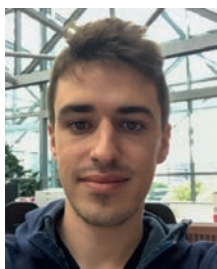


On the Ability of Nickel Complexes Derived from Tripodal Aminopyridine Ligands to Catalyze Arene Hydroxylations

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Abstract: The development of catalysts for the selective hydroxylation of aromatic C–H bonds is an essential challenge in current chemical research. The accomplishment of this goal requires the discovery of powerful metal-based oxidizing species capable of hydroxylating inert aromatic bonds in a selective manner, avoiding the generation of non-selective oxygen-centered radicals. Herein we show an investigation on the ability of nickel(II) complexes supported by tripodal tetradentate aminopyridine ligands to catalyze the direct hydroxylation of benzene to phenol with H₂O₂ as oxidant. We have found that modifications on the ligand structure of the nickel complex do not translate into different reactivity, which differs from previous findings for nickel-based arene hydroxylations. Besides, several nickel(II) salts have been found to be effective in the oxidation of aromatic C–H bonds. The use of fluorinated alcohols as solvent has been found to result in an increase in phenol yield; however, showing no more than two turn-overs per nickel. These findings raise questions on the nature of the oxidizing species responsible for the arene hydroxylation reaction.

Keywords: Aromatic C–H oxidation · Fluorinated solvents · Hydrogen peroxide · Nickel complexes · Phenols



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1. Introduction

Oxidations of organic compounds are essential reactions and have been intensively studied in academia as well as in the chemical industry.^[1,2] Interest stems from the fact that oxygenated organic molecules can be subsequently used to produce different

classes of chemicals. Nowadays, many improvements have been made in the development of different oxidation catalysts; however, the selective oxidation of organic substrates, such as aromatic compounds, still represents a critical challenge in modern chemical research.

Phenols are essential intermediates in the generation of a broad range of products such as pharmaceuticals and polymers.^[3–6] Currently, the industrial production of phenol from benzene is carried out *via* the cumene process, which suffers overall from low efficiencies in product yield.^[7] The direct introduction of a hydroxyl functionality through activation of an aromatic C–H bond is difficult because of the high stability of aromatic compounds and the high bond dissociation energy of an aromatic C–H bond (112 kcal mol^{–1}).^[8] To overcome this challenge, the generation of highly reactive and selective metal-oxygen species is necessary. However, often phenol products are more easily oxidized than non-oxidized aromatic compounds, causing a chemoselectivity issue. In addition, a lack of discrimination between different oxidation sites results in a regioselectivity issue, especially when substituted benzenes are used in which the oxidation of benzylic C–H bonds can be preferred over oxidation at the aromatic ring.

On the one hand, hydroxyl radicals, as well as hydroperoxyl radicals, are well known to oxidize aromatic compounds; however, poor selectivity is usually observed due to the non-discriminative reactivity of oxygen-centered radicals.^[9,10] On the other hand, metal-based oxidants are known to lead to more selective hydroxylation reactions.^[11] Along this line, some progress has been made in the direct hydroxylation of benzene to phenol using H₂O₂ as the benign oxidant catalyzed by homogeneous catalysts (Fig. 1), providing some mechanistic insights.^[12–19]

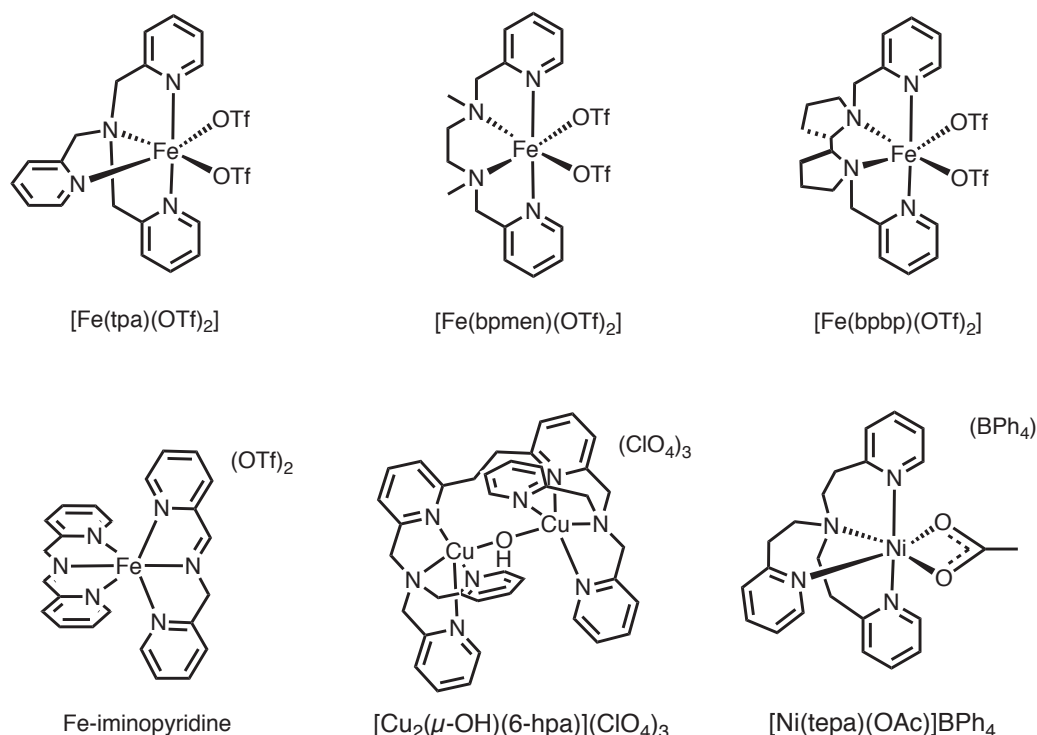
Over the last years, much interest has been devoted to the study of bioinspired iron complexes, which are minimalistic models of

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Fig. 1. Examples of metal complexes previously used in catalytic arene hydroxylation reactions with H_2O_2 .



natural oxygenase enzymes.^[20] These systems have been extensively studied for the oxidation of aliphatic C–H groups and epoxidation reactions with H_2O_2 ,^[21] whereas hydroxylation of aromatic compounds has remained challenging. The main problem is that the phenol products bind irreversibly to the iron center, which prevents catalytic turnover.^[22–24] For instance, several studies on the use of iron complexes supported by the tpa and bpmen aminopyridine ligands (tpa = tris(2-pyridylmethyl)amine) and bpmen = *N,N'*-dimethyl-*N,N'*-bis(2-picolyl)ethylenediamine) showed that these complexes were capable of oxidizing aromatic C–H bonds, but do not allow for catalytic turnover.^[22–24] Recently, a series of iron complexes supported by the bpbp type ligands (bpbp = *N,N'*-bis(2-pyridylmethyl)-2,2'-bipyrridine) were found to be active for the hydroxylation of aromatic substrates with H_2O_2 , but with poor selectivities due to the generation of overoxidation products.^[12–14] Non-heme imine-based iron complexes have also been investigated in the field of hydroxylation reactions.^[25] For instance, an iminopyridine iron(II) complex prepared *in situ* by self-assembly of commercially starting materials was found to be active for the hydroxylation of aromatic rings using H_2O_2 as the oxidant, likely through a metal-based electrophilic aromatic substitution mechanism.^[15]

Other first-row transition metals have also been shown to be capable of performing arene hydroxylation reactions with H_2O_2 as benign oxidant. Kodera and co-workers reported a dinuclear copper complex stabilized by the 6-hpa ligand (6-hpa = 1,2-bis{2-[bis(2-pyridylmethyl)aminomethyl]-6-pyridyl}ethane) for the selective hydroxylation of benzene to phenol with H_2O_2 , showing high activity for phenol formation.^[16] Another remarkable example is the selective hydroxylation of benzene catalyzed by a $[\text{Ni}(\text{tepa})(\text{OAc})]\text{BPh}_4$ (tepa = tris(2-pyridylethyl)amine)/ H_2O_2 system, which was reported to work through a metal-based mechanism, affording a maximum of 749 turnover numbers (TON) in 216 h at 60 °C for phenol production when using an 10000-fold excess of benzene with respect to the catalyst.^[18] The authors found that among a series of nickel complexes supported by tripodal tetradentate aminopyridine ligands, the one supported by the tepa ligand is able to chemoselectively catalyze the hydroxylation of benzene and alkylbenzenes at high H_2O_2 loadings, without the formation of substantial amounts of over-oxidized products.^[18] Remarkably though, when this complex was used in catalysis in

10 mol% loading with respect to the benzene substrate only 21% phenol (2.1 turnovers per nickel) was formed in 5 h reaction time at 60 °C. Based on the previous work from Itoh and co-workers, another recently reported study shows improved nickel-based catalysts for the selective oxidation of benzene to phenol through modifications of aminopyridine ligands by introduction of electron-rich pyridines, affording phenol with up to 820 TON in 5 h at 60 °C using 0.05 mol% loading of catalyst.^[19]

Many efforts have focused on the development of highly selective catalyst systems for phenol formation. These studies parallel the development of catalysts for the selective hydroxylation of aliphatic C–H bonds to the corresponding alcohols, avoiding the generation of overoxidized ketone products. In an effort to create more selective catalysts, several of the latter studies have described the use of fluorinated alcohol solvents, *i.e.* 2,2,2-trifluoroethanol (TFE) or 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) in hydroxylation reactions, showing improved selectivities for the first-formed hydroxylation product and avoiding overoxidation reactions.^[26–30]

Inspired by previous studies on arene hydroxylation catalyzed by nickel complexes,^[18,19] we studied the effect of different tripodal aminopyridine ligands for the direct hydroxylation of benzene to phenol with H_2O_2 by nickel under mild reaction conditions. Our findings show that the use of different tripodal tetradentate aminopyridine ligand designs in the nickel complexes does not lead to a different reactivity in arene hydroxylation reactions, showing that this type of ligand does not play an important role in catalysis. Besides, we show that the oxidation of benzene can be achieved using simple nickel salts with high chemoselectivity. The effect of solvents, such as fluorinated alcohols, is found to produce and enhance activity for phenol formation, highlighting the use of this kind of solvents on oxidation processes. On the basis of these results, we discuss some mechanistic considerations for arene hydroxylation using molecular nickel complexes derived from aminopyridine ligands.

2. Results and Discussion

2.1 Aminopyridine Ligands and Nickel Complexes

For our study, we investigated several nickel complexes supported by aminopyridine ligands as arene hydroxylation catalysts

with H_2O_2 as the benign oxidant under mild reaction conditions (Fig. 2). Our aim was to investigate if small modifications in the structure of the aminopyridine ligand would influence the reactivity of the complexes in arene hydroxylation reactions.

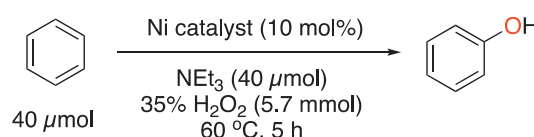
Based on the work of Itoh and co-workers,^[18] we focused on the use of tripodal tetradentate aminopyridine ligands, playing with the length of the arms. First, we synthesized the parent tpa ligand, containing three methylene arms, and the tepa ligand, which contains three ethylene arms. Of interest was also the pmea ligand (pmea = (2-(2-pyridylethyl))bis(2-pyridylmethyl)amine), and the pmap ligand (pmap = bis(2-(2-pyridylethyl))-2-pyridylmethylamine). Finally, we envisioned an enhancement of efficiency towards aromatic C–H oxidations by introducing electron-donating substituents into some of the pyridines, such as the 6-Me₂-tpa and 4-OMe-3,5-Me-pmap ligands (6-Me₂-tpa = bis(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine, and 4-OMe-3,5-Me-pmap = bis(2-(2-pyridylethyl))-(4-methoxy-3,5-dimethyl)-2-pyridylmethylamine). The benefit of such electron-rich pyridine donors has been shown for several C–H and C=C oxidation reactions with non-heme iron and manganese complexes,^[31–34] as well as for arene hydroxylation reactions with nickel complexes.^[19]

The corresponding nickel complexes were synthesized by mixing nickel acetate tetrahydrate with the different aminopyridine ligands; subsequent addition of sodium tetraphenylborate led to precipitation of the final complex. Several of the complexes were analyzed by X-ray single crystal structure determination, showing a mononuclear nickel(II) species exhibiting a distorted octahedral geometry. Details of the synthesis and characterization of the ligands and complexes can be found in the Supplementary Information.

2.2 Screening of Complexes

Next, we focused on the oxidation of benzene as model substrate to selectively screen for aromatic oxidation (Scheme 1). Catalytic experiments were carried out using 40 μmol of benzene, 40 μmol of triethylamine as a base, and 5.7 mmol of H_2O_2 (142 equiv.) in acetonitrile as solvent, with 10 mol% of catalyst; following the initial conditions described by Itoh.^[18] Reactions were run under air, at 60 °C, for 5 h using a closed reaction vessel. Crude mixtures were analyzed by GC, detecting mainly phenol as oxidized product, whereas formation of *para*-benzoquinone as an

over-oxidized by-product was not observed. Thus, all complexes tested show chemoselectivity for phenol formation, as was reported previously for similar Ni/ H_2O_2 systems.^[18,19] Furthermore, biphenyl was detected after analysis of the crude mixtures. The formation of biphenyl seems to originate from the tetraphenylborate counterion of the complex, since it is known that biphenyl can form through radical decomposition of tetraphenylborate.^[35,36] Similar oxidation experiments without benzene substrate afford biphenyl as well, corroborating that benzene is not the source of the biphenyl formation. Interestingly, acetamide was detected as the main product in the crude reaction mixtures. Acetamide may form through the oxidation of triethylamine, which can be oxidized in the presence of H_2O_2 .^[37,38] However, the amounts of acetamide obtained were higher than the amount of triethylamine used, suggesting that the acetonitrile solvent is hydrated to acetamide under our experimental conditions.



Scheme 1. Catalytic hydroxylation of benzene to phenol catalyzed by nickel(II) complexes with H_2O_2 under mild reaction conditions.

Overall, these first catalytic experiments using acetonitrile as solvent provided poor phenol yields, ranging from 9.0 to 10.5% (Table 1). These findings compare quite well with the initial experiments performed by Itoh and co-workers, for which they reported 2 TON for the oxidation of benzene catalyzed by Ni(*tepa*) under the same experimental conditions.^[18] Not only do our results represent a single turn-over per nickel, the differences in phenol yields between the different complexes lie within the experimental error of our GC analysis. Accordingly, these results indicate that no particular complex in the series of complexes tested catalyzes benzene hydroxylation more effectively than another complex. Our results might even indicate that the aminopyridine ligand plays no important role in performing the oxidation reaction. A control experiment without any complex as catalyst showed that no phenol product formation occurs in the absence of a nickel complex. Thus, we can confidently conclude that a nickel

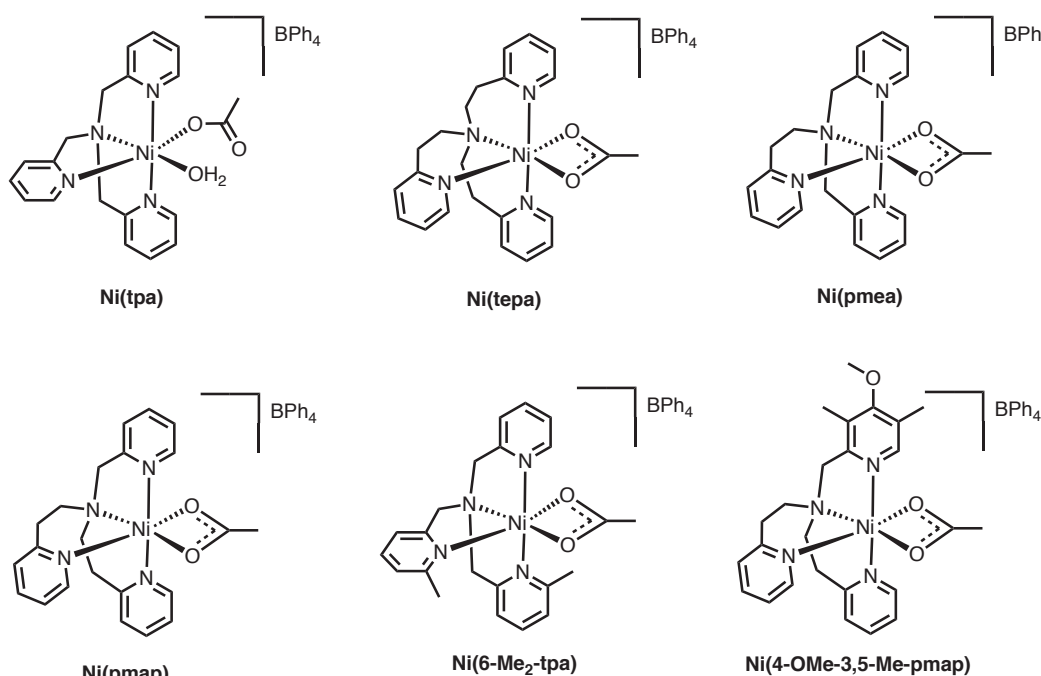


Fig. 2. Nickel(II) complexes supported by tripodal tetradentate aminopyridine ligands employed in this work.

Table 1. Direct hydroxylation of benzene to phenol employing Ni(II) complexes in acetonitrile.

Entry	Catalyst	Phenol Yield [%]
1	Ni(tpa)	9.6
2	Ni(tepa)	9.9
3	Ni(pmea)	9.7
4	Ni(pmap)	9.0
5	Ni(6-Me ₂ -tpa)	10.5
6	-	n.d.

n.d. = non-detected. ^aReaction conditions: benzene (40 μ mol), H₂O₂ (5.7 mmol), Ni complex (4 μ mol), and NEt₃ (40 μ mol) at 60 °C for 5 h in CH₃CN.

complex is involved in the oxidation reaction.

2.3 Different Reaction Solvents

Since the phenol yields were low, we decided to screen different solvents for the hydroxylation of benzene with the Ni(tepa) catalyst (Table 2). With acetonitrile, we could detect 4.7% phenol yield after 2.5 h, which increased to 9.9% when the reaction was run for 5 h (Table 2, entries 1 and 2). Next, fluorinated alcohols were tested, which have been reported to be suitable solvents in different hydroxylation reactions.^[26–30] TFE provided 7.6% phenol formation after 2.5 h, which slightly increased to 8% when the reaction was run for 5 h (Table 2, entries 3 and 4). Another fluorinated alcohol, HFIP, was also tested as solvent, providing an enhanced activity, with 11.8 and 15.3% phenol yield after 2.5 and 5 h of reaction time, respectively. Methanol afforded poor phenol formation (3.8% yield), whereas acetone did not provide any phenol product (Table 2, entries 7 and 8); showing that these two solvents are not suitable to perform arene hydroxylation reactions with nickel complexes.

Table 2. Screening of solvents for the direct hydroxylation of benzene to phenol catalyzed by Ni(tepa).^a

Entry	Solvent	Reaction Time [h]	Phenol Yield [%]
1	CH ₃ CN	2.5	4.7
2	CH ₃ CN	5	9.9
3	TFE	2.5	7.6
4	TFE	5	8.0
5	HFIP	2.5	11.8
6	HFIP	5	15.3
7	CH ₃ OH	5	3.8
8	(CH ₃) ₂ CO	5	n.d.
9 ^b	HFIP	5	14.8
10 ^c	HFIP	2.5	7.2

^aReaction conditions: benzene (40 μ mol), H₂O₂ (5.7 mmol), Ni complex (4 μ mol), and NEt₃ (40 μ mol) at 60 °C. ^b500 equivalents of H₂O₂ were used. ^cH₂O₂ was added slowly within 1 h with the use of a syringe pump. n.d. = non-detected.

From these results, we concluded that the fluorinated alcohol HFIP is the best solvent to perform the oxidation of benzene to phenol catalyzed by the Ni(tepa) complex. Next, we tried higher amounts of H₂O₂, which did not afford an increase in phenol formation (Table 2, entry 9). We also envisioned an increase in catalytic activity by delivering H₂O₂ slowly during catalysis, as has been shown for other C–H hydroxylation reactions using this oxidant.^[39,40] However, no improvement was observed, and phenol was formed in a much lower yield, highlighting that the disproportionation of H₂O₂ is not product-limiting, probably due to the high-excess conditions (Table 2, entry 10).

Next, we screened all nickel complexes for catalysis in the HFIP solvent (Table 3). Overall, we observed that for all complexes phenol yields increase when HFIP is used as the solvent compared to the use of acetonitrile, as was initially shown for the Ni(tepa) complex. While this observation highlights the use of a fluorinated alcohol solvent in arene hydroxylation catalysis by nickel(II) complexes, the overall yields still represent an average 1.5 TON per nickel. In addition, no distinctive differences in catalytic efficiencies are observed between the different complexes. Even the nickel complexes Ni(6-Me₂-tpa) and Ni(4-OMe-3,5-Me-pmap) supported by electron-rich tripodal ligands did not afford substantial changes in reactivity (Table 3, entries 5 and 6). Control experiments with HFIP as solvent showed that the reaction does not work in absence of a catalyst (Table 3, entry 7). Even though a solvent screening did result in some increase in catalytic efficiency, the small differences in product yields attainable with the current, yet limited, set of tripodal tetradentate aminopyridine ligands in our view does not allow for a rationalized ligand modification toward improved catalyst efficiency.

Interestingly, the simple salts nickel nitrate hexahydrate and nickel chloride hexahydrate led to 6.7 and 3.0% phenol yield, respectively, using our current conditions (Table 3, entries 8 and 9). However, the hydroxylation reaction did not work when nickel acetate tetrahydrate was used (Table 3, entry 10). Remarkably, these results show that aromatic C–H oxidations can be done using some simple commercial nickel(II) salts with high chemoselectivity, albeit in low efficiencies.

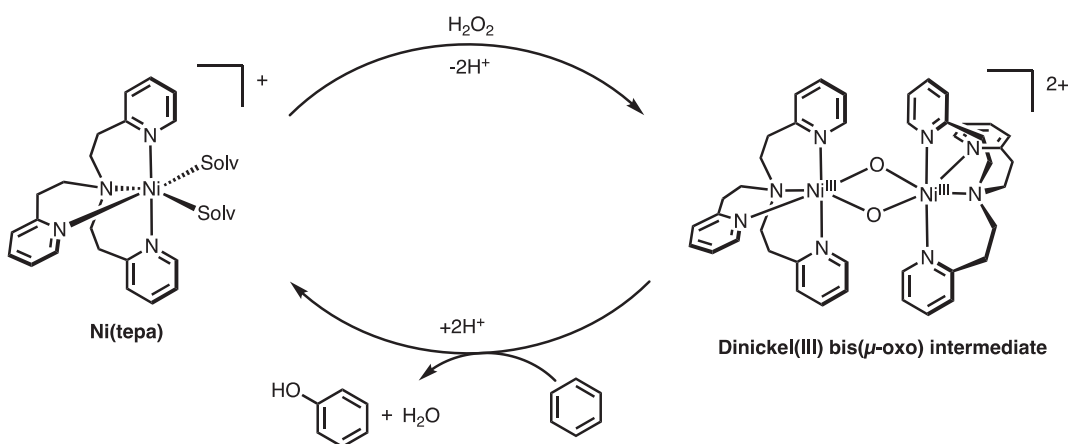
Table 3. Direct hydroxylation of benzene to phenol employing Ni(II) complexes in HFIP.

Entry	Catalyst	Phenol Yield [%]
1	Ni(tpa)	14.9
2	Ni(tepa)	15.3
3	Ni(pmea)	14.6
4	Ni(pmap)	16.4
5	Ni(6-Me ₂ -tpa)	15.0
6	Ni(4-OMe-3,5-Me-pmap)	17.4
7	-	n.d.
8	Ni(NO ₃) ₂ ·6H ₂ O	6.7
9	NiCl ₂ ·6H ₂ O	3.0
10	Ni(CH ₃ COO) ₂ ·4H ₂ O	n.d.

n.d. = non-detected. ^aReaction conditions: benzene (40 μ mol), H₂O₂ (5.7 mmol), Ni complex (4 μ mol), and NEt₃ (40 μ mol) at 60 °C for 5 h in HFIP.

2.4 Mechanistic Considerations

Finally, our efforts have been devoted to the understanding of the mechanism of the aromatic hydroxylation catalyzed by nickel complexes. In previous studies by Itoh and co-workers with the **Ni(tepa)** complex, it has been proposed that oxidation of benzene proceeds through a metal-based mechanism in which, after activation of H_2O_2 , a dinickel(III) bis(μ -oxo) species is formed as the active oxidant (Scheme 2).^[18] However, no direct evidence for the involvement of such species has been shown. A recent work by Mayilmurugan and co-workers on arene hydroxylations catalyzed by nickel complexes supported by similar tripodal tetradentate aminopyridine ligands, postulates the same dinuclear nickel species as the oxidant responsible for the oxidation of the aromatic ring.^[19] Only recently, Itoh and co-workers have shown an example of a dinickel(III) bis(μ -oxo) species with the dpema ligand (dpema = *N,N*-di-[2-pyridine-2-yl]ethyl)methylamine) displaying oxygenation reactivity towards external hydrocarbon substrates, however, no reactivity of such species towards external aromatics was reported.^[41]



Scheme 2. Proposed catalytic mechanism for the direct hydroxylation of benzene to phenol with nickel(II) complexes based on previous studies.^[18]

Here, we considered the role of triethylamine as a base, and how this component could affect catalysis. In these oxidation reactions triethylamine is thought to activate H_2O_2 and facilitate its reaction with the mononuclear nickel complex. Aqueous H_2O_2 solutions are acidic (pK_a of $\text{H}_2\text{O}_2 = 11.62$);^[42] therefore, the presence of a base in the catalytic reactions could help in the activation of H_2O_2 by deprotonating it. Indeed, we carried out some catalytic experiments using **Ni(tepa)** in acetonitrile without triethylamine, where we could observe a slight decrease in phenol formation (6.9% yield) in comparison with experiments using the base (compare with Table 1, entry 2); indicating the positive role of the amine in activating the oxidant.

However, the fluorinated solvent HFIP is rather acidic (pK_a of HFIP = 9.3)^[43] and could consequently affect the role of triethylamine (pK_a for the conjugate acid = 10.75)^[44] in the deprotonation of H_2O_2 . Carrying out a catalytic reaction with **Ni(pmea)** in HFIP and in the absence of triethylamine as a base gave a 15.4% phenol yield, which is similar to the yield obtained when triethylamine was employed (14.6%, see Table 3.). Thus, this observation made us conclude that triethylamine does not have an essential role in aromatic oxidations catalyzed by nickel complexes when HFIP is used as a solvent. Indeed, this fluorinated alcohol itself is known to activate H_2O_2 , as has been shown in some selective oxidation reactions such as the epoxidation of alkenes.^[45]

Overall, we believe that the reaction might proceed through a metal-based mechanism, since high chemoselectivity for the formation of phenol is observed. Generation of overoxidized products, such as hydroquinones or benzoquinones, easily occurs when oxygen-centered radicals are involved in catalysis.^[46–49] However, such products have not been observed in the current and in previous studies using aminopyridine-based nickel complexes.^[18,19]

On the other hand, we believe that some kind of deactivation of the catalyst occurs during catalysis, which prevents efficient and catalytic turnover. To further investigate catalyst stability, we have studied the formation of phenol over time using the **Ni(tepa)** complex with H_2O_2 , triethylamine and acetonitrile as the solvent, which showed that the phenol yield increases in the first few hours of reaction, to then come to a stop. Reaction analysis after 5 h provided us with 10% phenol yield, which remained the same for the next 24 h. Addition of an extra portion of catalyst and allowing the reaction to run for another 5 h resulted in an increase in phenol yield to 32%. Besides, attempts to obtain high turnover numbers by reproducing the same conditions described by Itoh and co-workers did not afford results that are consistent with the ones reported in the literature.^[18] Therefore, our results clearly differ from those reported by Itoh and co-workers, in which they describe up to 749 TON for phenol formation after 216 h of reaction time using the **Ni(tepa)** catalyst with H_2O_2 , triethylamine and acetonitrile.^[18]

3. Conclusions

We have presented a study on the effect of changes in the tripodal tetradentate aminopyridine ligand in nickel complexes used for the direct one-step hydroxylation of benzene to phenol in combination with H_2O_2 as benign oxidant under mild reaction conditions. Our results show that these modifications in the ligand structure do not translate into different activities in phenol formation, which differs from previous studies on nickel-based arene hydroxylations using similar tetradentate aminopyridine ligands.^[18,19] Remarkably, the oxidation of benzene could also be achieved using nickel(II) salts without the use of sophisticated ligand designs and using a fluorinated alcohol solvent, which seemed to improve phenol yields for the nickel complexes. The phenol yields obtained with the salts is significantly lower than with the complexes. The product selectivity obtained throughout our study, with no formation of catechols, hydroquinones or benzoquinones, points towards a metal-based mechanism, with no involvement of oxygen-centered radicals.

Our studies do corroborate the earlier findings of Itoh *et al.* concerning the catalytic performance of the nickel complexes at high catalyst loadings. Yet, attempts to reproduce the high turnover numbers achieved in the literature at low catalyst loadings were not successful. Together with the findings that catalytic performance is rather insensitive towards ligand structure variation and that simple nickel salts also are able to form phenol, the molecular nature of the catalyst involved in benzene hydroxylation by the nickel complexes can be questioned. Other than the involvement of a dinickel(III) bis(μ -oxo) species proposed earlier,^[18,19] we believe that some kind of decomposition of the nickel complexes occurs under the experimental conditions, possibly leading to the formation of nickel-based nanoparticles that are involved in ca-

talysis. Our future efforts will therefore be focused on identifying the actual nature of the hydroxylation catalyst and on the development of more active and stable catalyst systems based on nickel that allow for the high-turnover direct hydroxylation of benzene to phenol.

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Supplementary Information

Supplementary information is available on <https://www.ingentaconnect.com/content/scs/chimia>

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