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Rhodium-Catalyzed Carbonylative Synthesis of Heterocycles

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Abstract The main achievements in rhodium-catalyzed carbonylative synthesis of heterocycles are summarized and discussed.

Keywords Carbon monoxide · Carbonylation · Heterocyclic compounds · Organic synthesis · Rhodium catalyst

Contents

Nowadays, rhodium catalysts are 'star catalysts' in C–H activation reactions. Numerous synthetic systems have been developed based on Rh(I) or Rh(III) precursors. Compared with the achievements in C–H activation, the application of rhodium catalysts in carbonylation are less explored, except for the well-known Monsanto process which can transform methanol to acetic acid. In this chapter we summarize the established carbonylation procedures for the synthesis of heterocycles.

The carbonylation of acetylenes has received much attention because of its scientific and industrial importance. Various mono- and dicarboxylic acids, cyclic ketones, hydroquinones, butenolides, and other derivatives can all be produced from acetylenes [1]. Procedures for the synthesis of furanones catalyzed by Co [2, 3] and Pd [4] have been developed. In 1981, Mise and co-workers succeeded in developing a rhodium-catalyzed procedure for the synthesis of 5-alkyl-2(5*H*)-

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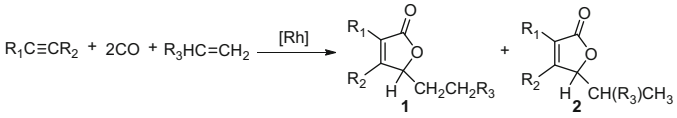


Scheme 1 General synthesis of furanones by carbonylation of acetylenes

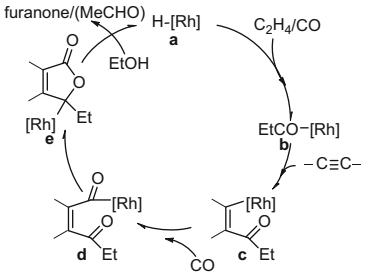
furanones from acetylenes. Rhodium carbonyl complexes and their precursors were tested in the presence of olefins and proton donors (Scheme 1) [5].

In this work, $Rh_4(CO)_{12}$ showed the best catalytic activity with different solvents acting as proton donors such as methanol, ethanol, propanol, and water. The formation of 5-ethyl-3,4-diphenyl-2(5*H*)-furanone and by-products indicated that the ethanol acted as both hydrogen donor and solvent medium in this reaction. Furthermore, 5-ethyl-3,4-dimethyl-2(5*H*)-furanone can also be produced from 2-butyne. Unfortunately, terminal acetylenes such as phenylacetylene and 1-hexyne did not give the desired products. Moreover, several mono-substituted olefins were used in the catalytic system with formation of the corresponding products in low yields. For the purpose of suppressing by-product formation, the influence of temperature was studied, results showing that a temperature of about 150°C is sufficient for maintaining yields and suppressing by-products. Finally, a possible mechanism was proposed by the authors and is shown in Scheme 2. It seems that the acyl complex **b** acted as an important intermediate given by stepwise insertion of ethylene and CO into the Rh-H intermediate. Then the subsequent addition of complex **b** to the acetylene and CO could give intermediate **d** and be converted to **e**, providing the final furanone.

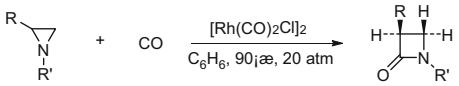
In 1983, Mise's group used $Rh_4(CO)_{12}$ as the catalyst to synthesize 5-ethoxy-3,4-diphenl-2(5*H*)furanone, and 72% yield of the corresponding product was formed. Interestingly, the addition of alkali metal salt to $Rh_4(CO)_{12}$ or its precursors can greatly improve the yield. A $Rh_4(CO)_{12}$/NaOAc system was found to be the best combination and gave the 5-ethoxyl-2(5*H*)-furanone in 87% yield [6]. Reasonable results could also be obtained by using Na_2CO_3 and $NaHCO_3$. Unfortunately, stronger bases such as NaOH and NaOEt gave no product. All of these results were dependent on the stability of $Na[Rh_6(CO)_{15}(COOR)]$ under the basic conditions [7]. Meanwhile, different rhodium catalysts such as Rh_2O_3, $RhCl_3{\cdot}3H_2O$, and $RhCl(PPh_3)_3$ were screened instead of $Rh_4(CO)_{12}$. The catalytic activities of the Rh_2O_3 and $RhCl_3{\cdot}3H_2O$ were nearly the same as the $Rh_4(CO)_{12}$ whereas the activity of $RhCl(PPh_3)_3$ was very low. All the results indicated that it was easy to obtain an (ethoxycarbonyl)rhodium intermediate by Rh_2O_3, $RhCl_3{\cdot}3H_2O$, and $Rh_4(CO)_{12}$, the triphenylphosphine ligand suppressing nucleophilic attack of an alkoxide ion on the coordinated carbon monoxide.

Later, Alper and Urso published a paper on the metal-catalyzed carbonylative ring expansion of aziridines to β-lactams [8]. To start with, they used the catalytic amount of $Pd(PPh_3)_4$ but, unfortunately, no β-lactams were formed. Then they used Rh salts as catalyst which can lead to the carbonylation of aziridines to β-lactams directly and regioselectively. It was found that when *N*-*tert*-butyl-2-phenylazirdine

Scheme 2 Proposed mechanism for the formation of furanone



Scheme 3 Carbonylation of *N-tert*-butyl-2-phenylaziridine



was treated with carbon monoxide in benzene with chlorodicarbonylrhodium (I) dimer as the catalyst at 90°C and 20 atm, the corresponding β-lactams can be produced in quantitative yield (Scheme 3).

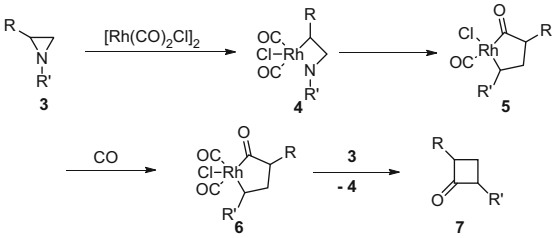
Other rhodium complexes were also taken into account, such as the 1,5-cyclo-octadienerhodium(I) chloride dimer, which is also an effective catalyst, whereas the dimers of 1,5-hexadiene-rhodium chloride and rhodium acetate were incapable of catalyzing this transformation. In this research, a mechanism was proposed whereby the oxidative addition of multi-substituted C–N bonds to Rh(I) afforded the corresponding Rh complex, then, followed by the migration of ligand and CO insertion, gave the desired product after reductive elimination (Scheme 4).

In 1989, Alper's group used 1,5-cyclo-octadienerhodium(I) chloride as catalyst and D- or L-menthol as an added chiral agent to study the asymmetric synthesis of β-lactams from aziridines [9]. To examine the ring-expansion process, *cis*-1-iso-propyl-3-methyl-2-phenylaziridine was subjected to benzene with $[Rh(CO)_2]Cl_2$ as the catalyst and the corresponding *cis*-3,4-disubstituted β-lactams was isolated in 81% yield, indicating that the carbonylation had taken placed with retention of the stereochemistry of the substituent groups (Scheme 5). Moreover, the remarkable regio-, stereo-, and enantiospecificity of the β-lactam synthesis suggested that it might be a promising route to synthesize corresponding asymmetric compounds from racemic aziridines in the presence of an appropriate chiral ligand.

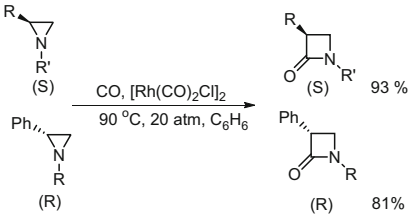
In 1990, Matsuda and co-workers synthesized β-lactones by rhodium-catalyzed cyclocarbonylation of substituted propargyl alcohols [10]. Because of the catalytic efficiency of Rh [11], an elegant cyclocarbonylation of acetylenic alcohols to form lactones with the assistance of an appropriate base and a catalytic amount of $Rh_4(CO)_{12}$ was demonstrated (Scheme 6).

The selectivity between the two products **9** and **10** can be tuned by the addition (or absence) of NEt_3. Preliminary research indicated that the propensity of β-lactones formation depended on both steric and electronic factors.

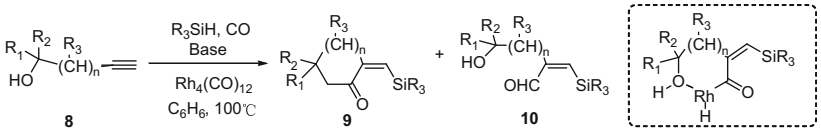
In 1990, Takahashi and co-workers found that the use of water instead of molecular hydrogen can give cyclocarbonylated products, 2(5*H*)-furanones, in excellent yield [12–14]. Later on, a novel rhodium-catalyzed carbonylation of



Scheme 4 Possible mechanism for the formation of β-lactams

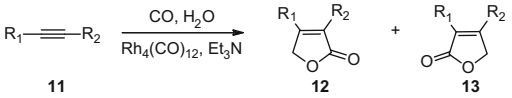


Scheme 5 Enantioselectivity of the carbonylation reaction

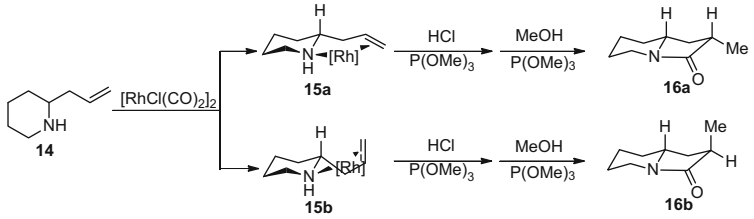


Scheme 6 Cyclocarbonylation of propargyl alcohols by the catalyst of rhodium

acetylenes was developed [15]. Under water-gas shift reaction conditions, internal acetylenes were selectively carbonylated to 3,4-disubstituted 2(5*H*)-furanones (Scheme 7). In addition, the reaction of D_2O instead of water gave the desired product 5,5-dideuteriofuran-2(5*H*)-one, indicating that the hydrogen came from water. Among the transition metal complexes, $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ were found to be the best catalysts. The effect of additives, solvents, the amount of H_2O in ethanol, and the pressure of CO were also examined. Thereby, the reactions can proceed with satisfactory yields by means of internal acetylenes bearing alky, alkenyl, and aryl substitutes. However, monosubstituted acetylenes such as phenylacetylene were of no use, possibly because the terminal acetylene has an active C–H bond. What should be pointed out is that, by employing a cyano group at the *para* position of one of the phenyl group of the acetylene, the reactivity was increased noticeably and the isomer **13** became the dominant product. In contrast, electron-donating groups could increase the isomer ratio of **12/13**. All of these results show that the electron density on the acetylene carbons have a strong effect on the product and that the carbonyl group of furanones is preferred to carbon atoms with lower electron densities.



Scheme 7 Carbonylation of acetylene to furanone by rhodium catalyst



Scheme 8 Synthesis of a bicyclic lactam through cyclocarbonylation of 2-allylpiperidine

A few years later, in 1993, Zhang and Ojima reported the synthesis of nitrogen heterocycles by direct hydrocarbonylation [16–21]. Based on previous research by Krafft et al. [22–24], Ojima and co-workers developed the diastereoselective annulation of 2-allylpiperidine **14** which it was thought could give a bicyclic lactam **16** (Scheme 8). During the process, it was found that the 2-allylpiperidine was processed highly stereoselectively and **16a** was given as the sole product in 43% isolated yield.

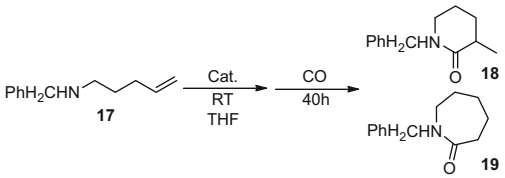
In addition, 5-benzylamino-1-pentene **17** was taken to examine catalytic and regioselective factors with a variety of rhodium complexes in the presence of hydrogen chloride. 1-Benzyl-3-methyl-2-piperidinone **18** and 1-benzyl-azepan-2-one **19** in ratios from 82:18 to 95:5 indicated that the amine-directed chelation control is effectively processed and is in favor of the formation of six-membered ring products (Scheme 9). However, the reactions gave lower conversion without hydrogen chloride, although good to excellent regioselectivities can be obtained with $HRh(CO)(PPh_3)_3$ or $Co_2Rh_2(CO)_{12}$.

In 1994, Khumtaveeporn and Alper used 1,3-thiazolidine as the substrate in the presence of catalytic amounts of chloro(1,5-cyclooctadiene)rhodium(I) dimer and potassium iodide to afford a thiazolidinone (Scheme 10) [25]. However, in the absence of KI, the six-membered ring thiazin-3-one becomes the primary product. Quantitative conversion was achieved and a ketene was produced as the by-product. Hence, the reaction involved a novel regiospecific insertion of carbon monoxide into one of two ring carbon–nitrogen bonds and a metal-catalyzed ketene elimination process. In this work, a serious of N-substituted thiazolidine derivatives were synthesized in dry benzene under 65 bar of carbon monoxide at 180°C for 48 h. In this catalytic system, complete conversion and good to excellent yields could be obtained.

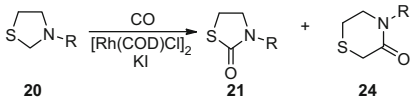
Under standard conditions, **21** was obtained in quantitative yield when **24** was used as the start material. All of this indicates that rhodium(I) not only catalyzed the ring expansion but also the subsequent ring contraction (Scheme 11).

In 1994, Joh and co-workers improved the reaction conditions for internal alkynes and extended the substrates to terminal alkynes. 3- and 4-substituted 2 (5*H*)-furanones were selectively produced (Scheme 12) [26].

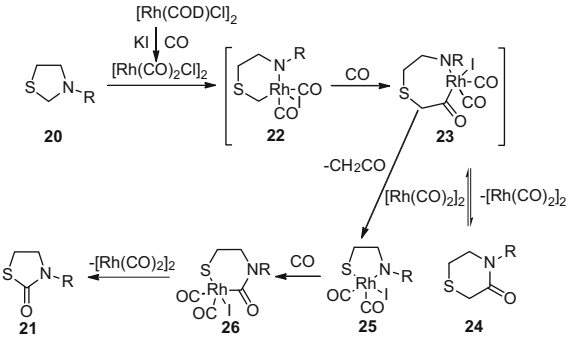
Scheme 9 Cyclocarbonylation of 5-benzylamino-1-pentene



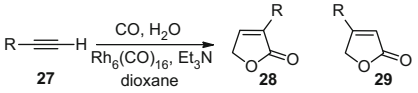
Scheme 10 Rhodium(I)-catalyzed carbonylation of 1,3-thiazolidines



Scheme 11 Mechanism of the rhodium-catalyzed carbonylation of 1, 3-thiazolidines



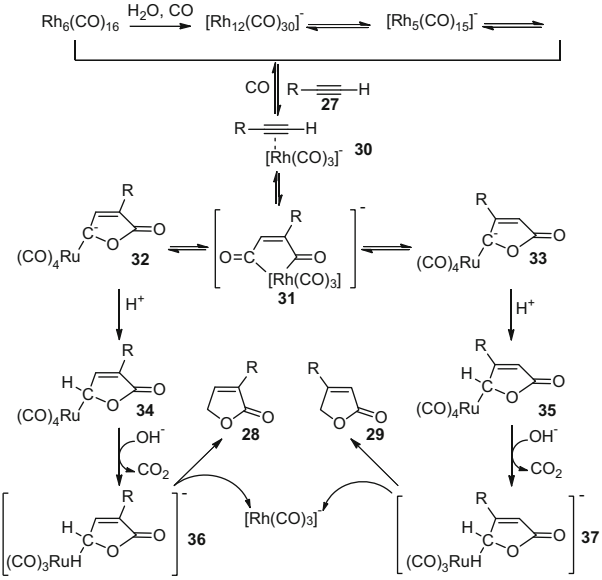
Scheme 12 Rhodium-catalyzed carbonylation of terminal alkynes



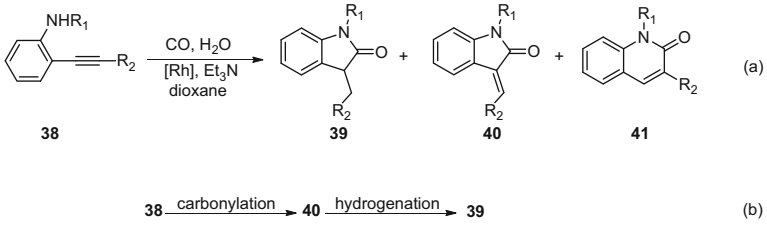
In the optimization process, the effect of solvent, concentration of Et_3N, alkyne, catalyst, and amount of water were all tested. Based on the observations described above, a new reaction pathway was given in detail (Scheme 13). Because there was no furanonyl product when the countercation of the intermediate was replaced with a cation with no hydrogen, it was considered that the most important step was the attack of a proton on the intermediate (**32**/**33**). Moreover, the amine may not only have promoted the attack of the OH^- anion but also have contributed to the stabilization of the anionic complex and transferred the proton to give the furanonyl complex.

In 1995, Takahashi and co-workers used 2-alkynylaniline as the start material to synthesize 1,3-dihydroindol-2-ones using the rhodium-catalyzed carbonylation process [27]. The typical experiment was performed under 100 bar of carbon monoxide in 1,4-dioxane containing water and triethylamine at 175°C for 14 h in the presence of $Rh_6(CO)_{16}$ (Scheme 14).

From the data obtained, it can be seen that the temperature affected the product distribution over a wide range. At low temperature, the main product was not **39** but



Scheme 13 Mechanism for rhodium-catalyzed carbonylation of terminal alkynes

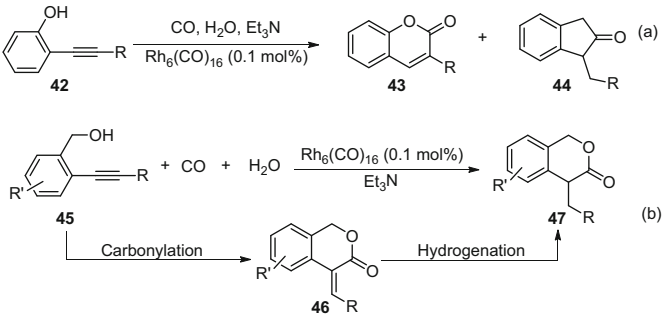


Scheme 14 Rhodium-catalyzed carbonylation of 2-alkynylaniline to dihydroindo-2-ones

40, which suggested that **40** was initially produced and then hydrogenated to **39** at higher temperature (Scheme 14b) and this was confirmed experimentally.

Later on, Takahashi's group succeeded in using *ortho*-substituted phenols as substrates to synthesize benzofuranones and coumarins also under water-gas shift reaction conditions [28]. The hydroxyl group adjacent to the carbon–carbon triple bond participates in the cyclic carbonylation with high yields up to 96% (43:44 = 65:35; Scheme 15a). The effects of solvent and additives were also investigated and 1,4-dioxane was found to be the best solvent for product selectivity, and both water and amines were compulsory for this system.

Taking the reaction mechanism into consideration, the hydroxy group of 2-alkynylbenzylalcohol may participate more effectively in the cyclic carbonylation of alkynes, and 2-alkynylbenzylalcohol was used in the presence of rhodium as catalyst to synthesize 3-isochromanone. The reaction proceeded via cyclic carbonylation under water-gas shift reaction conditions with highly selectivity and good yields (Scheme 15b) [29]. Interestingly, when 1,3,5-trimethylphenyl was used as a



Scheme 15 Rhodium-catalyzed carbonylation of 2-alkynyphenols

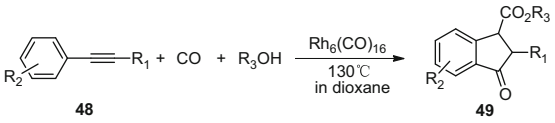
substitute group, no desired product was obtained but 71% yield of the intermediate. Hence the reaction involved two steps – carbonylation and hydrogenation.

In 1999, da Rosa and co-workers first reported the effects of chelating diphosphines on the rhodium-catalyzed carbonylation of allylamines [30]. The catalytic system was prepared in situ by mixing $RhCl_3 \cdot 3H_2O$ and equimolar amounts of the diphosphine ligands in THF. All the systems were tested and showed high conversion although, unfortunately, the selectivity decreased when the diphosphine carbon chain length increased. Hence there is a strong influence of the bite angle on both conversion and selectivity. The steric hindrance of the group attached to the allylamines nitrogen atom is also critical for the reaction.

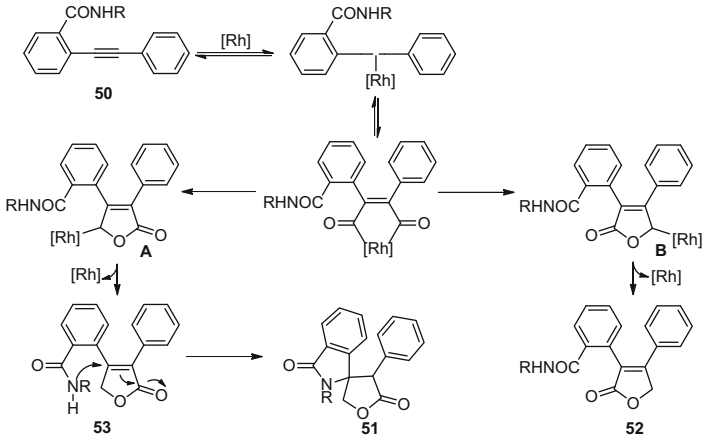
Carbonylation of alkynes under water-gas shift reaction conditions to give furan-2(5*H*)-ones in the presence of rhodium catalyst was reported. In 1999, the group of Takahashi used alcohol instead of water, and the corresponding 3-alkoxycarbonylindanones were obtained in good yield (up to 93%; Scheme 16) [31].

In the absence of methanol, the carbonylation of alkyne did not occur and the substrate was quantitatively recovered. The addition of 0.4 equiv. of methanol (based on the substrate) resulted in 52% conversion and a lower yield of about 32% when 1.0 equiv. of methanol was added, the reaction proceeding smoothly and completely. Rhodium complexes such as $[Rh(CO)_2Cl]_2$ and $RhCl_3$ showed almost the same activity as $Rh_6(CO)_{16}$ under the same reaction conditions. Moreover, study of the substrates indicated that primary alcohols gave higher yields of the corresponding indanone derivatives than secondary alcohols, possibly because of the acidity of the alcohols. It was found that alcohols with higher acidity gave better yields of the desired products.

Another example of rhodium-catalyzed cyclic carbonylation under water-gas reaction conditions was presented in 1999 by Takahashi's group. In this case, 2-phenylethynybenzamide was taken as the start material and treated with carbon monoxide in the presence of $Rh_6(CO)_6$, NEt_3, and H_2O in 1,4-dioxane at 80°C for 3 days. Two kinds of products **51**/**52** were obtained (Scheme 17) [32]. Normally, the amide group of the product was on the C=O side of the furanone ring. However, in the reaction of *N*,*N*-dimethyl-2-phenylethynylbenzamide, no further cyclization



Scheme 16 Rhodium-catalyzed carbonylation of alkynes in the presence of alcohol

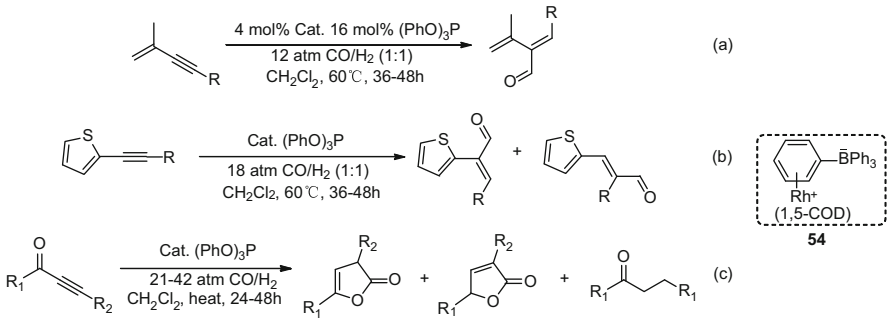


Scheme 17 Rhodium-catalyzed carbonylation of 2-phenylethynybenzamide

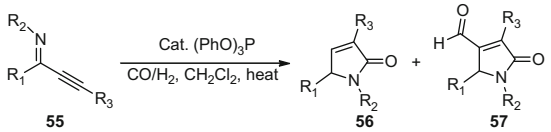
occurred and no spiro product was detected. All these results suggested that spiro compounds would be formed via a furanone intermediate with a structure similar to **53**, but it should have an N–H bond at the amide group.

In 1999, Alper and co-workers used the zwitterionic rhodium complex $(\eta^6\text{-}C_6H_5BPh_3)^-Rh^+(1,5\text{-COD})$ **54** as catalyst and triphenyl phosphite as ligand at moderate temperature and low pressure to study the hydroformylation of both enynes [33] and acetylenic thiophenes [34] (Scheme 18a, b). They used this catalyst system for the cyclohydrocarbonylation of multifunctionalized α-ketoalkynes in 2000. Good to excellent yield and good chemo- and regioselectivities could be obtained (Scheme 18c). The temperatures and pressures required were milder than those previously reported. In addition, good chemo- and regioselectivity were observed for a variety of multifunctionalized alkynones to give 2-, 2(3*H*)- and 2(5*H*)-furanones as the dominant products.

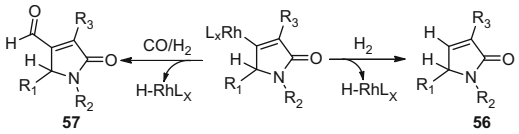
In 2001, Alper and co-workers described a novel chemo- and regioselective route to synthesize 4-carbaldehydepyrrolin-2-ones in the presence of zwitterionic rhodium complex **54** [35]. When the oxygen atom was replaced with nitrogen and under the same reaction conditions, 4-carbaldehydepyrrolin-2-ones **57** could be prepared in good yield (Scheme 19). R_1, R_2, and R_3 were replaced by different substitutes to investigate the electronic and steric effect in detail. Moreover, with some controlled experiments, together with the data obtained, the conversion of α-imino alkynes to 4-carbaldehydepyrrolin-2-ones was shown to be the minor route to **57** (Scheme 20).



Scheme 18 Hydrocarbonylation catalyzed by zwitterionic rhodium complex



Scheme 19 Rhodium-catalyzed cyclohydrocarbonylation/CO insertion of α-imino alkynes

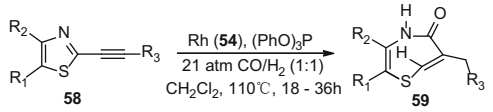


Scheme 20 Possible route to **56** and **57**

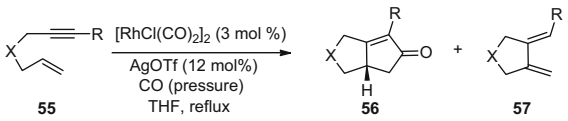
Another example of the application of a zwitterionic rhodium catalyst is the synthesis of 2-(*Z*)-6-(*E*)-4*H*-[1,4]-thiazepin-5-ones by cyclohydrocarbonylative ring expansion of acetylenic thiazoles (Scheme 21) [36], in the presence of 2 mol% Rh complex as the catalyst, 8 mol% ligand, 10 mL of CH_2Cl_2 in a 45-mL autoclave, at 110°C. In addition, a 1:1 ratio of CO/H_2 at a total pressure of 14 and 21 atm resulted in selectivity for the desired product of 89% and 90%, respectively.

In the substrates testing of this transformation, it is found that all the reactions can produce good to excellent isolated yields. Moreover, the reactions of thiazoles with different substitutes in the acetylenic unit seemed to proceed in a significantly temperature-dependent fashion.

Based on previous investigations, rhodium catalysts bearing bidentate phosphine ligands were also found to be effective for cyclization by tuning phosphine ligands [37]. Jeong and co-workers used $RhCl(CO)_2$ to study a rhodium-catalyzed asymmetric intramolecular Pauson–Khand-type reaction with (*S*)-BINAP as the ligand (Scheme 22) [38]. Even though using toluene as the solvent was more efficient, better enantioselectivity can be obtained in a coordinating solvent such as THF. In addition, the CO pressure was quite critical for the enantioselectivity and for the chemical yield. More Pauson–Khand reaction (PKR) products were favored under



Scheme 21 Zwitterionic rhodium-catalyzed cyclohydrocarbonylation of acetylenic thiazoles



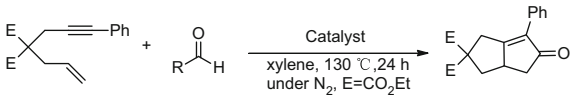
Scheme 22 Rh(I)-catalyzed enantioselective Pauson–Khand-type reaction

higher pressure, but better enantioselectivities might be obtained under lower CO pressure because the unfavorable equilibrium between potential catalysts is suppressed. In most cases, this transformation proceeded nicely to PKR products with good to excellent enantioselectivities in reasonable reaction times (4–6 h) under 1 atm of CO. Moreover, aryl-substituted acetylenes provided better chemical yields of PKR products but lower *ee* than alkyl-substituted acetylenes.

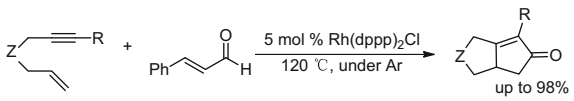
In 2002, Kakiuchi and co-workers used aldehydes as a source of carbon monoxide and investigated the Pauson–Khand-type reaction of enynes [39–42]. The reaction of enyne and benzaldehyde in the presence of catalytic amounts of [RhCl(cod)]$_2$ and dppp in xylene at 130°C for 24 h can afford the carbonylated product in 33% isolated yield although 66% of the starting material remains unreacted (Scheme 23). Additionally, a variety of aldehydes were examined and all the aromatic aldehydes were able to act as a carbon monoxide source. Aldehydes which contain electron-withdrawing substituents can donate CO moieties better [43]. Various enynes have been converted into the corresponding products with good to excellent yields. In addition, when two such groups were positioned on contiguous carbons of a ring system, the cyclocarbonylation proceeded diastereoselectively and tricyclic cyclopentenones were transformed in excellent yields.

Another example of carbonylation of alkene–alkyne using aldehyde as CO source and in the presence of Rh(dppp)$_2$Cl catalyst was reported by Shibata and co-workers in 2002 (Scheme 24) [44]. Among a variety of aldehydes, cinnamaldehyde showed the best efficiency as the CO source. It should be noted that the process was carried out under solvent-free conditions.

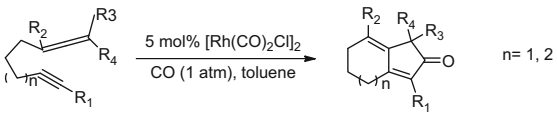
In 2002, Brummond and co-workers found that when alkynyl allenes were treated with [Rh(CO)$_2$Cl]$_2$ and processed via [2+2+1] cycloaddition reaction, a variety of 4-alkylidene cyclopentenones can be produced without α-alkylidenecyclopentenones (Scheme 25). The scope and limitations of the rhodium-catalyzed allenic Pauson–Khand-type reaction were examined in detail. All the result demonstrated that the ring system can be transformed from the distal double bond of the allene with highly regioselectivity. Another rhodium-catalyzed Pauson–Khand-type reaction was reported by Mukai and co-workers [45, 46]. 1-Phenylsulfonylallenes with a hexynyl appendage were treated with catalytic



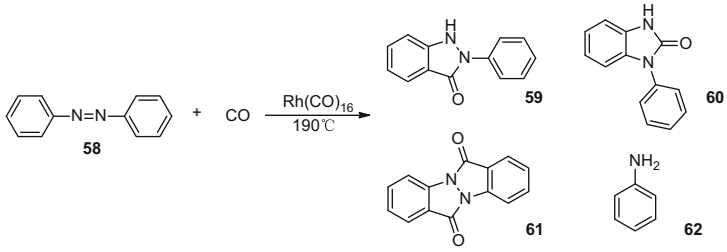
Scheme 23 Catalytic Pauson–Khand-type reaction of enyne with aldehyde as CO source



Scheme 24 Rhodium-catalyzed carbonylation of alkene-alkyne using aldehyde as CO source



Scheme 25 Rhodium-catalyzed carbonylation of alkynyl allenes



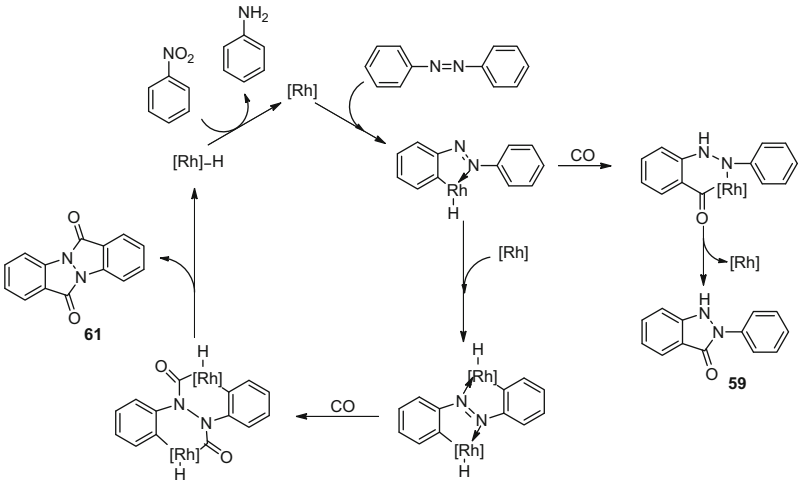
Scheme 26 Rhodium-catalyzed cyclocarbonylation of azobenzene

amounts of rhodium catalyst ($[RhCl(CO)_2]_2$ or [RhCl(CO)dppp]) in a carbon monoxide atmosphere and produced the corresponding bicyclo[5.3.0]dec1,7-dien-9-one via regioselective [2+2+1]-cycloaddition. Different substrates were also examined and produced acceptable yields.

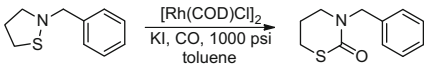
Later, Saito's group published relevant works on rhodium-catalyzed Pauson–Khand-type reactions for the synthesis of pyrrolo-indolones, pyrrolo-pyrrolinones [47], and pyrrolo[2,3-*b*]quinones [48]. As there are many research items and reviews published on the Pauson–Khand-type reaction, we do not discuss it extensively here [49–53].

Carbonylation of azobenzene derivatives catalyzed by rhodium carbonyls in the presence of nitrobenzenes was reported by Takahashi and co-workers [54]. Indazolo[2,1-*a*]indazole-6,12-dione was transformed from this novel cyclocarbonylation with C–H activation and CO insertion at each benzene nucleus of azobenzene (Scheme 26).

In this work, different carbonyl complexes and solvents were examined in detail, and it was found that the $[Rh(CO)_2Cl]_2$/nitrobenzene system showed the best



Scheme 27 Proposed mechanism for rhodium-catalyzed cyclocarbonylation of azobenzene

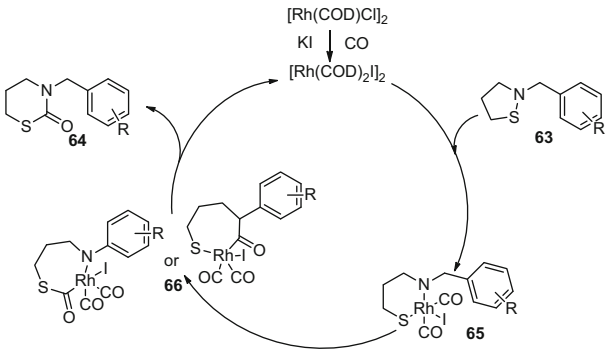


Scheme 28 Rhodium-catalyzed carbonylation of *N*-benzylisothiazolidine

selectivity for **61** synthesis. In addition, an Rh-H species is postulated as an active intermediate in this reaction, which it was also thought may cause the reductive cleavage of N=N bond to give aniline. Hence, the addition of nitrobenzene can depress the consumption of the azobenzene. After that, several azobenzene derivatives were used in this new type of cyclocarbonylation. Based on the result obtained and the previous literature, a tentative cyclocarbonylation mechanism was proposed as shown in Scheme 27.

In 2004, Dong and Alper used the carbonylation of *N*-alkylisothiazolidines in the presence of rhodium complex to produce the tetrahydro-2*H*-1,3-thiazin-2-ones [55], based on previous work on the rhodium-catalyzed carbonylation of isoxazolidines with regioselective insertion of CO into the N–O bond affording tetrahydro-1,3-oxazin-2-ones [56]. When *N*-benzylisothiazolidine is reacted with 5 mol% of (1,5-cyclooctadiene)rhodium(I) dimer in benzene in the presence of 1,000 psi of carbon monoxide at 130°C for 24 h, a 58% yield of 2*H*-1,3-thiazin-2-one can be achieved, and the addition of 5 mol% of potassium iodide can increase the yield to 70% (Scheme 28).

This reaction tolerates various substrates and can afford the corresponding products in 35–85% yields. Considering the isothiazolidines which contain one more CH_2 unit between the N atom and the phenyl ring, *N*-(2-phenylethyl) isothiazolidine was used and afforded 85% yield of the corresponding product. The mechanism of this carbonylation of *N*-alkylisothiazolidines as depicted consisted of three steps – oxidative addition, CO insertion, and reductive elimination (Scheme 29).



Scheme 29 Proposed mechanism of rhodium-catalyzed carbonylation of *N*-alkylisothiazolidines

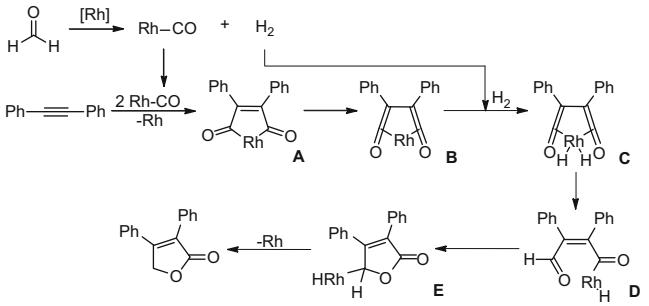
Later, in 2005, Kakiuchi and co-workers published a communication on rhodium-catalyzed cyclocarbonylation of alkynes to α,β-butenolides with formaldehyde [57–60]. In the presence of 5 mol% of $[RhCl(cod)]_2$ and 10 mol% of dppp in xylene, a variety of substrates were transformed with up to 95% yields. Generally, there are always two isomers produced because of the different locations of the of carbonyls. The mechanism of this reaction has been proposed (Scheme 30). In addition, the possibility of a lactonization process via **D** was demonstrated with *o*-phthalaldehyde, which was treated under the same reaction conditions, and 91% of benzolactone was transformed.

In 2006, an efficient and straightforward method to synthesize 5-aryl-2(5*H*)-furanones under the same conditions as for rhodium-catalyzed carbonylation of alkynes with aryl boronic acids was presented by Artok and co-workers (Scheme 31) [61].

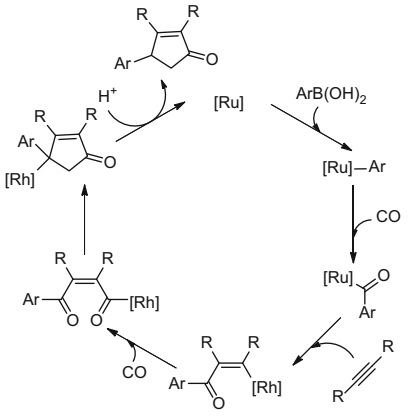
In the presence of 1 mol% of $[RhCl(COD)]_2$ in 1,4-dioxane under 20 atm of CO at 80°C for 16 h, 3,4,5-triphenylfuran-2(5*H*)-one can be obtained in 78% yield. The reaction proceeds efficiently when the aryl boronic acid contains an electron-donating functional group. A higher yield can also be obtained by increasing the amount of Rh catalyst to 3 mol%. Although moderate to excellent yields can be obtained under these conditions, no reaction occurs with terminal alkyne.

Chatani and co-workers used $[RhCl(cod)]_2$ as the catalyst in the reaction of alkynes with 2-bromophenylboronic which gave indenones in up to 97% yield (Scheme 32) [62]. In this reaction, it is found that some Rh complexes such as $[RhCl(CO)_2]_2$ and Rh(0) complexes such as $Rh_4(CO)_{12}$ show similar activities and give the corresponding product in good yield whereas rhodium phosphine complexes such as $RhCl(PPh)_3$ and $RhH(CO)(PPh_3)_3$ produce no activity. Moreover, alkenes were also examined with 2-bromophenylboronic. Unfortunately the styrene and cyclopentene showed no carbonylated products whereas norbornene gave the corresponding ketone in 80% yield.

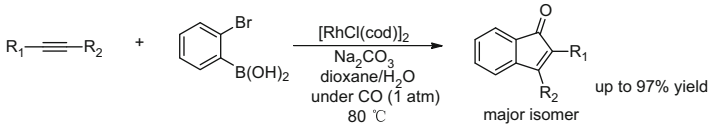
Regarding the reaction mechanism, a vinylrhodium intermediate could be generated by the addition of arylrhodium species to 2-bromophenyl(trimethylsilyl) acetylene followed by olefin isomerization to form the indenone as the sole product



Scheme 30 Mechanism for rhodium-catalyzed cyclocarbonylation of alkynes with formaldehyde



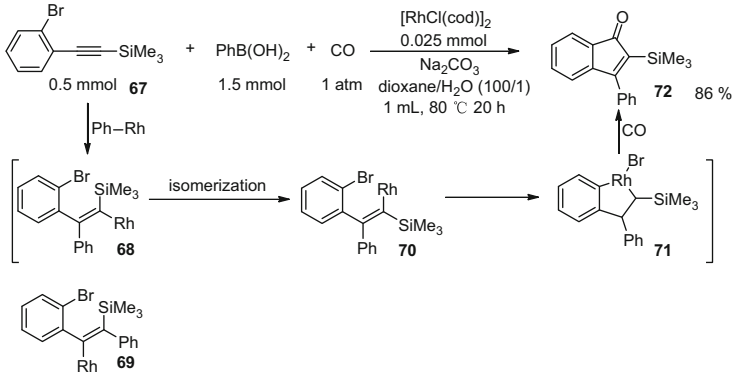
Scheme 31 Rhodium-catalyzed carbonylation of boronic acid to alkyne



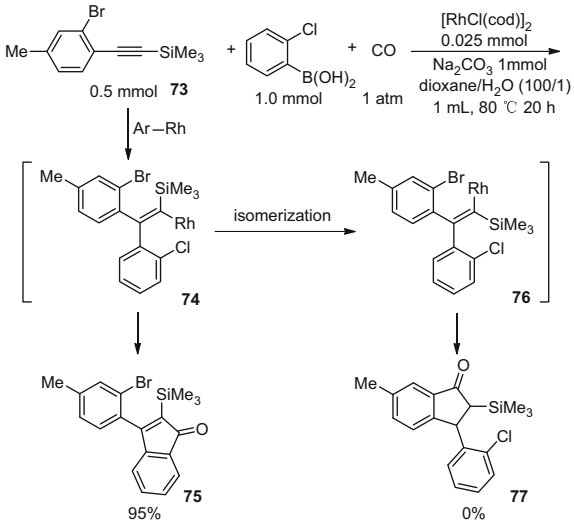
Scheme 32 Rhodium-catalyzed carbonylation of alkynes with 2-bromophenylboronoic acid

(Scheme 33). There were no regioisomeric indenones formed because the isomer **69** cannot be converted to indenones even if they were formed. Moreover, when trimethylsilyl was replaced with a *tert*-butyl, ester, and phenyl group, the corresponding product was not detected. All these indicated that a silyl group at the terminal acetylenic carbon is essential for the isomerization.

During this work, the *E*/*Z* isomerization of vinylrhodium complex was considered to act as a key step in the synthesis of indenone. Hence, to examine the isomerization, 2-bromo-4-methylphenyl(trimethylsilyl)acethylane was reacted with 2-chlorophenylbononic acid (Scheme 34). Theoretically, it forms two isomers with the oxidative addition of a C–Cl bond and a C–Br bond leading to two different



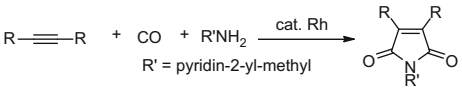
Scheme 33 Reaction of 2-bromophenyl(trimethylsilyl)acetylene with phenylboronic acid/CO



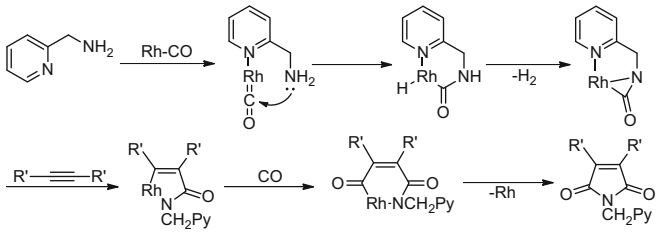
Scheme 34 Carbonylation of 2-bromo-4-methylphenyl(trimethylsilyl)acethylane with 2-chlorophenylbononic acid

products. Unfortunately, **77** was not detected although **75** was formed in 95% yield. All of these indicate that the isomerization of a vinylrhodium complex is not facile. In addition, the reaction of 1-(2-bromophenyl)-hept-2-yn-1-one with $PhB(OH)_2$ under similar conditions gave the carbonylative cyclization product indan-1,3-dione derivative in good yield. Finally, the rhodium-catalyzed regioselective addition of an arylrhodium(I) species to alkynes, followed by the oxidative addition of C–Br bonds in the adjacent phenyl ring afforded vinylrhodium(I) as the key step.

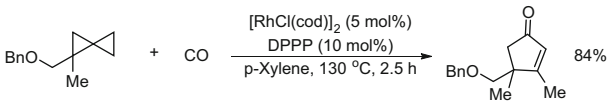
In the same year, Chatani and co-workers presented another report that on using $Rh_4(CO)_{12}/P(OEt)_3$ as the catalytic system to catalyze the carbonylation of alkynes with pyridin-2-ylmethylamine (Scheme 35) [63]. It is different from former



Scheme 35 Rh-catalyze carbonylation of alkynes with pyridin-2-yl-methylamine



Scheme 36 Proposed reaction mechanism of rhodium-catalyzed carbonylation of alkynes with pyridin-2-yl-methylamine



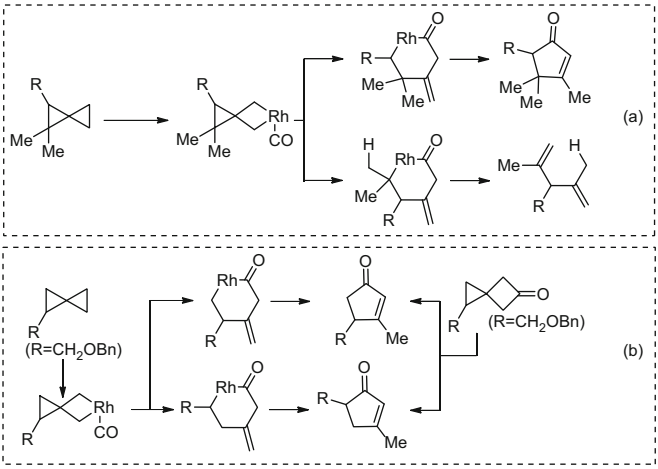
Scheme 37 Rhodium-catalyzed carbonylation of spiropentanes

literature on the carbonylation of alkynes with amines affording α,β-unsaturated amides [15, 64].

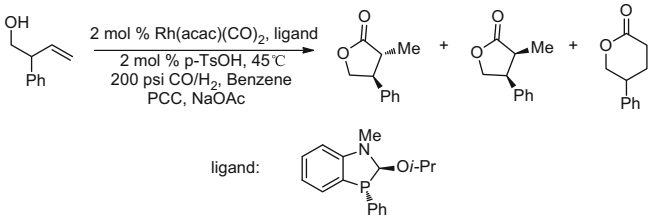
First, when 4-octyne was treated with pyridin-2-ylmethylamine under CO (3 atm) in toluene (1 mL) at 100°C in the presence of $Rh_4(CO)_{12}$ for 20 h, it afforded the corresponding product 3,4-dipropyl-1-(pyridin-2-ylmethyl)pyrrole-2,5-dione in 39% isolated yield. With increased temperature the yields of the corresponding products also increased. However, because the $Rh_4(CO)_{12}$ was decomposed there was no desired product when the reaction was carried out at 130°C. When the reaction was carried out at 120°C or lower, the color of the reaction mixture was red, whereas it would be black when the temperature was 130°C or higher. The yield can be significantly increased by the addition of P $(OEt)_3$. Both aliphatic and aromatic internal alkynes gave the corresponding products in good yield. Control experiments were performed and showed that the nitrogen of the pyridine is essential because the coordination of the pyridine nitrogen to the rhodium center facilitated the intramolecular attack of the amine on the coordinated carbon monoxide to give a rhodium hydride species (Scheme 36).

Later, Murakami and co-workers used 5 mol% of $[RhCl(cod)]_2$ and described a catalytic carbonylation reaction of spiropentanes to synthesize a series of 3-methylcyclopent-2-enones (Scheme 37) [65].

Various disubstituted spiropentanes were used under catalytic reaction conditions and afforded good yields. Trisubstituted spiropentanes were also examined, and the corresponding cyclopentenones were obtained with diene (Scheme 38a). However, when monosubstituted spiropentane was subjected to the reaction



Scheme 38 Rhodium-catalyzed carbonylation of tri- and 1; mono-substituted spiropentane

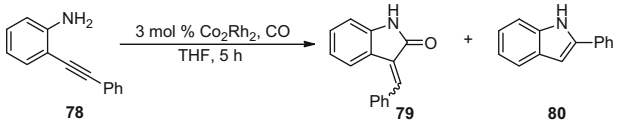


Scheme 39 Rhodium-catalyzed hydroformylation of terminal olefin

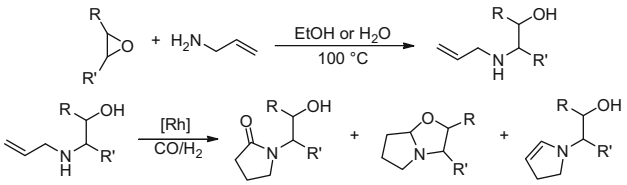
conditions, an isomeric mixture of cyclopentenones was transformed (Scheme 38b). This all indicates that the carbonylation of spiropentanes forming cyclopentenones also involves two successive carbon–carbon bond cleavage processes which were discussed in the former research [66].

In 2007, based on previous studies on hydroformylation [67–74], it seemed that the application of supramolecular catalysts could solve the problems with low regio-, diastereo-, and enantioselectivity [75–77]. Tan and co-workers synthesized a series of scaffolding ligands and tested them in the hydroformylation of terminal olefin (Scheme 39) [78]. With a range of substrates, the direct hydroformylation of them with an electron-rich and electron-deficient aromatic ring at the allylic position afforded good regio- and diastereoselectivities.

Cobalt/rhodium nanoparticles were also used as catalyst in the carbonylative cycloaddition of 2-alkylanilines to prepare oxindoles [79]. With the development of transition metal nanoparticles, they have been widely used as catalysts for organic synthesis because of their high catalytic activity and recyclability [80–85]. Chung and co-workers found that cobalt/rhodium nanoparticles derived from $Co_2Rh_2(CO)_{12}$ were useful as a catalyst in carbonylation reactions [86]. Co_2Rh_2-catalyzed carbonylative cyclization of 2-akynylanilines can form oxindoles



Scheme 40 Co_2Rh_2 catalyzed synthesis of oxindoles from 2-alkynylanilines

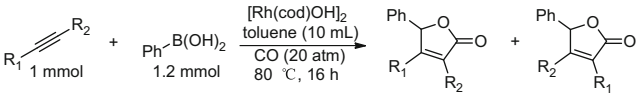


Scheme 41 Aminolysis of epoxides followed by carbonylation

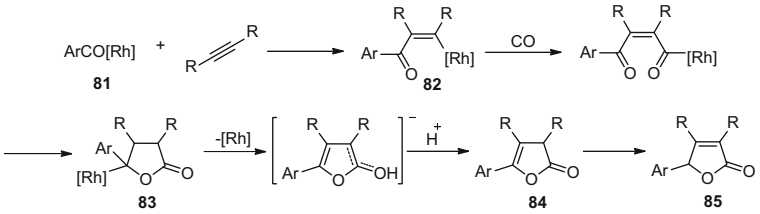
successfully and without any need for additives or promoters. The catalyst can be recycled several times without any significant loss of activity (Scheme 40). Various 2-alkynylanilines were screened under optimized conditions and gave the desired oxindoles in satisfactory yields. However, there was no desired product detected in the reaction of terminal alkynes.

In 2008, da Rosa and co-workers synthesized *N*-(2-hydroxy-alkyl)-γ-lactams and bicyclic oxazolidines by carbonylation of allylaminoalcohols in the presence of rhodium catalyst (Scheme 41) [87]. In this work, allylaminoalcohols from the aminolysis of cyclohexene oxide, styrene oxide, (*R*)-(+)-limonene oxide, and ethyl-3-phenyl-glicidate were used as the substrates. $RhClCO(PPh_3)_2$ was used as the catalyst, and moderate to excellent yields were obtained. The selectivity of the isomers can be optimized by controlling the CO/H_2 ratio. Excess CO provided a lactam selectivity of up to 90% although a higher quantity of H_2 gas can increase the selectivity of oxazolidines resulting from hydroformylation/cyclization. The kinetic studies indicated that oxazolidines and γ-lactams were formed through parallel routes. Moreover, two mechanisms for the two products were ascertained in detail, and the X-ray crystal structure of an iridium-carbamoyl complex prepared under the same reaction conditions was obtained which directly supported the assumption that the key step of the mechanism was the formation of a metal-carbonyl intermediate.

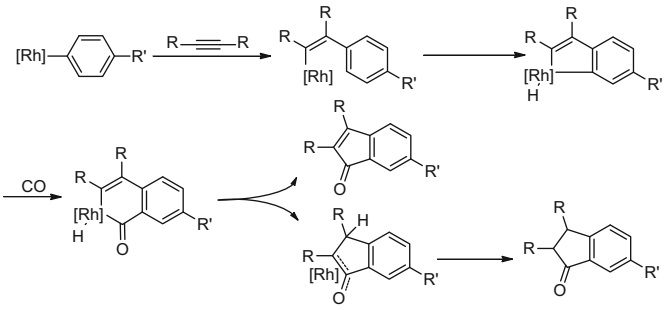
Aryl boronic reagents can be carbonylated with rhodium catalysts to give acyl rhodium species that are amenable to the addition of unsaturated C–C bonds [88–94]. In 2009 Artok and co-workers investigated a carbonylative reaction of various alkynes with aryl boronic acids in the presence of Rh complex and afforded 5-aryl-2(5*H*)-furanones (Scheme 42) [95]. In this catalytic system, the selectivities of the products were tunable by varying the reaction conditions and gave the desired 5-aryl-2(5*H*)-furanones in up to 90% yield. From the results obtained it can be seen that the relative formation of isomeric products was influenced by electronic and steric properties effects on the alkyne substrate. The acyl rhodium species **81** formed was considered subsequently to undergo 1,2-addition to the carbon–carbon



Scheme 42 Rhodium-catalyzed carbonylation of phenylboronic acid with alkynes



Scheme 43 Proposal mechanism of the formation of 2(5*H*)-furanone

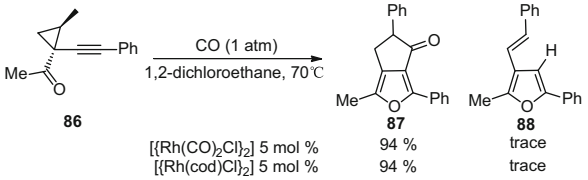


Scheme 44 Mechanism of indenone and indanone formation

triple bond, followed by the insertion of CO into the resulting β-aroyl alkenylrhodium(I) complex **82** and then by ring closure to form a *σ*-furanoyl complex **83**. Displacement of Rh from the cyclic complex and subsequent protonation leads to a 5-aryl-2(3*H*)-furanone molecule **84** which should undergo isomerization to a more stable structure, 5-aryl-2(5*H*)-furanone molecule **85** (Scheme 43).

Artok and co-workers also used the reaction to synthesize indanones by the reaction of alkynes and organoboranes under a CO atmosphere in the presence of 1.5 mol% of $Rh(cod)_2BF_4$ (Scheme 44).

A rhodium-catalyzed regio- and stereospecific carbonylation of 1-(1-alkynyl) cyclopropyl ketones to highly substituted 5,6-dihydrocyclopental[c]furan-4-ones was presented by Zhang and co-workers in 2009 [96]. Highly substituted furans as the key structure in bioactive natural compounds and pharmaceuticals, methodologies based on allenyl ketones [97–117], 3-alkyl-1-ones [111, 112, 118, 119], (*Z*)-2-en-4-yn-1-ols [120] and 2-(1-alkynyl)-2-alkens-1-ones [121–126], alkylidenecyclopropyl ketones [127–129], cyclopropenyl ketones [130, 131], etc., have been developed. The versatile compound 1-(1-alkynyl)cyclopropyl ketone has been



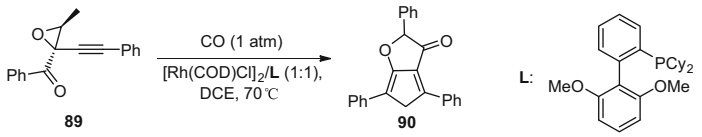
Scheme 45 Carbonylation of 1-(1-alkynyl)cyclopropyl ketones in the presence of Rh

successfully developed by Schmalz [132, 133] and Zhang [134, 135] as substrate for the production of highly substituted furans and other cyclic compounds using gold(I) complexes as catalyst. Based on previous research, it was thought that 1-(1-alkynyl)cyclopropyl ketones might undergo transformations initiated by rhodium(I) catalyzed activation of the carbon–carbon σ-bond of the cyclopropane ring [65, 136–142]. Hence, in the presence of 1 atm of CO and 5 mol% of [{Rh$(CO)_2Cl\}_2$] or [{Rh(cod)$Cl\}_2$], 1-methyl-3,5-diphenyl-5,6-dihydrocyclpenta[c]furan-4-one **87** can be detected in excellent yield in 1,2-dichloroethane at 70°C as the desired product by carbonylation of 1-(1-alkynyl)cyclopropyl ketones **86**. At the same time, (*E*)-2-methyl-5-phenyl-3-styrylfuran **88** as the sole and major by-product was formed (Scheme 45).

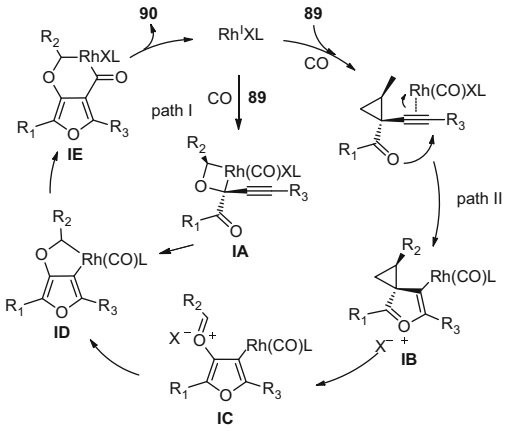
With 1-(1-alkynyl)oxiranyl ketone **89** as the substrate, formal [4+1] cycloaddition can occur in the presence of rhodium catalyst and finish with highly substituted furo[3,4-*b*]furan-3-(2*H*)-ones **90** as the products in good to excellent yields (Scheme 46) [143]. Two plausible reaction pathways were suggested by the authors (Scheme 47). In path **I**, it was considered that there was an oxidative addition of the C–C bond of epoxy motif of **89** and generated rhodaoctane **IA**, which would undergo rapid cycloisomerization to form intermediate **ID**. Then the insertion of CO and **90** was produced by reductive elimination of **IE**. In path **II**, the rhodium (I) coordination of the triple bond of **89** enhanced the electrophilicity of alkynes. The nucleophilic attack of the carbonyl oxygen on the rhodium(I)-activated alkyne would subsequently form the oxonium-containing vinyl-rhodium intermediate **IB**. Then the cleavage of C–C bond of **IB** would lead to intermediate **ID** and undergo the same process to afford **90**.

In 2011, a simple and highly efficient rhodium-catalyzed tandem heterocyclization and carbonylative [(3+2)+1] cyclization reaction that can afford furan scaffold **92** to be easily converted to highly substituted bicyclic phenols **93** was presented by Zhao and Zhang (Scheme 48) [144]. Based on previous research, the metallacycle intermediate **91** has been proposed which can afford fused tricycloheptadienes [145]. It was also considered that it can be trapped by CO, leading to a tricyclic scaffold. Different solvents, rhodium-complexes, and the amount of CO were examined. DCM was found to be the best solvent and this reaction can produce a better yield with a lower pressure of CO in the presence of 5 mol% $[RhCl(cod)]_2$.

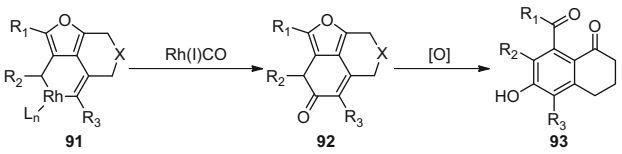
Rh(III)-complex-catalyzed formation of phthalimides by oxidative carbonylation of aromatic amides via C–H/N–H activation was developed by Rovis and co-workers in 2001 [146]. This was based on previous reports of coupling of



Scheme 46 Rhodium-catalyzed cycloaddition of 1-(1-alkynl)oxiranyl ketones

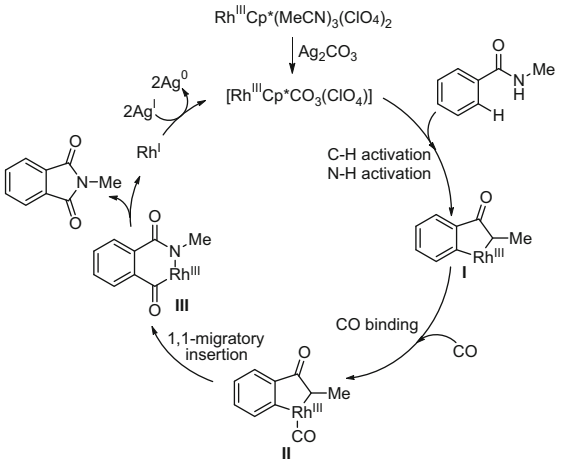


Scheme 47 Plausible mechanism of rhodium-catalyzed cycloaddition of 1-(1-alkynl)oxiranyl ketones



Scheme 48 Rhodium-catalyzed carbonylative [(3+2)+1] cyclization

benzamide and α,β-unsaturated amides with alkynes to produce isoquinolones and pyridones utilizing Rh(III)-catalyzed C–H activation [147–155]. It was considered that it could provide unique phthalimides via an analogous approach when the alkyne was replaced with CO. With a screening of different catalysts, solvents, and oxidants, the best results were obtained in the presence of 5 mol% RhCp* $(MeCN)_3(ClO_4)_2$, Ag_2CO_3 2 equiv., KH_2PO_4 2 equiv., and CO 1 atm. A number of different amides were tested under optimized conditions and indicated that the reactions of amides bearing alkyl groups at the nitrogen atom proceeded smoothly to deliver phthalimides in excellent yields of up to 95%. On the basis of the results obtained, a plausible mechanism for this RhCp*$(MeCN)_3(ClO_4)_2$-catalyzed oxidative carbonylation was proposed in detail (Scheme 49). It should be noted that the generated rhodium(I) species after reductive elimination is reoxidized by Ag_2CO_3 to close the catalytic cycle.



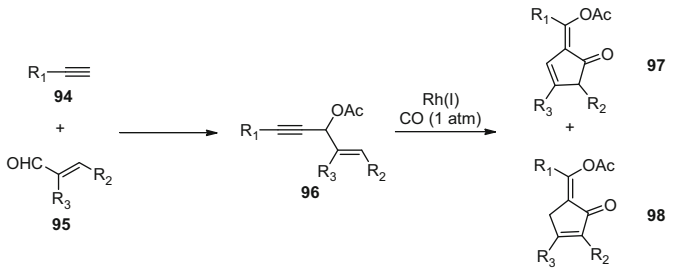
Scheme 49 Mechanism of rhodium-catalyzed oxidative carbonylation of benzamides with CO

In 2012, Tang and co-workers reported an efficient procedure for the synthesis of highly functionalized cyclopentenones **97** and **98** from 3-acyloxy-1,4-enyne **96** via a Rh(I)-catalyzed carbonylation reaction (Scheme 50) [156].

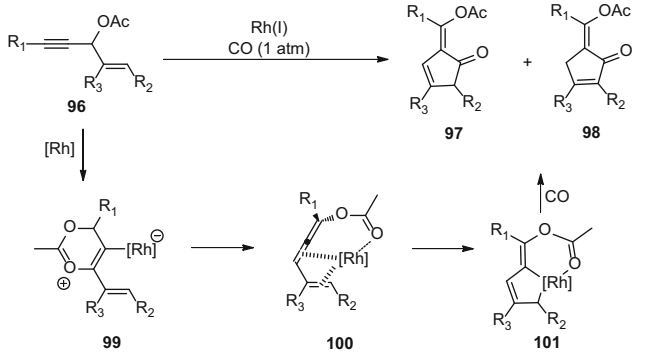
It has been demonstrated that 3-acyloxy-1,4-enynes with a terminal alkyne can serve as a five-carbon building block for [5+1] [157] and [5+2] [158] cycloadditions with CO and alkynes, respectively. Moreover, both of these cycloadditions involve a rhodium-catalyzed 1,2-acyloxy migration of propargyl esters which was reported in 1984 [159, 160]. With some elegant work in this field [161–163], cyclopentenones can also be produced with the use of rhodium catalyst $[Rh(COD)Cl]_2$ (Scheme 51). Here, the acyloxy group in the propargyl ester starting material not only eliminates the need for the preformation of allenes but also provides a useful handle for further selective functionalization of the cyclopentenone products.

In the same year, Tang and co-workers developed two different types of tandem reactions for the synthesis of highly functionalized cyclohexenones from cyclopropyl substituted propargyl esters (Scheme 52) [164]. First, different catalysts such as Au, Rh, Ag, and Pd were tested, but no reaction occurred or only the formation of enone. After this, it was found that alkylidene cyclohexenone was formed as a mixture of *E*/*Z* isomers (ratio = 1:1) in about 30% yield when in the presence of 20 mol% $[Rh(CO)_2Cl]_2$ in toluene (Scheme 53). However, the addition of different ligands (e.g., PPh_3, $P(OMe)_3$, $P(OPh)_3$, and pyridine) either decreased the conversion of the reaction or shut down the reaction completely. It should be noted that no reaction occurred for the secondary propargyl acetate although it can work well when replaced by pivalate.

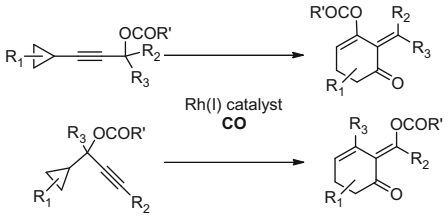
In 2015, Yu and co-workers first reported a rhodium-catalyzed benzo/[7+1] cycloaddition of cyclopropyl-benzocyclobutenes (CP-BCBs) and CO to benzocyclooctenones (Scheme 54) [165]. An appropriate R group in CP-BCBs can facilitate the ring opening of benzocyclobutene; more specifically, an electron-donating group could promote BCB's ring opening [166]. It should also



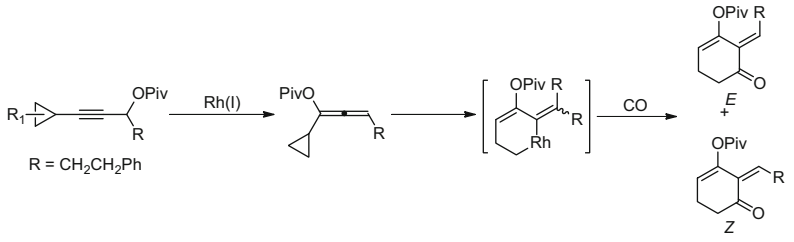
Scheme 50 Carbonylation of 3-acyloxy-1,4-enyne for the synthesis of cyclopentenones



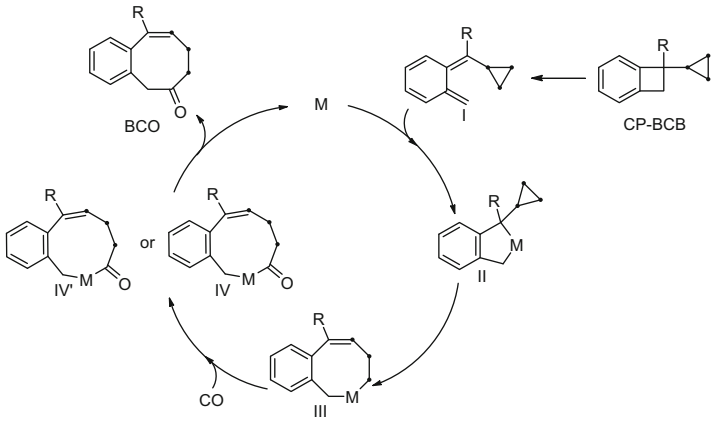
Scheme 51 Carbonylation of 3-acyloxy-1,4-enyne for the synthesis of cyclopentenones



Scheme 52 Rhodium-catalyzed carbonylation of cyclopropyl substituted propargyl esters



Scheme 53 Proposed mechanism for the formation of alkylidene cyclohexenone from cyclopropyl substituted propargyl ester



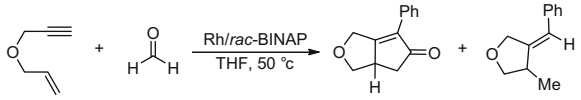
Scheme 54 Proposed benzo/[7+1] reaction pathway of CP-BCB with CO

be pointed out that the TBS protecting group is necessary for the success of the present reaction.

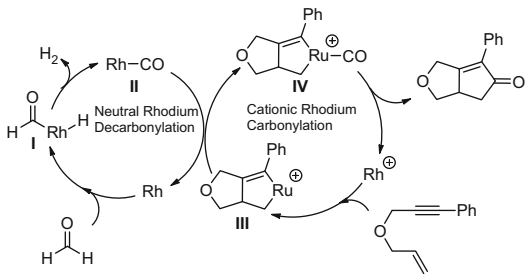
Under optimal reaction conditions, the reaction showed good tolerance with functional groups and substitution patterns on the phenyl ring. Moreover, substitutes on the cyclopropane ring can be tolerated and gave the corresponding products in moderate yields. The substrate with a methyl group at the nonfunctional position on the cyclopropane ring can also be tolerated with a little selectivity favoring the cleavage of the less-hindered C–C bond of the cyclopropane ring. However, when the methyl group was substituted on the four-membered ring there was no corresponding product, probably because of unfavorable steric hindrance.

Recently, Morimoto and co-workers reported an asymmetric Pauson–Khand-type reaction of 1,6-enynes that formaldehyde used as a carbonyl source in the presence of rhodium catalysts [167]. Initially, 1,6-enynes were treated with formaldehyde in the presence of $[RhCl(cod)]_2$ and *rac*-BINAP at 50°C; 18% conversion and 4% yield of the corresponding cyclocarbonylation product were the result (Scheme 55). After optimization, it was found that the cyclocarbonylation can occur even at 30°C. Other aldehydes were also examined although none of them can work as a carbonyl source. Then the role of each neutral and cationic Rh catalyst was examined. The result of ^{31}P NMR indicated that $[RhCl((R)\text{-binap})]_2$ is an effective catalyst for the carbonylation reaction at room temperature. Under the best reaction conditions, different substituted 1,6-enynes with oxygen tethers were converted into the corresponding bicyclic cyclopentenones in moderate yields with high enantioselectivities. However, when there was a sterically bulky substituent at the terminal alkyne, those containing a carbon(malonate)-tether were less reactive under the standard reaction condition. A proposed reaction pathway was that formaldehyde reacts with neutral rhodium to generate the carbonyl rhodium species **II** via the formation of a formyl rhodium complex **I**. Then the carbonyl moiety is directly transferred to the cationic rhodacycle **III**, followed by carbonylation to give the final product (Scheme 56).

Scheme 55 Rhodium-catalyzed cyclocarbonylation of 1,6-enyne



Scheme 56 Proposed mechanism of rhodium-catalyzed cyclocarbonylation of 1,6-enyne



In summary, the main contributions on rhodium-catalyzed carbonylative synthesis of heterocycles have been summarized and discussed. The related achievements have also been included, even though no heteroatom was involved. Most of the work is still limited with alkenes and alkynes, and the use of organohalides as substrates is still rare.

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