

Hydrogenation of organic substrates by an heterogenized catalyst based on a bis(diphenylphosphino)methane polymer-bound palladium(II) complex

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Abstract

$\text{Pd}(\text{OAc})_2$ undergoes easy and quantitative coordination to a cross-linked styrene/divinylbenzene resin functionalized with bis(diphenylphosphino)methane ligands to yield a supported palladium complex which behaves as a versatile and recyclable heterogenized catalyst for the hydrogenation of nitrocompounds and α,β -unsaturated aldehydes under mild conditions. Whereas nitrobenzene is converted only into aniline, cinnamaldehyde is selectively converted into hydrocinnamaldehyde. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Transition metal complexes have been successfully applied as homogeneous catalysts in a large variety of chemical reactions. On the other hand, immobilisation of homogeneous catalysts on insoluble reactive supports to yield well-defined heterogenized molecular complexes and their catalytic performances have recently been the focus of a great deal of interest [1,2]. Indeed, the main advantages of polymer-sup-

ported metal complexes are related to their enhanced stability as well as easy recovery and reuse in subsequent catalytic cycles, several benefits typical of the homogeneous counterparts, such as high selectivity and activity, being still retained.

Many palladium complexes are known to behave as highly efficient hydrogenation catalysts in homogeneous phase. In this context, particular attention has been devoted to mono- [3–5] and di-phosphine [6–10] modified complexes. Indeed, complexes of palladium(II) and (0) in combination with different tertiary phosphines have been employed as homogeneous

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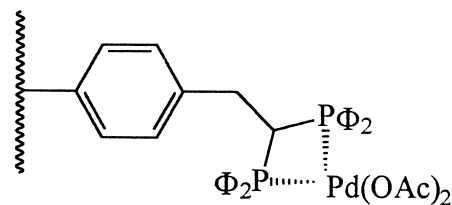
hydrogenation catalysts and although the identities of the active species remained unresolved, it was generally assumed that the active sites consist of palladium-derivatives, where ancillary phosphine ligands are permanently coordinated to the metal atom during the whole catalytic cycle [11,12].

Several attempts have been reported to afford heterogenized palladium complexes by anchoring the metal derivatives to polymer-based benzyl-diphenylphosphine ligands [13–15], to amino- and *N*-heterocyclic macromolecular ligands [16], to 2-amino-butanol functionalized styrene-divinylbenzene resins [17] or to a macroporous acrylate polymer network with pendant isocyanopropyl groups [18], the resulting heterogeneous analogues of $[\text{PdCl}_2(\text{PR}_3)_2]$ and $[\text{PdCl}_2(\text{CNR})_2]$ displaying enhanced hydrogenation activity and high selectivity.

On the other hand, immobilised catalysts were also prepared by contacting solutions of palladium-phosphine complexes with silica [19,20] or other inorganic supports such as pillared clays like montmorillonite [21] or zeolites [22]; even in the above cases, heterogenization offered enhanced stability and activity.

Very recently, the synthesis and molecular characterization of a novel diphosphine polymer-bound palladium complex was described by us [23]. The organic support was obtained by a functionalization pathway involving the reaction between a macroporous chloromethylated styrene-divinylbenzene resin and lithium bis(diphenylphosphino)methane and subsequent reduction of the anchored phosphinoyl moieties to yield a polymeric bis(diphenylphosphino)methane ligand. The above anchored palladium diphosphine complex Dow-DPPM-Pd(OAc)₂ (Chart 1) has been found to catalyse 1,3-butadiene telomerization with methanol to give with high activity and selectivity octadienyl ethers [24]. Moreover, the fact that catalytic performances remained unchanged after repeated reaction cycles and the recycled liquid reaction mixture was substantially inactive, allowed the conclusion that the above polymer-

bound palladium catalyst really works in heterogeneous phase. Therefore, it also appeared interesting to study the catalytic activity and selectivity of the Dow-DPPM-Pd(OAc)₂ complex in the hydrogenation of different organic substrates, as well as to check the really heterogeneous nature of the above catalytic system.



Dow-DPPM-Pd(OAc)₂

Chart 1.

2. Experimental

2.1. Materials

All manipulations were carried out under dry purified argon or nitrogen using standard Schlenk techniques.

The heterogenized Dow-DPPM-Pd(OAc)₂ catalyst precursor (2.83 wt.% of Pd, corresponding to 0.266 meq Pd/g of resin) was obtained, as previously reported [23], by reacting Pd(OAc)₂ with a macroporous cross-linked styrene (St)/divinylbenzene (DVB) resin (Dow-B) (specific surface area = 45 m²/g) containing 4.5 mol% of DVB co-units and functionalized with bis(diphenylphosphino)methane (DPPM) moieties (3.5 mol% of St-DPPM co-units).

Toluene (Baker) and *n*-hexane (Merck) were refluxed and distilled under dry argon over sodium and sodium-potassium alloy, respectively. Nitrobenzene (Merck) was treated with decolourising animal charcoal and purified by fractional distillation under reduced pressure in atmosphere of argon.

Decalin (Carlo Erba), cinnamaldehyde (Aldrich), hydrocinnamaldehyde (Aldrich) were dis-

tilled under reduced pressure immediately prior to the use; cinnamyl alcohol (Aldrich) was stored under argon and used as received.

2.2. Catalytic experiments and analyses

Catalytic experiments were carried out in a 300 ml mechanically stirred stainless steel autoclave, equipped with a glass inner beaker, a substrate inlet stopcock, a liquid sampling valve and a thermocouple for inner temperature control. In a typical procedure, the desired amount of catalyst precursor was introduced under inert atmosphere in the argon purged autoclave. The autoclave was then evacuated up to 0.5 mm Hg and the desired amounts of solvent (if required), substrate and toluene or *n*-hexane as internal standard were introduced inside. The autoclave was then pressurized with hydrogen and heated in a thermostatic oil bath.

Reaction mixture samples were periodically removed via the liquid sampling valve, collected in capped vials and immediately analysed by temperature-programmed GC.

When a pre-reduction of palladium catalyst was required, the desired amount of heterogenized complex and the solvent were introduced under argon atmosphere in the autoclave. The system was then pressurized with hydrogen and kept at the required temperature in a oil bath for the assigned time. Solvent was then removed via the liquid sampling valve and the autoclave was evacuated and charged again with solvent, unsaturated substrate and internal standard for GC analyses, pressurized with hydrogen and finally heated at the required temperature in a thermostatic oil bath.

Recycling experiments of the heterogenized catalyst were carried out in a similar manner;

Table 1

Hydrogenation of nitrobenzene in the presence of the heterogenized Dow-DPPM-Pd(OAc)₂ catalyst^a

Entry	Time (h)	Nitrobenzene conversion (mol%)					T.N. ^b (h ⁻¹)
		0.5	1	1.5	2	12	
1	1st cycle	33.3	80.5	97.0	100.0	–	566
2	2nd cycle	32.3	77.5	93.2	99.6	–	545
3	3rd cycle	33.8	68.2	85.6	99.6	–	479
4	4th cycle	36.5	59.7	82.2	95.9	–	420
5	5th cycle	36.5	67.3	80.5	95.7	–	473
6 ^c	liquid phase recycle	–	–	–	~ 0	–	0
7 ^d		–	–	–	–	22.1	283

^aReaction conditions: Pd: 1.38×10^{-2} mmol; solvent: methanol (25 ml); nitrobenzene/palladium: 700 mol/mol; temperature: 25°C; P_{H₂} = 1 MPa.

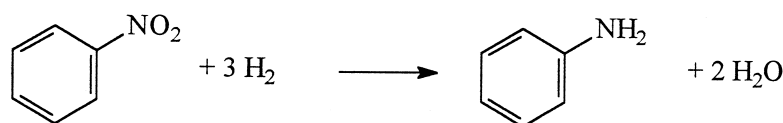
^bTurn over numbers evaluated after 1 h of reaction and expressed as: moles of converted nitrobenzene/(moles of palladium per hour).

^cRecycle of the liquid reaction mixture from entry 1, joined to a fresh amount of nitrobenzene, in the absence of solid catalyst.

^dRun carried out in the absence of solvent; nitrobenzene/palladium: 15,500 mol/mol; T.N. evaluated after 12 h of reaction.

after removing through the liquid sampling valve the liquid reaction mixture, the autoclave containing the heterogenized catalyst was evacuated and charged again for the subsequent catalytic cycle.

When the recycle of the liquid phase was investigated, the liquid reaction mixture was collected under inert atmosphere, joined to a fresh amount of unsaturated substrate, transferred in an evacuated autoclave free of the heterogenized catalyst, pressurised with hydrogen and heated at the desired temperature; the conversion obtained in the recycle experiment was evaluated by analysing the liquid mixture before and after the catalytic cycle and subtracting the amount of products formed in the preceding cycle.



Scheme 1. Hydrogenation of nitrobenzene to aniline.

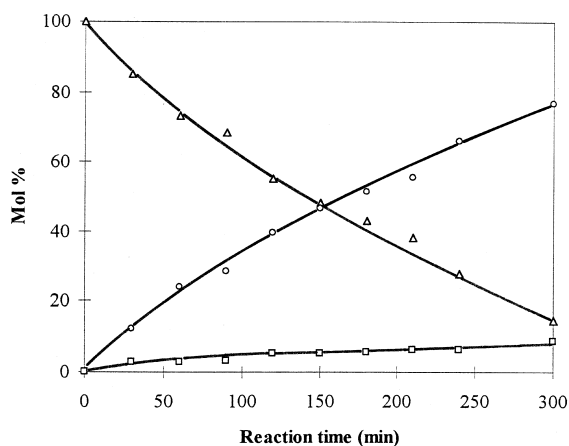


Fig. 1. Hydrogenation of cinnamaldehyde in decalin at 70°C and 0.5 MPa in the presence of the Dow-DPPM-Pd(OAc)₂ pre-reduced catalyst (entry 9): mole % vs. time. cinnamaldehyde (Δ); hydrocinnamaldehyde (○); 3-phenyl-1-propanol (□).

As the main goal of the anchorage of a metal catalyst on a polymer is the possibility of its recovery and recycle, the above catalytic system was employed in subsequent cycles and the analysis of the metal content was carried out after several cycles of use.

As shown in Table 1 (entries 2–5), the heterogenized catalyst was recycled with a substantial retainment of activity; moreover, when the liquid phase was separated from the heterogenized catalyst and fresh nitrobenzene was added, no further conversion of the nitro-compound was observed (entry 6, Table 1), thus confirming the absence of metal leaching and hence a really heterogeneous nature of the Dow-DPPM-

Pd(OAc)₂ complex. Indeed, even after five catalytic cycles, the catalyst showed a palladium loss ranging from 0.5 to 1% (in the limits of the experimental error), so that metal content in the catalyst could be assumed substantially unchanged with respect to the initial amount.

Besides, these experiments were particularly useful to test the stability of the catalyst towards water and aromatic amines. In fact, it was reported that addition of N-donors to palladium-phosphine homogeneous catalysts caused deactivation [27], thus suggesting that the availability of coordination sites is of critical importance. In this case no deactivation occurred in the presence of water and aniline, which are the hydrogenation products; moreover, when the hydrogenation of nitrobenzene was carried out in absence of solvent, thus increasing the concentration of the substrate and hence of the reaction products, an appreciable hydrogenation activity towards reduction of nitro-groups to amine moieties was still observed (entry 7, Table 1).

3.2. Hydrogenation of cinnamaldehyde

With the aim of studying the chemoselectivity of the supported palladium complex Dow-DPPM-Pd(OAc)₂, a typical bifunctional substrate such as cinnamaldehyde has been submitted to catalytic hydrogenation.

Table 3

Hydrogenation of cinnamyl alcohol (**II**) and hydrocinnamaldehyde (**I**) in the presence of the heterogenized Dow-DPPM-Pd(OAc)₂ catalyst^a

Entry	Substrate		Reaction time (min)						T.N. ^b (h ⁻¹)
			30	60	120	180	240	300	
11	Cinnamyl alcohol	Conversion (mol%)	14.3	25.7	50.3	74.5	92.9	–	463
		Selectivity (mol%) I	11.8	6.5	5.0	3.1	2.7	–	
		III	88.2	93.5	95.0	96.9	97.3	–	
12	Hydrocinnamaldehyde	Conversion (mol%)	5.7	7.4	8.6	11.7	12.7	15.3	133
		Selectivity (mol%) II	10.1	9.8	8.1	8.7	6.1	5.3	
		III	89.9	90.2	91.9	91.3	93.9	94.7	

^aPre-reduction conditions: solvent: decalin (25 ml); $P_{H_2} = 0.5$ MPa; time: 2 h. Reaction conditions: Pd: 1.30×10^{-2} mmol; solvent: decalin (25 ml); substrate/palladium: 1800 mol/mol; $P_{H_2} = 0.5$ MPa; temperature: 70°C.

^bTurnover numbers evaluated after 1 h of reaction and expressed as: moles of converted substrate/(moles of palladium per hour).

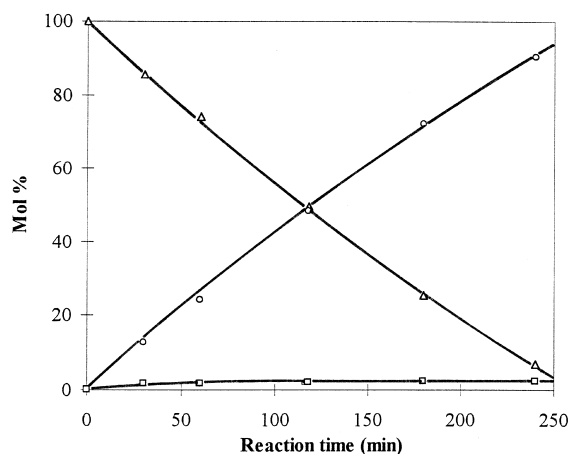


Fig. 2. Hydrogenation of cinnamyl alcohol in decalin at 70°C and 0.5 MPa in the presence of the Dow-DPPM-Pd(OAc)₂ pre-reduced catalyst (entry 11): mole % vs. time. cinnamyl alcohol (Δ); hydrocinnamaldehyde (□); 3-phenyl-1-propanol (○).

Indeed, hydrogenation of cinnamaldehyde may give rise, in principle, to three products, namely hydrocinnamaldehyde (**I**), cinnamyl alcohol (**II**) and 3-phenyl-1-propanol (**III**) as reported in Scheme 2.

Table 2 lists the hydrogenation experiments of cinnamaldehyde at 0.5 MPa pressure in decalin; the results are presented as percent conversion of cinnamaldehyde and selectivity to either hydrocinnamaldehyde (**I**) or 3-phenyl-1-

propanol (**III**). All the data clearly indicate that, under the adopted conditions, hydrogenation was preferentially directed towards the conjugated C=C double bond, yielding hydrocinnamaldehyde with high productivity, while no cinnamyl alcohol was detected in the reaction mixture. Better performances were obtained when catalytic precursor was pre-reduced under hydrogen atmosphere, both activity and selectivity resulting substantially increased (entry 9, Table 2). Moreover, the increase of reaction temperature from 70 (entry 9) to 100°C (entry 10) causes a remarkable improvement of activity (T.N. is almost doubled), the selectivity to hydrocinnamaldehyde being substantially retained.

As shown in Fig. 1, during the hydrogenation at 70°C of cinnamaldehyde by the pre-reduced Dow-DPPM-Pd(OAc)₂ catalyst the relative amount of hydrocinnamaldehyde with respect to that of 3-phenyl-1-propanol progressively increases in the reaction mixture; in fact, as reported in Table 2 for all the experiments, the selectivity to hydrocinnamaldehyde slightly increases on increasing the conversion of cinnamaldehyde, the reverse occurring for 3-phenyl-1-propanol. The above data clearly indicate that 3-phenyl-1-propanol does not seem to be originated from hydrocinnamaldehyde.

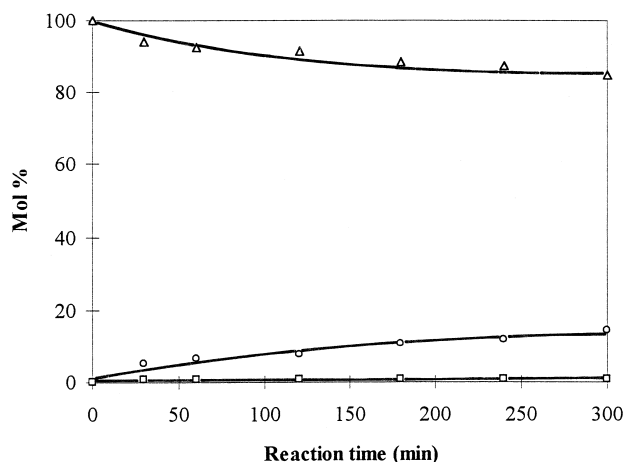
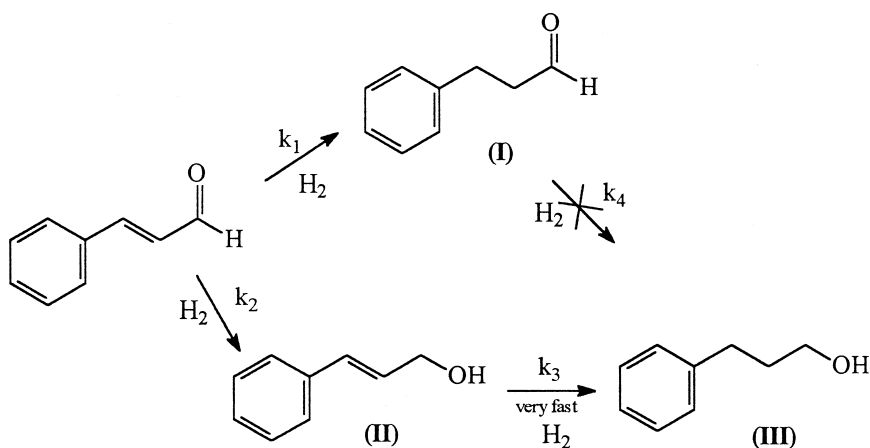


Fig. 3. Hydrogenation of hydrocinnamaldehyde in decalin at 70°C and 0.5 MPa in the presence of the Dow-DPPM-Pd(OAc)₂ pre-reduced catalyst (entry 12): mole % vs. time. hydrocinnamaldehyde (Δ); 3-phenyl-1-propanol (○); cinnamyl alcohol (□).



Scheme 3. Proposed reaction pathways for the hydrogenation of cinnamaldehyde.

In order to confirm this point, separate hydrogenation experiments on cinnamyl alcohol and hydrocinnamaldehyde were carried out, under the same conditions, over the heterogenized catalyst (Table 3). Cinnamyl alcohol was readily hydrogenated to 3-phenyl-1-propanol, with negligible isomerization to hydrocinnamaldehyde (Fig. 2), with a turnover number as high as 463 h^{-1} . On the contrary, hydrocinnamaldehyde was very slowly converted into 3-phenyl-1-propanol (Fig. 3), these results evidencing a higher catalytic activity of Dow-DPPM-Pd(OAc)₂ towards C=C double bond hydrogenation rather than C=O reduction. These observations can be explained in terms of greater affinity of palladium for C=C bonds than for C=O bonds [28]; indeed palladium catalysts are known to selectively adsorb and reduce alkenes [29]. There-

fore, it may be concluded that the hydrogenation of cinnamaldehyde substantially proceeds as reported in Scheme 3. Indeed, the hydrogenation of cinnamaldehyde affords hydrocinnamaldehyde (I) and cinnamyl alcohol (II), I being the major product ($k_1 \gg k_2$); however, II is not detectable because it is very quickly transformed ($k_3 \gg k_2$) into 3-phenyl-1-propanol (III), which in turn is not appreciably obtained by subsequent hydrogenation of I ($k_4 \approx 0$).

Finally, in order to test the stability of the catalyst and its really heterogeneous behaviour, the Dow-DPPM-Pd(OAc)₂ precursor was used in subsequent catalytic cycles, the results being summarised in Table 4.

Due to the fact that the catalyst was employed without a pre-reduction step, its performances appeared to improve cycle by cycle, up

Table 4

Hydrogenation of cinnamaldehyde in the presence of the heterogenized Dow-DPPM-Pd(OAc)₂ catalyst^a

Entry	Conversion (mol%)	Selectivity (mol%)		T.N. ^b (h ⁻¹)	
		Hydrocinnamaldehyde	3-Phenyl-1-propanol		
13	1st cycle	38.1	86.6	13.4	172
14	2nd cycle	48.8	91.5	9.5	220
15	3rd cycle	60.9	92.3	7.7	274
16	4th cycle	61.0	92.7	7.3	274
17	5th cycle	60.8	92.6	7.4	274
18 ^c	liquid phase recycle	~ 0	–	–	~ 0

^aReaction conditions: Pd: 1.38×10^{-2} mmol; solvent: decalin (25 ml); cinnamaldehyde/palladium: 1800 mol/mol; $P_{\text{H}_2} = 0.5$ MPa; temperature: 70°C; time: 4 h.

^bTurnover numbers evaluated after 4 h of reaction and expressed as: moles of converted cinnamaldehyde/(moles of palladium per hour).

^cRecycle of the liquid reaction mixture from entry 1, joined to a fresh amount of cinnamaldehyde, in the absence of solid catalyst.

to a nearly steady state with a conversion of about 60% after 4 h of reaction and a selectivity towards hydrocinnamaldehyde higher than 92 mol%. Negligible metal leaching was evidenced after five catalytic cycles; accordingly, the liquid reaction mixture of the 1st cycle, after separation from the solid catalyst, when joined to a fresh amount of substrate did not evidence any further cinnamaldehyde conversion.

4. Concluding remarks

On the basis of the obtained results the following concluding remarks can be drawn.

(i) The heterogenized Dow-DPPM-Pd(OAc)₂ catalyst precursor is able to hydrogenate nitrobenzene to aniline, under very mild conditions, with good productivity, no evidence of intermediate compounds being observed. Moreover, recycle experiments allow the conclusion that the catalyst retains its activity after several cycles, no metal leaching being substantially found. The lack of activity of the recycled liquid reaction products nicely confirms that the catalyst really works in the heterogeneous phase.

(ii) Dow-DPPM-Pd(OAc)₂ is also able to hydrogenate α,β -unsaturated aldehydes, such as cinnamaldehyde, to hydrocinnamaldehyde, with high activity and selectivity, thus indicating that, at least under the adopted mild conditions, the above palladium catalyst has greater affinity for carbon–carbon double bonds rather than for carbonyl groups. All the obtained results suggest that the observed minor amount of 3-phenyl-1-propanol is substantially derived from cinnamyl alcohol rather than from hydrocinnamaldehyde. Recycle experiments again show that the catalyst maintains its activity after several cycles and above all retains its heterogeneous character.

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