

# Direct Hydroxylation of Benzene to Phenol Using Hydrogen Peroxide Catalyzed by Nickel Complexes Supported by Pyridylalkylamine Ligands

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**S** Supporting Information

**ABSTRACT:** Selective hydroxylation of benzene to phenol has been achieved using H<sub>2</sub>O<sub>2</sub> in the presence of a catalytic amount of the nickel complex [Ni<sup>II</sup>(tpepa)]<sup>2+</sup> (**2**) (tpepa = tris[2-(pyridin-2-yl)ethyl]amine) at 60 °C. The maximum yield of phenol was 21% based on benzene without the formation of quinone or diphenol. In an endurance test of the catalyst, complex **2** showed a turnover number (TON) of 749, which is the highest value reported to date for molecular catalysts in benzene hydroxylation with H<sub>2</sub>O<sub>2</sub>. When toluene was employed as a substrate instead of benzene, cresol was obtained as the major product with 90% selectivity. When H<sub>2</sub><sup>18</sup>O<sub>2</sub> was utilized as the oxidant, <sup>18</sup>O-labeled phenol was predominantly obtained. The reaction rate for fully deuterated benzene was nearly identical to that of benzene (kinetic isotope effect = 1.0). On the basis of these results, the reaction mechanism is discussed.

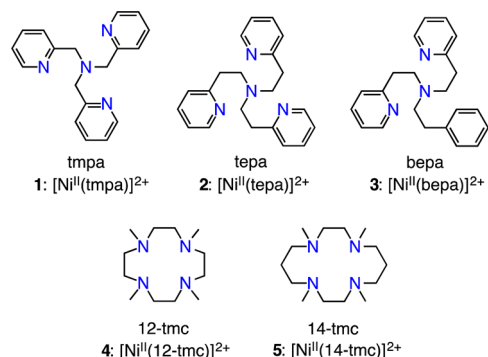
Phenol and its derivatives are an important class of chemicals as precursors of dyes, pharmaceuticals, polymers, etc.<sup>1</sup> Phenol and cresol are currently produced in industry by the cumene process, which consists of three chemical steps: propylation of benzene or toluene, autoxidation to the cumene hydroperoxide derivative, and Hock rearrangement.<sup>1,2</sup> These reactions are carried out under high temperature, high pressure, and strongly acidic conditions, and an equimolar amount of acetone is produced as a byproduct in the final step. In addition, the overall yield of phenol from benzene is very low (5%). Thus, a much simpler and more efficient process that proceeds under mild conditions is desired. In particular, a direct aromatic oxygenation reaction with an economically and environmentally benign oxidant such as O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> has remained a focal point for extensive research efforts.<sup>3–15</sup> However, the direct introduction of hydroxyl functionality into the aromatic C–H bond with such oxidants is challenging because of the notoriously low reactivity of aromatic C–H bonds and the low product selectivity caused by overoxidation of phenols.<sup>16–18</sup>

In the previous studies of transition-metal complexes of active oxygen species, dinuclear complexes such as dicopper(II)  $\mu$ - $\eta^2$ : $\eta^2$ -peroxide, dicopper(III) bis( $\mu$ -oxo), and dinickel(III) bis( $\mu$ -oxo) complexes supported by pyridylalkylamine ligands have been demonstrated to exhibit hydroxylation reactivity toward aromatic groups embedded in their supporting ligands.<sup>19–25</sup> To the best of our knowledge, however, there has been no report to

date of *intermolecular* hydroxylation of externally added benzene derivatives with transition-metal complexes supported by pyridylalkylamine ligands, although a large number of active-oxygen transition-metal complexes have been developed to date.<sup>26–29</sup> We herein report a benzene hydroxylation reaction employing nickel complexes supported by pyridylalkylamine ligands as the catalysts and H<sub>2</sub>O<sub>2</sub> as the oxidant under mild conditions.

We first examined the catalytic activity of [Ni<sup>II</sup>(tmpa)]<sup>2+</sup> (**1**) (tmpa = tris[2-(pyridin-2-yl)methyl]amine), [Ni<sup>II</sup>(tpepa)]<sup>2+</sup> (**2**) (tpepa = tris[2-(pyridin-2-yl)ethyl]amine), and [Ni<sup>II</sup>(bepa)]<sup>2+</sup> (**3**) (bepa = *N,N*-bis[2-(pyridin-2-yl)ethyl]-2-phenylethylamine) in the benzene hydroxylation reaction with H<sub>2</sub>O<sub>2</sub> (for the ligand structures, see Chart 1).<sup>30,31,25</sup> Treatment of benzene

**Chart 1. Ligands for Ni-Based Hydroxylation Catalysis**



(5.0  $\mu$ mol) with H<sub>2</sub>O<sub>2</sub> (2.5 mmol) in the presence of a catalytic amount of **1**, **2**, or **3** (0.50  $\mu$ mol, 10 mol %) and triethylamine (TEA) (5.0  $\mu$ mol) afforded phenol in 18%, 21%, or 2% yield based on benzene, respectively, after 5 h (Table 1, entries 1–3).<sup>32</sup> This is the first example of hydroxylation of benzene with H<sub>2</sub>O<sub>2</sub> catalyzed by nickel complexes. When **1** was employed as the catalyst, the overoxidation product benzoquinone (BQ) was also obtained in 9% yield. In contrast, only a negligible amount (<1% yield) of BQ was generated with catalyst **2** (Figure S1 in the Supporting Information (SI)). The 21% yield of phenol without formation of the overoxidation product (<1%) (entry 2) is the best result reported to date for homogeneous systems using H<sub>2</sub>O<sub>2</sub> (Scheme 1; for other systems, see Table S1 in the SI).<sup>33,34</sup>

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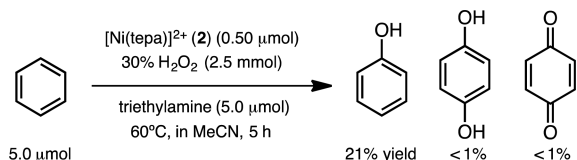
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Table 1. Catalytic Activity of Ni(II) Complexes

entry	cat	conv. (%)	yield (%)	selectivity (%)
1	1	27	18	66
2	2	23	21	>99
3	3	25	2	8
4	4	7	0	—
5	5	10	0	—

Conditions: benzene (5.0  $\mu\text{mol}$ ),  $\text{H}_2\text{O}_2$  (2.5 mmol), catalyst (0.50  $\mu\text{mol}$ ), and TEA (5.0  $\mu\text{mol}$ ) in MeCN for 5 h at 60  $^\circ\text{C}$ .

Scheme 1. Catalytic Hydroxylation of Benzene with 2



The reaction also proceeded at room temperature, but the yield was lower (14% in 5 h). When phenol was employed as the substrate (5.0 mol) with 2 under the same conditions, the hydroxylation reaction hardly took place (phenol was recovered almost quantitatively).

Nickel complexes supported by the tetraaza macrocyclic ligands such as  $[\text{Ni}^{\text{II}}(12\text{-tmc})]^{2+}$  (4) (12-tmc = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) and  $[\text{Ni}^{\text{II}}(14\text{-tmc})]^{2+}$  (5) (14-tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) did not show any catalytic ability for the reaction (entries 4 and 5).<sup>35,36</sup> Nickel(II) acetate alone or with 2,2'-bipyridine (bpy) as the ligand also did not work as the catalyst.

Since complex 2 showed the highest activity and selectivity, an endurance test was performed using 0.01 mol % 2, 0.10 mol % TEA, and 5.0 equiv of  $\text{H}_2\text{O}_2$ .<sup>37</sup> In this case, the turnover number (TON) of 2 reached 749 with a 7.5% yield of phenol after 216 h without the formation of substantial amounts of the over-oxidation products (Figure 1).<sup>38</sup> This is the highest TON

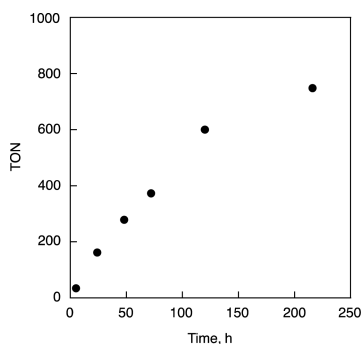


Figure 1. Time course of the turnover number in the catalytic oxidation of benzene (5.0 mmol) by  $\text{H}_2\text{O}_2$  (25 mmol) in the presence of 2 (0.50  $\mu\text{mol}$ ) and TEA (5.0  $\mu\text{mol}$ ) in 3.0 mL of MeCN at 60  $^\circ\text{C}$ .

reported for benzene hydroxylation reactions using transition-metal complexes as molecular catalysts; among molecular catalysts showing high selectivity (>95%), the polyoxometalate (POM) catalyst  $\text{Py}_1\text{-PMo}_{10}\text{V}_2\text{O}_{40}$  showed a TON of 21, which was the highest number reported previously (Table S1).

The system could also be applied to the hydroxylation of toluene. In the presence of 5 equiv of  $\text{H}_2\text{O}_2$  and 0.01 mol % 2, the TON reached 96 after 24 h to give cresol as the major product without the formation of quinone derivatives (Table 2, entry 1).

Table 2. Product Distributions in Catalytic Oxidation of Alkylbenzenes with 2

entry	substrate	BDE, kcal mol <sup>-1</sup>	sp <sup>2</sup> :sp <sup>3</sup> :q <sup>a</sup>	product, (o/m/p/i) <sup>b</sup>	selectivity, <sup>c</sup> %	TON <sup>d</sup>
1	toluene	90	90:10:<1	(57:18:25:0)	90	96
2	ethylbenzene	87	55:45:<1	(48:20:25:7)	51	91
3	cumene	84.5	71:29:<1	(42:21:27:10)	64	46

Conditions: substrate (5.0 mmol),  $\text{H}_2\text{O}_2$  (5 equiv), 2 (0.01 mol %), and TEA (0.10 mol %) in  $\text{CH}_3\text{CN}$  at 60  $^\circ\text{C}$  for 24 h. <sup>a</sup>Ratio of products given by aromatic hydroxylation (sp<sup>2</sup>), alkyl-substituted oxygenation (sp<sup>3</sup>), and quinone derivatives (q). <sup>b</sup>Ratio of products of hydroxylation at the ortho, meta, para, and ipso positions. <sup>c</sup>Selectivity for aromatic hydroxylation products except phenol. <sup>d</sup>Calculated on the basis of the amount of aromatic hydroxylation products, except for phenol, which was calculated on the basis of the substrate.

It should be noted that the aromatic sp<sup>2</sup> carbons were preferentially oxygenated with a high selectivity of 90% (Scheme S1 in the SI) despite the fact that the bond dissociation energy (BDE) of the C–H bond of a benzylic sp<sup>3</sup> carbon (90 kcal mol<sup>-1</sup>) is much lower than that of an aromatic C–H bond (112 kcal mol<sup>-1</sup>).<sup>39</sup>

Mizuno and co-workers reported selective aromatic oxygenation of toluene with  $\text{H}_2\text{O}_2$  using the POM catalyst  $[\gamma\text{-PW}_{10}\text{O}_{38}\text{V}_2(\mu\text{-OH})_2]^{3-}$ , where a high aromatic carbon to benzylic carbon selectivity of 98:2 was obtained. However, the total selectivity for cresol decreased to 86% as a result of overoxidation of cresol to methyl-*p*-quinone. Thus, the present system showed the highest selectivity for cresol formation from toluene with  $\text{H}_2\text{O}_2$ .<sup>40</sup> The regioselectivity of the present system was also different from that of Mizuno's system: with nickel catalyst 2, the ortho position was mainly oxygenated, whereas the para position of toluene was mainly oxygenated with Mizuno's system. Stimulated by this result, we examined the oxygenation of other alkylbenzene derivatives with more reactive benzylic C–H bonds, namely, ethylbenzene (BDE = 87 kcal mol<sup>-1</sup>) and cumene (BDE = 84.5 kcal mol<sup>-1</sup>), in the presence of a catalytic amount of 2 (0.01 mol %).<sup>39</sup> To our delight, oxygenation of the sp<sup>2</sup> carbons of those substrates also proceeded, although the selectivity for sp<sup>2</sup> carbons slightly decreased (Table 2, entries 2 and 3; for a comparison with previous reports, see Tables S3–S5). In these cases as well, no overoxidation products such as hydroquinone or quinone derivatives were obtained (Schemes S2 and S3). In the oxygenations of ethylbenzene and cumene, the ortho position was mainly attacked, as in the case of toluene oxygenation. However, the selectivity slightly decreased with increasing bulkiness of the substituent, and the selectivity for the ipso position to produce phenol increased.

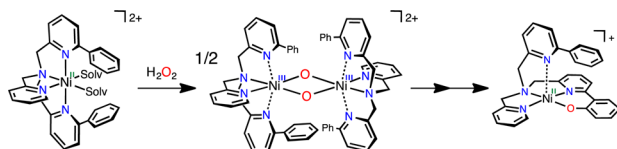
To gain insight into the reaction mechanism, the kinetic isotope effect (KIE) was examined using a 1:1 mixture of  $\text{C}_6\text{D}_6$  and  $\text{C}_6\text{H}_6$ . From the ratio of phenol to phenol-*d*<sub>5</sub>, the KIE value was determined to be 1.0, which is close to the KIE values for intramolecular aromatic hydroxylation of the dicopper(II)  $\mu$ -

$\eta^2:\eta^2$ -peroxide, dicopper(III) bis( $\mu$ -oxo), and dinickel(III) bis( $\mu$ -oxo) complexes (0.9–1.0).<sup>21–23</sup> Such a small or negligible KIE value is typical in aromatic hydroxylation by metal–active oxygen species via the electrophilic aromatic substitution mechanism.<sup>41</sup> Such a KIE value also suggests that a Fenton-type reaction is not likely to be involved, as the KIE value for the Fenton reaction was reported to be 1.7.<sup>42</sup> Metal insertion is not a plausible mechanism either, as the KIE value for C–H bond activation via Pd(0) insertion was reported to be 2.9–4.8.<sup>43</sup>

To verify the origin of the oxygen atom, benzene oxygenation was carried out using  $\text{H}_2^{18}\text{O}_2$  with 90% atom purity in  $\text{H}_2^{16}\text{O}$ . In this case,  $^{18}\text{O}$  was incorporated into the phenol product nearly quantitatively (92%), whereas no  $^{18}\text{O}$  atom was incorporated into the product when the reaction was carried out in  $\text{H}_2^{18}\text{O}$  using  $\text{H}_2^{16}\text{O}_2$ . These results unambiguously indicated that  $\text{H}_2\text{O}_2$  is the oxygen source in the present reaction.<sup>44</sup>

A number of nickel complexes supported by pyridylalkylamine ligands, including *N,N*-bis[( $\mu$ -phenylpyridin-2-yl)methyl]-*N*-[(pyridin-2-yl)methyl]amine ( $\text{Ph}_2\text{tmpa}$ ) and *bepa* have been demonstrated to generate dinickel(III) bis( $\mu$ -oxo) complexes in the reaction with  $\text{H}_2\text{O}_2$ . Moreover the Suzuki group and our group have independently reported intramolecular aromatic oxygenation in the dinickel(III) bis( $\mu$ -oxo) supported by pyridylalkylamine ligands under low-temperature conditions (Scheme 2).<sup>45</sup> In fact, a nickel(II) complex supported by

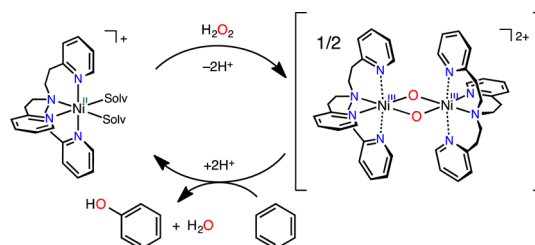
**Scheme 2. Intramolecular Aromatic Hydroxylation by a Dinickel(III) Bis( $\mu$ -oxo) Complex<sup>25</sup>**



$\text{Ph}_2\text{tmpa}$  could oxygenate benzene under the same reaction conditions as shown in Table 1, although the yield of phenol was only 3%. The low yield could be attributed to the competitive intramolecular reaction, as the product of intramolecular oxygenation of the phenyl group of the ligand was also found in the electrospray ionization (ESI) mass spectrum of the final reaction solution (Figure S2). Hydroxylation of aliphatic C–H bonds has also been demonstrated to be a characteristic feature of dinickel(III) bis( $\mu$ -oxo) complexes supported by pyridylalkylamine ligands, whereas aliphatic hydroxylated products are minor products in the present alkylbenzene oxygenation.<sup>46–49</sup> By contrast, nickel(II) complexes supported by the tetraaza macrocyclic ligands 12-tmc and 14-tmc have been shown to provide a mononuclear nickel(III) peroxide complex and a nickel(II) superoxide complex, respectively, in the reaction with  $\text{H}_2\text{O}_2$ ; neither Ni(III) peroxide nor Ni(II) superoxide species are known to have H-atom transfer reactivity.<sup>35,36,50–52</sup> It should be also noted that the reaction of ethylbenzene and *m*-chloroperoxybenzoic acid catalyzed by complex 2 exclusively provided 1-phenylethanol ( $\text{sp}^3$ -carbon oxygenation product) rather than ethylphenol, where we proposed that a Ni(II) oxyl radical-type species is involved as the key reactive intermediate.<sup>31</sup> On the basis of these results, we propose that a dinickel(III) bis( $\mu$ -oxo) complex is the most plausible reactive intermediate in the present reaction, as illustrated in Scheme 3.

In summary, we have demonstrated the catalytic ability of nickel complexes in direct benzene hydroxylation with  $\text{H}_2\text{O}_2$  for the first time. In particular, the nickel complex 2 supported by

**Scheme 3. Proposed Catalytic Mechanism**



*tepa* exhibited a prominent ability to produce phenol in 21% yield based on benzene without the formation of any overoxidation products. The total turnover number of the nickel complex supported by *tepa* reached 749, which is the highest value ever reported for molecular catalysts. The aromatic hydroxylation method has been shown to be applicable to oxygenation of alkylbenzene derivatives. The selectivity for *cresol* in the toluene hydroxylation reached 90%, which is also the highest reported value for direct hydroxylation of toluene to *cresol* with  $\text{H}_2\text{O}_2$  and a molecular catalyst. Details of the reaction mechanism and the reason for the bizarre selectivity are now under investigation.<sup>53</sup>

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b01814.

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### Notes

The authors declare no competing financial interest.

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- (33) A large part of the H<sub>2</sub>O<sub>2</sub> (44%) remained after the reaction.
- (34) For catalyst 3, we observed ligand hydroxylation at the benzylic position of the phenethyl arm in about 10% yield by <sup>1</sup>H NMR analysis, whereas we did not detect such a ligand-hydroxylated product with catalyst 2. For details, see the SI.
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