Asymmetric Epoxidation with a Photoactivated [Ru(salen)] Complex

Kenya Nakata, Tsuyoshi Takeda, Jun Mihara, Tetsuya Hamada, Ryo Irie, and Tsutomu Katsuki*[a]

Dedicated to Professor K. Barry Sharpless on the occasion of his 60th birthday

Abstract: (Nitrosyl)(salen)ruthenium(II) complex **1** was found to serve as an efficient catalyst for the epoxidation of conjugated olefins under photoirradiation, with 2,6-dichloropyridine *N*-oxide (**2**) or tetramethylpyrazine *N*,*N*′-dioxide as a stoichiometric oxidant. High enantioselectivity was achieved irrespective of the substitution pattern of olefins. The choice of solvent depends on stability of the resulting epoxides: high enantioselectivity is generally observed in the reaction with ethereal solvents, but use of benzene is recommended when the resulting epoxides are acid-sensitive.

Keywords: asymmetric catalysis · epoxidation · N,O ligands · photoactivation · ruthenium · salen

Introduction

Asymmetric epoxidation is a major topic in organic synthesis and much effort has been directed toward this goal. As a result, many efficient catalysts such as titanium-tartrate,[1] metalloporphyrins,[2] metallosalens,[3] and dioxiranes generated in situ from chiral ketones[4] have been introduced, and high enantioselectivity has been achieved in the epoxidation of a wide range of olefins. Among these catalysts, chiral metallosalens, especially (salen)manganese complexes (hereafter referred to as [Mn(salen)]) are efficient catalysts for asymmetric epoxidation of conjugated olefins.[3] However, good substrates for [Mn(salen)]-catalyzed epoxidation are mostly limited to conjugated *cis*-di-, tri-, and some tetrasubstituted olefins.[3, 5] Epoxidation of conjugated monosubstituted olefins such as styrene requires reaction temperatures as low as $-78\,^{\circ}C$.[6] On the other hand, recent studies on the asymmetric catalysis of chiral metallosalens uncovered that the stereochemistry of metallosalen-catalyzed reactions is dependent upon the metal ion, the chiral ligand, the apical ligand, the reaction temperature, and the solvent used.[3, 5–7] Therefore, the scope of metallosalen-catalyzed epoxidation was expected to be further expanded by tuning these factors appropriately.

Ru complexes are well known to serve as catalysts for oxidation[8] and some chiral Ru complexes, such as Ru–porphyrin,[9] Ru/Schiff base,[10] unsymmetric Ru/Schiff base,[11] and Ru–bis(oxazoline) complexes,[12] as well as [Ru(PPz)(bpy)] (PPz = 2,6-bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methanoindazol-2-yl]pyridine, bpy = bipyridine),[13] have been used for asymmetric epoxidation. Although the enantioselectivity so far obtained with these complexes is moderate, several interesting phenomena have been observed: 1) epoxidation of *p*-nitrostyrene with a Ru/Schiff base complex shows good enantioselectivity of 80% *ee*, though epoxidation of styrene is moderate (58% *ee*). [10, 14] 2) In contrast to epoxidations catalyzed by most metallosalens and metalloporphyrins, *trans*-β-methylstyrene shows better enantioselectivity than *cis*-β-methylstyrene in the epoxidation catalyzed by the Ru–bis(oxazoline) complex (62 and 25% *ee*, respectively),[12a] and in the epoxidation catalyzed by the dioxo-Ru complex (67 and 40% *ee*, respectively).[9d] 3) Epoxidation with Ru complexes as catalysts is stereospecific.[9d, 12a] These results suggested that the above-mentioned limitation of [Mn(salen)]-catalyzed epoxidation would be overcome by utilizing a [Ru(salen)] complex as the catalyst. Thus, we have synthesized optically active [Ru(salen)] complexes and examined their catalytic action in epoxidation reactions.[15]

Results and Discussion

We have reported that salen ligands which bear a chiral binaphthyl unit as a chiral element are excellent chiral auxiliaries for Mn-catalyzed asymmetric oxidations.[5b] To expand the scope of metallosalen-catalyzed epoxidation, we synthesized a chloro(nitrosyl)(salen)ruthenium(II) complex ([$RuCl(C_{60}H_{44}N_2O_2)(NO)$] (hereafter referred to as [Ru(salen)(NO)] complex (**1**)) and examined asymmetric

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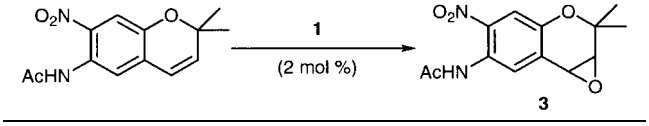
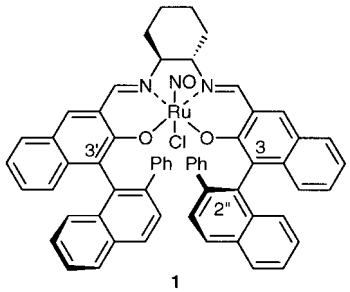
epoxidation of 6-acetamido-2,2-dimethyl-7-nitrochromene in the presence of various stoichiometric oxidants (Table 1). As expected, all the reactions showed good to high enantioselectivity, but the chemical yields of the epoxide **3** were poor except for the reaction with 2,6-dichloropyridine *N*-oxide (**2**),

Table 1. Asymmetric epoxidation of 6-acetamido-2,2-dimethyl-7-nitrochromene with **1** as a catalyst.



Entry	Oxidant	Time [h]	Yield [%]	*ee* [%][a]
1	PhIO[b]	2	1.9	85
2	$NaIO_4$[c]	24	2.9	82
3	oxone[c]	24	4	93
4	NaOCl[c]	24	4	76
5	2,6-$Cl_2C_5H_3NO$[d]	24	92	93

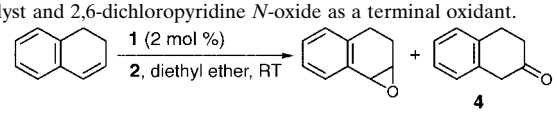
[a] Determined by HPLC analysis using optically active column (DAICEL CHIRALCEL OJ, hexane/2-propanol 1:1). [b] The reaction was carried out at 4 °C in CH_2Cl_2. [c] The reaction was carried out at 4 °C in CH_2Cl_2/H_2O. [d] The reaction was carried out in benzene at RT.



1

which was originally used as a stoichiometric oxidant for Ru/porphyrin-catalyzed epoxidation.[16] The first reaction that we tried with **2** proceeded with high enantioselectivity as well as high chemical yield (entry 4), but this result was found not to be very reproducible. Low reproducibility of enantioselectivity and chemical yield was also observed in the epoxidation of dihydronaphthalene under the same conditions. However, it was found that the epoxidation was greatly accelerated and reproducibility of the enantioselectivity was remarkably improved when the reaction vessel was exposed to incandescent or scattered sun light (Table 2). The reaction in the dark was sluggish (entry 4). It is also noteworthy that the enantiomeric excess of the resulting epoxide was diminished and formation of ketone **4** was detected as the reaction proceeded (entries 1–3). Ketone **4** was considered to be a rearrangement product of the epoxide. These results suggested that photoirradiation promoted dissociation of an apical ligand to generate a coordinatively unsaturated and Lewis acidic [Ru(salen)] complex, which catalyzed epoxidation through the corresponding oxo species and with simultaneous rearrangement of the resulting epoxide. Photoirradiation has also been found to promote dissociation of apical nitrosyl ligand.[17, 18]

Table 2. Asymmetric epoxidation of dihydronaphthalene with **1** as a catalyst and 2,6-dichloropyridine *N*-oxide as a terminal oxidant.

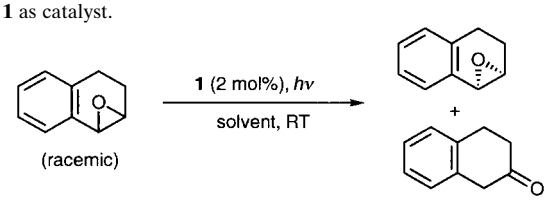


Entry	Time [h]	Yield [%][a]	*ee* [%][b]
1	2	19 (1)	87
2	6	57 (8)	84
3	15	58 (30)	78
4	15	3.3 (0.1)[c]	84

[a] The number in the parentheses is the yield of ketone. [b] Determined by HPLC analysis using optically active column (DAICEL CHIRALCEL OB-H, hexane/2-propanol 50:1). [c] The reaction was performed in the dark.

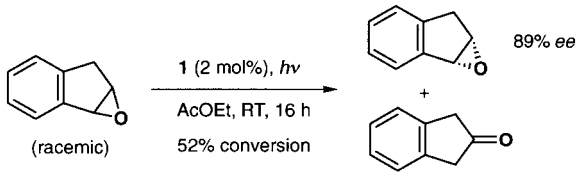
The coordinatively unsaturated [Ru(salen)] complex was considered to promote the rearrangement of the major enantiomer of the resulting epoxide in preference to that of the minor enantiomer, diminishing the enantiomeric excess of the epoxide. To prove enantiomer-differentiation by the [Ru(salen)] complex, we examined kinetic resolution of racemic 1,2-epoxy-3,4-dihydronaphthalene in the presence of complex **1** under irradiation of scattered sunlight (Table 3). As expected, the enantiomer corresponding to the major enantiomer of the epoxidation product preferentially rearranged to ketone, especially when diethyl ether or ethyl acetate was used as the solvent. No rearrangement of 1,2-epoxy-3,4-dihydronaphthalene was observed in the dark (entry 3). It is noteworthy that the rearrangement did not occur in the presence of **2** even under irradiation of scattered sunlight. This is probably due to the fact that **2** is more basic than the epoxide and binds to the coordinatively unsaturated [Ru(salen)] complex in preference to the epoxide. This result may also indicate that [Ru(salen)O] species generated from [Ru(salen)(**2**)] adduct does not catalyze the rearrangement of the epoxide. Kinetic resolution of racemic indene oxide was also effected ($k_{rel} = 30$) by using **1** as the catalyst under the same conditions (Scheme 1), but cyclohexene oxide was stable to the reaction conditions.

Table 3. Kinetic resolution of racemic 1,2-epoxy-3,4-dihydronaphthalene with **1** as catalyst.



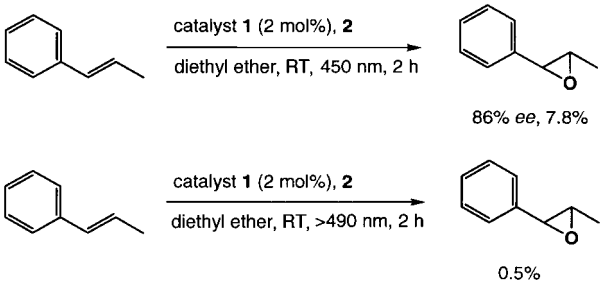
Entry	Solvent	Conversion [%][a]	*ee* [%][b,c]	k_{rel}
1	AcOEt	54	97.8	49
2	diethyl ether	54	99.0	61
3[d]	diethyl ether	< 1	–	–
4[e]	diethyl ether	< 1	–	–

[a] Conversion was determined by ^1H NMR analysis. [b] Percent *ee* of the unreacted epoxide. [c] Determined by HPLC analysis using optically active column (DAICEL CHIRALCEL OB-H, hexane/2-propanol 50:1, flow rate = 0.5 mL min^{-1}). [d] The reaction was carried out in the dark. [e] The reaction was carried out in the presence of 2,6-dichloropyridine *N*-oxide.



Scheme 1. Kinetic resolution of (±)-indene oxide.

We next examined the effect of the wavelength of light on the activation of catalyst **1** by using a xenon short arc lamp (Type UXL 500D-0, USHIO) and color filter glass (V-42 & UV-D33S, TOSHIBA). A solution of **1**, **2**, and *trans*-β-methylstyrene was exposed to light for 2 h (Scheme 2). Light

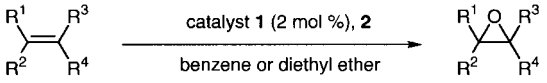


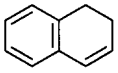
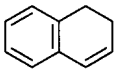
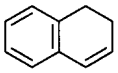
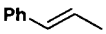
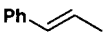
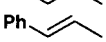
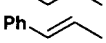
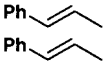
Scheme 2. Effect of wavelength of light on activation of catalyst **1**.

of around 450 nm accelerated the reaction the most effectively. The light of longer wavelength (>490 nm) was less efficient. Exposure of the reaction medium to UV light provided a complex product mixture. Based on these results, we used an incandescent or halogen lamp, which mostly emits visible and infrared light, as the light source in the following experiments.

We also examined solvent effect on enantioselectivity and chemical yield by using dihydronaphthalene and *trans*-β-methylstyrene as substrates and an incandescent lamp (100 V, 60 W) as the light source. Among the solvents (benzene, dichloromethane, diethyl ether, acetonitrile, ethyl acetate, and acetone) examined, use of polar ones such as ethyl acetate, acetone, and acetonitrile retarded epoxidation; the reactions were slow in acetone and ethyl acetate, and no reaction occurred in acetonitrile. In contrast, the reactions in diethyl ether and benzene proceeded smoothly, and high enantioselectivities were observed; however, the solvent of choice was dependent on the substrate used (Tables 2 and 4). Reduction of the enantiomeric excess of the epoxide and formation of ketone was also observed in the epoxidation of dihydronaphthalene in benzene, but the reduction of the enantiomeric excess in this reaction was less than that observed in the reaction in diethyl ether at the corresponding times [see Table 2 (entries 1 and 3) and Table 4 (entries 1 and 2)]. This is partly attributed to less efficient enantiomer differentiation in the rearrangement of epoxides with benzene as the solvent ($k_{rel} = 61$ and 30 in diethyl ether and benzene, respectively). On the other hand, enantiomeric excess of *trans*-β-methylstyrene oxide also gradually decreased, though ketone formation was not detected (entries 4, 5, 7, and 8). Again, reduction of enantiomeric excess of the epoxide was

Table 4. Asymmetric epoxidation of conjugated olefins with **1** as a catalyst.[a]



Entry	Substrate	Time [h]	Yield [%]	*ee* [%]	Configuration
1[b]		2	51 (5)[c]	87[d]	1*S*,2*R*
2[b]		6	70 (23)[c]	81[d]	1*S*,2*R*
3[e]		2	48 (4)[c]	80[d]	1*S*,2*R*
4[f]		2	26	86[g]	1*S*,2*S*
5[f]		32	64	75[g]	1*S*,2*S*
6[e]		7	60	81[g]	1*S*,2*S*
7[b]		6	28	82[g]	1*S*,2*S*
8[b]		20	75	80[g]	1*S*,2*S*

[a] The reaction was carried out under irradiation of visible light with incandescent or halogen lamp. [b] The reaction was carried out in benzene with **2** as a terminal oxidant. [c] The number in parentheses is the yield of the corresponding ketone or aldehyde. [d] Determined by HPLC analysis using optically active column (DAICEL CHIRALCEL OB-H, hexane/2-propanol 50:1). [e] The reaction was carried out in dioxane with tetramethylpyrazine *N*,*N*′-dioxide as a terminal oxidant. [f] The reaction was carried out in diethyl ether with **2** as a terminal oxidant. [g] Determined by GLC analysis using optically active column (SUPELCO β-DEX™ 225 fused silica capillary column, 30 m × 0.25 mm ID, 0.25 mm film: 90 °C).

slower in the reaction in benzene than in diethyl ether, but better enantioselectivity was observed in diethyl ether at the initial stage of the reaction (entries 4 and 7). These results suggested that reduction of enantiomeric excesses was attributed not only to enantiomer-differentiating rearrangement of the epoxides, but also to decay of the original catalyst into less efficient one(s) during epoxidation. This assumption was supported from the following observation: absorption maxima (λ_{max}) in the UV-visible spectrum of **1** in benzene (2.0×10^{-4} M) are 456 (ε 5.5×10^3) and 535 nm (ε 2.7×10^3), but the broad signal at 535 nm became gradually weak upon the exposure of complex **1** to incandescent light under the reaction conditions. To investigate the advantage of diethyl ether and benzene as solvents, we examined epoxidations in other ethereal and aromatic solvents (dioxane, THF, dimethoxyethane, and α,α,α-trifluoromethylbenzene). Though improvement in enantioselectivity was not obtained, the reactions in dioxane showed enantioselectivity almost equal to those observed in the reactions with benzene (entries 3 and 6).

Based on the above results, we examined epoxidation of various other olefins with diethyl ether, benzene, and dioxane as solvents. Hereafter, tetramethylpyrazine *N*,*N*′-dioxide[16] was mostly used as the terminal oxidant instead of 2,6-dichloropyridine *N*-oxide, because the resulting tetramethylpyrazine and tetramethylpyrazine *N*-oxide are chromatographically readily separable from the products, and the change of oxidant did not affect enantioselectivity. The best results obtained are summarized in Table 5. Epoxidation of

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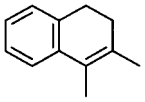
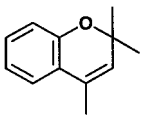
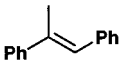
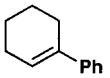
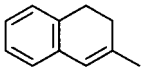
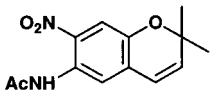
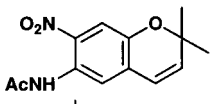
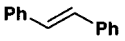
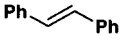
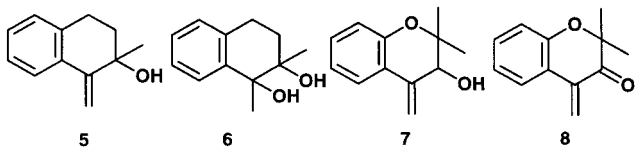
Table 5. Asymmetric epoxidation of conjugated olefins using **1** as a catalyst.[a]

Entry	Substrate	Time [h]	Yield [%]	*ee* [%]	Configuration[b]
1[c]		28	32[d]	82[e]	–
2[c]		16	54[f]	97[g]	3*S*
3[c]		17.5	83 (2)[h]	86[i]	1*R*,2*R*
4[c]		22	62	79[j]	1*R*,2*R*
5[c]		22	74	88[i]	–
6[k]		5	54	98[l]	3*S*,4*S*
7[m]		16	59	97[l]	3*S*,4*S*
8[m]		30	60	89[n]	1*S*,2*R*
9[m]		72	52	87[o]	1*R*,2*R*
10[c]		40	64	85[o]	1*R*,2*R*
11[c]		7	30 (2)[h]	83[p]	*S*
12[c]		14	63 (7)[h]	71[p]	*S*
13[m]		12	34 (<1)[h]	79[p]	*S*

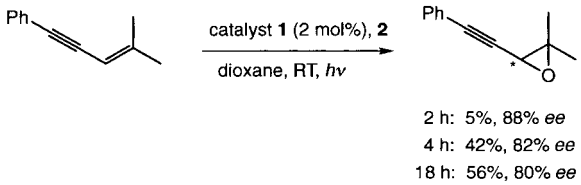
[a] Reactions were carried out under irradiation of visible light with incandescent or halogen lamp. [b] Configuration of major enantiomer was determined by comparison of elution order in HPLC analysis with the order of authentic sample. [c] The reaction was carried out in dioxane with tetramethylpyrazine *N*,*N*′-dioxide as a terminal oxidant. [d] Allylic alcohol **5** (10%) and diol **6** (3%, 73% *ee*) were also produced. [e] Determined by GLC analysis with an optically active column (HP-CHIRAL (20% permethylated β-cyclodextrin), 30 m × 0.25 mm ID, 0.25 mm film: 120 °C). [f] Product was a mixture of allylic alcohol **7** (54%, 97% *ee*) and enone **8** (4%). [g] Determined by HPLC analysis with an optically active column (DAICEL CHIRALCEL OB-H, hexane/2-propanol 50:1). [h] The number in parentheses is the yield of the corresponding ketone or aldehyde. [i] Determined by HPLC analysis with an optically active column (DAICEL CHIRALCEL OJ, hexane/2-propanol 50:1). [j] Determined by HPLC analysis with an optically active column (DAICEL CHIRALCEL OF, hexane/2-propanol 1000:1). [k] The reaction was carried out in diethyl ether with **2** as a terminal oxidant. [l] Determined by HPLC analysis with an optically active column (DAICEL CHIRALCEL OJ, hexane/2-propanol 1:1). [m] The reaction was carried out in benzene with **2** as a terminal oxidant. [n] Determined by GLC analysis with an optically active column (SUPELCO β-DEX™ 225 fused silica capillary column, 30 m × 0.25 mm ID, 0.25 mm film: 90 °C). [o] Determined by HPLC analysis using optically active column (DAICEL CHIRALCEL OJ, hexane/2-propanol 9:1). [p] Determined by HPLC analysis using optically active column (DAICEL CHIRALCEL OD-H, hexane/2-propanol 1000:1).



5 **6** **7** **8**

tetra-, tri-, *cis*-di-, *trans*-di-,[19] and monosubstituted olefins all showed good enantioselectivity greater than about 80% *ee*. Furthermore, as expected from previous reports,[9d, 12a] the present epoxidation was highly stereospecific: *cis*-olefins gave *cis*-epoxides and *trans*-olefins gave *trans*-epoxides exclusively. Formation of only a trace amount (<0.5%) of the isomerized *trans*-epoxides was detected in the epoxidation of *cis*-β-methylstyrene by GLC analysis (entry 8). The reaction of 1,2-dihydro-3,4-dimethylnaphthalene was slow, and the resulting epoxide was partly converted into the corresponding allylic alcohol and diol during the reaction (entry 1). Rearranged allylic alcohol was the major product in the epoxidation of 2,2,4-trimethylchromene (entry 2). In the epoxidations of (*E*)-1,2-diphenyl-1-propene and styrene, formation of a small amount of ketone and aldehyde was observed, respectively. In other reactions, epoxides were the only products.

In the above reactions, we used aryl-substituted olefins as the conjugated olefins due to ease of handling. We also examined the epoxidation of 4-methyl-1-phenyl-3-penten-1-yne. The reaction proceeded to give an epoxide as the sole product with high enantioselectivity, but the enantiomeric excess of the product decreased as the reaction time became long, because of decomposition of the catalyst (Scheme 3). These results may suggest the present reaction can be applied to various conjugated olefins.



Scheme 3. Asymmetric epoxidation of 4-methyl-1-phenyl-3-penten-1-yne.

To clarify the wide scope of asymmetric catalysis of **1**, we studied its structure. Complex **1** was recrystallized from chloroform and acetonitrile to afford single crystals **1**·(CH_3CN), the structure of which was unambiguously determined by X-ray crystallographic analysis (Figure 1). The geometry around the ruthenium ion was a slightly distorted octahedral with nitrosyl and chloride ligands as the apical ligands. The nitrosyl ligand behaved as a three-electron donor, and Ru-N(3)-O(3) is linear (176.0(9)°). The bond length of N(3)–O(3) (0.971(8) Å) is consistent with $(NO)^+$ coordinated to the metal ion, but the positive charge on the nitrosyl group is likely to be somewhat neutralized by a back donation of electron density from the ruthenium ion as indicated by a relatively short bond length of Ru–N(3) (1.862(6) Å). Due to the strong *trans* influence of the nitrosyl ligand, the Ru–Cl bond was lengthened to some extent (Ru-Cl 2.312(2) Å). Although these structural factors of **1** were comparable to the analogous [Ru(salen)] complexes so far reported,[20, 21] some other characteristic features of **1** were found: 1) a unique unsymmetrical stepped conformation of the salen ligand with the right half almost co-planar to the equatorial coordination plane defined by the N(1), N(2), O(1), and O(2) atoms and with the left half bent downward [the dihedral angle between the planes N(1)-C(7)-C(C8)-C(17)-O(1) and N(2)-C(34)-

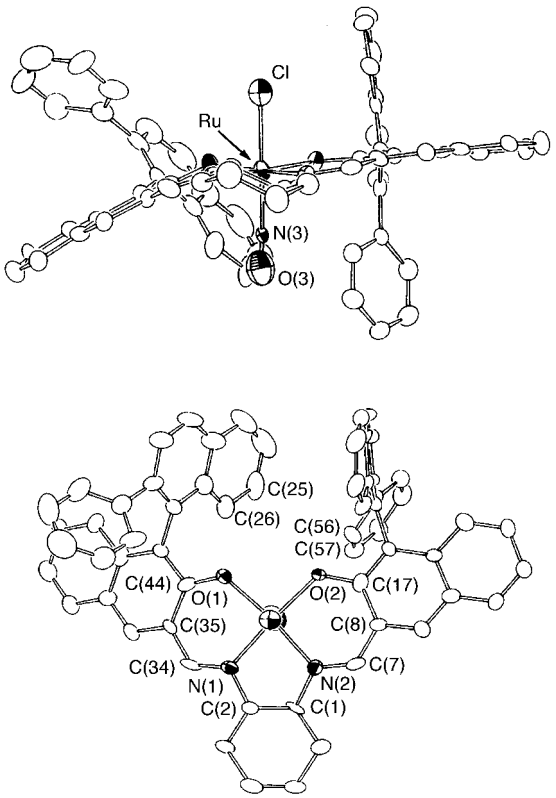
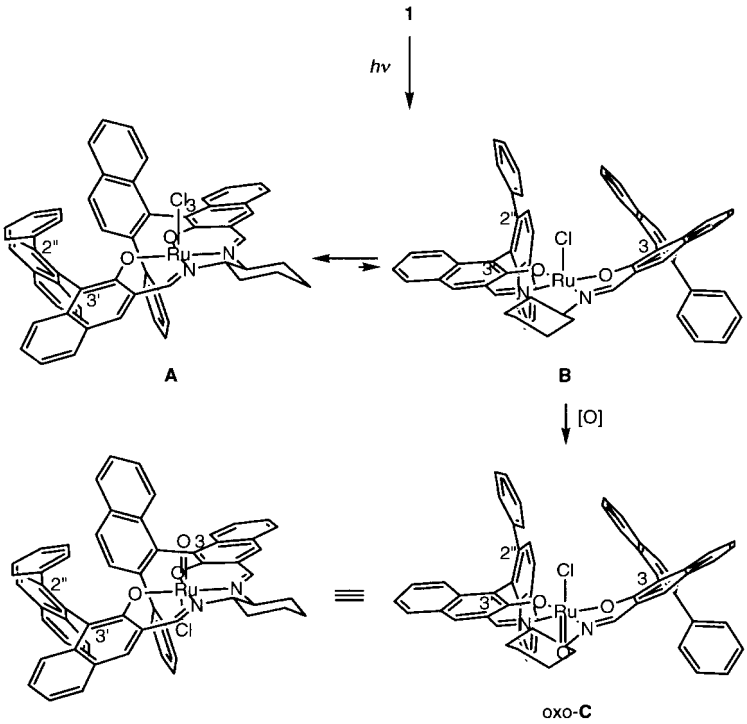


Figure 1. ORTEP diagrams for the crystal structure of **1**·(CH_3CN). Top: the side view from the cyclohexane ring. Bottom: the top view from the chloro ligand. The solvate molecule is omitted for clarification.

C(35)-C(44)-O(2) was ca. 16°: see the side view Figure 1 (top)]; 2) close proximity of C3-naphthyl and C2″-phenyl groups and the nitrosyl ligand, suggesting that some attractive interaction is working between them (C(25)–C(56) 3.47(1), C(25)–C(57) 3.71(1), O(3)–C(26) 3.84(1), O(3)–C(56) 3.63(1) Å). We have recently proposed that the conformation of the salen ligand of the related cationic chiral [Mn(salen)] complex bearing two apical aqua ligands is dictated by the chirality at the ethylenediamine part, the conformation of five-membered chelate ring (including manganese ion and ethylenediamine moiety), and the attractive interaction between two C3(3′) substituents and apical ligands.[22] Although the five-membered chelate ring in the [Mn(salen)] complex takes a half-chair conformation, the chelate ring in complex **1** adopts a distorted envelope conformation. Another difference between [Mn(salen)] and [Ru(salen)(NO)] complexes is the bond length between metal ion and equatorial oxygen atom; the Ru–O bond (2.03 – 2.04 Å) is longer than the Mn–O bond (1.84 – 1.87 Å). This longer bond length separates (2″-phenyl)naphthyl groups at C3 and C3′ and makes CH – π interactions between the 2″-phenyl ring at C3-substituent and the naphthyl ring at C3′ difficult. Thus, differing from [Mn(salen)] complex, two substituents at C3 and C3′ in **1** are not parallel to each other. The conformation of **1** reflects these differences between [Mn(salen)] and [Ru(salen)(NO)] complexes; the unique unsymmetrical conformation of **1** is mainly caused by the chelate ring conformation and amplified by the interaction of the C3′-substituent and the apical ligand. The contribution of the latter interaction to ligand conformation is supported by the fact that the nonsubstituted [Ru(salen)(NO)] complex has the five-membered chelate ring in a half-chair conformation and possesses an almost planar structure.[20]

The unsymmetrical non-planar ligand conformation of complex **1** is expected to be also reflected on the ligand conformation of a putative oxo(salen)ruthenium species (oxo-**C**) from the following consideration (Scheme 4). The apical



Scheme 4. Proposed structures of the photoactivated [Ru(salen)] and the oxo(salen)ruthenium species.

nitrosyl ligand of **1** is dissociated upon irradiation to give an active species **A**,[17, 18] which is equilibrated with another conformer **B**. The equilibrium between **A** and **B** is considered to favor **A** owing to the presence of unfavorable repulsion between 2″-phenyl group and the apical chloro ligand in **B**. However, the vacant apical site of **A** is sterically congested and its oxidation to the corresponding oxo species should be hampered. In contrast to this, the vacant apical site of **B** is sterically less congested and it is readily oxidized to oxo species (oxo-**C**). Thus, the oxo species derived from **1** is considered to have a structure similar to **1**. This deeply folded basal salen ligand and the largely inclined orientation of the C3 substituent endow oxo-**C** with an open asymmetric coordination sphere around the oxene atom, which could be responsible for the unique catalytic performance of **1**, and the highly enantioselective epoxidation of olefins irrespective of their substitution pattern. In conclusion, we were able to find a general methodology for the epoxidation of conjugated olefins.

Experimental Section

General considerations: ^{1}H NMR spectra were recorded at 400 MHz on a Bruker DPX400 or a Jeol GX400 instrument. All signals were expressed with respect to tetramethylsilane as an internal standard. IR spectra were

0947-6539/01/0717-3780 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 17

obtained with a Shimadzu FTIR-8600 instrument. Optical rotations were measured with a Jasco P-1020 polarimeter. Column chromatography was conducted on silica gel BW-820MH, 70–200 mesh ASTM, available from Fuji Silysia Chemicals. Preparative thin-layer chromatography was performed on a 0.5 mm × 20 cm × 20 cm Merck silica gel plate (60 F-254). Enantiomeric excesses were determined by HPLC analysis with Shimadzu LC-10AT-VP or by GLC analysis by using Shimadzu GC-17A or Perkin–Elmer Turbomas equipped with an appropriate optically active column, as described in the footnotes of the corresponding tables. Complex **1** was prepared to according to the reported procedure.[23] Tetrahydrofuran (THF), diethyl ether, and benzene were dried and deoxygenated over sodium benzophenone and distilled shortly before use. Anhydrous dioxane was purchased from Kanto Chemical Co. Reagents and solvents were used as received unless otherwise mentioned. Reaction temperature was controlled by using a water-circulating bath and by attaching a infrared filter to the light source. Equipment made with Pyrex glass were used in all the experiments. Reactions were carried out under an atmosphere of nitrogen.

General procedure for asymmetric epoxidation with complex 1 as the catalyst: Complex **1** (2.0 mg, 2 μmol) and tetramethylpyrazine *N,N′*-dioxide (16.8 mg, 0.10 mmol) were successively added to a solution of substrate (0.10 mmol) in dioxane (1.0 mL). The whole mixture was stirred for the period specified in the Tables 1, 2, 4 and 5 at room temperature under irradiation with a halogen (100 W or 150 W) or an incandescent lamp (60 W), and then concentrated in vacuo. The residue was purified by chromatography over short silica gel column (hexane/AcOEt 9:1 to 3:2). Enantiomeric excess and absolute configuration of the product were determined as described in the footnotes of Tables 1, 2, 4 and 5.

3,4-Dihydro-1,2-dimethylnaphthalene-1,2-oxide: Colorless oil; yield 32% (82% *ee*); $[\alpha]_{26}^{D} = -144.7$ ($c = 0.39$ in $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.55-7.51$ (m, 1H), 7.23–7.19 (m, 2H), 7.09–7.05 (m, 1H), 2.90 (ddd, $J = 6.4$, 14.3, 14.3 Hz, 1H), 2.49 (ddd, $J = 1.5$, 5.0, 14.3 Hz, 1H), 2.19 (ddd, $J = 1.5$, 6.4, 14.3 Hz, 1H), 1.86 (ddd, $J = 5.0$, 14.3, 14.3 Hz, 1H), 1.76 (s, 3H), 1.55 (s, 3H); IR (KBr): $\tilde{\nu} = 3429$, 2928, 1728, 1383, 1277, 1076, 1040, 883, 814, 760 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 174 (23) $[M]^+$, 159 (18), 146 (100), 131 (42), 115 (26), 91 (23); HRMS (EI, 70 eV): calcd for $C_{12}H_{14}O$: 174.1045; found: 174.1051; the absolute configuration was not determined.

3,4-Dihydro-2-methyl-1-methylenenaphthalene-2-ol: Colorless oil; yield 10%; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.61$ (m, 1H), 7.21–7.12 (m, 3H), 5.55 (s, 1H), 5.43 (s, 1H), 3.00 (ddd, $J = 5.5$, 5.5, 16.5 Hz, 1H), 2.90 (ddd, $J = 8.2$, 8.2, 16.5 Hz, 1H), 1.97–1.93 (m, 2H), 1.65 (brs, 1H), 1.40 (s, 3H); IR (KBr): $\tilde{\nu} = 3655$, 2928, 1720, 1454, 1381, 1290, 1258, 1150, 1101, 1076, 903, 762 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 174 (61) $[M]^+$, 156 (91), 141 (93), 131 (87), 115 (100), 91 (50); HRMS (EI, 70 eV): calcd for $C_{12}H_{14}O$: 174.1037; found: 174.1045.

3,4-Dihydro-1,2-dimethylnaphthalene-1,2-diol: Colorless oil; yield 3%; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.66$ (d, $J = 7.5$ Hz, 1H), 7.24–7.16 (m, 2H), 7.08 (d, $J = 7.5$ Hz, 1H), 3.03 (ddd, $J = 5.3$, 5.3, 17.2 Hz, 1H), 2.80 (ddd, $J = 8.5$, 8.5, 17.2 Hz, 1H), 2.61 (s, 1H), 2.46 (s, 1H), 2.03–2.00 (m, 2H), 1.47 (s, 3H), 1.37 (s, 3H); IR (KBr): $\tilde{\nu} = 3431$, 2982, 2936, 1454, 1373, 1119, 1080, 920, 764, 725 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 192 (9) $[M]^+$, 159 (100), 134 (16), 119 (100), 91 (50); HRMS (EI, 70 eV): calcd for $C_{12}H_{16}O_2$: 192.1150; found: 192.1148.

3-Hydroxy-2,2-dimethyl-4-methylenechromane: Colorless oil; yield 54% (97% *ee*); $[\alpha]_{28}^{D} = -22.9$ ($c = 0.38$ in $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.55$ (d, $J = 7.5$ Hz, 1H), 7.20 (t, $J = 7.5$ Hz, 1H), 6.92 (t, $J = 7.5$ Hz, 1H), 6.85 (d, $J = 7.5$ Hz, 1H), 5.64 (s, 1H), 5.22 (s, 1H), 4.06 (d, $J = 7.0$ Hz, 1H), 1.82 (d, $J = 7.0$ Hz, 1H), 1.38 (s, 3H), 1.28 (s, 3H); IR (KBr): $\tilde{\nu} = 2980$, 1481, 1456, 1375, 1304, 1256, 1144, 1097, 943, 899, 756 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 190 (100) $[M]^+$, 175 (15), 161 (33), 147 (83), 131 (23), 119 (30), 91 (51); HRMS (EI, 70 eV): calcd for $C_{12}H_{14}O_2$: 190.0994; found: 190.0992; the absolute configuration was not determined.

(*R*,*R*)-1-Methyl-1,2-diphenyl oxirane: Colorless oil; yield 83% (86% *ee*); $[\alpha]_{24}^{D} = +104.1$ ($c = 0.53$ in EtOH) ($[\alpha]_{25}^{D} = -113.9$ ($c = 0.9$ in EtOH) for the material of 95.5% *ee*[24]).

(1*S*,2*R*)-1-Phenylcyclohexene oxide: Colorless oil; yield 62% (79% *ee*); $[\alpha]_{25}^{D} = +79.7$ ($c = 0.59$ in benzene) ($[\alpha]_{25}^{D} = +116.7$ ($c = 1.21$ in benzene) for the material of 98% *ee*[24]).

2-Methyl-1,2-epoxy-1,2,3,4-tetrahydronaphthalene: Colorless oil; yield 74% (88% *ee*); $[\alpha]_{25}^{D} = -143.1$($c = 0.71$ in $CHCl_3$) ($[\alpha]_{33}^{D} = +50.5$ ($c = 1.02$ in $CHCl_3$) for the material of 49% *ee*[25]); the absolute configuration was not determined.

(3*S*,4*S*)-6-Acetamido-3,4-epoxy-2,2-dimethyl-7-nitrochromene: Colorless oil; yield 54% (98% *ee*); $[\alpha]_{25}^{D} = +19.9$ ($c = 0.42$ in $CHCl_3$) ($[\alpha]_{25}^{D} = +23.2$ (c 0.25 in $CHCl_3$) for the material of >99% *ee*[26]).

(1*S*,2*R*)-1,2-Epoxy-1-phenylpropene: Colorless oil; yield 60% (89% *ee*); $[\alpha]_{25}^{D} = +49.2$ ($c = 0.25$ in $CHCl_3$) ($[\alpha]_{25}^{D} = +28$ ($c = 0.41$ in $CHCl_3$) for the material of 68% *ee*[27]).

(1*S*,2*S*)-1,2-Epoxy-1-phenylpropene: Colorless oil; yield 26% (86% *ee*); $[\alpha]_{25}^{D} = -50.4$ ($c = 0.42$ in $CHCl_3$) ($[\alpha]_{25}^{D} = +47.8$ ($c = 1.04$ in $CHCl_3$) for the material of 95.5% *ee*[24]).

(1*R*,2*R*)-Stilbene oxide: Colorless oil; yield 52% (87% *ee*); $[\alpha]_{25}^{D} = +180.3$ ($c = 0.88$ in $CHCl_3$) ($[\alpha]_{25}^{D} = +126$ ($c = 0.88$ in $CHCl_3$) for the material of 48% *ee*[27]).

(1*S*,2*R*)-3,4-Dihydronaphthalene 1,2-oxide: Colorless oil; yield 59% (84% *ee*); $[\alpha]_{24}^{D} = -117.6$ ($c = 0.40$ in $CHCl_3$) ($[\alpha]_{25}^{D} = -144.9$ ($c = 0.33$ in $CHCl_3$) for the material of 98% *ee*[26]).

(*S*)-Styrene oxide: Colorless oil; yield 30% (83% *ee*); $[\alpha]_{28}^{D} = +36.9$ ($c =$ 0.18 in C_6H_6) ($[\alpha]_{18}^{D} = +44.5$ (c 1.05, in C_6H_6) for the material of 95% *ee*[28]).

3,4-Epoxy-4-methyl-1-phenylpent-1-yne: Colorless oil; yield 42% (82% *ee*); $[\alpha]_{24}^{D} = -14.7$ ($c = 0.17$ in $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.46-7.44$ (m 2H), 7.35–7.29 (m, 3H), 3.44 (1H, s), 1.51 (3H, s), 1.40 (3H, s); IR (NaCl): $\tilde{\nu} = 2990$, 2967, 2928, 1599, 1491, 1445, 1381, 1304, 1250, 1117, 1042, 881, 791, 758, 690, 569 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 172 (29) $[M]^+$, 156 (3), 143 (6), 129 (11), 114 (100), 88 (5); HRMS (EI, 70 eV): calcd for $C_{12}H_{12}O$: 172.088; found: 172.088; the absolute configuration was not determined.

X-ray crystal structure determination of 1: Recrystallization of **1** from chloroform and acetonitrile afforded single crystals **1**·(CH_3CN) suitable for X-ray structural analysis. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation. Structural analysis was performed by using the teXsan crystallographic software package. The structure was solved by heavy atom Patterson methods and expanded with Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Structural data and experimental detail are summarized in Table 6. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161815. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 6. Crystallographic data and experimental details of the structure determinations for complex **1**·(CH_3CN).

formula	$C_{62}H_{47}N_4O_3ClRu$
M_r	1032.60
crystal dimensions [mm]	0.20 × 0.15 × 0.35
crystal system	orthorhombic
space group	$P2_12_12_1$
a [Å]	18.215(4)
b [Å]	28.994(5)
c [Å]	9.241(2)
V [Å^3]	4880(1)
Z	4
ρ_{calcd} [g cm^{-3}]	1.405
$2\theta_{max}$ [°]	55
λ ($Mo_{K\alpha}$) [Å]	0.71069
scan mode	ω
T [K]	183
measured reflections	12614
unique reflections	8976
observed reflections [$I > 3\sigma(I)$]	6266
correction	Lorentz polarization
μ ($Mo_{K\alpha}$) [cm^{-1}]	4.29
R values [$I > 3\sigma(I)$]	$R = 0.055$, $R_w = 0.046$
refinement	full-matrix least squares against F^2
residual electron density [e Å^{-3}]	0.78/ −0.71

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