding alkylmagnesium halide and dialkylzinc are difficult to prepare, underwent 1,4-addition in spite of conceivable oxidative addition of the sp^3C-Br bond to the zerovalent nickel (entry 9).

Table 3. Nickel-catalyzed One-pot Hydroboration/1,4-Addition^a

entry	6	7	8 , yield (%) ^b
1	6a	7a	8a , 96
2 ^c	6b	7b	8b , 90
3	6c	7c	8c , 85
4	6d	7d	8d , 79
5	6e	7e	8e , 31

Table 3. (Continued)

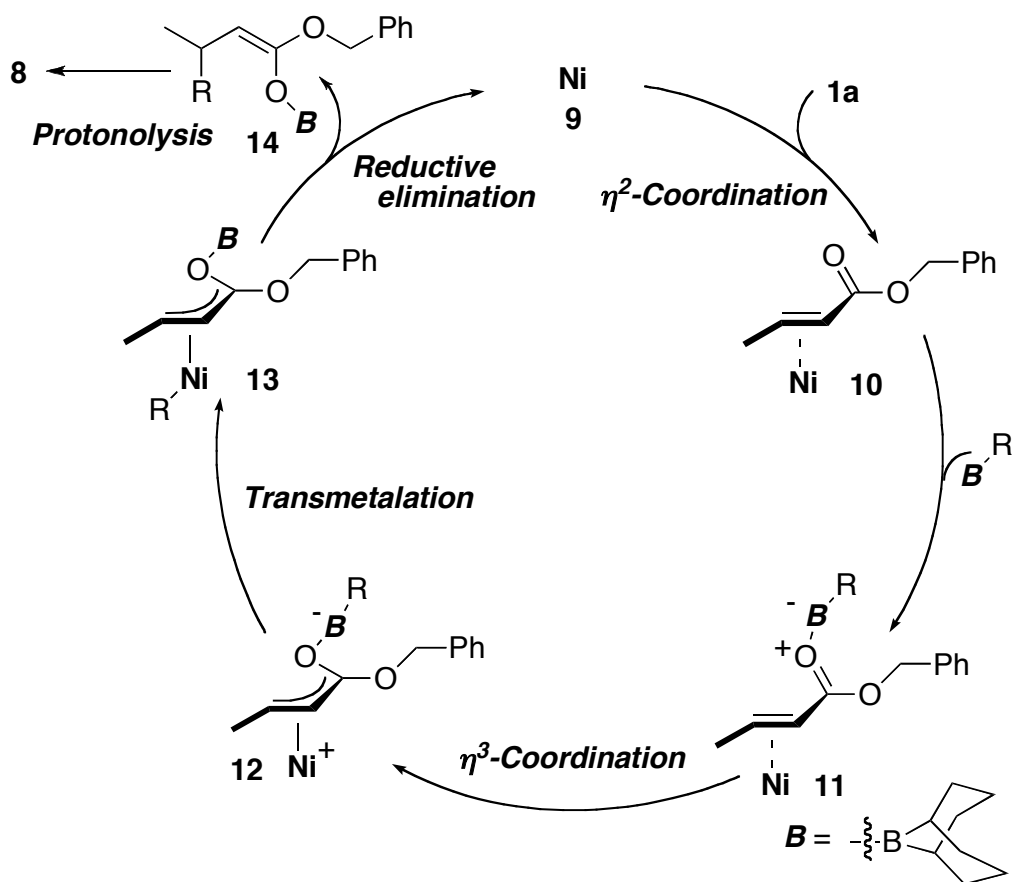
entry	6	7	8, yield (%)^b
6	PhMe ₂ Si-CH ₂ -CH=CH ₂ 6f	7f	8f, 59
7 ^d	<i>t</i> -BuMe ₂ SiO-(CH ₂) ₉ -CH=CH ₂ 6g	7g	8g, 58
8	Ph-C(=O)-O-(CH ₂) ₉ -CH=CH ₂ 6h	7h	8h, 73
9	Br-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂ 6i	7i	8i, 61

^a A mixture of **1** (0.50 mmol), **7** (3.0 equiv) prepared in advance from **6** and 9-BBN, MeOH (4.0 equiv), Ni(cod)₂ (8 mol%), P(*t*-Bu)₃ (19.2 mol%), and Cs₂CO₃ (3.0 equiv) was stirred in toluene (5.0 mL) for 6.5-10 h at room temperature.

^b Isolated yield. ^c Reaction time was 15 h. ^d Reaction time was 17 h.

The plausible mechanism of the reaction with 9-alkyl-9-BBN is shown (Scheme 5). A nickel(0) species **9** initially reacts with **1a** to generate η^2 -coordinated complex **10**. The coordination of the carbonyl moiety of **10** to the alkylborane gives the intermediate **11**.¹⁵ The Lewis acidity of the alkylborane promotes the formation of η^3 -coordinated complex **12** followed by transmetalation to furnish the alkylnickel species **13**.^{16,17} Finally, reductive elimination from **13** affords **14** and regenerates **9**. Protonolysis of **14** would provide **8**. The exact roles of cesium carbonate and methanol are not clear at this stage. They can enhance the transmetalation step through their coordination to the boron center of **12**. Moreover, methanol can be a good proton source for the intermediate **14**.

Scheme 5.



Conclusion

The author has developed 1,4-addition of trialkylboranes to α,β -unsaturated esters under nickel catalysis. Moreover, addition of methanol was found to dramatically enhance the nickel-catalyzed reactions of α,β -unsaturated esters with 9-alkyl-9-BBNs. The catalyst system allows trialkylboranes to serve as the promising alkyl sources for 1,4-addition to α,β -unsaturated esters.

Experimental Section

Instrumentation and Chemicals

^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were taken on Varian UNITY INOVA 500 spectrometers and were recorded in CDCl_3 . Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^1H and relative to CDCl_3 at 77.0 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was stored over slices of sodium. Triethylborane, tributylborane, and 9-borabicyclo[3.3.1]nonane (9-BBN) dimer were purchased from Aldrich. Tri(*tert*-butyl)phosphine was obtained from Wako Pure Chemical Co. Triethylborane and tri(*tert*-butyl)phosphine were diluted to prepare 1.0 M hexane solutions, which were stored strictly under argon. Bis(1,5-cyclooctadiene)nickel was available from Strem. All reactions were carried out under argon atmosphere.

Typical Procedure for the Nickel-Catalyzed 1,4-Addition of Trialkylboranes to α,β -Unsaturated Esters

Synthesis of 3a: With a glovebox filled with argon, $\text{Ni}(\text{cod})_2$ (11 mg, 0.040 mmol) and Cs_2CO_3 (489 mg, 1.5 mmol) were placed in a reaction flask. Toluene (3.0 mL) and $\text{P}(t\text{-Bu})_3$ (purchased from Wako and diluted to prepare a degassed hexane solution, 1.0 M, 0.096 mL, 0.096 mmol) were added dropwise. The suspension was stirred for 10 min at 0 °C. A solution of benzyl (*E*)-crotonate (**1a**, 88 mg, 0.50 mmol) in toluene (2.0 mL) and Et_3B (1.0 M hexane solution, 1.5 mL, 1.5 mmol) were then added. The mixture was allowed to warm to room temperature and stirred for 17 h. The resulting mixture was poured into 1.0 M hydrochloric acid

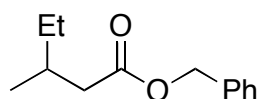
(10 mL). The product was extracted with hexane/ethyl acetate (20:1). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Silica gel column purification (hexane : ethyl acetate = 40 : 1) gave benzyl 3-methylpentanoate (**3a**, 91 mg, 0.44 mmol) in 88% yield.

Synthesis of 8a: With a glovebox filled with argon, 9-BBN dimer (commercially available from Aldrich, 183 mg, 1.5 mmol) was placed in a reaction flask. A solution of benzyl 11-undecenyl ether (**6a**, 469 mg, 1.8 mmol) in THF (3.0 mL) was added dropwise. The solution was stirred for 15 h at room temperature to prepare alkylborane **7a**. On the other hand, with a glovebox filled with argon, Ni(cod)₂ (11 mg, 0.040 mmol) and Cs₂CO₃ (489 mg, 1.5 mmol) were placed in another reaction flask. Toluene (3 mL) and P(*t*-Bu)₃ (1.0 M, 0.096 mL, 0.096 mmol) were added dropwise. The suspension was stirred for 10 min at 0 °C. Methanol (0.081 mL, 2.0 mmol) was added to **7a** prepared in advance and the solution was then transferred to the mixture of nickel catalyst and Cs₂CO₃ in toluene via a syringe under argon. Finally, a solution of benzyl (*E*)-crotonate (**1a**, 88 mg, 0.50 mmol) in toluene (2.0 mL) was added. After being stirred for 8.5 h at room temperature, the resulting mixture was poured into 1.0 M hydrochloric acid (10 mL). Extraction with hexane/ethyl acetate (20:1) followed by silica gel column purification afforded benzyl 14-benzyloxy-3-methyltetradecanoate (**8a**, 210 mg, 0.48 mmol) in 96% yield.

Characterization Data for Compounds

Compounds **3c**,¹⁸ **3d**,¹⁹ **3g**,²⁰ **5a**,²¹ and **5b**²² are found in the literature.

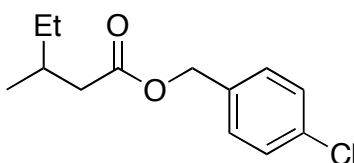
Benzyl 3-methylpentanoate (**3a**)



IR (neat) 3035, 2963, 2932, 2858, 1734, 1499, 1456, 1381, 1155, 1097, 981, 738, 697 cm⁻¹; ¹H NMR (CDCl₃) δ 0.90 (t, *J* = 7.5 Hz, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 1.19–1.28 (m, 1H), 1.33–1.41

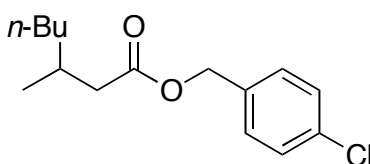
(m, 1H), 1.87–1.97 (m, 1H), 2.17 (dd, $J = 8.0, 15.0$ Hz, 1H), 2.38 (dd, $J = 6.0, 15.0$ Hz, 1H), 5.13 (s, 2H), 7.32–7.40 (m, 5H); ^{13}C NMR (CDCl_3) δ 11.25, 19.25, 29.30, 31.93, 41.45, 66.00, 128.13, 128.16, 128.51, 136.11, 173.23. Found: C, 75.90; H, 8.72%. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 75.96; H, 8.80%.

***p*-Chlorobenzyl 3-methylpentanoate (3b)**

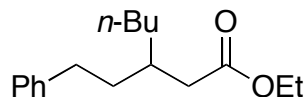


IR (neat) 2932, 2857, 1733, 1495, 1456, 1411, 1381, 1241, 1155, 1094, 1016, 982, 807 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.89 (t, $J = 7.5$ Hz, 3H), 0.93 (d, $J = 6.5$ Hz, 3H), 1.19–1.28 (m, 1H), 1.32–1.42 (m, 1H), 1.86–1.85 (m, 1H), 2.16 (dd, $J = 15.0, 8.0$ Hz, 1H), 2.37 (dd, $J = 15.0, 6.0$ Hz, 1H), 5.08 (s, 2H), 7.30 (d, $J = 8.5$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 11.23, 19.25, 29.29, 31.93, 41.38, 65.14, 128.70, 129.56, 134.02, 134.65, 173.06. Found: C, 64.84; H, 7.31%. Calcd for $\text{C}_{13}\text{H}_{17}\text{ClO}_2$: C, 64.86; H, 7.12%.

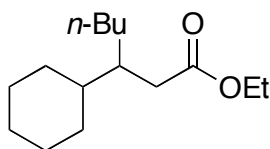
***p*-Chlorobenzyl 3-methylheptanoate (3h)**



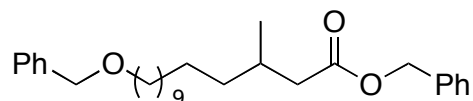
IR (neat) 2930, 2859, 1733, 1495, 1456, 1379, 1214, 1169, 1095, 806 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88 (t, $J = 7.0$ Hz, 3H), 0.93 (d, $J = 7.0$ Hz, 3H), 1.16–1.32 (m, 6H), 1.94–1.99 (m, 1H), 2.16 (dd, $J = 15.0, 8.0$ Hz, 1H), 2.34 (dd, $J = 15.0, 6.0$ Hz, 1H), 5.08 (s, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 14.01, 19.71, 22.74, 29.05, 30.35, 36.33, 41.78, 65.12, 128.68, 129.58, 134.02, 134.66, 173.03. Found: C, 67.31; H, 7.99%. Calcd for $\text{C}_{15}\text{H}_{21}\text{ClO}_2$: C, 67.03; H, 7.88%.

Ethyl 3-(2-phenylethyl)heptanoate (3i)

IR (neat) 3027, 2930, 2859, 1733, 1604, 1496, 1456, 1373, 1157, 1100, 1033, 747, 699 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.91 (t, $J = 7.5$ Hz, 3H), 1.24–1.44 (m, 6H), 1.27 (t, $J = 7.0$ Hz, 3H), 1.59–1.69 (m, 2H), 1.91–1.98 (m, 1H), 2.31 (d, $J = 6.5$ Hz, 2H), 2.62 (t, $J = 8.0$ Hz, 2H), 4.14 (q, $J = 7.0$ Hz, 2H), 7.17–7.20 (m, 2H), 7.27–7.30 (m, 3H); ^{13}C NMR (CDCl_3) δ 14.03, 14.25, 22.87, 28.62, 32.96, 33.40, 34.83, 35.82, 39.12, 60.13, 125.67, 128.28, 128.29, 142.55, 173.37. Found: C, 77.82; H, 10.21%. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$: C, 77.82; H, 9.99%.

Ethyl 3-cyclohexylheptanoate (3j)

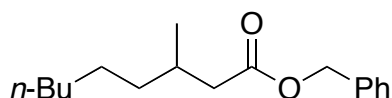
IR (neat) 2926, 2854, 1739, 1449, 1369, 1312, 1277, 1246, 1213, 1161, 1133, 1097, 1037 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.89 (t, $J = 7.5$ Hz, 3H), 0.94–1.05 (m, 2H), 1.06–1.16 (m, 1H), 1.16–1.39 (m, 9H), 1.26 (t, $J = 7.5$ Hz, 3H), 1.60–1.68 (m, 3H), 1.73–1.79 (m, 3H), 2.15 (dd, $J = 15.0, 7.5$ Hz, 1H), 2.31 (dd, $J = 15.0, 6.5$ Hz, 1H), 4.13 (q, $J = 7.5$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 14.05, 14.24, 22.94, 26.72, 26.76, 26.80, 29.13, 29.48, 29.95, 30.90, 36.60, 40.36, 40.52, 60.05, 174.25. Found: C, 74.89; H, 11.97%. Calcd for $\text{C}_{15}\text{H}_{28}\text{O}_2$: C, 74.95; H, 11.74%.

Benzyl 14-benzyloxy-3-methyltetradecanoate (8a)

IR (neat) 3033, 2927, 2855, 1733, 1498, 1456, 1380, 1362, 1259, 1168, 1103, 1029, 1002, 735, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.94 (d, $J = 6.5$ Hz, 3H), 1.18–1.39 (m, 18H), 1.60–1.66 (m, 2H),

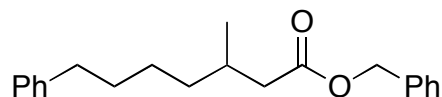
1.96–2.00 (m, 1H), 2.18 (dd, $J = 15.0, 8.0$ Hz, 1H), 2.36 (dd, $J = 15.0, 6.0$ Hz, 1H), 3.48 (t, $J = 7.0$ Hz, 2H), 4.52 (s, 2H), 5.13 (s, 2H), 7.27–7.39 (m, 10H); ^{13}C NMR (CDCl_3) δ 19.74, 26.19, 26.88, 29.47, 29.59 (Four signals were overlapped), 29.74, 29.77, 30.40, 36.71, 41.86, 65.97, 70.54, 72.84, 127.42, 127.59, 128.11, 128.17, 128.31, 128.50, 136.19, 138.75, 173.15. Found: C, 79.63; H, 9.61%. Calcd for $\text{C}_{29}\text{H}_{42}\text{O}_3$: C, 79.41; H, 9.65%.

Benzyl 3-methylnonanoate (8b)



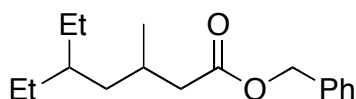
IR (neat) 3035, 2928, 2856, 2360, 1733, 1699, 1499, 1456, 1379, 1167, 1111, 1081, 1003, 736, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.89 (t, $J = 7.0$ Hz, 3H), 0.94 (d, $J = 6.5$ Hz, 3H), 1.16–1.31 (m, 10H), 1.97–2.00 (m, 1H), 2.18 (dd, $J = 14.5, 8.0$ Hz, 1H), 2.36 (dd, $J = 14.5, 6.0$ Hz, 1H), 5.13 (s, 2H), 7.32–7.40 (m, 5H); ^{13}C NMR (CDCl_3) δ 14.06, 19.74, 22.62, 26.83, 29.40, 30.41, 31.81, 36.71, 41.88, 65.98, 128.12, 128.18, 128.51, 136.19, 173.16. Found: C, 77.60; H, 9.80%. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$: C, 77.82; H, 9.99%.

Benzyl 3-methyl-7-phenylheptanoate (8c)



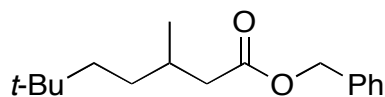
IR (neat) 3064, 3028, 2931, 2856, 1733, 1497, 1454, 1381, 1356, 1148, 1091, 1030, 982, 748, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.93 (d, $J = 6.5$ Hz, 3H), 1.18–1.26 (m, 1H), 1.28–1.43 (m, 3H), 1.56–1.63 (m, 2H), 1.95–2.02 (m, 1H), 2.18 (dd, $J = 14.5, 8.0$ Hz, 1H), 2.35 (d, $J = 14.5, 6.0$ Hz, 1H), 2.60 (t, $J = 7.5$ Hz, 2H), 5.13 (s, 2H), 7.17–7.20 (m, 3H), 7.27–7.30 (m, 2H), 7.32–7.39 (m, 5H); ^{13}C NMR (CDCl_3) δ 19.73, 26.54, 30.34, 31.52, 35.86, 36.48, 41.84, 66.01, 125.60, 128.15, 128.21, 128.23, 128.37, 128.52, 136.14, 142.67, 173.09. Found: C, 81.49; H, 8.69%. Calcd for $\text{C}_{21}\text{H}_{26}\text{O}_2$: C, 81.25; H, 8.44%.

Benzyl 5-ethyl-3-methylheptanoate (8d)



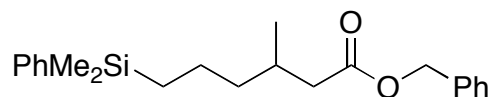
IR (neat) 2962, 2921, 2874, 1738, 1457, 1382, 1216, 1168, 1125, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.82 (t, $J = 7.0$ Hz, 3H), 0.84 (t, $J = 7.0$ Hz, 3H), 0.93 (d, $J = 6.5$ Hz, 3H), 1.06–1.12 (m, 1H), 1.16–1.36 (m, 6H), 2.01–2.11 (m, 1H), 2.17 (dd, $J = 14.5, 8.0$ Hz, 1H), 2.34 (dd, $J = 14.5, 6.0$ Hz, 1H), 5.13 (s, 2H), 7.32–7.40 (m, 5H); ^{13}C NMR (CDCl_3) δ 10.36, 10.78, 20.02, 24.97, 25.74, 27.96, 37.47, 40.53, 42.30, 65.99, 128.13, 128.23, 128.50, 136.18, 173.11. Found: C, 77.81; H, 10.24%. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$: C, 77.82; H, 9.99%.

Benzyl 3,6,6-trimethylheptanoate (8e)

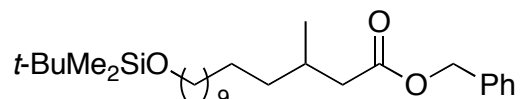


IR (neat) 3035, 2935, 2867, 1738, 1499, 1456, 1381, 1365, 1301, 1247, 1146, 1085, 982, 737, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.85 (s, 9H), 0.94 (d, $J = 7.0$ Hz, 3H), 1.10–1.31 (m, 4H), 1.88–1.95 (m, 1H), 2.18 (dd, $J = 14.5, 8.0$ Hz, 1H), 2.38 (dd, $J = 14.5, 6.0$ Hz, 1H), 5.13 (s, 2H), 7.31–7.39 (m, 5H); ^{13}C NMR (CDCl_3) δ 19.83, 29.32, 30.14, 31.13, 31.41, 41.15, 41.88, 65.99, 128.14, 128.21, 128.53, 136.18, 173.15. Found: C, 77.93; H, 10.13%. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$: C, 77.82; H, 9.99%.

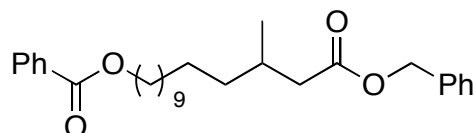
Benzyl 6-(dimethylphenylsilyl)-3-methylhexanoate (8f)



IR (neat) 2960, 2935, 2874, 1734, 1449, 1371, 1178, 1081, 994, 947, 748, 692 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.26 (s, 6H), 0.66–0.77 (m, 2H), 0.90 (d, $J = 6.5$ Hz, 3H), 1.20–1.25 (m, 1H), 1.27–1.39 (m, 3H), 1.95–2.02 (m, 1H), 2.15 (dd, $J = 15.0, 8.0$ Hz, 1H), 2.32 (dd, $J = 15.0, 6.0$ Hz, 1H), 5.12 (s, 2H), 7.34–7.38 (m, 8H), 7.49–7.53 (m, 2H); ^{13}C NMR (CDCl_3) δ -3.04, 15.70, 19.63, 21.15, 30.04, 40.60, 41.82, 65.98, 127.71, 128.13, 128.19, 128.51, 128.77, 133.52, 136.17, 139.50, 173.10. Found: C, 74.53; H, 8.72%. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}_2\text{Si}$: C, 74.53; H, 8.53%.

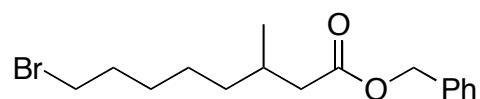
Benzyl 14-(*tert*-butyldimethylsiloxy)-3-methyltetradecanoate (8g)

IR (neat) 2928, 2855, 1739, 1463, 1256, 1165, 1100, 1006, 836, 775, 696 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.06 (s, 6H), 0.91 (s, 9H), 0.94 (d, $J = 6.5$ Hz, 3H), 1.18–1.29 (m, 18H), 1.49–1.55 (m, 2H), 1.97–2.00 (m, 1H), 2.17 (dd, $J = 15.0, 8.0$ Hz, 1H), 2.36 (dd, $J = 15.0, 6.0$ Hz, 1H), 3.61 (t, $J = 6.5$ Hz, 2H), 5.13 (s, 2H), 7.31–7.39 (m, 5H); ^{13}C NMR (CDCl_3) δ -5.26, 18.37, 19.74, 25.81, 25.99, 26.89, 29.45, 29.61 (Three signals were overlapped), 29.64, 29.75, 30.42, 32.90, 36.73, 41.88, 63.34, 65.98, 128.12, 128.18, 128.51, 136.20, 173.16. Found: C, 72.38; H, 10.72%. Calcd for $\text{C}_{28}\text{H}_{50}\text{O}_3\text{Si}$: C, 72.67; H, 10.89%.

Benzyl 14-benzoyloxy-3-methyltetradecanoate (8h)

IR (neat) 2927, 2855, 1720, 1452, 1314, 1275, 1176, 1113, 1070, 712, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.93 (d, $J = 6.5$ Hz, 3H), 1.19–1.36 (m, 16H), 1.42–1.48 (m, 2H), 1.75–1.81 (m, 2H), 1.94–2.01 (m, 1H), 2.17 (dd, $J = 14.5, 8.0$ Hz, 1H), 2.36 (dd, $J = 14.5, 6.0$ Hz, 1H), 4.33 (t, $J = 6.5$ Hz, 2H), 5.13 (s, 2H), 7.31–7.39 (m, 5H), 7.44–7.47 (m, 2H), 7.55–7.58 (m, 1H), 8.05–8.07 (m, 2H); ^{13}C NMR (CDCl_3) δ 19.72, 26.01, 26.86, 28.70, 29.25, 29.49, 29.53, 29.56 (Two signals were overlapped), 29.71, 30.38, 36.69, 41.85, 65.11, 65.96, 128.10, 128.15, 128.27, 128.48, 129.50, 130.56, 132.73, 136.16, 166.66, 173.13. Found: C, 77.02; H, 9.12%. Calcd for $\text{C}_{29}\text{H}_{40}\text{O}_4$: C, 76.95; H, 8.91%.

Benzyl 8-bromo-3-methyloctanoate (8i)



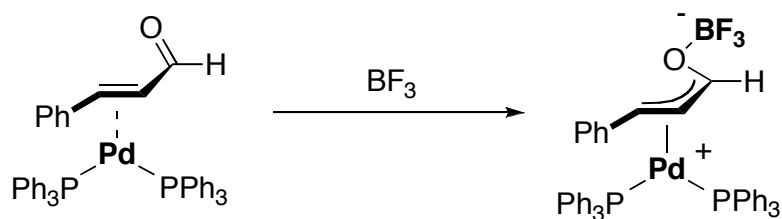
IR (neat) 2933, 2857, 1736, 1455, 1381, 1226, 1168, 1144, 982, 737, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.94 (d, $J = 7.0$ Hz, 3H), 1.16–1.26 (m, 1H), 1.27–1.46 (m, 5H), 1.81–1.87 (m, 2H), 1.95–2.02 (m, 1H), 2.19 (dd, $J = 15.0, 8.0$ Hz, 1H), 2.35 (dd, $J = 15.0, 6.0$ Hz, 1H), 3.40 (t, $J = 7.0$ Hz, 2H), 5.13 (s, 2H), 7.32–7.40 (m, 5H); ^{13}C NMR (CDCl_3) δ 19.70, 26.02, 28.22, 30.28, 32.69, 33.81, 36.37, 41.78, 66.03, 128.17, 128.22, 128.53, 136.12, 172.99. Found: C, 58.85; H, 6.98%. Calcd for $\text{C}_{16}\text{H}_{23}\text{BrO}_2$: C, 58.72; H, 7.08%.

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- (15) The fact that the electron rich substrate **1f** was more reactive than **1e** is highly suggestive of the existence and importance of the coordination (Table 1, entry 5 vs. entry 6). Namely, the more electron-rich carbonyl group of nickel-coordinated **1f** would have stronger interaction with alkylborane, which efficiently activates the carbonyl group of **1f**.
- (16) Ogoshi and Kurosawa reported that the η^2 -coordinated palladium complexes with cinnamaldehyde were converted to η^3 -coordinated ones in the presence of BF₃ with the aid of the Lewis acidity of boron (see the following equation) and proposed that the palladium-catalyzed 1,4-addition of trimethylaluminum to benzalacetone would proceed through a similar intermediate. (a) Ogoshi, S.; Yoshida, T.; Nishida, T.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 1944–1950. Also see: (b) Marshall, J. A.;

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Chapter 4

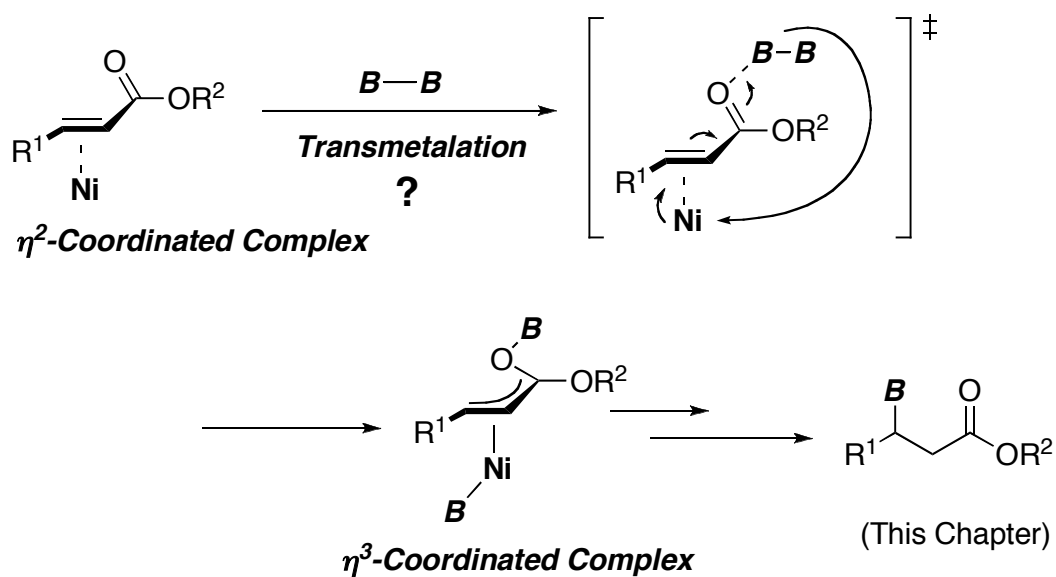
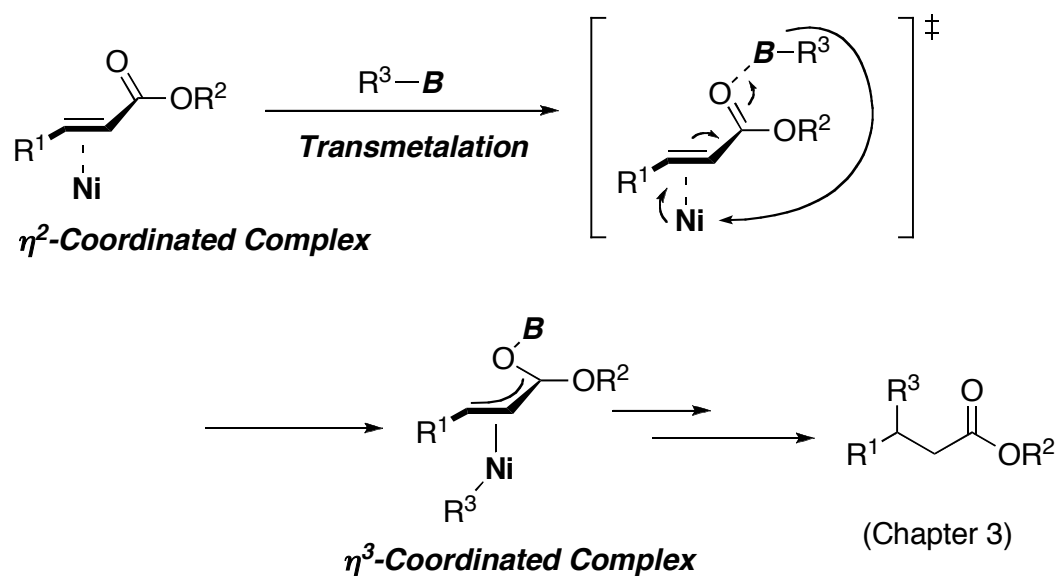
Nickel-Catalyzed β -Boration of α,β -Unsaturated Esters and Amides with Bis(pinacolato)diboron

A nickel catalyst system for β -boration of α,β -unsaturated esters and amides with bis(pinacolato)diboron has been developed. The catalyst system enables the boration of di-, tri-, and tetrasubstituted substrates in good yields. The reaction would proceed through a formation of η^3 -coordinated nickel complexes but not the oxidative addition of the B-B bond of the diboron to the low valent nickel complexes.

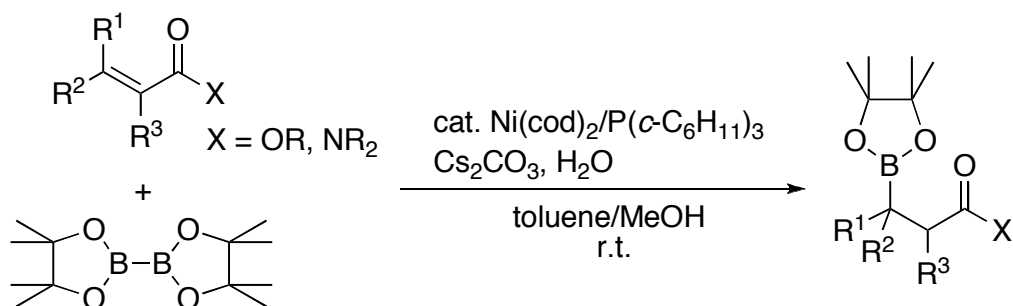
Introduction

Organoboron compounds are ubiquitous in organic synthesis¹ and can also display biological activity.² Transition-metal-catalyzed boration of unsaturated C–C bonds with diboron reagents is one of the most attractive methods for synthesis of organoboron derivatives. Since the pioneering work reported by Miyaura and Suzuki,³ a variety of catalysts for boration of various unsaturated molecules involving asymmetric variants have been explored.⁴ In the course of the development of this chemistry, β -boration of α,β -unsaturated carbonyl compounds with diborons ranks as the most important procedure for the preparation of organoborons having carbonyl functionalities at the β position. So far, platinum,⁵ rhodium,⁶ and copper⁷ complexes are known to catalyze the β -boration of α,β -unsaturated aldehydes and ketones. However, the β -boration of α,β -unsaturated esters and amides has been still challenging. Moreover, the reaction of sterically demanding multisubstituted esters and amides is not trivial. In chapter 3, the author has succeeded in nickel-catalyzed conjugate additions of trialkylboranes to α,β -unsaturated esters, which would involve the transformation of η^2 -coordinated nickel complexes with α,β -unsaturated esters to the corresponding η^3 -fashion with the aid of Lewis acidity of trialkylboranes.⁸ Given that diboron reagents have similar Lewis acidity to trialkylboranes, he expects that the catalyst and reaction system developed in Chapter 3 would be applicable to conjugate boration of α,β -unsaturated esters with diborons (Scheme 1). In Chapter 4, he discloses β -boration of α,β -unsaturated esters and amides with bis(pinacolato)diboron under nickel catalysis.⁹ The catalyst system enables the β -boration of di-, tri-, and tetrasubstituted substrates (Scheme 2).

Scheme 1.



Scheme 2.



Results and Discussion

His initial attempt on β -boration of crotonate ester **1a** with 1.2 equiv of bis(pinacolato)diboron (**2**) using 5 mol% of Ni(cod)₂/2P(*c*-C₆H₁₁)₃ as a catalyst in toluene at room temperature resulted in no conversion and the starting materials were recovered intact (Table 1, entry 1). On the basis of his previous observation,⁸ the effect of base as an activator of diboron **2** was examined. To his delight, an addition of cesium hydroxide monohydrate led to the formation of the desired product **3a** although the results were not reproducible and the yields varied from 2–40% (entry 2). After several attempts to optimize the yields, the use of a toluene/MeOH cosolvent system was found to be essential for good reproducibility (entry 3). This is probably because MeOH could be good proton source to boryl enolate formed in the catalytic cycle (*vide infra*). The combination of cesium carbonate and water instead of cesium hydroxide monohydrate improved the yield to 64% (entry 4). The boration of bulkier *tert*-butyl (*E*)-crotonate (**1b**) provided a better result (entry 5). Finally, with 1.5 equiv of diboron **2**, the borylated product **3b** was obtained in 77% yield (entry 6).¹⁰

Table 1. Optimization Studies^a

$\text{R} = \text{Et} \quad \mathbf{1a}$
 $\quad \quad \quad = t\text{-Bu} \quad \mathbf{1b}$

$\mathbf{2}$ (1.2 equiv)

$\text{Ni}(\text{cod})_2$ (5 mol%)
 $\text{P}(\text{c-C}_6\text{H}_{11})_3$ (10 mol%)
 additives (1.2 equiv)

$\xrightarrow{\text{solvent, r.t., 10-12 h}}$

$\mathbf{3}$

$\text{R} = \text{Et} \quad \mathbf{3a}$
 $\quad \quad \quad = t\text{-Bu} \quad \mathbf{3b}$

entry	1	additives	solvent	3 , yield (%) ^b
1	1a	none	toluene	3a , 0
2	1a	CsOH·OH ₂	toluene	3a , 2–40
3	1a	CsOH·OH ₂	toluene/MeOH	3a , 52
4	1a	Cs ₂ CO ₃ +H ₂ O	toluene/MeOH	3a , 64
5	1b	Cs ₂ CO ₃ +H ₂ O	toluene/MeOH	3b , 70
6 ^c	1b	Cs ₂ CO ₃ +H ₂ O	toluene/MeOH	3b , 77

^a A mixture of **1** (0.50 mmol), **2** (1.2 equiv), Ni(cod)₂ (5 mol%), P(c-C₆H₁₁)₃ (10 mol%), and additives (1.2 equiv) was stirred in toluene (5.0 mL) or toluene (5.0 mL)/MeOH (0.25 mL) for 10–12 h at room temperature.

^b Isolated yield.

^c With 1.5 equiv of **2**, Cs₂CO₃, and H₂O.

Subsequently, the β -boration was conducted with a range of substrates under the optimized conditions (Table 2). The reactions of phenylethyl- and cyclohexyl-substituted acrylates **1c** and **1d** gave **3c** and **3d** in 56% and 63% yields, respectively (entries 2 and 3). However, cinnamate ester **1e** was converted to the desired product in low yield (entry 4). Interestingly, the substitutions by methoxy and fluoro group on the benzene ring improved the yield (entries 5 and 6).¹¹ Heterocyclic compound **1h** took part in the reaction albeit the yield was moderate (entry 7). Fortunately, α -substituted substrate, methacrylate ester **1i**, also underwent the boration smoothly (entry 8). It should be noted that the borations of β,β -disubstituted esters **1j** and **1k** proceeded

to furnish **3j** and **3k** without any difficulties (entries 9 and 10). Moreover, tri- and tetrasubstituted substrates **1l** and **1m** participated in the reaction in spite of their steric hindrance (entries 11 and 12). The β -boration of α,β -unsaturated amides as well as esters was available, which is unprecedented to the best of our knowledge. Various substitution patterns were tolerant toward the conjugate boration as observed in the case of the boration of esters (entries 13–16). Notably, amides reacted with diboron **2** much faster than the corresponding esters. For instance, the boration of crotonamide **1n** was completed within 3 h to afford **3n** in 75% yield.

Table 2. Nickel-Catalyzed β -Boration of α,β -Unsaturated Esters and Amides with Bis(pinacolato)diboron^a

entry	1	time (h)	3 , yield (%) ^b
1	1b	11	3b , 77
2	1c	12	3c , 56
3	1d	11	3d , 63
4	1e	14	3e , 14

Table 2. (Continued)

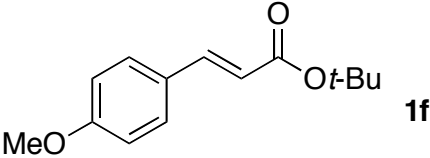
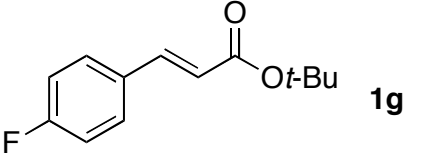
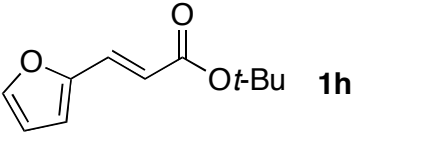
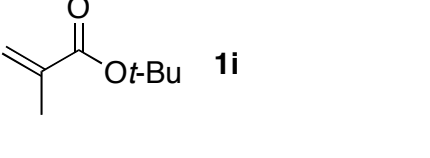
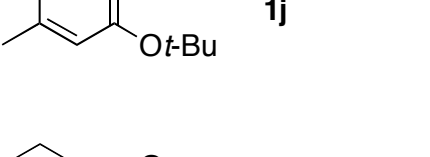
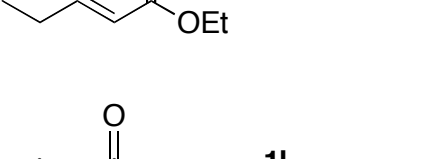

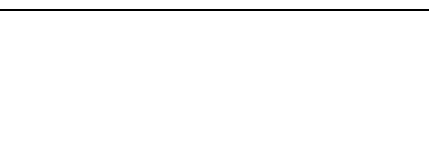
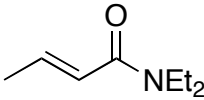
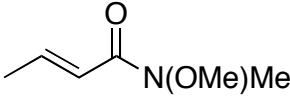
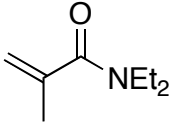
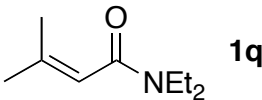
entry	1	time (h)	3, yield (%) ^b
5	 1f	10	3f , 72
6	 1g	10	3g , (50) ^c
7	 1h	12	3h , (47) ^c
8	 1i	12	3i , 71
9 ^d	 1j	10	3j , 60
10 ^d	 1k	12	3k , 76
11	 1l	7.5	3l , 82 ^e
12 ^d	 1m	12	3m , 83

Table 2. (Continued)

entry	1	time (h)	3 , yield (%) ^b
13	 1n	3	3n , 75
14	 1o	3	3o , 61
15	 1p	4	3p , 70
16	 1q	7	3q , 80

^a A mixture of **1** (0.50 mmol), **2** (1.5 equiv), Cs₂CO₃ (1.5 equiv), H₂O (1.5 equiv), Ni(cod)₂ (5 mol%), and P(*c*-C₆H₁₁)₃ (10 mol%) was stirred in toluene (5.0 mL)/MeOH (0.25 mL) at room temperature.

^b Isolated yield.

^c The borylated product was unstable so that the corresponding β -hydroxy ester was isolated after oxidation (See Experimental Section for the procedure).

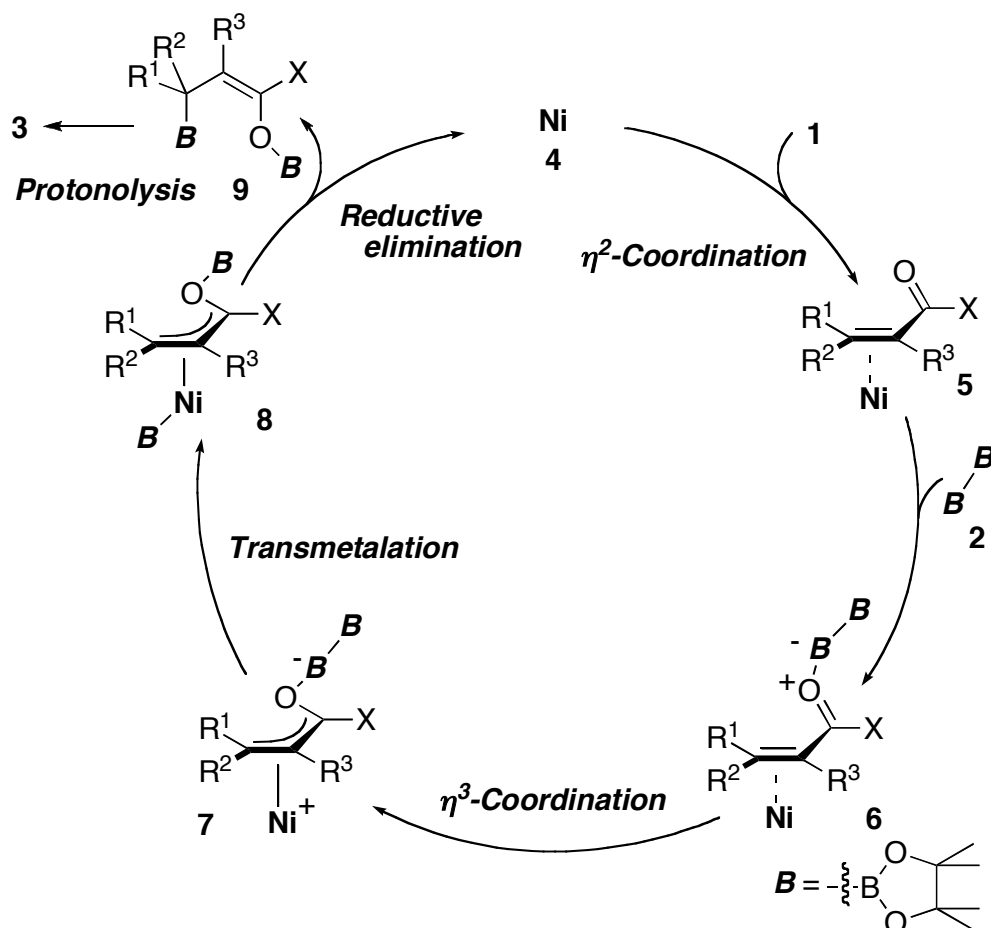
^d With 2.0 equiv of **2**, Cs₂CO₃, and H₂O.

^e A 1:1 mixture of diastereomers. The stereochemistry of each isomer was not determined.

The catalytic cycle of the present reaction is proposed as illustrated in Scheme 3. A nickel(0) species **4** initially reacts with **1** to generate η^2 -coordinated complex **5**. The coordination of the carbonyl moiety of **5** to diboron **2** gives the intermediate **6**.¹² The Lewis acidity of the boron promotes the formation of η^3 -coordinated nickel complex **7** followed by transmetalation of the boryl group to furnish the borylnickel species **8**.^{13,14} Finally, reductive elimination from **8** affords **9** along with the starting nickel complex to complete the catalytic cycle. Protonolysis of boryl enolate **9** with MeOH would provide **3**. The exact roles of cesium base are not clear at this stage. It can enhance the transmetalation step through its coordination

to the boron center of **7**.¹⁵

Scheme 3.



Conclusion

The author has developed the effective nickel catalyst system for the β -boration of α,β -unsaturated esters and amides with bis(pinacolato)diboron. The catalytic reaction provides a facile route to primary, secondary, and tertiary alkylboronates bearing esters and amides functionalities at the β position.

Experimental Section

Instrumentation and Chemicals

^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were taken on Varian UNITY INOVA 500 spectrometers and were recorded in CDCl_3 . Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^1H and relative to CDCl_3 at 77.0 ppm for ^{13}C unless otherwise noted. ^{19}F NMR spectra were obtained in CDCl_3 with fluorotrichloromethane as an external standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel 60 N (spherical neutral, obtained from Kanto Kagaku) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was stored over slices of sodium. Bis(1,5-cyclooctadiene)nickel and tricyclohexylphosphine were available from Strem. Tricyclohexylphosphine was diluted to prepare 0.50 M toluene solution, which was stored strictly under argon. Bis(pinacolato)diboron was purchased from Frontier Scientific. All reactions were carried out under argon atmosphere.

Typical Procedure for the Nickel-Catalyzed β -Boration of α,β -Unsaturated Esters and Amides with Bis(pinacolato)diboron

Synthesis of 3b: With a glovebox filled with argon, $\text{Ni}(\text{cod})_2$ (6.9 mg, 0.025 mmol) and Cs_2CO_3 (244 mg, 0.75 mmol) were placed in a reaction flask. Toluene (3.0 mL) and $\text{P}(c\text{-C}_6\text{H}_{11})_3$ (purchased from Strem and diluted to prepare a degassed toluene solution, 0.50 M, 0.10 mL, 0.050 mmol) were added dropwise. The suspension was stirred for 10 min at 0 °C. A solution of *tert*-butyl (*E*)-crotonate (**1b**, 71 mg, 0.50 mmol) and bis(pinacolato)diboron (**2**, 191 mg, 0.75 mmol) in toluene (2.0 mL) was then added. Finally, MeOH (0.25 mL) and water (14 μL , 0.75 mmol) were added, and the mixture was allowed to warm to room temperature and stirred for 11 h. The resulting mixture was poured into water (10 mL). The product was extracted with

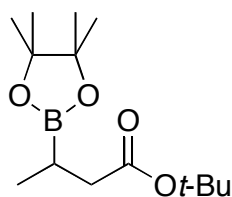
hexane/ethyl acetate (20:1). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Silica gel column purification (hexane : ethyl acetate = 40 : 1) gave *tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (**3b**, 104 mg, 0.385 mmol) in 77% yield.

Oxidation of 3g: According to the procedure described above, the β -boration was conducted with *tert*-butyl (*E*)-*p*-fluorocinnamate (**1g**, 111 mg, 0.50 mmol) instead of *tert*-butyl (*E*)-crotonate (**1b**) to provide the borylated product **3g**. The crude product obtained was oxidized with aq H₂O₂ (30%, 1.0 mL) and aq NaOH (3.0 M, 1.0 mL) in THF/EtOH (2.0 mL : 1.0 mL) at room temperature for 30 min. After aqueous sodium thiosulfate was added, extraction followed by purification on silica gel column with hexane/ethyl acetate (5:1) as an eluent provided *tert*-butyl 3-(*p*-fluorophenyl)-3-hydroxypropanoate (**3g'**, 60 mg, 0.25 mmol) in 50% yield.

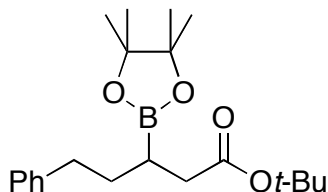
Characterization Data

Boronate **3a**^{7c} is found in the literature.

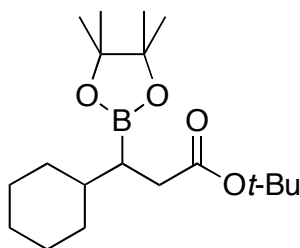
tert-Butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (**3b**)



IR (neat) 2979, 2933, 2876, 1729, 1464, 1417, 1370, 1348, 1318, 1274, 1236, 1214, 1143 cm⁻¹;
¹H NMR (CDCl₃) δ 1.00 (d, $J = 7.5$ Hz, 3H), 1.24 (s, 6H), 1.25 (s, 6H), 1.31–1.39 (m, 1H), 1.44 (s, 9H), 2.27 (dd, $J = 17.0, 7.5$ Hz, 1H), 2.35 (dd, $J = 17.0, 7.5$ Hz, 1H); ¹³C NMR (CDCl₃) δ 14.93, 24.65, 24.73, 28.12, 38.81, 79.82, 83.03, 173.28. The signal for the carbon which is attached to the boron atom was not observed. Found: C, 62.36; H, 10.26%. Calcd for C₁₄H₂₇BO₄: C, 62.24; H, 10.07%.

***tert*-Butyl 5-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3c)**

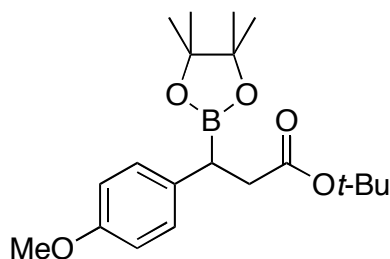
IR (neat) 2978, 2931, 2859, 1727, 1453, 1418, 1380, 1371, 1318, 1257, 1214, 1142 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.27 (s, 6H), 1.28 (s, 6H), 1.35–1.41 (m, 1H), 1.44 (s, 9H), 1.61–1.68 (m, 1H), 1.75–1.83 (m, 1H), 2.37 (dd, $J = 16.5, 7.0$ Hz, 1H), 2.42 (dd, $J = 16.5, 8.5$ Hz, 1H), 2.60–2.70 (m, 2H), 7.16–7.20 (m, 2H), 7.26–7.29 (m, 3H); ^{13}C NMR (CDCl_3) δ 24.73, 24.86, 28.12, 32.59, 35.20, 36.87, 79.94, 83.12, 125.61, 128.24, 128.40, 142.73, 173.23. The signal for the carbon which is attached to the boron atom was not observed. Found: C, 70.14; H, 8.96%. Calcd for $\text{C}_{21}\text{H}_{33}\text{BO}_4$: C, 70.01; H, 9.23%.

***tert*-Butyl 3-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3d)**

IR (neat) 2978, 2925, 2852, 1729, 1449, 1371, 1315, 1241, 1212, 1142 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.99–1.28 (m, 6H), 1.24 (s, 6H), 1.27 (s, 6H), 1.35–1.42 (m, 1H), 1.44 (s, 9H), 1.62–1.65 (m, 1H), 1.69–1.72 (m, 4H), 2.31 (dd, $J = 17.0, 6.0$ Hz, 1H), 2.39 (dd, $J = 17.0, 11.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 24.71, 25.02, 26.60, 26.70, 26.77, 28.13, 32.22, 32.56, 34.69, 39.10, 79.69, 82.99, 173.87. The signal for the carbon which is attached to the boron atom was not observed. Found: C, 67.58; H, 10.56%. Calcd for $\text{C}_{19}\text{H}_{35}\text{BO}_4$: C, 67.46; H, 10.43%.

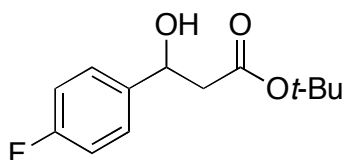
***tert*-Butyl 3-(*p*-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate**

(3f)



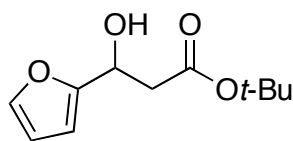
IR (neat) 2978, 2933, 1729, 1511, 1423, 1367, 1322, 1300, 1247, 1218, 1140, 1038, 848 cm^{-1} ;
 ^1H NMR (CDCl_3) δ 1.18 (s, 6H), 1.23 (s, 6H), 1.42 (s, 9H), 2.55 (dd, $J = 16.0, 6.5$ Hz, 1H), 2.65 (dd, $J = 10.0, 6.5$ Hz, 1H), 2.76 (dd, $J = 16.0, 10.0$ Hz, 1H), 3.78 (s, 3H), 6.81 (d, $J = 8.5$ Hz, 2H), 7.14 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 24.49, 24.64, 28.07, 38.66, 55.17, 80.05, 83.38, 113.82, 129.14, 133.53, 157.54, 172.82. The signal for the carbon which is attached to the boron atom was not observed. Found: C, 66.04; H, 8.79%. Calcd for $\text{C}_{20}\text{H}_{31}\text{BO}_5$: C, 66.31; H, 8.63%.

***tert*-Butyl 3-(*p*-fluorophenyl)-3-hydroxypropanoate (3g')**



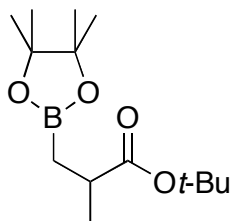
IR (neat) 3439, 2981, 2934, 1719, 1606, 1511, 1394, 1369, 1223, 1151, 838 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.46 (s, 9H), 2.62 (dd, $J = 16.5, 4.5$ Hz, 1H), 2.67 (dd, $J = 16.5, 8.0$ Hz, 1H), 3.51 (d, $J = 3.5$ Hz, 1H), 5.06–5.09 (m, 1H), 7.05 (tt, $J = 9.0, 2.0$ Hz, 2H), 7.36 (ddt, $J = 9.0, 5.0, 2.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 28.06, 44.21, 69.77, 81.68, 115.27 (d, $J = 21.6$ Hz), 127.39 (d, $J = 8.2$ Hz), 138.35, 162.23 (d, $J = 245.2$ Hz), 171.28; ^{19}F NMR (CDCl_3) δ -115.18. Found: C, 64.82; H, 7.19%. Calcd for $\text{C}_{13}\text{H}_{17}\text{FO}_3$: C, 64.99; H, 7.13%.

***tert*-Butyl 3-(2-furyl)-3-hydroxypropanoate (3h')**



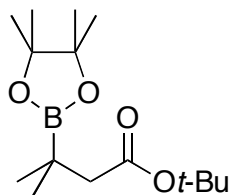
IR (neat) 3437, 2979, 2933, 1729, 1504, 1368, 1258, 1220, 1152, 1067, 1012, 955, 884, 846 cm^{-1} ;
 ^1H NMR (CDCl_3) δ 1.47 (s, 9H), 2.77 (dd, $J = 16.5, 4.0$ Hz, 1H), 2.83 (dd, $J = 16.5, 8.0$ Hz, 1H),
 3.37 (bs, 1H), 5.09 (dd, $J = 8.0, 4.0$ Hz, 1H), 6.28 (dt, $J = 3.5, 1.0$ Hz, 1H), 6.34 (dd, $J = 3.5, 2.0$
 Hz, 1H), 7.38 (dd, $J = 2.0, 1.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 28.04, 40.70, 64.34, 81.63, 106.15,
 110.17, 142.10, 154.92, 171.35. Found: C, 62.28; H, 7.73%. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_4$: C, 62.25; H,
 7.60%.

***tert*-Butyl 2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3i)**



IR (neat) 2979, 2935, 1728, 1369, 1319, 1273, 1223, 1144, 847 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88
 (dd, $J = 16.0, 7.5$ Hz, 1H), 1.10 (dd, $J = 16.0, 7.5$ Hz, 1H), 1.16 (d, $J = 7.0$ Hz, 3H), 1.24 (s, 6H),
 1.25 (s, 6H), 1.44 (s, 9H), 2.53–2.60 (m, 1H); ^{13}C NMR (CDCl_3) δ 19.26, 24.53 (Two peaks
 were overlapped.), 27.78, 36.06, 79.28, 82.80, 176.47. The signal for the carbon which is
 attached to the boron atom was not observed. Found: C, 62.28; H, 9.80%. Calcd for
 $\text{C}_{14}\text{H}_{27}\text{BO}_4$: C, 62.24; H, 10.07%.

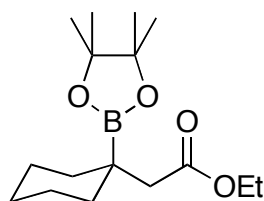
***tert*-Butyl 3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3j)**



IR (neat) 2978, 2936, 2907, 2866, 1726, 1477, 1448, 1389, 1369, 1345, 1312, 1237, 1213, 1142,

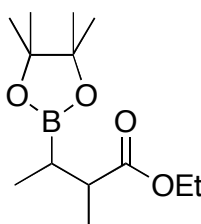
1115, 850 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.99 (s, 6H), 1.25 (s, 12H), 1.44 (s, 9H), 2.24 (s, 2H); ^{13}C NMR (CDCl_3) δ 24.57, 24.64, 28.17, 46.48, 79.83, 83.00, 172.78. The signal for the carbon which is attached to the boron atom was not observed. Found: C, 63.18; H, 10.05%. Calcd for $\text{C}_{15}\text{H}_{29}\text{BO}_4$: C, 63.39; H, 10.29%.

Ethyl 2-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl]acetate (3k)



IR (neat) 2978, 2927, 2853, 1733, 1452, 1389, 1379, 1371, 1309, 1237, 1167, 1144 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.05–1.10 (m, 2H), 1.25 (t, $J = 7.0$ Hz, 3H), 1.28 (s, 12H), 1.40–1.48 (m, 2H), 1.56–1.60 (m, 4H), 1.83–1.86 (m, 2H), 2.33 (s, 2H), 4.11 (q, $J = 7.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 14.33, 23.92, 24.84, 26.41, 34.44, 44.70, 59.98, 83.03, 173.07. The signal for the carbon which is attached to the boron atom was not observed. Found: C, 65.01; H, 9.86%. Calcd for $\text{C}_{16}\text{H}_{29}\text{BO}_4$: C, 64.88; H, 9.87%.

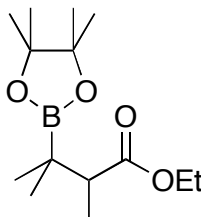
Ethyl 2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (a 1:1 mixture of diastereomers) (3l)



IR (neat): 2979, 2936, 2879, 1733, 1459, 1371, 1319, 1250, 1146, 1108, 1096, 1061, 850 cm^{-1} ; ^1H NMR (CDCl_3): δ 0.95 (d, $J = 7.0$ Hz, $0.5 \times 3\text{H}$), 0.96 (d, $J = 7.0$ Hz, $0.5 \times 3\text{H}$), 1.18 (d, $J = 7.5$ Hz, $0.5 \times 3\text{H}$), 1.24–1.27 (m, 17.5H), 2.55 (quint, $J = 7.0$ Hz, $0.5 \times 1\text{H}$), 2.60 (quint, $J = 7.0$ Hz, $0.5 \times 1\text{H}$), 4.08–4.19 (m, 2H); ^{13}C NMR (CDCl_3): δ 12.19, 12.58, 14.28, 14.33, 15.23, 16.35,

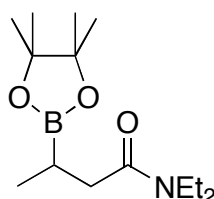
24.67, 24.70, 24.72, 24.73, 41.66, 41.86, 59.98, 60.09, 83.01, 83.07, 176.54, 176.96. The signals for the carbons which are attached to the boron atom were not observed. Found: C, 60.99; H, 9.56%. Calcd for $C_{13}H_{25}BO_4$: C, 60.96; H, 9.84%.

Ethyl 2,3-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3m)



IR (neat) 2979, 2942, 2870, 1729, 1466, 1448, 1390, 1357, 1311, 1272, 1184, 1145, 1123, 1086, 846 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.94 (s, 3H), 0.96 (s, 3H), 1.15 (d, $J = 7.5$ Hz, 3H), 1.25 (s, 6H), 1.26 (s, 6H), 1.26 (t, $J = 7.0$ Hz, 3H), 2.50 (q, $J = 7.5$ Hz, 1H), 4.11 (dq, $J = 11.0, 7.0$ Hz, 1H), 4.15 (dq, $J = 11.0, 7.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.10, 14.35, 21.01, 22.58, 24.62, 24.67, 46.96, 59.95, 82.90, 176.43. The signal for the carbon which is attached to the boron atom was not observed. Found: C, 62.39; H, 10.21%. Calcd for $C_{14}H_{27}BO_4$: C, 62.24; H, 10.07%.

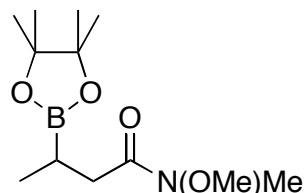
***N,N*-Diethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3n)**



IR (neat) 2995, 2935, 2872, 1638, 1462, 1448, 1421, 1380, 1369, 1313, 1276, 1252, 1224, 1144, 1081 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.00 (d, $J = 7.0$ Hz, 3H), 1.12 (t, $J = 7.0$ Hz, 3H), 1.18 (t, $J = 7.0$ Hz, 3H), 1.21–1.29 (m, 1H), 1.23 (s, 6H), 1.25 (s, 6H), 2.32 (dd, $J = 17.0, 8.0$ Hz, 1H), 2.55 (dd, $J = 17.0, 7.0$ Hz, 1H), 3.24–3.36 (m, 3H), 3.41–3.48 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 12.94, 13.96, 15.42, 24.86 (Two peaks were overlapped.), 37.74, 40.71, 42.03, 81.69, 174.20. The signal for the carbon which is attached to the boron atom was not observed. Found: C, 62.07; H, 10.73%.

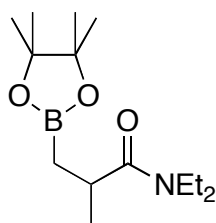
Calcd for $C_{14}H_{28}BNO_3$: C, 62.47; H, 10.48%.

***N*-Methoxy-*N*-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3o)**

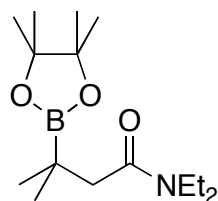


IR (neat) 2976, 2938, 2873, 1664, 1466, 1415, 1380, 1371, 1312, 1234, 1147, 1124, 1006 cm^{-1} ;
 1H NMR ($CDCl_3$) δ 1.02 (d, $J = 7.5$ Hz, 3H), 1.25 (s, 6H), 1.26 (s, 6H), 1.33–1.40 (m, 1H),
 2.53–2.55 (m, 2H), 3.17 (s, 3H), 3.69 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 12.94 (broad, very weak, the
 signal for the carbon which is attached to the boron atom), 15.26, 24.68, 24.71, 32.28 (very weak),
 35.63, 61.10, 82.86, 174.53 (very weak). Found: C, 55.88; H, 9.34%. Calcd for $C_{12}H_{24}BNO_4$:
 C, 56.05; H, 9.41%.

***N,N*-Diethyl-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanamide (3p)**



IR (neat) 2977, 2934, 2875, 1638, 1466, 1431, 1371, 1318, 1259, 1205, 1147, 1114, 970 cm^{-1} ;
 1H NMR ($CDCl_3$) δ 0.92 (dd, $J = 16.0, 7.0$ Hz, 1H), 1.10 (dd, $J = 16.0, 7.0$ Hz, 1H), 1.11 (t, $J =$
 7.0 Hz, 3H), 1.15 (d, $J = 7.0$ Hz, 3H), 1.21 (t, $J = 7.0$ Hz, 3H), 1.22 (s, 6H), 1.23 (s, 6H),
 2.82–2.89 (m, 1H), 3.33–3.38 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.01, 14.60, 20.42, 24.82, 24.83,
 32.08, 40.25, 41.80, 82.70, 177.00. The signal for the carbon which is attached to the boron
 atom was not observed. Found: C, 62.21; H, 10.37%. Calcd for $C_{14}H_{28}BNO_3$: C, 62.47; H,
 10.48%.

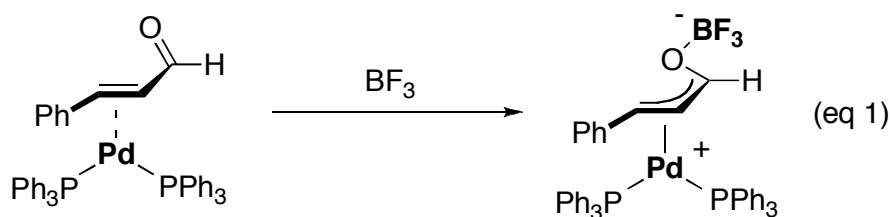
***N,N*-Diethyl-3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3q)**

IR (neat) 2974, 2936, 2904, 2861, 1635, 1475, 1448, 1385, 1365, 1301, 1223, 1145 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.96 (s, 6H), 1.13 (t, $J = 7.0$ Hz, 3H), 1.18 (t, $J = 7.0$ Hz, 3H), 1.23 (s, 12H), 2.34 (s, 2H), 3.29 (q, $J = 7.0$ Hz, 2H), 3.40 (q, $J = 7.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 12.88, 13.94, 24.96, 25.20, 41.04, 42.25, 46.05, 81.09, 173.26. The signal for the carbon which is attached to the boron atom was not observed. Found: C, 63.83; H, 10.39%. Calcd for $\text{C}_{15}\text{H}_{30}\text{BNO}_3$: C, 63.61; H, 10.68%.

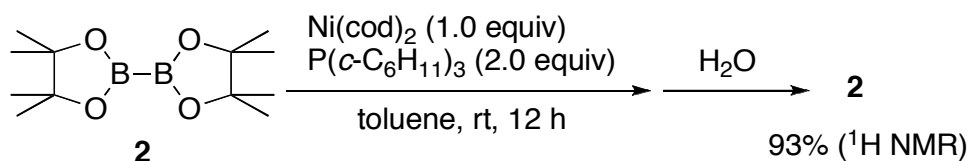
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- (9) Nickel-catalyzed reactions with diboron reagents are quite rare. See: (a) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435–3462. (b) Yu, C.-M.; Youn, J.; Yoon, S.-K.; Hong, Y.-T. *Org. Lett.* **2005**, *7*, 4507–4510.
- (10) The use of P(*t*-Bu)₃, P(*n*-Bu)₃, and PPh₃ instead of P(*c*-C₆H₁₁)₃ gave the product in lower yields (ca. <20%).
- (11) A similar trend was observed in our previous work. See ref 8c and ref 12.
- (12) The fact that the substrates **1f** and **1g** bearing π -donor substituents on the benzene ring were more reactive than **1e** is consistent with the existence and importance of the coordination (Table 2, entry 4 vs. entries 5 and 6). Namely, the more electron-rich carbonyl group of nickel-coordinated **1f** and **1g** would have stronger interaction with bis(pinacolato)diboron. The differences of reaction rates between amides and esters also support the assumption since the carbonyl group of amides would be more electron-rich than that of esters (Table 2, entries 13–16).
- (13) Ogoshi and Kurosawa reported that the η^2 -coordinated palladium complexes with cinnamaldehyde were converted to η^3 -coordinated ones in the presence of BF₃ with the aid of the Lewis acidity of boron (see eq 1). Furthermore, they also described that palladium-catalyzed 1,4-addition of disilanes to α,β -unsaturated aldehydes and ketones initiated by Me₃SiOTf would proceed through a similar η^3 -coordinated intermediate but not oxidative addition of the Si–Si bond of disilanes to the palladium complex. (a) Ogoshi, S.; Yoshida, T.; Nishida, T.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 1944–1950. (b) Ogoshi, S.; Tomiyasu, S.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2002**, *124*, 11598–11599.



- (14) Chlorotrialkylsilane is known to promote transformation of η^2 -coordinated nickel complexes with α,β -unsaturated aldehydes and ketones to the corresponding η^3 -complexes. (a) Grisso, B. A.; Johson, J. R.; Mackenzie, P. B. *J. Am. Chem. Soc.* **1992**, *114*, 5160–5165. (b) Ikeda, S.-i.; Sato, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5975–5976. In nickel-catalyzed 1,4-addition of allylboronic acid pinacol ester to styryl ketones, the η^3 -coordinated nickel complexes with the ketones formed by the action of the boronate was proposed as the key intermediate. (c) Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214–2215.
- (15) Although the mechanism involving the oxidative addition of B–B bond of bis(pinacolato)diboron (**2**) to the nickel complex could not be completely excluded, treatment of diboron **2** with a stoichiometric amount of $\text{Ni}(\text{cod})_2/2\text{P}(c\text{-C}_6\text{H}_{11})_3$ followed by quench with H_2O resulted in 93% recovery of **2**.



Chapter 5

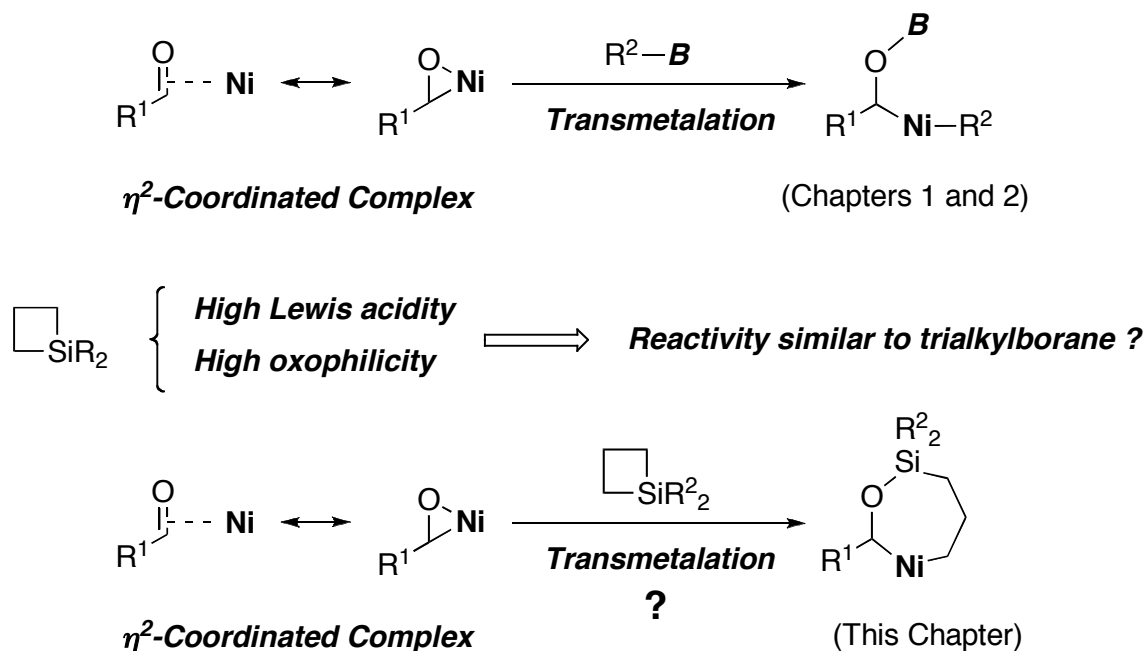
Nickel-Catalyzed Reactions of Silacyclobutanes with Aldehydes: Ring Opening and Ring Expansion Reaction

A nickel-catalyzed ring opening reaction of silacyclobutanes with aldehydes affords the corresponding alkoxyallylsilanes. In contrast, the ring expansion reaction of benzosilacyclobutene with aldehydes takes place under nickel catalysis to give oxasilacyclohexenes.

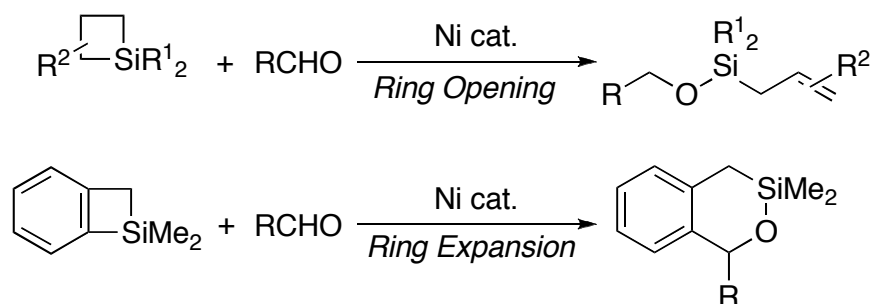
Introduction

Silacyclobutanes are an interesting class of compounds that have unique reactivity due to their ring strain and Lewis acidity.¹ Therefore, some groups^{2,3} have developed their synthetic utilities. Among them, palladium and platinum complexes are known to catalyze quite useful transformations including ring opening polymerization,⁴ cycloaddition with alkynes and allenes,⁵ and coupling reactions with acid halides.⁶ However, nickel-catalyzed reactions of silacyclobutanes have not been explored, although nickel belongs to the same group, group 10. In Chapters 1 and 2, the author has described nickel-catalyzed alkylation of aldehydes with trialkylboranes. The reaction mechanism would involve the η^2 -coordination between the nickel complexes and C=O moiety of aldehydes followed by transmetalation with trialkylboranes. The high Lewis acidity and oxophilicity of trialkylboranes would promote the transmetalation. On the basis of the high Lewis acidity and oxophilicity of silacyclobutanes, he assumes that silacyclobutanes have similar reactivities to trialkylboranes toward the η^2 -coordinated nickel complexes with aldehydes (Scheme 1). In Chapter 5, he describes nickel-catalyzed ring opening and ring expansion reactions of silacyclobutanes with aldehydes (Scheme 2). To the best of his knowledge, these are the first examples of nickel-catalyzed transformation of silacyclobutanes.

Scheme 1.



Scheme 2.

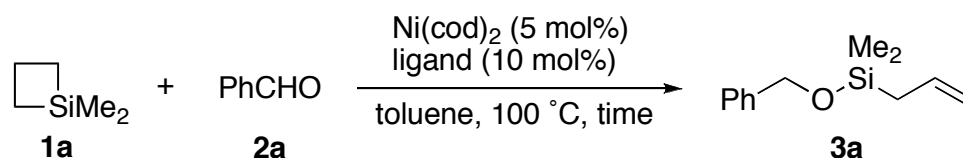


Results and Discussion

Treatment of 1,1-dimethylsilacyclobutane (**1a**, 0.5 mmol) with benzaldehyde (**2a**, 0.6 mmol) in the presence of 5 mol% of Ni(cod)₂ and 10 mol% of P(*c*-C₆H₁₁)₃ in toluene (5 mL) at 100 °C for 12 h afforded allylbenzyloxydimethylsilane (**3a**) in 20% yield (Table 1, entry 1).⁷ Apparently, a carbon-silicon bond cleavage was involved in this transformation, albeit the yield

was low. We then screened various ligands (Table 1). Although a number of phosphine ligands have poor to moderate activity for this reaction, PPh_2Me and $\text{P}(n\text{-Bu})_3$ showed high efficiency (entries 3 and 7). Finally, we found that the desired product was obtained in 88% yield with 10 mol% of $\text{Ni}(\text{cod})_2$ and 20 mol% of PPh_2Me in toluene (5 mL) at 100 °C (entry 10). This reaction is regarded as a hydrosilane-free reductive silylation of aldehydes.

Table 1. Optimization of the Ring Opening Reaction of 1,1-Dimethylsilacyclobutane (**1a**) with Benzaldehyde (**2a**)



entry	ligand	time (h)	yield of 3a (%)
1	$\text{P}(c\text{-C}_6\text{H}_{11})_3$	12	20
2	$\text{P}(t\text{-Bu})_3$	12	0
3	$\text{P}(n\text{-Bu})_3$	12	67
4	PMe_3	12	2
5	PPh_3	12	7
6	PPh_2Et	12	52
7	PPh_2Me	12	67
8 ^a	$\text{P}(n\text{-Bu})_3$	12	67
9 ^a	PPh_2Me	12	76
10 ^a	PPh_2Me	20	88

^a With 10 mol% of $\text{Ni}(\text{cod})_2$ and 20 mol% of ligand.

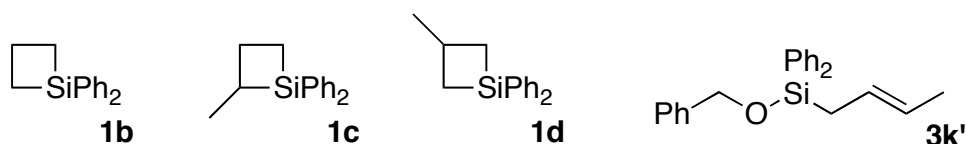
By using the optimal conditions, he surveyed the scope and limitation of this reaction (Table 2). Reaction of sterically hindered 2-methylbenzaldehyde (**2b**) proceeded smoothly to afford the corresponding alkoxyallylsilane (**3b**) in high yield (entry 1). Although reductive silylations of 4-methoxybenzaldehyde (**2c**) and 4-trifluoromethylbenzaldehyde (**2d**) resulted in low conversions (entries 2 and 3), the use of P(*n*-Bu)₃ instead of PPh₂Me as a ligand improved the yields to 53% and 77%, respectively (entries 4 and 5). Ester functionality was compatible under the reaction conditions (entry 6). Aliphatic aldehydes as well as aromatic aldehydes were converted to alkoxyallylsilanes. The reductive silylations of dihydrocinnamaldehyde (**2f**) and cyclohexanecarbaldehyde (**2g**) furnished **3f** and **3g** in 73% and 69% yields, respectively (entries 7 and 8). In the case of *trans*-cinnamaldehyde (**2h**), 1,2-reduction occurred preferentially to give allylcinnamyloxysilane **3h** as a sole product (entry 9). Other silacyclobutanes could be employed for the reaction. 1,1-Diphenylsilacyclobutane (**1b**) reduced aromatic and aliphatic aldehydes without any difficulties despite its increased steric hindrance (entries 10 and 11). With 1,1-diphenyl-2-methylsilacyclobutane (**1c**), cleavage of the primary carbon-silicon bond predominated over that of the secondary carbon-silicon bond to produce benzyloxydiphenyl(1-methyl-2-propenyl)silane (**3k**) as a major product (entry 12). The transfer of the primary alkyl carbon to the nickel center is preferable to that of the secondary one in the transmetalation step (*vide infra*).⁸ However, 1,1-diphenyl-3-methylsilacyclobutane (**1d**) did not react with benzaldehyde (**2a**) to recover the starting materials (entry 13). The reason for the unsuccessful conversion is not clear.

Table 2. Scope and Limitation
$$\begin{array}{c}
 \text{R}^2 \text{---} \text{SiR}^1_2 \\
 \text{1}
 \end{array}
 + \text{RCHO} \text{ (2)} \xrightarrow[\text{toluene, 100 }^\circ\text{C, 20 h}]{\text{Ni(cod)}_2 \text{ (10 mol\%)} \\ \text{ligand (20 mol\%)}}
 \begin{array}{c}
 \text{R} \text{---} \text{O} \text{---} \text{SiR}^1_2 \text{---} \text{CH}_2 \text{---} \text{CH}=\text{CH} \text{---} \text{R}^2 \\
 \text{3}
 \end{array}$$

entry	1 ^b	2	ligand	3 , yield (%)
1	1a	2-MeC ₆ H ₄ CHO (2b)	PPh ₂ Me	3b , 85
2	1a	4-MeOC ₆ H ₄ CHO (2c)	PPh ₂ Me	3c , 47
3	1a	4-CF ₃ C ₆ H ₄ CHO (2d)	PPh ₂ Me	3d , 48
4 ^a	1a	2c	P(<i>n</i> -Bu) ₃	3c , 53
5	1a	2d	P(<i>n</i> -Bu) ₃	3d , 77
6	1a	4-MeOCOC ₆ H ₄ CHO (2e)	P(<i>n</i> -Bu) ₃	3e , 53
7	1a	Ph(CH ₂) ₂ CHO (2f)	P(<i>n</i> -Bu) ₃	3f , 73
8 ^a	1a	<i>c</i> -C ₆ H ₁₁ CHO (2g)	P(<i>n</i> -Bu) ₃	3g , 69
9	1a	<i>trans</i> -PhCH=CHCHO (2h)	PPh ₂ Me	3h , 51
10	1b	2a	PPh ₂ Me	3i , 87
11	1b	2f	P(<i>n</i> -Bu) ₃	3j , 80
12	1c	2a	PPh ₂ Me	3k , 63 ^c
13	1d	2a	PPh ₂ Me	3l , 0

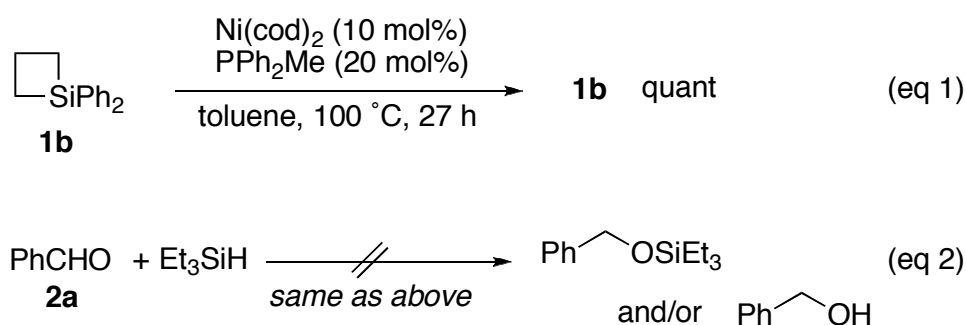
^a Reaction time was 12 h. ^b Structures of silacyclobutanes **1b-1d** are shown below.

^c Crotylsilane **3k'** was obtained in 24% yield as a byproduct.



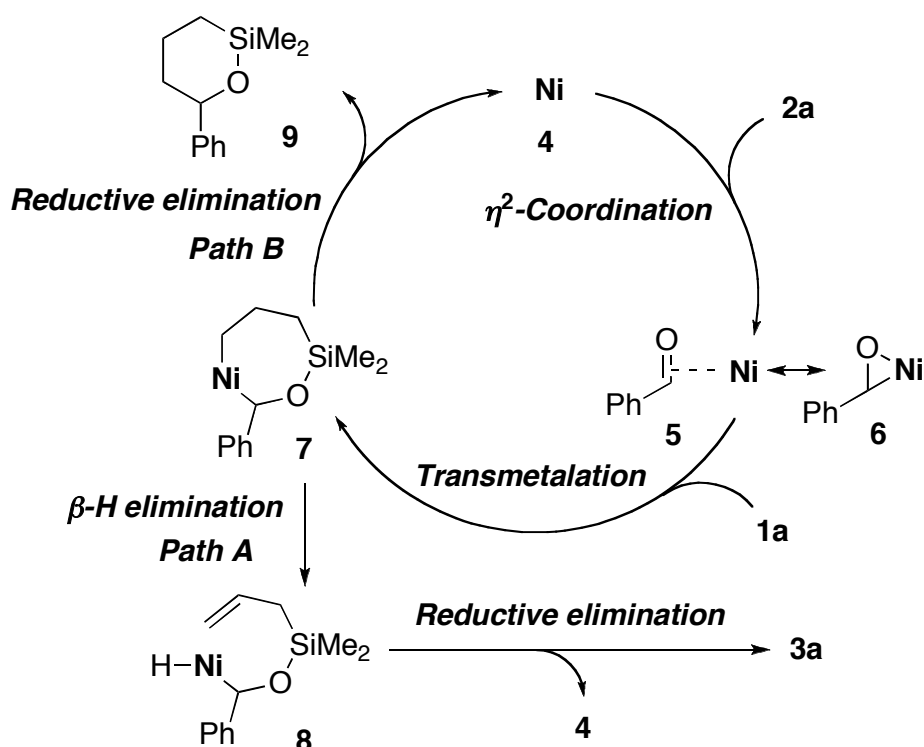
To determine the reaction mechanism, the author performed two experiments shown below (Scheme 3). Heating a solution of 1,1-diphenylsilacyclobutane (**1b**), Ni(cod)₂, and PPh₂Me in toluene at 100 °C for 27 h resulted in quantitative recovery of **1b** (eq 1).⁹ In addition, treatment of benzaldehyde (**2a**) with triethylsilane in the presence of Ni(cod)₂ and PPh₂Me in toluene at 100 °C did not afford the reduced products, that is, benzyloxytriethylsilane and/or benzyl alcohol, at all (eq 2).¹⁰ These facts excluded the possibility that isomerization of silacyclobutanes to allylhydrosilanes followed by hydrosilylation of aldehydes gives the products under nickel catalysis.

Scheme 3.



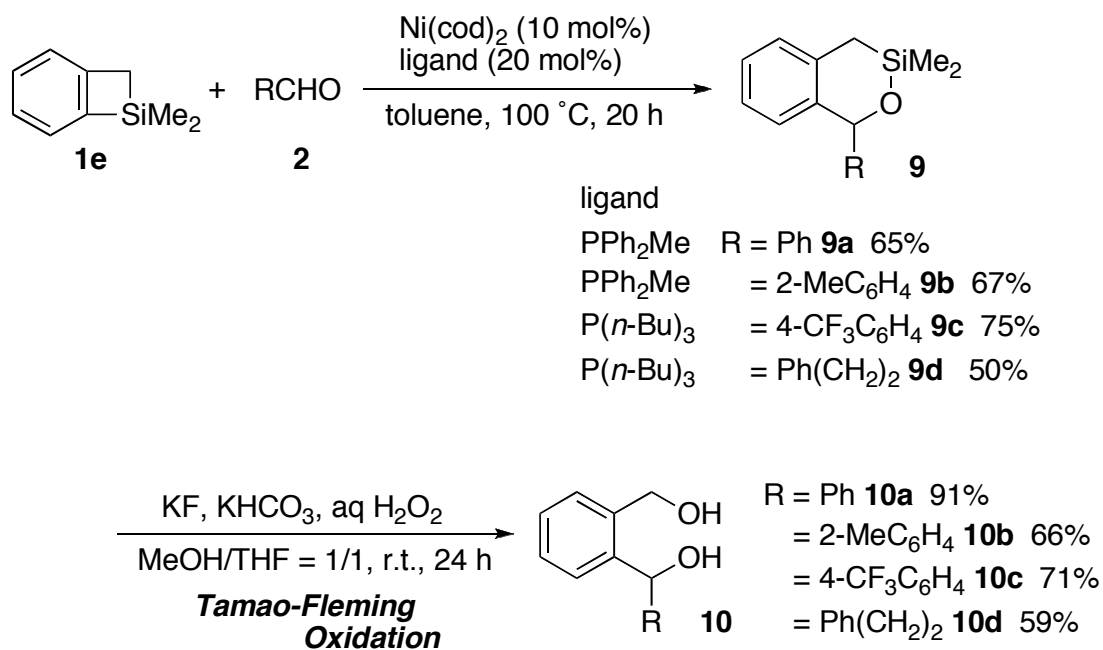
On the basis of the above results, he is tempted to assume the mechanism for the reductive silylation of aldehydes as follows (Scheme 4). A nickel(0) species **4** initially reacts with **2a** to generate η^2 -coordinated complex **5** or its resonance form **6**.¹¹ Subsequent transmetalation of **6** with silacyclobutane **1a** gives the intermediate **7**.¹² Subsequent β -H elimination and reductive elimination furnish **3a** and regenerate **4** (Path A).

Scheme 4.



It then occurred to him that, if the intermediate **7** had no hydrogens at the β -position, reductive elimination would proceed to afford the ring expanded product **9** (Path B). According to this assumption, benzosilacyclobutene **1e** was treated with benzaldehyde (**2a**) under the same conditions as those for the ring opening reactions (Scheme 5). To his delight, the desired oxasilacyclohexene **9a** was obtained in 65% yield. Interestingly, regioselective cleavage of the sp^2 carbon-silicon bond occurred, which was completely opposite to the cases of base-induced¹³ and photochemical¹⁴ ring expansion reactions of **1e** with aldehydes. This is probably because transmetalation of arylsilane is more favored than that of benzylsilane.¹⁵ Reactions with other aromatic and aliphatic aldehydes gave the corresponding ring-expanded products **9b–9d** in good yields. Tamao-Fleming oxidation could transform **9** to diols **10**. The overall transformations in Scheme 5 represent 2-(hydroxymethyl)phenylation of aldehydes.

Scheme 5.



Conclusion

The author has found two new transformations of silacyclobutanes with aldehydes under nickel catalysis. Ring opening products suggest that silacyclobutanes are equivalent to allylhydrosilanes ($\text{CH}_2=\text{CH}-\text{CH}_2\text{SiR}_2\text{H}$) for reductive silylation of aldehydes. Ring expansion reaction can provide a facile access to 1,2-bis(hydroxymethyl)benzenes from aldehydes.

Experimental Section

Instrumentation and Chemicals

^1H NMR (500 MHz), ^{13}C NMR (125.7 MHz), and ^{19}F NMR (282 MHz) spectra were taken on Varian UNITY INOVA 500 and Mercury 300 spectrometers. ^1H NMR and ^{13}C NMR spectra were obtained in C_6D_6 with tetramethylsilane as an internal standard. ^{19}F NMR spectra were obtained in C_6D_6 with fluorotrichloromethane as an external standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel 60 N (spherical neutral, obtained from Kanto Kagaku) was used for column chromatography. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was dried over slices of sodium. Bis(1,5-cyclooctadiene)nickel and diphenylmethylphosphine were purchased from Strem. Tri(*n*-butyl)phosphine was obtained from TCI. Diphenylmethylphosphine and tri(*n*-butyl)phosphine were diluted to prepare 0.25 and 1.0 M hexane solutions, respectively. The solutions were stored under argon atmosphere. 1,1-Dimethylsilacyclobutane and 1,1-dichlorosilacyclobutane were available from Shinetsu Silicone Chemicals. 1,1-Diphenylsilacyclobutane¹⁶ and 2,3-benzo-1,1-dimethylsilacyclobutene¹⁷ were prepared according to the reported procedures. 1,1-Diphenyl-2-methylsilacyclobutane¹⁸ was prepared from the corresponding dichloride.

Procedure for Ring Opening of 1,1-Dimethylsilacyclobutane (1a) with Benzaldehyde (2a)

With a glovebox filled with argon, Ni(cod)₂ (13.8 mg, 0.050 mmol) was placed in a reaction flask. Toluene (5.0 mL) and PPh₂Me (0.25 M hexane solution, 0.40 mL, 0.10 mmol) were added dropwise. The solution was stirred for 10 min at 0 °C. Benzaldehyde (**2a**, 64 mg, 0.60 mmol) and 1,1-dimethylsilacyclobutane (**1a**, 50 mg, 0.50 mmol) were then added and the resulting solution was heated at 100 °C. After being stirred for 20 h at the same temperature, the mixture was cooled to room temperature and concentrated. Purification by silica gel column

afforded allylbenzyloxydimethylsilane (**3a**, 93 mg, 0.44 mmol) in 88% yield.

Procedure for Ring Expansion of 2,3-Benzo-1,1-dimethylsilacyclobutene (1e) with Benzaldehyde (2a)

With a glovebox filled with argon, Ni(cod)₂ (13.8 mg, 0.050 mmol) was placed in a reaction flask. Toluene (3 mL) and PPh₂Me (0.25 M hexane solution, 0.40 mL, 0.10 mmol) were added dropwise. The solution was stirred for 10 min at 0 °C. Benzaldehyde (**2a**, 64 mg, 0.60 mmol) and a solution of 2,3-benzo-1,1-dimethylsilacyclobutene (**1e**, 74 mg, 0.50 mmol) in toluene (2 mL) were then added and the resulting solution was heated at 100 °C. After being stirred for 20 h at the same temperature, the mixture was cooled to room temperature and concentrated. The crude product was purified by column chromatography to provide 4,5-benzo-1,1-dimethyl-2-oxa-3-phenyl-1-silacyclohexene (**9a**, 85 mg, 0.33 mmol) in 65% yield.

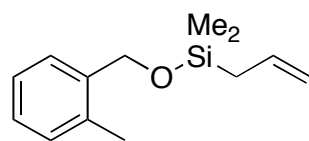
Procedure for Tamao-Fleming Oxidation of 4,5-Benzo-1,1-dimethyl-2-oxa-3-phenyl-1-silacyclohexene (9a)

A solution of 4,5-benzo-1,1-dimethyl-2-oxa-3-phenyl-1-silacyclohexene (**9a**, 25 mg, 0.10 mmol) in THF (1 mL) was added to a suspension of KF (12 mg, 0.20 mmol) and KHCO₃ (20 mg, 0.20 mmol) in MeOH (1.0 mL). Finally, aq. H₂O₂ (30–35%, 0.20 mL 2.0 mmol) was added dropwise. After being stirred for 24 h at room temperature, the resulting mixture was poured into aqueous sodium thiosulfate. Extraction with Et₂O followed by silica gel column purification furnished (2-hydroxymethylphenyl)phenylmethanol (**10a**, 19 mg, 0.091 mmol) in 91% yield.

Characterization Data

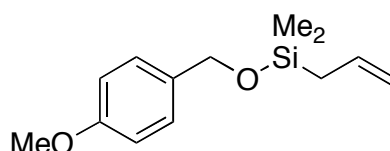
Spectral data for some compounds (**3a**¹⁹, **10a**²⁰, and **10b**²¹) are found in the literature.

Allyldimethyl(2-methylbenzyloxy)silane (3b)



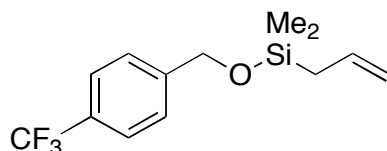
IR (neat) 3076, 2959, 2876, 1632, 1493, 1464, 1375, 1254, 1219, 1184, 1159, 1124, 1082, 1049, 991, 931, 895, 837 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.09 (s, 6H), 1.58 (dt, $J = 8.0, 1.0$ Hz, 2H), 2.11 (s, 3H), 4.58 (s, 2H), 4.91–4.95 (m, 2H), 5.75–5.84 (m, 1H), 7.00 (d, $J = 7.0$ Hz, 1H), 7.09 (td, $J = 7.5, 1.5$ Hz, 1H), 7.14 (td, $J = 7.5, 1.0$ Hz, 1H), 7.48 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (C_6D_6) δ -2.44, 18.57, 24.66, 63.47, 113.93, 126.14, 127.31, 127.50, 130.21, 134.22, 135.71, 139.06. Found: C, 70.73; H, 8.89%. Calcd for $\text{C}_{13}\text{H}_{20}\text{OSi}$: C, 70.85; H, 9.15%.

Allyldimethyl(4-methoxybenzyloxy)silane (3c)



IR (neat) 2957, 2872, 2835, 1630, 1614, 1514, 1466, 1302, 1250, 1302, 1171, 1159, 1086, 1038, 895, 835 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.10 (s, 6H), 1.59 (d, $J = 8.0$ Hz, 2H), 3.29 (s, 3H), 4.56 (s, 2H), 4.93–4.97 (m, 2H), 5.78–5.86 (m, 1H), 6.81 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (C_6D_6) δ -2.31, 24.74, 54.71, 64.79, 113.90, 113.99, 128.10, 128.25, 134.30, 159.43. Found: C, 65.79; H, 8.62%. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Si}$: C, 66.05; H, 8.53%.

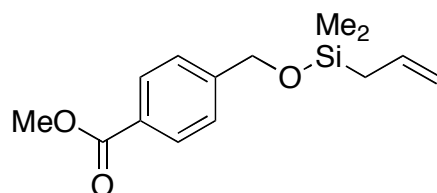
Allyldimethyl(4-trifluoromethylbenzyloxy)silane (3d)



IR (neat) 2961, 2882, 1622, 1421, 1377, 1327, 1258, 1209, 1067, 1018, 993, 932, 824, 750, 719 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.04 (s, 6H), 1.53 (dt, $J = 8.0, 1.0$ Hz, 2H), 4.37 (s, 2H), 4.91–4.95 (m, 2H), 5.72–5.81 (m, 1H), 7.07 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (C_6D_6) δ -2.57, 24.42, 63.97, 114.20, 123.97, 125.31, 125.34, 125.37, 125.40, 126.13, 126.46, 129.23,

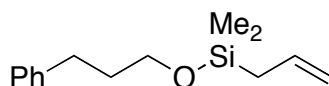
129.49, 133.84, 145.38 (The ^{13}C spectrum was very complex due to C-F coupling. All the signals observed were shown.); ^{19}F NMR (C_6D_6) δ -62.59. Found: C, 57.10; H, 6.35%. Calcd for $\text{C}_{13}\text{H}_{17}\text{F}_3\text{OSi}$: C, 56.91; H, 6.25%.

Allyldimethyl(4-methoxycarbonylbenzyloxy)silane (3e)



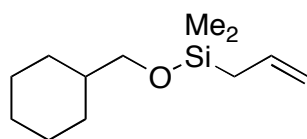
IR (neat) 2954, 2883, 1722, 1631, 1613, 1436, 1419, 1280, 1257, 1192, 1174, 1160, 1089, 1019, 932, 897, 839, 811 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.05 (s, 6H), 1.54 (dt, $J = 8.0, 1.0$ Hz, 2H), 3.48 (s, 3H), 4.45 (s, 2H), 4.90–4.94 (m, 2H), 5.72–5.81 (m, 1H), 7.22 (d, $J = 8.5$ Hz, 2H), 8.18 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (C_6D_6) δ -2.53, 24.47, 51.52, 64.29, 114.12, 126.19, 129.65, 129.95, 133.94, 146.49, 166.59. Found: C, 63.34; H, 7.45%. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{Si}$: C, 63.60; H, 7.62%.

Allyldimethyl(3-phenylpropoxy)silane (3f)



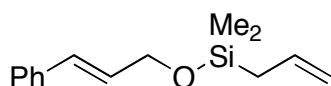
IR (neat) 3063, 3028, 2918, 2864, 1632, 1497, 1454, 1387, 1254, 1157, 1101, 1040, 964, 895, 835, 806 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.08 (s, 6H), 1.57 (dt, $J = 8.0, 1.0$ Hz, 2H), 1.73–1.79 (m, 2H), 2.61 (t, $J = 7.8$ Hz, 2H), 3.45 (t, $J = 6.3$ Hz, 2H), 4.93–4.97 (m, 2H), 5.78–5.86 (m, 1H), 7.05–7.17 (m, 5H); ^{13}C NMR (C_6D_6) δ -2.44, 24.65, 32.36, 34.63, 61.94, 113.80, 126.06, 128.61, 128.79, 134.37, 142.33. Found: C, 71.91; H, 9.52%. Calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}$: C, 71.73; H, 9.46%.

Allyl(cyclohexylmethoxy)dimethylsilane (3g)



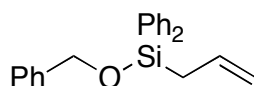
IR (neat) 2924, 2854, 1632, 1450, 1253, 1157, 1115, 1083, 1070, 1056, 1029, 932, 897, 836, 806 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.10 (s, 6H), 0.85–0.93 (m, 2H), 1.06–1.22 (m, 3H), 1.43–1.51 (m, 1H), 1.60 (dt, $J = 8.0, 1.0$ Hz, 2H), 1.58–1.63 (m, 1H), 1.66–1.70 (m, 2H), 1.74–1.79 (m, 2H), 3.33 (d, $J = 6.5$ Hz, 2H), 4.94–4.99 (m, 2H), 5.81–5.89 (m, 1H); ^{13}C NMR (C_6D_6) δ -2.45, 24.68, 26.27, 26.99, 29.99, 40.70, 68.63, 113.74, 134.47. Found: C, 67.80; H, 11.12%. Calcd for $\text{C}_{12}\text{H}_{24}\text{OSi}$: C, 67.86; H, 11.39%.

(*E*)-Allyl(cinnamyloxy)dimethylsilane (3h)



IR (neat) 3061, 3026, 2959, 2855, 1632, 1497, 1448, 1379, 1254, 1157, 1124, 1061, 966, 932, 839, 731, 692 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.12 (s, 6H), 1.61 (dt, $J = 8.0, 1.0$ Hz, 2H), 4.15 (dd, $J = 5.0, 1.5$ Hz, 2H), 4.94–4.99 (m, 2H), 5.80–5.88 (m, 1H), 6.18 (dt, $J = 16.0, 5.0$ Hz, 1H), 6.61 (dt, $J = 15.5, 1.5$ Hz, 1H), 7.03 (t, $J = 7.5$ Hz, 1H), 7.11 (t, $J = 7.5$ Hz, 2H), 7.26 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (C_6D_6) δ -2.30, 24.73, 63.63, 113.97, 126.71, 127.60, 128.82, 129.20, 129.94, 134.24, 137.48. Found: C, 72.10; H, 8.79%. Calcd for $\text{C}_{14}\text{H}_{20}\text{OSi}$: C, 72.36; H, 8.67%.

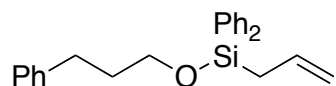
Allyl(benzyloxy)diphenylsilane (3i)



IR (neat) 2866, 2341, 1630, 1589, 1497, 1454, 1429, 1379, 1159, 1069, 1028, 997, 901, 833, 735, 698, 679 cm^{-1} ; ^1H NMR (C_6D_6) δ 2.14 (dt, $J = 8.0, 1.3$ Hz, 2H), 4.74 (s, 2H), 4.89–4.97 (m, 2H), 5.83–5.52 (m, 1H), 7.08 (t, $J = 7.5$ Hz, 1H), 7.16–7.18 (m, 8H), 7.30 (d, $J = 7.0$ Hz, 2H), 7.64–7.67 (m, 4H); ^{13}C NMR (C_6D_6) δ 22.16, 65.61, 115.35, 126.62, 127.34, 127.91, 128.50, 130.26, 133.13, 134.74, 135.17, 141.00. Found: C, 80.25; H, 6.78%. Calcd for $\text{C}_{22}\text{H}_{22}\text{OSi}$: C,

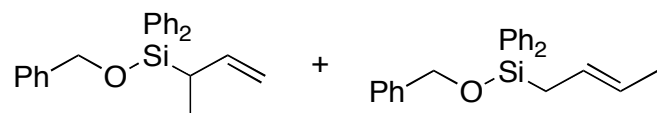
79.95; H, 6.71%.

Allyldiphenyl(3-phenylpropoxy)silane (3j)



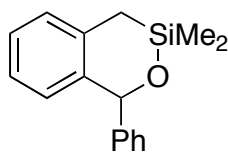
IR (neat) 2868, 2341, 1630, 1589, 1497, 1454, 1429, 1387, 1097, 1040, 966, 899, 735, 698, 675 cm^{-1} ; ^1H NMR (C_6D_6) δ 1.76–1.81 (m, 2H), 2.13 (dt, $J = 7.5, 1.5$ Hz, 2H), 2.61 (t, $J = 7.5$ Hz, 2H), 3.63 (t, $J = 6.0$ Hz, 2H), 4.91–4.99 (m, 2H), 5.85–5.94 (m, 1H), 7.03–7.07 (m, 3H), 7.11–7.21 (m, 8H), 7.65–7.67 (m, 4H); ^{13}C NMR (C_6D_6) δ 22.12, 32.30, 34.50, 62.85, 115.18, 126.01, 128.13, 128.58, 128.79, 130.18, 133.33, 135.11, 135.17, 142.24. Found: C, 80.16; H, 7.25%. Calcd for $\text{C}_{24}\text{H}_{26}\text{OSi}$: C, 80.39; H, 7.31%.

Benzyloxydiphenyl(1-methylpropenyl)silane (3k) and (*E*)-Benzyloxycrotyldiphenylsilane (3k')



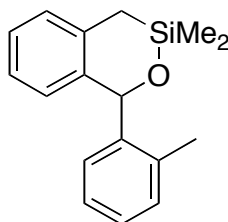
IR (neat) 3001, 2867, 1497, 1453, 1428, 1378, 1207, 1161, 1069, 1027, 998, 964, 900, 800 cm^{-1} ; ^1H NMR (C_6D_6) For **3k** δ 1.25 (d, $J = 7.5$ Hz, 3H), 2.38–2.45 (m, 1H), 4.73 (d, $J = 4.0$ Hz, 2H), 4.92–4.99 (m, 2H), 6.13 (ddd, $J = 17.5, 10.5, 7.0$ Hz, 1H), 7.06–7.09 (m, 1H), 7.17–7.20 (m, 8H), 7.29–7.33 (m, 2H), 7.67–7.72 (m, 4H). For **3k'** δ 1.48 (dq, $J = 6.5, 1.5$ Hz, 3H), 2.13 (dt, $J = 7.5, 1.5$ Hz, 2H), 4.76 (s, 2H), 5.27–5.34 (m, 1H), 5.50–5.57 (m, 1H), 7.06–7.09 (m, 1H), 7.17–7.20 (m, 8H), 7.29–7.33 (m, 2H), 7.67–7.72 (m, 4H); ^{13}C NMR (C_6D_6) For **3k** and **3k'** δ 12.98, 18.19, 20.25, 26.34, 65.60, 65.71, 112.60, 125.06, 125.83, 126.48, 126.61, 127.29, 127.91, 128.12, 128.48, 128.49, 130.19, 130.26, 133.43, 133.68, 135.11, 135.18, 135.62, 135.69, 139.89, 141.08. Found: C, 80.40; H, 6.99%. Calcd for $\text{C}_{23}\text{H}_{24}\text{OSi}$: C, 80.18; H, 7.02%.

4,5-Benzo-1,1-dimethyl-2-oxa-3-phenyl-1-silacyclohexene (9a)



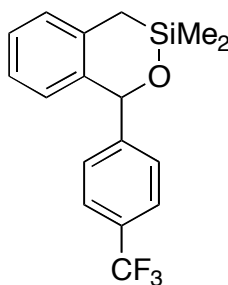
IR (neat) 3063, 2959, 1493, 1481, 1452, 1252, 1175, 1026, 843, 812, 748, 723 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.03 (s, 3H), 0.10 (s, 3H), 1.76 (d, $J = 15.5$ Hz, 1H), 1.82 (d, $J = 15.5$ Hz, 1H), 5.98 (s, 1H), 6.82–6.84 (m, 1H), 6.93–6.96 (m, 1H), 7.02–7.04 (m, 1H), 7.06–7.11 (m, 2H), 7.13–7.17 (m, 2H), 7.38–7.40 (m, 2H); ^{13}C NMR (C_6D_6) δ -0.54, 0.06, 20.22, 78.20, 125.23, 127.23, 127.37, 127.91, 128.12, 128.36, 131.09, 136.47, 141.24, 143.47.

4,5-Benzo-1,1-dimethyl-3-(2-methylphenyl)-2-oxa-1-silacyclohexene (9b)



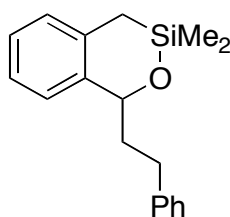
IR (neat) 3019, 2957, 1478, 1454, 1251, 1031, 878, 842, 808, 772, 739, 632, 610 cm^{-1} ; ^1H NMR (C_6D_6) δ -0.07 (s, 3H), 0.14 (s, 3H), 1.98 (s, 2H), 2.22 (s, 3H), 6.08 (s, 1H), 6.70 (d, $J = 7.5$ Hz, 1H), 6.85–6.88 (m, 1H), 7.07–7.12 (m, 5H), 7.47–7.49 (m, 1H); ^{13}C NMR (C_6D_6) δ -0.50, -0.45, 19.55, 20.48, 74.96, 125.45, 126.29, 127.02, 127.74, 127.95, 128.11, 130.59, 130.86, 136.73, 137.26, 140.39, 141.05. Found: C, 76.07; H, 7.54%. Calcd for $\text{C}_{17}\text{H}_{20}\text{OSi}$: C, 76.07; H, 7.51%.

4,5-Benzo-1,1-dimethyl-2-oxa-1-sila-3-(4-trifluoromethylphenyl)cyclohexene (9c)



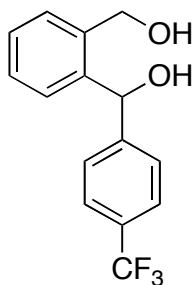
IR (neat) 2882, 1619, 1602, 1484, 1454, 1411, 1326, 1253, 1110, 1068, 1036, 1017, 813, 778, 744 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.00 (s, 3H), 0.06 (s, 3H), 1.66 (d, $J = 15.0$ Hz, 1H), 1.71 (d, $J = 15.0$ Hz, 1H), 5.80 (s, 1H), 6.68 (d, $J = 7.0$ Hz, 1H), 6.94 (td, $J = 7.5, 1.5$ Hz, 1H), 7.00 (d, $J = 7.5$ Hz, 1H), 7.09 (td, $J = 7.5, 1.5$ Hz, 1H), 7.20–7.22 (m, 2H), 7.32 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (C_6D_6) δ -0.71, -0.14, 20.10, 77.57, 125.25, 125.28, 125.35, 127.43, 127.91, 128.10, 128.45, 131.17, 136.30, 140.27, 147.40 (The ^{13}C spectrum was very complex due to C-F coupling. All the signals observed were shown.); ^{19}F NMR (C_6D_6) δ -62.62. Found: C, 63.14; H, 5.39%. Calcd for $\text{C}_{17}\text{H}_{17}\text{F}_3\text{OSi}$: C, 63.33; H, 5.31%.

4,5-Benzo-1,1-dimethyl-2-oxa-3-(2-phenylethyl)-1-silacyclohexene (9d)



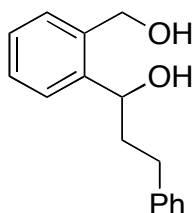
IR (neat) 3026, 2860, 1603, 1485, 1454, 1252, 1194, 1074, 1036, 955, 841, 812 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.03 (s, 3H), 0.15 (s, 3H), 1.76 (d, $J = 16.0$ Hz, 1H), 1.95 (d, $J = 16.0$ Hz, 1H), 1.90–1.97 (m, 1H), 2.03–2.10 (m, 1H), 2.74 (ddd, $J = 14.0, 10.0, 7.0$ Hz, 1H), 2.89 (ddd, $J = 14.0, 1.0, 4.5$ Hz, 1H), 4.80 (dd, $J = 9.0, 4.5$ Hz, 1H), 6.83 (d, $J = 7.5$ Hz, 1H), 6.98 (t, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 7.0$ Hz, 1H), 7.06–7.10 (m, 2H), 7.13–7.18 (m, 4H); ^{13}C NMR (C_6D_6) δ -0.51, 0.57, 19.60, 32.72, 40.01, 76.13, 125.39, 126.08, 126.55, 127.59, 128.66, 128.92, 131.61, 135.42, 141.79, 142.39. Found: C, 76.36; H, 7.89%. Calcd for $\text{C}_{18}\text{H}_{22}\text{OSi}$: C, 76.54; H, 7.85%.

(2-Hydroxymethylphenyl)(4-trifluoromethylphenyl)methanol (10c)



IR (neat) 3289, 2892, 1619, 1414, 1327, 1112, 1068, 1016, 951, 861, 799, 757, 726, 668 cm^{-1} ;
 ^1H NMR (CDCl_3) δ 2.50 (bs, 2H), 4.53 (d, $J = 12.5$, 1H), 4.71 (d, $J = 12.5$ Hz, 1H), 6.12 (s, 1H),
 7.18–7.20 (m, 1H), 7.32–7.35 (m, 3H), 7.52 (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H); ^{13}C
 NMR (CDCl_3) δ 64.22, 73.95, 123.06, 125.22 (q, $J = 3.8$ Hz), 126.64, 128.63, 128.84, 129.26,
 129.62, 130.44, 138.14, 142.00, 146.67; ^{19}F NMR (CDCl_3) δ -62.98.

1-(2-Hydroxymethylphenyl)-3-phenyl-1-propanol (10d)



IR (nujol) 3235, 2924, 2854, 1456, 1377, 1366, 1189, 1053, 1011, 922, 764, 749, 744 cm^{-1} ; ^1H
 NMR (CDCl_3) δ 2.10–2.17 (m, 1H), 2.23–2.30 (m, 1H), 2.50 (bs, 2H), 2.74 (ddd, $J = 14.0$, 9.5,
 7.0 Hz, 1H), 2.87 (ddd, $J = 14.0$, 9.5, 5.5 Hz, 1H), 4.65 (d, $J = 12.5$ Hz, 1H), 4.72 (d, $J = 12.5$ Hz,
 1H), 4.96 (dd, $J = 8.5$, 5.0 Hz, 1H), 7.20–7.23 (m, 3H), 7.28–7.37 (m, 5H), 7.47 (d, $J = 7.5$ Hz,
 1H); ^{13}C NMR (CDCl_3) δ 32.56, 38.44, 63.80, 70.63, 125.95, 126.42, 127.90, 128.43, 128.44,
 128.59, 129.79, 137.97, 141.63, 142.40. m.p. 73–74 $^\circ\text{C}$.

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- (11) η^2 -Coordinated nickel complexes with aldehydes have been reported. (a) Ogoshi, S.; Oka, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2004**, *126*, 11802–11803. The intermediate **5** or **6** was suggested in other nickel-catalyzed reactions. (b) Biswas, K.; Prieto, O.; Goldsmith, P. J.; Woodward, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 2232–2234. (c) Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2005**, *7*, 4689–4691. Nevertheless, oxidative addition of silacyclobutanes to palladium complexes is found to be an equilibrium reaction. Hence, it is also probable that initial oxidative addition of **1a** to **4** followed by subsequent direct insertion of **2a** generates **7**. See ref 9b.
- (12) The reaction of **5** with TMSOTf can promote the formation of the covalent bond between nickel and carbonyl carbon with the aid of the Lewis acidity of silicon. See ref 11a. Thus, it seems quite possible that this transmetalation would include a similar intermediate.
- (13) Takeyama, Y.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 6059–6062.
- (14) Okazaki, R.; Kang, K. T.; Inamoto, N. *Tetrahedron Lett.* **1981**, *22*, 235–238.
- (15) In the Hiyama cross-coupling reactions, to our knowledge, there are only two examples of benzyl group transfer from silicon. See: (a) Hatanaka, Y.; Hiyama, T.; *J. Am. Chem. Soc.* **1990**, *112*, 7793–7794. (b) Itami, K.; Mineno, M.; Kamei, T.; Yoshida, J. *Org. Lett.* **2002**, *4*, 3635–3638.
- (16) Sunderhaus, J. D.; Lam, H.; Dudley, B. *Org. Lett.* **2003**, *5*, 4571–4573.
- (17) Eaborn, C.; Walton, D. R. M.; Chan, M. *J. Organomet. Chem.* **1967**, *9*, 251–257.
- (18) Lanne, J. *J. Am. Chem. Soc.* **1967**, *89*, 1144–1147.
- (19) Wei, Z. Y.; Wang, D.; Li, J. S.; Chan, T. H. *J. Org. Chem.* **1989**, *54*, 5768–5774.
- (20) Gomez, C.; Huerta, F.; Yus, M. *Tetrahedron* **1998**, *54*, 1853–1866.
- (21) Bream, J. B.; Schmultz, J. *Helv. Chim. Acta* **1997**, *60*, 2872–2880.

Chapter 6

Nickel-Catalyzed Regio- and Stereoselective Silylation of Terminal Alkenes with Silacyclobutanes: Facile Access to Vinylsilanes from Alkenes

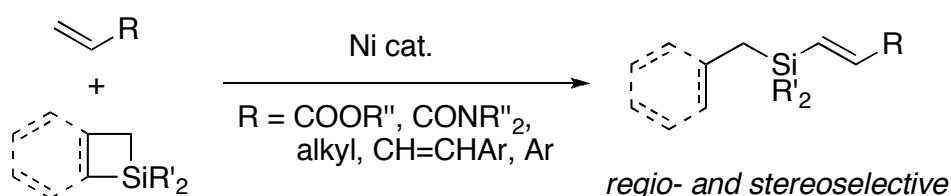
Treatment of terminal alkenes with silacyclobutanes under nickel catalysis resulted in silylation of the alkenes and yielded the corresponding vinylsilanes in a highly regio- and stereoselective fashion. The reaction provides a facile access to vinylsilanes starting from trivial terminal alkenes as well as styrenes, 1,3-dienes, and acrylate esters.

Introduction

Vinylsilanes constitute an important class of compounds in organosilicon chemistry and in organic synthesis. Transition-metal-catalyzed hydrosilylation¹ and silylmetalation² of alkynes are common routes to vinylsilanes. However, the reactions of terminal alkynes often encounter difficulty in controlling regio- and stereoselectivity of the reaction.³ On the other hand, dehydrogenative silylation of alkenes with hydrosilanes is an attractive alternative to the reactions mentioned above since vinylsilanes can be synthesized from alkenes in a highly regio- and stereoselective fashion. Although iron,⁴ ruthenium,⁵ cobalt,⁶ and rhodium⁷ complexes are known to catalyze the dehydrogenative silylation of alkenes with hydrosilanes, the substrates were still limited to activated alkenes such as α,β -unsaturated esters, styrenes, and 1,5-dienes. Moreover, the dehydrogenative silylations required a large excess of alkenes because the alkenes were hydrogen acceptors as well as substrates to be silylated.

Silacyclobutanes are interesting compounds that have unique reactivity based on their ring strain and Lewis acidity.⁸ Therefore, Oshima⁹ and others¹⁰ have developed their synthetic utilities. During his course of the studies on the reactivity of silacyclobutanes under nickel catalysis,¹¹ the author serendipitously has found nickel-catalyzed silylation of alkenes with silacyclobutanes. The silylation provides a new and efficient protocol for regio- and stereoselective synthesis of (*E*)-vinylsilanes from a variety of terminal alkenes (Scheme 1).

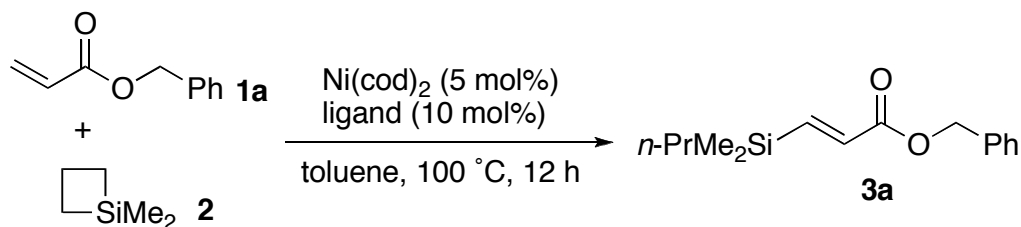
Scheme 1.



Results and Discussion

Benzyl acrylate (**1a**) and 1,1-dimethylsilacyclobutane (**2**) were chosen as model reactants

and the ligand effects were examined (Table 1). Regardless of the yields, high regio- and stereoselectivities were observed. $P(t\text{-Bu})_3$ and $P(o\text{-tolyl})_3$ showed no activity (entries 1 and 6) while $P(c\text{-C}_6\text{H}_{11})_3$ led to the formation of the desired product in 95% yield (entry 2). $P(n\text{-Bu})_3$, PMe_3 , and an *N*-heterocyclic carbene ligand, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), had similar activities (entries 3, 4, and 7). Notably, in the case of PPh_3 , **3a** was obtained in 81% yield (entry 5). These results indicate that the cone angles of the ligands play an important role in the reaction as well as their ability of σ -donation. Nevertheless, the effects of several other factors involving electronic ones could not be excluded completely. NiCl_2 instead of $\text{Ni}(\text{cod})_2$ did not catalyze the reaction even in the presence of $P(c\text{-C}_6\text{H}_{11})_3$ and 1,5-cyclooctadiene (COD). This is probably because the divalent nickel was not reduced to the zerovalent one under the reaction conditions so that the initial oxidative addition did not proceed (vide infra). The catalysts prepared from NiCl_2 , $P(c\text{-C}_6\text{H}_{11})_3$, and DIBAL-H failed to catalyze the reaction. The aluminum salt generated in situ would interfere the reaction. Although the exact role of COD is not clear at this stage, COD was known to work as an effective ligand in other nickel-catalyzed reactions.¹²

Table 1. Optimization for the silylation of benzyl acrylate (**1a**) with 1,1-dimethylsilacyclobutane (**2**)^a

entry	ligand	yield of 3a (%) ^b
1	P(<i>t</i> -Bu) ₃	0
2	P(<i>c</i> -C ₆ H ₁₁) ₃	95 ^c
3	P(<i>n</i> -Bu) ₃	22
4	PMe ₃	20
5	PPh ₃	81
6	P(<i>o</i> -tol) ₃	0
7	IMes ^d	11

^a A mixture of Ni(cod)₂ (0.025 mmol), ligand (0.050 mmol), **1a** (0.50 mmol), and **2** (0.60 mmol) was heated at 100 °C in toluene (5.0 mL) for 12 h.

^b ¹H NMR yields. ^c Isolated yield.

^d Generated in situ from 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride with *n*-BuLi.

With the optimal Ni(cod)₂/2P(*c*-C₆H₁₁)₃ catalyst system, the author performed the silylation reaction of a variety of terminal alkenes (Table 2). The reaction of **1a** with 1,1-diphenylsilacyclobutane (**2'**) proceeded without any difficulties to give **3a'** in 95% yield despite its increased steric hindrance (entry 2). Sterically demanding ester **1b** smoothly underwent the silylation (entry 3). The silylation of α,β -unsaturated amide **1c** provided **3c** in good yield albeit the product was obtained as a mixture of stereoisomers (entry 4). Styrene derivatives were converted to the corresponding silylated products in high yields with high regio-

and stereoselectivity except for electron-deficient **1g** (entries 5–8). A pyridine ring did not prevent the reaction (entry 9). It is worth noting that simple aliphatic terminal alkenes **1i–1l** participated in the reaction (entries 10–13). Moreover, silyl, siloxy, and ester moieties were tolerated under the reaction conditions.

Notably, the benzene-fused silacyclobutane **4** was also the suitable silylating agent (Table 3). In the reaction with **4**, the use of PPh_3 instead of $\text{P}(c\text{-C}_6\text{H}_{11})_3$ generally gave the better results. Styrene (**1d**) reacted with **4** to furnish the benzyldimethylsilyl-substituted styrene **5d** regio- and stereoselectively (entry 1). The palladium-catalyzed Hiyama cross-coupling reaction of **5d** with aryl halides would be available according to the reported procedures.¹³ Unfortunately, the reaction of **1i** with **4** furnished the silylated product **5i** with moderate stereoselectivity (entry 2). Conjugated 1,3-dienes also took part in the reaction. While the silylation of (*E*)-1-phenyl-1,3-butadiene (**1m**) took place to produce the corresponding silane **5m** in good yield, **5m** comprised an 83:17 mixture of (*E*)- and (*Z*) isomers (entry 3). A 1-naphthyl (1-Np) substitution led to the improvement of stereoselectivity (entry 4). As described above, the dienes obtained could be converted further to the corresponding asymmetrical 1,4-diaryl-1,3-dienes via palladium-catalyzed cross-coupling reaction with aryl halides.¹³

Table 2. Silylation with Dimethyl- or Diphenylsilacyclobutane^a

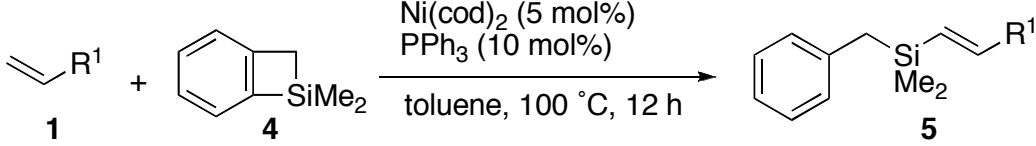
entry	1	R ¹	3	yield (%), <i>E/Z</i> ^b
1	1a	CO ₂ CH ₂ Ph	3a	95, >99:1
2 ^c	1a	CO ₂ CH ₂ Ph	3a'	95, >99:1
3 ^c	1b	CO ₂ <i>t</i> -Bu	3b'	95, >99:1
4 ^{d, e}	1c	CONEt ₂	3c	82, 88:12
5	1d	Ph	3d	98, >99:1
6	1e	2-MeC ₆ H ₄	3e	99, >99:1
7	1f	4-MeOC ₆ H ₄	3f	93, >99:1
8	1g	4-CF ₃ C ₆ H ₄	3g	trace
9 ^d	1h	2-Pyridyl	3h	71, >99:1
10	1i	<i>n</i> -C ₁₂ H ₂₅	3i	93, >99:1
11 ^{d, f}	1j	CH ₂ SiMe ₂ Ph	3j	82, >99:1
12 ^d	1k	(CH ₂) ₉ OSi <i>t</i> -BuMe ₂	3k	93, >99:1
13 ^d	1l	(CH ₂) ₉ OCO <i>t</i> -Bu	3l	81, >99:1

^a A mixture of Ni(cod)₂ (0.025 mmol), P(*c*-C₆H₁₁)₃ (0.050 mmol), **1** (0.50 mmol), and **2** (0.60 mmol) was heated at 100 °C in toluene (5.0 mL) for 12 h.

^b Isolated yields. *E/Z* ratios were determined by ¹H NMR.

^c Silacyclobutane **2'** was used instead of **2**. ^d With 1.0 mmol of **2**.

^e Reaction time was 15 h. ^f Reaction time was 8 h.

Table 3. Silylation with Benzene-Fused Silacyclobutane **4**^a


entry	1	R ¹	5	yield (%), <i>E/Z</i> ^b
1	1d	Ph	5d	64, >99:1 ^{c, d}
2 ^{e, f}	1i	<i>n</i> -C ₁₂ H ₂₅	5i	80, 70:30 ^{c, g}
3	1m	(<i>E</i>)-(CH=CH)Ph	5m	70, 83:17
4	1n	(<i>E</i>)-(CH=CH)(1-Np)	5n	88, 94:6

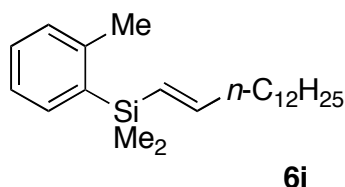
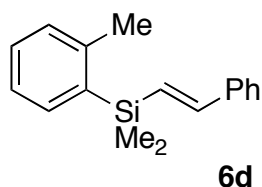
^a A mixture of Ni(cod)₂ (0.025 mmol), PPh₃ (0.050 mmol), **1** (0.50 mmol), and **4** (0.60 mmol) was heated at 100 °C in toluene (5.0 mL) for 12 h.

^b Isolated yields. *E/Z* ratios were determined by ¹H NMR. ^c ¹H NMR yield.

^d Dimethyl(2-methylphenyl)[(*E*)-2-phenylethenyl]silane (**6d**) was also obtained in 8% yield.

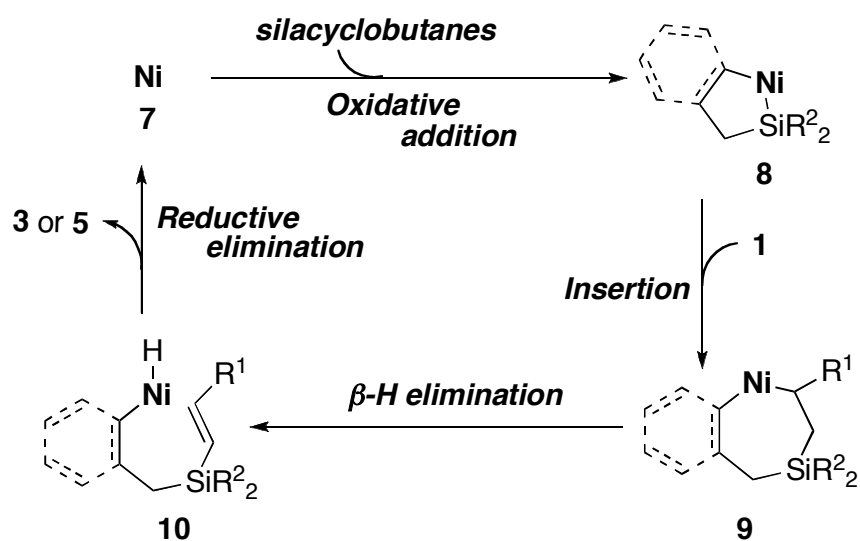
^e P(*c*-C₆H₁₁)₃ was used instead of PPh₃. ^f With 1.0 mmol of **4**.

^g Dimethyl(2-methylphenyl)[(*E*)-1-tetradecenyl]silane (**6i**) was also obtained in 12% yield.

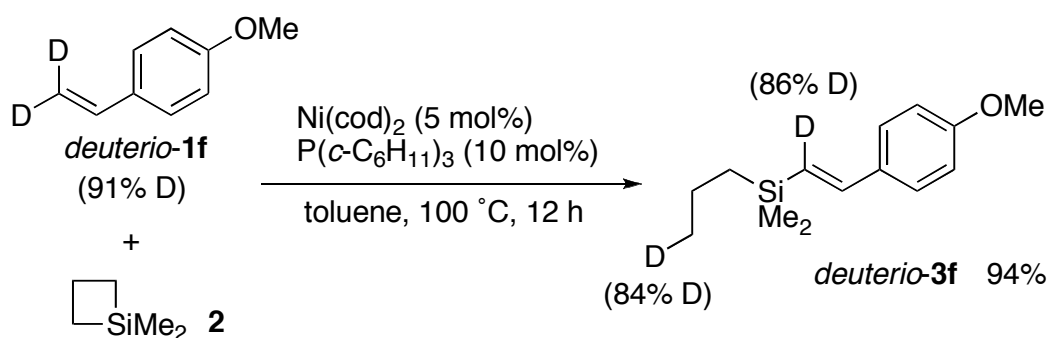


The author is tempted to assume the following reaction mechanism for the silylation of alkenes with silacyclobutanes (Scheme 2). Initial oxidative addition of silacyclobutanes to zerovalent nickel species **7** followed by insertion of alkene **1** to the Si-Ni bond of **8** gives the nickelasilacycle **9**.¹⁴ In the case of the benzene-fused silacyclobutane **4**, the oxidative addition of sp²C-Si bond to Ni(0) is preferable to that of the benzylic sp³C-Si bond.¹⁵ Subsequent β-H elimination¹⁶ followed by reductive elimination produces **3** or **5** along with the starting zerovalent nickel complex to complete the catalytic cycle. The result of the silylation of deuterio-**1f** was consistent with our plausible mechanism (Scheme 3).

Scheme 2.



Scheme 3.



Conclusion

The author has found the efficient nickel catalyst system for silylation of terminal alkenes with silacyclobutanes. The reaction provides a facile and straightforward access to vinylsilanes from terminal alkenes in a highly regio- and stereoselective manner.

Experimental Section

Instrumentation and Materials

^1H NMR (300 MHz), ^2H NMR (46 MHz), and ^{13}C NMR (75.3 MHz) spectra were taken on Varian Mercury 300 spectrometers and were recorded in CDCl_3 . Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^1H and relative to CDCl_3 at 77.0 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene and triphenylphosphine were purchased from Wako Pure Chemical Co. and toluene was stored over slices of sodium. Bis(1,5-cyclooctadiene)nickel and tricyclohexylphosphine were obtained from Strem. Tricyclohexylphosphine was diluted to prepare 0.5 M toluene solution, which was stored strictly under argon. 1,1-Dimethylsilacyclobutane and 1,1-dichlorosilacyclobutane were available from Shinetsu Silicone Chemicals. All reactions were carried out under argon atmosphere. 1,1-Diphenylsilacyclobutane¹⁷ and 2,3-benzo-1,1-dimethylsilacyclobutene¹⁸ were prepared according to the reported procedures. *Deuterio-1f* was prepared by Wittig olefination of 4-methoxybenzaldehyde with (trideuteriomethyl)triphenylphosphonium iodide.¹⁹

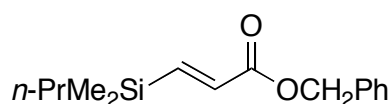
Typical Procedure for Nickel-Catalyzed Silylation of Terminal Alkenes with Silacyclobutanes

With a glovebox filled with argon, $\text{Ni}(\text{cod})_2$ (6.9 mg, 0.025 mmol) was placed in a reaction flask. Toluene (3.0 mL) and $\text{P}(c\text{-C}_6\text{H}_{11})_3$ (0.50 M toluene solution, 0.10 mL, 0.050 mmol) were added dropwise. The solution was stirred for 10 min at 0 °C. A solution of benzyl acrylate (**1a**, 81 mg, 0.50 mmol) in toluene (2.0 mL) and 1,1-dimethylsilacyclobutane (**2**, 60 mg, 0.60 mmol)

were then added and the resulting solution was heated at 100 °C. After being stirred for 12 h at the same temperature, the mixture was cooled to room temperature and filtered off. Concentration in vacuo followed by column chromatography on silica gel afforded benzyl (*E*)-3-(dimethylpropylsilyl)acrylate (**3a**, 125 mg, 0.475 mmol) in 95% yield.

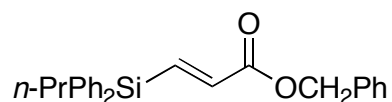
Characterization Data

Benzyl (*E*)-3-(dimethylpropylsilyl)acrylate (**3a**)



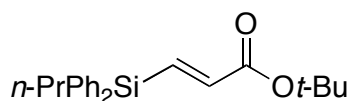
IR (neat) 2957, 2927, 2869, 1725, 1305, 1250, 1221, 1189, 1161, 997, 840, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.12 (s, 6H), 0.63 (t, $J = 8.0$ Hz, 2H), 0.97 (t, $J = 7.5$ Hz, 3H), 1.32–1.40 (m, 2H), 5.21 (s, 2H), 6.30 (d, $J = 18.5$ Hz, 1H), 7.32 (d, $J = 18.5$ Hz, 1H), 7.33–7.42 (m, 5H); ^{13}C NMR (CDCl_3) δ –3.60, 17.17, 17.48, 18.10, 66.35, 128.22, 128.30, 128.55, 133.83, 135.98, 149.82, 165.62. Found: C, 68.43; H, 8.29%. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Si}$: C, 68.66; H, 8.45%.

Benzyl (*E*)-3-(diphenylpropylsilyl)acrylate (**3a'**)



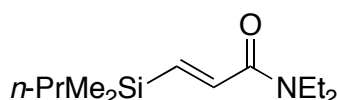
IR (neat) 3069, 2956, 2927, 2869, 1725, 1456, 1428, 1304, 1265, 1222, 1187, 1163, 1113, 998, 732, 699 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.01 (t, $J = 7.0$ Hz, 3H), 1.21 (t, $J = 8.5$ Hz, 2H), 1.44–1.53 (m, 2H), 5.21 (s, 2H), 6.34 (d, $J = 18.5$ Hz, 1H), 7.33–7.45 (m, 11H), 7.50–7.52 (m, 4H), 7.64 (d, $J = 18.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 15.32, 17.33, 18.33, 66.55, 128.02, 128.30, 128.42, 128.57, 129.74, 133.67, 135.18, 135.76, 137.01, 145.42, 165.40. Found: C, 77.72; H, 6.92%. Calcd for $\text{C}_{25}\text{H}_{26}\text{O}_2\text{Si}$: C, 77.68; H, 6.78%.

tert-Butyl (*E*)-3-(diphenylpropylsilyl)acrylate (**3b'**)



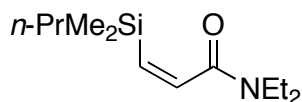
IR (neat) 2957, 1708, 1428, 1367, 1310, 1238, 1152, 1113, 998, 730, 700, 688 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.01 (t, $J = 7.0$ Hz, 3H), 1.21 (t, $J = 8.5$ Hz, 2H), 1.46–1.51 (m, 2H), 1.50 (s, 9H), 6.22 (d, $J = 18.5$ Hz, 1H), 7.34–7.44 (m, 6H), 7.46 (d, $J = 18.5$ Hz, 1H), 7.51–7.53 (m, 4H); ^{13}C NMR (CDCl_3) δ 15.46, 17.35, 18.34, 28.09, 80.66, 127.98, 129.64, 134.09, 135.22, 139.32, 142.82, 164.96. Found: C, 75.02; H, 7.96%. Calcd for $\text{C}_{22}\text{H}_{28}\text{O}_2\text{Si}$: C, 74.95; H, 8.01%.

***N,N*-Diethyl-(*E*)-3-(dimethylpropylsilyl)acrylamide [(*E*)-3c]**



IR (neat) 2957, 2932, 2908, 2871, 1638, 1597, 1445, 1426, 1379, 1264, 1249, 1138, 992, 853, 834 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.12 (s, 6H), 0.63 (t, $J = 8.0$ Hz, 2H), 0.97 (t, $J = 7.0$ Hz, 3H), 1.17 (t, $J = 7.0$ Hz, 3H), 1.22 (t, $J = 7.0$ Hz, 3H), 1.34–1.41 (m, 2H), 3.42 (q, $J = 7.0$ Hz, 2H), 3.45 (q, $J = 7.0$ Hz, 2H), 6.65 (d, $J = 18.5$ Hz, 1H), 7.16 (d, $J = 18.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ -3.33, 13.10, 14.85, 17.27, 17.77, 18.17, 41.01, 42.16, 133.83, 144.56, 165.56. Found: C, 63.19; H, 11.28%. Calcd for $\text{C}_{12}\text{H}_{25}\text{NOSi}$: C, 63.38; H, 11.08%.

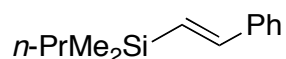
***N,N*-Diethyl-(*Z*)-3-(dimethylpropylsilyl)acrylamide [(*Z*)-3c]**



IR (neat) 2955, 2933, 2902, 2869, 1642, 1459, 1448, 1431, 1264, 1241, 1143, 841, 831, 810 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.15 (s, 6H), 0.70 (t, $J = 8.0$ Hz, 2H), 0.96 (t, $J = 7.5$ Hz, 3H), 1.16 (t, $J = 7.0$ Hz, 3H), 1.18 (t, $J = 7.0$ Hz, 3H), 1.34–1.39 (m, 2H), 3.36 (q, $J = 7.0$ Hz, 2H), 3.41 (q, $J = 7.0$ Hz, 2H), 6.20 (d, $J = 14.5$ Hz, 1H), 6.90 (d, $J = 14.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ -2.29, 13.06,

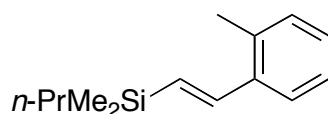
14.39, 17.49, 18.26, 18.66, 40.07, 42.36, 137.42, 143.74, 167.22. Found: C, 63.53; H, 11.32%.
Calcd for C₁₂H₂₅NOSi: C, 63.38; H, 11.08%.

Dimethyl[(*E*)-2-phenylethenyl]propylsilane (3d)



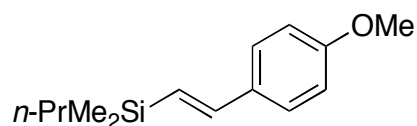
IR (neat) 2955, 2926, 2868, 1495, 1247, 989, 850, 803, 739, 724, 690 cm⁻¹; ¹H NMR (CDCl₃) δ 0.15 (s, 6H), 0.66 (t, *J* = 8.0 Hz, 2H), 0.99 (t, *J* = 7.0 Hz, 3H), 1.38–1.45 (m, 2H), 6.50 (d, *J* = 19.0 Hz, 1H), 6.89 (d, *J* = 19.0 Hz, 1H), 7.25–7.28 (m, 1H), 7.32–7.36 (m, 2H), 7.44–7.47 (m, 2H); ¹³C NMR (CDCl₃) δ -3.00, 17.41, 18.25, 18.35, 126.32, 127.87, 128.48, 128.73, 138.41, 143.86. Found: C, 76.34; H, 9.74%. Calcd for C₁₃H₂₀Si: C, 76.39; H, 9.86%.

Dimethyl[(*E*)-2-(2-methylphenyl)ethenyl]propylsilane (3e)



IR (neat) 3017, 2955, 2926, 2868, 1599, 1479, 1461, 1247, 1208, 1066, 989, 846, 803, 743, 665 cm⁻¹; ¹H NMR (CDCl₃) δ 0.16 (s, 6H), 0.66 (t, *J* = 8.0 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H), 1.38–1.46 (m, 2H), 2.39 (s, 3H), 6.37 (d, *J* = 19.0 Hz, 1H), 7.13 (d, *J* = 19.0 Hz, 1H), 7.13–7.21 (m, 3H), 7.52 (dd, *J* = 7.0, 2.0 Hz, 1H); ¹³C NMR (CDCl₃) δ -2.92, 17.44, 18.25, 18.39, 19.57, 125.28, 126.05, 127.63, 130.26, 130.59, 135.19, 137.78, 141.66. Found: C, 77.18; H, 10.37%.
Calcd for C₁₄H₂₂Si: C, 76.99; H, 10.15%.

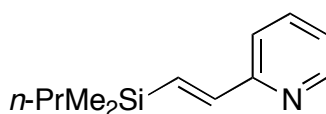
Dimethyl[(*E*)-2-(4-methoxyphenyl)ethenyl]propylsilane (3f)



IR (neat) 2955, 2927, 2868, 1607, 1510, 1465, 1304, 1295, 1251, 1172, 1038, 986, 843, 794, 739

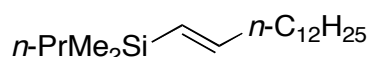
cm^{-1} ; ^1H NMR (CDCl_3) δ 0.13 (s, 6H), 0.64 (t, $J = 8.5$ Hz, 2H), 0.98 (t, $J = 7.0$ Hz, 3H), 1.36–1.44 (m, 2H), 3.83 (s, 3H), 6.30 (d, $J = 19.0$ Hz, 1H), 6.82 (d, $J = 19.0$ Hz, 1H), 6.87 (d, $J = 9.0$ Hz, 2H), 7.39 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ -2.93, 17.42, 18.25, 18.45, 55.28, 113.87, 125.89, 127.53, 131.47, 143.26, 159.51. Found: C, 71.61; H, 9.41%. Calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}$: C, 71.73; H, 9.46%.

2-[(*E*)-2-(Dimethylpropylsilyl)ethenyl]pyridine (3h)



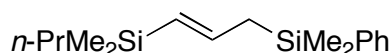
IR (neat) 3003, 2956, 2926, 2868, 1587, 1562, 1463, 1427, 1247, 1066, 994, 843, 808, 753 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.17 (s, 6H), 0.67 (t, $J = 8.0$ Hz, 2H), 0.98 (t, $J = 7.5$ Hz, 3H), 1.38–1.45 (m, 2H), 6.99 (s, 2H), 7.16 (ddd, $J = 7.5, 5.0, 1.5$ Hz, 1H), 7.39 (dt, $J = 7.5, 1.0$ Hz, 1H), 7.66 (td, $J = 7.5, 1.5$ Hz, 1H), 8.59 (dq, $J = 5.0, 1.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ -3.10, 17.38, 18.15, 18.24, 121.30, 122.38, 134.14, 136.48, 143.67, 149.52, 156.04. Found: C, 70.13; H, 9.51%. Calcd for $\text{C}_{12}\text{H}_{19}\text{NSi}$: C, 70.18; H, 9.32%.

Dimethylpropyl[(*E*)-1-tetradecenyl]silane (3i)



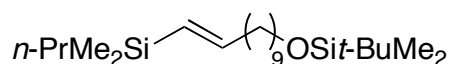
IR (neat) 2956, 2925, 2855, 1617, 1462, 1247, 989, 837, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.03 (s, 6H), 0.54 (t, $J = 8.0$ Hz, 2H), 0.89 (t, $J = 7.0$ Hz, 3H), 0.96 (t, $J = 7.0$ Hz, 3H), 1.27–1.42 (m, 22H), 2.08–2.13 (m, 2H), 5.60 (dt, $J = 18.5, 1.5$ Hz, 1H), 6.02 (dt, $J = 18.5, 6.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ -2.90, 14.10, 17.41, 18.26, 18.51, 22.68, 28.74, 29.17, 29.35, 29.51, 29.61, 29.66 (Two signals were overlapped), 29.69, 31.93, 36.82, 128.57, 147.78. Found: C, 76.86; H, 13.80%. Calcd for $\text{C}_{19}\text{H}_{40}\text{Si}$: C, 76.94; H, 13.59%.

(*E*)-2,6-Disila-2-phenyl-2,6,6-trimethyl-4-nonene (3j)



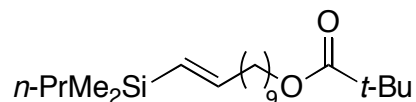
IR (neat) 2955, 2869, 1605, 1427, 1249, 1142, 1114, 987, 839, 757, 729, 698, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.00 (s, 6H), 0.28 (s, 6H), 0.51 (t, $J = 8.5$ Hz, 2H), 0.95 (t, $J = 8.0$ Hz, 3H), 1.28–1.36 (m, 2H), 1.87 (dd, $J = 7.5, 1.5$ Hz, 2H), 5.43 (dt, $J = 18.5, 1.5$ Hz, 1H), 6.00 (dt, $J = 18.5, 7.5$ Hz, 1H), 7.36–7.38 (m, 3H), 7.50–7.52 (m, 2H); ^{13}C NMR (CDCl_3) δ -3.50, -2.80, 17.43, 18.29, 18.62, 27.49, 127.67, 128.05, 128.95, 133.63, 138.67, 143.24. Found: C, 69.46; H, 10.48%. Calcd for $\text{C}_{16}\text{H}_{28}\text{Si}_2$: C, 69.49; H, 10.20%.

[(*E*)-11-(*tert*-Butyldimethylsiloxy)-1-undecenyl]dimethylpropylsilane (3k)



IR (neat) 2928, 2856, 1248, 1099, 836, 774, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.03 (s, 6H), 0.06 (s, 6H), 0.56 (t, $J = 8.0$ Hz, 2H), 0.91 (s, 9H), 0.96 (t, $J = 7.0$ Hz, 3H), 1.29–1.42 (m, 14H), 1.49–1.54 (m, 2H), 2.08–2.13 (m, 2H), 3.61 (t, $J = 6.5$ Hz, 2H), 5.60 (dt, $J = 18.5, 1.5$ Hz, 1H), 6.02 (dt, $J = 18.5, 6.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ -5.28, -2.92, 17.38, 18.24, 18.35, 18.48, 25.78, 25.97, 28.70, 29.13, 29.40, 29.41, 29.54, 32.78, 36.79, 63.31, 128.56, 147.72. Found: C, 68.81; H, 12.74%. Calcd for $\text{C}_{22}\text{H}_{48}\text{OSi}_2$: C, 68.67; H, 12.57%.

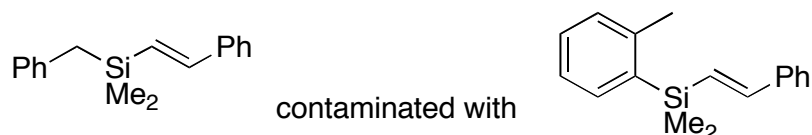
(*E*)-11-Dimethylpropylsilyl-10-undecenyl 2,2-dimethylpropanoate (3l)



IR (neat) 2927, 2855, 1732, 1616, 1480, 1462, 1398, 1258, 1247, 1153, 1066, 989, 772 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.03 (s, 6H), 0.54 (t, $J = 8.0$ Hz, 2H), 0.96 (t, $J = 7.5$ Hz, 3H), 1.21 (s, 9H), 1.29–1.41 (m, 14H), 1.60–1.65 (m, 2H), 2.08–2.12 (m, 2H), 4.05 (t, $J = 6.5$ Hz, 2H), 5.60 (dt, $J = 18.5, 1.5$ Hz, 1H), 6.02 (dt, $J = 18.5, 6.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ -2.90, 17.40, 18.26, 18.50, 25.91, 27.21, 28.62, 28.70, 29.11, 29.20, 29.38, 29.44, 36.79, 38.73, 64.45, 128.63, 147.68,

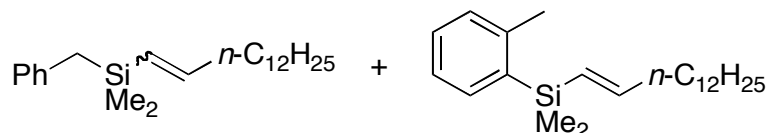
178.63. Found: C, 71.22; H, 12.13%. Calcd for $C_{21}H_{42}O_2Si$: C, 71.12; H, 11.94%.

Benzyl dimethyl[(*E*)-2-phenylethenyl]silane (5d, contaminated with 6d)



IR (neat) 3059, 3023, 2956, 1601, 1574, 1493, 1447, 1248, 1206, 1154, 989, 833, 813, 791, 761, 739, 699, 690 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.16 (s, 0.89 \times 6H, for **5d**), 0.51 (s, 0.11 \times 6H, for **6d**), 2.24 (s, 0.89 \times 2H, for **5d**), 2.49 (s, 0.11 \times 3H, for **6d**), 6.45 (d, $J = 19.0$ Hz, 0.89 \times 1H, for **5d**), 6.66 (d, $J = 19.0$ Hz, 0.11 \times 1H, for **6d**), 6.87 (d, $J = 19.0$ Hz, 0.89 \times 1H, for **5d**), 6.95 (d, $J = 19.0$ Hz, 0.11 \times 1H, for **6d**), 7.06 (d, $J = 7.5$ Hz, 0.89 \times 2H, for **5d**), 7.11 (t, $J = 7.5$ Hz, 0.89 \times 1H, for **5d**), 7.17–7.32 (m, 0.11 \times 3H, for **6d**), 7.24 (t, $J = 7.5$ Hz, 0.89 \times 2H, for **5d**), 7.28 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.44 (d, $J = 7.5$ Hz, 2H), 7.46–7.48 (m, 0.11 \times 1H, for **6d**); ^{13}C NMR ($CDCl_3$) For **5d**: δ -3.36, 26.12, 124.01, 126.39, 126.45, 127.36, 128.07, 128.13, 128.27, 128.51, 139.87, 144.69 Found: C, 81.11; H, 8.04%. Calcd for $C_{17}H_{20}Si$: C, 80.89; H, 7.99%.

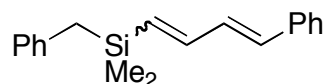
A mixture of benzyl dimethyl[(*E*)-1-tetradecenyl]silane [(*E*)-5i], benzyl dimethyl[(*Z*)-1-tetradecenyl]silane [(*Z*)-5i], and dimethyl(2-methylphenyl) [(*E*)-1-tetradecenyl]silane (6i)



IR (neat) 3024, 2956, 2925, 2854, 1617, 1602, 1494, 1452, 1247, 1206, 831, 817, 795, 698 cm^{-1} ; 1H NMR ($CDCl_3$) For (*E*)-**5i**: δ 0.03 (s, 6H), 0.90 (t, $J = 7.0$ Hz, 3H), 1.27–1.42 (m, 20H), 2.08–2.17 (m, 2H), 2.19 (s, 2H), 5.59 (dt, $J = 19.0, 1.5$ Hz, 1H), 6.01 (dt, $J = 19.0, 6.0$ Hz, 1H), 7.01 (d, $J = 7.5$ Hz, 2H), 7.07 (t, $J = 7.5$, 1H), 7.21 (t, $J = 7.5$ Hz, 2H), For (*Z*)-**5i**: δ 0.10 (s, 6H), 0.90 (t, $J = 7.0$ Hz, 3H), 1.27–1.42 (m, 20H), 2.08–2.17 (m, 2H), 2.17 (s, 2H), 5.44 (dt, $J = 14.0,$

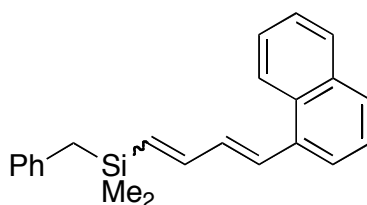
1.5 Hz, 1H), 6.35 (dt, $J = 14.0, 7.5$ Hz, 1H), 7.01 (d, $J = 7.5$ Hz, 2H), 7.07 (t, $J = 7.5$, 1H), 7.21 (t, $J = 7.5$ Hz, 2H), For **6i**: δ 0.38 (s, 6H), 0.90 (t, $J = 7.0$ Hz, 3H), 1.27–1.42 (m, 20H), 2.08–2.17 (m, 2H), 2.44 (s, 3H), 5.80 (dt, $J = 19.0, 1.5$ Hz, 1H), 6.10 (dt, $J = 19.0, 6.0$ Hz, 1H), 7.15–7.35 (m, 3H), 7.47–7.56 (m, 1H); ^{13}C NMR (CDCl_3) For (*E*)-**5i**: δ -3.31, 14.08, 22.66, 26.26, 28.63, 29.14, 29.33, 29.49, 29.59, 29.62, 29.66, 29.67, 31.90, 36.78, 123.80, 127.37, 127.98, 128.24, 140.25, 148.77. Found: C, 80.39; H, 11.58%. Calcd for $\text{C}_{23}\text{H}_{40}\text{Si}$: C, 80.15; H, 11.70%.

Benzyl dimethyl[(*E,E*)-4-phenyl-1,3-butadienyl]silane [(*E,E*)-5m**, contaminated with (*E,Z*)-**5m**]**



IR (neat) 3060, 3023, 2955, 1599, 1581, 1493, 1247, 1206, 1000, 857, 832, 818, 799, 748, 728, 699, 691 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.11 (s, $0.83 \times 6\text{H}$, for (*E,E*)-**5m**), 0.23 (s, $0.17 \times 6\text{H}$, for (*E,Z*)-**5m**), 2.19 (s, $0.83 \times 2\text{H}$, for (*E,E*)-**5m**), 2.27 (s, $0.17 \times 2\text{H}$, for (*E,Z*)-**5m**), 5.71 (d, $J = 13.5$ Hz, $0.17 \times 1\text{H}$, for (*E,Z*)-**5m**), 5.97 (d, $J = 18.5$ Hz, $0.83 \times 1\text{H}$, for (*E,E*)-**5m**), 6.54–6.58 (m, $0.17 \times 1\text{H}$, for (*E,Z*)-**5m**), 6.59 (d, $J = 16.0$ Hz, $0.83 \times 1\text{H}$, for (*E,E*)-**5m**), 6.64–6.70 (m, $0.17 \times 1\text{H}$, for (*E,Z*)-**5m**), 6.68 (ddd, $J = 18.5, 10.0, 0.5$ Hz, $0.83 \times 1\text{H}$, for (*E,E*)-**5m**), 6.80 (ddd, $J = 16.0, 10.0, 0.5$ Hz, $0.83 \times 1\text{H}$, for (*E,E*)-**5m**), 6.81–6.86 (m, $0.17 \times 1\text{H}$, for (*E,Z*)-**5m**), 7.02–7.04 (m, 2H), 7.08–7.11 (m, 1H), 7.22–7.25 (m, 2H), 7.25–7.27 (m, 1H), 7.32–7.35 (m, 2H), 7.42–7.43 (m, 2H); ^{13}C NMR (CDCl_3) For (*E,E*)-**5m**: δ -3.36, 26.09, 124.01, 126.57, 127.74, 128.13, 128.26, 128.61, 131.54, 132.63, 133.25, 137.13, 139.88, 145.16. Found: C, 81.93; H, 7.96%. Calcd for $\text{C}_{19}\text{H}_{22}\text{Si}$: C, 81.95; H, 7.96%.

Benzyl dimethyl[(*E,E*)-4-(1-naphthyl)-1,3-butadienyl]silane [(*E,E*)-5n**, contaminated with (*E,Z*)-**5n**]**



IR (neat) 3058, 3023, 2955, 2893, 1599, 1579, 1493, 1451, 1247, 1206, 1154, 1056, 1000, 831, 800, 774, 746, 699 cm^{-1} ; ^1H NMR (CDCl_3): δ 0.14 (s, $0.94 \times 6\text{H}$, for **(E,E)-5n**), 0.25 (s, $0.06 \times 6\text{H}$, for **(E,Z)-5n**), 2.22 (s, $0.94 \times 2\text{H}$, for **(E,E)-5n**), 2.29 (s, $0.06 \times 2\text{H}$, for **(E,Z)-5n**), 5.79 (d, $J = 14.0$ Hz, $0.06 \times 1\text{H}$, for **(E,Z)-5n**), 6.03 (d, $J = 17.5$ Hz, $0.94 \times 1\text{H}$, for **(E,E)-5n**), 6.50–6.62 (m, $0.06 \times 2\text{H}$, for **(E,Z)-5n**), 6.82 (dd, $J = 17.5, 10.0$ Hz, $0.94 \times 1\text{H}$, for **(E,E)-5n**), 6.87 (dd, $J = 15.0, 10.0$ Hz, $0.94 \times 1\text{H}$, for **(E,E)-5n**), 7.06 (d, $J = 7.5$ Hz, 2H), 7.11 (t, $J = 7.5$ Hz, 1H), 7.25 (t, $J = 7.5$ Hz, 2H), 7.38 (d, $J = 15.0$ Hz, 1H), 7.46–7.56 (m, 3H), 7.69 (d, $J = 7.0$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.86–7.88 (m, 1H), 8.17 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (CDCl_3) For **(E,E)-5n**: δ -3.35, 26.09, 123.43, 123.58, 124.03, 125.58, 125.78, 126.07, 128.14, 128.27, 128.43, 128.60, 129.98, 131.23, 132.97, 133.74, 134.30, 134.43, 139.87, 145.40. Found: C, 84.23; H, 7.44%. Calcd for $\text{C}_{23}\text{H}_{24}\text{Si}$: C, 84.09; H, 7.36%.

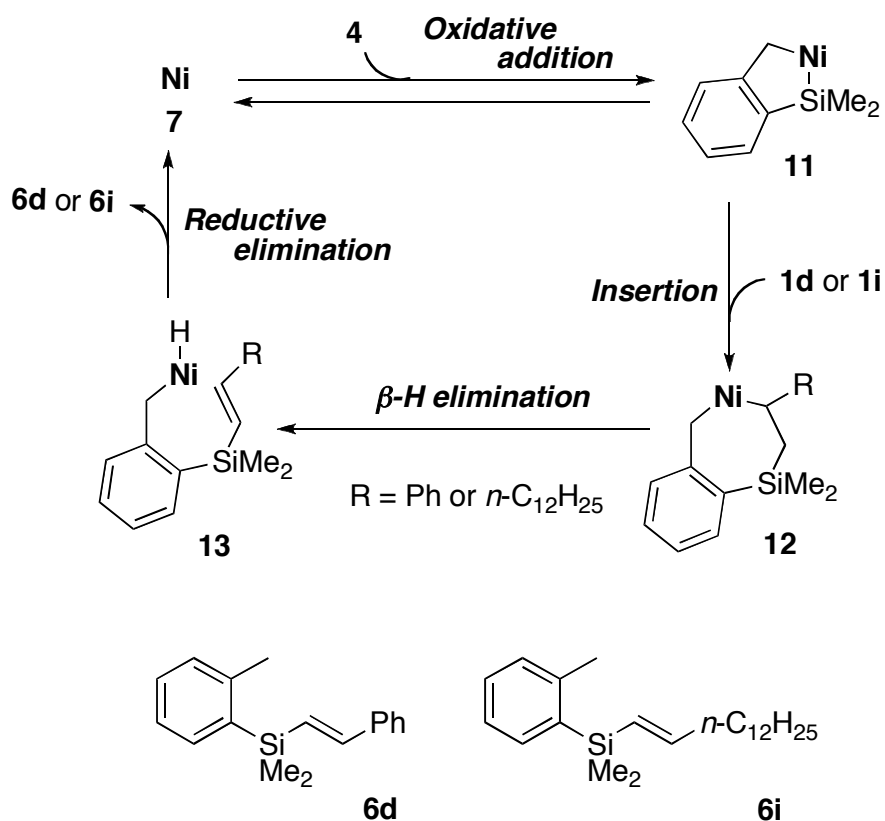
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(15) The oxidative addition of the benzylic sp^3C-Si bond to Ni(0) would cause the formations of **6d** and **6i** (Table 3, entries 1 and 2), which would proceed as follows (See the following scheme). Oxidative addition of the benzylic sp^3C-Si bond of **4** to Ni(0) followed by insertion of **1d** or **1i** gives the nickelasilacycloheptane **12**. Subsequent β -H elimination and reductive elimination produces **6d** or **6i** and regenerates the zerovalent nickel species. Nevertheless, in the reactions of dienes **1m** and **1n** with the benzene-fused silacyclobutane **4**, the byproducts corresponding to **6d** or **6i** were not detected (Table 3, entries 3 and 4). The finding suggests that the oxidative addition of the benzylic sp^3C-Si bond of **4** to Ni(0) would be reversible. Indeed, the oxidative addition of silacyclobutanes to palladium complexes is known to be in equilibrium (see ref 14b).



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