Conversion of chlorophenols into cyclohexane by a recyclable Pd-Rh catalyst

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Abstract

Mono and polychlorinated phenols that undergo only partial detoxification by conventional hydrogenation methods undergo exhaustive hydrogenation in the presence of a combined silica sol–gel entrapped catalyst composed of metallic palladium and chloro(1,5-cyclooctadiene)rhodium dimer. While the mono-, di-, tri- and tetrachlorophenols are converted into cyclohexane in a variety of solvents at 120 °C under 27.6 bar H_2, the pentachlorophenol requires the presence of toluene. Experiments conducted under milder conditions revealed that the hydrodechlorination of the chlorophenols proceeds via gradual evolvement of the chlorine atoms forming HCl and phenol. The C=C bonds of the latter compound are saturated stepwise. The 1-cyclohexenol accumulates as cyclohexanone and is further hydrogenated to cyclohexanol. HCl-catalyzed dehydration yields cyclohexene which is readily transformed to cyclohexane. The initial hydrodechlorination of 2-chlorophenol follows a first order rate law with rate constant $k = 5.0 \times 10^{-4}$ s^{-1} at 100 °C. The ceramic combined catalyst is leach-proof and recyclable and can be used in at lest six runs without loss in catalyst activity.
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1. Introduction

For many decades chlorophenols were regarded as useful industrial materials with a broad range of applications. They were used as versatile anti-microbial and disinfection agents, as fungicides, insecticides, ovicides, algicides, herbicides, as wood preservers and as plant growth regulators, they served as synthetic precursors for a variety of pharmaceuticals, glues, paints, dyestuffs and inks [1,2]. Owing to the recognition that the chlorophenols are also toxic and hazardous to the environment (e.g., [3,4]) their production and applications slowed down in recent years. Currently many efforts are even directed to destroy unwanted stocks and to depollute soils, ground and waste waters in which these compounds have accumulated. Among the most common technologies for the destructions of these chloroarenes are incineration, pyrolysis, hydrolysis, chemical and biochemical degradation [5,6]. Although each of these methods usually reduces the amount of the chlorine, they often form new

toxic compounds (see, e.g. [7]). Consequently, most attempts to destroy chlorophenols are associated today with catalytic hydrogenation processes. However, also these methods fail in general to completely detoxify these chloroarenes as they either lead to partial removal of the halogen atoms or to the formation of phenol which by itself in quite a hazardous compound (for some recent representative reports see references [8–13]). Only in a few cases have chlorophenols been converted (in part) during hydrogenation into non-aromatic cyclohexanone and cyclohexanol (e.g. [14–17]).

In this paper we report on conditions for clean one-pot catalytic hydrodechlorination and hydrodearomatization of the various chlorophenols to cyclohexane, and on evidence for the intermediates that take part in this multi-step process.

2. Experimental

2.1. Chemicals

All the chlorophenols and the hydrogenation products except the tetrachlorophenol were purchased from commercial sources.

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2,3,4,6-Tetrachlorophenol (**11**) [18] and the silica sol–gel entrapped Pd-[Rh(cod)(μ-Cl)]$_2$ catalyst [19] were prepared as described in the literature.

2.2. Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 instrument. Infrared spectra were run on a Bruker model Vector 22 FTIR. Mass spectra were measured on a Hewlett-Packard model 4989A mass spectrometer equipped with an HP gas chromotograph model 5890 series II. Gas chromatographic separations were carried out with the aid of a Hewlett-Packard model Agilent 4890D instrument using either a 15 m long capillary column packed with bonded and crosslinked (5% phenyl) methyl poly-siloxane (HP-5) or a 30 m long column bonded Carbowax 20 M poly(ethylene glycol) in fused silica (Supelco 25301-U). The hydrogenation experiments were performed within a glass-lined Parr microreactor model 4592 equipped with a temperature controller model 4842, a mechanical stirrer and a sampling device.

2.3. General procedure for the hydrodechlorination experiments

Typically, the microreactor was charged with the silica sol–gel entrapped catalyst that contained 0.11 mmol of palladium in the form of nanoparticles and 0.02 mmol of [Rh(cod)(μ-Cl)]$_2$, 2 mmol of the chlorinated phenol and 5 ml of the appropriate solvent. The sealed autoclave was flushed (3$\times$) with H$_2$ (atmospheric pressure) and heated to the desired temperature. After temperature equilibration, the reactor was pressurized to the required H$_2$ pressure and the stirring was operated at 150 rpm. Samples of 20 μl were withdrawn and analyzed periodically. After 3 h (or the desired reaction period) the autoclave was cooled to room temperature, the catalyst was removed by filtration and the filtrate analyzed by gas chromatography by direct comparison with authentic samples. The used catalyst was washed and sonicated for

30 min with CH$_2$Cl$_2$, dried at 0.1 mm and reused in a second run.

3. Results and discussion

We have already shown that a mixture of nanoparticles of palladium and a soluble rhodium complex entrapped in a silica sol–gel matrix yields an exceptionally potent catalyst for hydrogenation of aromatic C–C bonds [19], for hydrogenolysis of benzylic carbonyl functions [20], and for hydrodehalogenation of chlorinated dibenzodioxins and some other toxic aromatic chloroarenes [21]. Now we employ this catalyst for the transformation of the mono-, di-, tri-, and tetrachlorophenols **1–11** to cyclohexane. The best synthesis of the combined catalyst was accomplished by the method described previously [19] in which a methanolic solution of Na$_2$PdCl$_4$ was treated under N$_2$ with H$_2$N(CH$_2$)$_3$Si(OMe)$_3$ and NaBH$_4$ at room temperature. To a stirred suspension of the nanoparticles, so formed (cf. reference [22]), in THF was added tetramethoxysilane (TMOS) and a THF solution of [Rh(cod)(μ-Cl)]$_2$ followed by water ([H$_2$O]:[TMOS] = 6.4). After the gelation was complete and the resulting doped sol–gel was dried washed with CH$_2$Cl$_2$ and redried. The ceramic material was employed for hydrogenation of the chlorophenols **1–11** (in 1,2-dichloroethane) at 120 °C to give directly cyclohexane in 95–99% yield. At 80–100 °C it was possible to isolate some reaction intermediates as well as small amounts (0.9–5.0%) of chlorocylcohexane. The fully chlorinated pentachlorophenol, **12**, neither reacts in 1,2-dichloroethane nor in decalins at 120 °C, but forms cyclohexane at a reasonable rate when toluene is used as solvent. (Naturally, a part of the solvent is reduced to methylcyclohexane.) The results of the hydrodechlorination of compound **1–12** are summarized in Table 1.

Under the conditions of Table 1, the chlorinated phenols were shown to lose first part of the halogen atoms leaving traces of lower chlorinated or chlorine-free phenol (**13**). The latter is then further hydrogenated to give 1-cyclohexenol (**14a**), which accumulates as its keto tautomer, cyclohexanone (**14b**). Further

Table 1
Hydrodechlorination of mono- and polychlorophenols[a]

Entry	Starting compound	Composition of reaction mixture after 3 h (yield, %)												
		18	17	15	14	13	1	2	3	4	5	7	10	11
1	2-Chloro (**1**)	1.1	83	11	3.1	0.6								
2	3-Chloro (**2**)	0.9	79	15	3.0	0.6								
3	4-Chloro (**3**)	1.0	80	13	2.5	0.5								
4	2,3-Dichloro- (**4**)	1.3	79	11	7.0	2.1	0.2	0.1						
5	2,4-Dichloro- (**5**)	1.0	78	10	6.9	2.5	0.2		0.3					
6	3,4-Dichloro- (**6**)	1.7	80	8	7.1	1.9		0.2	0.2					
7	2,6-Dichloro- (**7**)	1.5	78	10	7.3	2.0	0.3							
8	2,3,6-Trichloro- (**8**)	3.9	79	6.3	10.5	0.1	0.2	0.3		0.3		0.2		
9	2,4,5-Trichloro- (**9**)	2.3	76	6.5	11.0	0.1	0.2	0.3			0.3			
10	2,4,6-Trichloro- (**10**)	2.8	77	6.7	12.5	0.2	0.2		0.3		0.2	0.1		
11	2,3,4,6-Tetrachloro- (**11**)	5.0	72	10.1	11.3	0.3	0.05		0.01		0.1	0.1		
12	Pentachloro- (**12**)[b]	4.0	70	5.0	15.0	0.1	0.1		0.1		0.5	0.2	0.3	3.0

[a] Reaction conditions for entries 1–11: 2 mmol substrate, 5 ml 1,2-dichloroethane, ceramic catalyst containing 0.02 mmol [Rh(cod)(μ-Cl)]$_2$ and 0.11 mmol palladium, 27.6 bar H$_2$, 3 h and 100 °C. The figures were determined by GC, and are the average of at least two experiments that did not differ by more than ±5%.
[b] The pentachlorophenol was dissolved in 6.7 ml toluene and hydrogenated for 6 h at 120 °C.

hydrogenation affords cyclohexanol (**15**), which, in the presence of HCl is dehydrated to cyclohexene (**16**). This cycloalkene undergoes rapid hydrogenation to cyclohexane (**17**) and therefore could not be traced in the reaction mixture. A small part of the cyclohexanol reacts with the HCl to give also chlorocyclohexane (**18**) which in contrast to the hydrogenation by silica supported nickel [23] is not dehalogenated under the reaction conditions of Table 1 and therefore it is regarded as a side product. The sequences of steps that take place during the hydrodechlorination process are given in Scheme 1. Fig. 1 displays the reaction profile of the hydrogenolysis of 2-chlorophenol at 100 °C. While the kinetics of a multi-step consecutive process such as described in Scheme 1 is quite complex, the analysis of the disappearance of the starting material as function of time is straight forward. We have asserted that the conversion of 2-chlorophenol under our conditions follows a first order rate law with observed rate constant $k = 5.0 \times 10^{-4}\,\text{s}^{-1}$. This is shown in Fig. 2 where $\ln(1-X)$ (X is conversion of 2-chlorophenol) is plotted versus time.

The observation (Fig. 1) that cyclohexanone (**14b**) reaches a maximum concentration of 0.16 M after 70 min and cyclohexanol (**15**) attains a maximum concentration of 0.08 M after approximately 120 min, suggests that the rate of formation of these intermediates is of the same order of magnitude as the rate of their consumption. Conversely, the conversion of the phenol intermediate (**13**), is relatively rapid and the latter could hardly be detected throughout the process.

Eventually, after 6 h, the ultimate products in the sequence, cyclohexane (**17**) builds up to its final concentration of 0.36 M.
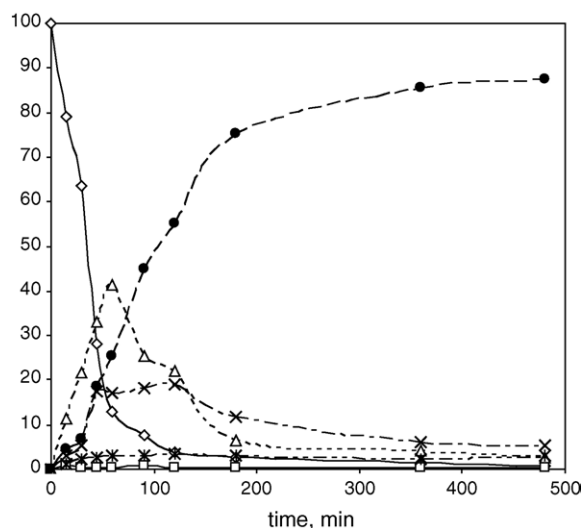

Fig. 1. Concentration–time profile for the reactant and products in the catalytic hydrogenation of 2-chlorophenol **1** (◇) to **13** (□), **14b** (△), **15** (×), **17** (●) and **18** (*) under the conditions of Table 1.

As the sol–gel entrapped catalyst is easily removed from the reaction mixture by filtration, it can be recycled. We usually reused the catalyst three to six times, and observed hardly any reduction in its activity during the advanced runs. A typical set of six runs of hydrogenation of 2,4,6-trichlorophenol (**10**) is shown in Table 2.
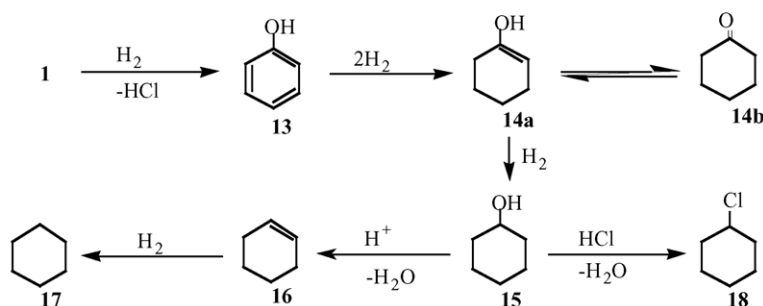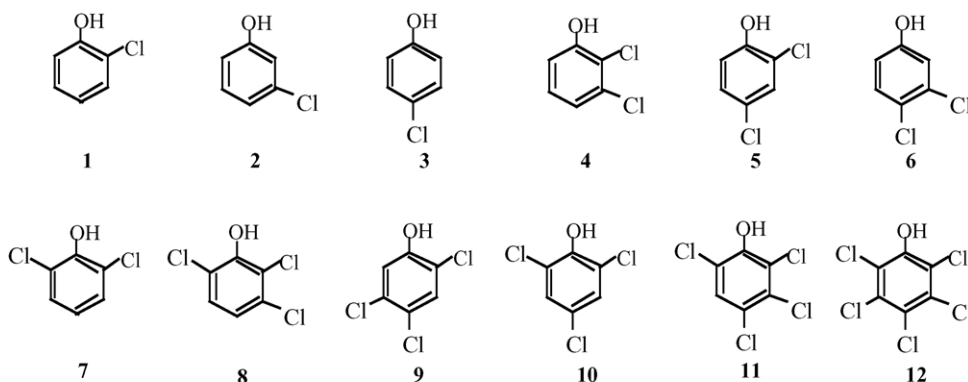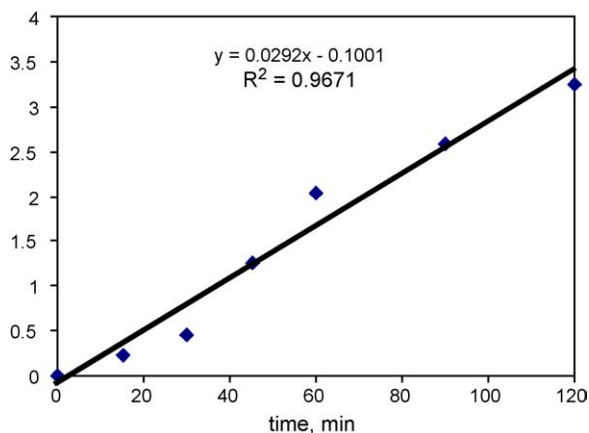

Scheme 1.

Fig. 2. Hydrodechlorination of 2-chlorophenol presented according to a first order rate equation.

The hydrodehalogenations of the chlorophenols **1–11** can be carried out in a variety of solvents such as *n*-decane, decalins, triethylamine and 1,2-dichloroethane. We chose the latter (although it gave a somewhat lower rate of conversion than the three former solvents) because its superior solvating properties. It should be noted that unlike in the hydrogenation of aliphatic chlorides by some other catalysts [24,25], the chlorine atoms in 1,2-dichloroethane are not dehydrochlorinated during the hydrogenation of the chlorophenols.

The sequences of reactions that take place during the hydrodehalogenation of the chlorophenols have been studied at a wide range of temperatures and pressures. We have carried out hydrogenations of each of the intermediates separately, as well as neutralization experiments of the liberated HCl. Changes in the temperature and pressure proved to affect differently the accumulation of the various intermediates. While, e.g., the reduction of the temperature from 100 to 20 °C in the hydrogenation of 2-chlorophenol causes under the conditions of Table 1, a decrease in the formation of cyclohexane (**17**) from 77 to 0.3%, the accumulation of the halogen-free phenol (**13**) increases from 0.5 to 0.8%. Likewise a change in the hydrogen pressure from 27.6 to 6.9 bar that lowers the yield of **17** from 77 to 0.9%, increases the amount of cyclohexanol from 6.7 to 26.4%. The accumulation of ketone **14b** is also strongly affected by the pressure: at 27.6 and 10.35 bar (at 100 °C), 11.9 and 36.7% of it were found in

Table 2

Hydrodechlorination of 2,4,6-trichlorophenol (**10**)[a,b]

Run no.	Yield of major products (%)			
	17	**15**	**14b**	**5**
1	77.5	6.7	13	0.2
2	76.6	7.3	13	0.4
3	77.2	7.5	12.7	0.4
4	77.1	6.5	13.0	0.2
5	76.9	6.9	13.5	0.2
6	77.6	6.9	14.8	0.1

[a] Reaction conditions as in Table 1.
[b] The minor products (**1** and **2**) as well as the chlorocyclohexane (**18**) have been omitted for the sake of brevity.

Table 3

Effect of the temperature on the distribution of the intermediates during the hydrogenation of **1**[a]

Compound	Yield of intermediates after 3 h (% at)				
	100 °C	80 °C	60 °C	40 °C	20 °C
13	0.5	0.6	0.8	0.8	0.8
14b	11.9	6.1	3.6	1.9	0.8
15	6.7	8.3	4.2	2.1	0.5
17	77.0	29	10	1	0.3

[a] Reaction conditions as in Table 1 except for the temperature.

the reaction mixture after 3 h. Some typical data on the temperature and pressure effects on the accumulation of the reaction intermediates in the hydrodechlorination of 2-chlorophenol are listed in Tables 3 and 4.

If the HCl, liberated during the initial stage of the hydrogenation, is neutralized by one equivalent of K_2CO_3, the progress of the reaction sequences practically stops after the formation of **15**. In this case only traces of **17** are formed. An excess of the base, which leads to the formation of sparingly soluble phenolates strongly slows down the whole process at the stage of **13**. (cf., the opposite acid and base effects observed in the hydrodechlorination of chlorophenols in the presence of some other catalysts [26,27].)

We have investigated the transformation of **1** to **17** also by hydrogenation of the individual intermediates under the conditions of Table 1. The hydrogenation of phenol (**13**) gave after 3 h 36% of cyclohexanone (**14b**), 2% of cyclohexanol (**15**) and traces of **17**. Upon addition of 20 μl of 2-chlorophenol (**1**) (or traces of dry HCl) the amount of **14b** did not change but that of **17** increased to 5%. Cyclohexanone alone gave practically only cyclohexanol (**15**) (30%). Upon addition of 20 μl of **1**, a substantial amount (29%) of **17** was formed and that of **15** decreased to 10.6%. Cyclohexanol did not react at all in the absence of a source of HCl. It was however, transferred to **17** upon addition of 20 μ of **1**. As mentioned above, the liberated HCl converts a small amount of cyclohexanol into chlorocyclohexane (**18**). The route to its formation is interesting as it may involve either HCl assisted nucleophilic substitution of the OH moiety in **15**, or HCl addition to **16**. In order to clarify this point we hydrogenated 4-chloro-2-methylphenol (**19**) which is expected to give 2-methylcyclohexanol (**20**) as a reaction intermediate. If the formation of 1-chloro-2-methylcyclohexane (**23**) proceeded by a Markovnikoff type addition of HCl, to the dehydration products of **20**, 1- and 3-methylcyclohexene (**21** and **22**,

Table 4

Effect of the hydrogen pressure on the distribution of the intermediates during the hydrogenation of **1**[a]

Compound	Yield of intermediates after 3 h (% under)				
	27.6 bar	13.8 bar	10.35 bar	6.9 bar	3.45 bar
13	0.5	0.5	0.5	0.5	0.3
14b	11.9	15.3	36.7	8.1	2.5
15	6.7	7.5	10.8	26.4	9.5
17	77.0	50.1	4.3	0.9	0.1

[a] Reaction conditions as in Table 1 except for the H_2 pressure.
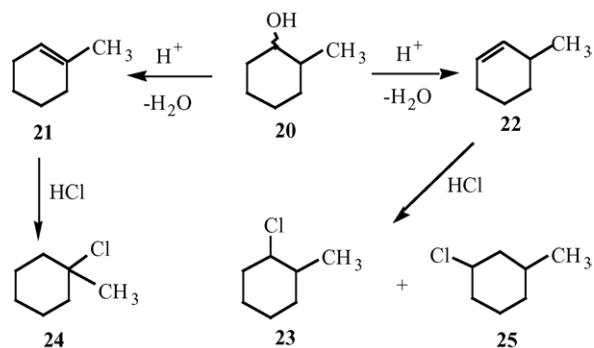
Scheme 2.

respectively) it would furnish, in addition to **23**, also 1-chloro- and 3-chloromethylcyclohexane (**24** and **25**, respectively) as shown in Scheme 2. An S_N2 reaction of HCl with the carbinol is expected to yield however, solely **23**. Since neither **24** nor **25** could be found in the reaction mixture, we speculate that the formation of the chlorocyclohexanes takes place by an S_N2 mechanism.

Several explanations have been suggested for the function of the metallic palladium and the rhodium complex in arene hydrogenation processes by analogous combined catalysts adsorbed on silica gel supports. A hydrogen spillover process [28] and a mechanism governed by synergistic effects [29] have been proposed. It seems however, that when Pd-[Rh(cod)Cl]$_2$ was encaged within a silica sol–gel matrix, the processes clearly involve a synergistic effect between the two metal nuclei [19–21]. Three parallel hydrogenation experiments of 2,4,6-trichlorophenol (**10**) have been performed under the conditions of Table 1, except that in the first experiment we used the entrapped combined catalyst, in the second one, we used only the sol–gel encapsulated palladium, and in the third experiment we used solely the entrapped [Rh(cod)(μ-Cl)]$_2$ component. The yields of phenol (**13**), cyclohexanone (**14b**), cyclohexanol (**15**) and cyclohexane (**17**) formed in the three experiments summarized in Table 5, indicate that the entrapped combined Ph-Rh catalyst is more efficient than each of the immobilized Pd and Rh components alone. It is notable that the hydrodehalogenation of 2,4,6-trichlorophenol (**10**) to **17** in the presence of the

entrapped combined catalyst is independent of the ratio [catalyst]:[substrate] between 1:100 and 1:200. When, however, the ratio is decreased the formation of **17** starts to slow down. For example, a ratio of 1:400 afforded after 3 h at 100 °C and 27.6 bar H$_2$, 27.4% of **14b** and only 60% of **17**. In addition to the three comparative experiments with the sol–gel encapsulated catalysts, we studied the hydrogenation of **1** in the presence of a non-entrapped Pd + [Rh(cod)(μ-Cl)]$_2$ mixture. The results given in Table 5 show that under our standard conditions, the formation of cyclohexane (**17**) is slow and the major product is phenol (**13**). The yield of **17** could be somewhat increased by increasing the stirring rate, but the formation of cyclohexane proved still slower than in the experiments shown as entries 1–3. We assume that the two metallic components that are placed in close proximity within the sol–gel cages are eventually too far apart under non-entrapped conditions despite the fact that the nanoparticles of Pd are always in excess. Therefore, no synergistic effect exists in the absence of a silica sol–gel matrix and consequently the mode of the hydrodehalogenation resembles in some respect the studies [9] with conventional catalysts.

4. Conclusions

The sol–gel entrapped system of metallic palladium and soluble [Rh(cod)Cl]$_2$ is an extremely powerful and recyclable catalyst for both dehalogenation and exhaustive hydrogenation of mono- and polychlorophenols to cyclcohexane. The catalyst dehalogenates selectively aromatic chlorine atoms. Under our standard reaction conditions it does not affect chloroalkanes. All three components of the catalyst (the palladium, the rhodium complex and the silica sol–gel matrix) have been shown to be essential for obtaining good yields of cyclohexane. The HCl liberated during the initial stages of the process plays a crucial role in the formation of the final cycloalkane as it promotes the dehydration of the cyclohexanol intermediate to cyclohexene. In the dehydrochlorination of 2-chlorophenol at 100 °C the first of the five-stages of the consecutive process proceeds according to a first order rate equation. Two intermediates build up significant transient concentrations of cyclohexanone reaching a maximum after 60 min and cyclohexanol with t(max) at 120 min.

Table 5
Hydrogenation of 2,4,6-trichlorophenol by different combinations of metallic Pd and [Rh(cod)(μ-Cl)]$_2$[a]

Entry	Catalyst system	Yield of major products (%)[b]			
		13	14	15	17
1	Pd-[Rh(cod)Cl]$_2$@sol–gel	0.5	12.5	6.7	77.6
2	Pd@sol–gel[c]	35.0	10.7	5.3	30.0
3	[Rh(cod)Cl]$_2$@sol–gel	44.9	9.8	5.8	25.5
4	Pd + [Rh(cod)Cl]$_2$ (non-entrapped)	45.1	9.6	7.8	19.0

[a] Reaction conditions: 2 mmol of 10, 5 ml ClCh$_2$CH$_2$Cl, 27.6 bar H$_2$, catalyst containing 0.11 mmol Pd (entries 1, 2 and 4) and 0.02 mmol Rh (entries 1, 3 and 4), 3 h, 100 °C), stirring rate 150 rpm.
[b] The yields were determined by GC and are the average of at least two experiments that did not differ by more than ±3%.
[c] No change in the yields was observed when 0.13 mmol of the Pd was used.

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