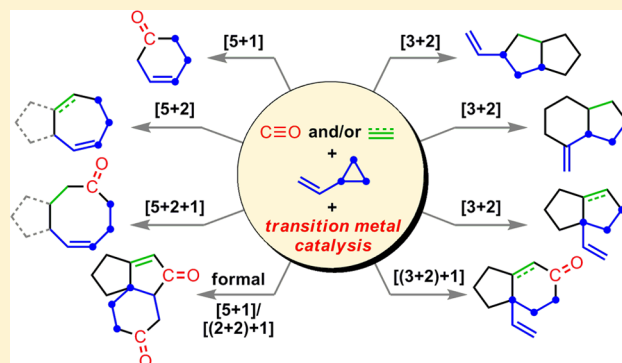# Vinylcyclopropane Derivatives in Transition-Metal-Catalyzed Cycloadditions for the Synthesis of Carbocyclic Compounds

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ABSTRACT: Vinylcyclopropane (VCP) derivatives participate in a variety of transition-metal-catalyzed multicomponent cyclo-additions to produce five- to eight-membered carbocycles. Various cycloaddition modes provide novel approaches to mono-, bi-, and polycyclic molecules. In this Synopsis, recent advances in transition-metal-catalyzed VCP cycloadditions are discussed, with a particular emphasis on the influence of VCP substitution pattern on cycloaddition modes. A tabular summary of applications of the VCP cycloadditions in natural product synthesis is also presented.

Cyclopropane derivatives are important small-ring compounds in modern synthetic organic chemistry[1−6] because these molecules can undergo various synthetically useful transformations, in which the cyclopropane ring is opened to form new chemical bonds. Reactive cyclopropane derivatives usually bear activating groups that can facilitate ring-opening and stabilize the ring-opened intermediate.[7−11] Vinylcyclo-propanes (VCPs) represent an important category of reactive cyclopropane derivatives[12,13] with rich cycloaddition chemistry (Scheme 1). The VCP motif can act as either an activated

Scheme 1. Reaction Modes of VCP Cycloadditions
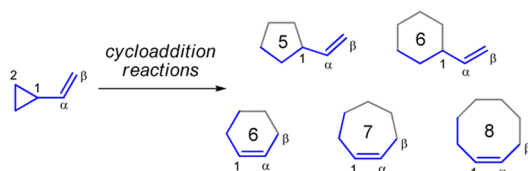
cyclopropane ring to undergo [3 + *x*] cycloadditions or a homologue of 1,3-butadiene to participate in [5 + *x*] cycloadditions.[14]

Most of these transformations are catalyzed by transition metals, and five- to eight-membered carbocyclic compounds are produced. An interesting feature in these reactions is that the substitution pattern of VCP substrates has a dramatic influence on the cycloaddition modes, particularly for those intramolecular cycloadditions. This Synopsis will focus on the most recent advances in this area with a particular emphasis on the cycloaddition chemistry of substituted VCPs. The cyclo-additions of VCPs with dipolar reagents (e.g., aldehydes, imines, and nitrones) for the synthesis of heterocycles are not included, and readers are directed to the cited reviews[4,10] and recent papers.[15−18]

■ EARLY STUDIES OF VCP CYCLOADDITIONS

Palladium-Catalyzed Tsuji-Type Cycloaddition. VCP derivatives were found to undergo an intermolecular [3 + 2] cycloaddition with electron-deficient olefins under Pd(0) catalysis in 1985 by Tsuji and co-workers (Scheme 2).[19] This

Scheme 2. Tsuji-Type [3 + 2] Cycloaddition
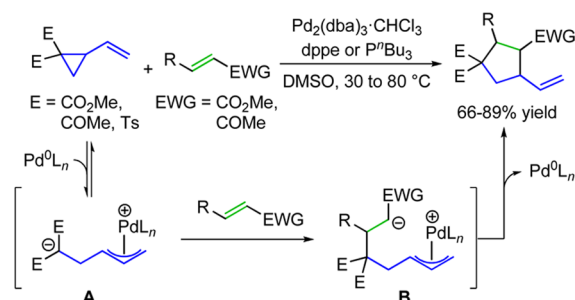
formal cycloaddition between the cyclopropane ring of VCP and a C=C bond afforded vinyl-substituted cyclopentanes in good yields. A stepwise ionic mechanism involving zwitterionic π-allylpalladium(II) intermediates **A** and **B** was proposed (Scheme 2). The Stoltz group used this [3 + 2] cycloaddition to construct the densely substituted cyclopentane core of the *Melodinus* alkaloids.[20] Asymmetric version of this [3 + 2] cyclo-addition was developed in the Trost group and the Shi group by employing chiral palladium complexes as catalyst.[21,22] The Plietker group recently found that nucleophilic ferrate can act as an alternative catalyst for this transformation.[17]

Radical-Mediated Cycloadditions. VCP derivatives were found to undergo radical-mediated [3 + 2] cycloaddition with alkenes or alkynes in the late 1980s.[23,24] Although beyond the range of transition-metal-catalyzed cycloadditions, this reaction is briefly introduced as a background of the VCP cyclo-addition chemistry. This radical [3 + 2] cycloaddition produced vinylcyclopentane or vinylcyclopentene cycloadducts in moder-ate to good yields through following a radical-mediated reac-tion sequence via intermediates **A−D** (Scheme 3). The reaction

Scheme 3. Radical-Mediated [3 + 2] Cycloaddition
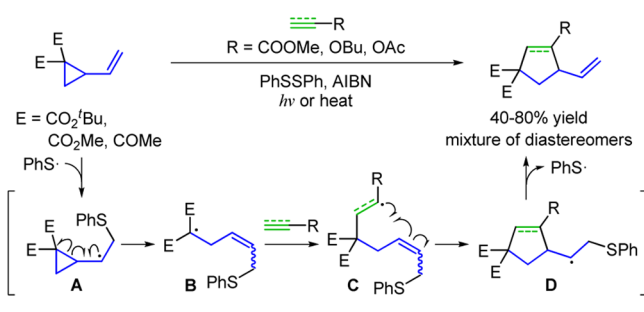
can also take place in an intramolecular fashion to generate bicyclic cycloadducts when the π-component was tethered to the 2-position of VCP.[24] In 2011, the Curran group applied the intramolecular radical [3 + 2] cycloaddition of 2-ene-divinyl-cyclopropane substrate as the key step in the total synthesis of *Melodinus* alkaloids meloscine and epimeloscine.[25]

These early studies established the utility of VCPs as cyclo-addition partners and opened up new possibilities for synthesiz-ing carbocycles. However, these cycloadditions suffered from drawbacks such as limited reaction modes, requirement of activa-tion groups on both VCP and the 2π cycloaddition partners, and unsatisfactory stereochemical control. Hence, more versatile and selective cycloadditions of VCPs were in high demand to provide tools for synthesis. This goal has been approached by transition-metal-catalyzed cycloadditions of VCPs, in which the transition-metal catalysts react with VCPs to form metallocarbocyclic species as key intermediates for further cycloadditions with dienophiles.

TRANSITION-METAL-CATALYZED [5 + X] CYCLOADDITIONS OF VCP SUBSTRATES

Since 1995, the combination of VCP and transition-metal catal-ysis has resulted in a renaissance of VCP chemistry, leading to the discovery of a series of novel [5 + x] cycloadditions. These include [5 + 1],[26−30] [5 + 2],[31−42] and [5 + 2 + 1][43−45] cycloadditions catalyzed by Fe, Co, Rh, and Ru complexes, in which the entire VCP motif is embedded in the formed rings to produce six- to eight-membered carbocycles (Scheme 4). Rh(I) complexes were found to be extremely general and efficient catalysts for these transforma-tions, and asymmetric [5 + 2] cycloaddition of β-ene-VCPs was achieved by using chiral Rh(I) complexes.[41,42]

Unlike the aforementioned zwitterion- and radical-mediated cycloadditions, these [5 + x] cycloadditions proceed via metallo-carbocyclic intermediates (Scheme 4, shown in brackets). For the Rh(I)-catalyzed [5 + 1], [5 + 2], and [5 + 2 + 1] cyclo-additions, the key intermediate is a metallocyclohexene (or isomeric alkyl π-allyl metal species) formed by ring-opening oxidative addition of VCP to the transition metal.[36] The reaction is then completed by complexation of the other cycloaddition partner (alkene, alkyne, allene, or CO), insertion, and reductive elimination. The Ru(II)-catalyzed [5 + 2] cycloaddition

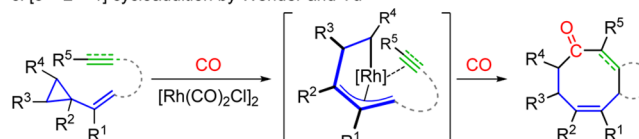**Scheme 4. Transition-Metal-Catalyzed [5 + x] Cycloadditions of VCPs**
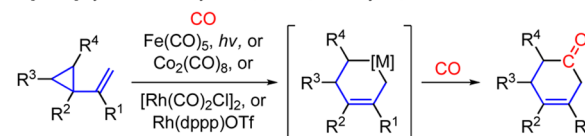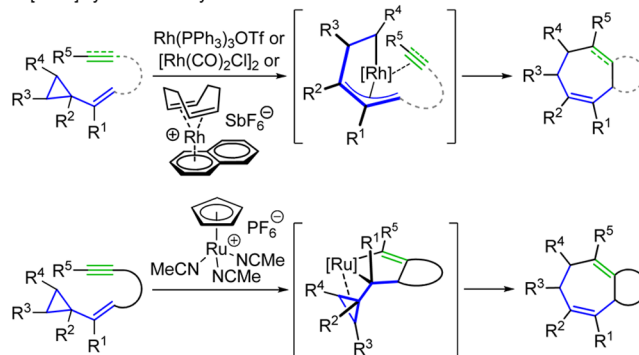
proceeds by following an alternative mechanism, in which oxidative cyclometalation between the VCP's vinyl group and the tethered C≡C bond generates a metallocyclopentene inter-mediate, followed by cyclopropane ring-opening and reductive elimination.[37−39] Since these reactions have been well-summarized by several review articles and book chapters,[3,26,46−50] this Synopsis will focus on more recent advances in transition-metal-catalyzed cycloadditions of VCPs.

NEW SUBSTITUTION PATTERNS OF VCP SUBSTRATES FOR CYCLOADDITIONS

Despite remarkable advances in VCP cycloadditions, the types of VCP substrates for intramolecular cycloaddition were still limited (Figure 1). In the transition-metal-catalyzed [5 + x]
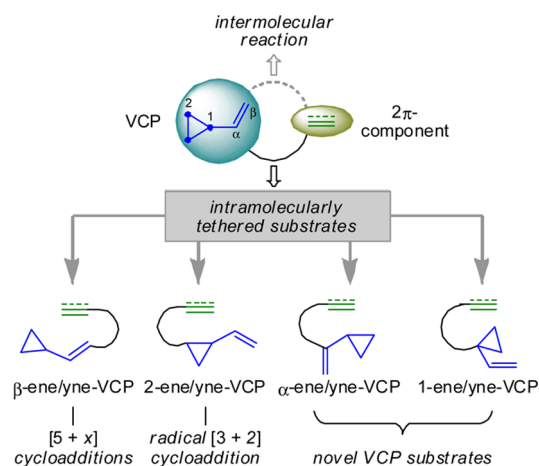

Figure 1. Types of intramolecularly 2π-component tethered VCPs.

cycloadditions, only VCP substrates with a 2π-component tethered to the β-position, namely, β-ene/yne-VCPs, were extensively studied. A limited number of 2-ene-VCPs were employed for intramolecular radical [3 + 2] cyclization,[24] and this substitution pattern was not tested for any transition-metal-catalyzed reaction. The α- and 1-ene/yne-VCPs are novel VCP substrates that had not been studied before 2010. Following a long-standing interest in the VCP chemistry, our research group set out to study the Rh(I)-catalyzed reaction of VCP derivatives with different substitution patterns.

Rh(I)-Catalyzed Intramolecular [3 + 2] Cycloaddition of *trans*-2-Ene-VCP Derivatives. In 2008, our group first investigated the Rh(I)-catalyzed intramolecular cycloaddition of 2-ene-VCP substrates, in which the alkene unit was tethered to the 2-position of the VCP with a 1,2-*trans* configuration. We found that, under Rh(I) catalysis, *trans*-2-ene-VCPs exhibited an unexpected intramolecular [3 + 2] cycloaddition rather than a [5 + 2] cycloaddition, affording *cis*-fused bicyclic cyclopentanes in good yields (Scheme 5).[51] Although this reaction resembled

Scheme 5. Rh(I)-Catalyzed [3 + 2] Cycloaddition
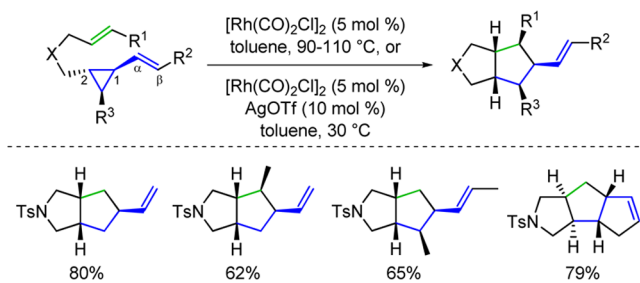
the intramolecular radical-type [3 + 2] cycloaddition,[24] it required no electron-withdrawing activation groups on the cyclopropane ring and afforded significantly better yields with excellent diastereocontrol. Unfortunately, *trans*-2-yne-VCPs are not suitable substrates for this transformation.

The reaction did not occur when vinyl moiety in 2-ene-VCPs was absent, indicating the role of VCP as an integrated cycloaddition partner. This is consistent with the proposed reaction mechanism involving a π-allyl rhodium intermediate (Scheme 6). Oxidative addition of VCP to Rh(I) produces

Scheme 6. Proposed Mechanism
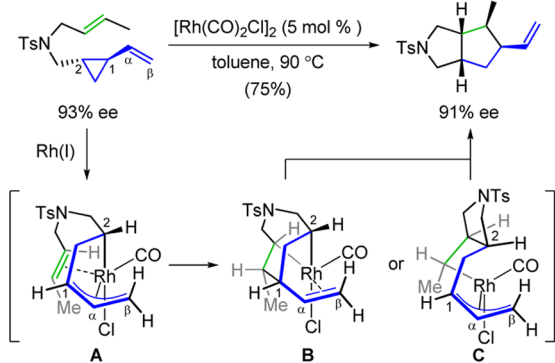
intermediate **A**, in which the cyclopropane ring is opened, and then the alkene moiety binds to the metal center proximal to C1. Alkene insertion affords intermediate **B** (insertion to the π-allylic C1−Rh bond) or **C** (insertion to the C2−Rh bond). Finally,

reductive elimination from intermediate **B** or **C** generates the bicyclic cycloadduct. The stereochemistry of VCP is conserved throughout this process, as indicated by the complete transfer of chirality from an optically active *trans*-2-ene-VCP substrate to the corresponding [3 + 2] cycloadduct (Scheme 6). Interestingly, when a *cis*-2-ene-VCP substrate was employed, a [5 + 2] cyclo-addition took place, showcasing the dramatic effect of VCP substitution pattern on the cycloaddition mode in Rh(I)-catalyzed cycloadditions (Scheme 7).

Scheme 7. [5 + 2] Cycloaddition of a *cis*-2-Ene-VCP
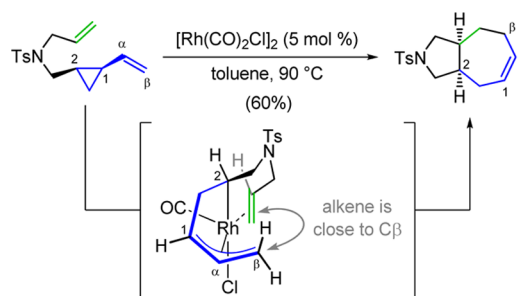
Rh(I)-Catalyzed Intramolecular [3 + 2] Cycloaddition of α-Ene-VCP Derivatives. The Rh(I)-catalyzed cycloaddition of novel α-ene-VCP substrates was reported by our group in 2010. An intramolecular [3 + 2] cycloaddition was observed between the alkene and cyclopropane moieties when a cationic Rh(I)−phosphine complex was employed as the catalyst (Scheme 8).[52]

Scheme 8. Rh(I)-Catalyzed [3 + 2] Cycloaddition
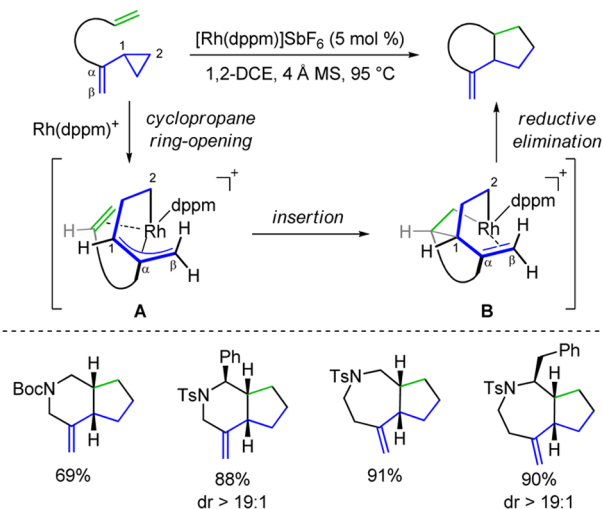
Both [5,6]- and [5,7]-bicyclic cycloadducts were obtained in good yields, and a pre-existing stereogenic center in the substrate resulted in excellent diastereocontrol. This [3 + 2] cycloaddition highlights the formation of seven-membered rings consisting of tether atoms in an intramolecular cycloaddition, which is uncommon in the transition-metal-catalyzed reactions. However, α-yne-VCPs are not compatible due to a competitive intra-molecular cyclopropanation reaction.[52]

This [3 + 2] reaction is proposed to start from the formation of π-allyl rhodium intermediate **A**. We think that substrate α-ene-VCP can transmit its substitution pattern to intermediate **A**, dictating its geometry and the stereochemistry of the followed C=C insertion process. Intermediate **B** then undergoes a

reductive elimination to afford the observed [3 + 2] cycloadduct (Scheme 8).

Rh(I)-Catalyzed Intramolecular [3 + 2] Cycloaddition of 1-Ene/Yne-VCP Derivatives. In line with the research on VCP cycloadditions carried out in our laboratory, we next explored the reactions employing 1-substituted VCP derivatives. The first reaction discovered was the intramolecular [3 + 2] cycloaddition of 1-ene/yne-VCPs (Scheme 9).[53] A cationic Rh(I)−phosphine
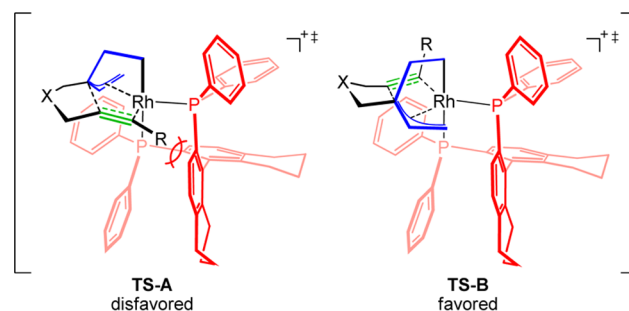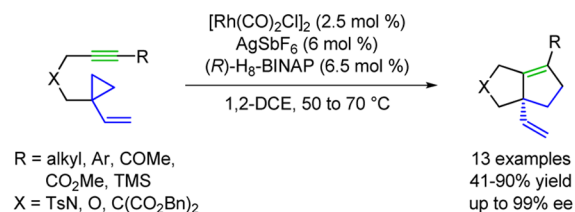
Scheme 9. Rh(I)-Catalyzed [3 + 2] Cycloaddition
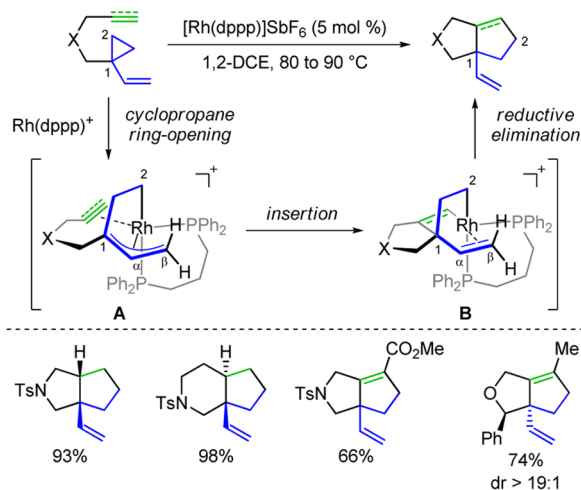
complex, [Rh(dppp)]SbF$_6$, was found to be an efficient catalyst for the cycloaddition between the C═C or C≡C bond and the cyclopropane unit in 1-ene/yne-VCP substrates. This cycloaddition delivered in good yields the bicyclic cyclopentane and cyclopentene derivatives, which bear a vinyl-substituted quaternary bridgehead stereocenter.

DFT studies of the reaction mechanism suggested that the [3 + 2] reaction is initiated by the formation of π-allyl rhodium species **A** (Scheme 9).[53,54] The π-component tethered to the 1-position of the VCP is placed proximal to C1 and distal to Cβ in intermediate **A**. Alkene or alkyne insertion into the C1−Rh bond generates intermediate **B**, which is the rate- and stereochemistry-determining step in this reaction. Reductive elimination from intermediate **B** forges the second C−C bond between C2 and the terminal carbon of the π-component to deliver the [3 + 2] cycloadduct.

Our group has developed an asymmetric Rh(I)-catalyzed [3 + 2] cycloaddition of 1-yne-VCPs by using (R)-H$_8$-BINAP as a chiral ligand. The reaction afforded a series of bicyclic cyclopentene products in good yields and excellent enantioselectivities (Scheme 10),[55] representing one of the few examples of asymmetric VCP cycloadditions. DFT calculations suggest that the enantioselectivity is controlled by the stereochemistry-determining alkyne insertion step, and transition state **TS-B** is favored over its diastereogenic counterpart **TS-A** by avoiding the repulsion between the alkyne substituent R and the H$_8$-BINAP backbone encountered in the latter transition state (Scheme 10).

Rh(I)-Catalyzed [(3 + 2) + 1] Cycloaddition of 1-Ene/Yne-VCP Derivatives. A follow-up study revealed that 1-ene/yne-VCPs can also undergo carbonylative cyclization. In a CO atmosphere, 1-ene/yne-VCPs underwent a carbonylative [(3 + 2) + 1] cycloaddition in the presence of catalytic amount of [Rh(CO)$_2$Cl]$_2$ (Scheme 11).[56] Bicyclic cyclohexanone/cyclohexenone products were obtained in good yields, rendering a homologous Pauson−Khand reaction under mild conditions.[57]

Scheme 10. Asymmetric [3 + 2] Cycloaddition

Scheme 11. Rh(I)-Catalyzed [(3 + 2) + 1] Cycloaddition
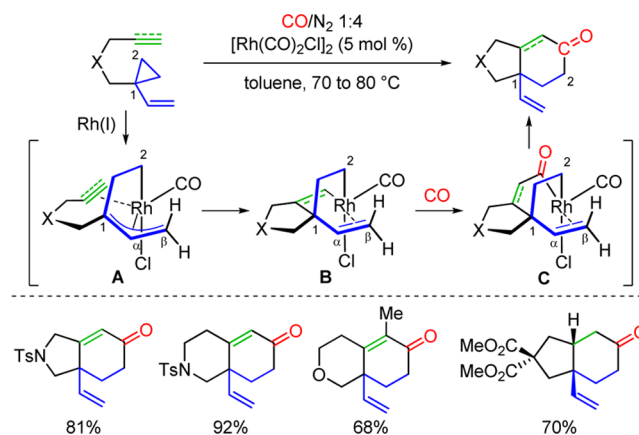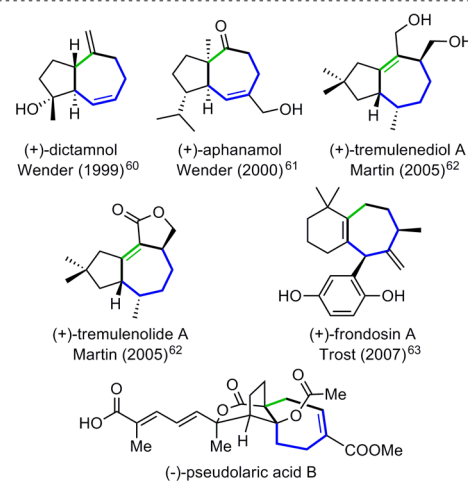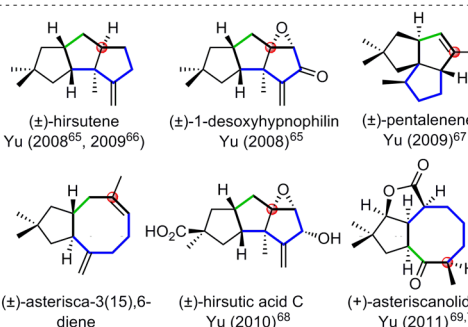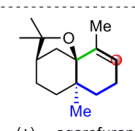
Scheme 12. Rh(I)-Catalyzed Formal [5 + 1]/[(2 + 2) + 1] Cycloaddition
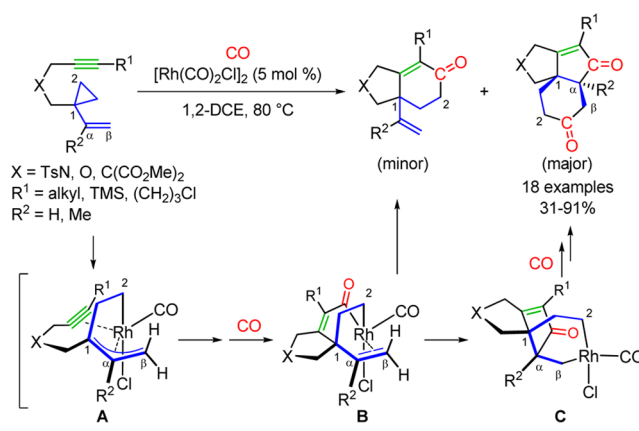
This reaction follows a similar mechanism as the [3 + 2] cycloadditions of 1-ene/yne-VCPs have (via intermediates **A** and **B**). In the presence of CO, intermediate **B** undergoes CO complexation and insertion, followed by reductive elimination to deliver the carbonylative cycloadduct. This reaction was successfully applied to the synthesis of a furanoid sesquiterpene natural product, α-agarofuran.[56]

Table 1. Application of VCP Cycloadditions in Total Synthesis[a]

key reaction	synthesized natural products

(±)-meloscine   (±)-epimeloscine
Curran (2011)[25]

(+)-dictamnol Wender (1999)[60]
(+)-aphanamol Wender (2000)[61]
(+)-tremulenediol A Martin (2005)[62]

(+)-tremulenolide A Martin (2005)[62]
(+)-frondosin A Trost (2007)[63]

(−)-pseudolaric acid B Trost (2007)[64]

(±)-hirsutene Yu (2008[65], 2009[66])
(±)-1-desoxyhypnophilin Yu (2008)[65]
(±)-pentalenene Yu (2009)[67]

(±)-asterisca-3(15),6-diene Yu (2009)[67]
(±)-hirsutic acid C Yu (2010)[68]
(+)-asteriscanolide Yu (2011)[69,70]

(±)-α-agarofuran Yu (2010)[56]

[a]The carbocycles formed by VCP cycloadditions are shown in bold. The blue portion comes from VCP, the green part comes from the 2π-component, and the red carbon comes from CO.
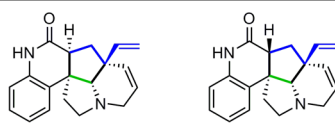
Rh(I)-Catalyzed Formal [5 + 1]/[(2 + 2) + 1] Cycloaddition of 1-Yne-VCP Derivatives. In 2011, our group discovered that 1-yne-VCPs with terminal alkyne substituents underwent a new and intriguing carbonylative cycloaddition under Rh(I) catalysis (Scheme 12).[58] In this reaction, two carbonyl groups and the entire VCP moiety are embedded into the generated cycloadducts, rendering an unprecedented bicarbonylative cycloaddition mode of 1-yne-VCP. This reaction was named as a formal [5 + 1]/[(2 + 2) + 1] cycloaddition, as it can be viewed as a reaction cascade consisting of a [5 + 1] cycloaddition (between the VCP and CO) and an intramolecular Pauson−Khand [(2 + 2) + 1] cycloaddition (between alkyne, in situ generated cyclohexenone, and CO). However, both experimental and DFT computational studies suggest an alternative mechanism involving multiple insertion/carbonylation processes on the Rh(I) center via intermediates **A**, **B**, and **C**. One of the limitations of

this cycloaddition is that 1-yne-VCPs must have an internal rather than a terminal alkyne. In addition, a remarkable amount of [(3 + 2) + 1] cycloadduct is generated as a competitive byproduct in the formal [5 + 1]/[(2 + 2)+1] cycloaddition. Despite this drawback, this reaction provides a concise approach to angular tricyclic [5,5,6] structure, which is found in natural products.

■ NATURAL PRODUCT SYNTHESIS UTILIZING VCP CYCLOADDITIONS

New reactions enable new strategies for complex molecule synthesis.[59] The rich cycloaddition chemistry of VCPs for the construction of polycyclic structures containing five- to eight-membered rings provides great opportunity to solve synthetic challenges. Compared with previous methods, VCP cyclo-additions allow for a multicomponent assembly of cyclic compounds bearing various functionalities for further elabo-rations, making them particularly valuable for complex molecule synthesis. Numerous total syntheses of natural products have been accomplished utilizing VCP's [3 + 2],[25] [5 + 2],[60−64] [(5 + 2) + 1],[65−70] and [(3 + 2) + 1][56] cycloadditions since 1999, in which the complex polycyclic skeletons of the natural products were created in a step-economical and stereoselective fashion (Table 1). This clearly demonstrates the impact of VCP chemistry on the science of synthesis.

In conclusion, in the past decades, VCPs have been utilized as multifunctional components in various cycloadditions. In particular, transition-metal catalysis (Co, Fe, Ru, and Rh) has significantly extended the scope of the VCP cycloaddition chemistry, enabling multicomponent cycloadditions to construct functionalized five- to eight-membered carbocycles. More recent advances have concentrated on exploration of unprecedented cycloaddition modes of VCPs by changing substitution patterns, as well as on the development of the corresponding asymmetric cycloadditions. Despite these advances, it remains desirable to develop cycloadditions of novel VCP substrates, as well as asymmetric carbonylative VCP cycloadditions. Reports of studies in this direction have already started to emerge in the literature,[71−73] and we believe that more exciting reactions from VCPs are to be discovered and more synthetic applications of these cycloadditions can be envisioned.

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Notes
The authors declare no competing financial interest.

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Lei Jiao completed his Ph.D. in Prof. Zhi-Xiang Yu's laboratory at Peking University in 2010 and is currently a postdoctoral fellow in the research group of Prof. Thorsten Bach at Technische Universität München.

Zhi-Xiang Yu obtained his Ph.D. in Prof. Yun-Dong Wu's group at the Hong Kong University of Science & Technology in 2001. After a three-year postdoctoral study with Profs. K. N. Houk (2001−2004) and M. Masca (2001−2002) at University of California, Los Angeles, he joined the faculty of Peking University as an associate professor in 2004 and was promoted to a full professor in 2008. With a research philosophy of *chem is try computationally and experimentally*, his laboratory focuses on application of computational and synthetic organic chemistry to study reaction mechanisms, develop new reactions and catalysts, and apply the new reactions discovered from the Yu group to synthesize natural and non-natural products.

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(14) In this Synopsis, we refer to these cycloadditions as the [*m* + *n*] cycloaddition, where brackets, instead of parentheses, are used in the nomenclature. Although, in principle, *m* and *n* do not stand for the number of electrons involved in these *formal* cycloadditions, we prefer to follow the nomenclature of most original publications, where brackets are used. The parentheses used in the nomenclature specify the cycloaddition partners from one molecule, while the number outside the parentheses stands for the cycloaddition partner from the other molecule. This nomenclature (see refs 45 and 49) will be used throughout the text.

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