The Pauson–Khand-Type Reaction Catalyzed by Transition Metal Nanoparticles

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Abstract: In this account, we survey our work on the use of transition metal nanoparticles as catalysts in Pauson–Khand-type reactions. Cobalt nanoparticles and Co/Ru, Co/Rh, and Co/Pd heterobimetallic nanoparticles have been used in Pauson–Khand-type reactions and related tandem reactions. In the case of Co/Ru nanoparticles, pyridylmethylformate can be used instead of carbon monoxide. We have developed environmentally friendly processes. The use of Co/Rh heterobimetallic nanoparticles allows the development of a new type of [2+2+1] cycloaddition of an α,β-unsaturated aldehyde with an alkyne.

1   Introduction

Transition metal-catalyzed coupling reactions have been established as one of the best methods in the synthesis of complex organic molecules.[1] Among them, the Pauson–Khand reaction (PKR) has been recognized as one of the best methods in the construction of 5-membered rings.[2] When the PKR was first disclosed,[3] the reaction conditions such as the reaction temperature and reaction time were harsh. Thus, only strained alkenes such as nor-bornene and norbornadiene were used as substrates. Initial studies on the PKR had focused on finding a promoter, which lowered the reaction temperature and lessened the reaction time.[4] Promoters such as TMO, NMO, alkaloid *N*-oxide, sulfide, amine, and sulfoxide were developed.[5] Recyclable polymer-supported amine *N*-oxide[6] was also developed as a promoter. After promoters were found, many research groups tried to find cobalt compounds, which easily provided an empty coordination site and was easily generated in solution. Actually, many useful catalytic systems such as (indenyl)Co(CO)$_2$, (indenyl)Co(cod), Co$_2$(CO)$_8$, and Co$_4$(CO)$_{12}$ were developed.[7] From the study on homogeneous catalytic systems, any system capable of generating in situ cobalt carbonyl species in a solution could be used as a catalyst. It became important how to generate in situ a cobalt carbonyl species in a solution. Thus, a reduction of Co(acac)$_2$ with NaBH$_4$ followed by treating with CO[8] had been tried. This system is quite active for PKR. However, when cobalt metal suspension was generated by a reduction of cobalt halide with sodium or lithium naphthalenide in THF, the cobalt metal suspension was sensitive to air and the handling of the cobalt metal suspension was not easy. How then can a cobalt metal suspension be stabilized? This Account highlights our progress in developing new heterogeneous catalysts based on transition metal nanoparticles that operate under mild reaction conditions.

Recently, transition metal nanoparticles are of considerable interest as catalysts in organic and inorganic transformations. Being small in size is expected to increase the nanoparticle surface tension. This makes surface atoms very active. In many cases, the inherent advantages of heterogeneous catalysts, such as ease of product separation and catalyst recycling, are observed. However, the activity and selectivity of catalyst nanoparticles are strongly dependent on their size, shape, surface structure, and their bulk and surface composition. A large number of review articles provide extensive coverage of the subject.[9] Moreover, the preparation, characterization, and mechanism of formation of transition metal nanoparticles have been extensively reviewed,[10] and therefore, these subjects are not included in this Account. For a complete overview of the nanocatalysis the reader is referred to literature.

2   Cobalt on Mesoporous Silica: The First Heterogeneous PKR Catalyst[11]

Until recently, most studies related to homogeneous catalysis. In order to commercialize a process, the development of a heterogeneous catalyst is a prerequisite. Thus, there have been many trials to achieve heterogeneous catalysis. For example, immobilization of cobalt carbonyls on polystyrene-PPh$_2$ resin and polyether dendron-functionalized polystyrene has been reported.[12]

Recently, mesoporous materials have attracted much attention due to their unique physical and chemical properties.[13] Particularly, they have high surface-to-volume ratio. They can be good candidates as supports. Thus, cobalt metal was deposited on mesoporous materials including MCM-41 and SBA-15 by reduction of cobalt halide or decomposition of $Co_2(CO)_8$ in the presence of mesoporous materials. Cobalt loading was adjusted to 9–10 wt%. The catalyst (Co/SiO$_2$) was easily recovered and reused several times without losing catalytic activity. However, the reaction conditions were quite harsh: 30 atm of CO, 130 °C, and 18 hours. The cobalt on a mesoporous material system is a quite effective catalyst for the intramolecular PKR, but displays low activity in the intermolecular PKR (Table 1). Furthermore, 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. After much experimentation, charcoal was our choice. Thus, cobalt metal was immobilized on charcoal
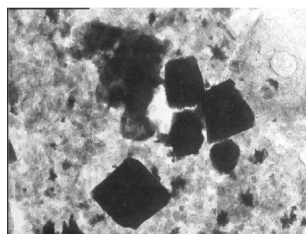

Figure 1   TEM images of Co on charcoal

(Figure 1) by refluxing $Co_2(CO)_8$ with charcoal in THF. The catalytic activity of Co/C strongly depends on the amount of cobalt on charcoal (wt%). The optimum cobalt loading on charcoal was about 12 wt%. The black Co/C shows ferromagnetism and is easily recovered by filtration or by using a magnet. Cobalt on charcoal was an effective catalyst for the intra- and intermolecular PKR (Table 2) and can be reused more than 10 times without losing catalytic activity.

The heterogeneous catalysts, Co/SiO$_2$ and Co/C, have many advantages such as stability, reusability, and ease of operation, but have disadvantages such as the high temperature and pressure of the CO. There have been a few reports on the cobalt-catalyzed PKR under mild reaction conditions.[14] However, additives such as molecular sieves, 1,2-dimethoxyethane, and water have to be added. Thus, catalytic systems without using other additives under mild reaction conditions have not been reported. While we were seeking a catalytic system under mild reaction conditions, transition metal nanoparticles had attracted our attention.

Biographical Sketches

Kang Hyun Park was born in AnGang, Gyeongju (Korea) in 1976. He studied chemistry at Kyungpook National University where he obtained his BS degree in 2000. He received his PhD in 2005 under the supervision of Y. K. Chung and was working on the synthesis of transition metal nanoparticles and their application in organic reactions. His main interests are in the field of organometallic chemistry and multi-step synthesis. In 2003, he was one of the Brain Korea 21 awardees for Outstanding Research Accomplishment in the Division of Chemistry and the College of Natural Sciences, SNU.
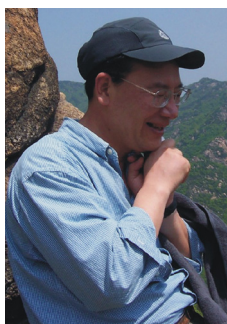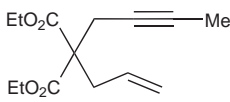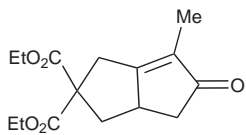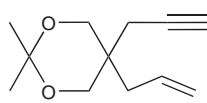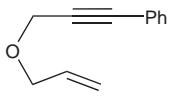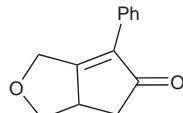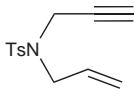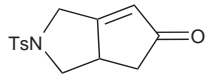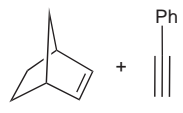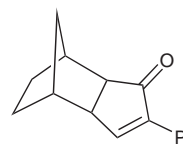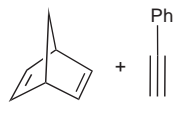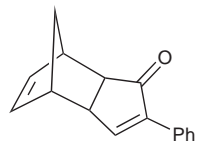
Young Keun Chung was born in Seoul, Korea, in 1953. He studied Chemistry at Seoul National University (BS in 1977) and received his PhD in 1984 from Brown University under the guidance of Prof. D. A. Sweigart. He did his postdoctoral work with Prof. P. C. Ford at University of California at Santa Barbara in 1984–1985. In 1985, he joined the Korea Institute of Science and Technology. In 1987, he was appointed as an Assistant Professor at Seoul National University and promoted to Associate Professor and Full Professor in 1991 and 1997, respectively. His research interests include the development of new transition metal-catalyzed reactions.

Table 1   Pauson–Khand Reaction Catalyzed by Co/SBA-15[a]

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			18	92
2			6.5	96
3			18	98
4			6.5	88
5			6.5	11[c]
6			6.5	36[c]

[a] Reaction conditions: 0.1 g of Co/SBA-15 (cobalt 9–10 w%), 1.26 mmol of substrate, 130 °C, CH_2Cl_2, 20 atm of CO.

[b] Isolated yield.

[c] Aromatic compound was isolated.

Table 2   Test for the Reusability of the Catalyst[a]

Runs	Catalyst	Yield (%)[b]
1	Co/Charcoal (12%)	91
2	Recovered from #1	98
3	Recovered from #2	95
4	Recovered from #3	97
5	Recovered from #4	98
6	Recovered from #5	95
7	Recovered from #6	98
8	Recovered from #7	98
9	Recovered from #8	98
10	Recovered from #9	98

[a] Reaction conditions: 0.1 g catalyst and 1.26 mmol substrate were used.

[b] Yield of isolated product.

3   Colloidal Cobalt Nanoparticles

3.1   The First Use of Transition Metal Nanoparticles in the PKR[15]

The transition nanoparticles have a characteristic high surface-to-volume ratio, and consequently a large fraction of the metal atoms are at the surface and hence are available for catalysis.[16] Many colloidal transition metal nanoparticles, especially noble metals, have been applied as catalysts for the hydrogenation of olefins, for carbon-carbon coupling reactions and for other reactions.[17] Thus, we studied the use of cobalt nanoparticles as catalysts in the PKR.

Several synthetic methods[18] have been applied in the fabrication of colloidal cobalt nanoparticles, including the thermal and sonochemical decomposition of organometallic compounds, and the reduction of metal salts. We have applied a recently developed synthetic method 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, dicobalt octacarbonyl, oleic acid, trioctyl phosphine, and dioctyl ether were mixed with stirring at room temperature. The mixture was heated slowly to

reflux and the refluxing was continued for 30 minutes, after which the reaction mixture was allowed to cool to room temperature. A black precipitate was obtained by adding ethanol followed by washing with acetone and drying in vacuo. The particles are quite stable even in air.

Figure 2 TEM image of collidal cobalt nanoparticle (a) before the reaction and (b) after the reaction

Scheme 1

As expected, the cobalt nanoparticles are more active than heterogeneous cobalt catalysts supported on either mesoporous silica or charcoal (Scheme 1). The colloidal cobalt (Figure 2) is very active with a high yield of product at 130 °C and a CO pressure of 5 atm (Table 3). The cobalt nanoparticles were quite effective for intra- and intermolecular PKR. However, when the substrates were heteroatom-bridged enynes, the reaction conditions were rather harsh, the pressure of CO being 10 atm. The reaction conditions are rather sensitive to the substrates.

Table 3 Pauson–Khand Reactions with Cobalt Nanoparticles[a]

Entry	Substrate	Product	Yield (%)[b]
1			97
2			97
3[c]			90
4[c]			85
5			94
6			97
7			93

[a] Reaction conditions: colloidal cobalt nanoparticles (25 mg, 45 wt% cobalt), substrate (0.42 mmol), CO (5 atm), THF, 130 °C, 12 h.
[b] Isolated yield.
[c] 10 Atm CO applied.

3.2 The First Catalytic PKR in Aqueous Media: Water-Stabilized Colloidal Cobalt Nanoparticles[19]

Although heterogenized catalysts can solve the separation problem, they still require an organic solvent as a reaction medium. Recently, the possibility of the substitution of conventional organic solvents by the supercritical fluids CO_2 or ethylene was demonstrated by Jeong and co-workers.[20] However, reaction conditions have not yet seen much improvement and are still quite harsh, requiring a long reaction time. Recently, as a consequence of the increasing demand for efficient, safe, and environmentally friendly processes, the application of homogeneous catalysts in aqueous solution and on liquid supports has attracted tremendous attention for many catalytic reactions. In these circumstances, the development of aqueous colloidal cobalt nanoparticles[21] has attracted our attention. We envisioned that the use of aqueous colloidal cobalt nanoparticles should provide an opportunity to study the PKR in an aqueous solution.

Aqueous colloidal cobalt nanoparticles were prepared by reducing an aqueous solution of cobalt acetate containing sodium dodecyl sulfate (SDS) surfactant. The cobalt nanoparticles were stable for a limited time, 2–3 days in air and quite stable without oxygen, and easy to handle.
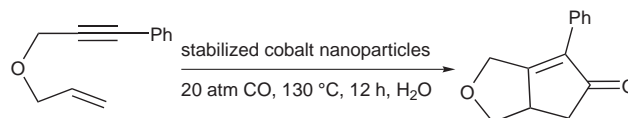
Scheme 2

We tested the catalytic reaction using the water-stabilized cobalt nanoparticles as catalysts (Scheme 2). The optimized reaction conditions were 20 atm of CO and 130 °C. Thus, the reaction conditions were not improved. The water-stabilized cobalt nanoparticles were quite effective for the intramolecular PKR (Table 4). However, we failed to obtain the intermolecular PKR products. We envisioned 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 substrate. Thus, there was no requirement to employ water-soluble substrates.

Recovery and reusability of the catalytic system were tested by carrying out consecutive cycles with the same catalyst in aqueous solution. The catalytic system can be recycled at least four times without loss of performance and without producing any waste.

Table 4 Pauson–Khand Reactions in Water[a]

Entry	Substrate	Product	Pressure (atm)	Yield (%)[b]
1			5	5
2			20	71
				24
3			20	90
4			20	92
5			20	88

[a] Reaction conditions: substrate (0.58 mmol), cobalt nanoparticle (23 mg, the amount of calculated Co), 130 °C, 20 atm CO, and 12 h.
[b] Isolated yield.

4   Immobilized Cobalt Nanoparticles on Charcoal
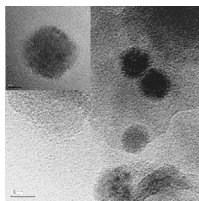
4.1   Pauson–Khand Reaction[22]

Figure 3   TEM image of cobalt nanoparticles on charcoal

The use of cobalt nanoparticle (Figure 3) as a catalyst in the PKR made a good contribution in the relief of harsh reaction conditions. However, there could be inconvenience in use and storage. To overcome the disadvantages of nanoparticles in catalysis, we researched how to combine the merits of conventional heterogeneous catalysts with the high catalytic activity of cobalt nanoparticles. We chose charcoal as a support and prepared cobalt nanoparticles on charcoal (**CNC**).

Refluxing the synthesized cobalt nanoparticles with dried charcoal yielded **CNC**. As expected, **CNC** is quite stable even in air for several months. Using **CNC** as a catalyst, we investigated the PKR (Table 5). To preserve high catalytic activity, the reaction temperature and CO pressure have to be maintained at a minimum of 130 °C and 5 atm of CO, respectively. The catalytic activity of **CNC** is slightly lower than that of the cobalt nanoparticles for the intermolecular reaction.

Table 5   Pauson–Khand Reaction with **CNC**[a]

Entry	Substrate	Product	Pressure (atm)	Yield (%)[b]
1			5	98
2			5	97
3			5	96
4			10	87
5			10	77
6			10	94
7			15	99
8			15	98

[a] Reaction conditions: CNC (0.1 g, 12 wt%), 0.48 mmol of enyne, THF, 130 °C, 18 h.
[b] Isolated yield.

4.2 The Catalytic Reductive Pauson–Khand Reaction[22]

Complexes of cobalt are known to be hydrogenation catalysts, but are mostly selective for conjugated systems.[23] The complex $Co_2(CO)_8$ and derivatives are known as hydrogenation catalysts for alkenes under specific conditions. In the previous section, we demonstrated that **CNC** is a quite effective catalyst for carbonylative cycloaddition reaction. Thus, we envision that **CNC** can be used as bifunctional catalyst in the PKR and hydrogenation (Scheme 3). To use **CNC** as a bifunctional catalysts in 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** for each reaction, and second, hydrogenation of substrates should not take place before a PKR of the substrate occurs.
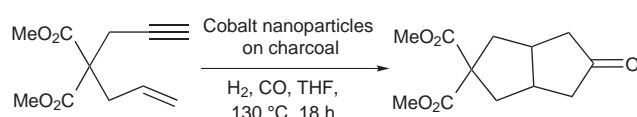
Scheme 3

Table 6 Hydrogenation of Enones under Various Conditions[a]

Entry	CO (atm)	H₂ (atm)	Yield (%)[b]
1		1	
2		5	90[c]
3	5	5	88[d]
4	10	5	93
5	20	5	95

[a] Reaction conditions: CNC (0.1 g, 12 wt%), 0.48 mmol of substrate, THF, 130 °C, 18 h.
[b] Isolated yield.
[c] Reactant (4 mol%) was recovered.
[d] Reactant (3 mol%) was recovered.

We first tested the catalytic activity of **CNC** for the hydrogenation of a PKR product (Table 6). With a pressure of 1 atm, no hydrogenation was observed. However, under 5 atm of H_2, 90% of the hydrogenated product was obtained with 4% recovery of the reactant. Interestingly, the presence of carbon monoxide did not interfere with the hydrogenation. After much experimentation, the optimum reaction conditions for the sequential PKR and hydrogenation were established: 130 °C under 5 atm of CO and 5 atm of H_2 for 18 hours. We screened various substrates for the sequential PKR and hydrogenation in a one-pot reaction (Table 7). Under our 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 ketones from enynes.

5 Heterobimetallic Nanoparticles

5.1 Ru/Co Heterobimetallic Nanoparticles: Catalytic Pauson–Khand Reactions in the Presence of Pyridylmethylformate[24]
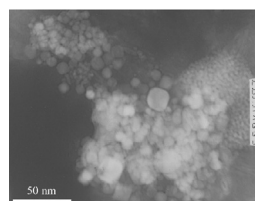
Figure 4 TEM image of **RuCNC**

Increasing environmental awareness has made the use of carbon monoxide undesirable and prompted the search for an alternative process that does not employ carbon monoxide or utilizes a substitute. In situ generated carbon monoxide could be a good candidate.[25] However, the synthetic utilization of generated carbon monoxide has been largely ignored. Recently, the use of decarbonylated CO from formates or aldehydes has been utilized in transition metal-catalyzed hydroxylcarbonylation, the Pauson–Khand reaction, and hydroesterification.[26] Thus, we have focused our efforts on the design and development of a new catalytic system consisting of immobilized transition metal nanoparticles with formate as an alternative to carbon monoxide.

Aldehydes and formates can be good candidates for our purpose because they have been studied with this aim for three decades.[27] We chose ruthenium metal as a decarbonylation catalyst.[28] The expected PKR product was obtained in a high yield when pyridylmethyl formate was used as with $Ru_3(CO)_{12}$ and cobalt nanoparticles, but no reaction product was obtained when cinnamaldehyde or benzyl formate was used. Thus, we decided to use pyridylmethyl formate instead of CO. The successful initial result encouraged us to make heterobimetallic Ru/Co nanoparticles immobilized on charcoal (**RuCNC**) and use them as catalysts in PKR (Scheme 4). The **RuCNC** (Figure 4) was prepared by the reaction of ruthenium nanoparticles on charcoal (in situ generated by the reaction of $RuCl_3$ with ethylene glycol followed by heating with charcoal) with cobalt nanoparticles in THF. TEM images of **RuCNC** revealed the cluster-in-cluster structure.

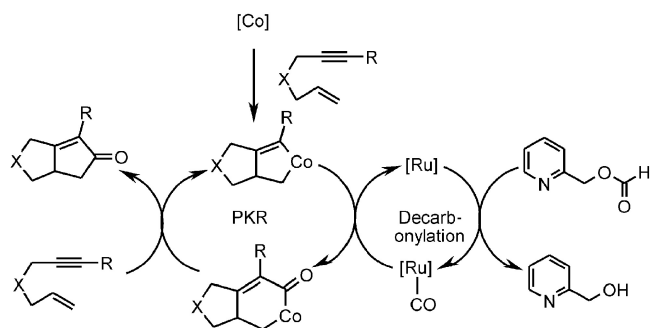**Table 7** Sequential Pauson–Khand Reaction and Hydrogenation[a]

Entry	Substrate	Product	Yield (%)[b]
1			98[c]
2			90
3			95
4			94
5			92
6			87
7			54[d]
8			43[d]

[a] Reaction conditions: CNC (0.1 g, 12 wt%), 0.48 mmol of substrate, THF, 130 °C, 18 h.
[b] Isolated yield.
[c] Co/C was used.
[d] A hydrofomylated compound was obtained as a minor product.

Scheme 4 A plausible reaction mechanism

RuCNC was quite an effective catalyst for the intra- and intermolecular PKR (Table 8). The optimized reaction conditions were established as follows: 1.5 equivalents pyridylmethyl formate, THF, 12 hours, and 130 °C. Interestingly, when the reactor was filled with nitrogen, a higher yield was obtained. For the intramolecular PKR, the catalyst system could be re-used five times without loss of activity; the maximum reusability has not yet been tested. The reusability can be understood when we consider that there is almost no leaching of cobalt and ruthenium from the charcoal surface. The intramolecular cycloaddition proceeded smoothly with mono-substituted olefins. Heteroatom-bridged enynes produced oxo- and aza-bicyclic compounds from the corresponding substrates. In most cases, the yields of the intramolecular reactions are

almost quantitative. For intermolecular cycloadditions with **RuCNC** catalyst, satisfactory results are obtained with simple terminal alkynes, a conjugated alkyne, and a diyne. In the case of the diyne substrate, a double PKR

occurred. Thus, Ru/Co nanoparticles on charcoal have been developed as highly effective catalysts for intra- and intermolecular PKR in the presence of pyridylmethyl formate instead of carbon monoxide.

Table 8   Pauson–Khand Reaction with **RuCNC**[a]

Entry	Substrate	Product	Yield (%)[b]
1			75
2			97
3			98
4			97
5			89
6			93
7			90
8			90
9			85

[a] Reaction conditions : THF, 12 h, 130 °C.
[b] Isolated yields.

5.2   Rh/Co Heterobimetallic Nanoparticle-Catalyzed Pauson–Khand-Type Reaction between Alkynes and Olefinic Aldehydes[29]

Recently, the use of heterobimetallic nanoparticles with a fixed stoichiometry as catalysts has attracted much attention because their catalytic performance is generally superior to that of a single nanometal by itself.[30] Thus, we decided to create heterobimetallic nanoparticles and to study their catalytic activity in the Pauson–Khand-type reaction. What kinds of heterobimetallic nanoparticles were suitable as catalysts? Studies on homogeneous rhodium catalysts might provide clues to the development of a heterogeneous catalytic system: when rhodium complexes were used as catalysts for the Pauson–Khand reaction, the pressure was usually 1 atm.[31] Thus, we decided to prepare Co/Rh heterobimetallic nanoparticles, immobilize them on charcoal, and study their use in Pauson–Khand-type reactions.
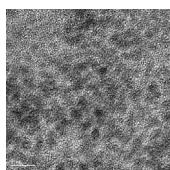

Figure 5   HRTEM image of **Co₂Rh₂**

In order to create bimetallic nanoparticles with a fixed stoichiometry, we employed the strategy of decomposition of bimetallic organometallic cluster compounds; it would appear that the use of molecular cluster compounds as precursors is one of the most attractive methods available.[32]

A solution containing the heterobimetallic carbonyl compound $Co_2Rh_2(CO)_{12}$ was injected into a solution of *o*-dichlorobenzene, oleic acid, and trioctylphosphine oxide at 180 °C. Heating the resulting solution at 180 °C for two hours afforded a black solution. The heterobimetallic carbonyl compound was fully decomposed to heterobimetallic nanoparticles. After removal of all the solvent, the black precipitates were re-suspended in THF. In order to immobilize Co/Rh nanoparticles (**Co₂Rh₂**) on charcoal, the THF solution of Co/Rh nanoparticles was refluxed with flame-dried charcoal in THF for 12 hours. According to the ICP-AES data of the immobilized Co/Rh heterobimetallic nanoparticles, the ratio of Co:Rh was 1.09:1. Thus, the method used in this study always gave fixed-stoichiometric Co/Rh bimetallic nanoparticles. The HRTEM (Figure 5) shows that the diameter of the resulting well-dispersed, isolated, and anchored bimetallic nanoparticles is approximately 2 nm. Thus, more than half of the atoms in the nanoparticles are exposed to reactant species in the reaction.[33]

The recent study of the use of an aldehyde instead of carbon monoxide in the PKR,[25] gave us the novel idea to use unsaturated aldehydes as a source of CO and alkene (Scheme 5). It has been well documented[34] that the reaction of aldehydes on metal surfaces releases hydrocarbons and carbon monoxide by decarbonylation. Thus, we studied the use of α,β-unsaturated aldehydes as a source of CO and alkene.
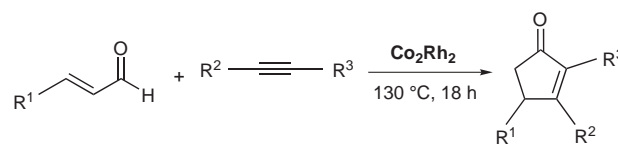
Scheme 5

Using **Co₂Rh₂** as a catalyst, α,β-unsaturated aldehydes such as acrolein, crotonaldehyde, and cinnamic aldehyde were screened (Table 9). As expected, a PKR product was obtained in reasonable to high yields with the concomitant formation of a coupling product in the case of acrolein. It is well known[35] that the PKR alkenes attached to electron-withdrawing groups (all π-conjugating) react anomalously, giving 1,3-dienes although some electron-deficient alkenes can be appropriate substances in the Pauson–Khand reaction under certain circumstances, such as in the presence of a promoter.[36] Thus, 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. Thus, α,β-unsaturated aldehydes have a dual function, slowly and continuously producing both olefin and CO in situ.

A few features have to be mentioned: when crotonaldehyde was used as a source of CO and propylene, the reaction was quite regioselective with respect to alkenes and alkynes. As with the traditional PKR, terminal alkynes yielded predominantly 2-substituted ketones. It is well known[37] that neither terminal nor internal alkenes usually demonstrate meaningful regioselectivity in reaction with alkynes. Thus, the high regiocontrol is highly noteworthy. When cinnamic aldehyde was used as a source of CO and styrene, under our reaction conditions, no polymers derived from free styrenes were found. Therefore, using these protocols, styrene might be slowly generated. In this case, it would seem to be the same situation as a highly diluted solution. When the re-usability 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.

When methacrolein was used, no reaction was observed, presumably due to the steric hindrance of the methyl group.

Unfortunately, the catalytic system was not effective for an intramolecular reaction. Further study will hopefully disclose a catalytic system that will be effective for an intramolecular reaction.

Table 9 Pauson–Khand-Type Reaction Catalyzed by Immobilized Co_2Rh_2 on Charcoal[a]

Entry	Substrate			Yield (%)
	R^1	R^2	R^3	
1	H	H	Ph	48[b]
2	H	H	Ph	49[b]
3	H	H	Ph	60
4	H	H	Bu	51
5	H	H	C_5H_{11}	54
6	H	H	TMS	43
7	H	Ph	Ph	74
8	H	Me	Ph	57
9	CH_3	H	Ph	77
10	CH_3	H	Bu	70
11	CH_3	H	TMS	56
12	CH_3	Ph	Ph	71
13	Ph	H	Ph	75
14	Ph	H	Bu	71
15	Ph	H	TMS	69
16	Ph	Ph	Ph	70
17[c]	Ph	H	Ph	72
18[d]	Ph	H	Ph	73
19[d]	Ph	H	Ph	73
20[d]	Ph	H	Ph	70

[a] Isolated yields. Reaction conditions: aldehyde (15.8 mmol), alkyne (9.1 mmol), catalyst (0.029 mmol), and THF (5 mL).
[b] 0.32 M THF solution.
[c] Catalyst : recovered from #13.
[d] Catalyst: recovered from the above entry.

5.3 Palladium and Cobalt Nanoparticles Immobilized on Silica: One-Pot Synthesis of Bicyclic Enones by Catalytic Allylic Alkylation and Pauson–Khand Reaction[38]

Recently, the use of bimetallic catalysts or bifunctional single catalysts in one-pot reactions has been developed.[39] Bimetallic nanoparticles have come to be of special interest 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 a specific reaction utilizing the synergistic effect between the different metal atoms but not for a sequential reaction of two specific reactions corresponding to two different metals.[40] We envision that catalytic multistep one-pot reactions can be carried out with the use of bi- or polymetallic nanoparticles as catalysts.

One of the challenging goals of synthetic chemistry is to discover reactions and strategies that allow the facile conversion of simple compounds into complex molecules. In this regard, we chose bicyclic enones as target molecules and studied the use of immobilized-palladium and cobalt nanoparticles on silica in the sequential allylic alkylation and Pauson–Khand reaction (Scheme 6). A similar homogeneous reaction was reported by Jeong's group.[41] They utilized a dual catalytic system to facilitate a one-pot palladium-catalyzed allylic alkylation followed by a rhodium-catalyzed PK annulation.

The palladium nanoparticles immobilized on silica (1 wt% of Pd) were prepared by the reaction of $Pd(OAc)_2$ with colloidal silica in a mixed solvent of ethanol and toluene (v/v, 6:94). We first tested the allylic alkylation catalyzed by Pd nanoparticles. We also screened the reaction conditions including reaction medium, base, and reaction times. The best yield (87%) was obtained when the reaction was carried out in THF using NaH as a base for six hours. As far as we are aware, this is the first palladium nanoparticle-catalyzed allylic alkylation.
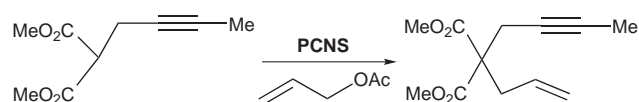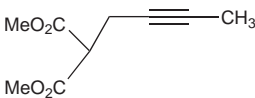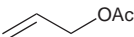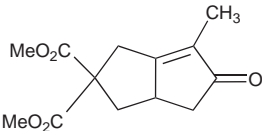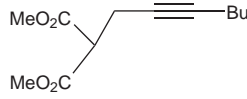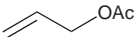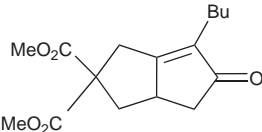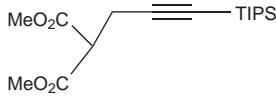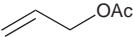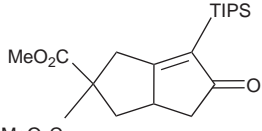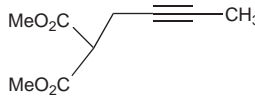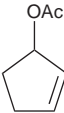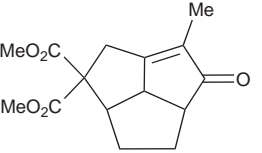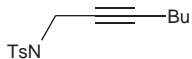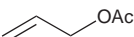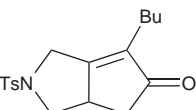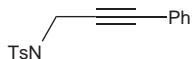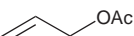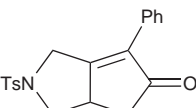
Scheme 6

We next synthesized palladium and cobalt nanoparticles immobilized on silica (**PCNS**) to use as a catalyst in the catalytic sequential allylic alkylation and PKR. The **PCNS** (14.5 wt% of Co and 1 wt% of Pd) was prepared by refluxing Pd on silica with colloidal cobalt in ethanol and was analyzed by TEM (and EDS).
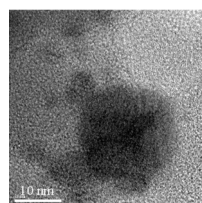
Figure 6 TEM image of **PCNS**

We investigated the catalytic sequential allylic alkylation and the PKR using **PCNS** (Figure 6) as a catalyst. 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. The **PCNS** catalyst sustained a degree of activity after three cycles, with 49% product yield being obtained. An ICP-AES study shows that the percentages of cobalt and palladium leached from **PCNS** after the first catalytic run were 0.9% of the original cobalt and 36% of the original palladium, respectively. Owing to the leaching of Pd, the reusability of the **PCNS** was greatly damaged. However, the **PCNS** may be used at least three times with moderate to high yields.

Table 10 Sequential Allylic Alkylation and Pauson–Khand Reactions[a]

Entry	Alkynes	Nucleophiles	Products	Yield (%)[b]
1				88
2				82
3				84
4				73
5				68
6				75

[a] Reaction condition: THF, NaH, substrate (0.54 mmol), **PCNS** (0.10 g), 130 °C, 10 atm CO, 18 h.
[b] Isolated yield.

We next investigated the versatility of the alkynes and nucleophiles (Table 10). The catalytic reaction was quite effective. Thus, we have shown that bimetallic Pd/Co nanoparticles immobilized on solid support can be used as multicomponent catalyst systems as well as multifunctional catalysts.

6.2   Use of a Combination of Cobalt Nanoparticles and Pd(II) Complex as a Catalyst in the Synthesis of Fenestranes[42]

In many cases, the usefulness of transition metal nanoparticles as catalysts is in their high reactivities, which are related to their high surface-to-volume ratio, compared to the heterogeneous bulk metal catalysts. In addition to the high surface-to-volume ratio, transition metal nanoparticles may have other unique properties, which cannot be reasonably explained right now. In order to demonstrate their usefulness in catalysis, we studied their use with a combination of other catalyst(s) in a one-pot reaction of a synthesis of complex organic molecules from readily available starting materials.

We chose fenestranes as target compounds since most of the known synthetic methods for fenestranes involve multiple steps and have been associated with separation problems.[43] Recently, we reported on the catalytic synthesis of fenestranes from dienediyne in the presence of $Co_2(CO)_8$ under carbon monoxide.[44] However, dienediynes have to be synthesized by multistep reactions.

A strategy for synthesizing fenestranes from commercially available starting materials was shown in Scheme 7. The first and second steps were easily accomplished by using cobalt on charcoal and Pd(II) catalysts, respectively. However, cobalt on charcoal was not effective in the third step. It appeared that the cobalt on charcoal system was damaged after the second step. However, cobalt nanoparticles were tolerant of all the reaction conditions and quite effective for both the first and third reactions. Thus, fenestranes were prepared from readily available chemicals in a three-step one-pot reaction (Scheme 8). This is a rare example of the use of transition metal nanoparticles as catalysts with the conventional homogeneous catalyst, Pd(II) in the synthesis of complex organic compounds in a one-pot reaction.
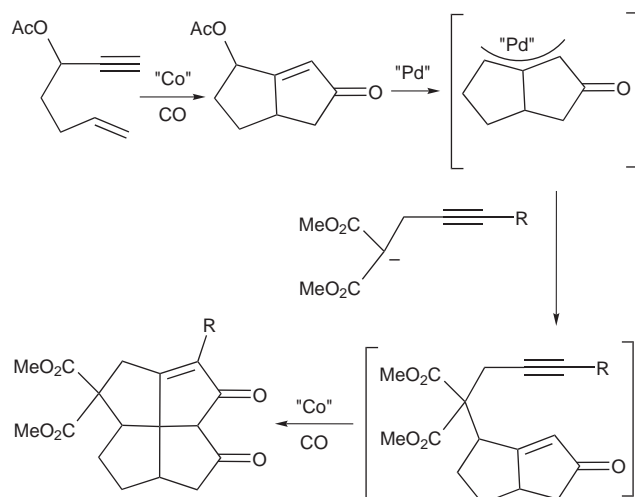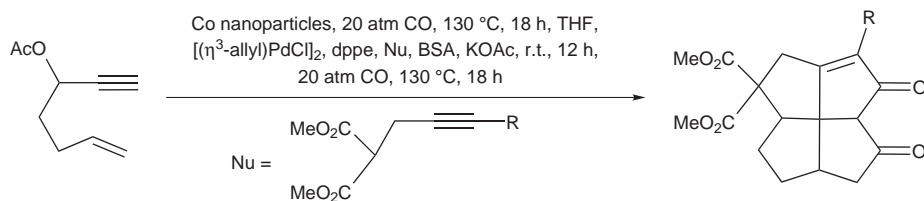
Scheme 7

7   Conclusion

We have developed transition metal nanoparticle-catalyzed Pauson–Khand reactions with the aim of the PKR becoming more useful, easy to use, safe, and an economical process. We believe that we have achieved our purpose to some degree. We expect that our methodology can be extended to other catalytic systems in the near future.

Acknowledgment

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Scheme 8

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