

Recent Advances in the Catalytic Pauson–Khand-Type Reaction

Takanori Shibata^{a,*}

^a Department of Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku, Tokyo, 169-8555, Japan
 Fax: (+81)-3-5286-8098; e-mail: tshibata@waseda.jp

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Abstract: The Pauson–Khand-type reaction is formally a [2+2+1] cycloaddition involving an alkyne, an alkene and carbon monoxide catalyzed or mediated by transition metal complexes. This review focuses on the catalytic reaction and describes the recent research on the Pauson–Khand-type reaction.

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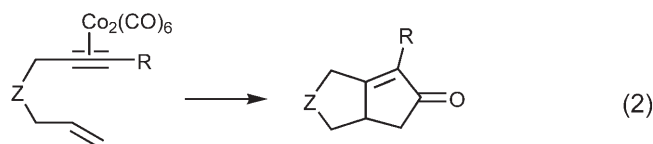
Keywords: asymmetric catalysis; carbonylation; cycloaddition; enones; enynes; transition metals

1 Introduction

In 1973, I. U. Khand and P. L. Pauson reported a [2+2+1] cycloaddition of an alkyne, an alkene and carbon monoxide. An alkyne- $\text{Co}_2(\text{CO})_6$ complex, which was prepared from $\text{Co}_2(\text{CO})_8$ and an alkyne along with the generation of carbon monoxide, reacted with an alkene to give a synthetically useful cyclopentenone.^[1] In the initial study of an intermolecular reaction, symmetrical and active alkenes, such as ethylene and norbornene, were used because four regioisomers, which are often difficult to separate, could be obtained when an unsymmetrical alkyne and alkene were used [Eq. (1)].

Use of the intramolecular reaction avoids the formation of the regioisomers. Carbonylative coupling of

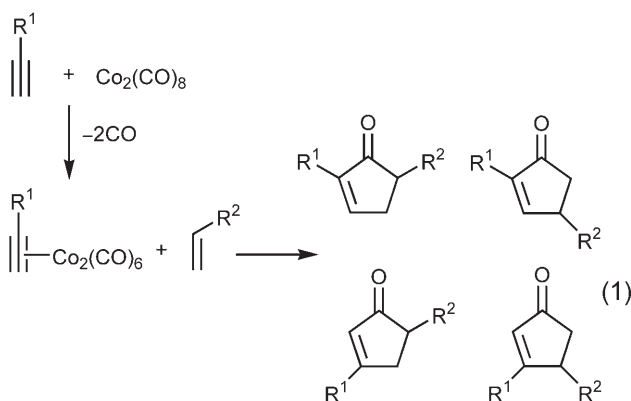
an enyne gives a bicyclic cyclopentenone [Eq. (2)]. In the 1980s, the Pauson–Khand reaction was recognized as a useful synthetic protocol and was used as a key reaction for the construction of carbocyclic skeletons in natural product syntheses.^[2]



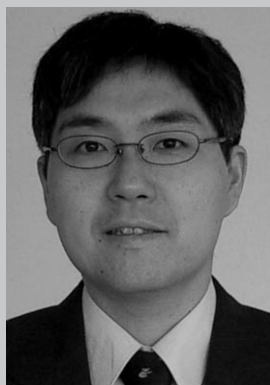
In this short review, I briefly summarize the early research on the catalytic Pauson–Khand reaction prior to 2000, and then summarize the recent reports, most of which were published after 2000.^[3]

2 The Road to the Catalytic Pauson–Khand(-Type) Reaction

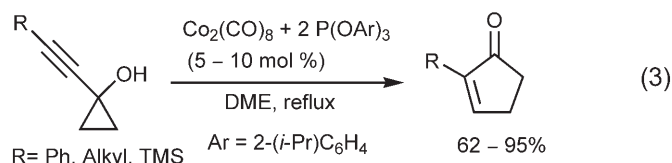
The proposed mechanism of the Pauson–Khand reaction is shown in Scheme 1.^[4] It suggests that a catalytic reaction could be possible under an atmosphere of carbon monoxide; however, there have been only a few limited examples, in which large excess amounts of active alkenes were needed under a high pressure of carbon monoxide. This would be probably because $[\text{Co}_2(\text{CO})_6]$ is readily transformed into more stable



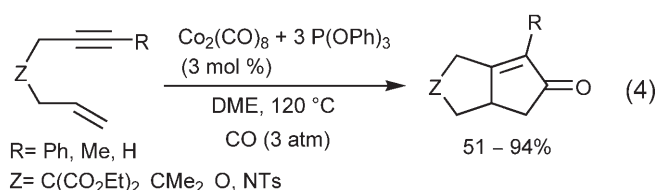
Takanori Shibata was born in 1966 in Tokyo, Japan. He studied chemistry at the University of Tokyo and earned his Ph.D in 1994 under the supervision of Prof. Koichi Narasaka. As a Research Associate, he moved to the Faculty of Science, Kitasato University (1994–1995), then to the Faculty of Science, Tokyo University of Science in the group of Prof. Kenso Soai (1995–1999). He was promoted to Associate Professor in 1999 at the Faculty of Science, Okayama University, then moved to Waseda University in 2003. He has been Professor of the School of Science and Engineering at Waseda University since 2006. He worked with Prof. E. J. Corey (Harvard University) as a postdoctoral fellow in 2001. He received the Daicel Award in 1997 and the Incentive Award in Synthetic Organic Chemistry, Japan in 2005. His current research interests concentrate on transition metal-catalyzed cycloadditions, especially asymmetric reactions.



cobalt carbonyl complex realized a catalytic reaction [Eq. (3)].^[5]

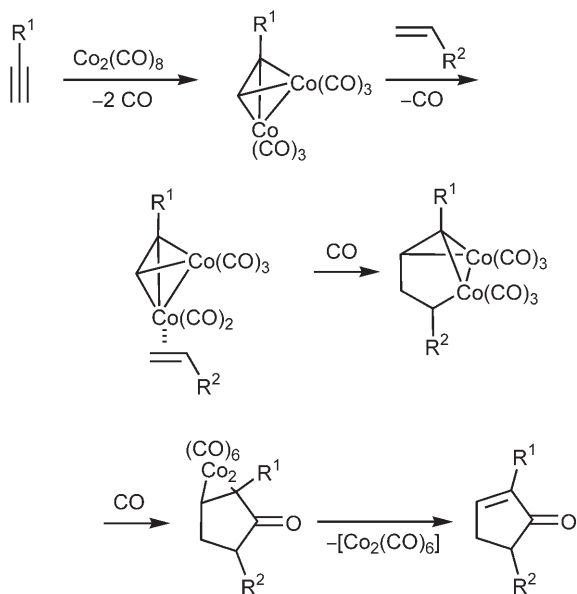
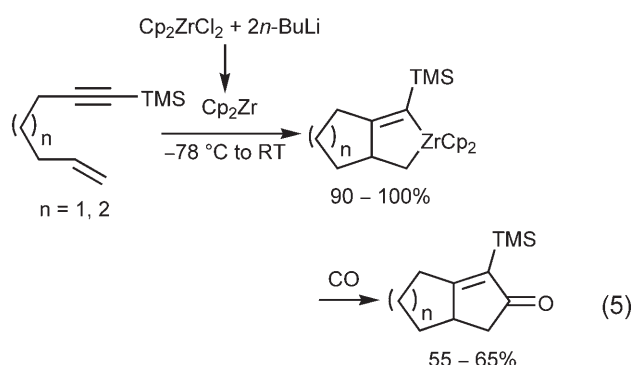


In 1994, Jeong disclosed a catalytic carbonylative coupling of enynes using Co₂(CO)₈ with triphenyl phosphite under the condition of pressurized carbon monoxide [Eq. (4)].^[6] This report represented the



starting point for catalytic and practical Pauson–Khand reactions, and various reaction conditions using a catalytic amount of cobalt carbonyl complexes were published.^[3]

In another approach to the synthesis of bicyclic cyclopentenones from enynes, Negishi reported a Zr-mediated reaction. The reaction of two-valent zirconium, which was prepared in situ from Cp₂ZrCl₂ and *n*-BuLi, with an enyne gave the metallacyclopentene, and this was readily transformed into a bicyclic cyclopentenone under an atmospheric pressure of CO [Eq. (5)].^[7]

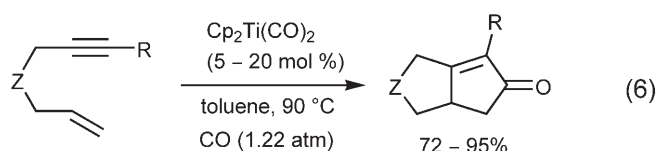


Scheme 1. Proposed mechanism of the Pauson–Khand reaction.

oligomeric cobalt complexes prior to the complexation with the alkyne.

In 1993, Iwasawa reported a Co-catalyzed rearrangement of alkynylcyclopropanols to cyclopentenones. Use of a triaryl phosphite as a ligand of the

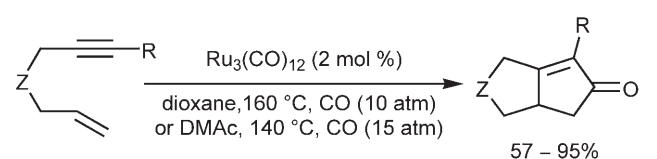
In 1996, Buchwald reported a Ti-catalyzed intramolecular coupling of various enynes under an atmosphere of carbon monoxide, and bicyclic cyclopentenones were directly obtained in good to excellent yields [Eq. (6)].^[8] The present reaction is recognized



R = Ar, Me, H
Z = C(CO₂Et)₂, CH₂, O, NPh

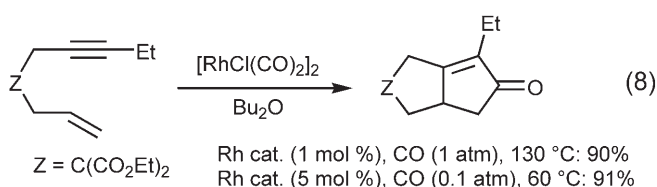
as the first catalytic Pauson–Khand-type reaction, which means a carbonylative coupling of an alkyne and an alkene catalyzed by transition metal complexes except for cobalt ones.

Ru₃(CO)₁₂ operated as an efficient catalyst under a high pressure of carbon monoxide at high temperatures [Eq. (7)].^[9] In the case of [RhCl(CO)₂]₂, the car-

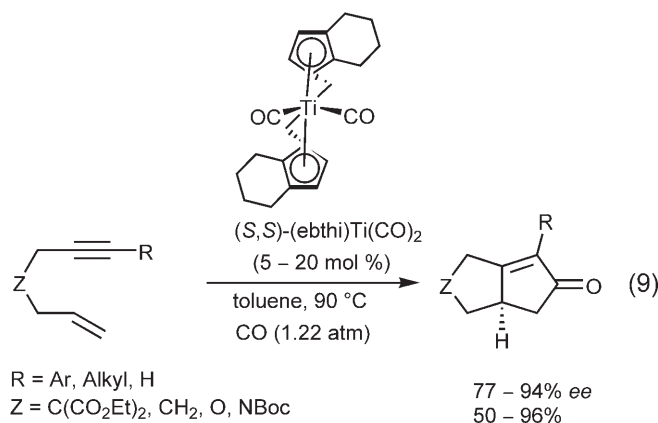


R = Ar, Alkyl, TMS
Z = C(CO₂Et)₂, O, NTs

bonylative coupling proceeded more smoothly under a lower partial pressure of carbon monoxide, probably because excess amounts of carbon monoxide deactivate the Rh catalyst by coordination to the metal center [Eq. (8)].^[10,11]



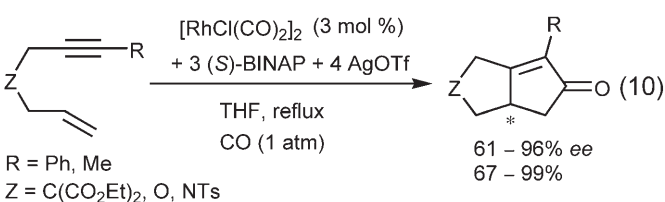
metal center by excess amounts of CO and part of the reaction proceeds by an achiral metal catalyst.^[13] Buchwald overcame the difficulty by using a chiral Ti complex in which the metal center and chiral moiety were connected by a σ -bond [Eq. (9)]. Various enynes



R = Ar, Alkyl, H
Z = C(CO₂Et)₂, CH₂, O, NBoc

were transformed into chiral bicyclic cyclopentenones by the chiral Ti-catalyzed highly enantioselective intramolecular Pauson–Khand-type reaction. However, several steps were needed for the preparation of the chiral ligand, and the Pauson–Khand-type reaction must be conducted in a glovebox because the low-valent Ti complex with a Ti–C σ -bonds is very sensitive to air and moisture.

In 2000, Jeong reported a cationic Rh-catalyzed, enantioselective Pauson–Khand-type reaction. The chiral catalyst was prepared *in situ* from [RhCl(CO)₂]₂ and BINAP by the addition of AgOTf [Eq. (10)].^[14] Recently, a spiro-monophosphoramidite was reported



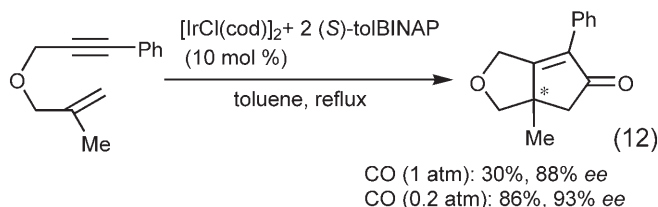
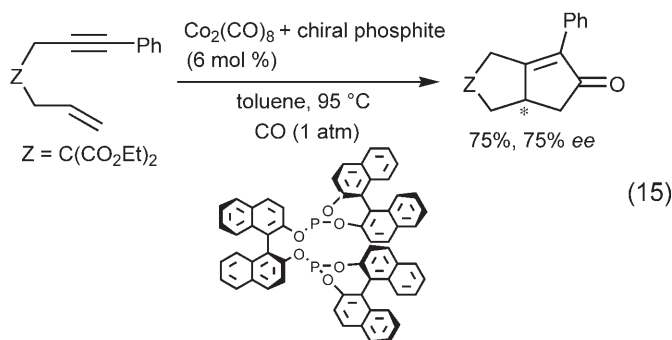
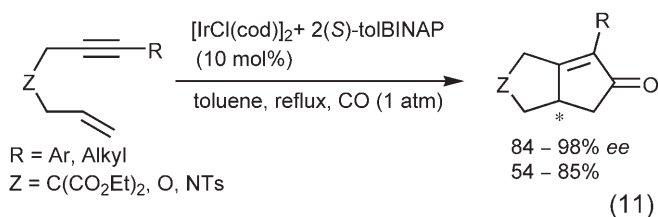
R = Ph, Me
Z = C(CO₂Et)₂, O, NTs

3 Enantioselective Pauson–Khand(-Type) Reaction

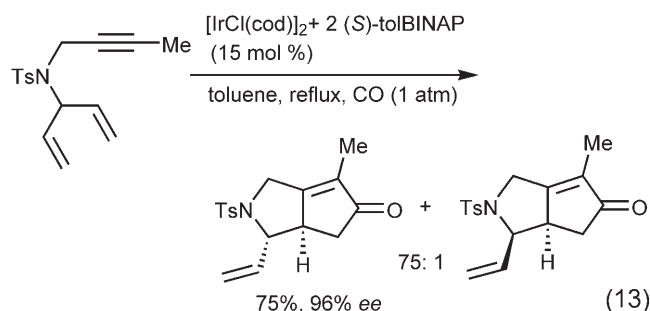
Diastereoselective Pauson–Khand reactions using enynes with chiral auxiliaries on the alkyne or alkene terminus or tethers have been reported as have also enantioselective reactions using a stoichiometric amount of chiral cobalt complexes.^[3a,d] However, a catalytic and enantioselective reaction had to wait till Buchwald's report in 1996.^[12] A highly enantioselective reaction under a CO atmosphere using a transition metal catalyst with a chiral ligand is rather difficult because the chiral ligand is dissociated from the

to be a chiral ligand for the Rh catalyst but the enantioselectivity did not exceed that achieved by BINAP.^[15]

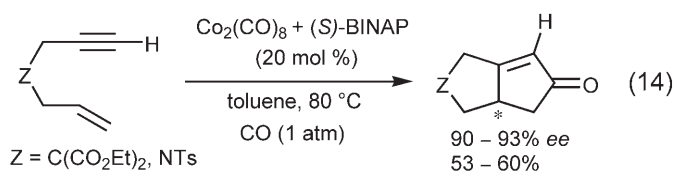
Quite independently, Shibata reported the catalysis by Ir-tolBINAP. The chiral Ir catalyst was readily prepared *in situ* from [IrCl(cod)]₂ and tolBINAP, both of which are commercially available and air-stable [Eq. (11)].^[16] The condition of low partial pressure of CO (0.2 atm) worked well also in the Ir-catalyzed enantioselective reaction: higher yield and enantioselectivity were achieved than under an atmospheric pressure of CO [Eq. (12)].



The chiral Ir catalyst was also used in the desymmetrization of *meso*-dienynes.^[17] A highly enantio- and diastereoselective Pauson–Khand-type reaction proceeded to give vinyl-substituted bicyclic cyclopentenones with two chiral centers [Eq. (13)].



Prior to the Rh- and Ir-catalyzed reactions, Hiroi reported a Co₂(CO)₈-BINAP complex-catalyzed reaction.^[18] High enantioselectivity was achieved; however, substrates were limited to enynes with no substitu-

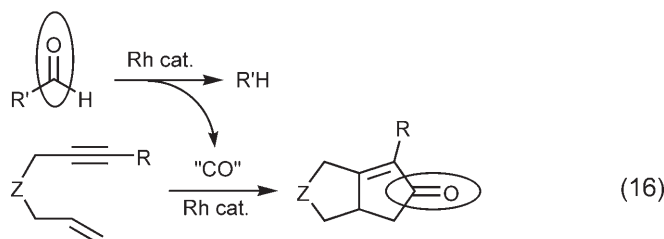


ent on the alkyne terminus [Eq. (14)]. A Co₂(CO)₈-chiral phosphite catalyst was also reported but the enantioselectivity and generality of enynes were inferior to those with chiral Ti, Rh and Ir catalysts as mentioned above [Eq. (15)].^[19]

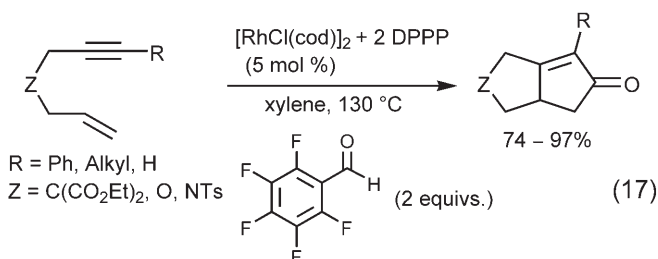
4 Pauson–Khand-Type Reactions Using Aldehydes as a CO Source

The transition metal-catalyzed decarbonylation of carbonyl compounds, such as aldehydes, ketones and acid chlorides, was already reported in the 1960s, and it was a key step in transition metal-catalyzed unique transformations.^[20] However, the use of generated carbon monoxide by a decarbonylation step was largely neglected.

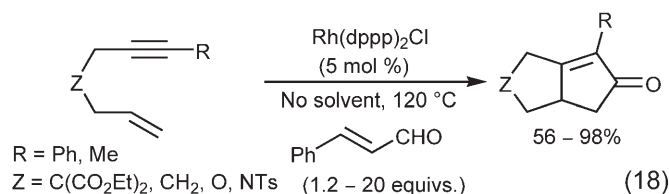
Rh complexes catalyze both the decarbonylation of aldehydes and the Pauson–Khand-type reaction, namely carbonylative coupling of enynes; therefore, a Pauson–Khand-type reaction using aldehydes as a CO source would be possible [Eq. (16)].



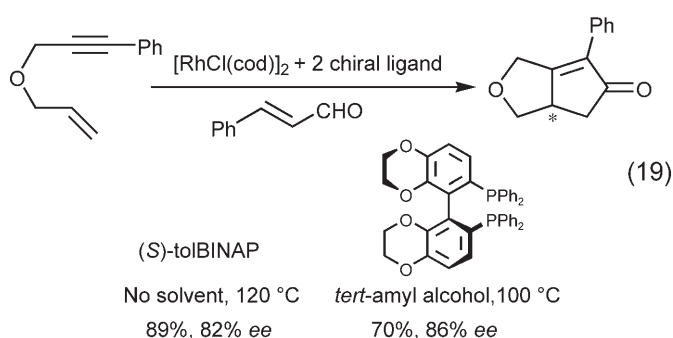
Morimoto realized the reaction using pentafluorobenzaldehyde as a CO source. Enynes were transformed into the corresponding bicyclic cyclopentenones under an atmosphere of nitrogen [Eq. (17)].^[21] Shibata independently disclosed the same type of reaction using cinnamaldehyde as a CO source [Eq.



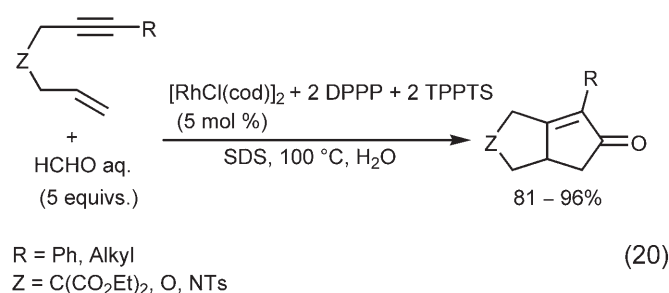
(18)].^[22] The reaction efficiently proceeded without solvent under an atmosphere of argon.



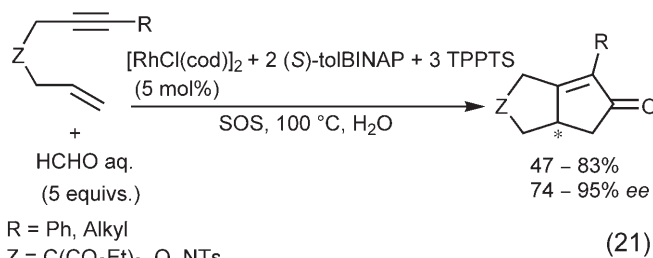
The reaction using cinnamaldehyde as a CO source could be applied for the enantioselective reaction using Rh-tolBINAP catalyst under no solvent conditions^[22b] and Rh-BisbenzodioxanPhos catalyst in *tert*-amyl alcohol^[23] [Eq. (19)].



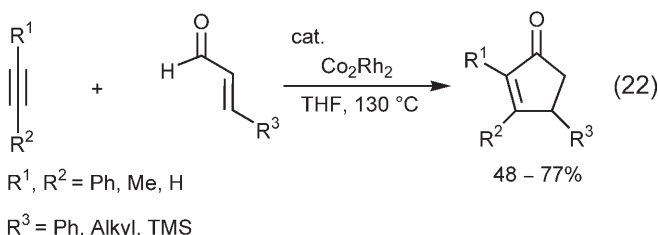
The present reaction provided a new protocol for carbonylation without the use of toxic carbon monoxide gas.^[24] However, from the viewpoint of atom-economy, pentafluorobenzene and styrene were wasted. Morimoto further developed the Pauson–Khand-type reaction using formaldehyde as a CO source under the aqueous conditions.^[25] The combined use of hydrophobic [DPPP = 1,3-bis(diphenylphosphino)propane] and hydrophilic (TPPTS = triphenylphospholane-3,3',3''-trisulfonic acid trisodium salt) phosphines with a surfactant (SDS = sodium dodecyl sulfate) was essential for high yield. Morimoto proposed that decarbonylation and carbonylation take place independently, and that the former proceed in an aqueous phase and the latter in a micellar phase [Eq. (20)]. In place of DPPP, tolBINAP was used as a



chiral and hydrophobic phosphine, and a highly enantioselective Pauson–Khand-type reaction using formalin (37% aqueous solution of formaldehyde) and sodium octadecyl sulfate (SOS) was achieved under the aqueous conditions [Eq. (21)].^[26]



The most atom-economical reaction is when an α,β -unsaturated aldehyde is used as both CO source and alkene moiety. Co/Rh heterobimetallic nanoparticles, derived from Co₂Rh₂(CO)₁₂, catalyzed the reaction of α,β -unsaturated aldehydes with alkynes to give cyclopentenones [Eq. (22)].^[27] Chung ascertained that the

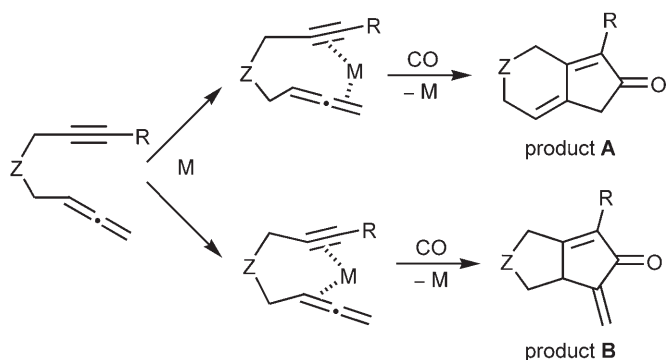


reaction is a carbonylative coupling of an alkyne and alkene, and that it is not a hydroacylation along with a cyclization.

5 Pauson–Khand-Type Reactions of Allenes

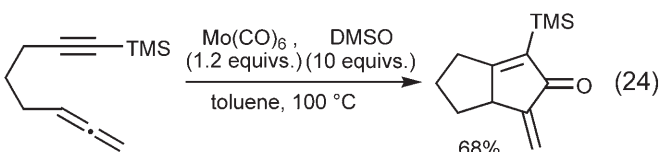
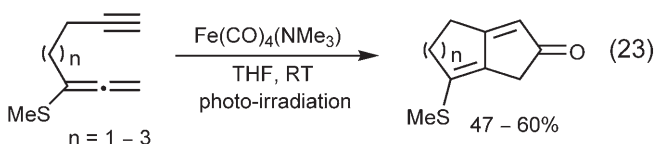
The Pauson–Khand-type reaction of an allene moiety as the ene component has been an intriguing topic.^[28] In the case of an intramolecular reaction of allenynes, there are two possible reaction pathways (Scheme 2). The reaction of an external π -bond of the allene moiety gives a bicyclic dienone (product **A**). On the other hand, the reaction of an internal π -bond gives a bicyclic cyclopentenone with an alkyldiene substituent (product **B**).

Narasaka and Shibata reported the first intramolecular Pauson–Khand-type reaction of allenyne using an iron carbonyl complex under irradiation conditions. Independent of the length of the tether between

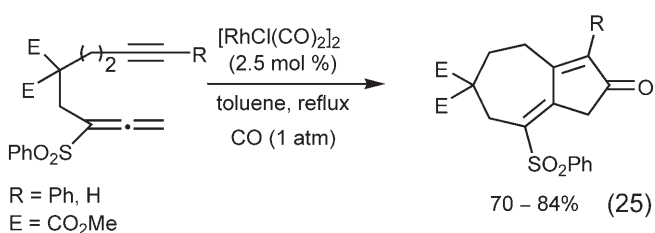


Scheme 2. Two reaction pathways of allenynes.

the allene and alkyne, bicyclic dienones (product **A**) were obtained [Eq. (23)].^[29] Brummond reported an Mo-mediated reaction in which α -methylene cyclopentenone (product **B**) was obtained [Eq. (24)].^[30] But these are both stoichiometric reactions.

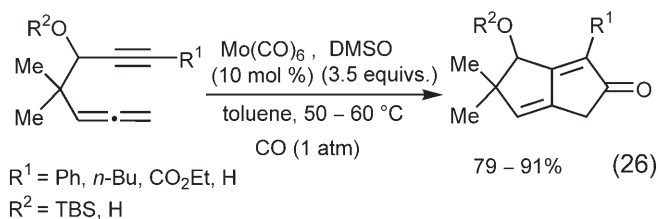


In the catalytic reaction using a Ti^[8b] or Rh^[10b] complex, product **A** was obtained. In the case of an Rh-catalyzed reaction, the construction of seven-membered ring systems was also possible [Eq. (25)].^[31]

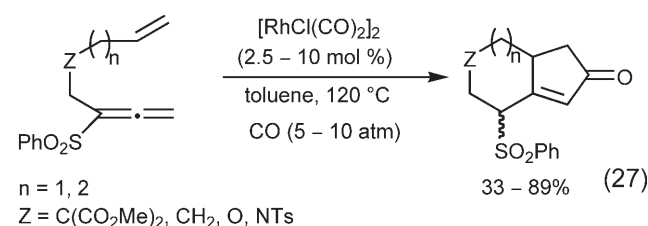


When allenynes with two-atom tethers were used under an atmospheric pressure of CO, the Mo(CO)₆-catalyzed reaction also gave product **A** because product **B** has a strained [3.2.0]heptenone skeleton [Eq. (26)].^[32]

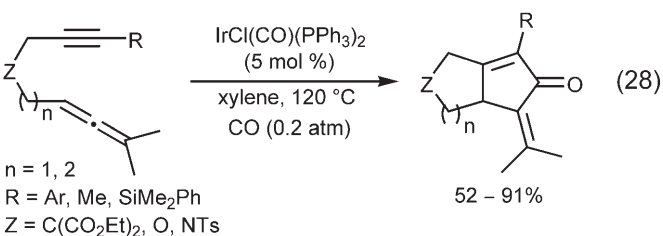
Recently, Mukai reported an Rh-catalyzed reaction of allenenes.^[33] An intramolecular carbonylative cou-



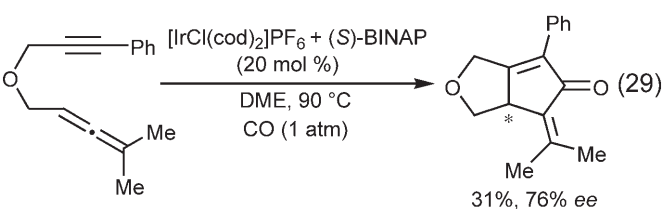
pling of an allene-alkene, which is tethered by three or four atoms, gave a bicyclic cyclopentenone with a 6–5 or 7–5 fused ring system along with the double bond isomerization [Eq. (27)].



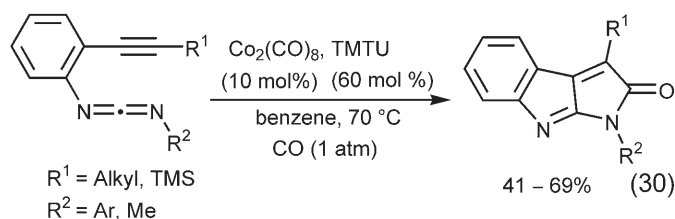
An Ir-catalyzed Pauson–Khand-type reaction resulted in a different regioselectivity. When allenynes with two substituents on the allene terminus were used under a low partial pressure of CO, the internal π -bond of allene moiety was the major reaction site and bicyclic cyclopentenones with an alkylidene substituent were obtained [Eq. (28)].^[34] When, in place



of IrCl(CO)(PPh₃)₂, RhCl(CO)(PPh₃)₂ was used as a catalyst under the same reaction conditions, reaction of the external π -bond of the allene moiety was the major pathway. The present transformation realized the first example of an enantioselective Pauson–Khand-type reaction of an allenyne, although the reaction conditions have not been optimized yet [Eq. (29)].^[35]

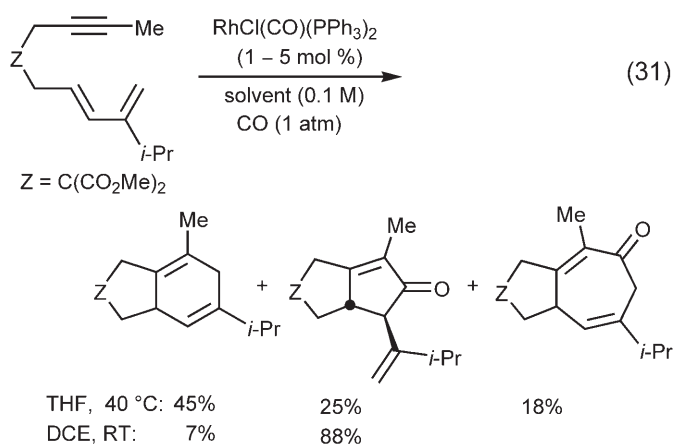


As a nitrogen analogue of an allene, a carbodiimide could also operate as an ene moiety in a Pauson–Khand reaction. After Saito's report of an Mo-mediated reaction,^[36] Mukai disclosed a $\text{Co}_2(\text{CO})_8$ -catalyzed hetero-Pauson–Khand reaction of an alkyne-carbodiimide in the presence of TMTU (tetramethylthiourea) [Eq. (30)].^[37]

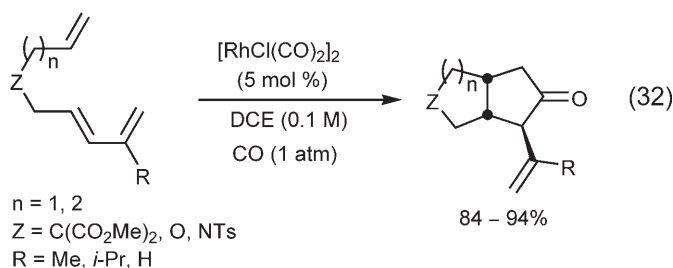


6 Pauson–Khand-Type Reactions of Dienes

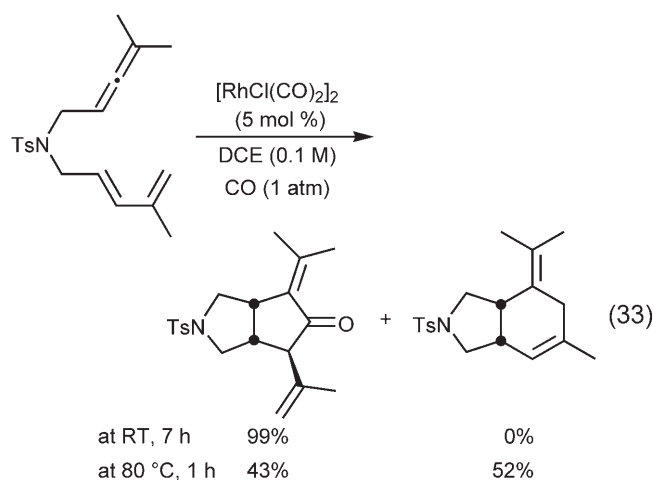
Wender studied Pauson–Khand-type reactions using dienes as the ene moiety. When the Rh-catalyzed reaction of 1,3-diene-yne was examined under an atmospheric pressure of CO at 40 °C in THF, a [4+2] cycloaddition proceeded as the major pathway, and [2+2+1] and [4+2+1] cycloadducts were minor products. On the other hand, when the reaction was examined at room temperature in 1,2-dichloroethane (DCE), a [2+2+1] cycloaddition predominantly and diastereoselectively proceeded to give a bicyclic cyclopentenone with an isopropenyl group [Eq. (31)].^[38] In



place of 1,3-diene-yne, 1,3-diene-ene also underwent the [2+2+1] cycloaddition to give bicyclic cyclopentenones as a single diastereomer [Eq. (32)].^[39] The diene component plays a pivotal role in the cycloaddition, and no cycloadduct was obtained from bis-ene.

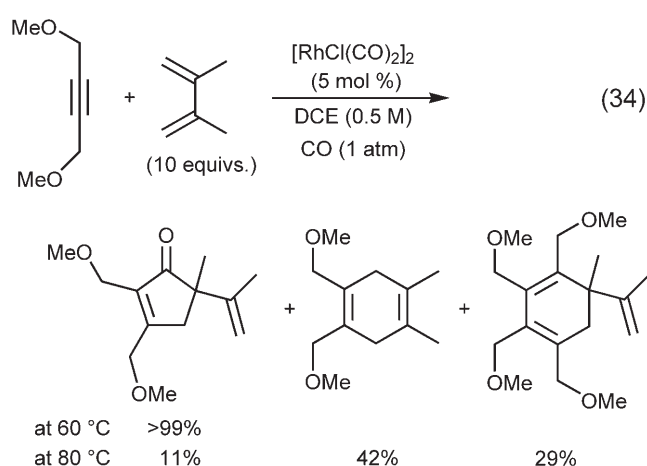


A [2+2+1] cycloaddition of a 1,3-diene-allene was also possible, and a bicyclic cyclopentanone with an alkylidene and a vinyl substituent was obtained at room temperature [Eq. (33)]. The reaction tempera-



ture determined the cycloaddition pathways, and a [4+2] cycloadduct was the major product at 80 °C.^[40]

The use of a diene moiety enabled the realization of an intermolecular Pauson–Khand-type reaction. The Rh-catalyzed reaction of 2,3-dimethylbuta-1,3-diene and an alkyne efficiently proceeded at 60 °C to give a cyclopentenone with an isopropenyl group [Eq. (34)]. The choice of the reaction temperature was cru-



cial also in this reaction, and two [4+2] cycloadducts were major products at 80°C.^[41]

7 Conclusion

This manuscript offers a brief summary of the catalytic Pauson–Khand(-type) reaction and the recent advances in this reaction type. In the 1990s, the Pauson–Khand reaction was dramatically developed into the Pauson–Khand-type reaction, and various transition metal catalysts including chiral species have been reported. Recently, modified (chiral) catalysts and reaction conditions, and new types of substrates, such as allenes and dienes, are major topics of interest. However, the limitation of alkynes and alkenes still exists, especially in enantioselective and/or intermolecular reactions. Therefore, further optimization of the catalysts and reaction conditions for the Pauson–Khand-type reaction is desired.

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