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Cyclobutanes

Cyclobutanes in Catalysis

*Tobias Seiser, Tanguy Saget, Duc N. Tran, and Nicolai Cramer**

C–C activation · cyclobutanes · homogeneous catalysis · ring expansion · ring strain

Dedicated to Professor Barry M. Trost on the occasion of his 70th birthday

The exploitation of ring strain as a driving force to facilitate chemical reactions is a well-appreciated principle in organic chemistry. The most prominent and most frequently used compound classes in this respect are oxiranes and cyclopropanes. For rather a long time, cyclobutanes lagged behind these three-membered-ring compounds in their development as reactive substrates, but during the past decade an increasing number of useful reactions of four-membered-ring substrates have emerged. This Minireview examines corresponding catalytic reactions ranging from Lewis or Brønsted acid catalyzed processes to enzymatic reactions. The main focus is placed on transition-metal-catalyzed C–C bond-insertion and β-carbon-elimination processes, which enable exciting downstream reactions that deliver versatile building blocks.

1. Introduction

Small and strained molecules have caught the interest of generations of chemists, for both theoretical and practical purposes.[1] Of the strained carbocycles, the cyclopropane ring has drawn most interest, whereas for a long time its homologue, the cyclobutane ring,[2] remained relatively underutilized. This difference is surprising, as often cyclobutane is considered the "big brother" of cyclopropane, with similar properties and reactivity (Figure 1). Intriguingly, the strain energy of cyclobutane (26.7 kcal mol^{-1}) is similar to that of cyclopropane (27.5 kcal mol^{-1}). This surprising result has been rationalized by the dissection of the strain into C–C and C–H bond-energy contributions.[3] Although the total C–C bond strain of cyclopropane is 10.1 kcal mol^{-1} higher than that of cyclobutane, this difference is mostly compensated by its stronger C–H bonds (8.0 kcal mol^{-1}).[4] Remarkably, it was calculated that *gem*-dimethyl substitution decreases the ring strain of cyclobutane by more than 8 kcal mol^{-1} as a result of the Thorpe–Ingold effect.[5] The ring strain liberated in ring-expansion or ring-cleavage reactions is a well-appreciated driving force that enables and accelerates otherwise sluggish reactions. Cyclopropanone is an unstable compound that reacts via its oxyallyl or diradical valence tautomer. In contrast, cyclobutanone is stable; however, it displays enhanced carbonyl reactivity that better resembles the behavior of aldehydes than that of ketones.

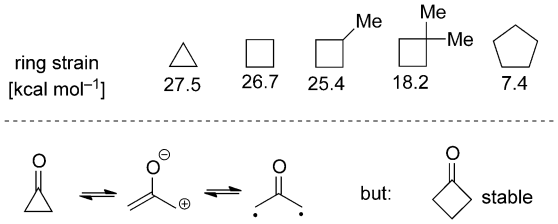

Figure 1. Comparison of the strain energies and properties of small rings.

Among classical cyclobutane-containing molecules, cubane (**1**) with its six cyclobutane rings is the prime example of an artificial, highly strained cyclobutane derivative (Figure 2).[6] The cyclobutane motif also occurs in natural products ranging from simple commodity terpenes, such as α-pinene (**2**), to the exotic and fascinating ladderanes.[7] One of the most prominent members of the ladderanes is pentacycloanammonic acid (**3**), which contains five fused cyclobutane rings.[8]

This natural occurrence has not only spurred the development of new synthetic methodologies for the construction of

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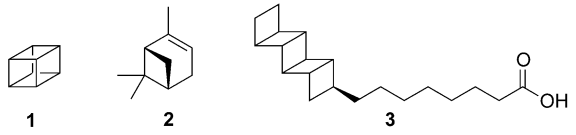


Figure 2. Prominent examples of cyclobutane-containing molecules.

these molecules and cyclobutane rings in general, but has also put a special focus on four-membered rings as an interesting substrate class. Several complementary methods enable efficient access to cyclobutanes; the most common are either photochemical or ketene [2+2] cycloadditions.[9] Recently cyclobutane syntheses based on transition-metal-catalyzed processes, such as the C(sp^3)–H functionalization reported by Baudoin and co-workers[10] or the gold-catalyzed reactions described by the research groups of Echavarren[11a] and Toste,[11b] have been developed as alternative methods. This Minireview covers the development of catalytic reactions of substrates with cyclobutane rings. In particular, it features reactions in which the four-membered ring is expanded or used as a four-carbon-atom component. In the following section, 1,2-carbon shifts initiated by various catalytic systems are examined. Section 3 highlights developments in the transition-metal-catalyzed C–C bond activation of cyclobutanes. In the last section, developments in the enantioselective Baeyer–Villiger oxidation of cyclobutanones are discussed.

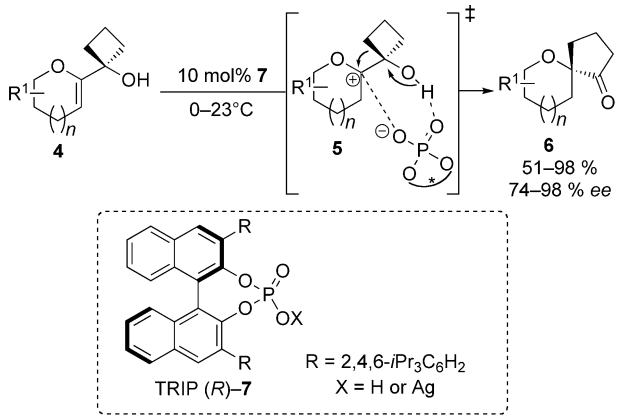
2. Ring Expansion through 1,2-Carbon Shifts

The inherent ring strain of cyclobutanes makes their σ bonds prone to Wagner–Meerwein-type 1,2-shift reactions of cyclobutylmethyl carbenium ions. These intermediates can be generated by a range of catalysts.

2.1. Organocatalytic Rearrangements

In 2009, Tu and co-workers developed a high-yielding Brønsted acid catalyzed enantioselective rearrangement of cyclobutanols **4** to chiral spiroethers **6** (Scheme 1).[12] They postulated that protonation of the enol ether moiety by the chiral phosphoric acid catalyst **7** initiates the asymmetric 1,2-migration. Hydrogen-bonding interactions in the chiral ion-pair transition state **5** were proposed to account for the high enantioselectivity.

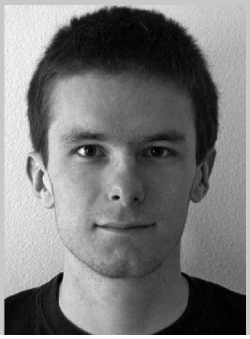
Tu and co-workers subsequently extended the reaction to vinylogous α-hydroxyketones **8** to obtain chiral spirocyclic



Scheme 1. Enantioselective semipinacol rearrangement.

Tobias Seiser studied chemistry at the University of Stuttgart, the TU Dresden (Germany), and the ECPM Strasbourg (France). Since completing his undergraduate degree at the TU Dresden under the guidance of Prof. Peter Metz in 2008, he has been a PhD student at the ETH Zurich in the group of Prof. Nicolai Cramer. He is interested in rhodium-catalyzed C–C bond activations.

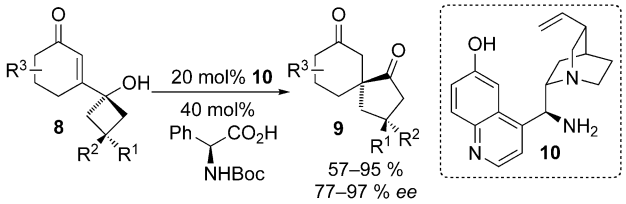
Duc N. Tran studied chemistry at the Institut Universitaire de Technologie du Mans (France). In 2006, he moved to the ENSC Montpellier (France), where he completed his "diplôme d'ingénieur" and his MSc in 2009. He then began PhD studies with Prof. Nicolai Cramer. His research focuses on enantioselective transition-metal catalysis.



Tanguy Saget graduated from the ENSC Montpellier (France) in 2008. He was awarded a Masters fellowship from the EPFL (Switzerland) to work on cationic cyclizations with Prof. Jérôme Waser. In 2009, he began his PhD studies on asymmetric C–H functionalization under the supervision of Prof. Nicolai Cramer, first at the ETH Zurich and since 2011 at the EPFL.

Nicolai Cramer completed his PhD at the University of Stuttgart (Germany) in 2005 with Prof. Sabine Laschat. After postdoctoral studies with Prof. Barry M. Trost at Stanford, he started his independent career as Habilitant under the guidance of Prof. Erick M. Carreira at the ETH Zurich in 2007. At the end of 2010, he took up his current position as Assistant Professor at the EPFL. His research interests include the development of selective C–H and C–C bond activations.

diketones **9** containing an all-carbon quaternary center (Scheme 2).[13] They discovered a very efficient catalytic system based on the cinchona alkaloid **10**. The use of a chiral acid cocatalyst (*N*-*tert*-butoxycarbonyl-L-phenylglycine) proved to be critical for high enantioselectivities to be attained.

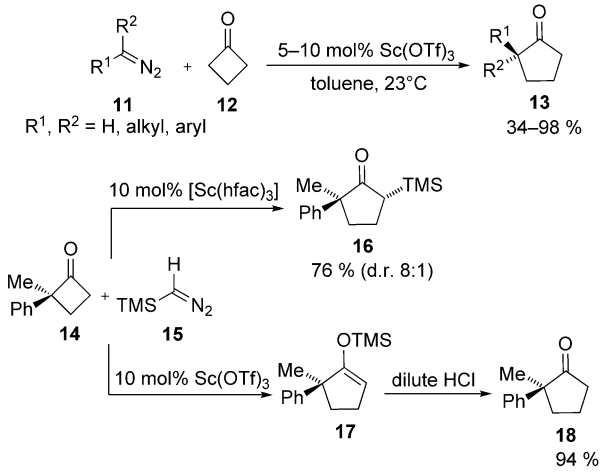


Scheme 2. Asymmetric vinylogous α-ketol rearrangement. Boc = *tert*-butoxycarbonyl.

2.2. Lewis Acid Mediated Ring Opening

2.2.1. Homologation of Cylobutanones

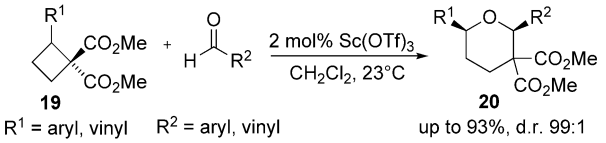
The treatment of cyclic ketones with diazoalkanes is an established method to promote ring expansion. Recently, Kingsbury and Moebius disclosed a catalytic and mild procedure to access substituted cyclopentanones **13** from cyclobutanone (Scheme 3).[14a] With $Sc(OTf)_3$ as a Lewis acid catalyst, a wide range of mono- and disubstituted diazoalkanes **11** can be used. Notably, when trimethylsilyldiazomethane (**15**) was used with cyclobutanone **14**, it was possible to obtain selectively either β-ketosilane **16** or silyl enol ether **17** by using different Sc^{III} salts.[14b]



Scheme 3. Scandium(III)-catalyzed ring expansion of cyclobutanones. hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate, Tf = trifluoromethanesulfonyl, TMS = trimethylsilyl.

2.2.2. Formal [4+2] Cycloaddition Reactions with Polarized Cyclobutanes

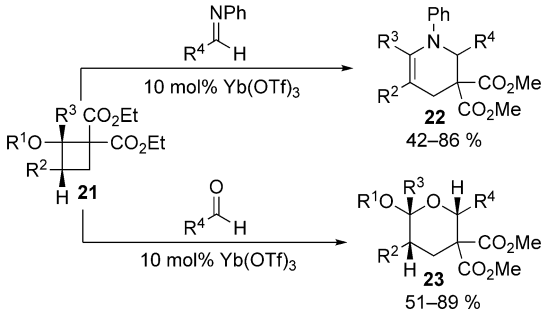
Lewis acid catalyzed dipolar [3+2] cycloaddition reactions involving donor–acceptor-substituted cyclopropanes are well-precedented.[15] Recently, this concept could be extended to cyclobutanes. The research groups of Johnson and of Christie and Pritchard independently reported [4+2] cycloaddition reactions of cyclobutanes, such as **19**, with aldehydes (Scheme 4).[16] The cycloaddition products **20** were obtained



Scheme 4. Formal [4+2] cycloaddition of cyclobutanes and aldehydes.

under mild conditions with excellent diastereoselectivity. Whereas Johnson and Parsons used aryl- and vinyl-substituted cyclobutanes to stabilize the charge during the reaction,[16a] Christie, Pritchard, and co-workers reported a similar reactivity of cyclobutanes substituted with a cobalt–alkyne complex.[16b]

In 2010, Pagenkopf and co-workers extended the scope of this strategy. They treated alkoxy-substituted cyclobutanes **21** with imines and aldehydes to afford tetrahydropyridines **22**[17a] and tetrahydropyrans **23**[17b] with excellent selectivity (Scheme 5).



Scheme 5. Synthesis of tetrahydropyridines and tetrahydropyrans through formal [4+2] cycloaddition reactions.

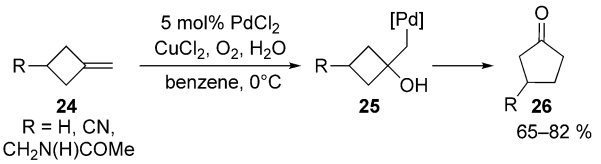
2.3. Transition-Metal-Catalyzed Ring Expansion

2.3.1. Palladium(II)-Catalyzed Oxidative Ring Expansion

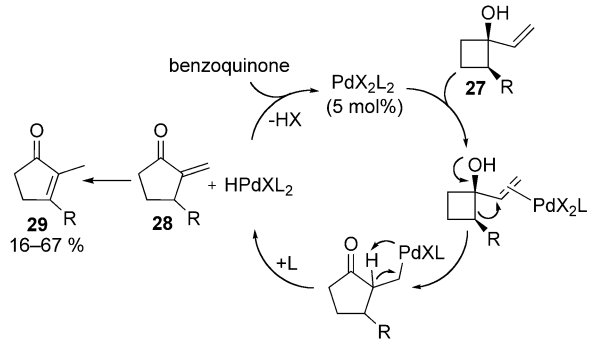
An early example of a transition-metal-catalyzed ring expansion of cyclobutanes was reported in 1977 by Grigg and Boontanonda.[18] Under Wacker-type conditions, methylenecyclobutanes **24** undergo a palladium(II)-catalyzed ring expansion to afford cyclopentanones **26** in good yields (Scheme 6).

In the mid-1980s, Clark and Thiensathit discovered that Pd^{II} complexes can be used to oxidatively expand 1-vinylcyclobutanols **27** to methylenecyclopentanones **28**, which then undergo isomerization to the final products **29** (Scheme 7).[19] The use of benzoquinone as a stoichiometric terminal oxidant reoxidizes Pd^0 to Pd^{II} and thus completes the catalytic cycle.

Since this seminal report, related methods have been reported[20] as well as applications of this ring expansion in the

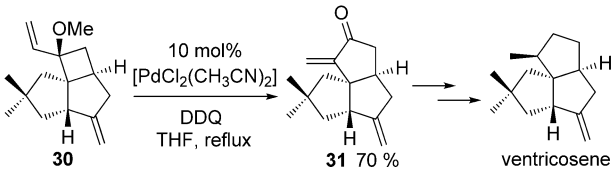


Scheme 6. Palladium-catalyzed oxidative ring expansion.



Scheme 7. Oxidative ring expansion of vinylcyclobutanols **27**.

context of natural product syntheses.[21] For example, Toste and co-workers converted **30** into **31** for a total synthesis of ventricosene (Scheme 8). They found that protection of the hydroxy group as a methyl ether was critical for the selective migration of the more substituted C–C bond.[21a]

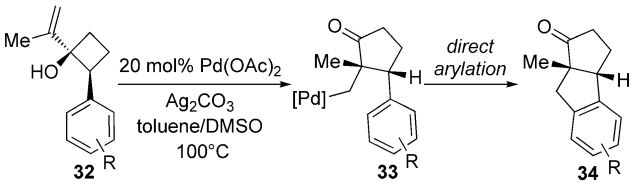


Scheme 8. Application of the oxidative ring expansion of vinylcyclobutanols in a synthesis of ventricosene by Toste and co-workers. DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone.

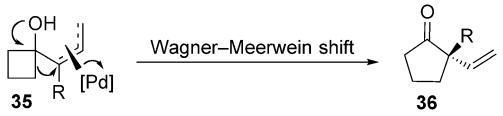
Recently, Orellana and co-workers coupled this ring expansion to a direct arylation with a tethered aryl substituent. This strategy provides access to benzoquinanes in moderate yields.[22] As no β-hydride elimination is possible from intermediate **33** formed by the initial 1,2-shift, a C–H group of the aromatic ring is activated (Scheme 9). Finally, reductive elimination affords the desired benzoquinane **34**. A mechanism involving a β-carbon elimination might be considered as an alternative possibility (see Section 3.2.3).

2.3.2. Palladium(0)-Catalyzed Ring Expansion

Another general way to promote the ring expansion of cyclobutanols involves the generation of a π-allyl palladium intermediate **35** (Scheme 10). Such species readily undergo a Wagner–Meerwein shift to form cyclopentanones **36.**

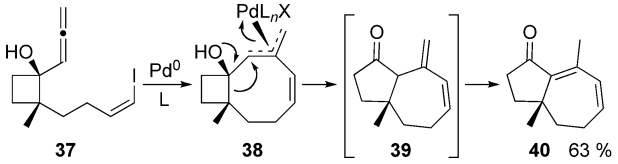


Scheme 9. Domino ring-expansion/direct-arylation sequence. DMSO = dimethyl sulfoxide.



Scheme 10. Ring expansion of π-allyl palladium species.

Nemoto et al. pioneered this approach with an intramolecular carbopalladation of allene **37** to generate the π-allyl palladium intermediate **38** (Scheme 11). The Wagner–

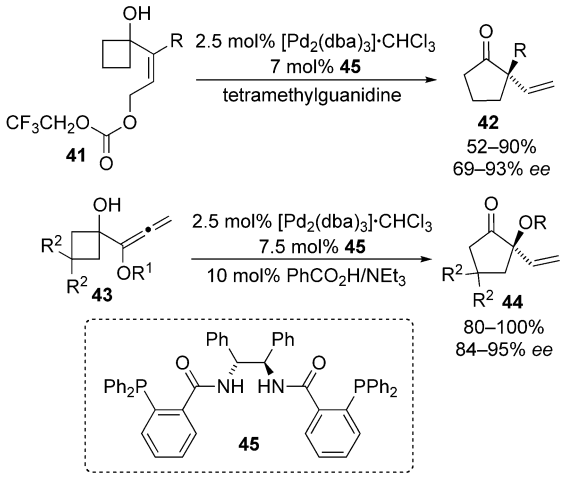


Scheme 11. Wagner–Merweein shift initiated by carbopalladation of an allene.

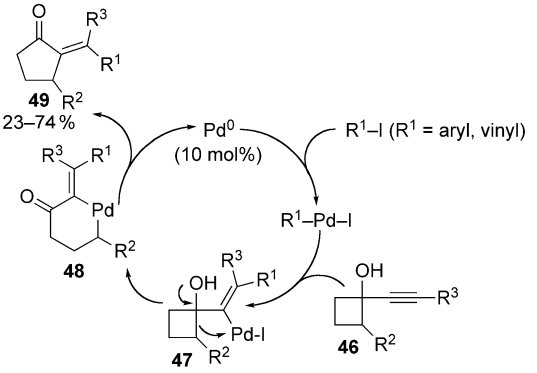
Meerwein shift yielded the fused bicycle **39**, which then isomerized to the more stable enone **40** as the final product.[23] These results led to the development of an intermolecular version of this reaction with external aryl halides.[24] Related transformations were also reported in which the crucial π-allyl palladium intermediate was generated from propargyl carbonates[25a,b] or by carbopalladation of conjugated dienes.[25c]

Trost and Yasukata developed an asymmetric version of this ring expansion. In this first approach, they generated the π-allyl palladium intermediate from allyl carbonate precursors **41** (Scheme 12).[26] High levels of enantioselectivity were achieved with the Trost ligand (**45**). Later, Trost and Xie developed another process based on a hydropalladation reaction of electron-rich alkoxy allenes **43** to trigger the Wagner–Meerwein shift.[27]

Larock and Reddy discovered a related but mechanistically distinct process for the synthesis of 2-alkylidenecyclopentanones from alkynyl-substituted cyclobutanols.[28] This reaction involves a regioselective carbopalladation of alkynes **46** to generate vinyl Pd^{II} intermediates **47**, which then promote the ring expansion to give six-membered palladacycles **48** (Scheme 13). Reductive elimination leads to cyclopentenones **49** in moderate to good yields.



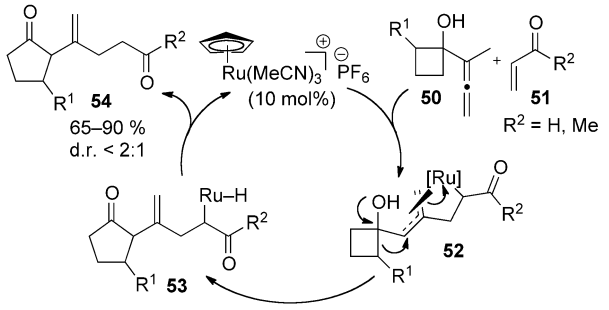
Scheme 12. Enantioselective Wagner–Meerwein shift described by Trost and Yasukata. dba = dibenzylideneacetone.



Scheme 13. Carbopalladation/ring-expansion sequence described by Larock and Reddy.

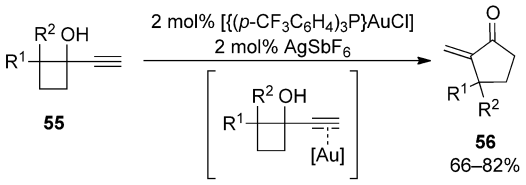
2.3.3. Ruthenium- and Gold-Catalyzed Ring Expansion

Ihara and co-workers reported the first ruthenium-catalyzed procedure for the synthesis of α-substituted cyclopentanones from allenyl cyclobutanols (Scheme 14).[29a] The reaction is proposed to proceed by the coordination of the allenyl cyclobutanol **50** and acrolein or methylvinylketone (**51**) to a cationic $CpRu^+$ fragment to give π-allyl ruthenium complex **52**. Ring expansion followed by reductive elimination then forms cyclopentanones **54** in good yields. The same group extended this transformation to alkynyl cyclobutanol substrates.[29b]



Scheme 14. Ruthenium(II)-catalyzed coupling/ring expansion described by Ihara and co-workers.

During the last decade, the propensity of gold complexes to act as carbophilic Lewis acids and to activate carbon–carbon π bonds has led to the discovery of numerous new synthetic methods. In this context, Toste and co-workers reported the ring expansion of alkynyl cyclobutanols **55** to methylenecyclopentanones **56** with cationic gold(I) complexes (Scheme 15).[30]

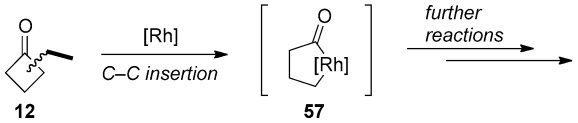


Scheme 15. Gold-catalyzed ring expansion of alkynyl cyclobutanols, as described by Toste and co-workers.

3. Metal-Catalyzed Activation of C–C Bonds

3.1. Insertion into the Acyl–Carbon Bond of Cyclobutanones

The direct oxidative insertion of a rhodium(I) complex into the acyl–carbon bond of a cyclobutanone forms a rhodacycle **57** (Scheme 16). Depending on the substrate substitution pattern, the metal complex used, and the reaction conditions, the acyl rhodium intermediate **57** can undergo a variety of transformations.

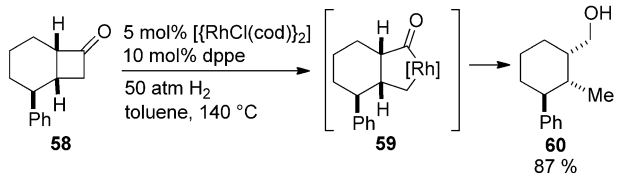


Scheme 16. Direct insertion of a Rh^I complex into an acyl–carbon bond.

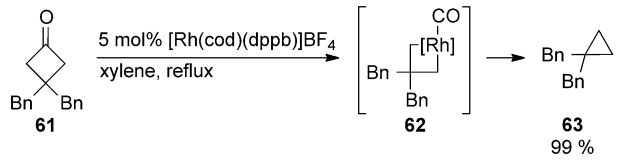
Ito and co-workers described in 1994 the first catalytic C–C activation of cyclobutanones with a rhodium(I) catalyst.[31a] As shown for cyclobutanone **58**, the rhodium complex inserts into the less substituted acyl–carbon bond to form the organorhodium species **59** (Scheme 17).[31a,b] Under an atmosphere of hydrogen, reductive ring cleavage occurs via an intermediary aldehyde delivering alcohol **60** as the terminal product.

An alternative reaction pathway of the acyl rhodium five-membered-ring intermediate is a decarbonylative ring contraction (Scheme 18).[31] In this case, metal insertion is followed by CO extrusion to afford after reductive elimination a cyclopropane in nearly quantitative yield.

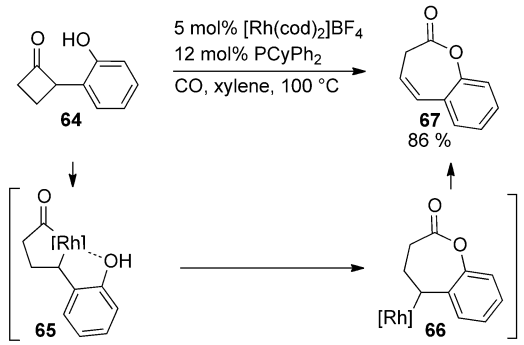
Ito and co-workers further showed that a rhodacyclopentanone can be intercepted by an adjacent phenolic hydroxy group, as in **65**, to give lactone **66** (Scheme 19).[32] Subsequent



Scheme 17. Reductive ring cleavage delivers primary alcohols, as described by Ito and co-workers. cod = 1,5-cyclooctadiene, dppe = 1,2-bis(diphenylphosphanyl)ethane.



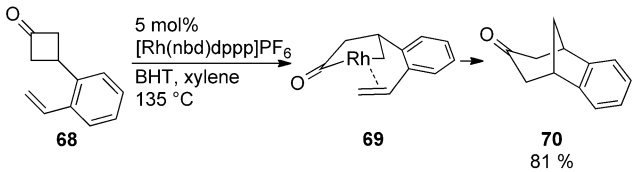
Scheme 18. Ito's decarbonylative ring contraction. Bn = benzyl, dppb = 1,4-bis(diphenylphosphanyl)butane.



Scheme 19. Intramolecular interception of **65** by a hydroxy group. Cy = cyclohexyl.

β-hydride elimination yielded **67**. It was essential to perform the reaction under a CO atmosphere to suppress the concurrent decarbonylation of **65**.

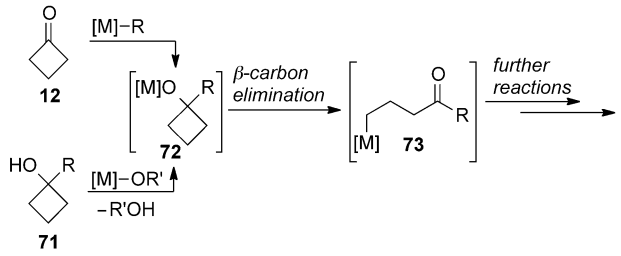
An alternative pathway was reported by Murakami and co-workers for rhodacycle **69**.[33] Intramolecular interception of this intermediate by an olefin provided the tricyclic ketone **70** in good yield through carborhodation and reductive elimination (Scheme 20).



Scheme 20. Intramolecular carborhodation of rhodacycle **69**. BHT = butylated hydroxytoluene, dppp = 1,3-bis(diphenylphosphanyl)-propane, nbd = norbornadiene.

3.2. β-Carbon Elimination from tert-Cyclobutanolates

Hartwig and co-workers thoroughly investigated the propensity of triaryl carbinols to undergo β-carbon elimination in the presence of a rhodium complex.[34] In analogy, cyclobutanolates **72** are in equilibrium with alkyl metal species **73** (Scheme 21). The latter are favored owing to the

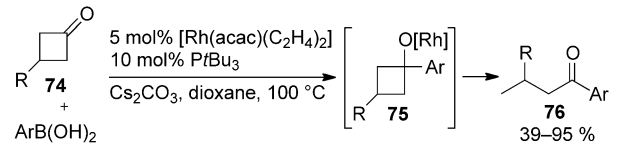


Scheme 21. β-Carbon elimination of *tert*-cyclobutanolates.

release of ring strain. This principle has evolved into a relatively robust method for the generation of highly reactive alkyl metal intermediates. Further downstream reactions enable access to a myriad of synthetically versatile products.[35] The important metal alcoholate **72** can be obtained either by the addition of organometallic reagents to cyclobutanone (**12**) or directly from the corresponding cyclobutanol **71** through ligand exchange.

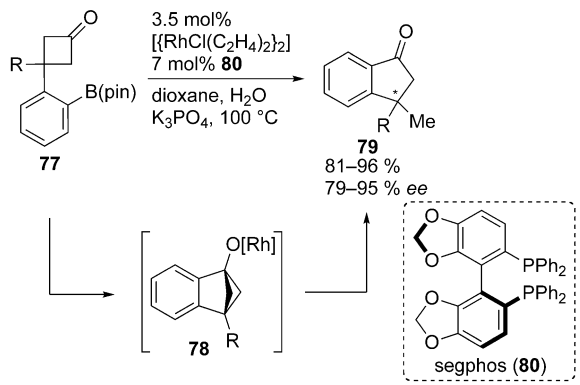
3.2.1. Generation of Rhodium tert-Cyclobutanolates by 1,2-Addition

In 2004, Murakami and co-workers reported an intermolecular 1,2-addition of aryl rhodium species generated from aryl boronic acids to give rhodium cyclobutanolates **75** (Scheme 22).[36] Subsequent β-carbon elimination and a series of β-hydride eliminations and readditions afforded an oxa-π-allylrhodium species, which was finally protonated to yield aryl ketones **76**. The reaction proceeded well with monosubstituted cyclobutanones **74**, whereas bulkier 3,3-disubstituted cyclobutanones were not suitable substrates.



Scheme 22. Intermolecular 1,2-addition of aryl rhodium species. acac = acetylacetonate.

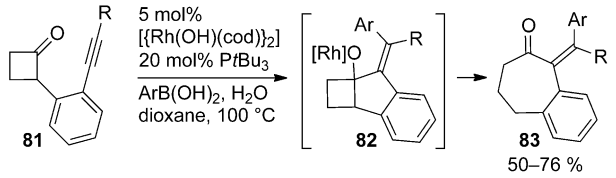
In contrast, 3,3-disubstituted cyclobutanones **77** perform well in an intramolecular reaction (Scheme 23).[37] In this case, 1,2-addition leads to a strained rhodium alkoxide **78**, which in turn undergoes β-carbon elimination to give an indanone **79**. Differentiation of the two enantiotopic C–C bonds of **78** in



Scheme 23. Intramolecular 1,2-addition followed by enantioselective β-carbon elimination. pin = pinacolato.

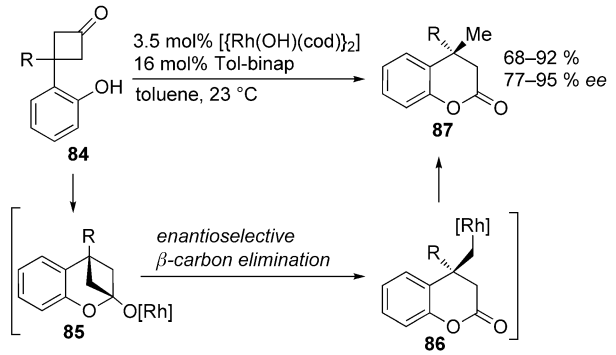
the β-carbon-elimination step through the use of segphos (**80**) as a steering ligand enables a highly enantioselective process.

A further extension is the intramolecular 1,2-addition of an adjacent vinyl rhodium moiety generated by a regioselective carborhodation of alkyne **81** (Scheme 24).[38] The regioselective β-carbon elimination of rhodium alkoxide **82** affords, after successive β-hydride elimination/readdition processes, benzoheptanones **83** upon protonolysis.



Scheme 24. Intramolecular 1,2-addition of vinyl rhodium species.

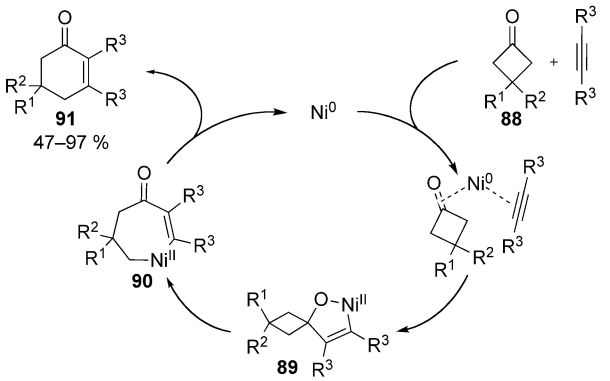
Murakami and co-workers also applied the concept to the intramolecular 1,2-addition of rhodium phenolates (Scheme 25).[39] The initial step of the reaction is believed to deliver hemiacetal **85**. Use of the chiral ligand tol-binap results in an enantioselective β-carbon elimination. Protodemetalation of the alkyl rhodium species **86** gives dihydrocoumarins **87** with good to excellent enantioselectivity. Placement of the phenol substituent in the 2- instead of the 3-position of the cyclobutanone provides access to five- and seven-membered-ring benzolactones.[39c]



Scheme 25. Intramolecular 1,2-addition of rhodium phenolates, followed by enantioselective β-carbon elimination. tol-binap = 2,2′-bis(di-*p*-tolylphosphanyl)-1,1′-binaphthyl.

3.2.2. Formation of Nickel Cyclobutanolates by Cycloaddition

Murakami et al. reported a nickel-catalyzed process in which cyclobutanones **88** serve as a four-carbon-atom component for a formal [4+2] cycloaddition with alkynes to provide cyclohexenones **91** (Scheme 26).[40] The proposed

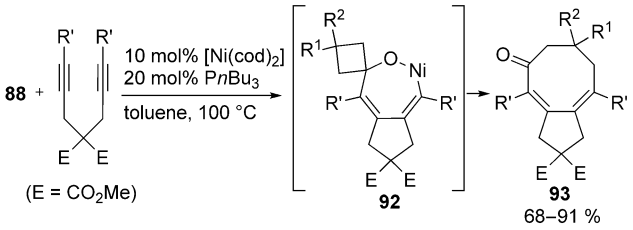


Scheme 26. Nickel-catalyzed [4+2] cycloaddition of cyclobutanones and alkynes.

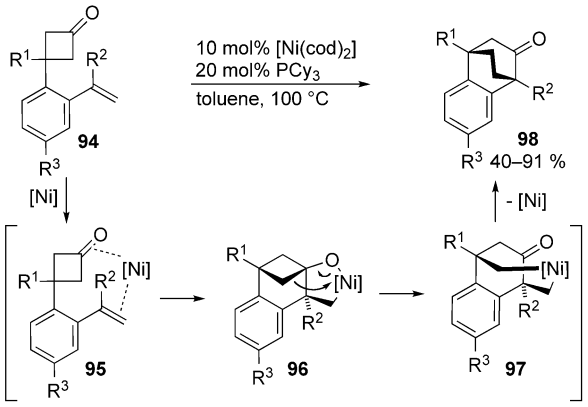
mechanism starts with the simultaneous coordination of **88** and the alkyne to a Ni^0 complex. The oxanickelacyclopentene **89** formed in the subsequent oxidative cyclization undergoes β-carbon elimination to give a seven-membered nickelacycle **90**. Reductive elimination then affords cyclohexenones **91** in moderate to excellent yields.

The reaction was extended to a formal [4+2+2] cycloaddition with diynes to give eight-membered carbacycles **93** (Scheme 27).[41] In close analogy to the previous process, oxanickelacycle **92** was proposed as a key intermediate. Opening of the cyclobutane ring and reductive elimination yields cyclooctadienones **93**.

An intramolecular version of the reaction also accommodates less reactive olefins as coupling partners (Scheme 28).[42] As before, an oxidative cyclization leads to an intermediate **96**, which undergoes β-carbon elimination to give a nickela-



Scheme 27. Nickel-catalyzed [4+2+2] cycloaddition of cyclobutanones and diynes.

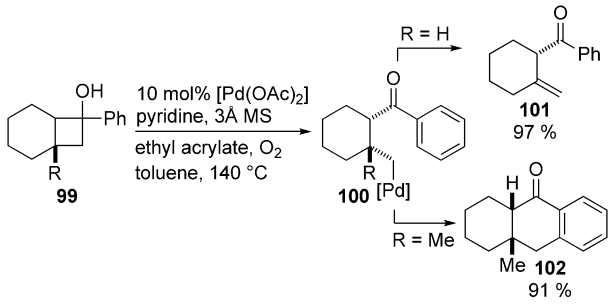


Scheme 28. Intramolecular cyclization with olefins.

cycle **97**. Reductive elimination completes the catalytic cycle and releases benzobicyclo[2,2,2]octenones **98**.

3.2.3. β-Carbon Elimination from tert-Cyclobutanols

In 1999, Uemura and co-workers reported the first example of a palladium-catalyzed β-carbon elimination from *tert*-cyclobutanols (Scheme 29).[43a] For example, the alkyl

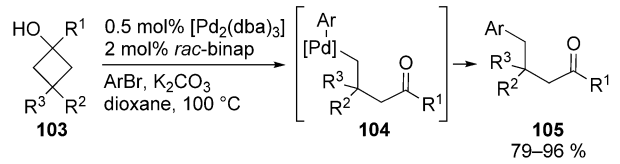


Scheme 29. Pioneering palladium(II)-catalyzed ring opening of *tert*-cyclobutanols, as described by Uemura and co-workers. MS = molecular sieves.

palladium species **100** was obtained from alcohol **99**. In the presence of a β-hydrogen atom (R = H), β-hydride elimination occurs and results in the formation of the β,γ-unsaturated ketone **101**. If no β-hydrogen atom is available (R = Me), **100** undergoes cyclization by C–H bond functionalization of the aryl substituent to yield the tricyclic ketone **102**.[43] Reoxidation of the palladium complex occurs under an oxygen atmosphere.

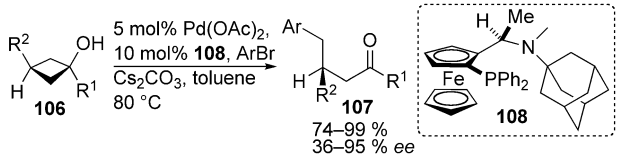
Nishimura and Uemura demonstrated that the alkyl palladium species formed can be intercepted with aryl halides (Scheme 30).[44] Oxidative addition of an aryl halide generates the requisite Pd^{II} species and β-C elimination delivers alkyl palladium intermediate **104**. Reductive elimination then leads to arylated ketones **105**.

In 2003, the same group reported an enantioselective version of this process.[45] By using the engineered bidentate P,N ferrocenyl ligand **108**, they obtained γ-arylated ketones



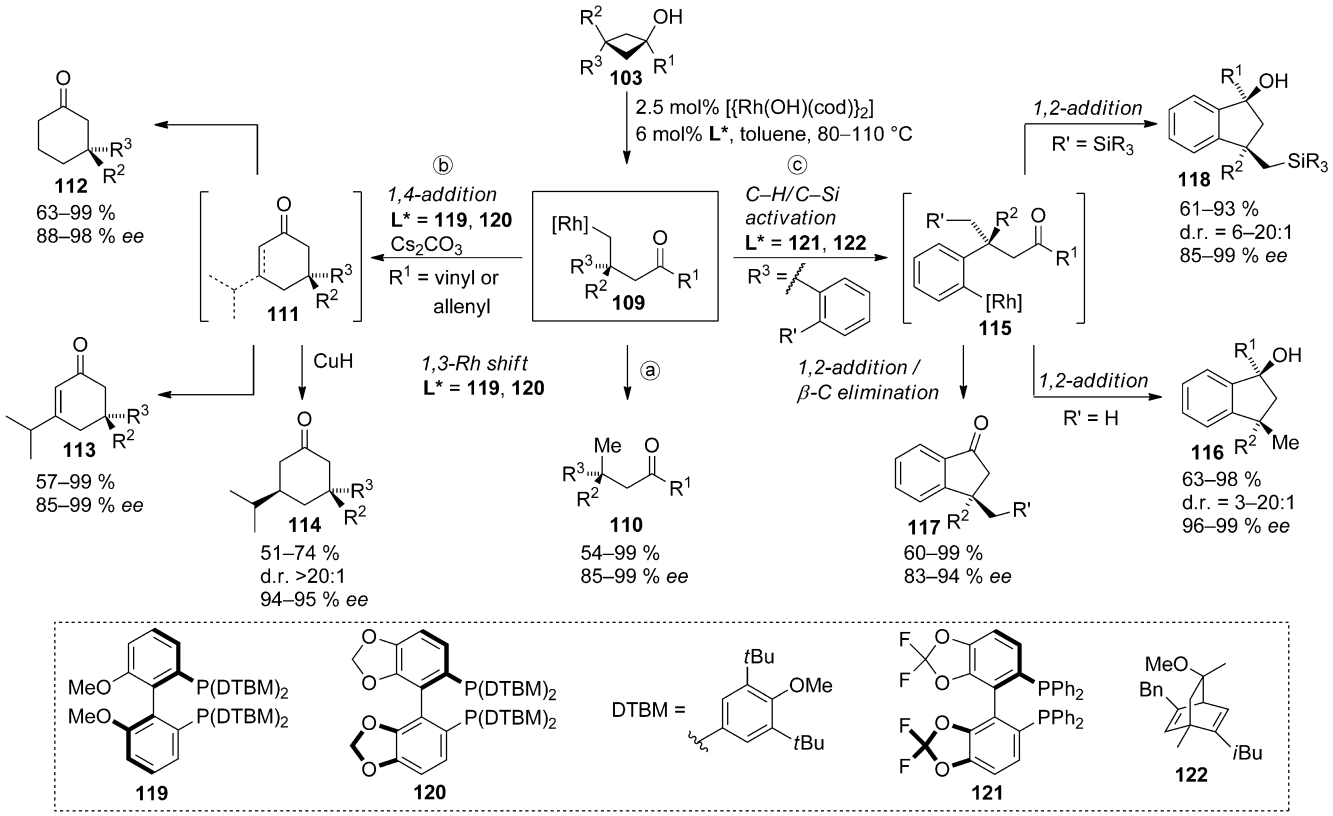
Scheme 30. β-Carbon elimination with subsequent arylation. binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl.

107 with a tertiary stereogenic center with excellent enantioselectivity (up to 95% *ee*; Scheme 31). Lower enantioselectivities that depended strongly on the substitution pattern were observed for 3,3-disubstituted cyclobutanols.



Scheme 31. Enantioselective palladium(II)-catalyzed β-carbon elimination.

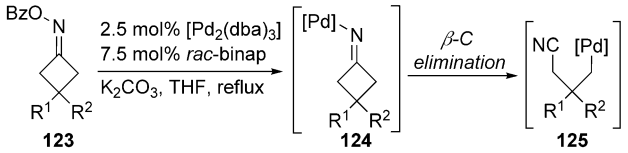
In 2008, we reported an enantioselective rhodium-catalyzed β-carbon elimination from cyclobutanols.[46a] Alkyl rhodium intermediates **109** bearing an all-carbon quaternary stereogenic center can be obtained from **103** with excellent enantioselectivity with a variety of chiral biphosphine ligands (Scheme 32). A number of different downstream reaction pathways enable access to a diverse range of products.[46] The protodemetalation of **109** affords acyclic ketones **110** (pathway **a**).[46b] Labeling experiments showed that the mechanism proceeds by a 1,3-rhodium shift to form an oxa-π-allylrhodium species before protonation occurs. The C–C bond cleavage of 1-vinyl- or 1-allenyl-substituted cyclobutanols **103** simultaneously generates an enone or allenone moiety, respectively. Subsequent cyclization of **109** by intramolecular 1,4-addition provides access to six-membered-ring compounds (pathway **b**). Depending on the reaction conditions and the substitution pattern, products **112**, **113**, and **114** can be obtained selectively.[46a,c] Intermediates **109** with an aromatic substituent R^2 or R^3 undergo a 1,4-rhodium shift through C–H bond activation (pathway **c**).[47] An intramolecular addition of the resulting aryl rhodium species **115** to the carbonyl group delivers substituted indanols **116** in a highly enantio- and diastereoselective manner.[46d,e] Remarkably, electron-rich aromatic substituents R^1, such as a 1-thienyl group, enable a second β-carbon elimination from the rhodium indanolate to provide ultimately indanones **117**.[46f] We further discovered that the alkyl→aryl rhodium shift is also possible through C–Si instead of C–H bond activation.[46g] This process introduces a functionalizable alkyl silyl group on indanols **118**. Generally, C–Si bond activation dominates over the competing C–H bond activation pathway with phosphine ligands. However, diene ligands, such as dolefin (**122**), are required to selectively activate C–Si bonds of bulkier silyl groups, which fail to react when phosphine ligands are used.[48]



Scheme 32. Reaction pathways of the alkyl rhodium intermediate **109** generated by β-carbon elimination from cyclobutanol **103**.

3.3. β-Carbon Elimination from Iminyl Palladium(II) Complexes

Uemura and co-workers showed that the same principle used for β-carbon elimination from *tert*-cyclobutanols can be applied to benzoylated oximes **123** with a Pd^0 catalyst (Scheme 33).[49] Oxidative addition generates iminopalladium(II) species **124**, which in turn undergo β-carbon elimination to give nitriles **125**.



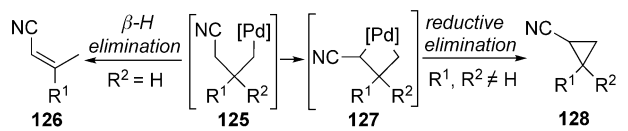
Scheme 33. β-Carbon elimination from iminyl palladium(II) complexes. Bz = benzoyl.

When possible, β-hydride elimination and migration of the formed double bond into conjugation yields α,β-unsaturated nitriles **126** (Scheme 34). If the β-H-elimination pathway is blocked, cyclopropanecarbonitriles **128** are obtained instead. The reaction proceeds presumably via palladacyclobutane **127**. With iridium complexes, a similar ring cleavage of oximes **123** is observed.[50] However, in this case, the reaction is believed to proceed through radical pathways.

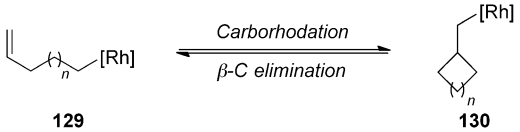
3.4. β-Carbon Elimination from Cyclobutylmethyl Rhodium Species

Reversal of the carborhodation of C–C double bonds is an attractive possibility for the activation of C–C bonds of cyclobutanes (Scheme 35). Owing to the release of ring strain, the equilibrium between carborhodation and β-carbon elimination lies on the side of the ring-opened compounds **129** for small rings ($n = 0,1$).

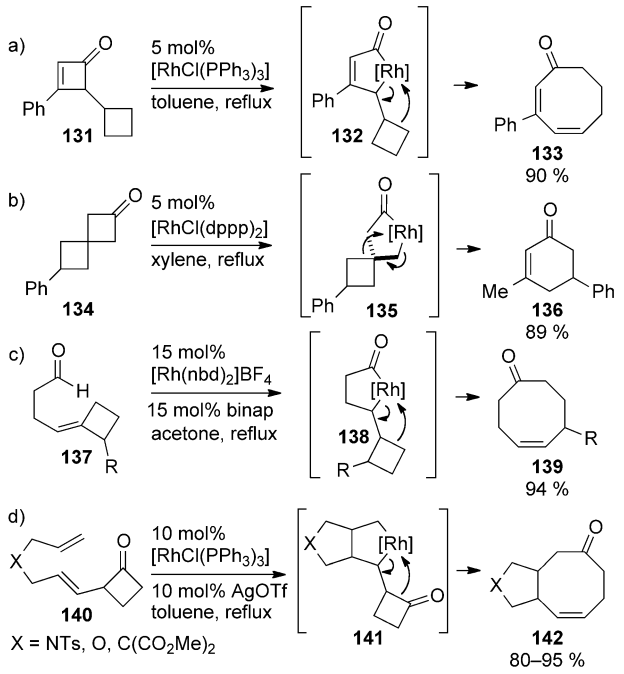
Several distinct methods for generating the required cyclobutylmethyl rhodium species **130** have been reported (Scheme 36).[51] In 1993, Liebeskind and Huffman investigated the C–C insertion of rhodium(I) complexes into cyclo-



Scheme 34. Downstream reactions of the alkyl palladium intermediate **125**.



Scheme 35. Equilibrium between carborhodation and β-carbon elimination: β-carbon elimination is dominant for small rings.

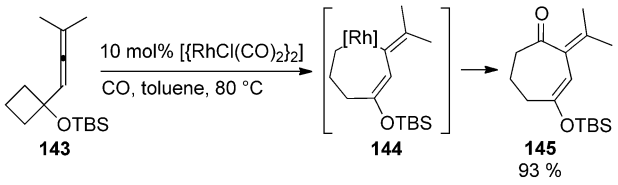


Scheme 36. β-Carbon elimination from cyclobutylmethyl rhodium species. Ts = *p*-toluenesulfonyl.

butenone **131**.[51a] Upon its formation, rhodacycle **132** underwent β-carbon cleavage of the adjacent cyclobutane, and subsequent reductive elimination provided cyclooctadienone **133**. Murakami et al. reported a related reaction of spirocyclobutanone **134**.[51b] Two consecutive C–C bond activations, first a C–C insertion into an acyl–carbon bond of **134** to form cyclobutylmethyl rhodium intermediate **135** and second a β-carbon elimination, afforded cyclohexenone **136**. Aïssa and co-workers used an intramolecular hydroacylation to obtain **138**, which collapsed to cyclooctenone **139**.[51c] Wender et al. accessed rhodacycles **141** through the cycloisomerization of dienes **140**.[51d] The adjacent four-membered ring was then opened by β-carbon elimination. In this case, the carbonyl group was required as an additional driving force to further facilitate ring opening.

3.5. Rhodium-Catalyzed C–C Activation of 1-Siloxy 1-Allenyl Cyclobutanes

The metal-catalyzed vinylcyclopropane rearrangement is a well-documented transformation.[52] Nevertheless, its extension to a homologous vinylcyclobutane rearrangement has proved difficult. Wender et al. successfully used siloxy substituents, which also facilitate the ring opening of vinylcyclopropanes. In combination with a chelating allenyl moiety, cyclobutane **143** underwent ring opening to yield rhodacycle **144** (Scheme 37).[53] As the reaction was performed under an atmosphere of carbon monoxide, a CO insertion occurred, and thus the synthetically valuable cycloheptenone **145** was obtained.



Scheme 37. Carbonylative [6+1] ring expansion described by Wender et al. TBS = *tert*-butyldimethylsilyl.

4. Asymmetric Baeyer–Villiger Reactions

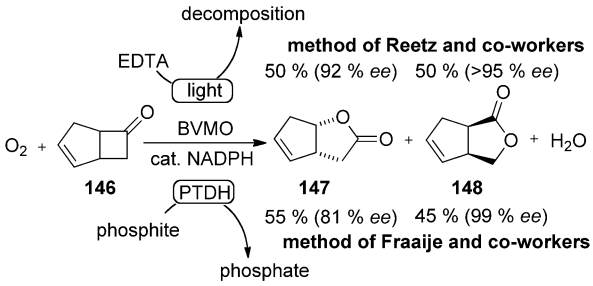
The Baeyer–Villiger (BV) oxidation of ketones to esters or lactones is an important reaction in organic chemistry.[54] Although the reaction is certainly not limited to cyclobutanones, this substrate class is often considered to be prototypical, and the resulting γ-lactones are synthetically useful. This section summarizes advances in bio-, organo-, and metal catalysis in the field of asymmetric BV reactions.

4.1. Enzymatic BV Reactions

Baeyer–Villiger monooxygenases (BVMOs) have been identified as a versatile class of enzymes for asymmetric BV reactions.[55] Optimization of these enzymes has provided highly robust BVMO mutants. For example, with these new enzymes the kinetic resolution of a racemic mixture of ketone **146** produced lactones **147** and **148**, both with excellent enantioselectivity [ratio **147** (94% *ee*)/**148** (98% *ee*): 48:52].[56] To avoid the use of a stoichiometric amount of the expensive cofactor NADPH, Reetz and co-workers developed a light-driven system in which NADPH is recycled in a coupled process.[57] Mihovilovic, Fraaije, and co-workers developed an alternative variant of the reaction by fusing a BVMO to a phosphite dehydrogenase (PTDH) that uses phosphite as a sacrificial reagent (Scheme 38).[58]

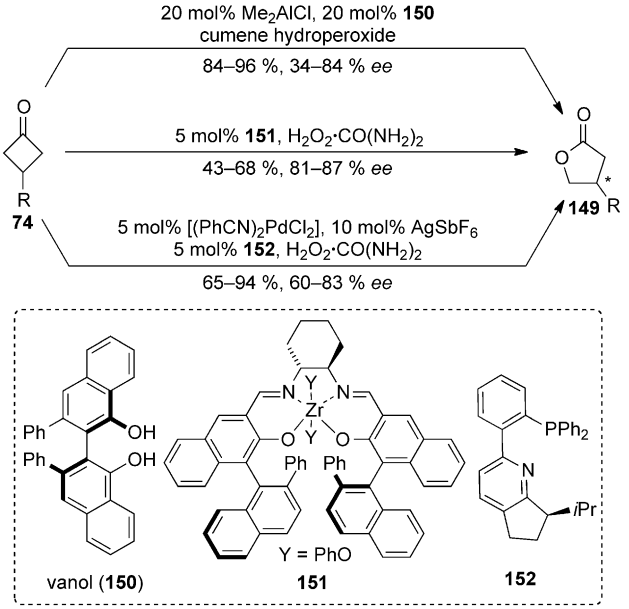
4.2. Enantioselective Metal-Catalyzed BV Reactions

Lopp et al. were the first to report an enantioselective metal-catalyzed BV oxidation of a cyclobutanone such as **74**;



Scheme 38. Enzymatic asymmetric BV reactions. EDTA = ethylenediaminetetraacetic acid; NADPH is the reduced form of nicotinamide adenine dinucleotide phosphate.

they carried out the transformation under Sharpless epoxidation conditions.[59] Since then, several other metal complexes have been identified that catalyze this transformation with moderate to good selectivity.[60–63] Bolm and co-workers reported several catalytic systems for this transformation, whereby they gradually improved the yield and selectivity of the reaction.[61] The latest system, a catalyst generated from Me_2AlCl and vanol (**150**), affords γ-lactones **149** with 34–84% *ee* (Scheme 39).[61d] Katsuki and co-workers improved



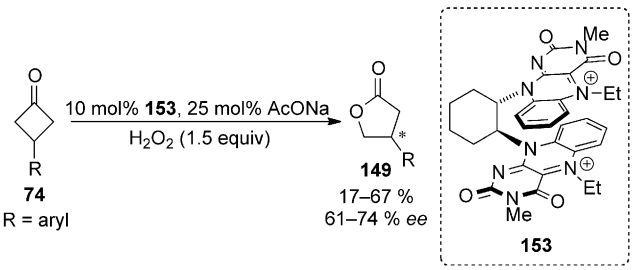
Scheme 39. Examples of metal-catalyzed asymmetric BV oxidations.

the selectivity with salen-type complexes **151** (M = Co^{III},[62a] Zr^{IV},[62b] Hf^{IV}[62c]) to 81–87% *ee*. They also discovered a cationic Pd^{II} catalyst based on the chiral P,N ligand **152** that efficiently promoted this transformation.[62d] Recently, Kočovský and co-workers reported a related system that afforded lactones **149** in excellent yields with comparable selectivity (55–81% *ee*).[63]

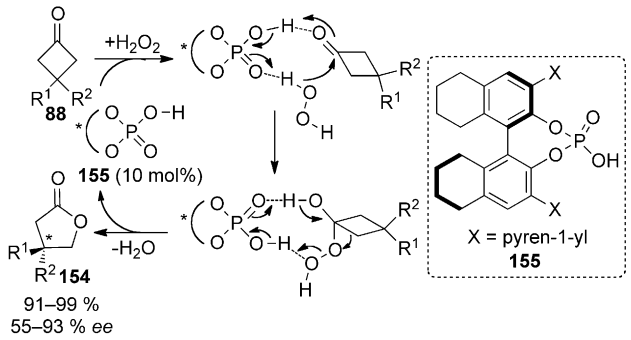
4.3. Organocatalytic BV Reactions

Flavin and derivatives thereof have been shown to be suitable catalysts for the BV oxidation of cyclobutanones.[64] Inspired by these results, Imada et al. designed the chiral bisflavin catalyst **153**, which promotes the enantioselective BV oxidation of 3-aryl cyclobutanones (Scheme 40).[65]

Ding and co-workers took another approach and investigated the potential of chiral phosphoric acids for this reaction.[66] High levels of enantioselectivity (up to 93% *ee*) and excellent yields were reported for the transformation of 3-substituted cyclobutanones with catalyst **155** (Scheme 41).[66a] Mechanistic studies suggest that the chiral phosphoric acid catalyst is involved in both the activation of the carbonyl group and the initiation of the rearrangement.[66b]



Scheme 40. Asymmetric BV reaction promoted by the chiral flavin catalyst designed by Imada et al.



Scheme 41. Brønsted acid catalyzed enantioselective BV reaction.

5. Conclusion

In this Minireview, we have highlighted recent advances in the use of four-membered rings as potent substrates in catalysis. This field has prospered over the past decade, and a myriad of intriguing and often highly selective reactions have emerged. Transition-metal catalysts, mainly rhodium and palladium complexes, have been successfully used for insertions into the acyl–carbon bond of cyclobutanones and for β-carbon eliminations of *tert*-cyclobutanols. These methods provide access to synthetically versatile building blocks and are complementary to traditional approaches. Some synthetic applications have already been reported. Although the successful transfer to cyclobutanes of reactions previously linked exclusively to cyclopropanes is highly remarkable, the majority of the examples described herein require the outstanding reactivity of four-membered rings. This aspect might be viewed as a limitation, but we tend to see it as an opportunity for the discovery of novel reactions. The next important step will be the extension of these reactions to further, less activated substrate classes.

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