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Pauson–Khand reactions catalyzed by entrapped rhodium complexes

Kang Hyun Park, Seung Uk Son and Young Keun Chung*

School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-747, South Korea

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Abstract—An entrapped Rh complex prepared by a sol–gel process has been used as a catalyst in the Pauson–Khand reaction under mild reaction conditions; the catalyst is easily recovered and reused at least 10 times without losing catalyst activity. © 2003 Published by Elsevier Science Ltd.

Since its discovery in the early 1970s, the cobalt-mediated carbonylative cocyclization of an alkyne and an alkene, known as the Pauson–Khand reaction, has become nowadays one of the most versatile methods for the synthesis of cyclopentenones.[1] In addition to cobalt, the use of other transition metals has been studied.[2] Among them, the most studied catalyst is based on the rhodium metal. Recent development of the heterogeneous catalytic version based on cobalt fulfils the principle of atom economy.[3] However, one of the disadvantages of the cobalt-catalyzed reaction is a harsh reaction condition, i.e. high temperatures and high pressures of CO. When rhodium complexes were used as catalysts, the Pauson–Khand reaction was conducted under relatively mild reaction conditions.[2] Thus, the use of rhodium in the Pauson–Khand reaction can solve the drawback of the Pauson–Khand reaction and is now quite common. Nevertheless, there are still some problems in the use of rhodium. Compared to cobalt, the rhodium is quite expensive. In order to commercialize the rhodium catalyzed-Pauson–Khand reaction, the rhodium complex should be recovered and reused. Thus, the development of the reusable rhodium catalysts is very important. However, there have been no reports on the recovery and reuse of the rhodium catalysts.

Heterogeneous catalysts are considered to be advantageous for the facile separation, as well as recovery and reuse. Thus, we tried to immobilize rhodium metals on supports. However, the rhodium metals on supports were not active as the homogeneous rhodium complexes. While studying the immobilization of rhodium complexes on the support, an entrapment of catalysts by sol–gel process has attracted our attention although entrapped or encapsulated catalysts have an inherent problem of the usually strong diffusion resistance due to the limited pore size.[4] However, in some cases, the activities and selectivities of entrapped catalyst have been found to be competitive with homogeneous catalysts.[5] We herein report the entrapment of rhodium complexes and their use in the catalytic Pauson–Khand reaction.

An entrapped rhodium catalyst was generated by silica sol–gel entrapment of $[Rh(cod)(\mu\text{-}Cl)]_2$ in THF solution.[6] Without modifying rhodium complex using silyloxy group for a covalent bonding, a non-modified

Table 1.

Entry	CO (atm)	Temp. (°C)	Yield (%)[a]
1	1	100	NR
2	3	100	65
3	5	60	73
4	5	100	90
5	5	130	90
6	Reuse from #4	100	91
7	Reuse from #5	100	90
8	Reuse from #6	100	88
9	Reuse from #7	100	89
10	Reuse from #8	100	87
11	Reuse from #9	100	90
12	Reuse from #10	100	88
13	Reuse from #11	100	88
14	Reuse from #12	100	90

[a] Isolated yields.

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* Corresponding author. Tel.: +82-2-880-6662; fax: +82-2-889-0310; e-mail: ykchung@plaza.snu.ac.kr

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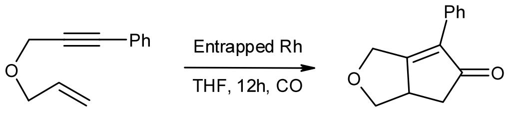
metallic complex was used for physical entrapment in sol–gel matrix.

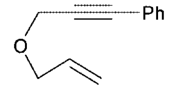
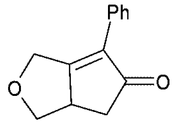
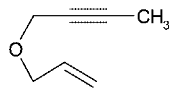
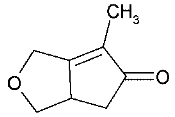
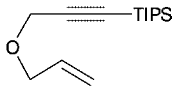
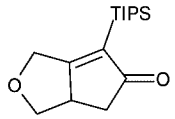
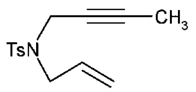
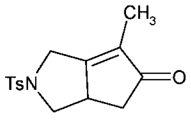
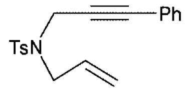
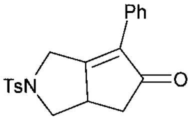
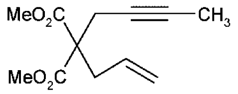
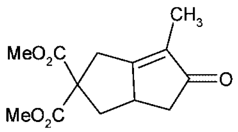
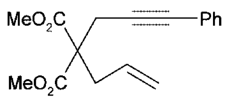
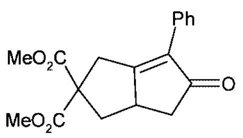


(1)

The intramolecular Pauson–Khand reaction of an enyne was investigated as a test reaction (Eq. (1)).[7] Table 1 summarizes the results of this reaction under various reaction conditions.

Entry 4 shows that the entrapped rhodium complex is very active with an isolated yield of product of 90% at 100°C and a CO pressure of 5 atm. Thus, the entrapped rhodium catalyst is more active than heterogeneous catalysts (130°C and 20 atm CO) based on metallic cobalt supported on mesoporous silica or charcoal, but it has a little lower catalytic activity than homogeneous rhodium catalysts.[8] However, when either the reaction temperature was decreased to 60°C or the CO pressure was lowered to 3 atm, the catalytic activity was found to decrease significantly (entries 1–3). Thus, to preserve a high catalytic activity, the reaction temperature and CO pressure have to be maintained at a minimum of 100°C and 5 atm of CO. To check the recyclability, the catalyst was separated and reused 10 times (entries 6–14). The results shown in Table 1 confirm that the catalyst maintained its high activity even after 10 cycles of recycling and reuse. After five times recycling, ICP-AES study showed that 0.278 ppm of rhodium, equal to leaching of 0.086% rhodium, was in solution. Recent study shows that the percentage of nickel bleed from

Table 2. Pauson–Khand reaction with various substrates[a]

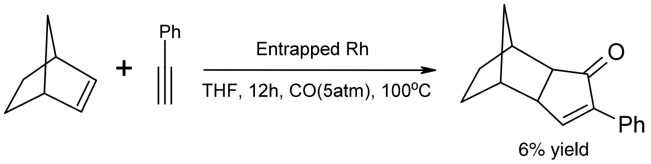
entry	substrates	products	yield(%)[b]
1			90
2			93
3			83
4			79
5			81
6			90
7			88

[a] Reaction conditions : THF, 12h, 5atm CO, 100°C

[b] Isolated yields.

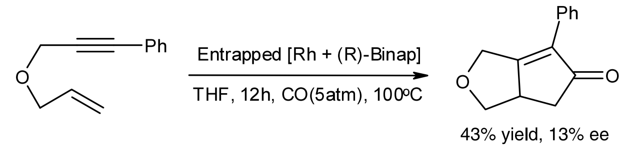
Ni/C after a catalytic reaction such as Suzuki coupling, Kumada coupling, and amination reaction was in the range of 0.4 to 3.0% of the original nickel used as Ni/C.[9] Compared to the case of Ni/C, the leaching of rhodium was negligible. This feature allows for effective recycling of the catalyst, since no rhodium is lost during filtration after completion of the reaction, and the catalyst displays identical activities in subsequent experiments.

To demonstrate the versatility of the entrapped rhodium catalyst, we screened various substrates for the catalytic Pauson–Khand reactions and the results are shown in Table 2. This catalytic reaction was quite effective with substituted enynes. The hetero-atom tethered substrates were tested to generate the corresponding products in high yields. However, this catalytic system is not quite effective for intermolecular Pauson–Khand reaction (Eq. (2)).



(2)

Next we investigated an asymmetric Pauson–Khand reaction using entrapped rhodium complexes $[Rh(cod)(\mu\text{-}Cl)]_2$ and $[Rh(acac)(CO)_2]$ and (*R*)-BINAP as chiral catalysts (Eq. (3)).



(3)

When 1 equiv. (*R*)-BINAP was used, the yield was 79–87% with 3–7% ee. An increase of the amount of (*R*)-BINAP to 2.5 equiv. led to increase the ee values up to 13% with a lower yield 43–65%. This ee value is quite poor, but is not meaningless. It gave us quite positive respect for the improvement of the asymmetric induction.

The ^{31}P NMR study of the entrapped catalyst in $CDCl_3$ shows phosphine–phosphine oxide as the sole species. Due to the low reactivity of rhodium complex of phosphine–phosphine oxide, it is not used as a catalyst in the Pauson–Khand reaction. Thus, it seems that the poor ee value was due to the presence of rhodium phosphine–phosphine oxide as a catalyst instead of rhodium diphosphine complex.

In conclusion, we have demonstrated that the entrapped Rh complex can be used as a catalyst in the Pauson–Khand reaction under mild reaction conditions and is easily recovered and reused at least 10 times without losing catalytic activity. However, the use of entrapped Rh complex and BINAP offered poor ee values (13% ee).

Acknowledgements

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6. (a) Abu-Rezig, R.; Avnir, D.; Miloslavski, I.; Schumann, H.; Blum, J. *J. Mol. Catal. A: Chem.* **2002**, *185*, 179; (b) To 10 mL of THF were added tetraethoxysilane (6.0 mL, 26.9 mmol), distilled water (2.0 mL), and triethoxysilane (0.3 mL). After, the solution was stirred at rt for 15 min, a solution of $[Rh(cod)(\mu\text{-}Cl)]_2$ (0.030 mg, 0.06 mmol) in 2 mL of THF was added. The resulting solution was heated at 60°C until gelation occurred. After drying in vacuum for 1 day, 1.80 g of entrapped rhodium complex was obtained. In order to induce an asymmetric Pauson–Khand reaction, a rhodium complex of chiral phosphine was entrapped by the sol–gel process. According to the ^{31}P NMR spectrum, the entrapped rhodium complex is rhodium complex of phosphine–phosphine oxide (^{31}P NMR ($CDCl_3$) δ 41.7 (d, $J_{Rh-P} = 171.3$ Hz), 41.7 (s) ppm; see the paper by Bunten, K. A.; Farrar, D. H.; Poë, A. J.; Lough, A. *Organometallics* **2002**, *21*, 3344. During the sol–gel process, one of the phosphines was oxidized to phosphine oxide.
7. General procedure for catalytic Pauson–Khand reactions: To a solution of 1,6-enyne (0.20 g, 1.2 mmol; entry 1 in Table 1) in 5 mL of THF was added entrapped Rh (12.5 mg, 0.12 mmol, 10 mol%). The reactor was charged with 5 atm of CO and heated at 100°C for 12 h. After the reactor

was cooled to rt, the solution was filtered, concentrated, and chromatographed on a silica gel column eluting with hexane and diethyl ether (v/v, 5:1). When the catalyst was recycled, the catalyst was filtered, dried in vacuum, and reused for the further catalytic reaction.

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