

Immobilized Co/Rh Heterobimetallic Nanoparticle-Catalyzed Pauson–Khand-Type Reaction

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Abstract: Co/Rh heterobimetallic nanoparticles were prepared from cobalt-rhodium carbonyl clusters $[\text{Co}_2\text{Rh}_2(\text{CO})_{12}]$ and $[\text{Co}_3\text{Rh}(\text{CO})_{12}]$ and immobilized on charcoal. HR-TEM revealed that the size of the heterobimetallic nanoparticles was *ca.* 2 nm and ICP-AES analysis showed a 2:2 and a 3:1 cobalt-rhodium stoichiometry (Co_2Rh_2 and Co_3Rh_1) in the heterobimetallic nanoparticles. The Co/Rh heterobimetallic nanoparticles immobilized on charcoal were used as a catalyst in the Pauson–Khand-type reaction under 1 atm of CO. The catalytic reactivity was highly dependent upon the ratio of Co:Rh with the highest reactivity being observed when the ratio was 2:2 (Co_2Rh_2). The Co_2Rh_2 immobilized catalyst is quite an effective catalyst for intra- and intermolecular Pauson–Khand-type reactions. When the immobilized

Co_2Rh_2 catalyst was used as a catalyst in the Pauson–Khand-type reaction in the presence of an aldehyde instead of carbon monoxide, the catalytic system was highly efficient. When the reaction was carried out in the presence of chiral diphosphines, *ee* values up to 87% were observed. The catalytic system can be reused at least five times in the presence of chiral diphosphines without loss of catalytic activity and enantioselectivity. The addition of $\text{Hg}(0)$, a known heterogeneous catalyst poison, completely inhibits further catalysis. Thus, an environmentally friendly and sustainable process was developed.

Keywords: aldehyde; asymmetric reaction; cobalt; heterogeneous catalyst; nanoparticles; Pauson–Khand reaction; rhodium

Introduction

Metal nanoparticles are a subject of great interest in chemistry and materials science because they display unusual physical and chemical properties, which are distinct from those of both the bulk phase and isolated molecules.^[1] Their unique features can be tailored by altering their size, the organization of the nanoparticle crystal lattice, and the microenvironment surrounding them. For noble metal nanoparticles, catalytic applications are considered, since a unique combination of reactivity, stability, and selectivity is expected. During the past decade, transition metal nanoparticles have been revealed as very efficient catalysts for various reactions, such as hydrogenation, oxidation, coupling reactions, and some photocatalytic reactions.^[2]

Since the initial discovery of the Pauson–Khand reaction,^[3] it has been extensively developed by numerous researchers. In particular, the development of a catalytic and asymmetric version of the Pauson–Khand reaction makes it one of the most convergent and versatile methods for the construction of 5-membered rings.^[4] In the beginning, dicobalt octacarbonyl had been used, but recently several other transition metal complexes^[5] including Ti, Ru, Rh, Ir, Ni, Mo, and W, and heterobime-

tallic complexes (Co/Mo and Co/W)^[6] have been employed in the Pauson–Khand reaction. Recently, the use of cobalt nanoparticles as catalysts was also reported by us.^[7]

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.

Recently, the use of heterobimetallic nanoparticles as catalysts has attracted much attention because their catalytic performance is generally superior to that of a single nanometal by itself.^[8] 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.^[9] Thus, we decided to prepare Co/Rh heterobimetallic nanoparticles, immobilize them on charcoal, and study the use of these immobilized Co/Rh

nanoparticles on charcoal as a catalyst in the Pauson–Khand-type reaction under 1 atm of carbon monoxide. Very recently, we reported the use of Co/Rh heterobimetallic nanoparticles in the carbonylative silylcarbocyclization of 1,6-enynes and Pauson–Khand-type reactions between alkynes and α,β -unsaturated aldehydes.^[10]

Recent increasing environmental awareness has made the use of carbon monoxide undesirable and prompted the search for an alternative process in which it is not used or a substitute is employed for carbon monoxide.^[11] Recently, the use of decarbonylated CO from formates or aldehydes has been utilized in the Pauson–Khand reaction.^[12] Thus, we also studied the use of the immobilized Co/Rh nanoparticles as a catalyst in the Pauson–Khand-type reaction in the presence of a substitute for carbon monoxide.

Here we report in detail the synthesis and use of immobilized Co/Rh heterobimetallic nanoparticles on charcoal as a catalyst in the Pauson–Khand-type reaction under 1 atm of CO and the Pauson–Khand-type reaction in the presence of aldehydes instead of carbon monoxide. An asymmetric intramolecular Pauson–Khand-type reaction in the presence of a chiral diphosphine and aldehyde is also described. To the best of our knowledge, such a heterogeneous catalytic system has not been reported previously.

Results and Discussion

Synthesis and Characterization of Co/Rh Heterobimetallic Nanoparticles and their Immobilization

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.^[13–15] Johnson et al.^[13,16] generated bimetallic nanoparticles by decarbonylation of mixed-metal carbonyl precursors such as $[\text{Ru}_5\text{PtC}(\text{CO})_{15}]^{2-}$, $[\text{Ru}_{10}\text{Pt}_2\text{C}_2(\text{CO})_{28}]^{2-}$, $[\text{Ru}_6\text{C}(\text{CO})_{16}\text{SnCl}_3]^-$, $[\text{Pd}_6\text{Ru}_6(\text{CO})_{24}]^{2-}$, and $[\text{Ru}_{12}\text{C}_2\text{Cu}_4\text{Cl}_2(\text{CO})_{32}]^{2-}$. Shapley et al. reported^[15] the preparation of two different compositions of Pt–Ru nanoparticles supported on carbons by reduction of the neutral precursors $\text{PtRu}_5\text{C}(\text{CO})_{16}$ and $\text{Pt}_2\text{Ru}_4(\text{CO})_{18}$ at elevated temperature in a hydrogen atmosphere.

The clusters $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ and $\text{Co}_3\text{Rh}(\text{CO})_{12}$ were prepared as previously reported.^[17] A solution containing the heterobimetallic 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. The evolution of the decomposition of the heterobimetallic carbonyl compound can be monitored by FT-IR spectroscopy following the distinct CO vibration peak. After removal of all the solvent, the black precipitates were re-suspended in THF. The THF suspension was used as a catalyst in the Pauson–Khand-type reaction.

Generally, immobilization of catalysts on a solid surface makes the work-up strikingly simple. Thus, we immobilized the Co/Rh heterobimetallic nanoparticles on charcoal. In order to immobilize Co/Rh nanoparticles on charcoal, the THF solution of Co/Rh nanoparticles was refluxed with flame-dried charcoal in THF for 12 h. After cooling and filtration of the solution under a nitrogen atmosphere, the precipitate was washed successively with diethyl ether, dichloromethane, acetone, and methanol and dried under vacuum. The immobilized black precipitate was used as a catalyst in the Pauson–Khand-type reaction. According to ICP-AES data of the immobilized Co/Rh heterobimetallic nanoparticles, 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/Rh heterobimetallic nanoparticles and the corresponding particle size distribution histogram are shown in Figures 1 and 2, respectively. HR-TEM shows that the diameter of the resulting well-dispersed, isolated, and anchored bimetallic nanoparticles is approximately 2 nm. Due to their small size, we could not characterize them any further.

We also prepared nanoparticles of cobalt (Co_4) and rhodium (Rh_4) from $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$, respectively. They also have the same diameter (*ca.* 2 nm). Thus, more than half of the atoms in the nanoparticles are exposed to reactant species in the reaction.^[14,18]

The Pauson–Khand-Type Reaction under 1 atm of CO

We first investigated the use of nanoparticles as catalysts in the intramolecular Pauson–Khand reaction of allyl propargyl ether. The results are summarized in Table 1. Under 1 atm of CO, no reaction was observed with cobalt nanoparticles (Co_4) on charcoal, and 23% of the reaction product was obtained with rhodium nanoparticles (Rh_4) on charcoal. When Co_3Rh was used, the expected product was obtained in 65% yield. The best result (87%) was obtained when Co_2Rh_2 was used as a catalyst. Interestingly, when a mixture 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 seemed that there arose some synergistic effects between cobalt and rhodium nanoparticles in the Co_2Rh_2 and Co_3Rh nanoparticles. However, the exact nature of the synergistic effects cannot be explained right now. Further study will provide clues to

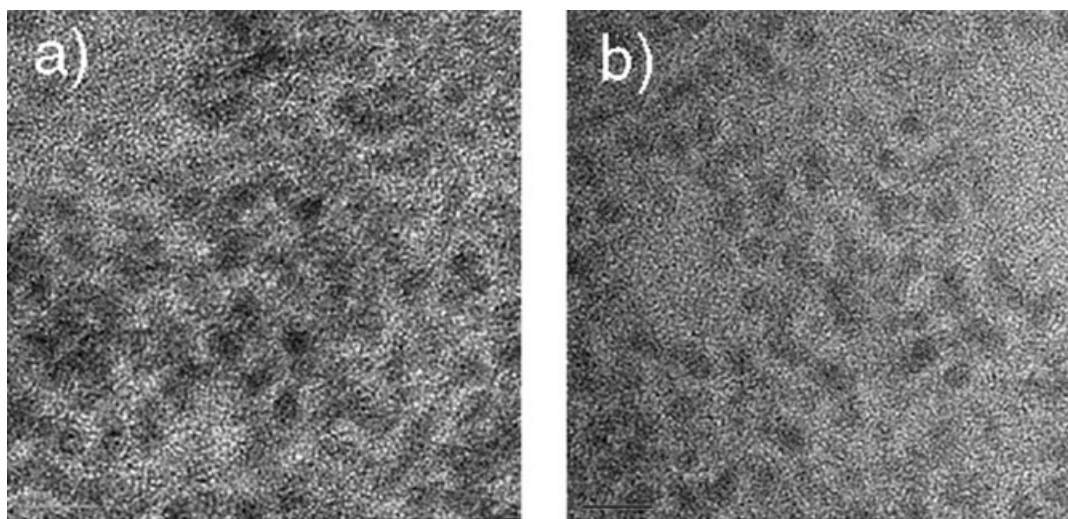


Figure 1. HR-TEM images of (left) Co_2Rh_2 (scale bar = 5 nm), (right) Co_3Rh (scale bar = 5 nm).

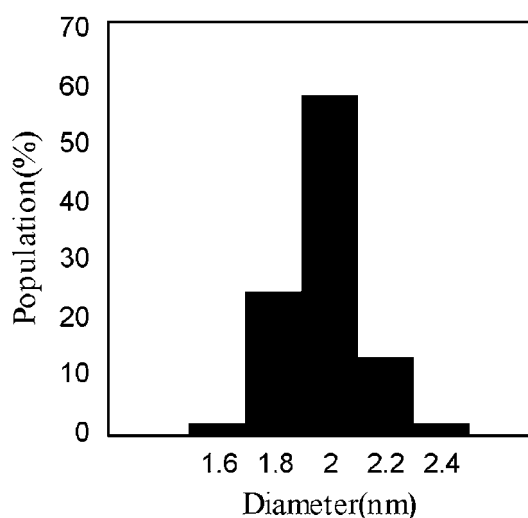


Figure 2. Particle size distribution of Co_2Rh_2 nanoparticles.

the nature of the synergistic effects. Therefore, the bimetallic nanoparticles were more reactive than the single nanometal on its own. Using Co_2Rh_2 as a catalyst, the optimized reaction conditions were established as 1 atm of CO, 130 °C, THF, and 18 h.

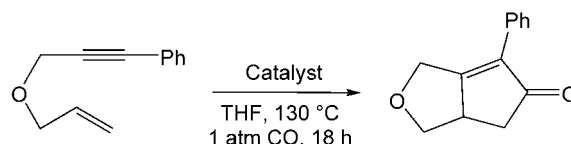
When Co_2Rh_2 nanoparticles immobilized on charcoal were used as a catalyst, the yield was 88%. Thus, immobilization of Co_2Rh_2 nanoparticles did not retard their catalytic activity. To inspect the recyclability, the immobilized Co_2Rh_2 was separated and reused several times. When the catalyst was recycled, the catalyst was filtered, dried under vacuum, and reused for the following catalytic reaction. The results shown in Table 1 confirm the catalyst maintained its high level of activity even after being recycled five times.

Next we investigated the versatility of intra- and intermolecular Pauson–Khand reactions under the optimized reaction conditions using immobilized Co_2Rh_2

as a catalyst (Table 2). For the intramolecular Pauson–Khand reaction, all the substrates including heteroatom-tethered enynes gave high yields (81–92%). The catalytic system is also effective for the intermolecular Pauson–Khand reaction although the yields (59–68%) are not comparable to those of the intramolecular reaction. It has been reported^[19] that catalytic and substoichiometric reactions based on cobalt carbonyls in the presence of additives such as phosphane sulfide and cyclohexylamine have been developed under 1 atm of CO. These processes are, at least, as effective as those reported here, especially in terms of the intermolecular Pauson–Khand cyclization. Many useful rhodium catalysts have been developed under similar mild conditions. However, they are generally less effective for the intermolecular Pauson–Khand reaction^[5d] and cannot be reused. Therefore, the Rh/Co bimetallic nanoparticles overcome the disadvantages of homogeneous rhodium catalysts.

The Pauson–Khand-Type Reaction in the Presence of Aldehydes

We first screened organic substrates that could be easily decarbonylated by transition metals. Aldehydes and formates are good candidates for our purpose because they have been studied with this end in mind for three decades.^[20] Using Co_3Rh or Co_2Rh_2 nanoparticles as catalyst, we screened aldehydes and formates as a substitute for carbon monoxide in an intramolecular Pauson–Khand-type reaction (Table 3). As shown in Table 3, aldehydes were quite effective in giving a carbonylative cycloaddition product, but 2-pyridylmethyl formate was ineffective. Especially, α,β -unsaturated aldehydes such as cinnamaldehyde, crotonaldehyde, and acrolein produced good results but aryl aldehydes such as benzal-

Table 1. Pauson–Khand reaction with various catalysts under 1 atm of CO.^[a]

Entry	Catalyst	Yield [%] ^[b]
1	Co ₂ Rh ₂	87
2	Co ₃ Rh	65
3	Cobalt nanoparticles on charcoal	0
4	Rhodium nanoparticles on charcoal	23
5	A mixture of cobalt nanoparticles and rhodium nanoparticles	12
6	Co ₂ Rh ₂ on charcoal	88
7	recovered from #6	89
8	recovered from #7	96
9	recovered from #8	87
10	recovered from #9	87

^[a] Reaction conditions: THF, 1 atm CO, 130 °C, 18 h, Co₂Rh₂ (Co = 8.93 mg, Rh = 15.6 mg), Co₃Rh (Co = 15.5 mg, Rh = 9.03 mg), Co₄ (24.5 mg), Rh₄ (24.5 mg).

^[b] Yields of isolated product.

dehyde and 1-naphthaldehyde gave poor results. When cinnamaldehyde was used, polystyrenes obtained as by-products had to be separated by column chromatography. However, in the case of crotonaldehyde or acrolein, propene or ethylene were produced and, accordingly, the purification of the Pauson–Khand reaction products was much more routine. As for crotonaldehyde and acrolein, the use of crotonaldehyde gave a slightly higher yield than acrolein. Thus, crotonaldehyde was our choice as the CO source. When Co₃Rh was used instead of Co₂Rh₂, the expected product was obtained in 80% yield. Moreover, the use of immobilized Co₂Rh₂ nanoparticles as catalysts gave the product in 93% yield. After much experimentation, optimized reaction conditions were established as follows: immobilized Co₂Rh₂ (0.05 g), enyne (0.96 mmol), crotonaldehyde (2.4 mmol), THF, 130 °C, and 18 h.

The most important advantage of heterogeneous catalysis over its homogeneous counterpart is the possibility of recovering the catalytic system. Thus, the reusability of the catalytic system was tested for the intramolecular Pauson–Khand-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 were leached. The maximum reusability of the catalytic system was not tested. However, the catalytic activity of Co₂Rh₂ nanoparticles was retained for at least five runs.

We next screened various enyne substrates for the intramolecular Pauson–Khand reaction under the optimized reaction conditions. As shown, the catalytic system is quite effective for giving high yields of the intra-

molecular Pauson–Khand reaction products. In homogeneous catalysis using rhodium catalysts, phosphine has to be added to enhance the catalytic reaction.^[21] However, no additives were added to enhance or promote the catalytic reaction. Moreover, multi-gram quantities of cyclopentenones were obtained without any difficulties.

Next we investigated the use of immobilized Co₂Rh₂ nanoparticles in the intermolecular Pauson–Khand-type reaction (Table 4). Immobilized Co₂Rh₂ nanoparticles are effective for the intermolecular Pauson–Khand-type reaction although the yields were not high, partly due to the trimerization of alkynes. When phenylacetylene was used as an alkyne substrate with norbornene, two reactions, the Pauson–Khand reaction and the trimerization of phenylacetylene, competed with each other. Thus, the Pauson–Khand reaction product and trimerization product were obtained in 64% and 23% yields (R = Ph), respectively. When trimethylsilylacetylene was used (again with norbornene) no trimerization of the acetylene was observed. However, the conversion was rather moderate (43%). Overall, our catalytic system is effective for the intra- and moderately effective for the intermolecular Pauson–Khand-type reactions.

Asymmetric Catalytic Pauson–Khand-Type Reaction in the Presence of an Aldehyde

We next investigated an asymmetric and catalytic intramolecular Pauson–Khand-type reaction. Much attention has been paid to the preparation of transition metal nanoparticles and their use in catalysis.^[1,2] However, much less attention has been paid to the combination

Table 2. Immobilized Co_2Rh_2 -catalyzed Pauson–Khand reaction of various substrates under 1 atm of CO .^[a]

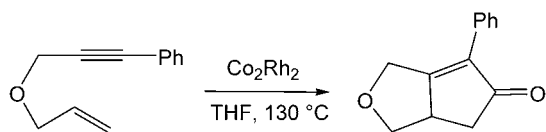
Entry	Substrates	Products	Yield [%] ^[b]
1 2		 R = Bu R = Ph	82 92
3 4		 R = Bu R = Ph	89 87
5 6		 R = Me R = Bu	81 91
7 8 9 10		 R = Bu R = Ph R = TMS R = Cyclohexene-1-yl	60 63 65 68
11		 R = Bu R = Ph R = TMS R = Cyclohexene-1-yl	59

^[a] Reaction conditions: THF, 1 atm CO , 130°C , 18 h.^[b] Yields of isolated product.

of optically active ligands with transition metal nanoparticles. Very recently, Fujihara and Tamura reported^[22] the synthesis of chiral bisphosphine BINAP-stabilized gold and palladium nanoparticles and their use in a catalytic asymmetric hydrosilylation of styrene. Enantiomeric excesses of up to 75% were obtained at room temperature and these increased to 95% when the hydrosilylation was carried out at 0°C .

First of all, we screened various C_2 -symmetrical chiral diphosphine ligands (Table 5). Enyne (0.96 mmol), crotonaldehyde (2.4 mmol), chiral phosphinine ligand (0.11 mmol), Co_2Rh_2 on charcoal (0.05 g), and THF (5 mL) were reacted in a stainless-steel bomb. After heating at 130°C for 18 h, the bomb was cooled to

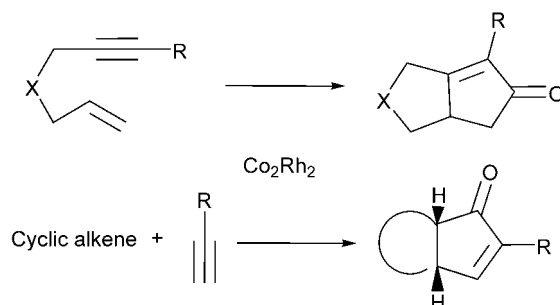
room temperature and the reaction product was isolated. As shown in Table 5, the presence of chiral ligands does not harm the yield of the reaction. Moreover, even when the lower quantities of catalyst were used (0.05 g), the yields were quite high (75–94%) but the ee values were highly dependent upon the chiral ligand itself. It has been documented^[23] that the use of (*S*)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl [(*S*)-BINAP] as a ligand was the most effective in cobalt-catalyzed reactions of 1,6-enynes. The use of (*R*)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl [(*R*)-BINAP] (entry 1) as a chiral ligand gave an ee value of 79%. Introduction of a methyl group to the phenyl group of (*R*)-BINAP [(*R*)-(+)-2,2'-bis(di-*p*-tolylphosphino)-1,1'-

Table 3. Immobilized Co/Rh-catalyzed intramolecular Pauson–Khand reaction using a substitute for carbon monoxide.^[a]

Entry	Ligand	Time [h]	Yield [%] ^[b]
1	Acrolein	18	87
2	Crotonaldehyde	18	91
3	Crotonaldehyde	18	93 ^[c]
4	Cinnamaldehyde	18	93
5	Benzaldehyde	18	43
6	1-Naphthaldehyde	18	35
7	2-Pyridylmethyl formate	18	–
8	Crotonaldehyde	12	85
9	Crotonaldehyde	6	81
10	Crotonaldehyde	18	80 ^[d]

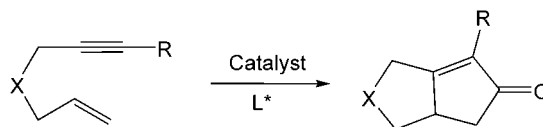
^[a] Reaction conditions: THF, 130 °C, and Co₂Rh₂.^[b] Yields of isolated products.^[c] Co₂Rh₂ immobilized on charcoal.^[d] Co₃Rh was used.

binaphthyl = (*R*)-Tol-BINAP] (entry 2) did not assist in raising the ee value (73%). When (*R*)-DIOP was used, the ee value dropped to 34% (entry 3). Strangely, in the case of (2*R*,3*R*)-(–)-2,3-bis(diphenylphosphino)-bicyclo[2.2.1]hept-5-ene [(*R,R*)-NORPHOS], a racemate was obtained (entry 4). However, surprisingly, the use of (2*S*,4*S*)-(–)-2,4-bis(diphenylphosphino)pentane [(*S,S*)-BDPP] gave a high ee value of 84% (entry 5). Considering both the yield and ee values, (*S,S*)-BDPP was the best choice for the asymmetric Pauson–Khand-type reaction. Thus, using (*S,S*)-BDPP as a chiral ligand, other enyne substrates were subjected to the Pauson–Khand reaction conditions (entries 6–12). The yields were high (75–94%) and the ee values were moderate to high (51–87%). The best ee value was 87% (entry 11). 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.^[21] Especially, the 84% ee value for enyne (entry 5) was greater than that (74%) obtained with the homogeneous rhodium catalysis. At present, a detailed mechanism for the asymmetric induction of our catalytic system in the presence of chiral diphosphines cannot be proposed. Further study, including theoretical calculations, will provide some clues for the rationalization of the asymmetric induction.

Table 4. Pauson–Khand reactions catalyzed by immobilized Co₂Rh₂.^[a]

Entry	Substrate	R	Yield [%] ^[b]
1	X = (MeO ₂ C) ₂ C	R = Bu	90
2	X = (MeO ₂ C) ₂ C	R = Ph	97
3	X = O	R = Bu	85
4	X = O	R = Ph	93
5	X = N-SO ₂ C ₆ H ₄ -CH ₃ - <i>p</i>	R = Me	87
6	X = N-SO ₂ C ₆ H ₄ -CH ₃ - <i>p</i>	R = Bu	90
7	Norbornene	R = Bu	65
8	Norbornene	R = Ph	64
9	Norbornene	R = TMS	43
10	Norbornene	R = Cyclohexen-1-yl	70
11	2,5-Norbornadiene	R = Ph	63
12	Cyclopentene	R = Ph	49
13	Cyclohexene	R = Ph	17

^[a] Reaction conditions: immobilized Co₂Rh₂ (0.05 g), enyne (0.96 mmol) for entries 1–6 or cyclic alkene (0.96 mmol) and terminal alkyne (1.15 mmol) for entries 7–11, crotonaldehyde (2.4 mmol), THF, 130 °C, and 18 h.^[b] Yields of isolated products.

Table 5. Immobilized Co₂Rh₂-catalyzed asymmetric Pauson–Khand reaction.^[a]

Entry	Catalyst	Substrate		Ligand	Yield [%] ^[b]	ee [%]
		X	R			
1	Co ₂ Rh ₂ on charcoal	O	Ph	(<i>R</i>)-BINAP	93	79
2	Co ₂ Rh ₂ on charcoal	O	Ph	(<i>R</i>)-Tol-BINAP	91	73
3	Co ₂ Rh ₂ on charcoal	O	Ph	(<i>R</i>)-DIOP	90	34
4	Co ₂ Rh ₂ on charcoal	O	Ph	(<i>R,R</i>)-NORPHOS	83	–
5	Co ₂ Rh ₂ on charcoal	O	Ph	(<i>S,S</i>)-BDPP	91	84
6	Co ₂ Rh ₂ on charcoal	O	Bu	(<i>S,S</i>)-BDPP	75	62
7	Co ₂ Rh ₂ on charcoal	O	CH ₃	(<i>S,S</i>)-BDPP	85	80
8	Co ₂ Rh ₂ on charcoal	N-SO ₂ C ₆ H ₄ -CH ₃ - <i>p</i>	Ph	(<i>S,S</i>)-BDPP	94	85
9	Co ₂ Rh ₂ on charcoal	(MeO ₂ C) ₂ C	CH ₃	(<i>S,S</i>)-BDPP	92	56
10	Co ₂ Rh ₂ on charcoal	(MeO ₂ C) ₂ C	Ph	(<i>S,S</i>)-BDPP	89	64
11	Co ₂ Rh ₂ on charcoal	(EtO ₂ C) ₂ C	CH ₃	(<i>S,S</i>)-BDPP	93	87
12	Co ₂ Rh ₂ on charcoal	(EtO ₂ C) ₂ C	Ph	(<i>S,S</i>)-BDPP	94	51
13	recovered from # 5	O	Ph	(<i>S,S</i>)-BDPP	90	85
14	recovered from # 13	O	Ph	(<i>S,S</i>)-BDPP	89	80
15	recovered from # 14	O	Ph	(<i>S,S</i>)-BDPP	93	83
16	recovered from # 15	O	Ph	(<i>S,S</i>)-BDPP	90	84

^[a] Reaction conditions: 1,6-enyne (0.96 mmol), crotonaldehyde (2.4 mmol), L* (0.11 mmol), immobilized catalyst (0.05 g, total weight of metals = 12.2 mg), THF, 18 h, 130 °C.

^[b] Yields of isolated products.

The reusability of the catalytic system was tested for the asymmetric Pauson–Khand-type reaction (entries 5 and 13–16). For the recyclization, the catalyst obtained by filtration was reused and the insufficient chiral diphosphine was supplemented by new chiral diphosphine. As shown, the yields and ee values were retained over at least five runs; the maximum reusability has not been tested. Elemental analysis (by ICP-AES) of the reaction mixture after completion of the three runs showed that 3.9 ppm of cobalt and 0.3 ppm of rhodium species were detected.

In many cases,^[24] 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.

Mercury-Poisoning Experiment

It seemed that the asymmetric Pauson–Khand-type reaction catalyzed by transition metal nanoparticles is rather unusual. Is this chemistry truly heterogeneous, i.e., catalyzed only by cobalt/rhodium nanoparticles attached to the charcoal support? If so, then in addition to such an association with charcoal, how can cobalt/rhodium nanoparticles accommodate both an oxidative ad-

dition and simultaneous coordination of diphosphine ligands, all within the coordination sphere of the metal? In order to obtain some evidence for distinguishing between homogeneous *versus* heterogeneous catalysis, we carried out a mercury-poisoning experiment.

The ability of added Hg(0) to poison metal(0) heterogeneous catalysts^[25] by amalgamating the metal catalyst or adsorbing onto its surface is the single most widely used test of homogeneous *versus* heterogeneous catalysis.^[26] The suppression of catalysis by Hg(0) is evidence for a heterogeneous catalyst; if Hg(0) does not suppress catalysis, the implication is that the catalysis is homogeneous. The Hg(0)-poisoning experiment is easy to perform, but is not definitive by itself, and not universally applicable because Hg(0) reacts with some single-metal complexes.^[25,26] Thus, this test inherently provides negative evidence (no poisoning) in cases where the catalyst is homogeneous.

With standard reaction conditions for the Pauson–Khand-type reaction, an experiment with Co₂Rh₂ was started as described above: [(3-allyloxy)prop-1-ynyl]-benzene (0.96 mmol), crotonaldehyde (2.4 mmol), and Co₂Rh₂ on charcoal (50 mg, 12 mg of Co₂Rh₂) in THF (5 mL) were reacted in a stainless-steel bomb. After about 5 h, the reaction was stopped, ~320 equivs. (0.175 g) of Hg(0) (vs. Co₂Rh₂) were added, and the reaction was then restarted. We used a large excess of Hg(0) in a well-stirred solution to ensure intimate con-

tact of the Hg(0) bead with the entire reactor. The addition of Hg(0) completely eliminated further catalysis (i.e., for the next 15 h over which it was monitored). The yield for 5 h was 31% and for an additional 15 h after the addition of mercury it was 32%. This result is consistent with and strongly supportive of heterogeneous metal(0) catalysis.^[25,27] Since the activity was completely poisoned, the heterogeneous metal(0) catalyst is the only active species present. A similar experiment in the presence of chiral diphosphine was also carried out. [(3-Allyloxy)prop-1-ynyl]benzene (0.96 mmol), crotonaldehyde (2.4 mmol), (*S,S*)-BDPP (0.11 mmol), and Co₂Rh₂ on charcoal (50 mg, 12 mg of Co₂Rh₂) in THF (5 mL) were put in a stainless-steel bomb. The yield and ee values for 5 h were 31% and 82% ee, respectively, and for an additional 15 h after the addition of mercury they were 32% and 79% ee, respectively. Thus, Hg(0) completely eliminated further catalysis.

Conclusion

We have demonstrated the usefulness of the combination of cobalt and rhodium nanoparticles in the intra- and intermolecular Pauson–Khand reactions under mild conditions. We have also achieved the development of environmentally safe, clean, and sustainable chemical processes for the asymmetric catalytic Pauson–Khand reaction. Multi-grams of cyclopentenones are obtained without any difficulties and the reuse of the catalyst has become a reality. Efforts to further delineate the asymmetric induction in asymmetric Pauson–Khand-type reactions and to validate its usefulness in natural product synthesis are underway in our laboratories. We expect that our methodology can be extended to other catalytic systems in the near future.

Experimental Section

General Remarks

All reactions were conducted under nitrogen using standard Schlenk-type flasks. Work-up procedures were done in air. All solvents were dried and distilled according to standard methods before use. THF was freshly distilled from sodium benzophenone ketyl prior to use. Reagents were purchased from Aldrich Chemical Co. and Strem Chemical Co. and were used as received. ¹H NMR spectra were obtained with a Bruker 300 MHz spectrometer. Elemental analyses were done at the National Center for Inter-University Research Facilities, Seoul National University. High resolution mass spectra were obtained at Korea Basic Science Institute (Daegu). High-performance liquid chromatography (HPLC) was conducted using a Hewlett-Packard 1100. Optical rotations were measured on a Jasco DIP360 instrument. Flash chromatography was performed using Merck Silica Gel 60 (230–400 mesh).

Preparation of M₄ Nanoparticles

To a two-neck flask were added *o*-dichlorobenzene (24 mL), oleic acid (0.2 mL), and trioctylphosphine oxide (0.4 g). While the solution was heated at 180 °C, a solution of metal carbonyl, Co₂Rh₂(CO)₁₂ (1.0 g), Co₃Rh(CO)₁₂ (1.08 g), Co₄(CO)₁₂ (1.19 g) or Rh₄(CO)₁₂ (0.89 g), in 6 mL of *o*-dichlorobenzene was injected into the flask. The resulting solution was heated at 180 °C for 2 h. After the solution was cooled, the solution was concentrated to a volume of ca. 10 mL by distillation. To the concentrated solution was added THF (200 mL). The progress of the decomposition of organometallic clusters can be monitored by checking the disappearance of one of the CO stretching frequencies: for Co₂Rh₂(CO)₁₂: 2074, 2064, 2059, 2058, 2030 cm⁻¹; for Co₃Rh(CO)₁₂: 2066, 2059, 2056, 2037, 2031 cm⁻¹; for Co₄(CO)₁₂: 2065, 2055 cm⁻¹; for Rh₄(CO)₁₂: 2075, 2043 cm⁻¹.

Immobilization of M₄ Nanoparticles on Charcoal

To a two-neck flask were added *o*-dichlorobenzene (24 mL), oleic acid (0.2 mL), and trioctylphosphine oxide (0.4 g). While the solution was heated at 180 °C, a solution of metal carbonyl, Co₂Rh₂(CO)₁₂ (1.0 g), Co₃Rh(CO)₁₂ (1.08 g), Co₄(CO)₁₂ (1.19 g), or Rh₄(CO)₁₂ (0.89 g), in 6 mL *o*-dichlorobenzene was injected into the flask. The resulting solution was heated to 180 °C for 2 h and then concentrated to a volume of 5 mL. The concentrated solution was cooled to room temperature. To the cooled solution were added 25 mL of THF. After the solution was well stirred for 10 min, flame-dried charcoal (2.0 g) was added to the solution. After the resulting solution had been refluxed for 12 h, the precipitates were filtered and washed with diethyl ether (20 mL), dichloromethane (20 mL), acetone (20 mL), and methanol (20 mL). Vacuum drying gave a black solid.

High Resolution Transmission Electron Microscopy (HR-TEM)

Co/Rh heterobimetallic nanoparticles immobilized on charcoal were investigated by transmission electron microscopy (TEM) on a JEM 100C transmission microscope. The samples were prepared by placing a drop of the solution on carbon-coated Cu grids and allowing this to dry in air. Counting 200 particles from enlarged TEM images monitored the particle size and size distribution.

Synthesis of Enynes

2-Allyl-2-(hept-2-ynyl)malonic acid dimethyl ester (entry 1 in Table 2):^[5a] To a solution of NaH (0.358 g, 60% dispersion in mineral oil) in 10 mL of THF was added dropwise a solution of dimethyl allylmalonate (1.0 mL, 6.22 mmol) in THF (10 mL) at 0 °C over a period of 15 min, and then the mixture was stirred at room temperature until the evolution of hydrogen gas subsided. The mixture was cooled to 0 °C, and a solution of 1-bromohept-2-yne (1.30 g, 7.42 mL) in THF (5 mL) was added dropwise over a period of 15 min. Stirring of the mixture at room temperature for 12 h afforded a brown solution with a white solid precipitate. Water (20 mL) was added,

and the organic layer was separated. The aqueous layer was extracted with ether (15 mL), and the combined organic layers were washed with water (20 mL) and brine (20 mL), dried over MgSO_4 , and concentrated under vacuum. The residue was purified by column chromatography on silica gel (ether/hexane, 10/90) to give the respective enyne; yield: 1.6 g (97%). ^1H NMR (CDCl_3): δ =5.69 (ddt, J =16.8, 9.7, 6.8 Hz, 1H), 5.18 (dm, J =16.3 Hz, 1H), 5.09 (dm, J =9.7 Hz, 1H), 3.73 (s, 6H), 2.80–2.73 (m, 4H), 2.16–2.10 (m, 2H), 1.42–1.38 (m, 4H), 0.89 (t, J =7.1 Hz, 3H).

2-Allyl-2-(3-phenylprop-2-ynyl)malonic acid dimethyl ester (entry 2 in Table 2):^[5a] The same procedure as the synthesis of the enyne (entry 1 in Table 2) was applied except using (3-bromoprop-1-yn-1-yl)benzene instead of 1-bromohept-2-yne. ^1H NMR (CDCl_3): δ =7.42–7.46 (m, 2H), 7.31–7.33 (m, 3H), 5.78 (m, 1H), 5.18 (dm, J =16.4 Hz, 1H), 5.14 (dm, J =9.8 Hz, 1H), 3.74 (s, 6H), 2.69–2.63 (m, 4H).

1-Allyloxyhept-2-yne (entry 3 in Table 2):^[5a] To a solution of NaH (0.513 g, 60% dispersion in mineral) in THF (10 mL) was added dropwise a solution of hept-2-yn-1-ol (1 g, 8.91 mmol) in THF (10 mL) at 0 °C over a period of 10 min, and then the mixture was stirred at room temperature until the evolution of hydrogen gas subsided. The mixture was cooled to 0 °C, and a solution of allyl bromide (0.93 mL, 10.7 mmol) in THF (5 mL) was added dropwise over a period of 10 min. The mixture was stirred at room temperature for 1 h. Water (20 mL) was added slowly at 0 °C, and the organic layer was separated. The aqueous layer was extracted with ether (15 mL), and the combined organic layers were washed with water (20 mL) and brine (20 mL), dried over MgSO_4 , and concentrated under vacuum. The residue was purified by column chromatography on silica gel (ether/hexane, 10/90) to give the enyne; yield: 1.3 g (96%). ^1H NMR (CDCl_3): δ =5.85 (ddt, J =16.8, 10.2, 5.3 Hz, 1H), 5.18 (dm, J =16.8 Hz, 1H), 5.17 (dm, J =9.9 Hz, 1H), 4.03 (t, J =1.7 Hz, 2H), 3.98–4.03 (m, 2H), 2.15–2.13 (m, 2H), 1.39–1.45 (m, 4H), 0.89 (t, J =7.1 Hz, 3H).

[(3-Allyloxy)prop-1-ynyl]benzene (entry 4 in Table 2):^[28] The same procedure as the synthesis of the enyne (entry 3 in Table 2) was applied except for using 3-phenylprop-2-yn-1-ol instead of hept-2-yn-1-ol. ^1H NMR (CDCl_3): δ =7.44–7.48 (m, 2H), 7.29–7.34 (m, 3H), 5.95 (ddt, J =17.3, 10.7, 5.4 Hz, 1H), 5.35 (dm, J =18.1 Hz, 1H), 5.24 (dm, J =12.0 Hz, 1H), 4.39 (s, 2H), 4.14 (dm, J =5.8 Hz, 2H).

N-Allyl-N-(but-2-ynyl)-4-methylbenzenesulfonamide (entry 5 in Table 2):^[5a] To a solution of NaH (0.217 g, 60% dispersion in mineral oil) in 10 mL of THF was added dropwise a solution of *N*-but-2-yn-1-yl-4-methylbenzenesulfonamide (1 g, 3.76 mmol) in DMF (10 mL) at 0 °C over a period of 10 min, and then the mixture was stirred at room temperature until the evolution of hydrogen gas subsided. The mixture was cooled to 0 °C, and a solution of allyl bromide (0.39 mL, 4.5 mmol) in THF (5 mL) was added dropwise over a period of 10 min. The mixture was stirred at room temperature for 1 h. Water (20 mL) was added slowly at 0 °C, and the organic layer was separated. The aqueous layer was extracted with ether (15 mL), and the combined organic layers were washed with water (20 mL) and brine (20 mL), dried over MgSO_4 , and concentrated under vacuum. The residue was purified by column chromatography on silica gel (ether/hexane, 20/90) to give the enyne; yield: 1.05 g (91%). ^1H NMR (CDCl_3): δ =7.71 (d, J =8.1 Hz, 2H), 7.33 (d, J =8.1 Hz, 2H), 5.79 (dm, J =

17.0 Hz, 1H), 5.29 (dd, J =16.9, 1.3 Hz, 1H), 5.28 (dd, J =9.8, 1.1 Hz, 1H), 4.29 (s, 2H), 3.77 (d, J =6.5 Hz, 2H), 2.29 (s, 3H), 1.66 (s, 3H).

N-Allyl-N-(hept-2-ynyl)-4-methylbenzenesulfonamide (entry 6 in Table 2):^[5a] The same procedure as the synthesis of the enyne (entry 5 in Table 2) was applied except for using *N*-hept-2-yn-1-yl-4-methylbenzenesulfonamide instead of *N*-but-2-yn-1-yl-4-methylbenzenesulfonamide. ^1H NMR (CDCl_3): δ =7.59 (d, J =8.5 Hz, 2H), 7.19 (d, J =8.5 Hz, 2H), 5.58 (dm, J =12.0 Hz, 1H), 5.19 (dd, J =16.8, 1.2 Hz, 1H), 5.15 (dd, J =9.7, 1.2 Hz, 1H), 4.01 (t, J =2.3 Hz, 2H), 3.29 (d, J =6.7 Hz, 2H), 2.33 (s, 3H), 1.78 (tt, J =6.7, 2.4 Hz, 2H), 1.2–1.19 (m, 4H), 0.80 (t, J =7.1 Hz, 3H).

Intra- and Intermolecular Pauson–Khand-Type Reactions under 1 atm of CO Catalyzed by Immobilized Co_2Rh_2 on Charcoal

General procedure for an intramolecular reaction (entries 1–6 in Table 2): To a solution of an enyne (1.2 mmol) in 10 mL of THF was added Co_2Rh_2 (0.05 g of the immobilized Co_2Rh_2). The reactor was charged with 1 atm of CO and heated at 130 °C for 18 h. After the reactor was cooled to room temperature, the solution was filtered, concentrated, and the product isolated and purified by chromatography on a silica gel column, eluting with hexane and diethyl ether (v/v, 5:1).

General procedure for an intermolecular reaction (entries 7–11 in Table 2): The same procedure as the above reaction was applied except using a cyclic alkene (0.96 mmol) and a terminal alkyne (1.15 mmol) instead of enyne (1.2 mmol).

Recycling experiment: In order to recycle the catalyst, it was filtered from the reaction mixture and dried in vacuum and then reused for the further catalytic reaction.

Intramolecular Pauson–Khand-Type Reactions under 1 atm of CO Catalyzed by Transition Metal Nanoparticles

The same procedure as the above reaction was applied except using a solution of transition metal nanoparticles in THF instead of immobilized Co_2Rh_2 on charcoal. When Co_2Rh_2 , Co_3Rh , Co_4 , and Rh_4 nanoparticles were used as a catalyst, the catalyst solution was prepared by dispersing nanoparticles [Co_2Rh_2 (Co = 8.9 mg, Rh = 15.6 mg), Co_3Rh (Co = 15.5 mg, Rh = 9.0 mg), Co_4 (24.5 mg), and Rh_4 (24.5 mg)] in 10 mL of THF.

6-Butyl-5-oxo-3,3a,4,5-tetrahydro-1H-pentalene-2,2-dicarboxylic acid dimethyl ester (entry 1 in Table 2):^[29] ^1H NMR (CDCl_3): δ =3.78 (s, 3H), 3.73 (s, 3H), 3.18 (s, 2H), 2.78–2.98 (m, 1H), 2.77 (dd, J =11.9, 6.9 Hz, 1H), 2.59 (dd, J =17.2, 6.0 Hz, 1H), 2.11–2.29 (m, 1H), 2.01–2.13 (m, 2H), 1.59 (dd, J =11.9, 12.0 Hz, 1H), 1.11–1.55 (m, 4H), 0.88 (t, J =7.3 Hz, 3H); IR: ν_{CO} =1732 cm^{-1} .

5-Oxo-6-phenyl-3,3a,4,5-tetrahydro-1H-pentalene-2,2-dicarboxylic acid dimethyl ester (entry 2 in Table 2):^[29] ^1H NMR (CDCl_3): δ =7.22–7.54 (m, 5H), 3.79 (s, 3H), 3.69 (s, 3H), 3.60 (d, J =18.7 Hz, 1H), 3.28 (d, J =18.5 Hz, 1H), 3.00–3.16 (m, 1H), 2.78–2.81 (m, 2H), 2.29 (dd, J =18.0, 2.9 Hz, 1H), 1.67 (dd, J =11.9, 11.8 Hz, 1H); IR: ν_{CO} =1735 cm^{-1} .

6-Butyl-3a,4-dihydro-1H,3H-cyclopenta[c]furan-5-one (entry 3 in Table 2):^[29] ¹H NMR (CDCl₃): δ = 4.49 (q, *J* = 13.8 Hz, 2H), 4.29 (s, 1H), 3.15 (d, *J* = 2.1 Hz, 2H), 2.66–2.58 (m, 1H), 2.22–2.29 (m, 1H), 2.10–2.15 (m, 2H), 1.21–1.25 (m, 4H), 0.90 (t, *J* = 6.6 Hz, 3H); IR: ν_{CO} = 1732 cm⁻¹.

6-Phenyl-3a,4-dihydro-1H,3H-cyclopenta[c]furan-5-one (entry 4 in Table 2):^[29] ¹H NMR (CDCl₃): δ = 7.13–7.31 (m, 5H), 4.56 (d, *J* = 15.8 Hz, 1H), 4.44 (d, *J* = 15.8 Hz, 1H), 4.27 (dd, *J* = 14.2 Hz, 1H), 3.07–3.14 (m, 2H), 2.58–2.69 (m, 2H); IR: ν_{CO} = 1734 cm⁻¹.

6-Methyl-2-(4-toluenesulfonyl)-2,3,3a,4-tetrahydro-1H-cyclopenta[c]pyrrol-5-one (entry 5 in Table 2):^[30] ¹H NMR (CDCl₃): δ = 7.75 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.27 (d, *J* = 16.5 Hz, 1H), 4.02–3.95 (m, 2H), 3.01 (br s, 1H), 2.64–2.54 (m, 2H), 2.22 (s, 3H), 2.07 (dd, *J* = 3.3 Hz, 1H), 1.68 (s, 3H); IR: ν_{CO} = 1730 cm⁻¹.

6-Butyl-2-(4-toluenesulfonyl)-2,3,3a,4-tetrahydro-1H-cyclopenta[c]pyrrol-5-one (entry 6 in Table 2):^[12c] ¹H NMR (CDCl₃): δ = 7.78 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.19 (q, *J* = 14.0 Hz, 2H), 4.00 (t, *J* = 2.4 Hz, 2H), 3.79 (d, *J* = 5.9 Hz, 2H), 2.42 (s, 3H), 2.01–1.92 (m, 2H), 1.31–1.24 (m, 4H), 0.85 (m, 3H); IR: ν_{CO} = 1700 cm⁻¹.

2-Butyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one (entry 7 in Table 2):^[12e] ¹H NMR (CDCl₃): δ = 7.09 (t, *J* = 1.2 Hz, 1H), 2.56 (s, 1H), 2.37 (s, 1H), 2.12–2.16 (m, 4H), 1.66 (m, 2H), 1.46 (m, 2H), 1.28 (s, 6H), 0.52–0.97 (m, 3H); IR: ν_{CO} = 1702 cm⁻¹.

2-Phenyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one (entry 8 in Table 2):^[31] ¹H NMR (CDCl₃): δ = 7.66–7.71 (m, 2H), 7.61 (d, *J* = 2.5 Hz, 1H), 7.22–7.41 (m, 3H), 2.60–2.69 (m, 1H), 2.48 (d, *J* = 3.6 Hz, 1H), 2.33 (d, *J* = 5.1 Hz, 1H), 2.23 (d, *J* = 3.8 Hz, 1H), 1.51–1.78 (m, 2H), 1.21–1.39 (m, 2H), 1.00–1.19 (m, 1H), 0.91–1.00 (m, 1H); IR: ν_{CO} = 1699 cm⁻¹.

2-Trimethylsilyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one (entry 9 in Table 2):^[32] ¹H NMR (CDCl₃): δ = 7.59 (d, *J* = 2.5 Hz, 1H), 6.27–6.31 (m, 2H), 2.77 (s, 1H), 2.69–2.71 (m, 3H), 2.50 (s, 1H), 1.89 (d, *J* = 6.3 Hz, 1H), 1.19 (d, *J* = 11.3 Hz, 1H), 0.98 (d, *J* = 11.3 Hz, 1H), –0.15 (s, 9H); IR: ν_{CO} = 1689 cm⁻¹.

2-Cyclohex-1-en-1-yl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one (entry 10 in Table 2):^[12e] ¹H NMR (CDCl₃): δ = 7.22 (d, *J* = 4.8 Hz, 1H), 6.81 (d, *J* = 3.7 Hz, 1H), 2.88–2.92 (m, 1H), 2.51 (m, 1H), 2.21–2.22 (m, 4H), 1.57–1.64 (m, 8H), 1.22–1.28 (m, 2H), 1.17 (m, 1H), 0.88 (m, 1H); IR: ν_{CO} = 1708 cm⁻¹.

2-Phenyl-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one (entry 11 in Table 2):^[33] ¹H NMR (CDCl₃): δ = 7.71–7.65 (m, 3H), 7.36–7.31 (m, 3H), 6.29 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.28 (dd, *J* = 5.6, 3.2 Hz, 1H), 3.02 (br s, 1H), 2.83 (m, 1H), 2.78 (br s, 1H), 2.46 (d, *J* = 5.4 Hz, 1H), 1.43 (d, *J* = 9.3 Hz, 1H), 1.33 (d, *J* = 9.3 Hz, 1H); IR: ν_{CO} = 1699 cm⁻¹.

Intra- and Intermolecular Pauson–Khand-Type Reaction in the Presence of an Aldehyde Catalyzed by Immobilized Co₂Rh₂ on Charcoal

For an intramolecular reaction, an enyne (0.96 mmol), crotonaldehyde (2.4 mmol), Co₂Rh₂ on charcoal (0.05 g), and THF (5 mL) were put in a stainless-steel bomb. The bomb was heated at 130 °C for 18 h. After this time, the solution was cooled

and the filtrate was evaporated to dryness. Chromatography on a silica gel column eluting with hexane and diethyl ether (v/v, 5:1) gave the product.

For an intermolecular reaction, the same procedure as the above reaction was applied except using a cyclic alkene (0.96 mmol) and a terminal alkyne (1.15 mmol) instead of an enyne (0.96 mmol).

2-Phenyl-4,5,6,6a-tetrahydro-3aH-pentalen-1-one (entry 12 in Table 4):^[32] ¹H NMR (CDCl₃): δ = 7.69–7.63 (m, 2H), 7.60–7.22 (m, 4H), 3.35–3.09 (m, 1H), 2.70–2.68 (m, 1H), 1.52–1.12 (m, 6H); IR: ν_{CO} = 1697 cm⁻¹.

2-Phenyl-3a,4,5,6,7,7a-hexahydroinden-1-one (entry 13 in Table 4):^[34] ¹H NMR (CDCl₃): δ = 7.71–7.66 (m, 2H), 7.61 (d, *J* = 2.5 Hz, 1H), 7.41–7.22 (m, 3H), 2.69–2.60 (m, 1H), 2.48 (d, *J* = 3.6 Hz, 1H), 2.33 (d, *J* = 5.1 Hz, 1H), 2.23 (d, *J* = 3.8 Hz, 1H), 1.78–1.51 (m, 2H), 1.39–1.21 (m, 2H), 1.19–1.00 (m, 1H), 1.00–0.91 (m, 1H); IR: ν_{CO} = 1704 cm⁻¹.

Synthesis of Multi-Gram Amounts of 6-Phenyl-3a,4-dihydro-1H,3H-cyclopenta[c]furan-5-one

[(3-Allyloxy-prop-1-ynyl)benzene (1.72 g, 0.01 mol), crotonaldehyde (0.24 mol), Co₂Rh₂ on charcoal (0.05 g), and THF (5 mL) were put in a stainless-steel bomb. The bomb was heated at 130 °C for 18 h. After the solution was cooled, the solution was filtered and the filtrate was evaporated to dryness. Chromatography on a silica gel column eluting with hexane and diethyl ether (v/v, 5:1) gave the product; yield: 1.46 g (73%).

Competition Between a Trimerization and a Pauson–Khand-Type Reaction

An alkyne (0.96 mmol), crotonaldehyde (2.4 mmol), Co₂Rh₂ on charcoal (0.05 g), and THF (5 mL) were put in a stainless-steel bomb. The bomb was heated at 130 °C for 18 h. After this time, the solution was cooled and filtered, and the filtrate was evaporated to dryness. Chromatography on a silica gel column eluting with hexane and diethyl ether (v/v, 10:1) gave the Pauson–Khand product as major product and trimerization product as minor product.

1,2,4-Tributylbenzene:^[34,35] Yield: 21%; ¹H NMR (CDCl₃): δ = 6.89–7.10 (m, 3H), 2.10 (m, 6H), 1.38 (m, 12H), 0.86 (t, *J* = 7.1 Hz, 9H).

1,2,4-Triphenylbenzene:^[36] Yield: 23%; ¹H NMR (CDCl₃): δ = 7.14–7.20 (m, 9H), 7.31–7.65 (m, 5H), 7.61–7.68 (m, 4H).

Asymmetric Intramolecular Pauson–Khand-Type Reaction Catalyzed by Immobilized Co₂Rh₂

An enyne (0.96 mmol), crotonaldehyde (2.4 mmol), chiral phosphinine ligand (0.11 mmol), Co₂Rh₂ on charcoal (0.05 g), and THF (5 mL) were put in a stainless-steel bomb. The bomb was heated at 130 °C for 18 h. After the reactor was cooled to room temperature, the solution was filtered and the filtrate was evaporated to dryness. Chromatography on a silica gel column eluting with hexane and diethyl ether (v/v, 5:1) gave the product and intact chiral diphosphine. For the recyclozation, the catalyst obtained by filtration was reused and

the insufficient chiral diphosphine was supplemented by new chiral phosphine.

Determination of Enantiomeric Purity

The enantiomeric excesses (% ee) were determined by chiral HPLC analysis. For entries 1, 2, 3, 4, 5, 6, 7, 9, 10, 12, 13, 14, 15 and 16 in Table 5, a CHIRALPAK AS 25 cm $\times$ 0.46 cm column (Daicel Chemical Ind., Ltd.) was used. For entry 8 in Table 5, a CHIRALPAK AD 25 cm $\times$ 0.46 cm column (Daicel Chemical Ind., Ltd.) was used. For entry 11 in Table 5, a CHIRALPAK OD-H 25 cm $\times$ 0.46 cm column (Daicel Chemical Ind., Ltd.) was employed.

6-Phenyl-3a,4-dihydro-1H,3H-cyclopenta[c]furan-5-one (entry 1 in Table 5):^[21] Yield: 93%, $[\alpha]_D^{20}$: -12.9 (c 1.80 in CH₂Cl₂); CHIRALPAC AS: 79% ee, 2-propanol/hexane = 10/90, flow rate = 1 mL/min, 1st product = 15.82 min, 2nd product = 17.91 min. The ¹H NMR spectrum matched the published spectrum.

6-Phenyl-3a,4-dihydro-1H,3H-cyclopenta[c]furan-5-one (entry 2 in Table 5):^[21] Yield: 91%, $[\alpha]_D^{20}$: -9.1 (c 1.50 in CH₂Cl₂); CHIRALPAC AS: 73% ee, 2-propanol/hexane = 10/90, flow rate = 1 mL/min, 1st product = 15.53 min, 2nd product = 17.44 min. The ¹H NMR spectrum matched the published spectrum.

6-Phenyl-3a,4-dihydro-1H,3H-cyclopenta[c]furan-5-one (entry 3 in Table 5):^[21] Yield: 90%, $[\alpha]_D^{20}$: -2.8 (c 1.3 in CH₂Cl₂); CHIRALPAC AS: 34% ee, 2-propanol/hexane = 10/90, flow rate = 1 mL/min, 1st product = 15.80 min, 2nd product = 17.68 min. The ¹H NMR spectrum matched the published spectrum.

6-Phenyl-3a,4-dihydro-1H,3H-cyclopenta[c]furan-5-one (entry 5 in Table 5):^[21] Yield: 91%, $[\alpha]_D^{20}$: -10.3 (c 1.50 in CH₂Cl₂); CHIRALPAC AS: 84% ee, 2-propanol/hexane = 10/90, flow rate = 1 mL/min, 1st product = 15.75 min, 2nd product = 17.66 min. The ¹H NMR spectrum matched the published spectrum.

6-Butyl-3a,4-dihydro-1H,3H-cyclopententa[c]furan-5-one (entry 6 in Table 5):^[21] Yield: 75%, $[\alpha]_D^{20}$: -32.1 (c 1.11 in CH₂Cl₂); CHIRALPAC AS: 62% ee, 2-propanol/hexane = 5/95, flow rate = 0.9 mL/min, 1st product = 10.26 min, 2nd product = 11.89 min. The ¹H NMR spectrum matched the published spectrum.

6-Methyl-3a,4-dihydro-1H,3H-cyclopenta[c]furan-5-one (entry 7 in Table 5):^[21] Yield: 85%, $[\alpha]_D^{20}$: -79.3 (c 0.90 in CH₂Cl₂); CHIRALPAC AS: 80% ee, 2-propanol/hexane = 10/95, flow rate = 1 mL/min, 1st product = 9.73 min, 2nd product = 10.53 min. The ¹H NMR spectrum matched the published spectrum.

6-Phenyl-2-(4-toluenesulfonyl)-2,3,3a,4-tetrahydro-1H-cyclopenta[c]pyrrol-5-one (entry 8 in Table 5):^[21] Yield: 94%, $[\alpha]_D^{20}$: +95.7 (c 0.57 in CH₂Cl₂); CHIRALPAC AD: 85% ee, 2-propanol/hexane = 20/80, flow rate = 0.9 mL/min, 1st product = 17.75 min, 2nd product = 22.66 min. The ¹H NMR spectrum matched the published spectrum.

6-Methyl-5-oxo-3,3a,4,5-tetrahydro-1H-pentalene-2,2-dicarboxylic acid dimethyl ester (entry 9 in Table 5):^[23b] Yield: 92%, $[\alpha]_D^{20}$: +57.5 (c 0.80 in CH₂Cl₂); CHIRALPAC AS: 56% ee, 2-propanol/hexane = 15/85, flow rate = 1 mL/min, 1st product = 11.83 min, 2nd product = 14.12 min. The ¹H NMR spectrum matched the published spectrum.

5-Oxo-6-phenyl-3,3a,4,5-tetrahydro-1H-pentalene-2,2-dicarboxylic acid dimethyl ester (entry 10 in Table 5):^[21] Yield: 89%, $[\alpha]_D^{20}$: +30.1 (c 1.3 in CH₂Cl₂); CHIRALPAC AS: 64% ee, 2-propanol/hexane = 15/85, flow rate = 1 mL/min, 1st product = 11.70 min, 2nd product = 14.53 min. The ¹H NMR spectrum matched the published spectrum.

6-Methyl-5-oxo-3,3a,4,5-tetrahydro-1H-pentalene-2,2-dicarboxylic acid diethyl ester (entry 11 in Table 5):^[37] Yield: 93%, $[\alpha]_D^{20}$: +85.6 (c 0.58 in CH₂Cl₂); CHIRALPAC OD-H: 87% ee, 2-propanol/hexane = 10/90, flow rate = 1 mL/min, 1st product = 6.53 min, 2nd product = 7.43 min. The ¹H NMR spectrum matched the published spectrum.

5-Oxo-6-phenyl-3,3a,4,5-tetrahydro-1H-pentalene-2,2-dicarboxylic acid diethyl ester (entry 12 in Table 5):^[36] Yield: 94%, $[\alpha]_D^{20}$: +43.9 (c 0.58 in CH₂Cl₂); CHIRALPAC AS: 51% ee, 2-propanol/hexane = 10/90, flow rate = 1 mL/min, 1st peak = 8.88 min, 2nd peak = 12.37 min. The ¹H NMR spectrum matched the published spectrum.

ICP-AES Analysis

Co and Rh contents were determined using inductive coupled plasma atomic emission spectroscopy (ICP-AES) with the Shimadzu ICPS-1000 IV device. The analysis showed that the cobalt-to-rhodium ratios were 1.09 for Co₂Rh₂ and 2.93 for Co₃Rh, respectively. When an ICP-AES analysis of the reaction mixture after completion of the reaction of crotonaldehyde with phenylacetylene was carried out, the contents of cobalt and rhodium were beyond the detection limit. For the test of the reusability of the catalytic asymmetric system (entries 5 and 13–16 Table 5), an ICP-AES experiment (elemental analysis) on the reaction mixture after completion of the three runs was carried out. The analysis showed that 3.9 ppm of cobalt and 0.3 ppm of rhodium species were present.

Mercury-Poisoning Experiment

Two batches were prepared for the experiment. The same amounts of enyne, crotonaldehyde, and chiral diphosphine were used for each experiment: [(3-allyloxy)prop-1-ynyl]benzene (0.96 mmol), crotonaldehyde (2.4 mmol), (S,S)-BDPP (0.11 mmol), and Co₂Rh₂ on charcoal (50 mg, 12 mg of Co₂Rh₂) in THF (5 mL) were put in a stainless-steel bomb. The bomb was heated at 130 °C for 5 h. After the reactor had cooled to room temperature, the solution was filtered and the filtrate was evaporated to dryness. Chromatography on a silica gel column eluting with hexane and diethyl ether (v/v, 5:1) gave the product in 31% yield with 82% ee.

For the mercury-poisoning experiment, the same procedure as above was applied except that the addition of Hg (0.175 g, 320 equivs. to Co₂Rh₂ used) was made after heating the reactor for 5 h. After the addition of Hg, the reactor was heated for 15 h. The usual purification procedure gave the product in 32% yield with 79% ee.

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