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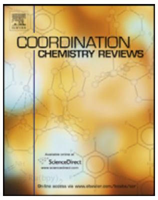

Review

Catalytic Pauson–Khand-type reactions and related carbonylative cycloaddition reactions

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Contents

Abbreviations: BSA, N,O-bis(trimethylsilyl)acetamide; CNC, cobalt nanoparticles immobilized on charcoal; PCNS, palladium and cobalt nanoparticles immobilized on silica; PKR, Pauson–Khand reaction; RuCNC, ruthenium and cobalt nanoparticles immobilized on charcoal.

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ABSTRACT

The development of a heterogeneous catalytic Pauson–Khand reaction and cobalt carbonyl-catalyzed tandem carbonylative cycloaddition reaction of unsaturated hydrocarbons studied in our laboratory are reviewed.

1. Introduction

The development of new processes that are simultaneously economically sustainable and environmentally responsible is a challenge for the twenty-first century [1]. In this respect, catalysis plays a central role in the development of environmentally safe and clean chemical processes. Thus, the design and development of new catalysts providing cleaner alternative synthetic pathways has attracted a lot of attention. The achievement of developing transition metal catalysts for the transformation of acyclic molecules into bicyclic carbocyclic species has been especially remarkable [2].

Cycloaddition reactions efficiently generate cyclic compounds from simple starting materials and carbonylation reactions introduce a ketone group. Both reactions are very important in organic chemistry. Each reaction can be used by itself or in combination. A representative combination reaction is the Pauson–Khand reaction (PKR hereafter) [3]. When the PKR was first discovered [4], it was considered to be a stoichiometric reaction and the alkene substrate was limited to strained olefins such as norbornene, norbonadiene, cyclopropenes, and bicyclo[3.2.0]hep-6-enes. However, since the first discovery of the catalytic version [5], many new catalytic versions [6] including many other types of metal catalysts based on Fe [7], Ni [8], Ti [9], Zr [10], Ru [11], Rh [12], and Ir [13] have been discovered and reaction pathways with much milder conditions have been developed [14]. Moreover, the scope of the olefin substrates have been widened by finding alkene equivalents such as dimethyl(pyridyl)(vinyl)silane [15], *o*-(dimethylamino)phenyl vinyl sulfoxide [16], and 2,3-disubstituted 1,3-butadiene [17]. It has been widely accepted [18] that electron-deficient alkenes, such as α,β-unsaturated aldehydes, ketones, esters and nitriles, are not suitable substrates for PKRs. However, under certain circumstances a relatively broad variety of electron-deficient alkenes can also be appropriate substrates in PKRs [19].

At present the PKR is recognized as one of the most important arsenal in synthesis of 5-membered compounds including cyclopentenones [6b,6c,20]. Cyclopentadienones can be easily generated by a reaction between two alkynes and carbon monoxide. Compared to the huge developments in the chemistry of cyclopentenones [6d,21], the chemistry of cyclopentadieneones remains relatively undeveloped, partly due to the inherent instability of free cyclopentadienones and their tendency to undergo dimerization. However, if cyclopentadieneones were generated *in situ* in the presence of another chemical species (and reacted subsequently with another chemical species) [22], then we could develop a whole chemistry of the unstable cyclopentadienes. This could be another example of a tandem reaction that incorporates multiple cycloaddition and carbonylation reactions and serves as the foundation for novel approaches to the preparation of polycyclic substances. The tandem reactions will provide the formation of multiple covalent bonds in a single step and a process with time- and cost-saving, atom economy, and environmental acceptability.

In this review, we will discuss the PKR and related reactions and show how they have been used in the synthesis of polycyclic compounds in a one-pot reaction. Reactions covered in our previous review [23] will not be commented on again herein.

2. Development of heterogeneous catalysts for Pauson–Khand reaction

Tremendous development has occurred in the field of homogeneous catalysis. Homogeneous catalysis may provide a high reaction rate and high turnover numbers (TON) and often affords high selectivity and yields. The properties of the catalysts can be tuned by ligands. Proper ligand design leads catalysts to exhibit higher TON and reaction rates, and to have improved lifetimes so that they are stable enough to run the reactions without the exclusion of water or air and to do so at lower temperatures. The structure of the catalytic species is often known, and structure–activity relationships could allow the development of new catalytic systems. On the other hand, homogeneous catalysis has a number of drawbacks, including lack of recovery/reuse of the catalyst. This leads to a loss of expensive metal and ligands and to impurities in the products and the need to remove residual metals [24]. These problems have to be overcome for the application of homogeneous catalytic reactions in industry and are still a challenge [25].

The heterogenization of homogeneous catalysts results in the advantages of both the homogeneous and heterogeneous catalytic

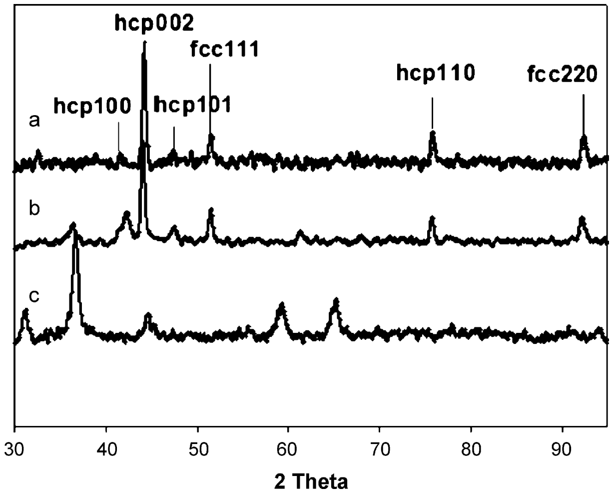


Fig. 1. XRD-graphic of cobalt on mesoporous silica: line (a) Co on SBA-15; line (b) Co on MCM-41; line (c) cobalt oxide.

modes [26]. Many ingenious methods have been used to immobilize such catalysts on the surface or within the interior structure of solid supports. In heterogenizing homogeneous catalyst systems, supports such as polymers [27], silica [28], and zeolites [29] have received the most attention. Various mesoporous silicas [30] with pore size ranging from 2 to 10 nm have been extensively applied as supports for many catalytically active metals and homogeneous catalysts, presumably due to their high surface areas.

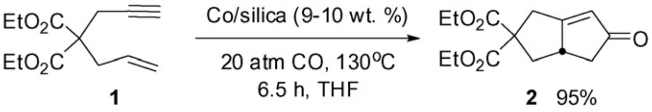
While a wide range of homogeneous catalysts for the Pauson–Khand reaction exist [9a,11,12a,31]. The first heterogeneous PK catalyst was developed by us in 2000 [32]. Since then, some useful variants have been reported [11], but it is still waiting further advances.

2.1. *Cobalt on mesoporous silica: [32,33] the first heterogeneous catalytic PKR*

Studies concerned with homogeneous catalysts for the PKR led to the insight that, if a cobalt carbonyl species could be generated during a reaction, it could act as a catalyst. This led to the study of some heterogeneous catalytic systems for the PKR. It was envisioned that mesoporous silicas deposited with cobalt metal would act as catalysts under a carbon monoxide atmosphere. Due to the high surface area, high catalytic activity could be expected. Based on this expectation, mesoporous silicas deposited by bulk cobalt were prepared and used as catalysts in the PKR.

Cobalt metal has been deposited with bulk cobalt on mesoporous silica supports, SBA-15 and MCM-41, by decomposing $Co_2(CO)_8$ in a refluxing toluene solution or using the conventional impregnation method using cobalt nitrate as a cobalt source. Cobalt loading was adjusted to 9–10 wt%. X-ray powder diffraction (XRD) patterns (Fig. 1) of the supported catalysts revealed face centered cubic (fcc) and hexagonal close packed (hcp) metallic cobalt peaks. No cobalt oxide peak was observed in the XRD.

The following intramolecular PKR of enyne was investigated as a test reaction (Scheme 1).



Scheme 1.

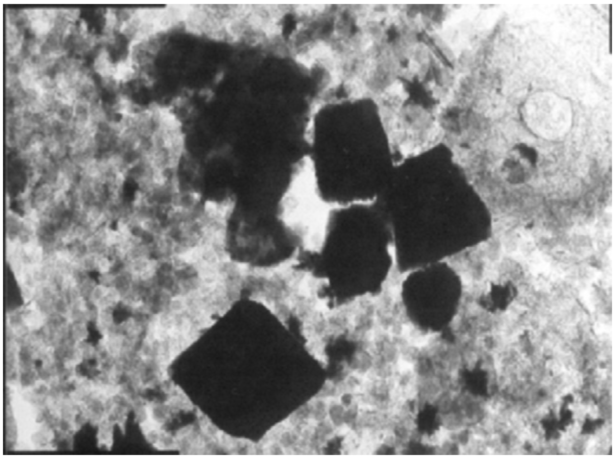


Fig. 2. TEM image of Co on charcoal. Reproduced from Ref. [34] with permission.

When either the reaction temperature or CO pressure was lowered, the activity of the catalyst decreased significantly. Thus, to keep a high level of catalytic activity, the reaction temperature and CO pressure have to be at least 130 °C and 20 atm, respectively. The catalyst system is metallic cobalt supported on mesoporous silica. As expected, the catalyst is air-stable and reusable, and exhibits an excellent catalytic performance for many intramolecular PKRs. However, there was no promotion in the reaction conditions, i.e. high temperatures and high pressures of CO.

2.2. *Cobalt on charcoal [34]*

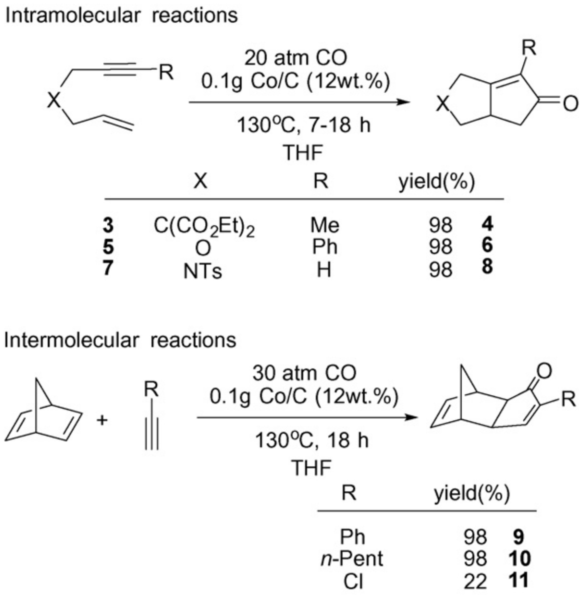
Cobalt on a mesoporous material system [32] is a fairly effective catalyst for the intramolecular PKR, but displays low activity in the intermolecular PKR. Moreover, mesoporous silica is not freely available. In view of the drawbacks of cobalt on mesoporous materials, much work has focused on finding more suitable supports, commercially available or easily synthesizable. Thus, a new catalyst system based on cobalt on charcoal (Co/C) has been developed.

This catalytic system was prepared by the thermal decomposition of $[Co_2(CO)_8]$ in the presence of commercially available charcoal bone in THF under reflux. The catalytic activity of Co/C strongly depends on the amount of cobalt on the charcoal (wt%). The optimum cobalt loading on charcoal was about 12 wt%. The XRD patterns of the supported catalysts revealed peaks of hexagonal close packed (hcp) metallic cobalt, as in the bulk phase [35]. A TEM study (Fig. 2) shows that cobalt atoms are not distributed homogeneously in the charcoal surface, but form metallic cobalt particles (100–1000 nm).

The black Co/C shows ferromagnetism and is easily recovered by filtration or by using a magnet. The catalytic system is stable and can be reused at least 10 times without losing any catalytic activity. This heterogeneous catalytic system exhibited an excellent catalytic performance for intra- and intermolecular PKRs (Scheme 2).

When graphite and mesoporous carbon has also been screened as a support, the catalytic activity of cobalt on graphite and mesoporous carbon are almost the same as that of cobalt on charcoal. They have different surface areas and structures, but the state of their metallic cobalt is the same (Fig. 3).

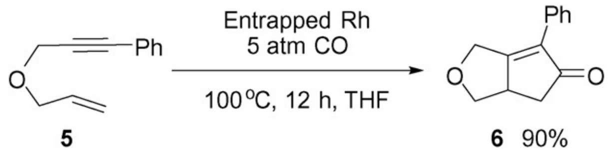
Thus, it seems likely that the catalytic activity depends on the state of the metallic cobalt on the support and not on the nature of the carbon support. The reaction temperature and CO pressure have to be at least 130 °C and 20 atm, respectively. Compared to those of Co/SiO_2, there is no improvement on the optimized reaction conditions.



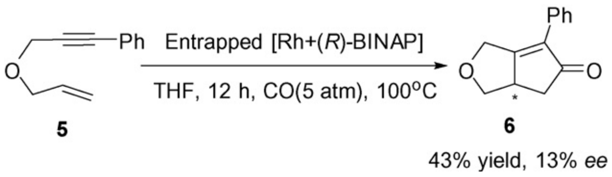
Scheme 2.

2.3. Entrapped rhodium catalysts [36]

Our previous studies [32,34] based on bulk cobalt on a support fulfil the principle of atom economy. However, one of the disadvantages of the cobalt-catalyzed reaction is its harsh reaction conditions, i.e. high temperatures and high pressures of CO. When rhodium complexes were used as catalysts, the PKR was conducted under relatively mild reaction conditions [11,12b,13,37]. The use of rhodium in the PKR can solve the drawback of this reaction and is now common. However, there have been no reports on the recovery and reuse of rhodium catalysts. The rhodium metals on supports were not as active as the homogeneous rhodium complexes. Thus, another immobilization method, an entrapment of catalysts by sol–gel process, has been used, although entrapped or encapsulated catalysts have an inherent problem, that of the usually strong diffusion resistance due to the limited pore size [38]. However, in some cases, the activities and selectivities of entrapped catalysts have been found to be competitive with homogeneous catalysts [39]. An entrapped rhodium catalyst was generated by the silica sol–gel entrapment of $[Rh(cod)(\mu\text{-Cl})]_2$ in THF solution. The intramolecular PKR of an enyne was investigated as a test reaction (Scheme 3).



Scheme 3.



Scheme 4.

The entrapped rhodium complex is very active, with an isolated product yield of 90% at 100 °C and a CO pressure of 5 atm. Thus, the entrapped rhodium catalyst is more active than heterogeneous catalysts (130 °C and 20 atm CO) based on metallic cobalt supported on mesoporous silica or charcoal [32,34], but it has a slightly lower catalytic activity than homogeneous rhodium catalysts [40]. The catalytic system is ineffective for intermolecular PKR. The catalyst maintained its high activity even after 10 cycles of recycling and reuse. After five times recycling, an ICP-AES study showed that 0.278 ppm of rhodium, equal to leaching of 0.086% rhodium, was in solution. Using entrapped rhodium complexes $[Rh(cod)(\mu\text{-Cl})]_2$ and $[Rh(acac)(CO)_2]$ and (*R*)-BINAP as chiral catalysts an asymmetric PKR was studied (Scheme 4).

When 1 equiv. (*R*)-BINAP was used, the yield was 79–87% with 3–7% ee. An increase of the amount of (*R*)-BINAP to 2.5 equiv. led to an increase in the ee values up to 13% with a lower yield of 43–65%. Although this ee value is low it is not meaningless and give us hope that future improvement in the levels of asymmetric induction may be made.

The ^{31}P NMR study of the entrapped catalyst in $CDCl_3$ shows phosphine–phosphine oxide as the sole species. Thus, it seems that the poor ee value may be due to the presence of rhodium phosphine–phosphine oxide as a catalyst instead of a rhodium diphosphine complex.

This study shows that an entrapment is a useful alternative method for immobilizations. Moreover, it also provides the possibility that reducing the formation of phosphine oxide may lead to a much higher ee value. Entrapment can be used for other reactions as well as the PKR.

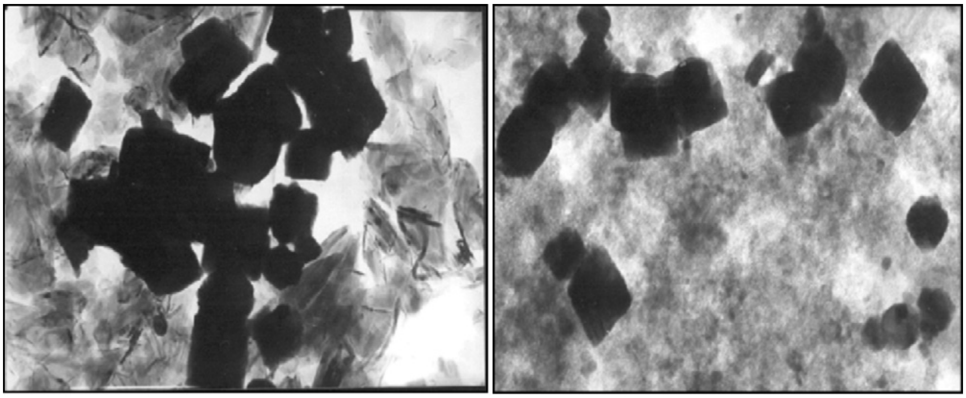
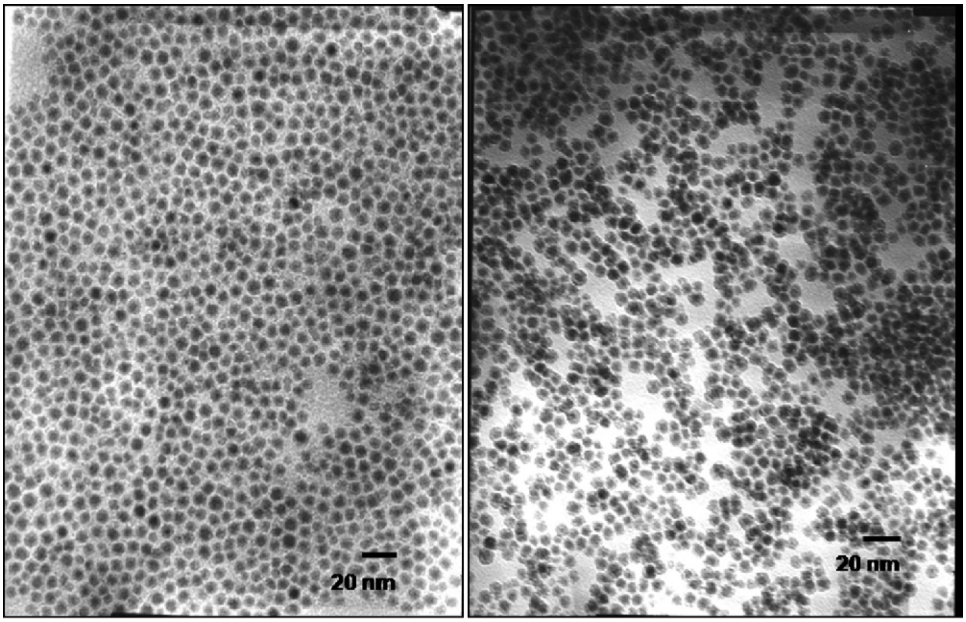

(a) Co on graphite (b) Co on mesoporous carbon

Fig. 3. TEM images of Co on carbon.



(a) Before (b) After

Fig. 4. TEM images of colloidal cobalt nanoparticle before the reaction (a) and after running four reaction cycles (b). Reproduced from Ref. [47] with permission.

3. Transition metal nanoparticle catalyst

The use of bulk cobalt metal as a catalyst was successful, but unsuccessful from the view-point of improvement of reaction conditions. Thus, development of another catalytic system, having the advantages of heterogeneous catalysts with high catalytic activity under mild reaction conditions, was needed. Under these circumstances, transition metal nanoparticles attracted our attention [41]. They are heterogeneous and have a characteristic high surface-to-volume ratio. Consequently a large fraction of the metal atoms are at the surface and hence are available for catalysis [42]. Many colloidal transition metal nanoparticles, especially noble metals, have been used as catalysts for the hydrogenation of olefin [43], for carbon–carbon coupling reactions, for other reactions [26b,44], and for oxidation [45]. However, colloidal nanoparticles of first-row transition metals have seldom been used as catalysts [46]. Transition metal nanoparticles would be effective catalysts under mild reaction conditions provided their special properties could be fully used in the catalytic reaction. With this expectation, transition metal nanoparticles were prepared and studied their use as catalysts in the PKR and related reactions.

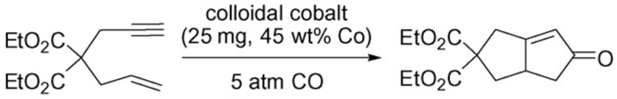
3.1. Colloidal cobalt nanoparticles [47]

In the previous studies [33,34], the first heterogeneous catalytic PKRs had been demonstrated using metallic cobalt supported on either mesoporous silica or charcoal. Even though these heterogeneous metallic cobalt catalysts exhibit good performance for many intramolecular and intermolecular PKRs, they require extreme reaction conditions of CO pressures >20 atm and temperatures >130 °C. The development of recyclable heterogeneous catalysts able to function in much milder conditions is desirable. Among several synthetic methods, a recently developed synthetic method was used to fabricate cobalt nanoparticles. This method comprises the formation of seed particles at low temperature and further aging at high temperature.

For the synthesis of cobalt nanoparticles, $Co_2(CO)_8$ (2.04 g, 6 mmol), oleic acid (1.68 g, 6 mmol), trioctylphosphine (0.6 mL) and dioctyl ether (20 mL) were mixed with stirring at room temperature. The mixture was heated slowly at reflux and the reflux was maintained for 30 min, after which the reaction mixture was allowed to cool to room temperature. A black precipitate was obtained by adding 50 ml of ethanol followed by washing with 20 ml of acetone and drying *in vacuo*. A TEM image (Fig. 4a) confirmed that the particles are well separated and that they are nearly monodisperse, having a mean diameter of 8 nm.

The intramolecular PKR of an enyne was investigated as a test reaction (Scheme 5).

Colloidal cobalt is very active, with an isolated yield of product of 97% at 130 °C and a CO pressure of 5 atm. The colloidal cobalt catalyst is more active than heterogeneous catalysts based on metallic cobalt supported on mesoporous silica or charcoal [32,34]. The catalyst maintained its high activity even after five cycles of recycling (yield: 97%, 94%, 94%, 94%, and 95%, respectively) and reuse. A TEM image (Fig. 4b) of the catalyst after running four reaction cycles showed that the particle size of the cobalt nanoparticles was unchanged and confirmed that no particle agglomeration was taking place. However, when either the reaction temperature was decreased to 110 °C or the CO pressure was lowered to 3 atm, the catalytic activity was found to decrease significantly.



1, 0.42 mmol **2**

temp(°C)	CO(atm)	yield(%)
130	5	97
110	5	26
130	3	45
130	1	0

Scheme 5.

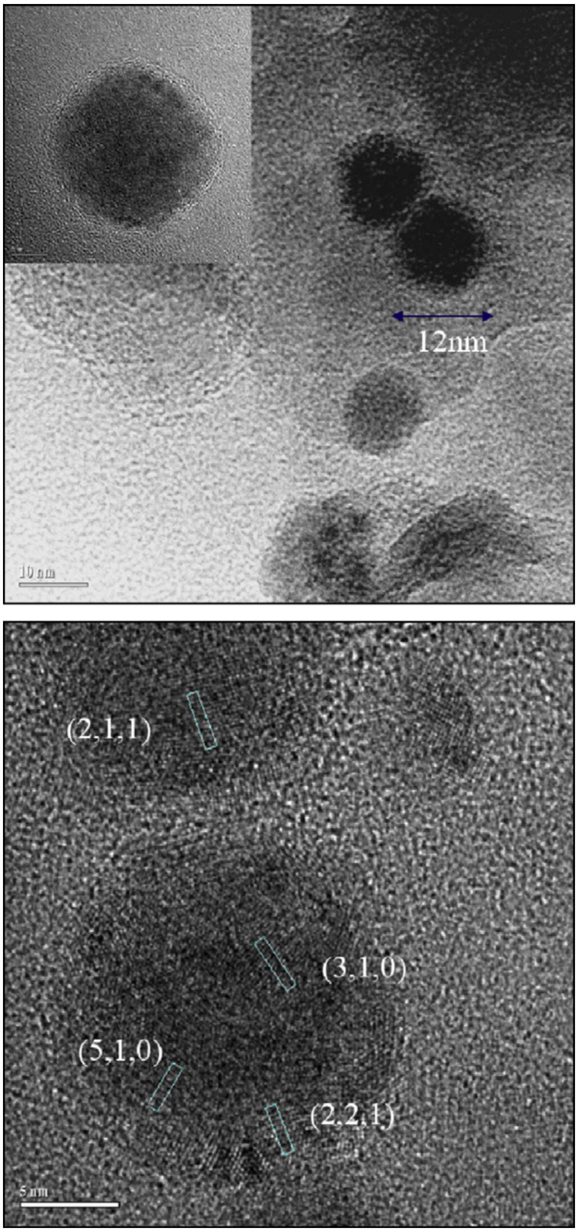


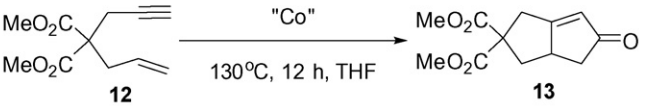
Fig. 5. HRTEM images of cobalt nanoparticle on charcoal. Reproduced from Ref. [48] with permission.

3.2. *Cobalt nanoparticles on charcoal [48]*

Although the cobalt nanoparticles are effective [47], they are more inconvenient to use than conventional heterogeneous catalysts such as Co on charcoal and Co on silica [32,34]. To combine the merits of conventional heterogeneous catalysts with the high catalytic activity of cobalt nanoparticles, cobalt nanoparticles on charcoal (**CNC**) were prepared.

3.2.1. *Synthesis of cobalt nanoparticles on charcoal (**CNC**)*

Surfactant-stabilized nanoparticles of cobalt were prepared by the thermal reduction of dicobalt octacarbonyl [49]. According to the TEM image, the particles are well separated and are nearly monodisperse, having a mean diameter of 12 nm. Heating the synthesized cobalt nanoparticles with dried charcoal in THF at reflux yielded cobalt nanoparticles on charcoal (**CNC**). The HRTEM study (Fig. 5) shows that the mean size of the nanoparticles is 12 nm, ranging from 7 to 18 nm. The crystal packing of **CNC** is an epsilon mode [50]. **CNC** is very stable even in air for several months.



colloidal cobalt nanoparticle	97%
cobalt nanoparticle on charcoal	98%

Scheme 6.

3.2.2. *The use of **CNC** in the Pauson–Khand reaction*

Under 5 atm of CO, cobalt nanoparticles also gave product in an almost quantitative yield (97%). When the same PKR was carried out using **CNC** as a catalyst, 98% of the product was isolated (Scheme 6).

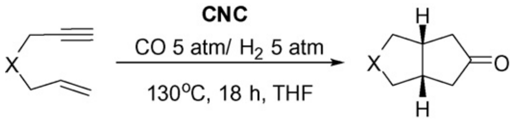
Thus, immobilization of cobalt nanoparticles did not retard their catalytic activity. The catalyst maintained its high activity even after being recycled five times (yield: 98%, 95%, 96%, 98%, and 98%, respectively).

While the normal intramolecular PKRs proceeded smoothly under 5 atm of CO, internal enyne and heteroatom-bridged enynes required a higher CO pressure of 10 atm. **CNC** is also effective for intermolecular PKR under 15 atm of CO. When the same reactions were carried out using colloidal cobalt nanoparticles as catalysts, the pressure of CO was 10 atm. Thus, the catalytic activity of **CNC** is slightly lower than that of the colloidal cobalt nanoparticles for the intermolecular PKR.

3.2.3. *The use of **CNC** as bifunctional catalysts: the reductive Pauson–Khand reaction in one pot*

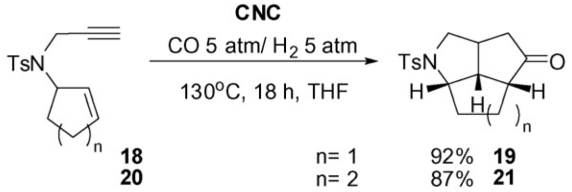
Complexes of cobalt are known to be hydrogenation catalysts but are mostly selective for conjugated systems [51]. $Co_2(CO)_8$ and its derivatives are known to be hydrogenation catalysts for alkenes under specific conditions, although they are decomposed to metal under a pure H_2 atmosphere. Although the sequential reaction of PKR and hydrogenation is a useful methodology for the synthesis of natural products [52], the known reductive PKRs use stoichiometric or substoichiometric amounts of cobalt complexes [53]. To use **CNC** as a bifunctional catalyst in the PKR and hydrogenation in a one-pot, tandem reaction, **CNC** had to satisfy the following conditions: first, carbon monoxide or hydrogen should not interfere with the catalytic activity of **CNC** in any reaction, and second, hydrogenation of substrates should not take place before a PKR of the substrate occurs. Fortunately, the **CNC** was effective for the reductive PKR (Scheme 7).

Under these optimized reaction conditions, no hydrogenation of enyne substrates was observed before the PKR occurred. This sequential reaction provides a straightforward approach to the bicyclic and tricyclic ketone frames derived from enynes. The structures shown in Scheme 8 appear as core skeletons in many natural syntheses such as those of the linear and angularly fused triquinane sesquiterpenes [54].



	X	yield(%)	
12	$C(CO_2Me)_2$	98	**14**
15	N(Boc)	90	**16**
7	NTs	94	**17**

Scheme 7.



Scheme 8.

CNC has a high activity in PKRs and can be used as a bifunctional catalyst in the PKR and hydrogenation in a one-pot reaction. **CNC** is easily recovered and can be reused many times without losing catalytic activity.

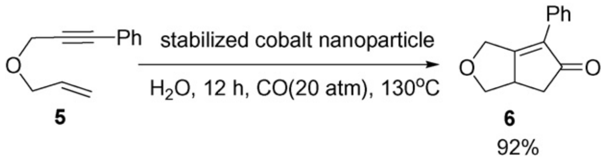
3.3. *Aqueous colloidal cobalt nanoparticles as catalysts [55]*

In the previous studies, the transition nanoparticles catalysts still require an organic solvent as a reaction medium. The possibility of substituting conventional organic solvents for the supercritical fluids CO_2 and ethylene have been demonstrated [31e,56]. The application of catalysts in aqueous solution and on liquid supports has attracted a great deal of attention and been applied to many catalytic reactions [57]. However, no catalytic systems that enable the use of water as a solvent in the PKR had been developed until we reported [55] the first PKR in water. Initially, the development of aqueous colloidal cobalt nanoparticles [58] attracted our attention.

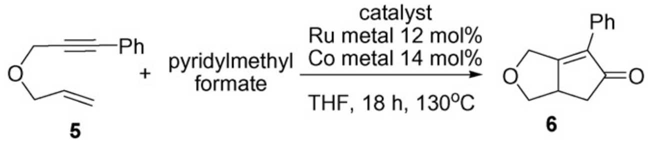
Aqueous colloidal cobalt nanoparticles were prepared by reducing an aqueous solution of cobalt acetate containing sodium dodecyl sulfate (SDS) surfactant [58b]. Aqueous colloidal cobalt nanoparticles are stable for a limited time (2–3 days) in air. However, in the absence of oxygen they are stable for a long time.

The optimum reaction conditions were 20 atm of CO at 130 °C, the yield of the reaction was 92% (Scheme 9). By contrast, the yields for $Co_2(CO)_8$ and cobalt on charcoal were 8% and 24%, respectively. We hypothesize that the stabilizing SDS surfactant micelles act as nanoreactors to induce better solubilization of organic reactants and ultimately allow the reactants to interact more intimately with the cobalt nanoparticles. The nonpolar alkyl chains remain in a nonpolar environment and the hydrocarbon chains can dissolve the organic substrates. Thus, there is no requirement to employ water-soluble substrates. The solubilized CO molecules might react with the outer surface of cobalt nanoparticles to generate *in situ* cobalt carbonyl species, which can act as catalysts for the carbonylative cycloaddition. Recovery and reusability of the catalytic system were tested by carrying out consecutive cycles, with the same catalyst in aqueous solution, carefully separated from the organic phase at the end of each run. The conversion yields were very high even at the fourth run (yield: 92%, 95%, 91%, 96%, and 95%, respectively). The relative invariance of the conversion yields means that the catalyst system is stable during recycling.

Aqueous colloidal cobalt nanoparticles are effective for intramolecular PKR. However, unfortunately, they are ineffective for intermolecular PKR. Thus, development of a new catalytic system that is effective for the intermolecular PKR in water is still needed.



Scheme 9.



catalyst	yield (%)
$Ru_3(CO)_{12}$ / **CNC**	98
$Ru_3(CO)_{12}$	-
CNC	-
RuCNC	98

Scheme 10.

3.4. *Immobilized heterobimetallic Ru/Co nanoparticle [59]*

Increasing environmental awareness has made the use of carbon monoxide undesirable and prompted the search for an alternative process that utilizes a substitute [60]. *In situ* generated carbon monoxide could be a good candidate, however, the synthetic utilization of generated carbon monoxide has been largely ignored [61]. The use of decarbonylated CO from formates or aldehydes has been utilized in transition metal-catalyzed hydroxycarbonylation [62], the PKR [63], and hydroesterification [64]. Thus, the research was focused on the design and development of a new catalytic system consisting of immobilized transition nanoparticles with formates as an alternative to carbon monoxide.

The metal ruthenium was chosen as a decarbonylation catalyst, stimulated by examples of its recent use [60,63] and organic substrates that could be easily decarbonylated by transition metals were screened. Aldehydes and formates are good candidates for our purpose because they have been studied with this aim for three decades [64,65]. Before using immobilized heterobimetallic ruthenium/cobalt nanoparticles as catalysts in the PKR, the use of a combination of $Ru_3(CO)_{12}$ and cobalt nanoparticles with pyridylmethyl formate instead of carbon monoxide was tested in the Pauson–Khand reaction (Scheme 10).

The expected PKR product was obtained in a high yield when pyridylmethyl formate was used with $Ru_3(CO)_{12}$ and cobalt nanoparticles. When either ruthenium carbonyl or colloidal cobalt nanoparticles were used as the catalyst in the presence of pyridylmethyl formate, no reaction product was obtained. The successful initial result encouraged us to make heterobimetallic ruthenium/cobalt nanoparticles immobilized on charcoal (RuCNC) and use them as catalysts in the PKR. These were prepared and characterized by TEM (Fig. 6).

The optimized reaction conditions were established as follows: 1.5 equiv. 2-pyridylmethyl formate, THF, 12 h, and 130 °C. The catalyst system could be re-used five times (yield: 97%, 98%, 98%, 97%, and 97%, respectively) without loss of activity. Elemental analysis (by ICP-AES) of the reaction mixture after completion of the reaction showed that less than 0.1 ppm of ruthenium and cobalt species were bled.

In this study, a catalytic system based on the Ru/Co nanoparticles on charcoal was developed as a highly effective catalyst for intra- and intermolecular Pauson–Khand-type reactions in the presence of pyridylmethyl formate instead of carbon monoxide.

3.5. *Heterobimetallic Co/Rh nanoparticles [66]*

Compared to dicobalt octacarbonyl, cobalt nanoparticles were quite active. However, when cobalt nanoparticles were used as a catalyst, the relatively high pressure (5 atm) of carbon monoxide was still an obstacle for use in an ordinary organic laboratory. Therefore, it is still necessary to develop a heterogeneous catalytic system for use under milder reaction conditions. The use of heter-

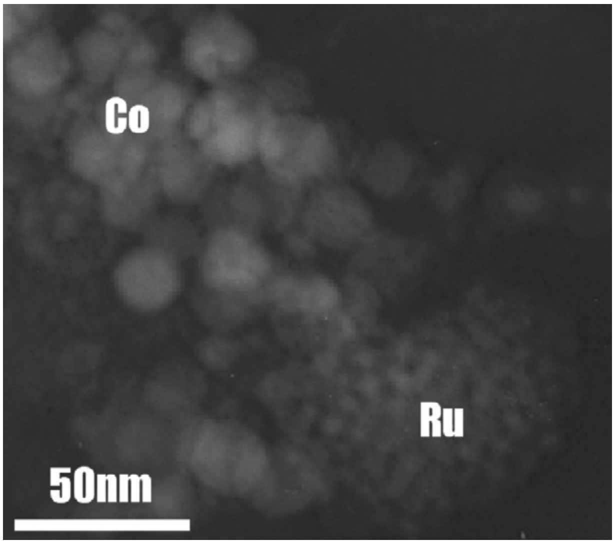


Fig. 6. TEM images of RuCNC. Reproduced from Ref. [59] with permission.

obimetallic nanoparticles as catalysts has attracted much attention because their catalytic performance is generally superior to that of a single nanometal by itself [67]. Furthermore, when rhodium complexes were used as catalysts for the PKR, the pressure was usually ≤1 atm [12,13,37b,68]. Therefore Co/Rh heterobimetallic nanoparticles were prepared, immobilized on charcoal, and their use in the PK-type reaction was studied.

3.5.1. Synthesis and characterization of Co/Rh heterobimetallic nanoparticles and their immobilization

In order to create bimetallic nanoparticles with a fixed stoichiometry, the strategy of the decomposition of bimetallic organometallic cluster compounds was employed; it would appear that the use of molecular cluster compounds as precursors is one of the most attractive methods available [69]. Ru/Pt, Ru/Sn, Ru/Pd, Ru/Cu nanoparticles were prepared by decarbonylation of mixed-metal carbonyl precursors.

The clusters $Co_2Rh_2(CO)_{12}$ and $Co_3Rh(CO)_{12}$ were prepared as previously reported [70]. A solution containing the cobalt–rhodium carbonyl compound was injected into a solution of *o*-dichlorobenzene, oleic acid, and trioctylphosphine oxide at 180 °C. Heating the resulting solution at 180 °C for 2 h afforded a black solution. The heterobimetallic carbonyl compound was fully decomposed to heterobimetallic nanoparticles. After removal of all the solvent, a black precipitates was obtained. The Co/Rh heterobimetallic nanoparticles were immobilized on charcoal by refluxing the precipitate with flame-dried charcoal in THF for 12 h. According to ICP-AES data on the immobilized Co/Rh heterobimetallic nanoparticles derived from $Co_2Rh_2(CO)_{12}$ and $Co_3Rh(CO)_{12}$, the ratios of Co:Rh were 1.09: 1 and 2.93: 1, respectively. Thus, the method used in this study always gave fixed stoichiometric Co/Rh bimetallic nanoparticles. HR-TEM photographs of the immobilized Co_2Rh_2 heterobimetallic nanoparticles and the corresponding particle size distribution histogram are shown in Figs. 7 and 8, respectively.

HR-TEM shows that the diameter of the resulting well-dispersed, isolated, and anchored bimetallic nanoparticles is approximately 2 nm.

3.5.2. The Pauson–Khand-type reaction under 1 atm of CO

Investigation of the use of nanoparticles as catalysts in the intramolecular PKR of allyl propargyl ether was carried out (Scheme 11).

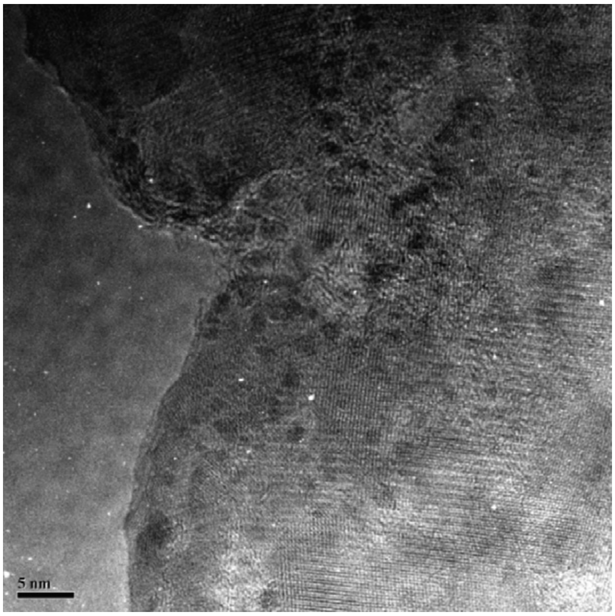


Fig. 7. HRTEM image of Co_2Rh_2 nanoparticle on charcoal. Reproduced from Ref. [66b] with permission.

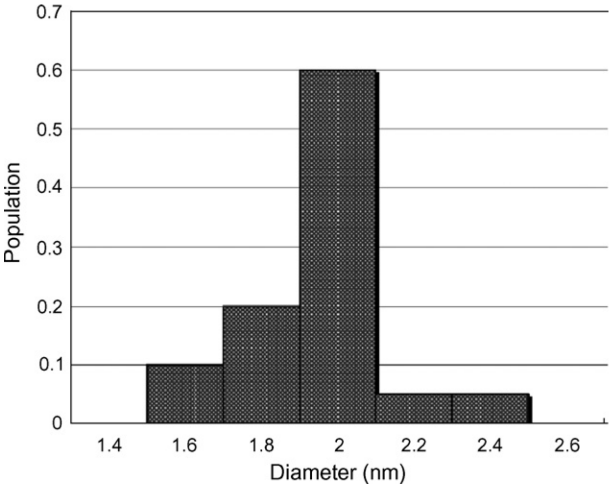
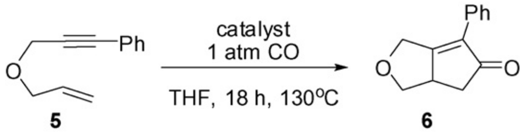


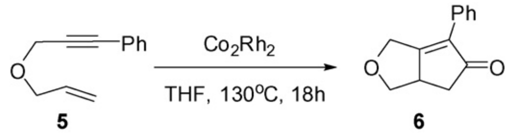
Fig. 8. Particle size distribution histogram of Co_2Rh_2 nanoparticle on charcoal. Reproduced from Ref. [66b] with permission.

When Co_3Rh nanoparticles (derived from $Co_3Rh(CO)_{12}$) were used, the expected product was obtained in 65% yield. The use of Co_2Rh_2 nanoparticles (derived from $Co_2Rh_2(CO)_{12}$) as a catalyst gave 87% of the reaction product. Interestingly, when a mixture



catalyst	yield (%)
Co_2Rh_2	87
Co_3Rh	65
Co nanoparticles on charcoal	0
Rh nanoparticles on charcoal	23
A mixture of Co and Rh nanoparticles	12

Scheme 11.



aldehyde	yield (%)
acrolein	87
crotonaldehyde	93
cinnamaldehyde	91
benzaldehyde	43
1-naphthaldehyde	35
2-pyridylmethyl formate	0

Scheme 12.

of colloidal cobalt and rhodium nanoparticles was used as a catalyst under the same reaction conditions, only 12% of the product was obtained. Thus, it seems that there arose some synergistic effects between cobalt and rhodium nanoparticles in the Co_2Rh_2 and Co_3Rh nanoparticles. Using Co_2Rh_2 as a catalyst, the optimized reaction conditions were established as 1 atm of CO, 130 °C, THF, and 18 h. When Co_2Rh_2 nanoparticles immobilized on charcoal were used as a catalyst, the yield was 88%. Thus, immobilization of Co_2Rh_2 nanoparticles did not retard their catalytic activity. When the catalyst was recycled, it maintained its high level of activity even after being recycled five times (yield: 97%, 89%, 96%, 87%, and 87%, respectively).

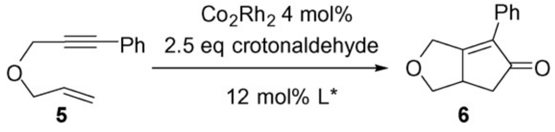
The catalytic system is effective both for the inter- and intramolecular PKR. Many useful rhodium catalysts have been developed under similar mild conditions. However, they are generally less effective for the intermolecular PKR [68a] and cannot be reused. Therefore, the Co_2Rh_2 bimetallic nanoparticles overcome the disadvantages of homogeneous rhodium catalysts.

3.5.3. The Pauson–Khand-type reaction in the presence of aldehydes

Aldehydes and formates are good candidates for our purpose because they have been studied with this end in mind for three decades [65]. Using Co_2Rh_2 nanoparticles as the catalyst, aldehydes and formates were screened as a substitute for carbon monoxide in an intramolecular PK-type reaction (Scheme 12).

Aldehydes proved to be effective in giving a carbonylative cycloaddition product, but 2-pyridylmethyl formate was ineffective. In particular, α,β-unsaturated aldehydes such as cinnamaldehyde, crotonaldehyde, and acrolein produced good results but aryl aldehydes such as benzaldehyde and 1-naphthaldehyde gave poor results. Crotonaldehyde was our choice as the CO source. Immobilized Co_2Rh_2 (0.05 g), enyne (0.96 mmol), crotonaldehyde (2.4 mmol), THF, 130 °C, and 18 h were established as the optimized reaction conditions. The reusability of the catalytic system was tested for the intramolecular PK-type reaction of cinnamic aldehyde with phenylacetylene by checking any leaching of cobalt and rhodium from the charcoal surface. Elemental analysis (by ICP-AES) of the reaction mixture after completion of the reaction showed that less than 0.1 ppm of cobalt and rhodium species had leached.

The catalytic system is effective for giving high yields of the intramolecular PKR products. The reaction needs no additives to enhance or promote the catalytic reaction. Moreover, multi-gram quantities of cyclopentenones were obtained without any difficulties. The catalytic system is also effective in the intermolecular PK-type reaction although the yields were not high, partly due to the trimerization of alkynes (yield: 17–70%).



ligand	yield (%)	ee
(*R*)-BINAP	93	79
(*R*)-Tol-BINAP	91	73
(*R*)-DIOP	90	34
(*R*,*R*)-NORPHOS	83	-
(*S*,*S*)-BDPP	91	84

Scheme 13.

3.5.4. Asymmetric catalytic Pauson–Khand-type reaction in the presence of an aldehyde

As mentioned above, much attention has been paid to the preparation of transition metal nanoparticles and their use in catalysis. However, much less attention has been paid to the combination of optically active ligands with transition metal nanoparticles. Recently, Fujihara and Tamura reported [71] the synthesis of chiral bisphosphine BINAP-stabilized gold and palladium nanoparticles and their use in a catalytic asymmetric hydrosilylation of styrene.

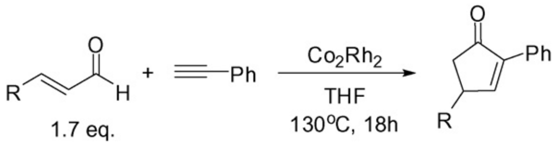
A number of catalytic asymmetric PKRs or PK-type reactions have been described [9c,13,33a,40b,75], however, there have been no reports on transition metal nanoparticle-catalyzed asymmetric PKRs. To study an asymmetric catalytic PK-type reaction in the presence of an aldehyde, various C_2-symmetrical chiral diphosphine ligands were first of all screened (Scheme 13).

The presence of chiral ligands does not harm the yield of the reaction, but the ee values are highly dependent upon the chiral ligand itself. The use of (*S*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*S*)-BINAP] as a ligand is the most effective in cobalt-catalyzed reactions of 1,6-enynes [72d,73] while using (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*R*)-BINAP] as a chiral ligand gave an ee value of 79%. Strangely, when (2*R*,3*R*)-(−)-2,3-bis(diphenylphosphino)-bicyclo[2.2.1]hept-5-ene [(*R*,*R*)-NORPHOS] was used, a racemate was obtained. However, surprisingly, the use of (2*S*,4*S*)-(−)-2,4-bis(diphenylphosphino)pentane [(*S*,*S*)-BDPP] gave a high ee value of 84%. Thus, (*S*,*S*)-BDPP was the best choice for the asymmetric Pauson–Khand-type reaction.

Using (*S*,*S*)-BDPP as a chiral ligand, when other enyne substrates were subjected to the PKR conditions, the yields were high (75–94%) and the ee values were moderate to high (51–87%). The best ee value was 87%. Interestingly, the ee values obtained were comparable to those obtained in homogeneous catalysis using rhodium catalysts derived from $[RhCl(CO)_2]_2$/(*S*)-BINAP and AgOTf [40b]. In particular, the 84% ee value for enyne was greater than that (74%) obtained with the homogeneous rhodium catalysis. The reusability of the catalytic system was tested for the asymmetric PK-type reaction. For the recyclization, the catalyst obtained by filtration was reused and the insufficient chiral diphosphine was supplemented by new chiral diphosphine. The yields and ee values were retained over at least five runs. Elemental analysis (by ICP-AES) of the reaction mixture after completion of the three runs showed that 3.9 ppm of the cobalt and 0.3 ppm of the rhodium species were detected.

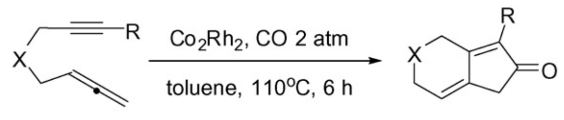
In many cases [74], chiral diphosphine ligands were oxidized to phosphine oxides during reaction or separation. However, (*S*,*S*)-BDPP was recovered in 87% yield from the reaction mixture after completion of the first run. Thus, the recovered (*S*,*S*)-BDPP can be used in further reactions.

The ability of added Hg(0) to poison metal(0) heterogeneous catalysts [75] by amalgamating the metal catalyst or adsorbing it onto its surface is the single most widely used test of homogeneous ver-



R	yield (%)	
H	60	**22**
Me	77	**23**
Ph	75	**24**

Scheme 14.



	X	R	yield(%)	
25	NTs	Me	85	**26**
27	NTs	H	69	**28**
29	NTs	TMS	71	**30**
31	$C(CO_2Me)$	Ph	73	**32**
33	O	Me	59	**34**

Scheme 15.

sus heterogeneous catalysis [76]. Thus, to obtain some evidence for distinguishing between homogeneous versus heterogeneous catalysis, a mercury-poisoning experiment was carried out. The addition of Hg(0) completely eliminated further catalysis. This result is consistent with and strongly supportive of heterogeneous metal(0) catalysis [75,77]. Since the activity was completely poisoned, the heterogeneous metal(0) catalyst is the only active species present.

This study demonstrated the usefulness of the combination of cobalt and rhodium nanoparticles in the intra- and intermolecular PKRs under mild conditions. Environmentally safe, clean, and sustainable chemical processes for the asymmetric catalytic PKR have been developed in this study.

3.5.5. *Olefinic aldehydes as an alkene and CO source [78]*

The PKR is a carbonylative cycloaddition reaction involving the selective incorporation of three different molecules, i.e., an alkyne, an alkene, and carbon monoxide. Substitution of one of the reaction components, carbon monoxide, by an aldehyde or a formate completely changes the reaction process. By extrapolation, if a substance could be used instead of both carbon monoxide and an alkene, a much simpler and cleaner process could be developed. Moreover, the application of cleaner heterogeneous catalysts with readily available starting materials would allow the minimization of inorganic as well as organic waste production.

The previous study [66] gave us the novel idea to use unsaturated aldehydes as a source of CO and alkene. The release of hydrocarbons and carbon monoxide from the reaction of aldehydes on metal surfaces has been well documented [79]. Organic substrates that could be easily decarbonylated by Co_2Rh_2, including α,β-unsaturated aldehydes, were screened (Scheme 14).

As expected, a PKR product was obtained in reasonable to high yields. It is very interesting that electron-deficient alkenes such as α,β-unsaturated aldehydes, known as poor substrates for the PKR, can be used as a source of CO and alkene. Acrolein, crotonaldehyde, and cinnamic aldehyde are good substrates. Thus, α,β-unsaturated aldehydes have a dual function, slowly and continuously producing both olefin and CO *in situ*. Moreover, the reaction was regioselective with respect to alkenes and alkynes.

When the reusability of the catalytic system was tested for the reaction between cinnamic aldehyde and phenylacetylene, the catalytic activity of Co_2Rh_2 nanoparticles was retained for at least five runs (yield: 75%, 72%, 73%, 73%, and 70%, respectively); the maximum reusability has not been tested. Elemental analysis (by ICP-AES) of the reaction mixture after completion of the reaction showed that less than 0.1 ppm of cobalt and rhodium species were present.

Thus, this study provides the conceptual basis for a new model of catalytic intermolecular PKR: a new catalytic protocol has been developed for the formal [2 + 2 + 1] cycloaddition reaction of alkynes and α,β-unsaturated aldehydes to 2-substituted cyclopentenones. The procedure can be characterized as environmentally friendly because the transformation occurs in the absence of additives except for the catalyst, and the catalyst can be reused semi-permanently without losing catalytic activity.

3.5.6. *Cobalt/rhodium heterobimetallic nanoparticle-catalyzed allenic Pauson–Khand reaction [80]*

The use of allenynes as substrates in the Co_2Rh_2-catalyzed allenic PKR was studied. Using an 1,7-allenyne in the presence of Co_2Rh_2 nanoparticles, the reaction condition was optimized as follows: 2 atm of CO, 110 °C, and 6 h. The cyclization occurs selectively with the distal double bond of the allene, to yield bicyclo[4.3.0]nonenone. The best yield was 85% and the catalyst maintained its high activity even after being recycled six times. The catalytic system was effective for various allenyne substrates (Scheme 15).

The reaction can be extended to a catalytic formation of bicyclo[5.3.0]dec-1,7-dien-9-ones from allenynes (Scheme 16). The same reaction using a homogeneous catalyst was reported by Mukai's and Brummond's groups [68b,81].

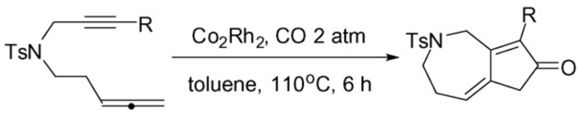
The bicyclo[5.3.0] skeleton was constructed in acceptable yields compared to those in previous works [81], and complete chemoselectivity was observed in the formal [2 + 2 + 1]-cycloaddition, leading to the exclusive construction of the bicyclo[5.3.0]dec-1,7-dien-9-one framework.

This study demonstrated that the Co_2Rh_2-catalyzed PKR of allenynes provides high yields of [5.6]- and [5.7]-bicyclic enones. The cyclization occurs selectively with the distal double bond of the allene. This is the first use of nanoparticles as catalysts in the allenic PKR.

3.5.7. *Cobalt/rhodium heterobimetallic nanoparticle-catalyzed carbonylative [2 + 2 + 1] cycloaddition of allenes [82]*

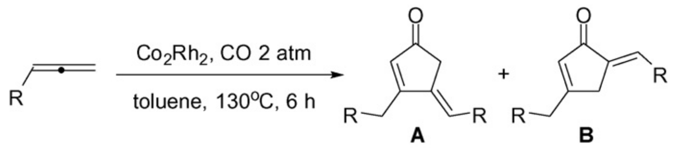
As an extension of the previous study [83], allenes were tested as substrates in an intermolecular PKR. When phenylallene in toluene was reacted with 2 atm of CO in the presence of a catalytic amount (5 mol%) of Co_2Rh_2 at 130 °C for 6 h, two carbonylated products were isolated in 68% and 12% yields, respectively.

The product was found to be a cyclic enone bearing two phenyl groups. Thus, the allenes formally serve both as an excellent alkene and alkyne-type moiety in Co_2Rh_2-catalyzed [2 + 2 + 1] cycloaddition with carbon monoxide when compared to the classical PK process. This was the first catalytic formation of cyclopentenones



	R	yield(%)	
35	H	64	**36**
37	Ph	72	**38**
39	Me	73	**40**

Scheme 16.



R	yield(A / B)(%)	
Phenyl	68 / 12	**41**
4-Tolyl	70 / 14	**42**
3,5-Dimethylphenyl	71 / 13	**43**
1-Naphthyl	72 / 20	**44**
4-Anisyl	61 / 0	**45**
4-Acetylphenyl	64 / 20	**46**
4-Chlorophenyl	68 / 8	**47**
n-Hexyl	52 / 7	**48**

Scheme 17.

via a [2 + 2 + 1] cycloaddition of two allenes and carbon monoxide. Moreover, the regiochemistry observed was different from a standard intermolecular PK process. Under the optimized reaction conditions, other allenes produced the corresponding cyclopentenones in high yields (Scheme 17).

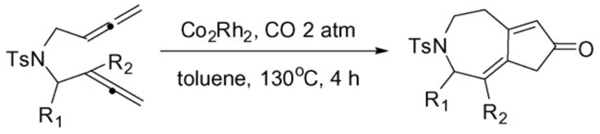
The use of bis-allenes as substrates in a Co_2Rh_2-catalyzed carbonylative cycloaddition reaction was also studied (Scheme 18). Compared to the use of allenes as substrates, the use of bis-allenes is rather uncommon, as seen from the fact that only a handful of reactions have been reported [83].

Under optimum reaction conditions (5 mol% Co_2Rh_2, toluene, 2 atm CO, 100 °C, and 4 h), each bis-allene yielded the corresponding intramolecular [2 + 2 + 1] cocyclization product in reasonable to high yield. The high regiocontrol observed is highly noteworthy.

This study demonstrated the first catalytic inter- and intramolecular [2 + 2 + 1] cocyclization of allenes and CO. This process provides a rapid and atom-economical method for the synthesis of a variety of cyclopentenones with an exocyclic double bond, or [5.3]bicyclic enones in one step.

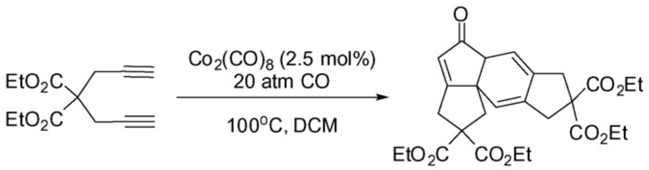
4. Cobalt carbonyl-catalyzed carbonylative cycloaddition of enyne, diynes, dienediynes, and triynes: tandem processes

Transition metal-catalyzed cycloaddition reactions of unsaturated substrates have provided many important methods for the construction of complex cyclic compounds [84]. Among them, the [2 + 2 + 1] cycloaddition [6d,85] provides a powerful tool for the assembly of five-membered rings containing polycyclic natural products. In particular, the PK cycloaddition has attracted much attention in the preparation of a variety of cyclopentenone systems [6c,72a,86]. However, cyclopentadienones [22] have played a minor role in five-membered ring construction due to their high reactivity in Diels–Alder reactions, even though some cyclopentadienone derivatives are known and are anticipated versatile building blocks in synthetic organic chemistry due to the formal ease with which a variety of functionalities at all positions on the ring can be introduced [22b,22e,87].



	R_1	R_2	yield(%)	
49	Me	H	67	**50**
51	H	Ph	74	**52**
53	H	Me	53	**54**

Scheme 18.



55

56 85 %

Scheme 19.

Transition metal-mediated [2 + 2 + 1] cycloaddition of two alkynes with CO can be a good way to generate and stabilize cyclopentadienones. However, the application of this method to organic synthesis has been hampered [88] by low yields, the requirement for the presence of specific substituents [89], and the necessity of a demetalation step [88d], even though $Fe(CO)_5$ [90] or $CpCo(CO)_2$ [91] have successfully been employed in some intramolecular carbonylative cycloaddition reactions. Furthermore, all the reported reactions are stoichiometric. A few examples of the use of cyclopentadienones in complex molecule synthesis have been reported [21e,85i].

Cyclopentadieneones are promising versatile intermediates for organic synthesis as long as their high reactivity can be controlled. One of the potentially useful reactions is the Diels–Alder reaction. The use of the high reactivity of cyclopentadienones will allow us to make a variety of cyclic compounds from the *in situ* generated cyclopentadieneones.

4.1. Cycloaddition of diynes

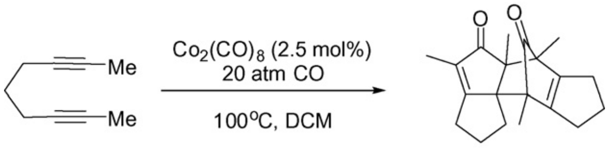
4.1.1. Cobalt carbonyl-catalyzed tandem [2 + 2 + 1]/[2 + 2 + 2] cycloaddition reaction of diynes [92]

In studying the PKR, the cycloaddition reaction of hepta-1,6-diynes employing cobalt carbonyl [$Co_2(CO)_8$] as catalyst attracted our attention because no successful examples of catalytic [2 + 2 + 1] cycloaddition reactions of α,ω-diynes had been reported. Moreover, it was expected that the $Co_2(CO)_8$-catalyzed tandem [2 + 2 + 1]/[2 + 2 + 2] cycloaddition reactions of diynes under CO would provide an easy construction pathway of unnatural novel tetracyclic compounds.

The treatment of diethyl dipropargylmalonate **55** in CH_2Cl_2 in the presence of 2.5 mol% $Co_2(CO)_8$ at 100 °C for 2 days under 20 atm of CO gave a tandem [2 + 2 + 1]/[2 + 2 + 2] cycloaddition reaction leading to production of the tetracyclic enone derivative **56** in 85% yield as the sole product (Scheme 19). No isomerized products were observed.

The reaction involves the formation of six carbon–carbon bonds. As we expected, it provides a unique pathway to a tetracyclic framework. All the terminal diynes except dipropargyl ether gave high yields. For the disubstituted 1,6-diyne **57**, a [4 + 2] cycloaddition between [2 + 2 + 1] cycloadducts gave **58** in 19% yield with the concomitant formation of unidentified polymeric materials (Scheme 20).

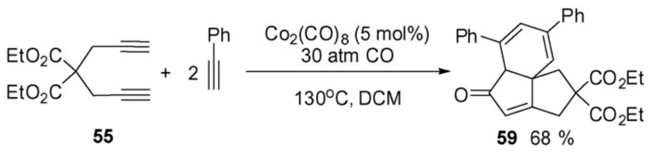
Thus, the steric effect of substituents at the external terminus of the diyne substrates is an important factor for the second [2 + 2 + 2] cycloaddition to proceed.



57

58 19 %

Scheme 20.



Scheme 21.

These experimental results suggested that the [2 + 2 + 2] cycloaddition reaction between diyne substrates does not occur before the [2 + 2 + 1] cycloaddition between CO and a substrate. Initially a [2 + 2 + 1] cycloaddition between a diyne and carbon monoxide catalyzed by $Co_2(CO)_8$ gives the corresponding bicyclic cyclopentadienone, and a subsequent [2 + 2 + 2] cycloaddition reaction between the bicyclic cyclopentadienone and diyne catalyzed by $Co_2(CO)_8$ leads to the tetracyclic cyclopentenone.

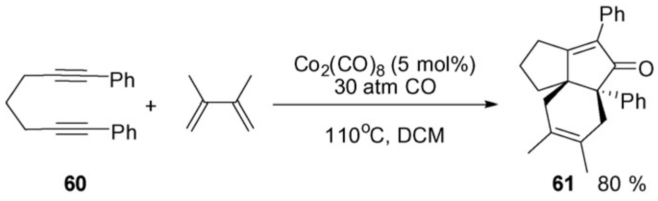
4.1.2. Cobalt carbonyl-catalyzed tandem [2 + 2 + 1] and [2 + 2 + 2] cycloaddition reaction of diynes with two phenylacetylenes [93]

As mentioned earlier, cyclopentadienone has played no role in five-membered ring construction due to its inherent instability and tendency to undergo dimerization. One of the potentially useful reactions is the use of the high reactivity of cyclopentadienones: a transition metal catalyzed [2 + 2 + 2] cycloaddition reaction of the olefinic double bond of cyclopentadienone with two alkynes. However, it seems to be very difficult to control the regioselectivity. No successful examples of catalytic tandem [2 + 2 + 1] and [2 + 2 + 2] cycloaddition reaction of diyne with alkynes have been reported, even though there has been much research in the [2 + 2 + 2] cycloaddition reaction of a diyne with an alkyne or alkene [84a,94]. Treatment of **55** and 2 equiv. phenylacetylene with $Co_2(CO)_8$ (5 mol%) at 130 °C under 30 atm CO for 18 h afforded a tricyclic product **59** in 68% yield (Scheme 21).

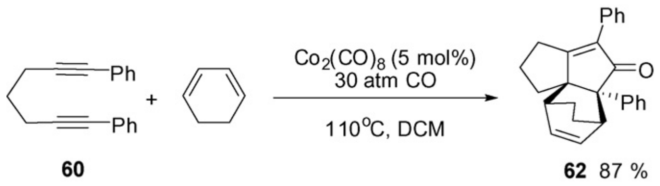
Compound **6** was derived from the reaction of carbonylative [2 + 2 + 1] cycloaddition of a diyne followed by [2 + 2 + 2] cycloaddition between the *in situ* generated bicyclic cyclopentadienone and two phenylacetylenes. Generally, intermolecular [2 + 2 + 2] cyclotrimerizations of alkynes encounter many difficulties [95]. Chemo- and regioselectivity problems lead to complex mixtures of products, which severely limit the utility of this reaction. However, in this reaction other isomers were not found, presumably due to steric congestion. Thus, the cycloaddition reaction is regioselective and can provide a very useful synthetic procedure. This study also demonstrates that the judicious choice of diyne substrate and an alkyne allows a cobalt carbonyl-catalyzed tandem [2 + 2 + 1] and [2 + 2 + 2] cycloaddition reaction giving tricyclic compounds.

4.1.3. Cobalt carbonyl-catalyzed tandem [2 + 2 + 1]/[4 + 2] cycloaddition reaction between diyne and diene [96]

There have been many studies [94a,94c,97] on the [2 + 2 + 2] cycloaddition reaction of a diyne with an alkyne or alkene but no successful examples of the catalytic tandem [2 + 2 + 1] and [4 + 2] cycloaddition reaction of a diyne with a diene under CO have been reported.



Scheme 22.



Scheme 23.

Treatment of **60** and 2,3-dimethyl-1,3-butadiene with $Co_2(CO)_8$ (5 mol%) in CH_2Cl_2 at 110 °C under 30 atm of CO for 18 h afforded 5.5.6 tricyclic enone **61** in 80% yield (Scheme 22).

Subjecting 1,3-cyclohexadiene to the same reaction conditions provided the expected tetracyclic enone **62** in 87% yield (Scheme 23).

The existence of phenyl groups at the external termini of the diyne substrate is an important factor for the tandem cycloaddition to proceed and the dicobalt octacarbonyl-catalyzed tandem [2 + 2 + 1] and [4 + 2] cycloaddition of diyne with diene is quite unique to 1,7-diphenyl-1,6-heptadiynes.

4.1.4. Cobalt carbonyl-catalyzed cycloaddition of diyne with cyclopentadiene [98]

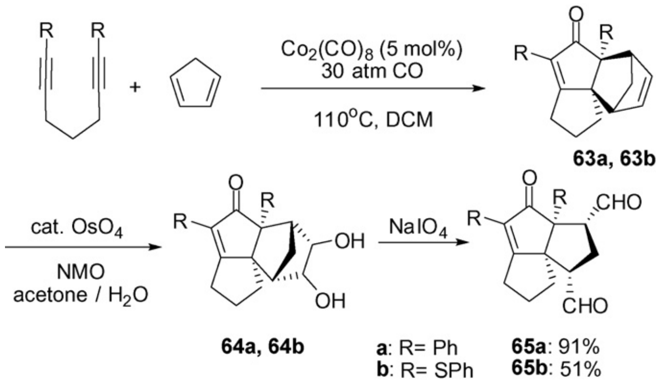
Polyquinane natural products have aroused a great deal of interest [99] because of their architecturally compact, complex molecular framework, and wide range of biological activities exhibited by some of their members. Numerous synthetic approaches toward the total synthesis of polyquinanes have been reported. However, most of the known synthetic methods involve multiple steps including a time-consuming separation step [100].

The previous studies [92,93,96] have demonstrated the usefulness of the dicobalt octacarbonyl-catalyzed tandem cycloaddition of triyne in the construction of complex molecular structures containing multiple unsaturations.

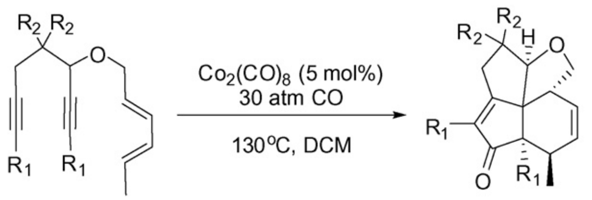
Cleavage of the double bond in **63a** leads to new synthetic sequences that permit the synthesis of an angular triquinane skeleton. Treatment of **63a** with NMO in the presence of a catalytic amount of OsO_4 led to the isolation of tetracyclic diol **64a**, and the subsequent oxidation of **64a** with $NaIO_4$ gave rise to tricyclic dialdehyde **65a** in 91% yield (Scheme 24).

Thus, an angular triquinane skeleton was easily obtained by a three-step reaction starting from readily available basic organic compounds and cyclopentadiene.

The presence of diphenyl groups at the terminal positions of diynes is a prerequisite for the tandem cycloaddition of a diyne and diene under carbon monoxide, eventually giving tetracyclic compounds. The existence of two phenyl groups on the terminal could limit the scope of diynes and diminishes the usefulness



Scheme 24.



	R_1	R_2	yield(%)	
66	Ph	Me	84	**67**
68	Ph	H	74	**69**
70	H	H	51	**71**

Scheme 25.

of this synthetic method. However, this drawback can be overcome by using 1,7-dithiophenyl-1,6-heptadiyne as a substrate when the corresponding tetracyclic enone **65b** was obtained in 51% yield. After the tandem cycloaddition, the SPh group can be easily removed [101]. Cyclopentadiene and cyclohexadiene were good substrates. However, other cyclic dienes such as furan, cycloheptadiene, cyclooctadiene and fulvalene were poor substrates for this tandem cycloaddition.

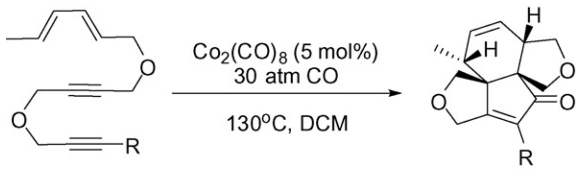
4.2. *Cycloaddition of dienediynes*

4.2.1. *Synthesis of fenestranes: cobalt carbonyl-catalyzed tandem cycloaddition of diendiynes—catalytic one-pot synthesis of [5.5.5.6]fenestrane systems [102]*

Most of the previous syntheses of fenestranes are based on the PKR [103], photocycloaddition [104], Pd-catalyzed carbonylative cyclization [105], aldolization [106] or cyclodehydration [107] as the key step(s). They gave only small quantities of the desired tetracycles and suffered from low selectivity and tedious separation problems. The dicobalt octacarbonyl-catalyzed carbonylative cycloaddition of a diene or triyne with/without diene or alkyne can produce up to four new five-membered rings in one step [99,100,103,108]. This success encouraged us to analyze the retrosynthesis of fenestranes.

After many experimental trials, dienediyne was chosen as a precursor to fenestrane. The treatment of dienediyne (0.68 mmol) with $Co_2(CO)_8$ (5 mol%) in dichloromethane at 130 °C under 30 atm of CO for 18 h yielded fenestrane derivatives in 51–84% yield (Scheme 25).

The reaction involves the formation of five carbon–carbon bonds. The dicobalt octacarbonyl-catalyzed carbonylative [2 + 2 + 1] cycloaddition of a diyne with carbon monoxide followed by a subsequent intramolecular [4 + 2] cycloaddition provides fenestrane derivative. The central triple bond acts as a double functionality that could be used in both cyclizations. Thus, a new catalytic route to fenestrane derivatives *via* the dicobalt octacarbonyl-catalyzed cycloaddition of dienediynes in a one-pot reaction was developed.



	R	yield(%)	
72	H	19	**73**
74	Me	64	**75**
76	*n*-Bu	57	**77**
78	Ph	73	**79**

Scheme 26.

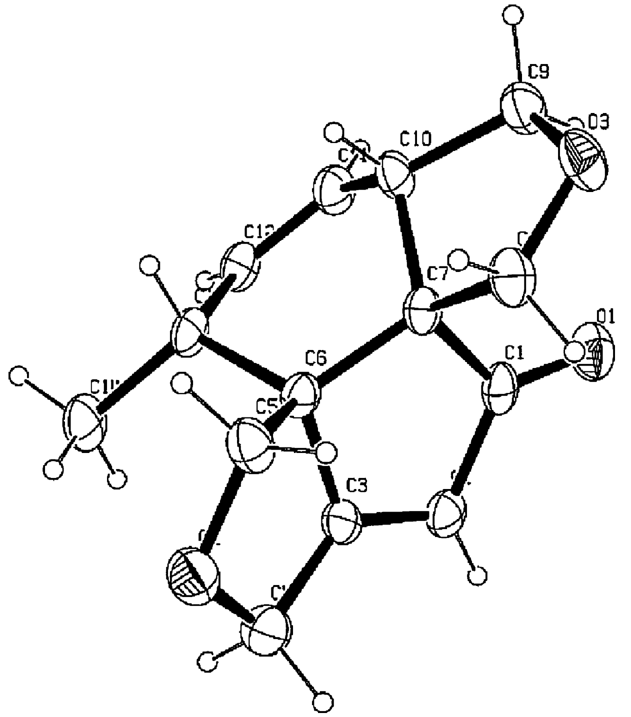


Fig. 9. X-ray structure of **73**. Reproduced from Ref. [108] with permission.

4.2.2. *Synthesis of tetracycle: cobalt carbonyl-catalyzed tandem [2 + 2 + 1]/[4 + 2] cycloaddition of dienediyne to new tetracycles [108]*

In a continuation of the previous study [109], the tandem PKR and Diels–Alder reaction of newly designed dienediyne substrates was explored to generate new polycyclic compounds.

Treatment of dienediyne with dicobalt octacarbonyl in dichloromethane at 130 °C under 30 atm of CO for 18 h yielded the tetracyclic compounds in poor to high yield (19–73%) (Scheme 26).

The structural skeleton of the synthesized polycyclic compounds is disclosed for the first time in this study, as far as we are aware. There are four stereocenters in the molecule. The crystal structure (Fig. 9) shows that the termini of the diene of the dienediyne rotate in opposite directions and each proton on the 1- and 4-positions of diene moiety faces the same direction.

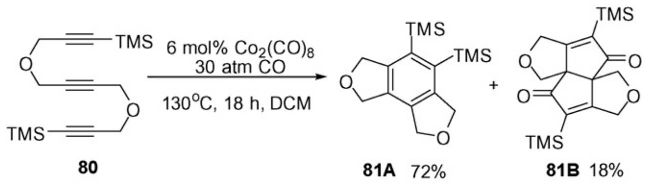
Thus, the disrotatory mode is allowed, as expected from the thermal Diels–Alder reaction. The yields were highly dependent upon the substrate itself. When the substrate was a terminal alkyne, the yield was rather poor, presumably due to side reactions, e.g. oligomerization of the substrate. Internal alkynes gave a much higher yield. Moreover, the introduction of a quaternary carbon center instead of a methylene group also promoted the yield to 55%, presumably due to the steric hindrance of the substituents on the quaternary carbon in the oligomerization.

4.3. *Cycloaddition of triynes*

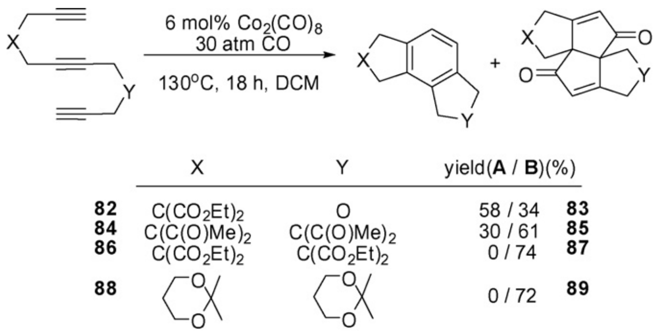
4.3.1. *Double carbonylative cycloaddition: $Co_2(CO)_8$-catalyzed double carbonylative [2 + 2 + 1] cycloaddition or [2 + 2 + 2] cycloaddition reaction of triynes [110]*

As an extension of the previous study [92], a cobalt carbonyl-catalyzed tandem [2 + 2 + 1]/[2 + 2 + 2] cycloaddition of triynes was studied.

Treatment of **80** with $Co_2(CO)_8$ (5 mol%) in CH_2Cl_2 at 130 °C for 18 h afforded a 4: 1 mixture of **81A** and **81B** in 90% yield (Scheme 27). Compound **81A** is a [2 + 2 + 2] cycloaddition product



Scheme 27.



	X	Y	yield(**A** / **B**)(%)	
82	$C(CO_2Et)_2$	O	58 / 34	**83**
84	$C(C(O)Me)_2$	$C(C(O)Me)_2$	30 / 61	**85**
86	$C(CO_2Et)_2$	$C(CO_2Et)_2$	0 / 74	**87**
88			0 / 72	**89**

Scheme 28.

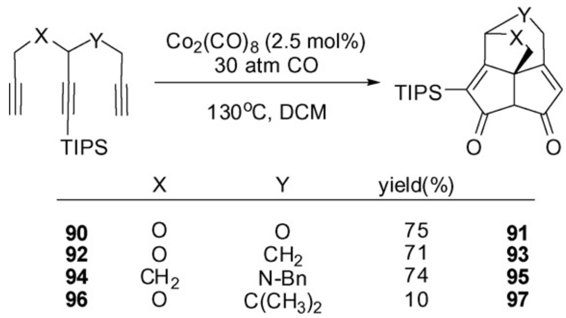
and **81B** is a new tetracyclic compound derived from a double [2 + 2 +1] cycloaddition.

Encouraged by the formation of **81B**, a variety of triynes was screened (Scheme 28).

When two oxygen bridges were changed to two carbon bridges, the ratio of **A**:**B** was completely reversed. The above results suggest that the oxygen atom of the ether linkage may play a key role in the transition state for the [2 + 2 +2] cycloaddition, the oxygen atom coordinating to the cobalt, thus positioning the triple bonds to yield [2 + 2 + 2] cycloaddition products. Therefore, for substrates with (an) oxygen bridge(s), the [2 + 2 + 2] cycloaddition is prevalent. A similar coordinating role for the oxygen atom of an ether linkage has been reported [94c] in other cycloaddition reactions. In the case of substrates without the oxygen bridge, the double [2 + 2 + 1] cycloaddition is more favored than the [2 + 2 + 2] cycloaddition. Thus, the reaction provides rapid access to tetracyclic skeletons of 5-5-5-5 and/or tricyclic skeletons of 5-6-5 ring systems depending upon the substrate used.

4.3.2. Synthesis of tetracycles: cobalt carbonyl-catalyzed carbonylated cycloaddition of triyne to functionalized tetracycle [111]

The synthesis of fenestranes [112] has attracted much attention due to the synthetic and theoretical points. For example, dienyne or ene-diyne [103a,113] have been successfully used in the synthesis of fenestrane derivatives. These studies suggest that triynes might be appropriate precursors for the construction of tetracycles possessing a fenestrane structure through two sequential [2 + 2 + 1] cycloaddition reactions.



	X	Y	yield(%)	
90	O	O	75	**91**
92	O	CH_2	71	**93**
94	CH_2	N-Bn	74	**95**
96	O	$C(CH_3)_2$	10	**97**

Scheme 29.

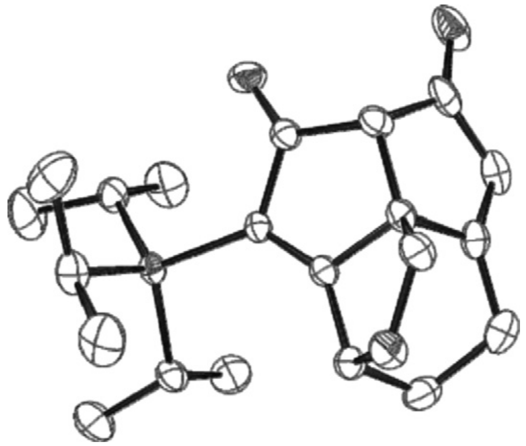


Fig. 10. X-ray structure of **93**. Reproduced from Ref. [111] with permission.

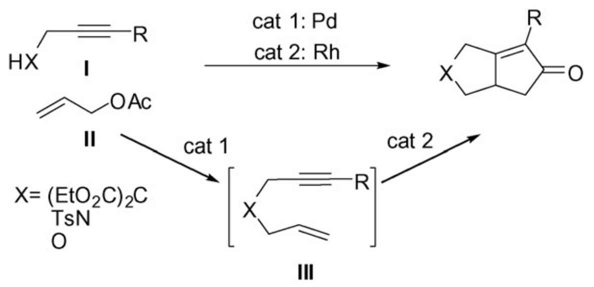
Treatment of triyne **23** with $Co_2(CO)_8$ (2.5 mol%) in CH_2Cl_2 at 130 °C for 1 day afforded the tetracyclic compound **24** in 75% yield (Scheme 29).

Instead of a fenestrane derivative, a novel 5.5.5.6 tetracyclic compound, which can be utilized as a versatile intermediate for polyquinane synthesis, was obtained. It is of particular note that, in one operation, six carbon-carbon bonds have been formed simultaneously, housing four rings in a single molecule. As expected, the double bond of the cyclopentadienone from the first cyclization had been used as an alkene part of the second PKR. However, as a result of the steric effect of the TIPS group, the second reaction occurred in the intermediate between the unsubstituted double bond and the triple bond. The structural proof of the tetracyclic structure was obtained through an X-ray study of **93** (Fig. 10).

Thus, the steric effect of the substituent in the inner triple bond plays an important role in controlling the destiny of the reaction path. Thus, the dicobalt octacarbonyl catalyzed double [2 + 2 + 1] carbonylative cycloaddition of triyne is unique for triynes in having a TIPS group in the inner triple bond. This study shows that by designing triynes bearing a proper steric group, a dicobalt octacarbonyl catalyzed double [2 + 2 + 1] carbonylative cycloaddition reaction of triyne can be carried out to yield a novel 5.5.5.6-tetracyclic di-enone system.

5. Sequential action of two different catalysts in one-pot reactions

Recent demands for environmentally friendly and economical synthetic processes have promoted the development of sequential transformations in one-pot reactions, in the presence of multiple catalysts and multiple components, to provide the desired products in the most efficient way [114]. They permit complex molecules to be constructed in only a few steps, thereby contributing to the protection of the environment. The understanding and practice of this concept may be taken from nature. Nature is highly selective and very efficient, employing sequential transformations: cellular reactions can be considered as a prototype [115]. Consequently, extensive studies have been conducted on the preparation and utilization of multi-functional catalyst systems in organic synthesis. However, in many instances, fundamentally new reaction sequences must be developed. For example, catalysts that contain both Lewis-acidic and -basic sites have been elegantly utilized for the simultaneous activation of substrates and reagents, making possible multiple cascade reactions in a one-pot reaction [116]. The tandem use of homogeneous catalysts



Scheme 30.

in a one-pot multistep transformation of substrates to products has been reported [117]. Despite the significant developments recently achieved, the development of a tandem reaction related to the PKR is relatively rare. The first demonstration was carried out by Jeong's group in 2000 [118]. They chose the following multiple C–C bond forming transformations for a demonstration (Scheme 30).

This transformation includes two reactions; the first allylation generates an enyne intermediate (**III**) via the Pd π-allyl complex [119] from a mixture of a propargyl compound (**I**) and allyl acetate (**II**). The following PKR of the resultant enyne yields a bicyclopentenone. They demonstrated a dual catalytic system that facilitated a one-pot palladium-catalyzed allylic alkylation followed by a rhodium-catalyzed PK annulation reaction. One year later, Evans and coworkers reported [37b] a single rhodium-catalyst to facilitate both transformations, allylic alkylation/PK annulation reaction, in a tandem sequence, using only the reaction temperature to modulate the catalytic activity.

5.1. A combination of Pd(II) and bulk Co on charcoal: catalytic asymmetric synthesis of cyclopentenones from propargyl malonates and allylic acetate in a one-pot reaction [120]

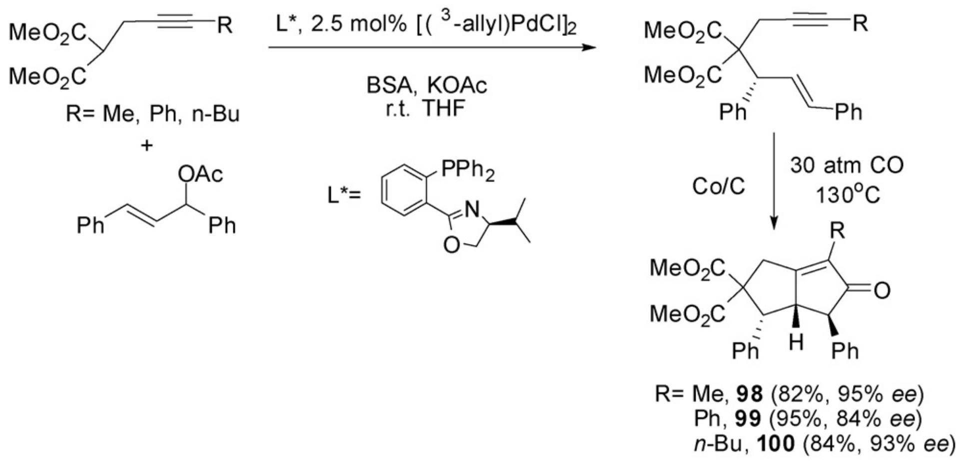
Much success has been achieved in the field of the transition-metal-mediated (or catalyzed) synthesis of cyclopentenones from readily available substrates [121]. However, demand for the development of a catalytic and enantioselective PK-type reaction remains high. The tandem use of two kinds of homogeneous catalyst in a one-pot multistep transformation of substrates to products has been reported [37b,118,122]. In particular, the use of a combination of Pd and Rh catalysts in the preparation of bicyclopentenones from propargyl malonates by Jeong's group [118] led us to study the use of Pd-catalyzed asymmetric allylic alkylation [123] to generate enynes in an enantioselective sense. The use of *in situ* generated enantiomerically enriched enynes as substrates in the PKR has not been reported even though increasing efforts are being devoted to the development of practical enantioselective versions of the PKR [124]. As the reaction shows, it should be a two-step one-pot reaction, the Pd(II)-catalyzed asymmetric allylic alkylation and cobalt-catalyzed PKR (Scheme 31).

After much experimentation, phosphinooxazoline ligand was chosen as the chiral ligand in the Pd-catalyzed asymmetric allylic alkylation and Co on charcoal was used as the catalyst in the PKR. Under these reaction conditions, bicyclic cyclopentenone was obtained in 95% with 96% ee. However, when $Co_2(CO)_8$ (20 mol%) instead of Co/C was used as a catalyst, only 2% of the product was isolated. Thus, the success of this tandem catalytic reaction is primarily due to the use of Co/C. In the Pd(II)-catalyzed allylic alkylation reaction, acetic acid was generated. The acid would then interact with the cobalt species in solution. However, the Co/C was found to be insensitive to acid or base. Generally, for good enantioinduction, low temperatures are required. However, our reaction conditions in the second step seem to be harsh: nevertheless no racemization occurred under these reaction conditions. When the reaction was carried out stepwise, the ee value of the final product was the same as that of the first. Thus, the ee value of the first asymmetric allylic alkylation reaction was maintained during the second cycloaddition reaction. This suggests that the first step is a stereoselective reaction and the second a stereospecific one.

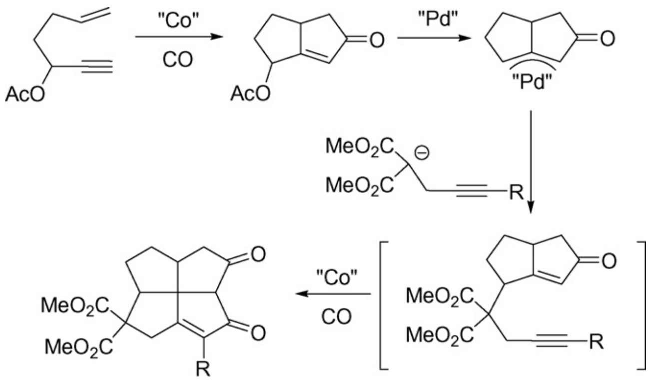
Thus, by using a combination of Pd(II) and cobalt on charcoal, a 'two-step one-pot' highly enantioselective PK-type reaction has been achieved. This was a rare example of the use of a combination of a homogeneous catalyst and a heterogeneous catalyst in a one-pot reaction.

5.2. Combination of cobalt nanoparticles and Pd(II) catalysts: three-step one-pot synthesis of fenestranes [125]

In the previous study [120], the usefulness of a combination of a homogeneous catalyst and a heterogeneous catalyst in the asymmetric synthesis of cyclopentenones was demonstrated. Thus, it was desirable to extend the same idea to the synthesis of fenestranes from readily available starting materials because most of the known synthetic methods for fenestranes involve multiple steps and have been associated with separation problems [112a,112b,113a,126]. The reaction should be a three-step one-pot synthesis of fenestranes from an enyne and alkyne diesters; the first step is a catalytic PKR, the second Pd(II)-catalyzed allylic alkylation, and the third another catalytic PKR (Scheme 32).



Scheme 31.



Scheme 32.

Treatment of **31** with **32** in the presence of cobalt nanoparticles and an allyl-Pd(II) complex led to the isolation of **33** in 84% yield (Scheme 33).

Two different catalysts, cobalt nanoparticles and allyl palladium chloride, were capable of promoting three sequential but independent catalytic cycles in the desired chronological order, thereby allowing a new molecular queuing process to take place. However, when a combination of Pd(II) and cobalt on charcoal catalysts was used, the cobalt on charcoal was not effective in the third step. Thus, this study demonstrated the usefulness of the combination of cobalt nanoparticles and Pd(II) catalysts in a three-step one-pot reaction for the construction of tetracyclic compounds, fenestranes.

5.3. Palladium and cobalt nanoparticles-immobilized on silica [127]

One of the challenging goals of synthetic chemistry is to discover reactions and strategies that allow for the facile conversion of simple compounds into complex molecules. In this regard, a variety of homogeneous catalysts have been used. The use of bimetallic catalysts (a combination of two catalysts) or bifunctional single catalysts in one-pot reactions has been developed [37b,118,122a]. Bimetallic nanoparticles have come to be of special interest [69i,128] because they may have great potential to be tailored with respect to the activity, selectivity, and stability of numerous possible combinations. The known combinations of bimetallic nanoparticles have been used as catalysts for specific single reactions utilizing the synergistic effect between the different metal atoms [69c,129] but not for a sequential reaction of two specific reactions corresponding to two different metals. It was envisioned that catalytic multistep one-pot reactions could be carried out by the use of bi- or poly-metallic nanoparticles as catalysts. Thus, the use of immobilized-palladium and cobalt nanoparticles on silica in the sequential allylic alkylation and Pauson–Khand reactions was studied.

The palladium nanoparticles immobilized on silica (1 wt% of Pd) were prepared by the reaction of $Pd(OAc)_2$ with colloidal silica in a mixture solvent of ethanol and toluene (v/v, 6:94) [130].

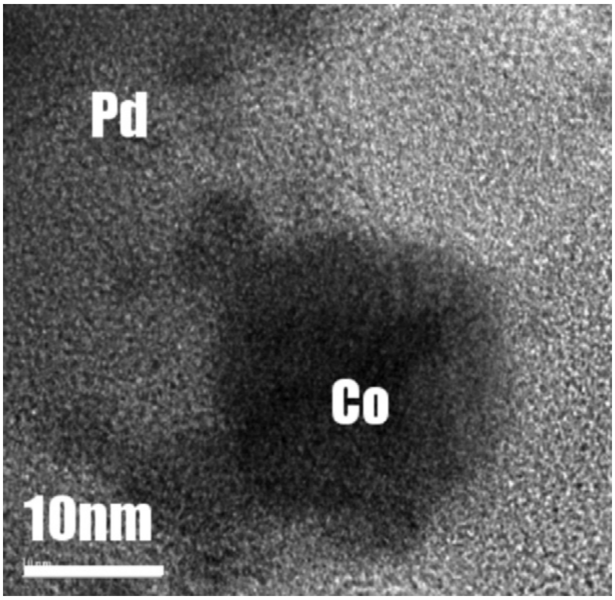
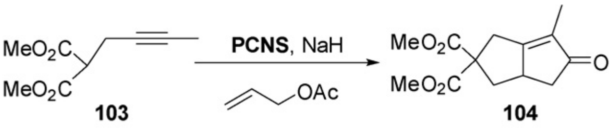


Fig. 11. TEM and EDS study of **PCNS**. Reproduced from Ref. [127] with permission.



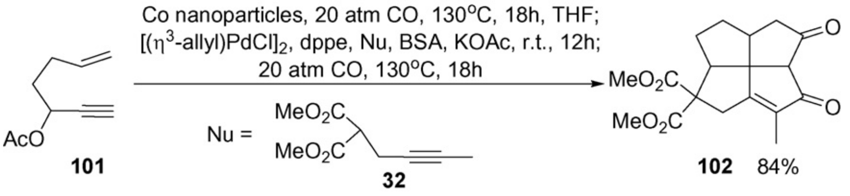
CO(atm)	temp(°C)	yield(%)
5	130	45
10	110	69
10	130	88

Scheme 34.

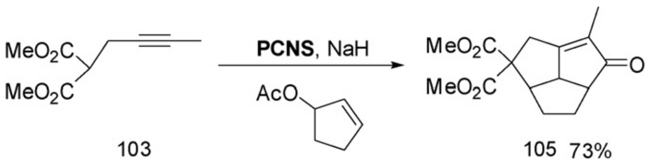
Although carbon–carbon bond formations catalyzed by palladium nanoparticles are well-known in Suzuki couplings [131] and Heck reactions [132], as far as we are aware, this is the first palladium nanoparticle catalyzed allylic alkylation. The reaction conditions including the reaction medium, base, and reaction time were screened for Pd-catalyzed allylic alkylation. The best yield (89%) was obtained when the reaction was carried out in THF and using NaH as a base for 6 h. When $NaHCO_3$ was used as a base in THF, the yield decreased slightly to 78%. Use of BSA as a base afforded only 23% of the product. When K_2CO_3 was used as a base in a mixture of THF and water (v/v, 5:1), no reaction was observed.

The palladium and cobalt nanoparticles immobilized on silica (**PCNS**) (14.5 wt% of Co and 1 wt% of Pd) was prepared by heating Pd on silica with colloidal cobalt in ethanol at reflux and was analyzed by TEM (and EDS) (Fig. 11). The HRTEM suggested that the bimetallic nanoparticles are in a cluster-in-cluster structure.

Using **PCNS** as a catalyst under various reaction conditions, the catalytic sequential allylic alkylation and PKR were studied (Scheme 34).



Scheme 33.



Scheme 35.

The **PCNS** is very active with an isolated product yield of 88% at 130 °C and a CO pressure of 10 atm. Thus, the **PCNS** catalyst is more active than heterogeneous catalysts (130 °C and 20 atm CO) based on metallic cobalt supported on mesoporous silica or charcoal [33,34]. However, when either the reaction temperature was decreased to 110 °C or the CO pressure was lowered to 5 atm, the catalytic activity decreases. Thus, to preserve a high catalytic activity, the reaction temperature and CO pressure have to be maintained at a minimum of 130 °C and 10 atm of CO, respectively.

When the recyclability of **PCNS** catalyst was checked, the **PCNS** catalyst sustained a degree of activity after three cycles (yield: 88%, 53%, and 49%, respectively). An ICPAES study shows that the percentages of cobalt and palladium bleed from **PCNS** after the first catalytic run are 0.9% of the original cobalt and 36% of the original palladium, respectively. Compared with the case of palladium, the leaching of cobalt was negligible. Owing to the bleeding of Pd, the reusability of the **PCNS** was greatly damaged. The catalytic reaction was effective with substituted enynes and allylic acetate. Especially when cyclic allyl acetate was used, a tricyclic enone was obtained in 73% yield (Scheme 35). The heteroatom-tethered substrates were tested to generate the corresponding products in high yields.

This study shows that bimetallic Pd/Co nanoparticles immobilized on solid support can be used as multicomponent catalyst systems as well as multifunctional catalysts. This strategy provides a facile methodology for the construction of bicyclic enones from easily available simple molecules. To the best of our knowledge, this is the first report of the use of immobilized bimetallic nanoparticles in two conceptually different catalytic reactions in a one-pot reaction.

6. Conclusion

This review focuses on the development of the catalytic Pauson–Khand reactions and related carbonylative cycloadditions studied in our laboratory. Many novel catalysts have been developed for the Pauson–Khand reactions. As can be seen, the catalytic systems for the Pauson–Khand reaction have now reached significant maturity. In particular, the utilization of heterobimetallic cobalt–rhodium nanoparticles as catalysts has uncovered several new novel reactions. The procedure can be characterized as environmentally friendly because the transformation occurs in the absence of additives except for the catalyst, and the catalyst can be reused semi-permanently without losing catalytic activity. In addition, a combination of two different metal nanoparticles, e.g. cobalt/palladium and cobalt/ruthenium, shows considerable potentials for future research developments of a combination catalyst, which may lead to new activities and other possibilities. Moreover, our results show that the combination of a homogeneous catalyst and a heterogeneous catalyst, e.g. a palladium complex and cobalt metal, may be a very useful catalytic system in a tandem reaction.

The cobalt carbonyl-catalyzed carbonylative cycloaddition of unsaturated hydrocarbons, such as diynes, dienynes, and triynes has been revealed to be a powerful synthetic tool in the construction of unnatural polycyclic compounds. Undoubtedly, the examples presented above represent only a part of the exciting and fascinating possibilities of the cobalt carbonyl-catalyzed tandem reactions in the synthesis of polycyclic compounds. The study of the cobalt carbonyl-catalyzed carbonylative cycloaddition reactions is now open for systematic investigations and many issues are still to be addressed.

Acknowledgments

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