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# Palladium complexes with 3-phenylpropylamine ligand: synthesis, structures, theoretical studies and application in the aerobic oxidation of alcohols as heterogeneous catalysts

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Reaction of 3-phenylpropylamine with Pd(OAc)<sub>2</sub> by heating in toluene, resulted in nearly square planar complex trans- $[Pd(C_6H_5(CH_2)_3NH_2)_2(OAc)_2]$  (1). Complex 1 reacted with NaCl in methanol to give corresponding product *trans*- $[Pd(C_6H_5(CH_2)_3NH_2)_2(Cl)_2]$  (2). Treatment of 2 with triphenylphosphine in dichloromethane afforded  $trans-[Pd(C_6H_5(CH_2)_3NH_2)_2(PPh_3)_2]2Cl$  (3). All of the palladium (II) complexes (1-3) were fully characterized by IR and NMR spectroscopies. In addition, the crystal structures of 1, 2 were determined by single-crystal X-ray diffraction analysis. In these structures, the acetate and chloride ligands are in trans geometry. Density functional theory (DFT) calculations gave bond lengths and angles in keeping with the experimental values. Palladium nanoparticles derived from complexes (1-3), were supported on cucurbit[6]uril (CB[6]) and identified by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), inductively coupled plasma analyzer (ICP) and high resolution X-ray powder spectroscopy (HR-XPS). CB[6]supported palladium nanoparticles (NP) were used as heterogeneous catalysts for the aerobic oxidation of alcohols to corresponding aldehydes or ketones without over oxidation. CB[6]-Pd NPs (3) (prepared from complex 3) shows better catalytic activity than CB[6]-Pd NPs (1), (2), as higher yield was observed with it in a relatively short time. The factors such as catalyst amount, solvent, temperature and reaction time were all systematically investigated to elucidate their effects on the yield of catalytic alcohol oxidation reactions. This catalytic system showed high activity and selectivity toward alcohols in mild conditions. The catalyst was reused five times without any significant loss in the catalytic activity.

# Introduction

Selective oxidation of alcohols to corresponding carbonyl compounds is an important transformation in the chemical industry [1,2]. The traditional oxidizing reagents, which have usually required stoichiometric amounts of inorganic oxidants such as chromate or permanganate, are expensive and have serious toxicity issues associated with them and are not acceptable from the green chemistry perspective [3,4]. Homogeneous transition metal-based catalysts such as palladium (II) complexes are known that can promote this reaction without the use of toxic oxidants [5].

Hydrogen peroxide is considered as one of the least toxic oxidants as it gives water as the only by-product. It also conforms with the environmental concerns, where development of catalytic systems

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that use molecular oxygen as the oxidant is of considerable interest [6-8]. Molecular oxygen is an inexpensive and abundant oxidant for the oxidation of alcohols.

The most important organic reactions have been performed with homogeneous palladium catalysts, that these catalysts possess many merits such as high turnover number, high activity and selectivity and excellent yields, but from economic and environmental standpoint, heterogeneous catalysts are highly desirable [9-14]. For this purpose, researchers have immobilized palladium complexes and nanoparticles on various supports such as polymers [15], silica [16], SBA-15/16 [17], MCM-41 [18], alumina [19], zeolite [20], carbon [21], clay [22], PEG [23] and TiO<sub>2</sub> [24], to create heterogeneous catalysts, because the heterogeneous systems are easy to handle and recover [25–33].

CB[6] is a family of macrocyclic molecules that can act as both support and capping agent (Fig. 1). CB[6] have been synthesized by condensation of formaldehyde with glycoluril [34–38] and it has two identical portals. At each entrance to the cavity, six polar carbonyl groups are located and provide two negative fringes of bonding to the surface of metals or nanomaterials. In spite of the polar fringed portals, the CB[6] is non-polar and thus nearly insoluble in all common organic solvents and water. In addition, CB[6] is the rigid cyclic structure that has high thermal and chemical stability against many oxidizing agents [39].

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<sup>&</sup>lt;sup>+</sup> Electronic supplementary information (ESI) available: NMR and FT-IR spectra of all complexes (1-3); single crystal data of 1 and 2 (CCDC 1060354 and 1060510), HR-XPS N1s spectra of fresh CB[6]-Pd NPs (3) and CB[6]-Pd NPs (3) after fifth runs.



Fig. 1 Illustration of Cucurbit[6]uril.

Here we report synthesis and characterization of palladium complexes derived from 3-phenyl prophyl amine. Theoretical studies were also carried out in order to investigate why we have obtained complex 2 instead of orthopalladate (our expectation). The optimized molecular parameters were close to the real structure that obtained by X-ray analysis. In addition the LUMO-HOMO energy gap and partial atomic charges of complex 2 (real product) and complex 2' (desired product) were obtained.

These complexes (1, 2 and 3) were used for preparation of heterogeneous Pd catalysts, which were deposited on CB[6] using a simple method. The supported Pd nanoparticles showed high activity and selectivity in the aerobic oxidation of alcohols under mild conditions. Finally, the catalyst was highly reusable at least five times.

### **Results and Discussion**

Scheme 1 shows the complexes prepared in this work and the labelling assigned to the methylene protons.



Scheme 1 (i)  $Pd(OAc)_2$  in toluene (60 °C, 24 h); (ii) excess NaCl in methanol (room temperature, 12 h); (iii) 2PPh<sub>3</sub> in dichloromethane (room temperature, 6 h).

#### Synthesis and structure of palladium complexes

The reaction of 3-phenylpropylamine  $Ph(CH_2)_3NH_2$  with  $Pd(OAc)_2$ in a 1:1 molar ratio was carried out in toluene at 60 °C to produce complex 1 trans-[Pd(C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>(OAc)<sub>2</sub>]. palladium Treatment of complex 1 with an excess of NaCl in methanol afforded the corresponding product trans- $[Pd(C_6H_5(CH_2)_3NH_2)_2(Cl)_2]$  (2). Complex 2 reacted with PPh<sub>3</sub> in a 1:2 molar ratio to give complex 3 trans- $[Pd(C_6H_5(CH_2)_3NH_2)_2]$  $(PPh_3)_2$  [2Cl<sup>-</sup> [40]. The mononuclear palladium complexes 1, 2 and 3 were characterized by IR and NMR spectroscopy. These spectra for complexes 1, 2 and 3 are given in the ESI (Fig. S1–S9<sup>†</sup>).

The IR spectrum of complex **1** shows characteristic bands due to the acetato ligand at 1573, 1388 cm<sup>-1</sup> [41] and two peaks corresponding to NH<sub>2</sub> at 3218, 3118 cm<sup>-1</sup>. <sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of complexes **1**, **2** and **3** were recorded in CDCl<sub>3</sub>. The <sup>1</sup>H NMR spectrum of complex **1** displays five sets of signals for the methylene protons, acetato-methyl and amine protons. The <sup>13</sup>C{<sup>1</sup>H}

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The IR spectrum of complex **2** shows two peaks corresponding to  $NH_2$  at 3223 and 3270 cm<sup>-1</sup> while acetato ligand peaks are not present. The <sup>1</sup>H NMR spectrum of complex **2** displays four sets of signals for the methylene protons and amine protons. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of complex **2** shows aliphatic and aromatic region and the carbon signals of CO and CH<sub>3</sub> are disappeared.

The IR spectrum of complex **3** shows two peaks corresponding to NH<sub>2</sub> at 3395 and 3451 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of complex **3** displays four sets of signals appear for the methylene protons and amine protons. The <sup>31</sup>P{<sup>1</sup>H} NMR of complex **3** shows a peak corresponding to PPh<sub>3</sub> at 23.26 ppm. Also this spectrum displays an additional peak with lower intensity at 17.86 ppm that belongs to PPh<sub>3</sub> in Pd(PPh<sub>3</sub>)<sub>4</sub> [42]. Molar conductance value for the complex **3** in acetone (1×10<sup>-3</sup> mol/cm<sup>3</sup>) is 110  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> which indicates its 1:2 electrolytic nature.

The single crystal structures of 1 and 2 were established with X-ray diffraction. However, attempts to crystallize complex 3 were unsuccessful. The single crystal X-ray diffraction study of complex 1, 2 confirmed the details of the proposed new structures.

Fig. 2 and 3 show ORTEP plot of complexes 1 and 2 with selected bond lengths and angles given in the figure caption. The crystal data and parameters concerning the data collection and structure solution and refinement are given in Table S1 of ESI<sup>†</sup>. Tables S2 and S3 in ESI<sup>†</sup> contain selected bond lengths and angles for complexes 1 and 2, respectively. H atoms in the figures as well as in the tables are omitted for clarity. The palladium metal exhibits a distorted squareplanar geometry in both the complexes and two acetates and two chlorides are *trans* to each other.

As indicated by the ligands at the Pd(II) center of complex 1, the angles subtended are varying from 85.0(5) to 95.4(5) and from 179.3(8) to 179.4(5). The summation of the bond angles around the palladium is 360.0. The Pd–N bond lengths, 2.057(12) and 2.059(14) Å of 1 are close to each other and greater than the value, 2.008(7) and 2.021(6) Å reported for palladium complex 2c [43]. Also the Pd–O bond distances (2.019(9) and 2.019(10) Å) of 1 have been found to be somewhat longer than the values 1.953(10) and 1.985(6) Å reported for palladium complex 2c [43].



Fig. 2 ORTEP diagram of *trans*- $[Pd(C_6H_5(CH_2)_3NH_2)_2(OAc)_2]$  (1) with 50% probability ellipsoids. All the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pd(1)–O(1), 2.019(9); Pd(1)–O(3), 2.019(10); Pd(1)–N(1), 2.057(12); Pd(1)–N(2), 2.059(14). Selected bond angles (°):O(1)-Pd(1)-N(1), 85.3(5); O(3)-Pd(1)-N(1), 94.3(5); O(3)-Pd(1)-N(2), 85.0(5); O(1)-Pd(1)-N(2), 95.4(5); O(1)-Pd(1)-O(3), 179.4(5); N(1)-Pd(1)-N(2), 179.3(8).



Fig. 3 ORTEP diagram of  $trans-[Pd(C_6H_5(CH_2)_3NH_2)_2(Cl)_2]$  (2) with 50% probability ellipsoids. All the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pd(1)-N(1), 2.0361(15); Pd(1)-Cl(1), 2.3031(5); Pd(1)-Cl(1<sup>i</sup>), 2.3031(5). Selected bond angles (°): N(1)-Pd(1)-Cl(1), 88.12(4); N(1)-Pd(1)-Cl(1<sup>i</sup>), 91.88(4); N(1<sup>i</sup>)-Pd(1)-Cl(1<sup>i</sup>), 88.12(4); N(1<sup>i</sup>)-Pd(1)-Cl(1), 91.88(4); Cl(1)-Pd(1)-Cl(1<sup>i</sup>), 180.0(5); N(1)-Pd(1)-N(1<sup>i</sup>), 180.0(5).

As indicated by the ligands at the Pd(II) center of the complex **2**, the angles are 88.12(4), 91.88(4), 88.12(4) and 91.88(4) for N(1)-Pd(1)-Cl(1), N(1)-Pd(1)-Cl(1<sup>i</sup>), N(1<sup>i</sup>)-Pd(1)-Cl(1<sup>i</sup>) and N(1<sup>i</sup>)-Pd(1)-Cl(1) respectively. The summation of the bond angles around the palladium is 360.0. In complex **2**, the Pd1-N1 (2.0361(15) Å) bond length is same as Pd1-N1<sup>i</sup> (2.0361(15) Å) distance. The Pd-Cl bond lengths of **2** (2.3031(5) Å) are in the normal range and consistent with the values reported for the Palladium(II) complexes [44].

The N-H···O interactions in the crystal of 1 result in the formation of a three dimensional structure shown in Fig. 4, where as N-H···Cl interactions shown in Fig. 5 result in the formation of three dimensional network in the case of 2.



Fig. 4 Intermolecular N–H…O interaction in complex 1.



Fig. 5 Intermolecular N–H····Cl interaction in complex 2.

# Synthesis and characterization of CB[6]-Pd NPs

Our goal for the synthesis of CB[6]-Pd NPs was to use simple methods. To achieve this goal, CB[6] was prepared in water, and Pd nanoparticles were dispersed on CB[6] in green solvents such as water and ethanol (Scheme 2). In these reactions palladium complexes 1-3 were used as precursor for the catalysts preparation. Previous studies show that CB[6] has two identical portals lined by carbonyl groups that provide two negative fringes capable of binding to the surface of metals or other nanostructures [45,46]. The Palladium ions can bind to carbonyl groups at the portal of CB[6] before reducing agent (NaBH<sub>4</sub>) is added to the reaction mixture [45,46]. When reducing agent is added to the reaction mixture, high percentage of Pd(II) were transformed to Pd(0). This synthesis procedure is based on the physical adsorption of Pd(0) on the surface of CB[6] support, by the electronic interaction between the electrons from Pd(0) and the vacant orbitals of C=O. However, electrostatic interaction between the surface atoms of Pd and CB[6] can effectively prevent the Pd NPs from agglomeration.



Scheme 2 Preparation of CB[6]-Pd NPs 1-3.

The XRD pattern of the fresh CB[6]-Pd NPs (**3**) exhibits a broad reflection peak belonging to the CB[6] at about  $23^{\circ}$  [48] and also shows the peaks at 40°, 46°, 68° and 82° corresponding to (111), (200), (220) and (311) crystallographic planes of Pd(0) nanoparticles with the face-centred cubic Pd lattice (Fig. 6a). This is in good agreement with the results achieved from literature (Fig. 6b) [49].



Fig. 6 X-ray powder diffraction pattern of (a) CB[6]-Pd NPs (3) (b) Pd(0) [46].

Fig. 7 shows the HR-XPS spectra of the CB[6]-Pd NPs (**3**). The Pd 3d spectra show the characteristic Pd  $3d_{5/2}$  and  $3d_{3/2}$  doublet peaks. The expected positions for the Pd(0) and Pd(II) species respectively at around 335.3 [50,52] and 337.6 eV [50,51] are shown.

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The Pd(II) peaks were fitted with a Gaussian Lorentzian peak shape, while the Pd(0) peaks were fitted with an asymmetric shape. The fitting indicates that the Pd in fresh CB[6]-Pd NPs (**3**) is a mix of Pd(II) and Pd(0) states (Fig. 7a). After the fifth runs, Pd(0) is seen in a higher proportion, indicating that after catalytic cycles, the Pd(II) cations were transformed to Pd(0).

The HR-XPS N 1s spectra of the fresh CB[6]-Pd NPs (**3**), and CB[6]-Pd NPs (**3**) after fifth runs show a single peak at around 400.0 eV attributed to C-N bonds [49] coming from the CB[6] and ligand. (Fig. S10†). After the fifth runs, C-N bonds is seen in a lower proportion, indicating that after catalytic cycles, the Pd(II) were transformed to Pd(0) and ligand removed from the complex **3**.



**Fig. 7** The XPS patterns of (a) High resolution Pd 3d of fresh CB[6]-Pd NPs (**3**), and (b) CB[6]-Pd NPs (**3**) after fifth runs.

Fig. 8 shows the FTIR spectra of palladium complex **3** (a) CB[6] (b) and CB[6]-Pd NPs (c). From the Fig. 8a it is clear that two bands at around 2924 and 2849 cm<sup>-1</sup> could be attributed to the asymmetric and symmetric stretching of CH<sub>2</sub> groups of 3-phenylpropylamine, respectively. The peak at 3048 cm<sup>-1</sup> exhibited the stretching vibration of CH in aromatic ring in palladium complex **3**. Three strong bands observed near 744, 693 and 518 cm<sup>-1</sup> in the complex were attributable to the coordinated PPh<sub>3</sub> ligand [53]. FTIR spectrum of CB[6] (Fig. 8b) shows the peak at 1726 cm<sup>-1</sup>. This peak was assigned to carbonyl stretching vibration at which no changes

between CB[6]-Pd NPs (**3**) (Fig 8c) and CB[6] (Fig. 8b) were observed, proving that there is no direct bonding between CB[6] and metal atoms [54]. In addition the absorption bands at 693 and 518 cm<sup>-1</sup> showed the existence of PPh<sub>3</sub> in CB[6]-Pd NPs (**3**) in a lower proportion (Fig. 8c), compared to palladium complex **3** (Fig. 8a).



**Fig. 8** FTIR spectra of (a) palladium complex **3** (b) CB[6] (c) CB[6]-Pd NPs.

The FE-SEM image of the corresponding CB[6]-Pd NPs (3) confirms the uniform distribution of Pd NPs onto CB[6] (Fig. 9).



Fig. 9 FE-SEM images corresponding to CB[6]-Pd NPs (3).

The corresponding TEM images reveal that the Pd NPs were formed and well dispersed through the support surface (Fig. 10). The average particle size of Pd(0) in the fresh CB[6]-Pd NPs based on more than 243 particle sizes resulted 3.11 nm (Fig. 10a). The TEM images after fifth runs are also shown in Fig. 10b. The average particle size of Pd(0) in CB[6]-Pd NPs after use is 2.62 nm. Also the TEM images show that aggregation of Pd NPs was not observed even after fifth runs.

Tabla 1



**Fig. 10** TEM images of (a) fresh CB[6]-Pd NPs (3) and (b) CB[6]-Pd NPs (3) after fifth runs: histogram illustrating the Pd nanoparticle size distribution.

#### Aerobic oxidation of alcohols by CB[6]-Pd NPs

Selective oxidation of alcohols to corresponding carbonyl compounds is one of the most important transformations in the synthesis of fine chemicals. Several excellent catalysts for the oxidation of alcohols to corresponding aldehydes or ketones have been disclosed, but most of them required heating and toxic oxidants which violate the requirements of the "green chemistry". We first examined the ability of CB[6]-Pd NPs (Cat 1–3) to actually catalyze the aerobic oxidation of benzyl alcohol. Initially, we focused our attention on the aerobic oxidation of benzyl alcohol under identical reaction conditions (90 °C, toluene as solvent,  $K_2CO_3$  as base, in air) in order to compare catalyst **3** with catalyst **1** and **2** (Table 1).

Table 1	
Optimizing of the catalyst for oxidation reaction of	of benzyl alco <u>hol<sup>a</sup></u>
<u> </u>	CUO

	OH Catalyst 1, 2 or 3 toluene, K <sub>2</sub> CO <sub>3</sub> 90 °C, 23 h	
Entry	catalyst	Conversion (%) <sup>b</sup>
1	1	36
2	2	39
3	3	60
4	3	52°
5	PPh <sub>3</sub>	5

**\*Reaction conditions:** alcohol (1 mmol), K<sub>2</sub>CO<sub>3</sub> (1 mmol), toluene (6 ml), catalyst (0.05 mol% Pd), 90 °C, 23 h, in air.

<sup>b</sup>Determined by GC using biphenyl as an internal standard. <sup>c</sup>Catalyst (0.025 mol% Pd).

Although all catalysts were able to furnish the corresponding benzaldehyde in good yield within the indicated time, catalyst 3 exhibited higher catalytic activity than that of catalysts 1, 2 (Table 1, entries 1, 2 and 3). This is due to the fact that by changing the ligands on the transition metal atom, the catalyst properties can be altered and bulky electron-rich phosphines tend to increase the reaction performance and they also act as catalysts themselves [55-57]. For further investigation, a blank experiment with only PPh<sub>3</sub> was performed ant it was found that PPh<sub>3</sub> could not act as catalyst by its own (Table 1, entry 5). In addition, two different amounts of CB[6]-Pd NPs (3) (0.025, 0.05 mol% of Pd) were used, keeping with all other reaction parameters fixed: namely temperature (90 °C), toluene (6 mmol), K<sub>2</sub>CO<sub>3</sub>, and reaction time (23 h) in the air. Indeed, the amount of catalyst had a significant effect on the oxidation of benzyl alcohol (Table 1, entries 3 and 4). The results are shown in Table 1, indicating 52 and 60 % conversion corresponding to 0.025 and 0.05 mol% of Pd catalyst, respectively. Lower conversion of benzyl alcohol into benzaldehyde with 0.025 mol% of Pd catalyst may be due to fewer catalytic sites. Therefore, 0.05 mol% of the Pd catalyst was taken to be optimal.

Our further investigation concerned the oxidation of benzyl alcohol using CB[6]-Pd NPs (**3**), toluene and atmospheric air as the source of molecular oxygen in the presence of various bases (Table 2).

It is reasonable that the base deprotonates the alcohol and starts the catalytic reaction, therefore the alcohol oxidation over Palladium based catalyst needs a base as a promoter generally [58]. Hence, different bases were used to promote the benzyl alcohol oxidation and  $K_2CO_3$  was found to be the most effective (Table 2, entry 7).

In addition, various solvents were investigated in the presence of K<sub>2</sub>CO<sub>3</sub> and it was found that solvents such as acetonitrile (CH<sub>3</sub>CN), N,N-dimethylformamide (DMF), acetone, MeOH and EtOH were not effective (Table 2, entries 15-19). The conversion of benzvl alcohol was low when H<sub>2</sub>O:EtOH (1:1, 1:2, 1:4) was used as the solvent (Table 2, entry 12-14) and toluene was the best choice for this catalytic reaction (Table 2, entry 7). Under air, the reaction time needed to be prolonged to 23 h at 90 °C. To reduce the reaction time, catalytic oxidation of benzyl alcohol was studied by performing the reaction of benzyl alcohol under air bubbling .In order to determine the effect of air bubbling on the oxidation reaction of benzyl alcohol, three different temperatures (rt, 40 °C and 90 °C) were investigated. The results show that 75, 85, and 77% conversion were found corresponding to rt, 40 °C and 90 °C, respectively (Table 2, entries 1, 4 and 6). At elevated temperature (90 °C), >95% benzyl alcohol conversion was found with 77% selectivity of benzaldehyde and 18% selectivity for benzoic acid which is due to over oxidation of banzaldehyde to benzoic acid at elevated temperature (Table 2, entry 6). Also, in the presence of CB[6] as catalyst, the reaction did not occur (Table 2, entry 20).

benzylic ring.

Table 3

oxidation reactions. High efficiency was obtained for 2-phenylethanol oxidation, where 100% conversion was observed at 2 h (Table 3, entry 2). CB[6]-Pd NPs (3) shows higher catalytic activity for substituted aromatic alcohols containing electrondonating groups (e.g., -OCH<sub>3</sub>) than those containing electron withdrawing group (such as  $-NO_2$ ) (Table 3, entry 7 and 8). Also this catalytic system was inactive toward linear alcohols (Table 3, entry 9 and 10). The results show that CB[6]-Pd NPs (3) was highly active and selective for the oxidation of alcohols that have at least a Aerobic oxidation of alcohols using CB[6]-Pd NPs (3).

	Alcohol	- Aldehyd	le/Ketone
	Toluene, $K_2C_0$	D <sub>3</sub>	
	40 °C, t		
Entry	Substrate	Time (h)	Conv. <sup>a</sup> (Yield) <sup>b</sup> (%)
1	Benzyl alcohol	4	85(81)
2	2-Phenylethanol	2	100(94)
3	1-Phenylethanol	4	98(91)
4	4-Hydroxybenzyl alcohol	4	96(90)
5	2-Chlorobenzyl alcohol	4	77(75)
6	2-Hydroxybenzyl alcohol	4	80(78)
7	7 4-Nitrobenzyl alcohol		84(81)
8	4-Methoxybenzyl alcohol	4	90(83)
9	3-Hexanol	10	Trace
10	2-methyl-1-propanol	10	Trace

Catalyst

corresponding aldehyde or ketone is high for all the alcohol

<sup>a</sup>Reaction conditions: alcohol (1 mmol), K<sub>2</sub>CO<sub>3</sub> (1 mmol), toluene (6 ml), catalyst (0.05 mol% Pd), 40 °C, under air bubbling.

<sup>a</sup>Determined by GC using biphenyl as an internal standard. <sup>b</sup> Isolated yields.

The catalytic activity of complex 3 was also studied in the aerobic oxidation of a variety of alcohols using the optimized heterogeneous reaction conditions. As presented in Table 4, in these homogeneous systems, different alcohols react to give the corresponding products. In comparison with homogeneous system, oxidation of alcohols in the presence of CB[6]-Pd NPs (3) (heterogeneous system) could be considered as efficient and versatile catalytic reactions for the aerobic oxidation of a variety of alcohols.

#### Table 4

Aerobic oxidation of alcohols using complex 3.

Alcohol $\longrightarrow$ Aldehyde/Ketone				
Toluene, $K_2CO_3$				
	40 °C, t			
Entry	Substrate	Time (h)	Conv. <sup>a</sup>	
1	Benzyl alcohol	4	88	
3	1-Phenylethanol	4	100	
4	4-Hydroxybenzyl alcohol	4	93	
5	2-Chlorobenzyl alcohol	4	76	
7	4-Nitrobenzyl alcohol	4	88	
8	4-Methoxybenzyl alcohol	4	93	
9	3-Hexanol	10	Trace	

<sup>a</sup>Reaction conditions: alcohol (1 mmol), K<sub>2</sub>CO<sub>3</sub> (1 mmol), toluene (6 ml), complex 3 (0.05 mol%), 40 °C, under air bubbling.

<sup>a</sup>Determined by GC using biphenyl as an internal standard.

### Table 2

Optimizing of the reaction condition for oxidation reaction of benzyl alcohol, using CB[6]-Pd NPs (3).

		ОН	Catalyst	CI	Ю	
		-	Solvent, Base T, t			
Entry	Solvent	Pd (mol %)	Base	Temp (°C)	Time (h)	Conv.
1	Toluene	0.05	K <sub>2</sub> CO <sub>3</sub>	40	4	85 <sup>b</sup>
2	Toluene	-	$K_2CO_3$	90	23	10
3	Toluene	0.05	-	rt	10	75 <sup>b</sup>
4	Toluene	0.05	$K_2CO_3$	rt	6	68 <sup>b</sup>
5	Toluene	0.025	K <sub>2</sub> CO <sub>3</sub>	90	6	70 <sup>b</sup>
6	Toluene	0.05	$K_2CO_3$	90	6	77 <sup>b</sup> (18) <sup>c</sup>
7	Toluene	0.05	$K_2CO_3$	90	23	60
8	Toluene	0.05	$K_3PO_4.3H_2O$	90	23	42
9	Toluene	0.05	NaOH	90	23	41
10	Toluene	0.05	КОН	90	23	13
11	Toluene	0.05	Na <sub>2</sub> CO <sub>3</sub>	90	23	28
12	EtOH:H <sub>2</sub> O (4:1)	0.05	K <sub>2</sub> CO <sub>3</sub>	90	23	31
13	EtOH:H <sub>2</sub> O (2:1)	0.05	$K_2CO_3$	90	23	43
14	EtOH: $H_2O$	0.05	$K_2CO_3$	90	23	55
15	Acetone	0.05	$K_2CO_3$	90	23	4
16	DMF	0.05	$K_2CO_3$	90	23	8
17	MeOH	0.05	$K_2CO_3$	90	23	8
18	EtOH	0.05	$K_2CO_3$	90	23	4
19	CH <sub>3</sub> CN	0.05	$K_2CO_3$	90	23	3
20 <sup>c</sup>	Toluene	0.05	$K_2CO_3$	40	4	_ <sup>b,d</sup>
21 <sup>d</sup>	Toluene	0.05	$K_2CO_3$	40	4	68 <sup>b,e</sup>
22 <sup>e</sup>	Toluene	0.05	K <sub>2</sub> CO <sub>3</sub>	40	4	$54^{b,f}$

<sup>a</sup>Reaction conditions: benzyl alcohol (1 mmol), base (1 mmol), solvent (6 ml), catalyst (0.025, 0.05 mol% Pd), in air.

<sup>a</sup>Determined by GC using biphenyl as an internal standard.

<sup>d</sup>The reaction was carried out in the presence of CB[6]

"The reaction was carried out in the presence of Pd(OAc)<sub>2</sub> supported on CB[6].

<sup>f</sup>The reaction was carried out in the presence of PdCl<sub>2</sub> supported on CB[6].

The scope of the catalytic system was then subsequently extended to the aerobic oxidation of a variety of alcohols under optimized conditions (Table 3). Several aromatic alcohols were employed to study the generality of CB[6]-Pd NPs (3) for alcohol oxidation, and the results are listed in Table 3, entry 1-8. The selectivity toward the

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<sup>&</sup>lt;sup>b</sup>Under air bubbling.

Benzoic acid conversion.

Further experiments were performed to confirm the recyclability of the solid catalyst. The consecutive oxidations of benzyl alcohol under air bubbling were also carried out at 40 °C using toluene as solvent. The results are summarized in Fig. 11. At palladium loading of 0.05 mol%, CB[6]-Pd NPs (**3**) afforded 85% conversion under air bubbling over 4 h. After the first reaction cycle, CB[6]-Pd NPs (**3**) catalyst was recovered by centrifugation and was washed with ethanol and water three times. The catalyst was dried overnight at 100 °C and for the second reaction cycle, the fresh benzyl alcohol was added and other conditions were the same as the first reaction cycle. A 87% conversion was obtained over 4 h. From the third to 5th reaction, there was no significant change observed in selectivity, and only little decrease in conversion was observed which showed that the catalyst was stable and can be regenerated for repeated use.



Fig. 11 A recyclability test for catalyst in the aerobic oxidation of alcohols.

ICP-OES analysis showed that palladium content of the fresh CB[6]-Pd NPs (**3**) was 11.9 wt%. The palladium content after 5 consecutive reaction cycles was almost the same as that of fresh catalyst, and palladium could not be detected in the filtrate after the reaction. Also the hot filtration test confirming no continued reaction after the catalyst was removed. These results confirm the heterogeneous character of the catalytically active species that limits pollution of the environment by the catalyst.

#### Comparison with the other studies

The catalytic performance of the catalyst CB[6]-Pd NPs (**3**) for the oxidation of alcohols was compared with some of the previous reported results using different types of the supports (Table 5) [15, 59-63]. As shown in Table 5, comparing with other supported palladium catalyst, CB[6]-Pd NPs (**3**) exhibited comparable yields

#### Table 5

Co	mparison	with	reported	results	for	Suzuki	reaction	on	supported	Pd	cataly	sts

Entry	Catalysts <sup>a</sup>	Reaction conditions solvent/base/temp./time/oxidant	Yields/% <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>b</sup>	References
1	Pd@SBA-15 (0.4)	toluene/K <sub>2</sub> CO <sub>3</sub> /80 °C/3.5 h/O <sub>2</sub>	83	59	[59]
2	PdNPs/PS (0.5)	toluene/K <sub>2</sub> CO <sub>3</sub> /85 °C/15 h/-	98	13	[15]
3	PdHAP-0 (0.6)	trifluorotoluene/-/90°C/1 h/O <sub>2</sub>	99	165	[60]
4	Pd/MIL-101 (1.5)	toluene/-/80 °C/1.5 h/O <sub>2</sub>	99	44	[61]
5	MS-PdG-G (1)	toluene/K2CO3/110 °C/10 h/O2	99	10	[62]
6	Pd(TOP)/MB-H <sub>2</sub> O <sub>2</sub>	solvent free/-/80 °C/24 h/-	29	36	[63]
7	CB[6]-Pd NPs (0.05)	toluene/K <sub>2</sub> CO <sub>3</sub> /40 °C/4 h/air bubbling	81	405	This work

<sup>a</sup>Data in parentheses indicate mol % of Pd used.

<sup>b</sup>The turnover frequency: mmol aldehyde product/(mmol catalyst × h reaction time).

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# Theoretical approaches

In order to investigate the structure of the prepared molecule 2 in the gas phase, theoretical calculations were performed. In the previous sections we described the synthetic methods for preparation of palladium complexes. According to our previous works [42(b)], with these reaction conditions, we expected to obtain orthopallated complex, but X-ray crystal structure confirmed *trans* geometry instead. Therefore, the optimizations of two structures (the real (2) and the expected (2') products) were performed to find a reason why the *trans* product results.

The optimized parameters of 2 are in good agreement with the experimental one determined by X-ray analysis. The most important calculated parameters for the optimized structure of 2 are listed in Table 6. The comparison between calculated parameters ( $2^*$ ) with its X-ray structure parameters (2) confirms that this structure is close to the real structure.

#### Table 6

Selected bond lengths (Å) and bond angles (°) for compound 2 (calculated  $(2^*)$  and X-ray structure (2)).

(		
Bond lengths	2	2*
Pd1-N1	2.0361(15)	2.058
Pd1-N1 <sup>i</sup>	2.0361(15)	2.057
Pd1-Cl1	2.3031(5)	2.466
Pd1-Cl1 <sup>i</sup>	2.3031(5)	2.466
Bond angles		
N1-Pd1-Cl1	88.12(4)	89.9
N1 <sup>i</sup> -Pd1-Cl1	91.88(4)	90.1
N1-Pd1-Cl1 <sup>i</sup>	91.88(4)	90.1
N1 <sup>i</sup> -Pd1-Cl1 <sup>i</sup>	88.12(4)	89.9
Cl1-Pd1-Cl1 <sup>i</sup>	180.0(5)	180.0
N1-Pd1-N1 <sup>i</sup>	180.0(5)	180.0

According to the X-ray structure, complex **2** has a *trans* geometry and calculation of the Gibbs free energies of both complexes showed that the *trans* structure (**2**) could be obtained more easily than the ortopalladate. The calculated  $\Delta G$  values for the reactions which produce **2** and **2'** are respectively -263.72 and -132.35 kcal/mol and  $\Delta H$  values are -305.40 and 151.25 kcal/mol in the gas phase. Therefore, the Gibbs free energy confirms the *trans* compound must be the major product. We also employed the population analyses for 2 and 2' to extract the energies of frontier molecular orbitals (FMOs). Graphical presentations of LUMO and HOMO and their related energy for both structures are shown in Fig. 12. Their energy gaps of 2 and 2' are respectively 0.0610 and 0.1647 eV. By comparison between the energies of frontier orbitals, the LUMO-HOMO energy gaps in 2 is less than that in 2', which shows this structure is more reactive. For a more exact determination of the partial atomic charges, NBO calculations were used. The results of these calculations for complex 2 shows that the partial charges of Cl atoms in the complex 2 are about -0.5. Also the charge of Pd in this complex is 0 that shows good interaction.

The second order perturbation energies (E2) obtained from the NBO calculations show that the Pd-ligand bonds are stronger in **2** compared with **2'**. The E2 interaction energies between Cl and Pd is 172 kcal/mol and between N and Pd is 154 kcal/mol for complex **2**, while the same values for complex **2'** are respectively 142 and 2 (Pd-C has a real covalent bond and its energy should be added to the E2 energy) kcal/mol. All these calculations confirm production of the complex **2**.



Fig. 12 Frontier molecular orbital diagrams of complexes 2 and 2'.

# Experimental

#### General

All reactants were purchased from Merck Chemical Company and Aldrich and used as received. Solvents were used without further purification or drying.

Fourier transform infrared (FTIR) spectra were measured in KBr pellets with a Jasco FT/IR 680 plus instrument. NMR spectra were obtained on a Bruker spectrometer at 400.13 MHz (<sup>1</sup>H). Elemental analysis was performed on LECO, CHNS-932 apparatus. Molar conductance of complex **3** was measured in acetone at  $1 \times 10^{-3}$  M using an Elmetron CC-505 conductivity meter.

Scanning electron microscopy (SEM) studies were recorded at 15 kV using a HITACHI S-4160 instrument (Japan). Transmission electron micrographs (TEM) were obtained with a JEOL JEM 1010 microscope operating at an acceleration voltage of 100 kV. Palladium content of the catalyst was measured by Inductively Coupled Plasma (ICP-OES) analyzer (Perkin–Elmer 7300DVspectrometer). X-ray powder diffraction (XRD) pattern was measured using a Scintag X-ray diffractometer with 1.54 Å (Cu K $\alpha$ ) X-ray radiation source. HR-XPS experiments were performed in a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray

source (Magnesium K $\alpha$  line of 1253.6 eV energy and a power applied of 250 W), placed perpendicular to the analyzer axis and calibrated using the  $3d_{5/2}$  line of Ag with a full width at half maximum (FWHM) of 1.1 eV. An electron flood gun was used during measurements to neutralize charging effects. The selected resolution for the spectra of the different elements was 15 eV of Pass Energy and 0.15 eV/step. All Measurements were made in an ultra high vacuum (UHV) chamber at pressure below  $8 \cdot 10^{-8}$  mbar. In the fittings Gaussian-Lorentzian and assymetric functions were used (after a Shirley background correction).

Conversions were monitored using an Agilent Technologies 6890N gas chromatograph equipped with a flame ionization detector (FID) and an HB-50<sup>+</sup> column (length = 30 m, inner diameter 320  $\mu$ m, and film thickness = 0.25  $\mu$ m). Products were identified by comparison with authentic samples.

# Crystallography

Crystals suitable for X-ray molecular structure determination of **1** and **2** were obtained by the diffusion method for a solution of 1 and **2** in dichloromethane/n-hexane (1:3 v/v) and chloroform/n-hexane (1:3 v/v) respectively. X-ray diffraction experiment was done at 120 K with the use of Agilent Gemini single crystal diffractometer (Cu K $\alpha$  radiation). The structure was solved using Superflip software [64] and further refined with Jana2006 [65]. MCE software [66] was used for Fourier maps visualization. The structure was refined by full matrix least squares on F squared value. The atoms of palladium complex were refined anisotropically, the positions of hydrogen atoms were kept in expected geometry with U<sub>iso</sub> set to 1.2 of U<sub>eq</sub> of the parent atom. The atoms O<sub>1</sub>, O<sub>2</sub> and O<sub>3</sub> were refined isotropically and they represented disordered solvent. The centers of these atoms do not represent actual atomic positions.

## **Computational methods**

DFT method was applied to optimize the structures and calculate molecular and spectral parameters of compounds in the gas phase. Gaussian 09 program package [67] was employed for optimizing the structures and calculation of molecular properties. To perform DFT calculations, Becke's three parameter exchange functional [68] was used in combination with the Lee-Yang-Parr correlation functional (B3LYP) with LANL2DZ basis set [69]. Molecules were used without any symmetry restriction and C1 symmetry

was assumed for all molecules. NBO analyses [70] were carried out as implemented in the Gaussian program package using B3LYP/LANL2DZ level of theory.

# Synthesis of *trans*-[Pd(C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>(OAc)<sub>2</sub>] (1)

Pd(OAc)<sub>2</sub> (0.0448 g, 0.2 mmol) was added to a solution of 3-phenylprophylamine (28  $\mu$ L, 0.2 mmol) in toluene (10 mL) and the resulting mixture was heated under reflux for 24 h. The solvent was then evaporated and the resulting yellow solid residue was dissolved in n-hexane (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (2 mL). A pale yellow solid immediately precipitated. The mixture was stirred for 2 h at room temperature and the resulting suspension was filtered. The pale yellow solid thus obtained and air dried to give (1).

Complex 1: yellow solid, Yield: (0.06533 g, 66%); m.p. 135 °C. IR:  $v_{ms}/cm^{-1}$  1573 and 1388 (CO), 3218 and 3118 (NH<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm): 1.85 (s, 3H, MeCO<sub>2</sub>), 2.04 (m, 2H, H<sub>2</sub>), 2.53 (m, 2H, H<sub>1</sub>), 2.60 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, H<sub>3</sub>), 3.77 (m, 2H, NH<sub>2</sub>), 7.17-7.30 (m, 5H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm): 23.51 (Me), 32.50 (C<sub>2</sub>), 32.90 (C<sub>3</sub>), 43.23 (C<sub>1</sub>), 126.15-140.85 (C<sub>aromatic</sub>), 180.18 (CO). Anal. calcd for C<sub>22</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>Pd: C,53.39; H, 6.52; N, 5.66. Found: C, 53.26; H, 6.65; N, 5.73.

# Synthesis of trans-[Pd(C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>(Cl)<sub>2</sub>] (2)

To a suspension of **2** in methanol was added excess NaCl and the resulting mixture stirred for 12 h at room temperature. The solvent was then evaporated and the resulting yellow solid residue was dissolved in n-hexane (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (2 mL). The mixture was stirred for 2 h at room temperature and the resulting suspension was filtered. The pale yellow solid thus obtained and air dried to give (**2**). Complex **2**: yellow solid, Yield: (0.04656 g, 52%); m.p. 170 °C. IR:  $v_{max}/cm^{-1}$  3223 and 3270 (NH<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm): 2.03 (m, 2H, H<sub>2</sub>), 2.67 (m, 2H, H<sub>1</sub>), 2.69 (m, 2H, H<sub>3</sub>), 2.78 (m, 2H, NH<sub>2</sub>), 7.17-7.31 (m, 5H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm): 32.85 (C<sub>2</sub>), 33.10 (C<sub>3</sub>), 44.87 (C<sub>1</sub>), 126.22-140.65 (C<sub>aromatic</sub>). Anal. calcd for C<sub>18</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>2</sub>Pd: C, 48.29; H, 5.85; N, 6.26. Found: C, 47.79; H, 5.92; N, 6.16.

# Synthesis of trans-[Pd(C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>)<sub>2</sub> (PPh<sub>3</sub>)<sub>2</sub>]2Cl<sup>-</sup> (3)

To a suspension of palladium complex 2 (0.275 g, 0.5 mmol) in dichloromethane (15 mL) was added PPh<sub>3</sub> (0.262 g, 1 mmol). The resulting solution was stirred for 6 h and then filtered through a plug of MgSO<sub>4</sub>. The filtrate was concentrated to ca. 2 mL, and n-hexane (10 mL) was added to the precipitate **3** as a pale yellow solid, which was collected and air-dried.

Complex **3**: yellow solid, Yield: (0.05047 g, 56%); m.p. 171 °C (dec.).  $\Delta_{M} (\Omega^{-1} \text{ cm}^{2} \text{ mol}^{-1}) 110$ . IR:  $v_{max}/\text{cm}^{-1} 3395$  and 3451 (NH<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm): 1.28 (m, 2H, H<sub>2</sub>), 2.09 (m, 2H, H<sub>1</sub>), 2.75 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H, H<sub>3</sub>), 3.06 (m, 2H, NH<sub>2</sub>), 7.28-7.75 (m, C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  (ppm): 23.26 (s, 1P, PPh<sub>3</sub> (complex **3**)), 17.85 (s, 1P, PPh<sub>3</sub> (Pd(PPh<sub>3</sub>)<sub>4</sub>).

# Preparation of Glycoluril and CB[6]

Glycoluril and CB[6] were prepared according to previous reports [71,72]. For preparation of glycoluril, to a solution of urea (60 g, 1 mol) in water (100 mL) was added a 40% aqueous solution of glyoxal (50 g, 0.345 mol) and concentrated HCl (8.6 mL). The resulting solution was heated at 90 °C until a heavy precipitate was formed. Then the reaction mixture was allowed to cool to room temperature and filtered. The precipitate was washed with copious amounts of water (200 mL) followed by acetone to remove residual water and dried under vacuum.

For synthesis of CB[6], a stirred mixture of glycoluril (1.5 g, 10.6 mmol), 37% aqueous formaldehyde solution (2.4 mL), concentrated sulfuric acid (1.43 mL) and water (10 mL) was heated several hours at 160 °C. The resulting reaction mixture was cooled to room temperature and poured into water (25 mL). A pale yallow precipitate was formed, which was filtered off and dissolved in concentrated hydrochloric acid and the solution was diluted with water. The precipitate was formed, which was washed several times with water and dried at 130 °C.

# Preparation of CB[6]-Pd NPs

CB[6]-Pd NPs catalysts were prepared according to the literature method [73]. For this purpose, 0.1 mmol palladium complex (1, 2 or 3) and 0.1 mmol (0.099 g) CB[6] were mixed in 10 mL water at room temperature. The mixture stirred for 30 min until a brown uniform suspension was formed. After this, a freshly prepared NaBH<sub>4</sub> in ethanol (1 mmol in 10 mL) was rapidly added to the reaction mixture and the reduction occurred instantaneously. The reduction was considered by a color change from brown to black. The mixture stirred at room temperature for another 3 h. The final reaction product was separated by centrifugation and washed several times with aqueous ethanol (v/v, 1:1) to remove excess salt. CB[6]-Pd NPs was dried at 70 °C for 10 h.

General procedure for the aerobic oxidation of alcohols

Benzyl alcohol (1 mmol), base (1 mmol), solvent (6 ml) and catalyst (0.05 mol% Pd) were combined in a dry flask and the mixture was stirred at given temperature in air or under air bubbling for a given time. After the reaction, the liquid was filtered and analyzed with GC to determine the conversion and selectivity.

# Recycle procedure for CB[6]-Pd NPs

Benzyl alcohol was used to test the recycle ability of CB[6]-Pd NPs (3) in the aerobic oxidation of alcohols. After the first run was complete, the CB[6]-Pd NPs (3) catalyst was separated by centrifugation and was washed several times with ethanol and water to remove adsorbed organic substrates and salt. The catalyst was dried overnight at 70 °C prior to being reused. Then the catalyst was used for the 2nd run without additional activation and the same process was repeated for the next run.

# Conclusions

In conclusion, we prepared three palladium complexes derived from primary benzylamine, we developed a simple method for their dispersion in a form of palladium nanoparticles on the surface of CB[6], and we tested application of these nanoparticles for the aerobic oxidation of alcohols in toluene using air as the source of molecular oxygen. The most promising catalytic effects exhibited nanoparticles of the complex **3**, CB[6]-Pd NPs (**3**), which were evaluated as an efficient catalyst for the aerobic oxidation of alcohols. Importantly, all reactions were performed at 40 °C and the corresponding products were obtained in good or excellent yields. The small size of the Pd particles explains the remarkably high activity of this particular catalyst. TEM and ICP of regenerated catalyst showed that it is stable under the present reaction conditions.

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