All reaction products described in the notes were identified by comparison of their physical data (m.s., n.m.r. and i.r.).

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4. Physical data of compound (3); an oil (172 mg, 33%), NMR (CDCl₃), δ 1.76 (6H, S, CH₃), 2.18 (3H, S, arom. CH₃), 3.85 (1H, brd, J=7.9 Hz, Benzylic H), 5.50 (1H, brs, olefinic H), 6.20 (2H, brs, arom. H); MS (107°) m/e, 260 (M⁺, 23), 190 (19), 175(100); IR (film), 3300, 1620, 1585, 1450 cm⁻¹.
5. Physical data of compound (4); an oil (213 mg, 42%); NMR (CDCl₃), δ 1.26 (3H, s, CH₃), 1.76 (6H, brs, CH₃), 2.18 (3H, S, arom. CH₃), 3.46 (2H, brd, J=7.7 Hz, benzylic H), 5.48 (1H, brs, olefinic H), 6.09 (1H, s, arom. H), 6.23 (1H, d, J=2.3 Hz, arom. H); MS (102°), m/e 260 (M⁺, 32), 175 (100); IR (film), 3425, 1628, 1585, 1450 cm⁻¹.
6. Physical data of compound (5); an oil (208 mg, 40%); NMR (CDCl₃), δ 0.94 (3H, d, J=7.1 Hz, CH₃), 1.08 (3H, d, J=7.9 Hz, CH₃), 1.33 (3H, s, CH₃), 2.20 (3H, S, arom. CH₃), 3.33 (2H, d, J=2.3 Hz, benzylic H), 6.11 (1H, s, arom. H), 6.26 (1H, S, arom. H); MS (59°), m/e 260 (M⁺, 15), 175 (100); IR (film), 3350, 1623, 1580, 1440 cm⁻¹.
7. The general procedure is as follows; BF₃-etherate (0.4 ml) was added under nitrogen to a stirred suspension of basic aluminum oxide (woelm, grade I) (4 g) in dry dichloromethane (40 ml). The mixture was stirred for 5 min, at room temperature. Nerol (1) (308 mg, 2.0 mmol) and orcinol (2) (284 mg, 2.0 mmol) in dichloromethane 6 ml) were added to the suspension by syring and the reaction was quenched after 5 min with 10% aqueous solution of sodium bicarbonate (20 ml). Ether (100 ml) and an additional proportion of the above sodium bicarbonate solution (100 ml) were added. The organic layer was washed with brine, dried and evaporated to dryness. The oil obtained was separated by Flash Chromatography (240-400 mesh ASTM, silica gel 60, for column chromatography; elution with ethyl ether to *n*-Hexane 5 : 95).

## Epoxidation of Styrene Catalyzed by Ni(II)- and Cu(II)-Macrocyclic Complexes

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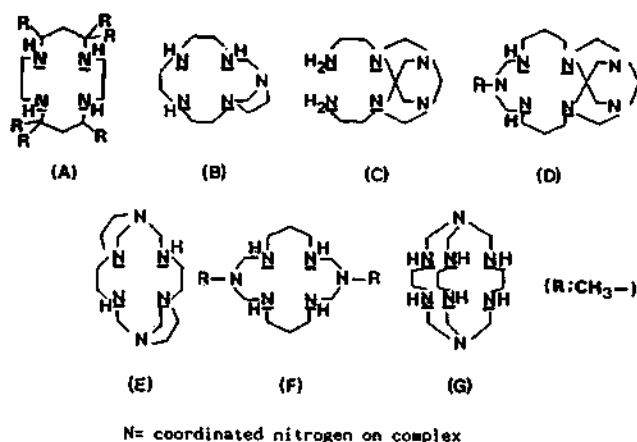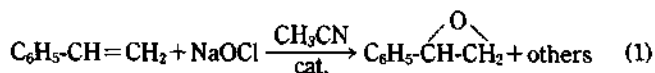N= coordinated nitrogen on complex

**Figure 1.**

The direct oxidation of olefins is a field of both academic and industrial importance and challenge. Catalysis by metal complexes plays a central role in partial selective oxidation of olefins to useful products. The use of transition metal complexes as catalysts for epoxidation reaction has received an increased attention during the past two decades. There are many reasons for this increased interest; e.g., the requirement for functionalization of lower alkenes formed as byproducts in the manufacture of gasoline by gas oil cracking, the interest in understanding reactions of biological importance, the need for partial selective oxidation, and the preparation of compounds with a specific spatial structure[1]. Recently epoxidation reaction by macrocyclic complexes has been studied in conjunction with mimicking the enzymatic reaction[2-5].

We now report that nickel(II) and copper(II) complexes of macrocyclic ligand ranging from tetraazamacrocycle to octaazamacrocycle are highly effective catalysts for styrene epoxidation by sodium hypochlorite in acetonitrile and that unlike previously reported systems, we observed various selectivity for styrene oxide depending on the types of polyaza-macrocyclic ligand coordinated to nickel(II) and copper(II).

The macrocyclic complexes used as catalysts were prepared by the literatures methods[6-10] and the ligands were shown in Figure 1.

The catalytic epoxidation of styrene by macrocyclic complexes could be described as Eq. (1).

$$C_6H_5\text{-}CH=CH_2 + NaOCl \xrightarrow[\text{cat.}]{CH_3CN} C_6H_5\text{-}\overset{\displaystyle O}{CH\text{-}CH_2} + \text{others} \quad (1)$$

In a typical experiment, sodium hypochlorite (4 mmol) was slowly added in the air over a period of 30 minutes to a solution of the complex (0.05 mmol) and styrene (1 mmol) in 5 ml of acetonitrile. The reaction was monitored by a Hwelett-Packard 5890 gas chromatography (GC) equipped with a 50 m FFAP capillary column and FID detector (oven temperature = 150°C ; carrier gas pressure = 30 psi; split ratio = 30 : 1).

In the absence of the metal complexes, conversions of styrene were about 5-6% and formation of styrene oxide was only trace. All the nickel(II) complexes were active catalysts for the styrene oxidation. Ni(A)²⁺ (tetraazamacrocyclic complex) gave 94% of styrene oxide and 1% of phenylacetalde-

**Table 1.** Catalytic Activities of Ni(II)-Macrocyclic Complexes for Oxidation of Styrene

| $(N_{uc}/N_t)^a$ | Styrene oxide | Benzaldehyde | Phenylacet-aldehyde |
|---|---|---|---|
| $A_1^b$ (0/4) | $94^d$ $(18.8)^e$ | 5 (1.2) | 1 (0.2) |
| $A_2^c$ (0/4) | 94 (18.2) | 7 (1.4) | 2 (0.4) |
| B (1/5) | 78 (15.6) | 6 (1.3) | 15 (3.1) |
| C (2/6) | 77 (15.4) | 14 (2.8) | 9 (1.8) |
| D (2/6) | 71 (14.2) | 9 (1.8) | 18 (3.6) |
| E (2/6) | 67 (13.4) | 5 (1.2) | 25 (5.1) |
| F (2/6) | 67 (13.4) | 8 (1.6) | 25 (5.1) |
| G (2/8) | 63 (12.6) | 7 (1.4) | 23 (4.7) |

Experimental conditions were complex (0.05 mmol), styrene (1 mmol), NaOCl (4 mmol), acetonitrile (5 ml), temp. (40℃), and time (5 hr). $^aN_{uc}$=un-coordinated nitrogen number on complex, $N_t$=total ni-trogen number in ligand. $^b$meso-, $^c$racemic-, $^d$Yields (%) were based on initial styrene concentrations. $^e$turnover.

**Table 2.** Catalytic Activities of Cu(II)-Macrocyclic Complexes for Oxidation of Styrene

| $(N_{uc}/N_t)^a$ | Styrene oxide | Benzaldehyde | Phenylacet-aldehyde |
|---|---|---|---|
| F (2/6) | 53 (10.6) | 27 (5.4) | 20 (4.0) |
| B (1/5) | 51 (10.2) | 27 (5.4) | 22 (4.3) |

All experimental conditions and explanations were the same as in Ni(II)-system.

hyde (yields based on styrene and turnovers based on complex). However, when ligands with uncoordinating nitrogen atoms were used (B-G) yield of styrene oxide decreased and that of phenylacetaldehyde increased. For example, Ni(G)²⁺ (octaazamacrocyclic complex) gave 63% of styrene oxide and 23% of phenylacetaldehyde. Role of the uncoordinating nitrogen atoms in the catalytic reaction is currently under investigation. Meso-Ni(A)²⁺ and racemic-Ni(A)²⁺ isomers showed almost the same product distribution which indicates that catalytic activity is not affected by the small steric effect due to the different methyl group arrangements of meso- and racemic-A. Small amounts (5-9%) of benzaldehyde as C=C cleavage product⁴ were observed in all nickel(II) complex systems except for Ni(C)²⁺ (non-cyclic hexaazaligand) (14 %). Cu(F)²⁺ and Cu(B)²⁺ were observed less effective catalysts for the formation of styrene oxide. However, yields of benzaldehyde were increased in copper(II) complexes more than nickel(II) complexes. Hydrogen peroxide and *tert*-butyl hydroperoxide were ineffective as an oxidant for styrene epoxidation.

$$LM^{II} \xrightarrow{\ OCl^-\ } L\overset{\overset{\textstyle O\cdot}{|}}{M^{III}}$$
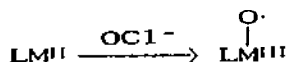
**1**

The mechanism of the present catalytic oxidation of styrene has not new elucidated. Several mechanisms have been proposed in the similar systems³⁻⁵. However, the structure of the active species generated from the reaction of nickel(II)

and copper(II) polyazamacrocyclic complexes with NaOCl was still unknown. Recently, structure **1** was reported a likely candidate for the active species formed with complex and OCl⁻. We believe that the same species might also be invaluable in our systems. **1** has considerable radical character at the oxygen, its addition to an styrene would proceed in stepwise to generate products observed.

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## Cyclopolymerization of 4-Hydroxy-4-phenyl-1,6-heptadiyne Containing Hydroxy Functional Group by Transition Metal Catalysts

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There have been many studies on polyacetylene¹ because of its unique properties. Polyacetylene is, however, unstable in air and insoluble in ususal organic solvents. Thus, though the electrical conductivity is somewhat low, studies of the synthesis and properties of substituted polyacetylene which