

# Hydrogenation of N-benzylideneaniline by palladium (II) catalysts with phosphorus-nitrogen ligands using formic acid as a renewable hydrogen source



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## ABSTRACT

This paper reports the hydrogenation of N-benzylideneaniline catalysed by Pd(II) compounds containing heterobidentated phosphorus-nitrogen (PN) ligands. The general formulas of the catalysts are *cis*-[PdCl<sub>2</sub>(L<sub>1</sub>)] and [PdCl(PPH<sub>3</sub>)(L<sub>1</sub>)]Cl (where L<sub>1</sub> = Ph<sub>2</sub>PCH<sub>2</sub>py, Ph<sub>2</sub>PNCH<sub>3</sub>py, Ph<sub>2</sub>PNHpy, Ph<sub>2</sub>PNHpym and Ph<sub>2</sub>Pqn). The hydrogenation of N-benzylideneaniline was carried out using propan-2-ol or formic acid as the hydrogen source. The catalytic activity was studied under different conditions by varying the base (NaOH and tert-butoxide) and the base/catalyst ratio (B/C = 20/1 and 50/1. Additionally, triethylamine was also used with a base/catalyst ratio of B/C = 500/1. It was found that palladium catalysts containing hemilabile heterobidentated ligands showed high catalytic activity and selectivity for the hydrogenation of N-benzylideneaniline. The catalysts *cis*-[PdCl<sub>2</sub>(Ph<sub>2</sub>PNHPy)] (2) and [PdCl(Ph<sub>2</sub>Pqn)(PPH<sub>3</sub>)]Cl (6) maintained the activities when the reactor was recharged with a fresh substrate (1000/1 substrate/catalyst ratio). It was also found that catalytic hydrogenation works well with only formic acid, with its activities ranging close to 100% for the 2 and 6 complexes.

## 1. Introduction

Conventional hydrogenation reactions involve the use of molecular hydrogen as a reagent. However, it is possible to carry out this reaction under safer conditions by using a donor molecule (DH<sub>2</sub>) that can transfer hydrogen to an unsaturated substrate (S), which acts as an acceptor (for example, imines). Formic acid (FA) and propan-2-ol are the commonly used donor molecules. While the latter also plays the solvent role, the former represents an alternative hydrogen source it is nontoxic and can be easily handled and transported. The hydrogen generated from FA enables the H<sub>2</sub> + CO<sub>2</sub> mixture, thus allowing an adequate hydrogen source. Additionally, the by-product CO<sub>2</sub> can be, in the presence of suitable catalysts, rehydrogenated back to FA, thus generating a zero carbon footprint cycle to store and release hydrogen [1–5].

The use of amines in medicine dates to at least a century [6,7]. Since they are essential in the preparation of pharmaceutical products as well as stimulants such as vasoconstrictors, decongestants, antihistamines, and antidepressants, the reduction of CN bonds is essential. Therefore, for the preparation of chiral amines, catalytic imine hydrogenation is an

important synthetic method.

Studies have revealed that the hydrogenation of nitro compounds, aldehydes, and Schiff bases can be carried out by using effective catalysts such as metal complexes of palladium, platinum, and rhodium [8,9]. Some authors have also reported the use of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> as a catalyst while using propan-2-ol as the hydrogen source and K<sub>2</sub>CO<sub>3</sub> as the base [10]. However, the Noyori group [11], in the asymmetric transfer of imines hydrogenation, reported the use of chiral ruthenium or rhodium as catalysts while using FA as the hydrogen source. Yields in both these cases have been excellent. In contrast, transfer hydrogenation of imines has been carried out using different transition metals such as Ru(II), Rh(III), Ir(III), and Ni(0) as catalysts [12–17]. It has also been reported that palladium complexes are also used as catalysts in the hydrogenation of different organic substrates under homogeneous and heterogeneous conditions [18–23].

In this study, the hydrogenation of N-benzylideneaniline is studied using molecular hydrogen as the hydrogen source, instead of using the usual triethylsilane which acts as a reducing agent. FA is better than other hydrogen sources because it is renewable and easier to handle (see Scheme 1). On the other hand, N-benzylideneaniline is used as a

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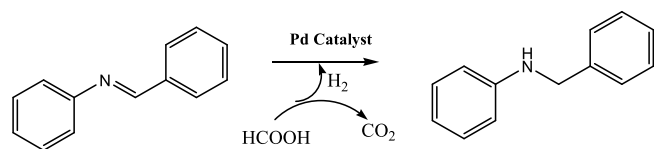
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**Scheme 1.** Transfer hydrogenation reaction of N-benzylideneaniline using formic acid as the hydrogen source.

model substrate for the imine hydrogenation study because when the catalyst shows low conversion, the obtained hydrolysed substrate gives both aniline and styrene. The presence of these products in the reaction is a clear indication that the catalysts will not be active with other imines.

The organometallic complexes containing ruthenium (II), nickel(II), iron(II), iridium (I) and palladium (II) have shown to be active in formic acid activation and hydrogenation reaction. The proposed mechanism for these transition metals includes the metal hydride pathway and the complexes containing phosphine, diphosphine or polypyridine ligands. These types of ligands stabilise the monohydride or dihydride metal complexes [24–36].

Our group has found that using ruthenium complexes that contain pincer phosphorus-nitrogen ligands [37] for the N-benzylideneaniline hydrogenation will help obtain a high conversion and selectivity rate. Meanwhile, palladium (II) complexes containing this type of ligands (such as  $\text{Ph}_2\text{PNHpy}$ ) have been used to generate efficient catalysts for the methoxycarbonylation of alkenes (namely styrene, cyclohexene, and 1-hexene) [38]. Heterobidentate P-, N-donor ligands represent an important class of ligands that have been used to prepare interesting catalytic systems [39–41].

In this study, we report the transfer hydrogenation of N-benzylideneaniline using different hydrogen sources. Palladium (II) with PN-type ligands ( $[\text{PdCl}_2\text{L}_1]$  where  $\text{L}_1 = \text{Ph}_2\text{PRpy}$  and  $\text{R} = \text{CH}_2$  **1**,  $\text{NH}$  **2**,  $\text{NCH}_3$  **3** and  $\text{Ph}_2\text{PNHpyN}$  **4**,  $\text{PdCl}_2(\text{Ph}_2\text{Pqn})$  **5**, and  $[\text{PdCl}(\text{Ph}_2\text{Pqn})\text{PPh}_3]\text{Cl}$  **6** were the catalysts used (see Scheme 2). They showed high activities with conversions between 54% and 99% when the reactions were made either using only formic acid or a mixture of formic acid and trimethylamine at reflux temperature.

## 2. Materials and methods

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Organic solvents and substrates were deoxygenated and purified prior to use by distilling them in sodium or  $\text{CaH}_2$ . The ligands and complexes were synthesized by reported procedures [38]. Conversions were obtained by GC on a Hewlett-Packard Agilent 6890 N chromatograph equipped with a flame ionization detector (FID) and a HP-5 column. GC–MS (HPG1800 A instrument) analyses were used to confirm the identity of the products. Samples of the reaction were periodically extracted to be analysed by

**Table 1**  
Hydrogenation of benzylideneaniline catalyzed palladium catalysts containing phosphorus-nitrogen Ligands.<sup>a</sup>

Entry	Catalyst	Base	B/C	TOF $\text{h}^{-1}$	% product
1	1	NaOH	20	2.0	4.0
2	1	NaOH	50	7.0	14.0
3	1	t-BuOK	20	5.0	11.0
4	1	t-BuOK	50	27.5	55.0
5	1*	t-BuOK	50	27.6	69.0
6	2	NaOH	20	0.2	1.0
7	2	NaOH	50	1.0	2.0
8	2	t-BuOK	20	0.0	0.0
9	2	t-BuOK	50	2.0	4.0
10	3	NaOH	20	1.5	3.0
11	3	NaOH	50	1.5	3.0
12	3	t-BuOK	20	0.6	1.0
13	3	t-BuOK	50	2.0	4.0
14	4	NaOH	20	1.0	2.0
15	4	NaOH	50	0.5	1.0
16	4	t-BuOK	20	0.2	0.4
17	4	t-BuOK	50	2.5	5.0
18	5	NaOH	20	2.5	5.0
19	5	NaOH	50	10.5	21.0
20	5	t-BuOK	20	2.5	5.0
21	5	t-BuOK	50	35.0	70.0
22	5*	t-BuOK	50	32.0	80.0
23	6	NaOH	20	3.0	6.0
24	6	NaOH	50	10.5	21.0
25	6	t-BuOK	20	6.5	13.0
26	6	t-BuOK	50	27.0	54.0
27	6*	t-BuOK	50	27.0	60.0

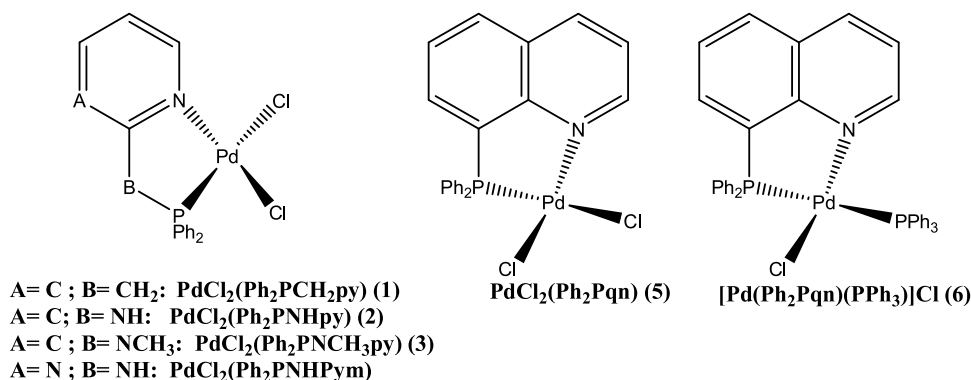
<sup>a</sup> Reaction conditions: 0.01 mmol of **1–6** catalysts and B/C: 50/1, 20/1; S/C ratio: 200/1 in 10 mL of solvent (propan-2-ol); time of reaction 4 h (\* 5 h); temperature: reflux.

GC-FID, and the pressure was adjusted whenever it was necessary.

The synthesis and characterization of the catalysts used in this work were reported by us [37,38] and also studied in other catalytic applications. The study of the hydrogen transfer reaction to imines was performed using two types of hydrogen sources (FA and propan-2-ol) and three types of bases (NaOH, t-BuOK, and  $\text{Et}_3\text{N}$ ). The catalytic reaction was carried out using a substrate/catalyst ratio of 200/1 and 500/1. The base/catalyst ratios were 20/1 and 50/1 for NaOH and t-BuOK respectively. When the co-catalyst was  $\text{Et}_3\text{N}$ , the base/catalyst ratio used was 500/1.

## 3. Results and discussion

In the first part of this study, the transfer hydrogenation of N-benzylideneaniline was studied using propan-2-ol as the hydrogen source under basic conditions. To study the effect of the base on the reaction, NaOH and t-BuOK were used. In the absence of a base, no reaction was observed. Similarly, in the absence of a catalyst, a series of control



**Scheme 2.** Palladium catalysts containing phosphorus-nitrogen ligands.

experiments which were conducted under the same conditions did not show any product formation.

Table 1 summarizes the results obtained using the Pd(II) complexes with NaOH or t-BuOK as the base. The catalyst load relative to the substrate (S/C) are in a 200/1 ratio, and the catalyst load relative to the base (B/C) are in 50/1 and 20/1 ratios.

These results show that the palladium complexes are efficient catalysts for the transfer hydrogenation of N-benzylideneaniline. Additionally, it also suggests that strong inorganic bases such as NaOH do not work well under the reaction conditions. The process is more active when t-BuOK is employed instead as the base. The best catalytic systems are those that included the complexes 1, 5, and 6, containing phosphine with phenyl or  $-\text{CH}_2-$  substituents. These types of ligands are more stable in a basic solution than aminophosphine; this is probably because the N–H bonds of the 2, 3, and 4 complexes decompose in a basic solution and deactivate the catalytic precursor. Conversions between 54% and 69% were obtained after 4 h of reaction. When the reaction was carried out in propan-2-ol, it required 10 h to get a 100% conversion for the catalysts 1, 5, and 6.

In the second part of this study, we changed the hydrogen source to FA and used the following two conditions: formic acid with triethylamine (500/1: base/formic acid ratio) and formic acid without triethylamine.

Table 2 summarizes the catalytic conversion of N-benzylideneaniline using a formic acid/ triethylamine = 500/1 ratio. All the catalysts studied under this condition even those that showed low activities in the propan-2-ol basic solution (2, 3 and 4) showed both high activity and selectivity. The observed conversions (between 42% and 88%) were obtained after 10 min. The maximum conversions were obtained after 1 or 3 h of the reaction depending on the type of catalyst studied. Furthermore, all the catalysts showed high selectivity with respect to N-benzylamine. The highest value for the turnover frequency ( $1080 \text{ h}^{-1}$ ) was obtained with the catalyst 2. The calculated TON (turnover number) shows that the catalysts are stable during the catalytic cycle, however, after one hour of reaction, the value obtained is lower than expected since the concentration of the substrate has decreased affecting the kinetic of the reaction. These results suggest that triethylamine facilitates the dehydrogenation of formic acid and promotes the formation of active hydride Pd–H species. It is well known that the presence of a base,  $\text{Na}_2\text{CO}_3$  or  $\text{Et}_3\text{N}$  for example, could enhance the activities and lifetime of the catalysts in the dehydrogenation of formic acid.

However, the hydrogenation can also be carried out by the metal complex without using triethylamine. Tianxiang et al. have studied the use of palladium complexes in the hydrogenation of different substrates

**Table 2**  
Hydrogenation of N-benzylideneaniline by formic acid / triethylamine using palladium catalysts that contain phosphorus-nitrogen ligands.<sup>a</sup>

Entry	Catalyst	B/C	Time of reaction	TON	TOF $\text{h}^{-1}$	% Product
1	1	500	10 min	176	1056	88
2	1	500	1 h	192	192	96
3	2	500	10 min	180	1080	90
4	2	500	1 h	192	192	96
5	3	500	10 min	152	912	76
6	3	500	1 h	190	190	95
7	4	500	10 min	84	504	42
8	4	500	1 h	194	194	97
9	5	500	10 min	160	960	80
10	5	500	1 h	170	170	85
11	6	500	10 min	138	828	69
12	6	500	1 h	154	154	77
13	6	500	3 h	188	63	94

<sup>a</sup> Reaction conditions: Compounds 1–6 (0.01 mmol); B/C: 500/1; S/C: 200/1; solvent: HCOOH (1.79 mL); base triethylamine and acetonitrile (7.5 mL); temperature: reflux.

with different phosphine ligands. In his study, only FA was used [25]. For selective hydrogen generation from formic acid, two general mechanisms can be considered (Scheme 3). One cycle starts with a metal hydride species that react with a FA proton to produce  $\text{H}_2$  and a metal formate intermediate a typical acid–base reaction between metal hydrides and a proton source. The catalytic cycle is completed with a  $\beta$ -hydride elimination ( $\beta$ -H) of the formate ligand to regenerate the metal hydride species. The other cycle starts with the oxidative addition (OA) of FA to a reduced metal complex to form a hydridometal formate complex. This complex subsequently undergoes the  $\beta$ -hydride elimination to produce a dihydride intermediate. The process continues with a reductive elimination (RE) of hydrogen and regenerate the reduced metal complex.

It is likely that  $\text{Et}_3\text{N}$  contributes to form the active species more easily when used with formic acid than when used with propan-2-ol (acid-base cycle). Therefore, the palladium complexes studied here could activate the formic acid without triethylamine and obtain a similar conversion after 1 h of reaction.

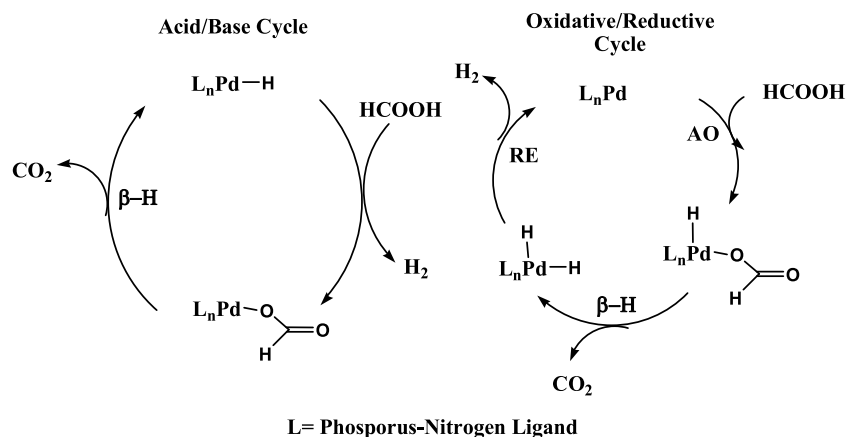
Table 3 summarizes the catalytic activities of palladium complexes containing phosphorus nitrogen ligands when FA was used as the hydrogen source. The catalysts 2 and 6 showed the best activity with conversions of 71% (TOF 852) and 80% (TOF 960) after 10 min of reaction. However, all the catalysts showed conversions of over 54% after 1 h of reaction. The catalysts 2 and 6 were studied using a 500/1 substrate/catalyst ratio and after 80 min of reaction, when the conversion was over 95%, the reactor was recharged with a fresh substrate (5 mmol, Table 4). After an additional 50 min of reaction, the conversion of catalysts 2 and 6 were 91% and 83% respectively. This result showed that the catalysts are active and stable when the substrate concentration is increased to a 1000/1 substrate/catalyst ratio.

Ruthenium and rhodium are also some catalysts that have been used successfully in hydrogenation reactions of ketones and imines using FA as the hydrogen source. These catalysts produce high conversion and selectivity; however, the duration of the reaction might range between 2–24 hours [42–47]. Recently, Burgess et al. found that palladium compounds containing pincer-type phosphorus ligands supported on zirconia were active in the hydrogenation of ketones that used FA as the hydrogen source. These catalysts showed conversions between 6% and 100%; however, their reaction times are 12 times higher than the palladium catalysts of our study [48].

Several authors have proposed an explanation for the role of triethylamine in the hydrogenation reaction using FA. The prevailing idea is that triethylamine prevents the inactivation of FA, favouring its deprotonation and increasing its reactivity instead. This theory might explain the significant difference in conversions during the first 10 min of the reaction when it was carried out using only FA and when FA/triethylamine was used (Tables 2 and 3). In the presence of a catalyst, FA is decomposed into  $\text{CO}_2$  and  $\text{H}_2$ . This explains the presence of molecular hydrogen in the catalytic reaction, which we detected by GC chromatography.

The mechanism proposed in this paper is based on previous studies reported in the literature [1,25]. In this mechanism, a metal-hydride species has been proposed, which would be the active species of the reaction. Based on this, it is possible to propose a likely mechanism to explain the active species formation during the hydrogenation process using palladium (II) catalysts with hemilabile phosphorus-nitrogen ligands. When FA is used without  $\text{Et}_3\text{N}$ , palladium dihydride is formed by the oxidative addition of FA, followed by  $\beta$ -elimination (see oxidative/reductive cycle in Scheme 3).

To determine effects of bases on the reaction, we conducted experiments using only FA. If triethylamine does not exert significant effects, the results should be similar to those obtained in the presence or absence of this base. The results achieved are summarized in Table 3. Under this condition, it was observed that the activities decreased after 10 min when compared to the results obtained when  $\text{Et}_3\text{N}/\text{HCOOH}$  was used (Table 2); however after 1 h, both the activities were similar. In



**Scheme 3.** Activation of palladium complexes containing PN ligands by formic acid.

**Table 3**

The effect of ligands in the transfer hydrogenation of N-benzylideneaniline with catalysts 1–6.<sup>a</sup>

Entry	Catalyst	Time of reaction (minutes)	TON	TOF h <sup>-1</sup>	% Product
1	1	10	60	360	30
2	1	60	160	160	80
3	1	120	176	88	88
4	2	10	142	852	71
5	2	30	180	360	90
6	2	60	198	180	99
7	3	10 min	80	480	40
8	3	60	108	108	54
9	3	120	162	81	81
10	4	10	112	672	56
11	4	30	168	336	84
12	4	60	182	182	91
13	5	10	70	420	35
14	5	60	152	152	76
15	5	120	160	80	80
16	6	10	160	960	80
17	6	60	182	182	91
18	6	120	184	92	92

<sup>a</sup> Reaction conditions: catalysts 1–6 (0.01 mmol); S/C ratio: 200/1; solvent: HCOOH (1.79 mL) and acetonitrile (8.21 mL).

**Table 4**

Recharge experiments for catalysts 2 and 6.<sup>a</sup>

Entry	Catalyst	Time of reaction (minutes)	TON	TOF h <sup>-1</sup>	% product
1	2	10	210	1260	42
2	2	30	435	870	87
3	2	60	480	480	96
4*	2	80	485	364	97
5	2	90	530	353	53
6	2	100	860	515	86
7	2	130	910	419	91
1	6	10	170	1020	34
2	6	30	380	760	76
3	6	60	465	465	93
4*	6	80	475	356	95
5	6	90	470	313	47
6	6	100	740	443	74
7	6	130	830	383	83

<sup>a</sup> Reaction conditions: catalysts (0.01 mmol); S/C ratio: 500/1; solvent HCOOH (1.79 mL) and acetonitrile (8.21 mL); \*substrate recharge: 5 mmol after 80 min of reaction.

the absence of Et<sub>3</sub>N, the system showed that the initial conversion was low, but after one hour it was nearly 90%. Only the catalyst 3 required 2 h of reaction to achieve an 80% conversion.

The formation of metal hydride (Pd-H) is so rapid that the conversion is observed just after 30 s. Unfortunately, after several experiments, we were not able to detect it by NMR.

Once the palladium hydride is formed, the reaction proceeds similarly as that observed in conventional hydrogenation catalysts. An interesting detail is how the catalyst is regenerated during its cycle (see Scheme 4). In this mechanism, we can observe the hemilabile behaviour of the PN ligand facilitates the coordination of FA. In addition the catalytic activity is low and palladium metal is observed if the reaction is performed in a non-coordinating solvent. It is likely that the coordinating solvent prevented the decomposition of palladium during the catalytic reaction.

Several authors have proposed that the palladium catalyst is decomposed into nanoparticles during the homogenous reaction [49–51]. For example, the dehydrolinalool and linalool transformations are catalysed by palladium nanoparticles [32]. These reactions include a hydrogenation pathway. In these experiments, it is possible to obtain a high conversion in the presence of nanoparticles; however, the duration of the reaction is 16 h. Another application of nanoparticles as a catalyst is in the Heck reaction, where the duration of the reaction is between 4 and 24 h. To examine if the nanoparticles played a catalytic role in our work, the hydrogenation of N-benzylideneaniline was studied using palladium nanoparticles that were prepared using the method reported by Tsvetkova [51]. Under these conditions, the system with the nanoparticles showed only 20% conversion after 1 h of reaction, and the hydrolysis of N-benzylideneaniline turned out to be 30% (see Fig. 1).

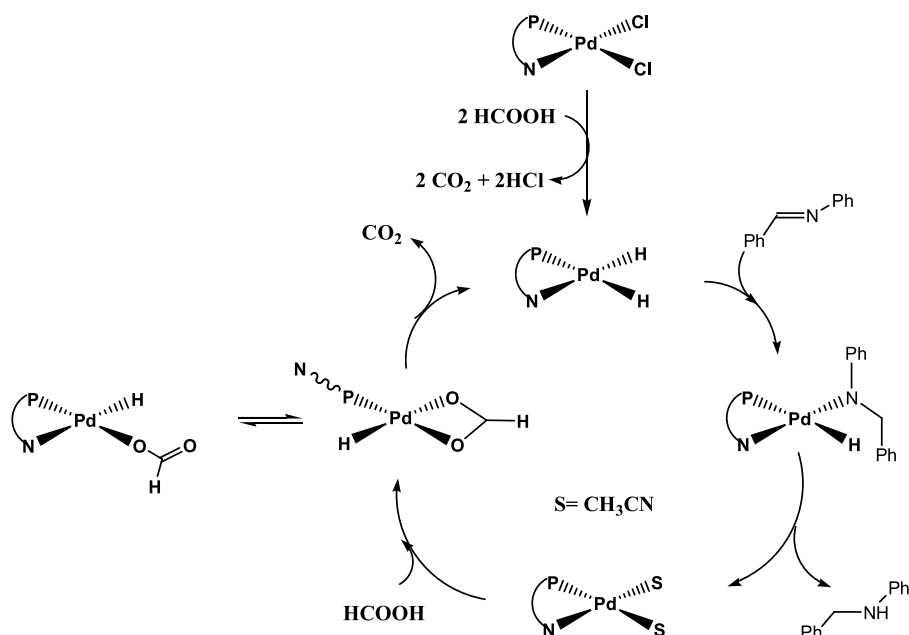
In this regard, when heterogeneous nanoparticles were used, the process required a higher reaction time and conversions were markedly lower compared to those obtained using homogeneous conditions (42% conversion after 10 min).

#### 4. Conclusions

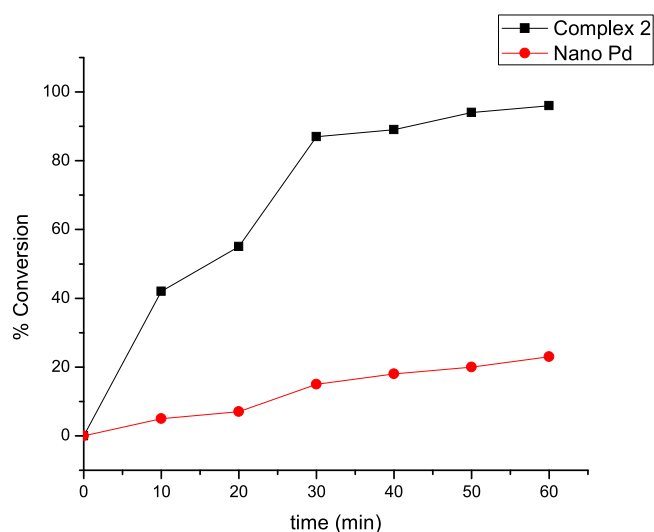
The palladium catalysts are active for the transfer hydrogenation of N-benzylideneaniline using 3 systems as the hydrogen source: (a) propan-2-ol in a basic solution, (b) triethylamine/formic acid, and (c) formic acid. The best results are obtained using formic acid and formic acid/triethylamine; however, the activities reported in formic acid without triethylamine turned out to be similar after 1 h of reaction.

The trimethylamine/formic acid medium only favours the initial reaction rate because it is likely that the triethylamine influences the formation of the active species in the reaction. However, once they are formed, the activities observed when using only formic acid are similar to those observed when triethylamine is used as the base.

Catalysts 2 and 6 show the best activities when only formic acid is used as the hydrogen source. The turnover numbers and the activities are maintained even after the systems are recharged. When the



**Scheme 4.** Proposed mechanism of hydrogenation of imines using formic acid with a palladium catalyst.



**Fig. 1.** Hydrogenation of N-benzylideneaniline using palladium phosphorus-nitrogen ligand (complex 2) and palladium nanoparticles (nano Pd).

substrate concentration is increased from a substrate/catalyst ratio of 200/1 to 500/1, their activities show an increase in the turnover frequency (TOF).

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