



The oxidative aromatization of Hantzsch 1,4-dihydropyridines by molecular oxygen using surface functionalized silica supported cobalt catalysts

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ABSTRACT

Cobalt complexes were covalently anchored onto the surface of silica by the complexation of organically modified silicas with $\text{Co}(\text{OAc})_2$ and CoCl_2 and investigated for the oxidative aromatization of Hantzsch 1,4-dihydropyridines using molecular oxygen. The catalyst obtained by the complexation of $\text{Co}(\text{OAc})_2$ with organically modified 3-aminopropyl silica (Cat **1**) was found to be most effective and stable under the reaction conditions. It can be easily recovered and recycled. The work-up procedure is simple and the corresponding pyridines were obtained in good to excellent yields.

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1. Introduction

Hantzsch 1,4-dihydropyridines are generally regarded as the models of the naturally reduced nicotinamide adenine dinucleotide [NADH] co-enzyme which functions as redox reagent for biological reactions. 1,4-Dihydropyridines (DHPs) are known to carry out many bioreductions by transferring a hydride ion or an electron to the surrounding substrate [1] and possess a high biological activity as a class of useful drugs for the treatment of cardiovascular disease [2]. Furthermore, these compounds are the starting materials for the synthesis of antibacterial 1,6-naphthyridines and 1,2-benzisoazalenes [3].

The oxidation of 1,4-DHPs to the corresponding pyridine derivatives constitute the principal metabolic pathway in biological systems [4], as well as providing facile access to the corresponding pyridine derivatives, which show anti-hypoxic and anti-ischemic activities [5]. Therefore, oxidative aromatization of DHPs has been a subject of great interest of organic and medicinal chemists and numerous reagents and procedures have been recommended for this oxidation [6]. Although a variety of reagents are capable of effecting these oxidations, this transformation is not always so easy and can be a difficult step if the substrate have functional groups sensitive to the oxidizing agent and reaction conditions. Most of the reported reagents produce by-products which are difficult to separate

from the products. Therefore, the development of an efficient, cost-effective and green method for the aromatization of 1,4-DHPs under milder conditions is still necessary.

The use of molecular oxygen has gained considerable attention in recent years [7], since it is considered as a green oxidant because by-product produced in these oxidations is water. However, oxygen is a weak, non-selective oxidation agent and therefore, transition metal complexes were employed as catalysts for its activation. Further, usually transition metal complexes were used in homogeneous media, which suffer from disadvantages such as difficult separation techniques, loss of precious metal complex after the reaction, side reactions, etc. These problems can be addressed by the heterogenization of the transition metal complexes. Heterogeneous catalysts which have been used for liquid phase oxidations are often based on transition metals, metal ion or metal complexes adsorbed on supports such as carbon, aluminas, silicas, zeolites, clays and ion-exchange resins [8]. However, these heterogeneous catalysts suffers from the serious problem of leaching of the active species and hence loss of recyclability. To overcome this problem, covalently anchored metal complexes based on chemically modified support materials have been developed [7d,9].

Among various transition metals, cobalt has been used extensively in catalyzing oxidation reactions [10]. Recently, cobalt complexes based on chemically modified silicas have been reported for catalyzing oxidations [11]. In this paper, we wish to report a mild and efficient method for the oxidative aromatization of Hantzsch 1,4-dihydropyridines by molecular oxygen in the presence of a catalytic amount of cobalt complexes covalently anchored onto silica

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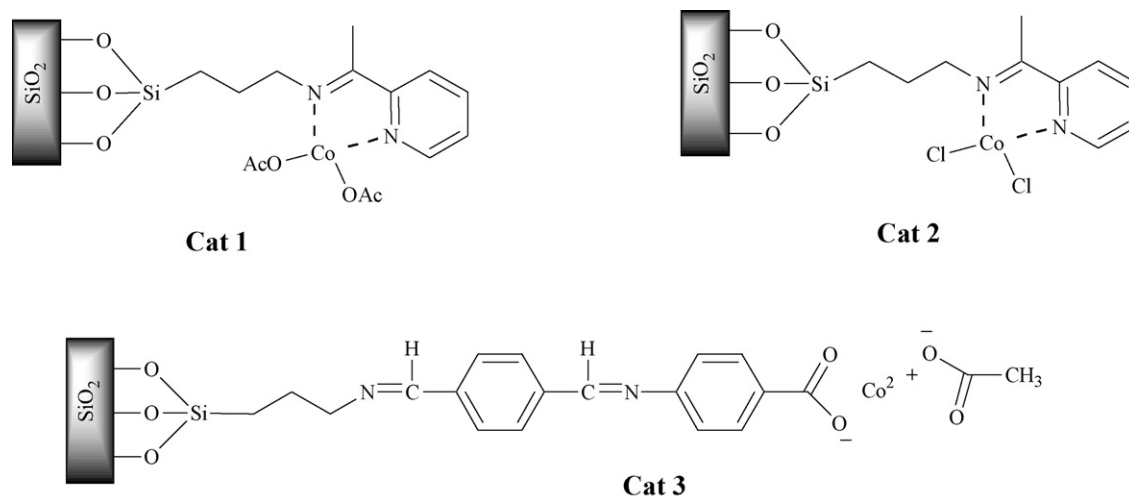
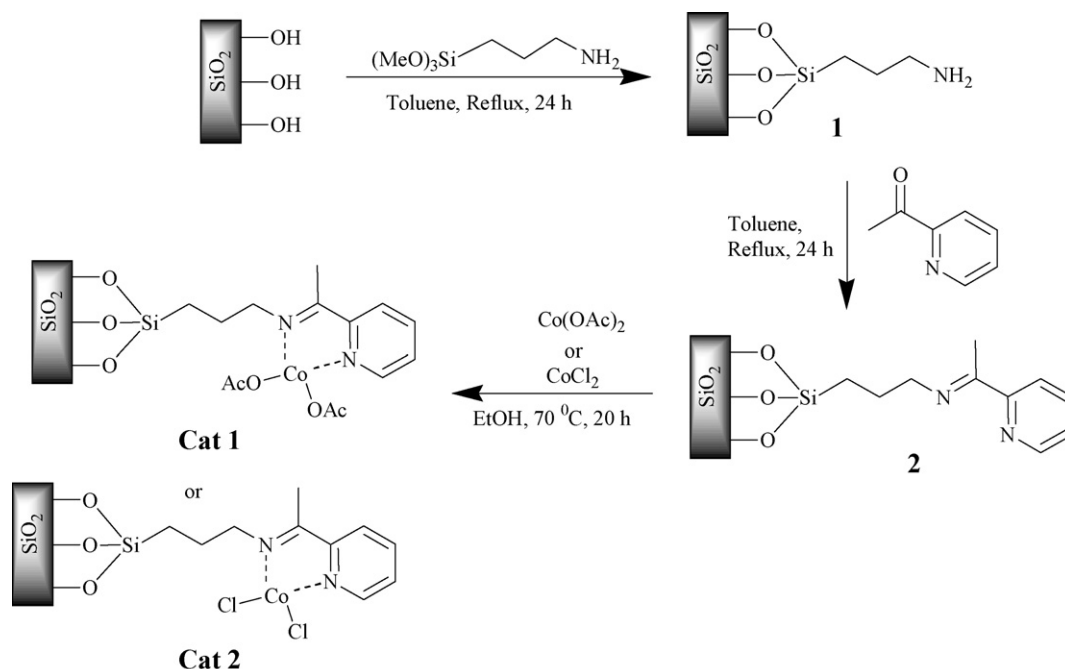


Fig. 1. Proposed structures of the catalysts.



Scheme 1. Synthesis of covalently anchored cobalt complexes onto silica (Cat 1 and Cat 2).

gel (Fig. 1, Cats 1, 2 and 3) under heterogeneous conditions. The preparation procedure for the Cats 1 and 2 is outlined in Scheme 1 and Cat 3 was prepared according to the literature method [11a].

2. Experimental

2.1. General remarks

Silica gel (K100, 0.063–0.200 mm) was purchased from Merck (Germany), and 3-aminopropyl(trimethoxy) silane and terephthaldehyde from Aldrich Chemical Company. Melting points were determined on a Perfit melting point apparatus and are uncorrected. ^1H NMR spectra were registered on a Bruker DPX-200 NMR spectrometer (200 MHz) in CDCl_3 using tetramethylsilane as an internal standard and IR spectra were recorded on a Perkin-Elmer FTIR spectrophotometer using KBr discs. Mass spectral data was recorded on a Bruker Esquire 3000 (ESI) spectrometer. Thermal analysis was carried out on a Shimadzu DTG-60 thermal analyzer at

the heating rate of 10°C/s and the amount of cobalt was determined on a double beam atomic absorption spectrophotometer (AAS), GBC 932 AB manufactured in Australia. The catalyst was stirred in dilute HCl for 10 h and the resulting filtrate was subjected to AAS analysis. Hantzsch 1,4-dihydropyridines were prepared by the literature method [12].

2.2. Grafting of ligand structure on the surface of silica gel (imine 2)

Silica (K100, 0.063–0.200 mm) was activated by refluxing in a mixture of conc. HCl and distilled water (1:1) for 24 h and then washed thoroughly with distilled water and dried at 110°C for 12 h. Activated silica (10 g) was added to a solution of 3-aminopropyl(trimethoxy) silane (10 mmol) in dry toluene and refluxed for 24 h. The 3-aminopropyl silica (AMPS) was filtered off, washed with hot toluene and dried at 110°C for 5 h to give the surface bound amino groups (AMPS). The oven dried AMPS (5 g)

was added to sodium-dried toluene (50 mL) in a round-bottomed flask (100 mL) followed by the addition of 2-acetylpyridine (0.605 g, 5 mmol). The reaction mixture was refluxed at 120 °C and water formed during the reaction was removed azeotropically by using a Dean-Stark apparatus. The ligand-grafted silica (imine **2**) was filtered at the reaction temperature and washed with hot toluene thoroughly to remove unreacted 2-acetylpyridine. It was dried in an oven at 100 °C for 10 h.

2.3. Synthesis of silica supported cobalt catalysts (Cats **1** and **2**)

The mixture of ligand-grafted silica (imine **2**, 5 g), Co(OAc)₂ (Cat **1**, 0.44 g, 2.5 mmol) or CoCl₂ (Cat **2**, 0.322 g, 2.5 mmol) in ethanol (50 mL) was stirred at room temperature for 15 h. The solid was filtered off with suction and washed with ethanol till washings were colourless. It was dried in an oven at 95 °C for 5 h and then conditioned for a total of 8 h (2 × 2 h each refluxing in acetonitrile and toluene). The conditioned catalysts were dried under vacuum for 5 h before use.

2.4. General procedure for the oxidative aromatization of Hantzsch 1,4-dihydropyridines

To a mixture of Hantzsch 1,4-dihydropyridine **3** (1 mmol) and Cat **1** (0.2 g, 3 mol% Co) in a three-necked round-bottomed flask, toluene (5 mL) was added. The flask was then evacuated with the help of a pump and re-filled with oxygen two times (using balloon filled oxygen) and the reaction mixture was stirred at 90 °C for an appropriate time (monitored by TLC). On completion, the reaction mixture was filtered while hot and the residue was washed with hot toluene (2 × 5 mL). The product was obtained after removal of the solvent under reduced pressure followed by crystallization or column chromatography. The catalyst was recovered from the residue after washing with CH₂Cl₂ (10 mL) followed by distilled water (200 mL) and then with CH₂Cl₂ (15 mL). It can be re-used after drying at 100 °C for 2 h.

The structures of the products were confirmed by spectral data and comparison with authentic samples prepared according to the literature methods [12,13]. The spectral data of some representative compounds is given below.

2.4.1. Diethyl 2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (**4a**)

¹H NMR (CDCl₃): δ 1.03–1.20 (t, 6H, *J* = 7.2 Hz, 2 × CH₂CH₃), 2.27 (s, 6H, 2 × CH₃), 4.01–4.21 (q, 4H, *J* = 7.2 Hz, 2 × CH₂CH₃), 7.18–7.38 (m, 5H, ArH). IR (KBr, ν_{max} in cm⁻¹): 3060, 2080, 1735, 1402. *m/z* (M+1)⁺ = 328.

2.4.2. Diethyl 2,6-dimethyl-4-(4-methoxyphenyl)pyridine-3,5-dicarboxylate (**4b**)

¹H NMR (CDCl₃): δ 1.05–1.21 (t, 6H, *J* = 7.3 Hz, 2 × CH₂CH₃), 2.21 (s, 6H, 2 × CH₃), 3.92 (s, 3H, OCH₃), 4.05–4.23 (q, 4H, *J* = 7.2 Hz, 2 × CH₂CH₃), 6.91 (d, 2H, *J* = 10 Hz, ArH), 7.20 (d, 2H, *J* = 8.9 Hz, ArH). IR (KBr, ν_{max} in cm⁻¹): 3065, 2825, 1730, 1407. *m/z* (M+1)⁺ = 359.

2.4.3. Diethyl 2,6-dimethyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate (**4d**)

¹H NMR (CDCl₃): δ 1.03–1.19 (t, 6H, *J* = 7 Hz, 2 × CH₂CH₃), 2.56 (s, 6H, 2 × CH₃), 4.04–4.22 (q, 4H, *J* = 7 Hz, 2 × CH₂CH₃), 7.45 (d, 2H, *J* = 8.6 Hz, ArH), 8.20 (d, 2H, *J* = 8.6 Hz, ArH). IR (KBr, ν_{max} in cm⁻¹): 3072, 2855, 1730, 1480, 1440. *m/z* (M+1)⁺ = 374.

2.4.4. Diethyl 2,6-dimethyl-4-(cinnamyl)pyridine-3,5-dicarboxylate (**4f**)

¹H NMR (CDCl₃): δ 1.10–1.27 (t, 6H, *J* = 7 Hz, 2 × CH₂CH₃), 2.52 (s, 6H, 2 × CH₃), 4.05–4.24 (q, 4H, *J* = 7.3 Hz, 2 × CH₂CH₃), 6.82 (d, 1H,

J = 16.5 Hz, =CH), 7.05–7.55 (m, 5H, ArH and d buried, 1H, =CH). IR (KBr, ν_{max} in cm⁻¹): 3036, 2865, 1727, 1540. *m/z* (M+1)⁺ = 355.

2.4.5. Diethyl 2,6-dimethyl-4-(2-furyl)pyridine-3,5-dicarboxylate (**4g**)

¹H NMR (CDCl₃): δ 1.03–1.19 (t, 6H, *J* = 7.4 Hz, 2 × CH₂CH₃), 2.53 (s, 6H, 2 × CH₃), 4.10–4.25 (q, 4H, *J* = 7.4 Hz, 2 × CH₂CH₃), 6.62–6.75 (m, 2H, ArH), 7.55 (m, 1H, ArH). IR (KBr, ν_{max} in cm⁻¹): 3068, 2865, 1726, 1463, 1045. *m/z* (M+1)⁺ = 319.

3. Results and discussion

The preparation procedure followed to obtain the catalysts (Cats **1** and **2**) is indicated in Scheme 1. It consists of building up a suitable ligand structure on the surface of a commercial silica gel (K100) followed by the complexation of cobalt(II) using cobalt acetate or cobalt chloride. Cat **3** was prepared according to a literature method [11a]. The characterization of the catalysts was done on the basis of simultaneous thermal analysis (STA), FTIR and AAS (Table 1). The simultaneous thermal analysis curve for Cat **1** shows an initial weight loss up to 90 °C and then a further weight loss from 320 to 574 °C. The weight loss up to 90 °C may be due to the loss of residual solvent and water present on the surface of Cat **1** and the further weight loss from 320 to 574 °C indicates that organic functionality is covalently bonded to silica gel. Similarly, for Cat **2**, initial weight loss up to 99 °C was attributed to the loss of residual solvent and water and further weight loss from 301 to 563 °C to the loss of organic functionality. The STA curve for Cat **3** shows the initial weight loss up to 95 °C (loss of residual solvent and water) and also from 390 to 600 °C (loss of organic functionality). Thus, the STA curves of Cats **1**, **2** and **3** indicate that catalysts are stable up to 320, 301 and 390 °C, respectively and hence it is safe to carry out the reaction at 90 °C.

The FTIR of 3-aminopropyl silica displays characteristic CH₂ stretching bands at 2933 and 2860 cm⁻¹ and aliphatic deformation bands at 1470 and 1445 cm⁻¹. The FTIR of chemically modified silica (imine) shows a sharp peak at 1638 cm⁻¹ due to a C=N bond, which on complexation with cobalt disappears and appear as a band at 1617 cm⁻¹ (Cat **1**) and 1632 cm⁻¹ (Cat **2**). The lowering in frequency of the C=N peak is indicative of the formation of metal–ligand bond. The FTIR of Cat **3** shows absorption bands at 1678 and 1684 cm⁻¹ due to C=N bonds and at 1584 and 1456 cm⁻¹ due to antisymmetric and symmetric stretching modes of the carboxylate group.

The amount of cobalt loaded on the surface of silica gel was determined by AAS analysis. The catalysts were stirred in dilute HCl and the solutions were then subjected to AAS analysis. Cats **1**, **2** and **3** were found to contain 0.0087, 0.0064 and 0.0084 g of cobalt per gram of the catalysts, respectively. To make the process completely heterogeneous, the catalysts were conditioned at reflux temperature in acetonitrile (2 × 2 h) and toluene (2 × 2 h).

Table 1
Characterization of the catalysts (FTIR and thermal analysis).

Catalyst	FTIR ^a (ν _{max} in cm ⁻¹)	Thermal analysis ^b (TGA)
Cat 1	1638 (C=N before complexation); 1617 (C=N after complexation)	Up to 90 °C (loss of residual solvent and H ₂ O molecule); 320–574 °C (loss of organic functionality)
Cat 2	1638 (C=N before complexation); 1632 (C=N after complexation)	Up to 99 °C (loss of residual solvent and H ₂ O molecule); 301–563 °C (loss of organic functionality)
Cat 3	1678 and 1684 (C=N); 1584 and 1456 (antisym. and sym. modes of carboxylate group)	Up to 95 °C (loss of residual solvent and H ₂ O molecule); 390–600 °C (loss of organic functionality)

^a FTIR was recorded on Perkin-Elmer FTIR spectrophotometer using KBr discs.

^b Thermal analysis was carried out on DTG-60 Shimadzu make thermal analyzer with heating rate of 10 °C/s.

Table 2
Effect of silica functionalized cobalt catalysts for the oxidative aromatization of **3a** with O₂ and H₂O₂ under heterogeneous conditions^a.

Catalyst	Oxidant	Time (h)	Yield (%) ^b
No catalyst	O ₂	20	Traces
Cat 1	O ₂	10	90
Cat 1	H ₂ O ₂	20	86
Cat 2	O ₂	20	38
Cat 2	H ₂ O ₂	20	25
Cat 3	O ₂	20	80
Cat 3	H ₂ O ₂	20	75

^a Reaction conditions: **3a** (1 mmol), catalyst (3 mol% Co), toluene (5 mL), oxidant (O₂-balloon; H₂O₂-0.5 mL), stirring at 90 °C.

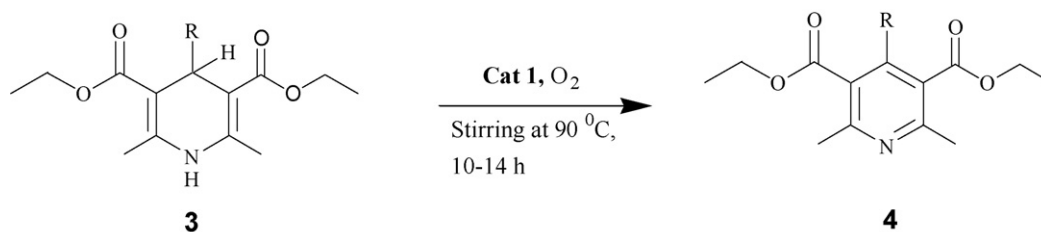
^b Yields after column chromatography.

The activity of the catalysts (Cats **1**, **2** and **3**) was tested in the oxidation of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate using molecular oxygen and hydrogen peroxide as oxidants, toluene as solvent, at 90 °C. The results are summarized in Table 2. Cat **1** was found to be the most effective with molecular

oxygen as the oxidant. With H₂O₂ using Cat **1**, the corresponding pyridine was obtained in 86% isolated yield in 20 h, whereas molecular oxygen gives 90% isolated yield in 10 h.

In comparison to H₂O₂, molecular oxygen is still considered as greener. Thus, Cat **1** was chosen to carry out the oxidation of various 1,4-dihydropyridines substituted with electron-releasing and electron-withdrawing groups using molecular oxygen as the oxidant (Scheme 2). All types of DHPs undergo oxidation efficiently and results are summarized in Table 3. In order to check the selectivity of the catalytic system in the case of the isopropyl group (which was reported to undergo dealkylation at the 4-position), we have carried out the oxidation of diethyl 2,6-dimethyl-4-isopropyl-1,4-dihydropyridine-3,5-dicarboxylate under similar conditions. It was found that in addition to oxidation product, 4-dealkylated product (15%, ¹H NMR yield) was also formed.

In the case of heterogeneous catalysts, two important points are always required to be addressed. One is the possibility of leaching of some active metal into the reaction medium, which in turn becomes responsible for the catalytic activity (homogeneous catalysis). To rule out the contribution of homogeneous catalysis, the reaction for



Scheme 2. Oxidative aromatization of Hantzsch 1,4-dihydropyridines in the presence of Cat **1** using O₂.

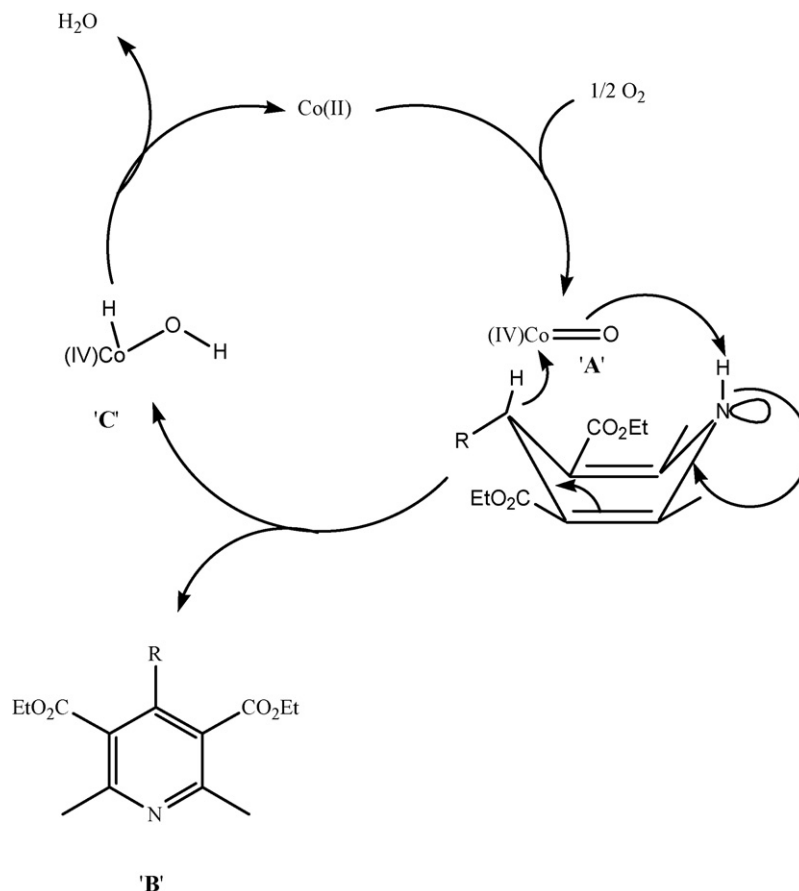


Fig. 2. Proposed catalytic cycle for the oxidative aromatization of Hantzsch 1,4-dihydropyridines.

Table 3

Oxidative aromatization of Hantzsch 1,4-dihydropyridines with molecular oxygen in the presence of Cat **1** under heterogeneous conditions.

Compound ^a	R	Time (h)	Yield (%) ^b	m.p./lit. m.p. (°C)
4a	C ₆ H ₅	10	90	62–63/62–64 [13]
4b	4-MeOC ₆ H ₄	10	90	57–58/55–57 [14]
4c	4-ClC ₆ H ₄	12	89	65–66/63–65 [13]
4d	4-NO ₂ C ₆ H ₄	12	87	113–114/114–116 [15]
4e	3-NO ₂ C ₆ H ₄	13	86	61–62/61–63 [16]
4f	Ph-CH=CH	12	87	87–89/88–90 [17]
4g ^c	2-Furyl	13	82	39–40/38–41 [18]
4h ^{c,d}	4-CH(CH ₃) ₂	14	65	Liquid/oil [19]

^a Structures of the products were confirmed by ¹H NMR, IR, mass spectral data and comparison with authentic samples prepared according to the known procedures.

^b Isolated yield.

^c The product was purified by passing through column of silica gel and elution with pet. ether:EtOAc (8:2).

^d 4-Dealkylated product (15%, ¹H NMR yield) was also formed.

entry **1** was carried out until the conversion was 36% (2.5 h) and at that point the solid was filtered off at the reaction temperature. The liquid phase was then transferred to another flask and again allowed to react, but no further significant conversion was observed. This indicates that no active species was present in the supernatant (no cobalt was detected in the supernatant by AAS analysis). The second point was the deactivation and recyclability of the catalyst, which becomes more important in the case of oxidation reactions. To test this, a series of three consecutive runs was carried out with the same sample (entry **1**) (1st use: 90% yield after 10 h; 2nd use: 85% yield after 12 h; 3rd use: 81% yield after 14 h). These recyclability data demonstrate the high stability of the catalyst under the reaction conditions.

A cyclic mechanism has been proposed for the oxidative aromatization of Hantzsch 1,4-DHPs using Cat **1** in the presence of molecular oxygen (Fig. 2). An oxygen molecule reacts with cobalt to form an oxocobalt complex **A**, which can deprotonate a 1,4-DHP molecule yielding product **B** and an intermediate **C**. Intermediate **C** then loses molecule of water and Co(II) is regenerated.

4. Conclusion

We have prepared recyclable covalently anchored cobalt complexes onto the surface of silica gel (Cats **1**, **2** and **3**) and employed for the catalytic oxidative aromatization of Hantzsch 1,4-dihydropyridines with green oxidant molecular oxygen under heterogeneous conditions. Cat **1** was found to be more effective than Cats **2** and **3**. Moreover, the mild reaction conditions, high yield of products, ease of work-up, compatibility with various functional groups, and the ecologically clean procedure will make the present method a useful and important addition to the present methodologies for the oxidation of dihydropyridines.

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