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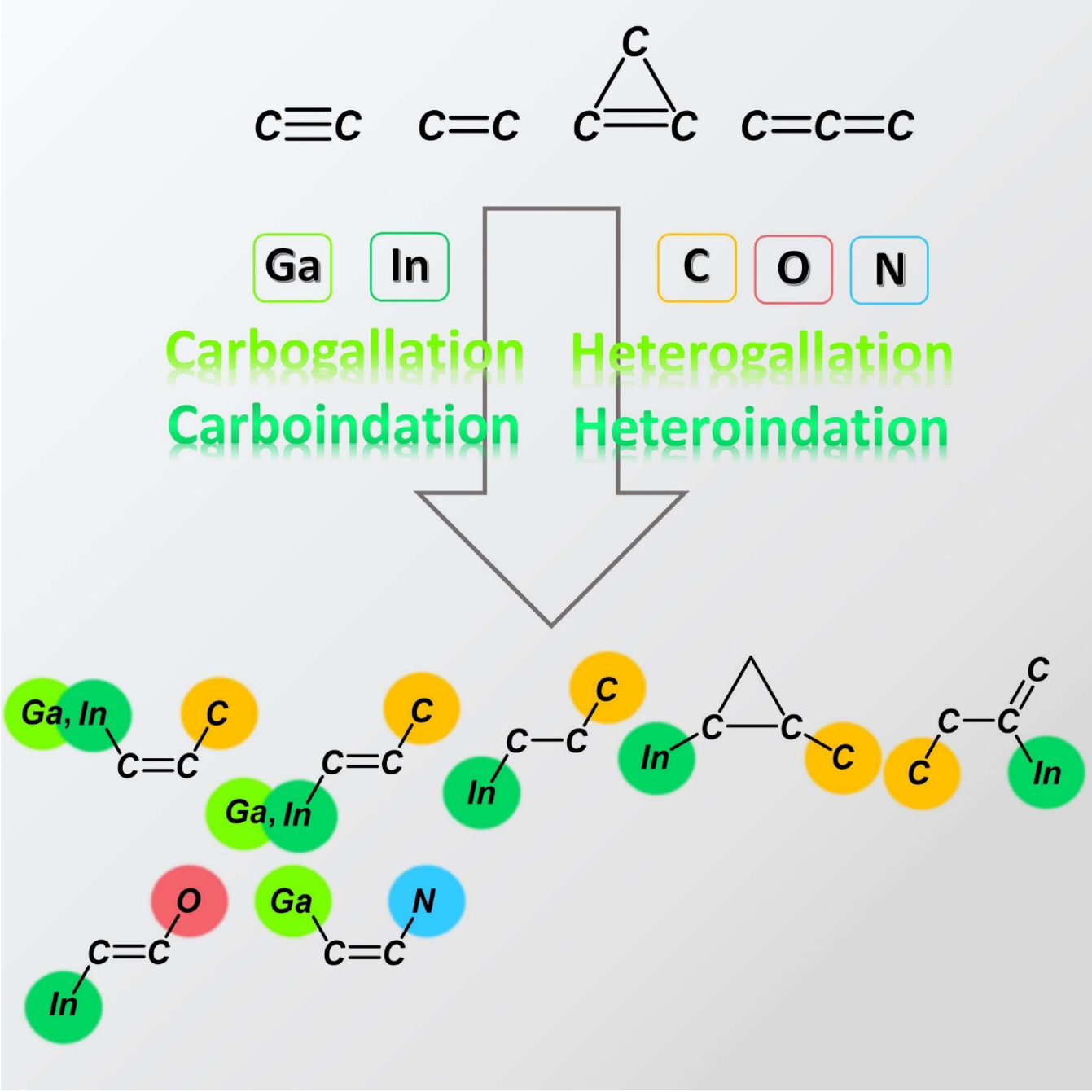
Special Collection

Carbometalation and Heterometalation of Carbon-Carbon Multiple-Bonds Using Group-13 Heavy Metals: Carbogallation, Carboindation, Heterogallation, and Heteroindation

Yoshihiro Nishimoto* and Makoto Yasuda*[a]



Abstract: Organogallium and -indium compounds are useful reagents in organic synthesis because of their moderate stability, efficient reactivity and high chemoselectivity. Carbogallation and -indation of a carbon-carbon multiple bond achieves the simultaneous formation of carbon-carbon and carbon-metal bonds. Heterogallation and -indation construct carbon-heteroatom and carbon-metal bonds. Therefore, these reaction systems represent a significant synthetic method for organogalliums and -indiums. Many chemists have attempted to apply various types of unsaturated compounds such as alkynes, alkenes, and allenes to these reaction systems. This minireview provides an overview of carboindation and -gallation as well as heteroindation and -gallation.

1. Introduction

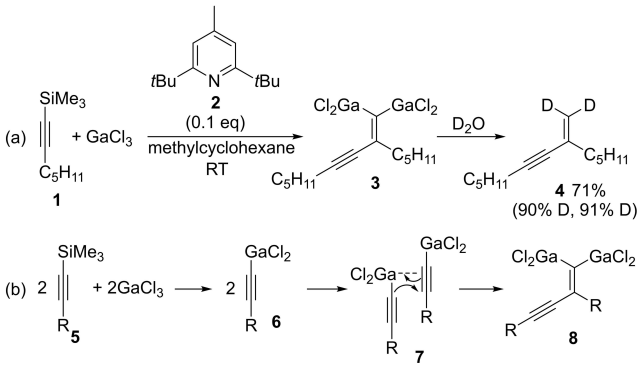
Carbometalation of a carbon-carbon multiple-bond is an important and powerful method for the synthesis of organometallic compounds because organometallics are produced by the formation of a new carbon-carbon bond.[1] There are many types of transition metal-catalyzed carbometalations, and most of them occur in a *syn*-addition fashion. Transition metal catalyst-free carbometalation is also an attractive reaction because toxic and expensive transition metals are not required. In several reports, highly reactive organometallic compounds such as organolithiums and Grignard reagents have been added directly to alkynes and alkenes. However, the high nucleophilicity of the organometallics that were used led to a lack of functional group tolerance. On the other hand, carbometalation using group-13 heavy metal species such as organogalliums and -indiums is a diverse reaction system with high chemoselectivity. This is because the Ga(III) and In(III) centers possess moderate Lewis acidity and high π-electron affinity that is caused by the large ionic radius, which leads to a compatibility with functional groups and to the activation of carbon-carbon multiple bonds, respectively.[2] Moderate reactivity of organogalliums and -indiums enables chemoselective reactions, and the organometallics produced by carbometalation are applicable to sequential reactions.[1,3] Carboindation via a radical mechanism is possible due to the stability of low-valent indium species. Therefore, the importance of carbogallation and carboindation has increased because of their usability and diversity. This review focuses on stoichiometric carbogallation and carboindation to synthesize organogalliums and organoindiums, respectively, and the application of these organometallic compounds to organic synthesis. Many excellent catalytic reactions, in which the catalytic cycle involves carbogallation and -indation, have been reported. In these cases, organogalliums and indium species are generated as transient intermediates, but are not afforded as final products. Therefore, the catalytic reactions are excluded in this review.[2] Additionally, heterometalation of carbon-carbon multiple bonds (heterogallation and heteroindation) is described. This is the reaction wherein new carbon-hetero atom bonds and new carbon-metal bonds are formed via the addition of hetero and metal atoms to the multiple bond.

2. Carbogallation of Carbon-Carbon Multiple-Bonds

2.1. Carbogallation with Organogalliums

The first carbogallation of alkynes was reported by Yamaguchi.[4] Treatment of alkynyltrimethylsilane with $GaCl_3$ in the presence of a catalytic amount of pyridine **2** gave dimeric product **4** after a workup with D_2O, and two deuterium atoms were introduced at an *exo*-methylene moiety of **4**, which suggested the possibility of a generation of **3** via carbogallation (Scheme 1a). The addition of pyridine **2** prevented origomerization of **4**. The reaction mechanism is shown in Scheme 1b. Transmetalation between **5** and $GaCl_3$ produces alkynylgallium **6**, and then carbogallation between two alkynylgallium **6** yields digallium compound **8**.

Allylgallium species generated by transmetalation between allylsilane **9** and $GaCl_3$ underwent *syn*-carbogallation (**13**) of alkynylsilane **1** (Scheme 2).[5] Takai reported that an allylgallium generated from allyl bromide **16** and Ga(0) was applicable to



Scheme 1. Carbogallation between alkynylgalliums generated by transmetalation of alkynylsilanes with $GaCl_3$.

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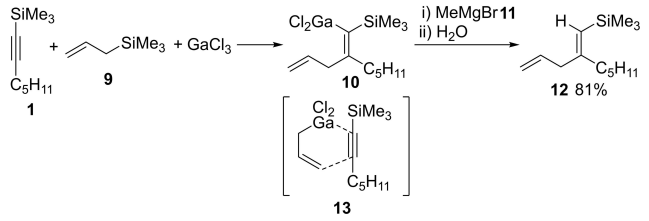
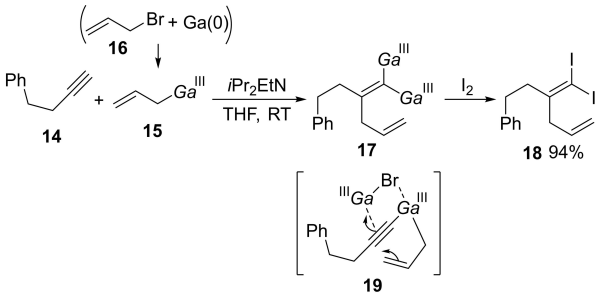


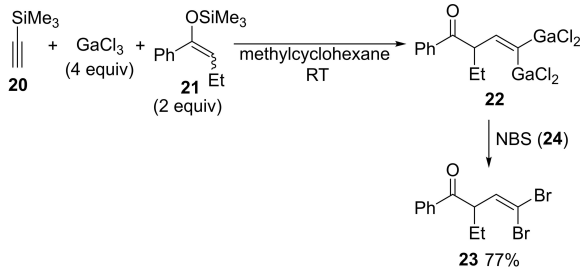
Scheme 2. Allylgallation of alkynylsilane with allylic gallium generated by transmetalation between allylic silane and $GaCl_3$.



Scheme 3. Allylgallation of terminal alkynes with allylic gallium generated from allylbromide and Ga(0).

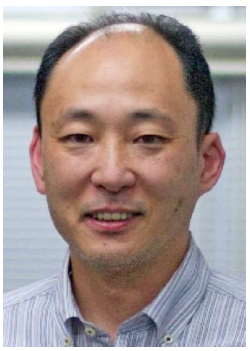
carbogallation of terminal alkynes (Scheme 3).[6] After alkyne **14** was reacted with allylic gallium **15**, quenching with I_2 gave 1,1-diiodoalkene **18**. Authors proposed the Ga(III)-assisted carbogallation of allyl alkynylgallium species **19**.

Yamaguchi reported that carbogallations of silyl acetylene **20** proceeded using $GaCl_3$ and silyl enolates (Scheme 4). Carbogallation of silylacetylene **17** with $GaCl_3$ and silyl enol ether was discovered.[7,8,9] Quenching with NBS (**24**) gave 1,1-dibromoalkene **23** (Scheme 4), which indicated the production of 1,1-dimetalated alkene **19** by carbogallation.



Scheme 4. Allylgallation of alkynylsilane with allylic gallium generated by transmetalation between allylic silane and $GaCl_3$.

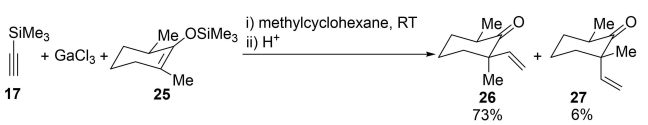
Yoshihiro Nishimoto received his Ph.D. degree in 2009 from Osaka University under the supervision of Prof. Akio Baba. He was appointed Assistant Professor at the Department of Applied Chemistry of Osaka University in 2009. At 2014, he moved to the Frontier Research Base for Global Young Researchers, Center for Open Innovation Research and Education (COiRE). He then became an Associate Professor (2020) at Department of Applied Chemistry of Osaka University. His research interests include the development of Lewis acid-catalyzed reactions and novel main-group metal catalysts.



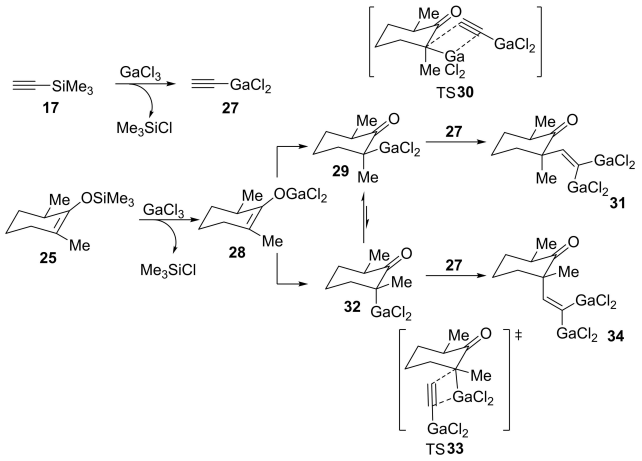
Makoto Yasuda received his Ph.D. degree in 1995 from Osaka University under the guidance of Prof. Akio Baba, and he was appointed Assistant Professor. During 1998–1999, he worked with Prof. J. M. Stryker as a postdoctoral fellow at the University of Alberta. After returning to Osaka University he was promoted to Associate Professor in 2004 and full Professor in 2014. He is currently interested in organic synthesis using main group metals, and in the development of new types of Lewis acids with a designed organic framework. He is also investigating reactive metal species that contribute to stereoselective carbon-carbon bond formation and their characterization based on spectroscopy and X-ray crystallographic analysis.

Carbogallation using silyl enol ether **25**, which is derived from a six-membered cyclic ketone, predominantly provided ethenylated cyclic ketone **26** with a equatorial vinyl group (Scheme 5).[10] Enolate ethenylation and alkylation display equatorial stereochemistry and axial stereochemistry, respectively. It is proposed that α-gallioketone is the reactive species rather than gallium enolate (Scheme 6). **25** and silyl acetylene **17** transmetalate with $GaCl_3$ to provide gallium enolate **28** and gallium acetylide **27**, respectively. **28** isomerizes to α-gallioketones **29** and **32**. There is an equilibrium between **29** and **32**, and **29** has a bulky $GaCl_2$ group at the equatorial position, which makes it more stable than **32**. Then, carbogallation of **27** with **29** preferentially proceeds to give 1,1-digallioalkene **31**.

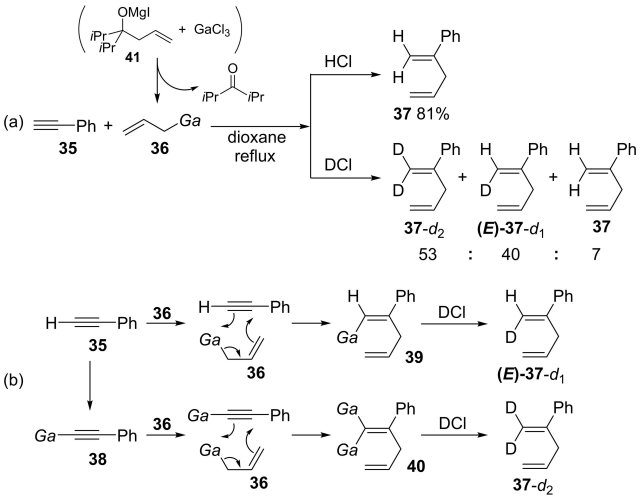
Yorimitsu and Oshima disclosed carbogallation of alkynes using allylic galliums generated by retro-allylation (Scheme 7a).[11] Allylic gallium **36** was produced by retro-allylation between homoallyl alkoxide **41** and $GaCl_3$, and then reacted with alkyne **35** to give product **37** after quenching with an aqueous solution of HCl. Quenching with DCl instead of HCl afforded di- and monodeuterated products (**37**-d_2 and (*E*)-**37**-d_1). Based on a DCl-quenching experiment, a *syn*-addition mechanism was proposed (Scheme 7b). Allylgallation of alkyne **35** with **36** proceeds via a six-membered transition state to give



Scheme 5. Carbogallation using silyl enol ether **25** derived from a six-membered cyclic ketone.



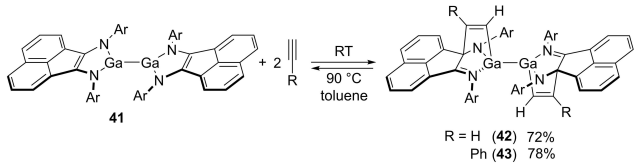
Scheme 6. Plausible reaction mechanism for carbogallation using silyl enolates and $GaCl_3$.



Scheme 7. Carbogallation of alkynes using allylic galliums produced by retro-allylation of homoallylic alcohols with $GaCl_2$.

alkenylgallium **39**. Meanwhile, deprotonation of alkyne **35** by basic allylic gallium gives alkynylgallium **38**. The *syn*-addition of **36** to **38** yields 1,1-metalated alkene **40**.

1,2-Bis(arylimino)acenaphthene (bian) ligands have attracted much attention. The synthesis of (dpp-bian)Ga–Ga(dpp-bian) complex **41** and reversible carbogallation of alkynes with **41** was reported (Scheme 8).[12] When treatment of a solution of **41** with acetylene or phenylacetylene was carried out, the Ga–N–C fragment was added to the alkynes to provide carbon-carbon and carbon-gallium bonds and to give alkenyl gallium



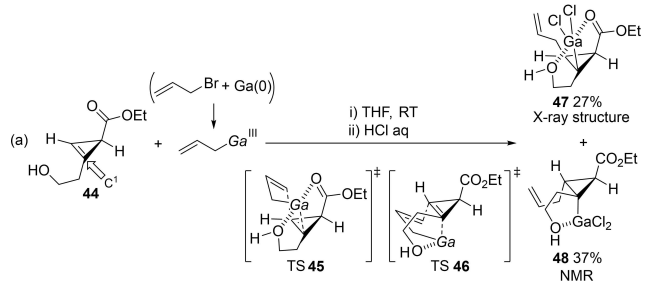
Scheme 8. Synthesis of (dpp-bian)Ga–Ga(dpp-bian) complex by carbogallation.

42 or **43**, respectively. These organogalliums were identified by single-crystal X-ray analysis. The carbogallation was reversible, and the equilibrium between **43** and **41** + phenyl acetylene was studied by ^{1}H NMR spectroscopy.

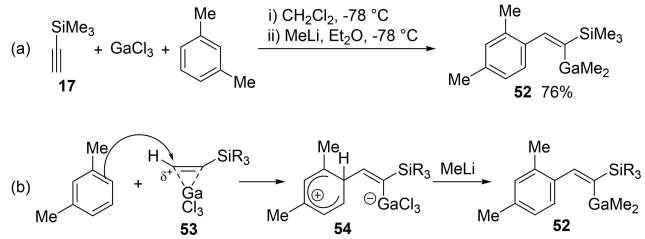
Carbogallation of a carbon-carbon double bond was established using allylgallium species. Araki reported a regioselective allylgallation of cyclopropenes (Scheme 9).[13] The reaction of the allylic gallium with cyclopropene **44** bearing a hydroxyalkyl group on the C^1 carbon gave cyclopropylgallium products **47** and **48**. The structure of **47** was revealed by X-ray diffraction analysis. Therefore, the coordination of the hydroxy group to a Ga atom in the allylic gallium was classified as *anti*-Markovnikov regioselectivity (TS **45** and TS **46**).

2.2. Carbogallation of Gallium Trihalide-Activated Carbon-Carbon Multiple-Bond

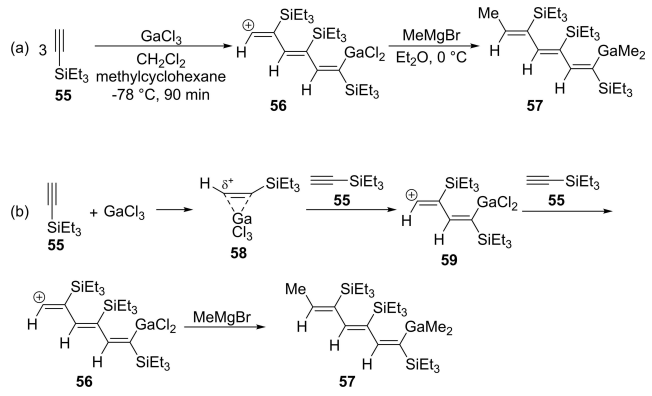
A reaction of silyl acetylene with $GaCl_3$ and nucleophilic arenes was carried out, followed by treatment with MeLi to gave alkenyldimethylgallium **52** (Scheme 10a).[14] π-Complex **53** was formed from $GaCl_3$ and vinyl *tert*-butyldimethylsilane and identified at −78 °C via NMR spectroscopy (Scheme 10b). Carbogallation proceeds via the regioselective nucleophilic attack of an arene at the β-carbon atom of a silyl group to give zwitterion intermediate **54**. Finally, a proton abstract and ligand exchange by MeLi produce alkenylgallium **52**. In the absence of nucleophilic arenes, ethynylsilane **55** was trimerized via alkenylgallation caused by $GaCl_3$ (Scheme 11a).[15] The reaction of $GaCl_3$ with 3 equivalents of **55** in CH_2Cl_2 and methylcyclohexane at −78 °C gave trienyl cation **56**. Interestingly, the cation intermediate **56** was identified by ^{1}H and ^{13}C NMR spectroscopies. MeMgBr in Et_2O was then added to the solution of **56** to



Scheme 9. Carbogallation of cyclopropenes using allylic galliums.



Scheme 10. Carbogallation of silyl acetylene with $GaCl_3$ and nucleophilic arenes.



Scheme 11. Trimerization of silyl acetylene via carbogallation.

produce alkenylgallium **57**. Proposed mechanism is shown in Scheme 11b. The reaction is initiated with the activation of **55** by $GaCl_3$, and then the nucleophilic addition of another **55** gives alkenyl cation **59**. The cation **59** is converted to trienyl cation **56** by the addition of **55**. Finally, the treatment of MeMgBr produces trienylgallium compound **57**.

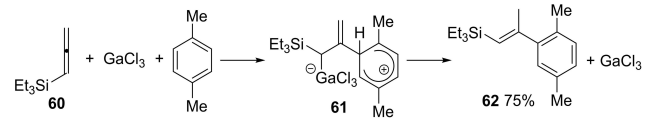
Silyl allene **60** also underwent carbogallation with $GaCl_3$ and *p*-xylene (Scheme 12).[16] In this case, however, an intramolecular proton transfer in zwitterion alkylgallium species **61**, which was formed by the carbogallation, occurred to give alkenylsilane **62** and $GaCl_3$, so a stable organogallium product was not obtained.

We reported the regio- and stereoselective *anti*-carbogallation of alkynes using $GaBr_3$ and silyl ketene acetals (Scheme 13).[17] Alkyne **63** was treated with $GaBr_3$ and silyl ketene acetal **64** to give dialkenylgallium **65** (Scheme 13a). The structure of **65** was determined by X-ray diffraction analysis after complexation with pyridine (**65**·pyridine). That result suggested carbogallation occurred as shown in Scheme 13b. The interaction between $GaBr_3$ and a carbon-carbon triple bond of alkyne **63** causes the regioselective nucleophilic attack of **64** from the opposite site of $GaBr_3$ to provide monoalkenylgallium **64** and Me_3SiBr.

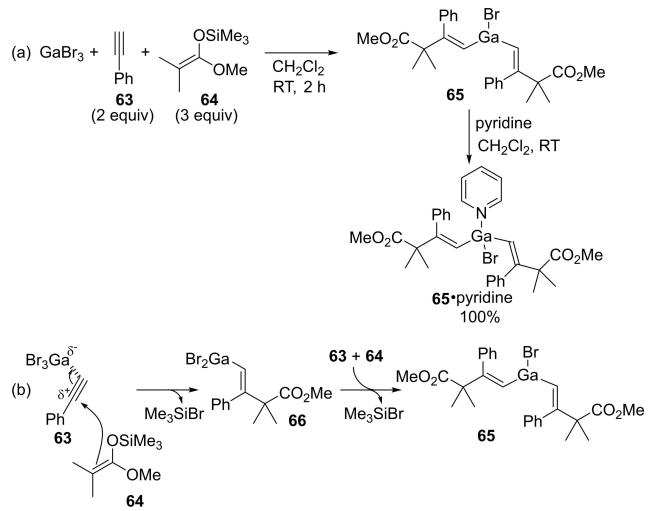
Synthesized alkenylgalliums were directly applied to Pd-catalyzed cross-coupling with aryl iodides (Scheme 14). Various types of functional groups were compatible with alkenylgalliums, and 4-acetyliodobenzene, 2-iodopyridine as well as iodobenzene smoothly coupled with alkenylgalliums (**65** or **66**) to give the corresponding trisubstituted alkene products (**67**, **68**, and **69**). The use of phosphine ligands for a Pd-catalyst is not necessary to the cross-coupling of organogalliums (and organoindiums) in highly-coordinative solvents such as DMF perhaps because the solvents could work as efficient ligands.

The developed process for trisubstituted alkene synthesis via carbogallation/cross-coupling was employed for the first total synthesis of nodosol **75** (Scheme 15). The key synthetic intermediate, diene **72**, was regio- and stereoselectively prepared by carbogallation of enyne **70** followed by cross-coupling using 4-bromoiodobenzene.

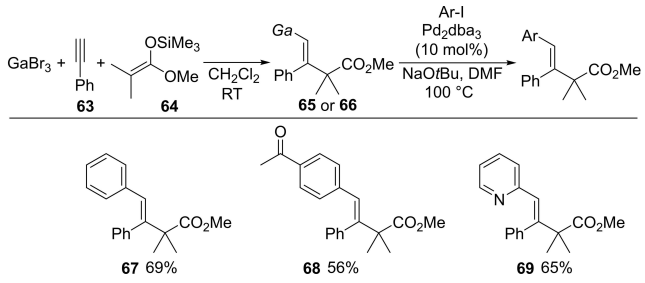
We discovered that vinyl ether **76** underwent carbogallation with $GaBr_3$ and silyl ketene acetal **77** at low temperature to give β-phenoxyalkylgallium species **78** (Scheme 16).[18] Interestingly, the *syn*-elimination of phenoxygallium from **78** via transition state **79** occurred at room temperature to give α-vinyl ester **80**.



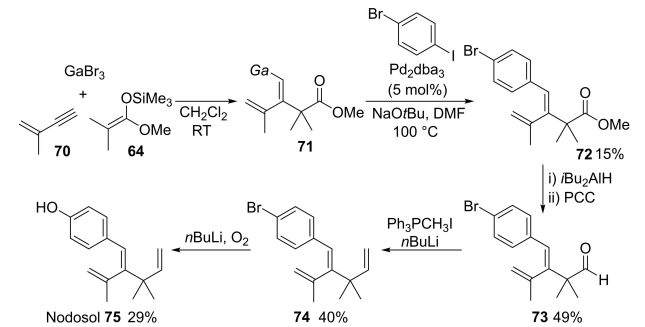
Scheme 12. Carbogallation of silyl allene with $GaCl_3$ with *p*-xylene.



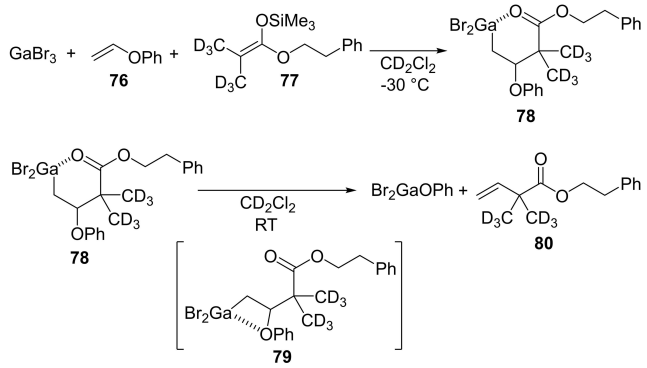
Scheme 13. Regio- and stereoselective *anti*-carbogallation of alkynes using $GaBr_3$ and silyl ketene acetals.



Scheme 14. Regio- and stereoselective synthesis of trisubstituted alkenes by using carbogallation/cross-coupling sequential process.

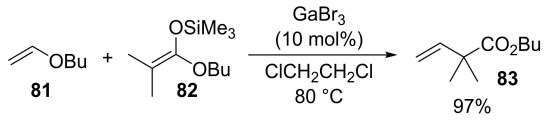


Scheme 15. The first total synthesis of nodosol via carbogallation/cross-coupling sequential process.



Scheme 16. Carbogallation of vinyl ether **76** with $GaBr_3$ and silyl ketene acetal **77**, and β-elimination of phenoxygallium to give α-vinyl ester **80**.

Therefore, the authors established the first catalytic cross-coupling of alkenyl ethers with silyl ketene acetals. Vinyl ether **81** was coupled with silyl ketene acetal **82** in the presence of $GaBr_3$ catalyst to produce α-vinyl ester **83** (Scheme 17). Silyl ketene imines were also applicable to this cross-coupling system.[19] A proposed catalytic cycle is shown in Figure 1. $GaBr_3$ is coordinated by alkenyl ether **1**, and then the anti-carbogallation of the activated **81** with silyl ketene acetal **82** occurs regioselectively to give alkylgallium **85** and Me_3SiBr. After conformation change from six-membered **85** to four-membered **86**, *syn*-elimination of Br_2GaOBu proceeds to give coupling product **83**. Finally, $GaBr_3$ is regenerated by transmetalation between Br_2GaOBu and Me_3SiBr.



Scheme 17. Catalytic coupling reaction of vinyl ether **81** with silyl ketene acetal **82.**

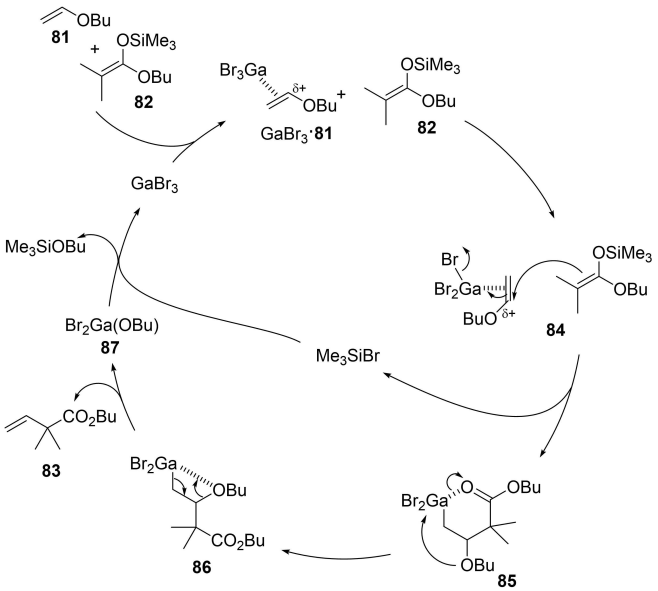
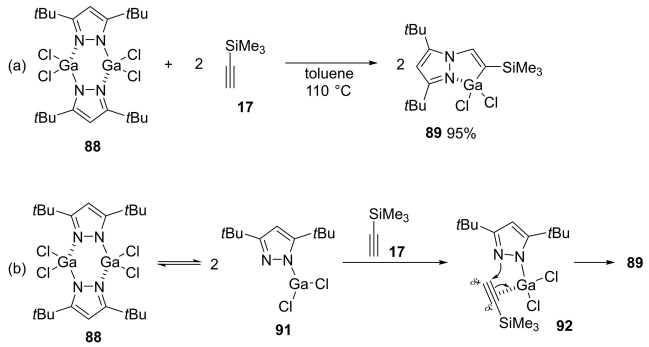


Figure 1. Proposed mechanism of $GaBr_3$-catalyzed cross-coupling between vinyl ethers with silyl ketene acetals.

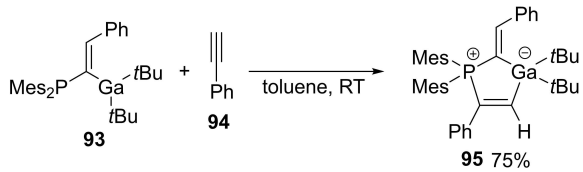
3. Heterogallation of Carbon-Carbon Multiple-Bonds

Zheng and Yang demonstrated the first synthesis and characterization of pyrazolato gallium dichlorides and its application to azagallation of alkynes.[20] When pyrazolato gallium dichloride **88** was mixed with silyl acetylene, azagallation of the carbon-carbon triple-bond gave pyrazolato alkenylgallium **89** (Scheme 18a). The reaction mechanism remains unclear, but the more reactive three-coordinated gallium species **91** is proposed (Scheme 18b). The gallium center of **91** activates silyl acetylene by π-coordination, and the intramolecular nucleophilic attack by a β-nitrogen of the Ga atom causes azagallation.

Uhl synthesized Ga/P complex **93** with the geminal arrangement of coordinatively unsaturated Ga and P atoms.[21] When **93** was mixed with alkyne **94**, phosphagallation of a carbon-carbon triple bond occurred to give five-membered heterocycle **95** involving P and Ga atoms (Scheme 19). The terminal C atom of alkyne **94** has its relatively high negative partial charge to bind to the electropositive Ga atom, and the relatively positive internal C atom binds to the electronegative P atom.



Scheme 18. Azagallation of alkyne with pyrazolato gallium dichloride **88.**



Scheme 19. Phosphagallation of a carbon-carbon triple bond by Ga/P FLPs complex.

4. Carboindation of Carbon-Carbon Multiple-Bonds

4.1. Carboindation with Organoindiums

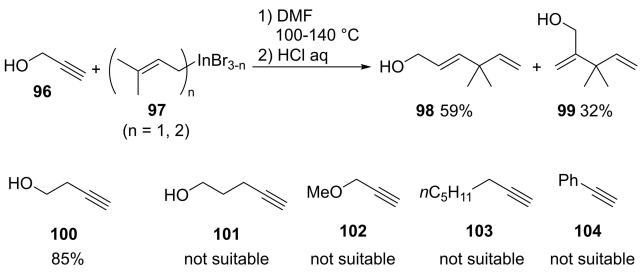
Various carboindations using allylindiums generated by the reaction of In(0) with allylic halides have been reported. Butsugan developed the first carboindation of alkynols in 1992 (Scheme 20).[22] The carboindation of alkynol **96** with allylic indium **97** proceeded via a syn addition mechanism to give *anti*-Markovnikov adduct **98** and Markovnikov adduct **99**. The reaction using 3-butyn-1-ol **100** gave a high yield, but 4-pentyn-1-ol **101**, 3-methoxy-1-propyne **102**, 1-octyne **103**, and phenylacetylene **104** were not suitable to these conditions. Therefore, a hydroxy group near the triple bond is important in the carboindation.

The regioselectivity depended on the structures of alkynols and allylic indiums (Scheme 21a). The reaction using sterically hindered alkynol **105** and allylic indium **106** showed perfect regioselectivity. A proposed reaction mechanism is shown in Scheme 21b. A hydroxy group coordinates to an indium atom of allylic indium **97**. The allyl group on the coordinated indium atom adds to the terminal carbon of alkynol **96** and the indium adds to the inner carbon.[23]

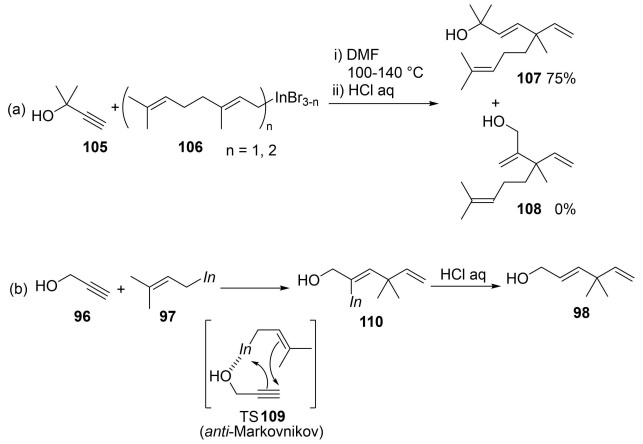
Yamamoto[24] and Ranu[25] independently reported the carboindation of unactivated alkynes using allylic indiums (Scheme 22). In contrast to the DMF solvent conditions, aromatic alkyne **111** and aliphatic alkyne **114** without a directing group such as a hydroxy group smoothly underwent carboindation using an allylic indium under THF solvent conditions to give dienes **113** and **115**, respectively (Scheme 22a and 22b). Quenching with DCl/D_2O afforded an *E/Z* mixture of deuterated diene product **115** (Scheme 22b). Therefore, the carboindation of an alkyne with an allylic indium proceeds via *syn*-addition fashion (**116**) to produce alkenyindium **117**, which undergoes *E-Z* isomerization (Scheme 22c).

Carboindation of alkynes using benzylic indiums was also reported by Yamamoto (Scheme 23).[24b] The benzylindation of aromatic alkyne **111** occurred in an *anti*-addition manner (Scheme 23a), while that of aliphatic alkyne **114** took place in a nonstereoselective fashion (Scheme 23b). As in the case of allylindation, *syn*-addition followed by *E-Z* isomerization occurred. The produced alkenylindium **122** coupled with benzyl iodide in the presence of a palladium catalyst to give three-component coupling product **123** in 49% yield (Scheme 23c).

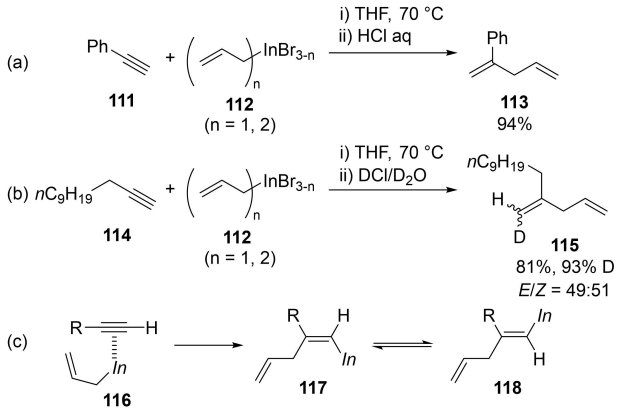
Intramolecular cyclizations of alkynes bearing an allylic bromide moiety via allylindation were reported. Salter discovered that In(0) mediated the cyclization of **123** to give cyclic compound **124** (Scheme 24a).[26] The allylic indium moiety of **125**, which generated by the reaction of allylic bromide **123** with In(0), adds to an intramolecular carbon-carbon triple bond in a *syn* fashion, giving alkenylindium **126**, regio- and stereo-



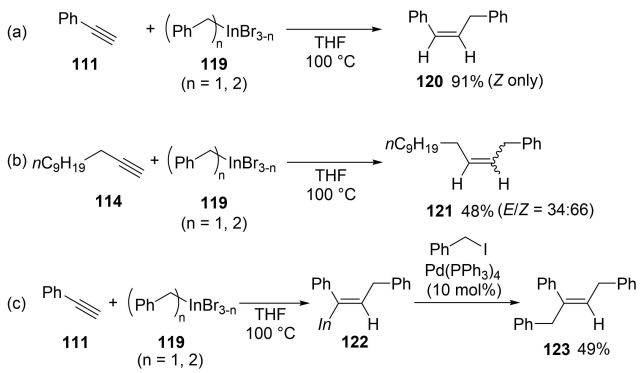
Scheme 20. Carboindation of a carbon-carbon triple-bond nearby a hydroxy group.



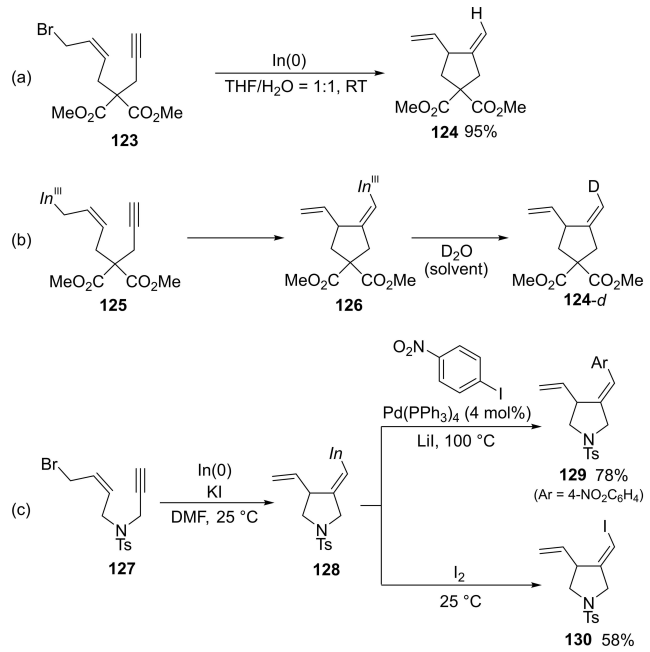
Scheme 21. Regioselectivity and plausible mechanism for carboindation of alkynols with allylic indiums.



Scheme 22. Carboindation of unactivated alkynes using an allylic indium.



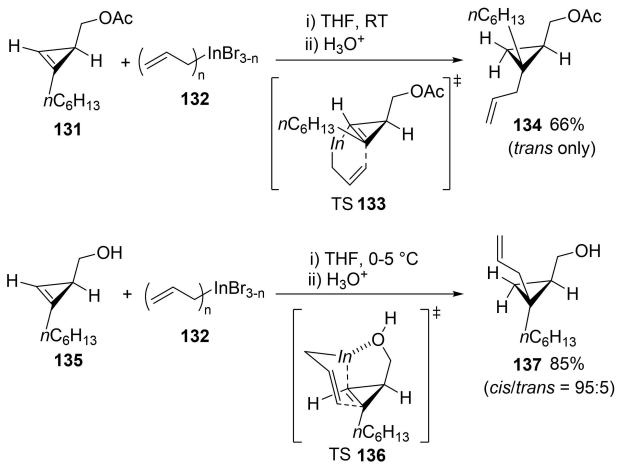
Scheme 23. Benzylindation of alkynes using benzylic indium species.



Scheme 24. Intramolecular allylindation via the addition of an allylindium moiety to a carbon-carbon triple bond.

selectively (Scheme 24b). Actually, the use of D_2O instead of H_2O stereoselectively gave deuterated product **124**-*d*. Lee reported an improved intramolecular cyclization system (Scheme 24c).[27] The cyclization of **127** in DMF smoothly proceeded without an H_2O co-solvent, and the addition of KI was a key factor. The produced alkenylindium 128 was successfully coupled with an aryl iodide or I_2.

Araki and Butsugan discovered the stereodivergent allylindation of cyclopropene derivatives (Scheme 25).[28] In a reaction of cyclopropene **131** with allylic indium **132**, the allylic indium was added preferentially from the anti-face of the acetoxymethyl group (TS **133**) to avoid steric repulsion with the acetoxymethyl group, and the allylic group was introduced to



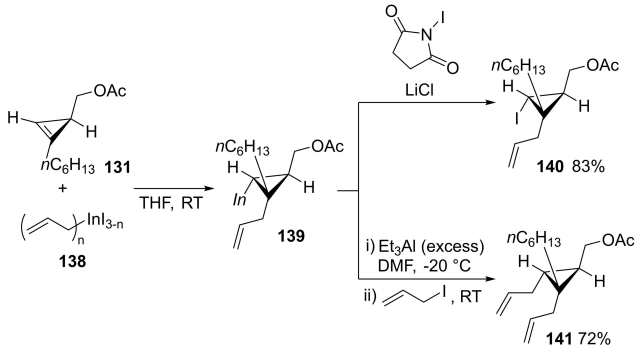
Scheme 25. Allylindation of cyclopropenes by allylic indiums and its stereoselectivity controlled by a functional group.

the substituted carbon of the cyclopropene double bond to give product **134**. In contrast, the stereoselectivity of allylindation into cyclopropene **135** was reversed to that of acetate **131**, although the regioselectivity was not changed. This result suggested that the coordination of the hydroxy group to an allylic indium species led to allylindation from the cis face of the hydroxymethyl group (TS**136**).

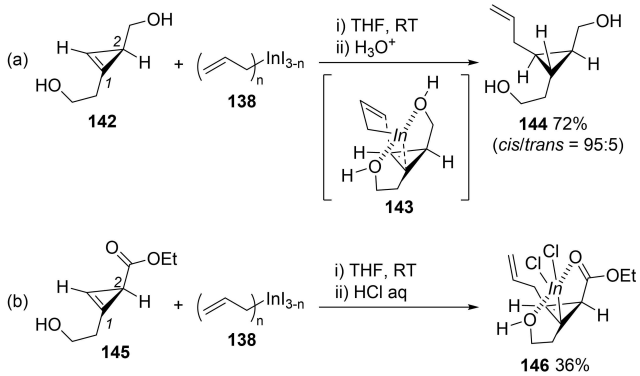
The generated cyclopropylindiums were applicable to further transformations (Scheme 26).[29] The treatment of generated cyclopropylindium **139** by I_2 and LiCl afforded iodo cyclopropane derivative **140**. In addition, cyclopropylindium **139** coupled with allyl iodide to give diallyl propane **141** in the presence of an excess amount of Et_3Al, in which a kind of cyclopropylindium ate-complex generated by the reaction of **139** with Et_3Al would be an active nucleophile.

Interestingly, the allylindation of cyclopropene **142** bearing a hydroxyalkyl group at a 1-position as well as at a 2-position took place with the opposite regioselectivity in the reaction of **135** (Scheme 27a).[30] The coordination of a hydroxy group hanging on the 2-position to an indium center of **142** in TS**143** caused a drastic change in the regioselectivity. The X-ray crystal structure of cyclopropylindium **146** synthesized by allylindation of cyclopropene **145** bearing 2-hydroxyethyl and ester groups at the C^1 and C^2 carbons, respectively (Scheme 26b).

Other strained olefins underwent carboindation with allylic indium reagents. Allylindation of norbornenol **147** regio- and



Scheme 26. Transformation of cyclopropylindiums produced by carboindation.

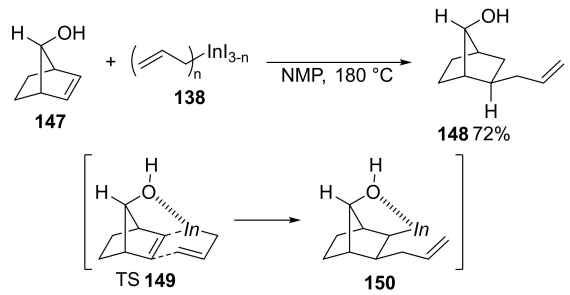


Scheme 27. Inverse of regioselectivity by coordination of a hydroxy group in carboindation of cyclopropenes.

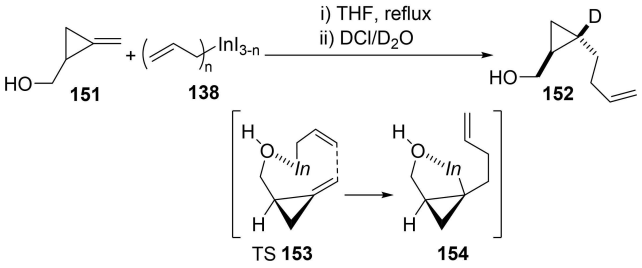
stereoselectively proceeded to give allylated product **148**, and the allylic group was installed exclusively from the *exo* face (Scheme 28).[31] Therefore, the hydroxy group of **147** acts as a director to lead the carboallylation on the *exo* face (TS **149**).

The reaction of methylenecyclopropane **151** with allylic indium species **138** exclusively gave deuterated cyclopropane **152** after carrying out a 1 M DCl/D_2O quench (Scheme 29).[32] Regio- and setereoselective allylindation occurred owing to the coordination of a hydroxyl of **151** to an indium center (TS**153**).

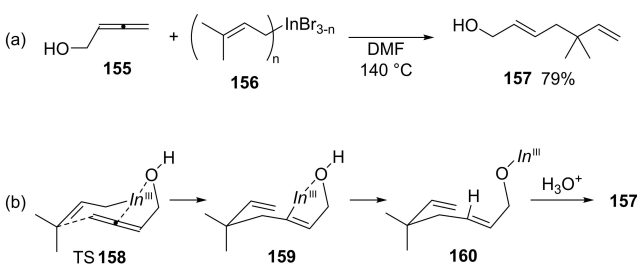
Araki and Butsugan developed carboindation of allenols using an allylic indium species.[33,34] The regio- and stereoselective addition of prenylindium species **156** to an allene moiety of allenol **155** proceeded to afford product **157** (Scheme 30a). *O*-protected allenols were not applicable to this carboindation system, which suggested the importance of an hydroxy group for effective carboallylation. A plausible reaction mechanism is shown in Scheme 30b. The carboindation regio- and stereoselectively proceeds through hydroxyl-chelated bicyclic transition state TS**158** to give alkenylindium **159**, and **159** was protonated by an internal hydroxy group to afford indium alkoxide **160**.



Scheme 28. Carboindation of norbornenol **147** with allylic indium **138.**



Scheme 29. Carboindation of methylenecyclopropane **10** with allylic indium **2.**



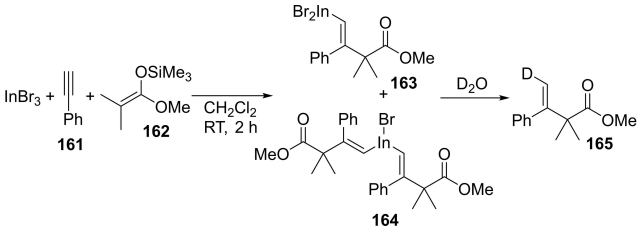
Scheme 30. Carboindation of allenols using an allylic indium species.

4.2. Carboindation of Indium Trihalide-Activated Carbon-Carbon Multiple-Bond

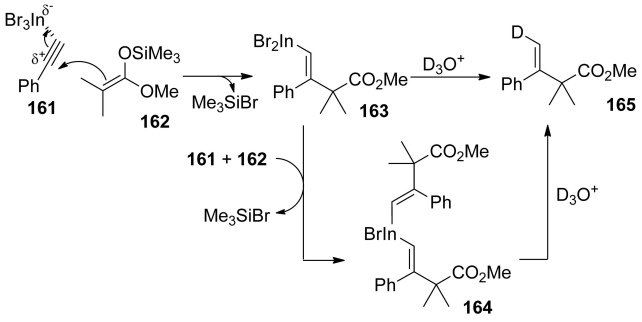
We reported the carboindation of alkynes using $InBr_3$ and silyl ketene acetals.[35] When alkyne **161** was treated with $InBr_3$ and silyl ketene acetal **162**, carboindation regio- and stereoselectively occurred to give alkenylindiums **163** and **164** (Scheme 30). The treatment of **163** and **164** with D_2O afforded deuterated **165**. The reaction mechanism is illustrated in Scheme 31. The activation of alkyne **161** by $InBr_3$ increase the positive charge on the internal carbon of **161**. The nucleophilic attack by silyl ketene acetal **162** to the internal carbon from the opposite side of the coordinated $InBr_3$ to give monoalkenylindium **163**. The successive addition of the resulting **163** to another **161** afforded dialkeynylindium **164** with the same selectivity. The moderate Lewis acidity and high π-electron affinity of $InBr_3$ plays an important role in the effective activation of alkynes in the presence of coordinative ketene silyl acetals. In contrast, the use of strong Lewis acids such as $AlCl_3$ and $BF_3{\cdot}OEt_2$ strongly interacted with an oxygen atom of ketene silyl acetals, which resulted in no reaction.

Scheme 32 illustrates the *anti*-carboindation mechanism. The activation of alkyne **161** by $InBr_3$ takes place to increase the positive charge on the internal carbon of the alkyne. Ketene silyl acetal **162** attacks the internal carbon from the opposite side of the $InBr_3$ to give monoalkenylindium **163**. The successive addition of **163** to another alkyne **161** produces dialkeynylindium **164**. Quenching with D_2O affords deuterated compound **165**.

The treatment with I_2 gave iodinated β,γ-unsaturated ester **166**, and Pd-catalyzed cross-coupling of the synthesized alkenylindium with iodobenzene in a one-pot manner gave



Scheme 31. Carboindation of alkynes using $InBr_3$ and silyl ketene acetals.



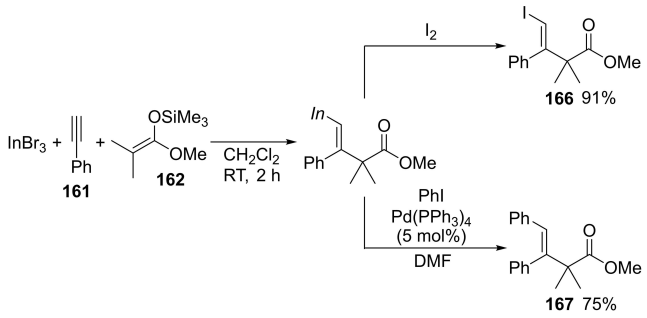
Scheme 32. Plausible reaction mechanism for carboindation of alkyne **161** using $InBr_3$ and silyl ketene acetal **162.**

coupling product **167** (Scheme 33). In both reactions, the configuration of the corresponding alkenylindium was retained.

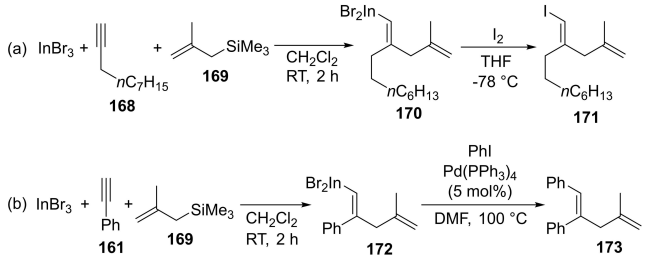
The regio- and stereoselective carboindation of alkynes using $InBr_3$ and allylic silanes was developed.[36] This is the first report of the stereoselective *anti*-allylindation of alkynes. The carboindation of 1-decyne **168** followed by the quenching of alkenylindium **170** with I_2 gave **171**, regio- and stereoselectively (Scheme 34a). The produced 1,4-dienylindium **172** was applicable to Pd-catalyzed cross-coupling (Scheme 34b).

We also established *anti*-carboindation of alkynyl ethers using InI_3 and organosilicons or –stannanes (Scheme 35).[37] The interaction between InI_3 and an alkynyl ether is accelerated by the conjugative electron-donation of an oxygen atom bonding an alkyne moiety, which revealed by DFT calculations. The carboindation of alkynyl ether **174** using InI_3 and silyl ketene acetal **175** gave metalated enol ether **176** (Scheme 35a). The iodination of **176** afforded trisubstituted enol ether **178** regio- and stereoselectively (Scheme 35b), as well as various nucleophiles such as silyl ketene imine **179**, alkynyl stannane **182** (Scheme 35c and 35d).

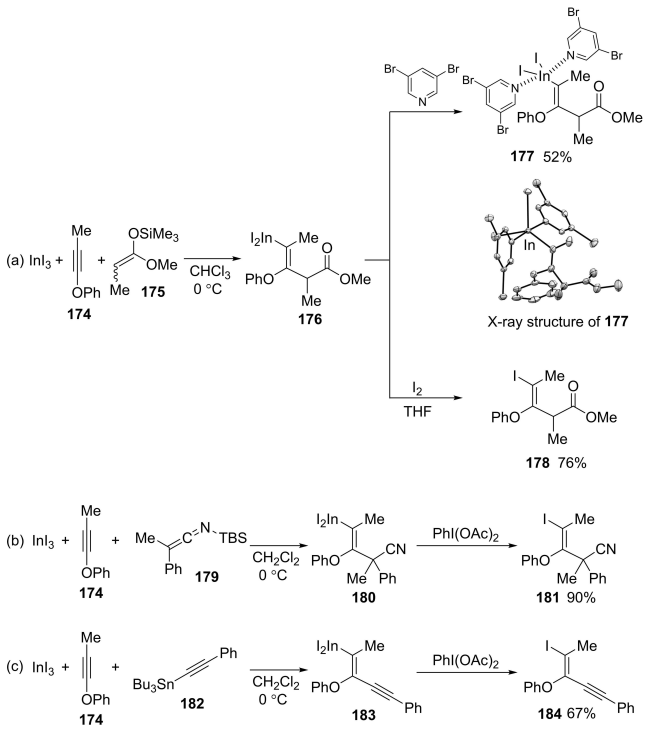
An indium trihalide effectively activates simple alkenes (Scheme 36).[38] The regioselective carboindation of 1-hexene **185** using $InBr_3$ and silyl ketene acetal **162** proceeded to give alkylindium **186** (Scheme 36a). The structure of **186** was revealed by X-ray diffraction analysis. The crystal structure of alkylindium **188** was afforded by the carboindation of cyclohexene **187** and showed an *anti*-addition mechanism (TS**189**) (Scheme 36b). Alkylindium **191** was treated with 1 M HBr and $PhI(OAc)_2$ to give the corresponding protonated product **192** and brominated product **193**, respectively (Scheme 36c).



Scheme 33. Transformation of alkenylindiums synthesized by carboindation.



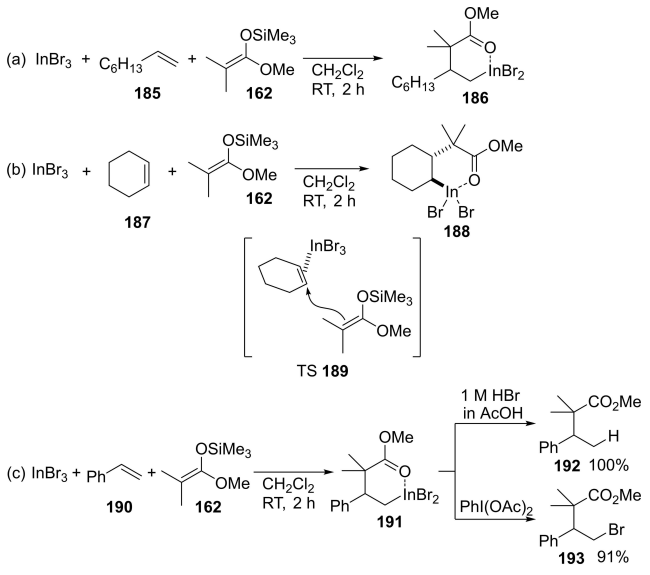
Scheme 34. *Anti*-allylindation of alkynes using $InBr_3$ and allylic silanes.



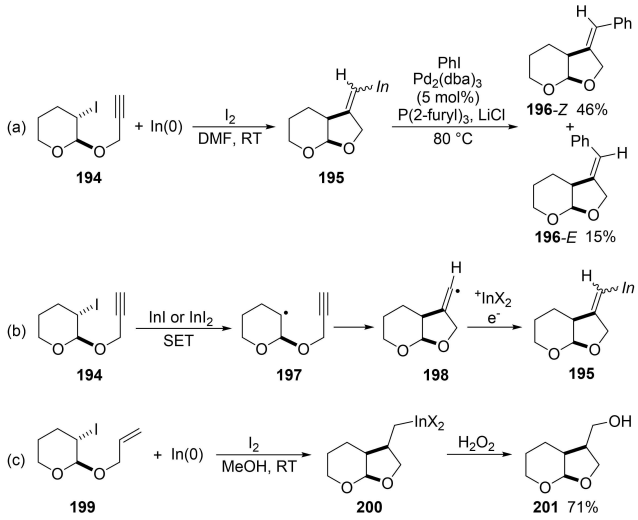
Scheme 35. *Anti*-carboindation of alkynyl ethers using $InBr_3$ and organosilicon- or stannane compounds.

4.2. Carboindation via Radical Mechanism

Takemoto discovered indium-mediated reductive radical cyclization of alkynes bearing an iodoalkane moiety by using a low-valent indium species (Scheme 35). Treatment of alkyne **194** with In(0) and I_2 promoted 5-*exo* cyclic carboindation to give alkenylindium **195** (Scheme 37a).[39] The generated alkenylindium **195** was coupled with iodobenzene in the presence of a Pd catalyst to give an *E*/*Z* isomer mixture **196**. A proposed



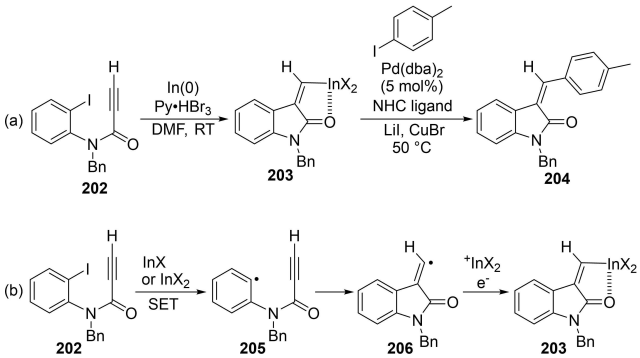
Scheme 36. Carboindation of unactivated alkenes and transformation of produced alkylindiums.



Scheme 37. Cyclic carboindation through alkyl radical intermediate produced by reduction of alkyl iodide with row-valent indium species.

mechanism is illustrated in Scheme 37b. The single electron transfer (SET) from a low-valent indium iodide species, which is generated from In(0) and I_2, to **194** provides alkyl radical **197**. The radical **197** then undergoes a radical cyclization to produce alkenyl radical **198**, and then the radical reductively combines with an indium cation ($^{+}InX_2$) to give the *E*/*Z*-mixture of alkenylindium **195**. Alkene **199** with an iodoalkyl moiety was also applicable to this reductive radical cyclization, and stable alkylindium **200** was isolated (Scheme 37c).[40] The alkylindium **200** underwent oxidation by H_2O_2 to give the corresponding primary alcohol **201**.

A reductive radical cyclization of iodoarene bearing an alkynylamide moiety by using In(0)/pyridinium tribromide ($PyHBr_3$) occurred regio- and stereoselectively to produce 3-alkylideneoxindoles **203** (Scheme 38a).[41] In the reaction mechanism (Scheme 38b), either InBr generated from In(0) or $InBr_2$ generated from $PyHBr_3$ could mediate the radical carboindation of iodoarene **202**, and the coordination of the amide group to an indium atom led to the high stereoselectivity. **202** underwent SET from a low-valent indium species to afford sp^2-σ radical **205**. The radical **205** produces alkenyl radical **206** via



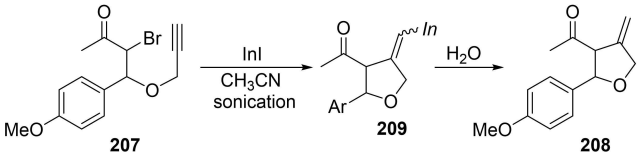
Scheme 38. Cyclic carboindation by reduction of aryl iodide with row-valent indium species.

radical cyclization, and then the radical exclusively gives an *E*-isomer of alkenykindium **203** due to the strong coordination of the amido moiety to the indium center. The generated alkenylindium **203** was applied to Pd-catalyzed cross-coupling with 4-iodo toluene.

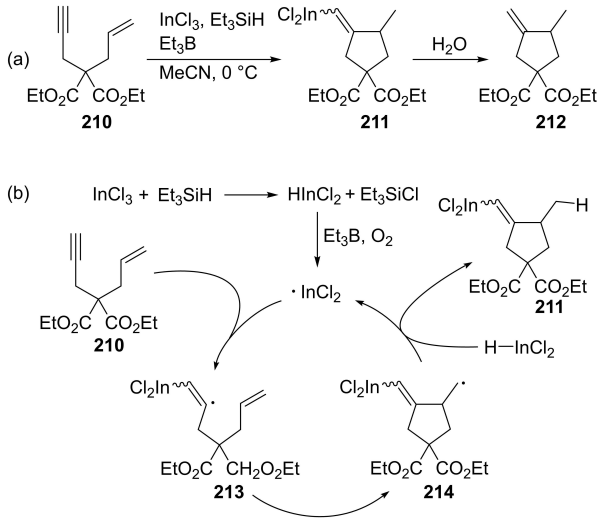
Ranu reported the InI-mediated cyclization of α-carbonyl bromo-alkynes (Scheme 39).[42] The treatment of α-carbonyl bromo-alkyne **207** with InI gave 4-methylene-tetrahydrofuran **208** via 5-*exo* cyclization. Alkenylindium **209** would be produced via InI-mediated reductive radical carboindation.

Shibata and Baba established the carboindation of alkynes and allenes via indium hydride-mediated radical cyclization. Enyne **210** underwent cyclization in the presence of $HInCl_2$, which was generated from $InCl_3$ and Et_3SiH, to give *exo*-methylene compound **212** through alkenylindium **211** (Scheme 40a).[43] A proposed mechanism is shown in Scheme 40b. Transmetalation between $InCl_3$ and Et_3SiH gives $HInCl_2$, and then the Et_3B/O_2 system generates a dichloroindium radical ($\cdot InCl_2$) from $HInCl_2$. The indium radical adds to an alkyne moiety of **210** to produce alkenyl radical **213**. Alkyl radical **214** is produced by the 5-*exo* cyclization of **213**, and then abstracts a hydrogen atom from $HInCl_2$ to give alkenylindium **211**.

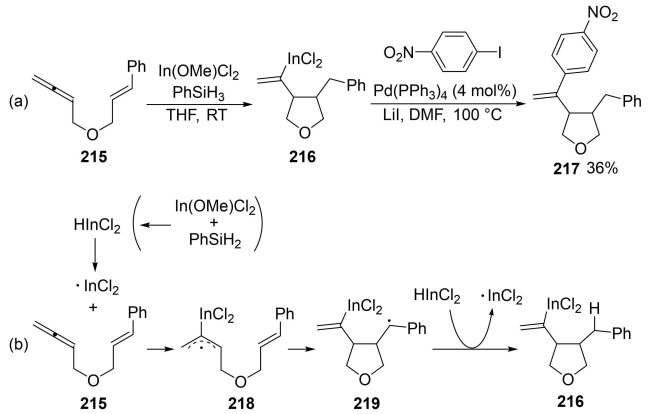
Carboindation of allenes by radical cyclization was also developed (Scheme 41a).[44] When allenene **215** was treated with $In(OMe)Cl_2$ and $PhSiH_3$, carboindation of an allene moiety and 5-*exo* cyclization proceeded to give alkenylindium **216**. In this case, an indium radical selectively adds to a central carbon of an allene moiety to provide allylic radical **218** (Scheme 41b).



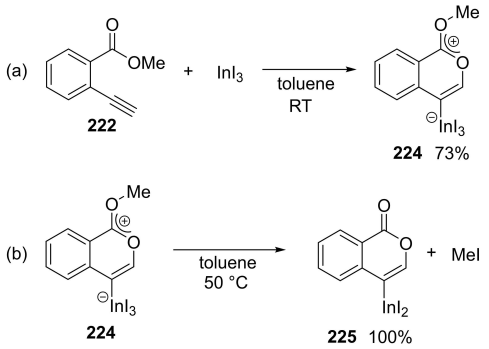
Scheme 39. Cyclic carboindation by reduction of α-bromo carbonyl moiety with row-valent indium species.



Scheme 40. Cyclization of enynes via indium hydride-mediated radical carboindation.



Scheme 41. Cyclization of allenynes via indium hydride-mediated radical carboindation.



Scheme 43. Isolation, characterization, and reactivity of zwitterion intermediate **3**.

The 5-*exo* cyclyzation of **218** followed by the hydrogen abstraction of alkyl radical **219** from $HInCl_2$ affords alkenylindium **216**. Then, Pd-catalyzed cross-coupling of the alkenyl indium **216** with an iodoarene successfully proceeds to yield **217**.

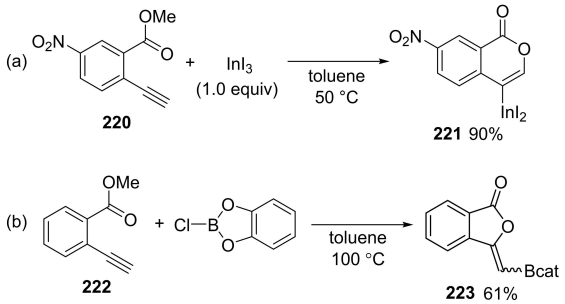
5. Heteroindation of Carbon-Carbon Multiple-Bonds

We reported the regioselective oxyindation of a terminal alkyne moiety in a 2-alkynyl benzoic ester.[45] The reaction of 2-alkynyl benzoic ester **220** with InI_3 at 50 °C exclusively gave 4-metalated isocoumarin **221** via oxyindation of an alkyne moiety (Scheme 42a). The 6-*endo* cyclization contrasts with the 5-*exo* cyclization caused by B-chlorocatecholborane (Scheme 42b), which was reported by Blum.[46] The obtained organoindium **221** was characterized by X-ray diffraction analysis.

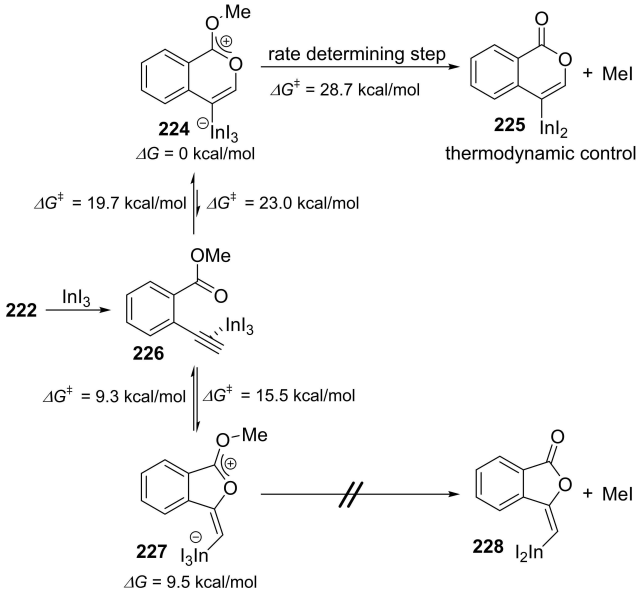
A reaction mechanism of the oxyindation was revealed by both experimental and theoretical studies. When the reaction of **222** with InI_3 was carried out at room temperature, zwitterion intermediate **224** with a new carbon-indium and carbon-carbon bonds was obtained and identified by X-ray diffraction analysis (Scheme 43a). Zwitterion **224** was heated at 50 °C, and then elimination of MeI occurred to give isocoumarin **225** bearing a carbon-indium bond at the 4-position (Scheme 43b). Based on experimental results, the details of the reaction mechanism were examined using theoretical calculation (Scheme 44), which showed that the activation energy of 5-*exo* cyclization is much smaller than that of the elimination of MeI so that 5-*exo* cyclization is reversible. Eventually, selective production of the thermodynamically stable 6-membered zwitterion **224** produced a remarkable level of 6-*endo* selectivity.

Alkenyl indium **229** was synthesized by the oxyindation of **222** using $InBr_3$ and applied to Pd-catalyzed cross-coupling with iodobenzene or benzoic chloride in a one-pot manner to afford 4-substituted isocoumarin **230** or **231**, respectively (Scheme 45).

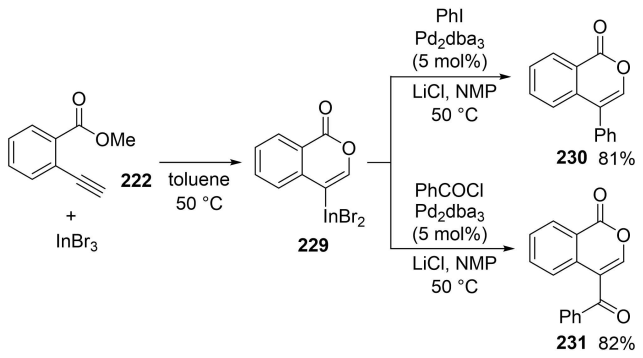
The formal total synthesis of oosponol was demonstrated by the present oxyindation (Scheme 46). Alkenylindium **234** was synthesized via the oxyindation of **233** with $InBr_3$, and then a one-pot process for the Pd-catalyzed cross-coupling of 2-



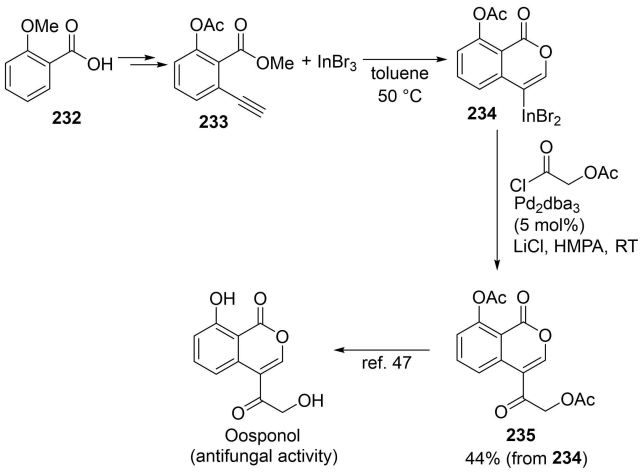
Scheme 42. Oxyindation of a terminal alkyne moiety in 2-alkynyl benzoic ester via 6-*endo* cyclization.



Scheme 44. Theoretical calculation study for 6-*endo* and 5-*exo* cyclic carboindation.



Scheme 45. Synthesis of 4-substituted isocoumarins by oxyindation/cross-coupling sequential process.

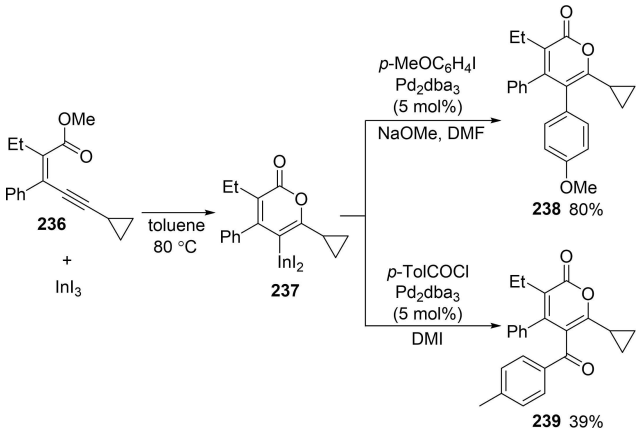


Scheme 46. Formal total synthesis of Oosponol.

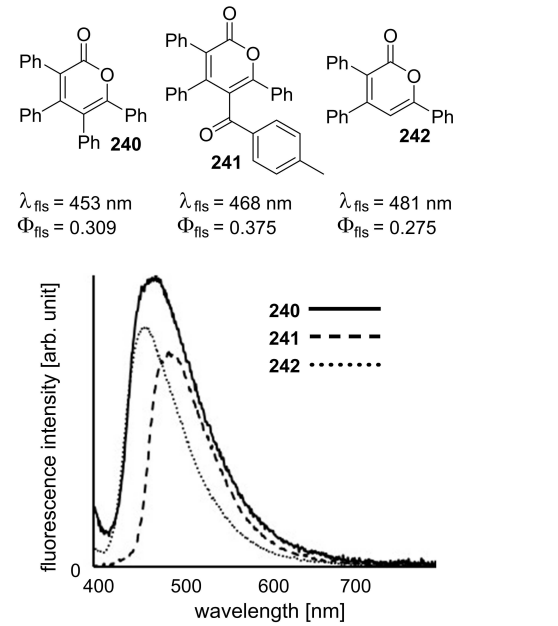
(acetyloxy)acetyl chloride provided a key isocoumarin precursor, **235**, for Oosponol.[47]

Carbonyl-ene-yne compounds are also applicable to oxyindation with indium trihalides to give 2-pyrones bearing a carbon-indium bond (Scheme 47).[48] The oxyindation of **236** using InI_3 produced tetrasubstituted metalated isocumarin **237**. Subsequently, the coupling reaction of **237** with either an aryl iodide or an aroyl chloride in the presence of a palladium catalyst led to 2-pyrones **238** or **239** bearing four different substituents, respectively. Tetrasubstituted 2-pyrones **240** and **241** exhibited an aggregation-induced emission (AIE) in the solid state (Scheme 48). It is noted that **240** and **241** exhibit greater quantum yields than triphenylated 2-pyrone **242**.[49]

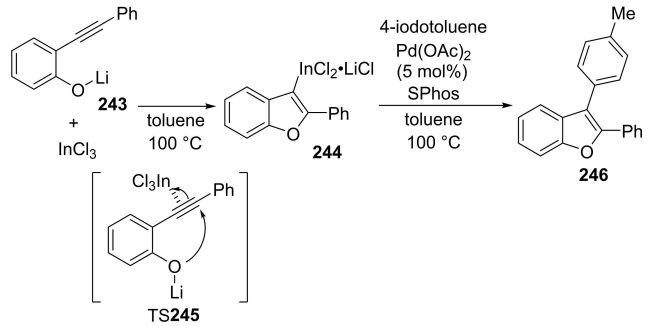
Gomez-Bengoa and Sestelo reported that cyclic oxyindation of lithium *o*-phenylethynylphenoxide **243** with $InCl_3$ proceeded to give alkenylindium **244** (Scheme 49).[50] In this case, the π-coordination of an alkyne moiety to $InCl_3$ followed by *endo*-cyclization induced by the nucleophilic attack of a lithium alkoxide moiety occurs (TS**245**). Organoindium **244** underwent Pd-catalyzed cross-coupling with 4-iodotoluene to afford benzo[*b*]furan **246**. The discovery of oxyindation provided important insight into the reaction mechanism of the In-catalyzed hydroalkoxylation of *o*-alkynylphenol derivatives.



Scheme 47. Cyclic oxyindation of carbonyl-ene-yne compounds and synthesis of tetrasubstituted pyrones.



Scheme 48. Cyclic oxyindation of carbonyl-ene-yne compounds and synthesis of tetrasubstituted pyrones.



Scheme 49. Cyclic oxyindation of lithium *o*-phenylethynylphenoxide **243** with $InCl_3$.

6. Conclusions and Outlook

We briefly summarized the history of carbogallation and -indation, and heterogallation and -indation of carbon-carbon multiple bonds. Carbogallation is divided into two main systems that are the addition of organogallium species and the addition of an external nucleophile to a gallium-activated alkyne. In the former system, allylgalliums, alkynylgalliums, and gallium enolates were used as organogallium species. In the latter, a gallium trihalide activates a carbon-carbon multiple-bond of alkynes, allenes, and alkenyl ethers, and carbogallation is then completed by the nucleophilic addition of various carbon nucleophiles. On the other hand, there are three types of carboindation. Two types are the same as carbogallation. A third type includes a radical pathway, which gives it broader diversity than carbogallation. A third type of carboindation involves a radical mechanism due to the stability of low-valent indium species. A few types of fascinating azagallation and oxyindation have been established. The moderate reactivity and stability of organogallium and -indium has resulted in high levels of compatibility with functional groups. Carbogallation, carboindation, heterogallation, and heteroindation are powerful tools available for the synthesis of highly functinalized organometallic compounds, and further development of this field of study will be extremely useful as more sophisticated organic syntheses are required in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Carbometalation · Gallium · Heterometalation · Indium · Metalation

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