

Palladium–Schiff base–triphenylphosphine catalyzed oxidation of alcohols

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Novel palladium(II)-*N*-(2-pyridyl)-*N'*-(5-*R*-salicylidene) hydrazine triphenylphosphine complexes were synthesized and characterized by UV, IR, ^1H NMR and ^{31}P NMR spectral analysis, C, H, N analysis and magnetic susceptibility measurements. The complexes were effective in the catalytic oxidation of primary and secondary alcohols in presence of *N*-methyl-morpholine-*N*-oxide as oxidant. The oxidation reactions were carried out in dichloromethane. A mechanistic study of the above reactions has been proposed. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: Pd complexes; schiff base; catalytic oxidation; NMO

Introduction

The selective oxidation of alcohols to carbonyl compounds is an important transformation in synthetic organic chemistry, as it is essential for the preparation of many key synthetic intermediates.^[1–4] Traditionally such transformations have been performed with inorganic oxidants, e.g. chromium (VI) compounds in stoichiometric quantities^[5,6] and in organic solvents.^[7] Issues such as product separation from the catalyst and catalyst recovery remain problematic. Over the last few years, many transition metals such as ruthenium,^[8] manganese,^[9] tungsten,^[10] rhenium,^[11] iron^[12] and vanadium^[13] have been used as catalysts for alcohol oxidation.

The Schiff base transition metal complexes are attractive oxidation catalysts because of their cheap, easy synthesis and their chemical and thermal stability. Considerable attention has been paid to the preparation of transition metal complexes of Schiff bases because they are considered to constitute new kinds of potential antibacterial and anticancer reagents. Palladium compounds are well known as very important reagents and catalysts in many organic reactions because of their stability and easy handling. Palladium(II) complexes with Schiff base ligands were found to be efficient homogeneous catalysts under mild reaction conditions.^[14] Herein, we present our attempts to synthesize a series of palladium triphenylphosphine complexes (**PdL1–PdL5**) containing *N*-(2-pyridyl)-*N'*-(salicylidene) hydrazine with its derivatives (Scheme 1) and their application as catalysts for the oxidation of alcohols to carbonyl compounds in dichloromethane using *N*-methyl-morpholine-*N*-oxide (NMO) as oxidant.

Results and Discussion

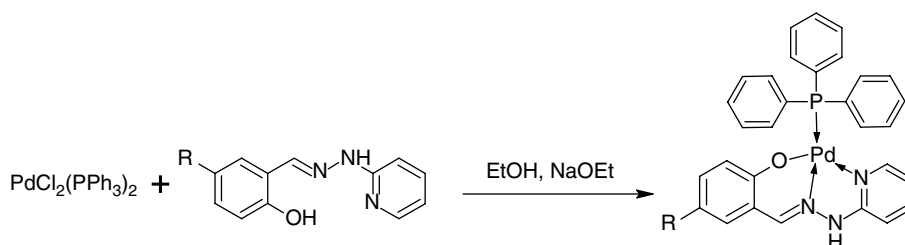
Synthesis and Characterization of Palladium Complexes

The electronic spectra of the complexes showed many bands in the region 250–490 nm. The bands appearing in the region 250–350 nm were assigned to intraligand transitions. A less intense band in the range 390–490 nm corresponded to the $d \rightarrow d$ forbidden transition. The IR spectra of the ligands exhibited a strong band around 1610–1620 cm^{-1} , which was assigned to $\nu(\text{C}=\text{N})$ vibration. As a result of coordination, this band was

altered in complexes. The band in the region 1315–1330 cm^{-1} , which was assigned to phenolic $\nu(\text{C}-\text{O})$ in the free ligand, was shifted to higher wavenumber in the complexes, suggesting the coordination of phenolic oxygen to metal ion. The $\text{N}-\text{H}$ stretching frequency occurred around 3100 cm^{-1} in ligands and was unaltered in complexes. The pyridine vibrations at 610 cm^{-1} (in-plane ring deformation) and 490 cm^{-1} (out of plane ring deformation) in the free ligand were found to be altered in the complexes, indicating the participation of pyridine ring in the coordination. The band at 550 cm^{-1} in the complex was assigned to $\nu(\text{Pd}-\text{O})$. Bands at 1440, 1090 and 690 cm^{-1} were assigned for the peaks due to triphenylphosphine.^[15] ^1H NMR spectra of the complexes exhibited a multiplet around 6.9–7.9 ppm which was assigned to the protons of phenyl groups present in Schiff base ligand and triphenylphosphine. A peak observed at 8.5 ppm in the complexes was assigned to azomethine proton ($-\text{CH}=\text{N}-$). The absence of a resonance at 10.3 ppm due to phenolic hydrogen indicated the deprotonation of the Schiff base.^[16] A broad singlet at 3.8 ppm was observed, which corresponded to the $\text{N}-\text{H}$ proton.^[17] In the ^{13}C NMR spectra of all the complexes, azomethine carbon resonances were observed in the 151.12–154.49 ppm range. The resonances for $\text{C}-\text{N}$, $\text{C}-\text{O}$ and $\text{C}-\text{P}$ were observed in the regions 147.32–149.99, 162.44–164.93 and 142.96–144.48 ppm, respectively.^[18] The ^{13}C NMR spectra of complexes revealed the presence of six different carbons (119.30, 129.46, 143.85, 143.98, 149.82 and 163.98 ppm). The three quaternary carbons arising from triphenylphosphine aromatic units were in same magnetic environments.^[18] ^{31}P NMR spectra exhibited a singlet at 23.3–23.8 ppm, suggesting the presence of one coordinated triphenylphosphine in the complexes. In order to obtain further structural information, the magnetic moments of the complexes were measured. The magnetic susceptibility

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Scheme 1. Synthesis of palladium complexes (**L1**: R = H, **L2**: R = Cl, **L3**: R = Br, **L4**: R = NO₂, **L5**: R = OCH₃).

Table 1. Optimization of reaction conditions for oxidizing benzyl alcohol to benzaldehyde^a

Entry	Amount of PdL1 (mmol)	Amount of NMO (mmol)	Yield (%)
1	0	1.0	1.5
2	0.01	1.0	29.9
3	0.02	1.0	89.1
4	0.03	1.0	89.1
5	0.04	1.0	89.3
6	0.05	1.0	89.2
7	0.02	0	23.1
8	0.02	0.5	48.2
9	0.02	1.0	89.1
10	0.02	1.5	89.2
11	0.02	2.0	89.1

^a 1 mmol benzyl alcohol, 20 ml CH₂Cl₂, 150 min, reflux.

measurements showed that the complexes are diamagnetic in nature and support square planar geometry.

Catalytic Oxidation of Alcohols

The optimization of the reaction conditions was studied by taking benzyl alcohol as substrate with **PdL1** in the CH₂Cl₂–NMO system (Table 1). The benzaldehyde formed was quantified by GC. In order to study the effect of time on the activity, the product analysis was done at regular intervals of time under similar reaction conditions (Fig. 1). It was observed that the total reaction time was only 150 min at reflux. This implies that the Pd (II)-complexes–CH₂Cl₂–NMO catalytic system showed good efficiency (Table 1). Therefore this catalytic system was studied in detail (Table 2). In order to study the effect of the concentration of catalyst with respect to substrate, the reaction was carried out at different substrate to catalyst ratios. A minimum amount of 12 mg (0.02 mmol) of catalyst was sufficient for the effective transformation of benzyl alcohol to benzaldehyde (Table 1, entry 3). The reaction was also studied in the absence of catalyst. The yield was insignificant in this case (Table 1, entry 1). This observation reveals the catalytic role of palladium complexes. The reaction was studied at various substrate-to-oxidant ratios. A minimum quantity of 1 mmol of the oxidant was sufficient for the effective oxidation of benzyl alcohol to benzaldehyde (Table 1, entry 9). All the alcohols were oxidized in good to excellent yields without the necessity of any additives. All the synthesized palladium complexes were found to catalyze the oxidation of alcohols to corresponding carbonyl compounds in 74–95% yield. Benzylic primary and secondary alcohols oxidized smoothly to give aldehydes and ketones respectively. Aliphatic alcohols were also oxidized to corresponding carbonyl compounds. All the

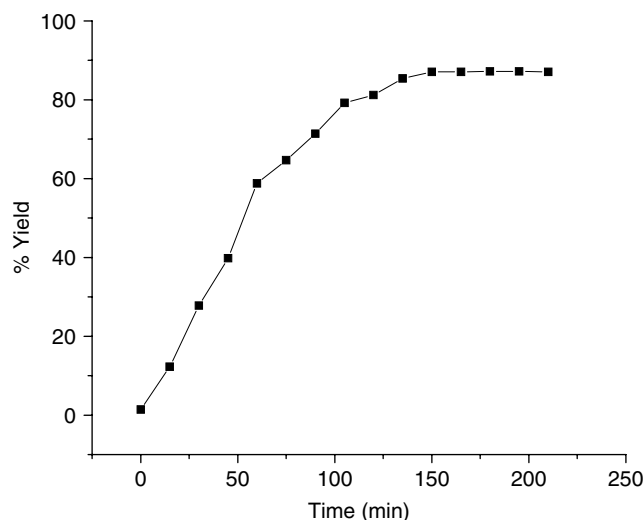


Figure 1. Effect of time on conversion of benzyl alcohol to benzaldehyde (1 mmol benzyl alcohol, 0.02 mmol **PdL1**, 1 mmol oxidant, 20 ml CH₂Cl₂).

experiments were carried out in an air atmosphere since there is no change in conversion if reaction is carried out under nitrogen. This indicates that air is not involved in oxidation process and palladium complexes are air-stable. A plausible mechanism for the oxidation of alcohols by palladium complexes in the CH₂Cl₂–NMO system is illustrated in Fig. 2.^[19,20]

Conclusions

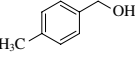
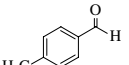
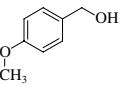
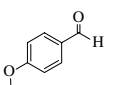
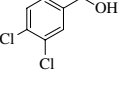
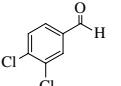
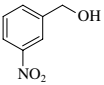
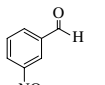
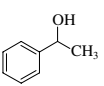
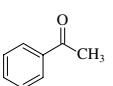
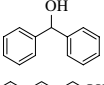
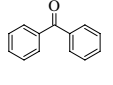
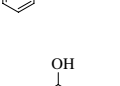
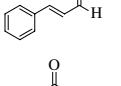
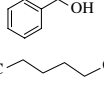
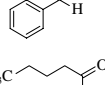
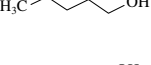
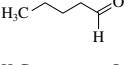
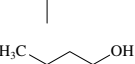
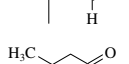
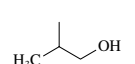
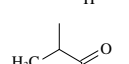
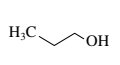
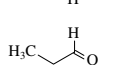
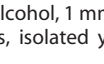
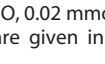
In summary, from readily available starting materials, a series of palladium complexes containing *N*-(2-pyridyl)-*N'*-(5-*R*-salicylidene) hydrazine and triphenylphosphine have been prepared and characterized. Oxidation of primary and secondary alcohols in the presence of the above synthesized complexes gave a yield of the corresponding carbonyl compounds. Further applications of the present catalytic system are ongoing and will be reported in due course.

Experimental

Materials and Methods

All the chemicals used were of analytical grade. Solvents were purified and dried according to standard procedures.^[21] Anhydrous PdCl₂ was purchased from Merck and was used without further purification. [PdCl₂ (PPh₃)₂] was prepared by the reaction of anhydrous PdCl₂ (CDH) and triphenylphosphine in

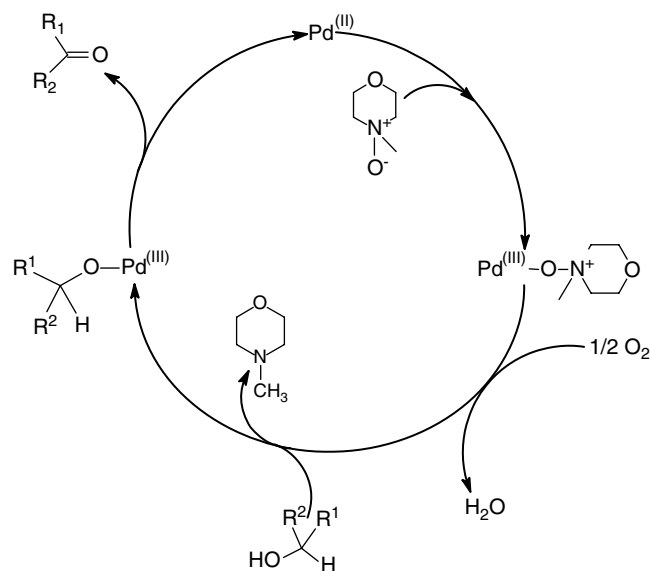
Table 2. Oxidation of alcohols catalyzed by Pd complexes^a

Entry	Alcohols	Product	Time (min)	Yield (%) ^b	TON ^c
1			150	89 (87)	445
2			150	87 (65)	435
3			150	89 (75)	445
4			180	88 (30)	440
5			150	89 (45)	445
6			150	95 (88)	475
7			120	93 (84)	465
8			120	88 (76)	440
9			90	82 (70)	410
10			150	85 (82)	425
11			120	81 (42)	405
12			120	81 (36)	405
13			120	75 (66)	375
14			120	78 (60)	390
15			120	74 (45)	370

^a 1 mmol alcohol, 1 mmol NMO, 0.02 mmol **PdL1**, 20 ml CH₂Cl₂, reflux.^b GC yields, isolated yields are given in parentheses, confirmed by derivative.^c TON = moles of product/moles of the catalyst.

tetrahydrofuran (Merck) under reflux for 5 h.^[22] The Schiff bases were prepared in 70–80% yield by condensation reactions of 2-hydrazinopyridine (Aldrich) with the corresponding 5-substituted salicylaldehyde (Loba) in methanolic media.^[23]

Electronic spectra were measured on a GBC Cintra 101 UV–vis double beam spectrophotometer in CH₃OH solution of the complexes in the 200–800 nm range. FT-IR spectra were recorded on a Thermo Nicolet Avatar FT-IR spectrometer as KBr powder in the

**Figure 2.** Proposed mechanism for palladium complex catalyzed oxidation of alcohols by NMO.

frequency range 400–4000 cm^{−1}. The C, H and N contents were determined by Thermoflash EA1112 series elemental analyzer. ¹H NMR and ¹³C NMR spectra were recorded in Bruker AV 400 instrument using TMS and H₃PO₄ as internal standards respectively. ³¹P NMR spectra were recorded in Bruker AV 400 instrument using H₃PO₄ as internal standard.

General Procedure for the Synthesis of Pd (II) Complexes

Complexes **PdL1–PdL5** were prepared by stirring a mixture of [PdCl₂(PPh₃)₂] in 3 ml of 0.1 M sodium acetate and the respective ligands in 15 ml alcohol in a 1 : 1 ratio for 5 h. The red solid was filtered off, washed with ethanol and dried in *vacuo*.

Data for the Complexes

PdL1

Yield: 79%. IR (KBr, cm^{−1}): 3105 (s), 623, 479 (m), 1592 (s), 1345 (w), 550 (m), 1446, 1095, 697. ¹H NMR (CDCl₃, δ ppm): 3.8 (s, 1H, N–H), 6.6–7.3 (m, 15H, Ar–H), 7.4–7.7 (m, 8H, Ar–H), δ 8.5 (d, 1H, –CH=N–). ¹³C NMR (ppm): 163.98 (C–O), 154.51 (C=N), 143.98 (C–P), 161.46, 147.57, 137.41, 114.05, 106.97 (carbon atoms in pyridine), 117.55, 119.84, 133.73, 136.92 (carbon atoms in salicylaldehyde). ³¹P NMR (H₃PO₄, δ ppm): 23.4. CHN found (calcd) for C₃₀H₂₅N₃OPd: C: 61.84 (62.02), H: 4.21 (4.34), N: 7.12 (7.23), Pd: 18.15 (18.32); UV–vis: λ_{max} (nm) intraligand interactions: 229, 272, 346, d → d forbidden transition: 441.

PdL2

Yield: 75%. IR (KBr, cm^{−1}): 3110 (s), 620, 478 (m), 1597 (s), 1330 (w), 545 (m), 1435, 1101, 690. ¹H NMR (CDCl₃, δ ppm): 3.8 (s, 1H, N–H), 6.6–7.3 (m, 15 H, Ar–H), 7.4–7.8 (m, 8 H, Ar–H), 8.5 (d, 1 H, –CH=N–); ¹³C NMR (ppm): 160.65 (C–O), 154.05 (C=N), 144.66 (C–P), 161.61, 147.17, 137.01, 114.55, 105.97 (carbon atoms in pyridine), 110.15, 118.99, 121.07, 133.51, 135.61 (carbon atoms in salicylaldehyde). ³¹P NMR (H₃PO₄, δ ppm): 22.3. CHN found (calcd) for C₃₀H₂₄ClN₃OPd: C: 58.25 (58.55), H: 3.68 (3.93), N: 6.46 (6.83), Pd: 17.19 (17.29); UV–vis: λ_{max} intraligand interactions: 233, 271, 346, d → d forbidden transition: 447.

PdL3

Yield: 72%. IR (KBr, cm^{-1}): 3106 (s), 630, 475 (m), 1585 (s), 1340 (w), 552 (m), 1439, 1093, 698. ^1H NMR (CDCl_3 , δ ppm): 3.8 (s, 1H, N–H), 6.7–7.3 (m, 15 H, Ar–H), 7.8–7.9 (m, 8 H, Ar–H), 8.5 (d, 1 H, –CH=N–); ^{13}C NMR (ppm): 160.55 (C–O), 153.46 (C=N), 144.48 (C–P), 161.61, 147.17, 137.01, 114.55, 105.97 (carbon atoms in pyridine), 111.34, 119.31, 121.77, 135.61, 139.63 (carbon atoms in salicylaldehyde). ^{31}P NMR (H_3PO_4 , δ ppm): 22.5. CHN found (calcd) for $\text{C}_{30}\text{H}_{24}\text{BrN}_3\text{OPPd}$: C: 54.48 (54.61), H: 3.45 (3.67), N: 6.19 (6.37), Pd: 16.05 (16.13); UV–vis: λ_{max} intraligand interactions: 231, 277, 346, d $\rightarrow$ d forbidden transition: 443.

PdL4

Yield: 72%. IR (KBr, cm^{-1}): 3099 (s), 619, 481 (m), 1595 (s), 1351 (w), 549 (m), 1429, 1087, 695. ^1H NMR (CDCl_3 , δ ppm): 3.8 (s, 1H, N–H), 6.6–7.4 (m, 15 H, Ar–H), 7.4–7.8 (m, 8 H, Ar–H), 8.6 (d, 1 H, –CH=N–); ^{13}C NMR (ppm): 166.18 (C–O), 153.39 (C=N), 144.42 (C–P), 161.61, 147.17, 137.01, 114.55, 105.97 (carbon atoms in pyridine), 119.03, 119.41, 129.81, 131.69, 140.73 (carbon atoms in salicylaldehyde). ^{31}P NMR (H_3PO_4 , δ ppm): 22.8. CHN found (calcd) for $\text{C}_{30}\text{H}_{24}\text{N}_4\text{O}_3\text{PPd}$: C: 57.26 (57.57), H: 3.67 (3.86), N: 8.72 (8.95), Pd: 16.83 (17.00); UV–vis: λ_{max} intraligand interactions: 233, 271, 346, d $\rightarrow$ d forbidden transition: 449.

PdL5

Yield: 75%. IR (KBr, cm^{-1}): 3109 (s), 618, 482 (m), 1586 (s), 1346 (w), 550 (m), 1428, 1105, 695. ^1H NMR (CDCl_3 , δ ppm): 3.8 (s, 1H, N–H), 6.6–7.3 (m, 15 H, Ar–H), 7.4–7.8 (m, 8 H, Ar–H), 8.5 (d, 1 H, –CH=N–); ^{13}C NMR (ppm): 156.06 (C–O), 154.11 (C=N), 143.61 (C–P), 161.21, 147.20, 137.86, 114.65, 106.27 (carbon atoms in pyridine), 115.24, 118.70, 120.10, 125.23, 152.78 (carbon atoms in salicylaldehyde), 55.89 ($\text{CH}_3\text{--O}$). ^{31}P NMR (H_3PO_4 , δ ppm): 22.6. CHN found (calcd) for $\text{C}_{31}\text{H}_{27}\text{N}_3\text{O}_2\text{PPd}$: C: 60.41 (60.94), H: 4.28 (4.45), N: 6.67 (6.88), Pd: 17.34 (17.42); UV–vis: λ_{max} intraligand interactions: 231, 273, 346, d $\rightarrow$ d forbidden transition: 442.

Catalytic Experiments

A solution of palladium complex (0.02 mmol) in 20 ml dichloromethane was added to the solution of substrate (1 mmol) and NMO (1 mmol). The mixture was stirred at room temperature. At the requisite times aliquots of the reaction mixture were removed and the alcohol and aldehyde/ketone extracted with ether. The ether solution was then analyzed by GC.

Product Analysis

The reaction product analysis was carried out using gas chromatography (GC) (Shimadzu 2014, Japan); the instrument has a 5% diphenyl and 95% dimethyl siloxane Restek capillary column

(30 m length and 0.25 mm diameter) and a flame ionization detector (FID). The initial column temperature was increased from 60 to 150 $^{\circ}\text{C}$ at the rate of 10 $^{\circ}\text{C}/\text{min}$ and then to 220 $^{\circ}\text{C}$ at the rate of 40 $^{\circ}\text{C}/\text{min}$. Nitrogen gas was used as the carrier gas. The temperatures of the injection port and FID were kept constant at 150 and 250 $^{\circ}\text{C}$, respectively, during product analysis. The retention times for different compounds were determined by injecting commercially available compounds under identical gas chromatography conditions. The oxidation products are commercially available, and were identified by GC co-injection with authentic samples. The products were isolated and were further confirmed by the derivative test.

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