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Sequential Actions of Palladium and Cobalt Nanoparticles Immobilized on Silica: One-Pot Synthesis of Bicyclic Enones by Catalytic Allylic Alkylation and Pauson–Khand Reaction

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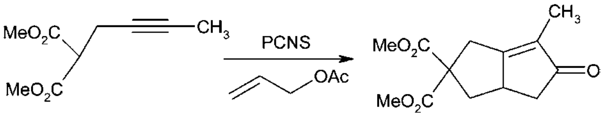
ABSTRACT



Palladium and cobalt nanoparticles immobilized on silica have been used as catalyst in a sequential allylic alkylation and Pauson–Khand reaction to form bicyclic enones.

One of the challenging goals of synthetic chemistry is to discover reactions and strategies that allow for the facile conversion of simple compounds into complex molecules. In this regard, a variety of homogeneous catalysts have been used. Recently, the use of bimetallic catalysts (a combination of two catalysts) or bifunctional single catalysts in one-pot reactions has been developed.[1]

Many transition-metal nanoparticles are highly active heterogeneous catalysts partly as a result of their high surface-to-volume ratio.[2] Recently, bimetallic nanoparticles have come to be of special interest[3] 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 single reaction utilizing the synergistic effect between the different metal atoms[4] but not for a sequential reaction of two specific reactions corresponding to two different metals. We envision that catalytic multistep one-pot reactions can be carried out by the use of bi- or poly-metallic nanoparticles as catalysts.

We herein report the use of immobilized-palladium and cobalt nanoparticles on silica in the sequential allylic alkylation and Pauson−Khand reaction. This strategy provides a facile methodology for the construction of bicyclic enones from easily available simple molecules. To the best of our knowledge, this is the first report of the use of immobilized bimetallic nanoparticles in two conceptually different catalytic reactions in a one-pot reaction. Recently,

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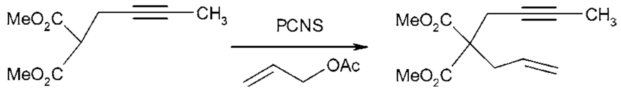
we reported[5] a sequential allylic alkylation and Pauson−Khand reaction catalyzed by a combination of cobalt nanoparticles and Pd(II) catalyst.

The palladium nanoparticles immobilized on silica (1 wt % of Pd) were prepared by the reaction of $Pd(OAc)_2$ with colloidal silica in a mixture solvent of ethanol and toluene (v/v, 6:94).[6] An HRTEM study showed that each nanoparticle was immobilized on silica. There were no agglomerations between different metals.

We first tested the allylic alkylation catalyzed by Pd nanoparticles. Although carbon−carbon bond formations catalyzed by palladium nanoparticles are well-known in Suzuki couplings[7] and Heck reactions,[8] as far as we are aware, this is the first palladium nanoparticle catalyzed allylic alkylation.

We screened the reaction conditions including reaction medium, base, and reaction time for Pd-catalyzed allylic alkylation (Table 1). The best yield (89%, entry 2) was obtained when the reaction was carried out in THF and using NaH as a base for 6 h. Compared to a short reaction time (entry 1), a long reaction time (entry 2) assisted the reaction yield. However, a prolonged reaction time (entry 3) did not improve the yield. When we used $NaHCO_3$ as a base in THF, the yield decreased slightly to 78%. Use of BSA as a base afforded only 23% of the product. When K_2CO_3 was used as a base in a mixture of THF and water (v/v, 5:1), no reaction was observed. Interestingly, when DMF was used as a reaction solvent (entry 7), 2-allyl-hex-4-ynoic acid methyl ester was obtained as the sole product.[9] During the reaction, one of the ester groups was removed.

Table 1. Allylic Alkylation under Various Conditions[a]



entry	solvent	base	time (h)	yield (%)[b]
1	THF	NaH	3	46
2	THF	NaH	6	89
3	THF	NaH	10	88
4	THF	K_2CO_3	6	nr
5	THF	BSA	6	23
6	THF	$NaHCO_3$	6	78
7	DMF	NaH	6	87[c]
8	CH_2Cl_2	NaH	6	60

[a] Reaction condition: substrate (0.54 mmol) and PCNS (0.10 g). [b] Isolated yield. [c] 2-Allyl-hex-4-ynoic acid methyl ester.

We next synthesized palladium and cobalt nanoparticles immobilized on silica (**PCNS**) to use as a catalyst in the catalytic sequential allylic alkylation and Pauson−Khand reaction. The **PCNS** (14.5 wt % of Co and 1 wt % of Pd) was prepared by refluxing Pd on silica with colloidal cobalt[10] in ethanol[11] and was analyzed by TEM (and EDS). The HRTEM (Figure 1) suggested that the bimetallic nanoparticles are in the cluster-in-cluster structure.

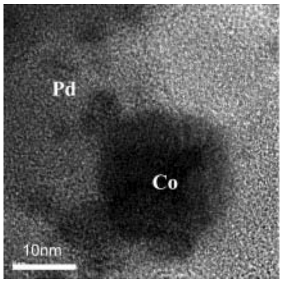
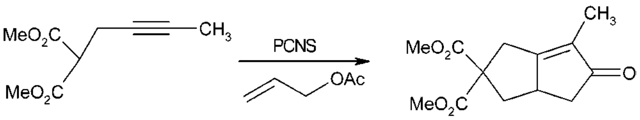


Figure 1. HRTEM image of **PCNS** catalyst.

We investigated the catalytic sequential allylic alkylation and the Pauson−Khand reaction using **PCNS** as a catalyst under various reaction conditions and also studied the reusability of the recovered **PCNS** (Table 2).

Entry 3 shows that the **PCNS** is very active with an isolated product yield of 88% at 130 °C and a CO pressure

Table 2. Sequential Allylic Alkylation and Pauson−Khand Reaction[a]



entry	catalyst	CO (atm)	temp (°C)	yield (%)[b]
1	PCNS	5	130	45
2	PCNS	10	110	69
3	PCNS	10	130	88
4	recovered from 3	10	130	53
5	recovered from 4	10	130	49
6	recovered from 5	10	130	23
7	recovered from 6	10	130	17

[a] Reaction conditions: substrate (0.54 mmol), NaH (0.8 mmol), and PCNS (0.10 g), THF. [b] Isolated yield.

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(6) (a) Horváth, A.; Beck, A.; Sárkány, A.; Guczi, L. *Solid State Ionics* **2002**, *148*, 219−225. (b) Dried colloidal silica (1.0 g, Aldrich Chemical Co., LUDOX HS-30) was suspended in 100 mL of ethanol and toluene (v/v, 6:94) for 10 h. To the suspended solution was added $Pd(OAc)_2$ (0.021 g). The resulting solution was stirred at room temperature for 12 h, filtered, and dried.

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of 10 atm. Thus, the **PCNS** catalyst is more active than heterogeneous catalysts (130 °C and 20 atm CO) based on metallic cobalt supported on mesoporous silica or charcoal. However, when either the reaction temperature was decreased to 110 °C or the CO pressure was lowered to 5 atm, the catalytic activity was found to decrease (entries 1 and 2). Thus, to preserve a high catalytic activity, the reaction temperature and CO pressure have to be maintained at a minimum of 130 °C and 10 atm of CO, respectively. To check the recyclability, the catalyst was separated and reused 5 times (entry 3−7).

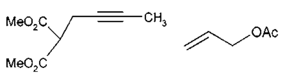
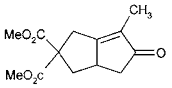
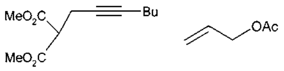
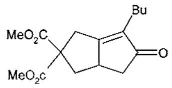
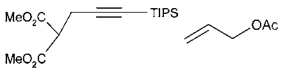
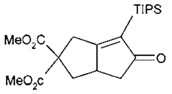
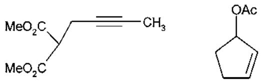
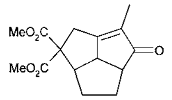
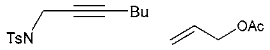
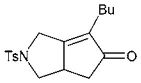
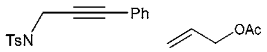
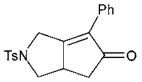
The **PCNS** catalyst sustained a degree of activity after three cycles, with 49% product yield being obtained. An ICP-AES study shows that the percentages of cobalt and palladium bleed from **PCNS** after the first catalytic run were 0.9% of the original cobalt and 36% of the original palladium, respectively. Compared to the case of palladium, the leaching of cobalt was negligible.

Owing to the bleeding of Pd, the reusability of the **PCNS** was greatly damaged. However, the yield of the second run was 53% and that of the third run was 49%. Thus, the **PCNS** may be used at least three times with moderate to high yields.

Next we investigated the versatility of the alkynes and nucleophiles (Table 3). The catalytic reaction (entries 1−3) was quite effective with substituted enynes and allylic acetate. Especially when cyclic allyl acetate was used (entry 4), a tricyclic enone was obtained in 73% yield. The heteroatom tethered substrates were tested to generate the corresponding products in high yields (entries 5 and 6).

In conclusion, we have shown that bimetallic Pd/Co nanoparticles immobilized on solid support can be used as multicomponent catalyst systems as well as multifunctional catalysts. It has been demonstrated that the bimetallic nanoparticles immobilized on solid support have great potential to be tailored with respect to the activity, selectivity, and stability of their numerous combinations.

Table 3. Sequential Allylic Alkylation and Pauson−Khand Reaction with Various Substrates

entry	substrates	products	yield(%)[a]
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.

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Supporting Information Available: Characterization data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The synthesized Pd/SiO$_2$ as in ref 10 was refluxed with colloidal cobalt (generated from 0.5 g of Co$_2$(CO)$_8$) in ethanol.