Some Typical Advances in the Synthetic Applications of Allenes

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1. Introduction

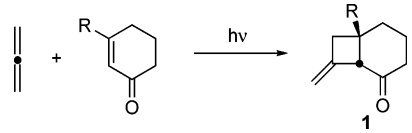
Allenes are a class of unique compounds with two π-orbitals perpendicular to each other. The first synthesis can be traced back to 1887.[1] They also exist in many natural products with interesting biological activities.[2] The development of IR and Raman spectroscopy promoted the development of allene chemistry greatly.[2] For a long period of time, allenes were considered as highly unstable, which retarded the development of the chemistry of allenes. However, during the last 8−10 years, allenes have been shown to demonstrate nice reactivities as well as selectivities, which can usually be tuned by the electronic or steric effects and the nature of the catalysts involved. This review will summarize some of the most typical advances on the chemistry of allenes, excluding those having been already included in the related reviews.[3−5] In some cases, to keep the chemistry complete, there may be some minor overlap with the contents in published reviews or books.[3−5]

2. Cycloaddition Reactions

2.1. [2+2]-Cycloaddition Reactions

In 1989, Kakiuchi et al. reported that under irridation propadiene can undergo [2+2]-cycloaddition with α,β-unsaturated cyclohexenones to afford methylene- cyclobutane-containing bicyclic products **1** (Scheme 1).[6]

Scheme 1



1

Shi et al. reported that under the catalysis of DABCO, *N*-tosylated imines **2** can undergo [2+2]-cycloaddition with 2,3-butadienoate or 3,4-pentadien-2-one to afford azetidine derivatives **3**.[7] The reaction proceeded via the nucleophilic addition of DABCO to the electron-deficient allene forming **4**- and **5**-type intermediate, which may undergo 1,2-addition with the imines to afford **6**. Intramolecular conjugate

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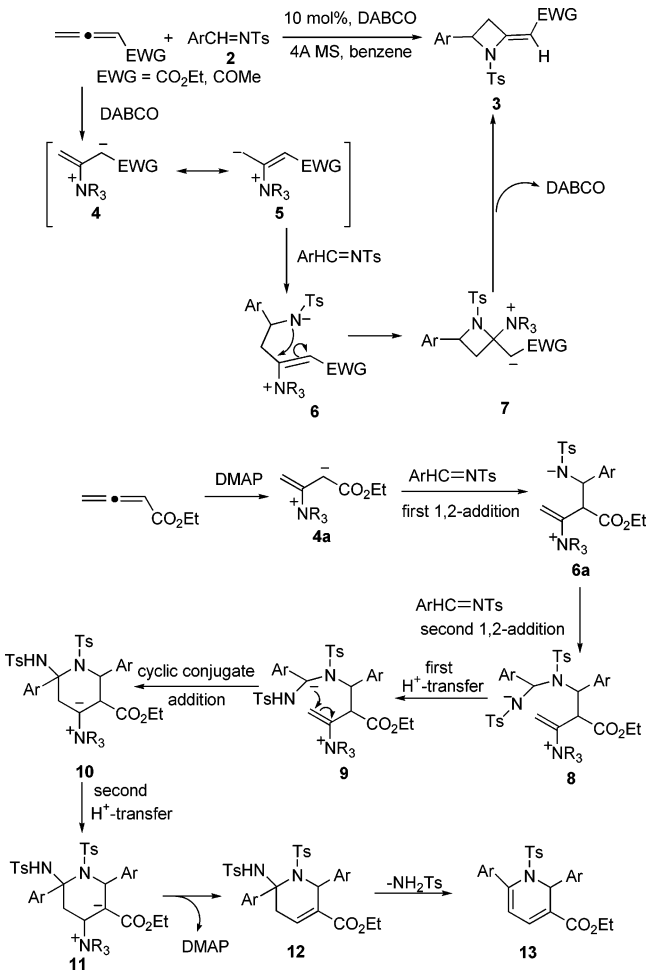
addition would form intermediate **7**, which may form azetidines **3** by the elimination of DABCO. With DMAP as the catalyst, dihydropyridine products **13** were formed via the double 1,2-addition/H^+-transfer,

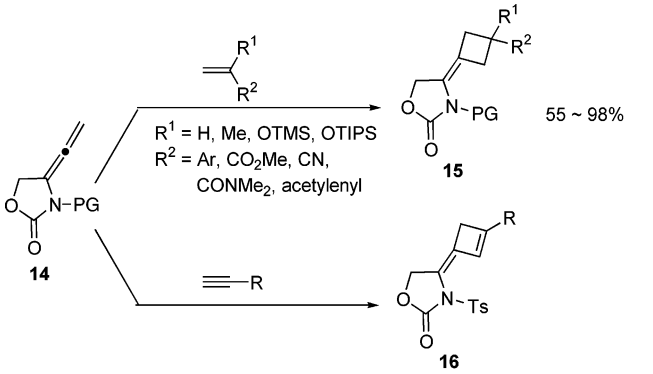
Scheme 2



cyclic conjugate addition, and NR_3 as well as NH_2-Ts-elimination (Scheme 2).[7]

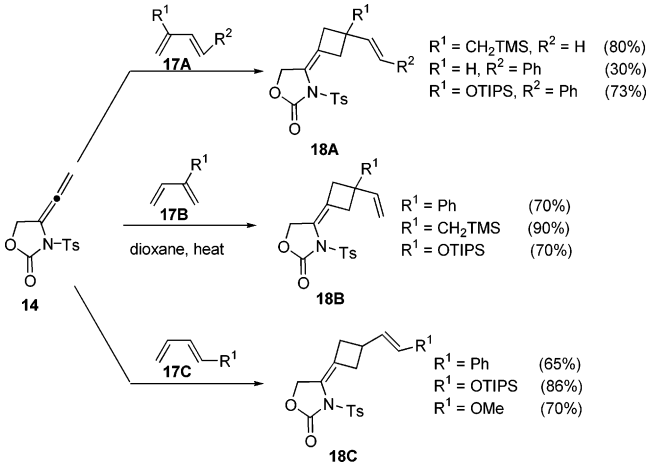
Tamaru et al. reported that the terminal C=C bond in 4-vinylidene-2-oxazolidinone **14** can readily undergo [2+2]-cycloaddition with alkenes or alkynes to afford cyclobutane derivatives **15** and cyclobutene derivatives **16** highly regioselectively (Scheme 3).[8]

Scheme 3



The reaction of 1,4-dienes **17A**−**C** with **14** also afforded [2+2]-products **18A**−**C**.[8] However, the regioselectivity for which the C=C bond participated in the reaction was strongly influenced by the electronic and the steric effects of R^1 and R^2 groups in **17A**−**C** (Scheme 4).

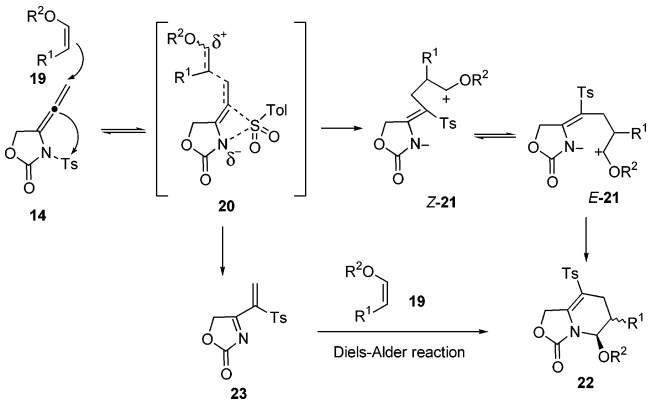
Scheme 4



Tamaru et al. also noticed that 4-vinylidene-1,3-oxazolidin-2-one **14** reacted with enol ethers **19** to provide different products, that is, bicyclic tetrahydropyridine derivatives **22**.[9] The reaction may proceed via the nucleophilic attack of the enol ethers **19** on the amino allene moiety in **14** followed by the 1,3-shift of the Ts group forming intermediate *Z*-**21**, which is in equilibrium with its stereoisomer *E*-**21** to afford the bicyclic products **22**. An alternative way for the formation of **22** is the Diels−Alder reaction of **23**, which was formed by the 1,3-Ts shift of **14**, with the enol ethers **19** (Scheme 5).

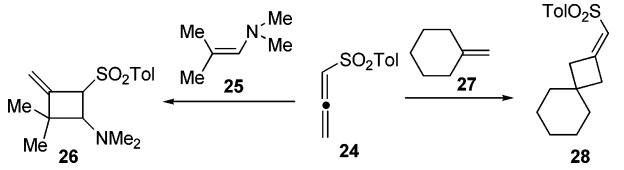
It has been reported that propadienyl sulfone **24** may undergo intermolecular [2+2]-cycloaddition with alkenes. With methylenecyclohexane, the [2+2]-cycloaddition reaction proceeded with the terminal C=C bond of propadienyl sulfones, while that of 1-(di-

Scheme 5



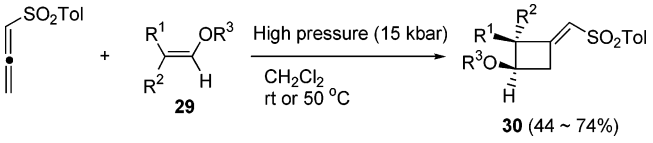
methylamino)-2-methylpropene **25** broke the C=C bond connected directly to the sulfonyl group (Scheme 6).[10]

Scheme 6



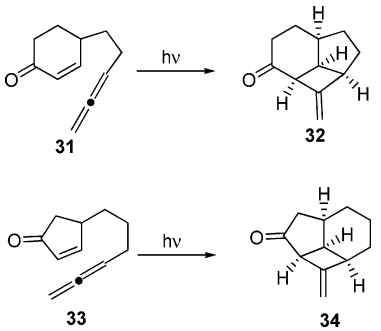
Scheeren et al. noticed that high pressure can promote the [2+2] cycloaddition of *p*-methylphenyl-1,2-propdienyl sulfone with enol ethers affording **30** highly selectively (Scheme 7).[11]

Scheme 7



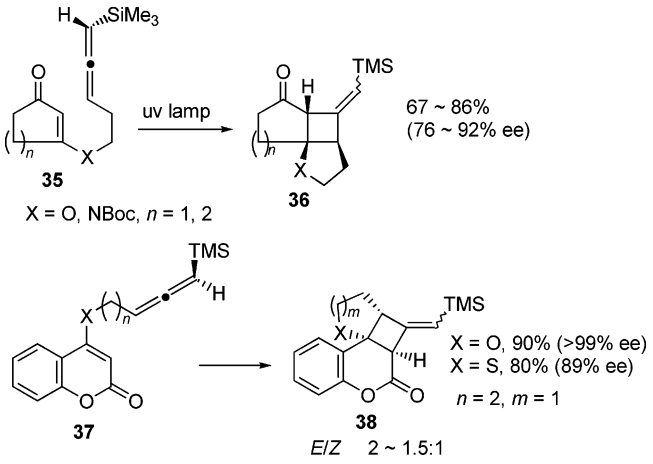
Dauben observed that a α,β-unsaturated cyclic enone can undergo intramolecular [2+2]-cycloaddition with the nonterminal C=C bond in the allene moiety in **31** or **33** to afford tricyclic products **32** and **34**. The selectivity depends largely on the size of the enone ring and the length of the tether between the two unsaturated moieties (Scheme 8).[12]

Scheme 8



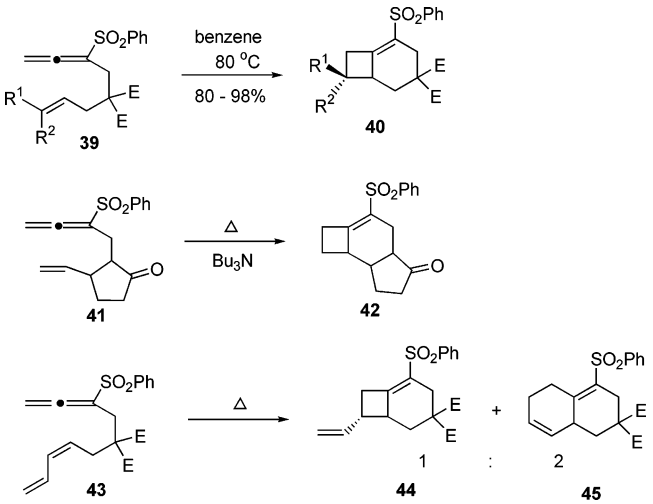
Carreira et al. observed an enantioselective photoinduced intramolecular [2+2]-cycloaddition of optically active allenyl silane with the C=C bond in α,β-unsaturated enone. The non silyl-substituted C=C bond in **35** or **37** in the allene moiety participated in the [2+2]-cycloaddition with high regioselectivity (Scheme 9).[13]

Scheme 9



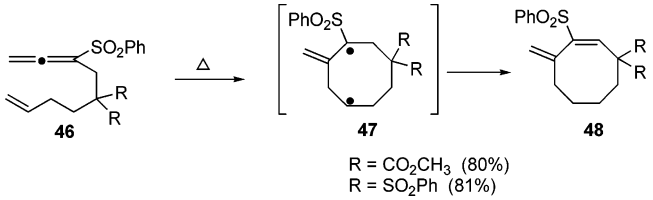
Padwa et al. demonstrated the intramolecular [2+2]-cycloaddition reaction of an alkene with the terminal C=C bond in the 1,2-allenyl sulfone moiety in **39** or **41**. The corresponding reaction of 1,2,7,9-tetraene **43** afforded the [2+2]-cycloaddition product **44** and [4+2]-cycloaddition product **45** (Scheme 10).[14]

Scheme 10



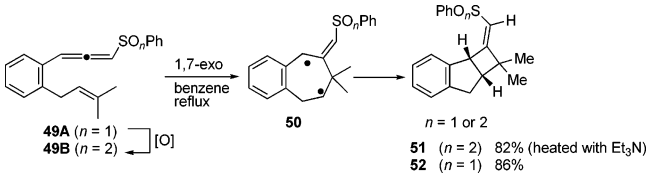
It is interesting to note that only the C1−C2 double bond of the allene moiety participated in the cycloaddition via a possible diradical mechanism. Thermolysis of 1,2,8-trienyl sulfones **46** underwent cyclization via a possible diradical intermediate **47**, which underwent transannular hydrogen abstraction to afford the eight-membered 3-methylenecyclooctene products **48** (Scheme 11).[14]

Scheme 11



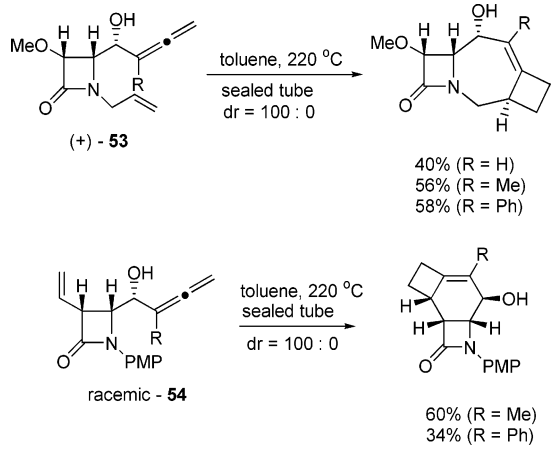
The oxidation of alkene-allenyl sulfoxide with a benzene core **49A** (n = 1) with oxone followed by heating in benzene at 60 °C produced the [2+2]-cycloaddition product of the non-S-substituted C=C bond with the alkene moiety **51**. Heating the sulfoxide **49A** without oxidation yielded the related [2+2]-product, that is, sulfoxide **52** (Scheme 12).[14b]

Scheme 12



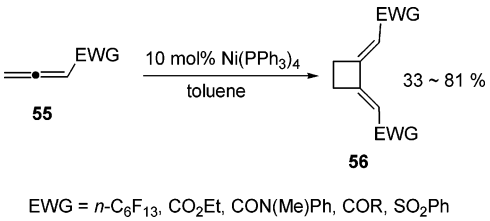
In 2003, Alcaide et al. reported the [2+2]-cycloaddition of the β-lactam-tethered alkene-α-allenols **53** and **54** yielding polycyclic lactams with a high selectivity toward the terminal C=C bond of the allene moiety (Scheme 13).[15]

Scheme 13



Under the catalysis of Ni(PPh$_3$)$_4$, electron-deficient allenes **55** can undergo a bimolecular cyclometalation and reductive elimination process to afford [2+2]-cycloaddition products, that is, 1,2-bis(alkylidene)-cyclobutanes **56** (Scheme 14).[16]

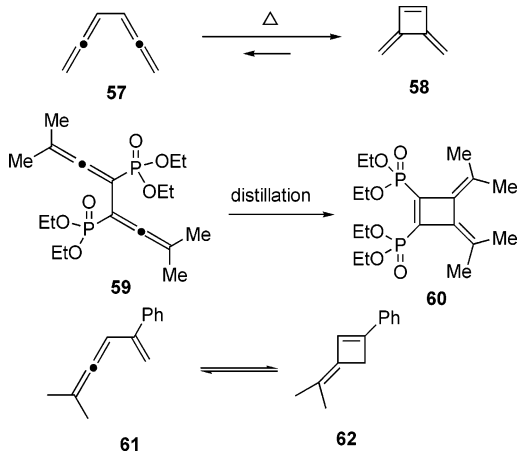
Scheme 14



In 1970, it was reported that 1,2,4,5-hexatetraene **57** underwent electronic ring closure reaction to afford 3,4-bis(methylene)cyclobutene **58**.[17a–d] 2,3,5,6-Octatetraene **59** would afford 3,4-bis(alkylidene)-cyclobutene **60** upon distillation via intramolecular [2+2]-cycloaddition of the 3,5-diene unit in **59**.[18] Pasto et al. observed that substituted vinyl allene **61** yielded an equilibrium mixture of **61** and **62** in a ratio of 19:81 at 360 °C (Scheme 15).[17e]

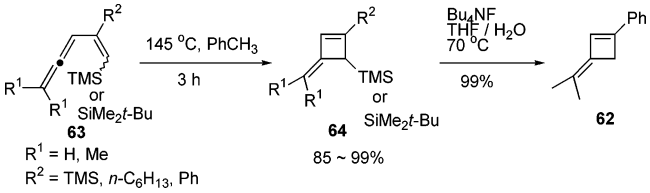
However, Murakami and Ito et al. observed an interesting effect of trimethylsilyl group on this

Scheme 15



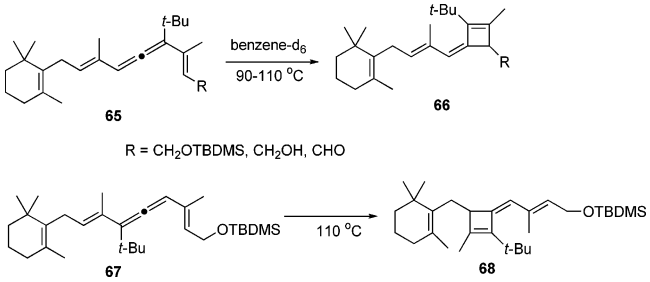
thermal electrocyclization leading to a complete convertion of **63** to alkylidenecyclobutene **64** in 85−99% isolated yields. R^2 can be Ph, TMS, or n-C$_6$H$_{13}$. The stereochemistry of the TMS-substituted double bond has no obvious effect on the cyclization reaction. The desilylation of **64** (R^1 = Me, R^2 = Ph) produced the pure **62** (Scheme 16).[19]

Scheme 16



1,3-Bis(vinylic) allenes **65** and **67** afforded alkylidenecyclobutene products **66** and **68**, respectively, in benzene-d_6 at 90−100 °C. The reaction of **65** with R = CHO is slower. Ab initio molecular orbital studies at the 6-31G* level with the Gaussian 92 program indicated that the regioselectivity was determined by the conformations of **65** and **67** (Scheme 17).[20]

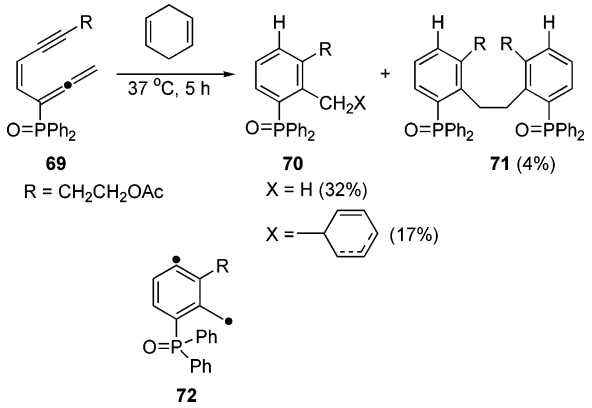
Scheme 17



2.2. Myers–Saito Cyclizations

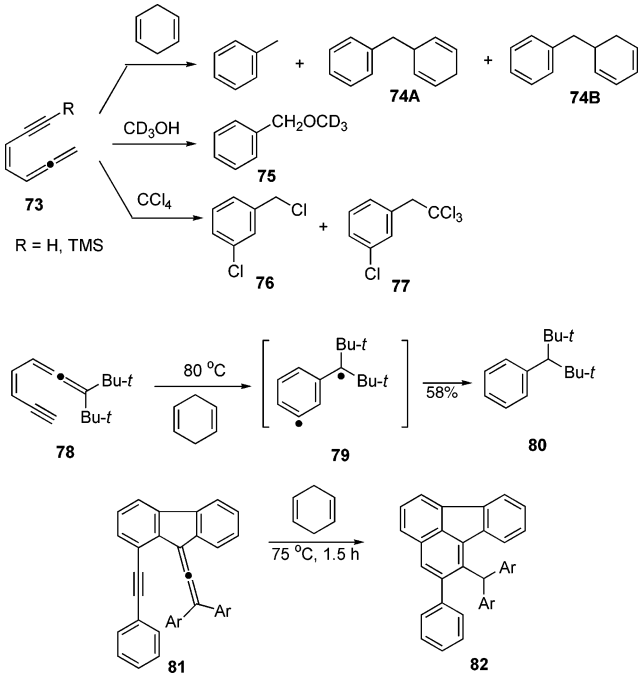
In 1989, Saito et al. reported the cyclization of enyne-allenyl phosphine oxide **69** in the presence of 1,4-cyclohexadiene leading to the formation of aryl phosphine oxide **70** together with the homocoupling product **71** of the possible diradical intermediate **72**. It is obvious that the regioselectivity is specifically forming a C−C bond between C2 and C7 atoms leading to the formation of the 1,4-diradical intermediate **72** (Scheme 18).[21]

Scheme 18



Almost at the same time, Myers et al. reported a similar reaction of 6-alkyn-1,2,4-triene **73** yielding benzene derivatives in the presence of different reagents.[22] Wang et al. also reported Myers−Saito cyclization of 1,2,4-trien-6-yne **78** and **81** with a benzene tether connecting the alkyne and the allene moiety (Scheme 19).[23,24]

Scheme 19

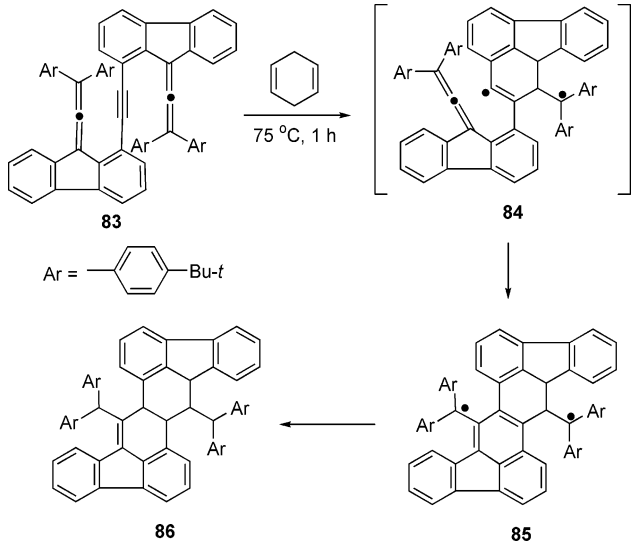


Wang et al. even prepared octacyclic product **86** from bis(allene)-alkynes with two benzene tethers **83** via this Myers−Saito reaction forming the diradical intermediate **84**, which underwent the intramolecular radical cyclization with the remaining allene moiety to form 1,6-diradical **85** (Scheme 20).[24]

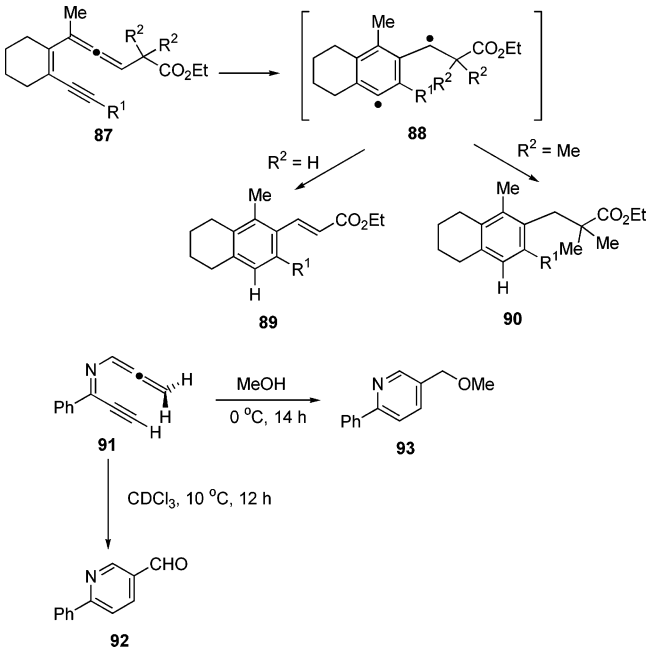
Allene-enynes **87** could also undergo the Myers−Saito aromatization reaction to afford benzocyclohexane derivatives **89** or **90** depending on the structure of R^2.[25] Recently, an aza-Myers−Saito cyclization of **91** forming pyridine derivative **92** or **93** was also reported (Scheme 21).[26]

Grissom et al. demonstrated the same diradical cyclization of 5-(*o*-(ethynyl)phenyl)-3,4-pentadienal **94** leading to naphthalene derivative **96**. The reaction

Scheme 20



Scheme 21



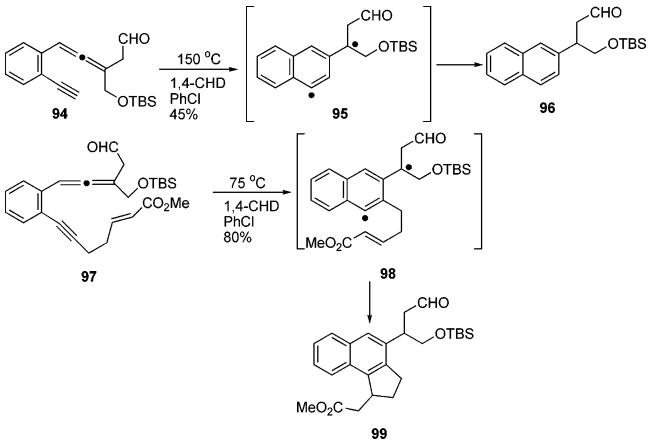
of **97**, which contains an extra conjugated C=C bond, formed tricyclic product **99** via the intramolecular radical cyclization of 1,4-diradical **98** (Scheme 22).[27]

The Myers−Saito reaction of **100** affording **101** has been successfully applied by Echavarren et al. to the synthesis of the benzo[*b*]fluorene core of kinamycins (Scheme 23).[28]

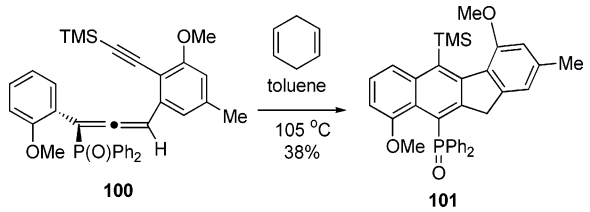
2.3. Schmittel Cyclizations

However, Schmittel et al. reported a new type of thermal cyclization of the similarly structured 3-(*o*-(1-alkynyl)phenyl)allenylphosphine oxide **102**. The reaction proceeded via the benzofulvene diradical intermediate **103**, which underwent radical addition with the nearby phenyl group to afford **104**. 1,5-H shift would afford the final product **105**. It should be noted here that the C−C bond was formed between the C2 and C6 atoms during the cyclization reaction (Scheme 24).[29]

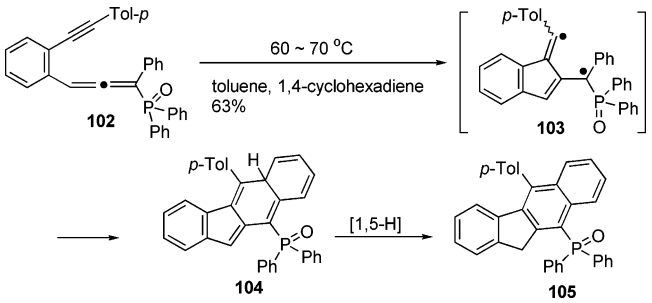
Scheme 22



Scheme 23

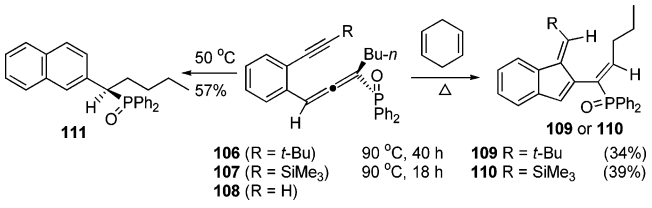


Scheme 24



With the change of the substituents of the alkyne and allene moieties, different products were formed via the **103**-type intermediate, indicating that the phenyl group in **102** is not necessary for the switch of the reaction pathway. However, the cyclization reaction of **108** (R = H) afforded Myers−Saito product **111**, indicating the importance of the steric effect of the R group (Scheme 25).[30] Similar phenomena have also been observed in other cases.[31]

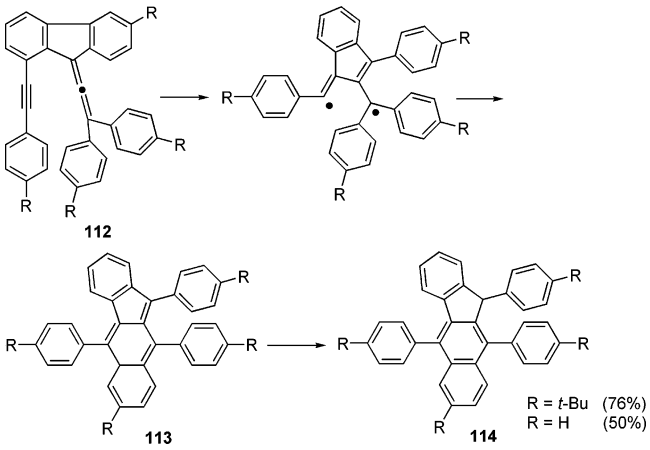
Scheme 25



Wang et al. noted that the steric effect of two aryl groups of the allene moiety also played an important role in determining the reaction pathway because the reaction of **112** afforded Schmittel product **114** (Scheme 26).[24]

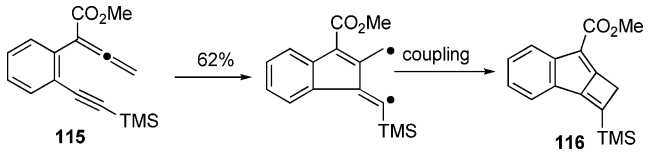
It is interesting to observe that similarly structured **115** with a benzene tether connecting the allene and

Scheme 26



the C−C triple bond underwent the Schmittel-type reaction, which was followed by the intramolecular coupling of the 1,4-diradical intermediate to afford tricyclic product **116** (Scheme 27).[32a] Ueda reported

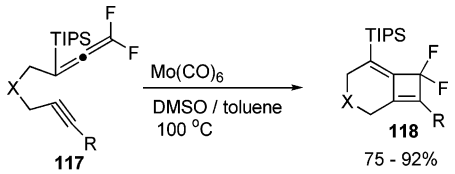
Scheme 27



a very similar reaction of *o*-(1-alkynyl)phenyl-2,3-allenols.[32b]

Hammond et al. noticed that 1,1-difluoro-1,2-allen-7-ynes **117** underwent $Mo(CO)_6$-mediated cyclometalation-reductive reaction to afford 4,6-fused bicyclic products **118** (Scheme 28).[32c]

Scheme 28

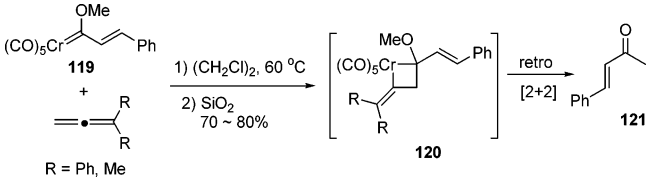


X = NTs, $C(CO_2Et)_2$; R = H, alkyl, Ph

2.4. Cycloaddition Reactions of Metallocarbenes with Allenes

Barluenga et al. reported the [2+2]-cycloaddition of the C−Cr double bond in alkenyl chromium carbene complex **119** with 1,1-disubstituted allenes leading to the formation of α,β-unsaturated enones **121** via the retro [2+2] cycloaddition of intermediate **120** (Scheme 29).[33]

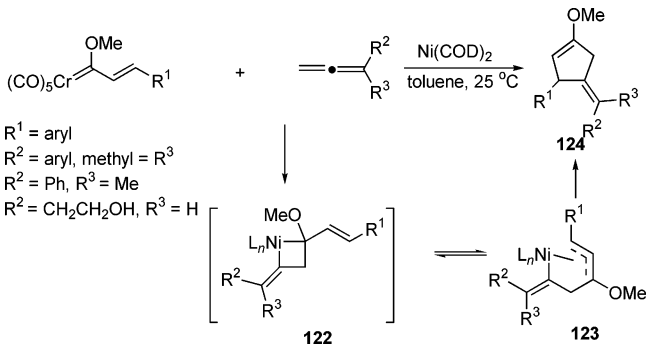
Scheme 29



However, in the presence of 1 equiv of $Ni(COD)_2$, four-membered intermediate **120** (Scheme 29) may

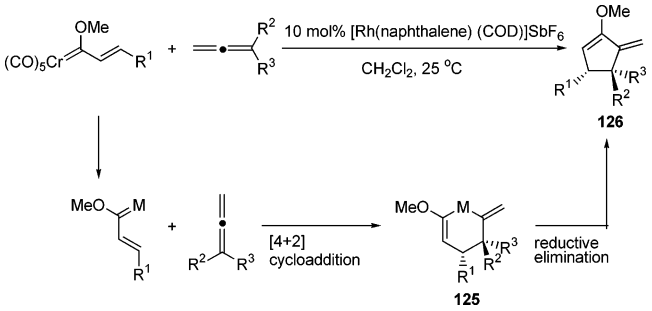
undergo Cr−Ni exchange to afford **122**, which would be followed by allylic rearrangement and reductive elimination to afford 4-alkylidenecyclopentenyl methyl ethers **124** (Scheme 30).[33]

Scheme 30



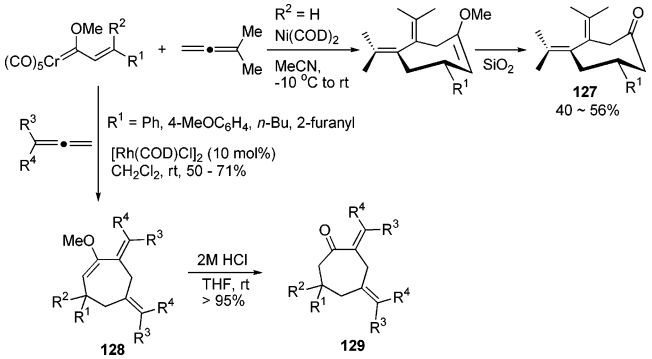
Under the catalysis of [(naphthalene)(COD)Rh]-[SbF_6], the reaction afforded the regioisomeric products 3-methylenecyclopentenyl methyl ethers **126** via the possible [4+2]-cycloaddition and reductive elimination mechanism via the intermediacy of metallocyclic intermediate **125** (Scheme 31).[33]

Scheme 31



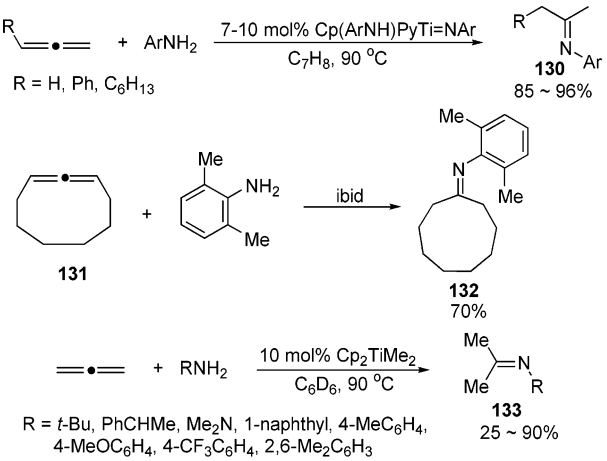
The Ni(0)-mediated [3+2+2] cycloaddition of alkenyl chromium carbene complexes with 2 molecules of allenes have also been demonstrated to afford 3,4-bis(alkylidene)cycloheptanones **127**. With [Rh(COD)-Cl]$_2$ as the catalyst, the related reaction yielded 3,5-bis(alkylidene)cycloheptenes **128**, which upon protonolysis afforded 2,4-bis(alkylidene)cycloheptanones **129** (Scheme 32).[34]

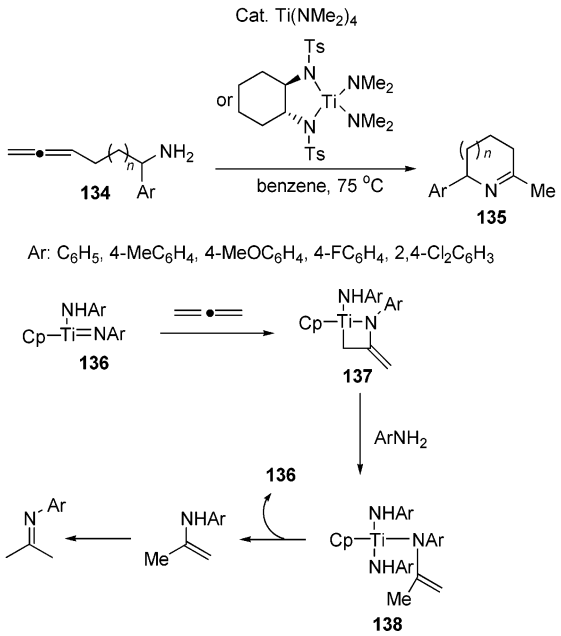
Scheme 32



Bergman et al. reported the Cp_2TiMe_2-catalyzed hydramination of allenes.[35] An intramolecular reaction has also been realized to afford heterocyclic products **135** in high yields via a similar mechanism.[36] A [2+2]-cycloaddition mechanism involving the reaction of a Ti=N bond in **136** and one of the two C−C double bonds in allenes forming methylenemetallocyclobutane intermediate **137**, which was followed by protonlysis with $ArNH_2$ and β-H elimination to afford the enamines, was proposed (Scheme 33).[35]

Scheme 33

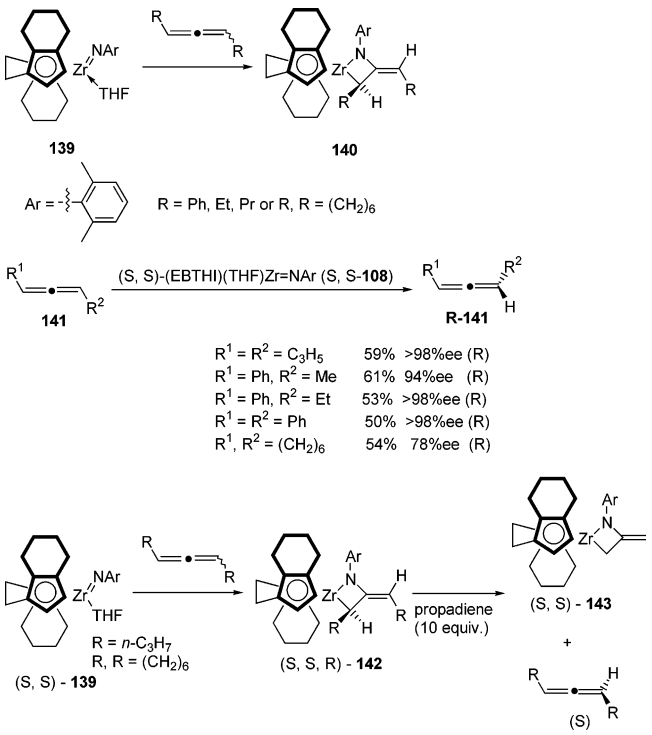




Racemic (EBTHI)(THF)Zr=NAr **139** can react with an allene in a [2+2] manner to afford β-methylenemetallocycle **140**. The reaction of enantiopure (*S*,*S*)-**139** with excess allenes provided an effective kinetic resolution of **141** even at room temperature. After this process, allenes with high enantiopurity (i.e., *R*-**141**) were formed.[37] By treating (*S*,*S*)-(EBTHI)-(THF)Zr=NAr (**139**) with slightly more than 2 equiv of 4,5-nonadiene, after removing the excess allene in vacuo, (*S*,*S*,*R*)-**142** could be isolated, which upon reacting with excess propadiene (10 equiv) at 23 °C produced (*S*,*S*)-**143** and (*S*)-4,5-nonadiene (Scheme 34).[37]

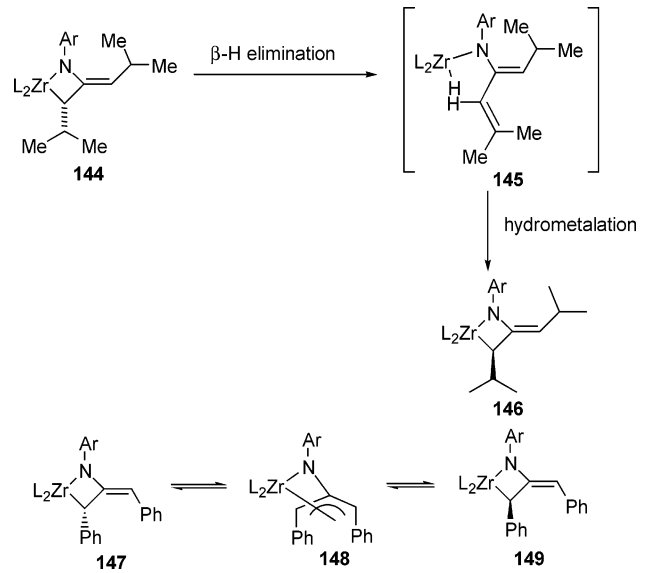
The reaction of (*S*,*S*)-**139** with 1 equiv of racemic 1,2-cyclononadiene yielded (*S*,*S*,*R*)-**142** (R, R= $(CH_2)_6$)

Scheme 34



as the only product, indicating that the slower reacting enantiomer of the allene reacted with (*S*,*S*)-**139** with the absolute configuration inverted. An explanation was recently disclosed; that is, the β-alkylidenemetallocyclic complex **144** may undergo β-H elimination forming **145**, which was followed by hydrometalation to induce the inversion. An alterative is the allylic rearrangement between **147**↔**148**↔**149** (Scheme 35).[38]

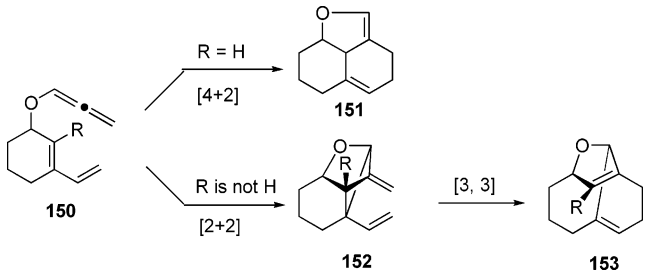
Scheme 35



2.5. The Substituent Switch between [2+2]- and [4+2]-Cycloadditions

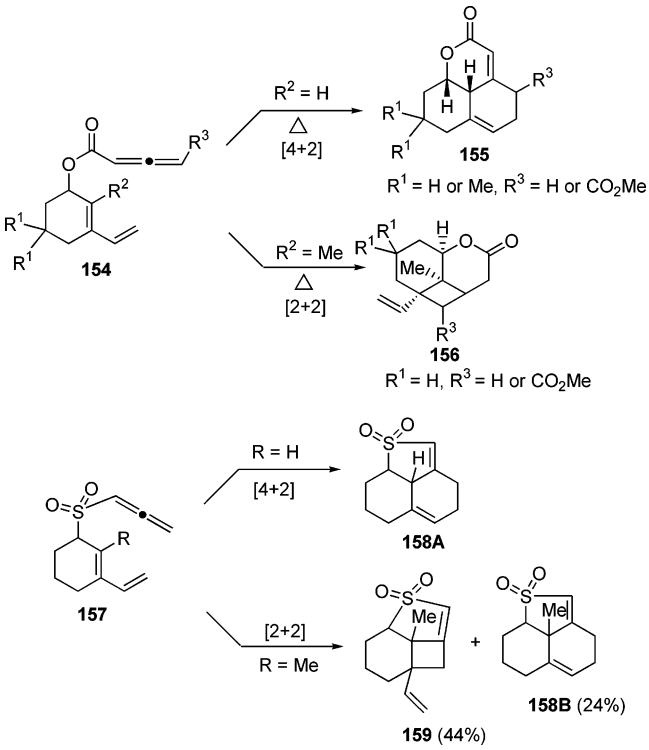
Kanematsu et al. observed an interesting and remarkable substituent (R) switch for the intramolecular [2+2]- and [4+2]-cycloaddition between an alkene and an allene in **150** affording **151** and **153**, respectively (Scheme 36).[39]

Scheme 36



Structurally related esters **154** behaved similarly; however, it should be noted that in these cases the formation of a cyclobutane ring, the normal [2+2] result, was observed (Scheme 37).[40]

Scheme 37



2.6. [4+2]-Cycloadditions

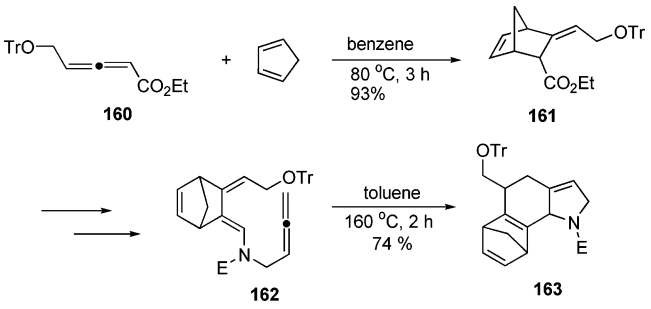
2.6.1. The Reactions of 1,3-Dienes with Allenes

Kanematsu et al. also reported the intermolecular [4+2]-cycloaddition of 2,3-allenoate **160** with cyclopentadiene leading to the formation of **161**.[41a] After several steps, **161** was converted to 1,3-diene-allene **162**, which underwent intramolecular [4+2]-cycloaddition to afford bridged tetracyclic product **163** (Scheme 38).[41a,42]

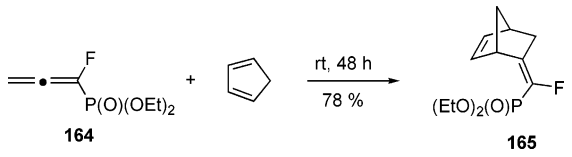
Hammond observed that 1-fluoropropadienyl phosphonate **164** could undergo intermolecular [4+2]-cycloaddition with cyclopentadiene at room temperature to afford the *endo*-product **165** with high selectivity (Scheme 39).[43]

Winkler applied the intermolecular Diels−Alder reaction of allenes with furans as the key step for

Scheme 38

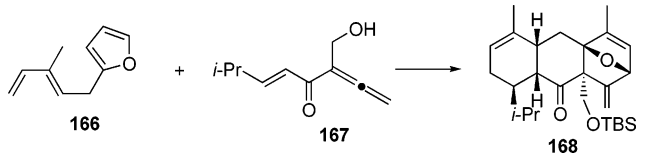


Scheme 39



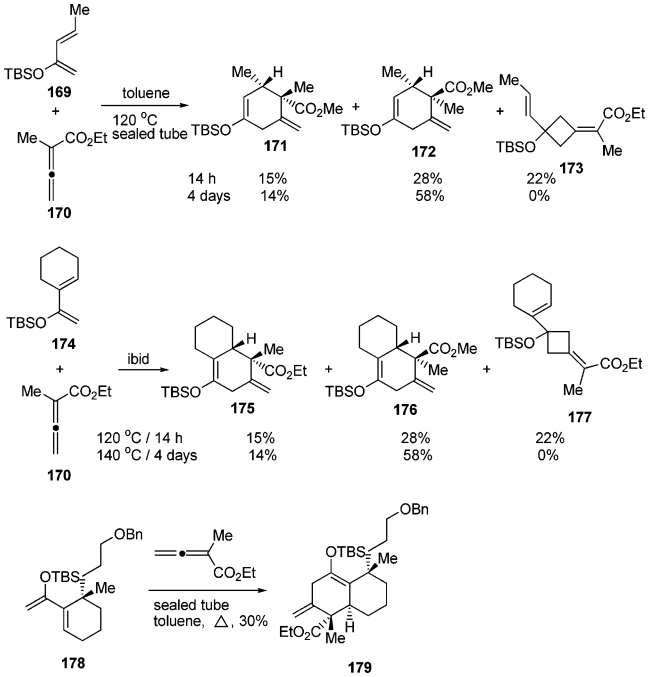
the synthesis of the carbon framework of the eleutherobin aglycone **168** (Scheme 40).[44]

Scheme 40



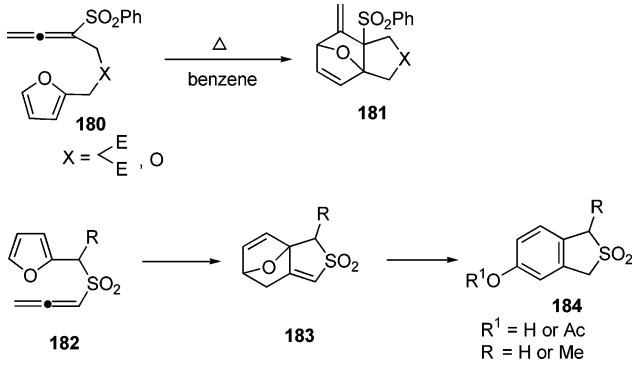
Jung et al. reported the [4+2]- and [2+2]-cycloaddition of 2-(silyloxy)-1,3-alkadienes **169** or **174** with 2-methyl-2,3-butadienoate **170**. The [2+2]-adducts **173** or **177** could be converted to the six-membered products **172** or **176**.[45] This protocol for the transformation from **178** to **179** had been successfully applied as the key step for the formal synthesis of (−)-dysidiolide (Scheme 41).[46]

Scheme 41



Intramolecular [4+2]-cycloadditions were observed between the nonterminal C=C bond in the 1,2-allenyl sulfone and furan moieties in **180**.[47,14c] Another example of intramolecular [4+2]-cycloaddition of furan with the terminal C=C bond of the 1,2-allenyl sulfone moiety in **182** was reported by Kanematsu et al. (Scheme 42).[48a] The Diels−Alder reaction of N-

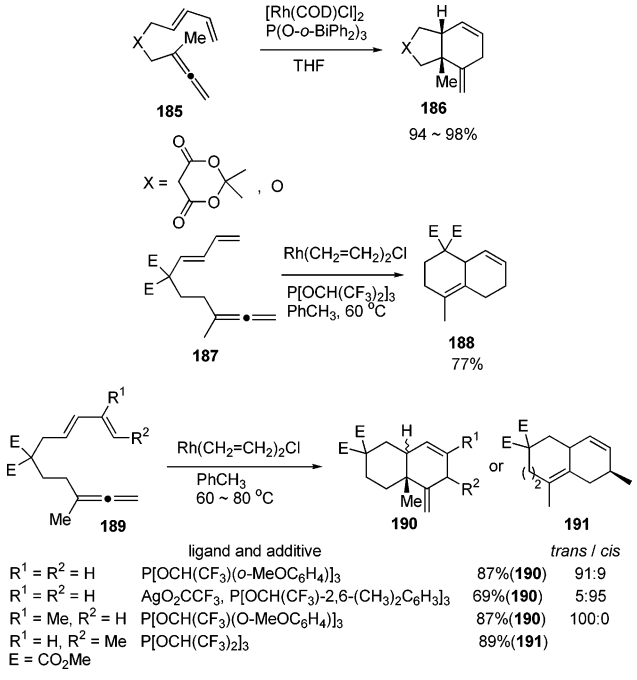
Scheme 42



protected pyrroles and allene-1,3-dicarboxylates has also been reported.[48b]

$Ni(COD)_2$ or $[Rh(COD)Cl]_2$ can catalyze the intramolecular [4+2] cycloaddition of acyclic 1,3-dienes and allenes in **185**, **187**, or **189** leading to the formation of different products due to the participation of different C=C bonds in the allene moiety (Scheme 43).[49]

Scheme 43



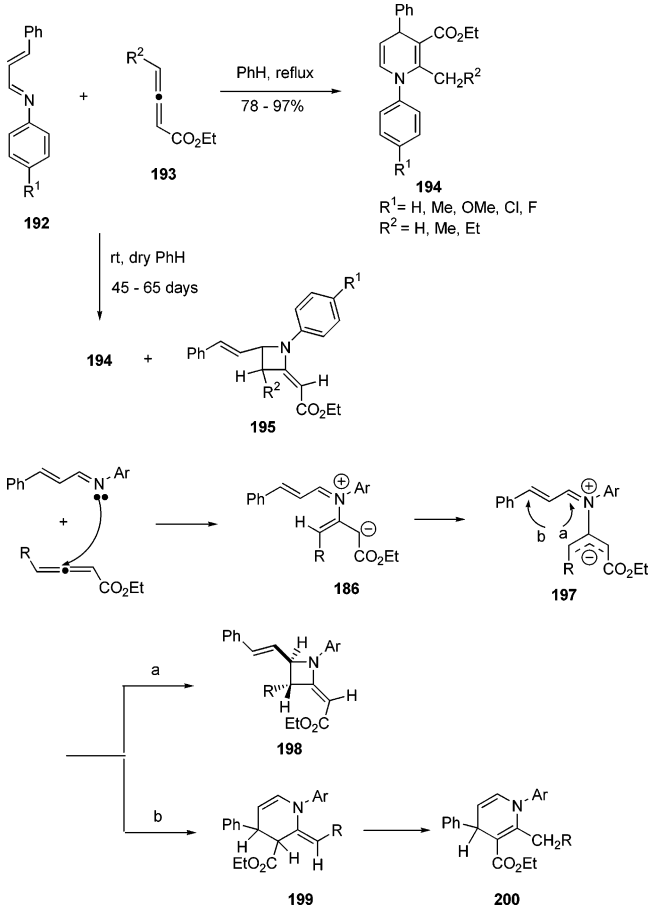
ligand and additive		*trans* / *cis*
$R^1 = R^2 = H$	$P[OCH(CF_3)(o\text{-}MeOC_6H_4)]_3$	87%(**190**) 91:9
$R^1 = R^2 = H$	AgO_2CCF_3, $P[OCH(CF_3)\text{-}2,6\text{-}(CH_3)_2C_6H_3]_3$	69%(**190**) 5:95
$R^1 = Me$, $R^2 = H$	$P[OCH(CF_3)(O\text{-}MeOC_6H_4)]_3$	87%(**190**) 100:0
$R^1 = H$, $R^2 = Me$	$P[OCH(CF_3)_2]_3$	89%(**191**)

E = CO_2Me

Ishar et al. observed that 1-aryl-4-phenyl-1-azadienes **192** could act as a 1,3-diene to react when heated with the relatively electron-deficient α,β-unsaturated C=C bond in 2,3-allenoates **193**. The same reaction at room temperature led to the formation of a mixture of **194** and a [2+2]-cycloaddition product azetidine **195**.[50] However, heating **195** in refluxing benzene failed to yield **194**. Thus, a reaction mechanism triggered by the nucleophilic conjugate addition of the iminyl nitrogen atom in **192** toward allenoates was proposed. The intramolecular 1,2- or

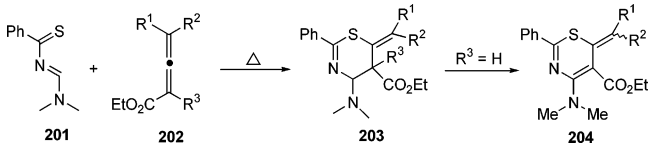
1,4-addition of π-allyl intermediate **197** would form the four-membered product **198** and the six-membered product **200**, respectively (Scheme 44).[50]

Scheme 44



2-Phenyl-4-(dimethylamino)-1-thia-3-azabuta-1,3-diene **201** underwent regio- and stereoselective [4+2] cycloadditions with 2,3-allenoates **202** in CH_2Cl_2−benzene to afford 6-alkylidene-6*H*-2-phenyl-5-ethoxycarbonyl-1,3-thiazines **204** (Scheme 45).[51]

Scheme 45

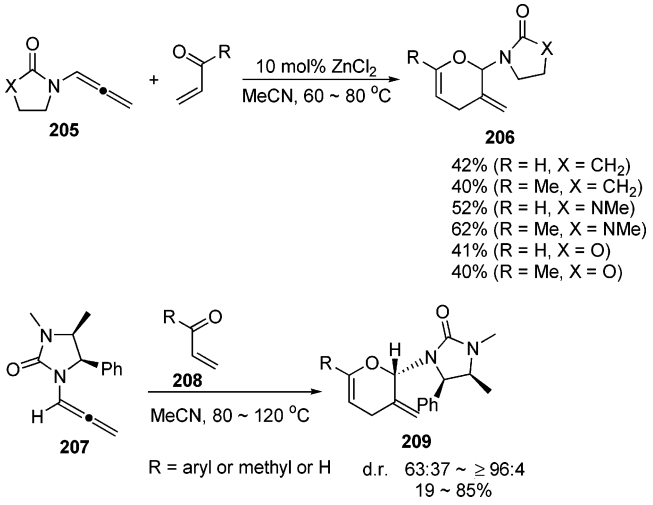


Hsung et al. noticed that allenamide **205** can undergo hetero [4+2]-cycloaddition with α,β-unsaturated enals or enones to afford dihydropyranyl derivatives **206**.[52] Greater than 92:8 de was observed for the reaction of optically active allenamide **207** with vinyl ketones **208**. Using propenals, the de is at the level of ~85:15 (Scheme 46).[53]

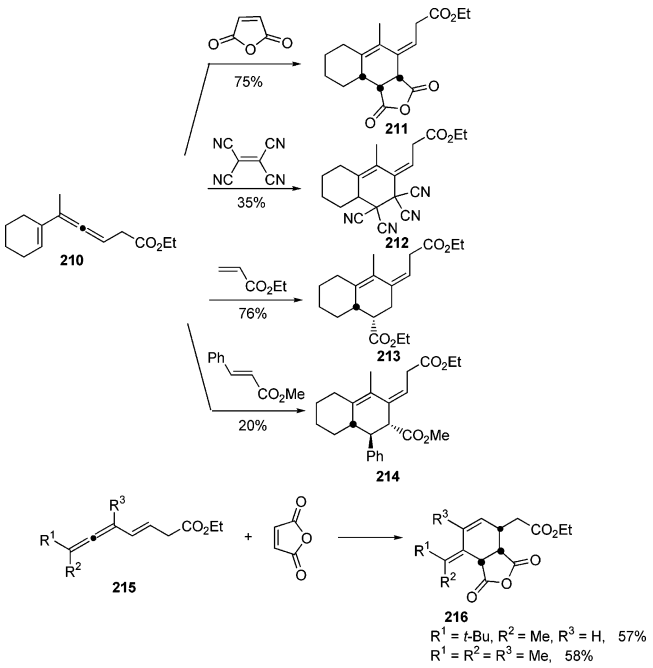
2.6.2. The Reactions of the 1,3-Diene Moiety in 1,3,4-Trienes with C═X Bonds (X = C, O, N)

Krause et al. studied the [4+2]-cycloaddition of 3,4,6-trienoates **179** with electron-deficient alkenes, in which the conjugated 4,6-diene moiety in **179** acted as the 1,3-diene. A similar Diels−Alder reaction was also observed in the reaction of **184** with maleic anhydride (Scheme 47).[54]

Scheme 46

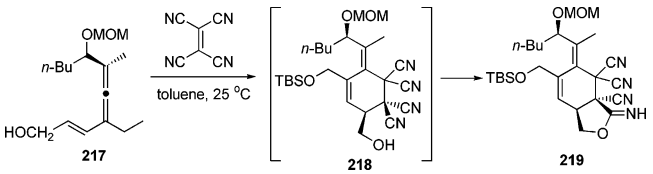


Scheme 47



Sipino et al. reported that 2,4,5-trienyl alcohol **217** and TCNE can undergo a similar [4+2]-cycloaddition forming cyclohexene derivative **218**, which was followed by the intramolecular attack of the hydroxyl group on the neighboring nitrile group to form bicyclic iminolactone **219** (Scheme 48).[55]

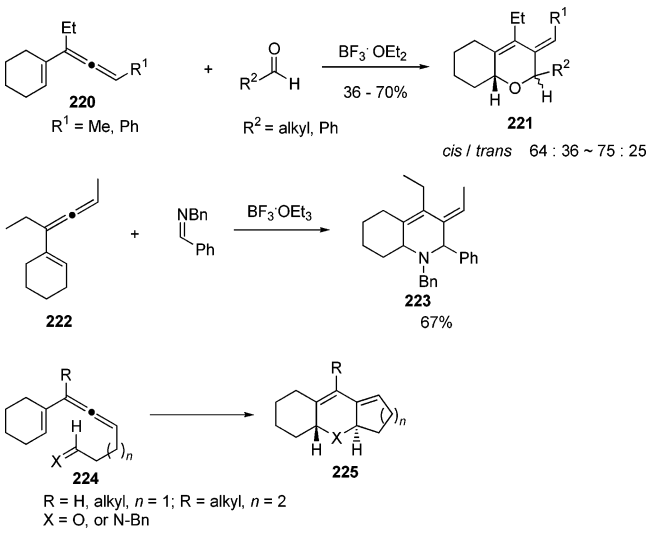
Scheme 48



Paleuzuela et al. observed the BF_3−OEt_2-catalyzed intramolecular hetero-Diels−Alder reaction of vinylic allenes **220** with aldehydes.[56] Imines can react simi-

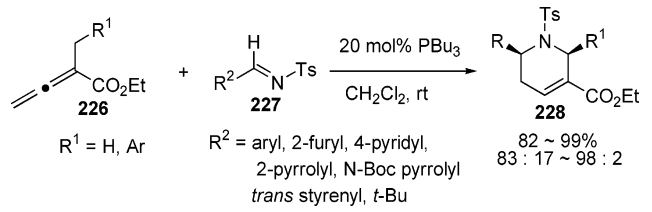
larly with vinylic allene **222**.[57] An intramolecular version of this type of reaction has also been demonstrated to afford fused tricyclic products **225** highly efficiently (Scheme 49).[58]

Scheme 49



Kwon et al. observed that under the catalysis of PBu_3, 2-substituted buta-2,3-dienoates **226** can undergo [4+2] reaction with imines **227** to afford tetrahydropyridine products **228** (Scheme 50).[59]

Scheme 50



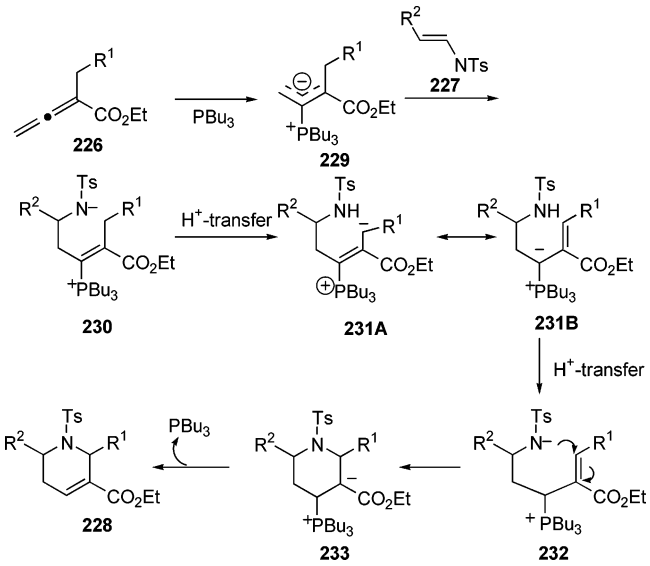
The reaction proceeded via the 1,2-addition of intermediate **229** with imines **227** producing **230**, which was followed by double intramolecular H^+-transfer induced C=C migration to afford **232**. Cyclic conjugate addition of **232** would yield the final six-membered products **228** via the releasing of PBu_3 from **233** to finish the catalytic cycle (Scheme 51).

2.7. [3+2]-Cycloadditions

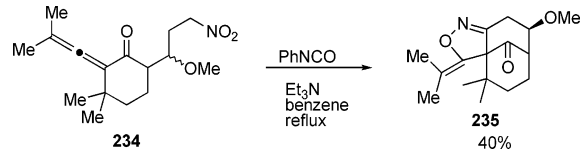
Young et al. established an intramolecular [3+2]-cycloaddition of the in-situ formed nitrile oxide with the allene part in **234** in their synthetic efforts toward hyperevolutin A acylated phloroglucinol ring system (Scheme 52).[60]

Eberbach reported the intramolecular electrocyclization reaction of conjugated allene-nitrones **237**, which were formed in-situ by the treatment of alkynes **236** with a base. A delocalized diradical intermediate **239**, formed from the homolytic cleavage of the N−O bond in **238**, would undergo an intramolecular radical coupling reaction to form 2-iminylphenylcyclopropanone intermediate **240**. [4+3]-Cycloaddition of **240** would form bicyclic intermediate **241**, which upon 1,5-H shift would afford the final product **242** (Scheme 53).[61]

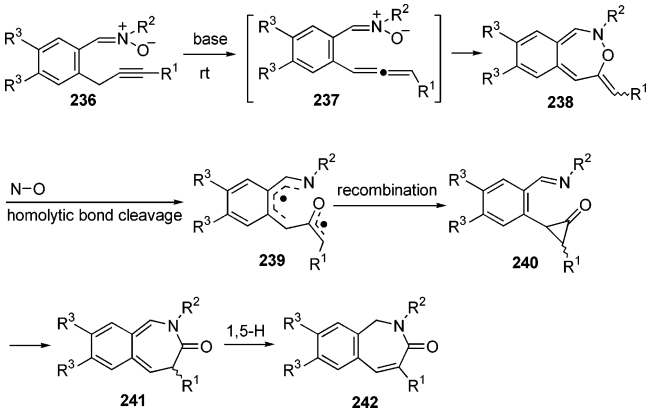
Scheme 51



Scheme 52

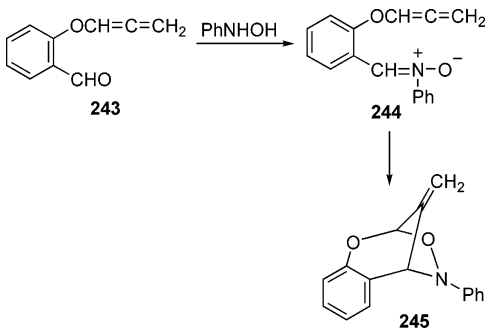


Scheme 53



Padwa et al. reported the intramolecular [3+2]-cycloaddition of nitrones with allenes (Scheme 54).[62]

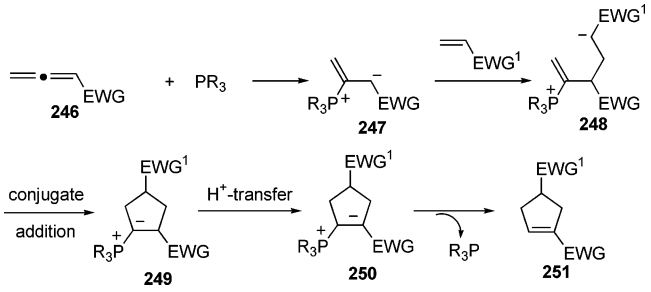
Scheme 54



Lu et al. established the PR_3-catalyzed [3+2]-cycloaddition of electron-deficient allenes **246** with alkenes bearing an electron-withdrawing group to afford cyclopentene derivatives **251**.[4k] The reaction

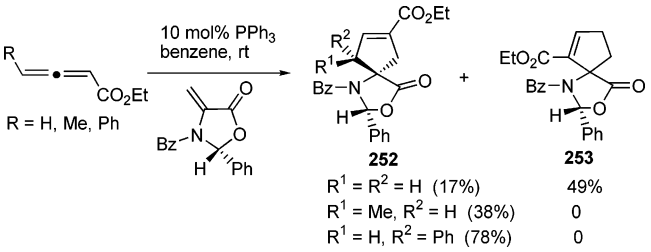
proceeded via the nucleophilic addition of **246** with PR_3 leading to the formation of intermediate **247**. Conjugate addition of **247** with an electronic-deficient alkene would afford **248**. Intramolecular conjugate addition, proton transfer, and PR_3-elimination afforded the final products **251** (Scheme 55).[63]

Scheme 55



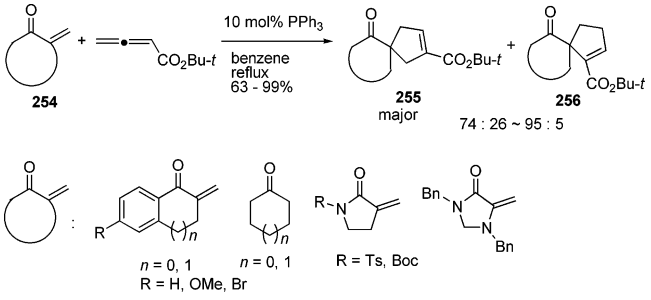
This type of reaction has been applied for the synthesis of cyclic amino acid derivatives **252** (and **253**) (Scheme 56).[64]

Scheme 56



Recently, spirocyclic compounds **255** and **256** have been prepared similarly with **255** being the major products (Scheme 57).[65]

Scheme 57

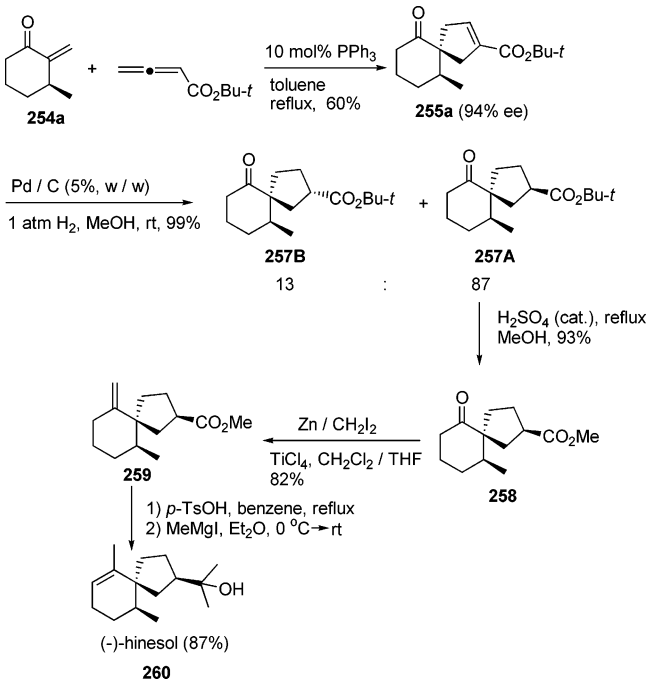


This protocol has been successfully applied to the first total synthesis of (−)-hinesol **260** using the [3+2]-cycloaddition of **254a** and *tert*-butyl butadienoate as the key step (Scheme 58).[66]

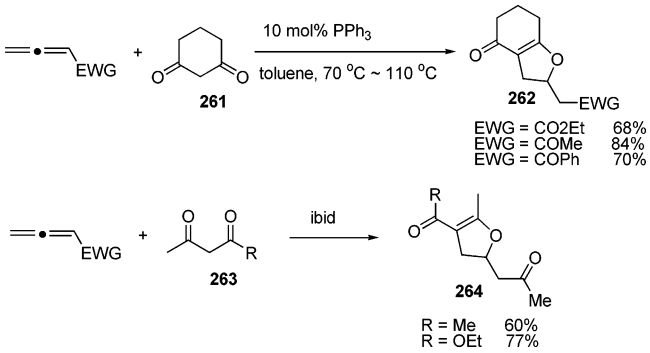
Lu et al. also reported that the PR_3-catalyzed reaction of electron-deficient allenes with compounds bearing two nucleophilic centers **261** and **263** would form dihydrofurans **262** and **264**, efficiently (Scheme 59).[67]

The reaction may proceed via the PR_3-catalyzed γ-addition of intermediate **266** with nucleophile **267**, intramolecular proton-transfer of **268**, and PPh_3-releasing from **269** forming intermediate **270**, which was followed by conjugate addition to afford **262** or **264** (Scheme 60).[67]

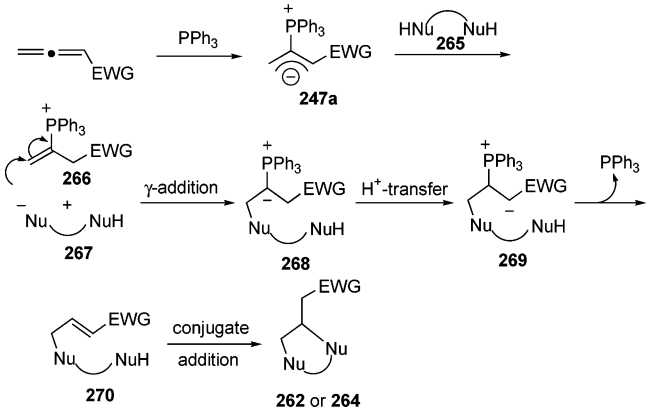
Scheme 58



Scheme 59



Scheme 60

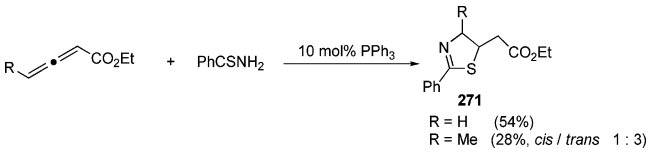


Under the catalysis of 10 mol % of PPh_3, thiobenzamide would also react with 2,3-alkadienoates to afford thiazolines **271** (Scheme 61).[68]

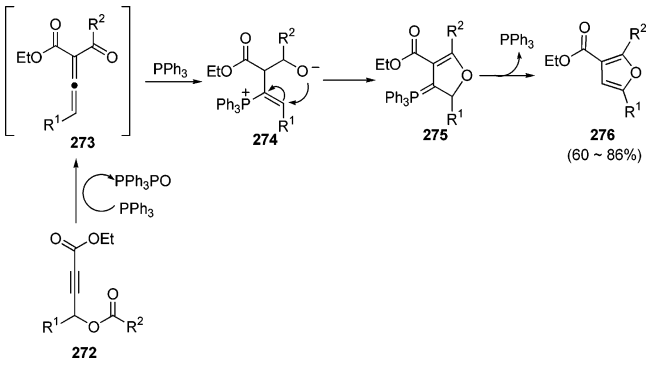
This type of reaction has also been observed with 2-acyl-2,3-alkadienoates **273** formed by the reaction of 4-acetoxy-2-alkynoates **272** with PPh_3 (Scheme 62).[69]

Ishar et al. has applied **247b**- or **247C**-type intermediate for the [3+2]-, [4+3]-, [8+2]-cycloaddition

Scheme 61

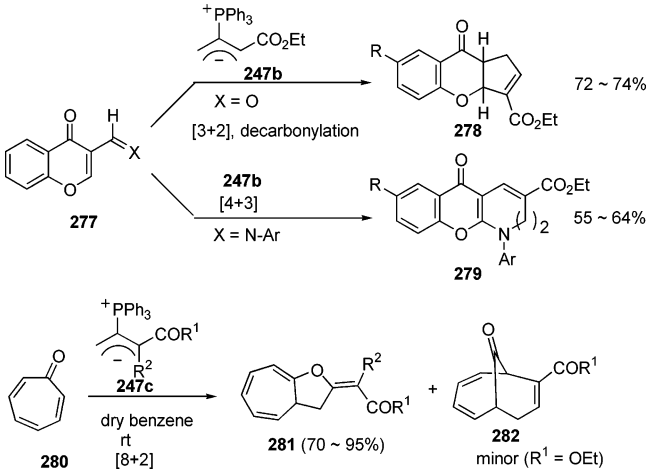


Scheme 62



with **277** or **280**, respectively, leading to the formation of tricyclic or bicyclic products **278**, **279**, **281**, and **282** (Scheme 63).[70,71]

Scheme 63

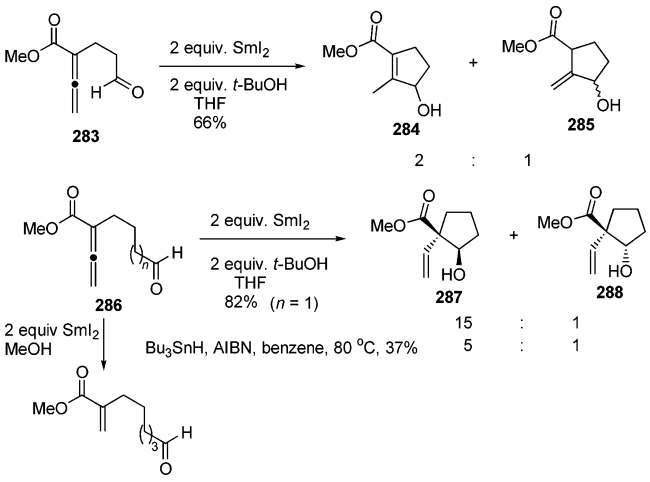


3. Radical Reactions

Gillman et al. studied the SmI_2-promoted intramolecular radical addition between the aldehyde and the allenoate moieties in **283** affording a mixture of C=C bond regioisomers **284** and **285**. When the carbon chain between the allene moiety and the aldehyde functionality was extended by one carbon, the highly selective reaction of the nonterminal C=C bond with the CHO group was observed to afford five-membered diastereomeric products **287** and **288**. The stereochemistry may be determined by the coordination of Sm with oxygen because the AIBN-initiated cyclization in the presence of Bu_3SnH afforded the same products with a much lower stereoselectivity (5:1). The formation of six-membered products was achieved in 78% yield, while the formation of seven-membered products was less successful with the conjugate reduction of the allenoate being the major pathway (Scheme 64).[72]

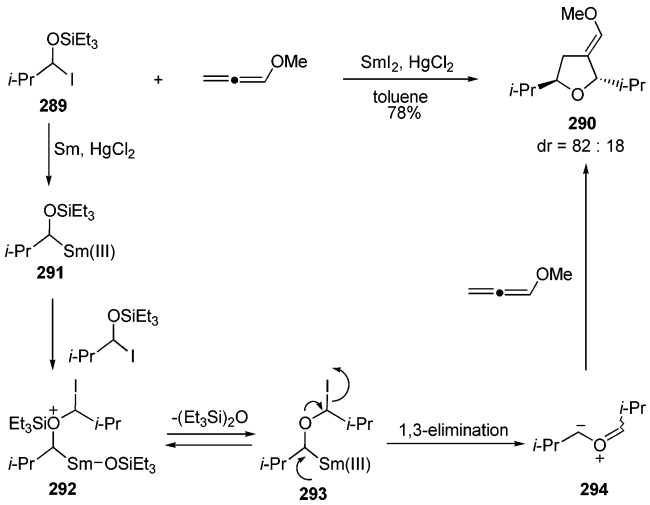
Hosomi et al. observed that 1-siloxyalkyl iodide **289** can react with propadienyl methyl ether in the

Scheme 64



presence of metallic Sm and $HgCl_2$ (0.2 equiv to Sm) to afford *trans*-3-methoxymethylenetetrahydrofuran **290** stereoselectively. The reaction may proceed via the nonstabilized carbonyl ylide **294** formed from the 1,3-elimination of **293**, which was produced by the reaction of **289** with its corresponding Sm reagent **291** (Scheme 65).[73]

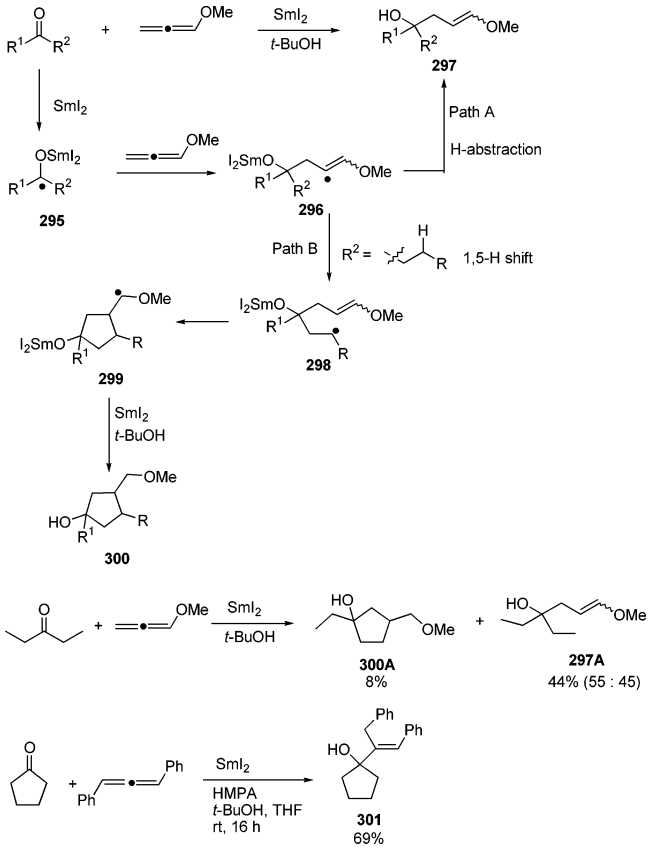
Scheme 65



Recently, Reissig et al. reported the intramolecular reaction of propadienyl methyl ether with ketones yielding homoallylic alcohol **297** via the addition of the in-situ formed ketyl radical **295** to allenyl methyl ether. In some cases, due to the presence of the R^2 group with a longer carbon chain, 1,5-H shift may lead to the formation of a new radical intermediate **298**, which may undergo a radical cyclization with the methyoxy-substituted C=C bond in **298** to afford cyclic alcohol **300**. The corresponding reaction of cyclopentanone and 1,3-diphenylallene afforded *E*-allyl alcohol **301** in 69% yield with high stereoselectivity (Scheme 66).[74]

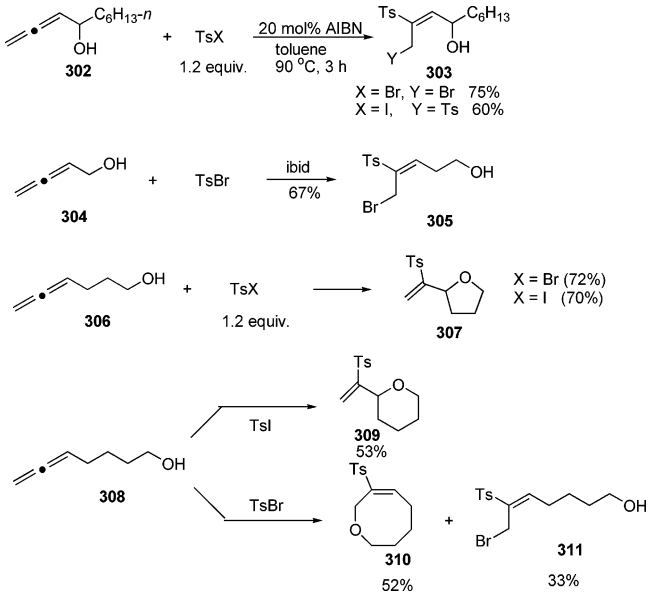
The AIBN-initiated radical addition reaction of *p*-toluenesulfonyl bromide or iodide with allenic alcohols **302** and **304** formed the addition products *E*-**303** and *E*-**305** with high stereoselectivity.[75a] The five-membered product **307** was formed from the reaction of 4,5-hexadienol **306**. The reaction of 5,6-

Scheme 66



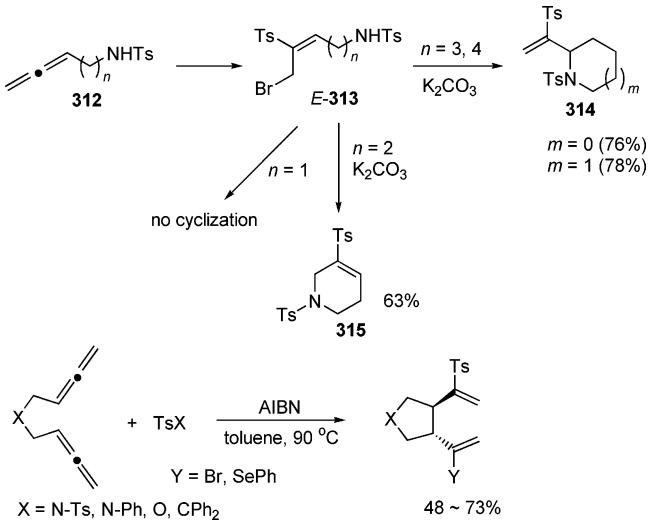
heptadienol **308** with TsI or TsBr afforded different cyclization products **309** or **310**, respectively (Scheme 67).[75a]

Scheme 67



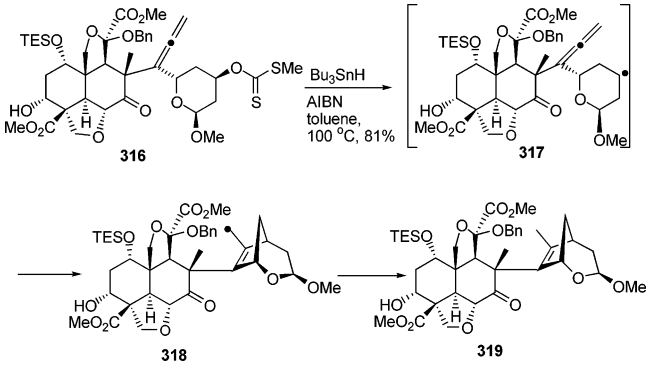
N-Allenyl sulfonamides **312** reacted with TsBr to afford the 1:1 radical addition products *E*-**313** highly stereoselectively, which cyclized in the presence of K_2CO_3 (1.2 equiv) at room temperature to afford **314** (n = 3, 4) or **315** (n = 2).[75a] The reaction of TsBr or TsSePh with 1,2,7,8-tetraenes afforded *trans*-1,2-vinylic five-membered products (Scheme 68).[75b]

Scheme 68



Ley et al. showed the intramolecular radical cyclization of an xanthate with an allene in **316** (Scheme 69).[76]

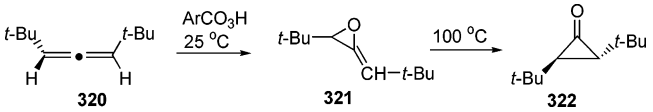
Scheme 69



4. Oxidations or Episulfidations

An early report showed that the photooxygenation of allenes with $^1O_2$ yielded unstable tetraoxaspirocycloheptenes, which underwent decomposition to yield aldehydes or ketones by releasing CO_2.[77] Reaction of 1,3-di(*tert*-butyl)allene **320** with *m*-CPBA in hexane afforded allene monoxide **321**, which may undergo rearrangement upon heating to form *trans*-2,3-di-(*tert*-butyl)cyclopropanone **322** (Scheme 70).[78]

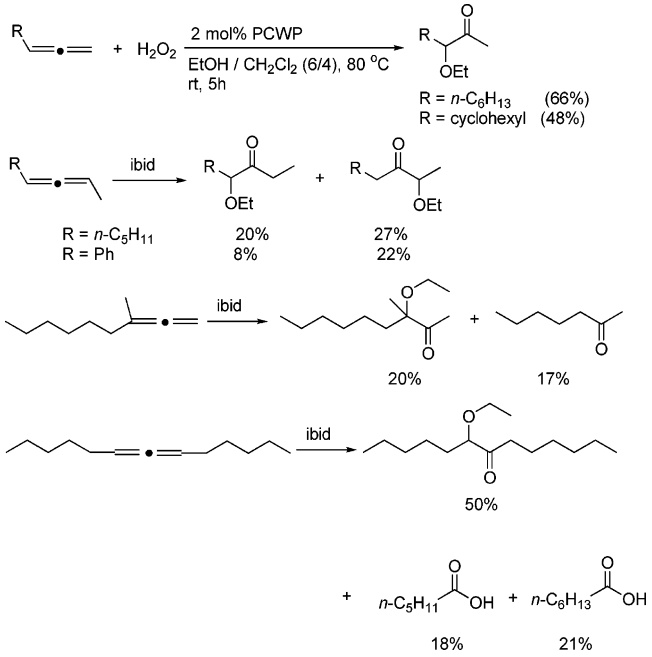
Scheme 70



Ishii reported that the oxidation of allenes with H_2O_2 under the catalysis of cetylpyridinium peroxotungstophosphate (PCWP) afforded α-ethoxy ketones.[79] The regioselectivity for monosubstituted allenes is very good, while the reaction of 1,3-disubstituted allenes yielded mixtures of α-ethoxyketones and carboxylic acids (Scheme 71).

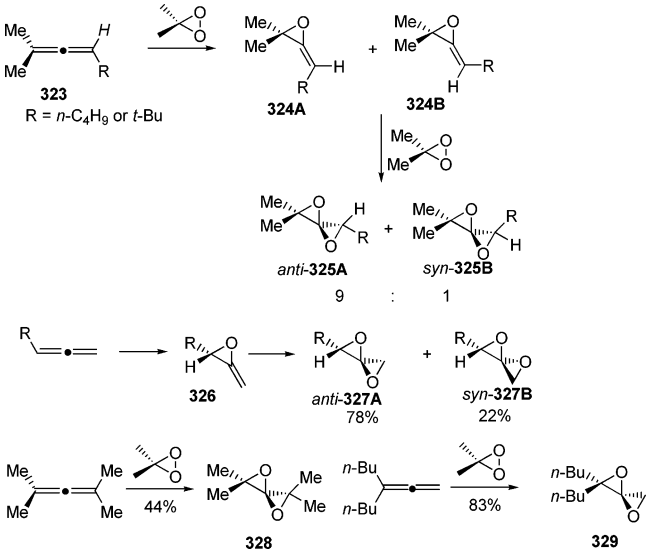
Crandall et al. demonstrated the bisepoxidation of allenes with dimethyldioxirane. The first epoxidation proceeded largely with the more substituted C=C

Scheme 71



bond of allenes. Mono- or trisubstituted allenes gave the anti diasteroisomers **325A** or **327A** as the major products. The same reaction of 2,4-dimethyl-2,3-pentadiene and 3-(*n*-butyl)-1,2-heptadiene yielded **328** and **329** in 44% and 83% yields, respectively (Scheme 72).[80]

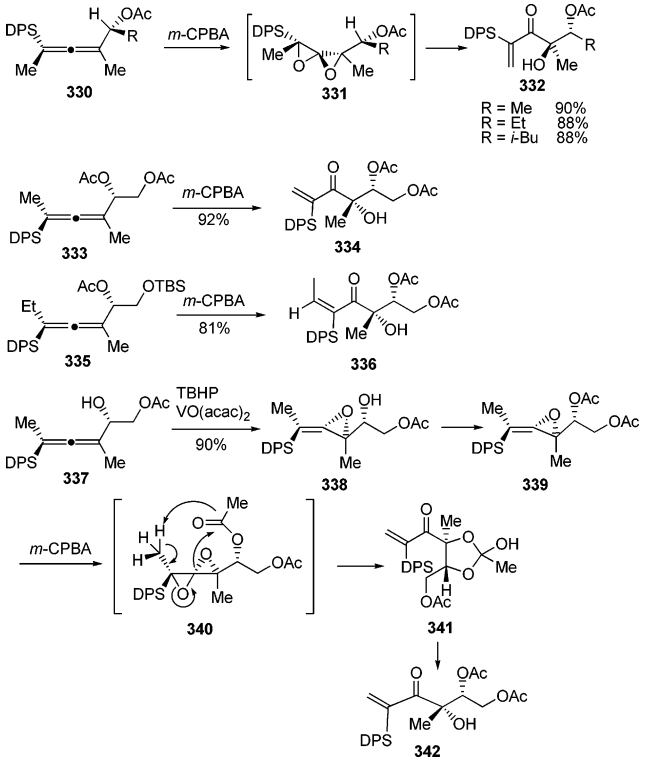
Scheme 72



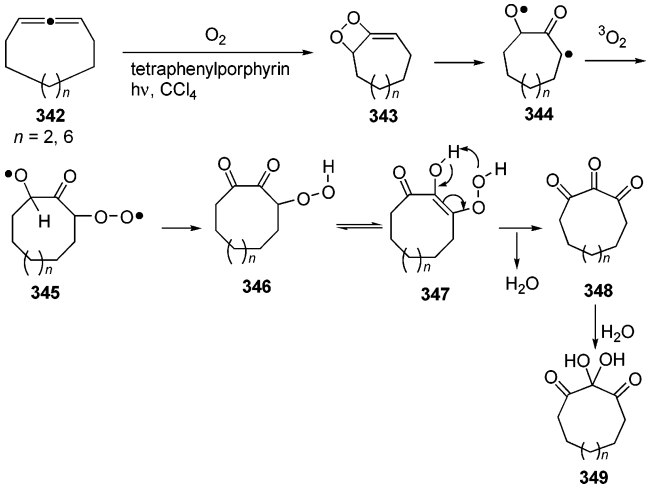
Marshall et al. reported the bisepoxidation of 2,3-allenyl acetates **330**, **333**, **335**, and **337** with *m*-CPBA leading to the formation of α,β-unsaturated ketones **332**, **334**, **336**, **342** via the **331** or **340**-type intermediates (Scheme 73).[81]

Cyclic allenes **342** can undergo monophotooxygenation with $^1O_2$ to afford **343**, which underwent the homolytic cleavage of the O−O bond to form the 1,4-diradical intermediate **344**. The addition reaction of the α-carbonyl radical in **344** with $^3O_2$ followed by H-abstraction would form α-hydroperoxy ketone **346**. Subsequent dehydration of its enol form **347** would afford trione **348** (Scheme 74).[82]

Scheme 73



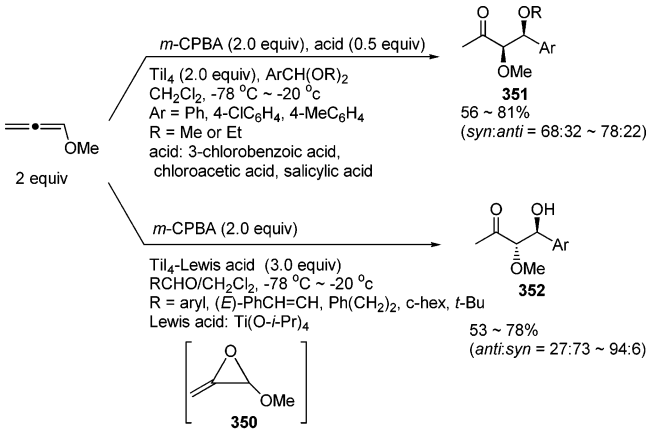
Scheme 74



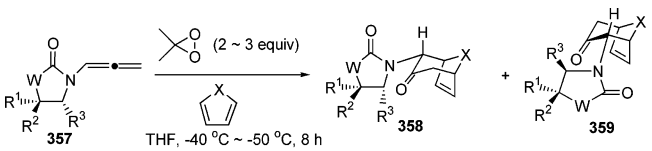
Monoepoxidation of methoxyallene can be regioselectively achieved with *m*-CPBA to give methoxyallene oxide **350**, which may undergo Aldol-type reaction with acetals or aldehydes to give β-alkoxy (or hydroxy)-α-methoxy ketones **351** or **352**, respectively, in the presence of 2.0 equiv of TiI_4.[83a] It should be noted that different stereoselectivity was observed with acetals and aldehydes, respectively, probably due to the difference in the coordination abilities of the alkoxy group and the hydroxy group. The epoxidation of allenoic acids **353** and **355** with dimethyldioxane followed by cyclization would afford lactones **354** and **356**, respectively (Scheme 75).[83b]

Hsung et al. studied the monoepoxidation of 1-aminoallenes **357** with dimethyl dioxirane and the subsequent reaction with furan or cyclopentadiene to afford **358** and **359** with high selectivity (Scheme 76).[84]

Scheme 75



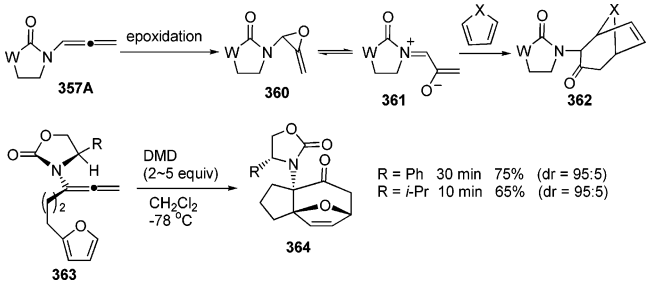
Scheme 76



X	W		$ZnCl_2$ (equiv)	
CH_2	O	$R^1 = R^2 = H$, $R^3 = Ph$	2.0	40% (¡Ý95:5)
O	NMe	$R^1 = Me$, $R^2 = H$, $R^3 = Ph$	2.0	60% (¡Ý95:5)
CH_2	NMe	$R^1 = Me$, $R^2 = H$, $R^3 = Ph$	2.0	83% (¡Ý96:4)
O	O	$R^1 = H$, $R^2 = H$, $R^3 = CHPh_2$	-	74% (¡Ý95:5)
CH_2	O	$R^1 = H$, $R^2 = H$, $R^3 = CHPh_2$	-	62% (93:7)
O	O	$R^1 = Ph$, $R^2 = Ph$, $R^3 = i$-Pr	-	72% (94:6)

The reaction may proceed via the [4+3]-cycloaddition reaction of the monoepoxidation product **360** with furan or cyclopentadiene via the intermediacy of zwitterion **361**.[84] An intramolecular version of this reaction has been recently disclosed by the same author (Scheme 77).[85]

Scheme 77

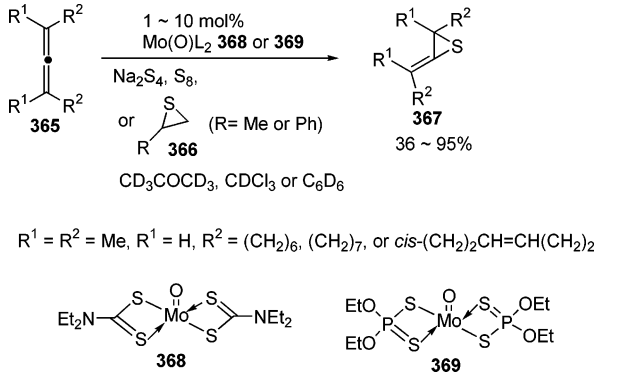


Recently, Bargon et al. demonstrated that under the catalysis of a molybdenum oxocomplex **368** or **369**, allenes **365** could undergo direct monoepisulfidation with thiirane **366** (Scheme 78).[86]

5. Nucleophilic Addition

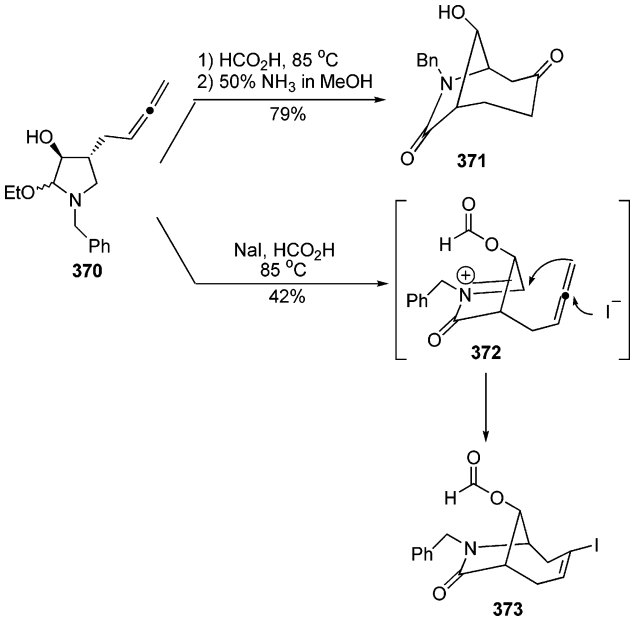
Hiemstra et al. noticed interestingly that the electron-rich allene moiety in **370** can accept the

Scheme 78



nucleophilic attack due to the presence of an iminium moiety in the **372**-type intermediates (Scheme 79).[87]

Scheme 79



Recently, intramolecular nucleophilic additions of 1,2-allenyl sulfones with different nucleophiles (alcohols, malonates, amines, etc.) have also been established to prepare cyclic products including the not readily available eight-membered ring products **375** ($n = 4$) (Scheme 80).[88]

6. Cyclometalation[89]

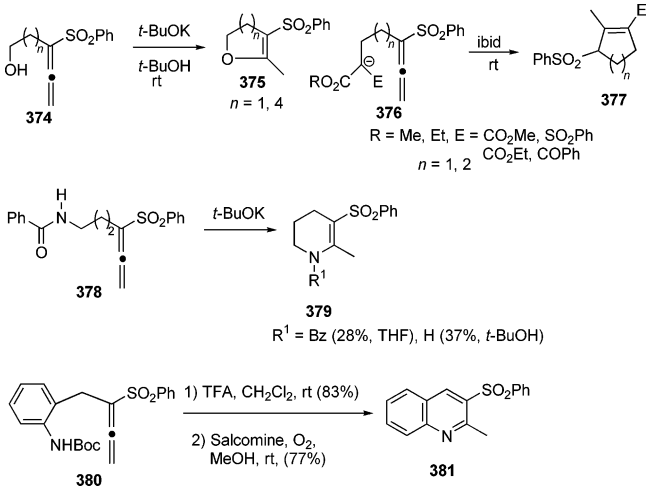
6.1. Intermolecular Reaction

6.1.1. Cyclometalation between Allenes and Alkynes

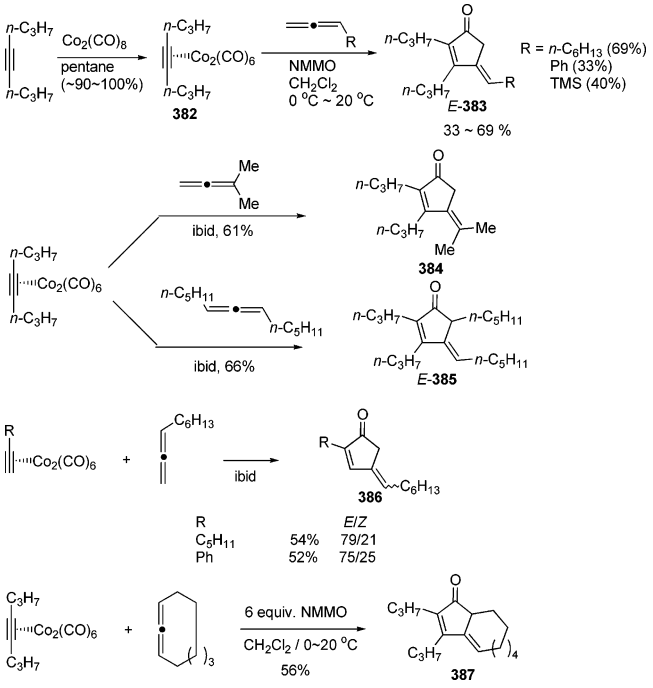
Cazes reported that *N*-methylmorpholine oxide can promote the intermolecular $Co_2(CO)_8$-mediated Pauson−Khand cyclization of alkyne and allenes leading to the formation of 4-alkylidene-2-cyclopentenones **383**−**387**.[90] In the cases of unsymmetric allenes, usually the less-substituted C=C bonds were cyclometalated. The reaction afforded *E*-isomers as the major products. The regioselectivity in terms of the C=C bonds in allenes bearing $SnBu_3$, $SiPhMe_2$, CO_2-Et, SO_2Ph groups is poor (Scheme 81).[91]

Furthermore, it was also observed that the silyl group in the alkyne moiety played an important role

Scheme 80



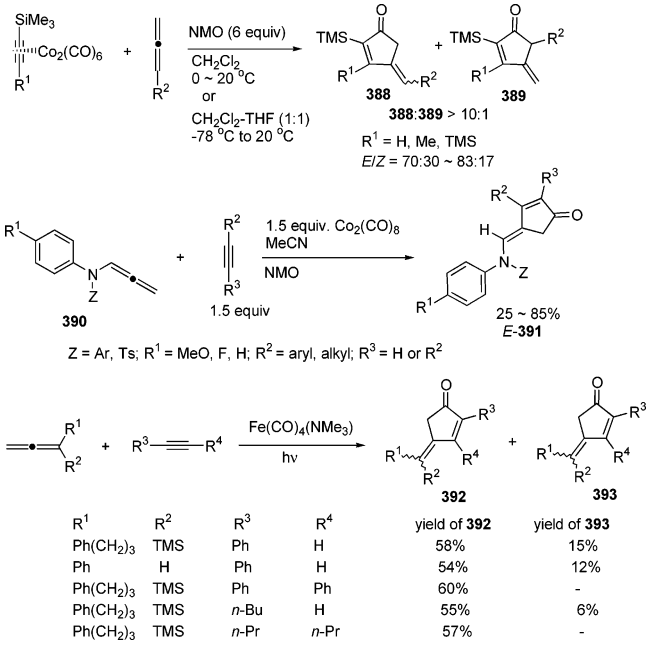
Scheme 81



in the regiocontrol of the Co-mediated intermolecular Pauson−Khand reaction of alkynes and allenes.[92] With R^1 being *n*-Bu, the *E*/*Z* ratio of **388** reached 100:0, while the reaction of the substrate with R^1 being *t*-Bu did not occur. The regioselectivity for the products was determined by the steric effect of both starting materials requiring the two relatively bulky groups located as far away as possible in the products. The intermolecular Pauson−Khand reaction of allenamides **390** and alkynes is also regio- and stereoselective forming *E*-**391** in 80% yield.[93] Intermolecular reaction between allenes and alkynes can also be mediated by $Fe(CO)_4(NMe_3)$ to afford cyclopent-2-enones **392**−**393**, selectively (Scheme 82).[94]

Cheng et al. developed the Ni-catalyzed cyclotrimerization of one allene and two 2-alkynoates affording polysubstituted arenes **395**. Different regiochemistry was observed with 3-phenylpropynoate affording benzene derivatives **396**, in which the two methoxycarbonyl groups are meta to each other.[95] A similar [2+2+2] reaction was also observed between

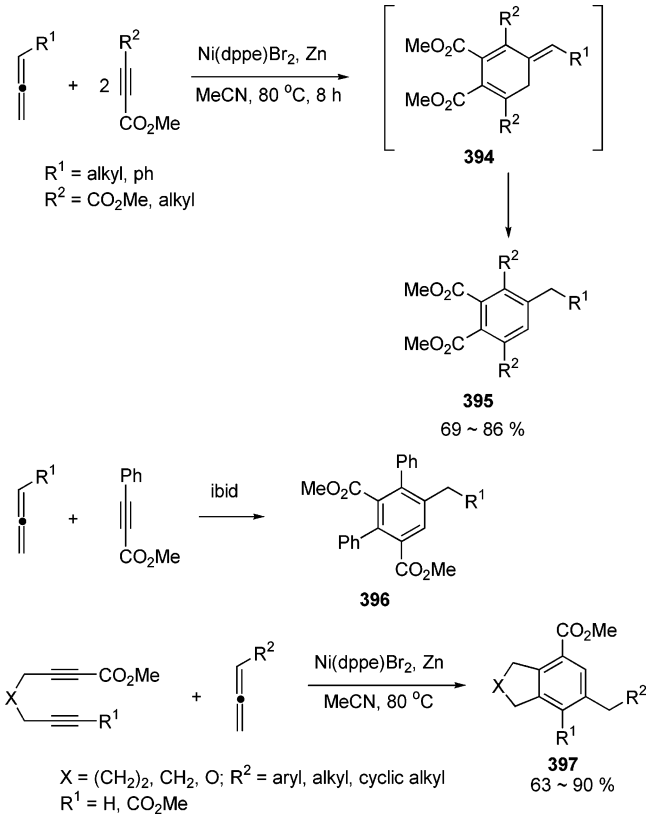
Scheme 82



R^1	R^2	R^3	R^4	yield of **392**	yield of **393**
$Ph(CH_2)_3$	TMS	Ph	H	58%	15%
Ph	H	Ph	H	54%	12%
$Ph(CH_2)_3$	TMS	Ph	Ph	60%	-
$Ph(CH_2)_3$	TMS	*n*-Bu	H	55%	6%
$Ph(CH_2)_3$	TMS	*n*-Pr	*n*-Pr	57%	-

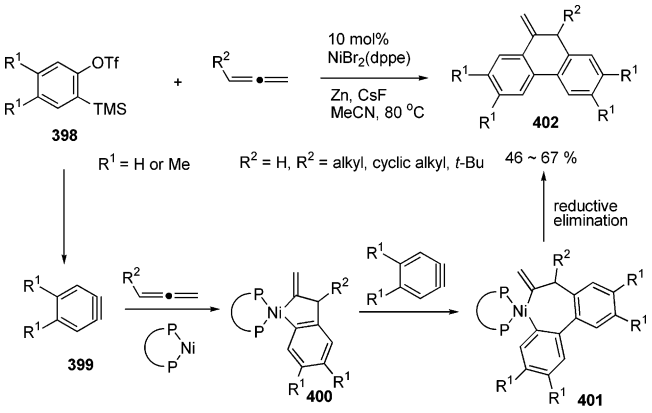
1,6- or 1,7-alkadiynoates and allenes to afford the benzocyclic products **397** efficiently.[96] With $R^1 = H$, the methoxycarbonyl group and the R^2CH_2 group are meta to each other in the newly formed benzene ring. The reaction proceeded via the cyclometalation of two C−C triple bonds forming a metallocyclopentadiene intermediate, which would undergo a sequential regioselective insertion with an allene, reductive elimination, and aromatization process to afford the polysubstituted arenes (Scheme 83).

Scheme 83



$NiBr_2$(dppe) can catalyze the cyclometalation of allenes with two molecules of the in-situ generated benzyne **399** to form the nonaromatic six-membered ring in **402** (Scheme 84).[97]

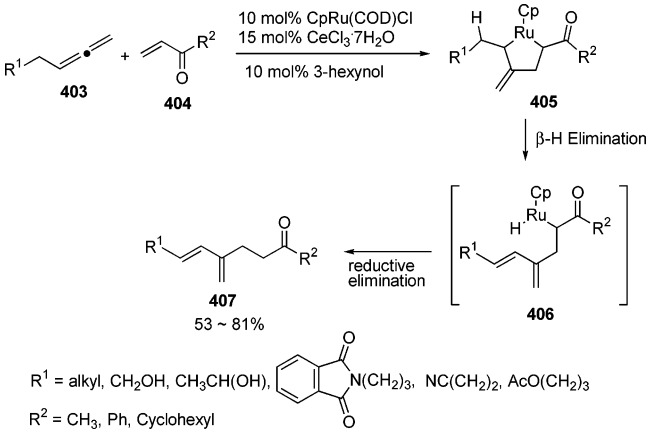
Scheme 84



6.1.2. Cyclometalation between Allenes and Alkenes

Trost et al. utilized the cyclometalation of terminal allenes with α,β-unsaturated enones and the subsequent β-H elimination-reductive elimination to prepare 3-methylene-4-(*E*)-alkenyl ketone **407** with high stereoselectivity (Scheme 85).[98]

Scheme 85



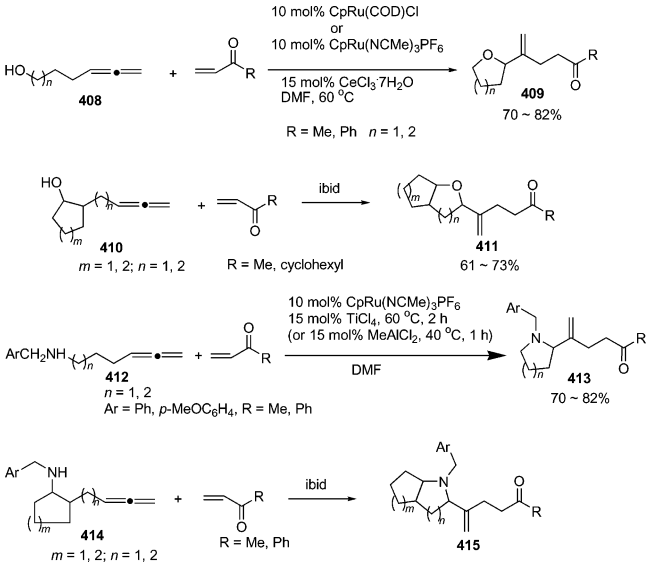
Furthermore, it is interesting to observe that when 4,5- or 5,6-allenols **408** or **410** were applied as the starting allenes, the allylic Ru moiety in the **405**-type intermediate may be attacked by the OH group to form cyclic ethers **409** and **411**.[99] Pyrrolidines or piperidines **413/415** can also be prepared from the reaction of 4,5- or 5,6-allenylamines **412** and **414** (Scheme 86).[100]

6.1.3. Cyclometalation between Two Allenes

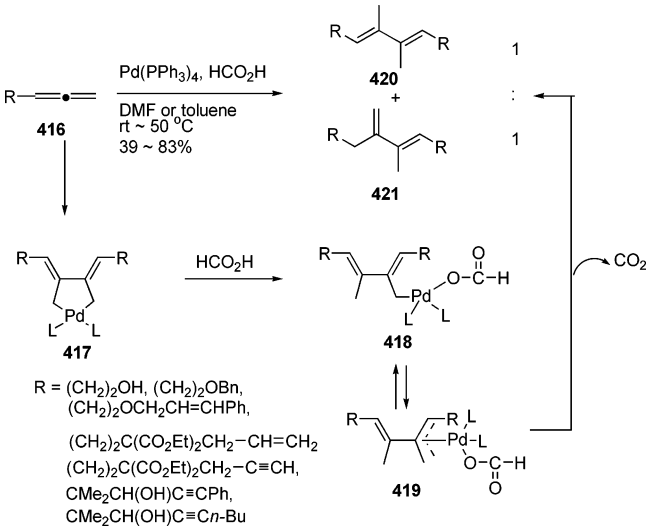
Oh et al. also reported the Pd-catalyzed dimerization of allenes **416** leading to the formation of conjugate dienes **420** and **421** via the monoprotonolysis of the metallocyclic intermediate **417**, forming **418** or **419**, which was followed by CO_2 elimination, and reductive elimination to afford a mixture of **420** and **421** (Scheme 87).[101]

(2-Propen-2-yl)propenylation of 4-hydroxylcumarin **422** or methylene pronucleophiles **425** or **427** with propadiene afforded **423**, **426**, or **428**, respectively.

Scheme 86



Scheme 87

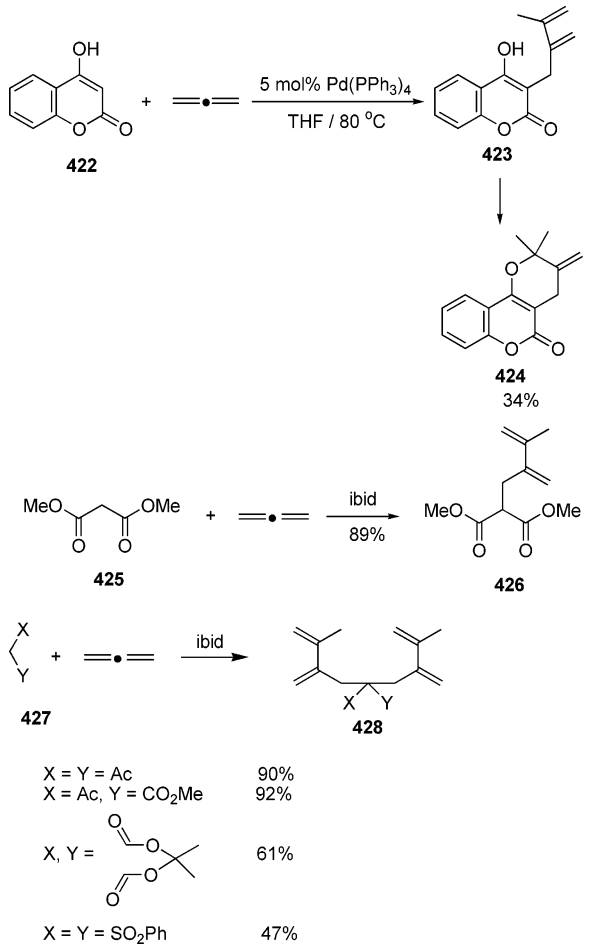


Product **423** undergoes further cyclization to form tricyclic compound **424** (Scheme 88).[102]

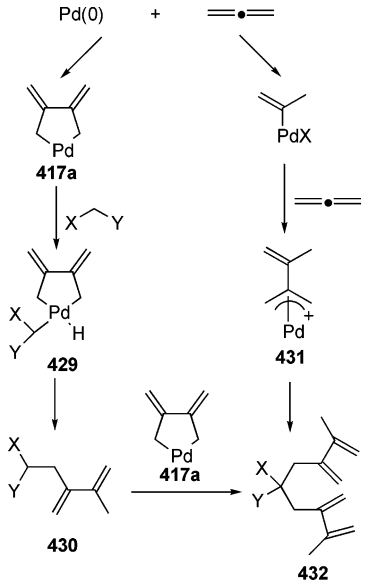
The reaction may proceed via the following mechanism: the cyclometalation of two molecules of propadiene would form metallocyclic intermediate **417** (R = H), which may undergo C−H oxidative addition reaction with a pronucleophile to form a tetravalent metallocyclic intermediate **429**. Double reductive elimination would afford monoalkylation product **430**, which would react with **417** in a similar way to afford the double alkylation product **432**. An alternative pathway is the regioselective hydropalladation of propadiene followed by carbopalladation of the second molecule of propadiene to form the 2-vinylic π-allyl palladium intermediate **431**. Double nucleophilic substitution would afford the product **432** (Scheme 89).

Recently, Ihara et al. observed the $CpRu(MeCN)_3PF_6$-catalyzed dimeric cyclometalation of 2,3-allenols **433** leading to the formation of 5-acetoxy-3-methylenealk-5-en-1,7-diols **437** via a cyclometalation/reductive elimination/intramolecular protonolysis (of the C−Ru bond in **435**) process (Scheme 90).[103]

Scheme 88



Scheme 89

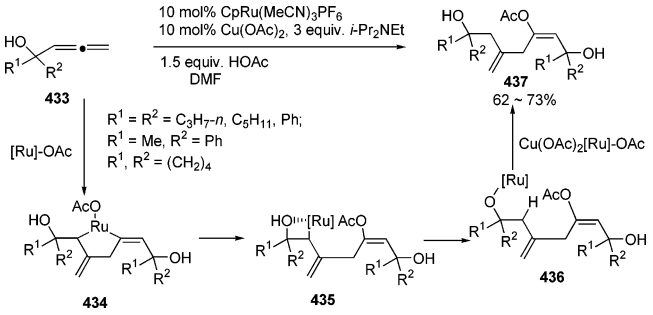


6.1.4. Cyclometalation between Allenes and CO_2

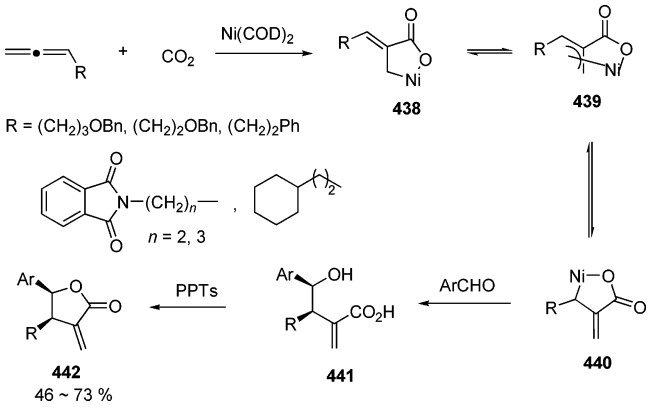
An allene can undergo cyclometalation with CO_2 to afford cyclic intermediates **438** or **439** or **440**, which would react with an aldehyde to afford **441** with high stereoselectivity. Upon lactonization, **441** would form *cis*-α-methylene-γ-butyrolactones **442** (Scheme 91).[104]

The $Ni(COD)_2$-mediated cyclometalation of CO_2 with 1-(trimethylsilyl)-1,2-allenes **443** led to the formation of metallocyclic intermediate **444**, which, upon sequential treatment with $R_2^1R^2SiH$, H_3O^+, and CH_2N_2, afforded 2-(trimethylsilylmethyl)-2(*E*)-alkenoates **445** with high selectivity. The yield was lower with Et_3SiH.[105] The Ni(II)-catalyzed electrocarboxylation of allenes with CO_2 afforded unsaturated carboxylic acids with a poor selectivity (Scheme 92).[106]

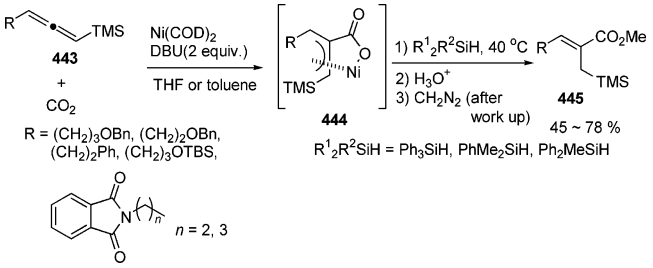
Scheme 90



Scheme 91



Scheme 92



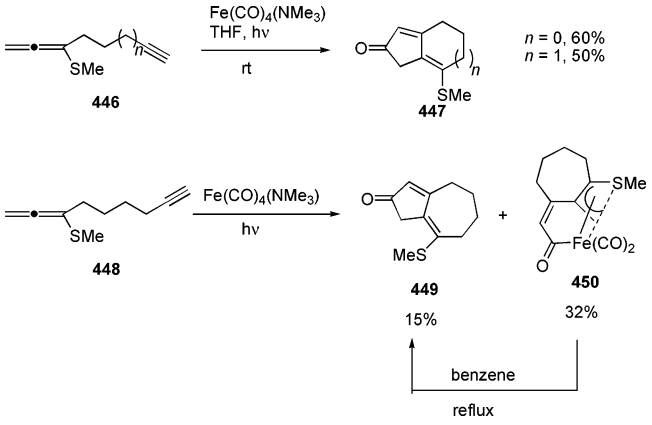
6.2. Intramolecular Reactions

6.2.1. Cyclometalation between Allenes and Alkynes

In 1995, Narasaka observed that $Fe(CO)_4(NMe_3)$ can promote the intramolecular coupling of allene-alkynes **446** to afford Pauson−Khand-type product **447** with the less substituted C=C bond of the allene moiety being reacted. The reaction of 3-methylthio-1,2-nonadien-8-yne **448** afforded 15% of the 5/7-fused bicyclic product **449** and π-allyl iron complex **450**, which can be converted to **449** by refluxing in benzene, indicating the intermediacy of **450** for this reaction (Scheme 93).[94]

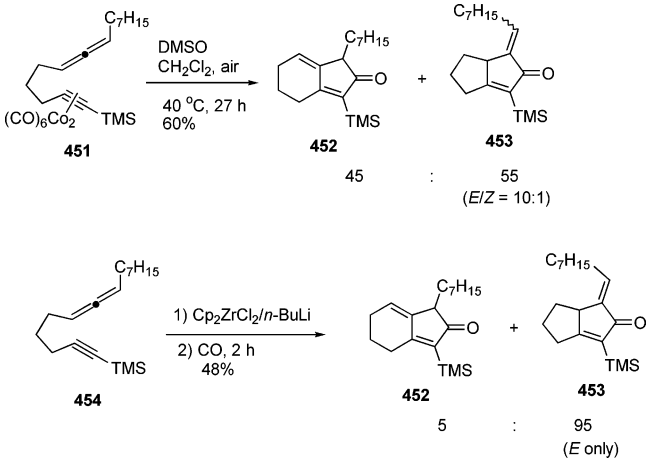
The Co-mediated intramolecular Pauson−Khand reaction afforded two products with a poor regioselectivity relative to the two C−C double bonds in the

Scheme 93



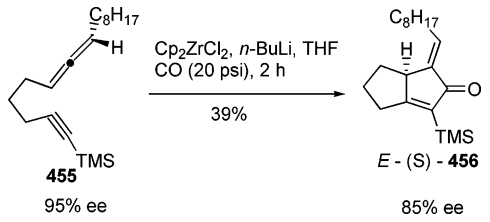
allene moiety.[107] When steric hindrance was increased by introducing the sterically bulky TMS group on the alkyne moiety, the reaction afforded the 5/6-fused bicyclic enone **452** together with 5/5-fused bicyclic product **453**. The reaction mediated by Cp_2ZrCl_2/*n*-BuLi afforded *E*-**453** with high selectivity (Scheme 94).[108]

Scheme 94



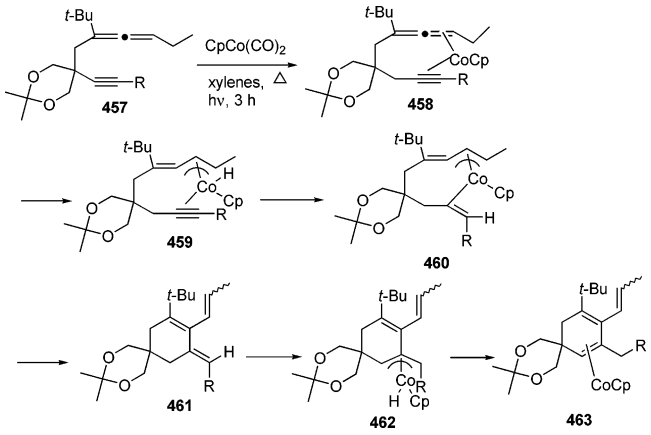
The reaction of optically active substrate **455** under the mediation of Cp_2ZrCl_2 and *n*-BuLi afforded optically active bicyclic enone *E*-(*S*)-**456** with the partial loss of the axial chirality of the allene moiety during the chirality transfer process, which may be explained by the formation of the *R*-product from the epimerization of *Z*-(*R*)-**456** during the reaction (Scheme 95).[109]

Scheme 95



However, the mechanism for the reaction of 5,6-alkadienynes **457** with $CpCo(CO)_2$ may not be cyclometalation. Malacria et al. reported the allylic C−H activation-hydrometalation-reductive elimination process forming cyclohexadiene derivatives **463**. The

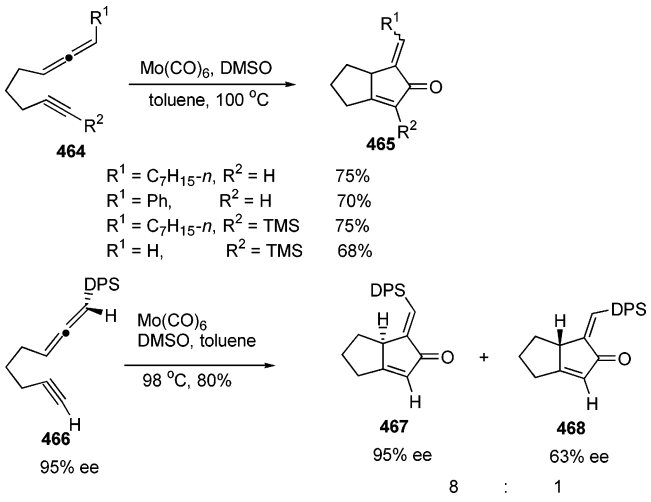
Scheme 96



second allylic C−H bond activation in **461** induced the migration of the C=C bond forming π-allylic cobalt complex **462** (Scheme 96).[110]

In 1995, Brummond reported the $Mo(CO)_6$-mediated Pauson−Khand reaction of alkyne-1,3-disubstituted allene compounds.[111] Compounds **464** afforded 5/5-fused bicyclic ketones **465** with the C=C bond in the allene moiety "closer" to the alkyne moiety being incorporated.[109,111] Under the mediation of $Mo(CO)_6$, the chirality in **466** could be transferred efficiently with a **467**:**468** ratio being 8:1 (Scheme 97).[109] In this

Scheme 97

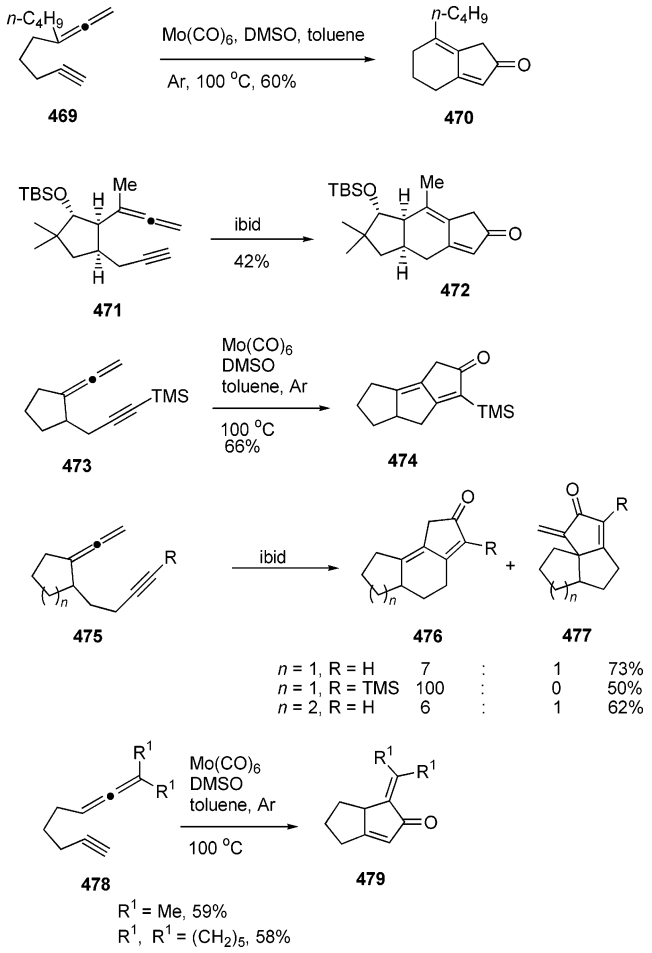


case, the favored formation of two five-membered rings may determine the regioselectivity.

The formation of 5/6-fused bicyclic enone skeletons became the only or major pathway when 3,3-disubstituted-1,2-allen-7-ynes **469** or **471** were studied. This was due to the incorporation of the less-substituted terminal C=C bond. The reaction of 3,3-disubstituted-1,2-allen-6-alkyne **473** with one CH_2 unit between the five-membered ring and the C−C triple bond that afforded the product **474** resulted from the reaction of the terminal C=C bond and the C−C triple bond. With the introduction of an extra CH_2 unit, the regioselectivity for the substrates with a terminal C−C triple bond in **475** is lower, affording a mixture of **476** and **477**. With the TMS-substituted alkyne, the regioselectivity is excellent, forming **476** as the only product. With 1,1,3-trisubstituted allene-

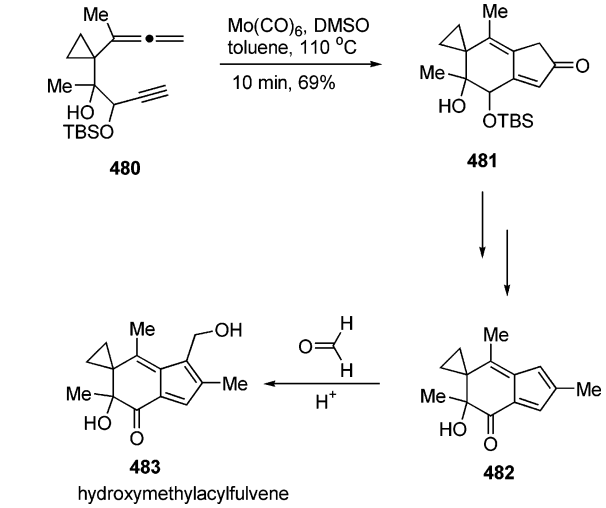
alkyne substrates **478**, the reaction underwent the Pauson−Khand-type reaction with the less-substituted C=C bond to afford the 5/5-bicyclic enones **479** with high selectivity (Scheme 98).[112]

Scheme 98



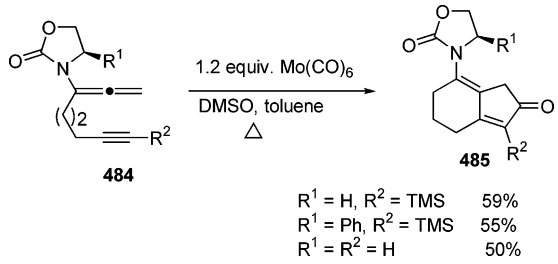
By applying this protocol, an efficient synthesis of the potent antitumor agent (±)-hydroxymethylacylfulvene **483** was developed (Scheme 99).[113]

Scheme 99



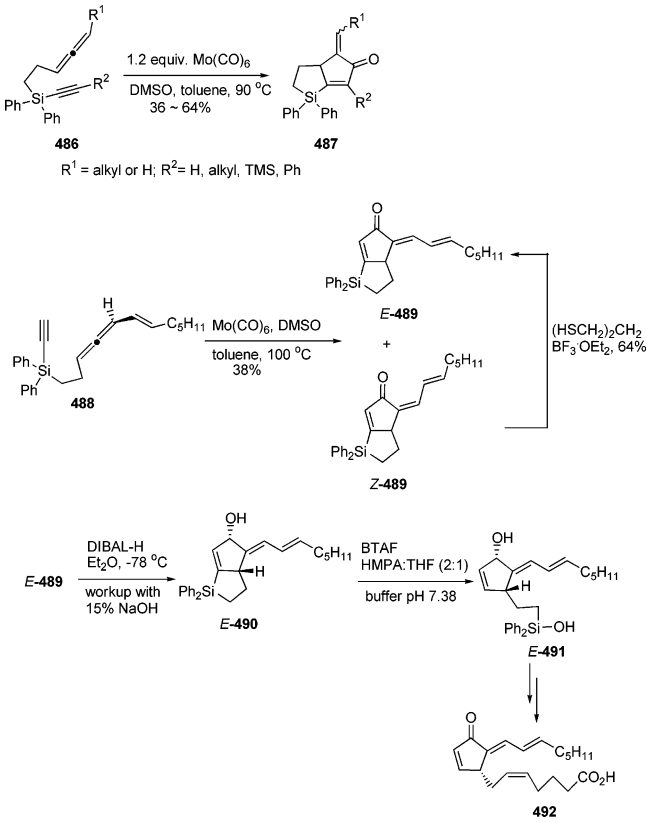
Hsung observed a similar sterically controlled regioselectivity in the reaction of allenamide-alkynes **484**.[114] On the basis of these results, it can be concluded that in the reaction of the 3,3-disubstituted substrates the relative steric hindrance of the two allenic C=C bonds determined the regioselectivity (Scheme 100).

Scheme 100



Pauson−Khand reaction of silicon-tethered 1,3-disubstituted allene-alkynes also yielded the 5/5-fused bicyclic ketones.[115] This reaction has been applied to the total synthesis of 15-deoxy-$\Delta^{12,14}$-prostaglandin J_2 **492**, which led to the unambiguous assignment of its C^{14} stereochemistry (Scheme 101).[116]

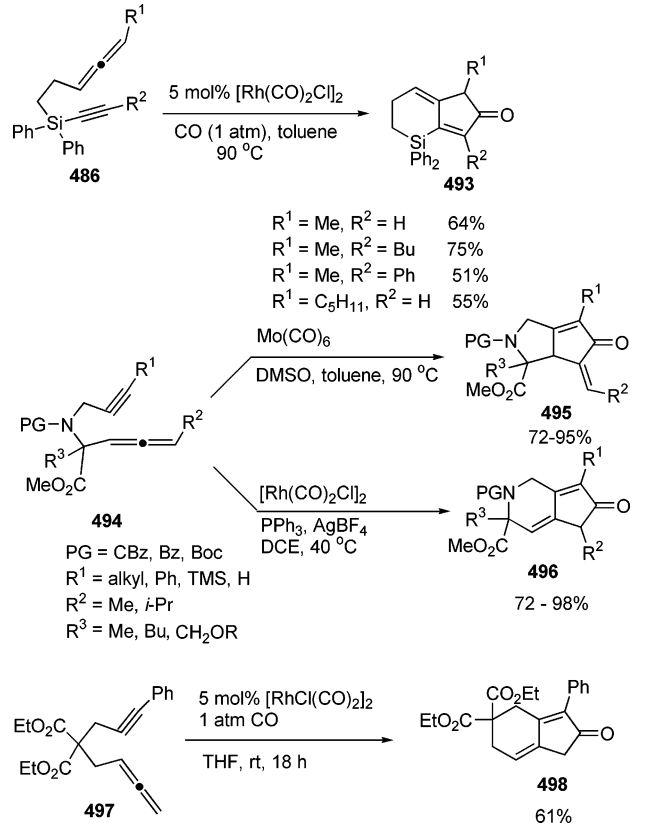
Scheme 101



It is also quite interesting to note that the Pauson−Khand reaction of **486** can also be realized by using a catalytic amount of $[Rh(CO)_2Cl]_2$ in the presence of CO (1 atm) in toluene with a different regioselectivity to afford the 5,6-fused bicyclic products **493** (Scheme 102).[115] A similar regioselectivity switch was also observed in some other cases.[117,118]

This Rh(I) or Ir(I)-catalyzed allene-alkynic Pauson−Khand-type reaction has been extensively studied. Regardless of the substitution pattern, the reaction of 1,2-allen-7-ynes **499** or **501** afforded the

Scheme 102



5/6-fused bicyclic products **500** and **502**.[119] 5,7-Fused bicyclic enones **504** or **506** were also prepared by applying the Pauson−Khand reaction between the 1,2-allenyl sulfone moiety and the C−C triple bond in **503** or **505** (Scheme 103).[120]

The carbon skeleton of guanacastepene A has been efficiently constructed by this Rh(I)-catalyzed transformation (Scheme 104).[121]

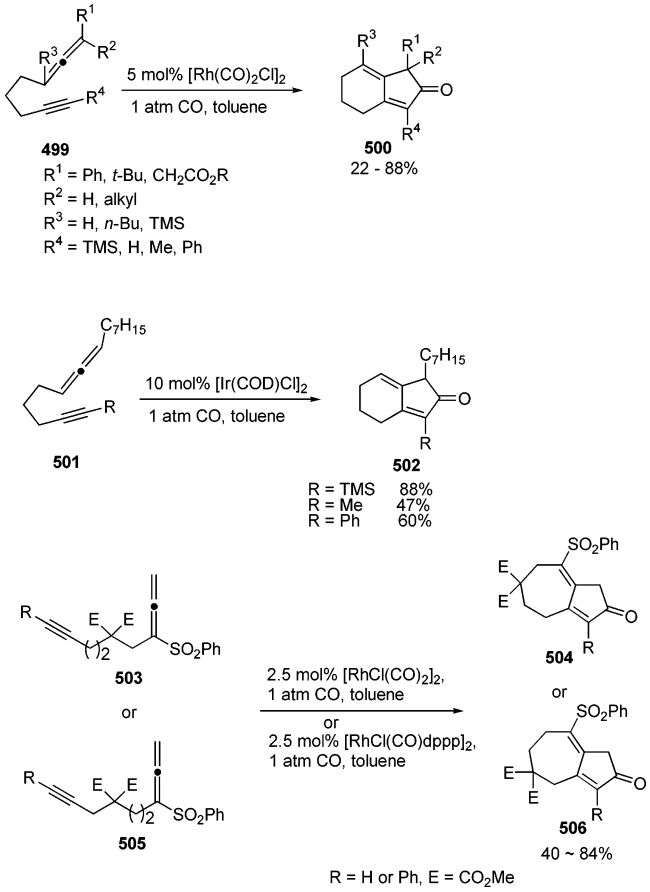
Buchwald noticed that 1,2-allen-6-yne **509** can undergo the Pauson−Khand-type reaction in the presence of $Cp_2Ti(CO)_2$ and CO (Scheme 105).[122]

In addition to the unique regioselectivity that is observed, another advantage of the Rh(I)-catalyzed reaction is that different products can be obtained by running the reaction in the absence of CO.[123] The reaction went through a cyclometalation reaction of **512** to afford the **514**-type intermediate, which underwent subsequent β-H elimination and reductive elimination to afford the product **513**. In some cases, a certain amount of this type of product was formed even when the reaction was conducted in the presence of CO (1 atm).[124] The cyclometalation-β-H elimination-reductive elimination of **515** afforded product **516** as the sole product under N_2.[124] In the case of tetrasubstituted 1,2-allenyl sulfones, that is, **517**, if the reaction was carried out in refluxing xylene, a further electrocyclization of **518** forming an extra cyclobutene ring was observed (Scheme 106).[124]

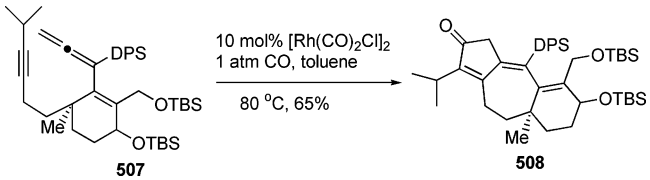
Recently, a double allene-alkynic cyclometalation reaction was demonstrated by Cook et al. to prepare tetracyclic products **521** and **522**, under different conditions (Scheme 107).[125]

Sato et al. reported the (η^2-propene)Ti(O-*i*-Pr)$_2$-mediated cyclometalation of 1,2-alkadien-7-ynes **523**.

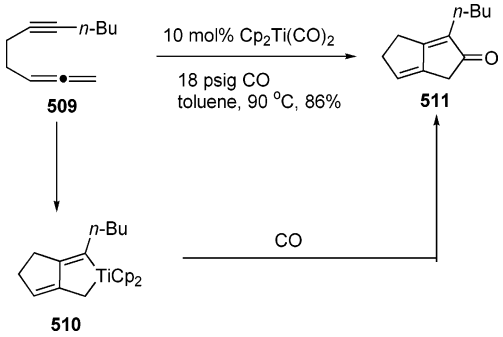
Scheme 103



Scheme 104

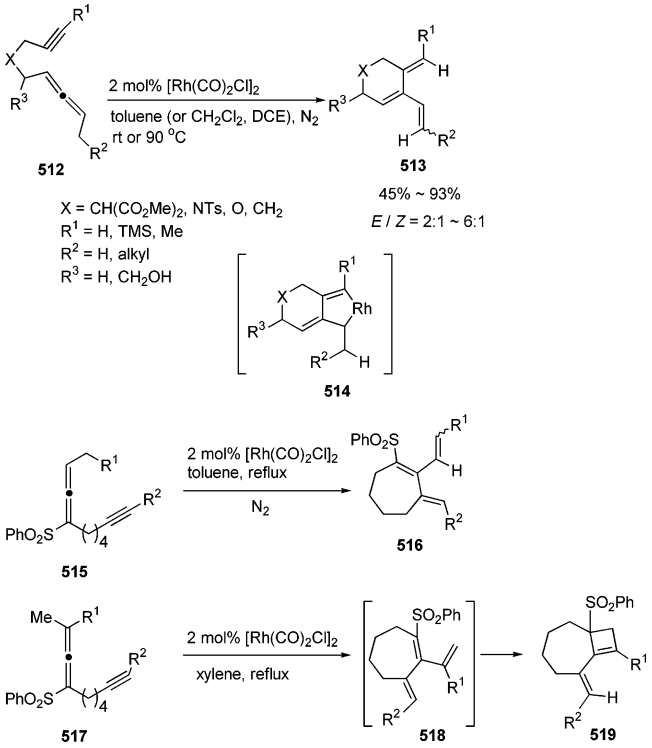


Scheme 105

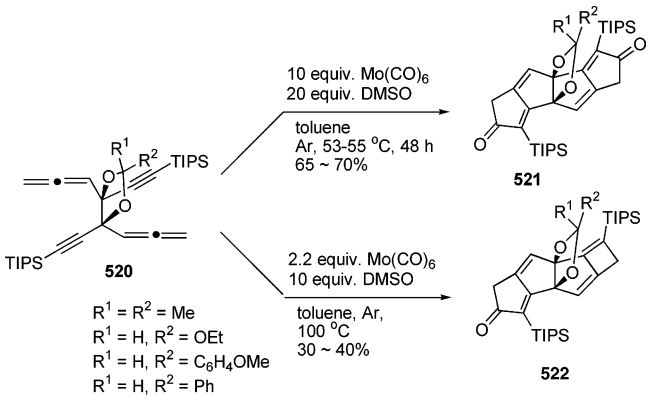


When R^2 was an alkyl group, the reaction afforded the products in a *Z*/*E* ratio of ~80:20, and when R^2 = SiR_3, only the *Z*-isomer was formed.[126] The stereoselectivity can be explained by the steric hindrance between the R^2 group and the Ti(O-*i*-Pr)$_2$ part in intermediate **524**.[126] The reaction of optically active substrate **523A** afforded the corresponding product **525A** without obvious loss of the chirality. When CO was added after the cyclometalation, bicyclic enone **528** was made in its optically active form starting

Scheme 106



Scheme 107



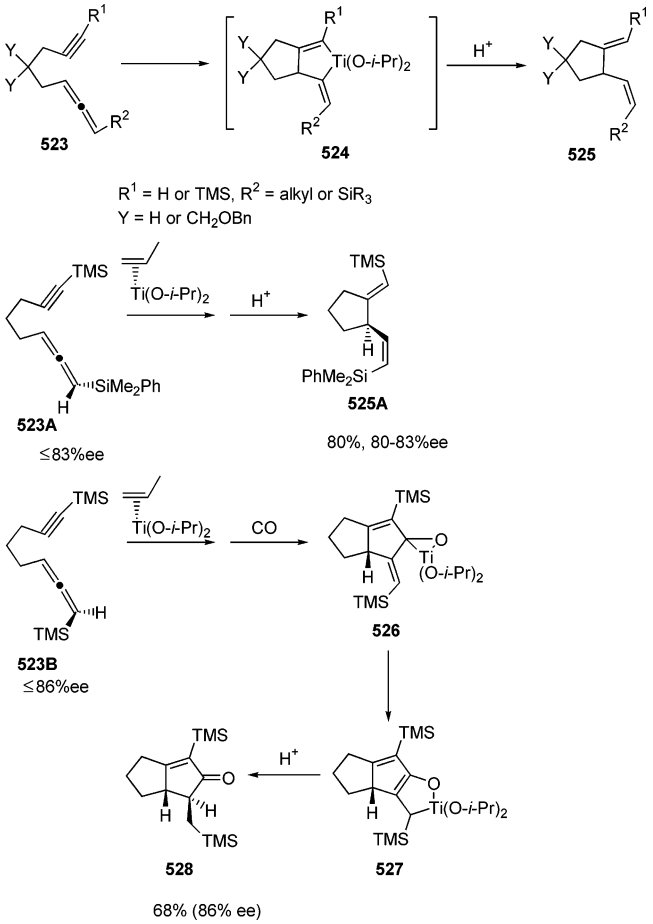
from the optically active substrate **523B** (Scheme 108).[126]

Starting from 1,2-alkadien-6-ynes **529**, the allylic Ti unit in the formed 5/5-fused metallobicyclic intermediates **530** may undergo regioselective addition with aldehydes to afford alcoholic products **531**.[126] The reaction of optically active 1,2-alkadien-6-yne **532** afforded the corresponding product **533** without obvious loss of the chirality (Scheme 109).[126]

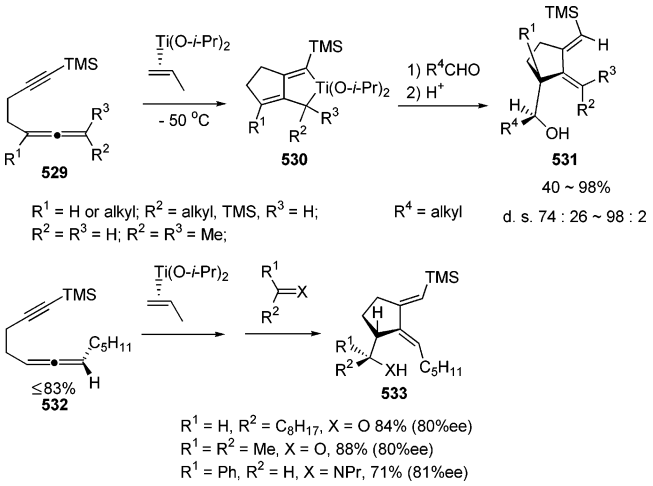
In a similar reaction, the stereoselectivity was effected by the presence of a hydroxyl methyl group (see **534**).[127] With 5,6-alkadien-1-ynes **536** bearing a CH_2X (X = leaving group), the reaction afforded β-heteroatom elimination products, that is, the cross-conjugated trienes **537** (Scheme 110).[128,129]

Shibata et al. used $RhCl(PPh_3)_3$ as the catalyst to catalyze this ene-type reaction of 2-methyl-2,3-allen-8 (or 9)-ynes **538**. The presence of the 2-methyl group provided a route for β-H elimination, which was followed by reductive elimination to afford the cyclic products **539** (Scheme 111).[130]

Scheme 108



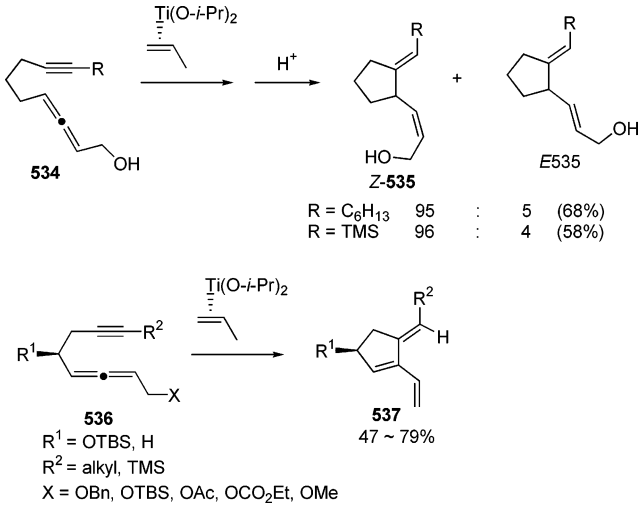
Scheme 109



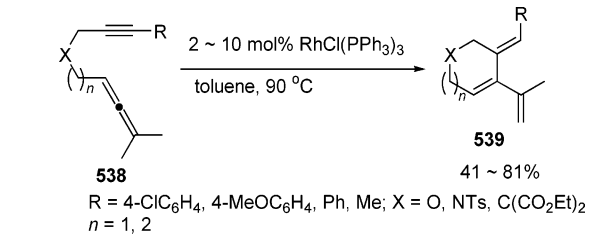
Quite recently, Malacria et al. noticed that under the catalysis of $PtCl_2$, the cyclization reaction of **540** afforded 3-allenylcyclohexenes **541**. The cyclization of the tetrasubstituted allene-alkyne substrates **542** with a terminal C−C triple bond afforded 5/6-fused bicyclic products **543**. It is surprising to note that the reaction of trisubstituted allene-alkyne **544** afforded 2-vinyl-3-methylenecyclohexene **545**, indicating the importance of the missing methyl group at the 4-position of **544** (the allene moiety) (Scheme 112).[131]

A cyclometalation mechanism leading to the formation of platinacyclopentene intermediate **547** was proposed. When $R^3 = CH_2R^4$, allylic β-H elimination

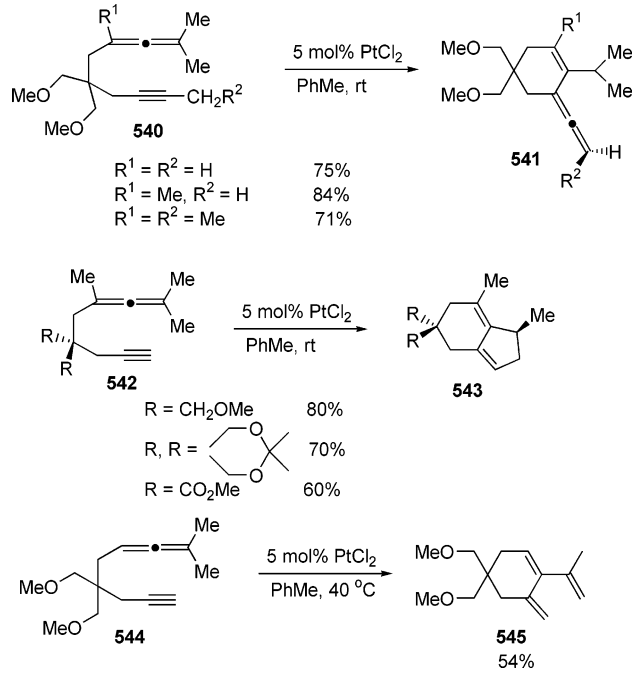
Scheme 110



Scheme 111

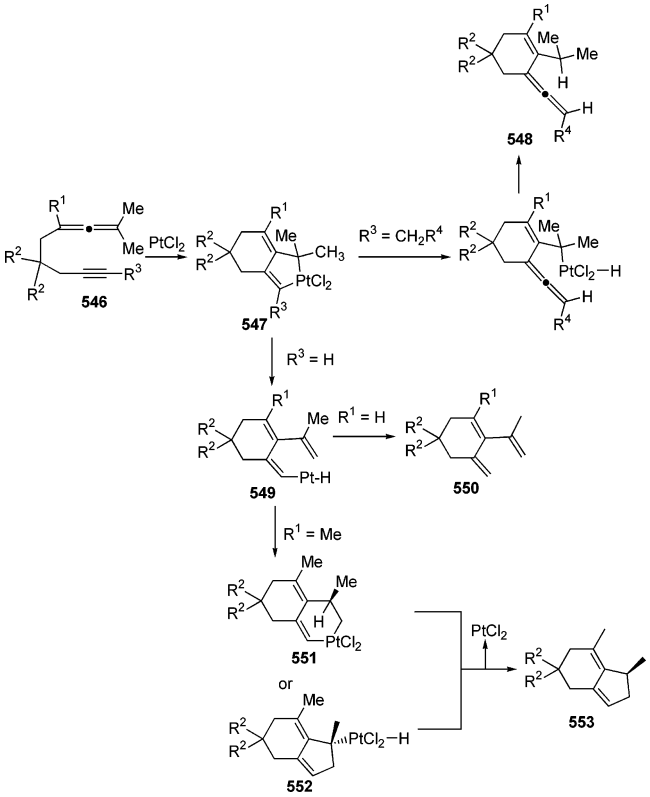


Scheme 112



and reductive elimination of **547** would form **548**. With R^3 being H, β-H elimination from the *gem*-dimethyl would occur to afford **549**. With R^1 = H, reductive elimination of **549** would afford **550**, while the presence of R^1 being Me would induce the second cyclization via hydro- or carbo-metalation forming either **551** or **552** and reductive elimination to afford **553** probably due to the repulsion of two methyl groups in **549**, which made the disubstituted C=C bond closer to the Pt atom (Scheme 113).

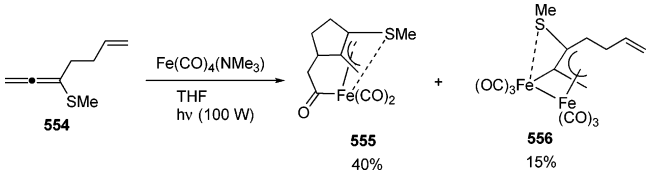
Scheme 113



6.2.2. Cyclometalation between Allenes and Alkenes

The intramolecular reaction of an alkylthio-substituted allene moiety with an alkene in 1,2,6-triene **554** led to the formation of the π-allyl iron complex **555** and the binuclear π-allyl iron complex **556** (Scheme 114).[94]

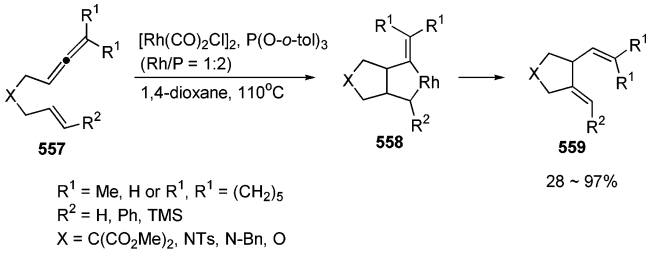
Scheme 114



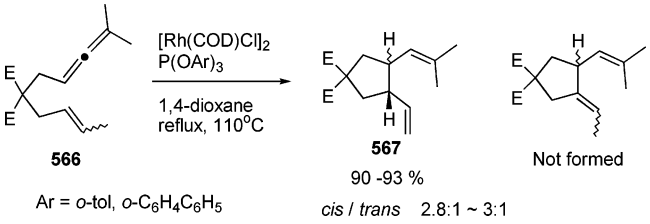
Itoh et al. established the $[RhCl(COD)]_2$-catalyzed cyclization of 1,2,7-trienes **557** (or **560**), in which the two "closer" C=C bonds (one each in the two moieties) was cyclometalated to form metallobicyclic intermediate **558**, which underwent β-H elimination and reductive elimination to afford the 2-vinylic alkylidenecyclopentanes **559** (or **561**).[132,133] Six-membered ring product **563** can also be prepared.[132] The ligand effect on the stereoselectivity of the C=C bond formed by reductive elimination was also demonstrated: with $P(O\text{-}o\text{-}PhC_6H_4)_3$, the *E*/*Z* ratio is much higher that those obtained with $P(O\text{-}o\text{-}tol)_3$ (Scheme 115).[133]

The reaction of the substrates bearing a disubstituted alkene **566** afforded 1,2-bis(vinylic) cyclopentanes **567**, indicating that the β-H elimination preferred to undergo the pathway forming a vinylic group instead of an alkylidene group, probably due to the *syn*-steric requirement for the β-H elimination (Scheme 116).[133]

Scheme 115

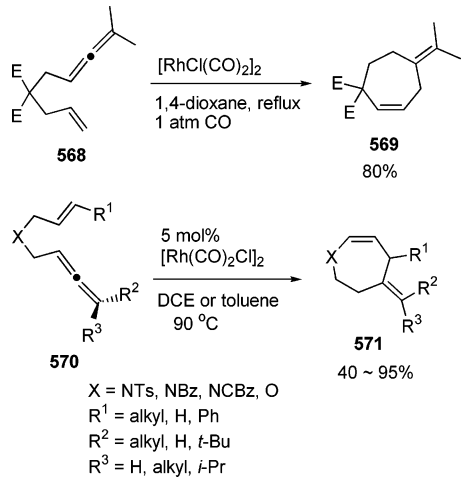


Scheme 116



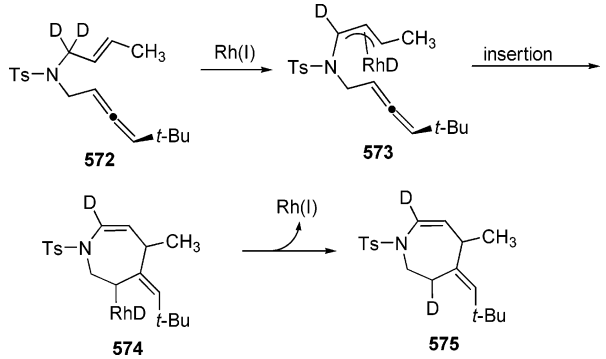
However, by using $[RhCl(CO)_2]_2$ as the catalyst, the reaction of **568** afforded 4-alkylidenecycloheptene **569**.[132] A similar phenomenon was also recently observed by Brummond et al. (Scheme 117).[134]

Scheme 117



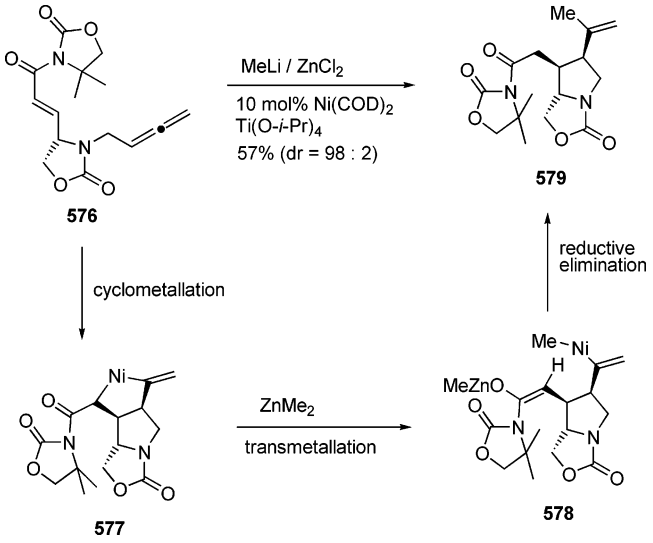
Through a deuterium-labeling study, a mechanism consisting of an allylic C−H bond cleavage forming π-allyl Rh intermediate **573**, *endo*-mode insertion, and reductive elimination was proposed (Scheme 118).[134]

Scheme 118



Nickel complexes are also good catalysts for cyclometalation of alkene-allenes. Montgomery et al. reported in 1999 that 2-alkenamide-allene **576** can be cyclized to afford 5/5-fused bicyclic product **579** via a sequential cyclometalation, transmetalation, and reductive elimination process (Scheme 119).[135]

Scheme 119

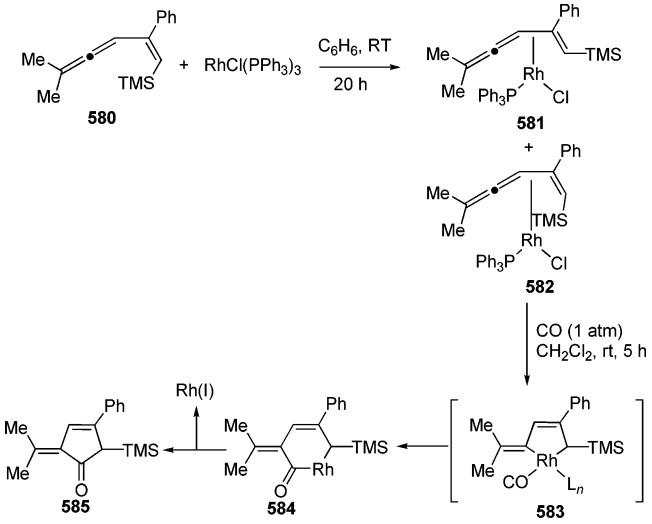


After studying the coordination chemistry of differently substituted vinyl allenes with $RhCl(PPh_3)_3$, it was observed that 1-(trimethylsilyl)-2-phenyl-5-methyl-1,3,4-hexatriene **580** reacted with $RhCl(PPh_3)_3$ to afford η^4-diene complexes *exo*-**581** and *endo*-**582**. The *endo*-**582** complex underwent cyclometalation in the presence of CO to afford the 2-alkylidene-3-cyclopentenone **585** via cyclometalation, CO insertion, and reductive elimination. This reaction is general for a variety of substituted vinylic allenes (Scheme 120).[136]

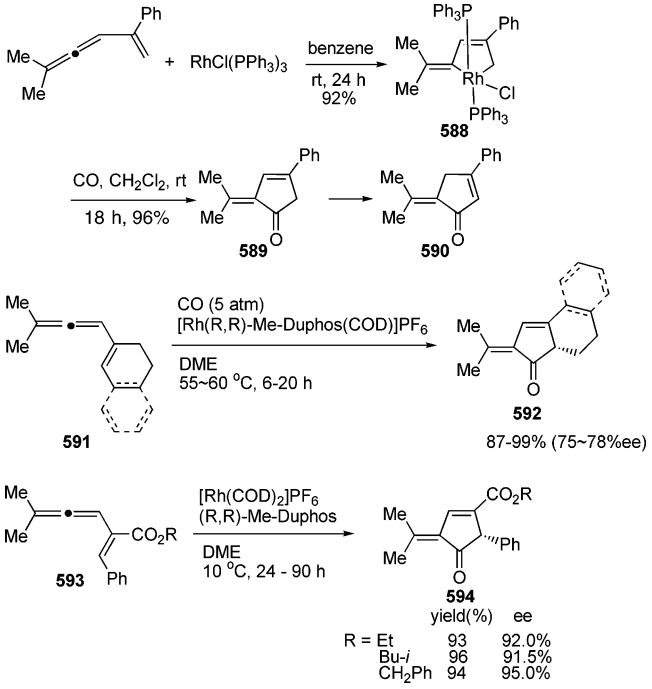
The mechanism was supported by the isolation of the five-membered metallocyclic complex **588**, which upon further carbonylation with CO afforded 5-alkylidenecyclopent-2-enone **590**.[137] Murakami and Ito et al. showed that with optically active [Rh(*R*,*R*)-Me-Duphos(COD)]PF_6 an enantioselective reaction can be achieved to afford **592** with moderate ee.[138] By introducing an ester and a phenyl group into the alkene moiety, the formation of **594** in >90% ee from **593** was observed (Scheme 121).[138]

It is also quite surprising to note that the Pd(0)-catalyzed [4+4+1]-cycloaddition reaction of two vi-

Scheme 120



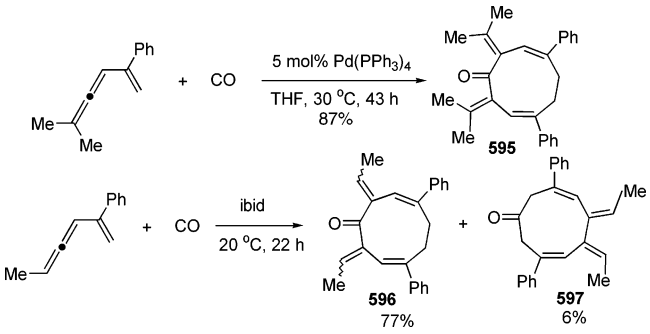
Scheme 121



nylic allenes with CO afforded nine-membered ring ketones **595**−**597** (Scheme 122).[139]

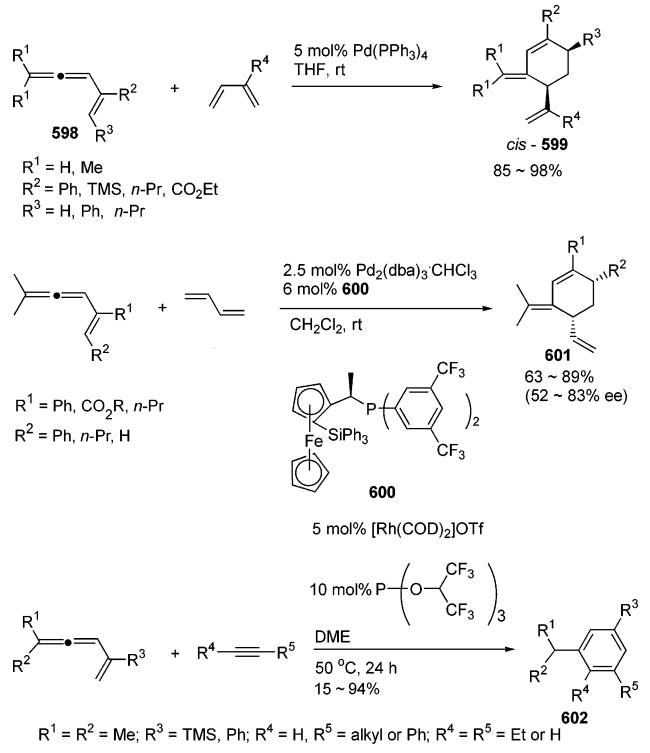
Under the catalysis of $Pd(PPh_3)_4$, vinylic allenes **598** can undergo [4+2]-cycloaddition with 1,3-dienes to afford the six-membered product *cis*-**599** with the less-substituted C=C bond in the 1,3-diene being the dienophile.[140] With optically active monophosphine ligand **600**, >52% ee was observed in the formation

Scheme 122



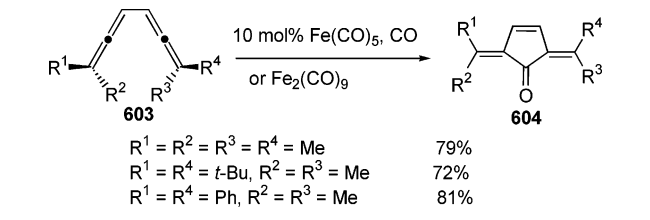
of the six-membered ring products **601**.[141] With terminal alkynes, polysubstituted arenes **602** were obtained with high regioselectivity (Scheme 123).[142]

Scheme 123



Eaton et al. reported the $Fe(CO)_5$-catalyzed [4+1]-cycloaddition of conjugated bisallene **603** forming 2,5-bis(alkylidene)cyclopent-3-enone **604** (Scheme 124).[143]

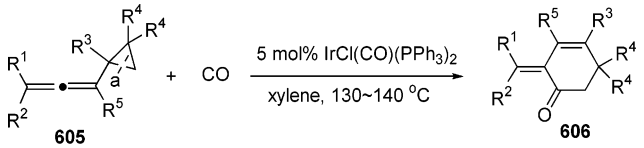
Scheme 124



6.2.3. Cyclometalation between Allenes and Cyclopropanes

trans-$IrCl(CO)(PPh_3)_2$ can catalyze the reaction of 1,2-allenyl cyclopropanes **605** with CO to afford 2-alkylidene-3-cyclohexenones **606** (Scheme 125).[144]

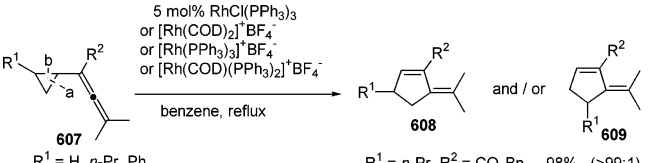
Scheme 125



R^1 = Me, Ph; R^2 = Me, H; R^3 = OEt, H; R^4 = H or Ph; R^5 = H, Ph

Under the catalysis of $RhCl(PPh_3)_3$, allenylcyclopropanes **607** would yield 3-alkylidenecyclopentenes **608** and **609**.[145] The selectivity depends largely on the nature of R^1 and R^2. Products **608** were formed via the cleavage of the bond "a", while products **609** were produced via cleavage of the bond "b" (Scheme 126).

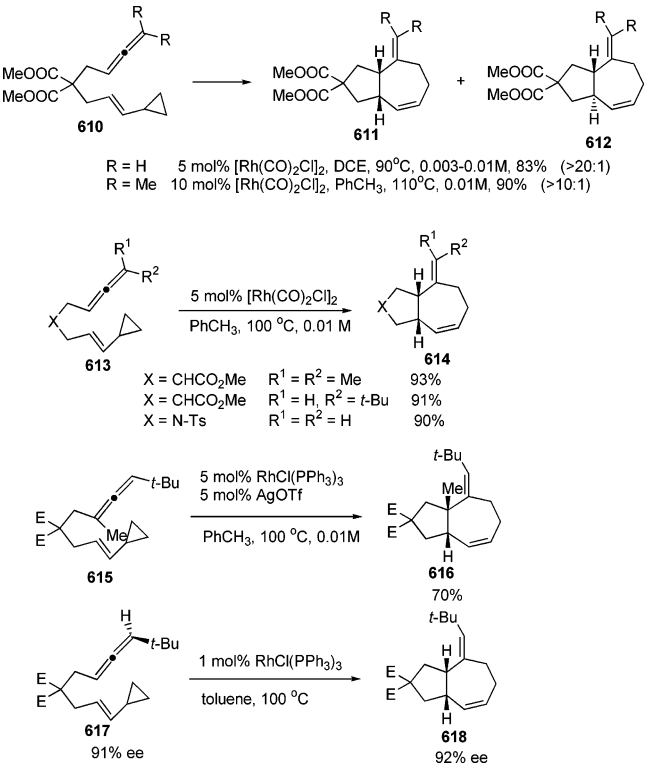
Scheme 126



6.2.4. Cyclometalation between Allenes and Vinylic Cyclopropanes

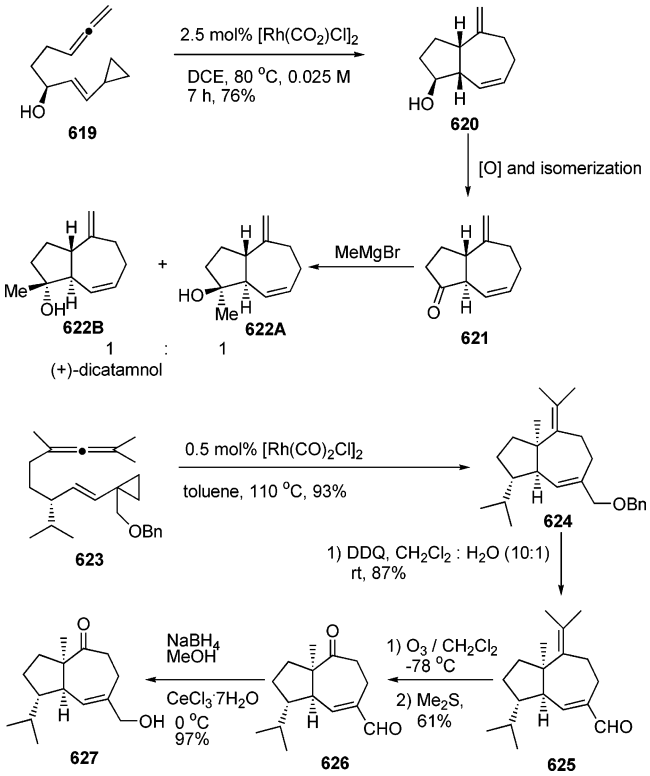
Wender et al. demonstrated the Rh(I)-catalyzed [5+2] intramolecular cycloaddition of allene-vinyl cyclopropanes **610**, **613**, and **615**.[146] The reaction afforded the *cis*-5/7-fused bicyclic compounds, such as **611**, **614**, and **616**, as the only or major products. The axial chirality of the allene moiety in **617** was transferred with high efficiency to the final product **618** (Scheme 127).

Scheme 127



This methodology has been successfully applied to the total synthesis of (+)-dictamnol **622B**[147] and (+)-aphanamol **627** (Scheme 128).[148]

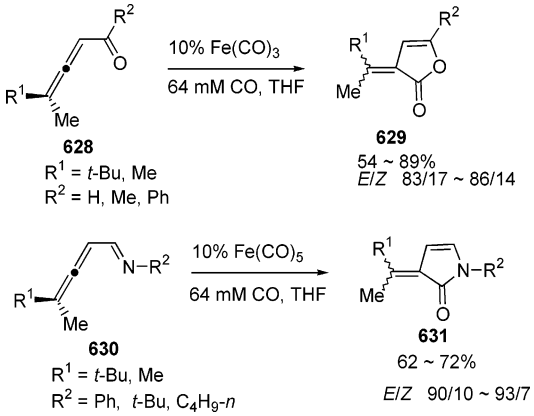
Scheme 128



6.2.5. Reactions between Allenes and C=X Bonds (X = O, N)

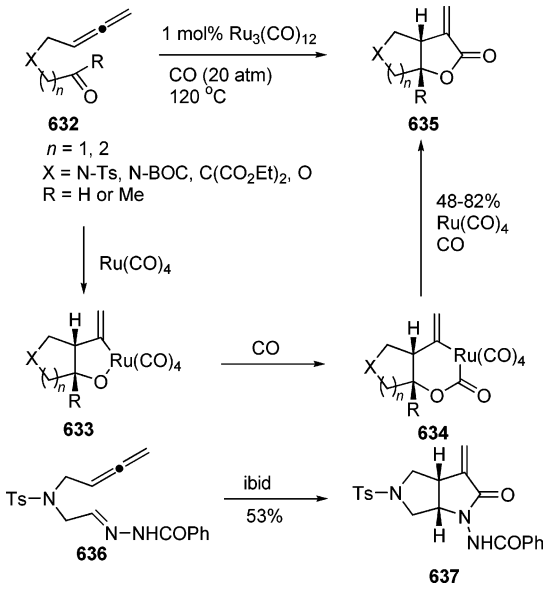
Eaton et al. reported that 1,2-allenyl ketones **628** can undergo cyclization in an atmosphere of CO under the catalysis of $Fe(CO)_5$ forming lactones **629**.[149] Similar reactions were also observed with 1,2-allenyl imines **630** to afford lactams **631** (Scheme 129).[150]

Scheme 129



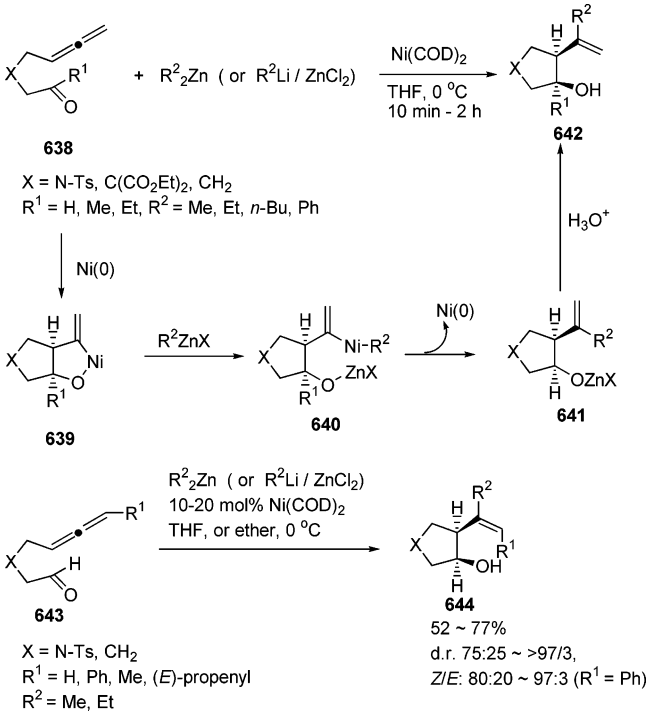
Kang et al. reported that the $Ru_3(CO)_{12}$-catalyzed cyclization of 5,6- or 6,7-alkadienyl aldehydes or ketones **632** or hydrazone **636** in the presence of CO afforded *cis*-fused bicyclic α-methylene-γ-butyrolactones **635** or -lactam **637** in good yields with high stereoselectivity (Scheme 130).[151]

Scheme 130



In the absence of CO, the same substrates under the catalysis of $Ni(COD)_2$ afforded *cis*-2-vinylic five-membered cyclic alcohols highly stereoselectively with an extra R^2 group being introduced by using organozinc reagents.[152] Montgomery et al. reported similar results almost at the same time (Scheme 131).[153]

Scheme 131

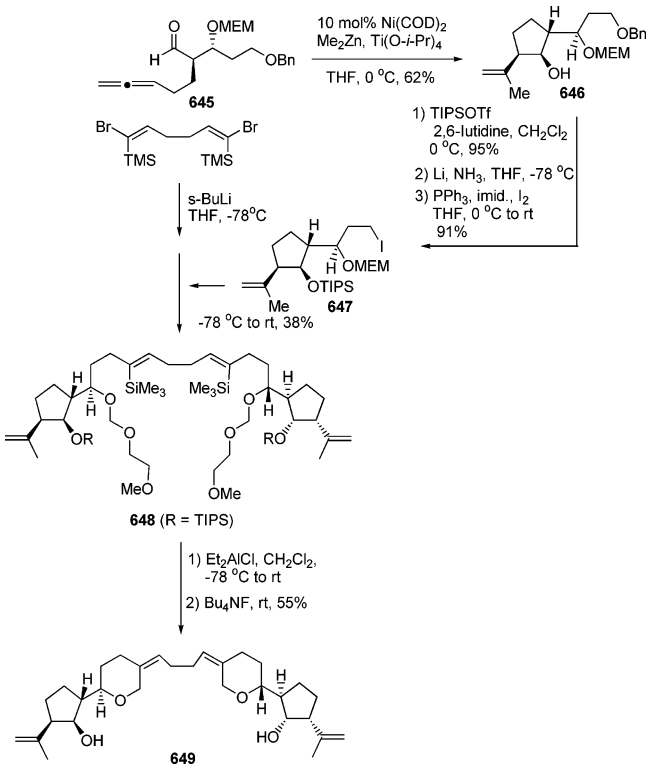


The reaction was conducted in the absence of a phosphine ligand, such as PPh_3, PBu_3, or $P(OMe)_3$, etc. This protocol has been applied to the enantioselective total synthesis of (+)-testudinariol A **649** (Scheme 132).[154]

7. Hydrometalation Reactions

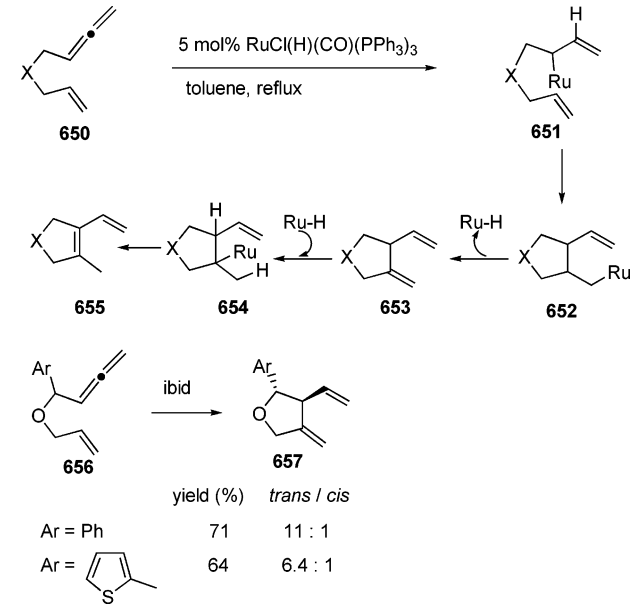
By using $Ru(H)Cl(CO)(PPh_3)_3$ as the catalyst, Kang et al. observed intramolecular hydrometalation-

Scheme 132



insertion-β-H elimination-hydrometalation-β-H elimination reaction of 1,2,7-trienes **650** forming vinyl cyclopentene derivatives **655**. In most cases, the conjugated 1,3-dienes were obtained. However, for related ethers, 1,4-dienes **657** were formed as the only product as a trans/cis mixture with the trans isomer being major, indicating that the reaction stopped at the stage of **653** (Scheme 133). [155]

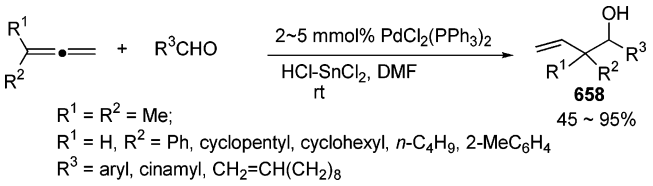
Scheme 133



Cheng et al. reported the Pd-catalyzed reaction of allenes with $SnCl_2$ and RCHO in the presence of HCl afforded homoallylic alcohols **658**.[156] The reaction was believed to proceed via the hydropalladation of allenes forming a π-allyl palladium intermediate, which

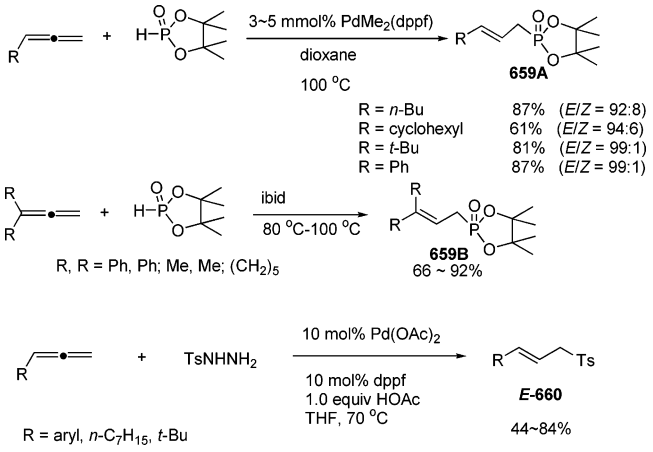
upon reacting with $SnCl_2$ was converted to an allylic trichlorotin reagent. The reaction of the allylic trichlorotin reagent with aldehyde and subsequent hydrolysis yielded homoallylic alcohol **658**. The regioselectivity is very high affording the products with a terminal C=C bond (Scheme 134).

Scheme 134



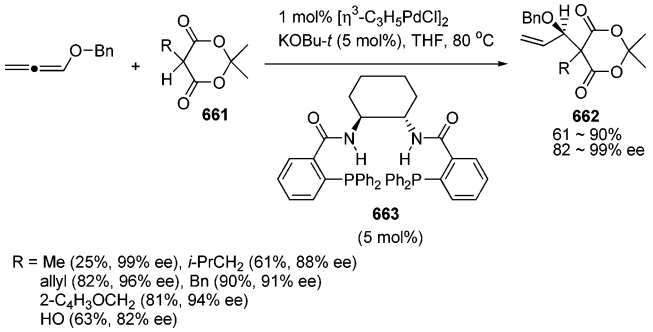
Han and Tanaka et al. reported Pd(0)-catalyzed hydrophosphorylation-reductive elimination of allenes yielding *E*-allylic phosphonates **659A** or **659B**.[157a] However, the ytterbium-imine complex-catalyzed hydrophosphination of Ph_2PH with allenes yielded vinylic phosphine oxides upon further oxidation with a poor selectivity.[157b] Yamamoto et al. observed that $Pd(OAc)_2$-dppf can catalyze the hydrosulfination reaction of allenes with $TsNHNH_2$ yielding linear allylic sulfones *E*-**670** with high selectivity (Scheme 135).[157c]

Scheme 135



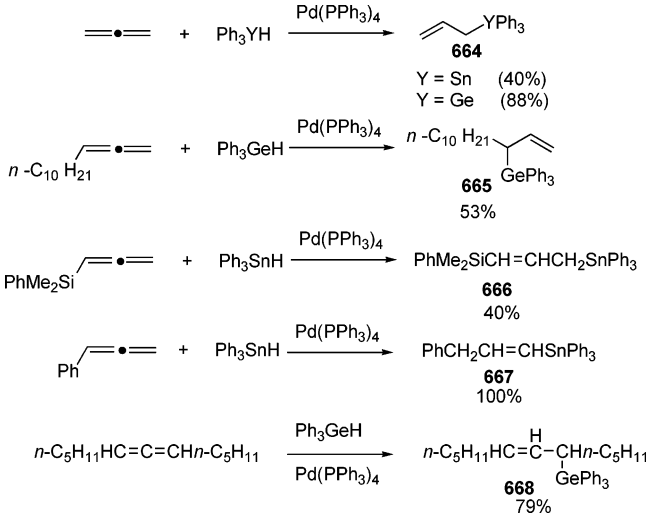
Trost et al. established the Pd-catalyzed enantioselective addition reaction of a pronucleophile with propadienyl benzyl ether via the hydropalladation and enantioselective nucleophilic allylic substitution mechanism (Scheme 136).[158]

Scheme 136



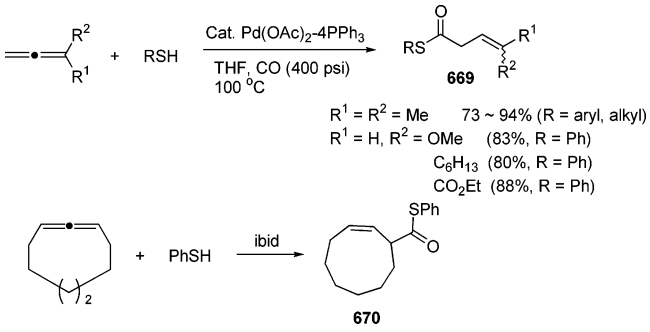
The $Pd(PPh_3)_4$-catalyzed hydrostannation and hydrogermylation of propadiene afforded allyl stannane or germannane **664** with a high regioselectivity.[159] The reaction of 1,2-tridecadiene with Ph_3GeH afforded allylic germanane with a terminal C=C bond **665**. The reaction of $PhMe_2SiCH=C=CH_2$ with Ph_3GeH afforded a mixture of regioisomeric allylic germanes in a low selectivity, while that with Ph_3SnH afforded nonterminal allylic tin product **666**. The $Pd(PPh_3)_4$-catalyzed hydrostannation reaction of phenyl propadiene with Ph_3SnH afforded vinylic stannane **667** in 100% yield. Under the catalysis of $Pd(PPh_3)_4$, Ph_3GeH reacted with trideca-6,7-diene to afford allylic germannane **668** (Scheme 137).

Scheme 137



Alper et al. reported an efficient thiocarbonylation of allenes with thiophenols or thiols. The reaction of monosubstituted or unsymmetrical 1,3-disubstituted allenes afforded the products where the carbonylation occurred at the less sterically hindered C=C bond. The stereoselectivity is, in most cases, not high (Scheme 138).[160]

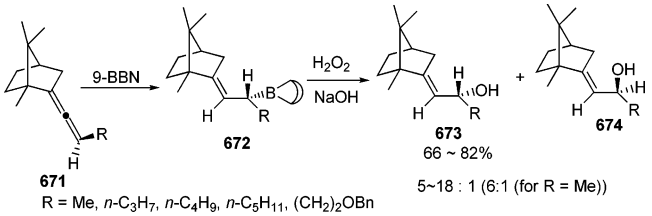
Scheme 138



The hydroboration of chiral allenes **671** yielded allylic alcohols **673** or **674** upon oxidation of the in-situ formed allylic borane **672** (Scheme 139).[161]

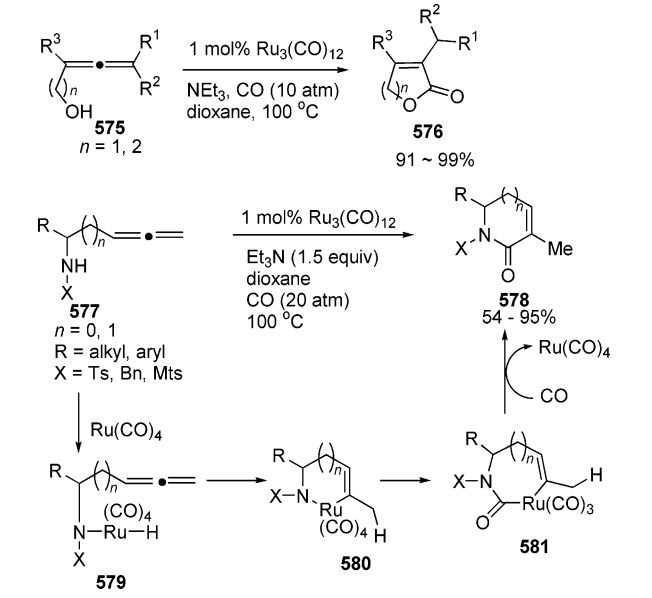
The cyclic carbonylation of α- or *β*-allenyl alcohols is reported to form α,*β*-unsaturated lactones **576** in very high yields.[162] Kang observed a similar reaction of α- or *β*-allenylamines. The reaction may proceed via the hydrometalation, carbonyl insertion, and reductive elimination mechanism.[163] In both reports,

Scheme 139



the C=C bond remote from the OH or amine functionality was highly regioselectively hydrometalated probably due to the coordination of the heteroatom with the metal in **579**, which would facilitate the *syn*-hydrometalation of the terminal C=C bond forming metallocyclic intermediate **580** (Scheme 140).[163]

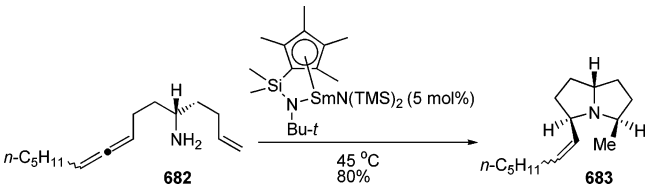
Scheme 140



8. Nucleometalation Reactions

McDonald and Marks et al. reported the Cp^*_2-$SmCH(TMS)_2$-catalyzed double cyclic hydroamination of 1-(3′-butenyl)-4,5-allenylamines **682** via the insertion of the C=C bond closer to the amine group in the allene moiety and the isolated terminal C=C bond into the N−Sm bond to afford the bicyclic product **683** (Scheme 141).[164]

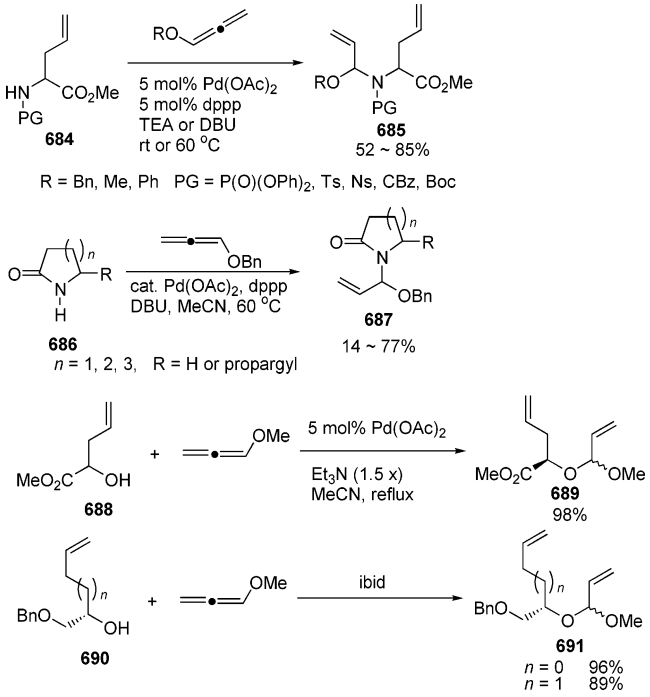
Scheme 141



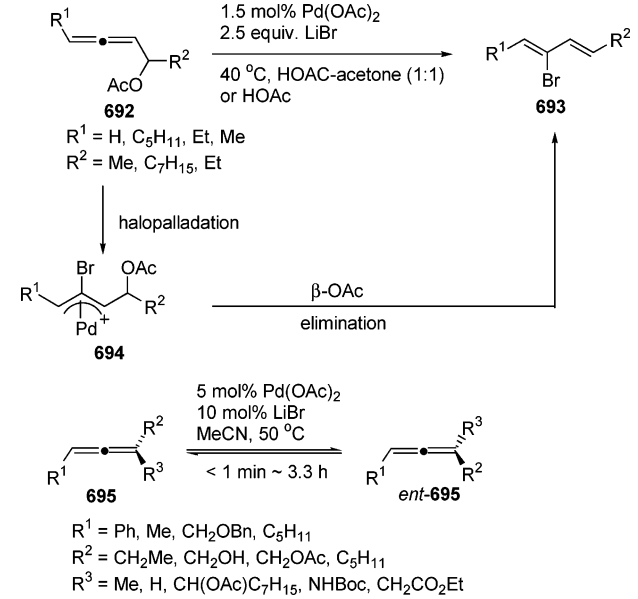
Rutjes et al. observed the amidopalladation of alkoxyallenes forming **685**.[165] Cyclic amides can also undergo a similar reaction. The reaction of alcohols with propadienyl ether under the catalysis of 5 mol % $Pd(OAc)_2$ afforded acetals **689** and **691** via the same oxypalladation process (Scheme 142).[166]

Hirao et al. reported the Pd-catalyzed hydroselenation of monosubstituted allenes with PhSeH affording vinylic selenides with a poor regioselectivity via a selenopalladation mechanism.[167a] Bäckvall et al. used the halopalladation of 2,3-allenyl acetates to prepare 2-bromo-1(*Z*),3(*E*)-diene. The stereoselectivity may be determined by the *syn*-*syn*-orientation of intermediate **694**.[167b] This halopalladation protocol has been applied to achieve the racemization of a variety of optically active allenes (Scheme 143).[168]

Scheme 142

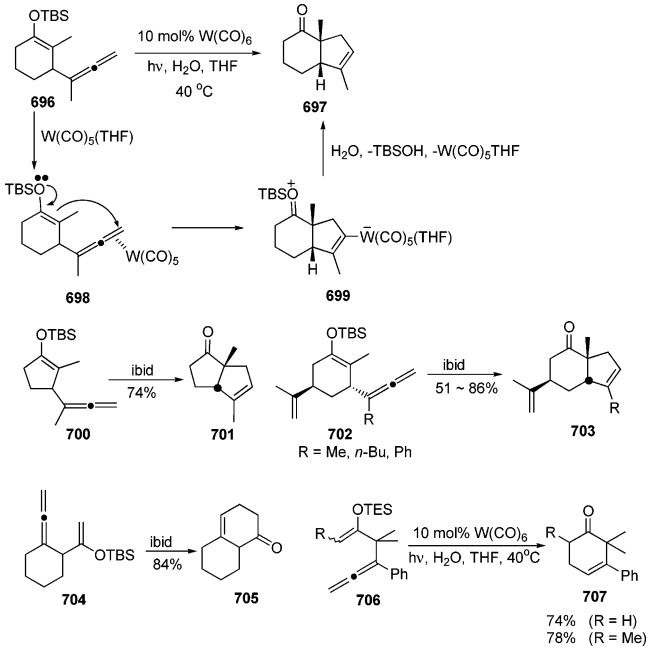


Scheme 143



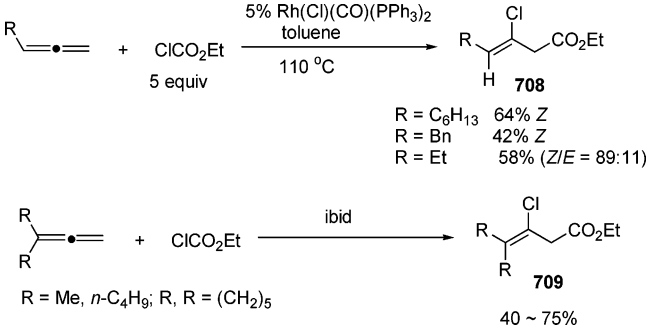
Lee and Iwasawa et al. reported that under the catalysis of $W(CO)_6$ (10 mol %) the allene moiety in **696** can undergo intramolecular *endo*-mode cyclization with the enol silyl ether moiety. Activation of the terminal C=C bond in the allene moiety by the coordination with $W(CO)_5THF$ may direct the attack of the carbon nucleophile to form **699**, which upon protonolysis would afford **693** (Scheme 144).[169]

Scheme 144



Tanaka et al. disclosed the Rh(I)-catalyzed stereoselective additions of chloroformate with allenes yielding 3-chloro-3(*Z*)-alkenoates **708** and **709** with a regioselectivity of >91% via chlororhodation and a reductive elimination mechanism. The reaction of phenylallene is low-yielding and much less regioselective (Scheme 145).[170]

Scheme 145



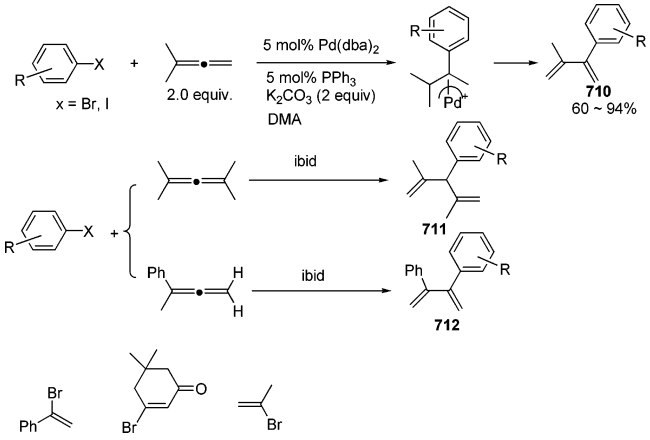
9. Carbometalation Reactions

Cheng et al. demonstrated the carbopalladation-β-H elimination process for the efficient synthesis of 1,3-dienes **710**−**712**. 4-Acyl(or nitro)phenyl chloride yielded the products in 21−29% yields. Alkenyl bromides shown in Scheme 126 could also be applied for this transformation. The reaction with 1-phenyl-1,2-butadiene or cyclohexylpropadiene yielded regioisomeric mixtures. In addition, the stereoselectivity of this reaction is poor (Scheme 146).[171]

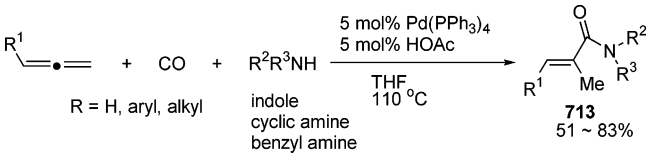
This Pd(0)-catalyzed reaction of aryl halides with allenes usually ended up with the formation of a π-allyl palladium intermediate, which may also undergo Tsuji−Trost-type chemistry with nucleophiles.[172] Grigg et al. reported the efficient synthesis of α,β-unsaturated *E*-enamides from the acylpalladation of allenes in the presence of an amine (Scheme 147).[173]

The Pd(0)-catalyzed four-component reaction of aryl halide, CO, amine, and a polymer-supported

Scheme 146

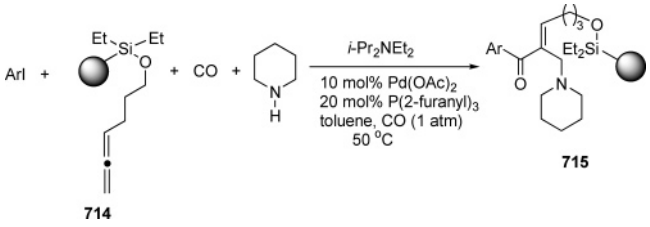


Scheme 147



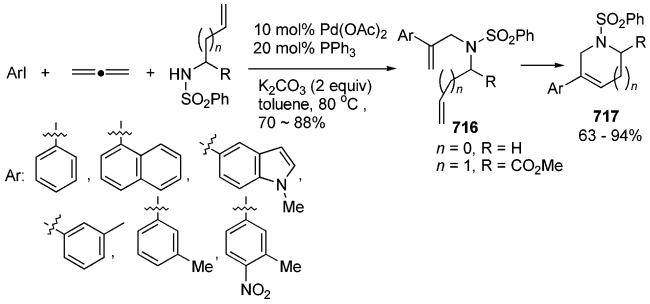
allene **714** leading to the highly selective formation of 2-acyl allylic amines **715** has also been disclosed (Scheme 148).[174]

Scheme 148



An intermolecular carbopalladation of propadiene then intermolecular allylic substitution with tosylamines[175a−e] bearing a terminal C=C bond afforded a diene **716**, which would undergo a RCM reaction to afford N-heterocycles (Scheme 149).[175f]

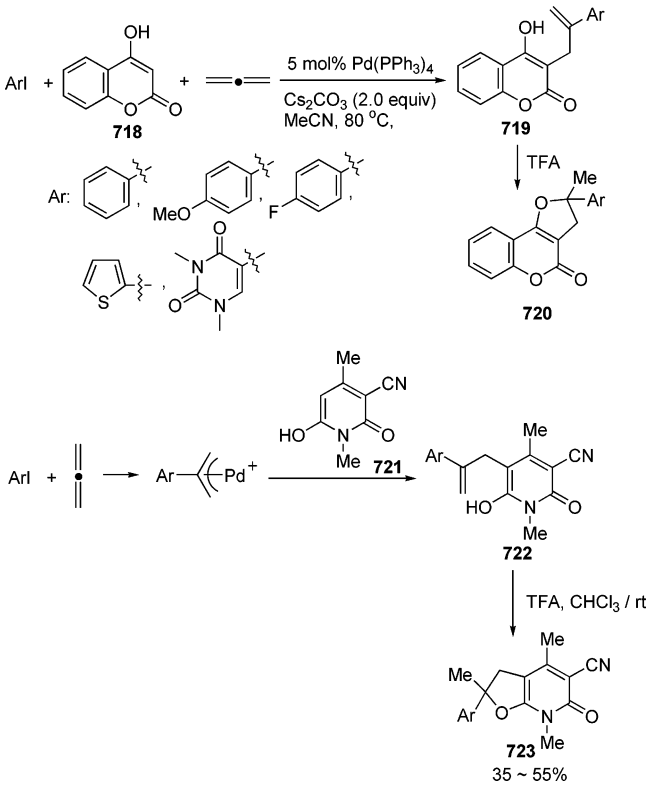
Scheme 149



A three-component reaction of aryl halides, propadiene, and 4-hydroxycoumarin **718** was conducted in a Schlenk tube to afford C-allylation products **719**, which undergo further cyclization under the catalysis of TFA to afford tricyclic product **720**.[176a] A similar process was also observed with 4-hydroxy-2-quinolone **721**,[176a] azides,[176b] or phenols (Scheme 150).[176c]

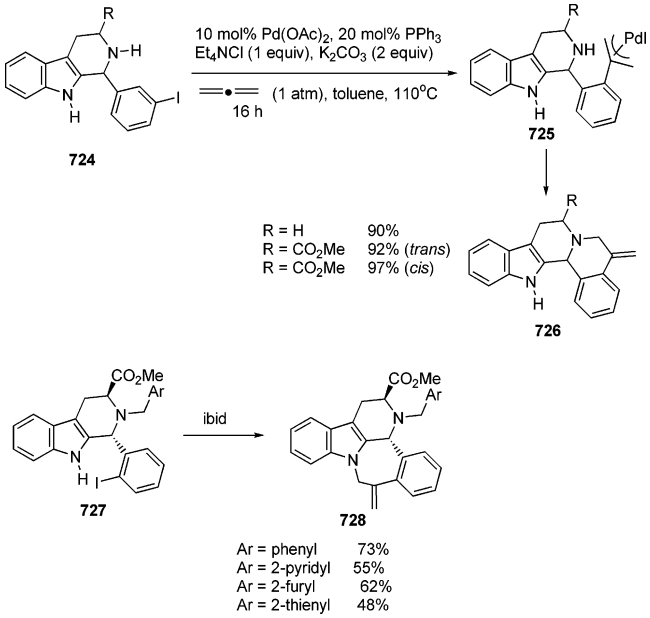
Grigg et al. reported the intermolecular carbopalladation of propadiene and intramolecular allylic

Scheme 150



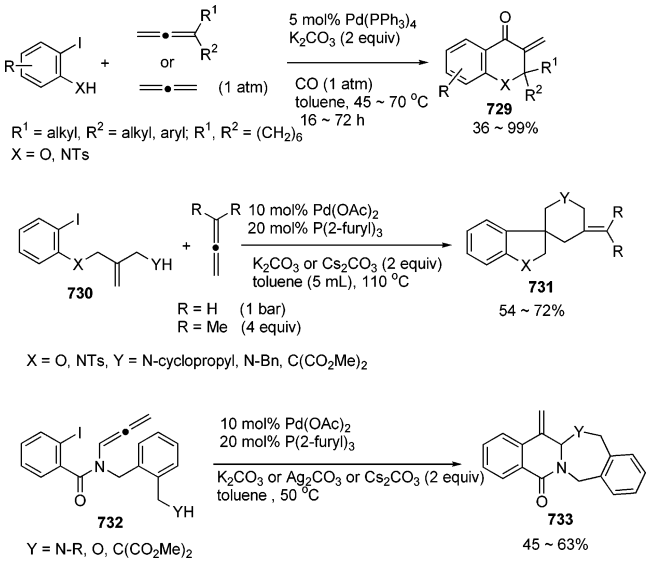
amination of **724** or **727** affording indole-containing polycyclic products **726** or **728** efficiently (Scheme 151).[177]

Scheme 151



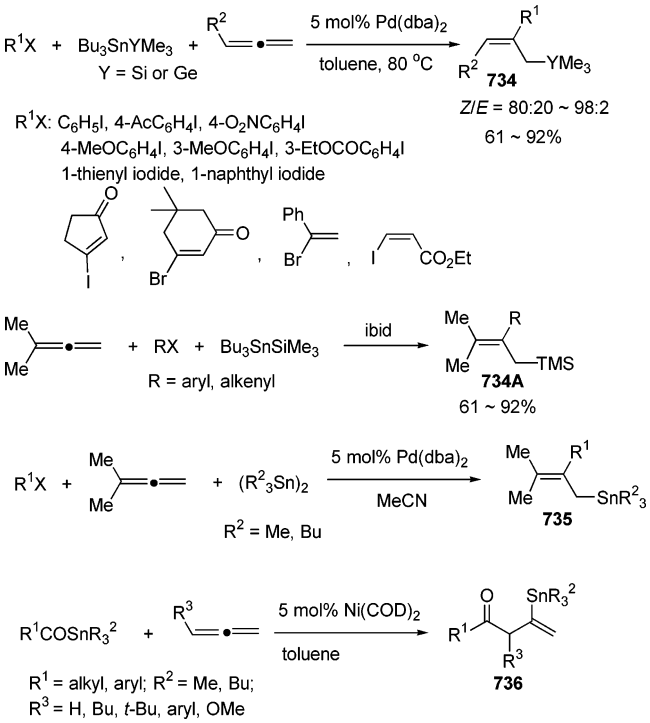
A similar protocol has been established with 2-iodophenols or 2-iodoaniline derivatives. It is interesting to note that the allylic substitution occurred at the more substituted alkene.[178] A sequential intramolecular carbopalladation of an alkene-intermolecular carbopalladation of an allene-intramolecular allylic subsitution process has also been demonstrated forming polyheterocyclic products **731**.[179a] An example of intramolecular carbopalladation-intramolecular nucleophilic substitution was shown to yield tricyclic products **733** (Scheme 152).[179]

Scheme 152



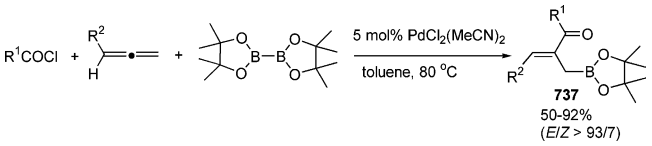
Cheng et al. reported the Pd(0)-catalyzed three-component reaction of organic halides, allenes, and Bu_3SnYMe_3(Y = Si or Ge). Allylic silanes or germanes **734** were prepared efficiently via the oxidative addition, carbopalladation, transmetalation, and reductive elimination process. 3-Methyl-1,2-butadiene also reacted smoothly affording allylic silane **734A**.[180a] Allylic tins **735** were also prepared in a similar way by using R_3SnSnR_3[181] instead of $Bu_3SnSiMe_3$. For monosubstituted allenes, the stereoselectivity is poor with the *Z*-isomer being the major product. β-Organostannyl-β,γ-unsaturated enones **736** could be prepared by the Ni(COD)$_2$-catalyzed reaction of R^1COSnR_3[2] and allenes in toluene (Scheme 153).[182]

Scheme 153



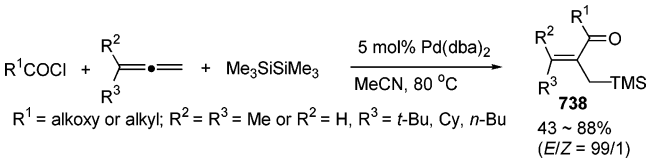
The $PdCl_2(MeCN)_2$-catalyzed three-component reaction of acyl chlorides, allenes, and diboronate in toluene at 80 °C yielded 2-acylallylic boronates *E*-**737** efficiently and stereoselectively.[183] The stereoselectivity may be determined by the repulsion between R^1CO and R^2 groups during the reaction (Scheme 154).

Scheme 154



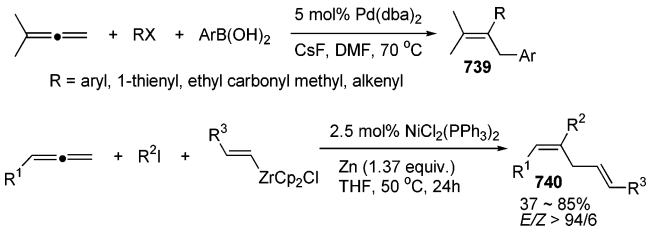
With acyl halides (or chloroformate), allenes, and $(SiMe_3)_2$, 2-acyl allylic silanes **738** can be prepared in good yields (Scheme 155).[183]

Scheme 155



This type of three-component reaction could also proceed with organic halides, allenes, and organic boronates affording tetrasubstituted alkenes **739**.[184] For monosubstituted allenes, a *E*/*Z* mixture (*E*/*Z* ≥ 73:27) was formed with the ratio depending on the nature of the substituent of the allene. By using $NiCl_2(PPh_3)_2$ as the catalyst, 1-alkenyl zirconium reagents can be used instead of organic boronate leading to an efficient and stereoselective synthesis of 1,4-dienes *E*-**740**.[185] These reactions may proceed via an oxidative addition of the Pd(0) with organic halides to form organic palladium halides, which would undergo carbopalladation to form π-allyl palladium intermediates with high stereoselectivity. Subsequent transmetalation and reductive elimination would form the coupling products and regenerate the catalytically active Pd(0) species (Scheme 156).

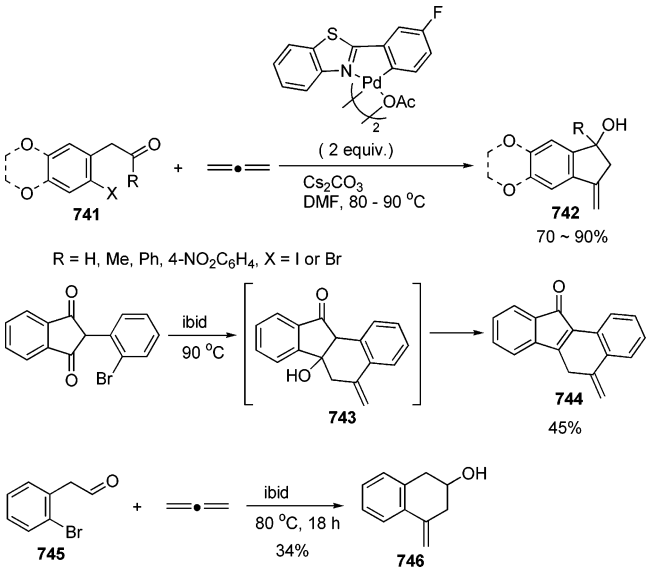
Scheme 156



This type of π-allyl palladium intermediate may react intramolecularly with an aldehyde or a ketone to afford five-membered cyclic alcohols **742**.[186a] Compound **744** was formed via the further dehydration of **743**. The yield for the formation of a six-membered ring in **746** is much lower (Scheme 157).

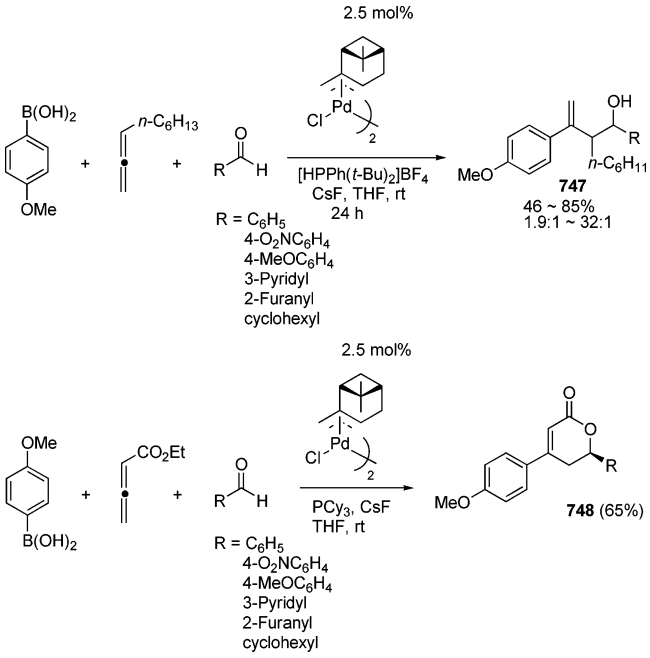
For the corresponding intermolecular reactions with aldehydes[186b] or imines,[186c] the addition of indium for umpolung selectivity was required. Malinakova et al. developed an efficient Pd(II)-catalyzed three-component reaction of aryl boronic acid, 1,2-

Scheme 157



nonadiene, and aldehydes yielding homoallyl alcohols with a terminal C=C bond **747**.[187] With ethyl 2,3-butadienoate, six-membered lactone products **748** were obtained in 65% yield (Scheme 158).

Scheme 158

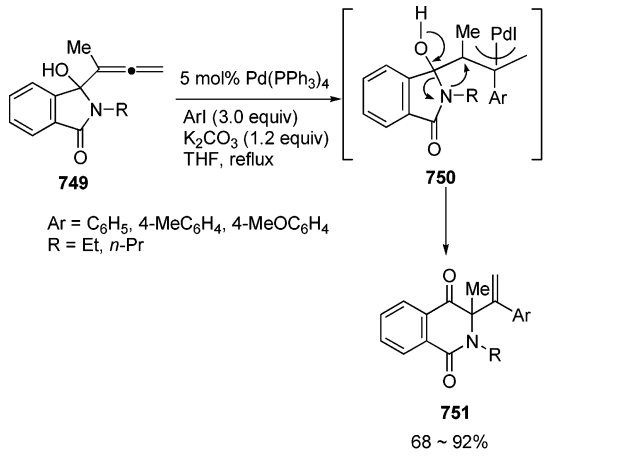


Nagao et al. observed that the **750**-type π-allyl palladium intermediate formed by the carbopalladation of an allene may undergo ring expansion to afford benzocyclohexadione derivatives **751**, **753**, **754**, or **757** (Scheme 159).[188]

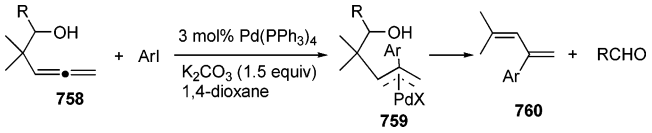
Oh et al. even observed a C−C bond cleavage reaction in the Pd-catalyzed intermolecular reaction of 3,4-allenols **758** with ArI. The reaction may proceeded via the intermediacy of **759** to afford 1,3-diene **760** and an aldehyde (Scheme 160).[189]

Bates et al. noticed that $MeCOCo(CO)_4$ can mediate the cyclization of 4,5-alkadienylamines **761** via a π-allyl cobalt intermediate **762** (Scheme 161).[190]

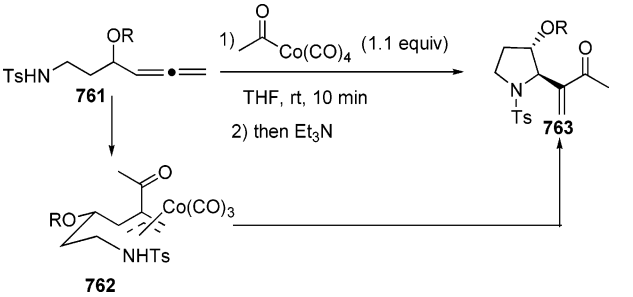
Scheme 159



Scheme 160



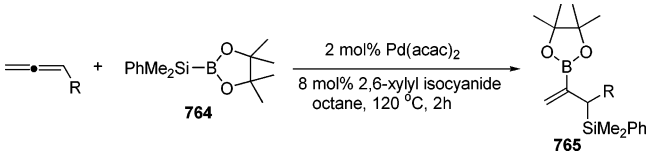
Scheme 161



10. Palladium-Catalyzed Silylboration Reactions

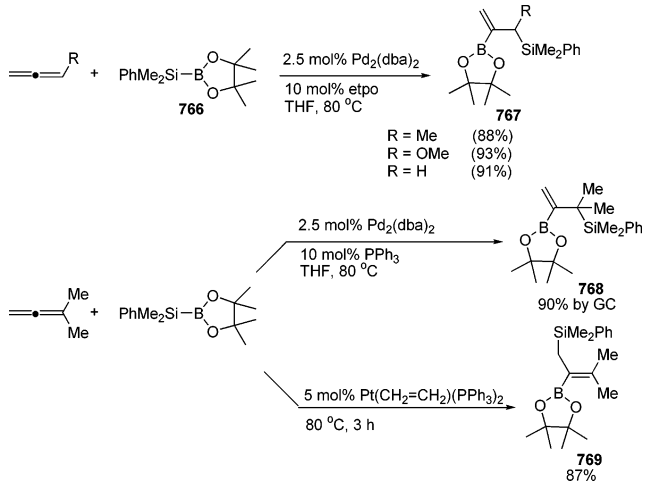
Ito et al. observed that $Pd(acac)_2$ can catalyze the highly regioselective silaboration of allenes forming allylic silanes **765** with the boron being introduced to the central carbon atom and the silyl group connected with the more substituted terminal of allenes.[191,192] With R = $Ph(CH_2)_2$, Cy, OMe, the regioselectivity is >99:1. With R being Ph or *t*-Bu, 6% and 14% of the regioisomeric allylic silanes were also formed respectively as byproducts.[191] An oxidative addition of the Si−B bond with Pd(0) followed by boropalladation of an allene and reductive elimination was proposed (Scheme 162).[192]

Scheme 162



Tanaka et al. also observed the silylboration reaction of allenes with **766** using $Pd_2(dba)_3$-etpo (etpo = $P(OCH_2)_3CEt$) or PPh_3 as the catalyst. For 1,1-disubstituted allenes, the reaction using etpo as the ligand yielded the related products in a poor regioselectivity. With $Pd_2(dba)_2-PPh_3$ and $Pt(CH_2{=}CH_2)(PPh_2)_2$ as the catalysts, different allylic silanes **768** and **769** can be prepared respectively from 3-methyl-1,2-butadiene (Scheme 163).[193]

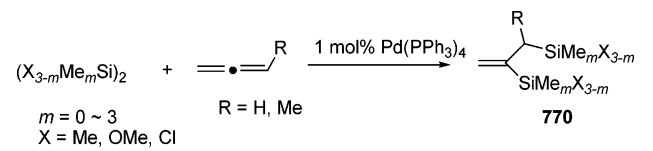
Scheme 163



11. Pd-Catalyzed Disilylation, Distannylation, Silylstannylation, and Diboration Reactions

In 1981, Watanabe et al. reported the $Pd(PPh_3)_4$-catalyzed disilylation of allenes. The regioselectivity is very high; that is, only the allylic silanes with a terminal C=C bond **770** were formed (Scheme 164).[194]

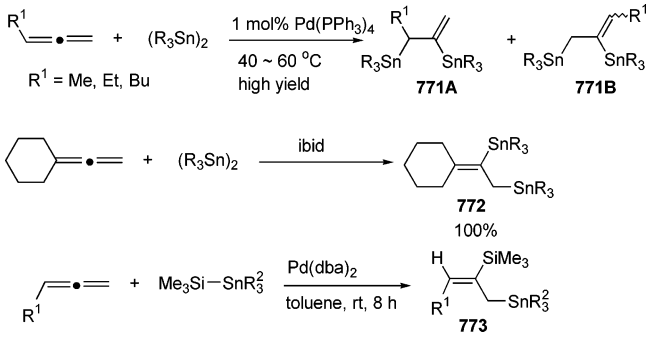
Scheme 164



Mitchell et al. noticed that the $Pd(PPh_3)_4$-catalyzed distannylation of allenes is reversible leading to the formation of a mixture of products derived from distannylation of both C=C bonds of allenes **771A/**

B. Usually 2-stannyl-(*E*)-allylic tin is the major product.[195] The reaction of $Me_3SiSnMe_3$ with allenes is not reversible forming a mixture of regioisomeric 2-(trimethylsilyl)allylic tins in good yields.[196a] However, with a phosphine free palladium complex, that is, $Pd(dba)_2$, as the catalyst the reaction is highly regio- and stereoselective affording **773** (Scheme 165).[196b]

Scheme 165



The Pd(0)-catalyzed diboration of allenes can be accomplished in the presence of 5 mol % of 3-iodo-2-methyl-2-cyclohexenone **775**. The diboration occurred with the terminal C=C bond. Through control and cross-addition studies, it was found that the halide **775** may react with the allene and the diboron reagent **774** under the catalysis of $Pd(dba)_2$ to yield allylic boronate **777** and iodoboronate **778**. The real catalytic cycle involves the oxidative addition of the B−I bond in **778**, which may be followed by the sequential insertion of an allene, transmetalation, and reductive elimination to yield the diboration product **776A**. The iodoboronate **778** was regenerated after transmetalation (Scheme 166).[197]

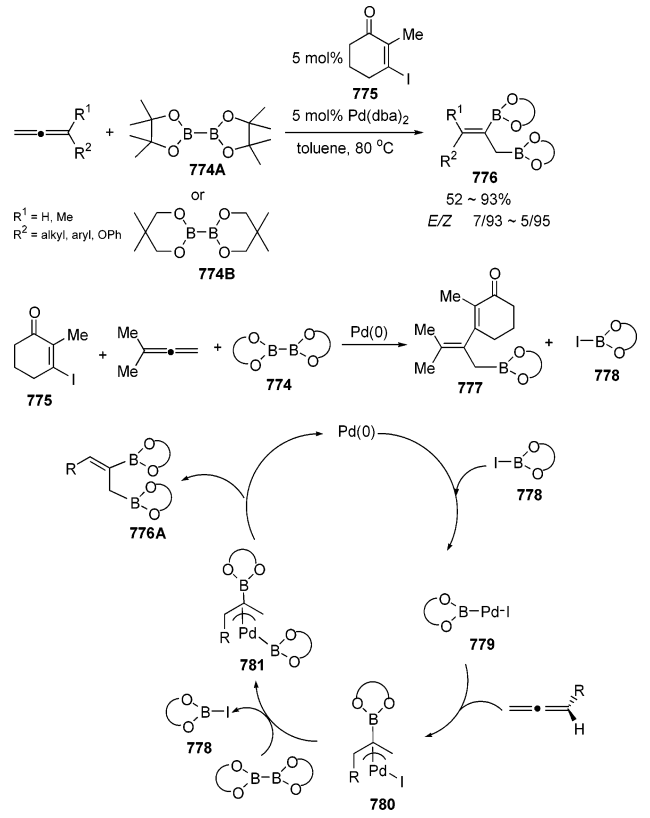
Recently, Morken et al. reported the enantioselective diboration of the nonterminal C=C bond in monosubstituted allenes.[198] In this reaction, the regioselectivity is similar to what was observed with disilylation shown in Scheme 164 (Scheme 167).[198]

12. Stannylcupration

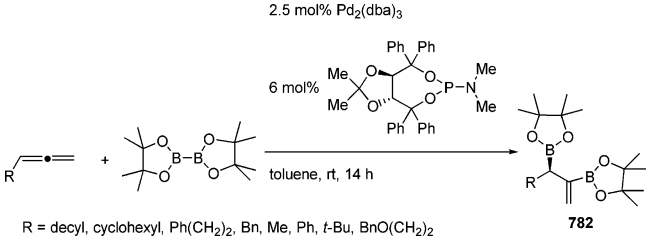
$(Bu_3Sn)_2CuLi$ reacted with allenes to form either 1-alkenylic stannane **783** or allylic stannanes **784** depending on the nature of the substituted allenes. The author also noticed that the regiochemistry strongly depended on the reaction temperature and the electrophiles used at that temperature. The reaction of propadiene with $(Bu_3Sn)_2CuLi$ at −100 °C followed by quenching with MeOH, CH_3COCl, or Br_2 (conditions A) yielded allylic stannanes **786**. When the same reaction was conducted at −100 °C for 1 h followed by warming to 0 °C for over 1 h and then quenching at −100 °C with MeOH, CH_3COCl, ethylene epoxide, or CO_2 (conditions B), vinylic stannanes **788** were formed (Scheme 168).[199]

The stannylcupration of propadiene with a halide-free copper reagent behaved similarly; that is, different electrophiles afforded different products.[199] With a mixed silyl(stannyl)cuprate, a selective transfer of the stannyl group was observed for the reaction

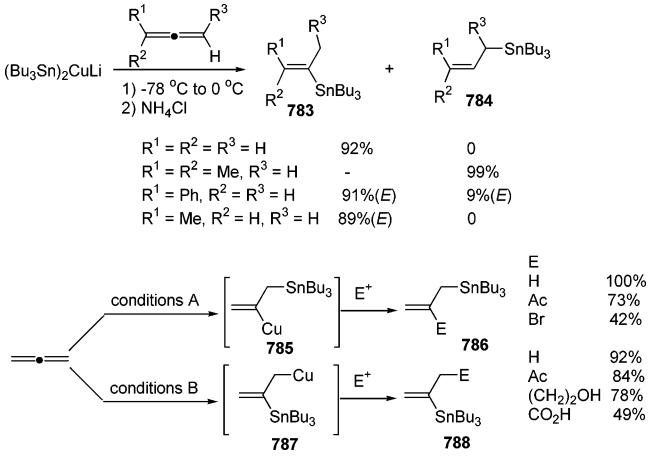
Scheme 166



Scheme 167



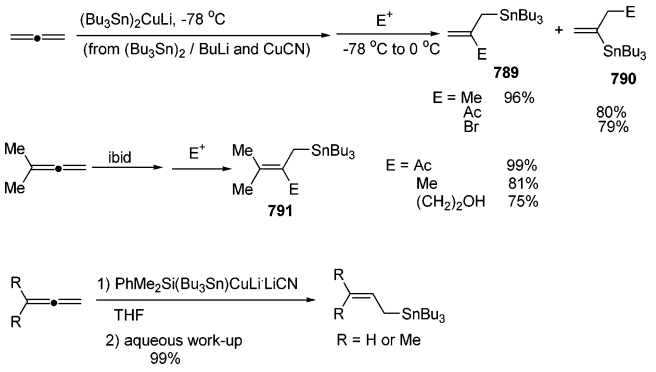
Scheme 168



with propadiene and 3-methyl-1,2-butadiene.[200] With monosubstituted allenes the selectivity is poor (Scheme 169).[201]

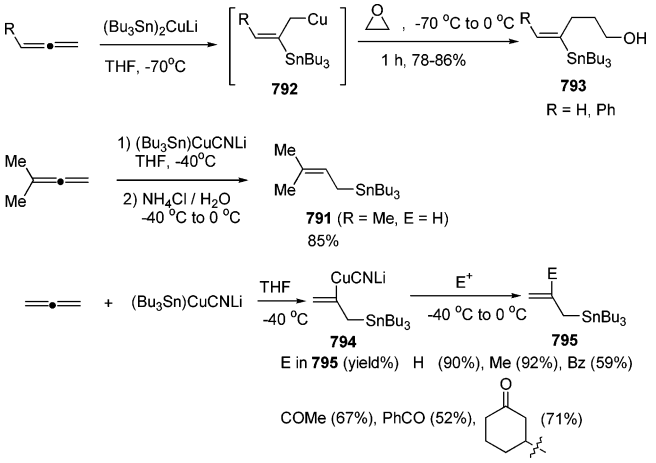
In a later report, Pulido et al. observed that phenylpropadiene or propadiene can react with $(Bu_3Sn)_2CuLi$ in THF at −70 °C followed by a subsequent reaction with an epoxide to afford 4-(tributylstannyl)-

Scheme 169



4(*E*)-pentenols **793** in 78−86% yield.[202] Recently, the same author reported that with a low order cuprate, that is, (Bu_3Sn)CuCNLi (prepared from 1 equiv of Bu_3SnLi and CuCN at −20 °C in THF for 30 min), the stannylcupration of propadiene or 3-methyl-1,2-butadiene at −78 to −40 °C followed by the reaction with E^+ yielded allylic stannanes **791** or **795** almost exclusively (Scheme 170).[203]

Scheme 170



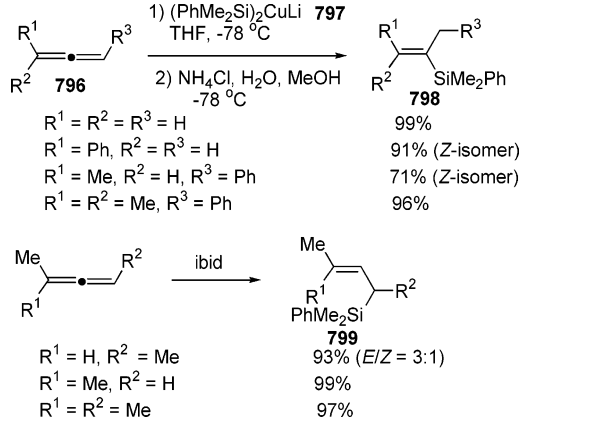
13. Silylcupration

Silylcupration of allenes with $(PhMe_2Si)_2CuLi$ at −78 °C in THF also yielded vinylic silanes or allylic silanes depending on the structure of the allenes. Propadiene or phenyl-substituted allenes yielded vinylic silanes **798**. The corresponding reaction of 1,1-disubstituted allenes or 1,1,3-trisubstituted allenes afforded allylic silanes **799**.[204] However, the reaction of 1,2-heptadiene yielded a mixture of vinylic silane and allylic silane in 78% and 29%, respectively (Scheme 171).[204]

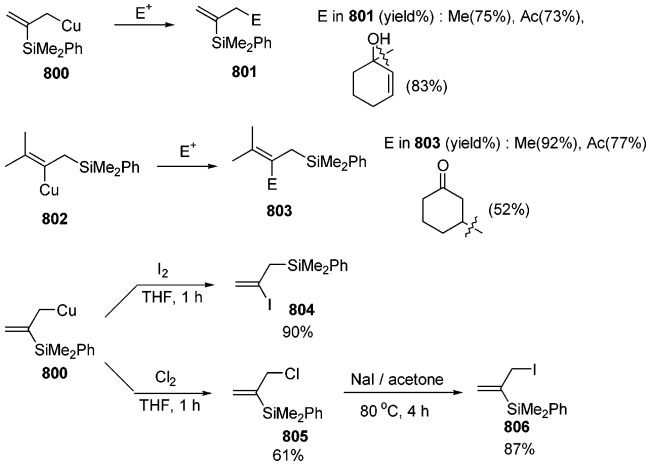
The vinylic cuprate or allylic cuprate formed can react with MeI or CH_3COCl. The reaction of **800** with cyclohex-2-enone afforded the 1,2-addition product, while that of the vinylic copper reagent **802** yielded the 1,4-addition product. Further study indicated that the reaction of cuprate **800** with I_2 yielded 2-iodoallyl silane **804** in 90% yield, although the corresponding reaction with Cl_2 yielded the normal vinylic silane **805** (Scheme 172).[205]

The silylcupration with (t-$BuPh_2Si)_2CuLi$ (**807**) or t-$BuPh_2SiCu{\cdot}LiCN$ (**808**) at −78 or −40 °C, respectively, led to the formation of vinylic cuprate **809** with

Scheme 171

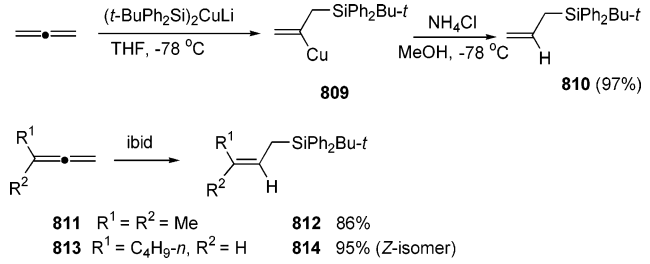


Scheme 172



high selectivity, which undergoes 1,2-addition with aldehydes, ketones, α,β-unsaturated enones, or enals.[206] Conjugate addition products were also formed with 2-alkenoates. In addition, the vinyl cuprate will undergo reactions with I_2, epoxide, CH_3COCl, or MeI to yield the expected products. The silylcupration reaction can also proceed with 3-methyl-1,2-butadiene **811** or 1,2-heptadiene **813** to afford allylic silanes **812** or **814** in high yield and stereoselectivity (Scheme 173).

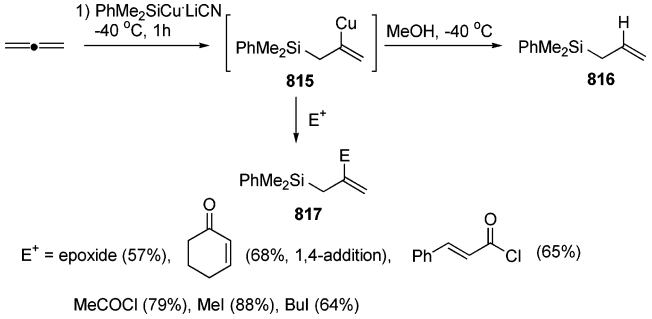
Scheme 173



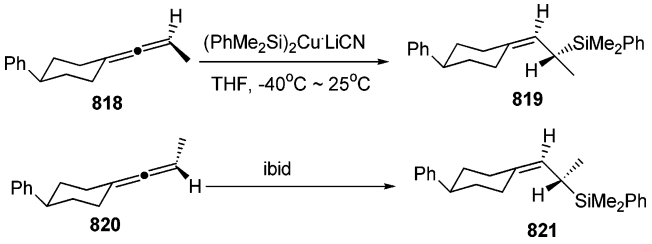
The vinylic copper reagent **815** prepared from the reaction of propadiene with $(PhMe_2)SiCu{\cdot}LiCN$ at −40 °C reacted with different electrophiles to afford allyl silanes **816** and **817** (Scheme 174).[207]

The corresponding results of stereochemically defined allenes **818** and **820** proved that the siylcupration is a stereospecific *syn*-addition process (Scheme 175).[208]

Scheme 174

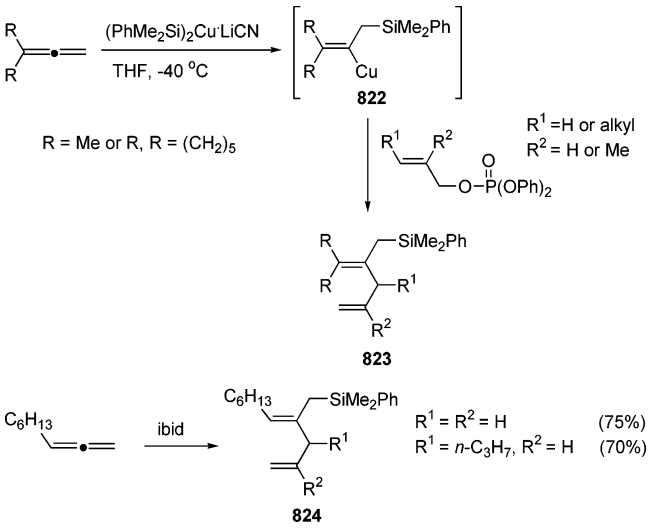


Scheme 175



Bäckvall et al. reported the sequential silylcupration of allenes and the subsequent trapping with allylic phosphates leading to 1,4-dienes **823** and **824** with high efficiency. The reaction of phenylpropadiene with 1-substituted allyl phosphates afforded mixtures of *Z*/*E*-isomers (Scheme 176).[209]

Scheme 176

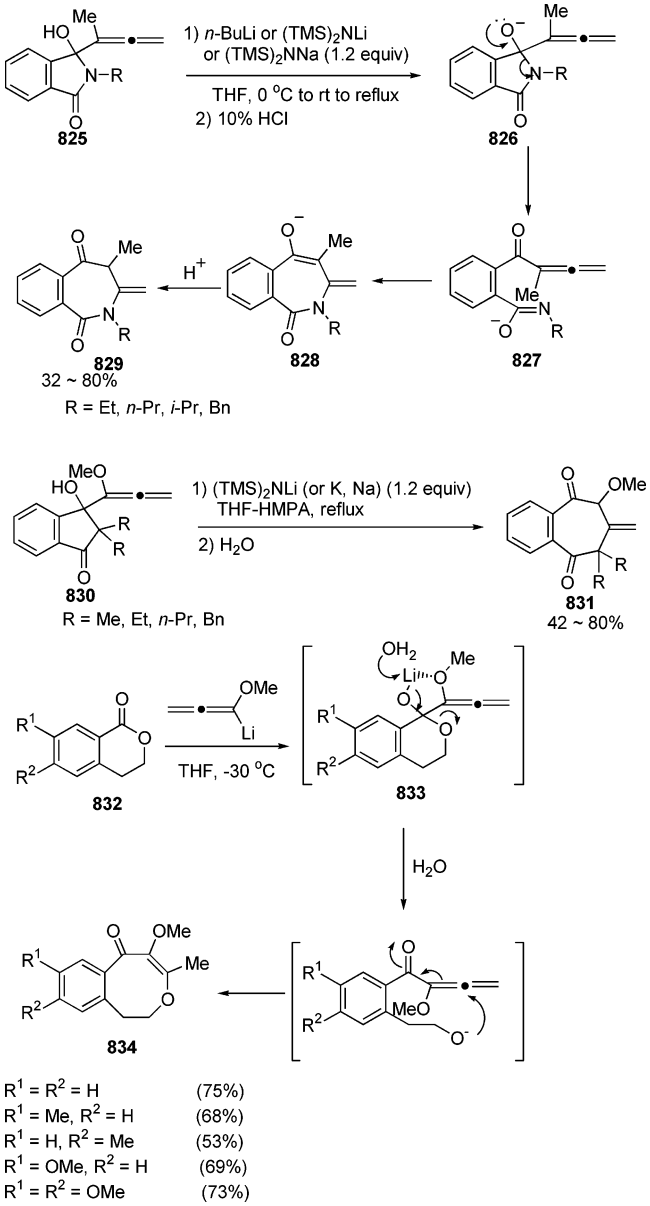


14. Miscellaneous Reactions

2,3-Allenols **825** can be converted to 3-methylenebenz[*c*]azepines **829** via the ring-opening reaction of **826** forming **827**, which may undergo intramolecular conjugate addition with the 1,2-allenyl ketone moiety.[210] A similar ring expansion reaction was also observed with benzocyclopentanones **830**[211] and benzocyclotetrahydropyrans **833** (Scheme 177).[212]

An oxy-Cope rearrangement reaction has been reported for the 1,2,6-triene **836** to form the ring expansion product **837**, which would react further via the intramolecular condensation of the vinylic silyl ether moiety with the ketone to afford **838**. Direct protonlysis would produce fused bicyclic product **839** (Scheme 178).[213]

Scheme 177



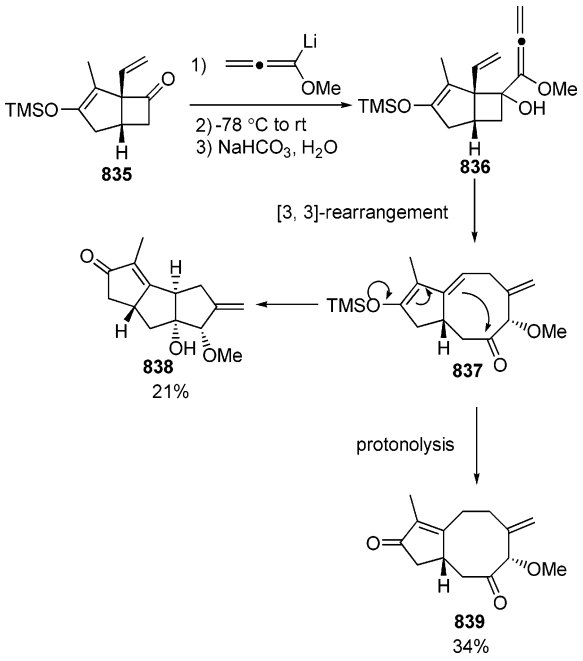
A Claisen rearrangement of 1,2-allenyl allyl ethers was also nicely demonstrated to afford 2-methylene-4-alkenals **840** (Scheme 179).[214]

Yu et al. observed a Rh-catalyzed silylcarbocyclization of allenyl aldehydes and ketones **841** via the silylrhodation of the allene-1,2-addition to the C=O bond-reductive elimination mechanism to afford 2-vinylic cyclic alcohols *cis*-**842**.[215] Recently, Shibata et al. disclosed a similar process with 6,7-allen-1-ynes **843** to afford 2-(1′-silylvinyl)alkylidenecyclopentane derivatives **844** (Scheme 180).[216]

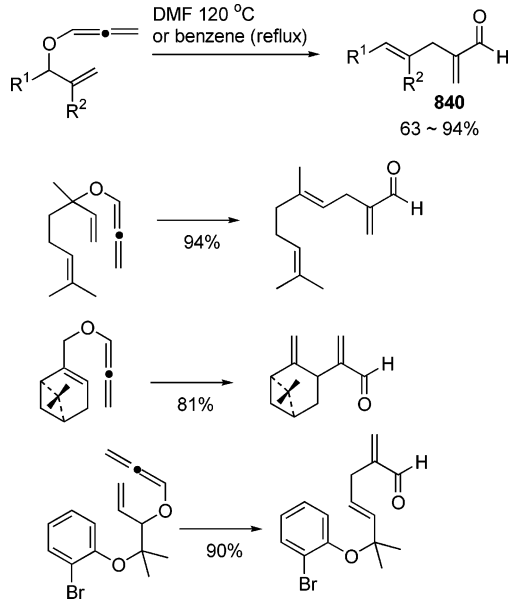
We observed a Pd(II)-catalyzed coupling between 1,2-allenyl sulfoxide and allyl bromide to form 2-vinylic-1(*E*),4-alkadienyl phenyl sulfoxides (Scheme 181).[217] The reaction was induced by the nucleophilic addition of the relatively electron-rich C=C bond of the allene moiety to $PdCl_2L_2$.

A cross-metathesis reaction of monosubstituted allenes has been shown to afford 1,3-disubstituted

Scheme 178



Scheme 179

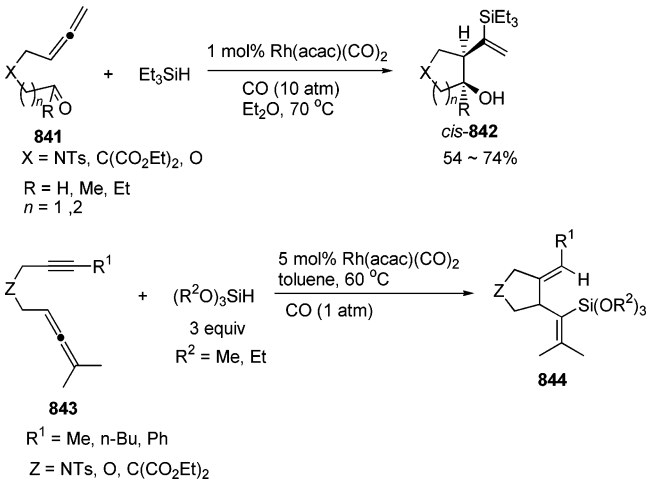


allenes. When R = Ar, only polymeric products were formed (Scheme 182).[218]

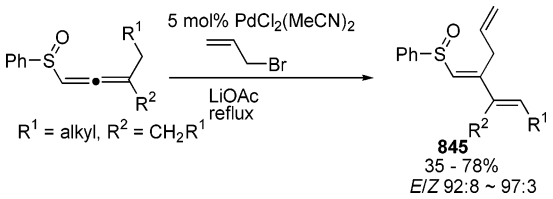
Yoshida and Ihara et al. reported the Pd(0)-catalyzed synthesis of 1,3-dienes **847** from 2,3-allenols **846** using organic boronic acids. The hydrogen bond between the hydroxyl group in allenols and the boronic acid may promote the oxidative addition of allenols with Pd(0) to form a dienyl Pd intermediate, which may undergo transmetalation and reduction elimination to form the product and regenerate Pd-(0) (Scheme 183).[219]

Trost et al. demonstrated the vanadium-catalyzed aldol-type addition of 2,3-allenic alcohols with aldehydes. The reaction of $VO(OSiPh_3)_3$ with allenols **850** would lead to the formation of vanadium enolates **852**, which may react with aldehydes to form **853**. Hydrolysis of **853** with Ph_3SiOH would form the

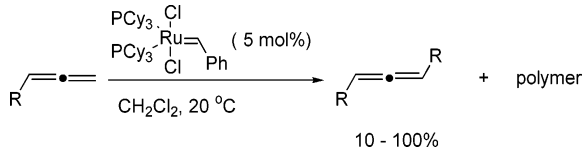
Scheme 180



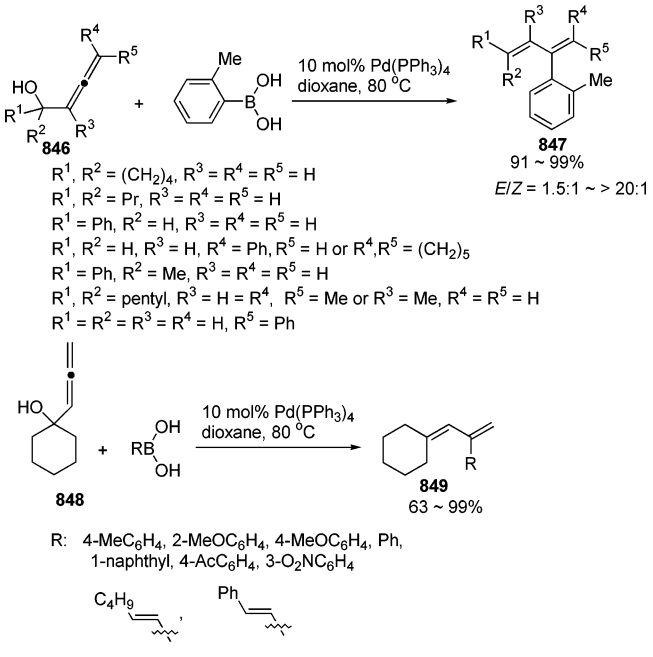
Scheme 181



Scheme 182



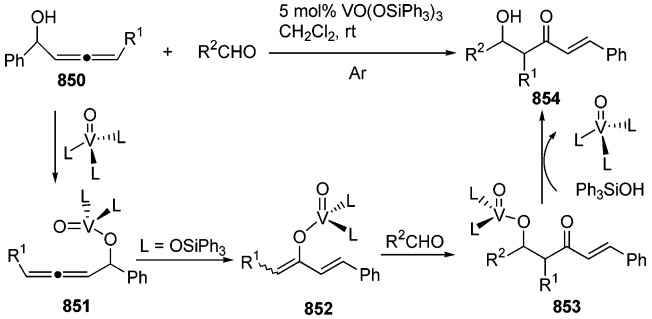
Scheme 183



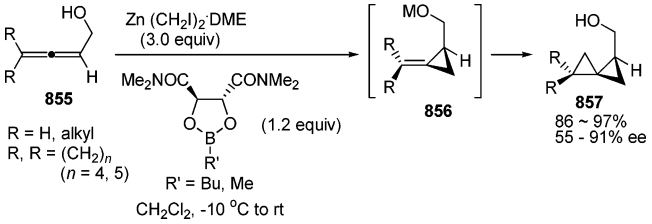
products **854** and regenerate $VO(OSiPh_3)_3$ (Scheme 184).[220]

The enantioselective double cyclopropanation of 2,3-allenols **855** afforded spiropentanes **857** efficiently with a moderate to high ee. With R = Ph, the yield is very low (7%) (Scheme 185).[221]

Scheme 184

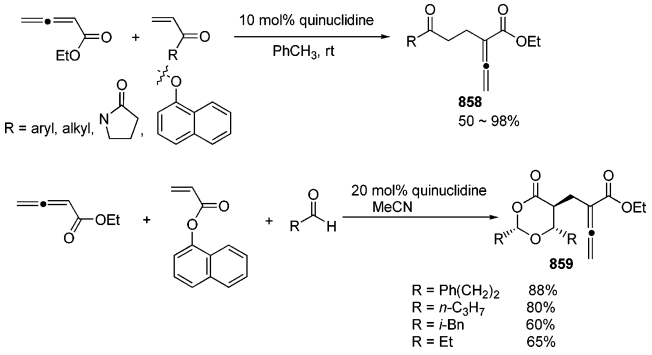


Scheme 185



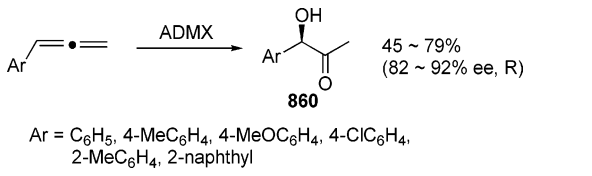
It has been clearly shown that phosphines can catalyze the [3+2] cycloaddition of 2,3-alkadienoates with α,β-unsaturated alkenoates.[3c] However, Miller et al. showed that quinuclidine (10 mol %) leads the reaction in a different route, forming 2-substituted-2,3-alkadienoates **858**.[222] No reaction was observed with an α,β-unsaturated enone bearing an α-substituent. Three-component coupling of ethyl butadienoate, aldehydes, and acrylate has been established to afford **859** (Scheme 186).

Scheme 186



Most recently, Fleming et al. showed that arylpropadienes can undergo enantioselective dihydroxylation to afford chiral 1-hydroxyl-1-aryl acetones **860** with >82% ee (Scheme 187).[223]

Scheme 187



15. Concluding Remarks

As compared to the chemistry of alkenes and alkynes, which has been extensively studied and well established, allenes, an important class of unsaturated hydrocarbons, have not been well documented. In the past 10 years, the situation has changed dramatically. Many new reactions of allenes have been discovered showing nice reactivity and selectivity. Due to the substituent-loading capability and axial chirality, allenes will continue to play a more important role in selective modern organic synthesis. It is believed that with this continued investigation of allenes many more interesting reactions will be discovered. Another direction of allenes will be the new methods for the stereoselective preparation of optically active allenes, which may be the starting materials for many optically active interesting compounds with new structural features and properties. The golden age for the chemistry of allenes is just around the corner.

16. Abbreviations

acac	acetylactonyl
9-BBN	9-borabicyclo[3.3.1]nonane
BTAF	benzyltrimethylammonium fluoride
1,4-CHD	1,4-cyclohexadiene
COD	cyclooctadiene
Cp	cyclopentadienyl
(*R*,*R*)-Me-Duphos	1,2-bis(2,5-dimethylphosphorano)benzene
m-CPBA	3-chloroperoxybenzoic acid
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DIBAL-H	di(iso-butyl)aluminum hydride
DMA	dimethylacetamide
DMD	dimethyldioxirane
DME	ethylene glycol dimethyl ether
DMF	dimethylformamide
dppp	1,3-bis(diphenylphosphino)propane
dppe	1,2-bis(diphenylphosphino)ethane
DPS	diphenyl-*tert*-butylsilyl
EBTHI	bis(tetrahydroindenyl)ethane
HMPA	hexamethylphosphoramide
MEM	(2-methoxy)ethoxymethyl
NMMO(NMO)	*N*-methylmorpholine oxide
TBAB	tetrabutylammonium bromide
TBHP	*tert*-butyl hydroperoxide
THF	tetrahydrofuran
TEA	triethylamine
Ts	4-toluenesulfonyl

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18. Note Added after ASAP Publication

This article was published ASAP on June 9, 2005. It was temporarily withdrawn later that day while some changes were made in the schemes and references. It was reposted on June 27, 2005.

19. References

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