Poly(ethylene glycol) stabilized Co nanoparticles as highly active and selective catalysts for the Pauson–Khand reaction†

Jean-Luc Muller,[a] Jürgen Klankermayer[a] and Walter Leitner*[ab]

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PEG-stabilized cobalt nanoparticles were prepared by thermal decomoposition of [$Co_2(CO)_8$] in PEG and were shown to be highly active and selective catalysts, for intra- and intermolecular Pauson–Khand reactions (PKR), in organic solvents or aqueous media.

The [2 + 2 + 1] cycloaddition of alkynes with alkenes and carbon monoxide (CO) to form cyclopentenones is known as Pauson–Khand reaction (PKR).[1] The original reaction setup[2] required a stoichiometric application of cobalt complexes derived from [$Co_2(CO)_8$], but catalytic versions were developed more recently.[3,4] Nevertheless the practical utility of this synthetic method is still limited by problems of catalyst separation and the volatile and toxic nature of cobalt carbonyls.[1]

Our group recently demonstrated that commercially available Raney cobalt acts as active and recyclable catalyst for inter- and intramolecular PKR.[5] Raney cobalt can be efficiently separated and reused by filtration and/or exploiting its ferromagnetic properties. Chung and co-workers deposited cobalt particles by thermal decomposition of [$Co_2(CO)_8$] onto various supports and demonstrated the catalytic activities of the resulting materials for the PKR.[6,7] Colloidal cobalt nanoparticles in supported or unsupported form were also used as reusable catalysts for this reaction.[8,9] Cobalt nanoparticles, for the intramolecular PKR in aqueous solution, stabilized by sodiumdodecylsulfate (SDS) were reported.[10] All these nanoparticle catalysed systems require very high catalyst loadings approaching stoichiometric ratios in many cases. So far only heterobimetallic Co/M (M = Rh,[11] Ru[12]) nanoparticles on charcoal lead to active catalytic systems that operate at loadings of a few mol%.

Here we report that poly(ethylene glycol) PEG-stabilized cobalt nanoparticles serve as readily available, highly active and partly recyclable catalysts for the PKR. The catalysts are compatible with organic solvents and aqueous solutions as reaction media. PEG-stabilized cobalt nanoparticles were prepared by thermal decomposition of [$Co_2(CO)_8$] in molten PEG at 80–100 °C. PEG of molecular weight 1000 and 5000 was used. Transmission electron microscopic (TEM) pictures confirmed that the particles stabilized either with PEG_{1000} or PEG_{5000} were smaller than 1.6 nm and well dispersed (Fig. 1). The IR spectra of the catalysts showed no carbonyl absorptions, indicating a complete decomposition of the metal carbonyl. In a first set of experiments the intramolecular PKR (Scheme 1) catalyzed by the PEG-stabilized cobalt nanoparticles was investigated. Under optimized reaction conditions conversions of **1** were almost quantitative using catalyst loadings of only 3.3 mol% (Table 1). By using higher catalyst loadings a significant decrease of the pressure under otherwise identical conditions was possible (Entry 3–4, Table 1).

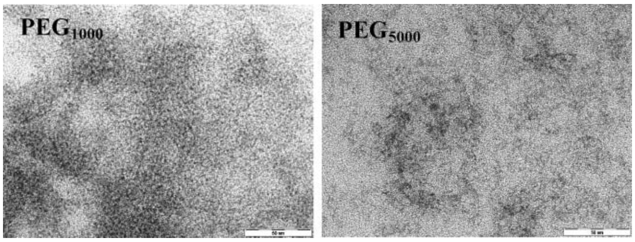
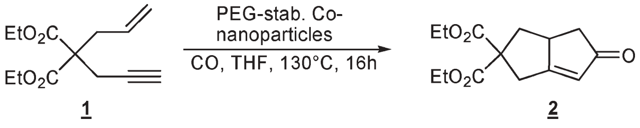


Fig. 1 PEG-stabilized Co-nanoparticles.

The scope of this new protocol was tested in a variety of different intra- and intermolecular PKRs. Representative results obtained under standard conditions are given in Table 2. Almost quantitative conversions were achieved with both catalysts for the malonate derived enynes **1** and **3** as well as for the diol **5**. The PEG-stabilized cobalt nanoparticles were also active for the intramolecular PKR in water, giving high yields of cyclic products (Scheme 2). Interestingly the decarboxylated compound **16** was formed to a large extent under these conditions. In contrast, the literature reported hydrogenation of the double bond in water, was not observed.[10,13]

The intermolecular PKR of norbonene **7** with different alkynes occurs also smoothly with both catalysts, also a higher catalyst loading and and increased CO pressure was required. Again, protic functional groups were tolerated (Table 2, entry 3, 5) and excellent conversions and selectivities were obtained in all cases. The performance of the two different types of nanoparticles was largely identical for the various substrates.

The workup of the reaction mixture is particularly straight forward with the PEG_{5000}-stabilized Co-nanoparticles. These materials are readily separated from the reaction mixture using



Scheme 1 Intramolecular PKR reaction with PEG-stabilized Co-nanoparticles.

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[a] *Institut für Technische und Makromolekulare Chemie, RWTH Aachen, Worringerweg 1, 52074, Aachen, Germany*
[b] *Max Planck Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470, Mülheim an der Ruhr, Germany*

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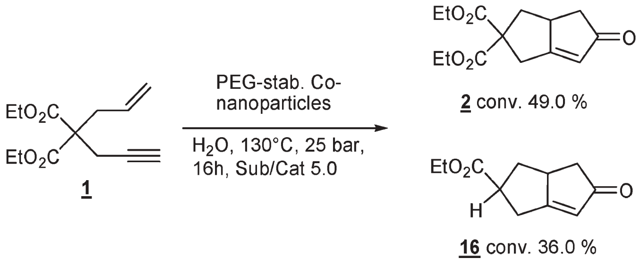
Table 1 Pressure dependence of the PKR catalysed by the PEG-stabilized Co-nanoparticles

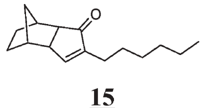
Entry	Co [mol%]	Pressure/bar[a]	Conversion [%]	Selectivity for **2** [%]
1	3	23	⩾99.0	98.0
2	3	10	35.1	89.8
3	50	10	97.4	98.2
4	50	5	84.5	91.8

[a] Pressure in the autoclave at 130 °C. Reaction conditions: All reactions were performed in 4 mL THF, in a 10 mL window equipped steel autoclave. Reaction time 16 h. Catalyst: PEG_{5000}-stabilized Co-nanoparticles.



Scheme 2 Intramolecular PKR in water.

Table 3 Recycling of PEG_{5000}-Co-nanoparticles with $scCO_2$

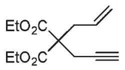
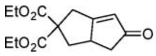
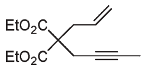
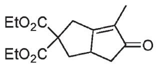
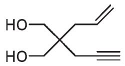
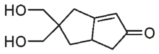
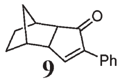
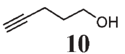
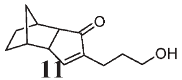
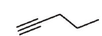
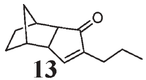
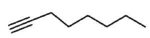
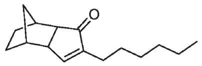
Entry	Product	Conversion [%]	Selectivity [%]
1	 **15**	99.0	97.0
2		77.9	99.0
3		72.3	99.0
4		32.2	99.0

Reaction conditions: All reactions were performed in 2 mL THF, in a 10 mL, window equipped steel autoclave at 130 °C and 35 bar CO pressure. Reaction time 16 h. **14**/Catalyst 20.0. Extraction conditions: 130 bar, 80 °C, 10 l/h, 2.5 h.

either Et_2O or $scCO_2$ as extraction media for the products. Fair to excellent yields of the pure products were obtained after separation of the catalyst with Et_2O (Table 2). NMR spectra of the products showed that they contained no or only trace amounts of PEG in the product so that a simple and effective procedure for the product isolation and catalyst separation is available. Contamination with cobalt was found to be in the range of 19 to 120 ppm for the examples in Table 2. The recyclability of these PEG_{5000}-Co catalysts was tested for both methods with different products (Table 3 and 4). Pressurizing the reaction mixture with $scCO_2$ leads to precipitation of the PEG-stabilized nanoparticles, similar to what has been observed for PEG-modified organometallic complexes.[14] The activity of the recycled catalyst remained reasonable over three runs but decreased sharply in the fourth run (Entry 4, Table 3). A comparable deactivation was observed using the Et_2O extraction protocol (Table 4). Nevertheless the selectivity for the formation of the desired products **11** and **15** remained uniformly high in both series of experiments. The total turnover number (TON) achieved for the Et_2O extraction and recycling experiments amounts to 58.3 mol of **11** per mol of cobalt. This corresponds to 203.8 g of **11** per gram of cobalt.

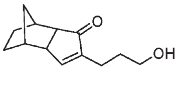
The deactivation of the catalytic system results partly from the as yet noticeable cobalt leaching (up to 0.74% per cycle based on the contamination in the product). Other factors such as changes in the particle morphology can, however, not be excluded. TEM

Table 2 Inter- and intramolecular PKR with PEG-stabilized cobalt nanoparticles

			PEG_{1000} stab. Co-nanoparticles		PEG_{5000} stab. Co-nanoparticles		
Entry	Substrate	Product	Conversion [%]	Selectivity [%]	Conversion [%]	Selectivity [%]	Yield [%][a]
1	 **1**	 **2**	⩾99.0	98.0	99.0	98.0	88.7
2	 **3**	 **4**	⩾99.0	99.0	99.0	95.0	89.9
3	 **5**	 **6**	99.0	94.0	98.0	86.2	73.5
4	 **7**  **8**	 **9**	94.3	95.1	98.9	91.1	87.5
5	 **7**  **10**	 **11**	99.0	85.0	98.5	85.0	81.5
6	 **7**  **12**	 **13**	⩾99.0	94.2	85.0	90.4	71.5
7	 **7**  **14**	 **15**	99.0	95.5	99.0	99.0	85.5

[a] Yield of isolated product. Reaction conditions: all reactions were performed in 4 mL THF, in a 10 mL window equipped stainless steel autoclave. Reaction time: 16 h. Entry 1–3: substrate/Co 30.0. CO pressure 23 bar at 130 °C. Entry 4: substrate/Co 30.0. CO pressure 35 bar at 130 °C. Entry 5–7: substrate/Co 20.0. CO pressure 35 bar at 130 °C.

Table 4 Recycling of PEG_{5000}-Co-nanoparticles with Et_2O

Entry	Product	Conversion [%]	Selectivity [%]
1	 **11**	98.5	85.0
2		98.0	83.0
3		69.0	82.6
4		25.8	97.0

Reaction conditions: All reactions were performed in 4 mL THF, in a 10 mL, window equipped steel autoclave at 130 °C and 35 bar CO pressure. Reaction time 16 h. **10**/Catalyst 20.0.

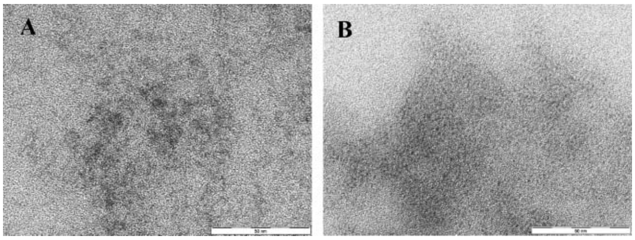


Fig. 2 PEG_{5000}-stabilized Co-nanoparticles before reaction (A) and after the recycling experiments (B).

micrographs of the same catalyst before and after the recycling series (summarized in Table 4) show no significant increase in the size of the primary particles, but indicate a reduced degree of dispersion within the PEG matrix (Fig. 2). Possibilities to ameliorate both leaching and agglomeration include the further development of supported PEG-phase systems.[15]

In conclusion, we have shown that Poly(ethylene glycol) (PEG) stabilized cobalt nanoparticles could be synthesized by thermal decomposition of $[Co_2(CO)_8]$ in molten PEG. These PEG-stabilized cobalt nanoparticles are broadly applicable as catalysts in intra- and intermolecular Pauson–Khand reactions, in organic solvents or aqueous phase. The activities of these new materials compare favourably with that of previously described nanoparticle-based systems and heterogeneous catalysed PKR reactions. The PEG-stabilized cobalt nanoparticles are easy to handle, stable over weeks and can be effectively separated from the reaction products by using diethyl ether or supercritical carbon dioxide. The principle recyclability of the catalysts has been demonstrated, albeit further optimization is necessary to minimize the metal leaching and catalyst deactivation.‡

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Notes and references

‡ *Catalyst preparation*. After degassing of $PEG_{1000}(OMe)_2$ (1.1 g, 1.1 mmol) for 3 h at 80 °C, a solution of $[Co_2(CO)_8]$ (170.0 mg, 0.5 mmol) in 10 mL toluene was injected to the molten PEG under counter current flow of argon. The reaction solution was heated to 100 °C for 20 min under rigorous shaking and was concentrated afterwards over 1 h under reaction conditions leading to a green black waxy precipitate. The PEG_{1000}-stabilized cobalt nanoparticles were analysed by IR and TEM. Preparation of PEG_{5000}-stabilized Co nanoparticles is achieved using an identical procedure.

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