



Catalytic oxidation of alcohols by nickel(II) Schiff base complexes containing triphenylphosphine in ionic liquid: An attempt towards green oxidation process

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ABSTRACT

A series of square planar nickel(II) complexes containing N,O donor Schiff base ligand, i.e. N-(2-pyridyl)-N'-(5-substituted-salicylidene)hydrazine and triphenylphosphine, have been synthesized and characterized by analytical and spectral methods. Catalytic activities of all the complexes have been studied for the oxidation of alcohols in ionic liquid media using NaOCl as oxidant.

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1. Introduction

Oxidation of alcohols into carbonyl compounds is one of the most pivotal functional group transformations in organic synthesis. Use of some homogeneous catalysts such as metal complexes of Ru [1–7], Pd [8–10], Co [11,12], Os [13] and Cu [14,15] has achieved high catalytic activity and selectivity for this reaction. Tertiary phosphine complexes of nickel, palladium and platinum have played an extremely important role in the development of homogeneous catalysis [16]. In particular, nickel catalysis is of great interest due to the fact that it is cheaper. It is well known that the wide spread use of traditional organic solvents in many chemical processes is an issue of great environmental concern. Hence, the use of ionic liquids as reaction medium is a topic of much current interest in the context of environmentally friendly chemical reactions [17].

In a recent study, it is found that a Schiff base ligand, N-(2-pyridyl)-N'-(salicylidene)hydrazines and its derivatives can coordinate a vanadium(IV) ion via the pyridine-N, the imine-N and the phenolate-O atoms [18]. We intend to investigate the coordination behavior of N-(2-pyridyl)-N'-(5-salicylidene)hydrazine and its derivatives with Ni(II). Herein, we present a series of nickel(II)-triphenylphosphine complexes with derivatives of N-(2-pyridyl)-N'-(salicylidene)hydrazine (NiL1–NiL5) and their catalytic application for the oxidation of alcohols to carbonyl compounds in ethylmethyl imidazolium (EMIM) ionic liquid.

2. Experimental

[NiCl₂(PPh₃)₂] was prepared by the reaction between NiCl₂·6H₂O and triphenylphosphine in glacial acetic acid [19]. The Schiff bases were prepared in 70–80% yield by condensation reactions of 2-hydrazinopyridine with the corresponding 5-substituted salicylaldehyde in methanol [18].

2.1. Synthesis of complexes

Complexes NiL1–NiL5 were prepared by refluxing a solution of [NiCl₂(PPh₃)₂] (0.2 mmol) in CH₂Cl₂ (20 mL) and ligand (0.2 mmol) for 3 h. The solvent was stripped by evaporation. The residue was washed with diethyl ether and dried in vacuo to form green color complexes. They were soluble in CH₃OH, CH₃CN, C₆H₆, DMSO, DMF and CHCl₃.

NiL1: Yield: 62%. IR (KBr, cm^{−1}): 3100, 610,490, 1607, 1334, 528, 457, 1433, 1095, 691. ¹H NMR (CDCl₃, δ ppm): 6.8–7.4 (m, 15H, Ar–H), 7.8–8.2 (m, 8H, Ar–H), 8.6 (d, 1H, –CH=N–); ³¹P NMR (H₃PO₄, δ ppm): 22.5; CHN found (calc.) for C₃₀H₂₅ClN₃OPNi, C: 61.77 (61.90), H: 4.82 (5.02), N: 5.78 (5.95); UV–vis: λ_{max} (nm) intraligand transitions: 213, 259, d → d: 422.

NiL2: Yield: 60%. IR (KBr, cm^{−1}): 3100, 610,490, 1615, 1341, 532, 455, 1435, 1096, 693. ¹H NMR (CDCl₃, δ ppm): 6.8–7.4 (m, 15H, Ar–H), 7.9–8.2 (m, 8 H, Ar–H), 8.6 (d, 1H, –CH=N–); ³¹P NMR (H₃PO₄, δ ppm): 22.3; CHN found (calc.) for C₃₀H₂₄Cl₂N₃OPNi, C: 61.08 (61.95), H: 4.07 (4.66), N: 5.45 (5.60); UV–vis: λ_{max} (nm) intraligand transitions: 216, 269, d → d: 413.

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NiL3: Yield: 65%. IR (KBr, cm^{-1}): 3100, 610,490, 1619, 1325, 527, 455, 1434, 1093, 695. ^1H NMR (CDCl_3 , δ ppm): 6.8–7.4 (m, 15H, Ar–H), 7.9–8.2 (m, 8H, Ar–H), 8.6 (d, 1H, $-\text{CH}=\text{N}-$); ^{31}P NMR (H_3PO_4 , δ ppm): 22.4; CHN found (calc.) for $\text{C}_{30}\text{H}_{24}\text{BrClN}_3\text{OP-Ni}$, C: 62.29 (62.90), H: 5.02 (5.20), N: 5.22 (5.40); UV–vis: λ_{max} (nm) intraligand transitions: 213, 269, d $\rightarrow$ d: 419.

NiL4: Yield: 60%. IR (KBr, cm^{-1}): 3100, 610,490, 1603, 1326, 529, 459, 1437, 1098, 694. ^1H NMR (CDCl_3 , δ ppm): 6.8–7.4 (m, 15H, Ar–H), 7.8–8.2 (m, 8H, Ar–H), 8.6 (d, 1H, $-\text{CH}=\text{N}-$); ^{31}P NMR (H_3PO_4 , δ ppm): 22.8; CHN found (calc.) for $\text{C}_{30}\text{H}_{24}\text{ClN}_4\text{O}_3\text{PNi}$, C: 59.31(59.47), H: 4.07(4.42), N: 7.01(7.55); UV–vis: λ_{max} (nm) intraligand transitions: 212, 258, d $\rightarrow$ d: 414.

NiL5: Yield: 55%. IR (KBr, cm^{-1}): 3100, 610,490, 1598, 1321, 529, 456, 1435, 1097, 695. ^1H NMR (CDCl_3 , δ ppm): 6.8–7.4 (m, 15H, Ar–H), 7.8–8.2 (m, 8H, Ar–H), 8.6 (d, 1H, $-\text{CH}=\text{N}-$); ^{31}P NMR (H_3PO_4 , δ ppm): 22.5; CHN found (calc.) for $\text{C}_{31}\text{H}_{27}\text{ClN}_3\text{O}_2\text{PNi}$, C: 63.59 (64.26), H: 4.15 (4.38), N: 4.66(4.95); UV–vis: λ_{max} (nm) intraligand transitions: 211, 265, d $\rightarrow$ d: 417.

2.2. Catalytic experiments

A solution of nickel(II) complex (0.02 mmol) in 0.1 mL EMIM was added to the solution of substrate (1 mmol) and NaOCl (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.

2.3. Product analysis

The reaction product analysis was carried out using GC (Shimadzu 2014) equipped with 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 a 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 pure compounds under identical conditions.

3. Results and discussion

3.1. Synthesis and characterization of nickel complexes

The electronic spectra of the complexes (NiL1–NiL5) in CH_3OH showed three bands in the region 198–431 nm. The bands appeared in the region 198–350 nm have been assigned to intra ligand transitions. A less intense band in range 410–431 nm corresponds to d $\rightarrow$ d forbidden transition [20,21]. The IR spectra of the ligands exhibit a strong band around 1610–1622 cm^{-1} , which is assigned to $\nu(\text{C}=\text{N})$ vibration. As a result of coordination, this band shifts to higher wave number in complexes [21,22]. The band in the region 1304–1323 cm^{-1} which is assigned to phenolic $\nu(\text{C}-\text{O})$ in the free ligand, is shifted to higher wave number in the complexes suggesting the coordination of phenolic oxygen to nickel ion. The N–H stretching frequency occurs around 3100 cm^{-1} in ligands is unaltered in complexes. The pyridine vibrations at 610 cm^{-1} (in-plane ring deformation) and 490 cm^{-1} (out of plane ring deformation) were also unchanged in complexes [23]. These factors reveal the non participation of $-\text{NH}$ group and pyridine-N in coordination. The bands around 530 and 460 cm^{-1} in all the complexes are assigned to $\nu(\text{Ni}-\text{O})$ and $\nu(\text{Ni}-\text{N})$, respectively [24]. Bands due to triphenylphosphine are also appeared in the expected region [25]. ^1H NMR spectra of all the complexes exhibit a

multiplet around 6.3–8.1 ppm which confirms the protons of phenyl groups present in triphenylphosphine and Schiff base ligand. A doublet observed at 8.6 ppm in the complexes has been assigned to azomethine proton ($-\text{CH}=\text{N}-$). The absence of a resonance at 10.3 ppm due to phenolic hydrogen indicates the deprotonation of the Schiff base [26]. ^{31}P NMR spectra exhibits a singlet at 22.3–22.8 ppm suggesting the presence of one coordinated triphenylphosphine in the complexes [27]. The magnetic susceptibility measurements show that the complexes are diamagnetic [27].

3.2. Catalytic oxidation

The optimization of the reaction conditions was studied by taking benzyl alcohol as substrate with NiL1 in EMIM–NaOCl 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 15 min even at room temperature. This implies that Ni(II)-complex/EMIM–NaOCl catalytic system showed good efficiency (Table 1, entry 3). Therefore this catalytic system was studied in detail (Table 2). The catalytic activity of complexes varies with the size of substituent. It was observed that the activity decreases with increase of bulkiness of the substituents. This may be due to steric

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

Entry	Amount of NiL1 (mmol)	Amount of NaOCl (mmol)	Conversion ^b (%)
1	0	1.0	1.5
2	0.01	1.0	65.2
3	0.02	1.0	90.6
4	0.03	1.0	89.6
5	0.04	1.0	89.4
6	0.05	1.0	89.3
7	0.02	0	2.6
8	0.02	0.5	44.6
9	0.02	1.5	90.6
10	0.02	2.0	90.5

^a 1 mmol benzyl alcohol, 0.2 mL EMIM, 15 min, room temperature.

^b Average of three trials.

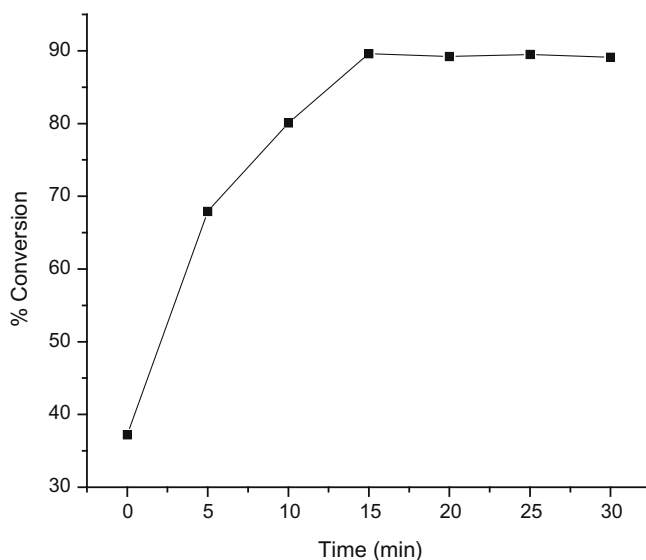
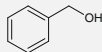
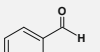
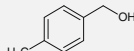
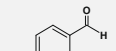
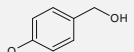
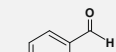
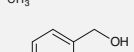
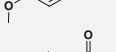
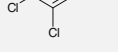
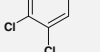
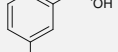
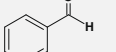
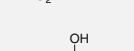
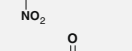
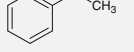
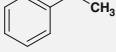
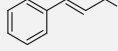
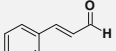
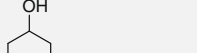
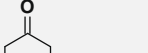
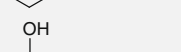
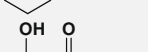
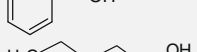
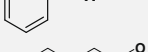
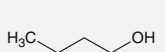
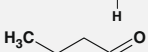
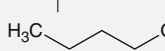
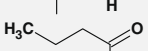


Fig. 1. Effect of time on conversion of benzyl alcohol to benzaldehyde (1 mmol benzyl alcohol, 0.02 mmol NiL1, 1 mmol oxidant, 0.3 mL EMIM).

Table 2
Oxidation of alcohols catalyzed by Ni(II) complexes.^a

Entry	Alcohols	Product	% Conversion of carbonyl compound ^b				
			NiL1 ^c	NiL2 ^c	NiL3 ^d	NiL4 ^c	NiL5 ^e
1			90.6	83.1	80.2	79.7	86.1
2			88.2	93.0	87.1	77.7	83.2
3			88.4	92.2	82.5	77.0	81.5
4			88.7	97.8	88.1	80.1	81.3
5			89.5	78.7	86.0	72.3	79.6
6			95.9	92.3	79.9	79.6	83.6
7			93.4	91.0	88.7	78.1	85.1
8			91.7	91.2	82.7	74.5	77.2
9			94.8	91.5	86.3	73.4	78.6
10			84.1	82.8	80.9	80.0	85.0
11			77.3	76.5	77.0	74.6	72.6
12			80.5	77.6	75.6	79.1	75.5
13			76.7	75.2	71.6	74.6	73.2
14			73.6	73.5	72.1	70.6	71.3
15			69.5	68.6	66.3	63.1	60.8

^a 1 mmol alcohol, 1 mmol NaOCl, 0.2 mmol Ni(II) complex and 0.1 mL EMIM stirring at room temperature.

^b GC yield average of three trials.

^c Reaction time 15 min.

^d Reaction time 20 min.

^e Reaction time 30 min.

hindrance caused by the substituent, which can affect the planarity of the ligand in the complexes.

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 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 nickel(II) complexes. The

reaction was studied at various substrate to oxidant ratios (Table 1). A minimum quantity of 1 mmol of the oxidant was sufficient for the effective oxidation of benzyl alcohol to benzaldehyde (Table 1, entry 3). All the alcohols were oxidized in good to excellent conversions without the necessity of any additives. All the synthesized nickel(II) complexes were found to catalyze the oxidation of alcohols to corresponding carbonyl compounds in a conversion range of 60–96%. It is clear from GC analysis that no side reaction took place during the course of catalytic oxidation. Hence alcohols are

converted into only aldehydes and ketones which were quantified by comparing with authentic samples on GC–FID. Benzylic primary and secondary alcohols oxidize smoothly to give aldehydes and ketones, respectively. Oxidation of allylic alcohols to α,β -unsaturated carbonyl compounds has long been of interest. It was found that cinnamaldehyde was obtained from cinnamyl alcohol in ~90% conversion after 30 min of stirring whereas $\text{NaIO}_4/2,2,6,6$ -tetramethylpiperidine-1-oxyl/ NaBr system gives only 18% of aldehyde from the same substrate [28]. Cyclohexanol is also converted into cyclohexanone in ~90% yield; the conversion is better than recently reported $\text{Ru(III)}/\text{H}_5\text{IO}_6\text{--H}_2\text{O}$ catalytic system [29]. Interestingly, catalytic property of nickel(II) complexes is not affected even for chelating substrate (*o*-hydroxy benzylalcohol) as it is in many homogeneous catalytic systems. Aliphatic alcohols were also oxidized to corresponding carbonyl compounds. All the experiments are carried out in air atmosphere since there is no change in conversion if reaction is carried out under argon. This indicates that air is not involved in oxidation process and nickel(II) complexes are air stable. Further, ionic liquid (EMIM) was recycled up to 92% along with the catalyst. Both the ionic liquid and catalyst can be reused at least for ten times. No solvent vapors released and minimum wastage of reagents during the catalytic reaction makes this as 'green' process.

4. Conclusion

In conclusion, the present green catalytic system offers an efficient oxidation of primary and secondary alcohols to corresponding carbonyl compounds. The ready availability of the reagents and the ease of preparation, together with rapid oxidation and high yields are the good features of this approach. Hence the procedure is versatile, greener, particularly where, environmentally benign, rapid and mild oxidizing conditions are required.

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