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Recent advances of Pd-π-allyl zwitterions in cycloaddition reactions ☆

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ABSTRACT

Palladium-catalyzed cycloaddition reactions *via* Pd-π-allyl zwitterions have been established as significant synthetic transformations to enable numerous carbon- or heterocycles compounds that are key constituents of various biologically active natural products and pharmaceuticals. In addition to the well-known Pd-π-allyl zwitterions, including palladium-trimethylenemethane and Pd-1,3/1,4-zwitterions, chemists have recently discovered new applications of several long ago reported but less-studied Pd-π-allyl zwitterions, which can straightforwardly and efficiently construct novel cyclic architectures. Meanwhile, some impressive newly designed zwitterions have been also developed. Those zwitterions are diverse and can serve as transient and highly reactive intermediates for the subsequent cyclization with various acceptors. In this review, we highlight recent advances in applications of these two types of zwitterions in the synthesis of complex polycyclics and medium-sized cyclic compounds.

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1. Introduction

Dipolar cycloaddition reactions are of fundamental importance to organic synthesis, as they provide access to cyclic motifs in an efficient and convergent manner, particularly, the capability to rapidly access fused-/bridged-ring systems and medium-sized rings (7 to 11-membered rings) which are common core structures in various bioactive natural products and drugs [1–11]. As a result, this strategy has attracted the attention of numerous synthetic chemists. In addition to relatively stable classical 1,3-dipoles [12–15], 1,n-dipole variants which are not fully conjugated chemical species, are difficult to generate using non-catalytic methods. Among them, transition metal Pd-catalyzed dipolar cycloadditions have been one of the most straightforward and powerful strategy to this end. Most of dipolar intermediates are a short-lived, non-isolable species and the dipole species could be a zwitterion rather than a true dipole. In 1980s, the best-known palladium-mediated dipole, palladium-trimethylenemethane (Pd-TMM), was firstly generated by Trost's group [16], which is an all-carbon 1,3-dipole. Thereafter, Shintani and Hayashi *et al.* designed γ-methylene-δ-pentyl lactone as a precursor of all-carbon 1,4-dipole compound to access larger ring sizes (Scheme 1a) [17,18]. It has been used extensively in the preparation of a variety of cyclic products, since it reacts with a multitude of acceptors. With the rapid development of these early studies, increasingly profound dipoles have been emerged and are widely used (Scheme 1a). As shown in Scheme 1a, compared to Pd-TMM dipoles, those new dipoles are designed by introducing heteroatoms, growing carbon chains or designing dipoles containing delocalized anions, which not only allow to construct a larger ring system, but also have more reaction pathways for cyclization reactions. This type of dipolar reaction is characterized by the formation of exocyclic unsaturated bonds.

Around the same time as the development of the [3 + 2] Pd-TMM cycloadditions, an alternative [3 + 2] cycloaddition strategy was realized by Tsuji and co-workers [19] *via* a zwitterion generated *in situ* by the reaction of Pd with activated vinylcyclopropanes. Since then, the Pd-catalyzed intermolecular [3 + *n*] and [5 + *n*] cycloadditions have been a powerful, atom-economic tool for the construction of various carbon- and heterocycles through the *in situ* generated Pd-π-allyl 1,3- or 1,5-zwitterions by the reaction of Pd(0) with vinyl three-membered cycles and their analogues [20–30]. Meanwhile, Pd-π-allyl zwitterions derived from vinyl benzoxazinanones were first developed as a type of 1,4-dipole by Tunge's group in 2008 [31], and subsequently gained widespread use [32–39]. Several related reviews have been reported (Scheme 1b) [18,40].

☆ Dedication to Prof. Lixin Dai on the Occasion of His Centenary Birthday.

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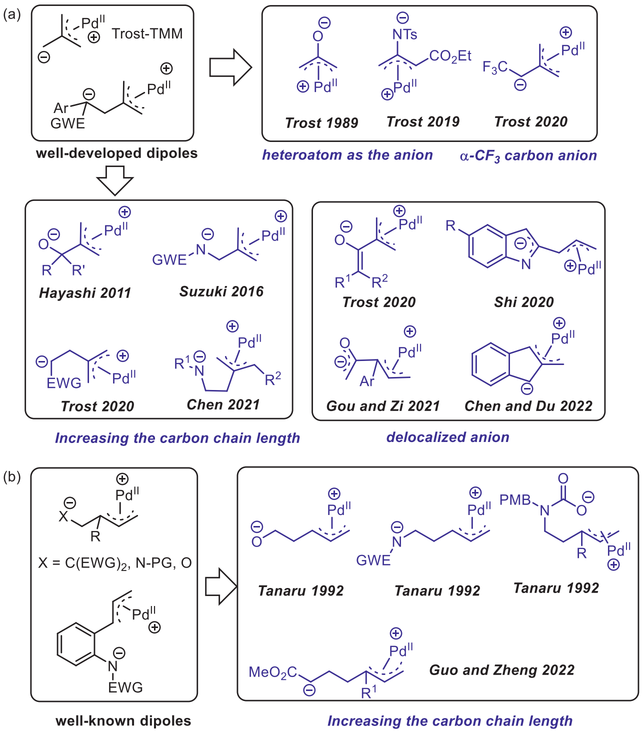


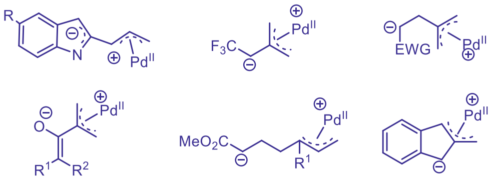
Scheme 1. Representative Pd-π-allyl zwitterions.

In recent years, along with the expansion and applications of those dipoles, some other dipoles that had little application after their initial discovery have recently received renewed attention in palladium-catalyzed cycloaddition reactions and have been rapidly developed (Scheme 1b). Compared to dipoles derived from vinyl three-membered cycles, these newly applied dipoles have longer chains to enable larger cyclization products. It is worth noting that the reaction products usually containing multiple chiral centers can be constructed in one step through cycloaddition reactions of those Pd-π-allyl zwitterions under asymmetric catalysis, which is usually difficult to obtain with other methods.

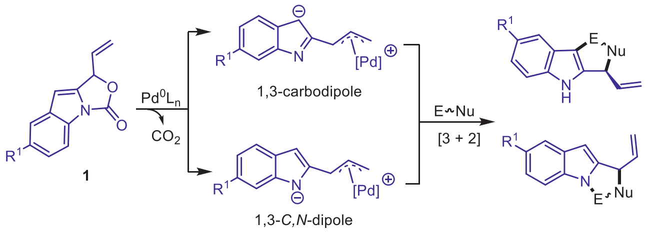
The discovery of new Pd-π-allyl zwitterions has enabled the construction of the diverse set of carbon- and heterocyclic compounds and improves the high potential of such transformation for the synthesis of highly complex organic molecules. However, the design and exploration of unprecedented dipolar cycloadditions is particularly challenging because these dipole intermediates are often highly reactive and short-lived, leading to multiple unexpected reaction pathways. This paper reviews representative advances in Pd-π-allyl zwitterions in organic synthesis over the past five years in two aspects: (1) different kinds of new Pd-π-allyl zwitterions and their applications as different kinds of synthons in cycloaddition reactions; (2) recent advances in the early zwitterions that were hardly applied after their initial discovery. Although several related reviews have been reported [20,41-44], there is no comprehensive summary for the recent development of Pd-π-allyl zwitterions. This review will provide a systematic and overall summary of the recent developments of Pd-π-allyl zwitterions, including three different types of Pd-stabilized zwitterions (bearing a carbanion, *O*-centered anion or *N*-centered anion), as well as the related substrate applicability and reaction mechanisms.

2. Pd-π-allyl zwitterions bearing a carbanion

A wide assortment of compounds, including γ-methylene-δ-pentyl lactones, vinylcyclopropanes, and silylated allylic substrates were commonly used to generate Pd-zwitterionic species with a carbanion. In the past years, several novel Pd-π-allyl zwitterions were developed by using new precursors (Scheme 2). They can serve as C3, C4, and C6 synthons to participate in cycloaddition reaction with various dipolarophiles.



Scheme 2. Pd-π-allyl zwitterions bearing a carbanion.



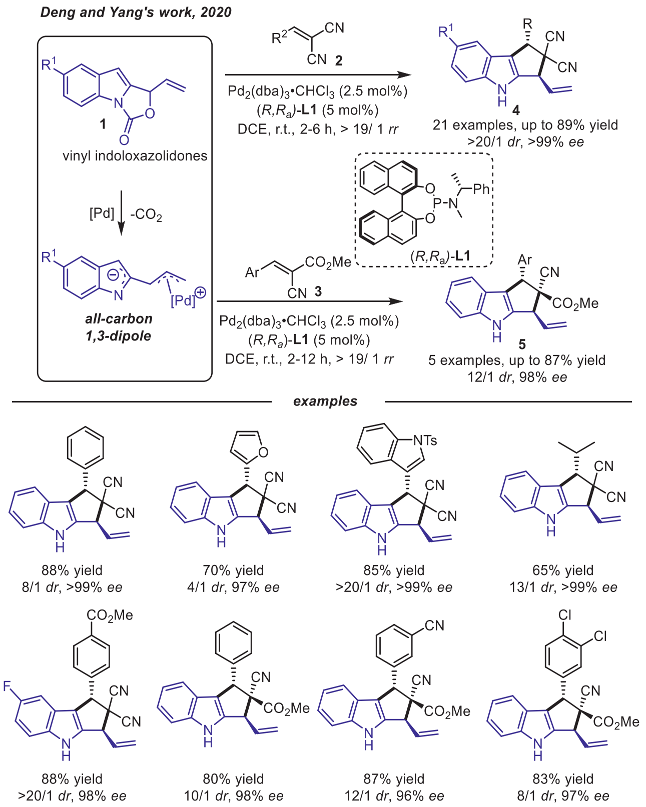
Scheme 3. The general process of cycloaddition reactions of vinyl indoloxazolidones.

2.1. Pd-π-allyl 1,3/5-zwitterions

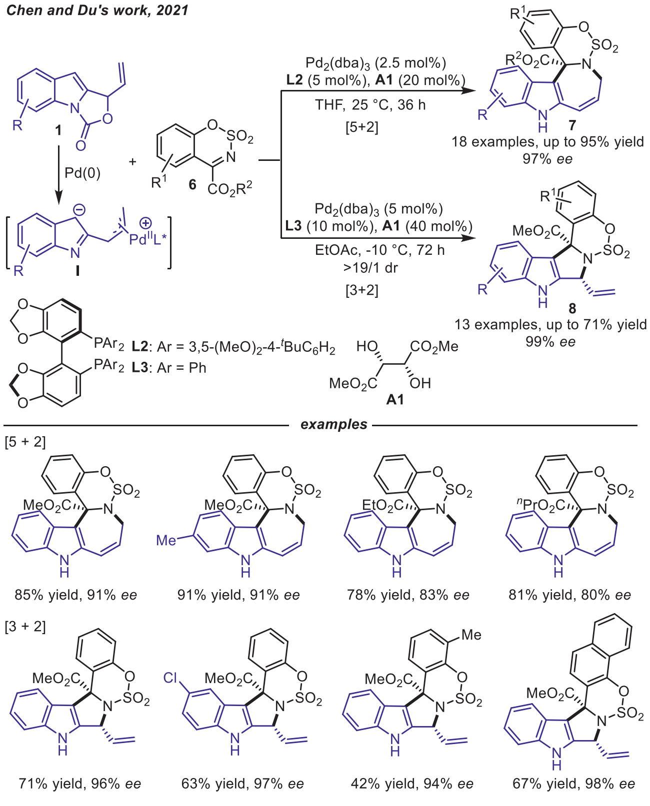
In 2020, vinyl indoloxazolidones **1** were reported as either 1,3-C,N-dipole or 1,3-carbodipole precursors in Pd-catalyzed [3 + 2] cycloaddition reactions by Shi group [45] and Deng group [46], respectively (Scheme 3). The indolyl substituted Pd-π-allyl zwitterionic intermediates were derived from the palladium catalyzed decarboxylation reaction of vinyl indoloxazolidones **1**, which could serve as both all-carbon 1,3-dipoles and aza-1,3-dipoles through the anionic delocalization, providing a new platform for the divergent synthesis of polycyclic indoles. The reactions in which they participate as all-carbon 1,3-dipoles are presented firstly, and the reactions in which vinyl indoloxazolidones act as 1,3-C,N-dipoles will be presented later (*vide infra*).

Deng and coworkers [46] first applied vinyl indoloxazolidones **1** that selectively served as all-carbon 1,3-dipole precursors in the asymmetric [3 + 2] cycloaddition with electron deficient alkenes **2** or **3**, furnishing polysubstituted cyclopenta[*b*]indoles **4** and **5** with high regio- and stereo-selectivities in the presence of phosphoramidite ligand **L1** (Scheme 4).

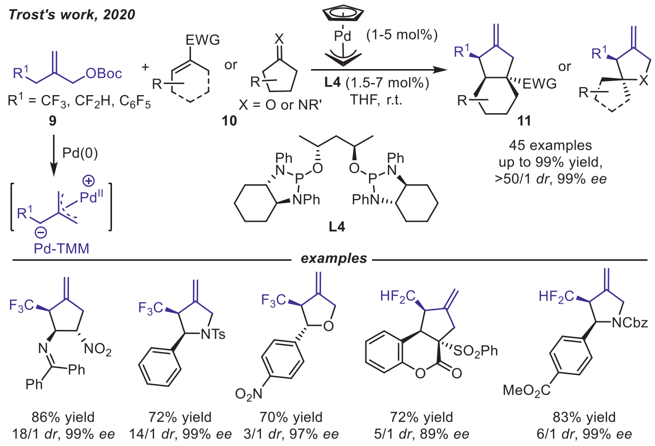
The next year, Chen and coworkers [47] also disclosed a palladium-catalyzed regiodivergent asymmetric cycloadditions of vinyl indoloxazolidones **1**, which could serve as unusual 1,5-carbodipole or 1,3-carbodipole precursors by tuning chiral bisphosphine ligands and reaction conditions, in the assemblies with sulfamate-derived cyclic imines **6** (Scheme 5). A diversity of [5 + 2] cycloaddition products **7** were generally constructed with up to 95% yields and 97% enantioselectivities by employing the combination of $Pd_2(dba)_3$ and chiral bisphosphine ligand **L2**. Remarkably, by tuning the structure of bisphosphine ligand from a sterically bulky **L2** to a less sterically demanding **L3**, the asymmetric [3 + 2] cycloaddition products **8** between the same substrate assemblies could be separated as the major ones in excellent stereoselectivity since the congested feature of the π-allyl palladium complex would be beneficial for the [3 + 2] cycloaddition pathway. During this process, the chiral tartrate **A1** was found to be beneficial for the enantioselectivity and reactivity, probably acting as a hydrogen donor co-catalyst after assembly with the palladium(II) intermedi-



Scheme 4. Pd-catalyzed $[3+2]$ cycloadditions of vinyl indoloxazolidones.



Scheme 5. Pd-catalyzed $[3+2]$/$[5+2]$ cycloadditions of vinyl indoloxazolidones.



Scheme 6. Pd-catalyzed $[3+2]$ cycloadditions *via* α-CF_3 carbanion Pd-TMM.

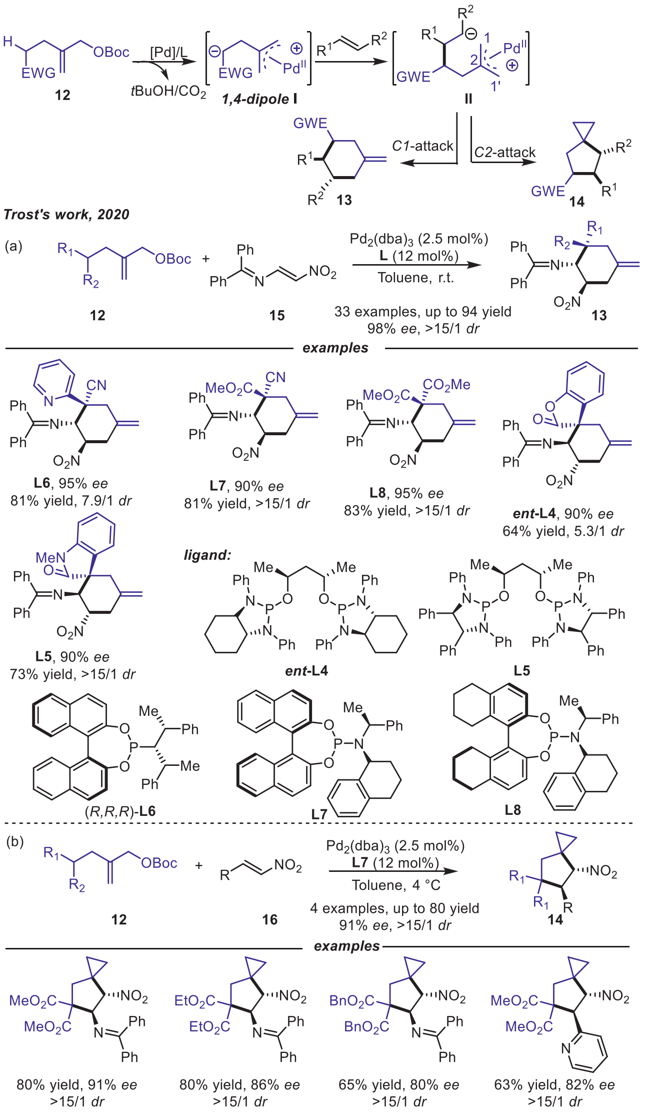
ate *via* coordination. Moreover, this delocalized Pd-π-allyl zwitterions **I** are similar to the zwitterionic species formed from vinylethylene carbonates (VECs) or vinyloxiranes [48–53] under Pd catalysis, which could perform as either 5-atom synthons or 3-atom synthons for cycloaddition reactions.

Since the seminal study by Trost and Can in 1979 [16], five-membered ring structures, such as cyclopentanes, pyrrolidines and tetrahydrofurans, have been well constructed through asymmetric $[3+2]$ cyclizations of Pd-TMM with 2π-dipolarophiles. In 2020, Trost and coworkers developed a Pd-TMM containing an α-trifluoromethyl carbanion (Scheme 6) [54]. The unique charge distribution of the cationic palladium π-allyl motif may stabilize the adjacent fluorocarbanion and prevent the elimination of fluoride. Thus, asymmetric $[3+2]$ cycloadditions of Pd-TMM intermediate with a vast array of acceptors **10** were realized to deliver valuable CF_3-substituted five-membered rings **11** including cyclopentanes, pyrrolidines and tetrahydrofurans in high yields and stereoselectivities. In addition, other five-membered rings containing polyfluorinated substituents such as difluoromethyl, were also successfully provided using this approach.

2.2. Pd-π-allyl 1,4-zwitterions

In 2007, γ-methylidene-δ-valerolactones were first designed and used as precursors of 1,4-zwitterionic specie by Shintani and Hayashi group [17]. Since then, this type of precursors has been rapidly developed by reacting with many acceptors as an all-carbon four-atom synthon for $[4+n]$ cycloadditions [55–59]. Despite its great reactivity, γ-methylidene-δ-valerolactones require an electron-rich or neutral aromatic ring at the α-position of its ester group to enable the key palladium-mediated decarboxylation, which would limit the further functionalization and applications of the products. Thus, the need of more general dipole precursors and the possibility of achieving high enantioinduction have prompted chemists to explore and develop new atom-economic pathways to construct functionalized carbo- and heterocycles.

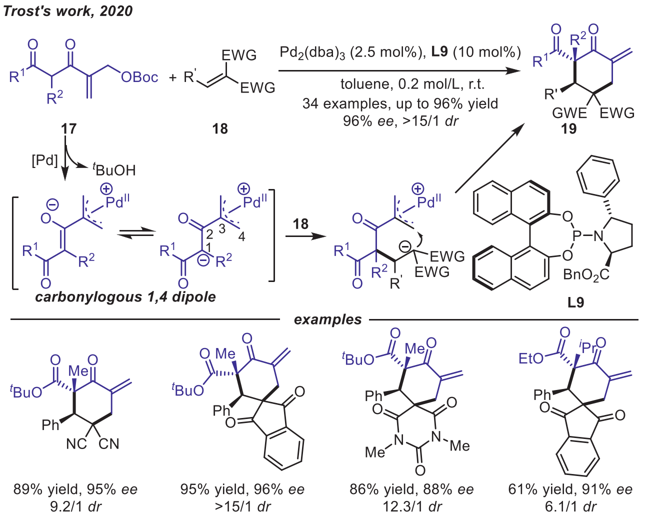
Until 2020, Trost and coworkers designed and applied a new 1,4-zwitterionic intermediate precursor that could be accessible in one step, greatly simplifying the synthesis (Scheme 7) [60]. The allyl carbonates **12** would undergo ionization in the presence of Pd(0) complex and subsequently abstract the homoallylic proton, acidified by the electron withdrawing group, with release of ^tBuOH and CO_2. The corresponding Pd-stabilized zwitterion **I** was generated, which can then be add to electron-deficient olefins **15** or **16** to deliver intermediate **II**. While the subsequent ring closure of intermediate **II** can yield different products because both C1 and



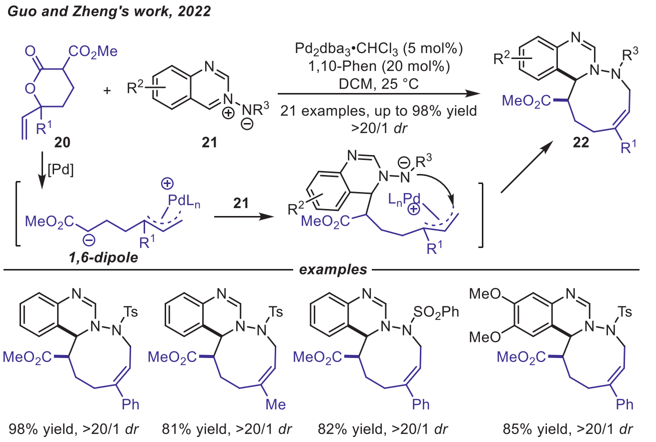
Scheme 7. Pd-catalyzed cycloadditions *via* aliphatic 1,4-dipoles.

C2 centers are electrophilic. Nucleophilic attack at the C1 terminus *via* a classic Tsuji-Trost type mechanism afforded 6-membered adducts **13** in up to 94% yield, 98% *ee* and >15/1 *dr* (Scheme 7a), while attack at the C2 position yielded a palladacyclobutane intermediate which subsequently would undergo reductive elimination to form the spirocyclic compounds **14** (Scheme 7b). Various chiral 6-membered rings and spiro[2.4]heptanes were prepared in high yields and selectivity through ligand-controlled and substrate induced regio- and diastereoselectivity.

In the same year, Trost and coworkers [61] also developed another novel palladium-mediated carbonylogous 1,4-dipole by *in situ* deprotonation from **17** (Scheme 8). In contrast to the well-developed palladium-mediated dipole precursors that usually used electron-neutral or rich olefins, such as cinnamyl, methylmethylene. In this process, electron-deficient system was reported as the precursor. By using their developed C2-unsymmetric phosphoramidite ligand **L9**, this novel dipole could be used for asymmetric [4 + 2] cycloaddition reactions with various electron-deficient alkenes **18** to produce chiral cyclohexanones **19** in good to excellent results.



Scheme 8. Pd-catalyzed cycloadditions *via* carbonylogous 1,4-dipoles.

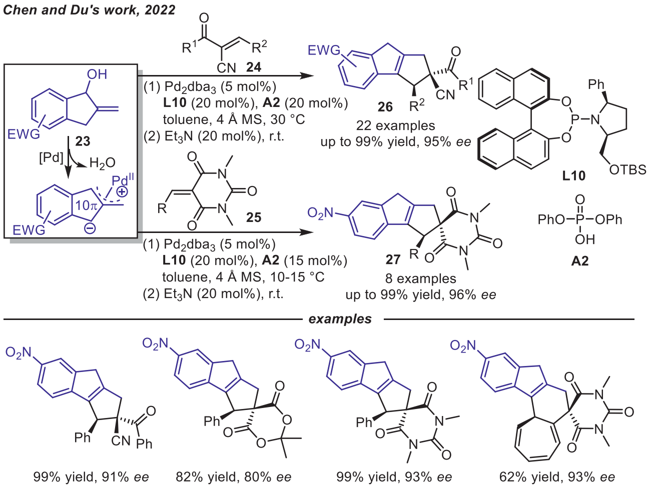


Scheme 9. Pd-catalyzed [6 + 3] cycloadditions of δ-vinylvalerolactone.

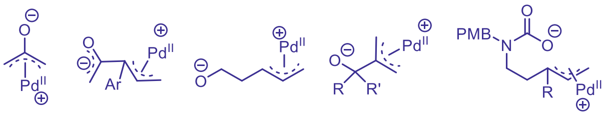
2.3. Pd-π-allyl 1,6-zwitterions and others

In 2022, a new precursor of π-allylpalladium zwitterion, δ-vinylvalerolactone **20**, was designed for the [6 + 3] decarboxylative cycloaddition reactions with azomethine imines **21** by Guo and coworkers (Scheme 9) [62]. A range of nine-membered 1,2-dinitrogen-containing heterocycles **22** were synthesized in 77%–98% yields with >20/1 *dr*. δ-Vinylvalerolactones **20** with aryl, 2-naphthyl, thienyl and methyl-substituted all displayed well reactivity, affording the corresponding products.

In 2022, Chen and coworkers designed novel π-allylpalladium dipolar 10π-cycloaddends derived from 2-methylene-1-indanols **23** *via* oxidative addition under Pd(0) catalysis and deprotonation (Scheme 10) [63]. Thus, an asymmetric [10 + 2] cycloaddition reaction of **23** with diverse activated alkenes was developed under double activation of Pd(0) and phosphoric acid. By employing a newly designed chiral phosphoramidite ligand **L10**, various polycyclic frameworks embedding an indene core were obtained in moderate to excellent yields with high enantioselectivities. Notably, introducing an electron-withdrawing group at the indane ring is required to enhance the acidity of the benzylic C-H. The addition of phosphoric acid as a co-catalyst may be beneficial for the oxidative addition of Pd(0) to allyl alcohol and may also facilitate enantiomeric control. Besides, apart from α-cyano chalcones **24** and barbiturate-derived alkenes **25**, other types of activated



Scheme 10. Pd-catalyzed $[10+n]$ cycloadditions of 2-methylene-1-indanols.



Scheme 11. Pd-π-allyl zwitterions bearing an *O*-centered anion.

alkenes can also be employed to construct polycyclic frameworks with more structural diversity through asymmetric $[10+8]$ and $[10+4]$ cycloaddition reactions.

3. Pd-π-allyl zwitterions bearing an *O*-centered anion

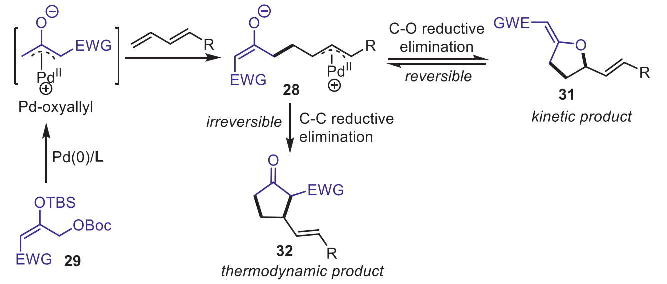
Novel Pd-π-allyl zwitterions bearing an *O*-centered anion have also been rapidly developed and can be used as versatile multiatomic synthons depending on the reaction conditions and the variation of dipolarophiles (Scheme 11), however, the control of the reaction site as well as the stereoselectivity is difficult. Nevertheless, with the continuous efforts of chemists, numerous carbon- or heterocycles compounds have been successfully furnished.

3.1. Pd-π-oxyallyl 1,3-zwitterions

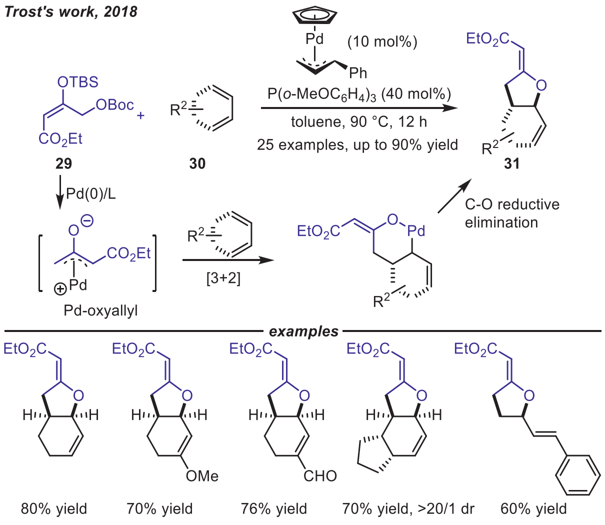
Pd-oxyallyl intermediates have attracted the attention of researchers since the 1990s [64–66]. They were generated from different precursors and were all found to react only with norbornene type strained alkenes to yield unexpected cyclopropanation products. However, it was not until very recently that a catalytic Pd-oxyallyl-mediated $[3+2]$ cycloaddition was achieved by Trost and coworkers in 2018 [67]. The key to success was the introduction of an additional electron-withdrawing group (EWG) on the Pd-oxyallyl intermediate, which could drive the equilibrium toward $[3+2]$ cycloaddition products (Scheme 12). The Pd-oxyallyl intermediated *in situ* generated by the reaction of Pd(0) with precursor **29** acted as an electrophile, which differed from the analogous Pd-TMM intermediates that are nucleophiles. Subsequently, the new Pd-allyl zwitterionic intermediate **28** would be generated by the addition of Pd-oxyallyl to the conjugated diene, and this Pd-allyl transfer process would be followed by C-O or C-C reductive elimination to form the five-membered rings **31** or **32**, respectively. In addition, it was found that the kinetic products **31** would be converted to thermodynamic products **32** *via* the intermediate **28**.

In this work, a tailored bifunctional precursor **29** and 1,3-dienes **30** including cyclohexadienes and linear dienes were chosen as substrates (Scheme 13). A wide variety of tetrahydrofurans **31** containing an exocyclic double bond were delivered in good to high yields, which was quite different from those obtained *via* the $[3+2]$ cycloadditions of vinyl three-membered cycles with olefins [68–71].

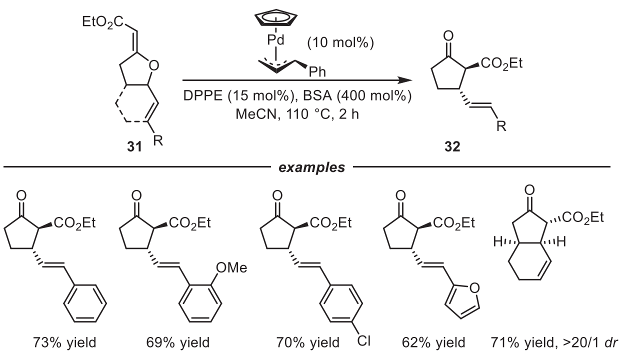
In addition, the heterocycles **31** could smoothly be converted to the thermodynamically more stable carbocyclic cyclopentanones **32** in 62%-73% yields by using CpPd(cinnamyl)/1,2-bis(diphenylphosphino)ethane (dppe) as the catalyst under elevated temperature that can facilitate the irreversible C–C bond reductive elimination (Scheme 14). Subsequently, to rationalize the regioselectivity of these reactions, Houk *et al.* performed density functional theory (DFT) calculations, which revealed that the C-O reductive elimination step is kinetically favorable [72]. The DFT calculations also revealed that the electron-withdrawing ester substituent was crucial as it could decrease the LUMO energy of the



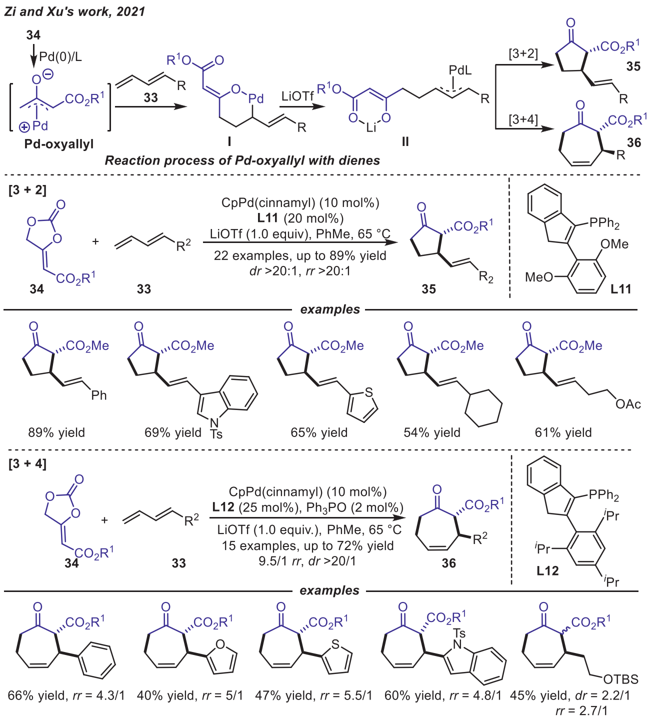
Scheme 12. General reaction process of Pd-catalyzed cycloadditions *via* Pd-oxyallyl intermediates.



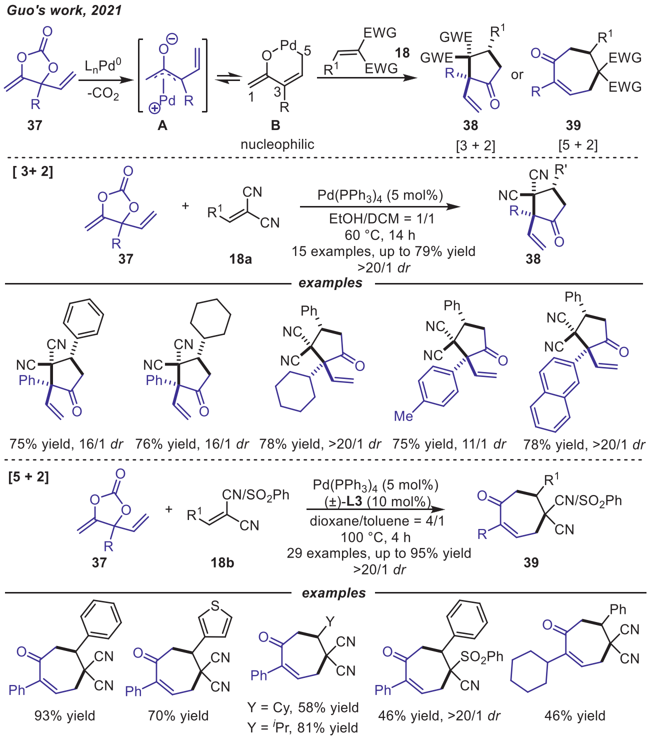
Scheme 13. Pd-catalyzed $[3+2]$ cycloadditions *via* Pd-oxyallyl intermediates.



Scheme 14. Pd-catalyzed conversion of tetrahydrofurans to cyclopentanones.



Scheme 15. Pd-catalyzed cycloadditions of MECs.



Scheme 16. Pd-catalyzed [3 + 2]/[5 + 2] cycloadditions of VMCCs.

Pd-oxyallyl species, leading to a more favorable energy match with the HOMO of the dienes.

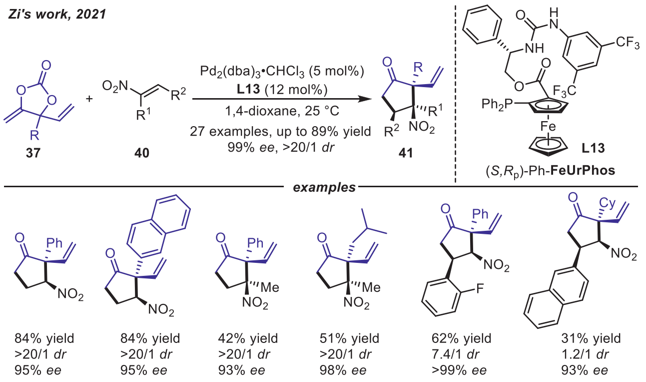
Despite the aforementioned successes, because C-O bond formation is kinetically favored, the [3 + 2] cycloadditions directly involving C-O reductive elimination are more general. In contrast, catalytic cycloaddition reactions of Pd-oxyallyl species directly through C-C reductive elimination to provide cyclic ketones remain challenging. In 2021, Zi and coworkers developed a method of lithium triflate-promoted [3 + 2] cycloaddition reactions of Pd-oxyallyl intermediates with 1,3-dienes (Scheme 15) [73]. The key to the success of this method was the coordination of the lithium ion with the alkoxide moiety, and this coordination disrupted the C-O reductive elimination pathway and promoted to form the metalenolate tethered Pd-π-allyl intermediate **II** that then could undergo intramolecular allylic attack by the enolate moiety to form the carbocyclic products **35** or **36**. Methylene ethylene carbonates (MECs) **34** were chosen as the precursors for the Pd-oxoallyl intermediate because they can be easily prepared by a one-step gold-catalyzed cyclization reaction [74]. The corresponding five-membered carbocycles **35** were delivered in good to high yields with high regioselectivities through [3 + 2] cycloadditions. Furthermore, the competitive [4 + 3] cycloaddition reactions were also accomplished by tuning the steric properties of the ligands. A larger sterically hindered ligand **L12** facilitated delivery of [4 + 3] products **36**. Importantly, DFT calculations indicated that when **L12** was used as the ligand, the activation energies of the [3 + 2] and [4 + 3] cycloadditions differed in the intramolecular allylic substitution step. The former is higher than the latter. Therefore, the [4 + 3] cycloaddition reaction was favored over the [3 + 2] cycloaddition, which was consistent with experimental observations.

In 2022, Zhang and coworkers developed asymmetric [3 + 2] cycloaddition reactions of Pd-oxyallyl specie precursors **29** or **34** with cyclic or acyclic 1,3-dienes to provide various tetrahydrofuran rings in high yields and selectivities, with 10 examples in yields up to 91% and *ee* values up to 98% [75]. In this process, a rationally designed chiral sulfinamide phosphine (Sadphos) type ligand was employed to improve the reaction efficiency and enantioselectivity.

With the development of heterocycles decarboxylative process, Guo's or Zi's groups respectively designed new cyclic carbonates vinyl methylene cyclic carbonates (VMCCs) that can provide carbon-carbon zwitterion species under palladium catalysis in 2021 [76,77].

Guo and coworkers [76] designed a series of vinyl methylene cyclic carbonates **37** as substrates that could be used as 1,3- or 1,5-zwitterion intermediates under palladium catalysis (Scheme 16). The general process of the reaction is briefly described. The VMCCs could react with Pd(0) to form vinyl-substituted Pd-oxyallyl species **A** with the loss of one molecular CO_2. The charge delocalization led to the equilibrium between **A** and Pd-oxypentadienyl species **B**. The C1 position of **B** had some nucleophilicity, allowing for the realization of an inverse electron demanding cycloaddition, which was quiet unlike the above electrophilicity of Pd-oxoallyl intermediate shown in Scheme 12. The five-membered carbocycles **38** were delivered through a [3 + 2] cycloaddition reaction in the presence of $Pd(PPh_3)_4$ catalyst with good to high yields and high diastereoselectivity and regioselectivity at 60 °C. Interestingly, by adding the ligand **L3** and increasing the temperature, the regioselectivity was completely reversed to [5 + 2] cycloadditon, yielding the seven-membered products **39**. In addition, in order to broaden the applicability of this reaction, the asymmetric examples were also explored, but the results were not satisfactory.

Almost at the same time, Zi and coworkers [77] realized an asymmetric [3 + 2] cycloaddition reaction of VMCCs **37** as precursors of vinyl-oxyallyl-Pd species (Scheme 17). In this case, Pd-oxoallyl was predicted by DFT calculations to be a highly electrophilic intermediate, and previously only electron-rich olefins could be available as cycloaddition partners. In contrast, the vinyl-oxoallyl-Pd species exhibited nucleophilicity, and its application would expand the range of olefins. Thus, the first enantioselective [3 + 2] cycloaddition reactions of vinyl-oxoallyl-Pd with electron-deficient nitroalkenes **40** were realized. Different ligands,



Scheme 17. Pd-catalyzed enantioselective [3 + 2] cycloadditions of VMCCs.

including Binap, ^{i}Pr-PhOX, Phosferrox, and DACH-PhTrost ligand, failed to enable the desired [3 + 2] cycloaddition. Only using phosphoramidite-type ligands can provide the cycloaddition product **41** in 40% yield with >20:1 *dr* and 40% *ee*. Inspired by the application of noncovalent interactions in asymmetric transition-metal catalysis [78–80], a new type of hydrogen-bond-donating phosphine ligand **L13** containing a tethered urea moiety was designed. Ligand **L13** can form hydrogen bonds with the electron-rich oxygen of Pd-oxyallyl, and this interaction has the potential to enhance chiral induction. Cyclopentanones **41** containing three contiguous stereocerters with *ee* values up to 99% and *dr*>20/1 were obtained by employing rationally designed FeUrPhos **L13**. The R group of **37** could be aryl, benzyl, alkyl, terminal alkenyl. In addition, not only various β-aryl nitroethylenes **40** but also α-methyl nitroethylenes **40** were well employed.

Recently, Liu and coworkers realized another [3 + 2] cycloaddition reaction of VMCCs **37** with [60]fullerenes in the presence of $Pd(PPh_3)_4$ [81]. In this process, VMCCs also participated in the cycloadditions as 1,3-C,C-zwitterion intermediates, which further demonstrated the reaction versatility and broad substrate applicability of VMCCs **37** as dipolar precursors.

In 2022, inspired by the above works, by using chiral H8-BINOL-derived bis-phosphite ligand **L14**, Cao and coworkers [82] developed Pd-catalyzed enantioselective [3 + 2] cycloaddition reactions of vinyl-substituted oxyallyl carbonates **42** with activated carbonyl compounds trifluoromethyl aryl ketones **43** or isocyanates **44**, delivering 1,3-dioxolanes **45** with up to 98% *ee* and 94/6 *dr* value or oxazolidinones **46** with up to 98% *ee*, respectively. In addition, an aminoketone **47** with α-chiral tetrasubstituted carbon was produced through ring-opening hydrolysis of **46** under basic conditions in 70% yield and 91% *ee* (Scheme 18).

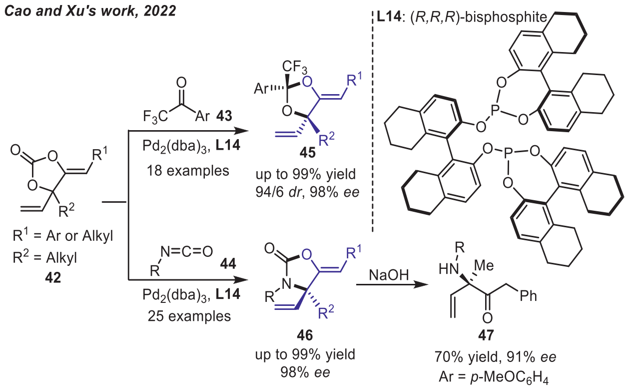
3.2. Pd-π-oxyallyl 1,4-zwitterions

Since the discovery of newly designed vinyl methylene cyclic carbonates (VMCCs), Guo and coworkers has achieved several Pd-catalyzed decarboxylative cyclizations to construct carbon- or heterocycles. During the process, they unexpectedly discovered the formation of pyrrole products when the reactions proceeded in the presence of amine nucleophile reagents [83]. The synthesis of a series of polysubstituted pyrroles **49** was then achieved under Pd catalysis (Scheme 19a). This decarboxylative protocol generated only CO_2 and H_2O as byproducts and operated at room temperature in air. Mechanistic investigations suggested that the stereoselective formation of the (*Z*)-configured γ-amino ketone intermediate **A** was crucial for the success of the reaction. The (*E*)-**A** was stable and isolatable. In contrast, the intramolecular nucleophilic attack of (*Z*)-**A** readily occurred to give intermediate **B**, which was subsequently dehydrated to give the corresponding pyrrole compounds **49**.

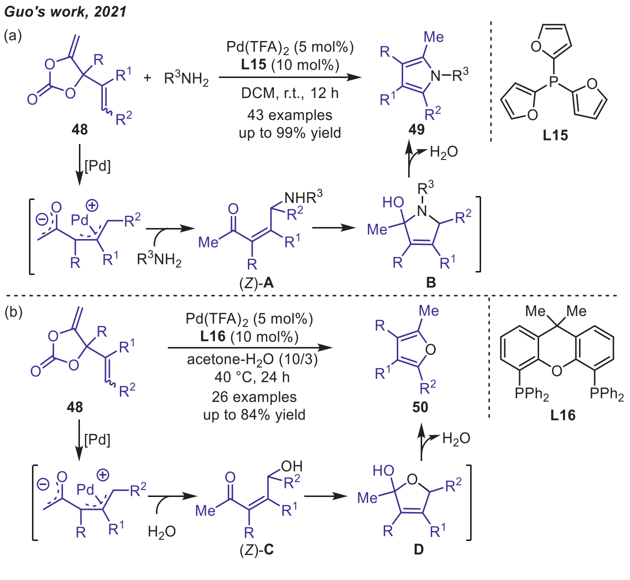
In the same year, Guo and coworkers reported a water-mediated catalytic decarboxylation process to form a series of polysubstituted furans **50** (Scheme 19b) [84]. This protocol also utilized VMCCs **48** as reaction substrates with broad functional group tolerance in the presence of $Pd(TFA)_2$ and **L16** in a mixed solvent of acetone and H_2O.

3.3. Pd-π-oxyallyl 1,5-zwitterions

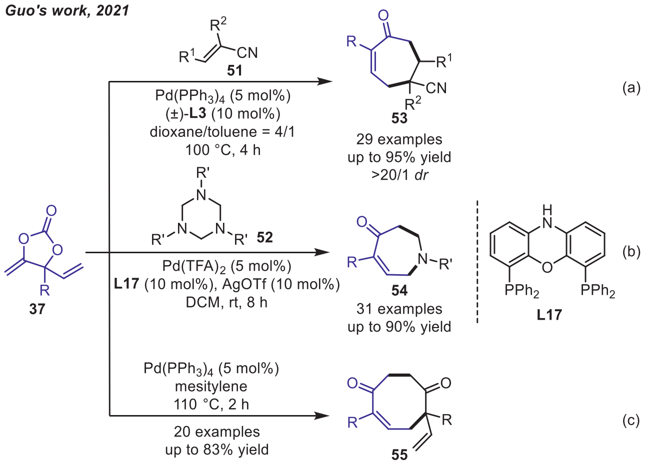
In addition to acting as three-atom synthons, VMCCs can also serve as five-atom synthons for [5 + 2] cycloadditions. Guo and coworkers obtained the [5 + 2] cycloaddition products **53** from the reaction of VMCCs **37** and activated alkenes **54** with high selectivity and good to high yields under $Pd(PPh_3)_4$ and ligand **L3** co-catalysis (Scheme 20a) [76]. When the reaction substrates were switched from olefins **51** to triazines **52**, non-fused *N*-aryl azepane derivatives **54** were obtained *via* [5 + 2] cycloaddition reactions promoted by Pd catalysis and AgOTf [85]. In this process, in order to gain insights into the reaction pathways, DFT calculations showed that the origin of the exclusive [5 + 2] rather than the [3 + 2] cycloaddition process was due to a much lower barrier for the formation of azepanes **54** (Scheme 20b). Besides, the same group [86] found that two molecules of vinyl Pd-oxyallyl species



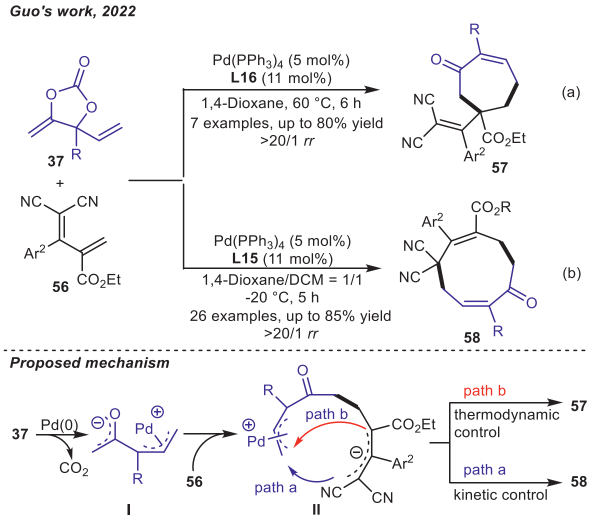
Scheme 18. Pd-catalyzed enantioselective [3 + 2] cycloadditions of VMCCs with aryl ketones or isocyanates.



Scheme 19. Pd-catalyzed [4 + 1] cycloadditions of VMCCs.



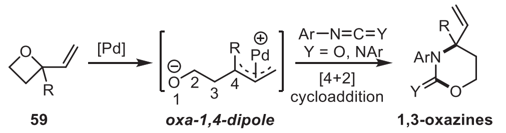
Scheme 20. Pd-catalyzed $[5+n]$ cycloadditions of VMCCs.



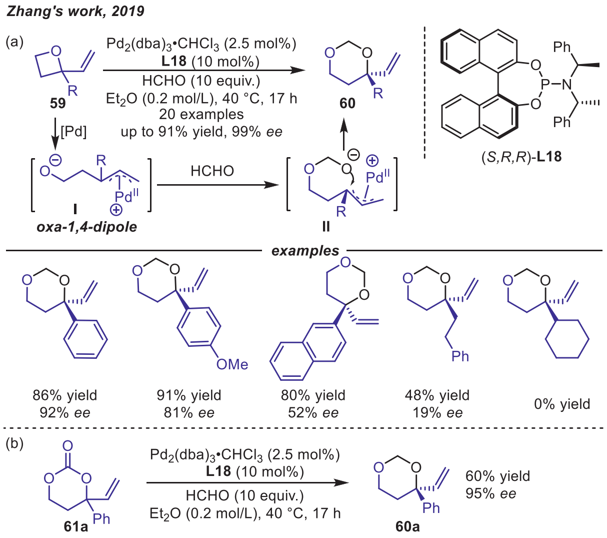
Scheme 21. Pd-catalyzed $[5+n]$ cycloadditions of VMCCs and allylidenemalononitriles.

could dimerize regiospecifically to form highly functionalized nonbridged cyclooctanoids **55**. This methodology demonstrated the vinyl Pd-oxyallyl species possessing both electrophilic and nucleophilic properties (Scheme 20c).

Guo and coworkers also reported ligand-controlled Pd-catalyzed decarboxylative $[5+4]$ and $[5+2]$ cycloadditions by utilizing VMCCs **37** as C5-synthons [87]. When using a diphosphine ligand **L16**, only the thermodynamically favorable $[5+2]$ cycloaddition products **57** were given (Scheme 21a). The utilization of a monophosphine ligand **L15** could switch the regioselectivity, prompting the challenging nine-membered compounds **58** to be the major products *via* the $[5+4]$ cycloadditions (Scheme 21b). A reaction mechanism was proposed. First, cyclic carbonate **37** underwent decarboxylation in the presence of a palladium catalyst to give the zwitterionic Pd-π-allyl enolate intermediate **I**. Followed by nucleophilic attack on dienes **56**, the new zwitterionic intermediate **II** was generated. The regio-divergent nucleophilic cyclization under kinetic (path a) or thermodynamic control (path b) generated the corresponding nine- or seven-membered carbocycles, respectively, with the regeneration of the palladium catalyst.



Scheme 22. General Pd-catalyzed reactions of vinyl oxetanes.



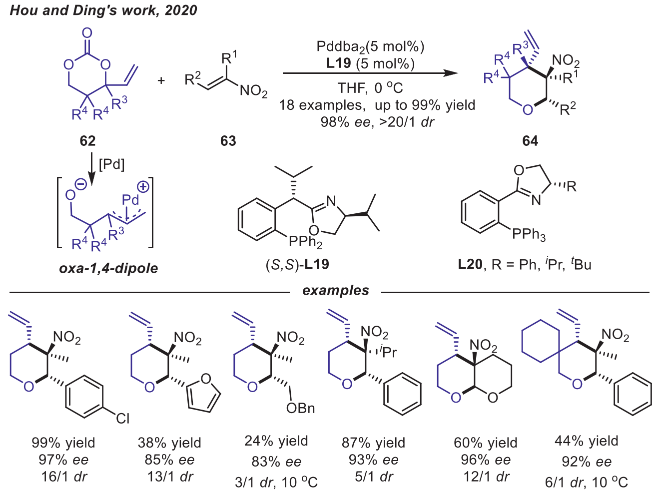
Scheme 23. Pd-catalyzed $[4+2]$ cycloadditions of vinyl oxetanes.

3.4. Pd-π-allyl 1,4-zwitterions derived from vinyl oxetanes and their analogues

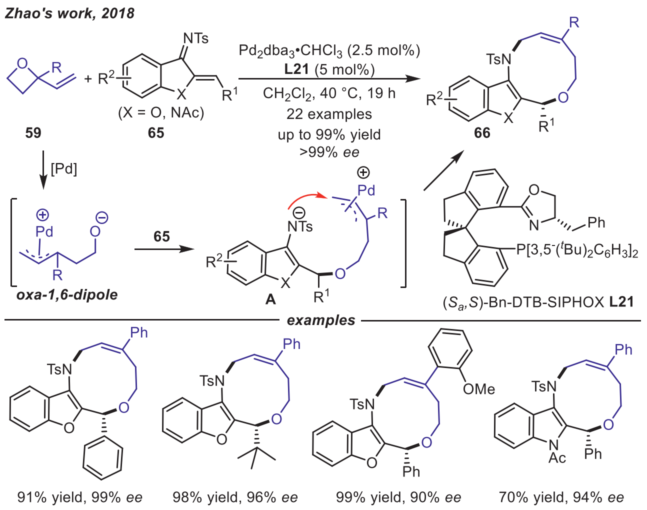
Since Alper and coworkers reported the Pd-catalyzed allylic cycloaddition of vinyloxetanes **59** with isocyanates/carbodiimides to provide compounds 1,3-oxazines in a racemic form in 1999 [88], which was the first report on the oxa-1,4-dipoles (Scheme 22). In addition to cycloaddition reactions, vinyloxetanes **59** also delivered acyclic products [89,90] and dihydropyrans [91] *via* ring-opening allylic substitution and ring-expansion reactions. However, metal-catalyzed asymmetric cycloaddition reactions of vinyloxetanes remained to be unknown for a long time.

In 2019, Zhang and coworkers [92] achieved an asymmetric $[4+2]$ cycloaddition of vinyloxetanes **59** with an abundant feedstock formaldehyde in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ and phosphoramidite ligand **L18** under mild conditions to provide 4-substituted 4-vinyl-1,3-dioxanes **60** in high yields with good to excellent enantioselectivities (Scheme 23a). Vinylpropylene carbonate (VPC) **61a**, which was synthesized from the corresponding 1,3-diol [93], was also tested instead of vinyl oxetanes **59** for this cycloaddition reactions. As shown in Scheme 23b, the same reaction conditions were effective for the cycloaddition of VPC **61a** with formaldehyde to furnish 1,3-dioxane **60a** in 60% yield with high enantioselectivity (95% *ee*).

Almost at the same time, Hou and coworkers [94] paid attention to the oxa-1,4-dipoles and developed the first asymmetric $[4+2]$ cycloaddition reaction of VPCs **62** with singly activated electron deficient alkenes **63** catalyzed by a combination of Pd and the newly developed benzyl-substituted P,N-ligand **L19** (Scheme 24). A range of tetrahydropyrans **64** containing three continuous chiral centers were obtained in high yields with high diastereo- and enantioselectivities. Reactions using commercial P,N-ligands **L20** produced **64** in high yields with varied enantioselectivities, but with very low diastereoselectivities. Excitingly, if benzylic substituted P,N-ligand (*S,S*)-**L19** with isopropyl as a substituent at the



Scheme 24. Pd-catalyzed [4+2] cycloadditions of vinylpropylene carbonates (VPCs).

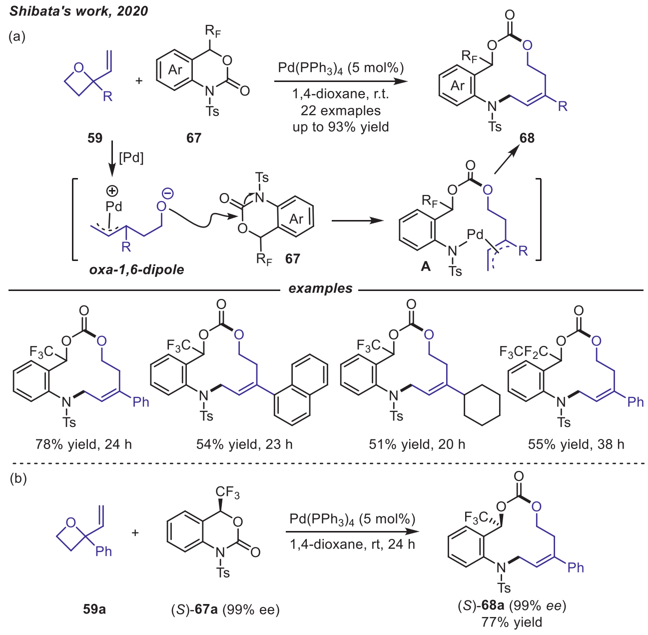


Scheme 25. Pd-catalyzed [6+4] cycloadditions of vinyl oxetanes.

benzylic position was used, both the yields and diastereo- and enantioselectivities were significantly improved. This class of benzylic substituted P,N-ligands was further applied in the palladium-catalyzed asymmetric [3+2] cycloadditions of vinyl epoxides with alkynyl esters as well [95].

3.5. Pd-π-allyl 1,6-zwitterions derived from vinyl oxetanes and their analogues

Vinyl oxetanes **59** are commonly used as 1,4-zwitterionic precursors to achieve Pd-catalyzed [4+2] cycloaddition reactions [96]. Until 2018, Zhao and coworkers reported the first Pd-SIPHOX **L21** complex-catalyzed enantioselective [6+4] cycloaddition reactions of vinyl oxetanes **59** with azadienes **65** (Scheme 25) [97]. Various benzofuran- as well as indole-fused heterocycles **66** could be accessed in excellent yields and enantioselectivities. In this context, vinyl oxetanes were involved in the reaction as oxa-1,6-dipole precursors *via* oxidative addition of Pd(0). Then, the alkoxide moiety of oxa-1,6-dipoles underwent Michael addition with azadienes **65** to give intermediate **A**. Finally, the [6+4] cycloaddition products were obtained through intramolecular *N*-allylic substitution. In fact, the preparation of ten-membered rings by cycloaddition reactions remains scarce in organic synthesis. This reaction provided a fast and efficient method to construct of chiral 10-membered rings.

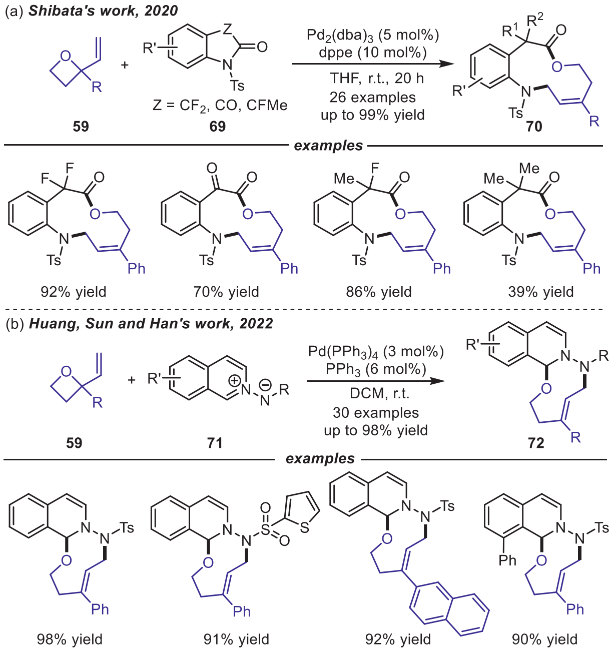


Scheme 26. Pd-catalyzed [6+6] cycloadditions of vinyl oxetanes.

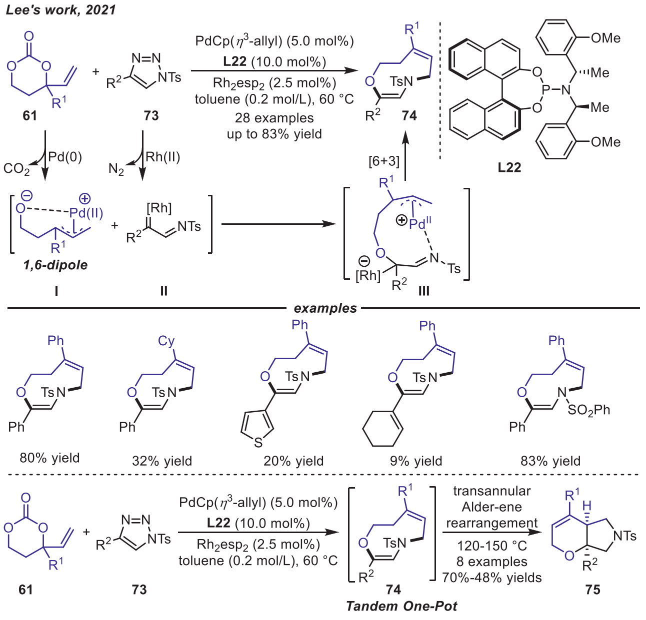
In 2020, Shibata and co-workers reported another reaction on the use of vinyl oxetanes **59** as 1,6-dipoles *via* Pd catalysis (Scheme 26) [98]. In this case, a non-decarboxylated Pd-catalyzed [6+6] cycloaddition of six-membered trifluoromethyl benzo[*d*][1,3]oxazinones **67** with vinyl oxetanes **59** was developed, which was an efficient way for the synthesis of trifluoromethylated 12-membered heterocycles **68**. The possible reaction mechanism was shown in Scheme 26. First, the oxa-1,6-dipoles were generated *in situ* by the reaction of Pd with vinyl oxetanes **59**. Then, nucleophilic attack on the carbonyl moiety of **67** by the oxygen anion of the oxa-1,6-dipoles induced ring opening *via* C-N bond breakage of **67**, which led to the formation of the Pd complex intermediate **A** that was confirmed by LC-MS analysis ($m/z = 940.0$, M+Na). Finally, the reductive elimination of the Pd complex **A** provided [6+6] cycloaddition products **68**. In addition, the reaction of vinyl oxetane **59a** with (*S*)-**67a** under standard conditions afforded the chiral trifluoromethyl-substituted 12-membered heterocycle (*S*)-**68a** in 77% yield and 99% *ee* without any loss of the enantiopurity compared to the starting material (*S*)-**67a**.

In the same year, Shibata and co-workers [99] altered six-membered trifluoromethyl benzo[*d*][1,3]oxazinones **67** into difluorooxindoles, isatins or their analogs in reaction system, thus producing functionalized 11-membered heterocycles **70** in good to high yields by Pd-catalyzed [6+5] cycloadditions (Scheme 27a). In this process, vinyl oxetanes **59** smoothly *in situ* generated oxa-1,6-dipoles in the present of $Pd_2(dba)_3$ and dppe. The reaction mechanism was similar to the catalytic cycle of Scheme 26.

Recently, Huang and coworkers achieved a palladium-catalyzed selective [6+3] cycloaddition reaction of 2-vinyl oxetanes **59** and *N*-iminoisoquinolinium ylides **71** to deliver 9-membered *N,N,O*-heterocycles **72** in moderate to high yields (Scheme 27b) [100]. A range of 2-aryl-2-vinyl oxetanes **59** were examined, while 2-methyl-2-vinyl oxetanes failed to provide the corresponding heterocycle, possibly owing to the poor stability of the generated zwitterionic allylpalladium intermediates.

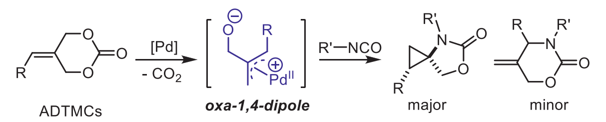


Scheme 27. Pd-catalyzed [6 + 5]/[6 + 3] cycloadditions of vinyl oxetanes.

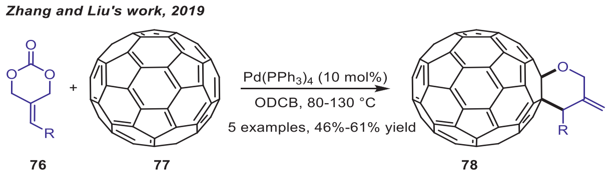


Scheme 28. Pd-catalyzed [6 + 3] cycloadditions of vinylpropylene carbonates.

VPCs can also act as 1,6-dipole precursors, which is similar to vinyl oxetanes. VPCs could undergo oxidative addition catalyzed by palladium catalysis followed by spontaneous decarboxylation to produce oxa-1,6-dipoles. In 2021, Lee and coworkers [101] reported a novel Pd(0)/Rh(II) dual catalytic strategy to enable [6 + 3] cycloadditions between VPCs **61** and *N*-sulfonyl-1,2,3-triazoles **73** to provide nine-membered 1,4-oxazonines **74** in moderate to high yields (Scheme 28). The plausible reaction pathway was depicted. First, the Pd(0) and Rh(II) catalysts selectively activated **61** and **73**, respectively, to generate 1,6-dipole **I** and 1,3-dipole equivalent α-imino rhodium(II) carbenoid intermediate **II**. Then, the oxygen anion of intermediate **I** could be added nucleophilically to the electrophilic carbenoid carbon of intermediate **II** to deliver the Pd/Rh-bimetalated intermediate **III**. Finally, nine-membered oxazonines **74** were formed through intramolecular cyclization pathways. Moreover, the nine-membered oxazonines **74** could be further converted to the corresponding *cis*-fused bicyclic hexahydropyranopyrroles **75** in moderate to good yields through the transannular Alder-ene rearrangement in one pot.



Scheme 29. General Pd-catalyzed cycloaddition of alkylidenetrimethylene carbonates (ADTMCs).



Scheme 30. Pd-catalyzed [4 + 2] cycloadditions of ADTMCs and fullerene.

3.6. Pd-π-allyl zwitterions derived from alkylidenetrimethylene carbonates (ADTMCs)

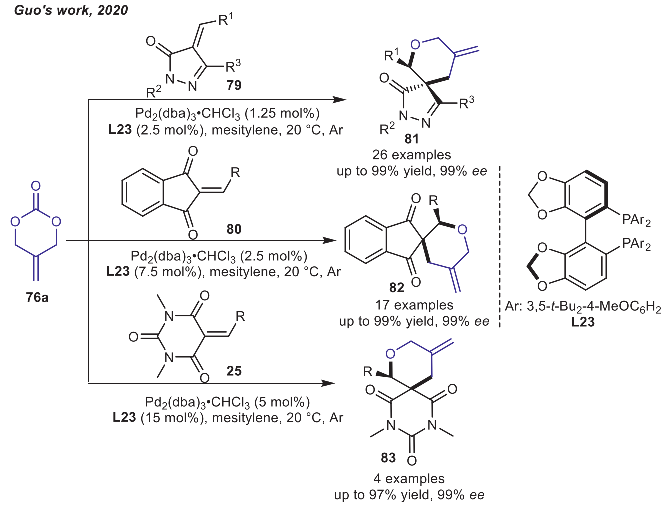
In addition to VPCs, 2-alkylidenetrimethylene carbonates (ADTMCs), first reported by Tsuji and coworkers [102] in 1984, were also applied to Pd-catalyzed cycloaddition reactions with isocyanates by Hayashi and co-workers in 2011 (Scheme 29) [103]. The application of ADTMCs has developed rapidly in recent years. Interestingly, compared to VPCs or vinyl oxetanes, ADTMCs were used only as 1,4-dipole species for Pd-catalyzed intermolecular cycloadditions with different dipolarophiles, and the cycloaddition products contained an exocyclic double bond.

In 2019, Liu and coworkers [104] explored a Pd-catalyzed [4 + 2] cycloaddition between ADTMCs **76** and fullerene **77** to afford fullerene-fused tetrahydropyrans **78** in medium to good yields (Scheme 30). Although there were only 5 examples, this methodology revealed the application of ADTMCs as oxa-1,4-dipolar precursors under palladium catalysis.

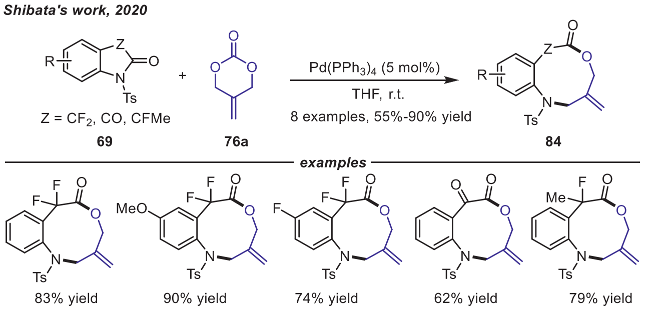
In 2020, Guo and co-workers [105] realized palladium-catalyzed asymmetric [4 + 2] cycloadditions of ADTMCs **76a** with olefins derived from pyrazolones **79**, indandiones **80** or barbiturates **25** to provide pharmacologically interesting chiral tetrahydropyrane-fuse spirocyclic scaffolds **81-83** in good to excellent yields and high enantioselectivities (Scheme 31). The chiral diphosphine ligand **L23** was proved to be the best choice. In this process, ADTMCs were designed to generate oxa-1,4-dipoles *via* palladium-catalyzed oxidative addition followed by spontaneous decarboxylation.

In the same year, Shibata and coworkers [99] applied **76a** in the Pd-catalyzed [4 + 5] cycloaddition reactions with isatins and their analogs to access 9-membered heterocycles **84** in good to excellent yields (Scheme 32). The highly electron withdrawing nature of the Z group in combination with the nucleophilic attack of the *in-situ* generated 1,4-dipole species induced the C-N bond breakage of substrates **69**. The desired products **84** were obtained by subsequent intramolecular cyclization.

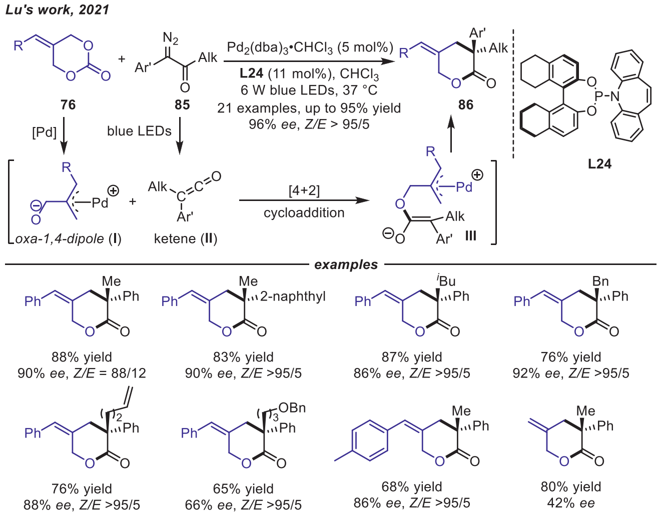
In 2021, Lu and co-workers successfully completed the Pd-catalyzed, visible-light-induced asymmetric [4 + 2] cycloaddition reaction of ADTMCs **76** with α-adiazoketones **85** (Scheme 33) [106]. The proposed mechanism began with the generation of oxa-1,4-dipole intermediates **I** from the reaction of ADTMCs and Pd(0) catalyst. Meanwhile, ketenes **II** were readily generated from α-diazoketones **85** *via* a photo-Wolff rearrangement under blue LEDs.



Scheme 31. Pd-catalyzed [4 + 2] cycloadditions of ADTMCs and alkenes.

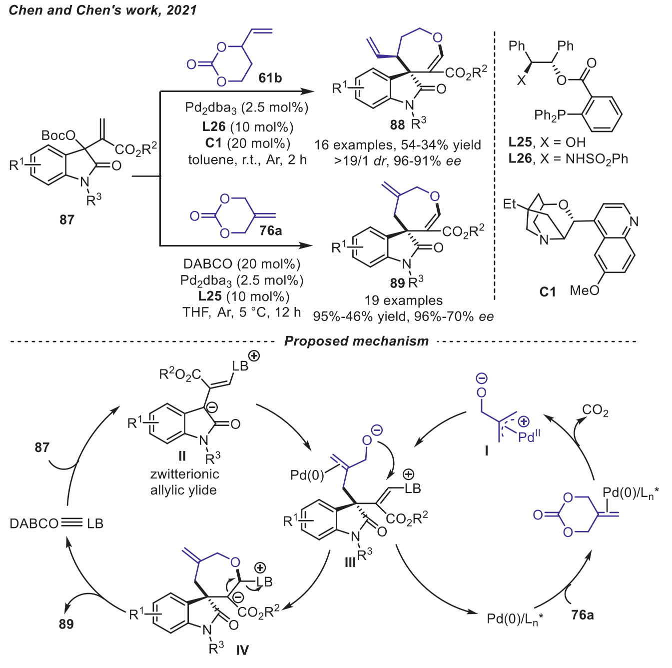


Scheme 32. Pd-catalyzed [4 + 5] cycloadditions of ADTMCs.

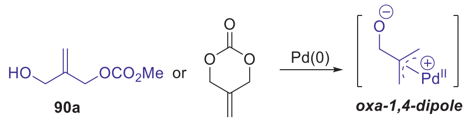


Scheme 33. Pd-catalyzed [4 + 2] cycloadditions of ADTMCs and ketenes.

Then, intermolecular nucleophilic addition/intramolecular asymmetric allylic alkylation sequence produced 6-membered lactones **86** bearing exocyclic olefin. The chiral phosphoramidite ligand **L24** proved to be efficient and provided chiral products **86** in 50%-95% yields with high selectivities. The reaction had a wide range of substrate applicability, allowing the use of α-diazoketones containing Me, Et, *n*Bu, *i*-Bu, Bn and so on. Aryl substituted ADTMCs with different electrical properties could be employed. Moreover, unsubstituted ADTMCs also reacted smoothly; whereas alkyl-substituted ADTMCs failed to produce the desired lactone products under the standard conditions.



Scheme 34. Pd-catalyzed [4 + 3] cycloadditions *via* Pd-1,4-oxa-dipoles.

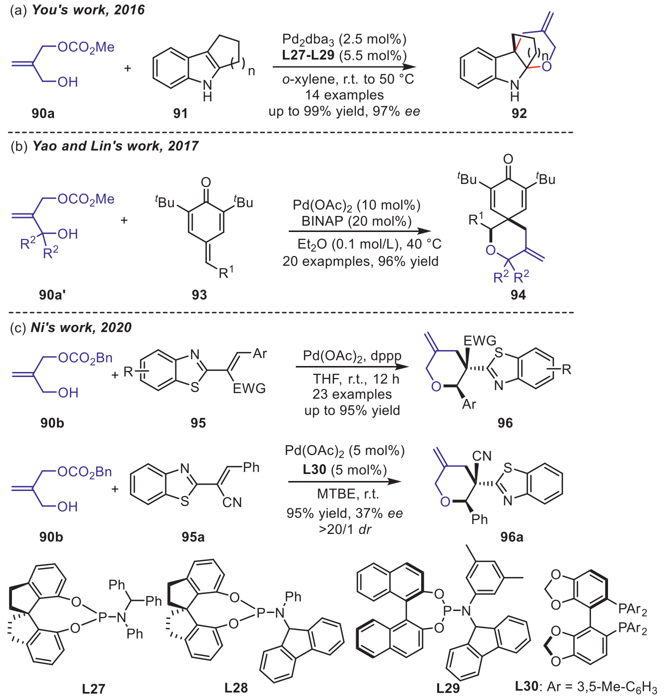


Scheme 35. The formation of oxa-1,4-dipole from ADTMC and 3-hydroxy-2-methylenepropyl methyl carbonate.

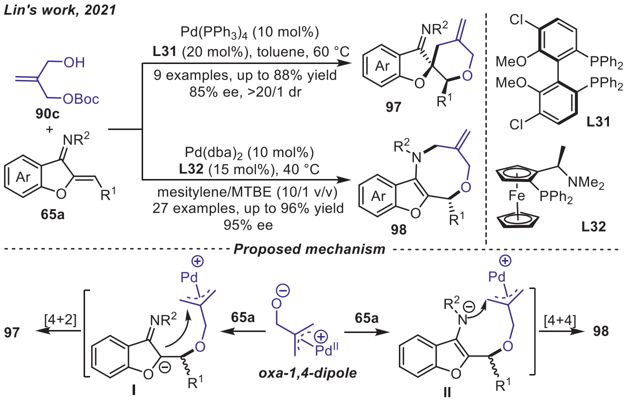
Chen and coworkers [107] achieved that the isatin-derived Morita-Baylis-Hillman (MBH) carbonates **87** could *in situ* form zwitterionic allylic ylides **II** under the catalysis of Lewis bases (LBs), such as DABCO, DMAP or PPh_3 (Scheme 34). ADTMCs **76a** or VPCs **61b** would readily generate zwitterionic Pd-π-allyl intermediates upon Pd-catalyzed CO_2 dissociation. Therefore, an asymmetric [4 + 3] cycloaddition reaction between isatin-derived MBH carbonates **87** and oxygen-containing 1,4-dipoles through the process of intermolecular allyl substitution/intramolecular cyclization was realized (Scheme 34) [108]. A range of spirooxindoles incorporating an oxepane frameworks **88** or **89** were smoothly constructed in moderate to good yields with high stereocontrol. Phosphine ligands bearing hydrogen bonding motifs were suitable, such as **L25**, **L26**, which could be readily obtained from chiral 1,2-aminoalcohol or 1,2-diol, respectively [77,109]. In this process, the hydrogen bonding interactions played a pivotal role in enhancing reactivity and enantiocontrol.

3.7. Pd-π-allyl zwitterions derived from 3-hydroxy-2-methylenepropyl carbonates

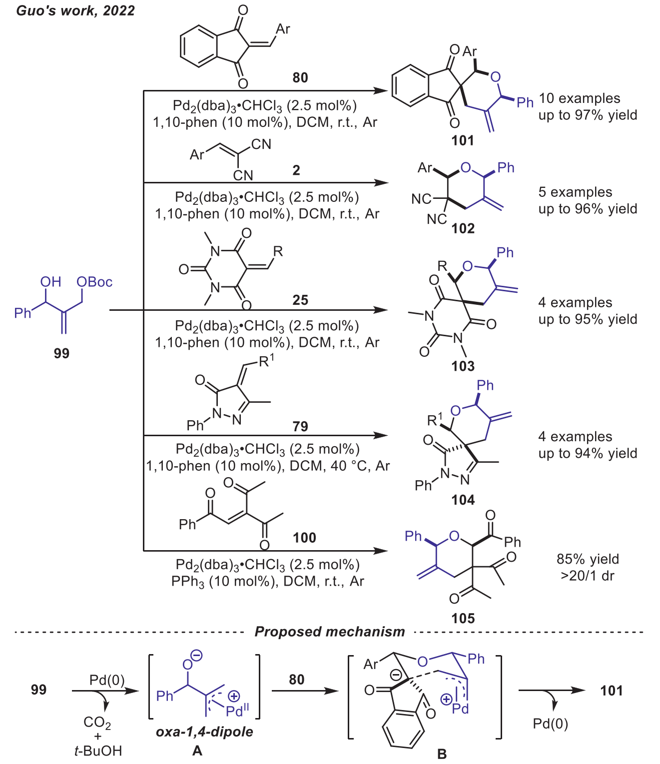
Analogous to ADTMCs, 3-hydroxy-2-methylenepropyl carbonates could be transformed *in situ* into the same oxa-1,4-dipole intermediate under palladium catalysis (Scheme 35). The 3-hydroxy-2-methylenepropyl methyl carbonate **90a**, first reported by Pátek and co-workers in 1996 [110], was synthesis in one step. The allyl carbonates bearing a nucleophilic alcohol side chain have been applied in Pd-catalyzed [4 + 2] cycloadditions with indoles **91** or *para*-quinone methides **93** by You's [111] or Yao's groups [112] in



Scheme 36. Pd-catalyzed [4 + 2] cycloadditions of 3-hydroxy-2-methylenepropyl methyl carbonate.



Scheme 37. Pd-catalyzed [4 + 2] and [4 + 4] cycloadditions of *tert*-butyl[2-(hydroxymethyl)allyl] carbonate.



Scheme 38. Pd-catalyzed [4 + 2] cycloadditions of hydroxy-tethered allyl carbonate.

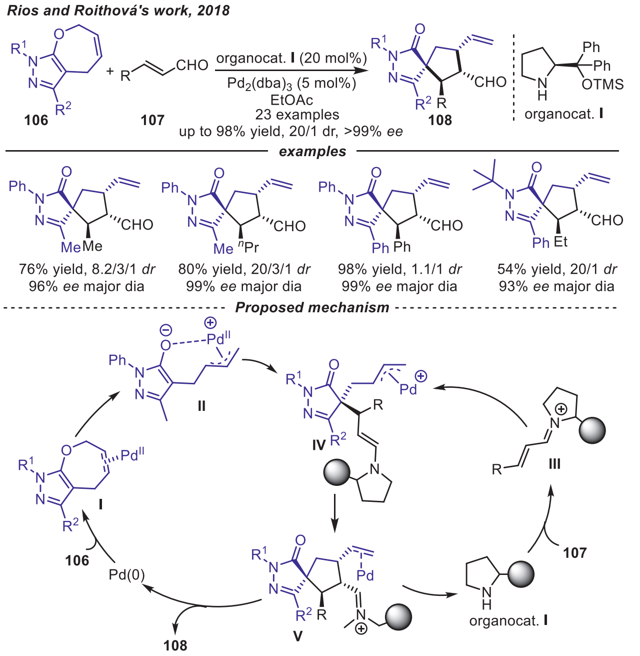
2016 and 2017, respectively (Schemes 36a and b). Since then, the application of 3-hydroxy-2-methylenepropyl carbonates with a nucleophilic alcohol side chain in cycloadditon reactions has been opened.

In 2020, 3-hydroxy-2-methylenepropyl carbonate **90b** was further used to deliver an array of 3-methylenetetrahydropyrans **96** in good to excellent yields *via* [4 + 2] cycloadditon reactions with 2-alkenylbenzothiazoles **95** by Ni and coworkers (Scheme 36c) [113]. When asymmetric syntheses were attempted, Trost ligands or monodentate phosphoramidite ligands were tested. Unfortunately, neither was able to yield the product of the [4 + 2] cycloaddition reaction. Chiral bidentate ligands were also tested, and only axially chiral bisphosphine ligand **L30** realized the enantioselectivity and gave **96a** in 95% yield and 37% *ee*.

Subsequently, Lin and coworkers [114] developed the ligand-controlled asymmetric [4 + 2] or [4 + 4] cycloaddition reactions of *tert*-butyl[2-(hydroxymethyl)allyl]carbonate **90c** with benzofuran-derived azadienes **65a** by palladium catalysis (Scheme 37). Using chiral P,P-ligand (*S*)-ClMeO-BIPHEP **L31**, the tetrahydropyran-fused spirocyclic compounds **97** with good to high enantio- and diastereoselectivities were obtained in good yields *via* the [4 + 2] cycloaddition reactions of intermediate **I** (Scheme 37). When taking advantage of chiral P,N-ligand (*S*,R_p)-PPFA **L32**, the chemo- and regio-selectivities were switched to synthesize a variety of benzofuro[2,3-*c*][1,5] oxazocines **98** in good yields with excellent enantioselectivities *via* the [4+4] cycloaddition reactions of intermediate **II**. The C- or N-nucleophilic sites could be specifically discriminated during the subsequent intramolecular allylic substitution processes after initial oxo-Michael addition due to the inherent steric and electronic effects of two different chiral ligands.

Almost simultaneously, Archambeau and coworkers [115] also realized a similar [4 + 4] cycloadditon reaction using dppe as the ligand between benzofuran-derived azadienes **65a** with *tert*-butyl[2-(hydroxymethyl)allyl] carbonate **90c**. In contrast to the above work, the difference was the absence of asymmetric examples. Noticeably, linear azadienes were also involved and yielded monocyclic eight-membered heterocycles with complete regioselectivity.

In 2022, Guo and coworkers [116] achieved the construction of tetrahydropyran derivatives **101**-**105** in moderate to high yields with excellent *dr* values (>20:1 *dr*) *via* palladium-catalyzed [4 + 2] cycloaddition reactions of hydroxy-tethered allyl carbonate **99** with five electron-deficient alkenes, including indandione-based alkene **80**, 1,1-dicyanoalkenes **2**, barbiturate-derived alkenes **25**, pyrazolone-derived alkenes **79**, and acyl-substituted alkene **100** (Scheme 38). Interestingly, compared with the previous 3-hydroxy-2-methylenepropyl carbonates, the α-position of oxygen atom in the dipole precursors has one extra substituent in **99**, and therefore the α-position of the oxygen atom in the corresponding tetrahydropyran products also has an additional chiral center. The possible mechanism is described using **99** and indandione-based alkenes **80** as substrates. First, the oxa-1,4-dipole intermediate **A** is produced by palladium-catalyzed decarboxylation/deprotonation



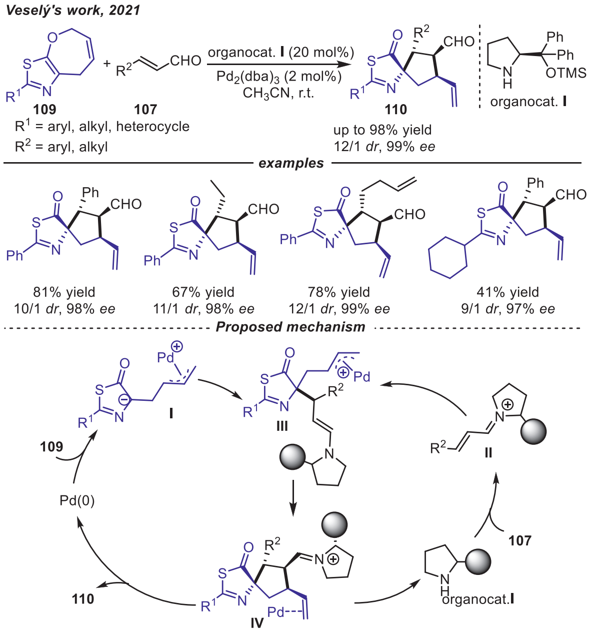
Scheme 39. Pd-catalyzed ring contraction/formal cycloadditions with pyrazolone derivatives.

of substrate **99** to release of CO_2 and *t*-BuOH. The intermediate **A** subsequently attacks indandione-based alkenes **80** to give the intermediate **B**. The two aryl groups in the six-membered ring transition state of **B** are located at equatorial positions, so that the *cis*-isomer serves as the major product when undergoing intramolecular cyclization.

Very recently, Yuan and coworkers also developed the [4+2] cycloaddition reaction of 2-alkylidenetrimethylene carbonates **76** or 2-(hydroxymethyl)-3-arylallyl carbonates **90** with 3-nitroindoles to deliver a wide range of indoline-fused tetrahydropyrans in good yields with excellent diastereoselectivities [117]. That was due to the formation of the same oxa-1,4-dipole intermediate catalyzed by palladium using different dipole precursors. Unexpectedly, Liu and coworkers also involved 2-alkylidene-trimethyl carbonates (ADTMCs) as 1,3-all-carbon dipoles in the [3+2] cycloaddition reactions with [60]fullerenes [81].

3.8. Miscellaneous

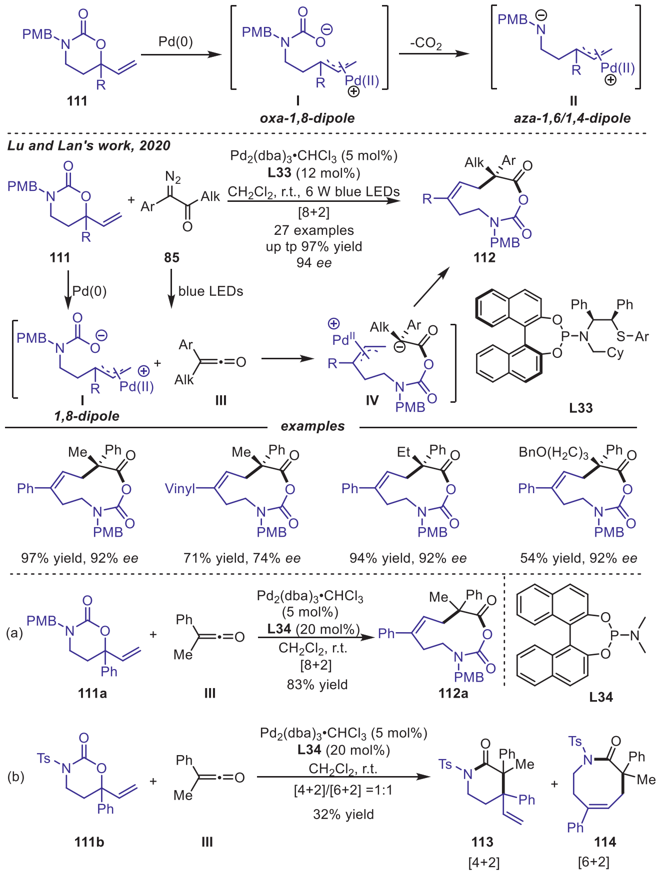
In 2018, Rios and coworkers [118] successfully reported the first ring contraction/formal [6+2] cycloaddition of pyrazolone derivatives **106** with α,β-unsaturated aldehydes **107** in synergistic Pd(0)/chiral secondary amine catalysis to obtain [5,5]-spiropyrazolone derivatives **108** in excellent yields and stereoselectivities (Scheme 39). The reaction mechanism started with the coordination of palladium to the double bond of substrates **106**. Palladium not only interacted with the C=C double bond, but also coordinated with one molecule of acetonitrile to form complex **I**. Complex **I** rearranged to form intermediate **II**. Meanwhile, iminium intermediate **III** was formed *via* condensation of enal **107** with a chiral secondary amine, which underwent conjugate addition with intermediate **II** to give complex **IV**. The desired products **108** were afforded after intramolecular allylic substitution and hydrolysis of iminium. In addition, the protonated form of the key palladium-activated intermediate **II** can be detected by mass spectrometry and its structure was characterized by infrared spectroscopy and DFT calculations.



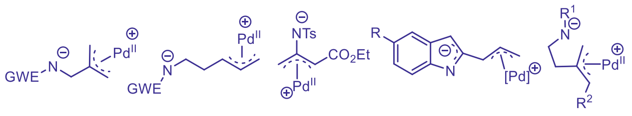
Scheme 40. Pd-catalyzed ring contraction/formal cycloadditions with thiazole derivatives.

In 2021, Veselý and coworkers [119] also developed similar cycloadditions between thiazole derivatives **109** and α,β-unsaturated aldehydes **107**. The reactions were catalyzed by the cooperative achiral Pd(0) complex and a chiral secondary amine to deliver the corresponding chiral spirothiazolones **110** in yields up to 98%, as well as 12/1 *dr* and 99% *ee* values (Scheme 40). The process proceeded by forming the transient zwitterionic π-allyl palladium intermediates **I** and chiral α,β-unsaturated iminium ions **II**. Next, iminium intermediate **II** underwent conjugate addition to intermediate **I**, affording enamine **III**. After intramolecular 5-*exo-trig* cyclization and hydrolysis of iminium, spirocycles **110** were formed and Pd(0) was returned to the catalytic cycle.

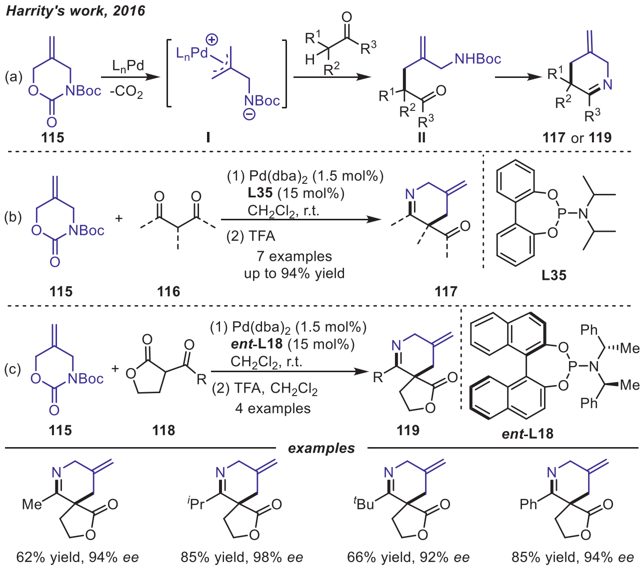
The development of 1,8-dipoles has lagged significantly compared to Pd-π-allyl 1,4- or 1,6-dipoles. In 2020, Lu and coworkers [120] developed Pd-catalyzed [8+2] cycloaddition reactions with α-diazoketones **85** using carbamates **111** as non-decarboxylated Pd-containing 1,8-dipoles **I** rather than decarboxylated intermediate **II** to provide various 10-membered monocyclic products **112** bearing chiral quaternary stereocenters in the presence of chiral ligand **L33** under mild conditions (Scheme 41). Decarboxylation occurred in most dipole cycloaddition reactions based on the palladium-catalyzed reactions involving carbamate substrates, producing active Pd-π-allyl zwitterionics by releasing CO_2 [44]. Interestingly, in this process, the carbonate anions of dipoles **I** could attack the ketenes **III** *via* nucleophilic addition to produce intermediates **IV**, and subsequently intramolecular allylation of the enolate intermediates **IV** would yield 10-membered monocyclic products **112**. Moreover, the electronic effect of the amine played a key role in the stability of the reaction intermediates. Under the same conditions, tosyl (Ts)- and 4-MeO-benzyl (PMB)-substituted vinyl carbamates gave very different results (Scheme 41b *vs.* 41a). The former reaction provided an inseparable mixture of 6- and 8-membered cycloadducts **113** and **114**, neither of which retained the CO_2 unit (Scheme 41b). While the latter reaction did delivere the desired 10-membered monocyclic compound **112a** (as racemate) in a good yield (Scheme 41a). These results are similar to that of γ-methylidene-δ-valerolactones, where the electron-rich α-substituted of γ-methylidene-δ-valerolactones could act as 1,6-dipoles by inhibiting the decarboxylative process [56].



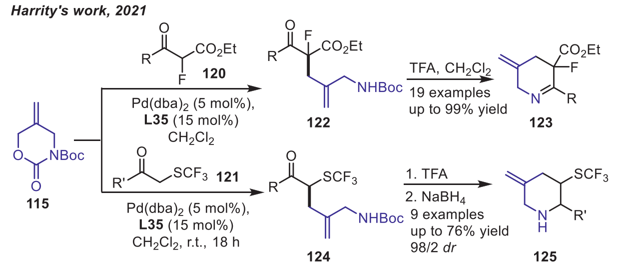
Scheme 41. Pd-catalyzed [8 + 2] cycloadditions of vinyl carbamates.



Scheme 42. Pd-π-allyl zwitterions bearing a *N*-centered anion.



Scheme 43. Pd-catalyzed [4 + 2] cycloadditions of carbamate **115**.



Scheme 44. Pd-catalyzed [4 + 2] cycloadditions of carbamate **115** with α-fluoro β-ketoesters or α-SCF$_3$-substituted ketones.

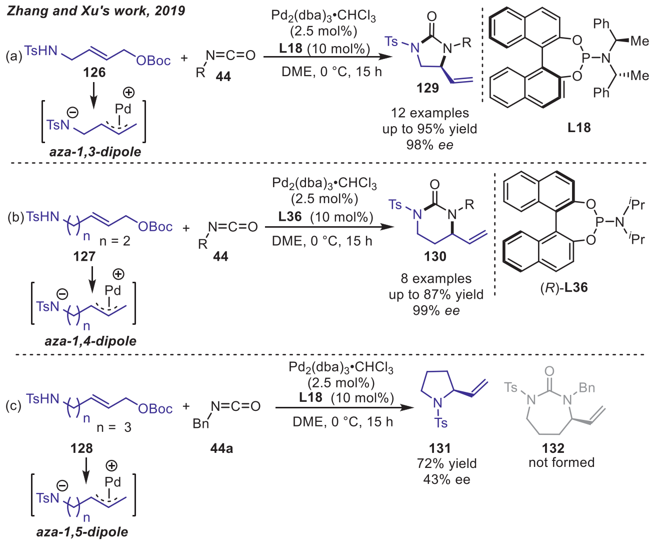
4. Pd-π-allyl zwitterions bearing a *N*-centered anion

N-Heterocycles have received widespread attention due to their bioactivities and pharmaceutical applications [121–123]. Therefore, it is necessary to develop facile and efficient dipolar cycloaddition reactions for the selective and diverse construction of various *N*-heterocycles. In addition to the well-known vinyl aziridines as aza-dipole precursors, in 2006, Tunge and coworkers [124] observed for the first time aza-1,4-zwitterionic Pd complexes generated by palladium catalyzed decarboxylation of 6-vinyl-1,3-oxazinanones, undergoing [4 + 2] cycloaddition with electron-deficient olefins. On the basis of those preliminary studies, several new 1,*n*-C,N-dipoles have been recently developed (Scheme 42).

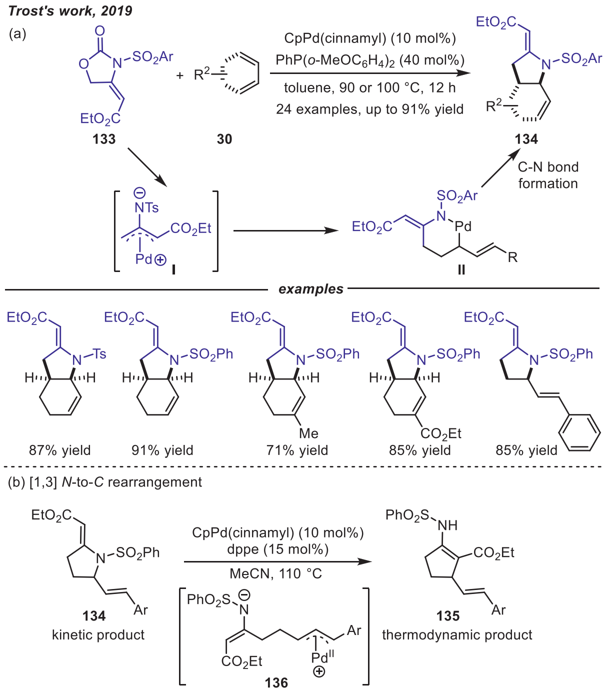
In 2016, Harrity and coworkers [125] established a short and scalable synthetic route to carbamate **115**, which was able to adapt the sequence developed by Suzuki [126]. Then, the [4 + 2] cycloaddition reactions of carbamate **115** that was used as a precursor of 1,4-C,N-dipole intermediate, with 1,3-dicarbonyl substrates **116** or **118** were realized by using a catalyst system comprising Pd(dba)$_2$ and phosphoramidite ligands (Scheme 43). When achiral phosphoramidite ligand **L35** was employed, a range of piperidines **117** were constructed in good to high yields (Scheme 43b). When using chiral ligand *ent*-**L18**, increasing the steric encumbrance of R group of ketoesters **118** had varying effects on the selectivity, where the isopropyl group produced the best enantiomeric excess. The corresponding piperidines **119** were obtained in high yields and enantioselectivities (Scheme 43c).

In 2021, the same group [127] achieved another [4 + 2] cycloaddition between carbamate **115** and α-fluoro β-ketoesters **120** or α-SCF$_3$-substituted ketones **121** to construct 3-fluoro- or trifluoromethylthio-piperidines **123** and **125** with imine, ester, and alkene functional groups in good to high yields *via* **122** or **124** intermediates, respectively (Scheme 44). This method is a new and efficient way to introduce 3-trifluoromethylthio-group into piperidines, providing a general approach for these important scaffolds.

In 2019, acyclic allylic carbonates **126**-**128** can be readily obtained in a one-step synthesis. A Pd-catalyzed asymmetric [3 + 2] cycloaddition reaction of nitrogen-containing allylic carbonate **126** with isocyanates **44** was first reported by Zhang and coworkers (Scheme 45a) [128]. A practical and efficient method for obtaining imidazolidinones **129** in high yields and enantioselectivities in the presence of chiral binol-derived phosphoramidite ligand **L18** and palladium co-catalysis was developed. Allylic carbonate **126** could afford stable 1,3-zwitterionic allylpalladium intermediate similar to 5-vinyloxazolidin-2-ones or vinylaziridine [20,129]. In addition, a Pd-catalyzed asymmetric [4 + 2] cycloaddition of nitrogen-containing allylic carbonate **127** with isocyanates **44** was also developed (Scheme 45b) [128]. Allylic carbonate **127** could provide stable 1,4-zwitterionic allylpalladium intermediate similar to 6-vinyl-1,3-oxazinanones under palladium catalysis. A series of chiral tetrahydropyrimidinones **130** could be obtained in up to 87% yield and 99% *ee* under ligand **L36** and palladium co-catalysis.



Scheme 45. Pd-catalyzed [*n* + 2] cycloadditions of acyclic allylic carbonates.

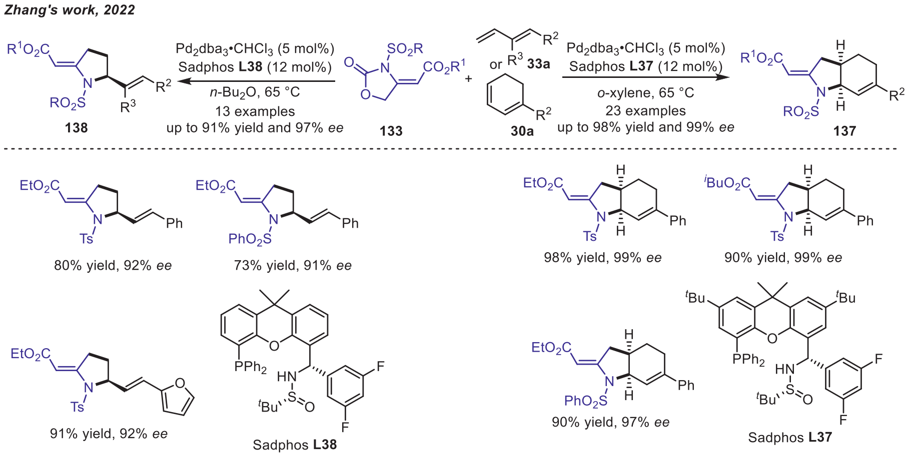


Scheme 46. Pd-catalyzed [3 + 2] cycloadditions *via* Pd-aminoallyl intermediates.

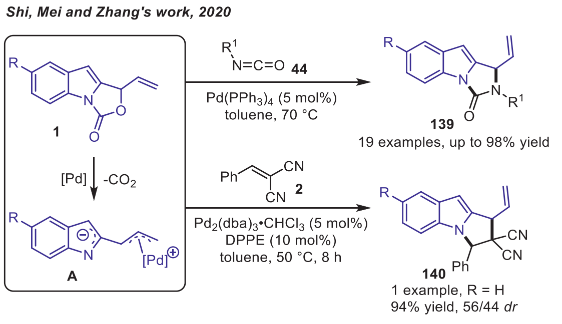
When the reaction of allyl carbonate **128** with benzyl isocyanate **44a** under the same reaction conditions as that of **126** was investigated, only pyrrolidine **131** was obtained in 72% yield and 43% *ee*. No cycloadduct **132** was observed (Scheme 45c). This result suggested that allyl carbonate **128** underwent intramolecular cyclization to produce pyrrolidine **131** through the generation of 1,5-zwitterionic allylpalladium intermediate.

In 2019, Trost and coworkers designed a new Pd-aminoallyl precursors **133** and applied them to the [3 + 2] cycloaddition reactions with dienes (Scheme 46a) [130]. Compared with their previous reports, an electron withdrawing group on the Pd-oxyallyl precursors was essential for the smooth [3 + 2] cycloaddition with conjugated dienes [67]. Thus, the electron-withdrawing ester motif was also indispensable for the [3 + 2] cycloaddition involving the Pd-aminoallyl precursors. A variety of pyrrolidines **134** were produced in moderate to high yields via the C-N reductive elimination. The Pd-aminoallyl precursors **133** were prepared from commercially available substrates in a single step by Tamaru and coworkers in 1994 [131]. Notably, similar to Pd-oxyallyl intermediate, the heterocycle adducts **134** can be readily isomerized to thermodynamically more stable carbocycles **135** *via* intermediate **136** in the present of bidentate dppe ligand and CpPd(cinnamyl) (Scheme 46b). Thus, the five-membered carbocyclic **135** could be formed by palladium-catalyzed [1,3] N-to-C rearrangement.

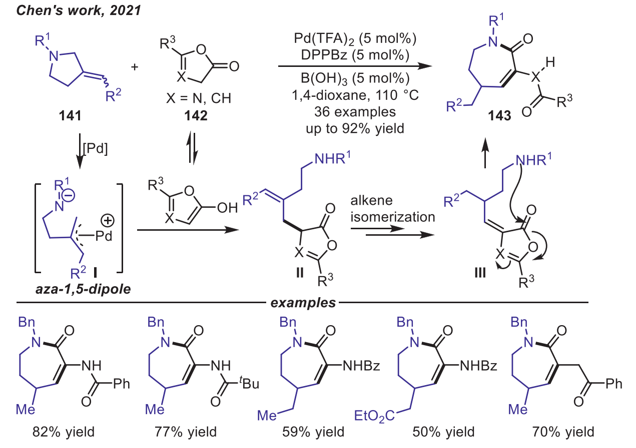
Additionally, Zhang and co-workers achieved highly substituted or fused pyrrolidines in asymmetric cycloaddition reactions of Pd-aminoallyl intermediates with 1,3-dienes in 2022 (Scheme 47) [75]. The cyclic or acyclic 1,3-dienes reactions with Pd-aminoallyl intermediates were catalyzed using chiral ligands Sadphos **L37** or **L38** respectively, in which aminoallyl precursors had a large range of ester groups, including Et, Me, ^{n}Bu, ^{i}Bu, Ph and Bn. Control experiments indicated that the apparent matched/mismatched effect of substrates was influenced by *cis*/*trans*-configuration of aminoallyl precursor and dienes. The cycloaddition products could not be obtained for *E*-**133** and *Z*-**33a**. The asymmetric version required the aminoallyl precursor **133** with exclusive *Z*-geometry since it could reduce the activation entropy of the transition state generated by Pd/Sadphos-aminoallyl zwitterion. Moreover, a Pd-



Scheme 47. Pd-catalyzed asymmetric [3 + 2] cycloadditions *via* Pd-aminoallyl intermediates.



Scheme 48. Pd-catalyzed [3 + 2] cycloadditions of vinyl indoloxazolidones.



Scheme 49. Pd-catalyzed [5 + 2] cycloadditions of 3-alkylidenepyrrolidine.

catalyzed [1,3] N-to-C rearrangement with the achiral ligand could also be achieved.

In 2020, Shi and coworkers [45] continued to expand the application of vinyl indoloxazolidones **1**, which could be convert to Pd-π-allyl zwitterion intermediate **A** specifically used as a nitrogen-carbon-carbon building block (Scheme 48). Thus, palladium-catalyzed decarboxylative [3 + 2] cycloaddition reactions were achieved by reaction with isocyanates **44**. Nevertheless, different chiral ligands (including chiral phosphoramidites and chiral bidentate phosphine ligands) could hardly control the enantioselectivity (<8% *ee*) of the [3 + 2] cycloaddition reaction. Furthermore, when the electron-deficient olefin benzylidene malononitrile **2** was used as a dipolarophile for the reaction with oxazoloindol-3-one **1** under palladium catalysis, the product **140** was produced in 94% yield with a diastereoselectivity of 56/44.

Interestingly, in 2021, Chen and coworkers disclosed the first use of pyrrolidines **141** [132,133] for the palladium-catalyzed [5 + 2] cycloaddition reactions with azlactones or butenolides to produce seven-membered azepines **143** (Scheme 49) [134]. A wide range of substrate scope was suitable. R^3 on **142** could be aryl, vinyl, alkyl. Moreover, the substituent on the nitrogen atom of substrates **141** could contain PMB, cyanide, phthalimide, or ester groups. A possible reaction pathway was depicted. Firstly, with the assistance of $B(OH)_3$, the palladium catalyst underwent oxidative addition with 3-alkylidenepyrrolidines **141** to yield *N*-zwitterionic intermediate **I** through an inert C-N bond cleavage. The substrates **142** acted as a two-atom synthon to capture intermediate **I** to give intermediate **II**. Subsequently, 1,1-disubstituted alkene on intermediate **II** may isomerized to form conjugated azlactone intermediate **III**. The final azepines **143** were generated by an intramolecular lactamization step.

5. Summary and outlook

As described in this review, the palladium-catalyzed intermolecular cycloaddition reactions of 1,n-dipoles with different dipolarophiles in the present of ligands can be an effective and practical strategy for constructing structurally diverse 5- to 12-membered cyclic compounds, which are widely found in many natural products and pharmaceutical molecules and have received significant attention from synthetic chemists. We mainly summarize the progress of Pd-π-allyl zwitterions in the past 5 years, including newly designed Pd-π-allyl zwitterionics and several zwitterionics that have received renewed attention, which have also been designed and applied to diverse reaction partners to achieve new cyclic compounds that may be difficult to construct by other conventional methods.

Despite these great achievements allow for the rapid and convenient construction of complex polycyclics or medium-sized cycles exclusively with relatively simple substrates under mild conditions. There are several areas still need improvement. First of all, such transformations are often plagued by competitive reaction pathways and low levels of site- and stereoselectivity, and improvements in new catalytic systems may depend heavily on the design and discovery of new dipoles and chiral ligands. Secondly, the corresponding precursors of these key species are far from adequate, especially for 1,6- or 1,8-zwitterionic π-allyl palladium species, and their applications are still rare. Moreover, studies on the direct application of cycloaddition reactions *via* Pd-π-allyl zwitterion intermediates to the total synthesis of natural products, bioactive molecules, and pharmaceuticals are still scarce [135,136], even though this aspect is of great importance. Therefore, the design and discovery of novel zwitterionic π-allyl palladium species will be crucial to the continuous advancement of this field and the direct application of this reaction strategy to the synthesis of drug-containing or active molecules.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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