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# Syntheses of monomeric iron and manganese complexes using bulky tripodal ligands: catalytic alkene epoxidations

Jinyuan Chen, L. Keith Woo *

*Department of Chemistry, Iowa State University, Gilman Hall, Ames, IA 50011-3111, USA*

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**Abstract**

Sterically encumbered monomeric transition-metal complexes were examined as epoxidation catalysts. Bulky ligands such as tetradentate triamidoamines of the type $[(RNCH_2CH_2)_3N]^{3-}$ and tridentate tris(3-*t*-butylpyrazolyl)borate were used to diminish the deactivation of the catalysts via μ-oxo dimerization. Several monomeric manganese and iron complexes, including $M[(RNCH_2CH_2)_3N]$ [R = trimethylsilyl: $M = Mn^{3+}$ (**1**); $R = C_6F_5$: $M = Fe^{3+}$ (**2**), $Mn^{3+}$ (**3**)], $\{\eta^3\text{-HB(3-}^t\text{BuPz)}_3\}$MCl [$M = Fe^{2+}$ (**4**), $Mn^{2+}$ (**6**)] and $\{\eta^3\text{-HB(3-}^t\text{BuPz)}_3\}$FeOTf (**5**), were synthesized and examined as possible catalysts for the selective epoxidation of norbornylene and styrene. Oxygen atom sources were PhIO or molecular $O_2$–isobutyraldehyde. With PhIO as the oxidant, complexes **1**, **3**, and **6** oxidized norbornylene and styrene catalytically to the corresponding epoxides in high selectivity, while complexes **2** and **4** exhibited low epoxidation activity. By using $O_2$ with isobutyraldehyde as a co-reductant, complexes **1**, **3**, **4**, and **6** showed efficient catalytic activity with high selectivity and reaction rate for epoxidation, in comparison to control experiments without a catalyst. Complex **4** with $O_2$ and isobutyraldehyde also catalyzed the epoxidation of stilbenes to epoxides. Both *cis*- and *trans*-stilbenes are converted mainly to the *trans*-stilbene oxide. The possible role of the metal complexes as the active epoxidation catalysts is discussed. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Oxidation; Epoxidation; Catalysis; Iron; Manganese

## 1. Introduction

Epoxides are one of the most versatile and important intermediates for the synthesis of oxygen-containing organic compounds both in industry and in academic laboratories. During the past 15 years, significant effort has been directed towards finding synthetically useful and economically affordable transition-metal complexes for selectively catalyzing the epoxidations of olefinic compounds with common oxidants, such as iodosobenzene, peroxides ($^t$BuOOH, $H_2O_2$ etc.), and sodium hypochlorite [1]. To date, numerous manganese(III) and iron(III) porphyrins including cytochrome *P*-450 have been studied as monooxygenation catalysts [2]. Non-heme complexes such as manganese Schiff base complexes [3], titanium–tartrate complexes [4], manganese triazacyclononane complexes [5], methyltrioxorhenium [6], ferric bleomycin [7], and other transition-metal complexes [8] have also been developed to catalyze olefin epoxidations. Recently, selective olefin epoxidation using molecular oxygen under mild reaction conditions has also been studied intensively. Several catalytic systems including iron(III) porphyrins–$O_2$–$H_2$ on colloidal platinum [9] and (tetra-mesitylporphinato)ruthenium [10] have been employed successfully for this purpose. Another simple catalytic system, which combines molecular oxygen, primary or secondary aldehydes (or alcohols) and transition-metal complexes, also selectively epoxidizes alkenes under mild temperature and pressure. For example, nickel(II) bis(1,3-diketonato) complexes [11,12], oxovanadium(IV) bis(2-alkyl-1,3-diketonato) complexes [12,13], Fe(III) tris(1,3-diketonato) complexes [12,14], and several polyoxoanion-supported precursors (such as $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$) [15], etc. can selectively convert olefins to epoxides in high to quantitative yields by the combined use of an atmosphere of oxygen in the presence of aldehydes or alcohols. From this previous research, it was found that

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* Corresponding author. Fax: + 1-515-2949623.

*E-mail address:* kwoo@iastate.edu (L.K. Woo)

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epoxidations are dependent upon the solvent, the types of aldehydes, the metal complexes used, and the reaction conditions.

One of the major problems in the application of homogeneous transition-metal complexes as catalysts for selective olefin epoxidation results from catalyst decomposition or degradation. Deactivation pathways include autoxidation, dimerization through the formation of μ-oxo bridges [16a] or oxidative degradation via the formation of multinuclear μ-oxo complexes [16b]. Decreasing the degradative dimerization of the catalytic centers has been achieved by methods such as intercalation or encapsulation of the metal complex in layered compounds or within the cavities of a porous solid (e.g. zeolites) [17], binding the metal complex to a polystyrene matrix [18], and using steric hindrance [19].

In this study, we synthesized several monomeric iron and manganese complexes with sterically demanding ligands including $[Mn(N_3N)]$ ($N_3N = [N(CH_2CH_2NSi(CH_3)_3)_3]$), $[M(N_3N)']$ ($M = Fe(III), Mn(III)$, $(N_3N)' = [N(CH_2CH_2NC_6F_5)_3]$), and several (tris(3-*tert*-butylpyrazolyl)hydroborato)iron(II) and manganese(II) complexes [20], to study their catalytic activity for alkene epoxidation. Several transition-metal complexes utilizing similar ligands have been used as model compounds to mimic the dioxygen binding sites in enzymes [16b]. However, their use as alkene epoxidation catalysts has not been reported to the best of our knowledge. Several related μ-oxo binuclear iron complexes with Tp ligands (Tp = general hydrotris(pyrazolyl)borato ligand) were used for the oxidation of alkanes and hydroxylation of alkanes and arenes [21].

## 2. Experimental

All of the following reactions were carried out under an $N_2$ atmosphere using standard Schlenk or glovebox techniques [22], unless specified. Diethyl ether, tetrahydrofuran, hexanes, benzene and toluene were dried over purple solutions of Na–benzophenone, degassed with three freeze–pump–thaw cycles, and stored in a glovebox after being vacuum-distilled. Methylene chloride was prepared similarly, except $CaH_2$ was used as the drying agent. Styrene (Aldrich) was dried with $CaH_2$ and stored at −30°C in a glovebox after being degassed and vacuum-distilled. Norbornylene (Aldrich) was dried by heating with Na in an evacuated, sealed flask and vacuum-distilled. Isobutyraldehyde (Aldrich) was distilled under $N_2$ and stored in a sealed bottle at −30°C before use. Anhydrous $MnCl_2$ was obtained via dehydration of $MnCl_2 \cdot 4H_2O$ in refluxing thionyl chloride [23]. PhIO [24], $Li_3(Me_3SiNCH_2CH_2)_3N(THF)_2$ [25], $MnCp_2$ (Cp = cyclopentadienyl) [26], $[FeCp_2]OTf$ (OTf = trifluoromethylsulfonate) [27], $Fe[N(SiMe_3)_2]_3$ [28], $Mn[N(SiMe_3)_2]_3$ [29], and $N(CH_2CH_2NHC_6F_5)_3$ [30] were prepared according to literature procedures. Potassium hydrotris(3-*tert*-butylpyrazol-1-yl)borate was a gift from Professor Gerard Parkin, which was synthesized following the literature procedure [31]. Other reagents were used as received without further purification.

Elemental analyses were performed in house on a Perkin–Elmer CHNS/O analyzer, or by Quantitative Technologies Inc., Whitehouse, NJ. NMR spectra were obtained on a Varian VXR-300 spectrometer. Infrared spectra were obtained as Nujol mulls with an IBM/Bruker IR-98 spectrometer. Gas chromatography was performed on Hewlett 5890 Series II gas chromatograph. HPLC was performed on a Millipore Waters chromatograph (model 501) with a 3.9 × 150 mm column packed with Nova-Pak $C_{18}$.

### 2.1. Preparation of $Mn[N_3N]$, ($N_3N = N(CH_2CH_2NTMS)_3$) (**1**)

The preparation of $Mn[N_3N]$ was similar to that reported for $Mn[N(CH_2CH_2N(SiMe_2{}^tBu))_3]$ [32]. To a stirred solution of $MnCp_2$ (0.309 g, 1.67 mmol) in 20 ml THF, white microcrystals of $Li_3(Me_3SiNCH_2CH_2)_3N(THF)_2$ (0.876 g, 1.67 mmol) were added slowly. After 7 h, the solution was dried in vacuo and the residue was redissolved in 30 ml pentane. The pentane solution was filtered through a layer of Celite, the filtrate was concentrated to 4 ml under reduced pressure, and cooled to −30°C to deposit light pink crystals. $Li(THF)[Mn(N_3N)]$ was isolated by filtration and dried in vacuo (0.45 g in three crops, 53%). To a stirred solution of $Li(THF)[Mn(N_3N)]$ (0.439 g, 0.864 mmol) in 40 ml $Et_2O$ at −40°C was added $[FeCp_2]OTf$ (0.290 g, 0.865 mmol). The color of the solution changed immediately to dark green. The solution was warmed to ambient temperature, stirred for 2 h, and then taken to dryness in vacuo. The residue was extracted with 30 ml pentane and the pentane solution was filtered to remove LiOTf. The filtrate was taken to dryness in vacuo and $FeCp_2$ was sublimed from the residue at < 0.002 Torr for 5 h. The solid was then redissolved in a minimum amount of pentane (5 ml). Slow evaporation of pentane at ambient temperature resulted in the precipitation of brown crystals. $Mn[N_3N]$ was isolated after filtration and dried in vacuo (0.15 g, 42%). MS: *m*/*e* 414 [$M^+$ 414.7]. $^1H$-NMR shows no signals between −30 and 100 ppm. Anal. Calc. for $MnC_{15}H_{39}N_4Si_3$: C, 43.45; H, 9.48; N, 13.51. Found: C, 41.01; H, 8.79; N, 12.33%.

### 2.2. Preparation of $Fe[N_3N]'$ ($[N_3N]' = N(CH_2CH_2NC_6F_5)_3$) (**2**)

Benzene (20 ml) was added to a flask containing $Fe[N(SiMe_3)_2]_3$ (0.298 g, 0.554 mmol) and $N(CH_2CH_2$

$NHC_6F_5)_3$ (0.352 g, 0.546 mmol). The solution was refluxed for about 64 h until almost no starting materials were observed by $^1$H-NMR. The solution was dried and the residue was redissolved in a minimum amount of hexanes (3 ml). The hexanes solution was cooled to −35°C to deposit dark brown crystals. Fe[$N_3N$]′ was isolated by filtration and dried in vacuo (0.082 g, 21%). MS: *m*/*e* 697 [M$^+$ 697.2]. Anal. Calc. for $FeC_{24}H_{12}F_{15}N_4$: C, 41.35; H, 1.73; N, 8.00. Found: C, 41.18; H, 1.92; N, 7.92%.

### 2.3. Preparation of Mn[$N_3N$]′ ([$N_3N$]′ = $N(CH_2CH_2NC_6F_5)_3$) (**3**)

To a stirred, cold solution of $N(CH_2CH_2NHC_6F_5)_3$ (0.0877 g, 0.136 mmol) in about 12 ml hexanes (−34°C) was added a $Mn[N(SiMe_3)_2]_3$ (0.0724 g, 0.135 mmol) solution in 3 ml hexanes (also cooled to −34°C). After the solution was warmed to room temperature (r.t.) and stirred for an additional 6.5 h, an aliquot of the violet solution was dried in vacuo and dissolved in $C_6D_6$. $^1$H-NMR spectroscopy indicated that the reaction was not complete. The reaction mixture was refluxed for an additional 12 h. The color of the solution changed to colorless and some light brown precipitate was formed. The precipitate was isolated by filtration and dried in vacuo to produce 0.047 g Mn[$N_3N$]′ in 50% yield. MS: *m*/*e* 696 [M$^+$ 696.3].

### 2.4. Preparation of {$\eta^3$-HB(3-$^t$BuPz)$_3$}FeCl (**4**) [20]

The following synthesis was modified from a literature procedure [20]. Either anhydrous $FeCl_2$ or $FeCl_2 \cdot 4H_2O$ can be used as the starting material. A typical procedure using anhydrous $FeCl_2$ is described. Anhydrous $FeCl_2$ (0.112 g, 0.0881 mmol) was added to a stirred solution of KHB(3-$^t$BuPz)$_3$ (0.368 g, 0.0881 mmol) in 10 ml THF. After 23 h, the mixture was dried in vacuo and the residue was extracted with toluene. After filtering the toluene solution, the filtrate was concentrated to 4 ml and cooled to −35°C to deposit {$\eta^3$-HB(3-$^t$BuPz)$_3$}FeCl (**4**) as white crystals. The product was isolated by filtration, washed with 1 ml hexanes and dried in vacuo (0.137 g in two crops, 33%). IR data (Nujol mull, NaCl plates, cm$^{-1}$): 2523 (*w*) $\nu$(B–H). $^1$H-NMR ($CDCl_3$): $\delta$ −11.9 (br, s, 27H, $^t$Bu), 45.2 (br, s, 3H, $C_3N_2H_2$), 62.3 (br, s, 3H, $C_3N_2H_2$), 48.93 (br, 1H, B*H*). $^1$H-NMR ($C_6D_6$): $\delta$ −13.99 (s, 27 H), 48.48 (s, 3 H), 54.75 (br, s, 1 H), 61.24 (s, 3 H), and 2.10 (s, 0.12 H, $C_6H_5CH_3$). Anal. Calc. for {$\eta^3$-HB(3-$^t$BuPz)$_3$}FeCl·0.04toluene ($FeC_{21}H_{34}BClN_6 \cdot 0.04C_7H_8$): C, 53.66; H, 7.26; N, 17.64. Found: C, 54.02; H, 7.49; N, 17.89%. The toluene solvate (0.04 equivalents) was observed in the $^1$H-NMR spectrum of the sample submitted for elemental analysis. IR and $^1$H-NMR data are similar to those reported in the literature [20].

### 2.5. Preparation of {$\eta^3$-HB(3-$^t$BuPz)$_3$}FeOTf (**5**)

A solution of AgOTf (0.0199 g, 0.0775 mol) in about 2 ml toluene was added slowly to a stirred solution of {$\eta^3$-HB(3-$^t$BuPz)$_3$}FeCl (0.0362 g, 0.0766 mmol) in 10 ml toluene. A white precipitate formed immediately. After stirring for about 3.5 h, the mixture was filtered and the filtrate was dried in vacuo. The residue was redissolved in a minimum amount of toluene–$CH_2Cl_2$ (1:1, 2 ml). The solution was then layered with pentane and cooled to −35°C, to produce light pink crystals. The product was isolated via filtration and dried in vacuo (0.0155 g, 34%). $^1$H-NMR ($CDCl_3$): $\delta$ −3.42 (br, 27H, $^t$Bu), 31.11 (s, 3H, $C_3N_2H_2$), 67.53 (s, 3H, $C_3N_2H_2$), and 2.34 (s, 3H, $C_6H_5CH_3$). IR data (Nujol mull, NaCl plates, cm$^{-1}$): 2515 (*w*) $\nu_{(B–H)}$; 1238 (s), 1199 (s), 1015 (s) and 629 (s) $\nu(CF_3SO_3^-)$. Anal. Calc. for {$\eta^3$-HB(3-Bu$^t$Pz)$_3$}FeOTf·$C_6H_5CH_3$ [$FeC_{29}H_{42}BF_3N_6O_3S$]: C, 51.31; H, 6.24; N, 12.39. Found: C, 50.62; H, 6.17; N, 12.86%.

### 2.6. Preparation of {$\eta^3$-HB(3-$^t$BuPz)$_3$}MnCl (**6**)

The following synthesis was modified from a literature procedure [20]. THF (15 ml) was added to a flask charged with 0.0735 g of anhydrous $MnCl_2$ (0.584 mmol) and 0.245 g of KHB(3-$^t$BuPz)$_3$ (0.583 mmol). The mixture was heated at reflux for 16 h and filtered. The filtrate was taken to dryness in vacuo and the residue was dissolved in a minimum amount of toluene (2 ml). On cooling the toluene solution to −35°C, white crystals precipitated. {$\eta^3$-HB(3-$^t$BuPz)$_3$}MnCl (**6**) was isolated by filtration and dried in vacuo (0.103 g, 37%). MS: *m*/*e* 472 [M$^+$: 471.7]. Anal. Calc. for $MnC_{21}H_{34}BClN_6$: C, 53.47; H, 7.27; N, 17.81. Found: C, 53.50; H, 7.42; N, 17.57%.

### 2.7. Alkene epoxidation procedures

Styrene and norbornylene were used as the substrates for catalytic epoxidation reactions mediated by iron and manganese complexes. PhIO and $O_2$–isobutyraldehyde were used as the oxidants during the reactions. The products were identified by comparing the $^1$H-NMR spectra and the GC and HPLC retention times of the products with those of the authentic compounds.

With PhIO, a typical reaction procedure was as follows. $CH_2Cl_2$ (10 ml) was added to a flask charged with about 100 mg of substrate, excess PhIO (one to two equivalents), and 0.75 ~ 3 mol% catalyst. The mixture was stirred at ambient temperature. Dodecane was added as an internal standard. The conversion of substrate and the yield of products could be determined from GC, or determined from $^1$H-NMR by filtering the reaction mixture through a layer of celite and concentrating the filtrate under reduced pressure.

When $O_2$–isobutyraldehyde was employed as the oxidant, two slightly different methods were followed. Method A: about 100 mg of substrate, dodecane, and 0.75–2 mol% catalyst were dissolved in about 10–15 ml $CH_2Cl_2$ in a two-necked flask with a side-arm stopcock. The flask was connected to the Schlenk line. One atmosphere of $O_2$ was bubbled gently through the stirred solution and isobutyraldehyde was added via a syringe. Method B is similar to Method A, but after the flask was connected to the Schlenk line, the solution in the flask was degassed after being cooled with liquid $N_2$. The flask was then put under 1 atmosphere of $O_2$ and the solution was warmed to r.t. Isobutyraldehyde was then added by syringe to the stirred solution.

To determine the catalytic efficiency of the alkene epoxidation using $O_2$–isobutyraldehyde as the oxidant, several control reactions without catalyst were also done. To avoid the contamination of traces of metal complexes completely, the reaction was done as follows. A clean two-necked flask charged with about 100 mg of substrate and dodecane was connected to a Schlenk line. The $CH_2Cl_2$ solvent and the required amount of isobutyraldehyde were vacuum-transferred to the reaction flask. Then the flask was put under an atmosphere of $O_2$ and the solution was warmed to r.t. and stirred.

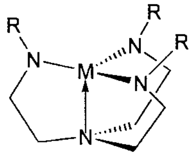
During product analysis by GC, styrene oxide decomposed to acetophenone in the GC injector. $^1$H-NMR and HPLC analyses of the reaction mixture indicated the presence of only styrene oxide and benzaldehyde as the major and minor products. Thus, the amount of acetophenone detected by GC was included in the yield of styrene oxide.

The epoxidation of *cis*- or *trans*-stilbene with isobutyraldehyde and $O_2$ with a catalytic amount of FeTp$^{t\text{Bu}}$Cl was performed as follows. A flask was charged with 100 mg of substrate, dodecane (GC standard), $Ph_3CH$ (NMR standard), ca. 2 mol% of FeTp$^{t\text{Bu}}$Cl, and 10–15 ml of $CH_2Cl_2$. After the flask was connected to a Schlenk line, the solution in the flask was frozen at −196°C and degassed. The flask was then put under 1 atmosphere of $O_2$. After the solution was warmed to r.t., isobutyraldehyde was added by syringe to the stirred solution. The conversion of stilbene and the yield of products were determined by GC. At the end of the reaction, the solution was taken to dryness under a flow of $N_2$ gas. The residue was redissolved in $CDCl_3$ and the products were also analyzed by $^1$H-NMR spectrum. Since the epoxidation products (*cis*- and *trans*-stilbene oxides) were decomposed partially to unknown substances under GC analysis, the yield of *cis*- and *trans*-stilbene oxides were determined by $^1$H-NMR analysis using $Ph_3CH$ as the internal standard.

## 3. Results and discussion

### 3.1. Characterization of metal complexes

Complexes Mn[$N_3N$] (**1**), Fe[$N_3N$]′ (**2**) and Mn[$N_3N$]′ (**3**) use the trianionic tetradentate triamidoamines of the type $[RNCH_2CH_2)_3N]^{3-}$ (R = trimethylsilyl and pentafluorophenyl) as sterically demanding ligands. Many transition-metal complexes that contain these types of ligands are well known, including the first-row transition metals from Ti to Fe, and heavier congeners such as Ta, W, and Mo [32,33]. The bulky R group usually forces the metal complexes either to adopt relatively rigid, distorted trigonal bipyramidal geometries when the amine coordinates to the metal in an apical position, or to have a trigonal monopyramidal structure when no ligand is in the apical site *trans* to the amine donor [30,32,34]. Mn[$N_3N$] (**1**) is similar to Mn{[$^t$BuMe$_2$SiNCH$_2$CH$_2$]$_3$N} [32], except that the R group in the latter complex is bulkier than in the former. Several molybdenum and tungsten complexes with a trigonal bipyramidal geometry are reported with the more electron-deficient $[N(CH_2CH_2NC_6F_5)_3]^{3-}$ ligand [30]. The mass spectra of complexes **1**, **2**, and **3** and the elemental analysis of **2** confirm the formation of monomeric metal complexes with these trisamidoamine ligands. It appears that complexes **1**, **2**, and **3** all adopt a similar trigonal monopyramidal geometry (shown below).



**1**: M = Mn, R = $Si(CH_3)_3$
**2**: M = Fe, R = $C_6F_5$
**3**: M = Mn, R = $C_6F_5$

The complexes {$\eta^3$-HB(3-$^t$BuPz)$_3$}FeCl (**4**) and {$\eta^3$-HB(3-$^t$BuPz)$_3$}MnCl (**6**) were first synthesized by Gorrell and Parkin [20]. The molecular structure of **4** was also determined by single-crystal X-ray diffraction analysis [20]. The modified synthesis procedures used in this work to prepare **4** and **6** produced materials with $^1$H-NMR and IR data that were identical with the reported values [20]. The coordination sphere of the triflate-derivative {$\eta^3$-HB(3-$^t$BuPz)$_3$}FeOTf (**5**) appears to differ from those of complexes **4** and **6**. From a comparison of the IR spectra of complexes **5** and **4**, the vibration bands due to $CF_3SO_3^-$ were assigned as 1238, 1199, 1054, and 629 cm$^{-1}$. The highest energy IR band for the triflate ligand serves as a marker for its coordination mode. For example, the ionic triflate in [L$^{iPr_3}$Cu(CH$_3$CN)]CF$_3$SO$_3$ (L = 1,4,7-triisopropyl-1,4,7-triazocyclononane) has its highest frequency at 1225 cm$^{-1}$ in KBr [35]. Also, the weakly coordinated triflate

Table 1
Epoxidation of alkenes by using PhIO as oxidant in $CH_2Cl_2$

| Substrate | Metal complex | Mole ratio of substrate:PhIO:metal complex [a] | Time (h) | Conversion of substrate (%) | Yield of epoxide (%) [b] | Epoxide turnover number | Other products |
|---|---|---|---|---|---|---|---|
| Styrene | **1** | 1:1.1:0.018 | 38 | 23 [c] | 23 [c] | 13 | |
| Norbornylene | **1** | 1:1.1:0.0075 | 45 | 31 [c] | 31 [c] | 41 | |
| Styrene | **2** | 1:1.0:0.012 | 21 | 0 [d] | 0 [d] | 0 | |
| Styrene | **3** | 1:1.2:0.010 | 14 | 16 [d] | 15 [d] | 15 | PhCHO: 1% |
| | | | 41.5 | 23 [d] | 17 [d] | 17 | PhCHO: 6% |
| Styrene | **4** | 1:2.1:0.030 | 50 | 0 [d] | 0 [d] | 0 | |
| Styrene | **5** | 1:1.5:0.012 | 22 | 3 [d] | 0.5 [d] | 0.4 | PhCHO: $<0.5\%$ |
| Norbornylene | **6** | 1:1.4:0.010 | 72 | 78 [d] | 20 [d] | 20 | |
| Styrene | **6** | 1:1.3:0.010 | 44 | 40 [c] | 40 [c] | 40 | |

[a] Typical quantities used in each reaction: 100 mg substrate, 10 ml $CH_2Cl_2$, at about 22°C.

[b] Yield was according to the total substrate.

[c] Determined by $^1$H-NMR.

[d] Determined by GC.

Table 2
The epoxidation of alkenes using transition-metal catalysts and $O_2$–isobutyraldehyde

| Substrate | Metal complex | Mole ratio of substrate:isobutyraldehyde:metal complex [a] | Time (h) | Conversion of substrate (%) [b] | Yield of epoxide (%) [b] | Epoxide turnover number | Other products (%) |
|---|---|---|---|---|---|---|---|
| Styrene | **1** | 1:7.2:0.012 | 1 | 99 | 41 | 34.2 | PhCHO: 15 |
| Norbornylene | **1** | 1:7.0:0.0057 | 1 | 100 | 71 | 124.6 | |
| Styrene | **2** | 1:6.0:0.022 | 5.6 | 9 | 1 | 0.5 | PhCHO: 1 |
| Styrene | **3** | 1:6.4:0.010 | 2 | 100 | 54 | 54.0 | PhCHO: 10 |
| Styrene | **4** | 1:6.0:0.010 | 2.5 | 99 | 89 | 89.0 | PhCHO: 6 |
| Norbornylene | **4** | 1:6.0:0.010 | 3.5 | 100 | 79 | 79.0 | |
| Styrene | **5** | 1:6.0:0.010 | 5.5 | 45 | 15 | 15.0 | PhCHO: 13 |
| Styrene | **6** | 1:6.0:0.010 | 3 | 99 | 47 | 47.0 | PhCHO: 13 |
| Norbornylene | **6** | 1:6.0:0.010 | 2.5 | 82 | 44 | 44.0 | |
| | | | 6 | 97 | 73 | 73.0 | |
| Styrene [c] | **4** | 1:6.0:0.012 | 10.5 | 13 | 0 | 0 | PhCHO: $<2$ |
| | | | 18.5 | 17 | 0 | 0 | PhCHO: $<2$ |
| Norbornylene [d] | $Ni(dmp)_2$ [d,e] | 1:2.0:0.01 [d] | 3 [d] | 100 [d] | 100 [d] | 100 [d] | NA |
| Styrene [f] | $Fe(dmp)_3$ [e,f] | 1:6.0:0.01 [f] | 10 [f] | 82 [f] | 82 [f] | 82 [f] | NA |

[a] Typical quantities used in each reaction: 100 mg substrate, 10–15 ml $CH_2Cl_2$, at about 22°C.

[b] Products were detected with GC; conversion and yield were calculated according to the total substrate.

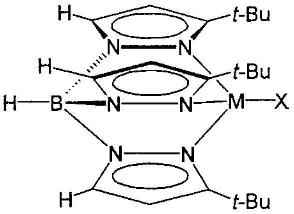
[c] 0.23 equivalents of di-*tert*-butyl nitroxide was also added to the solution before the addition of isobutyraldehyde.

[d] Ref. [11a].

[e] dmp = 1,3-bis(dimethyoxyphenyl)-1,3-propandionato.

[f] Ref. [14].

in tetrakis(5-$^t$butylpyrazole)iron(II) trifluoromethanesulfonate has its highest frequency at 1310 cm$^{-1}$ [34b]. It is apparent that the triflate ligand in **5** is probably not bound to Fe.



**4**: M = Fe, X = Cl
**5**: M = Fe, X = OTf
**6**: M = Mn, X = Cl

### 3.2. Epoxidation with PhIO

Our first epoxidation studies focused on the use of iodosobenzene as the oxygen atom source with styrene and norbornylene as substrates. The epoxidations of styrene with complexes **1**–**6** are summarized in Table 1. The manganese complexes **1**, **3** and **6** catalyze the selective conversion of styrene and norbornylene to the corresponding epoxides, i.e. styrene oxide and *exo*-norbornylene oxide, with turnovers between 12 and 40. When Mn[N$_3$N] (**1**) and {η$^3$-HB(3-$^t$BuPz)$_3$}MnCl (**6**) were used (entries 1, 2, 7 and 8), styrene oxide and *exo*-norbornylene oxide were the only products as determined by $^1$H-NMR analysis. When Mn[N$_3$N]′ (**3**) was employed (entry 4), the main product was still styrene oxide, but a small amount of PhCHO (1%) also formed. With increasing reaction time, the appearance of PhCHO increased dramatically while the amount of epoxide produced remained relatively unchanged. Compared to the result in entry 1 where Mn[N$_3$N] (**1**) was used, it appears that the electron-deficient triamidoamine ligand in Mn[N$_3$N]′ has a slight influence on the selectivity. As shown in entries 3 and 5, it is clear that the iron complexes including {η$^3$-HB(3-$^t$BuPz)$_3$}FeCl (**4**) and Fe[N$_3$N]′ (**2**) have no catalytic epoxidation capability with PhIO. The complex {η$^3$-HB(3-$^t$BuPz)$_3$}FeOTf (**5**) is also not an efficient epoxidation catalyst, as only trace amounts of benzaldehyde and styrene oxide were formed in 22 h when PhIO was employed as the oxidant (entry 6).

### 3.3. Epoxidation with $O_2$–isobutyraldehyde

Because of the modest epoxide yields with PhIO, a better oxygen source was desired. Table 2 shows the results of the epoxidation of styrene and norbornylene with 1 atmosphere of molecular oxygen in the presence of isobutyraldehyde using Mn[N$_3$N] (**1**), Fe[N$_3$N]′ (**2**), Mn[N$_3$N]′ (**3**), {η$^3$-HB(3-$^t$BuPz)$_3$}FeCl (**4**), {η$^3$-HB(3-$^t$BuPz)$_3$}FeOTf (**5**) or {η$^3$-HB(3-$^t$BuPz)$_3$}MnCl (**6**) as catalysts at ambient temperature. Since it is well known that the epoxidation reaction with O$_2$–aldehyde–metal complex proceeds via a radical route and can take place without metal catalysts [18], control experiments were undertaken. Table 3 shows the results without the addition of metal catalysts. Without a metal catalyst, the epoxidation reaction is slow. In 6.5 h, only 21% of norbornylene is converted to epoxide. In contrast, when metal complexes **1** and **4** were used (shown in Table 2), norbornylene is consumed completely and *exo*-norbornylene oxide was the only identified product in 3.5 h in 70–80% yield. When {η$^3$-HB(3-$^t$BuPz)$_3$}MnCl (**6**) was used as the catalyst, the conversion of norbornylene was 97% with a 73% yield of epoxide. Although complex **6** is an efficient catalyst, it is less active than complex **4** under the same conditions. However, complex **6** can epoxidize styrene with PhIO, while complex **4** cannot (Table 1). From Table 2, it is also clear that complex **3** is an efficient catalyst for the epoxidation of styrene, but complexes **2** and **5** exhibited low epoxidation activity. The last entries in Table 2 provide epoxidation results for the best known catalysts, Ni(dmp)$_2$ and Fe(dmp)$_3$ (dmp = 1,3-bis(dimethyoxyphenyl)-1,3-propandionato), when using the O$_2$–aldehyde oxidant. These both provide high yields of epoxides. Complex **4** compares favorably with Fe(dmp)$_3$ for the epoxidation of styrene.

Table 3 also shows the control experiments with styrene. Entries 2 and 3 are the results obtained by following the identical reaction procedures as above,

Table 3
The controlling epoxidation of alkenes with O$_2$–isobutyradehyde as co-oxidants and without metal catalyst

| Substrate | Mole ratio of substrate:isobutyraldehyde [a] | Time (h) | Conversion of substrate (%) [b] | Yield of epoxide (%) [b] | Other products (%) |
|---|---|---|---|---|---|
| Norbornylene | 1:6.0 | 6.5 | 80 | 21 | |
| Styrene | 1:6.0 | 26 | 25 | 10 | PhCHO: 10 |
| | | 46.5 | 56 | 21 | PhCHO: 21 |
| Styrene | 1:6.0 | 3.5 | 2 | 0.2 | PhCHO: 0.4 |
| | | 32 | 99 | 40 | PhCHO: 42 |

[a] Typical quantities used in each reaction: 100 mg substrate, 10–15 ml CH$_2$Cl$_2$, at about 22°C.

[b] Products were detected with GC; conversion and yields were calculated according to the total substrate.

Table 4
Epoxidation of styrene with complex **4** [a]

| Aliquot | Time (h) | Conversion of styrene (%) | Yield of styrene oxide (%) | Epoxide turnover numbers | Yield of PhCHO (%) |
|---|---|---|---|---|---|
| First | 1.5 | 100 | 53.5 | 32 | 17.9 |
| Second | 16.5 | 90.0 | 42.5 | 25 | 14.3 |

[a] The molar ratio of styrene:complex **4**:isobutyraldehyde = 1:0.017:7.3. The second aliquot of styrene was added after the completion of the first batch. Isobutyraldehyde was also added to keep the ratio of styrene:isobutyraldehyde unchanged. The yields were determined from GC and based on the total substrate.

but without catalyst added. In 3.5 h, only traces of styrene oxide and benzaldehyde were formed with no catalyst. But with increasing reaction time, the results are irreproducible, and the qualitative reaction rate and the yield of products are different. This suggests that the reaction proceeds via a free-radical process without the employment of a radical initiator (such as ROOH, R = cyclohexen-2-yl) [18]. In the absence of metal complex, the two control reactions produced styrene oxide and PhCHO in essentially the same ratio (1:1). When $\{\eta^3\text{-HB(3-}^t\text{BuPz)}_3\}$FeCl (**4**) was employed as catalyst (entry 5 in Table 2), styrene was almost completely converted to styrene oxide with 89% yield with only 6% yield of PhCHO. Thus, complex **4** is very effective for the selective epoxidation of styrene. When Mn[$N_3$N], Mn[$N_3$N]′ or $\{\eta^3\text{-}^t\text{BuPz})_3\}$MnCl were employed, styrene oxide is still the major product (41–54%), but the amount of PhCHO increased to 10–15%.

To test the stability of complex **4** during the catalytic reaction, a typical catalytic reaction using about 100 mg styrene (the molar ratio of styrene:complex **4**:isobutyraldehyde = 1:0.017:7.3) was done in $CH_2Cl_2$ solution. After the consumption of the first batch of substrate, a second aliquot of styrene (about 100 mg) was added to the reaction mixture via syringe. Isobutyraldehyde was also added to return the amount of styrene and isobutyraldehyde to the starting ratio of 1:7.3. Table 4 shows the corresponding results. It was clear that the catalyst decomposed gradually, as indicated by the slower conversion of the substrate in the second batch reaction. However, the selectivity of styrene oxide over PhCHO remained constant over time. It can be seen also that the selectivity of epoxide was varied and dependent on the ratio of substrate, **4** and isobutyraldehyde, as compared to the result of entry 5 in Table 2 (the ratio of styrene:isobutyraldehyde:**4** = 1:6.0:0.010), where the yields of styrene oxide and PhCHO were 89 and 6%, respectively.

### *3.4. Epoxidation of stilbenes*

In order to compare our catalysts to epoxidations with metal macrocycle complexes, the common substrates *cis*- and *trans*-stilbenes were used with catalyst **4**. These results are summarized in Table 5. In general, our observations parallel those of Nam et al. shown at the bottom of Table 5 [36]. In our examples, a stronger selectivity for the *trans*-stilbene oxide is found. Notably, complex **4** has a much higher selectivity for the *trans*-product relative to the porphyrinato and cyclam complexes used by Nam et al. When oxygen-atom sources such as iodosylbenzene, peracids, or hypochlorite are used with metalloporphyin catalysts, the conversion of *cis*-stilbene to epoxides is generally highly selective for the *cis*-product [2a,37]. Product ratios of *cis*-stilbene oxide/*trans*-stilbene oxide as high as 170:1 have been reported [2a]. However, the product ratio depends on the nature of the metalloporphyrin catalyst and reaction conditions. For example, *trans*-stilbene oxide is sometimes the major product in the epoxidation of *cis*-stilbene with manganese(III) porphyrins [38].

### *3.5. Proposed mechanism for the alkene epoxidation with $O_2$–isobutyraldehyde*

Mechanisms for metal-catalyzed epoxidation of substrates with $O_2$ and aldehydes often invoke high-valent metal-oxo species. Given the poor epoxidation results of complexes **1**–**6** with PhIO as the oxygen source, a high-valent oxo species seems unlikely with these catalytic systems. Moreover, the epoxidation of alkenes in the metal complex–$O_2$–aldehyde system (such as Cr(TPP)Cl, Fe(TPP)Cl, TPP = *meso*-tetraphenylporphyrin dianion) involves a purportedly radical-chain process [15a,36]. The epoxidation can proceed via the autoxidation of the aldehyde to form peracid and acylperoxy radicals as the intermediates. The radical character of this process was checked with the use of radical inhibitors with complex **4** (entry 10 in Table 2). When 0.23 equivalents of radical inhibitor di-*tert*-butyl nitroxide were added to the reaction mixture before the addition of isobutyraldehyde, no epoxidation was observed and only trace amounts of PhCHO formed in 18.5 h. The yields of oxidation products were also much lower than that of the control experiment where catalyst was not added. Thus, the formation of a radical intermediate (acylperoxy radical) is important for the epoxidation of alkene in this system. The metal complex must react effectively with isobutyraldehyde and

Table 5
Epoxidation of stilbenes [a]

| Substrate | Metal complex | Mole ratio of substrate:isobutyraldehyde:metal complex | Time (h) | Conversion of substrate (%) | PHCHO (%) | *cis*-Stilbene oxide (%) | *trans*-Silbene oxide (%) | *cis*:*trans* Ratio | Epoxide turnover number |
|---|---|---|---|---|---|---|---|---|---|
| *trans*-Stilbene | FeTp$^{tBu}$Cl | 1:6.0:0.022 | 3 | 100 | 3 [b] | 0 [c] | 97 [c] | 0 | 44.1 |
| *trans*-Stilbene | FeTp$^{tBu}$Cl | 1:6.0:0.022 | 3 | 100 | 3 [b] | 0 [d] | 97 [d] | 0 | 44.1 |
| *cis*-Stilbene | FeTp$^{tBu}$Cl | 1:6.0:0.020 | 3 | 93.3 [d] | 4.2 [d] | 5.4 [d] | 83.4 [d] | 0.065 | 44.4 |
| | | | | 89.6 [b] | 5.6 [b] | 6.7 [b] | 81.4 [b] | 0.082 | 44.1 |
| *cis*-Stilbene | FeTp$^{tBu}$Cl | 1:6.0:0.018 | 2 | 95 [c] (80 [b]) | 4.9 [b] | 6.6 [c] | 78.7 [c] | 0.084 | 47.4 |
| *cis*-Stilbene | None | 1:6.0:0 | 22 | 0 [b] | 0 [b] | 0 [b] | 0 [b] | – | 0 |
| *cis*-Stilbene | Cr(TTP)Cl [e] | 1:17:0.02 [e] | 18 [e] | 33 | 1 [e] | 7 [e] | 25 [e] | 0.28 [e] | 16 |
| *trans*-Stilbene | Cr(TTP)Cl [e] | 1:17:0.02 [e] | 18 [e] | 48 | 2 [e] | 7 [e] | 39 [e] | 0.18 [e] | 23 |
| *cis*-Stilbene | Fe(TTP)Cl [e] | 1:17:0.02 [e] | 18 [e] | 67 | 2 [e] | 15 [e] | 50 [e] | 0.30 [e] | 33 |
| *trans*-Stilbene | Fe(TTP)Cl [e] | 1:17:0.02 [e] | 18 [e] | 78 | 2 [e] | 12 [e] | 64 [e] | 0.19 [e] | 38 |
| *cis*-Stilbene | Fe(cyclam)$^{2+}$ [e] | 1:17:0.02 [e] | 18 [e] | 17 | 1 [e] | 3 [e] | 13 [e] | 0.23 [e] | 8 |
| *trans*-Stilbene | Fe(cyclam)$^{2+}$ [e] | 1:17:0.02 [e] | 18 [e] | 76 | 2 [e] | 7 [e] | 67 [e] | 0.10 [e] | 37 |
| *cis*-Stilbene | Cu(cyclam)$^{2+}$ [e] | 1:17:0.02 [e] | 18 [e] | 35 | 1 [e] | 7 [e] | 27 [e] | 0.26 [e] | 17 |
| *trans*-Stilbene | Cu(cyclam)$^{2+}$ [e] | 1:17:0.02 [e] | 18 [e] | 99 | 2 [e] | 4 [e] | 93 [e] | 0.04 [e] | 49 |
| *trans*-Stilbene | Fe(dmp)$_3$ [f] | 1:6:0.01 [f] | 14 [f] | 99 | – | – | 99 [f] | – | 99 |

[a] The yield of products was based on the total substrate.

[b] Determined with GC using dodecane as a reference.

[c] Determined with $^1$H-NMR using $-CH_3$ of dodecane as an internal standard.

[d] Determined with $^1$H-NMR using $Ph_3CH$ as internal standard.

[e] From Ref. [36].

[f] From Ref. [14].

$O_2$ to generate the acylperoxy radical. Mizuno et al. [15] found that polyoxoanion-supported catalyst precursors catalyzed the formation of the acylperoxy radical, but did not improve the selectivity for the epoxide. However, the metal complexes examined here increased the selectivity for epoxidation products greatly. Formation of the side product PhCHO was reduced greatly. Thus, the metal complex must also be involved in the final epoxidation step. A mechanism for this process, modified from a pathway first proposed by Fdil et al. [12] is shown in Scheme 1. The improved selectivity for epoxidation with a metal catalyst indicates that path A contributes significantly to the product formation. When no metal compound is used in the control experiment, the acylproxyl radical can only react with substrate via path B to form styrene oxide and PhCHO. It is well known that the formation of PhCHO involves a free-radical process [36].

Possible mechanisms for metal-catalyzed epoxidation of olefins by dioxygen with the co-oxidation of aldehydes were studied by Nam et al. [36,39].

$$\mathrm{RCHO} + \mathrm{M}^{n+} \rightarrow \mathrm{M}^{n-1} + \mathrm{R\dot{C}O} + \mathrm{H}^{+} \tag{1}$$

$$\mathrm{M}^{n+} + \mathrm{O_2} \rightarrow (\mathrm{M}-\mathrm{OO})^{n+} \xrightarrow{\mathrm{RCHO}} (\mathrm{M}-\mathrm{OOH})^{n+} + \mathrm{R\dot{C}O} \tag{2}$$

$$(\mathrm{M{-}OOH})^{n+} + \mathrm{R\dot{C}O} \rightarrow \mathrm{M}^{n+} + \mathrm{RCO_3H} \tag{3}$$

Eqs. (1)–(3) can proceed to initiate the radical process [35,36]. For $\{\eta^3\text{-HB(3-}^t\text{BuPz)}_3\}\text{FeCl}$ (**4**), it is unlikely that the acyl radical can be formed via Eq. (1) because Fe(I) complexes are rare and unstable towards disproportion to Fe(0) and Fe(II) [40]. The acyl radical initiation is presumably via Eq. (2). Although the $O_2$ adduct in Eq. (2) is shown as monomeric, its formulation is unclear. For trispyrazolyborate complexes, the bulkiness of the substituent at the three-position is important in the nuclearity of $O_2$ adducts. For example, $\text{HB(3,5-}^i\text{Pr}_2\text{pz)}_3\text{Fe(OAc)}$ was shown to reversibly bind $O_2$ at low temperature to form a μ-peroxo dimer (Eq. (4)) [16b].

$$2\mathrm{Tp}^{3,5^i\mathrm{Pr}}\mathrm{Fe(OAc)} + \mathrm{O_2} \rightarrow \mathrm{Tp}^{3,5^i\mathrm{Pr}}(\mathrm{OAc})\mathrm{Fe{-}O{-}O{-}Fe(OAc)}\mathrm{Tp}^{3,5^i\mathrm{Pr}} \tag{4}$$

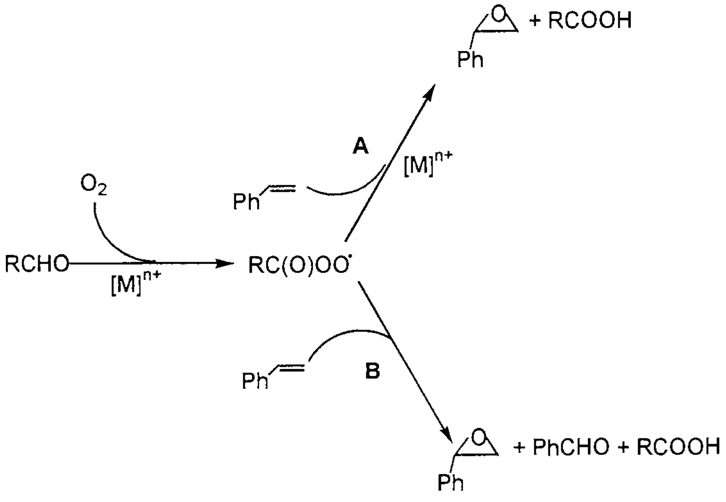
Fujisawa et al. also found that the bulkiness of the Tp ligands could influence the dioxygen adduct structures of the TpCu(I) complexes [41]. The reaction between dioxygen and $\text{Cu(I)(HB(3,5-}^i\text{Pr}_2\text{Pz)}_3)$ results in instantaneous formation of the μ-$\eta^2$:$\eta^2$-peroxo dinuclear copper(II) complex (Eq. (5)) [41b].

$$2\mathrm{Cu(HB(3,5\text{-}}^i\mathrm{Pr_2Pz)_3)} + \mathrm{O_2} \rightarrow [\mathrm{Cu(HB(3,5\text{-}}^i\mathrm{Pr_2Pz)_3)}]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{O_2}) \tag{5}$$

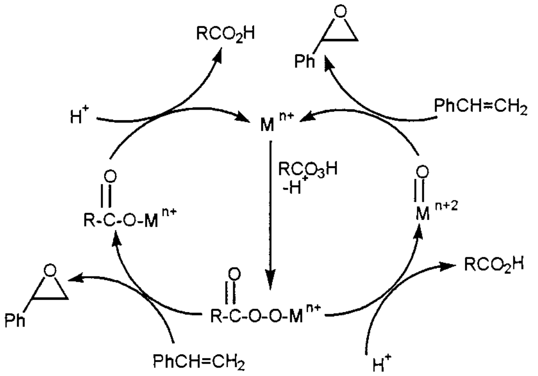
However, the reaction between dioxygen and $\text{Cu(HB(3-}^t\text{Bu-5-}^i\text{PrPz)}_3)$ affords the formation of a monomeric superoxocopper(II) species $\text{Cu(O}_2\text{)(HB(3-}^t\text{Bu-5-}^i\text{PrPz)}_3)$ (Eq. (6)) [41a].

$$\mathrm{Cu(HB(3\text{-}}^t\mathrm{Bu\text{-}5\text{-}}^i\mathrm{PrPz)_3)} + \mathrm{O_2} \rightarrow \mathrm{Cu(O_2)(HB(3\text{-}}^t\mathrm{Bu\text{-}5\text{-}}^i\mathrm{PrPz)_3)} \tag{6}$$

The bulkiness of $\text{Tp}^{3\text{-}^t\text{Bu}}$ used in this research is very similar to that of $\text{Tp}^{3\text{-}^t\text{Bu-5-}^i\text{Pr}}$. Thus, it is possible that a superoxo intermediate is formed during the reaction between **4** and $O_2$, although attempts at characterizing this transient species by IR or Raman spectroscopies have been inconclusive. Moreover, catalysis with complex **4** increases the selectivity for epoxide formation greatly. Thus, the metal complex appears to play an important role in the epoxidation process. A possible mechanism is shown in Scheme 2. This mechanism is analogous to that proposed by Nam et al. However, in our systems we propose that the metal complex is involved intimately in the epoxidation step since our



Scheme 1.



Scheme 2.

selectivities are much higher. This catalytic cycle suggests that the formation of PhCHO due to over oxidation should be reduced. Indeed, production of PhCHO in our metal-catalyzed systems is lower that those in the non-metal-catalyzed reactions.

## 4. Conclusions

Several monomeric manganese and iron complexes with sterically demanding tetradentate trisamidoamines of the type $[RNCH_2CH_2)_3N]^{3-}$ (R = trimethylsilyl, pentafluorophenyl) or tris(3-$^t$butylpyrazolyl)borate as the coordinating ligands were synthesized and characterized. Mn[$N_3$N] (**1**), Mn[$N_3$N]′ (**3**) and {$\eta^3$-HB(3-$^t$BuPz)$_3$}MnCl (**6**) catalytically epoxidized norbornylene and styrene to the corresponding epoxides with high selectivity using PhIO as oxidant, while the analogous iron complexes (**2** and **4**) did not exhibit catalytic epoxidation activity. By using $O_2$ with isobutyraldehyde as a co-reductant, the catalytic efficiency of metal complexes including Mn[$N_3$N] (**1**), Fe[$N_3$N]′ (**2**), Mn-[$N_3$N]′ (**3**), {$\eta^3$-HB(3-$^t$BuPz)$_3$}FeCl (**4**), {$\eta^3$-HB(3-$^t$BuPz)$_3$}FeOTf (**5**), and {$\eta^3$-HB(3-$^t$BuPz)$_3$}MnCl (**6**) was studied. The selectivity for epoxide and the reaction rate were improved greatly when complexes **1**, **3**, **4**, and **6** were employed as catalysts, in comparison to control experiments where no metal complex was used. Complex **4** was the most efficient catalyst with a yield of styrene oxide as high as 89% in 2.5 h. The metal complexes deactivated slowly during the catalytic reaction conditions. This suggests that either the bulkiness of the ligands was not sufficient to prevent μ-oxo deactivation, or that the ligand itself decomposed gradually during the epoxidation reactions. From a discussion of the epoxidation mechanism, it is likely that the catalyst enhances the formation of an acylperoxy radical. Moreover, the high selectivity for epoxide product suggests that a metal complex must be involved directly in the epoxidation step.

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