Catalytic Alkane Hydroxylation Reaction with Nickel(II) Complexes Supported by Di- and Triphenol Ligands

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Ni^{II}-complexes supported by the tetradentate ligands containing two or three 2,4-di-*tert*-butylphenol groups were synthesized and structurally characterized. The Ni^{II}-complex of the diphenol ligand has been found to act as a very efficient turnover catalyst in the alkane hydroxylation reaction with *m*-chloroperbenzoic acid (*m*-CPBA).

A variety of transition-metal complexes such as Fe, Co, Mn, Ru, and Cu-complexes have extensively been examined as the catalysts for selective hydroxylation of alkanes (saturated hydrocarbons) with various oxidants in synthetic organic chemistry and industrial chemistry.[1–6] Especially, a great deal of attention has been paid to the heme and non-heme iron complexes due to their high catalytic activity and biological relevance.[2]

Recently, we have found that a simple Ni^{II}-complex such as $[Ni^{II}(TPA)(OAc)(H_2O)]BPh_4$ [TPA = tris(2-pyridylmethyl)amine] works as an efficient catalyst for alkane hydroxylation with *m*-CPBA (Scheme 1).[7] The overall catalytic efficiency (catalytic activity, product selectivity, and stability) of Ni^{II}(TPA) was higher than that of Fe^{II}, Mn^{II}, and Co^{II}-complexes of the same ligand (TPA), suggesting that nickel is an attractive transition metal for the development of efficient catalysts for alkane-hydroxylation.[7] Furthermore, we have examined the ligand effects on the alkane hydroxylation reaction catalyzed by a series of Ni^{II}-complexes to demonstrate that the supporting ligands greatly affect both the reactivity and the product-selectivity (alcohol vs ketone).[8] One of the intriguing results of such study was that the Ni^{II}-complex **1** supported by monophenol ligand L1H (see Chart 1) gave a higher catalytic activity as compared to that of Ni^{II}(TPA).[8] These results stimulated us to examine further the catalytic efficiency of the Ni^{II}-catalysts supported by diphenol and triphenol ligands such as $L2H_2$ [*N*-(2-pyridylmethyl)-*N*,*N*-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine] and $L3H_3$ [tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine] shown in Chart 1. The structure and catalytic activity of the Ni^{II}-complexes have been examined in detail to gain deeper insight into the ligand effects on the catalytic activity of Ni^{II}.

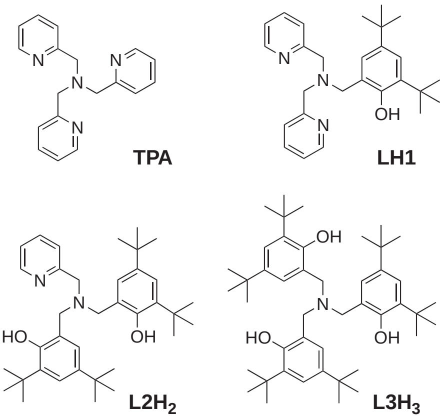


Chart 1. Supporting ligands.

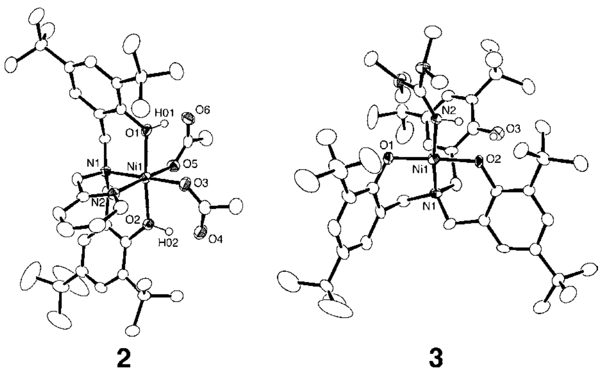
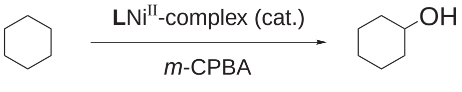


Figure 1. ORTEP drawings of $[Ni^{II}(L2H_2)(OAc)_2]$ (**2**) (left) and $[Ni^{II}(L3H)(TMG)]$ (**3**) (right) showing 50% probability thermal ellipsoids. The hydrogen atoms attached to the carbon atoms are omitted for clarity.

The Ni^{II}-complex supported by the diphenol ligand, $[Ni^{II}(L2H_2)(OAc)_2]$ (**2**), was synthesized in 73% by mixing $L2H_2$ and an equimolar amount of $Ni^{II}(OAc)_2{\cdot}4H_2O$ in CH_2Cl_2/MeOH mixed solvent system.[9] Complex **2** was recrystallized from acetonitrile to afford pale-blue single crystals suitable for X-ray crystallographic analysis.[9] Complex **2** exhibits a slightly distorted octahedral geometry with an N_2O_4 donor set provided by the ligand and two monodentate acetate counter anions as shown in Figure 1 (left). It should be noted that both phenol protons in **2** are retained and involved in the strong hydrogen-bonding interaction with the carbonyl oxygen atom of the monodentate acetate co-ligands. (H(01)–O(6) 1.46 Å and H(02)–O(4) 1.49 Å).



Scheme 1.

In the case of triphenol ligand $L3H_3$, however, just mixing the ligand and $Ni^{II}(OAc)_2{\cdot}4H_2O$ did not afford any Ni^{II}-complex under the same experimental conditions. On the other hand, addition of a slightly excess of 1,1,3,3-tetramethylguanidine (TMG) as a base gave a Ni^{II}-complex, $[Ni^{II}(L3H)(TMG)]$ (**3**), although the yield was not sufficient enough (24% isolated yield).[9] Single crystals suitable for X-ray crystallographic analysis were obtained from a hexane solution of **3**.[9] Complex **3** shows a four-

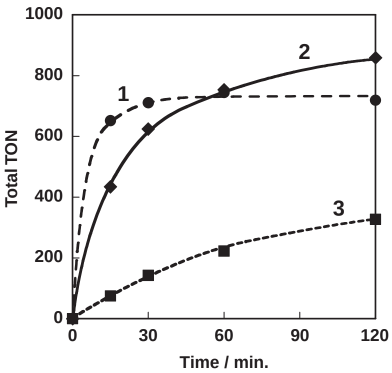


Figure 2. Time courses for the oxidation of cyclohexane (2.5 M) with *m*-CPBA (0.33 M) catalyzed by **1** (●), **2** (◆), and **3** (■) (0.33 mM) in CH_2Cl_2/CH_3CN (v/v = 3/1, total 6 mL) at room temperature.

coordinate distorted square planer geometry with an N_2O_2 donor set, in which two deprotonated phenolate oxygen atoms O(1) and O(2), tertiary amine nitrogen N(1), and the imine nitrogen N(2) of the TMG co-ligand are involved (Figure 1, right). Thus, one of the phenol groups of the ligand is free from coordination.

Catalytic activity of the Ni^{II}-complexes was examined using cyclohexane as the substrate and *m*-CPBA as the oxidant (Scheme 1).[9] Figure 2 shows the time courses of total turnover number (TON) of the catalysts. In all the cases, cyclohexanol was obtained as a major product together with a small amount of cyclohexanone and a trace amount of over oxidation product ε-caprolactone. As reported previously, the monophenol complex **1** acted as an efficient turnover catalyst to give total TON as 719 and alcohol product selectivity (A/K; alcohol/ketone ratio) as 7.2 after 2 h. When the diphenol complex **2** was employed as the catalyst, the total TON and A/K values became larger as 858 and 7.7, respectively, although the turnover rate at the initial stage of the reaction (ca. 30 min) was little lower (Figure 2).[10] On the other hand, complex **3** exhibited relatively low catalytic activity as compared to **1** and **2**, whereas the A/K value (65) of **3** was much higher than that of others.

Although the details of the catalytic mechanism have yet to be clarified, we proposed that a nickel–oxo (Ni^{II}–O• or Ni^{III}=O) species is involved as a key reactive intermediate for the alkane-hydroxylation.[7,8] Introduction of the additional phenol group into L1H to give $L2H_2$ may enhance the durability of the catalyst. Namely, self-degradation of the catalyst may be suppressed in **2**, allowing the high TON, even though the turnover rate became a little lower (Figure 2). On the other hand, the triphenol ligand $L3H_3$ itself may not fit to the octahedral geometry, which is required for the *m*-CPBA-binding to generate the nickel–oxo species. Thus, **3** may exhibit the lower catalytic activity. Nonetheless, significantly high alcohol selectivity (A/K = 65) of **3** is noteworthy.

Another advantage of catalyst **2** is its high solubility to non-polar organic solvent. Thus, the oxidation of cyclohexane (15 mmol, 1.62 mL) with **2** (0.002 mmol) in the presence of *m*-CPBA (0.4 mmol, suspended) can be carried out without adding any other solvent to yield cyclohexanol in 93% together with a small amount of cyclohexanone (7%) based on the oxidant (the oxidant efficiency was 100%, A/K = 13.3).[9]

In summary, we have succeeded in developing a significantly efficient Ni^{II}-catalyst for the alkane hydroxylation reaction with *m*-CPBA using diphenol ligand $L2H_2$. Optimization of the reaction conditions as well as characterization of the active oxygen species is now under investigation.

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9 Supporting Information (experimental procedures and X-ray stractural determination) is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html. Crystallographic data of **2** and **3** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-640872 and -640873, respectively.

10 After a prolonged reaction time (24 h), the total TON reached ca. 1000 and all the *m*-CPBA (0.33 M) was consumed. Thus, the product yield based on the oxidant was ca. 100%, demonstrating the high durability of the catalyst.