Contribution

Fascination of metallosalen complexes: Diverse catalytic performances and high asymmetry-inducing ability

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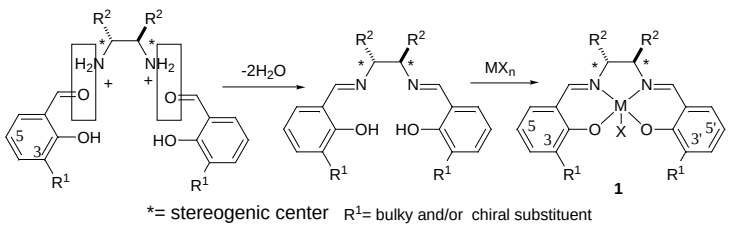
Introduction

Studies on asymmetric reactions using optically active metallosalen complexes as catalyst have recently been rapidly increasing. This is attributable to the facts that various derivatives of salen complexes can be easily synthesized and they exhibit distinctive catalytic performances. During a recent two-decade period, various metallosalen complexes have been introduced and conspicuous development has been made in the chemistry of "metallosalen complex." This paper reports on the basic structural features and catalytic performances of metallosalen complexes, as well as recent developments in asymmetric reactions using them as catalyst, focusing on the author's studies.

1. Synthesis of metallosalen complexes and their structural features

Salen ligand [*N,N'*-bis(salicylidene)ethylenediamine] and its derivatives can be synthesized by the dehydration condensation reaction of salicyl aldehydes and ethylenediamine derivatives. The formation of metallosalen complex (**1**) can be achieved by simply mixing the ligand with a metal ion after its conversion to the corresponding phenoxide ion derivative or under basic conditions (**Scheme 1**). Most metal ions can form salen complexes, with the exception of alkali, alkaline-earth and some of the rare-earth metals. Of these complexes, trivalent chromium, cobalt, and manganese complexes that are widely used as catalyst are synthesized by aerobic or chemical oxidation of the corresponding divalent complexes. Since synthetic methods for the various 3-substituted or 3,5-disubstituted salicyl aldehydes and for optically active diamines have already been established (some of which are commercially available), a variety of salen complexes with different central metals are now easily available.

The important structural features of salen complexes are the existence therein of an ethylene unit located adjacent to a metal ion and that of the large space between the 3- and 3'- positions. These features allow the reaction field around the metal ion, to be tailored to fit with specific reactions through the introduction of suitable substituents at the ethylene and the 3- and 3'-positions. Another important feature of salen complexes is the structural-flexibility that is provided by the existence of the ethylene unit. Most of the salen complexes have an octahedral structure, and in many cases the salen ligand coordinates tetravalently with the central ion on the same plane (*trans*-isomer, **2**). Namely, four of the coordinating atoms (N, N, O, O) of the ligand occupy equatorial positions and the other ligands (X, Y) bind at the apical positions (**Figure 1**). [1)]



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Scheme 1.

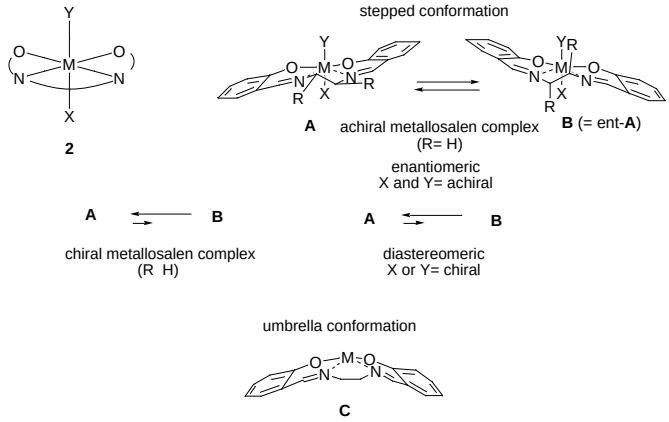
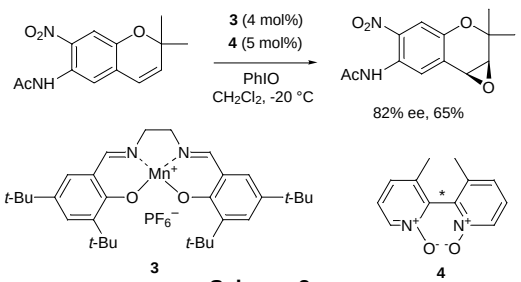


Figure 1.

Although salen ligands coordinate tetravalently on a single plane, this does not mean that the ligands adopt planar structures. A five-ring chelate constituted from ethylene diamine and a central ion can adopt a half-chair conformation, an envelope conformation or a slightly distorted form of one of these. Consequently, salen complexes adopt a conformation that is either stepped (**A** and **B**), an umbrella (**C**) or a slightly distorted form of either.[1] The stepped conformation is chiral, but the umbrella is achiral. The substituents introduced at the ethylene unit occupy the stable pseudo-equatorial position and they are gauche to each other. Thus, the stepped conformation (**A**) has some advantage over the conformation (**B**) in which the substituents occupy the pseudo-axial position or the umbrella conformation (**C**) with an eclipsed relationship between both substituents. This means that the introduction of the substituents not only creates asymmetry at the ethylene site, but also makes the salen skeleton chiral.[2] An achiral complex with no substituent (R = H) generally exists as an equilibrium mixture of two enantiomers [A and B (= ent-**A**)]. However, if an apical ligand (X or Y) is chiral, the enantiomers (**A** and **B**) become diastereomeric, and therefore the equilibrium tends towards one or other of the isomers. By leveraging this phenomenon, asymmetric synthesis using an achiral complex as the catalyst becomes possible.[3] In fact, when using achiral manganese(salen) complex (**3**) as the catalyst in the presence of chiral bipyridine-*N,N'*-oxide (**4**), the epoxidation proceeds in a highly enantioselective manner (**Scheme 2**).[4] These studies were the first examples of asymmetric synthesis using a conformationally controlled achiral metal complex as catalyst. Similar attempts were widely undertaken afterwards.[5]

Another major feature of salen complexes is the existence of coordination isomers. As stated above, many of the salen ligands primarily adopt a planar-tetravalent coordination, however, they can adopt *cis*-coordination where one oxygen atom on the salen ligand shifts to the apical position, when a bidentate additive (X-Y) coordinating with the metal ion is added (**Figure 2**).[6] Salen complexes of metal ions of second and third series such as Zr, Ru, Hf, *etc.* sometimes adopt *cis*-β coordination without the existence of a bidentate ligand. Unlike planar tetravalent complexes, these *cis*-β complexes are chiral at the first coordination sphere of the complex, and therefore possess a significant advantage in terms of the construction of an asymmetric field. More specifically, a *cis*-β complex can exist as the Δ or Λ isomer with an enantiomeric relationship in which the central metal ion is chiral. The chirality of this central metal atom is generally determined by asymmetry of the diamine portion. If the design of a ligand that can utilize this feature of a *cis*-β complex proves to be possible, then the design of a catalytic agent with higher asymmetry-inducing ability is expected to become a reality. In particular, it is believed that a *cis*-β complex could provide an effective reaction field for substrates that can take a bidentate coordination or intermolecular reactions between substrates with a coordinating functional moiety. Although salen complexes are able to take a conformation in which two oxygen molecules coordinate at apical positions (*cis*-α isomer), they are normally unstable and there are almost no reports on their application to chiral catalytic reactions, and their chemistry is not dealt with in this paper.



Scheme 2.

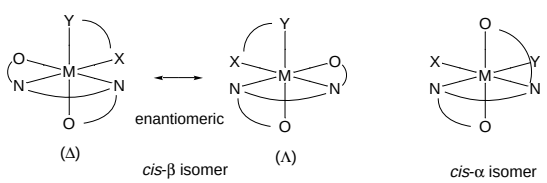
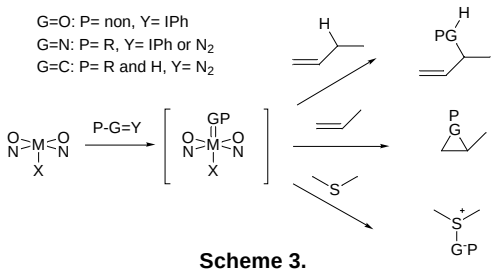


Figure 2.

2. Asymmetric atom transfer reactions using square planar salen complexes

By reacting with appropriate precursors, the square planar salen complexes afford oxenoid, nitrenoid or carbenoid intermediates that undergo addition reactions to olefins or hetero-atoms or insertion reactions to C-H bonds.



Scheme 3.

For effective and highly-stereoselective atomic transfers to be performed, the following requirements need to be fulfilled: i) the selection of central metal atoms that are suitable for the the oxenoid, nitrenoid or carbenoid formation and ii) the appropriate design of salen ligands that take into account the structures of the intermediates. Fujita *et al.* reported the asymmetric oxidation of sulfides using optically active vanadium(salen) complex (**5**) as catalyst in 1986.[7] In 1990, Jacobsen *et al.*[8] and the present authors *et al.*[9] independently reported on asymmetric epoxidation using manganese complexes (**6**[8], **7**[9]), which revealed the usefulness of salen ligands bearing bulky constituents at the 3-position (**Scheme 4**). These reports led to the initiation of active studies on asymmetric oxidation using metallosalen complexes. The stereoselectivity of the reactions (taking epoxidation for example) are dependent on the direction from which the oxenoid species (oxo species in Scheme 3, G = O, P = none) are approached by the substrate and the orientation of the substrate during this process. In other words, high-stereoselectivity can be achieved during the reaction by controlling the direction of approach and the orientation. Although controversy still exists regarding the exact mechanism for controlling the direction of approach and the orientation, in this report the author describes his own hypothesis, which is based on experimental results. As mentioned earlier in this report, it was assumed that oxo compounds could adopt the stepped conformation as suggested by the experimental results of asymmetric epoxidation using achiral salen complexes.[3,4] This assumption is supported by the calculated results.[10] In the case where bulky substituents (R^1) exist at the 3,3'-positions, olefins approach the oxo compound along the N-M bond axis near to the downward-bent benzene ring, thereby directing the bulkier substituent (R_L) away from the bulky 3- or 3'-substituents (R^1) (**Figure 3**).[2] The alternative approach pathway along the N-M bond axis is considered to be less effective due to a repulsive interaction with the upward-bent benzene ring. With a bulky substituent (R^2) at the 5-position (complex **8**[11]), an approach from the direction of the upwardly-bent benzene ring becomes even less effective, and thus the enantioselectivity of the reactions improves (**Scheme 4**).[11] Although Jacobsen *et al.* (who introduced compound (**8**)) claim that olefins approach from the diamine side to avoid the 3,5-substituents,[11] this argument does not agree with the results reported later on.[2b] *tert*-Butyl group is often used as bulky 3 and 3'-substituents, and this leads to favorable results in asymmetric epoxidation. However, in atom-transfer reactions other than epoxidation, the results are not always favorable.

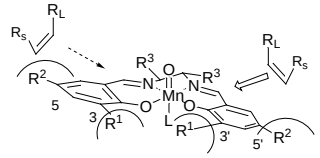
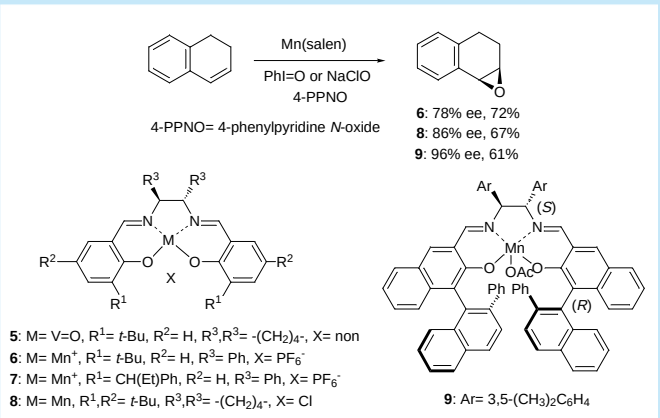


Figure 3.

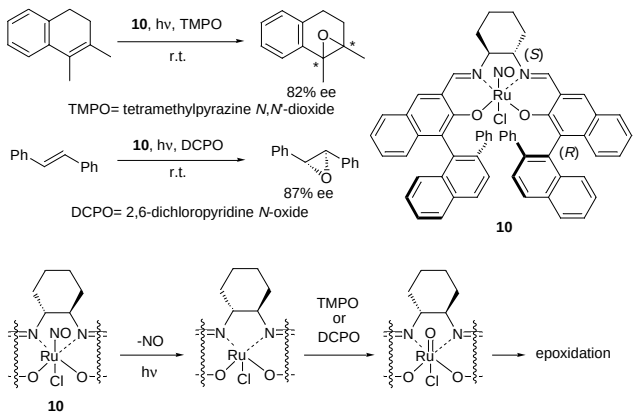
The authors expected that if the 3,3'-substituents were configured closer to the oxo bond, the orientation of the olefins could be more stringently regulated, resulting in improved enantioselectivity. Therefore, we constructed a new salen complex (**9**) bearing 2-phenylnaphthyl groups as 3,3'-substituents instead of *tert*-butyl groups.[12a] In this complex, the 2-phenyl groups on the naphthyl ring face toward the oxo-bond, which are then configured in the desired space. This was later confirmed by X-ray structural analysis.[13] Epoxidation using complex (**9**) provided significantly improved enantioselectivity, as expected. In the epoxidation of *cis*-2-substituent and 3-substituent olefins, high enantioselectivity (greater than 90% *ee*) is generally achieved.[12] Enantioselectivity during epoxidation is affected by the characteristics of the apical ligands, and 4-phenylpyridine *N*-oxide (4-PPNO) is usually added in the reaction (**Scheme 4**). However, due to the facts that manganese complexes adopt a relatively little-stepped conformation and the reactions proceed *via* radical intermediates, good selectivity cannot be achieved during the epoxidation of *trans*-2-substituent olefins or terminal olefins.[12b]



Scheme 4.

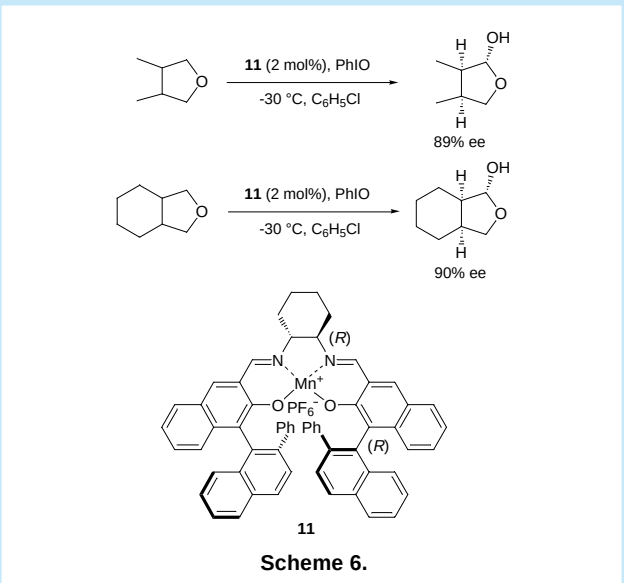
Recently, we discovered that ruthenium(salen) complex (**10**) served as an efficient catalyst for the epoxidation of olefins, and high-enantioselectivity was achieved, irrespective of the substitution pattern of the olefins (**Scheme 5**).[14] Complex (**10**) adopted a distorted stepped conformation,

so *trans*-di-substituted or tetra-substituted olefins could approach the oxo species.[15] These reactions are stereospecific, so *cis*-epoxides can be obtained from *cis*-olefins and *trans*-epoxides from *trans*-olefins. It is noteworthy that photo-radiation activates complex (**10**) to exhibit catalytic performance for asymmetric epoxidation. In short, complex (**10**) is coordinatively-saturated and catalytically inactive; however, photo-irradiation promotes the dissociation of the nitrosyl groups and makes it coordinatively-unsaturated and catalytically active.



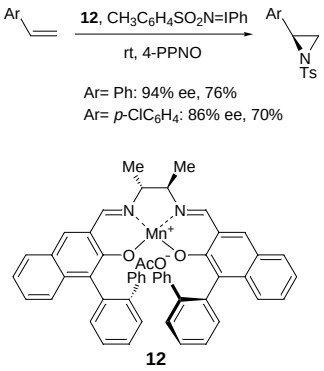
Scheme 5.

The oxenoid species (oxo species) catalyze both the epoxidation and hydroxylation of C-H bonds. However, since the appropriate structures of the manganese complexes and the reaction conditions used in both reactions are different from each other, it was assumed that the mechanism for asymmetric induction in both reactions is different. *R,R*-type complex (**11**) rather than *R,S*-type is appropriate to desymmetrization of *meso*-tetrahydrofuran *via* C-H oxidation and the reaction obtains a high-selectivity of 90% *ee*.[16] Unlike the epoxidation reaction, the addition of 4-PPNO results in decreased selectivity.



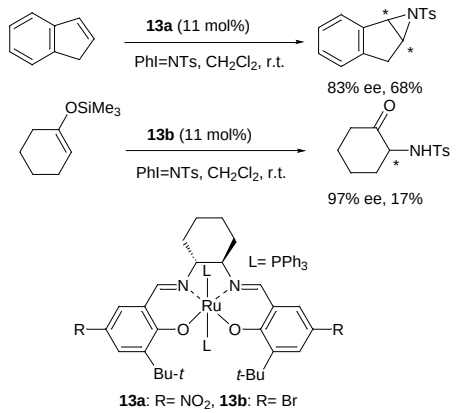
Scheme 6.

Nitrenoids are active species that possess the same electronic structure as oxenoids. However, they have a substituent on the nitrogen atom, and its orientation has a great influence on the asymmetric environment of the reaction site. This affects on the orientation of the approaching substrates. Therefore, rapid application of complex (**11**) that is a good catalyst for hydroxylation, to aziridination cannot lead to sufficient selectivity. However, complex (**12**) designed by taking into consideration that the orientation of the *p*-toluenesulfonyl group can achieve high-enantioselectivity in the aziridination of styrene and its derivatives (**Scheme 7**).[17]



Scheme 7.

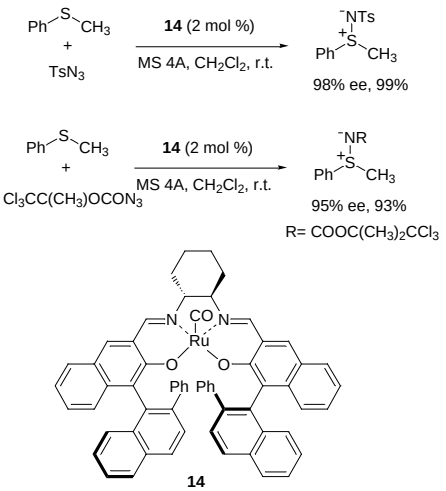
Recently, Che *et al.* reported that salen ruthenium complexes (**13**) can effectively catalyze nitrogen transfer reactions. Although the yield needs to be improved, significant selectivity in the amination of enols has been achieved (**Scheme 8**).[18] However, since *N*-(*p*-toluenesulfonyl)iminophenyliodinane was used as the nitrene precursor in these reactions, iodobenzene was generated as a by-product as the reaction progressed, and atom-economy of the reaction is inefficient. Use of a more atom-efficient precursor is required.



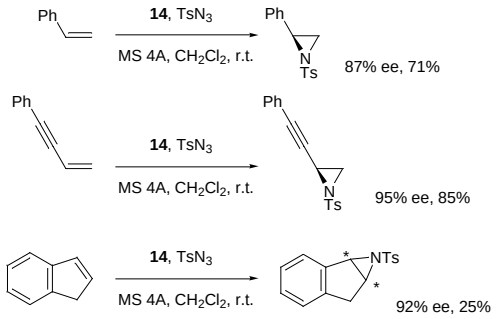
Scheme 8.

The atom economy of nitrene precursors should be significantly improved if toluenesulfonyl azide could be used, instead of the corresponding phenyliodinane derivative. Jacobsen *et al.* have reported that Cu-diimine complexes catalyze aziridination with TsN_3 as the precursor. However, the enantioselectivity that was obtained was insufficient, besides that UV irradiation was required for

the decomposition of the azide.[19] The authors *et al.* have discovered that ruthenium(salen) complex (**14**), which bears a CO ligand at the apical position, promotes the decomposition of azide at room temperature in the presence of sulfide groups and affords the corresponding sulfimides in a highly enantioselective manner (**Scheme 9**). In addition to *N*-arylsulfonylazide,[20] a carbamoylazide that possesses a bulky and electron-withdrawing alkyl group can be used as the precursor.[21] The aziridination of styrene derivatives can also be performed with high-enantioselectivity by using TsN_3 (**Scheme 10**) .[22]

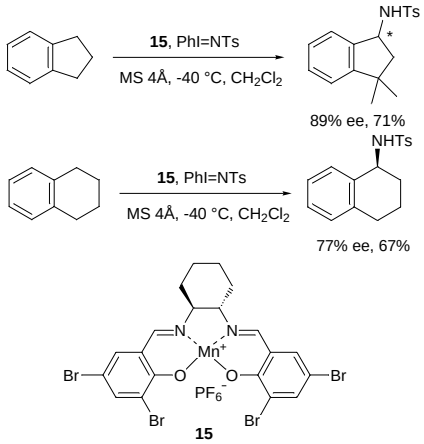


Scheme 9.



Scheme 10.

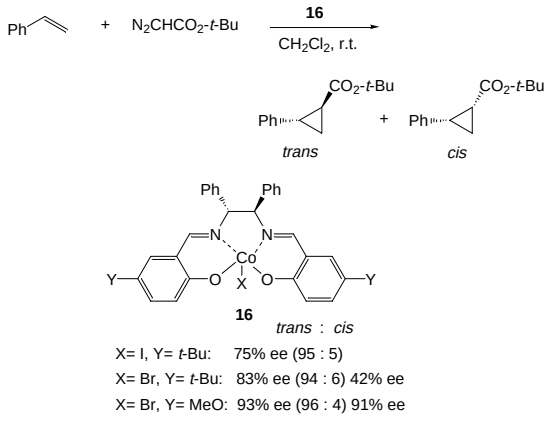
In a similar way to the oxenoid species, nitrenoid species can be inserted into active C-H bonds at benzylic or allylic positions. C-H amination and aziridination can occur competitively, when the substrates are olefins. However, amination becomes the dominant reaction if a catalyst bearing an electron-withdrawing groups is used as the catalyst. The use of the suitably brominated manganese(salen) complex (**15**) realized high enantioselectivity of 89% *ee* in C-H amination (**Scheme 11**).[23] However, there is a room for improvement in the atom economy, because *N*-sulfonyliminoiodinane has been used as the precursor.



Scheme 11.

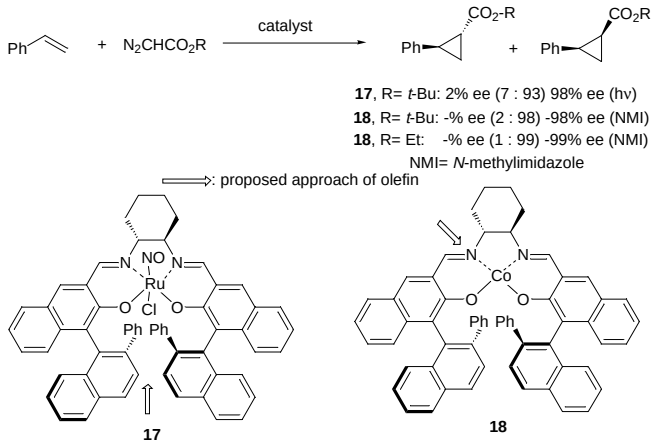
Diazo-compounds are widely used as precursors for asymmetric cyclopropanation *via* carbenoid intermediates. Inspired by the epoch-making Aratani's achievement, various excellent methods for asymmetric cyclopropanation using copper, rhodium and ruthenium catalysts have been reported. Most of these reactions are *trans*-selective.[24, 25]

The authors also discovered that cobalt(III)(salen) complex (**16**) can serve as the catalyst for highly *trans*- and highly enantio-selective cyclopropanation using a diazo ester (**Scheme 12**). Interestingly, the electronic effect of the 5-substituent (Y) and the *trans*-effect of the apical ligand (X) exert a favorable effect on the enantioselectivity of the reaction. On the other hand, since the presence of the 3,3'-substituents vitiates the catalysis, it is very likely that olefins approach the carbenoid intermediate along the O-Co bond axis (**Scheme 12**).[26]

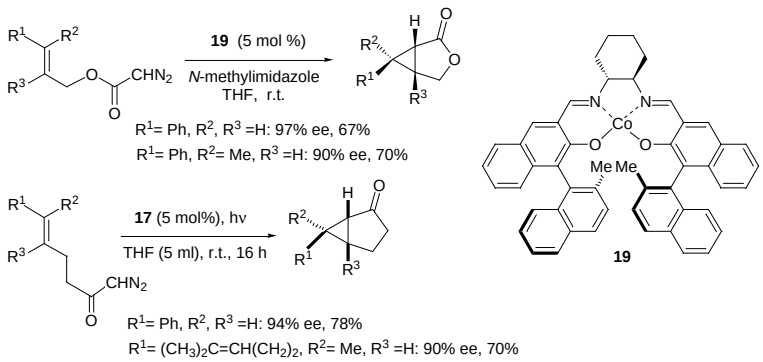


Scheme 12.

On the contrary, ruthenium(salen) complex (**17**) catalyzes cyclopropanation under photo-irradiation, despite the existence of substituents at the 3,3'-positions. This reaction exhibits high *cis*-selectivity and high enantioselectivity (**Scheme 13**).[27] This is the first example in which high *cis*-selectivity was observed in the cyclopropanation of a simple olefin. As described in the chapter on



Scheme 13.



Scheme 14.

epoxidation, the ruthenium(salen) complex adopts a distorted-stepped conformation and a large inter-atomic space exists between the substituents at the 3,3'-positions. The orientation of the olefin passing through the space can be controlled, resulting in high-*cis* selectivity. Cobalt(II)(salen) complex (**18**) bearing the same ligand also exhibit a similar catalytic action. Although both **17** and **18** show high-*cis* enantioselectivity, the senses of asymmetric induction for **18** and **17** are opposite to each other.[28)] This suggests that olefins approach **18** and **17** along different access routes. In reactions using the cobalt(II) complex (**18**), as with the cobalt(III) complex (**16**), the substituents at the 3,3'-positions is considered to hamper the approach of the olefin along the O-Co bond axis. This means that the olefin approaches along the N-Co bond axis in the reaction with **18**. This direction of approach is impossible when using **16**, but the reason for this difference in substrate-approach is still unclear. On the other hand, the following results support the notion that different access routes are used by **18** and **17**. When derivatives of **17** and **18** (without any chirality at the diamine site) are used as catalysts for cyclopropanation, the derivative of **17** shows similar enantioselectivity to **17** but the derivative of **18** does not exhibit any enantioselectivity.[28b)] Furthermore, complex (**18**) also shows high *cis*- and high enantioselectivity even in reactions using commercially-available ethyl diazoacetate as a precursor of carbene.

Intramolecular cyclopropanation of alkenyl diazoacetate is catalyzed with high enantioselectivity by complex **19**, a modified complex of **18**, while intramolecular cyclopropanation of alkenyl diazo ketone by using complex **17** as catalyst (**Scheme 14**). [29)]

As described so far, the stereochemistry of oxenoid, nitrenoid and carbenoid transfer reactions can be highly controlled by using properly-designed salen complexes of square planar coordination.

3. Asymmetrical synthesis using *cis*-β salen complexes

As described in Section 1, most of the metallosalen complexes adopt the square planar structure (*trans*-configuration). However, if a bidentate ligand such as oxalate ions or acetylacetone is coordinated, they will transform to the *cis*-β structure. The *cis*-β salen complexes show various features that cannot be obtained in the square planar structure, in addition to the feature whereby the central metal is chiral. Some salen complexes (including titanium salen complexes) form dimers *via* μ-oxo bonds (**Figure 4**). In the μ-oxo *trans*-complexes, the two apical ligands (L_1, L_2) are distant and the intramolecular reaction

between them is impossible. However, when the ligands adopt the *cis*-β structure, the ligands are equatorially coordinated and the intramolecular reaction becomes possible. Furthermore, as shown in Figure 2, the *cis*-β complexes are expected to provide excellent reaction sites for reactions using bidentate substrates or reagents (X-Y).

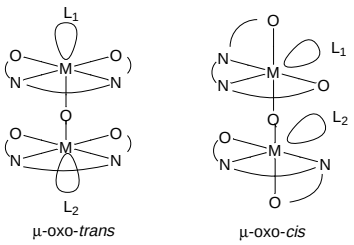
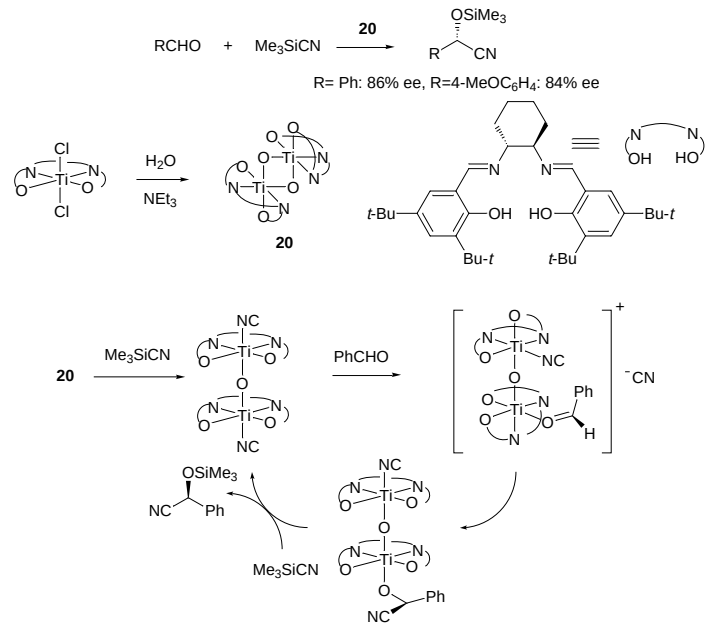


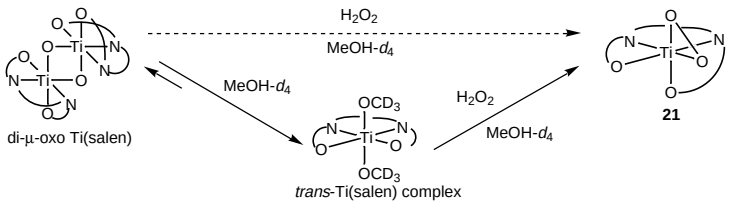
Figure 4.

In order to exploit the characteristics of *cis*-β-μ-oxo complexes, Belokon' *et al.* reported highly-enantioselective trimethylsilyl cyanation.[30] When a Ti salen complex is treated with water in the presence of an amine, it affords the di-μ-oxo complex (**20**), which bears the salen ligands of *cis*-β geometry. Upon treatment with aldehyde and trimethylsilyl cyanide, one of the two μ-oxo bond in complex **20** is cleaved and a μ-oxo complex bearing the aldehyde and the cyanide is generated. Each salen ligand then adopts the *cis*-β structure, so the aldehyde and cyanide can take part in an intramolecular reaction. Since both the substrate and agent are coordinated to the optically active Ti-ions, the reaction progresses with high-enantioselectivity.

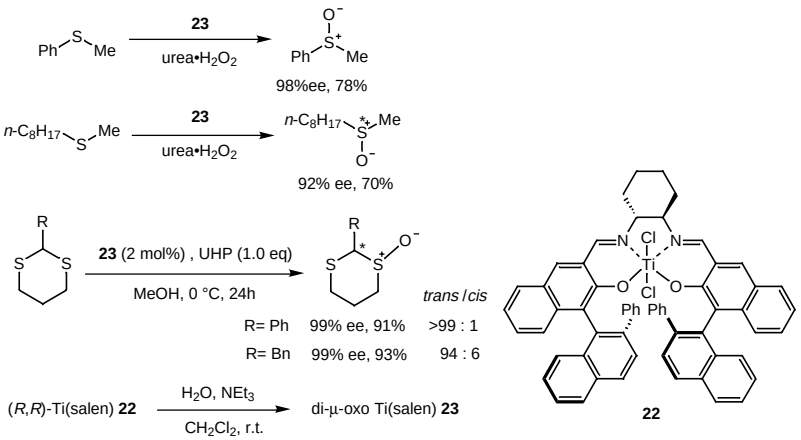
Taking into consideration the facts that alkoxide exchange on titanium ion is rapid and that peroxo-hydrogen is a bidentate ligand, the authors assumed that the di-μ-oxo complex would be converted into a *cis*-β peroxo Ti complex (**21**) (**Scheme 16**). In **21**, the peroxo-portion is fixed in asymmetric space; therefore, asymmetric oxidation using **21** attracted some attention. After the Ti complex (**22**) was converted to the corresponding di-μ-oxo complex (**23**), subsequent treatment with urea•hydrogen peroxide adduct gave the peroxo-complex that was used for various sulfoxidation reactions. It was found that not only alkyl aryl sulfides, but also dialkyl sulfides and dithianes can be oxidized with high enantioselectivity (**Scheme 17**).[31] In the following study, it was revealed that **21** cannot be obtained directly from the di-μ-oxo complex, but is actually generated *via* the *trans*-complex (**Scheme 16**).[31b]



Scheme 15.

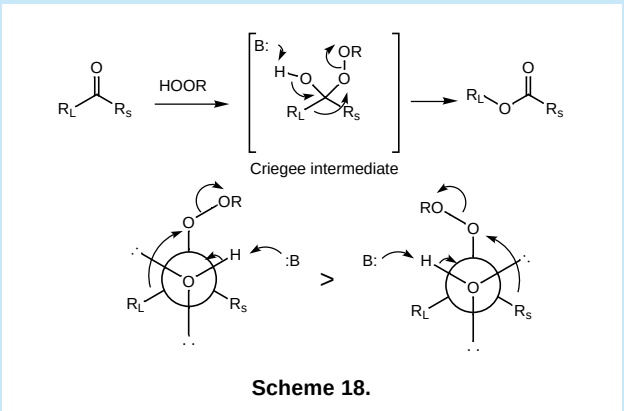


Scheme 16.



Scheme 17.

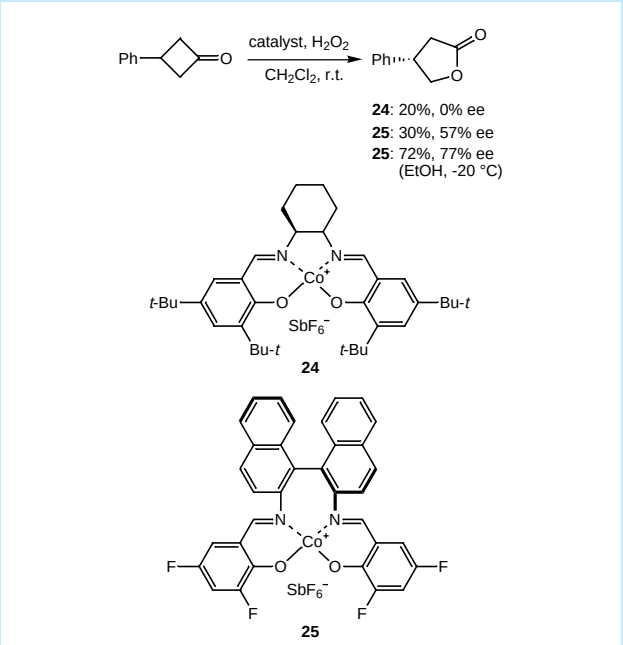
The Baeyer-Villiger reaction is the most convenient method of transforming carbonyl compounds into esters or lactones (**Scheme 18**).



Scheme 18.

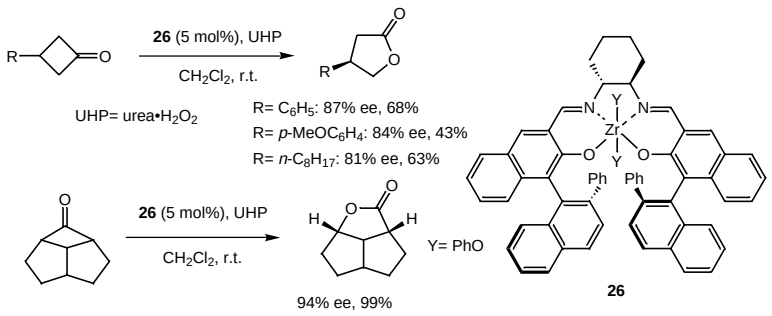
The reaction proceeds through the migration of the Criegee intermediate. It is essential for the migration that the alkyl group is anti-periplanar to the O-O bond for stereoelectronic reason (σ-σ* interaction). In general, more ramiform alkyl group shows higher nucleophilicity and the more ramiform group (R_L) migrates in preference to the less ramiform one (R_S), if the conformation of the O-O bond is not regulated. Therefore, if the conformation is controlled somehow, it was expected that the less nucleophilic R_S group could migrate preferentially. Such examples are known in enzymatic reactions, and a similar reaction has been reported in the case of asymmetric Baeyer-Villiger reaction,[33] although the mechanism is unclear.[34] Therefore, if the conformation of the intermediate could be controlled by using a catalyst, the catalyst was expected to show high selectivity comparable to that observed in enzymatic reactions.

The Criegee intermediate (R = H) that is obtained with hydrogen peroxide as an oxidant is considered to be a bidentate ligand; therefore it is expected to form chelate compounds with *cis*-β complexes. By properly controlling the chelate conformation, the stereochemistry of the Baeyer-Villiger reaction could also be controlled. Based on this idea, the catalytic performances of the *trans*-cobalt complex (**24**) and the *cis*-β complex **25** were compared. Although both the complexes showed catalytic activity, the former did not show any enantioselectivity at all; however, the latter showed moderate selectivity (**Scheme 19**) .[35,36]

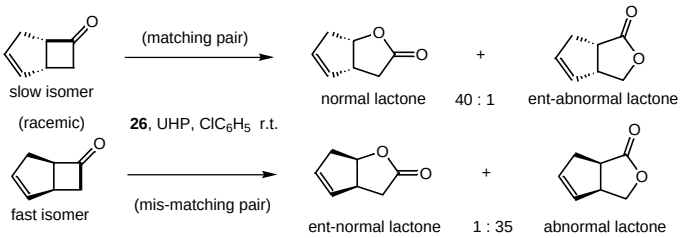


Scheme 19.

Then, we attempted to control the stereochemistry of the Baeyer-Villiger reaction by using a catalyst that, despite its original *trans*-conformation, can form a *cis*-β chelate upon the coordination of the Criegee intermediate in the reaction. As the result, the reaction using the salen zirconium complex (**26**) was found to show good selectivity of more than 80% *ee* (**Scheme 20**).[37] More interestingly, an investigation of the reactions using racemic ketones as the starting materials revealed that the topos selectivity induced by the catalyst was beyond the regular migratory aptitude of Baeyer-Villiger reactions; one enantiomer gave a normal-lactone, which was generated



Scheme 20.



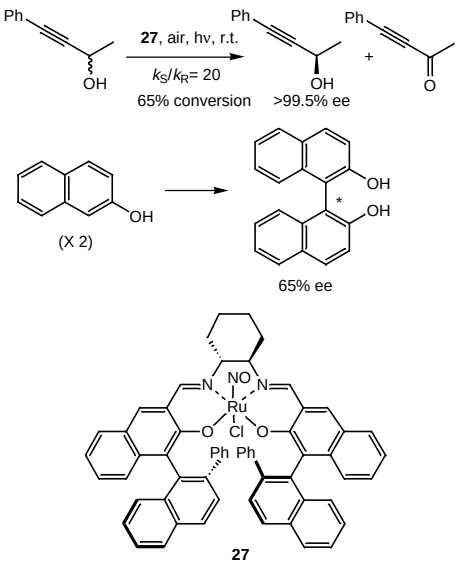
Scheme 21.

by methine carbon migration, and the other enantiomer yielded an abnormal-lactone generated by methylene carbon migration (**Scheme 21**).[38] This topos selectivity is comparable to that of enzymatic reaction.

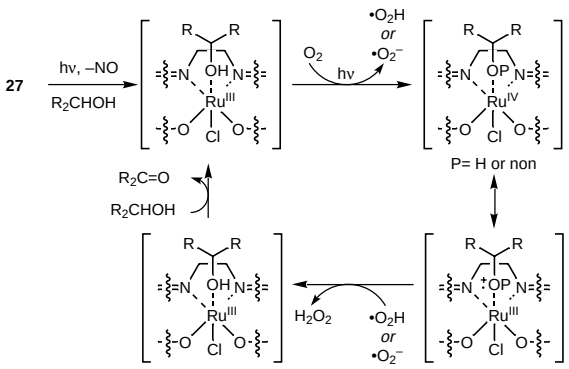
4. Applications to aerobic oxidation

As described in the preceding sections, salen manganese and ruthenium complexes are excellent asymmetric oxidation catalysts. However, each reaction requires stoichiometric chemical oxidants. From the viewpoints of atom economics and environmental friendliness, the development of an efficient method for the use of molecular oxygen (particularly air) has been keenly sought. Recently, the authors discovered that salen ruthenium complexes are excellent catalysts for aerobic oxidation.

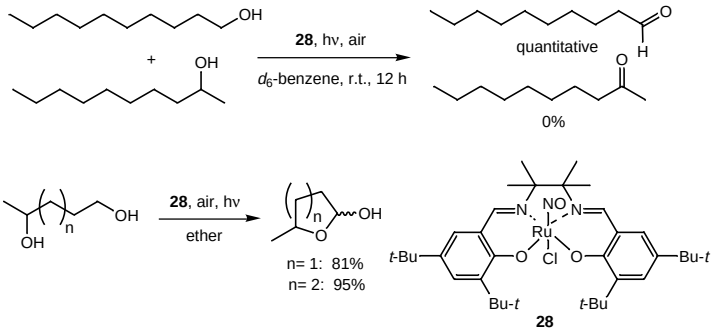
Under irradiation with visible light, ruthenium complex (**27**) and a racemic secondary alcohol were stirred in air, resulting in the kinetic resolution of the alcohol (**Scheme 22**). The relative reaction rate was 11 – 20. This was the first example of oxidative kinetic resolution using oxygen.[39] Although the reaction mechanism is not clear, it was considered to proceed in such a way that the ruthenium ion coordinated by an alcohol undergoes single-electron oxidation, generating an alkoxy radical, since optically active binaphthol is obtained from 2-naphthol under the same conditions (**Scheme 23**). However, it is unclear at the moment how the single-electron transfer accompanies proton shift.



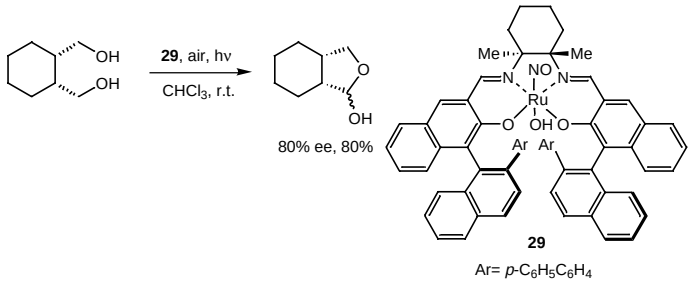
Scheme 22.



Scheme 23.



Scheme 24.



Scheme 25.

With the thought in mind that oxidation proceeds *via* the coordination of an alcohol to ruthenium, it was expected that if the diamine portion near to the ions could be made bulkier, then the primary alcohol and the secondary alcohol would be oxidized individually. In fact, the use of complex (**28**) (which is derived from 1,2-tetramethylethylene diamine) as a catalyst oxidized the primary alcohol selectively (**Scheme 24**).[41] In the case of diol, the terminal alcohol is selectively oxidized resulting in lactole.[42] No excess oxidation to carboxylic acid or lactone was observed in either reaction.

Therefore, by using an optically active ruthenium salen complex as catalyst, it was expected that the oxidation of *meso*-diol would generate optically active lactol. The asymmetric oxidation of *meso*-diols has been widely examined, but enzymatic or chemical methods afford optically active lactones as the product. As a result of extensive examination, when complex (**29**), which has hydroxyl group at the apical position, was used in the oxidation of *meso*-1,2-di(hydroxymethyl)cyclohexane, enantioselectivity of 80% *ee* was observed (**Scheme 25**).[43] Recently, the scope of this oxidation and its mechanism have been examined in detail.

In conclusion

In addition to the catalytic activities described here, the metallosalen complexes show various asymmetric catalytic activities, including Lewis acid catalysis. Not all of these can be described here due to limitations of space. We would ask you to refer to reviews[45] for further information.

The results presented in this article were achieved due to the enthusiasm and careful observations made by those who are listed in the references as co-workers. I would like to extend my sincere appreciation to all of them. Appreciation is also due for the financial support granted by the Ministry of Education, Culture, Sports, Science and Technology and by CREST, Japan Science and Technology Agency.

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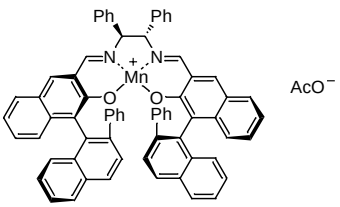
Tsutomu Katsuki obtained his M.S. Degree from Kyushu University in 1971 and served as a research associate at Kyushu University. He then became a post-doctoral fellow with Professor K.B. Sharpless at Stanford University and at Massachusetts Institute of Technology. He has held the post of Professor at Kyushu University since 1989. He has held his current position since 2000. He was awarded the Inoue Science Award in 1996, the Synthetic Organic Chemistry Award in 1998 and the Molecular Chirality Award and the Japanese Society of Chemical Association Award in 2001.

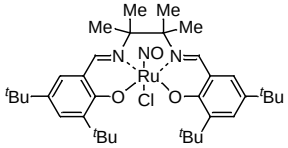
[Specialties] Asymmetric catalysis, synthetic reactions and the synthesis of natural organic compounds.

(Received February, 2006)

TCI's Metallosalen Complexes



(1*S*,2*S*)-*N*,*N*′-Bis[(*R*)-2-hydroxy-2′-phenyl-1,1′-binaphthyl-3-ylmethylene]-1,2-diphenylethylenediaminato Manganese(III) Acetate 100mg [B2409]



Chloronitrosyl[*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,1,2,2-tetramethylethylenediaminato]ruthenium(IV) 100mg [C1944]