DOI: 10.1002/ejoc.200900001

Rhodium-Catalyzed Tandem Transformations with Organoboron Reagents: Sequential Multiple C–C Bond Formations

So Won Youn*[a]

Keywords: Rhodium / Domino reactions / C–C coupling / Carbocycles / Heterocycles

Tandem transformations represent one of the most efficient methods for the synthesis of complex molecules from readily available starting materials, as evidenced by the intense research activity and the plethora of literature published in this area. This review highlights recent developments of rhodium(I)-catalyzed tandem transformations with organoboron compounds involving the formation of multiple carbon–carbon bonds.

Introduction

In recent years, transition-metal-catalyzed transformations have been increasingly employed as important tools for C–C bond formation. In particular, transition-metal-catalyzed tandem reactions, which consist of multiple C–C bond-forming reactions, are powerful methods for the synthesis of structurally complex molecules from relatively simple starting materials in a convergent way.[1] The advantages of these transformations are the one-pot formation of several bonds using a single catalyst in one operation without isolation of the intermediates, change of the reaction conditions, or addition of reagents, high efficiency, atom economy, and favorable environmental considerations.

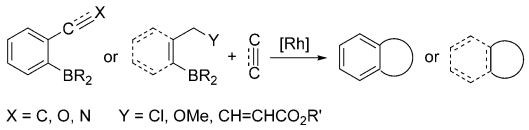
Recently there has been considerable research interest in rhodium(I)-catalyzed tandem transformations with organoboron reagents for the formation of acyclic or cyclic compounds.[1f–1g] Two strategies have been developed for this process. First, a tandem reaction between alkenes or alkynes and ambiphilic bifunctional organoboron molecules that contain an electrophilic functional group, which can eventually accept an organorhodium(I) species at a later stage (Scheme 1, a). Secondly, tandem reactions of two or more unsaturated functionalities in a molecule or in separate molecules with external organoborons can occur to form acyclic or cyclic compounds (Scheme 1, b). Because an organorhodium(I) species generated by the transmetalation of organoborons can undergo facile addition to unsaturated functionalities such as alkyne, alkene, carbonyl, imine, and cyano groups,[2] molecules containing two or more different unsaturated bonds at appropriate positions, which can act as acceptors of an organorhodium(I) species, are particularly useful substrates for such tandem reactions involving multiple C–C bond formations to construct a cyclic skeleton. The more reactive functional group provides the entry point for the addition of an organorhodium species by way of initial intermolecular carborhodation, which triggers the second carborhodation on the less reactive functionality in an intra- or intermolecular way.

This review will cover both Rh^{I}-catalyzed inter- and intramolecular tandem reactions for the synthesis of both acyclic and cyclic compounds. This review has been divided into three main sections: Rh^{I}-catalyzed tandem transformations triggered by i. alkyne additions, ii. conjugate additions, and iii. strained alkene additions. And each section has been further divided into several classes of secondary electrophiles.

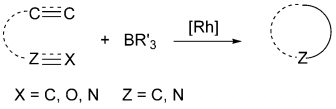
[a] Department of Chemistry, Pukyong National University, Busan 608-737, Korea
Fax: +82-51-629-5583
E-mail: sowony@pknu.ac.kr

So Won Youn was born in Gyung-gi, Korea, in 1973. She studied chemistry at Yonsei University, where she received her B. S. degree in 1996. She received her M. S. in 1998 and Ph. D. in 2001 under the supervision of Prof. Yong Hae Kim at the Korea Advanced Institute of Science and Technology. After a two-year postdoctoral stay with Prof. Dalibor Sames at Columbia University, she was appointed as a full time instructor at Pukyong National University in 2003 and promoted to Assistant Professor in 2005 and Associate Professor in 2009. Her research interests are the development of new synthetic methodology and transition-metal catalysis.

(a) Tandem reactions of ambiphilic bifunctional organoboron compounds with alkynes or alkenes for the synthesis of carbocycles



(b) Tandem reactions between two or more unsaturated functionalities and external organoboron compounds for the synthesis of acyclic, carbocyclic, or *N*-heterocyclic compounds



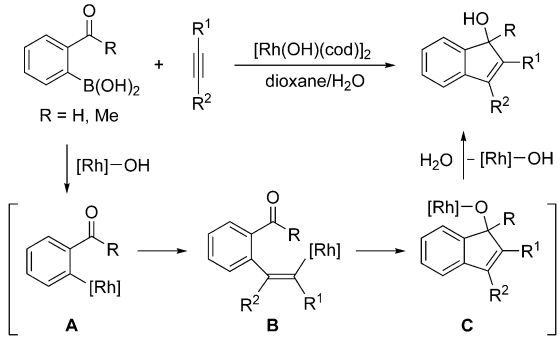
Scheme 1. Rhodium-catalyzed tandem transformations.

Rh^{I}-Catalyzed Tandem Transformations Triggered by the Addition of Organoborons Across Alkynes

In 2001 Hayashi et al. reported the seminal work on the Rh-catalyzed hydroarylation of alkynes with organoboronic acids.[3]

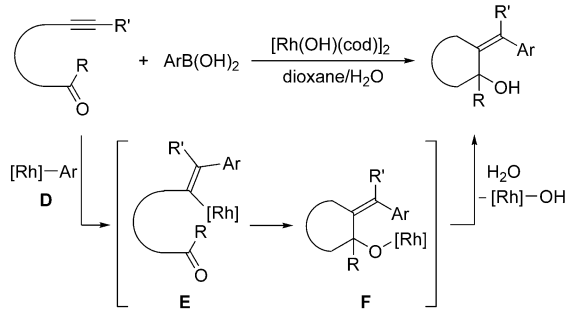
Carbonyl Group as a Secondary Electrophile

The Rh-catalyzed synthesis of indenols has been developed through the coupling of alkynes with *ortho*-carbonylated arylboronic acids (Scheme 2).[4] High regioselectivities were observed with unsymmetrical alkynes and *o*-acetylphenylboronic acid required more forcing conditions than *o*-formylphenylboronic acid. The reaction has also been applied to its asymmetric variant through the use of chiral diene ligands, achieving high enantioselectivity. Arylrhodium species **A** generated by transmetalation adds to the alkyne in a *syn* fashion to form **B**, which undergoes intramolecular addition to the carbonyl group to give rhodium(I) alkoxide **C**. Protonolysis produces the desired indenol and regenerates the hydroxorhodium(I) species.



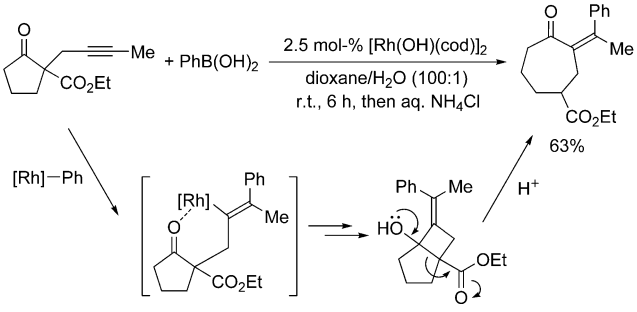
Scheme 2.

Sequential addition/cyclization of arylboronic acids to alkynals or alkynones has been achieved to afford four-, five-, or six-membered cyclic allylic alcohols with a tetrasubstituted olefin (Scheme 3).[5] The regioselective 1,2-addition of an arylrhodium(I) species **D** across the alkyne is followed by intramolecular nucleophilic addition of the resulting vinylrhodium(I) species **E** to the carbonyl group. Higher enantiomeric excesses as well as better chemical yields were obtained by the use of chiral diene ligands rather than phosphorus-based ligands.



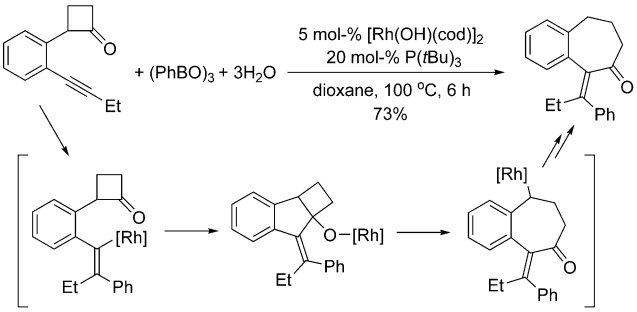
Scheme 3.

On the other hand, 4-alkyn-1-ones having a two-carbon tether and a carbonyl substituent at the C2 position undergo sequential 1,2-addition to an alkyne, 4-*exo*-trig cyclization, and retro-aldol reaction (Scheme 4).[5c,6] This acyl 1,3-migration reaction can produce medium-sized (seven-, eight-, and ten-membered) carbocycles through a two-carbon ring-expansion process.



Scheme 4.

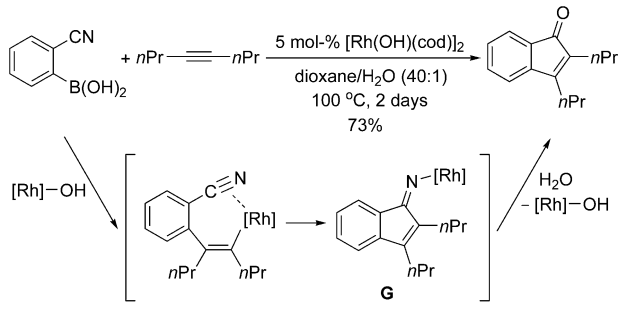
Another method for the construction of seven-membered-ring skeletons has been shown by a Rh-catalyzed ring-expansion reaction (Scheme 5).[7] When a cyclobutanone moiety is used as a secondary electrophile, addition of a vinylrhodium(I) species to the carbonyl group of the cyclobutanone produces rhodium cyclobutanolate, which undergoes ring-opening by β-carbon elimination followed by successive β-hydride elimination, readdition, and protonolysis.



Scheme 5.

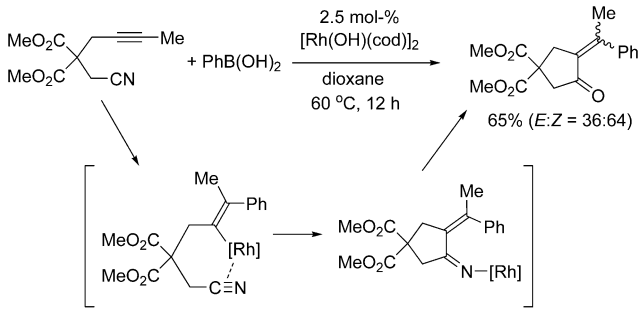
Cyano Group as a Secondary Electrophile

Cyano groups can act as a secondary electrophile, accepting the organorhodium(I) intermediate in an intramolecular way even though they are much less reactive in intermolecular cases. 2-Cyanophenylboronic acid has been used as an ambiphilic bifunctional substrate for [3+2] annulation reactions (Scheme 6).[8] The alkenylrhodium(I) intermediate resulting from sequential transmetalation and 1,2-addition across the alkyne undergoes an intramolecular addition to the cyano group to give the *N*-rhodium(I) imine **G**, which is hydrolyzed to the corresponding indenone. Interestingly, when ethyl 2-hexynoate was used as the alkyne, the seven-membered ring benzotropone derivative was obtained as a major product instead of the five-membered ring through a further intermolecular carborhodation onto a second ethyl 2-hexynoate unit followed by 7-*exo*-dig ring closure.

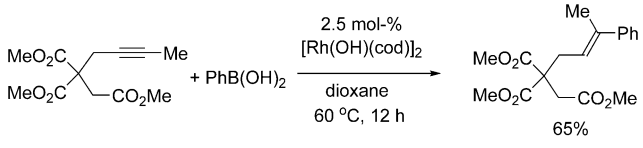


Scheme 6.

Cyclization reactions of cyano-substituted alkynes with arylboronic acids have been reported in which the alkenylrhodium(I) species undergoes intramolecular nucleophilic addition to the cyano group to give cyclic α,β-unsaturated ketones (Scheme 7).[9] In this report, the higher reactivity of the cyano group towards the alkenylrhodium(I) species relative to the alkoxycarbonyl group was demonstrated, which suggested that the reactivity order of the cyano and ester groups is the opposite to that for organolithium and -magnesium reagents (Scheme 8).



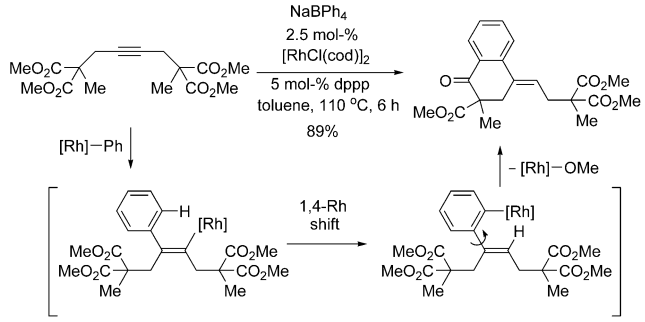
Scheme 7.



Scheme 8.

Ester Group as a Secondary Electrophile

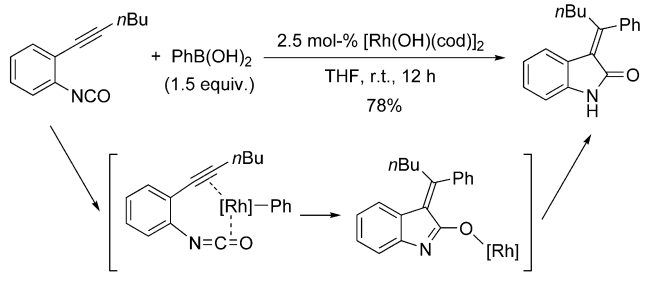
In contrast, the use of $NaBPh_4$ under strictly anhydrous conditions led to acylation with the ester to give α-tetralone derivatives without formation of the 1,2-addition product (Scheme 9 vs. Scheme 8).[10] Addition across the alkyne in a *syn* fashion followed by a sequential 1,4-shift of rhodium and acylation with the ester group produces an α-tetralone derivative with concomitant regeneration of the catalytically active methoxorhodium(I).



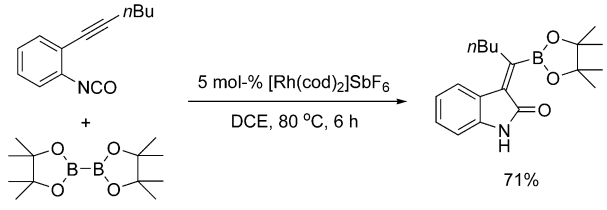
Scheme 9.

Isocyanate Group as a Secondary Electrophile

The Rh-catalyzed cyclization reactions of 2-alkynylaryl isocyanates with organoborons have been developed to afford 3-alkylideneoxoindoles in a stereoselective manner (Scheme 10).[11] Recently, the incorporation of a carbon–boron linkage into the 3-alkylideneoxoindole skeleton has been achieved (Scheme 11).[12] The stereoselective synthesis of borylated 3-alkylideneoxoindoles was successfully performed by the Rh-catalyzed reaction of alkynylaryl isocyanates with bis(pinacolato)diboron through simultaneous C–B and C–C bond formations.



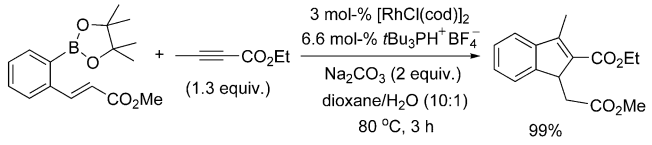
Scheme 10.



Scheme 11.

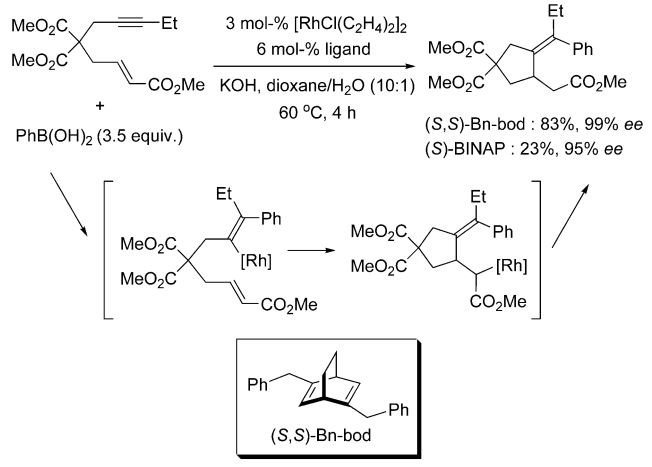
α,β-Unsaturated Carbonyl Group as a Secondary Electrophile

Arylboronate esters bearing an electron-deficient olefin at the *ortho* position have been used for Rh-catalyzed tandem cyclization reactions with activated alkynes to afford 1*H*-indenes (Scheme 12).[13] The catalytic system involved the use of electron-rich, sterically bulky ligands stabilizing the organorhodium intermediates.



Scheme 12.

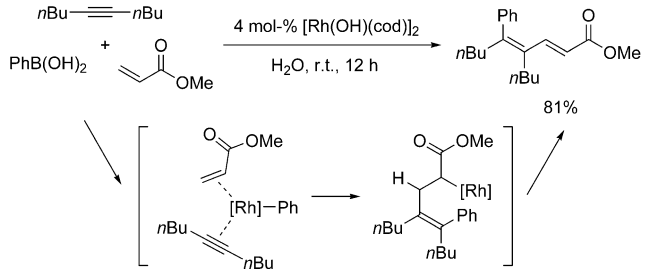
It has been demonstrated that a Rh–diene catalyst rather than a Rh–bis-phosphane catalyst can promote the arylative cyclization of alkyne-tethered electron-deficient olefins more effectively with high chemo- and enantioselectivities (Scheme 13).[14] The observed chemoselectivity, which involves initial carborhodation of the triple bond instead of the conjugated double bond, is in accord with the observation that a Rh–diene catalyst displays higher activity in the arylation of alkynes than in the 1,4-addition to α,β-enoates, whereas a Rh–bis-phosphane catalyst behaves in the opposite manner.



Scheme 13.

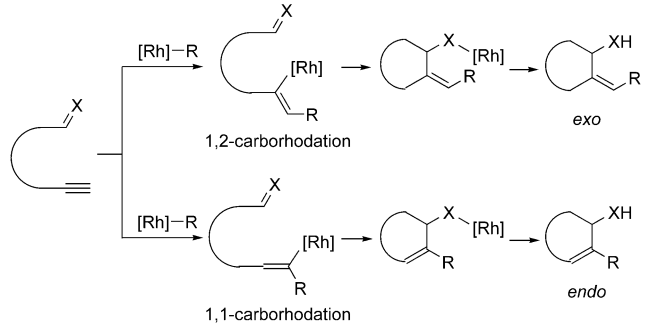
The Rh-catalyzed intermolecular reactions of arylboronic acids with internal alkynes and acrylates have been reported in which functionalized dienes were obtained in water through an arylrhodation/Heck-type addition sequence (Scheme 14).[15]

1,2-Addition of organorhodium(I) species across alkynes in a *syn* fashion has been pivotal in the Rh-catalyzed intermolecular coupling reactions of alkynes with organoboron reagents, resulting in the formation of *exo*-olefin cyclic compounds through a tandem process (Scheme 15). Recently, Chen and Lee demonstrated the occurrence of the 1,1-carborhodation pathway, which can afford an *endo*-olefin cyclic product (Scheme 16).[16] This new addition/cyclization

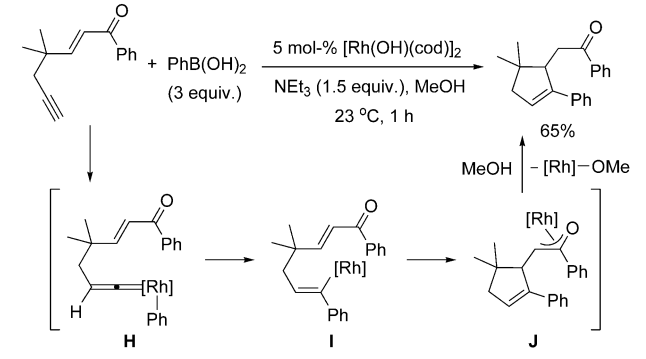


Scheme 14.

reaction occurred through a vinylidenerhodium-mediated 1,1-carborhodation process. Following the formation of vinylidenerhodium **H**, α-migration of the aryl group from the Rh center to the vinylidene ligand provides alkenylrhodium intermediate **I**, which then undergoes addition to the pendant enone to give rhodium enolate **J**. Finally, protonation of **J** produces cyclopentene derivatives and regenerates the methoxorhodium(I) species.



Scheme 15.

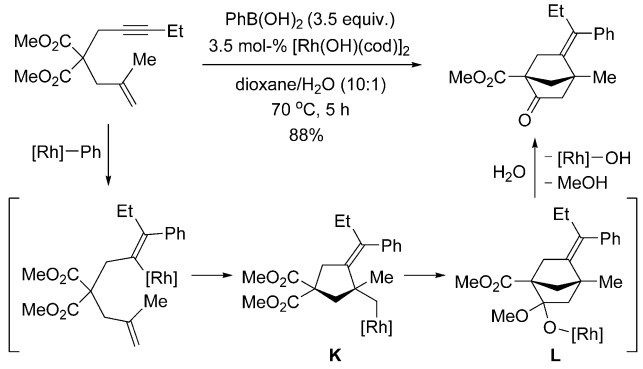


Scheme 16.

Alkene Group as a Secondary Electrophile

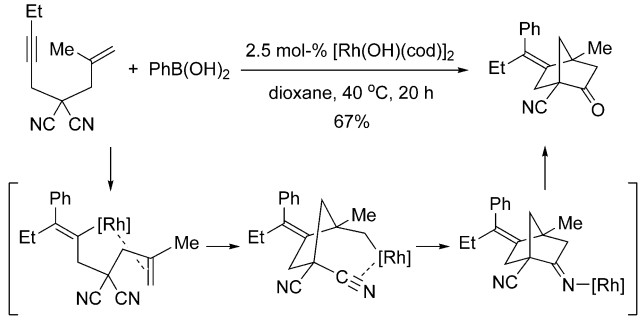
Tandem reactions of 1,6-enynes tethered through a methyl malonate group proceeded through three sequential C–C bond-forming reactions to give bicyclic compounds (Scheme 17).[5a,10] Initially, 1,2-addition of phenylrhodium(I) species across the carbon–carbon triple bond gives an alkenylrhodium(I) intermediate. Then intramolecular carborhodation to a pendant methallyl moiety occurs in a 5-*exo*-trig mode, leading to the alkylrhodium(I) intermedi-

ate **K**. Finally, intramolecular acylation with the ester group by addition/elimination affords the bicyclo[2.2.1]heptan-2-one derivatives with generation of the catalytically active hydroxorhodium(I).



Scheme 17.

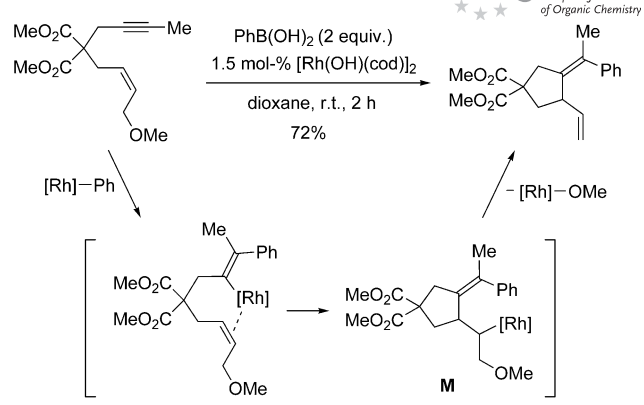
In the case of 1,6-enynes tethered through a malononitrile group, an analogous tandem reaction occurred to afford the corresponding bicyclic compounds by intramolecular nucleophilic addition of the alkylrhodium(I) intermediates onto one of the nitrile groups (Scheme 18).[9]



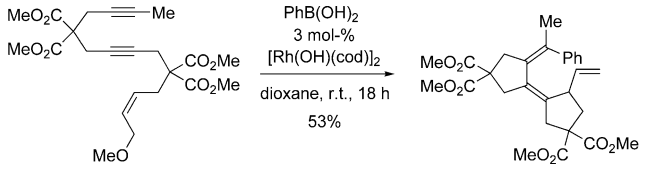
Scheme 18.

When 1,6-enynes possess a methoxy group in an allylic position, the tandem reaction proceeds in a different way. The alkylrhodium(I) intermediate **M** generated by intramolecular carborhodation to the pendant allylic double bond in a 5-*exo* mode undergoes β-elimination of the methoxy group rather than acylation with an ester group to afford vinylcyclopentane derivatives and catalytically active methoxorhodium(I) (Scheme 19).[17] An analogous reaction could occur with enediyne substrates through multiple carborhodations and β-elimination of the methoxy group (Scheme 20).[16]

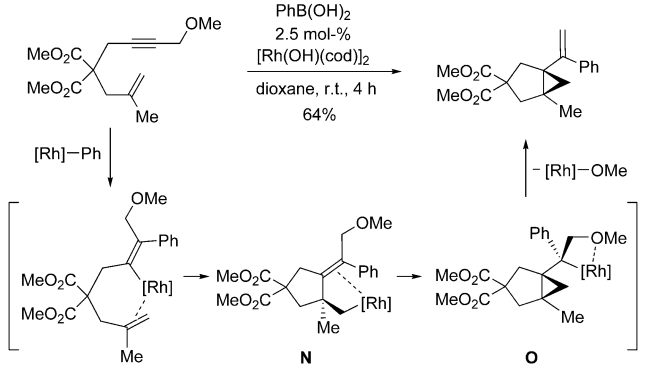
It also has been reported that 1,6-enynes bearing a methoxy group at the propargylic position instead of the allylic position undergo multiple carborhodation steps and β-oxygen elimination to afford vinylcyclopropanes (Scheme 21).[18] Interestingly, a second intramolecular carborhodation to the allylic double bond occurred in a 3-*exo*-trig mode (**N** → **O**), despite the developing ring strain, rather than acylation with an ester (Scheme 21 vs. Scheme 17). Finally, β-elimination of the methoxy group afforded vinylcyclopropanes fused with a cyclopentane ring along with a catalytically active methoxorhodium(I) species. It is conceivable that the three-membered ring-closure from **N** to **O** is facilitated by the developing coordination of the methoxy group to rhodium. Formation of the methoxorhodium(I) species by β-oxygen elimination would drive the reaction forward.



Scheme 19.



Scheme 20.

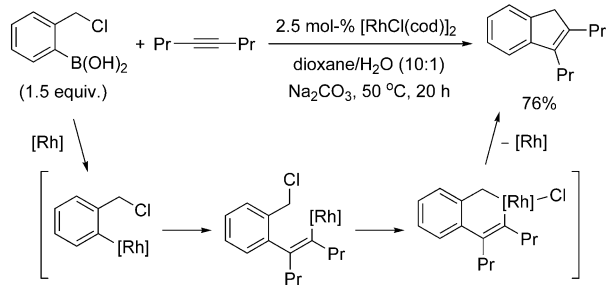


Scheme 21.

Alkyl Chloride Group as a Secondary Electrophile

Recently, the Rh-catalyzed reaction of 2-(chloromethyl)-phenylboronic acid with internal alkynes has been developed to afford substituted indenes (Scheme 22).[19] The reaction involves the addition of an arylrhodium(I) species to alkynes and the oxidative addition of the C–Cl on the phenyl ring to the resulting vinylrhodium(I), which undergoes reductive elimination. Terminal alkynes, alkynes having a silyl or ester group, and alkenes were not suitable

for this reaction. Electron-deficient olefins gave simple 1,4-addition products, which suggests that protonation of the initially generated rhodium enolate is much faster than intramolecular nucleophilic substitution of a chloride.



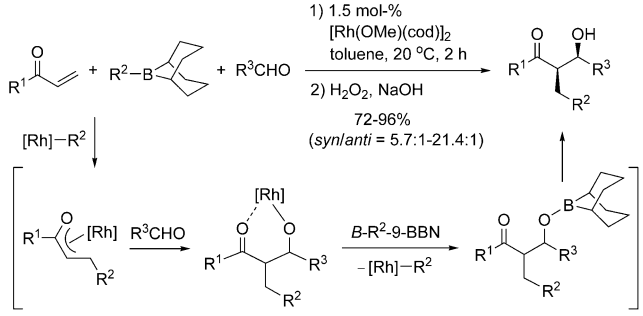
Scheme 22.

Rh^{I}-Catalyzed Tandem Transformations Triggered by the Conjugate Addition of Organoborons

Tandem transformations triggered by the conjugate addition of organoborons to electron-deficient alkenes followed by inter- or intramolecular trapping of the resulting enolate intermediate are gaining in popularity due to the seminal study by Miyaura and co-workers, who reported the Rh-catalyzed conjugate addition of organoboronic acids to enones.[20]

Carbonyl Group as a Secondary Electrophile

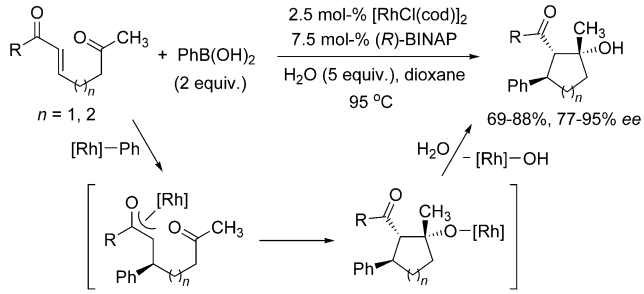
A tandem 1,4-addition/aldol reaction has been realized in an intermolecular way in which the two C–C bond-forming reactions, the 1,4-addition and aldol reaction, are catalyzed by a rhodium complex in single catalytic cycle (Scheme 23).[21] This process consists of the 1,4-addition of an organorhodium(I) species to an α,β-unsaturated ketone and the aldol addition of the resulting (oxa-π-allyl)rhodium(I) intermediate to an aldehyde to form rhodium aldolate, which undergoes transmetalation of the aryl or alkenyl group from 9-BBN to give the boron aldolate and the organorhodium species. The high *syn* selectivity may suggest a six-membered-ring transition state of the rhodium (*Z*)-enolate in the aldol reaction. The use of 9-BBN reagents



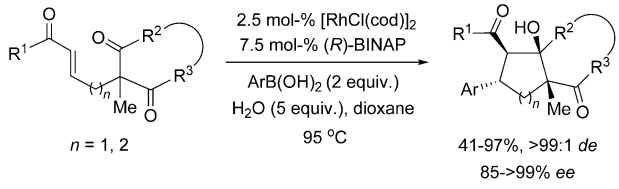
Scheme 23.

was essential for this reaction, whereas organoboron reagents in which boron is bonded to oxygen ligands gave no detectable amounts of the desired products.

An analogous intramolecular tandem conjugate addition/aldol cyclization has been developed to afford five- and six-membered-ring products (Scheme 24).[22a] Tandem cyclization of keto-enones with phenylboronic acid could be conducted in the presence of an excess amount of water. In contrast, α,β-unsaturated esters underwent conjugate addition, but cyclization did not occur. In a single manipulation, three contiguous stereogenic centers were created with high levels of relative and absolute stereochemical control. Given these results, the application of this methodology has been explored in the desymmetrization of ene-diones, which results in the formation of two C–C bonds and four contiguous stereogenic centers (Scheme 25).[22b] This transformation enables the rapid assembly of complex polycyclic ring systems from simple precursors with high levels of diastereo- and enantiocontrol.



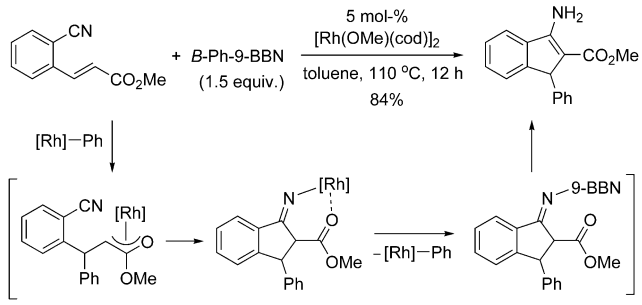
Scheme 24.



Scheme 25.

Cyano Group as a Secondary Electrophile

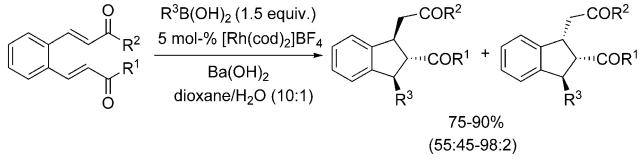
Unsaturated esters possessing a pendant cyano moiety have been utilized for Rh-catalyzed tandem cyclization triggered by the conjugate addition of arylboron reagents to form five- and six-membered β-enamino esters (Scheme 26).[23] An (oxa-π-allyl)rhodium(I) intermediate, generated by the initial conjugate addition of an arylrhodium(I) species, undergoes a facile intramolecular addition to the cyano group followed by sequential transmetalation with *B*-Ar-9-BBN, hydrolysis, and tautomerization.



Scheme 26.

α,β-Unsaturated Carbonyl Group as a Secondary Electrophile

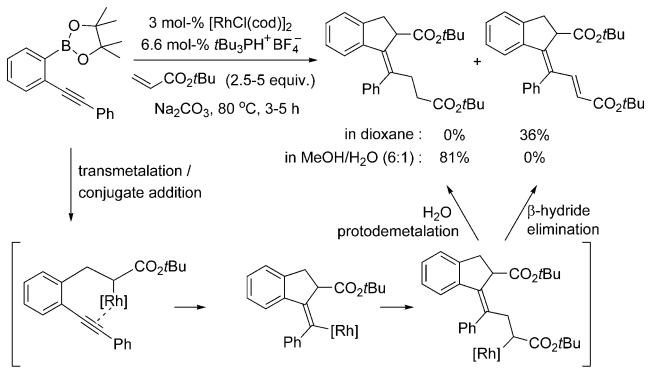
A stereoselective Rh-catalyzed tandem annulation reaction triggered by the conjugate addition of arylboronic acids to enones followed by an intramolecular Michael reaction to enones has been reported (Scheme 27).[24] This sequence afforded 1,2,3-trisubstituted indanes in a highly regio- and diastereoselective fashion. On the other hand, the corresponding reactions with α,β-unsaturated esters gave rise to a complex mixture of reaction products.



Scheme 27.

Alkyne Group as a Secondary Electrophile

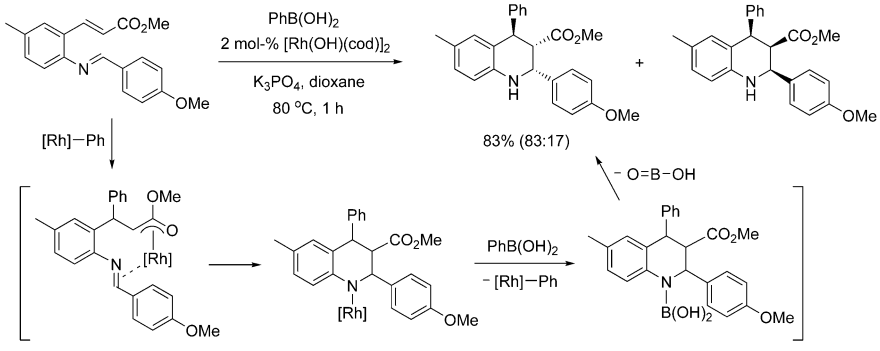
An arylboronate ester bearing a pendant alkyne underwent a tandem intramolecular cyclization reaction with *tert*-butyl acrylate (Scheme 28).[13] In this reaction, a third carborhodation occurred and a mixture of two products was obtained with the ratio depending mainly on the solvent mixture. When the reaction was conducted in dioxane without water, the unsaturated product was formed as a result of β-hydride elimination. In contrast, when the reaction was performed in a mixture of methanol/water (6:1), only the saturated product resulting from protodemetalation was obtained.



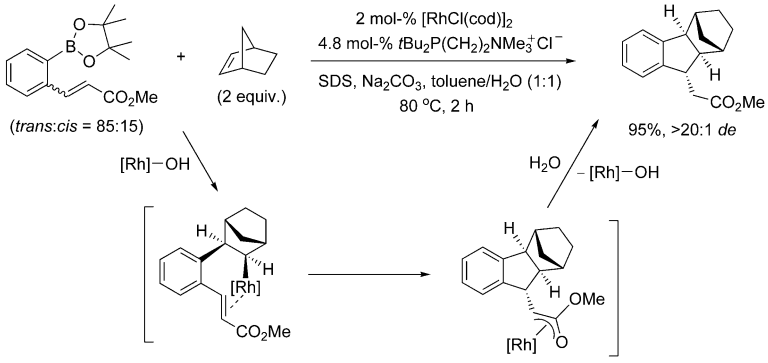
Scheme 28.

Imine Group as a Secondary Electrophile

As shown in this review, in recent years several examples of Rh-catalyzed tandem annulations with organoboron reagents have been demonstrated in which the sequential process was triggered by conjugate addition or 1,2-addition across alkynes and followed by intramolecular addition to a secondary electrophile such as a carbonyl, cyano, alkyne, alkene, or isocyanate group, which mostly provides carbocycles with the exception of the isocyanate group.[11,12] However, the process involving an imine group as the secondary electrophile has not been explored, probably due to its low reactivity and instability relative to other functional groups. As both α,β-unsaturated carbonyl compounds and imines are good acceptors of organorhodium(I) species,[2] we envisioned that electron-deficient alkenes bearing an imine moiety placed at an appropriate position would be interesting bifunctional substrates with regard to the possibility of a tandem cyclization reaction that could afford *N*-heterocycles such as tetrahydroquinolines. Finally, we have developed a new Rh-catalyzed tandem conjugate addition/Mannich cyclization reaction of imine-substituted electron-deficient alkenes with arylboronic acids (Scheme 29).[25] This process represents the first example in which an imine



Scheme 29.



Scheme 30.

group serves as a secondary electrophile that accepts the (oxa-π-allyl)rhodium(I) intermediate in an intramolecular way. Note that this process can tolerate various functional groups and the arylboronic acids act as a proton source as well as a carbon nucleophile.

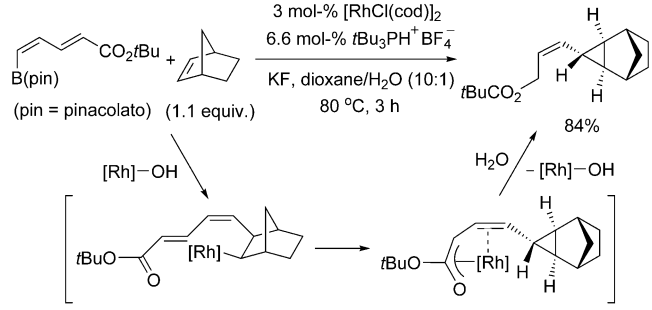
Rh^I-Catalyzed Tandem Transformations Triggered by the Addition of Organoborons to Strained Alkenes

In 2000 the first example of a Rh-catalyzed alkylation reaction of arylboronic acids with a strained alkene, 2-norbornene, was described by Miura and co-workers.[26]

Electron-Deficient Alkene Group as a Secondary Electrophile

A Rh-catalyzed tandem cyclization involving arylboronate esters bearing a pendant Michael acceptor alkene and various strained olefins has been developed to give highly functionalized polycyclic systems (Scheme 30).[27] The catalytic system involved the use of an electron-rich, sterically bulky ligand to stabilize the organorhodium intermediate and reduce the incidence of protodeboronation in aqueous media. The arylrhodium(I) species generated by transmetalation adds to the carbon–carbon double bond on the *exo* face. In the resulting alkylrhodium(I) species, rhodium is presumably coordinated to the internal pendant olefin. Subsequent carborhodation occurs by a 5-*exo*-trig process to generate the rhodium(I) enolate, which is rapidly protodemetalated by water. Finally, the fused indane product is released with regeneration of the hydroxorhodium(I) species.

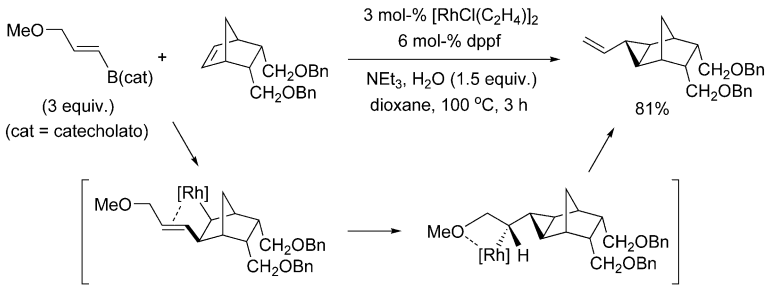
A similar Rh-catalyzed tandem cyclization reaction has been achieved by using a vinylboronate ester with extended conjugation (Scheme 31).[28] A vinylcyclopropanation reaction occurred through a rare 1,6-addition of an alkylrhodium(I) species in preference to 1,4-addition. The exclusive formation of a *Z* olefin was thought to be favored due to internal coordination of the carbonyl group, which locks the (oxa-π-allyl)rhodium(I) into one conformation.



Scheme 31.

Alkene Group as a Secondary Electrophile

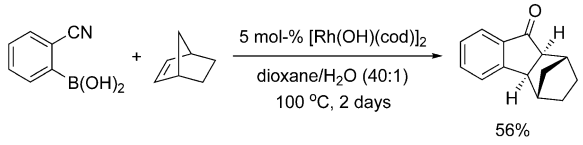
A vinylcyclopropanation reaction of a strained alkene has also been achieved by using an alkenylboronate ester bearing a methoxy group as a potential leaving group at the allylic position (Scheme 32).[18] The alkenylrhodium(I) species generated by transmetalation acts as an allylic carbene equivalent.



Scheme 32.

Cyano Group as a Secondary Electrophile

A [3+2] annulation has been reported in which 2-cyanoboronic acid reacted with strained alkenes despite the failure of the reaction with ordinary alkenes (Scheme 33).[8] When a chiral diene ligand was used, the corresponding indanone product was formed with good enantioselectivity (80% *ee*).



Scheme 33.

Conclusions

As shown in this review, Rh^I-catalyzed tandem transformations are of particular significance and a number of exciting protocols have been developed in recent years because these processes are powerful and straightforward tools for accessing complex structures from readily available starting materials. Although much progress has been made in this area, many challenges remain to be addressed. The development of asymmetric versions of some of these processes and their application in the synthesis of natural products or their analogues would significantly expand the scope of these methods. Undoubtedly, the title processes will continue to play a vital role in the synthesis of, in particular, cyclic compounds. Further exciting developments in this and related fields and further improvements in terms of the efficiency and scope of the reactions can be expected.

Acknowledgments

This work was supported by a Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea Government (MEST) (No. R01-2008-000-20332-0). We are grateful to the BK21 Foundation for generous support.

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Received: January 2, 2009
Published Online: March 12, 2009

