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[5] J. V. Greenhill, P. Lue, *Prog. Med. Chem.* **1993**, *30*, 203 – 326.
[6] All reactions were carried out under argon. Optimization experiments were carried out in Schlenk tubes in a 10-well reactor thermostated at the required temperature and each well independently stirred (Stem ReactoStation, model RS900).
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Cobalt on Charcoal: A Convenient and Inexpensive Heterogeneous Pauson – Khand Catalyst**

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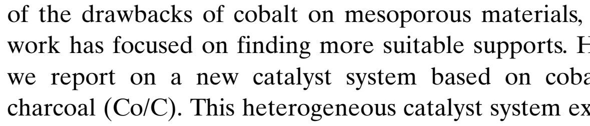
Although much success has been achieved in the field of transition metal mediated (or catalyzed) synthesis of cyclopentenones from readily available substrates,[1] industrial applications are surprisingly still undeveloped. In order to develop large-scale processes, it is extremely important and prerequisite to heterogenize homogeneous systems. Recently we published[2] the first heterogeneous catalyst system for the Pauson – Khand reaction based on cobalt on mesoporous silica. Polymer-supported cobalt carbonyl complexes have been reported[3] as catalysts of the intramolecular Pauson – Khand reaction, but the catalytic activity was low. The cobalt on a mesoporous material system is a quite effective catalyst for the intramolecular Pauson – Khand reaction, but displays low activity in the intermolecular Pauson – Khand reaction. 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. Herein we report on a new catalyst system based on cobalt on charcoal (Co/C). This heterogeneous catalyst system exhibits an excellent catalytic performance for intra- and intermolecular Pauson – Khand reactions [Eq. (1)]. The catalyst system is quite stable and can be reused. Recently, catalyst systems based on transition metals on charcoal have attracted much attention.[4]



(1)

The catalyst system was prepared by thermal decomposition of $[Co_2(CO)_8]$ in the presence of commercially available charcoal bone in THF under reflux.[5] The catalytic activity of Co/C strongly depends on the amount of cobalt on charcoal (wt %). When the cobalt loading on charcoal was less than 7.5 wt %, no catalytic reaction was observed. The optimum cobalt loading on charcoal was about 12 wt %. The IR spectra of the supported catalysts show no carbonyl absorptions, confirming a complete decomposition of the metal carbonyl. X-ray powder diffraction (XRD) patterns of the supported catalysts revealed peaks of hexagonal close packed (hcp) metallic cobalt, as in the bulk phase.[6] A transmission electron microscopic (TEM) study (Figure 1) shows that cobalt atoms are not distributed homogeneously in the charcoal surface, but form metallic cobalt particles (100 – 1000 nm). The black Co/C shows ferromagnetism and is easily recovered by filtration or by using a magnet.

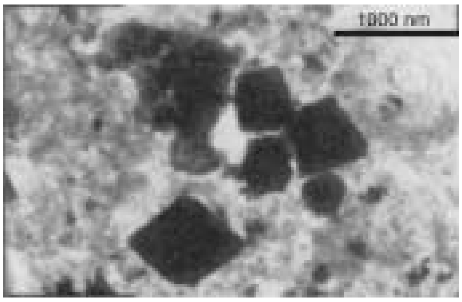


Figure 1. Transmission electron micrograph of Co/C.

The scope of application of this catalyst was examined with a number of substrates both in inter- and intramolecular variants of the Pauson – Khand reaction. Several representative results obtained under standard conditions are given in Table 1. The intramolecular cycloaddition proceeded smoothly with monosubstituted olefins regardless of the substitution pattern of alkynes (Table 1, entries 1 – 4), although the internal olefin substrate (Table 1, entry 5) needs a relatively long reaction time. Heteroatom-bridged enynes produced aza- (Table 1, entry 4) and oxobicyclic compounds (Table 1, entries 3 and 5) from the corresponding substrates. In most cases, the yields of the intramolecular reactions are almost quantitative. For intermolecular cycloadditions with the Co/C system the substrate structure has little influence on the results. Satisfactory results are obtained with simple terminal alkynes (Table 1, entries 6 and 7), a conjugated alkyne (Table 1, entry 8), and a diyne (Table 1, entry 10). In contrast, an *n*-alkyl halide substituted alkyne (Table 1, entry 9)[7] was not a suitable substrate for the Co/C system. In the case of the diyne substrate (entry 10), a double intermolecular Pauson – Khand reaction[8] occurred and no [2+2+2] cycloaddition product was observed.

The most important advantage of heterogenous catalysis over its homogeneous counterpart is the possibility of recovering the catalyst after reaction by simple filtration. For the intramolecular Pauson – Khand reaction according to

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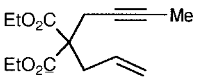
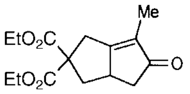
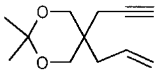
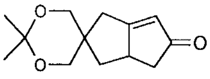
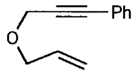
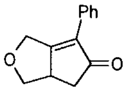
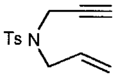
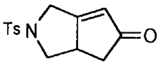
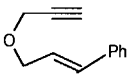
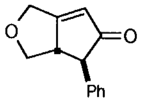
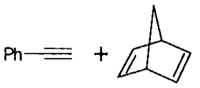
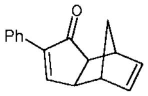
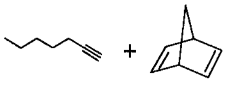
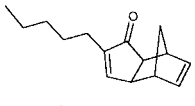
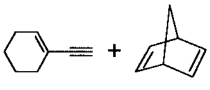
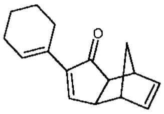
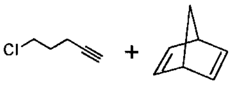
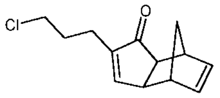
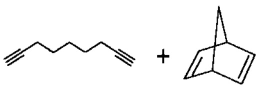
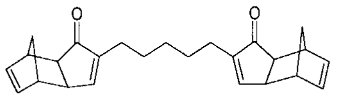
1433-7851/00/3922-4158 $ 17.50+.50/0

Table 1. Pauson–Khand reaction with various substrates.[a]

Entry	Substrate	Product	p [atm]	t [h]	Yield[b] [%]
1			20	18	98
2			20	7	93
3			20	18	98
4			20	7	98
5			30	24	61
6			30	18	98
7			30	18	98
8			30	18	98
9			30	18	22
10			30	48	89

[a] 0.1 g Co/charcoal (12wt.%) catalyst and 1.26 mmol (entries 1–5) or 1.64 mmol (entries 6–10) substrate were used. $TsH_3CC_6H_4SO_2$. [b] Yield of isolated product.

Equation (1), the catalyst system could be reused 10 times without loss of activity (Table 2); the maximum reusability has not been tested. The reusability can be understood when we consider almost no bleeding of cobalt from the charcoal surface. Elemental analysis (by inductively coupled plasma atomic emission spectroscopy (ICP-AES)) of the reaction mixture after completion of the reaction showed that less than 0.1 ppm of cobalt species was bled.

Table 2. Test for the reusability of the catalyst. The reaction given in Equation (1) was selected as the test reaction.[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	95

[a] 0.1 g catalyst and 1.26 mmol substrate were used. [b] Yield of isolated product.

We have screened graphite and mesoporous carbon as a support. Interestingly, the catalytic activities of cobalt on graphite and mesoporous carbon are almost the same as that of cobalt on charcoal even though they have quite different surface areas and structures. Furthermore, XRD and TEM studies on cobalt on graphite and mesoporous carbon likewise show peaks for hexagonal close packed metallic cobalt similar in intensity to those for cobalt on charcoal. Thus, it seems likely that the catalytic activity depends on the state of metallic cobalt on the support and not on the nature of the carbon support.

In conclusion, cobalt on charcoal has been developed as an inexpensive, heterogeneous, and highly effective catalyst for intra- and intermolecular Pauson–Khand reactions. The reusability of the catalyst and the experimental simplicity are especially attractive and should encourage the use of this catalyst system among synthetic chemists and in industrial applications.

Experimental Section

The enyne shown in Equation (1) (0.30 g, 1.26 mmol) and Co/C (0.10 g, 12.2 wt% Co) in THF (15 mL) was heated under carbon monoxide (20 atm at room temperature) at 130 °C for 7 h. After workup and column chromatography, the corresponding cyclopentenone derivative was obtained 92% yield.

Characterization of the product of entry 10 in Table 1: IR (NaCl): $\tilde{\nu} = 1690$ (s; ν(CO)) cm^{-1}; m.p. 51 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.16$ (s, 2H), 6.28 (m, 2H), 6.20 (m, 2H), 2.90 (br.s, 2H), 2.70 (br.s, 2H), 2.66 (br.s, 2H), 2.27 (m, 2H), 2.15 (t, $J = 7.3$ Hz, 4H), 1.49 (q, $J = 7.4$ Hz, 4H), 1.37 (q, $J = 7.3$ Hz, 2H), 1.36 (d, $J = 9.2$ Hz, 2H), 1.19 (d, $J = 9.2$ Hz, 2H); elemental analysis (%): calcd: C 83.29, H 7.89; found: C 83.36, H 7.97.

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[5] Charcoal (2.0 g, WAKO Pure Chemical Industry) in a Schlenk flask was flame-dried under vacuum and cooled to room temperature. [Co$_2$(CO)$_8$] (0.50 g), THF (30 mL) and charcoal (1.0 g) were put in a 50 mL of Schlenk flask and the mixture was refluxed for 12 h. After the solution was cooled to room temperature, the solid was filtered off, washed with hexane, diethyl ether, and CH$_2$Cl$_2$, and dried under vacuum for one day. Cobalt on charcoal (Co/C, 1 g) was obtained with a cobalt loading of 12.2 wt% (analyzed by ICP-AES).

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(CuI)$_2$P$_8$Se$_3$: An Adduct of D_3-Symmetrical P$_8$Se$_3$ Cage Molecules with Cu$_2$I$_2$ Rhomboids[**]

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Copper(I) halides have been established as a preparative tool for neutral and low charged molecules of the group 15 and 16 elements. Thus, several adducts of polymers, either of phosphorus or chalcogens, could be prepared in a crystalline state and characterized.[1] By this approach, the β-P$_4$Se$_4$ cage, which was not previously accessible, was synthesized in (CuI)$_3$P$_4$Se$_4$. This compound is an adduct of a neutral phosphoselenide cage with copper iodide.[2] Lowering the annealing temperature of the starting materials, copper iodide, phosphorus, and selenium, yields (CuI)P$_4$Se$_4$,[3] in which phosphorus and selenium are arranged as polymers consisting of P$_4$Se$_3$ cages, analogous to norbornane, bridged by selenium atoms. This finding is consistent with the behavior of free equimolar mixtures of phosphorus and selenium, that, at low temperatures, form a polymer[4] which depolymerizes at higher temperatures.[5] The depolymerization processes in phosphorus–selenium melts were subject of a series of experiments.[5] By means of NMR techniques, it was shown for P–Se mixtures of 48% P that, at about 375 °C, the depolymerization and the formation of oligomers becomes significant.[6] However, to date only four further phosphoselenide binary compounds have been crystallographically characterized. These compounds are P$_2$Se$_5$,[7] P$_{14}$Se,[8] P$_4$Se$_5$,[9] and P$_4$Se$_3$.[10] Therefore, information on the molecular structures of phosphoselenides is rather limited as compared to phoshosulfides.[11] The major problem that hinders the preparation of phosphoselenides seems to be their tendency to form amorphous polymers at ambient temperatures. Since oligomeric and polymeric P$_4$Se$_4$ can be obtained in copper iodide at different temperatures, we were encouraged to explore the system CuI-P-Se for the existence of further adducts of either oligomeric or polymeric phosphoselenides with copper iodide. Herein, we report the synthesis and the structural characterization of (CuI)$_2$P$_8$Se$_3$.

The adduct (CuI)$_2$P$_8$Se$_3$ was obtained as a red crystalline material from the reaction of stoichiometric mixtures of CuI, P, and Se (CuI:P:Se = 2:8:3). The crystal structure was determined from single crystals.[12] It consists of planar Cu$_2$I$_2$ rhomboids and P$_8$Se$_3$ phosphoselenide cages. It has been recently discussed that this building unit can adapt to a given coordination necessity due to the flexibility of both the $\sphericalangle$(Cu-I-Cu) and the $\sphericalangle$(I-Cu-I) angles.[3] Typical measures for these rhomboids are, for example, the distance d(Cu-Cu) and the angles mentioned above. For (CuI)$_2$P$_8$Se$_3$, the following

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