Metal Carbenes

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# New Approaches to the Synthesis of Metal Carbenes

*Minqiang Jia and Shengming Ma**

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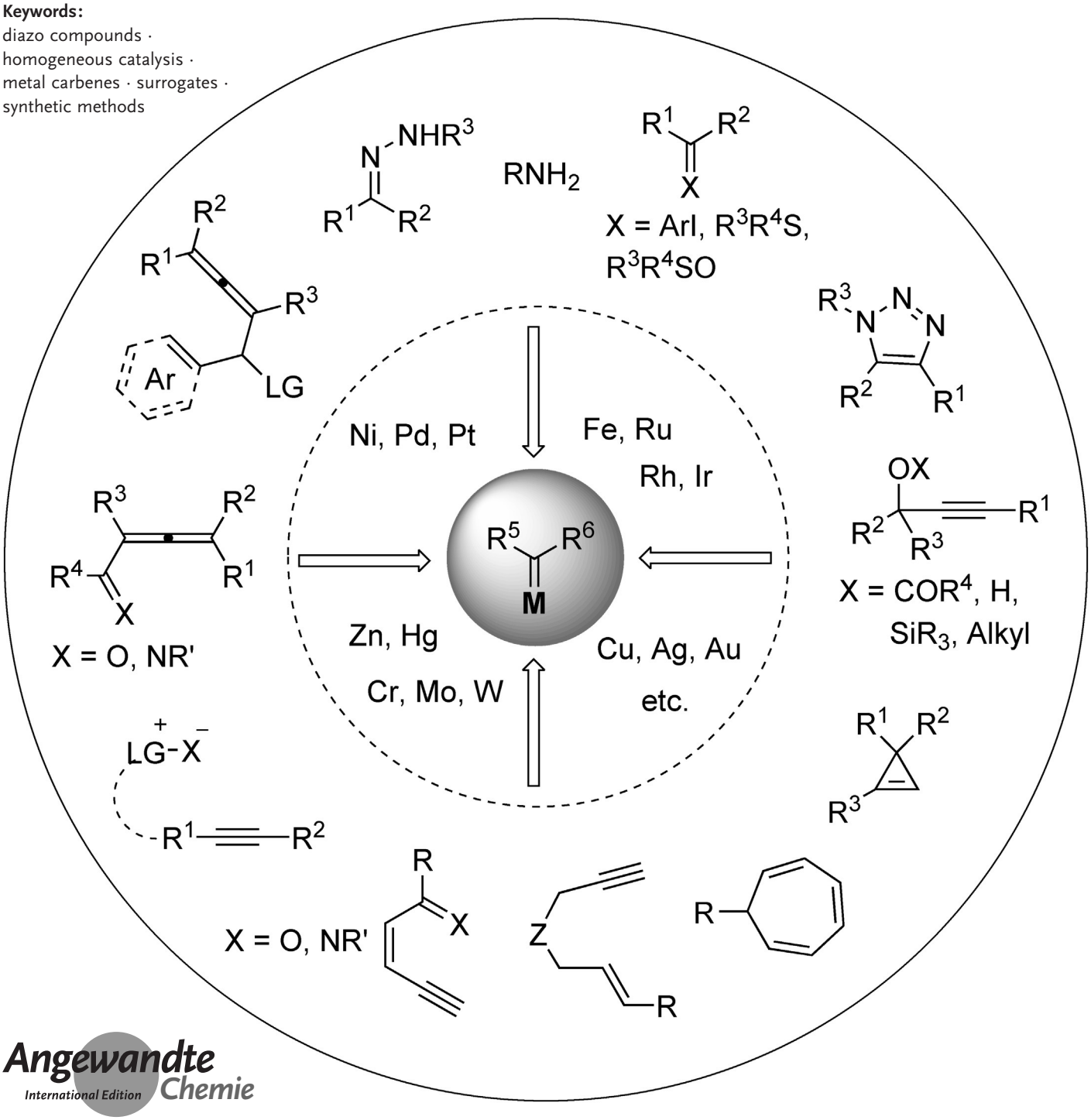


*Metal carbenes usually possess versatile reactivities that are controlled by the presence of both the metals and the ligands. Diazo compounds are commonly used for the generation of such species through elimination of nitrogen. However, they are often unstable, explosive, and toxic, which limits their applications in large-scale syntheses. Thus, identifying sustainable and safe surrogates for the generation of metal carbenes has attracted great attention. In this Review, we summarize some of the most important breakthroughs in the generation, catalytic reactions, and selectivity control of metal carbenes from non-diazo starting compounds.*

## From the Contents



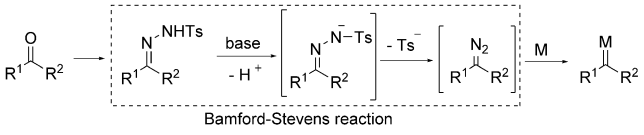
## 1. Introduction

One of the most important applications of diazo compounds is their decomposition through the release of one molecule of nitrogen to generate the corresponding carbenes or metal carbene species, which may readily undergo various types of synthetically attractive transformations,[1] such as cyclopropanations, dipolar cycloadditions,[2] XH (X = C,[3] Si, O, S, N, etc.) insertions,[4] reactions with nucleophiles,[5] and migratory insertions with different metals, including Rh,[6] Cu,[7] Au,[8] Pd,[9] Fe,[10] Ru,[11] Co,[12] Ir,[13] and Ag.[14] In this Review we summarize some of the most important progress made in the generation of metal carbenes from non-diazo starting materials, together with their reactions.

## 2. Hydrazones

### 2.1. Tosylhydrazones

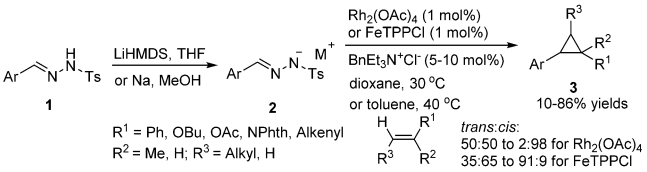
Tosylhydrazones, which are readily available from aldehydes or ketones,[15] can generate diazo compounds through a gentle Bamford–Stevens reaction under basic conditions (Scheme 1). Electron-rich tosylhydrazones are usually more stable than the electron-poor ones, and can serve as alternatives to unstable diazo compounds.[16]




***Scheme 1.*** Synthesis of metal carbenes from tosylhydrazones.

#### 2.1.1. Cyclopropanation Reactions

$Rh_2(OAc)_4$ or FeTPPCl (TPP = tetraphenylporphyrin) can catalyze the cyclopropanation of electron-rich alkenes with tosylhydrazones (Scheme 2):[17] Electron-rich alkenes, such as alkoxy-substituted alkenes, provided high yields, while alkenes bearing β-carbonyl groups showed very high *cis* selectivity. Such a ruthenium(II) porphyrin catalyzed cyclopropanation of electron-rich alkenes was also realized with just 0.1 mol% catalyst.[18]




***Scheme 2.*** Cyclopropanation of electron-rich alkenes.

#### 2.1.2. X–H Insertion Reactions

Carbene insertions into N–H bonds of imidazoles and benzimidazoles **5**,[19] normal amines **7**,[20] and P–H bonds of phosphine oxides **9**[21] have been realized with different copper catalysts (Scheme 3).

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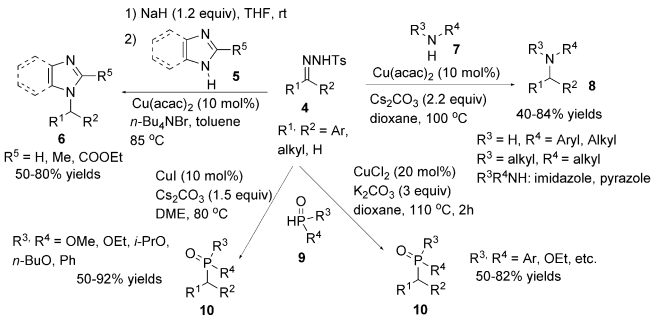



***Scheme 3.*** Cu-catalyzed X–H insertion reactions.

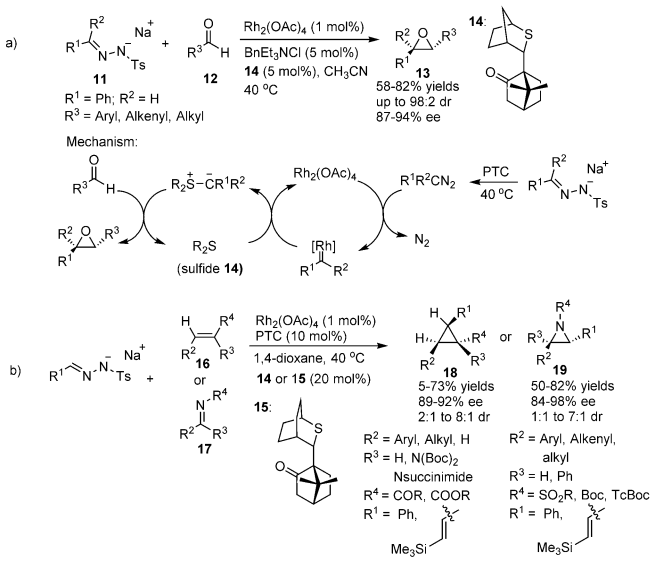
### 2.1.3. *Reactions with Nucleophiles*

In 2001, Aggarwal et al. reported the first example of the trapping of such Rh carbenes with tetrahydrothiophene to form sulfur ylides, which underwent epoxidation with aromatic aldehydes. The enantioselective reaction was accomplished by introducing chiral sulfide **14**, which provided optically active epoxides **13** in high yields and high stereoselectivities (Scheme 4a).[22] Aggarwal et al. also realized the catalytic asymmetric aziridination of imines **17** and the cyclopropanation of electron-deficient alkenes **16** with excellent enantioselectivity, although with moderate yields and diastereoselectivities, mediated by chiral sulfide **14** or **15** (Scheme 4b). Chiral sulfide **15** provided higher yields than sulfide **14** in the cyclopropanation reactions.[23]

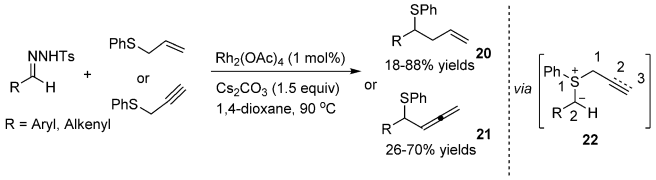
Such an ylide formation may also be applied to the synthesis of homoallyl sulfides **20** or 2,3-allenyl sulfides **21** through the [2,3] sigmatropic rearrangement of ylide intermediate **22** (Scheme 5).[24] By using CuI[25] or $FeCl_3$[26] as the catalyst, the research groups of Yu and Barluenga achieved the synthesis of sulfones from *N*-sulfonylhydrazones in moderate to good yields by nucleophilic attack of the oxygen atom of the sulfonyl anion at the C($sp^2$) atom of the metal carbene intermediate.

### 2.1.4. *Migratory Insertions*

In 2007, Barluenga et al. observed that the arylpalladium halides effected dediazoniation of the in situ generated diazo




***Scheme 4.*** Asymmetric epoxidation, cyclopropanation, and aziridination.




***Scheme 5.*** Rh-catalyzed reactions with sulfides.

compound to produce the Pd-carbene intermediate **24**, which may undergo intramolecular migratory insertion of the carbene unit ($R^1CHR^2R^3C$=) into the Ar–Pd single bond to form **25**. A subsequent β-H elimination provided the olefin product **23** (Scheme 6).[27]

Such a migratory insertion with β-bromostyrenes **27** would generate an allylic palladium intermediate **30**. A subsequent intramolecular nucleophilic substitution would then provide 2*H*-chromenes **28** (Scheme 7a).[28] Such reactions were also observed with the aryl metal species generated by C–H functionalization using CuI[29,30] and $[Cp^*RhCl_2]_2$[31]

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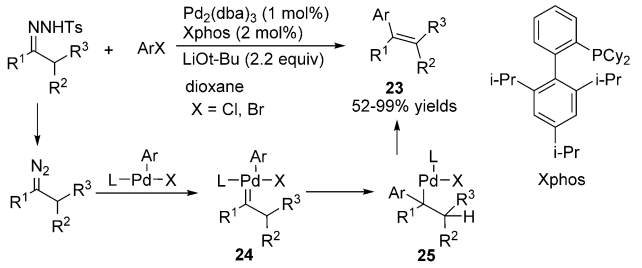
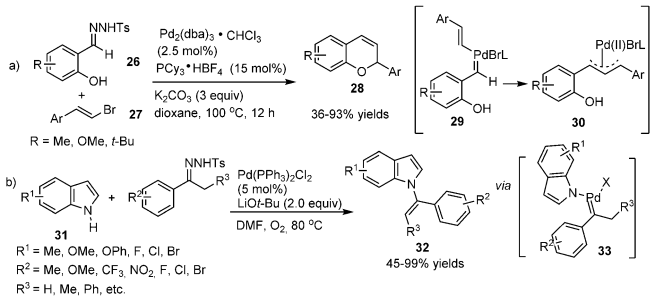


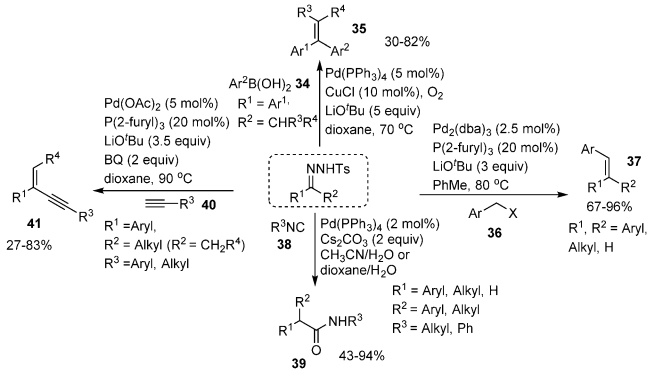

***Scheme 6.*** Pd-catalyzed reactions with aryl halides.




***Scheme 7.*** Pd-catalyzed migratory insertions.

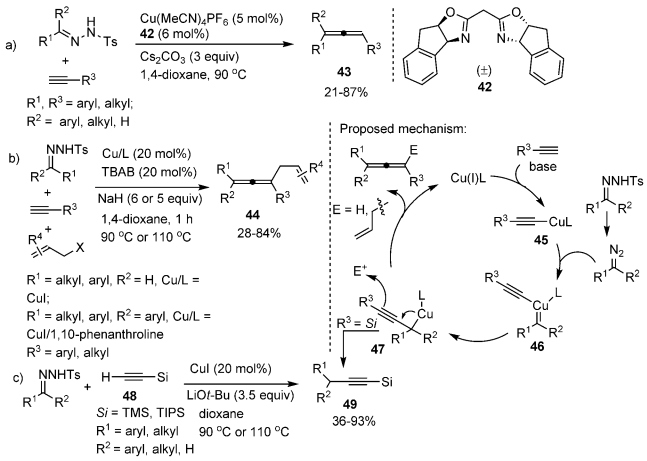
as the catalyst. Insertion into the Pd–N bond of palladium carbene intermediate **33** provided *N*-vinylic indoles **32** with high stereoselectivity (Scheme 7b).[32]

Different coupling partners such as arylboronic acids **34**,[33] benzyl halides **36**,[34] isocyanides **38**,[35] and terminal alkynes **40**[36] can all be applied to form different products (**35**, **37**, **39**, and **41**; Scheme 8).[37]




***Scheme 8.*** Pd-catalyzed migratory insertions.

Furthermore, by using CuI as the catalyst, alkynylcopper carbene intermediate **46** could be generated via the alkynylcopper intermediate **45**.[38] The migratory insertion forms propargylic copper intermediate **47**, which reacts smoothly with protons or allyl halides at the γ position to afford allenes **43** and **44** (Scheme 9a,b).[39–41] Interestingly, when trialkylsilylethynes were applied, 1-alkynylsilanes were formed instead through α-protonation (not γ) because of the steric effect of

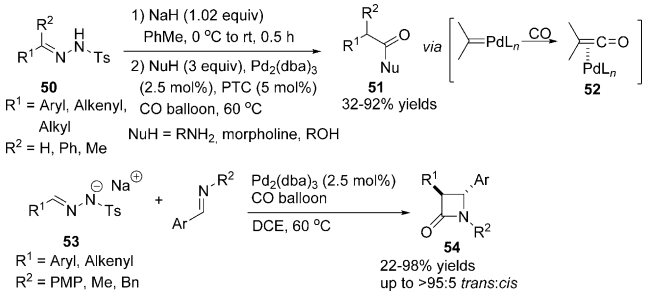



***Scheme 9.*** Cu-catalyzed synthesis of allenes from hydrazones.

the silyl group (Scheme 9c).[42] An interesting alkyne formation from *N*-tosylhydrazones, terminal alkynes, and aryl halides was also observed under the co-catalysis of $Pd^0$ and $Cu^I$.[43]

### 2.1.5. *Reactions with CO*

Palladium carbene intermediates can also be trapped with CO to form ketene intermediate **52**, which can readily react with different nucleophiles such as alcohols, amines, and imines to provide carbonyl compound **51** or β-lactam derivatives **54** (Scheme 10).[44]




***Scheme 10.*** Pd-catalyzed carbonylation of *N*-tosylhydrazones.

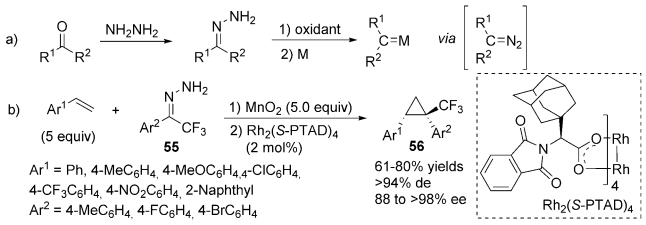
### 2.1.6. *Intramolecular Dimerizations*

$Rh_2(OAc)_4$-catalyzed intramolecular carbene dimerization has also been applied by Wang and co-workers to prepare polycyclic compounds containing a naphthylene unit from bis(*N*-tosylhydrazone)s.[45]

## 2.2. *Oxidation of Hydrazones*

Besides tosylhydrazones, hydrazones themselves may also be used as carbene precursors under oxidative conditions, thereby avoiding the use of a strong base[46] (Scheme 11a).

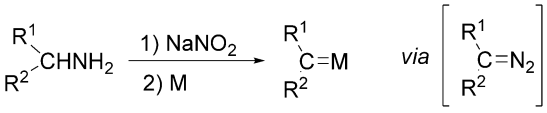



***Scheme 11.*** Preparation of metal carbenes from hydrazones and their enantioselective cyclopropanation.

Doyle et al. found that the application of this method to a cycloproanation reaction led to low yields.[47a,b] In 2007, Davies and co-workers successfully developed the $Rh_2(S\text{-PTAD})_4$-catalyzed enantioselective cyclopropanation reaction of alkenes for the synthesis of trifluoromethyl-substituted cyclopropanes **56** in high diastereoselectivity and enantioselectivity by using $MnO_2$ as the oxidant (Scheme 11b).[47c] Doyle et al. also observed that the oxidation of the hydrazones led to a carbene dimerization reaction with remarkable *Z*/*E* selectivity.[47b] Other reaction types, such as O–H insertion reactions of carboxylic acids, were also reported.[48a,b]

## 3. Amines

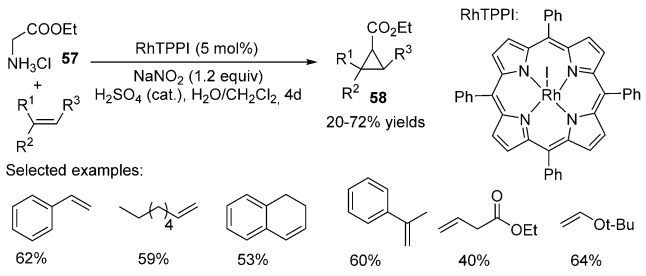
An alternative synthesis for metal carbenes is the diazotization of amines with sodium nitrite under aqueous conditions (Scheme 12).




***Scheme 12.*** Formation of metal carbenes from amines.

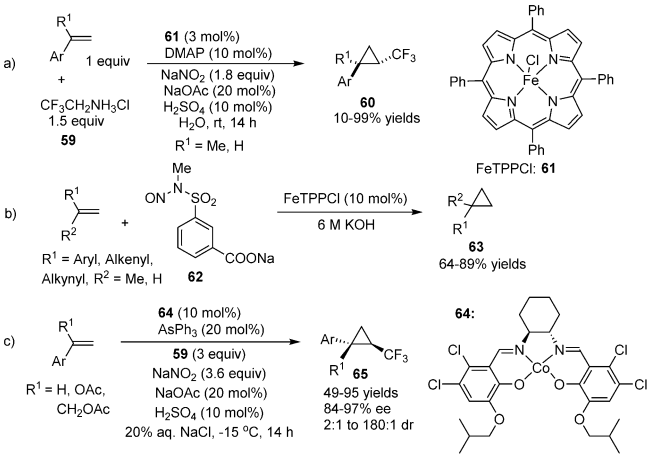
### 3.1. Cyclopropanation and Related Reactions

The cyclopropanation of alkenes with glycine ester hydrochloride **57** (1 equiv) in the presence of $NaNO_2$ (1.2 equiv) and sulfuric acid (5 mol%) at room temperature with RhTPPI (0.5 mol%) as the catalyst proceeded slowly (4 days) with a diastereoselectivity of 1:1 (Scheme 13).[49,50]




***Scheme 13.*** RhTPPI-catalyzed cyclopropanation.

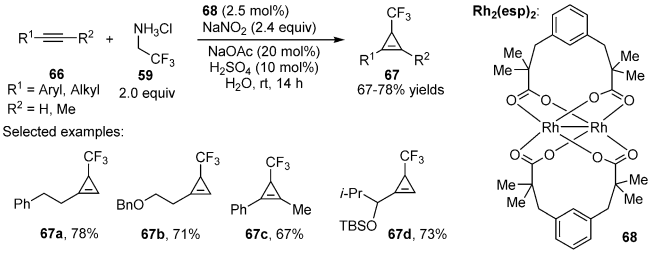
Interestingly, the FeTPPCl-catalyzed cyclopropanation of substituted styrenes with trifluoroethylamine hydrochloride **59** provided **60** in good yield and excellent diastereoselectivity (Scheme 14a).[51] This catalyst may be used for the conversion




***Scheme 14.*** Amine-based cyclopropanations catalyzed by Earth-abundant metals.

of glycine ethyl ester hydrochloride **57** (up to 79% yield, d.r. 10:1)[52] or a commercially available precursor **62** as a safe and user-friendly alternative to diazomethane (Scheme 14b).[53] The same research group also developed an enantioselective cyclopropanation by using 2,2,2-trifluoroethylamine salt **59** and the chiral salen-Co complex **64** as catalyst to generate the $CF_3$-containing cyclopropanes **65** in good yields and diastereoselectivities with up to 97% *ee* (Scheme 14c).[54]

$Rh_2(esp)_2$ **68** has been introduced for cyclopropenation with alkynes **66**, including unactivated aliphatic alkynes, monosubstituted and disubstituted aliphatic alkynes, and phenylpropyne (Scheme 15).[55] However, the use of terminal alkynes and CuI as catalyst led to alkyne products in 80–97% yields through insertion of the metal carbene into the C(sp)–H bond of the terminal alkynes.[56]



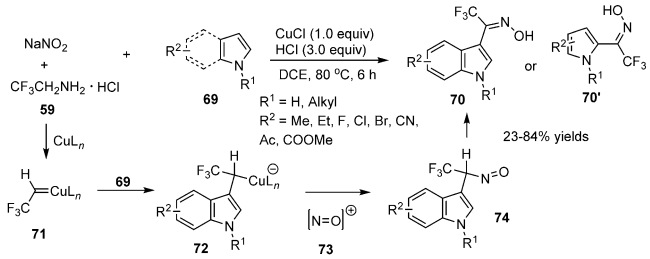

***Scheme 15.*** $Rh_2(esp)_2$-catalyzed cyclopropenation with 2,2,2-trifluoroethylamine.

### 3.2. Reactions with Nucleophiles

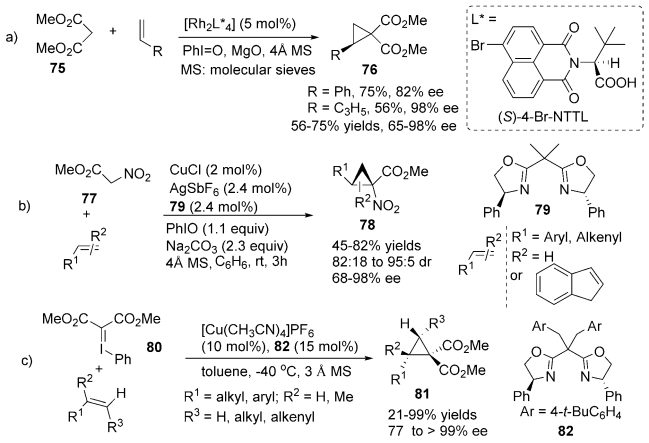
The reaction of indoles/pyrroles **69** with **59** in the presence of $NaNO_2$ proceeded through nucleophilic attack of the

indole C3 atom at the copper carbene intermediate **71** to form intermediate **72**, which was attacked by nitrosonium species **73** to generate **74**. Isomerization of the N=O bond provided the final (*E*)-3-indolyl/2-pyrrolyl trifluoromethylketoxime products **70** and **70′** (Scheme 16).[57]




***Scheme 16.*** Cu-catalyzed reaction with indoles/pyrroles.

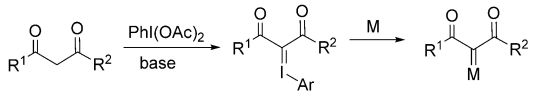



***Scheme 18.*** Enantioselective cyclopropanations with phenyliodonium ylides.

## 4. Phenyliodonium and Sulfonium Ylides

### 4.1. Phenyliodonium Ylides

Phenyliodonium ylides,[58,59] which are easily prepared by the reaction of compounds bearing an acidic methylene unit with PhIO or $PhI(OAc)_2$,[60] can also react with metal complexes to generate metal carbenes (Scheme 17), although an ionic mechanism initiated by the electrophilic iodonium center is also proposed.[61] Since there are already some detailed reviews on this topic,[59] we will only introduce some of the most important recent advances.

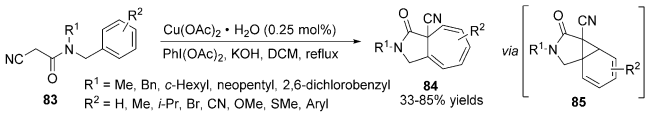



***Scheme 17.*** Formation of metal carbenes from phenyliodonium ylides.

#### 4.1.1. Cyclopropanations

Based on their previous cyclopropanation with in situ generated phenyliodonium ylides,[62a] Müller et al. developed an enantioselective cyclopropantion of terminal alkenes with malonate **75** and PhIO to provide cyclopropanes **76** in good to excellent enantioselectivities (Scheme 18a).[62b] Moreau and Charette also developed a cyclopropanation of mono- or disubstituted alkenes with methyl nitroacetate **77** and PhIO (Scheme 18b).[63] Furthermore, cyclopropanation of numerous multisubstituted olefins with phenyliodonium ylide **80** was realized in high yields and excellent enantioselectivities by Tang and co-workers by using a chiral dibenzyl-substituted bisoxazoline **82**/$Cu^I$ complex (Scheme 18c).[64]

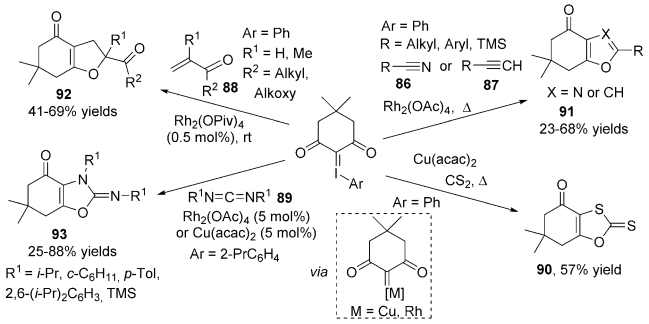
Even benzene may be intramolecularly cyclopropanated to generate tricyclic intermediate **85**. Subsequent ring expansion afforded differently fused cyclohepta-1,3,5-triene derivatives **84** in up to 85% yield (Scheme 19).[65]




***Scheme 19.*** Cu-catalyzed intramolecular Buchner reaction.

#### 4.1.2. Cycloaddition Reactions

Phenyliodonium ylides were also used in a series of cycloaddition reactions, such as [3+2] additions with carbon disulfide,[66] nitriles **86** or terminal alkynes **87**,[67] alkenes **88**,[68] and carbodiimides **89**,[69] to produce heterobicycles **90–93** (Scheme 20).

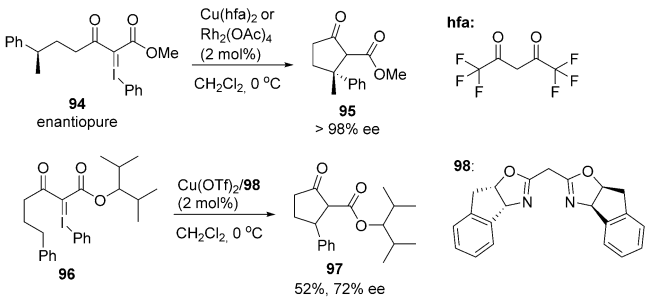



***Scheme 20.*** Metal-catalyzed cycloadditions with phenyliodonium ylides.

#### 4.1.3. X–H Insertion Reactions

The intramolecular insertion of enantiopure substrate **94** led to a complete retention of configuration; however, such enantioselective C–H insertions under Cu catalysis in the presence of chiral bisoxazoline ligand **98** provided only moderate enantioselectivity (Scheme 21).[70]

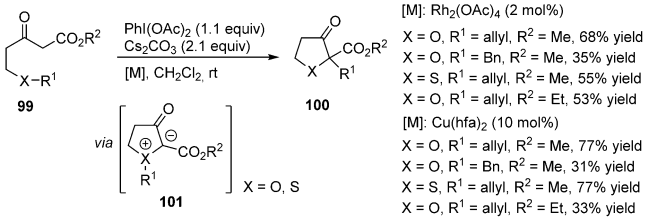
  




***Scheme 21.*** C–H insertion reactions based on phenyliodonium ylides.

#### 4.1.4. *Reactions with Nucleophiles*

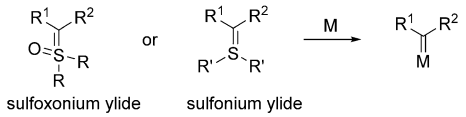
The $Rh_2(OAc)_4$ or $Cu(hfa)_2$ (hfa: hexafluoroacetylacetonate) catalyzed reactions of acyl acetates **99** with intramolecular etheric oxygen or sulfur as the nucleophile formed oxonium or sulfonium ylides **101**, which underwent 1,2-$R^1$ transfer to afford cyclic ketones **100** (Scheme 22).[71]




***Scheme 22.*** Rh- and Cu-catalyzed generation of ylides and their rearrangement.

### 4.2. *Sulfonium and Sulfoxonium Ylides*

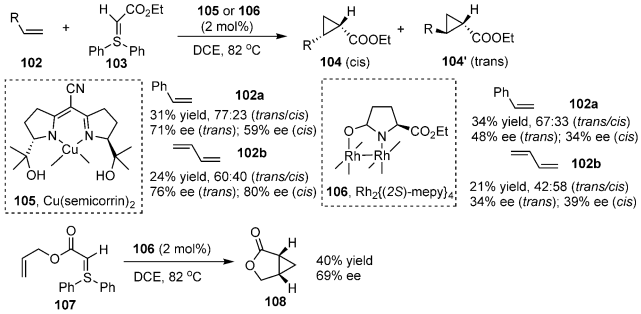
Sulfonium and sulfoxonium ylides may also serve as carbene precursors in metal-catalyzed reactions (Scheme 23)[59a,72] or under metal-free conditions.[73] In contrast to phenyliodonium ylides, which require two electron-withdrawing substituents ($R^1$, $R^2$ in Scheme 23) at the ylide center to be isolable, only one (or even no) such substituent is required for sulfonium or sulfoxonium ylides.




***Scheme 23.*** Formation of metal carbenes from sulfoxonium or sulfonium ylides.

#### 4.2.1. *Cyclopropanation Reactions*

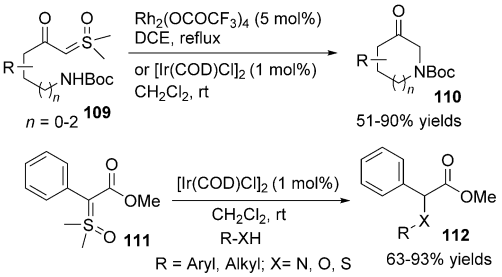
Although the first example of the generation of a metal carbene from sulfur ylides was reported in 1966 with $CuSO_4$ as the catalyst,[74] chiral rhodium- or copper-catalyzed intermolecular or intramolecular cyclopropanations of olefins with sulfonium ylides to provide **104'** and **108** has not been very successful (Scheme 24).[75,76]




***Scheme 24.*** Cu- and Rh-catalyzed cyclopropanation reactions.

#### 4.2.2. *X–H Insertion Reactions*

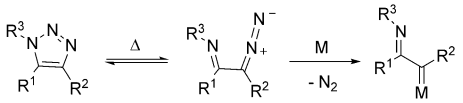
An intramolecular insertion reaction of sulfoxonium ylides **109** with polar N–H bonds was realized by using $[Rh_2(OCOCF_3)_4]$ or $[Ir(COD)Cl]_2$ as the catalyst, which afforded lactam products **110** (Scheme 25).[77,78] The intermolecular insertion reactions of sulfoxonium ylides **111** into X–H (NH, OH, SH) bonds catalyzed by $[Ir(COD)Cl]_2$ has also been reported (Scheme 25).[78]




***Scheme 25.*** Rh- or Ir-catalyzed X–H insertion of sulfoxonium ylides.

## 5. Triazoles

Different types of 1,2,3-triazoles, which exist in equilibrium with their diazoimine tautomer with proper substituents at the N1-, C4-, and C5-positions upon heating, may serve as stable precursors for α-iminyl metal carbenes under metal catalysis (Scheme 26).[79]

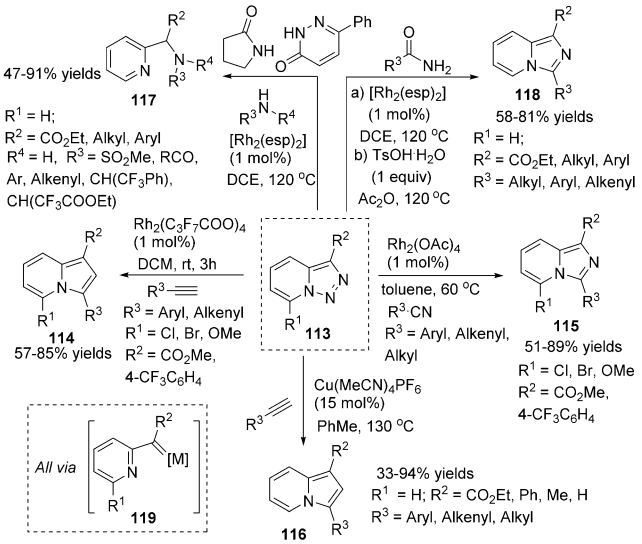



***Scheme 26.*** Formation of metal carbenes from 1,2,3-triazoles.

### 5.1. Pyridotriazoles and Triazoloindoles

#### 5.1.1. Pyridotriazoles

7-Substituted pyridotriazoles **113** have been introduced as convenient precursors for Rh carbene **119**, which readily undergoes cycloaddition reactions with alkynes or nitriles to provide indolizines **114** or imidazoles **115**, respectively.[80] Recently, a Cu-catalyzed cycloaddition of pyridotriazoles with terminal alkynes was developed that provided indolizines **116**. This reaction could be carried out under aerobic conditions, had a broader substrate scope, and with no need of an activating group $R^1$. Aliphatic alkynes are also competent partners.[81] The insertion of pyridyl carbenes **119** into the N–H bonds of carbamates, amides, ureas, oxazolidin-2-one, and 3(2-*H*)-pyridazinone, as well as aromatic and aliphatic amines were realized and provided pyridinylmethylamines **117** in good to excellent yields. The authors also developed a [$Rh_2$-(esp)$_2$]-catalyzed one-pot N–H insertion/cyclization reaction of pyridotriazoles **113** with primary amides to provide **118** (Scheme 27).[82]

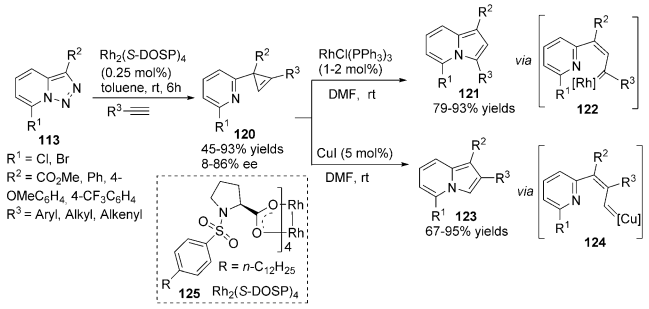



*Scheme 27.* Rh- or Cu-catalyzed reactions of pyridotriazoles **113**.

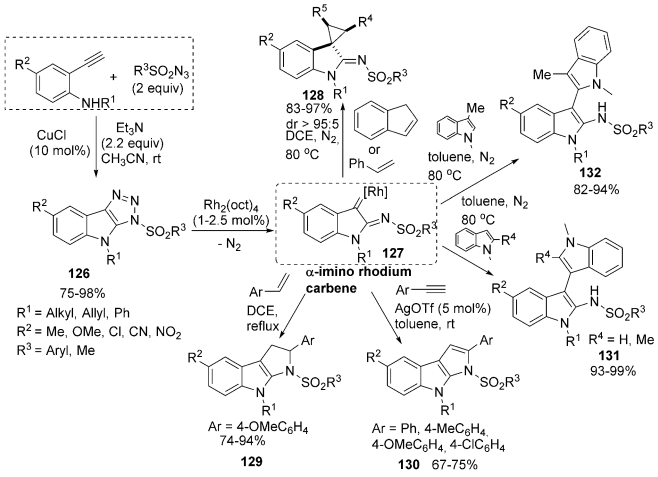
However, the $Rh_2$(*S*-DOSP)$_4$-catalyzed cyclopropenation of 7-substituted pyridotriazoles **113** with terminal alkynes provided cyclopropenes **120** with only poor to moderate enantioselectivities. Interestingly, such cyclopropenes may undergo different ring-opening cyclizations with $RhCl(PPh_3)_3$ or CuI to provide the 1,3-substituted indolizines **121** and 1,2-substituted *N*-fused pyrroles **123**, respectively (Scheme 28).[83]

#### 5.1.2. Triazoloindoles

Triazoloindoles **126** served as precursors of α-imino rhodium carbene **127** with an indole skeleton. Various types of reactions, such as cyclopropanation with alkenes to generate **128**, cycloaddition with electron-rich terminal aryl alkenes or alkynes to provide tricyclic products **129** or **130**, C–H insertion into 1,2- or 1,3-disubstituted indoles to produce **131** or **132**, have been realized (Scheme 29).[84]




*Scheme 28.* Rh-catalyzed cyclopropenation and subsequent cyclizations.




*Scheme 29.* Synthesis and reactions of triazoloindoles **126**.

### 5.2. Simple Triazoles

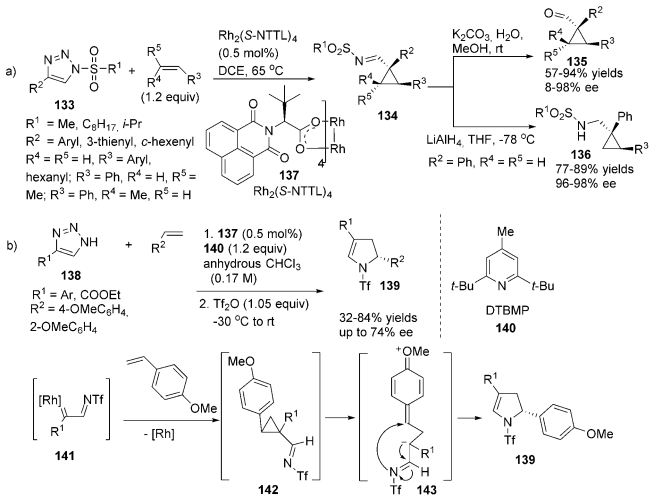
Simple 1,2,3-triazoles are readily available from alkynes and azides[85] and were found to act as metal carbene precursors under metal (Rh, Ni) catalysis.

#### 5.2.1. Cyclopropanations and Related Reactions

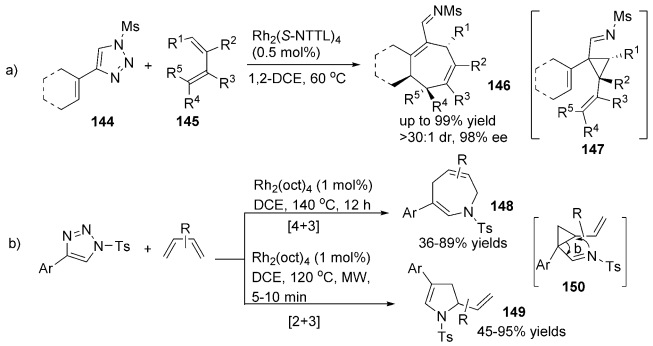
In 2009, the Fokin research group developed the enantioselective cyclopropanation of olefins with simple 1,2,3-triazoles **133** to afford the cyclopropanes **134** containing the sulfonylimine group (Scheme 30a).[86] The $Rh^{II}$-catalyzed asymmetric formal [3+2] cycloaddition of *NH*-1,2,3-triazoles **138** with 2-methoxy- or 4-methoxy-substituted styrene provided 2,3-dihydropyrroles **139** in moderate to good yields and enantioselectivities (Scheme 30b). The OMe group triggers the ring opening of the cyclopropane ring in intermediate **142**.[87]

The cyclopropanation of the less-substituted C=C bond in conjugated 1,3-dienes **145** with alkenyl-substituted 1-sulfonyl-1,2,3-triazoles **144** can be combined with a Cope rearrange-



***Scheme 30.*** Rh-catalyzed cyclopropanation and related reactions.



***Scheme 31.*** Formal [4+3] and [3+2] cycloaddition reactions of triazoles **144**.

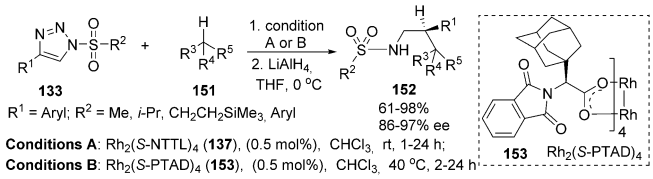
ment to afford formal [4+3] cycloaddition products **146** in acceptable yields with excellent control over the diastereoselectivity and enantioselectivity (Scheme 31 a).[88] In the case of aryl-substituted triazoles, the cyclopropanation product **150** would undergo an aza-Cope rearrangement to generate the formal [4+3] product **148**, or a cyclopropylimine rearrangement (nitrogen atom of imine attacks the cyclopropane) to provide the [3+2] products **149** under different reaction conditions (Scheme 31 b).[89]

### 5.2.2. *X–H Insertion Reactions*

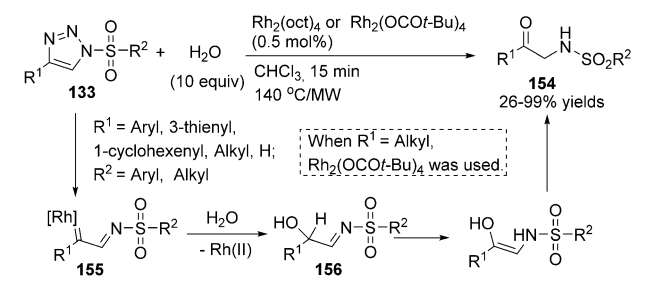
The enantioselective insertion of unactivated alkane C–H compounds **151** with in situ generated iminyl Rh carbenes afforded a series of highly optically active sulfonamides **152** after workup with $LiAlH_4$ (Scheme 32).[90]

Such insertion reactions with water provided α-amino ketones **154** through an O–H insertion and tautomerization (Scheme 33).[91]

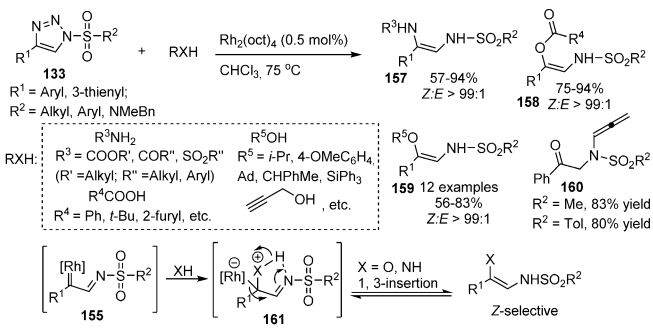
Primary amides, bulky carboxylic acids, aromatic carboxylic acids, and bulky alcohols are aslo applicable for generating the X–H insertion products **157–159** with very high stereoselectivity. When propargylic alcohols were used, O–H



***Scheme 32.*** Rh-catalyzed C–H insertion based on triazoles **133**.



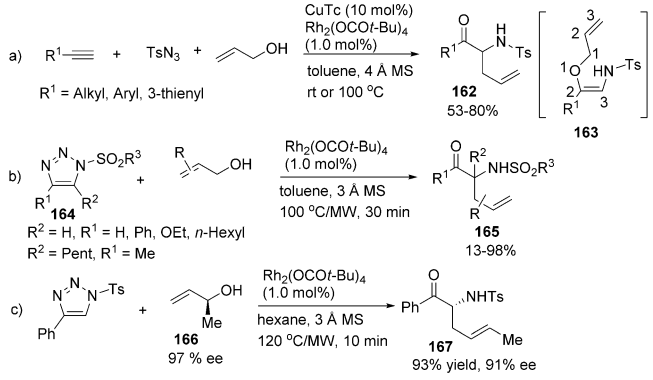
***Scheme 33.*** Rh-catalyzed O–H insertion reactions.



***Scheme 34.*** Rh-catalyzed triazole-based X–H insertion reactions.

insertion occurred first, followed by a 3,3-rearrangement to provide the allene products **160** in yields of 72–87 % (Scheme 34).[92]

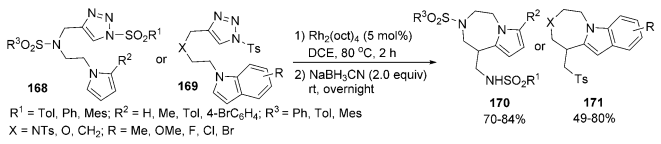
Similarly, such reactions with allylic alcohols in the presence of a $Cu^{I}$ or $Rh^{II}$ catalyst yielded amides **162**, **165**, and **167** with an acceptable chirality transfer (Scheme 35).[93]



***Scheme 35.*** Rh-catalyzed O–H insertion and rearrangement of allylic alcohols.

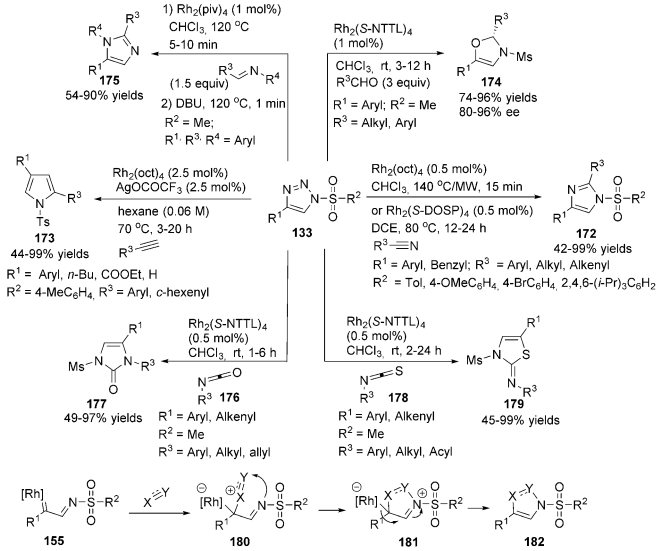
Intramolecular insertion into the C–H bond of pyrroles or indoles provided polycyclic azepine derivatives **170** and **171** efficiently (Scheme 36).[94]




***Scheme 36.*** Rh-catalyzed intramolecular C–H insertions of pyrroles and indoles.

### 5.2.3. *Reactions with Nucleophiles*

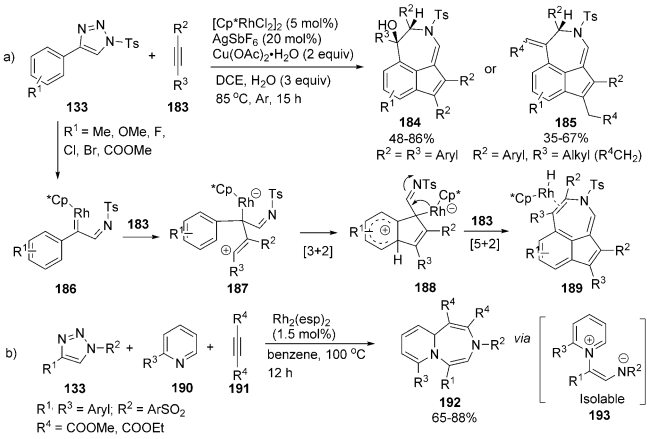
Imino-substituted Rh carbenes **155** can also react with different unsaturated compounds, such as nitriles, to generate imidazoles **172**,[95] terminal alkynes to produce pyrroles **173**,[96,97] aldehydes or aldimines to provide oxazolines **174** or imidazoles **175** by elimination of one molecule of sulfinic acid under basic conditions,[98] as well as isocyanates **176** and isothiocyanates **178** to deliver imidazolones **177** and thiazoles **179** (Scheme 37).[99] Mechanistically speaking, the generated




***Scheme 37.*** Rh-catalyzed cycloaddition of triazoles with unsaturated compounds.

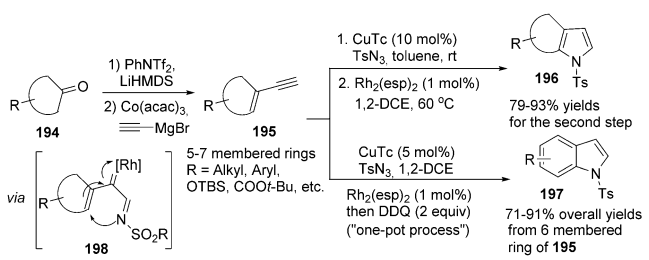
rhodium carbene **155** was nucleophilically attacked by the unsaturated compounds to form the zwitterionic species **180**. A subsequent *N*-initiated cyclization provided zwitterionic intermediate **181**, which underwent elimination of the Rh catalyst to form the products **182**.

A $Rh^{III}$-catalyzed [3+2]/[5+2] cycloaddition of aryl triazoles **133** with internal alkynes **183** led to the formation of the indeno[1,7-*cd*]azepin-1-ols **184** or 1-methyleneindeno[1,7-*cd*]azepines **185** in acceptable yields. The nucleophilic attack of alkynes **183** on rhodium carbene intermediate **186** followed by Friedel-Craft-type cyclization would form the [3+2] bicyclic intermediate **188**. A second [5+2] reaction with the alkynes then provides the Cp*(H)Rh-coordinated tricyclic intermediate **189**. Finally, the reaction of water with the coordinated C=C bond provides the product **184**; a highly regioselective hydrometalation and β-H elimination then leads to **185** (Scheme 38a).[100] In the presence of substituted pyridines and activated alkynes **191**, [5+2] products of 1,4-diazepines **192** could be obtained in good yields via isolable 1,5-dipoles **193** (Scheme 38b).[101]




***Scheme 38.*** Rhodium-catalyzed [3+2] and [5+2] cycloadditions.

An efficient synthesis of 2,3-disubstiuted pyrroles **196** or indoles **197** was realized by a rhodium-catalyzed intramolecular cyclization of in situ generated 4-alkenyl-1-sulfonyl-1,2,3-triazoles from enynes **195**. The presence of an extra C=C bond led to the Michael addition of the iminyl nitrogen atom at the conjugated metal alkenyl carbenes **198** (Scheme 39).[102]

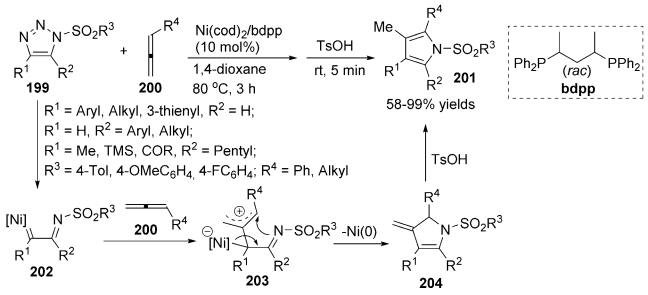



***Scheme 39.*** Synthesis of pyrroles and indoles from enyne substrates **195**.

Allenes **200** reacted efficiently in the $Ni^0$-catalyzed [3+2] transformation with 1-sulfonyl-1,2,3-triazoles **199** to produce pyrroles **201** via zwitterionic intermediate **203**, which was generated by nucleophilic attack at the nickel carbene **202** with allene **200**. An allylic cyclization triggered by the iminyl nitrogen atom generated isopyrroles **204**, which were further converted into polysubstituted pyrroles **201** through aromatization (Scheme 40).[103]

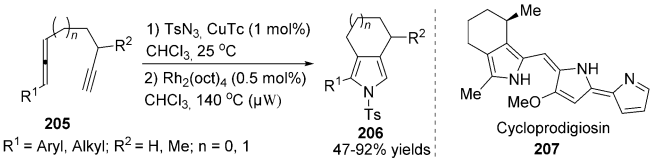
An intramolecular reaction of allene-terminal alkyne substrates **205** was developed by Schultz and Sarpong for



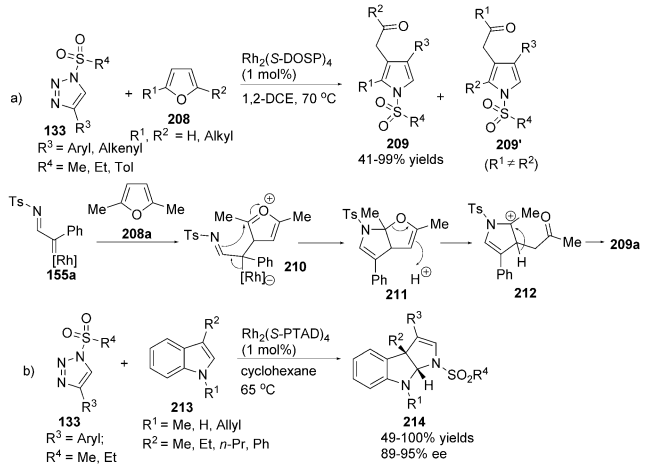

***Scheme 40.*** Ni-catalyzed cycloadditions of triazoles with allenes.

the efficient synthesis of 2-substituted 3,4-fused pyrroles **206** in a one-pot process. This approach has been applied to the efficient synthesis of the natural product cycloprodigiosin **207** (Scheme 41).[104]




***Scheme 41.*** Cu/Rh-catalyzed synthesis of bicyclic pyrroles.

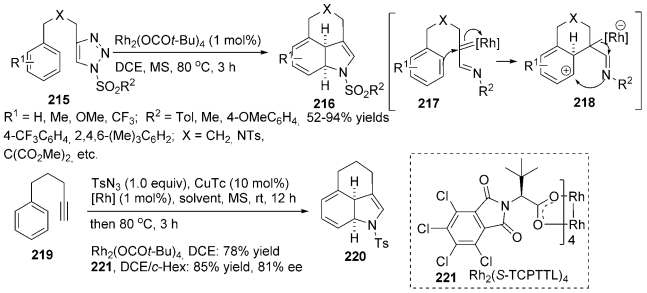
These imino-substituted rhodium carbenes may even react with 2,5-disubstituted furans **208** to allow preparation of the substituted pyrroles **209** (and **209′**). The generated metal carbene **155a** was attacked by the C3 carbon atom of furan to generate the zwitterion **210**, and a subsequent ring closure provides the formal [3+2] product of hemiaminal **211**. Ring opening of **211** under mild acidic conditions and rearomatization provided pyrroles **209a** with an aldehyde or ketone functionality. Low selectivity was observed with unsymmetrical 2,5-disubstituted furans **208** (Scheme 42a).[105] An enantioselective reaction of indoles led to the highly efficient construction of tricyclic pyrroloindolines **214** in




***Scheme 42.*** Synthesis of pyrroles and pyrroloindolines.

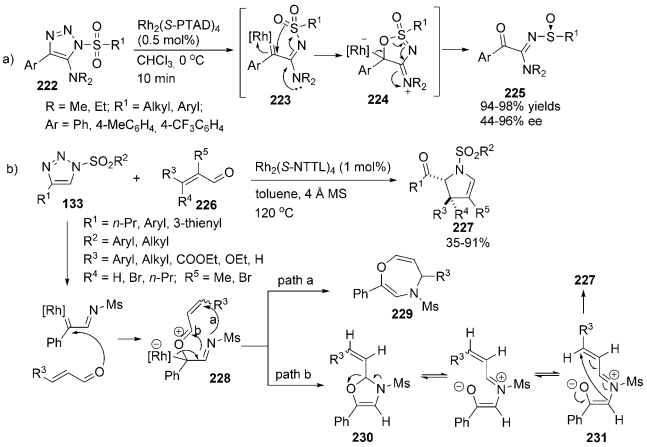
moderate to good yields and with excellent control over the enantioselectivity (Scheme 42b).[106]

An intramolecular dearomatizing [3+2] reaction of triazoles with an aryl ring in **215** was reported with $Rh_2(OCOtBu)_4$, which afforded 3,4-fused dihydroindoles **216**. The reaction with $Rh_2(S\text{-TCPTTL})_4$ **221** led to **220** in 81% *ee* (Scheme 43).[107]




***Scheme 43.*** Cycloadditions of rhodium carbenes with benzene rings.

The Fokin research group observed that the oxygen atom from the generally considered inert *N*-sulfonamide may also act as a nucleophile to enantioselectively attack the in situ generated rhodium carbene **223** to form the optically active sulfinylamidines **225** (Scheme 44a).[108] In 2013, Murakami




***Scheme 44.*** Reactions of rhodium carbenes with oxygen nucleophiles.

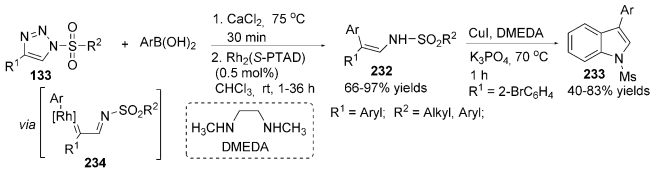
and co-workers identified that the oxygen atom in the carbonyl group of α,β-unsaturated enals **226** may also act as nucleophiles to generate the zwitterionic intermediate **228**. The presence of a C=C bond leads to two possible pathways: Attack at the β-position provides the minor product 4,5-dihydro-1,4-oxazepine **229** (path a), while attack at the carbonyl carbon atom generates the 4-oxazoline intermediate **230** (path b). The C–O bond of the *N*,*O*-aminal moiety of **230** is then selectively cleaved to yield the more stable *E* isomer of enolate-iminonium intermediate **231**. Subsequent conjugate addition of the enloate carbon atom affords 2,3-dihydropyrroles **227** (Scheme 44b).[109] A Cu- or Rh-catalyzed nucleo-

philic reaction with allylic sulfides afforded homoallylic sulfides through a [2,3] sigmatropic rearrangement process.[110]

#### 5.2.4. Migratory Insertions

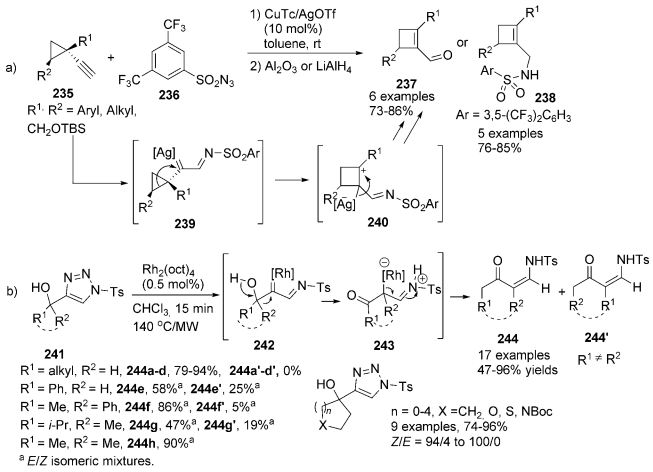
Stereoselective arylation of in situ generated imino-substituted $Rh^{II}$ carbenes **234** with aryl boronic acids provided 2,2-diaryl enamines **232** with good *cis* selectivity in regard to the coupling Ar group (5:1 to >10:1, Scheme 45).[111]




***Scheme 45.*** Rh-catalyzed migratory insertion reaction of triazoles with boronic acids.

#### 5.2.5. 1,2-Migration Reactions

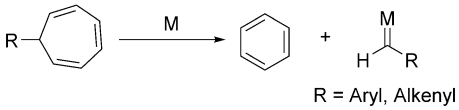
When a metal carbene is adjacent to a highly strained cyclopropane, for example, in intermediate **239**, it may undergo a ring expansion to generate intermediate **240**, thereby producing the multisubstituted cyclobutenes **237** or **238** with excellent regioselectivity (>20:1, Scheme 46a).[112] When an alcohol unit replaced the three-membered ring, such a reaction provided β-aminoenones **244** and/or **244′** in good to excellent yields (47–96%) by a 1,2-migration/ring-expansion reaction (Pinacol rearrangement process). The migratory aptitude follows the order H > phenyl > primary alkyl > secondary alkyl (Scheme 46b).[113]




***Scheme 46.*** Catalyzed 1,2-migrations.

## 6. 1,3,5-Cycloheptatrienes

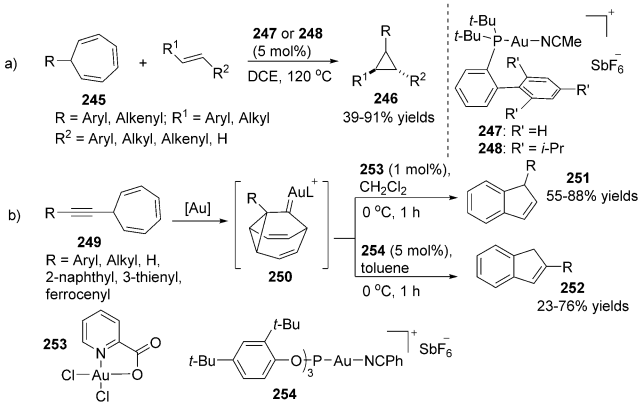
A Retro-Buchner reaction of 7-substituted 1,3,5-cycloheptatrienes can generate metal carbenes by releasing a molecule of benzene (Scheme 47).




***Scheme 47.*** Formation of metal carbenes from cycloheptatrienes.

### 6.1. Cyclopropanations and Related Reactions

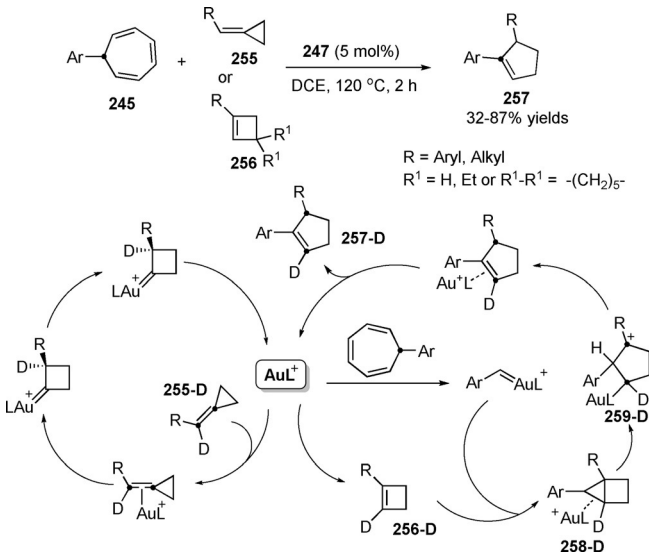
In 2011, Echavarren and co-workers reported that a $Au^I$ carbene generated from **245** may be trapped by monosubstituted or disubstituted alkenes to provide cyclopropanes **246** (Scheme 48a).[114] 7-Alkynyl-1,3,5-cycloheptatrienes **249** behaved differently under gold(I) or gold(III) catalysis, with generation of the fluxional barbaralyl gold carbene cations **250**. Two cycloisomerization reactions with different catalysts occurred to produce different indene products **251** and **252** (Scheme 48b).[115]




***Scheme 48.*** Au-catalyzed cyclopropanation and cycloisomerization.

In the case of methylenecyclopropanes **255** or cyclobutenes **256**, [4+1] cycloaddition occurred to afford the cyclopentene products **257**. Cyclobutenes **256-D** were first formed from methylenecyclopropanes **255-D**. Subsequent cyclopropanation formed bicyclic intermediates **258-D**, which was followed by selective ring expansion of the three-membered ring to generate the cyclopentyl gold intermediate **259-D** with a carbocationic center at the 3-position. A concerted 1,2-H shift/gold(I) elimination provided the final cyclopentene product **257-D** (Scheme 49).[116]

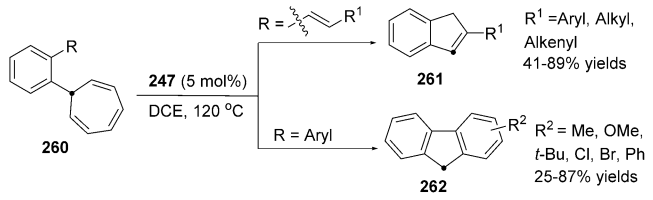
  




*Scheme 49.* Au-catalyzed [4+1] cycloadditions.

### 6.2. Reactions with Nucleophilic Olefins or Arenes

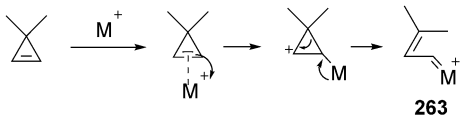
The intramolecular reaction of *ortho*-alkenyl- or aryl-substituted 7-aryl-1,3,5-cycloheptatrienes **260** produced indenes **261** and fluorenes **262** (Scheme 50).[117]




*Scheme 50.* Au-catalyzed reaction of *ortho*-substituted substrates **260**.

## 7. Cyclopropenes

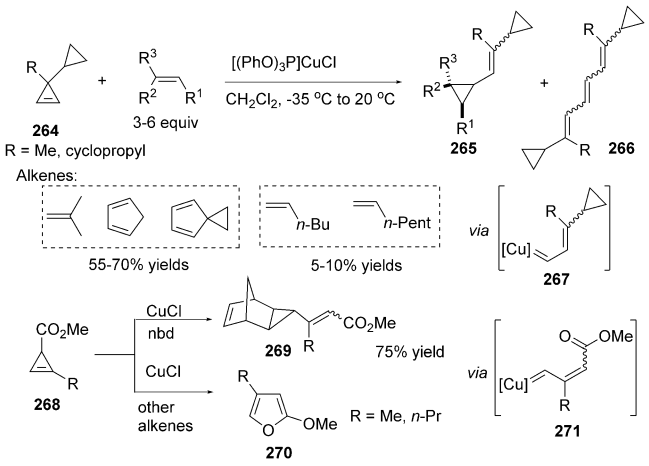
Cyclopropenes can generate metal carbene intermediates **263** under quite mild conditions because of their intrinsic ring strain (Scheme 51). The double bond in **263** may be easily oxidized to an aldehyde unit and, thus, such cyclopropenes can be considered as α-diazo aldehyde (ketone) surrogates.[118]




*Scheme 51.* Formation of metal carbenes **263** from cyclopropenes.

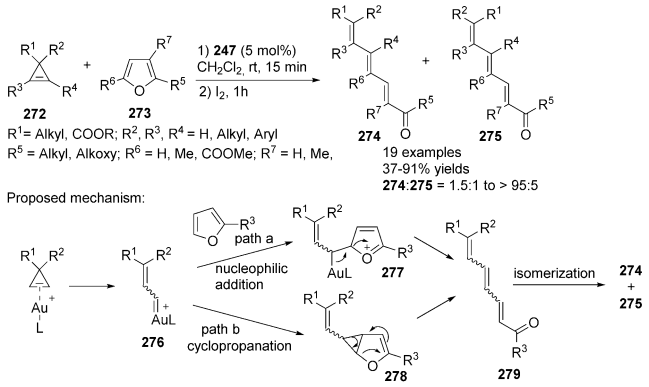
### 7.1. Cyclopropanations

In 1974, Binger and McMeeking reported the first intermolecular cyclopropanation of highly electron-deficient olefins with nickel carbene species generated by ring opening of 3,3-dimethylcyclopropene.[119] The intermolecular cyclopropanation reaction of unactivated internal olefins with cyclopropenes **264** was achieved by Nefedov and co-workers in 1982 by using a $Cu^{I}$ catalyst.[120] In the case of methoxycarbonyl-substituted cyclopropene **268**, the proposed vinylcarbene intermediate **271** was trapped by norbornadiene (nbd) to provide monocyclopropanation product **269**. However, alkenes not as reactive as norbornadiene did not undergo such a reaction, instead furan products **270** were formed by nucleophilic attack of the ester and isomerization (Scheme 52).[121]



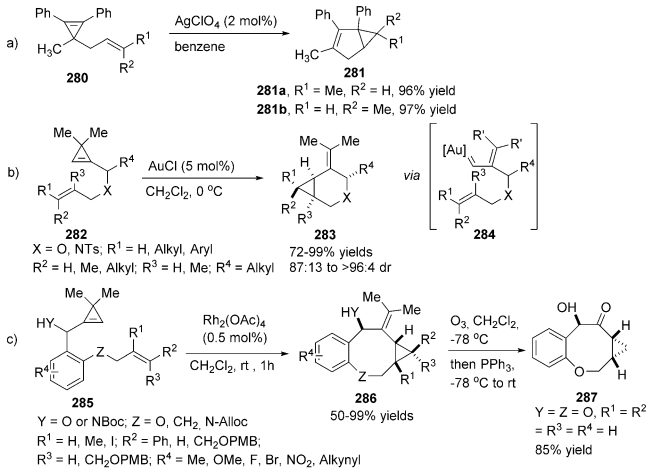

*Scheme 52.* Cu-catalyzed cyclopropanations and cycloisomerization.

In 2009, Toste and co-workers proposed an Au carbene intermediate in the $Au^{I}$-catalyzed ring opening/cyclopropanation of cyclopropene with *cis*-1,2-diphenylethene.[122] However, a carbenoid-type intermediate is also possible (see Section 12). This was further demonstrated by Hadfield and Lee in the intermolecular reaction of cyclopropenes **272** with furans **273** to provide the conjugated trienylcarbonyl compounds **274** and **275** at room temperature with 0.01 mol% of catalyst **247**. Here, both a Friedel–Crafts-type mechanism (via **277**) or cyclopropanation with furans (via **278**) are possible (Scheme 53).[123]




*Scheme 53.* Au-catalyzed reaction of cyclopropenes with furans.

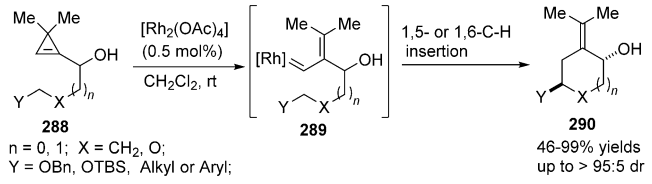
Intramolecular cyclopropanations of alkenes were also observed, and led to the efficient formation of strained bicyclic products **281**, **283**, and **286** (Scheme 54).[124–126]




***Scheme 54.*** Cyclopropene-based intramolecular cyclopropanations.

### 7.2. X–H Insertion Reactions

An intramolecular C($sp^3$)–H insertion reaction of cyclopropenes **288** proceeded via carbene intermediate **289**, thereby providing cyclic products **290** (Scheme 55).[127]



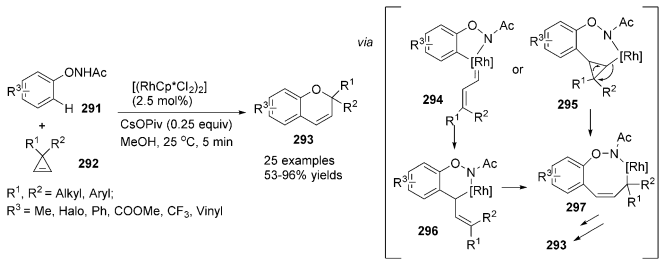

***Scheme 55.*** Rh-catalyzed intramolecular insertions in C–H bonds.

### 7.3. Reactions with Nucleophiles

Rhodium carbene intermediates may also be trapped by allylic sulfides or propargylic sulfides to provide 1,5-dienyl or 1,2-5-trienyl sulfides in good to excellent yields. An enantioselective version of this reaction was also attempted, but gave disappointing results.[128] When alcohols were used as the nucleophiles, conjugate addition provided the corresponding terminal *tert*-allylic ethers in moderate to good yields. Oxidation formed the corresponding 2-enals with poor stereoselectivity.[129] In addition, conjugate addition of a benzene ring was also observed, although a Friedel–Crafts type reaction mechanism may also be possible.[130]

### 7.4. Migratory Insertions

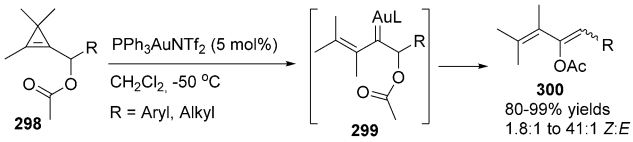
2*H*-Chromenes **293** were prepared from the ring-opening cyclization of *N*-phenoxyacetamides **291** with cyclopropenes **292** in the presence of [($RhCp^*Cl_2$)$_2$] as the catalyst through a migratory insertion of carbene **294** to generate allylic Rh intermediate **296**. Allylic rearrangement and reductive elimination provided **293** (Scheme 56).[131]




***Scheme 56.*** Rh-catalyzed cyclization based on migratory insertion.

### 7.5. 1,2-Migrations

(*Z*)-Acetoxydiene **300** may be prepared through a gold-catalyzed rearrangement of cyclopropenylmethyl acetates **298** by 1,2-acetoxy migration of carbene intermediate **299** (Scheme 57).[132]




***Scheme 57.*** Au-catalyzed 1,2-OAc migration.

## 8. Propargylic Esters and Alcohols

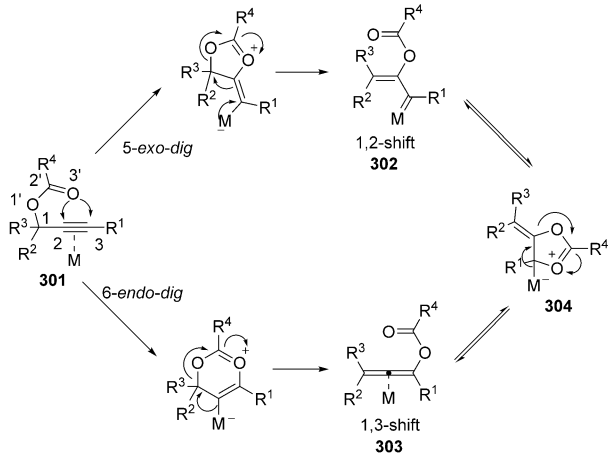
### 8.1. Propargylic Esters

Transition-metal-catalyzed rearrangement of propargylic esters has been extensively explored for the formation of different metal carbenes by using Pd, Pt, Au, Ru, Rh, etc.[133] Two pathways are possible: 5-*exo*-*dig* cyclization provided the metal carbene intermediate **302** through a 1,2-shift process; alternatively, a 1,3-shift process proceeding through a 6-*endo*-*dig* cyclization provides the allene product **303**, which can also be converted into **302** via cyclic intermediate **304** (Scheme 58).[134]

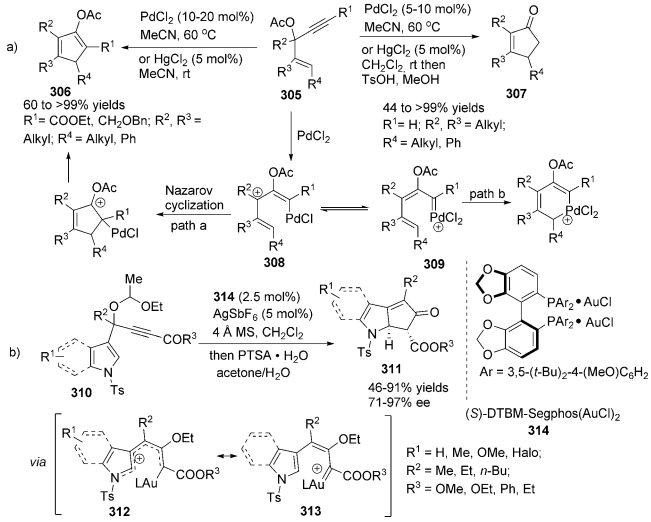
#### 8.1.1. Rautenstrauch Rearrangement/Pentannulation

In 1984, Rautenstrauch first reported the $PdCl_2(MeCN)_2$-catalyzed cyclization of 1-ethynyl-2-propenyl acetates to form 2-cyclopentenones via a possible Pd carbene intermediate.[135] Later, Caruana and Frontier carefully studied this reaction of differently substituted propargylic acetates **305** by using $PdCl_2$ or $HgCl_2$ as the catalyst. A Nazarov cyclization mechanism was proposed to be the most likely pathway (via intermediate **308**, path a). However, the metal carbene mechanism (via intermediate **309**, path b) cannot be ruled out completely




***Scheme 58.*** Migration of an acetoxy group of propargyl esters.



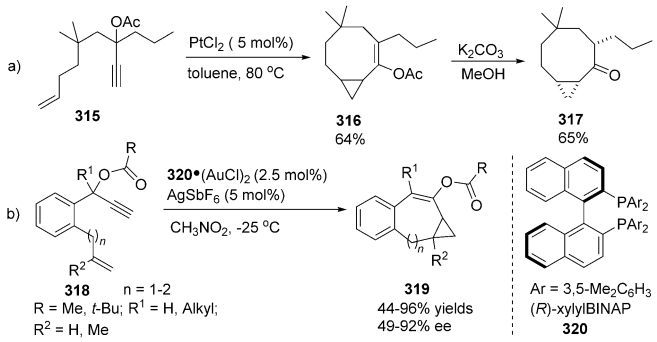

***Scheme 59.*** Transition-metal-catalyzed Rautenstrauch rearrangement.

(Scheme 59a).[136] Sarpong and co-workers reported an analogous $PtCl_2(PPh_3)_2$-catalyzed cyclization.[137] A highly enantioselective Rautenstrauch rearrangement was realized by Toste and co-workers when an indole or pyrrole unit replaced the C=C bond and using (*S*)-DTBM-Segphos$(AuCl)_2$/$AgSbF_6$ as the catalyst (Scheme 59b).[138]

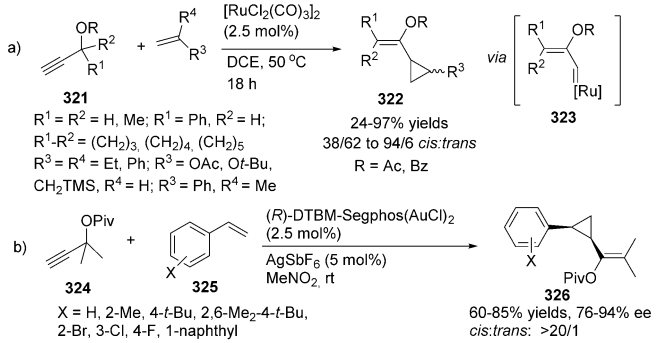
### 8.1.2. *Cyclopropanations and Related Reactions*

An elongated chain between the propargylic ester unit and the C=C bond allowed intramolecular cyclopropanations to afford bicyclic products **316**.[139–141] An enantioselective intramolecular cyclopropanation to provide tricyclic products **319** efficiently was realized by using a (*R*)-xylylBINAP-$(AuCl)_2$/$AgSbF_6$ system (Scheme 60).[142]

Intermolecular cyclopropanations have been realized with Ru or Au catalysts.[143] With the exception of some cyclic substrates, $Au^I$-catalyzed cyclopropanations usually provide poor *cis*/*trans* selectivities. Interestingly, the chiral DTBM-



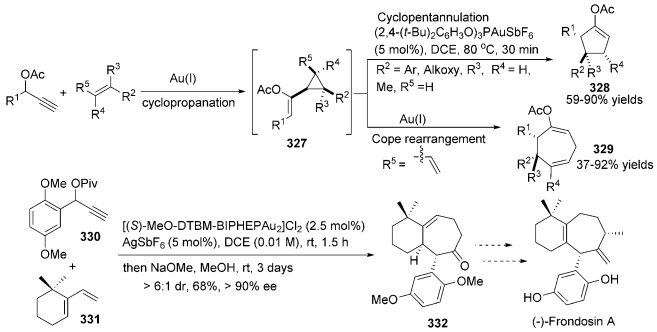

***Scheme 60.*** Intramolecular cyclopropanations.




***Scheme 61.*** Ru- and Au-catalyzed intermolecular cyclopropanation reaction.

Segphos-$Au^I$ complex catalyzes this reaction to provide **326** with high stereoselectivity (Scheme 61).[144]

The cyclopropanation products **327** may further undergo cyclopentannulation or Cope rearrangement to produce five- (**328**) or seven-membered rings (**329**). This principle has been successfully applied to the formal enantioselective synthesis of marine norsesquiterpenoids frondosins A and B (Scheme 62).[145]

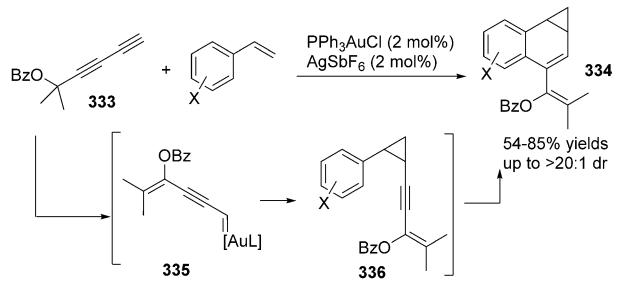



***Scheme 62.*** Au-catalyzed [3+2] and [4+3] reaction through cyclopropanation.

Interestingly, the reaction of 2-methyl-3,5-hexadiyn-2-yl benzoate (**333**) with the additional terminal C–C triple bond led, after 1,2-OBz migration, to the formation of enynyl gold carbene **335**, which can react with styrenes to form cyclo-

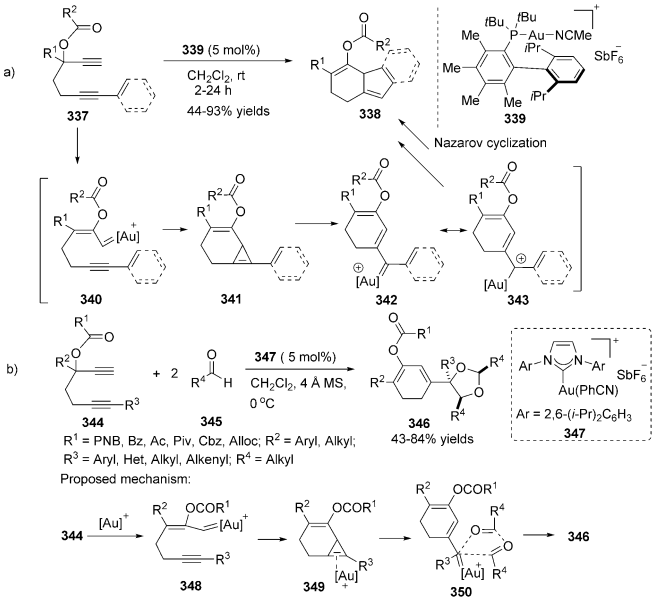
propanation product **336**. Further metal-mediated *endo* cyclization produced the final tricyclic products **334** efficiently (Scheme 63).[146]




***Scheme 63.*** Au-catalyzed cyclopropanation from diynyl esters.

### *8.1.3.* ***Cyclopropenation and Related Reactions***

The cyclopropenation reaction of 1,6-diyn-3-yl carbonates or esters **337** catalyzed by $Au^{I}$ complex **339** was initiated by 1,2-acyloxy migration to deliver Au carbene **340**. A subsequent cyclopropenation provided cyclopropenes **341** and ring opening generated the second Au carbene **342**, which was in resonance with gold-stabilized carbocation **343**. A Nazarov cyclization of **343** provided the final product **338** (Scheme 64 a).[147] Gold carbene **350** could also react with two molecules of aldehydes **345** to generate the [2+2+1] products **346** (Scheme 64 b).[148]



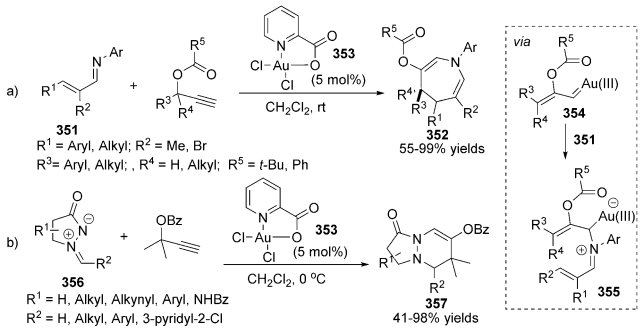

***Scheme 64.*** Au-catalyzed cyclopropenation and cycloisomerization reactions.

In accordance with such a process, a 1-naphthylmethylene gold intermediate generated from *o*-acetylenylphenyl terminal propargylic acetate may also undergo intermolecular cyclopropantion with different substituted alkenes to provide 1-naphthylcyclopropanes.[149]

### *8.1.4.* ***Formal Cycloaddition Reactions***

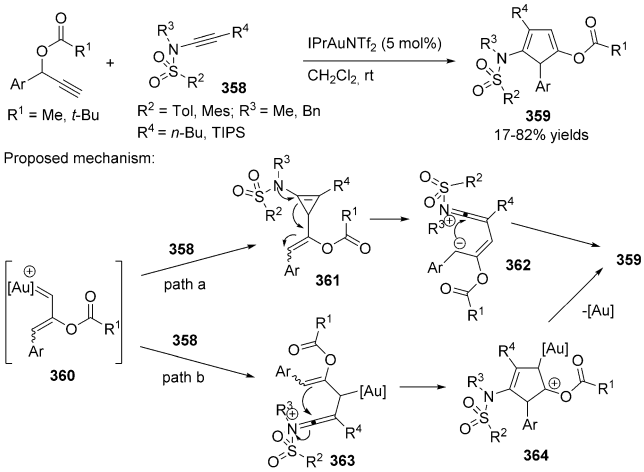
#### *8.1.4.1.* ***Au-Catalyzed Reactions***

Azepines **352** were synthesized from the intermolecular [4+3] cycloaddition of propargylic esters with 2-alkenyl imines **351** catalyzed by $Au^{III}$ complex **353**. The nucleophilic attack of the iminyl nitrogen atom on gold carbene intermediate **354** resulted in formation of the key α-iminiumyl allylic gold intermediate **355** in this reaction (Scheme 65 a).[150] A similar reaction with azomethine imines **356** would afford tetrahydropyridazine derivatives **357** (Scheme 65 b).[151]




***Scheme 65.*** Au-catalyzed [4+3] and [3+3] cycloadditions.

Ynamides **358** was also found by Hashmi and co-workers to be suitable substrates for $Au^{I}$-catalyzed formal [3+2] cycloaddition reactions with propargylic esters to generate cyclopentadienes **359** (Scheme 66). Cyclopropenation of ynamide **358** with gold carbene **360** generates the cyclopropenation product **361**. Ring opening then delivers the zwitterionic intermediate **362**. Subsequent anionic ring closure would then form cyclopentadienes **359** (path a). As an alternative, the carbene carbon atom of **360** may be attacked by the nucleophilic carbon atom of the ynamide to generate keteniminum intermediate **363**. Subsequent ring closure and



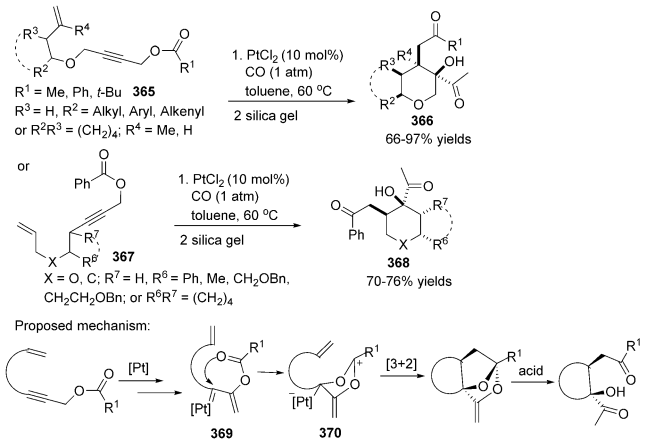

***Scheme 66.*** Au-catalyzed [3+2] cycloadditions with ynamides **358**.

elimination of the $[Au]^+$ species provides the final product **359** (path b).[152]

#### 8.1.4.2. *Pt-Catalyzed Reactions*

The propargylic ester unit in enynyl esters **365** and **367** firstly formed the platinum carbene intermediate **369** by 1,2-acyloxy migration, which was followed by the nucleophilic addition of an intramolecular carbonyl compound to deliver the 1,3-dipolar intermediate **370**. A subsequent [3+2] cycloaddition with the intramolecular alkene and hydrolysis affords pyran derivatives **366** and **368** (Scheme 67).[153]

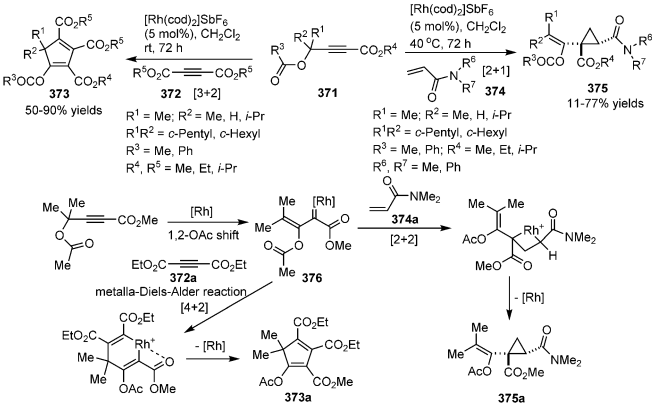



***Scheme 67.*** Pt-catalyzed [3+2] cycloadditions of enynyl esters.

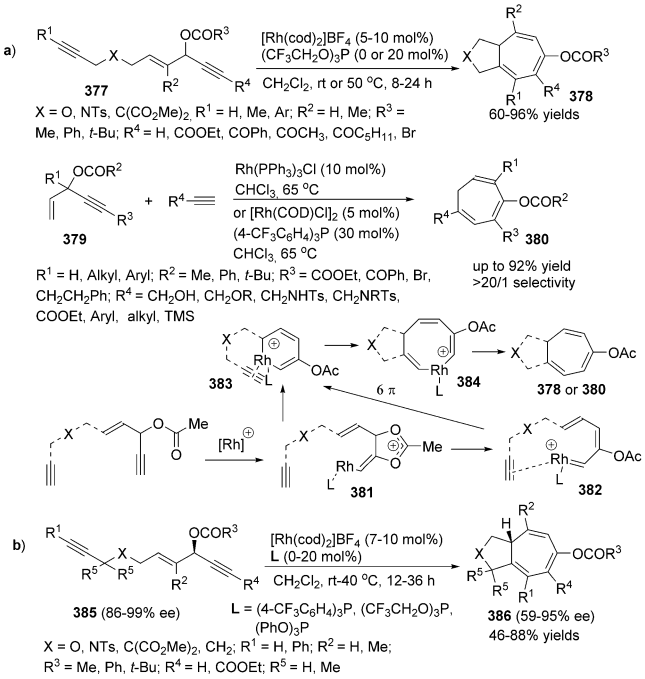
#### 8.1.4.3. *Rh-Catalyzed Reactions*

The Rh carbene intermediate **376** may undergo a [4+2] metalla-Diels–Alder reaction with **372** or a [2+2] cycloaddition with **374** followed by reductive elimination to form the final products **373** or **375** (Scheme 68).[154]

The rhodium carbene **382** generated from 3-acyloxy-4-en-1,9-diyne **377** or **379** underwent a 6π-cyclization to afford the six-membered key intermediate **383**. Insertion and reductive elimination provided trienes **378** or **380** (Scheme 69a).[155] Fair



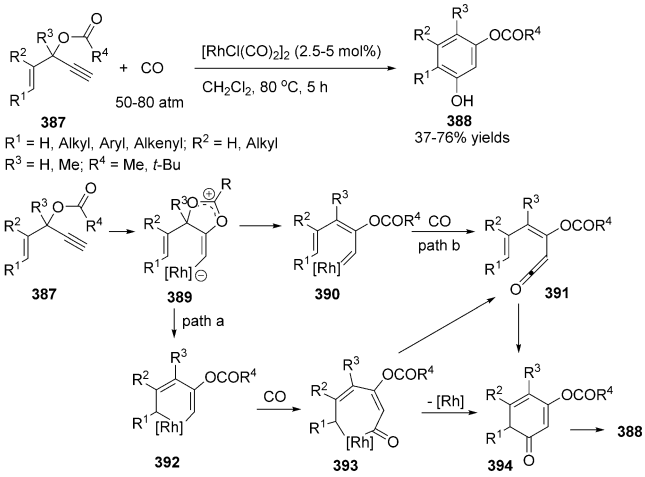

***Scheme 68.*** Rh-catalyzed [3+2] and [2+1] cycloaddition reactions.




***Scheme 69.*** Rh-catalyzed [5+2] cycloaddition reactions.

to good chirality transfer was observed in this reaction (Scheme 69b).[156]

The rhodium carbene intermediate **390** genertated from 3-acyloxy-1,4-enynes **387** can react with CO to form ketene **391**. A subsequent 6π electrocyclization would finally afford phenols **388**, although another mechanism involving compounds **392** to **394** is also possible (Scheme 70).[157]




***Scheme 70.*** Rh-catalyzed [5+1] cycloadditions with 3-acyloxy-1,4-enynes.

#### 8.1.5. *1,2-Migration Reactions*

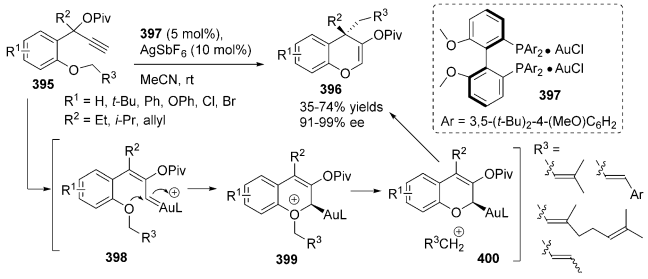
A stereoselective synthesis of (1*Z*,3*E*)-2-pivaloxy-1,3-dienes from propargylic pivalates by an irreversible 1,2-

hydride migration of such formed gold carbene has also been reported.[158]

### 8.1.6. Reactions with Nucleophilic Species

Oxonium intermediate **399** could be formed from propargylic esters **395**, which contains an aryl ether unit, by the intramolecular nucleophilic attack of an ether oxygen atom at the gold carbene **398**. Then allylic gold(I) intermediate **400** was generated together with the cationic $R^3CH_2$ species, which would be retrapped by the chiral allylgold(I) unit to provide benzopyrans **396** containing a quaternary stereocenter with excellent enantioselectivities (Scheme 71).[159]




*Scheme 71.* Au-catalyzed enantioselective synthesis of benzopyrans.

The oxidation of a metal carbene intermediate derived from terminal 1-phenyl-2-propynyl pivalate with diphenyl sulfoxide to form aldehydes with high *Z* stereoselectivity has also been reported.[160]

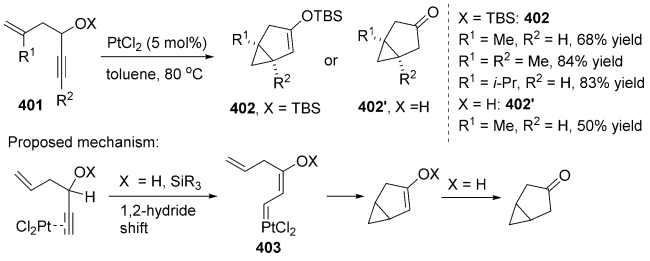
### 8.1.7. Carbene Dimerization

The Ru-catalyzed hetero-dimerization of such metal carbenes with diazo compounds provided the conjugated dienes in good yields on addition of styrene, which may temporarily protect the coordinatively unsaturated ruthenium carbene species. The formation of the TMS-connected *cis*-C=C bond is attractive.[161]

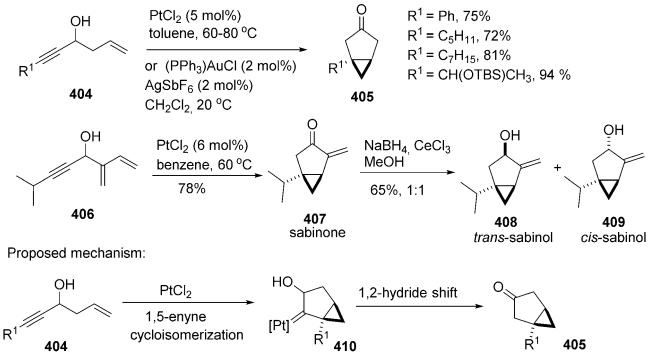
## 8.2. Propargylic Alcohols

1,5-Enynes **401** bearing a free hydroxy or OTBS group were introduced by Fensterbank, Malacria, Marco-Contelles et al. and provided cyclopropanation products **402** or **402′** in good yields in the presence of $PtCl_2$. A 1,2-hydride shift mechanism was proposed for the generation of Pt carbene intermediate **403** (Scheme 72).[140a]

However, Fürstner and co-workers proposed a different mechanism for the $PtCl_2$- or $(PPh_3)AuCl/AgSbF_6$-catalyzed intramolecular cyclopropanation reaction of propargylic alcohols **404**: the platinum carbene **410** was formed by an enyne cyclization mechanism (see Section 9), followed by a 1,2-hydride shift to provide the final ketone product **405** (Scheme 73). This procedure was efficiently applied to the concise total synthesis of the terpenes sabinone **407** and sabinol (**408** and **409**).[141a]

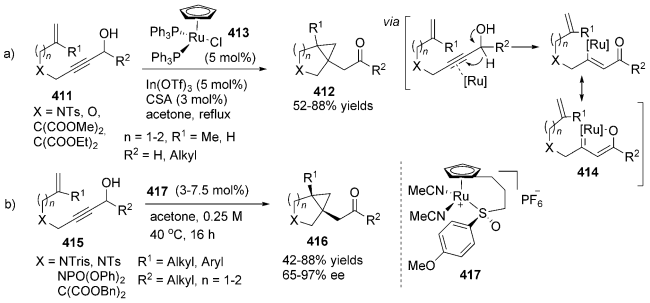



*Scheme 72.* Pt-catalyzed intramolecular cyclopropanations from **401**.




*Scheme 73.* Intramolecular cyclopropanations of alcohols.

The reaction of ω-alken-2-ynols **411** catalyzed by a ruthenium complex **413** was reported by Trost et al. in 2011.[162a,b] Reactive β-oxoruthenium carbene **414** was proposed to be generated through a 1,2-hydride shift, and this intermediate could be trapped efficiently by an intramolecular alkene (Scheme 74a).[162c,d] An asymmetric intramolecular cyclopropanation reaction was also realized using the chiral ruthenium complex **417** (Scheme 74b).[163]

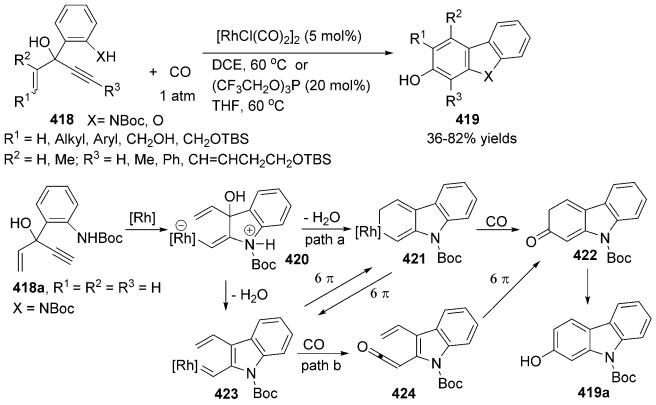



*Scheme 74.* Ru-catalyzed intramolecular cyclopropanation with propargylic alcohols.

The Rh-catalyzed tandem cyclization and [5+1] cycloaddition of 3-aryl-3-hydroxy-1,4-enyne **418** in the presence of CO provided differently substituted carbazoles, dibenzofurans, and tricyclic compounds containing a cyclohexadienone moiety. The amide group could imitate well the acetoxy group: Firstly, intramolecular nucleophilic attack of the nitrogen atom on the propargylic alcohol generated the vinylrhodium species **420**, which was followed by elimination

of water to generate rhodium carbene intermediate **423**. Similar to a 1,2-acetoxy migration process,[157a] two possible pathways via intermediates **421** and **423** were proposed (paths a and b, Scheme 75).[164]

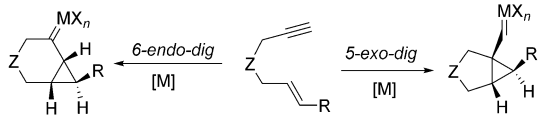



***Scheme 75.*** Rh-catalyzed [5+1] cycloadditions of 3-hydroxy-1,4-enyne **418**.

## 9. Enynes

### 9.1. 1,*n*-Enyne Cyclizations

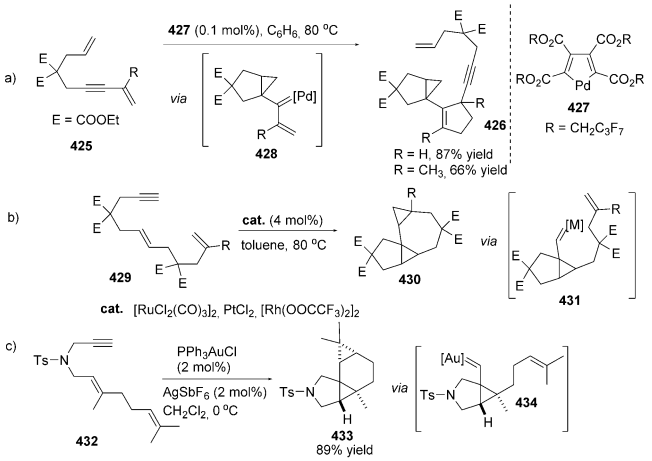
1,*n*-Enynes ($n = 5$, 6, 7, etc.) are another type of readily available precursors for the generation of metal carbenes whereby the C=C bond acts as the nucleophile (Scheme 76).[165] Products not easily available from diazo compounds can be obtained by careful design of the stable and readily available substrates.




***Scheme 76.*** Generation of different metal carbenes from 1,6-enynes.

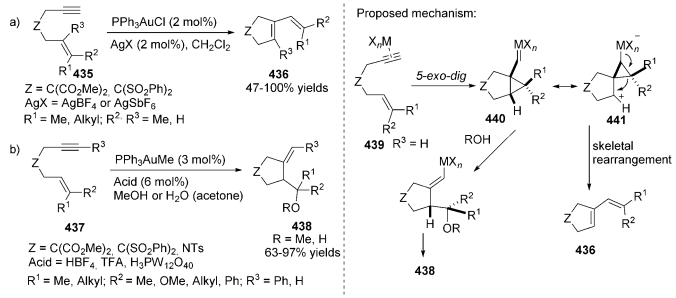
#### 9.1.1. *5-exo-dig Cyclization*

An early study by Trost et al. on the rearrangement of the skeleton of 1,6-enynes with palladium catalysts that provided dimeric product **426** in good yields disclosed that the reaction may proceed through a palladium carbene intermediate **428** (Scheme 77 a).[166] In 1994, Murai and co-workers reported the efficient cycloisomerization of 1,6- and 1,7-enynes catalyzed by $[RuCl_2(CO_3)]_2$.[167] They also noticed that Ru, Rh, and Pt complexes could catalyze the intramolecular cycloisomerization of **429**. The proposed metal carbene intermediate **431** could be trapped by an intramolecular alkene to produce **430** (Scheme 77 b).[168] Detailed research later revealed that $PtCl_2$ was a quite efficient catalyst for the cycloisomerization reactions of enynes.[169] Echavarren (Scheme 77 c), Genêt, and co-workers also proposed Pd, Pt, and Au carbene intermediates during the cyclization of enynes.[170–172]




***Scheme 77.*** Cyclopropanation based on dienynes.

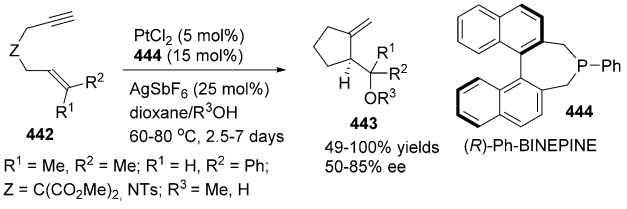
Cationic $Au^I$ complexes are efficient and selective catalysts for the cycloisomerization of simple 1,6-enynes to afford vinylcyclopentenes **436** or the alkoxycyclization products **438** via the intermediacy of **441** and **440**, respectively (Scheme 78).[171]




***Scheme 78.*** $Au^I$-catalyzed cycloisomerization of 1,6-enynes.

An enantioselective alkoxycyclization of 1,6-enynes was developed by Michelet, Gladiali, Genêt, and co-workers, with $PtCl_2$ and (*R*)-Ph-BINEPINE **444** found to be the optimal catalyst system (Scheme 79).[173]

A mechanism corresponding to the $Au^I$-catalyzed reactions of 1,6-enynes was also observed in the 1,5-,[174] 1,7-,[167,175] and higher analogues with a longer tether.[176] Furthermore,



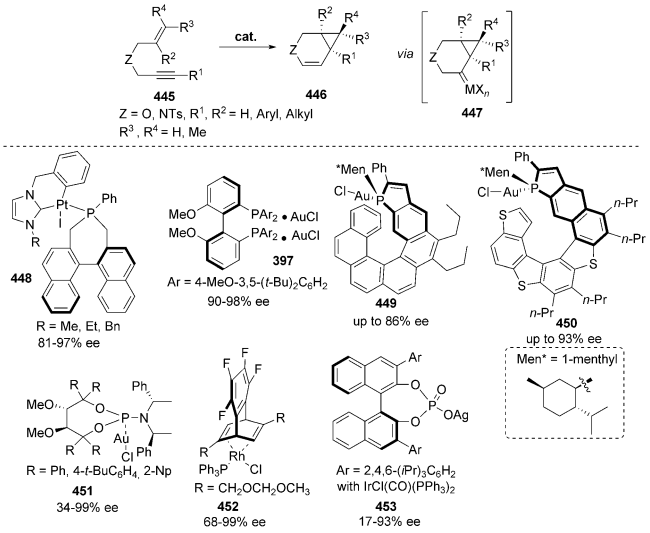

***Scheme 79.*** Pt-catalyzed enantioselective alkoxycyclization of 1,6-enynes.

intermolecular reactions between alkyne and alkene substrates to generate the cyclobutene products were also realized by López-Carillo and Echavarren.[177] Two reviews have since then appeared on $Au^I$-catalyzed cycloisomerization reactions and cyclopropyl gold carbene intermediates. We will not discuss this topic here in detail.[133e,165d,178]

#### 9.1.2. 6-endo-dig Cyclization

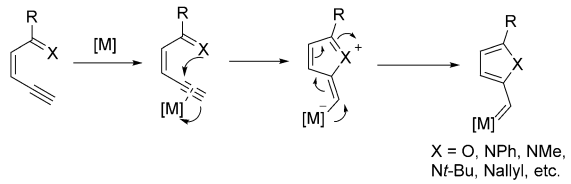
The products generated from metal carbene intermediate **447** were first discovered by Blum et al. in 1995 by using $PtCl_4$.[179] Since then, many other π-acidic transition-metal catalysts such as Pt, Au, Rh, and Ir have been reported for this reaction.[180] The first enantioselective version was developed in 2009 almost at the same time and independently by the Marinetti and Michelet groups.[181,182] This was followed by contributions by the groups of Fürstner,[183] Voituriez and Marinetti,[184] Hayashi,[185] as well as Fensterbank and Gandon[186] (Scheme 80).




***Scheme 80.*** Enantioselective 6-*endo* cycloisomerizations of 1,6-enynes.

### 9.2. Enynyl Ketones or Imines

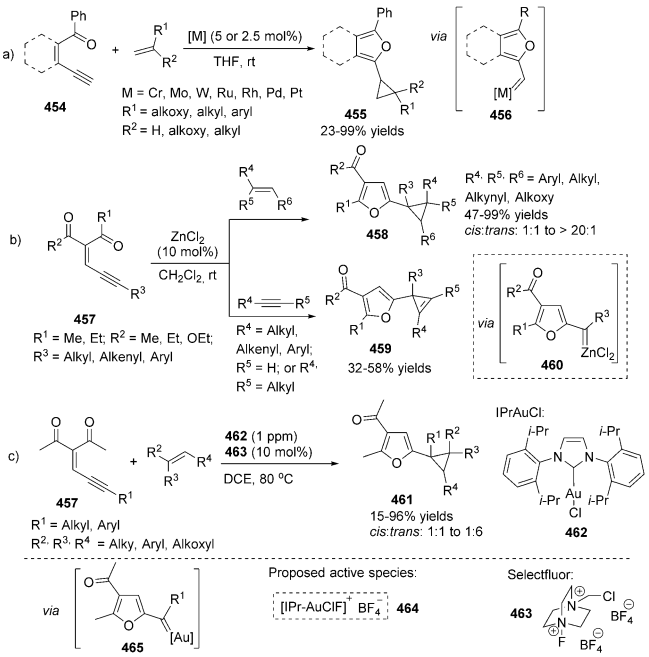
Enynyl-substituted ketones or imines can also generate 2-furyl or 2-pyrrolyl metal carbenes under metal catalysis through 5-*exo* cyclization (Scheme 81).[187]




***Scheme 81.*** Generation of metal carbenes from ene-yne ketones or imines.

#### 9.2.1. Cyclopropanations and Related Reactions

Ohe, Uemura, and co-workers reported that chromium carbene intermediate **456** could be trapped efficiently by electron-rich alkenes to afford the cyclopropanation products **455**. Other transition-metal complexes, such as $Mo(CO)_5$-(THF), $W(CO)_5$(THF), $[RuCl_2(CO)_3]_2$, $[RhCl(cod)]_2$, $PdCl_2$, and $PtCl_2$ were also found to be effective (Scheme 82 a).[188]



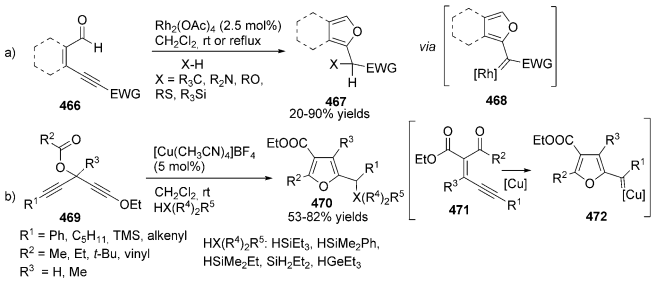

***Scheme 82.*** Catalyzed cyclopropanations/cyclopropenations based on ene-yne ketones.

Gold-catalyzed intramolecular cyclopropanations[189] and their application to the synthesis of furylcyclopropane and furfurylidene-containing polymers was also reported.[190] Interestingly, in 2012, González, López, and Vicente even observed an efficient generation of 2-furyl-substituted zinc carbene **460** from ene-yne-ketone **457** with 10 mol% $ZnCl_2$. Subsequent cyclopropanations/cyclopropenations with alkenes[191] as well as terminal and internal alkynes[192] worked efficiently at room temperature to afford **458** and **459**. Excellent diastereoselectivities can be obtained for **458** only when $R^3$ was an alkyl group (Scheme 82 b). A highly efficient IPrAuCl/Selectfluor system was also reported for such cyclopropanation via Au carbene **465**, although with poor diastereoselectivity (Scheme 82 c).[193] Likewise, 2-pyrrolyl-substituted metal carbenes can be generated from conjugated 3-alkyn-2-enyl imines with $[Rh(OAc)_2]_2$ to afford bicyclic or tricyclic cyclopropanation products in moderate to good yields.[194]

#### 9.2.2. X–H Insertion Reactions

Rhodium carbene **468** can undergo insertions into C–H, N–H, O–H, Si–H, and S–H bonds to provide **467** (Scheme




***Scheme 83.*** X–H insertion reactions with 2-furyl-substituted metal carbenes.

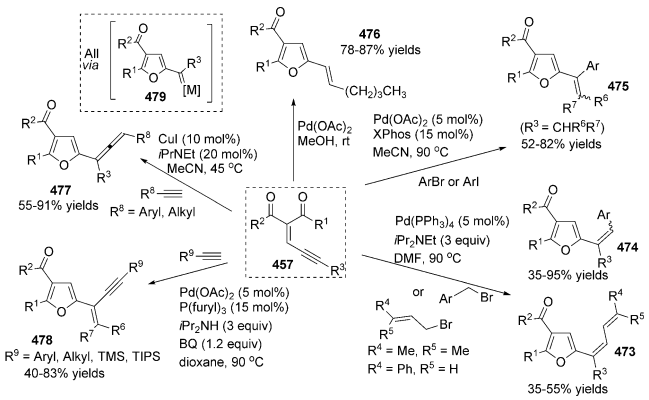
83 a).[195] Barluenga et al. also reported the insertion of in situ generated 2-furyl-substituted copper carbene **472** into Si–H and Ge–H bonds to efficiently deliver **470** (Scheme 83 b).[196] $ZnCl_2$-catalyzed insertion of the generated 2-furyl-substituted zinc carbene into Si–H bonds was also realized.[191,197] IPrAuCl/Selectfluor can catalyze efficient insertion into O–H, N–H, and Si–H bonds via Au carbene **465**.[193]

#### 9.2.3. Reactions with Nucleophiles

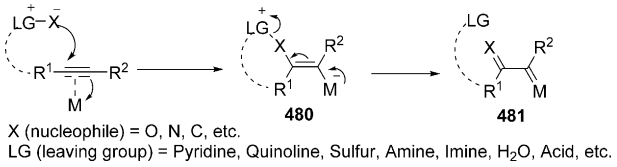
Similar reactions with allylic sulfides to afford furan-containing homosulfides have also been demonstrated. In the case of diallyl sulfides, a further Diels–Alder reaction would provide the polycyclic products.[198] Au- or Cu-catalyzed oxidatons to form 2-acylfurans have also been observed.[199] The furanyl-substituted zinc carbene can react with diazo compounds to provide alkenes with a very attractive C=C bond stereoselectivity.[200]

#### 9.2.4. Migratory Insertions

Palladium-catalyzed carbene migratory insertions with benzyl, aryl, or allyl bromides also provided various 2-alkenyl-substituted furans **473**–**475**.[201] At the same time, Cao and co-workers also reported the palladium-catalyzed synthesis of 2-vinylfurans **476** through a final 1,2-H shift process of the palladium carbene intermediate **479**.[202] Wang and co-workers reported the CuI-catalyzed coupling of conjugated yne-ne ketones **457** and terminal alkynes to form furan-substituted allenes **477**.[203] The palladium-catalyzed oxidative coupling of conjugated ene-yne ketones **457** and terminal alkynes was also reported recently to provide the *trans* conjugated enynes **478** highly selectively (>20:1, Scheme 84).[204]




***Scheme 84.*** Metal-catalyzed migratory insertions of metal carbene **479**.




***Scheme 85.*** Generation of metal carbenes from alkynes.

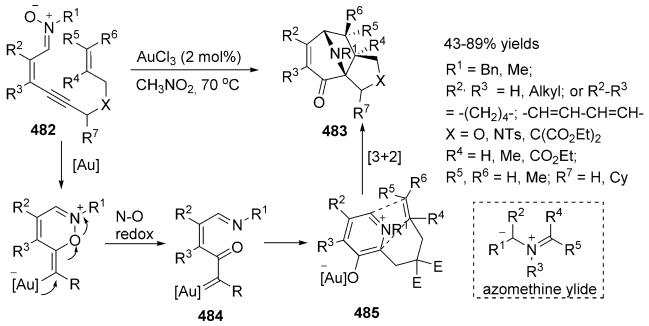
### 10. Alkynes

The attack of alkynes by a nucleophilic entity containing a leaving group is another reliable approach for the generation of metal carbenes via the intermediacy of vinyl metal species **480**, which bears a negative charge at the metal center, triggering the elimination of leaving group to form the metal carbene **481** bearing an α-C=X unit (Scheme 85).[205]

#### 10.1. Intramolecular Reactions with Alkynes

#### 10.1.1. Cycloaddition Reactions

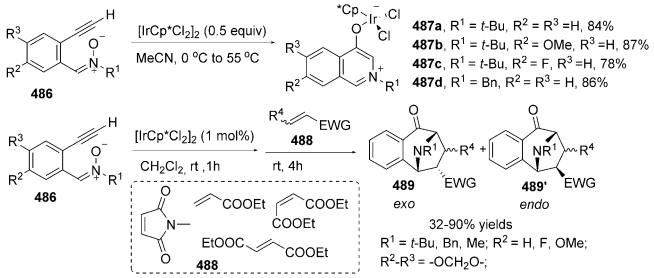
The gold carbene intermediate **484** can be generated from dienyne **482** with a tethered nitrone. This intermediate could be attacked by the in situ generated imine to afford the azomethine ylide equivalent **485**, which could undergo an intramolecular [3+2] cycloaddition reaction with an alkene to provide the final product **483** (Scheme 86).[206]



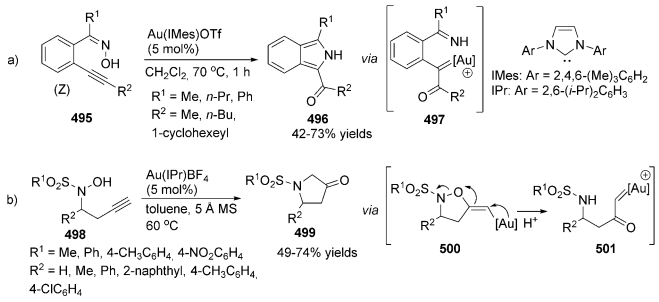

***Scheme 86.*** Intramolecular redox reaction with nitrone **482**.

The iridium azomethine ylide equivalent **487 a** generated from the redox cyclization of alkynyl nitrone **486** with $[Cp^*IrCl_2]_2$ has been confirmed by X-ray single-crystal analysis. $[\{Ru(p\text{-cymene})Cl_2\}_2]$ may also catalyze such an intermolecular [3+2] cycloaddition efficiently with 1–2 mol% catalyst loading. The in situ generated azomethines **487** reacted smoothly with activated alkenes **488** to provide the diastereomers **489** and **489'** (Scheme 87).[207] An auxiliary-




***Scheme 87.*** Isolation and reactions of iridium azomethine ylide.

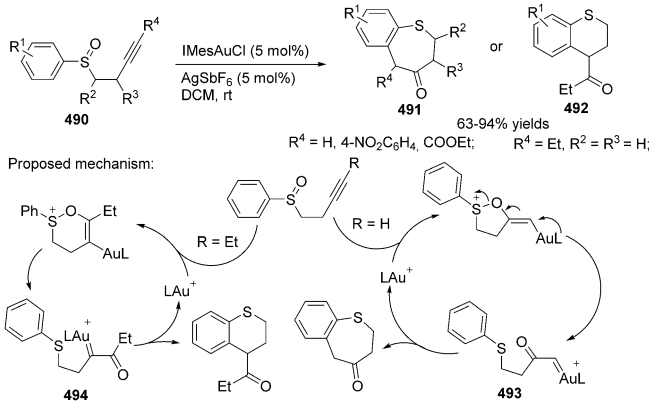



***Scheme 89.*** N–H insertions of gold carbenes.

controlled asymmetric intramolecular [3+2] dipolar cycloaddition was also realized by introducing the chiral *N*-(1-(4-nitrophenyl)ethyl)hydroxyamine as a chiral auxiliary, thereby providing the final products in excellent diastereoselectivities and enantioselectivities.[208]

### 10.1.2. *X–H Insertion Reactions*

In $Au^I$-catalyzed rearrangements of alkynyl sulfoxides **490**, the sulfoxide unit functioned as the oxidant to generate gold carbene intermediates **493** and **494**, thereby providing benzothiepinones **491** or benzothiopines **492** (Scheme 88).



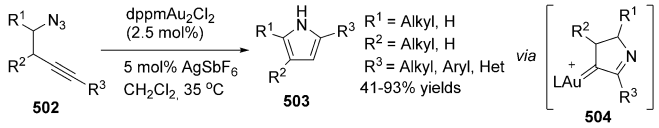

***Scheme 88.*** $Au^I$-catalyzed rearrangement of alkynyl sulfoxides.

Alternatively, a mechanism involving a [3,3] sigmatropic rearrangement was also possible for this reaction.[209]

Ketoximes may also be used for the synthesis of isoindole **496** via α-oxo-gold carbene intermediate **497**, which then undergoes N–H insertion and elimination of gold (Scheme 89a).[210] Shin and co-workers also observed the gold-catalyzed NH insertion reaction from *N*-sulfonylhydroxylamines **498** via carbene intermediate **501**, with formation of 3-pyrrolidinones **499** (Scheme 89b).[211]

### 10.1.3. *1,2-Migration*

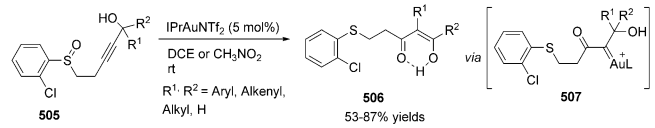
Homopropargyl azides **502** were treated with $Au^I$ catalysts by Toste and co-workers to synthesize multisubstituted




***Scheme 90.*** Generation of Au carbenes from homopropargyl azides.

pyrroles **503** through a 1,2-H shift of Au carbene **504** (Scheme 90).[212]

The $Au^I$-catalyzed synthesis of 1,3-diketones **506** from the intramolecular reaction of sulfinyl alkynes **505** with an extra hydroxy group, via an α-oxo gold carbene intermediate **507**, was realized by Li and Zhang in 2007 (Scheme 91). The 1,2-migration of carbene intermediate **507** was highly selective: the aryl group migrated preferably over alkyl and H; an alkenyl group migrated preferably over H.[213]



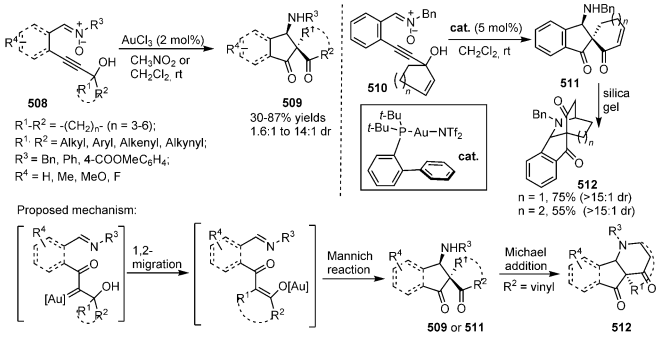

***Scheme 91.*** Generation of Au carbenes and their 1,2-migration.

A cascade reaction of 1,2-migration followed by a Mannich (Michael) reaction from nitrone substrates **508** and **510** was developed by Shin and co-workers, and provided various synthetically important skeletons, such as spirocycles, 1-aminoindanes, and 5,6-fused azacycles. The reaction was initiated by an intramolecular oxidation of an alkyne with a nitrone to afford a gold carbene, which underwent a 1,2-migration to provide the metal enolate. The Mannich (Michael) reaction then gave the final products **509**, **511**, and **512** (Scheme 92).[214]

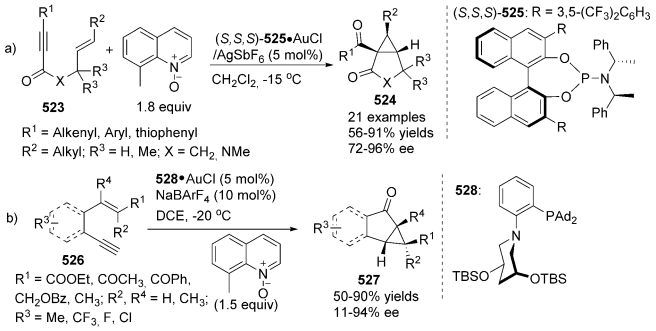
### 10.2. *Intermolecular Reactions with Alkynes*

The scope of such intramolecular oxidations is relatively narrow and, thus, reactions with an external oxidant have been developed.



***Scheme 92.*** Au-catalyzed intramolecular cascade reactions.

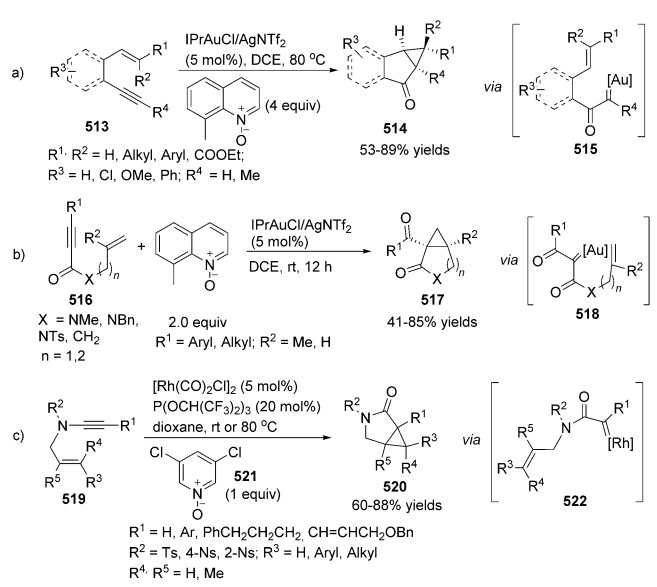


***Scheme 94.*** Enantioselective cyclopropanation with α-oxo gold carbenes.

#### 10.2.1. *Cyclopropanation Reactions*

The $Au^I$-catalyzed intramolecular cyclopropanation of 1,5-enynes **513** with quinoline *N*-oxide as the oxidant was reported by Liu and co-workers in 2011 via α-oxo gold carbene intermediate **515**, which provided the cyclopropylindanone products **514** (Scheme 93 a).[215] Zhang and co-workers realized the cyclopropanation reaction with 1,6-enynes and 1,7-enynes **516** via α-oxo gold carbene intermediate **518** to provide various carbo- and hetero[*n*.1.0] bicyclic products **517** (Scheme 93 b).[216] The efficient generation of α-oxo Rh carbene **522** from ynamides **519** and pyridine *N*-oxide **521** with $[Rh(CO)_2Cl]_2$/$P[OCH(CF_3)_2]_3$ as catalyst afforded the cyclopropanation product **520** (Scheme 93 c).[217]

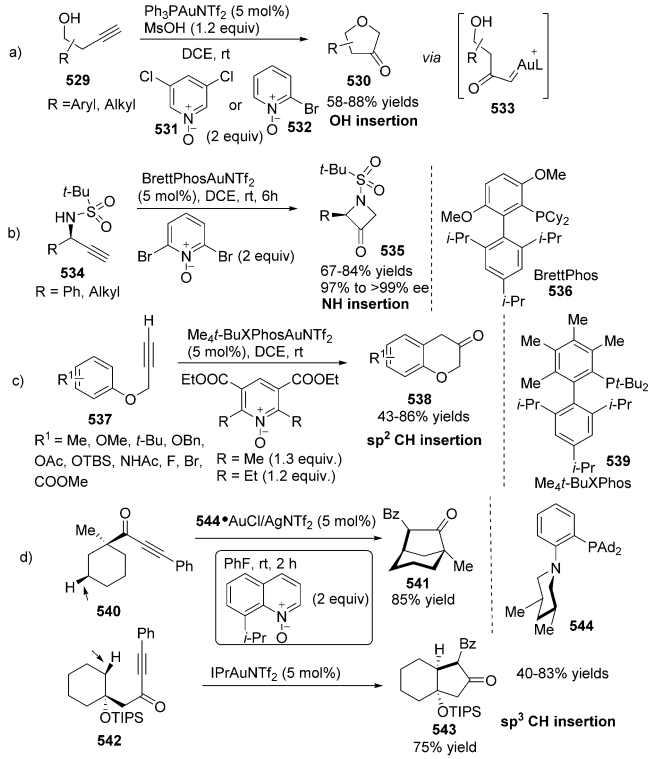
Similar $Au^I$-catalyzed enantioselective cyclopropanations have been developed by using chiral phosphoramidite ligand **525** and *P*,*N*-bidentate ligand **528** (Scheme 94).[218,219]



***Scheme 93.*** Intramolecular cyclopropanations of α-oxo gold carbenes.

#### 10.2.2. *X–H Insertion Reactions*

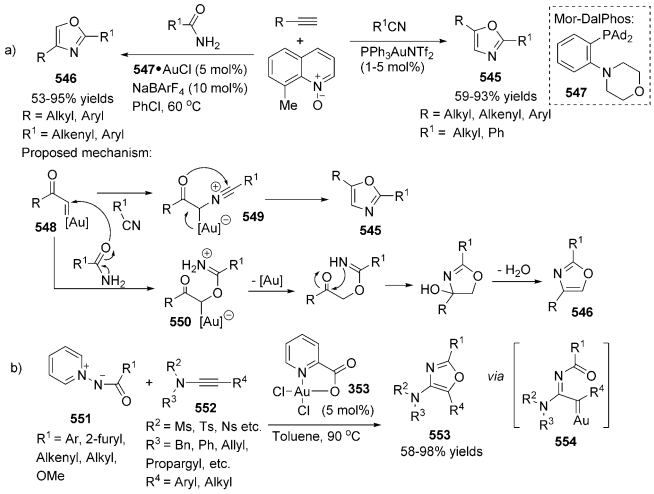
α-Oxo gold carbene intermediate **533** generated with pyridine *N*-oxide **531** or **532** could be trapped intramolecularly by a hydroxy group to generate substituted dihydrofuranones **530** (Scheme 95 a).[220] Similarly, pyridine *N*-oxide was found to be the most efficient oxidant for the generation of metal carbenes with a terminal alkyne in different intramolecular X–H insertion reactions, including N–H insertion (Scheme 95 b),[221] $C(sp^2)$–H insertion (Scheme 95 c),[222] and $C(sp^3)$–H insertion (Scheme 95 d),[223] with optimized ligands and oxidants. The generated α-oxo gold carbenes could also be trapped intermolecularly with carboxylic acids[224] or MsOH.[225]



***Scheme 95.*** X–H insertions of α-oxo gold carbenes.

#### 10.2.3. Reactions with Nucleophiles

Allylic sulfides can also trap carbene intermediates to provide homoallylic sulfides with an acyl unit.[226] The α-oxo gold carbene intermediate **548** formed from the oxidation of terminal alkynes can be trapped intermolecularly with excess nitrile, which serves as the solvent, to provide 2,5-disubstituted oxazoles **545**,[227] or amides to generate 2,4-disubstituted oxazoles **546** (Scheme 96a).[228] Highly selective intermolecular [3+2] cycloaddition reactions of pyridine-derived *N*-ylides **551** and ynamides **552** catalyzed by $Au^{III}$ compound **353** were realized that provided substituted 1,3-oxazoles **553** in good to excellent yields (Scheme 96b).[229]

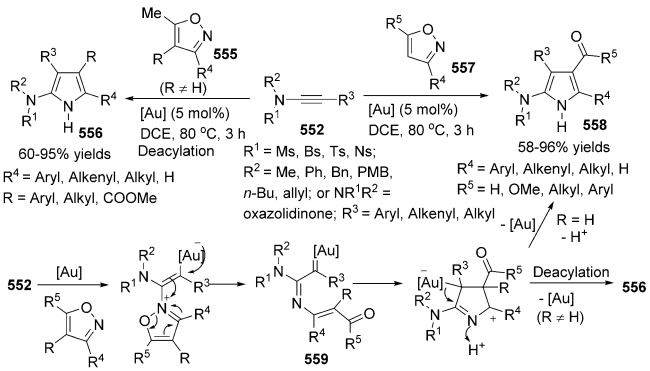



***Scheme 96.*** Reaction of Au carbenes with different nuleophiles.

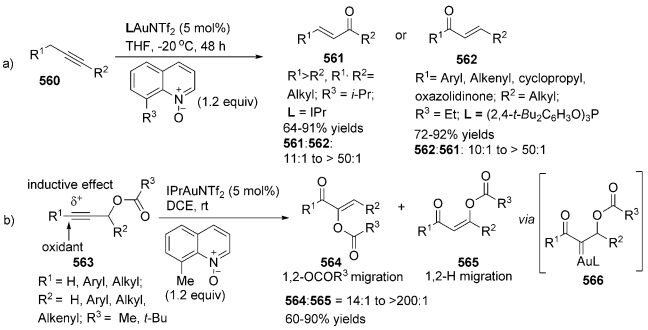
Electron-rich alkynamides can also react intermolecularly with nitrones or nitrosobenzenes to provide oxoamination products or various 2-oxoiminylamides, respectively, via gold carbene intermediates.[230] Furthermore, isoxazoles **555** and **557** were also identified as optimal oxidants by Ye and coworkers for the oxidative generation of α-imino gold carbene **559** from ynamides **552**. Their formal [3+2] cycloaddition reaction was also realized and provided polysubstituted 2-aminopyrroles **556** and **558** in moderate to excellent yields (Scheme 97).[231]

#### 10.2.4. 1,2-Migrations

Regioselectivity is an issue in reactions of internal alkynes: When one end of the C–C triple bond is sterically biased, steric control by using a bulkier oxidant, such as 8-isopropylquinoline *N*-oxide, provided **561** or **562** with good selectivity (Scheme 98a).[232] Inductive polarization of the C–C triple bond also provided good regioselectivity. Propargylic carboxylates, which have an electron-withdrawing carboxy group providing the electrically biased triple bond, generated gold carbene **566** regioselectively. A subsequent highly selective 1,2-OAc migration provided **564** as the major product (Scheme 98b).[233,234]




***Scheme 97.*** Intermolecular reactions of isoxazoles with ynamides.

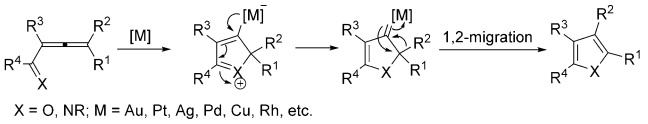



***Scheme 98.*** 1,2-Migration of α-oxo gold carbenes.

## 11. Allenes

#### 11.1. Allenyl Ketones and Imines

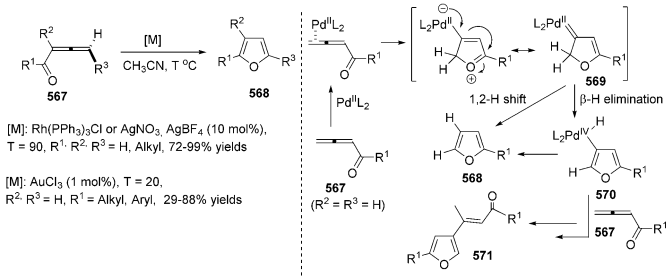
Allenyl ketones and imines may also serve as precursors for the generation of metal carbenes to afford furans or pyrroles through 1,2-migration (Scheme 99). Marshall et al. reported the $Rh^{I}$- and $Ag^{I}$-catalyzed efficient synthesis of furan derivatives **568** from allenyl ketones in good to excellent yields.[235] Hashmi et al. also demonstrated that $Pd^{II}$ and $AuCl_3$ served as efficient catalysts for the synthesis of furans, although dimer **571** was the major product under palladium catalysis. A possible mechanism via a palladium carbene intermediate **569** followed by a 1,2-hydride shift was proposed for the generation of furan **568** and dimerization product **571** (Scheme 100).[236]




***Scheme 99.*** Preparation of metal carbenes from allenyl ketones and imines.

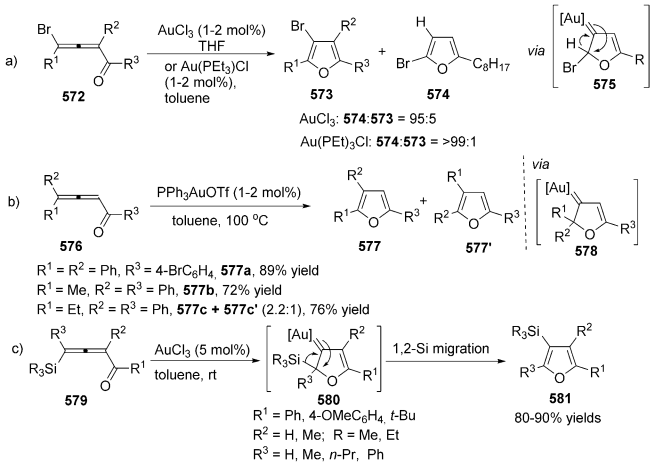
The Gevorgyan group reported that the $AuCl_3$- and $Au(PEt_3)Cl$-catalyzed 1,2-hydride migration reaction of halo-



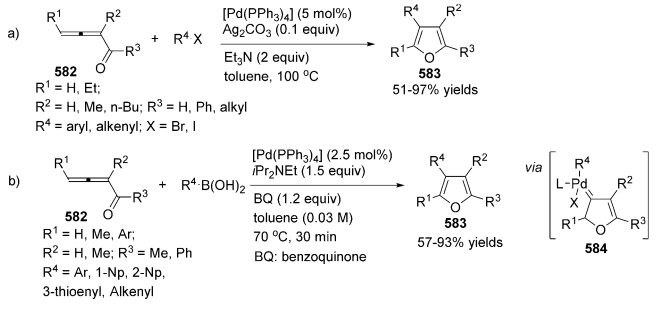

***Scheme 100.*** Synthesis of furans from allenyl ketones.

allenyl ketones produced the 2-halofurans **574** via Au carbene intermediate **575**.[237] A dramatic counterion effect was also observed in this reaction.[238] Such 1,2-alkyl or silyl group migration was also observed in the synthesis of furans **577** (**577′**) and **581** (Scheme 101).[239]




***Scheme 101.*** Au-catalyzed selective 1,2-migrations of H, alkyl, and silyl groups.

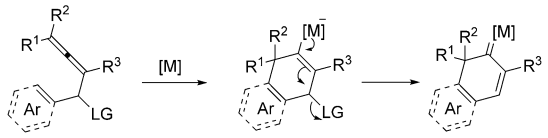
Our group as well as the Wang research group also reported the reaction of aryl or 1-alkenyl halides or boronic acids with 1,2-allenyl ketones **582** to generate the polysubstituted furans **583** via the possible metal carbene **584** (Scheme 102).[240,241]




***Scheme 102.*** Pd-catalyzed migratory insertions based on allenyl ketones.

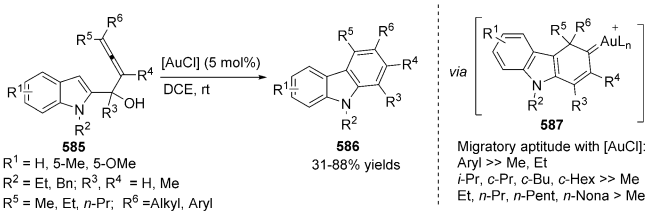
### *11.2. 2,3-Allenols and Their Derivatives*

Carbazole and naphthalene products could be synthesized via a metal carbene intermediate when an electron-rich aromatic ring was introduced into 2,3-allenol substrates as nucleophiles (Scheme 103). In 2009, our group reported a $PtCl_2$-catalyzed reaction of 1-(indol-2-yl)-2,3-




***Scheme 103.*** Generation of metal carbenes from 2,3-allenols and their derivatives.

allenols that provided various substituted carbazoles in good yields via a platinum carbene intermediate.[242,243] When aryl- or methyl-substituted substrates were introduced, the 1,2-aryl migration product could be obtained selectively, thereby disclosing that 1,2-aryl migration was favorable.[244] AuCl had a much broader scope and better selectivity, and was applied to the syntheses of a series of naturally occurring carbazole alkaloids (Scheme 104).[245,246] The indole unit can also be




***Scheme 104.*** Au/Pt-catalyzed synthesis of carbazoles.

replaced with electron-rich benzenes, thiophenes, furans, and benzofurans to produce polyarenes although through a mixed mechanism of both gold carbene and alkenyl gold intermediate.[247] A combination of the in situ generation of allene substrates from the 1,3-migration of a benzoate group from 4-benzoxyl-1-(indol-2-yl)-2-alkynols with $Au^I$-catalyzed cyclization to produce the carbazoles was also developed, which was applied to the first synthesis of the carbazole alkaloid karapinchamine A.[248]

## *12. Conclusions and Outlook*

It should be mentioned that transmetalation of a preformed metal carbene complex is another pathway for the generation of transition-metal carbene complexes.[249] The first example of transmetalation was reported by Fischer and Beck in 1970. The molybdenum carbene complexes was successfully transformed to iron carbene complexes under UV irradiation.[250] Fañanás-Mastral and Aznar[251] as well as

Fürstner and co-workers[252,253] prepared the cationic alkenyl Fischer-type $Au^I$ complexes by transmetalation of chromium or rhodium carbene complexes with gold compounds. X-ray single-crystal diffraction analysis indicated a typical single C–Au bond and a cyclopropanation reaction revealed the reactivity of the Au carbene species; such carbon species are usually called "carbenoids".[8d,e,122,252,253] Many cycloaddition reactions[249] with alkenes,[254] alkynes,[255] allenes,[256] or alkylidenecyclopropanes[257] involving such transmetalations were also reported.

Identifying new surrogates for diazo compounds is a really dynamic area in organic synthsis because of the rich and useful chemistry of metal carbenes. Hydrazones and amines are used for the in situ generation of diazo compounds. The generation of metal carbenes from hydrazones under basic conditions is well-established and can be combined perfectly with a second reaction partner such as arylboronic acids, alkynes, halides, nucleophiles (ROH, $R_2NH$ etc.) or even a third partner such as CO and allyl halides. Phenyliodonium ylides and sulfonium ylides are other alternatives that are not often used, partly because of stability and purification issues. Triazoles are another recently developed surrogate for cyclopropanation reactions, cycloaddition reactions, X–H insertions, and reactions with different nucleophiles (sulfide, aldehyde etc.), which mainly used a rhodium catalyst. 1,3,5-Cycloheptatrienes and cyclopropenes are also two interesting methods that are waiting more applications. Different alkyne derivatives, such as propargyl esters and alcohols, enynes, and simple alkynes are well-explored surrogates for the efficient construction of complex molecular structures. Allenes are also promising substrates for the generation of metal carbenes, but are much less explored than their alkyne partners. Different transition metals, such as Au, Pt, Rh, Ru, Cu, Ir, Ni, Pd, Fe, and Zn may work for the generation of such metal carbenes. Ligands play an important role in tuning the reactivities and selectivity of the reactions involving metal carbenes.

In the future, 1) cheap metals such as Fe, Ru, Co, Ni, Cu, and Zn rather than Rh, Ir, and Au may be considered as catalysts. 2) By applying different ligands and introducing newly designed ligands, the reactivities may be tuned and excellent enantioselective control may also be further developed. 3) With a deep understanding of the mechanism, the reactivities of different surrogates will be extensively shown. 4) In addition, applications in the efficient and highly stereoselective synthesis of biologically interesting molecules with chiral center(s) will be very promising.

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