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Review

Transition metal-catalyzed cyclocarbonylation in organic synthesis

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Contents

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ABSTRACT

Cyclocarbonylation reactions proceed mainly by the coupling reactions of carbonylation components with cyclization components having an unsaturated π-electron bond, in the presence of transition metal compounds. The representative reactions are cyclocarbonylation of alkynes by carbon monoxide such as Pauson–Khand reactions, hetero Pauson–Khand reactions, cyclocarbonylation of alkynyl alcohols, cyclocarbonylation of alkynyl amines, cyclocarbonylative alkyne–alkyne coupling reactions, and reductive cyclocarbonylation of alkynes. The other reactions are cyclocarbonylation of alkenes by carbon monoxide such as alkene–alkene coupling reactions, cyclocarbonylation with aldehydes, ketones, amines or imines, cyclocarbonylation of alkenyl alcohols. Carbonylation via cyclometalation, carbonylative ring expansion reactions, cyclocarbonylation by aldehydes, carboxylic acids or carboxylic acid esters are also cyclocarbonylation reactions. These reactions are conveniently used for organic syntheses, especially, for the syntheses of pharmaceutical intermediates.

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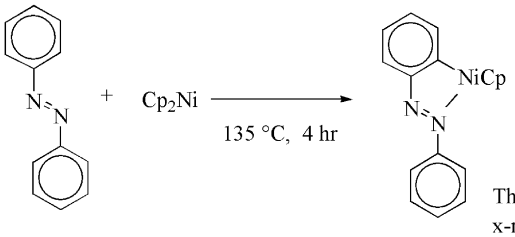
1. Introduction

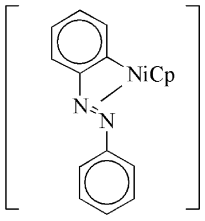
Cyclometalation was first reported in 1955 as synthetic reactions involving main group metal compounds, e.g., organoaluminium compounds [1]. On the other hand, the reaction of azobenzene with nickelocene reported in 1963 as shown in Eq. (1) [2], is generally considered as the first reaction to concern the cyclometalation by transition metal compounds. The number of articles on cyclometalation reactions has increased dramatically since 1970s, and reviews [3,4] and books [5] have been published.

I studied the characteristic reactions of transition metal compounds including Pauson–Khand reactions together with this cyclometalation and, now embark on cyclocarbonylation. This cyclocarbonylation includes the Pauson–Khand reaction and cyclometalation. Pauson–Khand reactions have been reviewed often [6]. In 2006, Vasapollo and Mele [7] reported, via cyclocarbonylation, the synthesis of lactones, lactams, pyrrolidinones, etc. with mainly palladium compounds, and the other catalysts such as Rh, Ru, Co, Ni and Ti metal compounds. Many other reviews [8,9] and examples of transition metal-catalyzed cyclocarbonylation reactions have appeared in monographs [10,11] and reviews [12–30].



The structure was confirmed by the x-ray diffraction study in 1989.[2b]

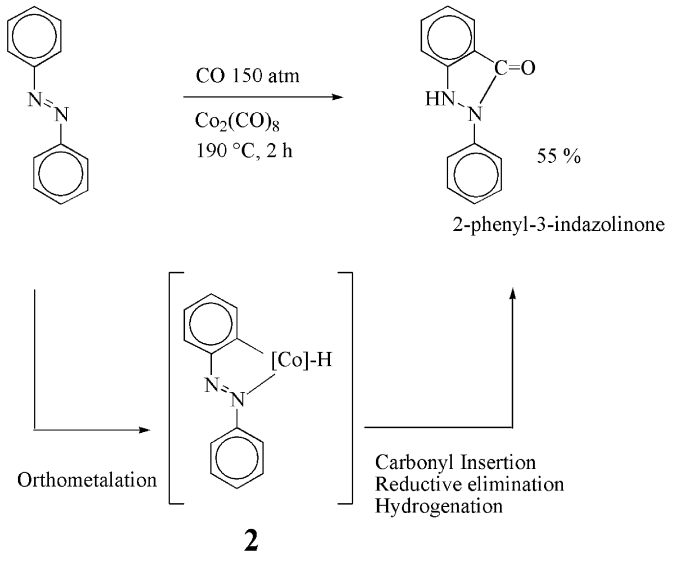
1



The original structure was published in 1963.[2a]

(1)

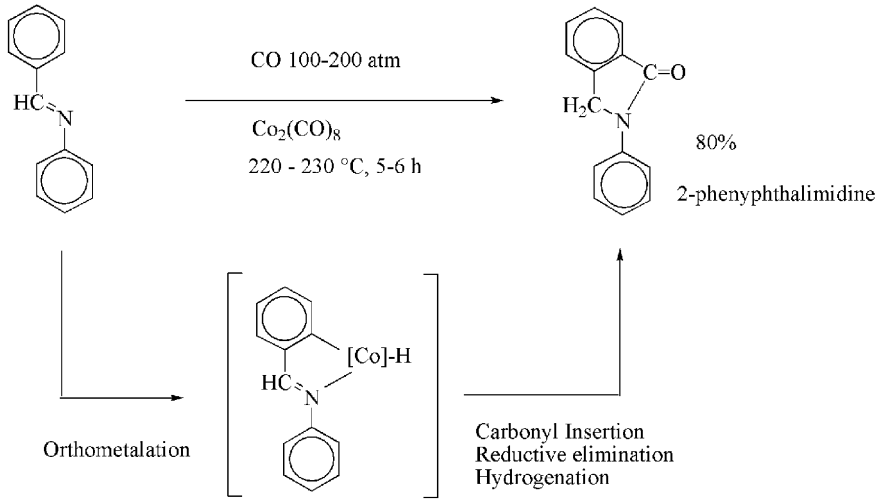
In 1956, the cyclocarbonylation of azobenzene using transition metal compounds, e.g., cobalt carbonyl, was reported as shown in Eq. (2) [31]. Cyclocarbonylation was presumed to proceed, at first, by orthometalation through an intermediate **2**, which was not isolated, followed by the insertion of carbon monoxide into a bond between a cobalt atom and a carbon atom at an *ortho* position, 2-phenyl-3-indazolinone is then formed by reductive elimination and hydrogenation [32] (see Schemes 9 and 10).



2

(2)

Furthermore, one year before that, in 1955, the similar cyclocarbonylation of benzylideneaniline with cobalt carbonyl as shown in Eq. (3), was also reported [33]. In this cyclocarbonylation, cyclometalation is presumed to proceed followed by carbonyl insertion, reductive elimination, and hydrogenation to give a product [32].



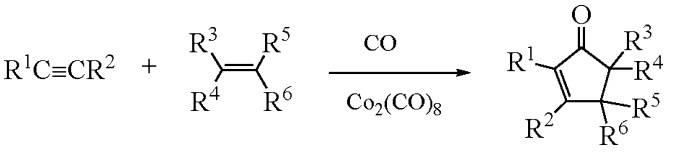
3 (3)

Hence, in the latter cyclocarbonylation published in 1955, it is presumed that the cyclometalation proceeds via an orthometalated compound **3** though the intermediate compound was not isolated [32].

From these reactions as shown in Eqs. (2) and (3), the organocobalt compounds are very reactive towards carbon monoxide. The high reactivities of organocobalt compounds towards the carbonyl group is one of the following three characteristic reaction properties of organocobalt compounds [32].

First, cobalt has high reactivity towards carbon–carbon π-bonds or carbon–nitrogen π-bonds. Secondly, cobalt has high reactivity towards carbonyl groups. The third one, B_{12}-type reaction property, is due to the fact that cobalt tends easily to form six-coordinate octahedral structures with four nitrogen atoms or two nitrogen atoms and two oxygen atoms and one or two carbon atoms at an axial position [32].

The first type characteristic reactions are the most representative reactions of organocobalt compounds via a mutually bridged bond between the two π-bonds of acetylene and the cobalt–cobalt bond of hexacarbonyldicobalt. These reactions are represented by three kinds of reactions, i.e., the Pauson–Khand reactions, the Nicholas reactions and the reactions of a $Co_2(CO)_6$ protecting group with a reactive acetylene bond. The "Pauson–Khand reactions" are reactions which exploit the strong reactivity of cobalt metal to both of the unsaturated π-bonds and the carbonyl groups. Hence, the Pauson–Khand reactions have the first and the second characteristic reaction properties of the organocobalt compounds. The reactions are shown in Eq. (4) [32].



(4)

Properly speaking, Pauson–Khand reactions are reactions using cobalt catalysts. However, the same type of reaction proceeds with other transition metal compounds [6,32,34,35]. Hence, these reactions are also called Pauson–Khand reactions. The other transition metals are Ti (group 4), Cr, Mo and W (group 6), Mn (group 7), Fe, Ru and Os (group 8), Rh and Ir (group 9), Ni, Pd and Pt (group 10), Cu, Ag and Au (group 11) [32,35].

The Pauson–Khand reactions are representative cyclocarbonylation reactions. This is because in these reactions two kinds of useful components, alkynes and carbon monoxide, are used. The alkynes bond with the *d*-orbitals of the transition metal because the alkynes have two π-bonds at the p_y and p_z planes. Carbon monoxide also easily bonds with transition metals by CO–metal σ-donation and metal–CO π back bonding [36].

The cyclocarbonylation proceeds via carbonyl components and cyclization components having an unsaturated π-electron bond. The carbonyl components are carbon monoxide, metal carbonyls, aldehydes, ketones, carboxylic acids, carboxylic acid esters, ketenes, amides, isocyanides, carbon dioxide, etc. The cyclization components having unsaturated π-electron bonds are alkynes, alkenes, aryl compounds, allyl compounds, allenes, dienes, nitriles, isonitriles, etc.

This review describes the many types of cyclocarbonylation in the presence of transition metal compounds, and especially, the cyclocarbonylation of alkynes by carbon monoxide, and cyclocarbonylation of alkenes by carbon monoxide, and cyclocarbonylation by the other carbonylation components, etc.

2. Cyclocarbonylation of alkynes by carbon monoxide

2.1. Introduction

The reactive components of Pauson–Khand reactions are alkynes, carbon monoxide and alkenes as described in the previous section. The alkynes are the most reactive cyclization components having two π-electron bonds (one p_y π-bond and one p_z π-bond) [35b], and carbon monoxide is the most reactive carbonylation components. In the Pauson–Khand reaction, the so-called hetero Pauson–Khand reaction is the reaction with aldehydes (C=O π-bond), ketones (C=O π-bond) or imines (C=N π-bond) instead of the alkenes as a C=C π-bond source in the presence of the transition metal catalysts.

The above reactions have been reported in three reviews concerning organocobalt compounds [32], alkynes [35a] and group 9 metal compounds [35b], therefore, in these reactions, only the transition metal atoms used as the catalysts are shown in Table 1 [6,10–30,32,35–47].

Other hetero Pauson–Khand reactions, include cyclocarbonylation of alkynyl alcohols, cyclocarbonylation of alkynyl amines, cyclocarbonylative alkyne–alkyne coupling reactions, reductive cyclocarbonylation of alkynes, cocyclization of two alkynes and two

Table 1
Cyclocarbonylation of alkynes by carbon monoxide and other moieties.

Entry	Reaction name	Other moieties	Products	Metal atoms in catalysts	References
1	Pauson–Khand reactions, [2 + 2 + 1] cycloaddition	C=C	Cyclopentenones	Co	[6,11]
2	Pauson–Khand reactions, [2 + 2 + 1] cycloaddition	C=C	Cyclopentenones	Ti, Zr, Cr, Mo, W, Fe, Ru, Rh, Ir, Ni, Pd, Co/C, Co/Rh, Pd/Rh	[34,35]
3	Hetero-Pauson–Khand reactions, [2 + 2 + 1] cycloaddition	>C=O	Butenolides	Mo, Ru, Rh, Ni	[10,11,22,37]
4	Hetero-Pauson–Khand reactions, [2 + 2 + 1] cycloaddition	>C=N–	Lactams	Mo, Ru, Co, Rh	[24,38]
5	Cyclocarbonylation of alkynyl alcohols	OH	Lactones	Co, Rh, Pd, Pt, Co–Rh	[10,11,22,39]
6	Cyclocarbonylation of alkynyl amines	NR^1R^2	Lactams	Rh, Pd	[10,40]
7	Cyclocarbonylative alkyne–alkyne coupling reactions, [2 + 2 + 1] cycloaddition	C≡C	Cyclopentadienes	Fe, Co, Rh, Ir, Pd	[11,24,27,41]
8	Reductive cyclocarbonylation of alkynes, [2 + 2 + 1] cycloaddition	H_2O	Furanones	Ru, Rh, Ni, Pd, Co/Rh	[10,22,42]
9	Cocyclization of two alkynes and two carbon monoxides, [2 + 2 + 1 + 1] cycloaddition	C≡C, CO	*p*-Benzoquinones	Fe, Co, Rh	[27,43]
10	Reductive cocyclization of alkynes, alkenes and two carbon monoxides, [2 + 2 + 1 + 1] cycloaddition	C=C, CO	Hydroquinones	Fe, Ru, Co, Rh	[27,43a,44]
11	Cyclocarbonylative coupling reaction of alkynes, amines, two carbon monoxides, [2 + 1 + 1 + 1] cycloaddition	CO, RNH_2	Maleimides	Rh	[45]
12	Cyclocarbonylation with ketones, [3 + 2 + 1] cycloaddition	>CO	Lactones	Ru, Pd	[46]
13	Reductive cyclocarbonylation of arylalkynes, [2 + 2 + 1] cycloaddition	Aryl group	Cycloketones	Fe, Co	[47]

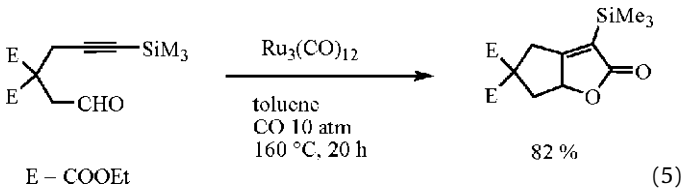
carbon monoxides, reductive cocyclization of alkynes, alkenes and two carbon monoxides, cyclocarbonylative coupling reactions of alkynes, amines and two carbon monoxides, cyclocarbonylation of ketones, and reductive cyclocarbonylation of arylalkynes.

2.2. Hetero Pauson–Khand reactions

The Pauson–Khand reactions yield cyclopentenones by the reactions of alkynes, carbon monoxide (or cobalt carbonyls) and alkenes in the presence of transition metal compounds as described above [32,35].

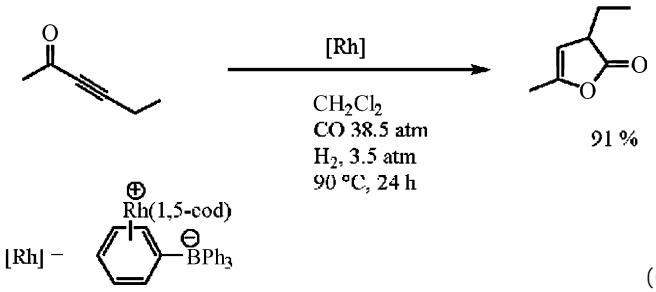
However, hetero Pauson–Khand reactions yield butenolides (unsaturated lactones such as 2(5*H*)-furanones and 2(3*H*)-furanones) [10,22,37] or lactams [26,38] by the reactions of alkynes, carbon monoxide and carbonyl moieties or imine moieties instead of the alkene moieties in the Pauson–Khand reactions.

When formyl group is used as the carbonyl moiety, ruthenium [37a] and molybdenum [37b] are used as the catalysts. For example, the reaction of an alkyne having a formyl group at its terminal position with carbon monoxide in the presence of a ruthenium compound yields a bicyclic α,β-unsaturated γ-butyrolactone in high yield as shown in Eq. (5) [37a].



(5)

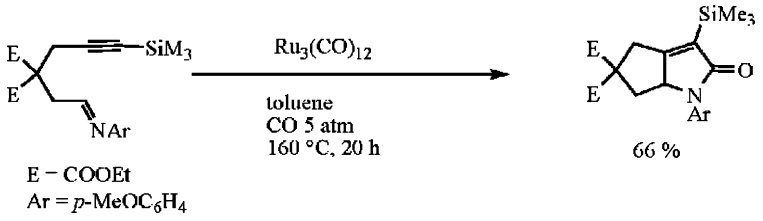
On the other hand, the reaction of an alkynone having a keto carbonyl group with carbon monoxide in the presence of a rhodium compound yields an α,β-unsaturated γ-butyrolactone in high yield as shown in Eq. (6) [37c].



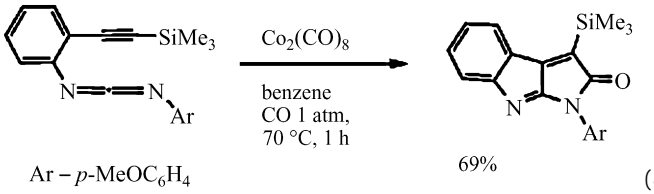
(6)

Yne-imines and yne-diimides are available as the latter imino group. Mo, Ru, Co and Rh metal compounds are used as the catalysts in these reactions [10,38]. For example, the reaction of a trimethylsilylyne-imine with carbon monoxide in the presence of $Ru_3(CO)_{12}$ in toluene at 160 °C for 20 h gave a bicyclic α,β-unsaturated lactam in 66% yield as shown in Eq. (7) [38a].

The reactions of yne-diimides are applied for the synthesis of precursor of an indole alkaloid (±) physostigmine. Ru, Rh, Co and Mo metal compounds are used as catalysts. A compound, $Co_2(CO)_8$, gives most reasonable yields as a catalytic amount in the reaction of an alkynecarbodiimide with carbon monoxide as shown in Eq. (8) [38b].



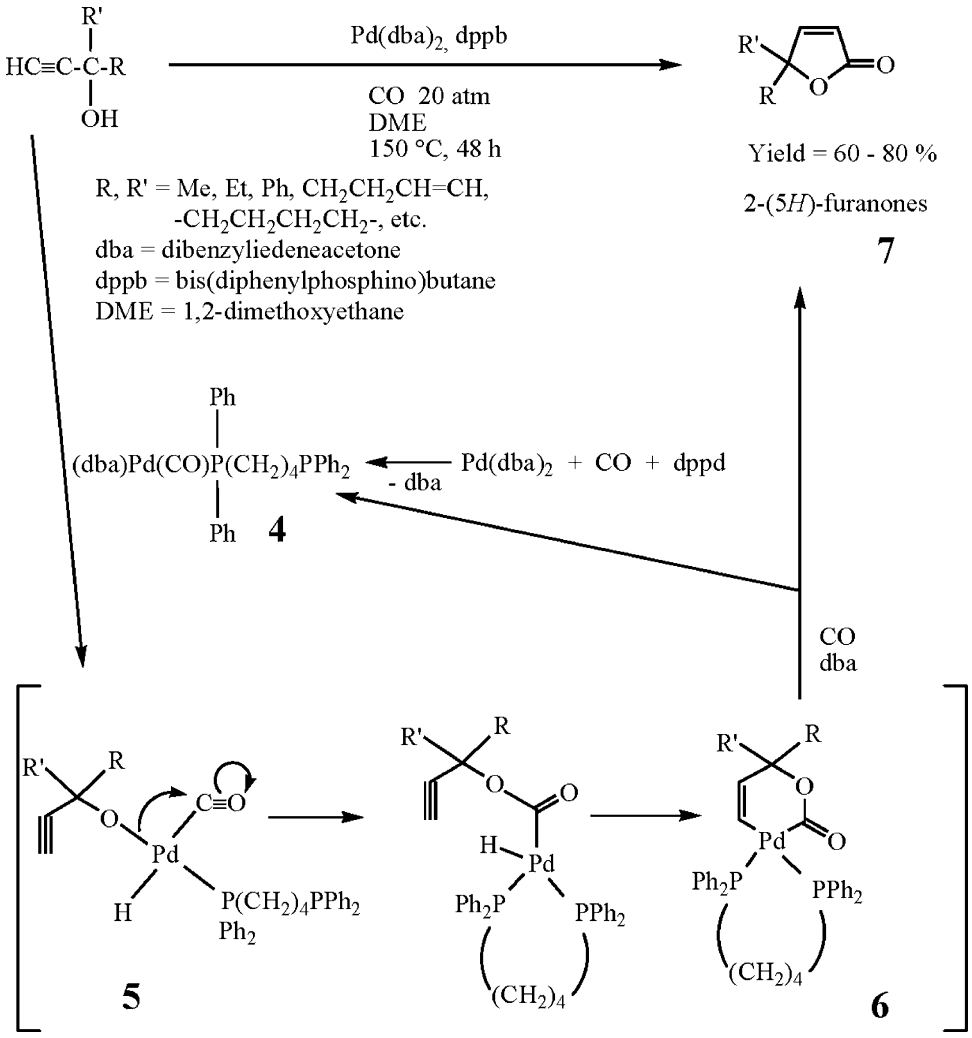
(7)



(8)

2.3. Cyclocarbonylation of alkynyl alcohols

The cyclocarbonylation of alkynyl alcohols with carbon monoxide in the presence of transition metal compounds yields lactones,



Scheme 1.

for example, intramolecular cyclocarbonylation of an alkynol in the presence of bis(benzylideneacetone)palladium (0) ($Pd(dba)_2$) and 1,4-bis(diphenylphosphino)butane (dppb) under CO pressure gave 2-(5*H*)-furanones **7** in a good yield as shown in Scheme 1 [39a].

The reaction of $Pd(dba)_2$ with dppb and carbon monoxide may give the palladium phosphine carbonyl complex **4**. The complex can undergo insertion into the oxygen–hydrogen bond of the alkynol, to give the palladium hydride complex **5**. The insertion of carbon monoxide into the palladium–oxygen bond by ligand migration and the intramolecular addition of palladium hydride to the triple bond would form metallacycles **6**. The conversion of the metallacycles **6** to the γ-lactone **7** would then occur by reaction with carbon monoxide and dba, together with the regeneration of a palladium phosphine carbonyl complex **4** in the process [39a].

On the other hand, the reaction of the alkynoyl with palladium dichloride is shown in Scheme 2 [39b]. The coordination of the oxygen atom and the triple bond of the alkynyl alcohol to $PdCl_2$ gave a complex **8**, which was followed by *cis*-chlorometalation to give a complex **9**. The subsequent coordination and insertion of CO gave a metallocyclic intermediate **10**, which was followed by reductive elimination to give a β-lactone **11**. $PdCl_2$ was regenerated by the oxidation reaction of *in situ* generated Pd(0) with $CuCl_2$ as shown in Scheme 2 [39a].

These cyclocarbonylation of the alkynyl alcohols are carried out mainly with palladium catalysts and the other catalysts such as Zr, Rh, Pt, and Co–Rh metal compounds [39].

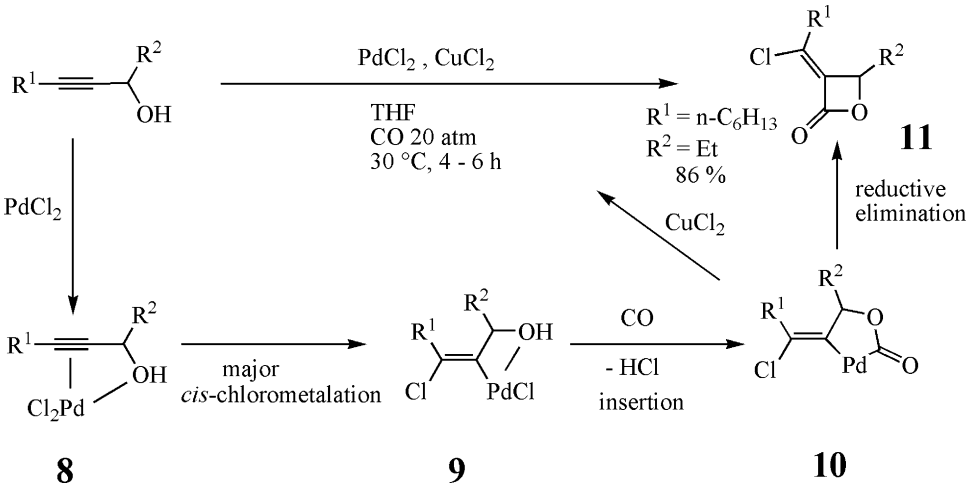
The cyclocarbonylation of the alkynols to form lactones also proceeds in the reaction of alkynes with carbon monoxide and alcohols [22,39a,39r], however, the cyclocarbonylation of alkynes with *o*-iodophenol as the alcohol component gives chromone derivatives in high yield [39s].

On the other hand, the cyclocarbonylation with allenyl alcohols instead of alkynyl alcohols in the presence of ruthenium catalysts also gives the lactones in a good yield [39t].

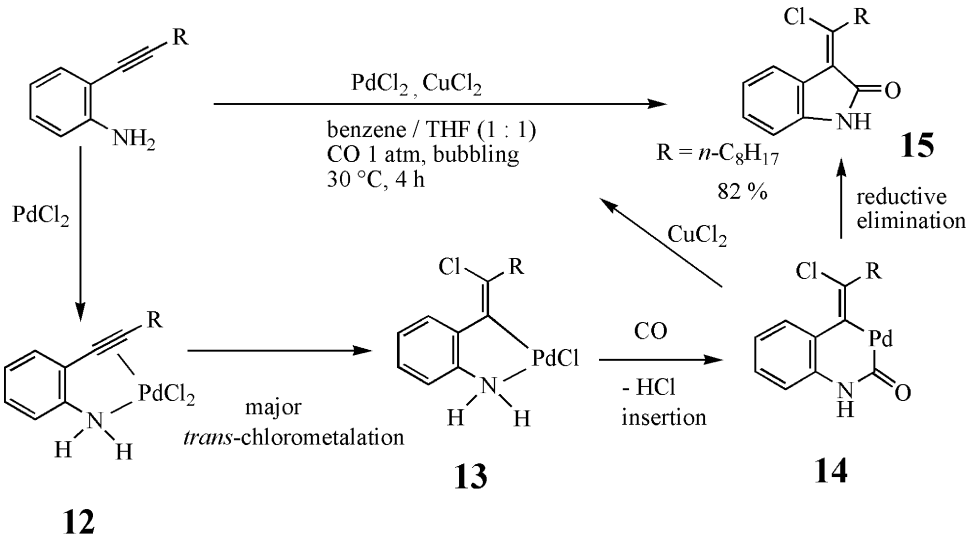
2.4. Cyclocarbonylation of alkynyl amines

The cyclocarbonylation of alkynyl amines in the presence of transition metal compounds gave lactames. Palladium and rhodium compounds are used as the transition metal catalysts [10,26,40], for example, the reaction mechanism using the palladium catalyst is similar to that of the cyclocarbonylation of alkynyl alcohols with the palladium dichloride as shown in Scheme 3.

The coordination of a nitrogen atom and the triple bond of the alkynes to $PdCl_2$ gives an intermediate **12**, which is followed by *trans*-chloropalladation (less steric hindrance) to generate an intermediate **13**. The subsequent coordination and insertion of CO with the intermediate **13** to give an intermediate **14**. The intermediate **14** undergoes reductive elimination, and readily forms the desired lactams such as 3-(halomethylene)indolin-2-ones, **15**, and a Pd(0) species. The active Pd(II) species can be regenerated by the oxida-

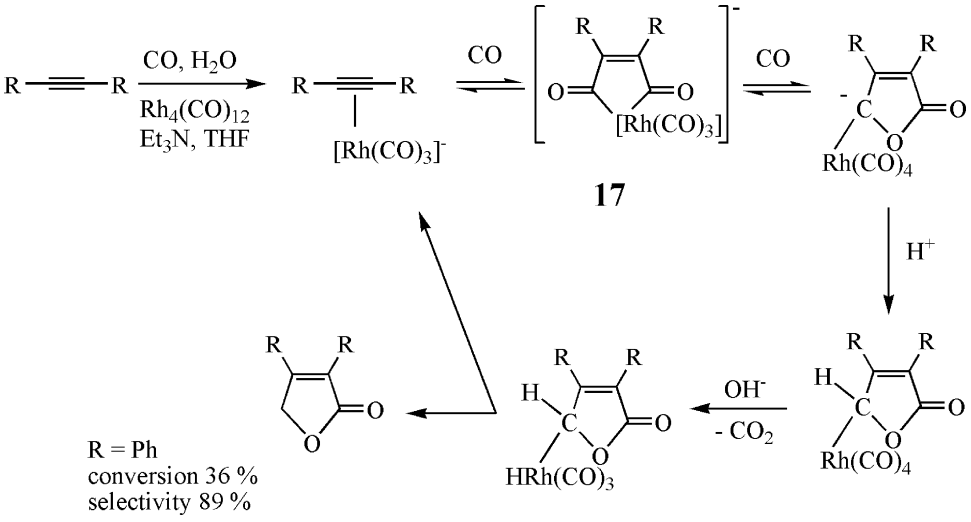


Scheme 2.



R = H, *t*-Bu, C_5H_{11}, *n*-C_8H_{17}, *p*-MeC_6H_4, *p*-$NO_2C_6H_4$, etc.

Scheme 3.



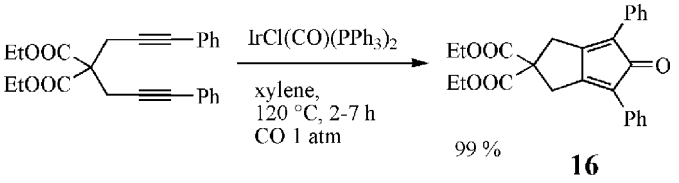
Scheme 4.

tion reaction of the Pd(0) with $CuCl_2$ to start a new catalyst cycle [40a].

2.5. Cyclocarbonylative alkyne–alkyne coupling reactions

The cyclocarbonylative alkyne–alkyne coupling reactions are the cyclocarbonylation of two C≡Cs and one CO. The products are cyclopentadienenones. Fe, Co, Rh, Ir and Pd metal compounds are used as transition metal catalysts [10,24,27,28,41].

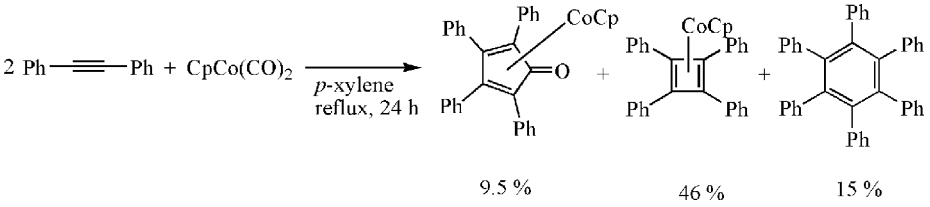
For example, the cyclocarbonylation of a 1,6-diyne with carbon monoxide at an atmospheric pressure in the presence of Vaska's complex ($IrCl(CO)(PPh_3)_2$) yields a bicyclic cyclopentadienenone **16** in a high yield as shown in Eq. (9) [41a].



(9)

The cyclocarbonylation of 1,8-diynes with carbon monoxide in the presence of iron carbonyl compounds yields bicyclic cycloheptane–cyclopentadienones in good yields [41b]. These intramolecular alkyne–alkyne coupling reactions show generally high yields and high stereoselectivities.

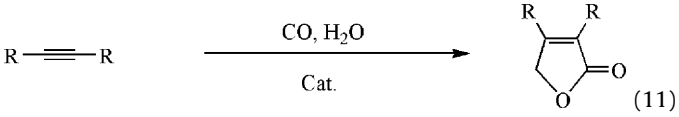
However, intermolecular cyclocarbonylative alkyne–alkyne coupling reactions do not have high yields. For example, the reaction of diphenylacetylene with cyclopentadienyldicarbonylcobalt in xylene gives cyclopendienylpentadienonecobalt only in 9.5% yield as shown in Eq. (10) [41c].



(10)

2.6. Reductive cyclocarbonylation of alkynes

The cyclocarbonylation of alkynes with carbon monoxide in the presence of water and transition metal compounds gives furanones. Ru, Rh, Pd and Co–Rh metal compounds are used as catalysts in these reactions [10,22,42].



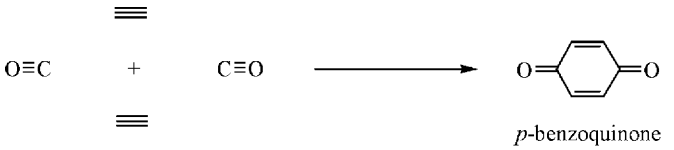
(11)

Jo et al. [42a] reported the reaction mechanism with rhodium carbonyl catalysts. The internal alkyne mechanism is shown in Scheme 4 [42a]. At first, the rhodium metal is coordinated by the triple bond of alkynes, followed by double carbonylation, protonation, and reductive elimination, furanones are formed, and the catalyst is regenerated.

2.7. Cocyclization of two alkynes and two carbon monoxides, [2+2+1+1] cycloaddition

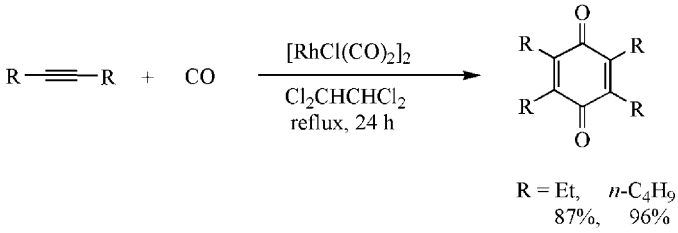
In the alkyne–alkyne coupling reactions, the reaction components are two alkynes and one carbon monoxide. The product is cyclopentadienone as described in the former section.

On the other hand, in the cyclization of alkynes and carbon monoxide, if the reaction components are two alkynes and two carbon monoxides, the products are *p*-benzoquinones as shown in Eq. (12) [43a]. Rh and Fe metal compounds are used for these reactions [43].



(12)

For example, dialkyl acetylene reacts with carbon monoxide in 1,1,2,2-tetrachloroethane, while bubbling CO/N_2 (CO/N_2 = 1:1, 1.5–20 mL min^{-1}) in the presence of $[RhCl(CO)_2]_2$, and refluxing for 24 h to yield *p*-benzoquinone in high yield as shown in Eq. (13) [43a].

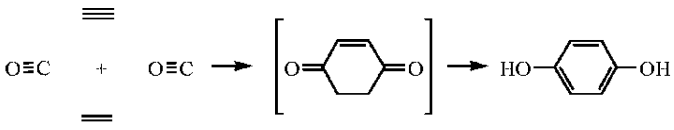


(13)

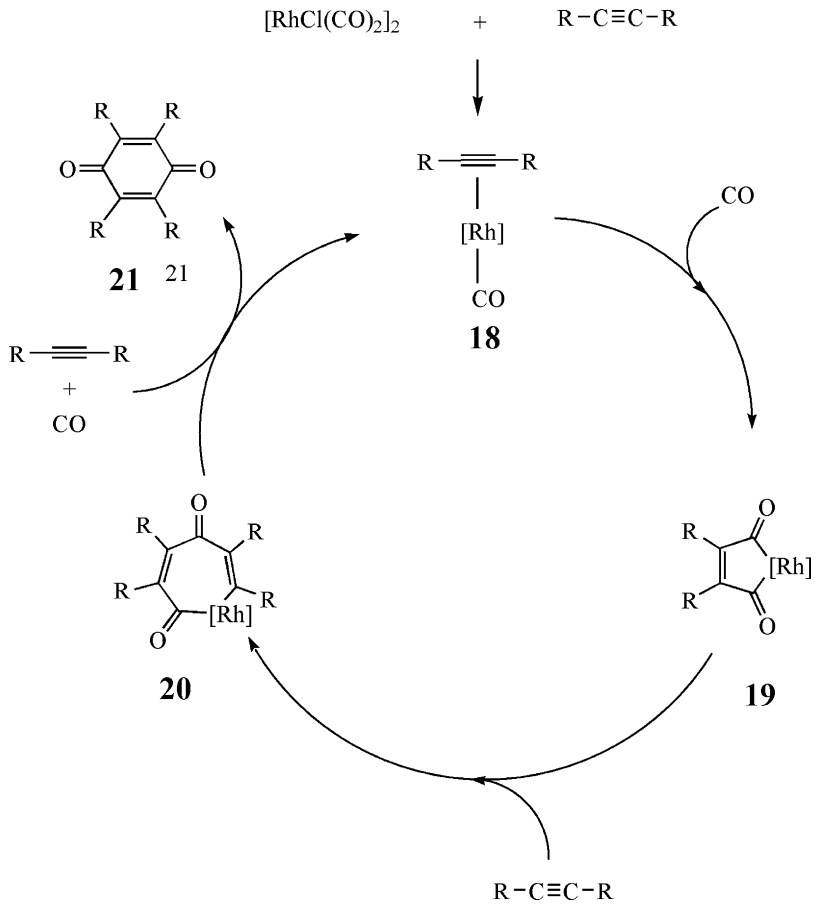
The reaction mechanism is proposed in Scheme 5 [43a]. The rhodium atom is first coordinated by alkynes. The oxidative coupling of the coordinated alkyne **18** with CO generates a five-membered rhodacycle **19** which is the double carbonylation product corresponding to the compound **17** (Scheme 4), and then the insertion of another alkyne into the rhodium–carbon bond follows to form a seven-membered rhodacycle **20**. The carbon–carbon bond formation by reductive elimination furnishes a benzoquinone **21** and regenerates the coordinated alkyne **18** [43a].

2.8. Reductive cyclocarbonylation of alkynes, alkenes and two carbon monoxides, [2+2+1+1] cycloaddition

The cyclization of two alkynes and two carbon monoxides yields *p*-benzoquinones as shown in Eq. (12), however, the cyclization of alkynes, alkenes and two carbon monoxides is the reaction with one alkene instead of one alkyne in the former reaction. The final products are hydroquinones. Ru, Fe, Co and Rh metal compounds are used as catalysts [43a,44].

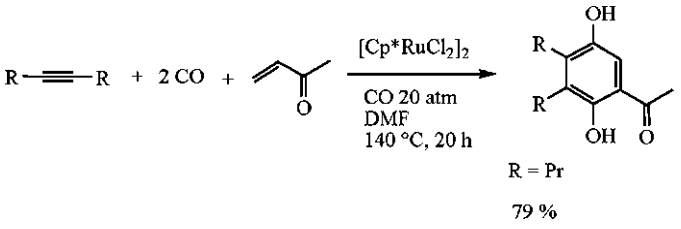


(14)



Scheme 5.

For example, the cyclization of dipropylacetylene, allyl methyl ketone and carbon monoxide gives a hydroquinone in 79% yield as shown in Eq. (15) [44a].



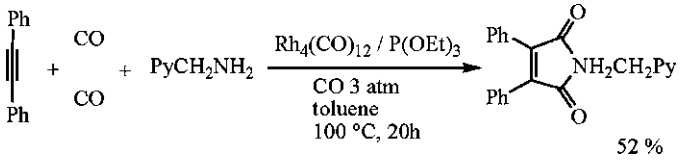
(15)

The reaction mechanism for the cyclization reaction is the similar to that described in Scheme 5 [44a]. The ruthenium atom is first coordinated by alkynes. The double carbonylation of the coordinated alkyne **22** forms a maleoylruthenium complex **23**. Then, the maleoylruthenium complex reacts with alkenes to yield seven-membered ruthenacycles **24** by the insertion of the alkene into a bond between a rhodium atom and a carbonyl carbon atom. Reductive elimination gives 2-cyclohexene-1,4-dione **25**. The diketones **25** easily isomerize to the dienols that is hydroquinone **26**, by enolization since the enol forms is more stable by aromatic resonance stabilization [44a] (Scheme 6).

2.9. Cycylocarbonylative coupling reactions of alkynes, amines and two carbon monoxides, [2 + 1 + 1 + 1] cycloaddition

Cyclocarbonylative coupling reactions of alkynes, carbon monoxide and amines are the reactions of one alkynes, two carbon monoxides and one amine, that is, [2 + 2 + 1 + 1] cycloaddition.

For example, the reaction of diphenylacetylene with CO and pyridin-2-ylmethylamine in the presence of $Rh_4(CO)_{12}/P(OEt)_3$ results in the incorporation of two molecules of CO leading to a maleimide derivative as shown in Eq. (16) [45].



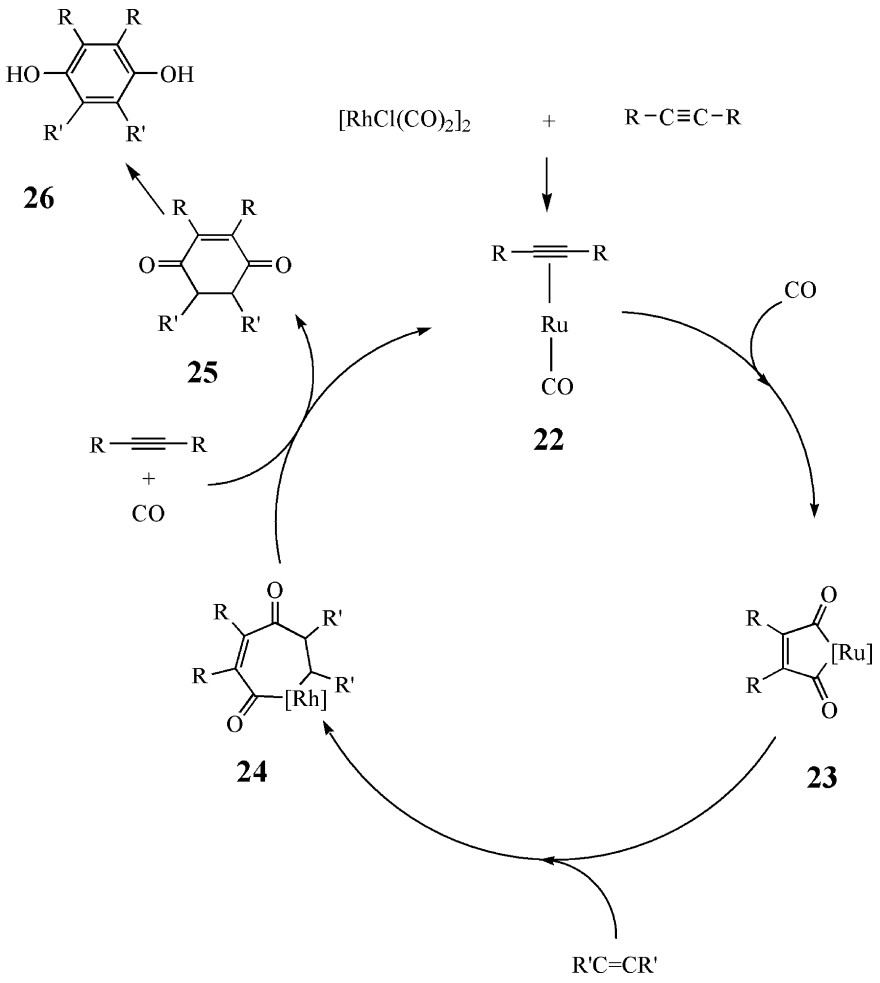
(16)

In the reaction of a reactive pyridinylamine, the coordination of pyridine nitrogen and amine nitrogen to a rhodium center, and then to the rhodium carbonyl forms an η^2-isocyanate–rhodium complex **27**, and the insertion of an alkyne gives a rhodacycle **28**. The insertion of carbon monoxide in the complex **28** was followed by reductive elimination to afford a maleimide **29**, and the rhodium catalyst is regenerated as shown in Scheme 7 [45].

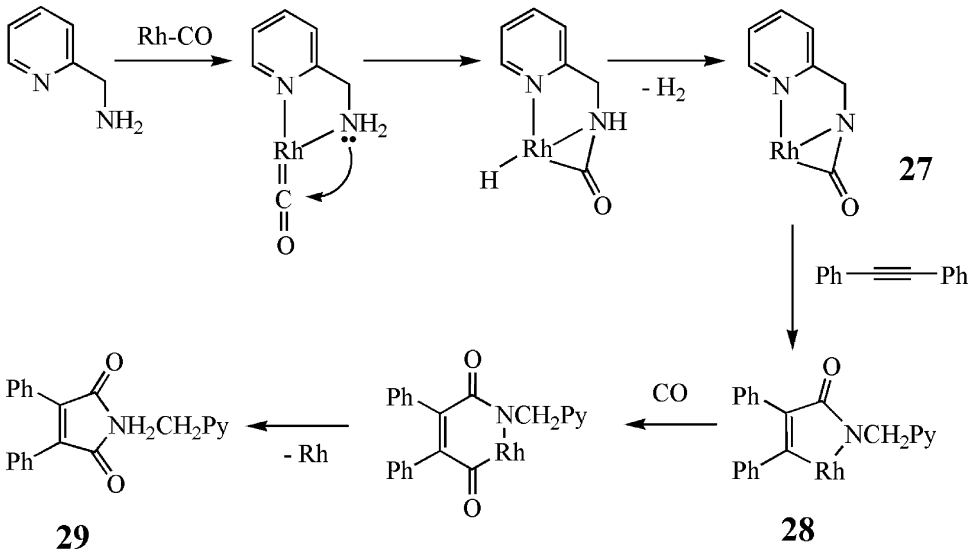
2.10. Cyclocarbonylation with ketones, [3 + 2 + 1] cycloaddition

In the cyclocarbonylation of alkynes and carbon monoxide, the reactions of α,β-unsaturated ketones or 1,3-diketones as a third cyclization component in the presence of a transition metal compound, generate unsaturated δ-lactones.

For example, the reaction of 1-(trimethylsilyl)-2-phenylacetylene with ethyl vinyl ketone and CO with pressure of 20 atm in the presence of $Ru_3(CO)_{12}$ and $Et_2MeN{\cdot}HI$ gives a

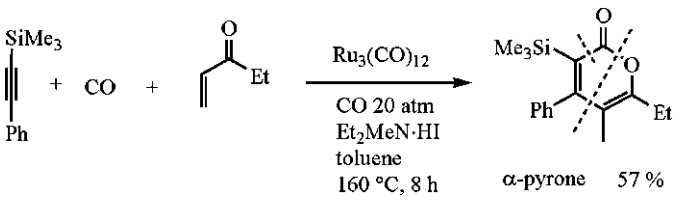


Scheme 6.



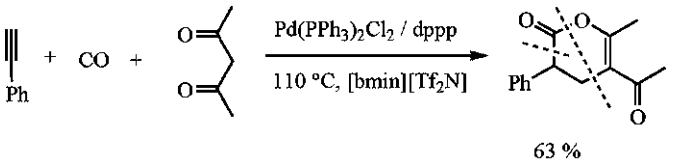
Scheme 7.

α-pyrone in 57% yield as shown in Eq. (17) [46a].



(17)

On the other hand, the reaction of alkynes with 1,3-diketones and carbon monoxide in the presence of palladium catalyst gives an unsaturated endocyclic enol lactone via the carbonylation coupling reaction of the alkyne and 1,3-diketone [46b].



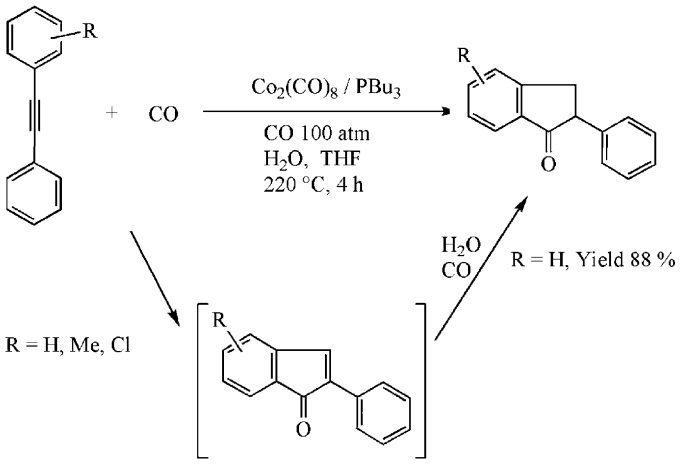
dppp = 1,3-bis(diphenylphosphino)propane
[bmin][Tf_2N] = ionic liquid [46c]

(18)

2.11. Reductive cyclocarbonylation of arylalkynes, [2 + 2 + 1] cycloaddition

Arylalkynes have two cyclization components of one carbon–carbon triple bond and one aryl carbon–carbon bond. The cyclocarbonylation of the arylalkynes proceeds with carbon monoxide in the presence of transition metal compounds.

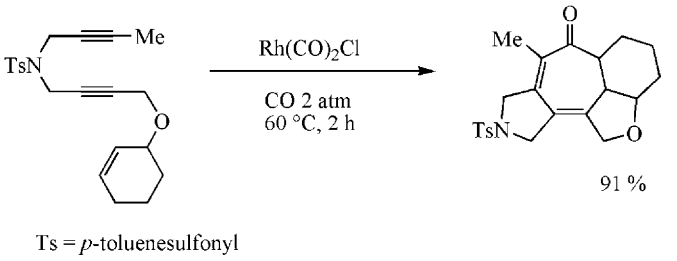
For example, the carbonylation of diphenylacetylene derivatives with cobalt carbonyl catalysts gives indan-1-ones in good yields. Using D_2O instead of H_2O, diphenylacetylene gave the deuterated indanone, which indicates that hydrogen comes from water. The use of molecular hydrogen as a hydrogen source gave only bibenzyl ($PhCH_2CH_2Ph$) in 85% yield. Hence, water gas shift conditions may be indispensable for the formation of indanones from acetylenes. As the reaction path, it is supposed that the indenone derivatives are formed through the cyclocarbonylation of diphenylacetylene at its first step, and followed by hydrogenation to afford indanones as shown in Eq. (19a) [47a].



(19a)

2.12. Others

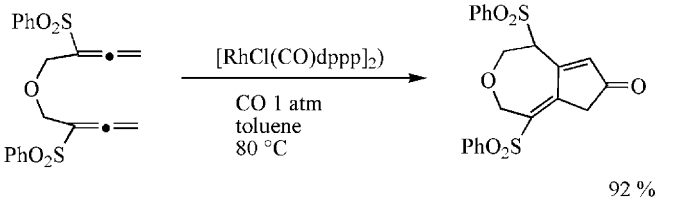
Recently, the cyclocarbonylation of compounds having two ynes and one ene with carbon monoxide, that is, [2 + 2 + 2 + 1] cycloaddition reaction was reported. One-step formation of fused tetracyclic skeletons from cyclohexene-diynes and carbon monoxide through a rhodium catalyzed cycloaddition reaction proceeds as shown in Eq. (19b) [47b].



Ts = *p*-toluenesulfonyl

(19b)

Allenes are used as alkyne or alkene components for the cyclocarbonylation reactions. for example, intramolecular carbonylative [2 + 2 + 1] cycloadditions proceed with bis(allene)s with carbon monoxide in the presence of rhodium catalysts as shown in Eq. (19c) [47c].



dppp = 1,3-bis(diphenylphosphino)propane

(19c)

3. Cyclocarbonylation of alkenes by carbon monoxide

3.1. Introduction

Alkenes have only one carbon–carbon π-electron bond, as compared to alkynes, hence, the reactivity of alkenes is generally lower than that of alkynes as the cyclization component. Therefore, there are fewer reaction types, then those of alkynes, for the cyclocarbonylation of alkenes with carbon monoxide as shown in Table 2.

The cyclocarbonylation of alkenes by carbon monoxide mainly follows four reactions.

1. Cyclocarbonylative alkene–alkene coupling reactions.
2. Cyclocarbonylation with aldehydes or ketones.
3. Cyclocarbonylation with amines or imines.
4. Cyclocarbonylation of alkenyl alcohols.

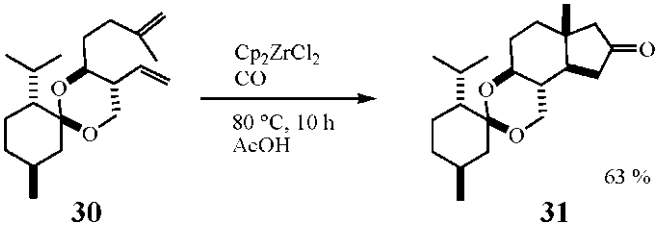
3.2. Cyclocarbonylative alkene–alkene coupling reactions, [2 + 2 + 1] cycloaddition

Cyclocarbonylative alkene–alkene coupling reactions proceed via both of intramolecular reactions and intermolecular reactions [11,48], for example, the intramolecular alkene–alkene coupling reactions of a diene **30** yields a tetracyclic ketone **31** as the precursor of (−)-androst-4-ene-3,16-dione **32** in 63% yield as shown in Eq.

Table 2
Cyclocarbonylation of alkenes by carbon monoxide.

Entry	Reaction name	Other moieties	Products	Metal atoms in catalysts	References
1	Cyclocarboylative alkene–alkene coupling reactions, [2 + 2 + 1] cycloaddition	C=C	Cyclopentanones	Zr, Co, Rh, Pd	[11,26,48,49]
2	Cyclocarbonylation with aldehydes or ketones	>C=O	Lactones	Ti, Mo, Fe, Ru, Pd	[24,26,50]
3	Cyclocarbonylation with amines or imines	C–NR^1R^2, >C=N–	Lactams	Mo, Fe, Ru, Co, Rh, Ir, Pd	[10,24,26,29,51]
4	Carbonylation of alkynyl alcohols	OH	Lactones	Ru, Rh, Ni, Pd	[10,11,24,52,53]

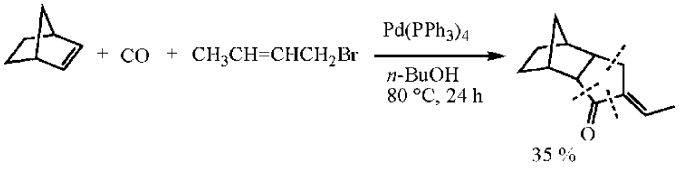
(20) [48a].



(-)-androst-4-ene-3,16-dione

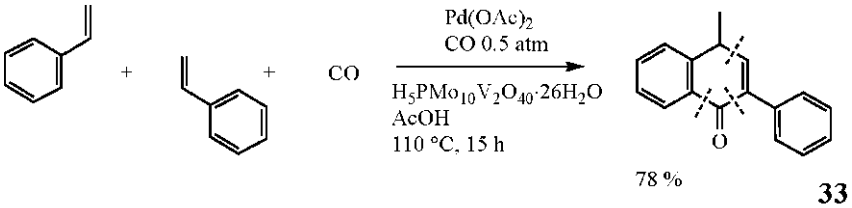
(20)

On the other hand, as the intermolecular reaction of the cyclocarbonylation of 2-norbornene (bicyclo[2.2.1]-2-heptene) and *E*-1-bromo-2-butene under CO in *n*-butanol in the presence of $Pd(PPh_3)_4$ gives a cyclocarbonylation product in 35% yield as shown in Eq. (21) [48b].



(21)

Cyclocarbonylative alkene–aryl or aryl–aryl coupling reactions proceed in a similar way as the cyclocarbonylative alkene–alkene coupling reactions [10a,49], for example, the carbonylation reaction of 2 moles of styrene with carbon monoxide in the presence of $Pd(OAc)_2$ gives a naphthalenone **33** in good yield as shown in Eq. (22) [49a].



4-methyl-2-phenyl-1(4*H*)-naphthalenone

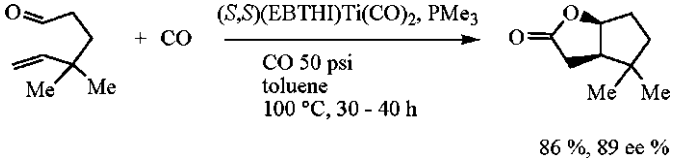
(22)

However, the final products of cyclocarbonylation of allylaryl compounds in the presence of palladium catalysts are phenol acetates instead of carbonyl compounds, because of aromatic resonance stabilization as the enol form is more stable as shown in Scheme 6 [49b,49c,49d]. For example, the palladium-catalyzed cyclocarbonylation of 3,3-diarylallyl acetates affords 4-aryl-substituted 1-naphthyl acetates. The reaction mechanism is proposed via two kinds of paths. Path A is intramolecular electrophilic attack of the acyl group coordinated to palladium on the aromatic ring. Path B is cyclization proceeding via an alkenylketene intermediate formed by the β-elimination of a butenoyl–palladium complex as shown in Scheme 8 [49b].

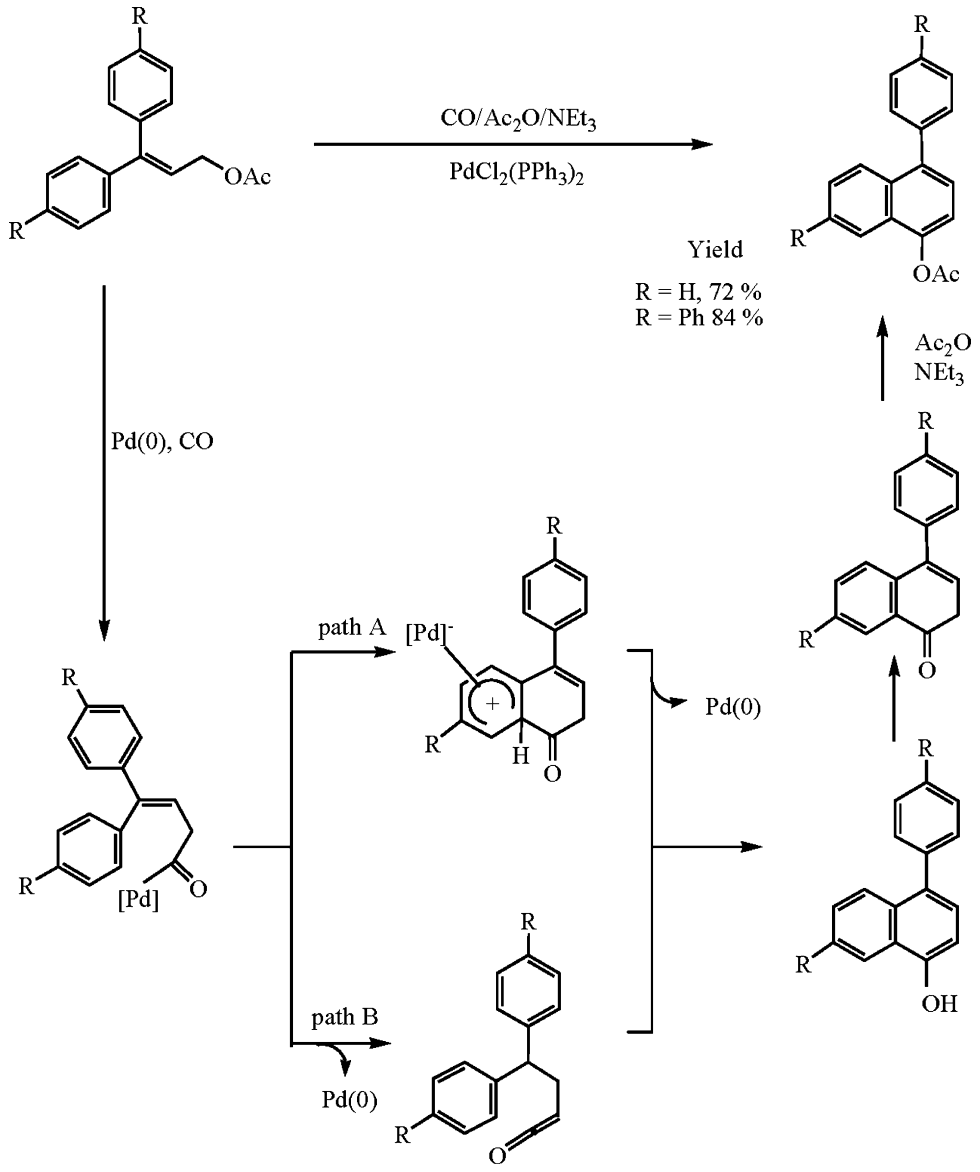
3.3. Cyclocarbonylation with aldehydes or ketones

In hetero Pauson–Khand reactions, the reaction components are alkynes, carbon monoxide, and aldehydes or ketones, and the products are butenolides (unsaturated lactones such as 2(5*H*)-furanones and 2(3*H*)-furanones) as described in Section 2.2. However, the reactions with alkenes instead of alkynes yield γ-butyrolactones [50].

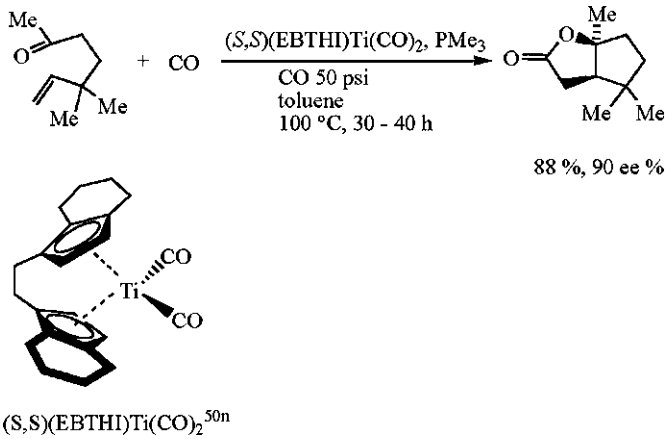
For example, the cyclocarbonylation of an aldehyde or a ketone in the presence of enantiomeric pure (*S*,*S*)(EBTHI)$Ti(CO)_2$ yields γ-butyrolactones in high yield and high enantioselectivity as shown in Eq. (23) or (24), respectively [50a]. Ti, Mo, Fe, Ru and Pd metal compounds are used for these cyclocarbonylation reactions [50].



(23)



Scheme 8.

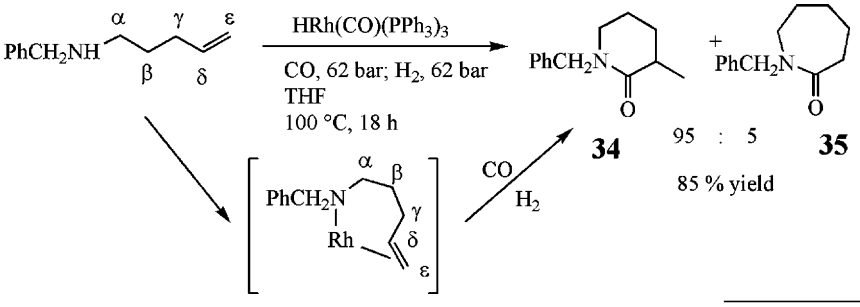


(S,S)(EBTHI)Ti(CO)$_2$ [50n]

3.4. Cyclocarbonylation with amines or imines

In the hetero Pauson–Khand reactions, the reaction of alkynyl imines in the presence of transition metal catalysts give unsaturated lactames as shown in the former section, however, instead of the reactions of the alknyl-imines in the hetero Pauson–Khand reactions, the reactions of alkenyl-amines (or -imines), allenyl-amines (or -imines), alkenylarylamines (or -imines), give the corresponding lactams. Mo, Ru, Co, Rh and Pd metal compounds are used as catalysts for the above reactions [51].

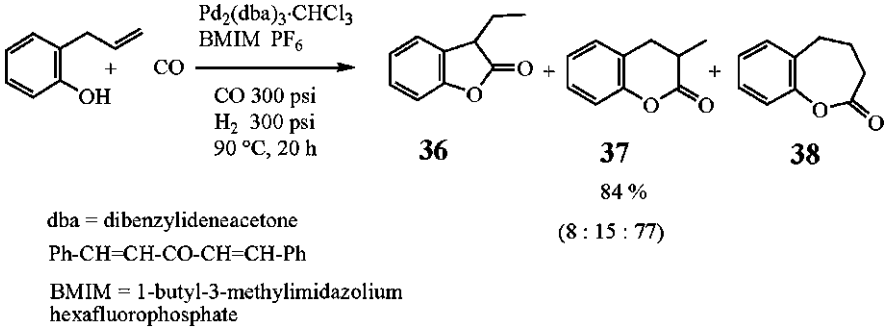
Mechanistically a metal atom is first coordinated by a nitrogen atom, followed by the insertion of CO, and the reductive elimination of the metal to yield a lactam ring, for example, the cyclocarbonylation of 5-benzylamino-1-pentene in the presence of a rhodium catalyst, carbon monoxide and hydrogen proceeds via the coordination of the nitrogen atom, followed by the insertion of CO, and the reductive elimination of the rhodium atom to yield mainly a 2-piperidinone **34** as shown in Eq. (25) [10,24,26,29,51a].



(25)

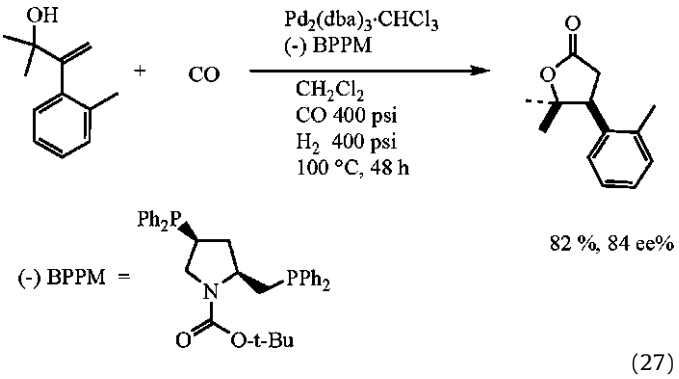
3.5. Cyclocarbonylation of alkenyl alcohols

The cyclocarbonylation of alkynyl alcohols yields lactones as described in Section 2.3. The cyclocarbonylation of alkenyl alcohols also generally yields the corresponding lactones, although the cyclization reactivity and selectivity decrease [52]. For example, the cyclocarbonylation of 2-allylphenol in the presence of a palladium catalyst in ionic liquid (BMIM PF_6) yields three kinds of lactones as shown in Eq. (26) [52a]. A seven-membered ring lactone **38** which is cyclized at its terminal carbon, is produced as a main product. However, the five- and six-membered lactones are also produced.



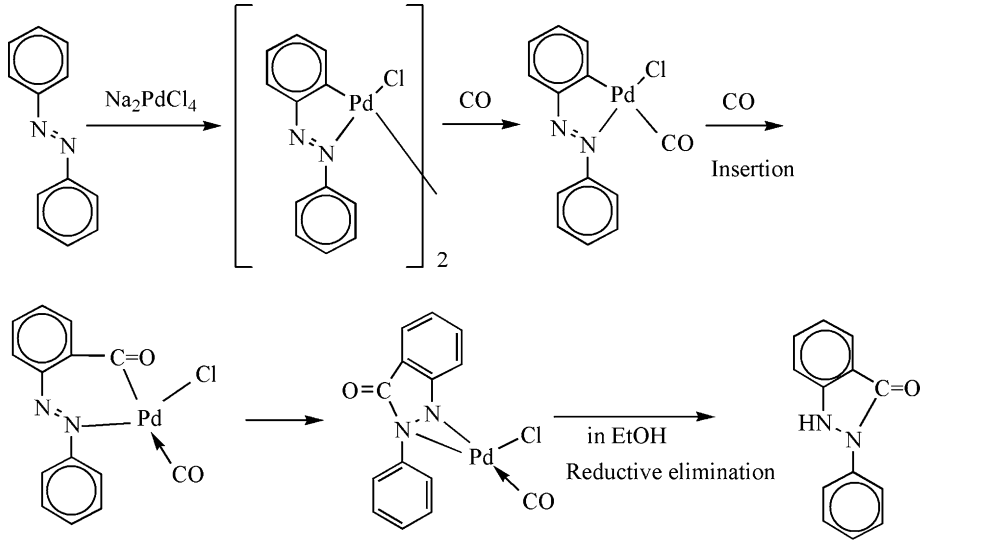
(26)

The cyclization reaction of an alkenyl alcohol having a bulky group improves the stereo selectivity of the reaction as shown in Eq. (27) [52b].



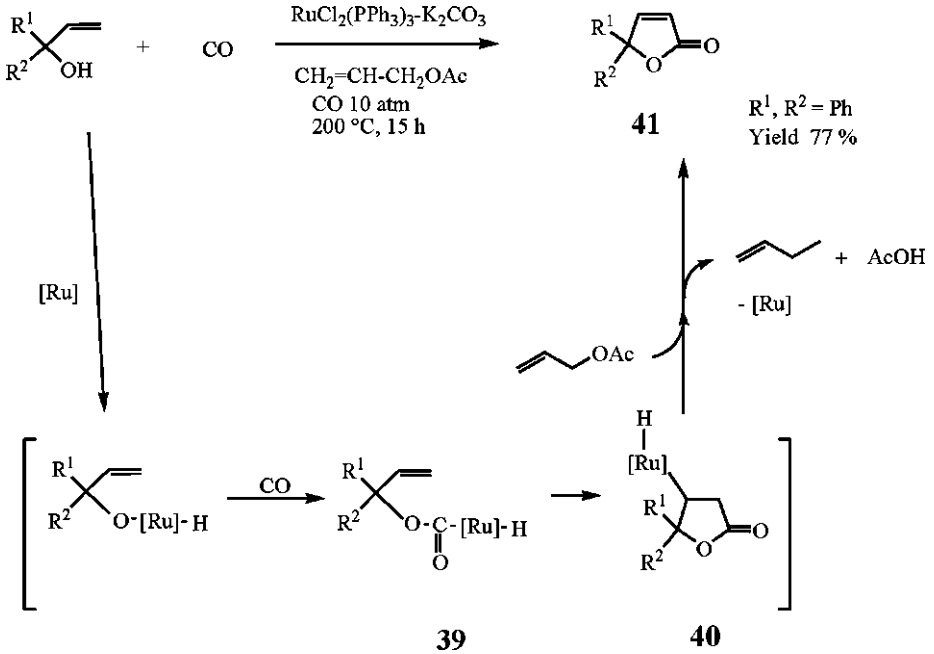
(27)

Palladium catalysts are used mainly for these cyclization reactions [10,11,24,52].



Scheme 9.

However, Ru, and Rh metal compounds are also used for these cyclocarbonylation [53]. The ruthenium catalyzed reaction proceeds in the oxidative cyclocarbonylation of allylic alcohols at a high temperature under a CO pressure to give directly 2(5*H*)-furanone in good yield as shown in Eq. (28) [53a].



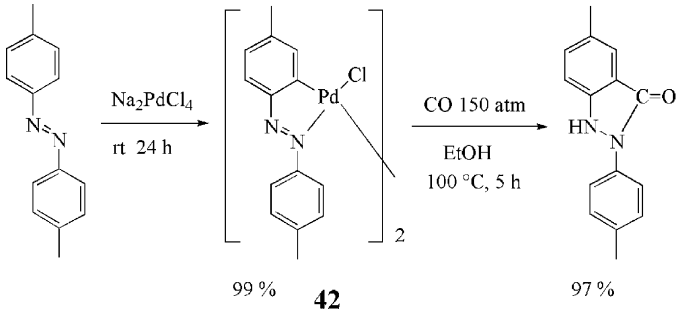
(28)

The reaction is presumed to proceed as follows: at first, the oxidative addition of a ruthenium compound to hydroxy group in an allylic alcohol and the insertion of carbon monoxide into an O–Ru bond gives a carboxylate **39**, followed by the insertion of an alkenyl group to the carboxylate to give an intermediate **40**, subsequently, β-hydride elimination affords a 2(*5H*)-furanone **41** together with the regeneration of an active ruthenium species by hydrogen transfer (hydrogenolysis) to allyl acetate [53a].

4. Cyclocarbonylation via cyclometalation

The presumption of cyclocarbonylation via cyclometalation at a high temperature and under a high CO pressure is shown in Eqs. (2) and (3) in Section 1.

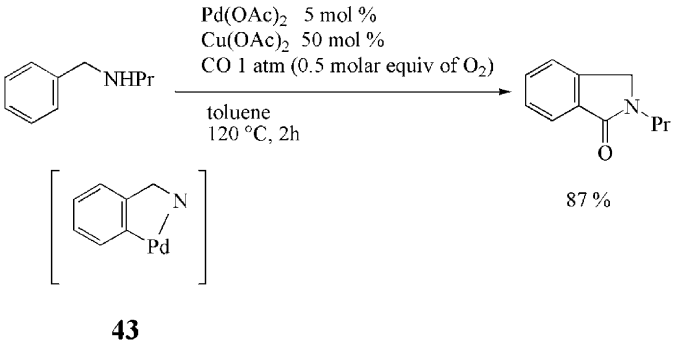
This presumption was founded on the following cyclopalladation and carbonylation reactions as shown in Eq. (29) and Scheme 9 [54]. With palladium catalysts, the cyclopalladation of azobenzene easily proceeds at room temperature for 24 h to give a cyclopalladated product **42** in almost quantitative yield as shown in Eq. (29), however, the carbonylation requires a high temperature and a high CO pressure atmosphere to yield a product as shown in Eq. (29).



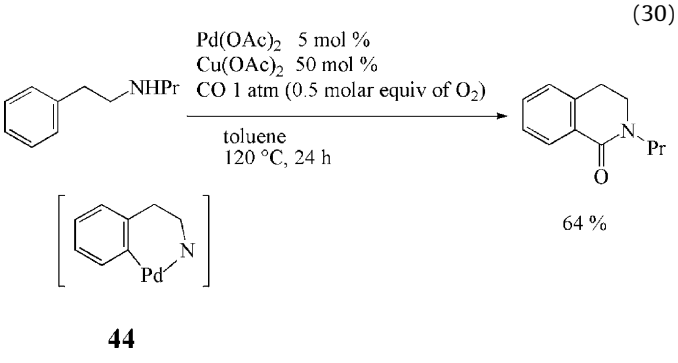
(29)

Hence, the cyclocarbonylation of azobenzene proceeds in the presence of a palladium catalyst under carbonylation reaction conditions via cyclometalated intermediates **42** as shown in Eq. (29). The palladium catalyzed cyclocarbonylation of azobenzene is presumed as at first, the cyclometalation proceeds, followed by CO insertion and reductive elimination with protonation by ethanol to give a 2-aryl-3-indazolinone as shown in Scheme 9.

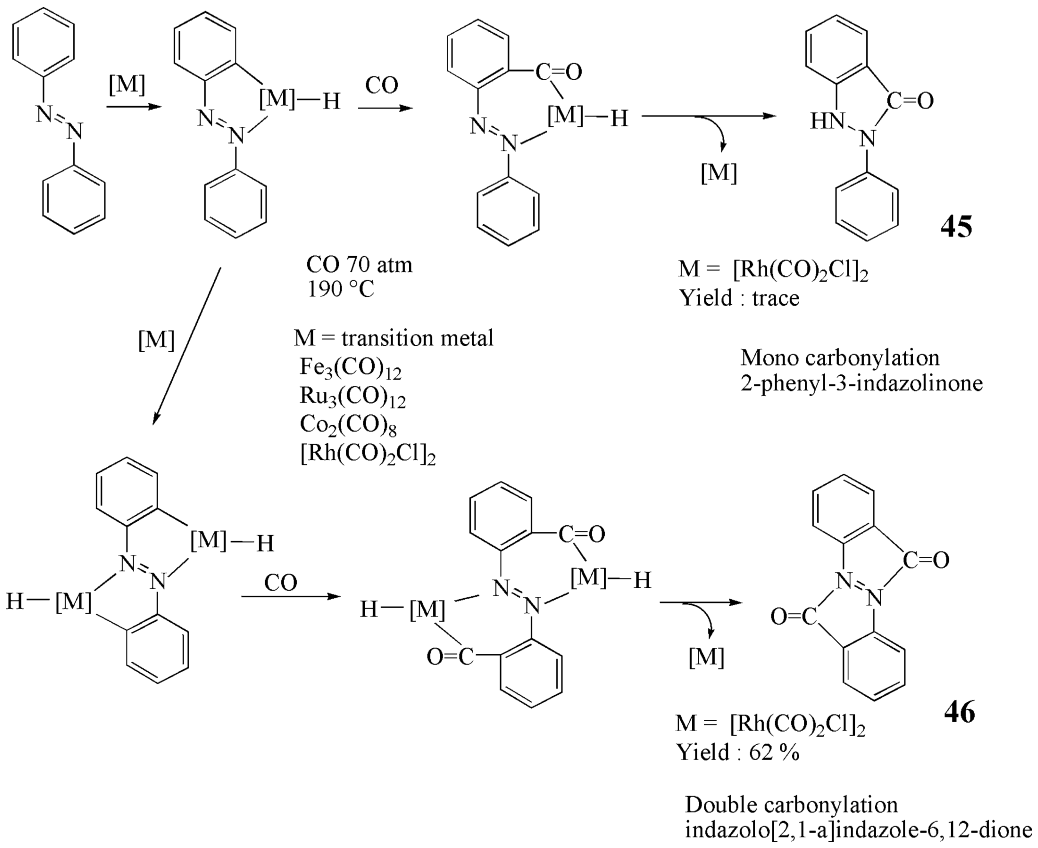
Recently, the preparation of various kinds of benzolactams by palladium-catalyzed cyclocarbonylation was reported [55]. The cyclocarbonylations of *N*-propylbenzylamine and propylphenethylamine are shown in Eqs. (30) and (31), respectively [55]. The yield of cyclocarbonylation of propylphenethylamine, though the reaction time is twelve-times longer, is lower than that of *N*-propylbenzylamine. The reaction also shows that the formation of the five-membered ring structure **43** is much easier than that of six-membered ring structure **44** [5].



(30)



(31)

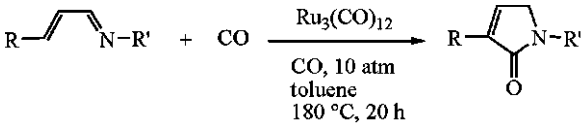


Scheme 10.

Takahashi et al. [56] reported on both of the mono and double cyclocarbonylation of azobenzene with $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Co_2(CO)_8$ and $[Rh(CO)_2Cl]_2$, which proceed at 190 °C and CO 70 atm in a small amount of solvent. The double cyclocarbonylation with the $[Rh(CO)_2Cl]_2$ in nitrobenzene as the solvent show the highest yield in these reactions as shown in Scheme 10 [56]. Under these reaction conditions, the monocarbonylation product is produced only in trace amount. The monocarbonylation and double carbonylation reactions proceed via different reaction routes as shown in Scheme 10 [56]. The mono cyclocarbonylation proceeds via one orthometalation, CO insertion, reductive elimination and protonation. On the other hand, the double cyclocarbonylation proceeds via double orthometalation, double CO insertion, and double reductive elimination as shown in Scheme 10 [56].

Both the mono cyclocarbonylation in Eq. (2) and the double cyclocarbonylation at a higher temperature, are shown in Scheme 11 [31]. These reaction conditions are compared with the reaction conditions shown in Scheme 10. In the latter reaction conditions, the mono cyclocarbonylation reaction is performed under a higher CO pressure of 150 atm, and the double cyclocarbonylation is performed under the higher CO pressure of 150 atm, and also at a higher temperature of 230 °C. The double cyclocarbonylation proceeds via the mono cyclocarbonylation. The mono cyclocarbonylation is the same in the both reactions of Schemes 10 and 11, that is, initially, orthometalation occurs followed by carbonyl insertion, reductive elimination and protonation, however, in the double cyclocarbonylation a cobalt atom bonds with a reactive amino nitrogen atom, followed by the carbonyl insertion and reductive elimination as shown in Scheme 11 [31].

The cyclocarbonylation of conjugated imines easily proceed under a low CO pressure in the presence of ruthenium compounds by [4 + 1] cycloaddition as shown in Eq. (32) [57a]. The reaction is presumed to proceed via the intramolecular five-membered ring structure to give unsaturated γ-lactams as shown in Scheme 12 [57a].

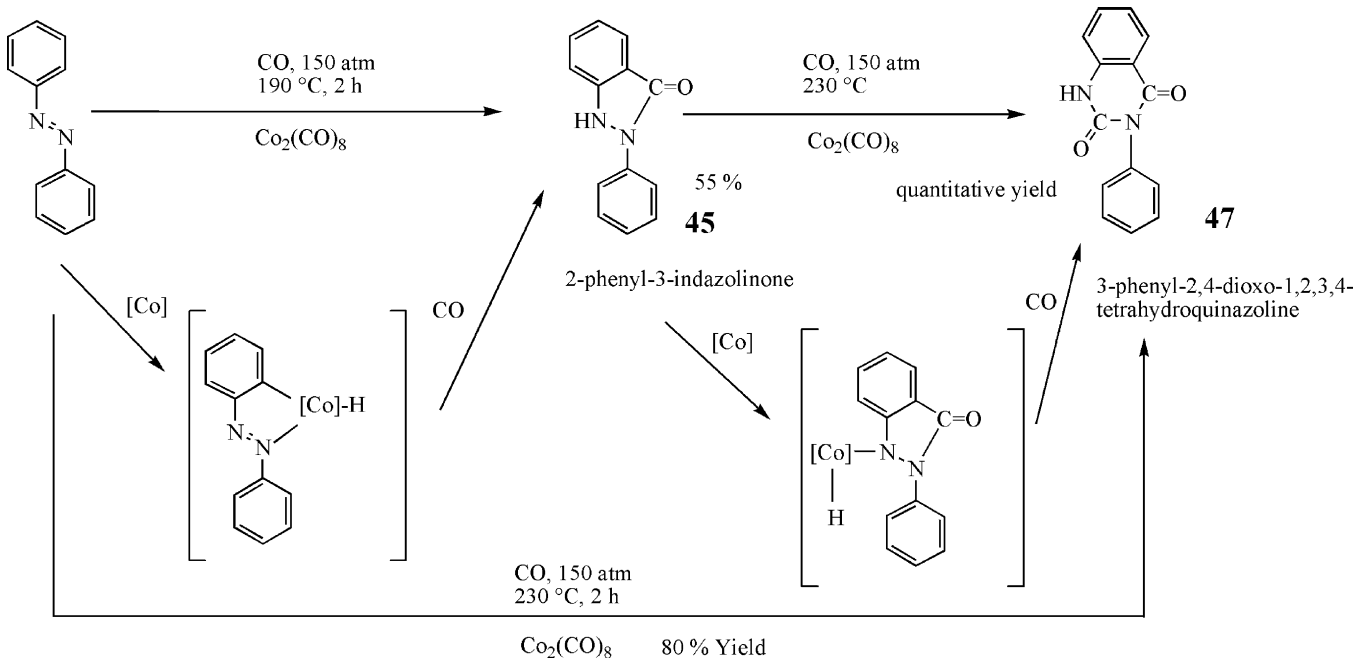


(32)

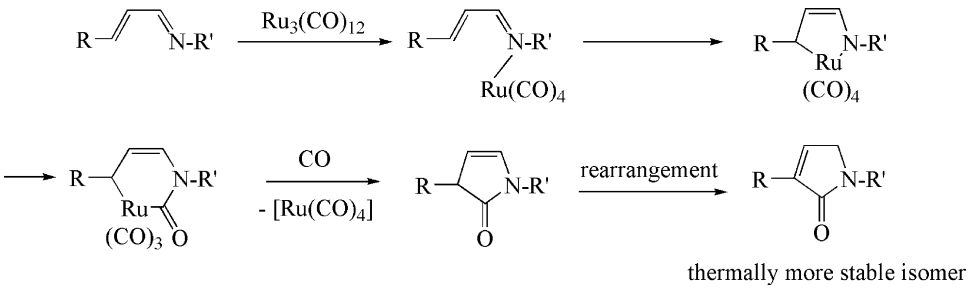
Recently, Chatani et al. [57b] also reported on the cyclocarbonylation of aryl amides for the synthesis of phthalimides with carbon monoxide via cyclometalation reactions.

5. Carbonylative ring expansion reactions

Carbonylation compounds are also prepared by the carbonylative ring expansion reactions of small ring compounds such as cyclopropanes [58], epoxides [59], aziridines [60], cyclobutanes [61] and others, such as oxazolines [62] and triazolidines [63], with carbonyl components such as carbon monoxide, metal carbonyls and isocyanates [58]. Their carbonylative ring expansion reactions are shown below: heptylidenecyclopropane was treated with one equivalent of $Co_2(CO)_8$ in THF at 50 °C for 12 h and this led to a mixture of (2*E*)-and (2*Z*)-2-heptylidenecyclobutanones in 85% yield as

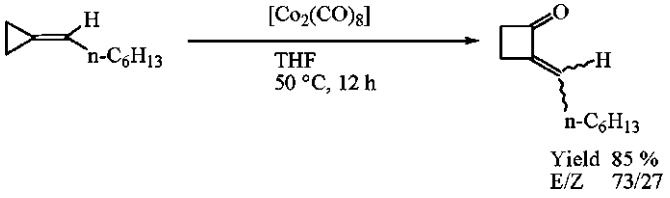


Scheme 11.



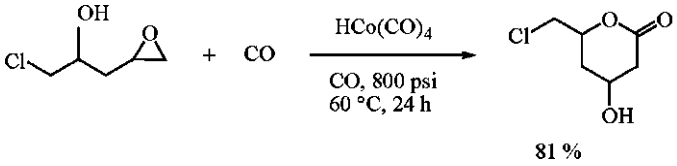
Scheme 12.

shown in Eq. (33) [58a].



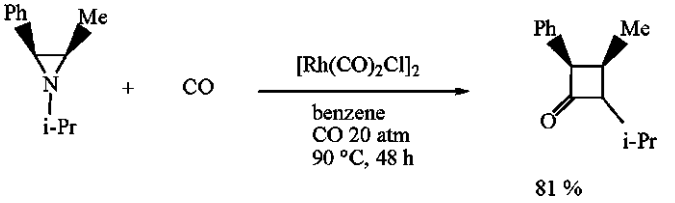
(33)

The carbonylative ring expansions of the epoxides such as 4-hydroxy-1,2-epoxides, with carbon monoxide in the presence of a cobalt catalyst, ($HCo(CO)_4$), give valuable intermediates in the synthesis of pharmaceuticals and other biologically active natural products. The products are the substituted 3-hydroxy-δ-lactones that are the important synthetic intermediates of statin drugs [59a].



(34)

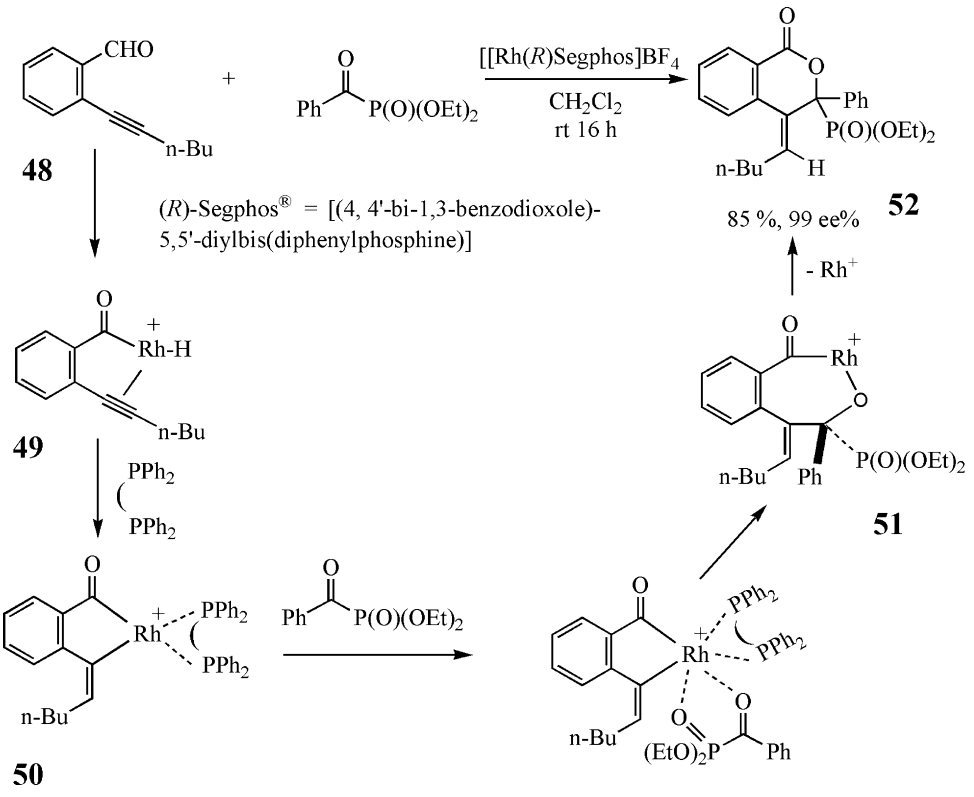
Cis-1-isopropyl-3-methyl-2-phenylaziridine reacts with carbon monoxide in the presence of $[Rh(CO)_2Cl]_2$ in benzene to give ring expansion β-lactams as shown in Eq. (35) [60a].



(35)

6. Cyclocarbonylation by aldehydes

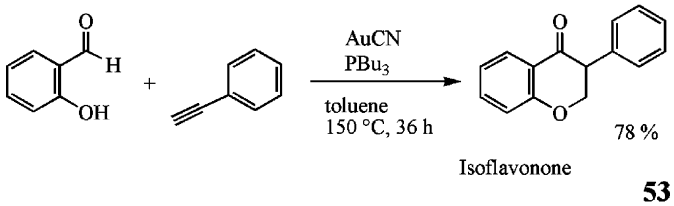
Aldehydes are used as one of the carbonyl components instead of carbon monoxide described in Sections 2 and 3 [12–16,24,64–69]. A representative substrate is a 2-alkynylbenzaldehyde (e.g., compound **48**), for example, in the reaction of the 2-alkynylbenzaldehyde **48** with acyl phosphonates, via [4+2] annulation gave the benzopyranones **52** as shown in Scheme 13 [64]. At first, the oxidative addition of the aldehyde's C–H bond to rhodium(I) affords a rhodium acyl hydride **49**. The *cis*-addition of the rhodium acyl hydride to a metal-bound alkyne then provides five-membered acyl rhodium intermediate **50**. The regio- and stereoselective insertion to the intermediate forms an oxarhodacycle **51**. The reductive elimination of the oxarhodacyle



Scheme 13.

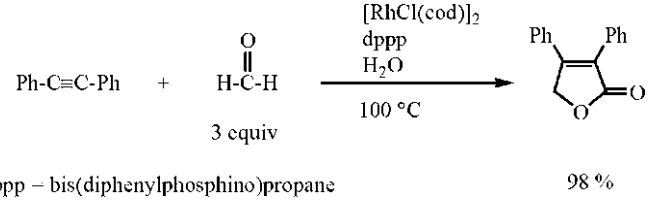
furnishes a benzopyranone **52** and regenerates the rhodium catalyst [64].

The reaction of salicylaldehyde with phenyl acetylene to form an isoflavanone **53** and the reactions of 4-alkynals with an acetylene to form the cyclohexenones **54**, are [4+2] annulation as shown in Eqs. (36) [65] and (37) [66], respectively.

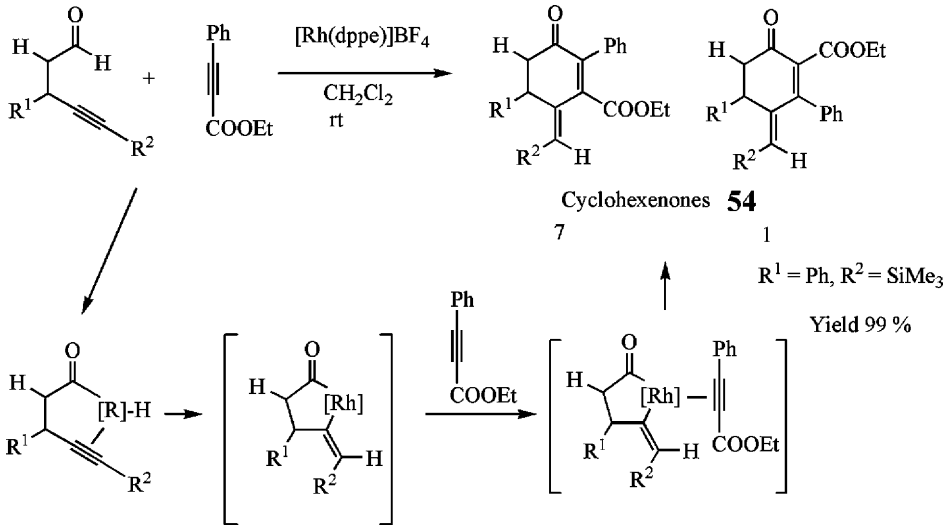


(36)

The rhodium(I)-catalyzed reaction of alkynes with formaldehyde proceeds via the double incorporation of a carbonyl moiety from formaldehyde, resulting in a CO gas-free cyclohydrocarbonylation leading to α,β-butenolides as shown in Eq. (38) [67].

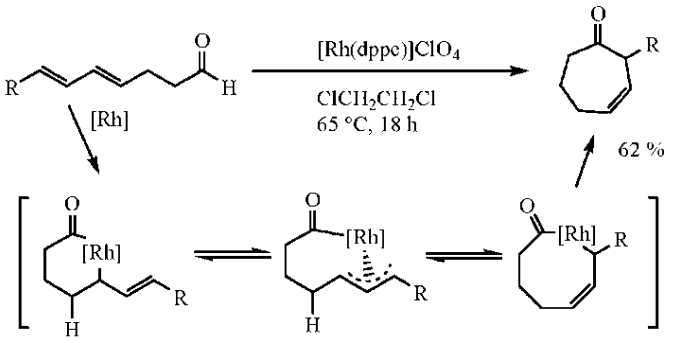


(38)



(37)

The cyclizations of alkenes or dienes having a formyl group at the terminal position proceed in the presence of a transition metal catalyst, for example, the intramolecular hydroacylation of a 4,6-dienal proceeds in the presence of a rhodium catalyst to give a cycloheptenone as shown in Eq. (39) [68].



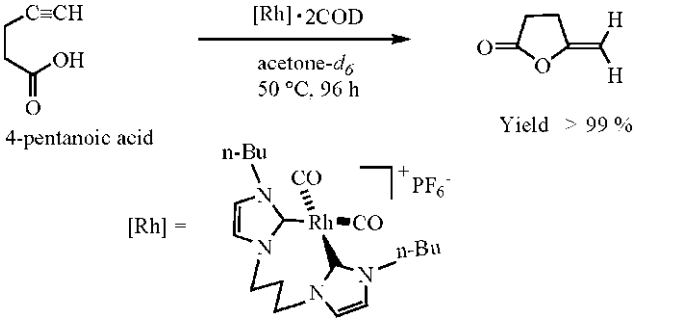
R = CH_2CH_2Ph dppe = bis(diphenylphosphino)ethane

(39)

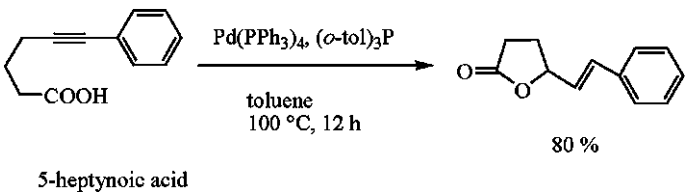
7. Cyclocarbonylation by carboxylic acids or carboxylic acid esters

Carboxylic acids [12–15,17–19,22,70–73] or carboxylic acid esters [12,15,27,74–77] are used as one of carbonyl components for the cyclocarbonylation reactions. These reactions, generally, proceed by using the carbonyl group in the carboxyl groups or alkoxycarboxyl groups at the terminal position. Both of these intramolecular and intermolecular reactions proceed with cyclization components such as alkynes, alkenes, aryl compounds, etc. to give the various lactones.

The intramolecular cyclocarbonylation reactions of alkynylcarboxlic acids proceed in the reactions of 4-pentanoic acid or 5-heptanoic acid in the presence of transition metal catalysts such as rhodium metal or palladium compounds to give γ-lactones as shown in Eq. (40) or (41), respectively [70,71].

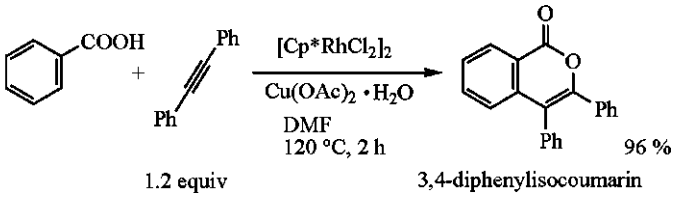


(40)

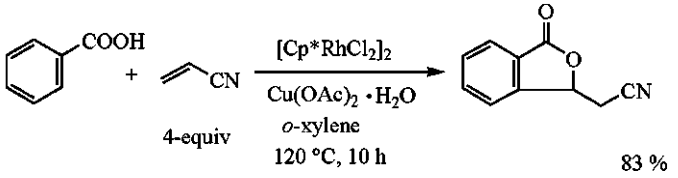


(41)

On the other hand, intermolecular cyclocarbonylation reactions also proceed in the reactions of benzoic acid with diphenyl acetylene or acrylonitrile in the presence of a rhodium metal compound to give an unsaturated δ-lactone or γ-lactone, respectively [72,73].

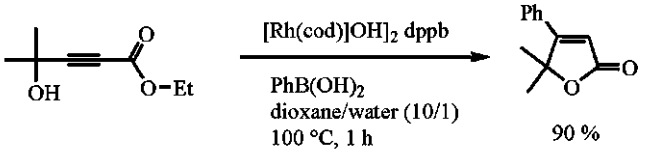


(42)



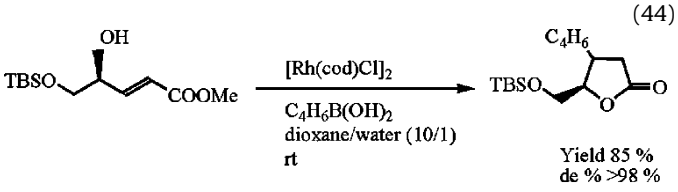
(43)

The cyclization of 4-hydroxy-2-alkynyl carboxylic acid esters or 4-hydroxy-2-alkenyl carboxylic acid esters with organoboron compounds proceed in the presence of rhodium catalysts to give lactones as shown in Eq. (44) or (45), respectively [74,75]. These reactions are intramolecular cyclocarbonylation of an alkoxycarbonyl group at the terminal positions.



dppb = bis(diphenylphosphino)butane

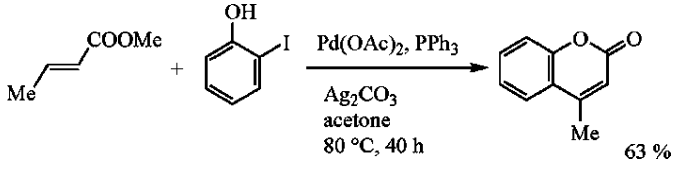
(44)



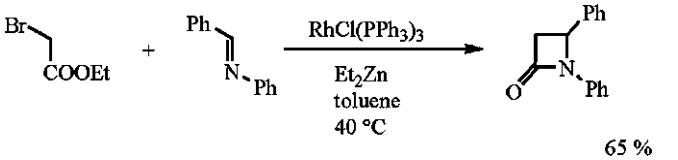
(45)

The intermolecular cyclocarbonylation of an alkoxycarbonyl group at the terminal position also proceeds with aryl compounds or imines as the cyclization components. The cyclization of *ortho*-iodophenols with methyl crotonate in the presence of a palladium catalyst gives lactones as shown in Eq. (46) [76].

On the other hand, the cyclization of α-bromoethylacetate with diphenylimine in the presence of rhodium catalyst gives lactams as shown in Eq. (47) [12,77].



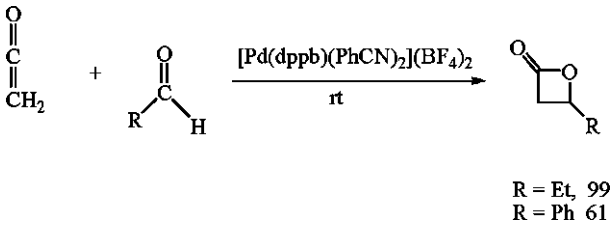
(46)



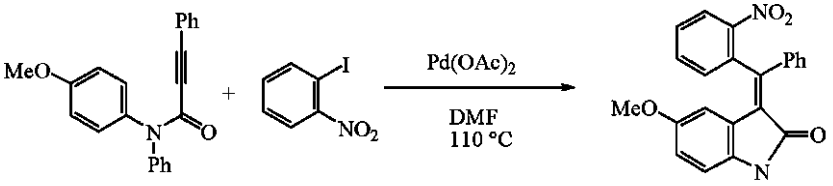
(47)

8. Cyclocarbonylation by other carbonyl components

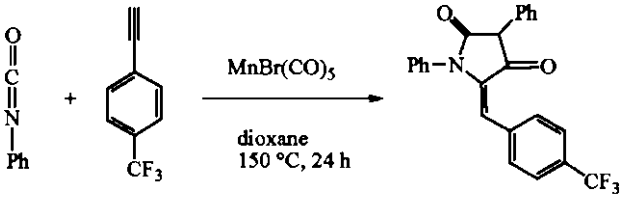
Amides, isocyanates, carbamates, ketenes, ureas and acyl chlorides are also used as the other carbonylation components. These cyclocarbonylation regarding carbonyl components such as amides [78], isocyanates [21,28,27,28,79], carbamates [80], ketenes [81], and acyl chorides [82], are shown Eqs. (48)–(53), respectively.



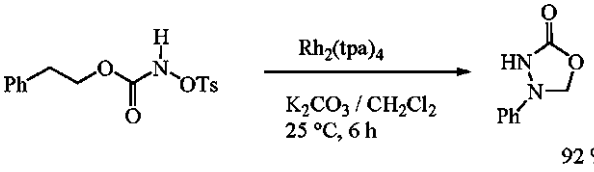
(51)



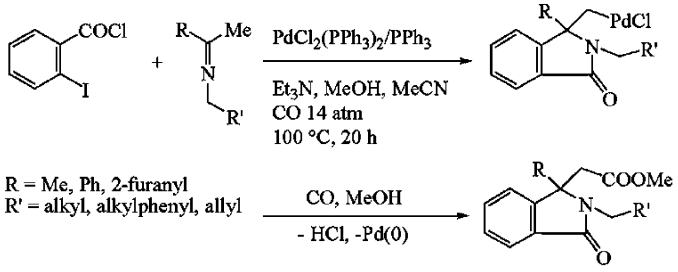
(48)



(49)

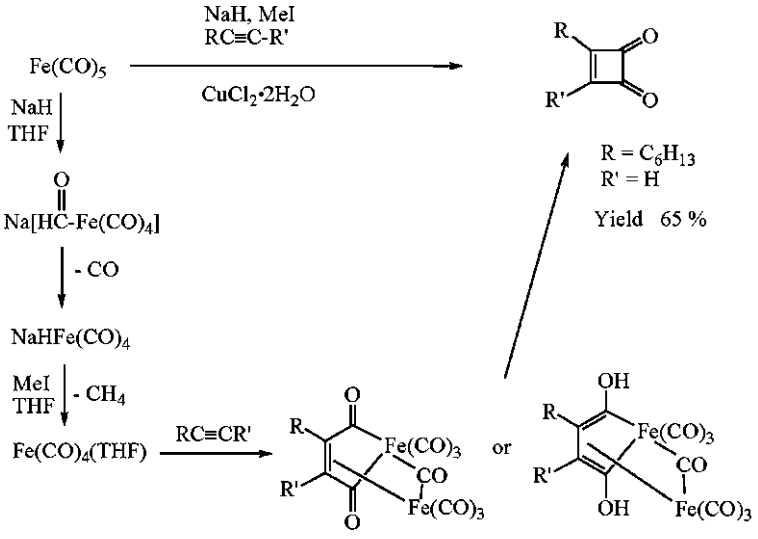


Rh(tpa)4 = rhodium (II) triphenylacetate dimer complex (50)

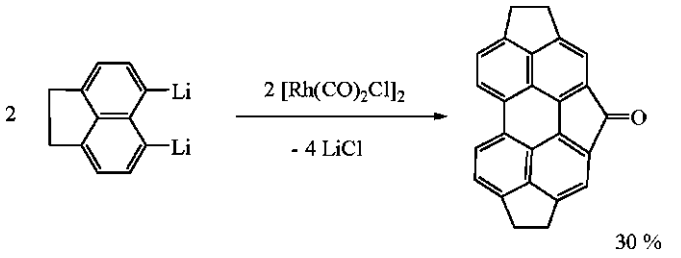


(52)

Further, metal carbonyls and carbon dioxide are also used as the other carbonylation components. As the metal carbonyl, cobalt carbonyls are already shown in the Pauson–Khand reactions (e.g., $Co_2(CO)_8$, in Eq. (4), the reaction of carbonylative alkyne–alkyne reactions (e.g., $CoCo(CO)_2$ in Eq. (10), and carbonylative ring expansion reactions ($Co_2(CO)_8$ in Eq. (33).



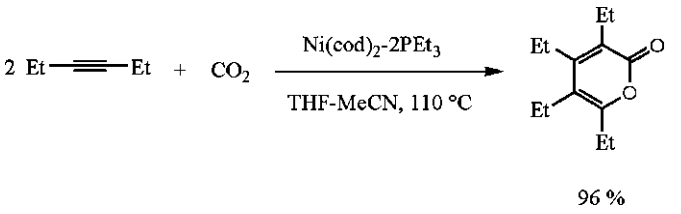
(53)



(54)

The other examples of the metal carbonyls as the carbonyl components, are $Fe(CO)_5$ [83a] and $[Rh(CO)_2Cl]_2$ [83b] shown in Eqs. (53) and (54), respectively [10,22,27,28,83].

Cyclocarbonylation by carbon dioxide proceeds in reactions with dienes, allenes, alkynes, dialkynes, and epoxides [10,11,18,21,24,26,28,84]. These reactions were already reported in detail in the review "Aspects of Carbon Dioxide Utilization" [84]. therefore, in this review, only one example is shown below: the reaction of alkynes with carbon dioxide in the presence of nickel catalysts give a doubly substituted pyrone by the [2 + 2 + 2] cycloaddition of two akynes and one carbonyl group in carbon dioxide as shown in Eq. (55) [84].



(55)

9. Concluding remarks

The cyclocarbonylation reactions proceed mainly by the coupling reactions of carbonylation components with cyclization components having an unsaturated π-electron bond in the presence of transition metal compounds. The carbonylation components are carbon monoxide, metal carbonyls, aldehydes, ketones, carboxylic acids, carboxylic acid esters, ketenes, isocyanides, acyl compounds, carbon dioxide, etc. The cyclization components are alkynes, alkenes, allenes, dienes, aryl compounds, imines, nitriles, diazo compounds, etc.

These cyclocarbonylation reactions are Pauson–Khand reactions, Hetero Pauson–Khand reactions, the cyclocarbonylation of alkynyl alcohols, the cyclocarbonylation of alkynyl amines, the cyclocarbonylative alkyne–alkyne coupling reactions, the reductive cyclocarbonylation of alkynes, the cocylization of two alkynes and two carbon monoxides, the reductive cocylization of alkynes, alkenes and two carbon monoxides, the cyclocarbonylative coupling reactions of alkynes, amines and two carbon monoxides, the cyclocarbonylation of alkynes with carbon monoxide and ketones, the reductive cyclocarbonylation of arylalkynes, cyclocarbonylative alkene–alkene coupling reactions, the cyclocarbonylation of alkenes with aldehydes or ketones, the cyclocarbonylation of alkenes with amines or imines, the cyclocarbonylation of alkenyl alcohols, carbonylation via cyclometalation, carbonylative ring expansion reactions, cyclocarbonylation by aldehydes, cyclocarbonylation by carboxylic acids or carboxylic acid esters, and cyclocarbonylation by other carbonyl compounds. These reactions are conveniently used for organic syntheses, especially, for the syntheses of pharmaceutical intermediates.

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