

Palladium-Catalyzed Cyclization Reactions of Allenes in the Presence of Unsaturated Carbon–Carbon Bonds

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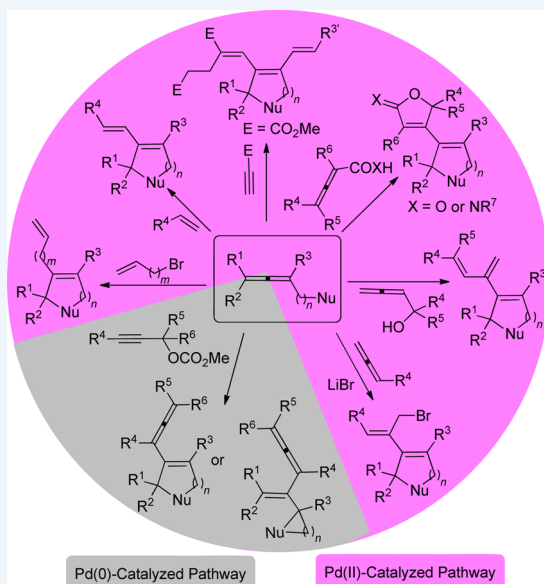
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CONSPECTUS: Modern synthetic chemists have looked for rapid and efficient ways to construct complex molecules while minimizing synthetic manipulation and maximizing atom-economy. Over the last few decades, researchers have made considerable progress toward these goals by taking full advantage of transition metal catalysis and the diverse reactivities of allenes, functional groups which include two cumulative carbon–carbon double bonds.

This Account describes our efforts toward the development of Pd-catalyzed cyclization reactions of allenes in the presence of compounds that contain unsaturated carbon–carbon bonds such as alkenyl halides, simple alkenes, allenes, electron-deficient alkynes, or propargylic carbonates. First, we discuss the coupling-cyclization reactions of allenes bearing a nucleophilic functionality in the presence of alkenyl halides, simple alkenes, functionalized and nonfunctionalized allenes, or electron-deficient alkynes. These processes generally involve a Pd(II)-catalyzed sequence: cyclic nucleopalladation, insertion or nucleopalladation, and β -elimination, reductive elimination, cyclic allylation or protonation. We then focus on Pd(0)-catalyzed cyclization reactions of allenes in the presence of propargylic carbonates. In these transformations, oxidative addition of propargylic carbonates with Pd(0) affords allenylpalladium(II) species, which then react with allenes via insertion or nucleopalladation. These transformations provide easy access to a variety of synthetically versatile monocyclic, dumbbell-type bicyclic, and fused multicyclic compounds. We have also prepared a series of highly enantioenriched products using an axial-to-central chirality transfer strategy.

A range of allenes are now readily available, including optically active ones with central and/or axial chirality. Expansion of these reactions to include other types of functionalized allenes, such as allenyl thiols, allenyl hydroxyl amines, and other structures with differing steric and electronic character, could allow access to cyclic skeletons that previously were difficult to prepare. We anticipate that other studies will continue to explore this promising area of synthetic organic chemistry.



INTRODUCTION

Nowadays allenes have been recognized as reasonably stable organic compounds with two cumulated C=C bonds, of which two π -orbitals are perpendicular to each other. This unique structure together with the substituent-loading capability has endowed them with distinctive reactivity and great potentials in organic synthesis.¹

Palladium is one of the most powerful transition metals in organic synthesis,² with Pd(0) and Pd(II) complexes being the most widely observed ones. It has long been recognized that Pd(0) preferentially undergoes oxidative addition in the presence of organic halides or their equivalents, whereas Pd(II) tends to promote the reaction of coordinated unsaturated carbon–carbon bonds with nucleophiles to promote nucleopalladation or

undergo insertion.² These basic principles constitute the foundation of all the work discussed below.

This Account will demonstrate our recent efforts on the cyclization reactions of allenes in the presence of C=C bonds, C \equiv C bonds, and cumulated C=C bonds under Pd catalysis. Generally speaking, two mechanistically different reaction pathways are involved in these transformations (Scheme 1): (a) a Pd(II) catalyst preferentially coordinates with one of the C=C bonds of allenes **1** to promote cyclic nucleopalladation leading to intermediate **Int1**, which then undergoes insertion with various unsaturated carbon–carbon bonds to give intermediates **Int2–Int4** or an extra cyclic nucleopalladation to

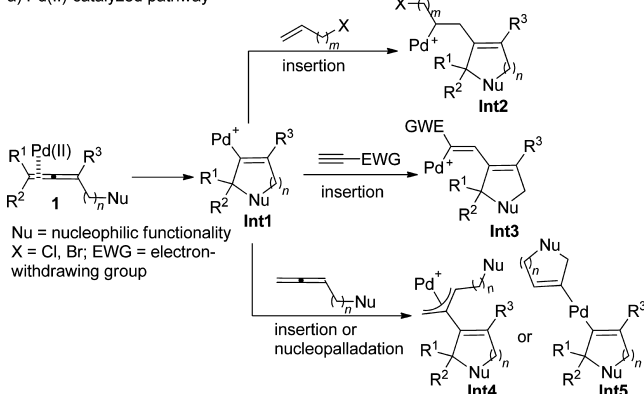
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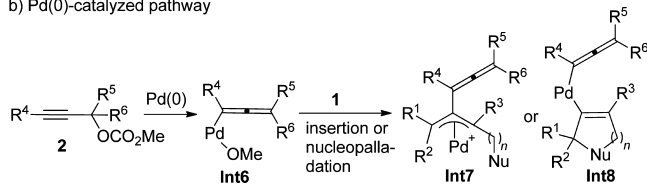
afford **Int5**; (b) Pd(0)-catalyzed oxidative addition of propargylic carbonates **2** affords Pd(II) species **Int6**, which will react with functionalized allenes **1** to generate intermediate **Int7** or **Int8** via insertion or nucleopalladation, respectively.

Scheme 1

a) Pd(II)-catalyzed pathway



b) Pd(0)-catalyzed pathway



1. CYCLIZATION REACTIONS OF ALLENES IN THE PRESENCE OF ALKENYL HALIDES, ALKENES, ALLENES, OR ELECTRON-DEFICIENT ALKYNES

1.1. Cyclization Reactions of Allenes in the Presence of Allylic or Other Terminal-Alkenyl Halides

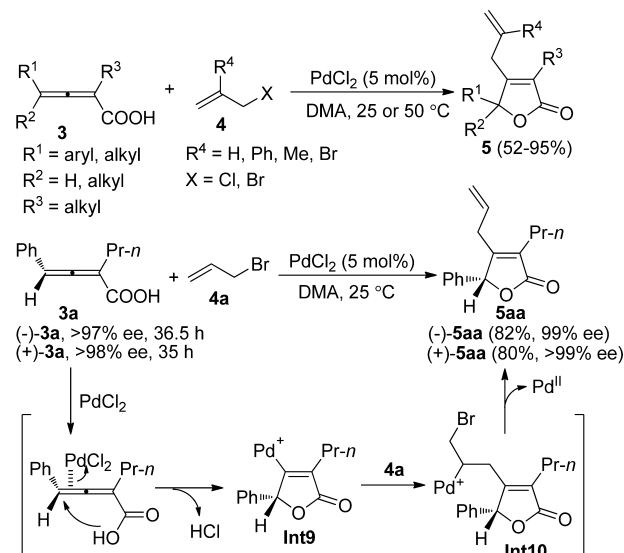
2,3-Allenic Acids. Butenolides are important structural unit widely existed in many natural products and biologically active molecules.³ Thus, a Pd-catalyzed cyclization reaction of 2,3-allenoic acids **3** in the presence of allylic halides was developed, affording β -allyl polysubstituted butenolides **5** in moderate to excellent yields (Scheme 2).⁴ Highly enantio-enriched products (+)- and (-)-**5aa** could be obtained via the efficient axial-to-central chirality transfer.

Furthermore, this coupling-cyclization strategy may be extended to the reactions of 2,3-allenoic acids with terminal alkenyl bromides **6** to afford β -alkyl substituted butenolides **7** in reasonable yields (Scheme 3).⁵

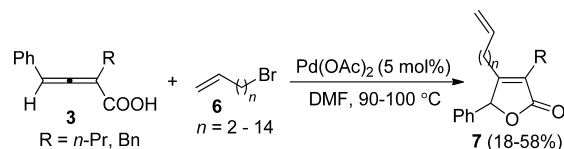
When deuterated homoallyl bromide [D_2]-**6a** was utilized in the presence of 2,3-allenoic acid **3a**, [D_2]-**7aa** was obtained in 52% yield (Scheme 4). Notably, the two deuterium atoms were located at the terminal carbon atom of the noncyclic C=C bond, indicating that the reaction may proceed via cyclic oxypalladation, carbopalladation of the terminal C=C bond, repeated dehydropalladation/hydropalladation, and finally dehalopalladation.

2,3-Allenates. 2,3-Allenic acids are usually prepared from the hydrolysis of 2,3-allenotes. However, in some cases, the hydrolysis affords 2-alkynoic acids instead of 2,3-allenoic acids or a mixture of both. Thus, direct cyclization of 2,3-allenates with allyl bromides is highly desirable. Toward this end, a $FeCl_3$ /PdCl₂-cocatalyzed coupling-cyclization of 2,3-allenates **8** with allylic bromides was developed, furnishing β -allyl polysubstituted

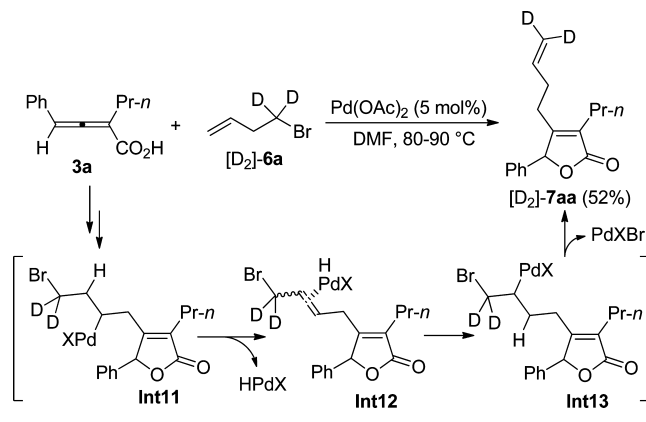
Scheme 2



Scheme 3



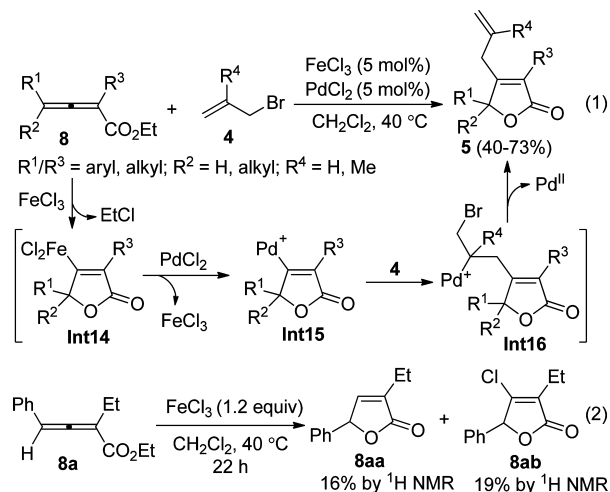
Scheme 4



butenolides **5** in practical yields (eq 1, Scheme 5).⁶ Control experiments revealed that no reaction occurred in the absence of $FeCl_3$. In addition, when 2,3-allenoate **8a** was treated with a stoichiometric amount of $FeCl_3$ in the absence of $PdCl_2$ and allylic bromide, 16% of 2(*SH*)-furanone **8aa** and 19% of 3-chloro-2(*SH*)-furanone **8ab** were formed (eq 2, Scheme 5). Thus, 2(*SH*)-furanonyl iron species **Int14** was proposed for this reaction, which then underwent transmetalation with $PdCl_2$ to form the 2(*SH*)-furanonyl palladium species **Int15** and regenerate $FeCl_3$.

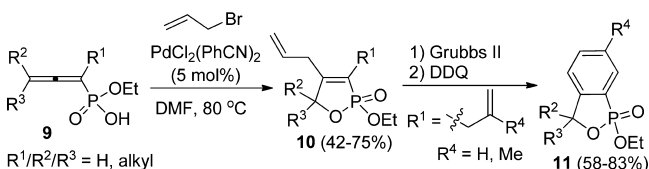
1,2-Allenyl Phosphonic Acids Monoesters. Phosphorus-containing heterocycles, important skeletons widely existing in bioactive molecules, such as 4-allyl-2,5-dihydro[1,2]-oxaphosphole 2-oxides **10**, may also be prepared via the coupling-cyclization of monoesters of 1,2-allenyl phosphonic acids **9** in the presence of allylic bromide in 42–57% yields (Scheme 6).⁷ Further elaboration of the products via RCM

Scheme 5



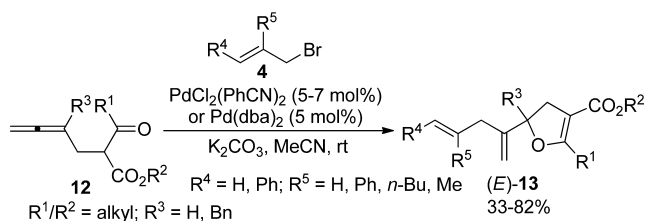
reaction and oxidation afforded biologically active 1,3-dihydro-[2,1]benzoxaphosphole 1-oxide derivatives **11** in moderate to good yields.

Scheme 6



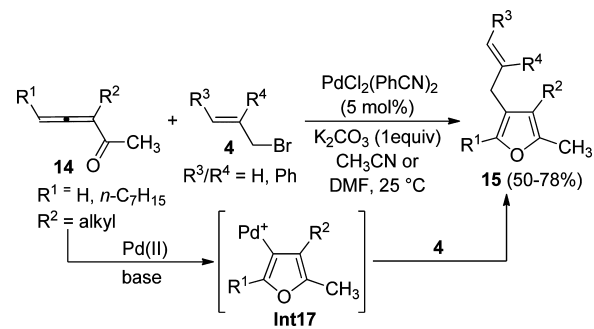
2-(2',3'-Allenyl)acetylacetates. For allenes bearing an acetylacetate functionality, two types of cyclization patterns are possible, that is, C-attack versus O-attack.⁸ Interestingly, in the Pd-catalyzed coupling-cyclization reactions of 2-(2',3'-allenyl)-acetylacetates **12** with allylic halides, only O-attack *exo*-cyclization products 4,5-dihydrofuran derivatives **13** were obtained in 33–82% yields (Scheme 7).⁹ High regioselectivity and *E/Z* stereoselectivity was observed when nonsymmetric allylic halides ($R^4 \neq \text{H}$) were employed.

Scheme 7



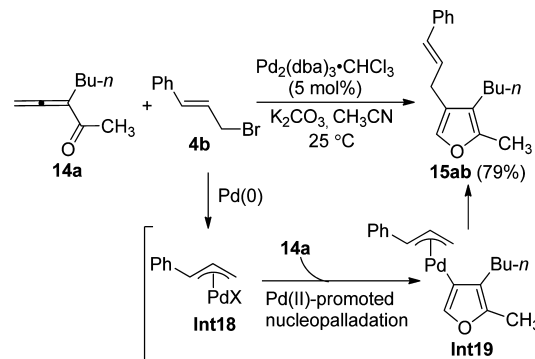
1,2-Allenyl Ketones. Such regio- and stereoselectivity have also been observed with 1,2-allenyl ketones **14**, where addition of 1 equiv of K_2CO_3 as the base has been observed to be critical for the coupling-cyclization reactions with allylic bromide, providing *endo*-cyclization products 3-allyl polysubstituted furans **15** in decent yields (Scheme 8).¹⁰ The furanyl palladium species **Int17**, which was generated similarly via a cyclic oxypalladation of 1,2-allenyl ketone **14**, was proposed to react with allyl bromide to give product **15** and regenerate Pd(II) species possibly via a direct replacement of the bromine atom as indicated by the stereoselectivity of the noncyclic C=C bond.

Scheme 8



Interestingly, however, it was noted that the reaction could also be catalyzed by Pd(0) species (Scheme 9), which may proceed via cyclic oxypalladation of **14a** with Pd(II) species **Int18** followed by regioselective reductive elimination. This may also nicely account for the regioselectivity of the nonsymmetric allylic halides that has been observed in the cases of 2-(2',3'-allenyl)acetylacetates **12**.

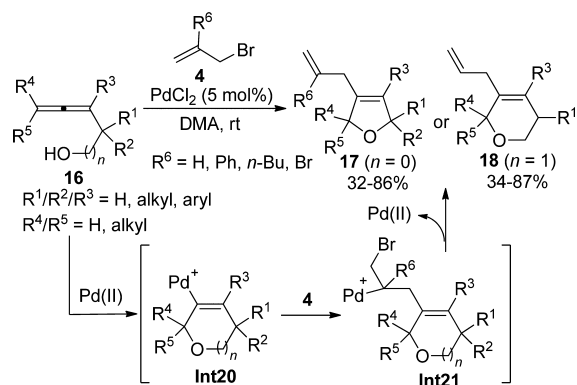
Scheme 9



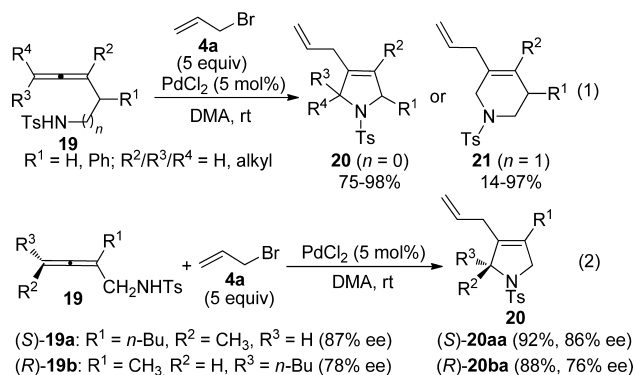
2,3- or 3,4-Allenols. 2,5-Dihydrofurans and 5,6-dihydro-2H-pyran units are commonly observed in natural products.¹¹ Under the catalysis of PdCl_2 , the coupling-cyclization reactions of 2,3- or 3,4-allenols **16** with allylic bromides afforded polysubstituted 2,5-dihydrofurans **17** or 5,6-dihydro-2H-pyrans **18** containing a modifiable allylic group in practical yields (Scheme 10).¹² Primary, secondary, and tertiary alcohols with various substituents on the allene moiety are all compatible. However, nonsubstituted 2,3-allenols furnished the desired products in very low yields probably due to substantial dimerization, which will be discussed in detail in section 1.3. The reactions most likely proceed via Pd(II)-catalyzed cyclic oxypalladation, insertion, and dehalopalladation.

2,3- or 3,4-Allenyl Amines. When the hydroxyl group of 2,3- or 3,4-allenols was replaced by a more nucleophilic amine functionality, the resulting 2,3- or 3,4-allenyl amines **19** may react with allylic bromide in a similar manner to give 2,5-dihydro-1H-pyrroles **20** or 1,2,3,6-tetrahydropyridines **21** (eq 1, Scheme 11).¹³ When an enantioenriched 2,3-allenyl amine (*S*)-**19a** or (*R*)-**19b** was subjected to the standard conditions, optically active 2,5-dihydropyrrole (*S*)-**20aa** or (*R*)-**20ba** was obtained without obvious loss of enantiopurity, respectively (eq 2, Scheme 11), supporting that this reaction may also proceed via a Pd(II)-catalyzed pathway.

Scheme 10



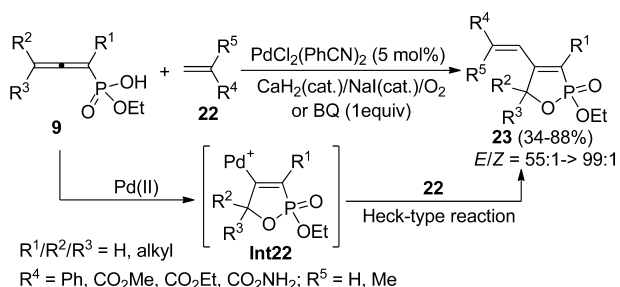
Scheme 11



1.2. Cyclization Reactions of Allenes in the Presence of Simple Alkenes

Although the coupling-cyclization reactions of allenyl halides have been extensively studied, the cyclization-Heck reactions of functionalized allenyl phosphonic acids **9** reacted with simple alkenes **22** to afford 4-1(*E*)-alkenyl-2-ethoxy-2,5-dihydro[1,2]-oxaphosphole 2-oxides **23** via a Heck-type reaction (Scheme 12).¹⁵ The in situ formed Pd(0) can be reoxidized to the catalytically active Pd(II) species by using either the combination of CaH_2 (cat.)/NaI (cat.)/ O_2 or benzoquinone (BQ).

Scheme 12



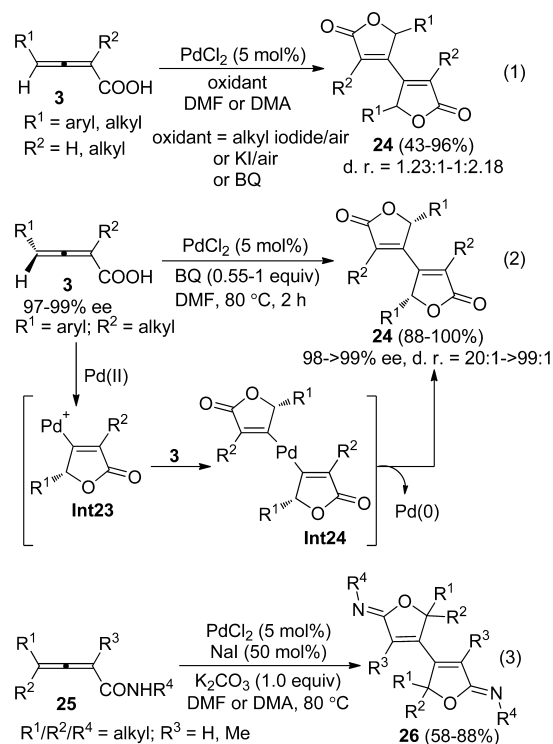
1.3. Cyclization Reactions of Allenes in the Presence of Allenes

1.3.1. Double Cyclization Protocols. Homodimerization of 2,3-Allenic Acids. Previously, we have studied the Pd(0)/ Ag^+ -cocatalyzed coupling-cyclization reactions of 2,3-allenoic acids **3** with aryl or alkenyl iodides for the synthesis of β -aryl or

alkenyl substituted butenolides.¹⁶ However, β -alkyl substituted butenolides were not accessible via this strategy as alkylpalladium species undergoes β -H elimination preferentially.² Thus, a Pd(II)-catalyzed approach involving oxypalladation forming furanonyl palladium was proposed for the preparation of this type of compounds from 2,3-allenoic acids **3** and alkyl iodides.

Quite unexpectedly, in the presence of PdCl_2 and an alkyl iodide, homodimerization reactions of 2,3-allenoic acids **3** were observed instead to afford dumbbell-type bibutenolides **24** in moderate to excellent yields in open air, albeit as a mixture of diastereoisomers (eq 1, Scheme 13).^{17a} Gratifyingly, excellent diastereoselectivity (d.r. $\geq 20:1$) was observed when enantiopure 2,3-allenoic acids were utilized with benzoquinone (BQ) as the oxidant: optically active bisbutenolides **24** were obtained in high yields with complete retention of enantiopurity (eq 2, Scheme 13),^{17b} suggesting that the reaction was most likely proceed via a double oxypalladation followed by a reductive elimination.¹⁸ Control experiments indicated that the alkyl iodide may just release I^- , which would be oxidized to the real oxidant I_2 with the aid of O_2 in air. In fact, the oxidant could be replaced with two alternative oxidation systems: KI/air or benzoquinone.^{17b}

Scheme 13

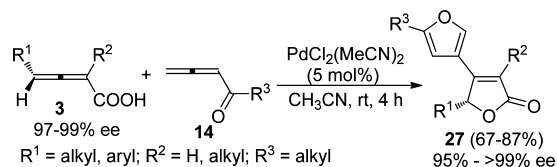


Homodimerization of 2,3-Allenamides. Under the standard conditions for the homodimerization reactions of 2,3-allenoic acids, 2,3-allenamides **25** failed to give the corresponding dimerization products. However, when 1 equiv of K_2CO_3 was added as the base in the presence of PdCl_2 and NaI, dimerization products *Z*-bis(furanimine) derivatives **26** were obtained in 58–88% yields (eq 3, Scheme 13).¹⁹ I_2 generated in situ from the oxidation of NaI with the O_2 in air may act as the oxidant for the regeneration of Pd(II) species. Interestingly, *N*-attack cyclization products γ -lactams were not observed.²⁰

Cyclization of 2,3-Allenic Acids in the Presence of 1,2-Allenyl Ketones. In the homodimerization reactions of 2,3-

allenoic acids, an external oxidant was needed to achieve the turnover efficiency of the Pd(II)-catalyst. However, in the heterodimeric cyclization reactions of 2,3-allenoic acids **3** with 1,2-allenyl ketones **14**, no external oxidant was required.²¹ Starting from highly enantioenriched axially chiral 2,3-allenoic acids, optically active polysubstituted 4-(3-furanyl)-2(5H)-furanones **27** have been obtained without obvious loss of enantiopurity (Scheme 14).^{21b}

Scheme 14

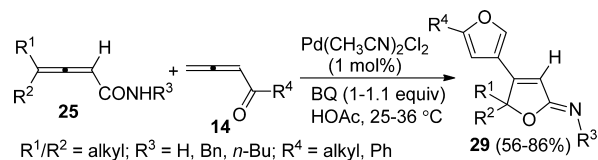


The reaction is believed to proceed via a double cyclic oxypalladation forming **Int19** that underwent subsequent reductive elimination (Scheme 15). Isolation of the byproducts **28a–c** from the reaction mixture indicated that Pd(0) species may be converted back into catalytically active Pd(II) species as follows: an initial bimolecular cyclometalation of allenyl ketones **14b** with Pd(0) involving the two nonterminal C=C bonds affords intermediate **Int26**, which would be protonated by the in situ generated HCl to give Pd(II) species and diketone **28a**, which would isomerizes to its isomers **28b,c**.

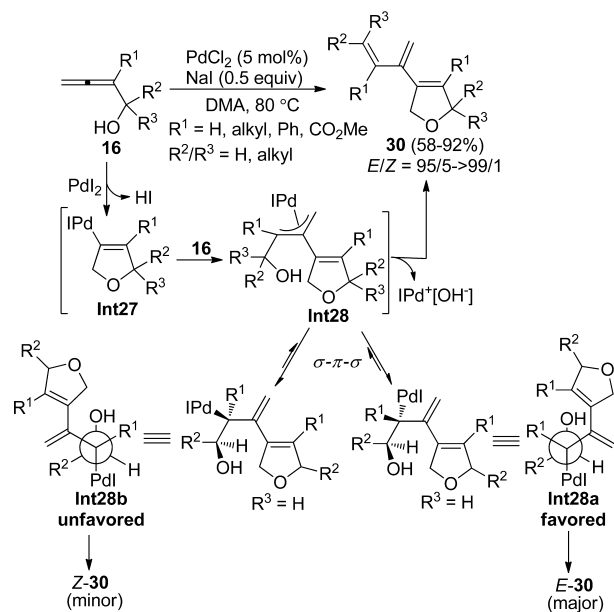
Cyclization of 2,3-Allenamides in the Presence of 1,2-Allenyl Ketones. The heterodimeric cyclization reactions of 2,3-allenamides with 1,2-allenyl ketones afforded 4-(furan-3-yl)-furanimines **29** in practical yields in a similar way (Scheme 16).²² Benzoquinone was found to be the most effective oxidant in this case.

1.3.2. Mono-Cyclization Protocols. Dimeric Cyclization of 2,3-Allenols. In the homodimerization reactions of 2,3-allenoic acids and 2,3-allenamide, both allenes underwent cyclization to form the dumbbell-type products. However, in the homodimerization of 2,3-allenols **16**, a very different reaction pattern was observed: one molecule of 2,3-allenol underwent cyclization while the other one formed a 1,3-diene unit obviously via β -OH elimination, leading to 4-(1,3-dien-2-yl)-2,5-dihydrofuran derivatives **30** in moderate to good yields with high stereoselectivity (Scheme 17).²³ Control experiments indicated

Scheme 16

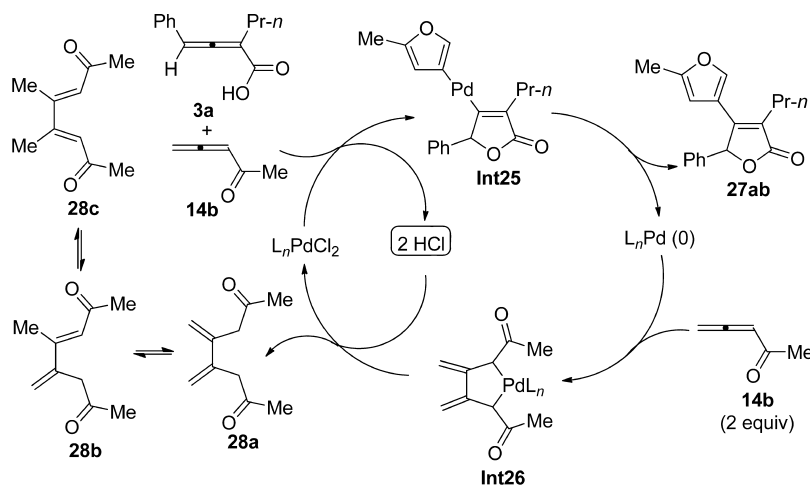


Scheme 17



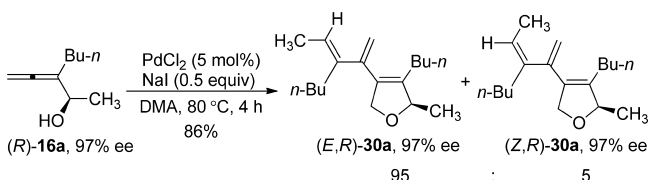
that PdI₂, which was formed in situ from mixing PdCl₂ with NaI, may be the catalytically active species. Cyclic oxypalladation of 2,3-allenol followed by carbopalladation with another molecule of 2,3-allenol would form π -allyl palladium species **Int28**, which underwent *trans*- β -OH elimination to afford the coupling products **30**. The IPd⁺[OH⁻] species was converted back into PdI₂ by its reaction with HI generated in the first step (Scheme 17). The high *E/Z* stereoselectivity observed in the cases of secondary 2,3-allenols (R² = alkyl, R³ = H) may be attributed to the fact that the intermediate **Int28a** was more favored for its thermodynamic stability than **Int28b** due to the intrinsic σ - π - σ rearrangement.

Scheme 15



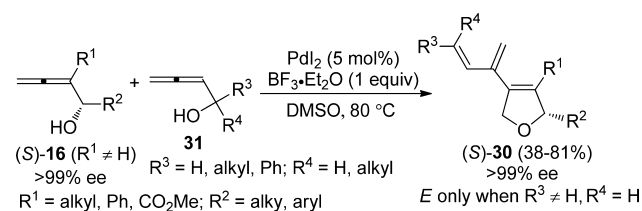
Highly enantioenriched 2,5-dihydrofurans **30a** could also be prepared in good yields with a high *E/Z* stereoselectivity from optically active 2,3-allenols (*R*)-**16a** (Scheme 18).

Scheme 18



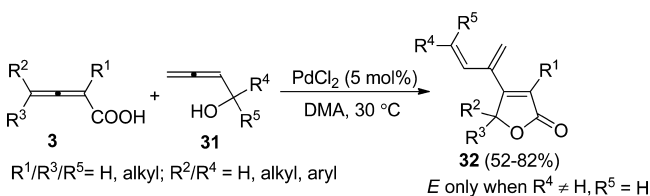
Furthermore, two different 2,3-allenols may undergo this type of reactions with 2-substituted 2,3-allenols **16** being cyclized and 2-unsubstituted 2,3-allenols **31** forming the 1,3-diene unit in the presence of PdI₂ and BF₃·Et₂O,²⁴ indicating the unique effect of the substituent at 2-position of 2,3-allenols on the reactivity (Scheme 19).

Scheme 19



Cyclization of 2,3-Allenolic Acids in the Presence of 2-Unsubstituted 2,3-Allenols. In the heterodimerization reactions of 2,3-allenoic acids in the presence of 2-unsubstituted 2,3-allenols, 2,3-allenoic acid underwent cyclization to form the butenolide skeletons whereas 2,3-allenol **31** was acting as the precursor of a 1,3-diene unit (Scheme 20).²⁵ When secondary 2,3-allenols were used, only (*E*)-**32** was formed.

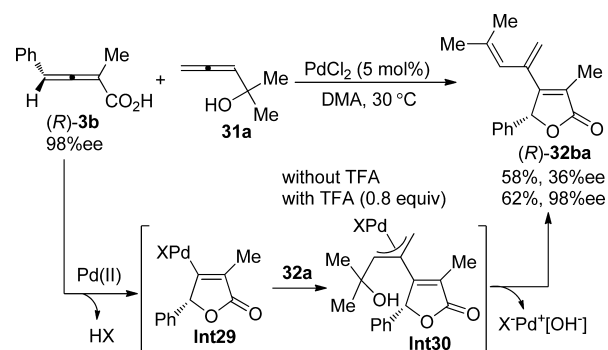
Scheme 20



When enantiopure 2,3-allenoic acid (*R*)-**3b** was subjected to the standard conditions in the presence of 2,3-allenol **31a**, the coupling-cyclization product (*R*)-**32ba** was obtained with a serious racemization (Scheme 21). Interestingly, when 0.8 equiv of TFA (CF₃CO₂H) was added, complete axial-to-central chirality transfer was achieved, indicating that the racemization-inducing basic [OH⁻] species may be formed during the reaction. Thus, we proposed that the reaction may proceed via cyclic oxypalladation, carbopalladation, and β-OH elimination to afford the products and XPd⁺[OH⁻] species, which was converted to PdX₂ via protonation with H⁺.

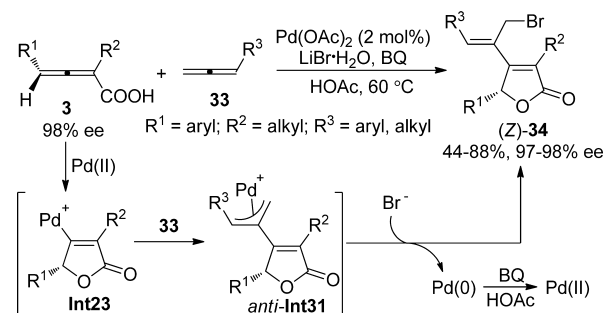
Cyclization of 2,3-Allenolic Acids in the Presence of Simple Allenes. In all these reactions discussed above, the Int1-type cyclic alkenyl palladium species may undergo insertion with the C=C bond of functionalized allenes; thus, we envisioned such a cyclization in the presence of simple allenes. In fact, in the

Scheme 21



presence of a nucleophile (LiBr) and an oxidant (BQ), the Pd(II)-catalyzed cyclization reactions of 2,3-allenoic acids **3** with nonfunctionalized simple alkyl or aryl-substituted allenes **33** afforded butenolides (*Z*)-**34** bearing an allylic bromide unit in moderate to good yields. Excellent axial-to-central chirality transfer was also observed (Scheme 22).²⁶ The reaction proceeds via cyclic oxypalladation, carbopalladation, and nucleophilic allylic bromination. The exclusive *Z* stereoselectivity observed may be explained by the fact that formation of π -allyl palladium species *anti*-Int31 with the *R*³ group *anti* to the relatively bulky furanone moiety was more favorable than that of *syn*-Int31.

Scheme 22

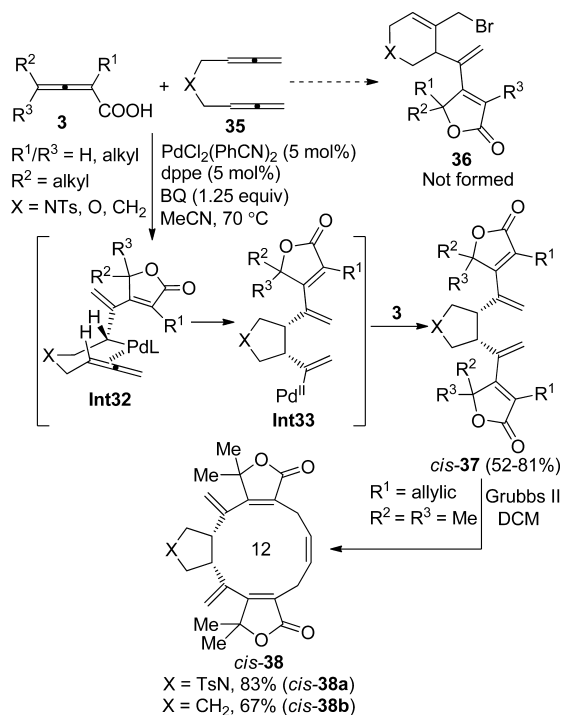


When this strategy was extended to the reactions of 2,3-allenoic acids with 1,5-bisallenenes **35**, the desired **36**-type bicyclic products were not formed. Interestingly, we found that unexpected tricyclic “sandwich-type” products *cis*-**37** were obtained in decent yields when the reactions were carried out in the presence of 5 mol % of PdCl₂(PhCN)₂ with 1,2-bis(diphenylphosphino)ethane (dppe) as the ligand and benzoquinone (BQ) as the oxidant (Scheme 23).²⁷ Notably, when the α -position of the lactone (*R*¹) is an allyl group, twelve-membered rings **38** containing three (*Z*)-C=C bonds were obtained in practical yields via RCM reactions.

A possible mechanism was proposed for this transformation (Scheme 23). Cyclic oxypalladation followed by intermolecular carbopalladation of one allene moiety in bisallene **35** would form π -allyl palladium species Int32, which underwent intramolecular carbopalladation to generate vinyl palladium species Int33. Int33 would trigger a cyclic oxypalladation of another molecule of 2,3-allenoic acid, which was followed by a reductive elimination to furnish the final tricyclic product **37**.

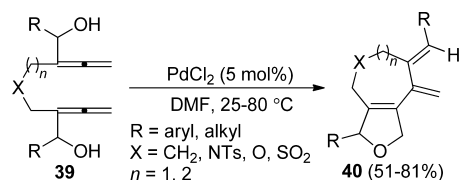
1.3.3. Intramolecular Reactions. 1, ω -Bisallenols. When two 2,3-allenol units were combined into a molecule, intramolecular cyclization reactions of the resulting 1, ω -bisallenols **39**

Scheme 23



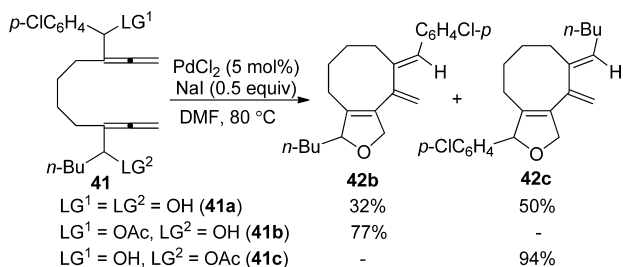
afforded 2,5-dihydrofuran-fused bicyclic skeletons **40** in 51–81% yield under Pd catalysis (Scheme 24).²⁸

Scheme 24



When “unsymmetric” 1,6-bisallenol **41a** was used, a mixture of bicyclic products **42b** and **42c** were obtained. Gratifyingly, when one of the hydroxyl groups was protected as an ester group as reported by Alcaide et al.,²⁹ the reaction afforded **42b** or **42c** exclusively in 77% and 94% yield, respectively (Scheme 25).

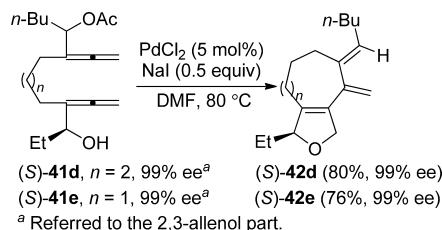
Scheme 25



Using this strategy, optically active substrates (*S*)-**41d** and (*S*)-**41e** were converted into the corresponding bicyclic products **42** without racemization (Scheme 26).

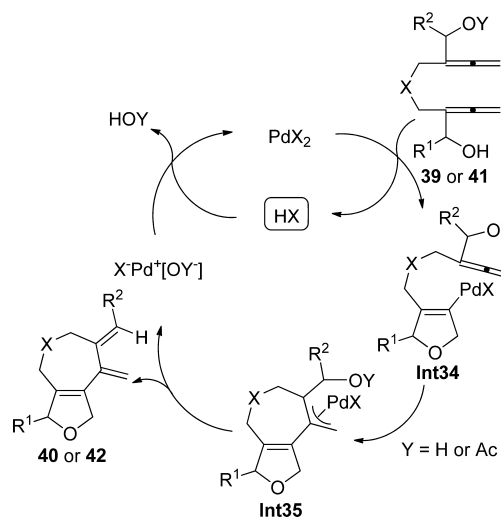
A rationale was proposed for this reaction (Scheme 27). Cyclic oxypalladation of the 2,3-allenol moiety with Pd(II) would form intermediate **Int34**, which underwent intramolecular carbopalla-

Scheme 26



ation with the remaining allene moiety to afford π -allyl palladium intermediate **Int35**. Subsequent β -hydroxide or acetate elimination gave the bicyclic product highly stereoselectively.

Scheme 27

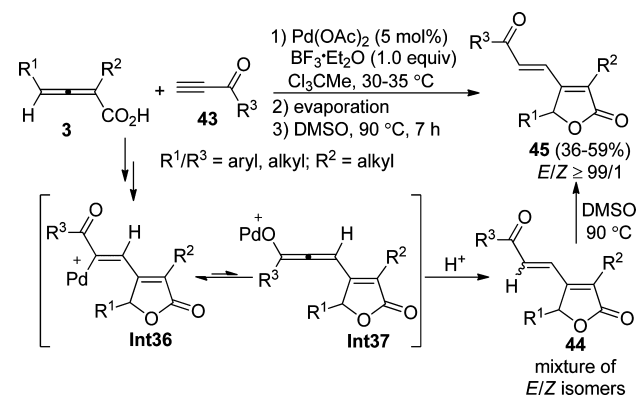


1.4. Cyclization Reactions of Allenes in the Presence of Electron-Deficient Alkynes

Electron-deficient alkynes could also be used as the coupling partner in the cyclization reactions of functionalized allenenes. For example, the Pd(OAc)₂-catalyzed cyclization reactions of 2,3-allenoic acids with α,β -unsaturated alkynes **43** yielded the coupling-cyclization product **44** as a mixture of *Z/E* isomers in moderate yields in the presence of BF₃·Et₂O, which acted as a Lewis acid to improve the reactivity of α,β -unsaturated alkynes **43**. Gratifyingly, heating the reaction mixture in DMSO at 90 °C for 7 h allowed for exclusive isomerization of the *Z* isomers to *E* isomers (Scheme 28).³⁰

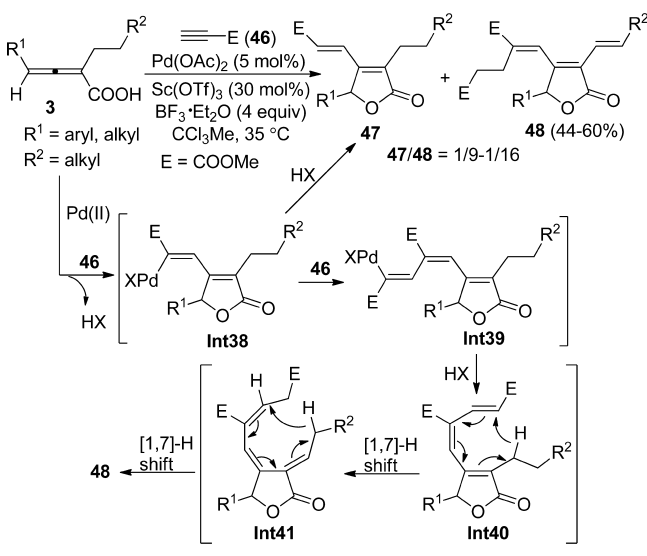
Interestingly, when methyl propiolate **46** was utilized instead of α,β -unsaturated alkynes **43**, the 1:2 adducts **48** with the C=C bonds migrated via double [1,7]-H shift were obtained as the major products in 44–60% yields together with a minor amount of 1:1 adducts **47** (Scheme 29),³¹ indicating that further carbopalladation of intermediate **Int38** with the second molecule of methyl propiolate proceeded much faster than its protonolysis. The double [1,7]-H shift from **Int40** to final product **48** was supported by deuterium experiments. The sharp difference between methyl propiolate and α,β -unsaturated alkynes in these reactions may be attributed to stronger electron-withdrawing ability of the ketonic carbonyl group than the ester group, which makes intermediate **Int36/Int37** prone to protonolysis while **Int38** is stable enough to undergo an insertion with second molecule of propiolate **46**. An excess

Scheme 28



amount of BF₃·Et₂O was added in this case to release Sc(OTf)₃ from the products as it has been reported that the Lewis acid coordinates preferentially with the methyl acrylate derivative products.³²

Scheme 29



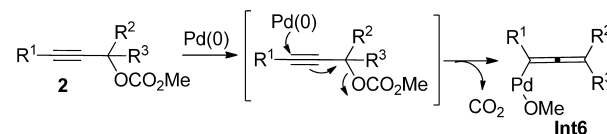
2. CYCLIZATION REACTIONS OF ALLENES IN THE PRESENCE OF PROPARGYLIC CARBONATES

2.1. Intermolecular Reactions

Palladium-catalyzed reactions of propargylic carbonates have become a powerful tool for constructing carbon–carbon and carbon–heteroatom bonds since Tsuji's pioneering work in 1985.³³ In the facile irreversible oxidative addition of propargylic carbonate with Pd(0), a molecule of CO₂ is released with concomitant formation of an allenylpalladium species **Int6** (Scheme 30), which may participate in a wide range of transformations to provide allene-containing products in a quite efficient manner.³⁴

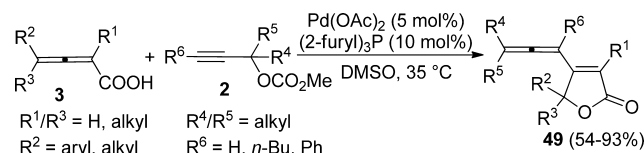
2,3-Allenic Acids. In 2006, we developed a Pd(0)-catalyzed “allene-to-allene” approach for the synthesis of β-allenyl butenolides **49** from 2,3-allenoic acids and propargylic carbonates (Scheme 31).³⁵ The allenylpalladium species **Int6** may react with 2,3-allenoic acids via either insertion followed by nucleophilic substitution or nucleopalladation followed by reductive elimination to give the vinylallene product **49**, which

Scheme 30



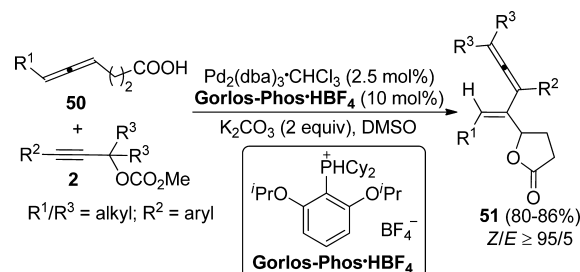
can be further converted into various more complicated polycyclic compounds via pericyclic reactions such as Diels–Alder reaction,³⁵ [1,*n*]-H shift, and 6*π*- or 8*π*-electrocyclization.³⁶

Scheme 31



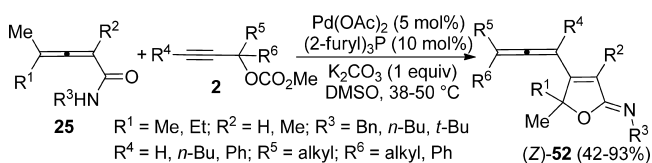
4,5-Allenic Acids. When 4,5-allenoic acids **50** were utilized instead of 2,3-allenoic acids, *exo*-cyclization was observed, providing 5-(1,3,4-alkatrien-2-yl)-4,5-dihydro-2(3*H*)-furanones **51** in good yields (Scheme 32).³⁷ Rigorous *Z/E* stereocontrol of the nonallenyl C=C bond was achieved by employing the sterically hindered monophosphine ligand **Gorlos-Phos·HBF₄** recently developed in our group.³⁸ Control experiment revealed that the Brønsted acid HBF₄, which was utilized to stabilize the phosphine ligand, has no influence on the reaction outcome.

Scheme 32



2,3-Allenamides. The Pd(0)-catalyzed cyclization reactions of 2,3-allenamides with propargylic carbonates afforded *O*-attack cyclization products β-allenyl furanamines **52** in 42–93% yields (Scheme 33).³⁹ Again, *N*-attack²⁰ cyclization products were not observed.

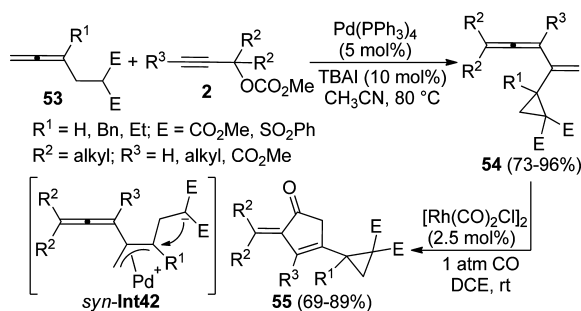
Scheme 33



(2,3-Butadienyl)malonate or Bis(phenylsulfonyl)-methane. The reactions of (2,3-butadienyl)malonate or bis(phenylsulfonyl)methane **53** with propargylic carbonates yielded *exo*-cyclization products tetrasubstituted allenes with a cyclopropylvinyl substituent **54** in 73–96% yield, possibly via the π-allyl palladium intermediate *syn*-**Int42** (Scheme 34),⁴⁰ probably due to the unfavorable steric compulsion between Pd

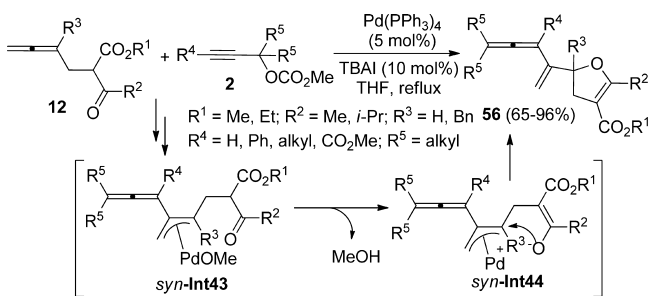
and the relatively bulky nucleophilic moiety in the *anti* configuration. The in situ generated methoxy anion was acting as the base to deprotonate the activated methylene group in **53**, thus, no external base was required. The vinylallene products can be efficiently converted to polysubstituted cyclopentenone derivatives **55** via Pauson-Khand reaction under mild conditions.

Scheme 34



2-(2',3'-Allenyl)acetylacetates. Interestingly, the reactions of 2-(2',3'-allenyl)acetylacetates **12** with propargylic carbonates afforded five-membered 1,3,4-alkatrien-2-ylidihydrofurans **56** rather than cyclopropane derivatives, albeit also via *exo*-cyclization (Scheme 35),⁴¹ which may be explained by the formation of the enolate intermediate *syn*-**Int44** due to the presence of a neighboring acyl group.

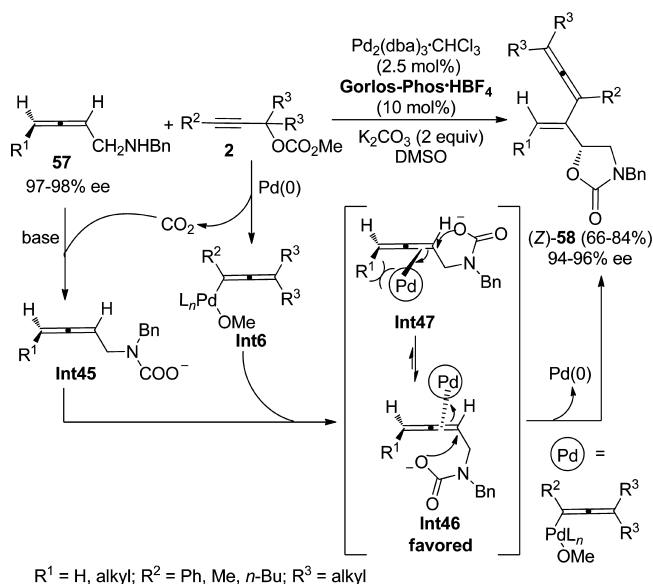
Scheme 35



2,3-Allenyl Amines. In the previously discussed Pd(0)-catalyzed cyclization reactions of functionalized allenes with propargylic carbonates, the CO₂ generated in situ via oxidative addition of propargylic carbonate with Pd(0) was uselessly released. Based on previous studies in this area,⁴² we developed an atom-economic CO₂-recycling⁴³ reaction for the synthesis of medicinally active oxazolidin-2-one skeletons **58** from 2,3-allenyl amines and propargylic carbonates (Scheme 36).^{37,44} Control experiments confirmed that the –COO– unit in the oxazolidin-2-one **58** came from propargylic carbonate rather than carbonate salt such as K₂CO₃. When 4-monosubstituted 2,3-allenyl amines were employed, (*Z*)-**58** were formed exclusively by utilizing **Gorlos-Phos·HBF₄** as the ligand. Efficient axial-to-central chirality transfer was also achieved, suggesting that the reaction was more likely proceed via a cyclic oxypalladation followed by reductive elimination mechanism.¹⁸ Due to the unfavorable steric repulsion between R¹ and the to-be-coordinated palladium species in **Int47**, *Z* isomers of **58** were obtained via the intermediacy of **Int46**.

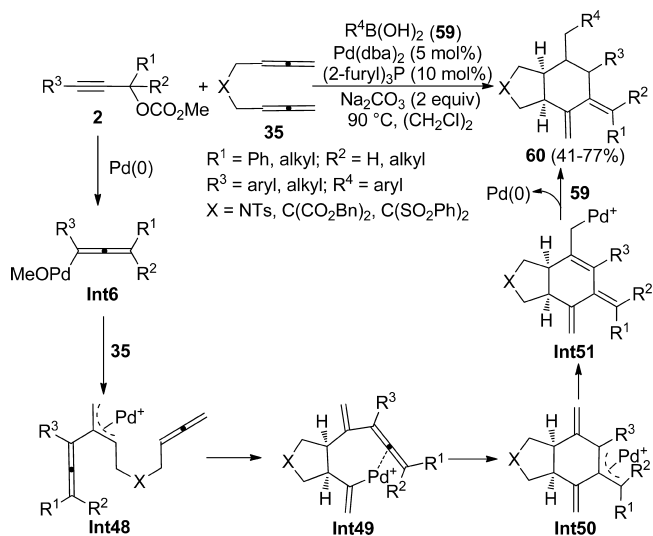
1,5-Bisallenenes.⁴⁵ When the nucleophilic functionality of the aforementioned allene moiety was replaced by another simple allene unit, the resulting 1,5-bisallenenes **35** reacted with

Scheme 36



propargylic carbonates in the presence of organoboronic acids to afford *cis*-fused bicyclo[4.3.0]nonenes **60** in reasonable yields in a single operation with high regio- and stereoselectivity (Scheme 37).⁴⁶ A plausible mechanism was proposed for this reaction. The allenylpalladium species **Int6** first underwent intermolecular carbopalladation with one allene moiety of 1,5-bisallene to form the π -allyl palladium species **Int48**. Subsequent double intramolecular carbopalladation followed by isomerization would generate the intermediate **Int51**, which then gave the final product **60** via a Suzuki coupling reaction.

Scheme 37

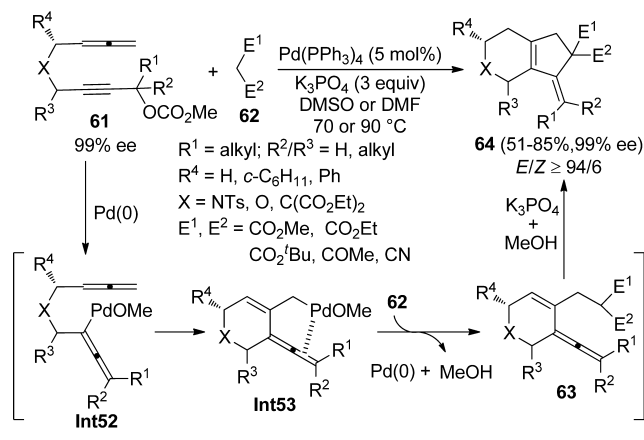


2.2. Intramolecular Reaction

Previous studies have been focused on the intermolecular reactions of allenes with propargylic carbonate, we recently developed a Pd(0)-catalyzed intramolecular cyclization reactions of the allene-propargylic carbonates **61** in the presence of geminal bisnucleophiles **62**, furnishing synthetically versatile bicyclo[4.3.0] skeletons **64** in up to 85% yield with a high *E/Z* stereoselectivity ($\geq 94/6$) in a single operation (Scheme 38).⁴⁷

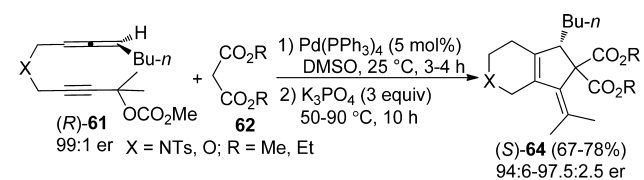
Control experiments revealed that **63**-type monocyclization products were first formed in this transformation, possibly via an oxidative addition, intramolecular carbopalladation and regioselective intermolecular nucleophilic allylation sequence. The monocyclization products **63** then underwent further cyclization and C=C bond migration to furnish the final bicyclic products **64** with the aid of K_3PO_4 and the in situ generated MeOH.

Scheme 38



When enantioenriched axially chiral allene-propargylic carbonates (*R*)-**61** was subjected to the standard reaction conditions, the corresponding bicyclic products was obtained with serious racemization, which is not surprising as racemization of the **Int53**-type π -allyl palladium species via a σ - π - σ process has been observed in previous studies.¹⁸ Fortunately, we found that when the reaction was carried out in a one-pot two-step manner with the first step being conducted at room temperature, efficient axial-to-central chirality transfer was achieved, affording optically active bicyclic products in practical yields with only a slight decrease of enantiopurity (Scheme 39). The coordination of Pd with the allene moiety in **Int53** may be critical for its η^1 -nature at room temperature explaining such a high efficiency of chirality transfer.

Scheme 39



CONCLUSIONS AND PERSPECTIVES

In this Account, we summarized our recent studies on Pd-catalyzed cyclization reactions of allenes in the presence of unsaturated carbon-carbon bond-containing compounds such as alkenyl halides, alkenes, allenes, electron-deficient alkynes, or propargylic carbonates, which have enabled expeditious synthesis of a wide range of synthetically versatile monocyclic, dumbbell-type bicyclic, and fused polycyclic compounds. Efficient axial-to-central chirality transfer has been accomplished in certain types of reactions and application of this strategy to other cases may be possible, thanks to the remarkable progress made in the area of enantioselective synthesis of axially chiral allenes in recent years.⁴⁸ On the other hand, developing asymmetric versions of

these reactions should also be a promising area of future endeavors given the vast potentials of transition metals and various types of chiral ligands.

Further efforts to expand these reactions to other types of functionalized allenes, such as allenyl thiols and allenyl hydroxylamines, or different combinations of reaction partners bearing different steric and electronic nature will allow for more accesses to some privileged skeletons that are otherwise difficult to prepare. It will also be highly desirable to investigate the possibility of constructing medium or macrocycles by extending the length of the carbon chain between allene moiety and the nucleophilic functionality. Finally, more attention will be paid to the applications of these methodologies in target synthesis in the coming years.

AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

Biographies

Juntao Ye was born in 1986 in Hubei, China. He received his B.S. degree in applied chemistry from Huazhong University of Science and Technology (HUST) in 2008. He was then admitted to Shanghai Institute of Organic Chemistry (SIOC) and got his Ph.D. degree in June 2013 under the supervision of Prof. Shengming Ma. His doctoral research was focused on the synthesis and cyclization reactions of allenes. Currently, he is a post-doctoral fellow in Prof. M. Lautens' group at the University of Toronto.

Shengming Ma was born in 1965 in Zhejiang, China. He received his Ph.D. from Shanghai Institute of Organic Chemistry (SIOC) and became an assistant professor there in 1991. After postdoctoral research at the ETH with Prof. Venanzi and Purdue University with Prof. Negishi, he returned to SIOC in 1997. From February 2003 to September 2007, he was jointly appointed by SIOC and Zhejiang University (ZJU). In October 2007, he moved to East China Normal University to help build the research program in organic chemistry. Currently, he is also a research professor at SIOC and Qiu Shi Adjunct Professor at ZJU and CUHK. He received the Mr. & Mrs. Sun Chan Memorial Award in Organic Chemistry (2004), OMCOS Springer Award (2005), National Award for Research in Natural Science in China (Second-Class, 2006), and Natural Science Awards of Shanghai (First-Class, 2010). The work discussed in this Account has been conducted at SIOC and ZJU.

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