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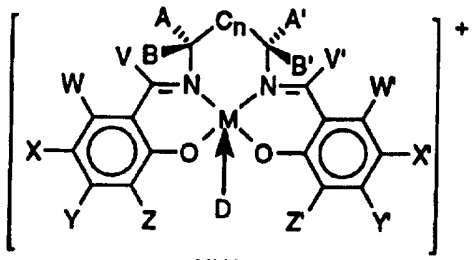

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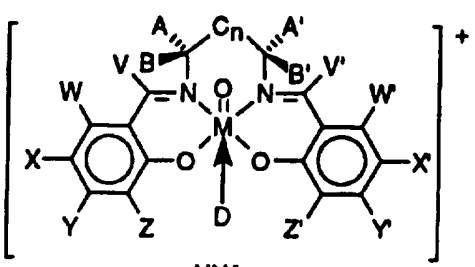

(II)

(57) Abstract

The present invention relates to a transition metal cationic chiral non-racemic complex containing a substituted or unsubstituted tetradentate or quinquedentatate ligand derived from two salicylaldimine units, the cationic complex including a non-nucleophilic anion NNA and, optionally, an oxygen atom bonded to the transition metal and, optionally, a neutral donor ligand D capable of coordinative bonding to the transition metal, the cationic chiral complex and the cationic chiral oxo-complex having structural formulae (I and II), respectively. The complex of formula (II) is useful for stereoselectively epoxidising an alkene and for stereoselectively oxidising a tertiary amine, an organic sulphide or a racemic tertiary phosphine.

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COMPLEXES, PROCESSES FOR THEIR PREPARATION AND THEIR USE

The present invention concerns complexes, processes for their preparation and their use.

The complexes of the present invention are useful in accelerating the reaction between a prochiral alkene (**1**) and an oxygen source (**2**) to yield a chiral epoxide (also called an oxepin, **3**). It is very desirable industrially to identify a catalytic process in which only one of the possible enantiomeric end products (**3a**) or (**3b**) predominates, *i.e.* is in enantiomeric excess (ee).

The catalyst used will usually be chiral and, while there have been a large number of such catalysts reported in the past[1], only two of these have successfully yielded one chiral epoxide in enantiomeric excess (ee), those of Sharpless[2] and Jacobsen[4].

Sharpless[2] found in 1980 that, if the prochiral alkene also bore an alcohol unit (*i.e.* an allylic alcohol **4**), then using a catalyst based on a titanium tartrate complex and a hydroperoxide as the oxygen source was very effective, giving consistently high (>90%) enantiomeric excess (ee). However, this suffers from the disadvantage that only alkenes which are also allylic alcohols can be epoxidised.

A method for epoxidising alkenes not bearing an alcohol directive group is highly desirable. There have been a number of attempts to do this since the work of Sharpless and the catalysts reported are mainly based on either metal-porphyrin[3] or metal-salen complexes[4]. In the latter context, in 1985 Kochi and co-workers[5] published a detailed account of their investigation into the epoxidation of alkenes using chromium salen complexes of the type (**5**: M = Cr, Y = H, Cl, OMe, NO_2) and in 1986 they published a similar account[6] for the related manganese salen complexes (**5**: M = Mn). In both cases the oxygen source was iodosylbenzene. They showed that the active

species in both cases was probably the metal oxo salen complex (**6**) but that only in the chromium case was this species isolatable. The use of bleach as stoichiometric oxidant (attractive industrially) was developed for metal-porphyrin catalysts by Meunier[7] and applied to metal-salen catalysis by Burrows[8].

Chiral metal-salen complexes are known[9] and had been assayed for catalytic hydrogenation but their first use for catalytic asymmetric oxidation seems to have been the vanadium catalysed asymmetric oxidation of sulphides by Fujita[10]. Later Nishinaga[11] reported the use of similar cobalt-based catalysts for styrene oxidation.

Recently both Jacobsen[4,12] and Katsuki[13], but especially the former, have reported that useful ees can be achieved in the epoxidation of prochiral alkenes using the manganese system with chiral salen ligands such as (**7**). In particular Jacobsen has shown that the epoxidation of certain *cis*--1,2-disubstituted[4] and trisubstituted[12b] alkenes (**1**: $R^1 = R^3 = H$ or only $R^1 = H$) can be achieved with high ee in a preparatively useful system with bleach as the oxygen source. Also, with the addition of a chiral phase transfer catalyst, the *cis*-alkenes can be converted to the *trans*-epoxides[12c]. Other workers subsequently disclosed related systems[14]. However the more industrially attractive conversion of *trans*-alkenes to *trans*-epoxides has not been reported to date and remains a challenging problem. Indeed it has been speculated[12c] that this may never be possible with these sorts of systems if the widely held hypothesis for the side-on approach mechanism[3,4,15] (see later) holds true.

According to a first aspect of the invention, there is provided a transition metal cationic chiral non-racemic complex containing a substituted or unsubstituted tetradentate or quinquedentate ligand derived from two salicylaldimine units, the cationic complex including

a non-nucleophilic anion NNA and, optionally, an oxygen atom bonded to the transition metal and, optionally, a neutral donor ligand D capable of coordinative bonding to the transition metal.

The cationic chiral complex and the cationic chiral oxo-complex have the structural formulae (I) and (II), respectively, given hereinafter, in which:

M is a transition metal atom;

NNA is a non-nucleophilic anion;

D, which may be present or absent, is a neutral donor ligand;

C_n represents a connecting chain of atoms in which is n is 0 to 4, preferably 0, 1 or 2;

A, A', B and B' are each a non-oxidisable group or atom, or A and B' or B and A' together with their respective intermediate carbon atoms, each form a substituted or unsubstituted ring structure, or A and B or A' and B' together form a substituted or unsubstituted spiro ring structure; and

V, V', W, W', X, X', Y, Y', Z and Z' are each a non-oxidisable group or atom or any two of V, W, X, Y and Z and/or any two of V', W', X', Y' and Z' together with their respective intermediate carbon atoms may form a substituted or unsubstituted ring structure or V and V' or W and W' or X and X' or Y and Y' or Z and Z' together with their respective intermediate carbon atoms may form a substituted or unsubstituted ring structure.

D may be bonded to at least one of A, A', B, B' V, V', W, W', X, X', Y, Y', Z and Z', to provide the quinquedentate ligand.

Preferably, NNA is a non-coordinating species selected from hexafluorophosphate, trifluoromethanesulphonate, tetrahalogenoborates, substituted or unsubstituted arylmethanesulphonates and tetraarylborates, where aryl is phenyl, toluyl or mesityl, or trifluoroacetate.

Most preferably, NNA is hexafluorophosphate or trifluoromethanesulphonate.

Preferably, D is selected from:

a phosphine oxide *e.g.* triphenylphosphine oxide, diphenylmethylphosphine oxide, triethylphosphine oxide, (RS)- or (R)- or (S)-anisylmethylphenylphosphine oxide, (RS)- or (R)- or(S)-naphthylmethylphenylphosphine oxide, (RS)- or (R)- or (S)-anisylnaphthylphenylphosphine oxide, trimesitylphosphine oxide, trimesitylphenylphosphine oxide, tributylphosphine oxide, trioctylphosphine oxide, trichlorophosphine oxide (phosphoryl chloride);

a phosphine sulphide *e.g.* triphenylphosphine sulphide, triethylphosphine sulphide, (RS)- or (R)- or (S)-anisylmethylphenylphosphine sulphide, (RS)- or (R)- or (S)-methylnaphthylphenylphosphine sulphide, (RS)- or (R)- or (S)-anisylnaphthylphenylphosphine sulphide;

a phosphine imine *e.g.* triphenylphosphine imine, (RS)- or (R)- or (S)-anisylmethylphenylphosphine imine;

an alkyl/aryl phosphonate *e.g.* methyl diphenylphosphonate, methyl dimethylphosphonate, (RS)- or (R)- or (S)-methyl methylphenylphosphonate, any isomer of menthyl methylphenylphosphonate;

an alkyl/aryl phosphinate *e.g.* dimethylphenyl-phosphinate, dimethyl methylphosphinate;

an alkyl/aryl phosphate *e.g.* trimethyl phosphate, triphenyl phosphate, trihexyl phosphate, tritolyl phosphate, tris(2-ethylhexyl) phosphate, triethyl phosphate;

a phosphoramide *e.g.* hexamethylphosphoramide, tripyrrollidinylphosphine oxide; a phosphinamide; a phosphonamide;
a phosphine borane *e.g.* triphenylphosphine borane, (RS)- or (R)- or (S)-anisylmethylphenylphosphine borane;
an amine oxide *e.g.* pyridine-N-oxide, 4-phenylpyridine-N-oxide, 2-picoline-N-oxide, 3-picoline-N-oxide, 4-picoline-N-oxide, trimethylamine-N-oxide;
a sulphoxide *e.g.* dimethylsulphoxide, diphenylsulphoxide, benzyltert-butylsulphoxide, anisyltoluylsulphoxide;
a sulphone *e.g.* dimethylsulphone, diphenylsulphone, benzyltert-butylsulphone, anisyltoluylsulphone, sulpholane;
an amide *e.g.* dimethylformamide, phenylmethylformamide;
an ester *e.g.* ethyl acetate; a ketone *e.g.* acetone; urea; a carbamate; a carbonate; an α-aminoamide; an α-aminoester; or an unsaturated system capable of coordinative bonding to the transition metal *e.g.* benzene, napthalene.

More preferably, D is triphenylphosphine oxide, (RS)-anisylmethylphenylphosphine oxide, N,N-dimethylformamide, dimethylsulphoxide, trimesitylphosphine oxide, tributylphosphine oxide, trioctylphosphine oxide, trihexyl phosphate, tritolyl phosphate, triethyl phosphate, tris(2-ethylhexyl) phosphate, pyridine-N-oxide or 4-phenylpyridine-N-oxide.

M is preferably selected from Cr, Ni, Co, Fe, Ti, Mo, W or V, and is most preferably Cr.

Preferably, A, A', B, B', V, V', W, W', X, X', Y, Y', Z and Z' are each selected from:

hydrogen, halogen (F, Cl, Br, I),
OH, OR,
SH, SR, S(O)R, $S(O_2)R$, SO_3H, SO_3R,
NH_2, NHR, NRR', NO_2,

PRR', PR(OR'), P(OR)(OR'), P(O)RR', P(O)R(OR'), P(O)(OR)(OR'),
optionally substituted alkyl, alkoxy, cycloalkyl, carboalkoxy, heterocycle, aryl or carboaryloxy, $CHal_3$, $CHal_2R$, $CHalRR'$, C(O)R, CO_2H, CO_2R, $C(O)NH_2$, C(O)NHR, C(O)NRR', CN, SiRR'R'', Si(OR)(OR')(OR''), $OSiR_3$, SiR_3, OSiRR'R", OSi(OR)(OR')(OR"),

wherein R, R' and R'' are each optionally substituted alkyl, cycloalkyl or aryl; carboalkoxy, carboaryloxy, acyl, carbamyl or halogen (F, Cl, Br, I).

More preferably, V, V' are each hydrogen; W and W' are each hydrogen or chloride, X and X' are each hydrogen, fluoride, chloride, bromide, iodide, lower alkyl such as methyl, tert-butyl or lower alkoxy such as methoxy, or W and X and W' and X' each together with their respective intermediate carbon atoms form a benzo ring; Y and Y' are each hydrogen or diethylamine; and Z and Z' are each hydrogen, fluoride, chloride, bromide, iodide, lower alkyl such as methyl or tert-butyl, lower alkoxy such as methoxy or substituted or unsubstituted aryl such as benzyl or phenyl.

Advantageously, V, V', W, W', X, X', Y and Y' are each hydrogen and Z and Z' are selected from fluoride, chloride, methyl, tert-butyl, benzyl or phenyl. Alternatively, V, V', W, W', Y and Y' are each hydrogen and X, X', Z and Z' are selected from fluoride, chloride, methyl or tert-butyl. Alternatively, V, V', Y and Y' are each hydrogen and W, W', X, X', Z and Z' are selected from fluoride, chloride or tert-butyl. Alternatively, V, V', W, W', Y, Y', Z and Z' are each hydrogen and X and X' are selected from chloride or bromide.

Preferably, A and B' or B and A' together comprise cyclohexane and A' = B = H or B' = A = H, respectively, n is 0 and the ligand is tetradentate, *i.e.*, the ligand is a salen ligand ((*S,S*) or (*R,R*)-*N,N'*-bis(salicylidene)-1,2-cyclohexanediamine).

In a particularly preferred embodiment of formula (I) or (II), A and B or B and A together comprise cyclohexane and A' and B are each hydrogen or B' and A are each hydrogen, respectively, M is Cr, n is O and at least one of V, V', W, W', X, X', Y, Y', Z and Z' is halogen.

Preferably, V and V' or W and W' or X and X' or Y and Y' or Z and Z' are each halogen. More preferably, Z and Z' are each halogen. Advantageously, Z and Z' are each F or Cl.

The complex according to the present invention is chiral because:

(i) either A is not identical with B or A' is not identical with B';

(ii) the groups A, A', B, B', C_n are part of an atropisomeric system;

(iii) the donor ligand D, if present, is chiral;

(iv) one or more of V, V', W, W', X, X', Y, Y', Z or Z' is a chiral group, especially Z and/or Z', or any combination of (i), (ii), (iii) and (iv).

According to a second aspect of the invention, there is provided a process for preparing a complex of the formula (I), which process comprises:

(i) contacting a complex of the formula (I) in which D is replaced by halide, with a salt of a NNA in a suitable solvent; or

(ii) contacting an appropriate quadridentate or quinquedentate ligand of the formula (13) with either a chromium salt and a salt of a NNA or, alternatively, a chromium NNA salt in a suitable solvent.

Preferably, the complex of formula (I) in which D is replaced by halide, is prepared by contacting an appropriate quadridentate or quinquedentate ligand with a chromium halide in a suitable solvent.

More preferably, the chromium salt is a chromium (II) halide, most preferably chromium dichloride, and the salt of the NNA is an alkali metal salt of the NNA, most preferably potassium hexafluorophosphate.

A donor ligand D may be added to the complex (I) prepared in accordance with the second aspect of the invention, where a complex of the formula (I) with donor ligand D is desired. The complex (I) with donor ligand D is preferably prepared *in situ* in the alkene epoxidation reaction described hereinafter.

According to a third aspect of the invention, there is provided a process for preparing a complex of the formula (II), which process comprises contacting an appropriate complex of the formula (I) with an oxygen source in a suitable solvent and, optionally, with a donor ligand D.

It will be appreciated that a complex of the formula (II) may be prepared *in situ* in the alkene epoxidation reaction described hereinafter.

According to a fourth aspect of the invention, there is provided a process for stereoselectively epoxidising an alkene, which process comprises contacting the alkene with a complex of the formula (II) in a suitable solvent, optionally in the presence of an oxygen source.

Preferably, the complex of the formula (II) is formed *in situ*, by contacting a complex of the formula (I) with an oxygen source.

The term "stereoselectively" as used herein is intended to mean that one of the possible stereoisomeric epoxide products is produced in excess.

If the alkene is prochiral or chiral and non-racemic, then the stereoselective process is an enantioselective process in that one of the possible enantiomeric epoxide products is produced in enantiomeric excess (ee). If the alkene is racemic, it is expected from the experimental findings of Sharpless[2] that kinetic resolution should occur, *i.e.*, that the stereoselective process is a diastereoselective process in that one of the possible diastereomers is produced in excess.

The enantioselective epoxidation reaction may be catalytic, or stoichiometric *i.e.* using about one equivalent of the complex of formula (II) in the presence of one equivalent of alkene in the absence of an oxygen source. Preferably, the complex according to the invention acts as a catalyst and an oxygen source is present. The ratio of catalyst complex to alkene to oxygen source is in the range of from about 1:10:1 to 1:1000:1, preferably about 1:20:1.

The diastereoselective epoxidation reaction may be catalytic, or stoiochiometric *i.e.*, using about 0.5 equivalents of the complex of formula (II) in the presence of one equivalent of alkene in the absence of an oxygen source. Preferably, the complex according to the invention acts as a catalyst and an oxygen source is present. The ratio of catalyst complex to alkene to oxygen source is in the range of from about 1:10:0.5 to 1:1000:0.5, preferably about 1:20:0.5.

The stoichiometric reaction can advantageously be used to assess and fine-tune the maximum efficiency for any alkene to be epoxidised or, indeed, any substrate to be oxidised. The efficiency of the stoichiometric reaction predicts the efficiency of the catalytic reaction.

The term "alkene" is intended to embrace any compounds, whether cyclic or non-cyclic, having at least one double bond such as, for example, mono-substituted alkenes, 1,2-disubstituted alkenes (both *cis* and *trans*), 1,1-disubstituted alkenes, trisubstituted alkenes and tetrasubstituted alkenes and any cyclic hydrocarbons having at least one double bond.

Preferably, the alkene is a *E*-1,2-disubstituted alkene, more preferably, *E*-ß-methylstyrene or *E*-stilbene. Alternatively, the alkene is selected from anethole, *Z*-ß-methylstyrene, *α*-methylstyrene, styrene, *E*-ß-hexene or 1,2-dihydronaphthalene.

The oxygen source used in any of the above-described processes according to the present invention may be any suitable oxygen source, such as for example, iodosylarenes (*e.g.* iodosylbenzene), hypohalites (*e.g.* bleach), perhalates (*e.g.* sodium periodate, perbromate, perchlorate), halates (*e.g.* barium chlorate), electrochemical oxidants (*e.g.* the iron (II/III) ferricyanide couple), the combination of t-butylhydroperoxide and pyridine, oxone, molecular oxygen in the presence of a suitable sacrificial co-reductant, *e.g.* an aldehyde, or the combination of N-methylmorpholine-N-oxide and m-chloroperbenzoic acid (MCPBA).

Preferably, the solvent used in any of the above-mentioned processes according to the present invention is an organic solvent such as, for example, dichloromethane, acetonitrile, N,N-dimethylformamide, chloroform, acetone, ethyl acetate, tetrahydrofuran, dimethylsulphoxide, toluene or ether. Dichloromethane and acetonitrile are preferred.

The extent of crossover in the Cr epoxidation reaction is negligible (less than 0.5%), thus the epoxidation of an *E*-alkene yields the *threo*-epoxide product with only very small amounts of the *erythro* isomer *i.e.* the one which would be derived from the equivalent *Z*-alkene isomer. This is in contrast to the case of $M = Mn^4$.

Oxo-complexes of the formula (II), or complexes of the formula (I) which, in the presence of a suitable oxygen source, generate complexes of the formula (II), are efficient catalysts for the asymmetric or enantioselective epoxidation of prochiral alkenes with high enantiomeric excess, particularly when iodosylbenzene or bleach is used as the oxygen source. High ee values can be obtained for catalytic epoxidation reactions. For example, epoxidation of *E*-ß-methylstyrene (1:$R^1 = R^4 = H$; $R^2 = Ph$; $R^3 = Me$) with a complex of the formula (II) in which M = Cr, n = 0, AB' or BA' = cyclohexane and A' = B = H or B' = A = H, respectively; V = V' = W = W' = Y = Y' = H and X = X' = Z = Z' = Cl, D = triphenylphosphine oxide, gives 73% ee in the resulting epoxide at room temperature.

High ee values can also be obtained for stoichiometric epoxidation reactions. For example, epoxidation of *E*-ß-methylstyrene (1:$R^1 = R^4 = H$; $R^2 = Ph$; $R^3 = Me$) with a complex of the formula (II) in which M = Cr, n = 0, AB' or BA' = cyclohexane and A' = B = H or B' = A = H, respectively; V = V' = W = W' = X = X' = Y = Y' = H, Z = Z' = Cl, D = triphenylphosphine oxide, gives 86% ee in the resulting epoxide at 0°C.

The nature of the donor ligand D (which may also be chiral) is very significant for the success of these epoxidation reactions. For example, in the case of M = Cr, a large number of possible species can be used with enormous effects on the ee value achieved. This is in contrast to the case of M = Mn where only simple anions are effective[4].

The nature of the substitution pattern on the aromatic rings of the salicylaldimine units of the quadridentate or quinquedentate ligand is also significant for the attainment of high ee values in the epoxidation reaction and, here again, there are significant differences between the chromium and manganese[4] cases. The number of possible

substituents is very high because of the large number of reported[16] substituted salicylaldimines from which the chiral complex according to the present invention may be derived.

A further significant difference between chromium and manganese is that the profile of epoxide product configurations is different; thus *R,R*-Cr complex gives 1*R*,2*R*-1-phenylpropylene oxide from *E*-ß-methylstyrene (same as Mn-analogue[4]) but 1*S*,2*R*-1-phenyl-propylene oxide from *Z*-ß-methylstyrene (opposite to Mn-analogue[4]).

The rate of the epoxidation reaction can be controlled by variation of the substituents on the aromatic rings of the salicylaldimine units. For example, halo-substitution accelerates the reaction rate considerably.

A significant advantage of the preferred enantioselective epoxidation reaction described herein is that both enantiomers of the epoxide end product can be produced because the complex according to the invention can be derived from either enantiomer of the initial tetradentate or quinquedentate ligand. The reaction tolerates many different solvents as indicated hereinabove and a wide temperature range, *e.g.* from -78 to 110°C.

We expect that the success gained so far with the chromium system should be capable of extension to other transition metal ion systems. The insights gained from the results of the stoichiometric selectivities measured in the chromium case; the considerations used to develop the neutral donor ligand concept for chromium; and the dramatic rate accelerations seen with, for example, halo-substitution on the aromatic rings of the salicylaldimine units can equally be applied to the transition metals vanadium, nickel, cobalt, iron, titanium, molybdenum and tungsten, particularly vanadium.

According to a fifth aspect of the invention there is provided a process for stereoselectively oxidising a tertiary amine or an organic sulphide, which process comprises contacting the tertiary amine or sulphide with a complex of the formula (II) in a suitable solvent optionally in the presence of an oxygen source.

Preferably, the complex of the formula (II) is formed *in situ*, by contacting a complex of the formula (I) with an oxygen source. The oxidation reaction may be catalytic, or stoichiometric. The catalytic reaction is preferred.

According to a sixth aspect of the invention there is provided a process for stereoselectively oxidising a racemic tertiary phosphine, which process comprises contacting the tertiary phosphine with a complex of the formula (II) in a suitable solvent.

Preferably, the ratio of complex to tertiary phosphine should not exceed 1:2.

It is further expected that the complexes according to the present invention will be useful for oxidations other than of alkenes. This follows from the work of Sharpless who found that a slight modification of his titanium/tartrate/ hydroperoxide system was also useful for the stereoselection of certain ß-hydroxyamines[2]. Furthermore Kagan has found that another modification of the Sharpless system is useful for asymmetric oxidation of sulphoxides[17]. Therefore we expect that good stereoselectivity may be achieved in the oxidation of tertiary amines to amine oxides, sulphides to sulphoxides and, by analogy to these, that there should be stereoselection in the oxidation of racemic tertiary phosphines with the complexes according to the present invention.

THREE-DIMENSIONAL STRUCTURE OF THE CATALYST

Structural formulae (I) and (II) are not meant to specify the three-dimensional structure of the catalysts, which is not known at present. Thus Kochi[5] determined by single crystal x-ray crystallography the structure of the achiral chromium-salen complex (**8**: D = pyridine-N-oxide) which was found to have the salen ligand disposed all in one plane with D and =O in the *trans* relation shown. However, other workers[18] have found that salen and salen-like ligands do not take up a planar disposition around the metal atom. Indeed in solution it is possible that there will be an equilibrium between some of the various possible isomers (**9-12**). It is quite possible that only one of these isomers is the active one or, if all are active, only one gives high ee.

MECHANISM OF EPOXIDATION

That *cis*-alkenes had previously shown the best enantioselectivity in epoxidation reactions was not considered surprising because this had been invariably found for the porphyrins and is explained by the widely accepted side-on approach mechanism[3,4,12c,13c,15], wherein there is a less hindered approach for the *cis*-alkene, as diagrammatically shown in the accompanying Figure. This idea, originally proposed by Groves[15], has become a useful working model in the design of transition metal-based epoxidation catalysts[3]. Moderate ees had been achieved in the epoxidation of *trans*-alkenes, notably by Katsuki[13d], but in relevant cases the *cis*-isomer still gave a higher selectivity.

Indeed, Jacobsen[12c] has stated "If the side-on approach mechanism is correct and general, it is possible that *trans*-olefins will always be poor substrates for catalysts bearing salen, porphyrin, and related tetradentate ligands". Therefore, it is all the more remarkable that the complexes according to the present invention work best as epoxidation catalysts for the *trans*-alkenes.

PREPARATION OF COMPLEXES OF FORMULAE (I) AND (II)

The complexes of the invention are exemplified by, but are not limited to, the series based on 1,2-diaminocyclohexane. Racemic 1,2-diaminocyclohexane was purchased from Aldrich Chemical Co.; resolved as the tartrate salt and, if desired, released with base according to the method of Galsbol *et al*[19].

Synthesis of Quadridentate Ligands (13) - Method A

To 1 equivalent of resolved 1,2-diaminocyclohexane in sufficient absolute ethanol is added 2 equivalents of the appropriate salicylaldehyde portion-wise at room temperature. The solution turns yellow and a yellow precipitate starts to appear (except in the case of vanillin and 5-methylsalicylaldehyde). The mixture is refluxed for one hour, allowed to cool and then stand for 24 hours. The resulting precipitated Schiff base is collected by filtration and washed with cold ethanol. In the case of 5-methylsalicylaldehyde, precipitation is achieved by concentration of the solution and in the case of vanillin by the addition of ether and in both these cases the ethanol washing is omitted.

Synthesis of Quadridentate Ligands (13) - Method B

To 1 equivalent of the tartrate salt of resolved 1,2-diaminocyclohexane dissolved in sufficient ethanol/water (4:1) is added 2 equivalents of potassium carbonate and 2 equivalents of the appropriate salicylaldehyde portion-wise at room temperature. The solution turns yellow and a yellow precipitate starts to appear (except in the case of vanillin and 5-methylsalicylaldehyde). The mixture is refluxed for one hour, allowed to cool and then stand for 24 hours. The resulting precipitated Schiff base is collected by filtration and washed with cold ethanol. In the case of 5-methylsalicylaldehyde, precipitation is achieved by concentration of the solution and in the case of vanillin by the addition of ether and in both these cases the ethanol washing is omitted.

Tables 1 and 2 list the salen ligands (13) made in accordance with Methods A and B hereinabove.

Synthesis of Cr(III)salen intermediate complexes

The appropriate quadridentate ligand (**13**) (1 equivalent of salen ligand) is dissolved in either acetone/methanol (4:1, 50 ml/g) or neat acetone (150 ml/g) at room temperature. In some cases (*e.g.* the 3,3',5,5'-tetratert-butyl derivative), this may take a significant period of time (up to 12 hours) in which case an alternative is to use twice the amount of solvent at 50°C. To this solution is added, dropwise under nitrogen at room temperature, an aqueous solution of 1.5 equivalent of chromium dichloride ($CrCl_2$, obtained by the reduction of $CrCl_3.6H_2O$ with amalgamated zinc - 10g Zn for 1g of $CrCl_3.6H_2O$ in 30 ml water). The initial yellow solution turns brown. After addition is complete (approximately 45 minutes), the mixture is left under nitrogen for 30 minutes and is then exposed to air for 20 hours. A precipitate, which may occur in the case of halogeno-substituted salen ligands, is removed by filtration. The remaining brown solution is concentrated by evaporation of all the organic solvents usually resulting in a brown precipitate which is filtered and washed several times with water and dried. Failing precipitation, one of three remedies may employed: (i) addition of water to the concentrated solution of the crude mixture in methanol usually results in precipitation of the chromium complex; (ii) failing the above, the crude mixture is further concentrated to leave a dark brown viscous oil to which water (20ml) is added followed by the same volume of diethyl ether; shaking of the flask leads to the formation of a brown solid which is the desired complex; (iii) failing both of the above, the brown oil was triturated with chloroform; this washes away an impurity but also reduces the yield. Remedy (i) was employed, for example, with halogeno derivatives; remedy (ii) was employed, for example, for naphthalene derivatives; and remedy (iii) was employed, for example, for tetrachloro derivatives.

Tables 3 and 4 list the chromium(III)salen intermediate complexes made in accordance with this method.

Synthesis of Cr(III)salen hexafluorophosphate complexes of formula (I: NNA = PF_6^-, no D) - Method A

The final precipitate from the previous procedure is dissolved in just sufficient methanol, with the addition of a small percentage of acetone if the dissolution is difficult, and treated with 2 equivalents of potassium hexafluorophosphate dissolved in just sufficient water. The mixture is allowed to stand overnight. Removal of the methanol and acetone, if present, yields a precipitate which is filtered. In the case of the 5,5'-dimethoxy- and 5,5'-dimethyl- derivatives, the aqueous potassium hexafluorophosphate solution is added directly to the initial residue obtained after evaporation of the acetone, if present, and methanol.

Synthesis of Cr(III)salen hexafluorophosphate complexes of formula (I: NNA = PF_6^-, no D) - Method B

The appropriate quadridentate ligand (**16**) (1 equivalent of salen ligand) is dissolved in either acetone/methanol (4:1, 50 ml/g) or neat acetone (150 ml/g) at room temperature. In some cases (*e.g.* the 3,3',5,5'-tetratert-butyl derivative), this may take a significant period of time (up to 12 hours) in which case an alternative is to use twice the amount of solvent at 50°C. To this solution is added, dropwise under nitrogen at room temperature, an aqueous solution of 1.5 equivalent of chromium dichloride ($CrCl_2$, obtained by the reduction of $CrCl_3.6H_2O$ with amalgamated zinc - 10g Zn for 1g of $CrCl_3.6H_2O$ in 30 ml water) and 1.5 equivalents of potassium hexafluorophosphate. The initial yellow solution turns brown. After addition is complete (approximately 45 minutes), the mixture is left under nitrogen for 30 minutes and is then exposed to air for 20 hours. A precipitate, which may occur in the case of

halogeno-substituted salen ligands, is removed by filtration. The remaining brown solution is concentrated by evaporation of all the organic solvents usually resulting in a brown precipitate which is filtered and washed several times with water and dried. Failing precipitation, one of three remedies may employed: (i) addition of water to the concentrated solution of the crude mixture in methanol usually results in precipitation of the chromium complex; (ii) failing the above, the crude mixture is further concentrated to leave a dark brown viscous oil to which water (20ml) is added followed by the same volume of diethyl ether; shaking of the flask leads to the formation of a brown solid which is the desired complex; (iii) failing both of the above, the brown oil was triturated with chloroform; this washes away an impurity but also reduces the yield. Remedy (i) was employed, for example, with halogeno derivatives; remedy (ii) was employed, for example, for naphthalene derivatives; and remedy (iii) was employed, for example, for tetrachloro derivatives.

Tables 5 and 6 list the chromium(III)salen complexes made in accordance with Methods A and B hereinabove.

Synthesis of Cr(V)oxosalen hexafluorophosphate complexes of the formula II

To 1.1 mmol of the appropriate Cr(III) salen hexafluorophosphate complex (I) in acetonitrile (approx. 25 ml) at room temperature is added, with stirring, iodosylbenzene (1.27 mmol). The solution becomes very dark green or black with suspended solid. The suspension is stirred for 30 minutes, filtered to remove unreacted iodosylbenzene and then treated with diethylether which precipitates the very dark green or black complex. In the case of 3,3'5,5'-tetrahalogeno derivatives, the acetonitrile has to be evaporated before addition of the diethylether. Halogeno derivatives may have to be washed with chloroform.

1 equivalent of the appropriate donor ligand may then be added to a solution of 1 equivalent of the appropriate Cr(V)oxosalen hexafluorophosphate complex (II) in sufficient acetonitrile. The solution becomes green. After stirring for 30 minutes, the acetonitrile is evaporated leaving the green Cr(V)oxosalen-donor ligand hexafluorophosphate complex (II).

Table 7 lists the chromium(V)oxosalen complexes made in accordance with the present synthesis process.

PROCESSES FOR THE EPOXIDATION OF ALKENES

Method A. First process for catalytic epoxidation of alkenes with Cr(III)salen hexafluorophosphate complexes (I) using iodosylbenzene as oxygen source.

To a solution of alkene (0.2 mmol), donor ligand D (if to be used, 0.02 mmol) and Cr(III)salen hexafluorophosphate complex (I) lacking donor ligand (0.02 mmol) in acetonitrile or dichloromethane (1 ml) is added at room temperature iodosylbenzene (75 mg). The solution becomes green and is allowed to stir overnight or longer when it has turned orange. It is then filtered to remove iodosylbenzene. The solution is then evaporated and the residue subjected to short path chromatography on silica gel (elution with dichloromethane) or alumina (elution with ether) before being analysed for yield and enantiomeric excess of the resultant epoxide by either chiral gas-liquid chromatography or chiral high performance liquid chromatography.

Method B. Second process for catalytic epoxidation of alkenes with Cr(III)salen hexafluorophosphate complexes (I) using iodosylbenzene as oxygen source.

To a solution of alkene (0.2 mmol), donor ligand D (if to be used, 0.02 mmol) and Cr(III)salen hexafluorophosphate complex (I) lacking donor ligand (0.02 mmol) in acetonitrile or dichloromethane (1 ml) is added at room temperature iodosylbenzene (75 mg in 5mg portions as the green colour is discharged each time, over approximately one or two days). It is then filtered to remove iodosylbenzene. The solution is then evaporated and the residue subjected to short path chromatography on silica gel (elution with dichloromethane) or alumina (elution with ether) before being analysed for yield and enantiomeric excess of the resultant epoxide by either chiral gas-liquid chromatography or chiral high performance liquid chromatography.

Method C. Process for catalytic epoxidation of alkenes with Cr(III)salen hexafluorophosphate complexes (I) using bleach as oxygen source.

To a solution of alkene (1.3 mmol) and Cr(III)salen hexafluorophosphate complex (I) lacking donor ligand (0.06 mmol) and donor ligand D (if to be used, 0.06 mmol) in dichloromethane (2 ml) was added 6 ml of aqueous bleach solution (2% available chlorine) buffered to pH9 with sodium dihydrogen phosphate. The mixture is stirred vigorously overnight or longer at room temperature. The phases are separated and the organic phase dried, evaporated and the residue subjected to short path chromatography on silica gel (elution with dichloromethane) or alumina (elution with ether) before being analysed for yield and enantiomeric excess of the resultant epoxide by either chiral gas-liquid chromatography or chiral high performance liquid chromatography.

Table 8 lists alkenes epoxidised by Methods A, B or C hereinabove using various Cr(III)salen complexes, together with their respective reaction times (approximate time to discharge of green colour).

Method D. Process for stoichiometric epoxidation of alkenes with Cr(III)salen hexafluorophosphate complexes (I).

To a solution of Cr(III)salen hexafluorophosphate complex (I) lacking donor ligand (0.04 mmol) in acetonitrile (3 ml) is added iodosylbenzene (0.45 mmol). The black mixture is allowed to stir for 30 minutes, filtered to remove unreacted iodosylbenzene and treated with donor ligand D (if to be used, 0.04 mmol). The solution becomes green and is allowed to stir for 10 minutes. It is then cooled to 0°C and treated with alkene (0.2 mmol) and the solution turns orange when oxidation is complete, which may take from 1 minute to one week depending on the combination of alkene, salen ligand and donor ligand. The solution is then evaporated and the residue subjected to short path chromatography on silica gel (elution with dichloromethane) or alumina (elution with ether) before being analysed for yield and enantiomeric excess of the resultant epoxide by either chiral gas-liquid chromatography or chiral high performance liquid chromatography.

Tables 9-11 list alkenes epoxidised by Method D, together with their respective reaction times (approximate time to discharge of green colour), enantiomeric excesses and yields, where available.

Method E. Process for stoichiometric epoxidation of alkenes with Cr(V)oxosalen hexafluorophosphate complexes (II).

To a solution of alkene (0.2 mmol) and donor ligand D (if to be used, 0.02 mmol) in acetonitrile or dichloromethane (1 ml) at 0°C is added Cr(V)oxosalen hexafluorophosphate complex (II) lacking donor ligand (0.02 mmol). The solution becomes green initially and when the reaction is over it turns orange. This process may take from 1 minute to 1 week depending on the combination of alkene, salen ligand and donor ligand. The solution is then evaporated and the residue subjected to short path chromatography on silica gel (elution with dichloromethane) or alumina (elution with ether) before being

analysed for yield and enantiomeric excess of the resultant epoxide by either chiral gas-liquid chromatography or chiral high performance liquid chromatography.

Method F. Process for stoichiometric epoxidation of alkenes with Cr(V)oxosalen-donor ligand hexafluorophosphate complexes (II).

To a solution of alkene (0.2 mmol) in acetonitrile or dichloromethane (1 ml) at 0 °C is added Cr(V)oxosalen-donor ligand hexafluorophosphate complex (II) (0.02 mmol). The solution becomes green initially and when the reaction is over it turns orange. This process may take from 1 minute to 1 week depending on the combination of alkene, salen ligand and donor ligand. The solution is then evaporated and the residue subjected to short path chromatography on silica gel (elution with dichloromethane) or alumina (elution with ether) before being analysed for yield and enantiomeric excess of the resultant epoxide by either chiral gas-liquid chromatography or chiral high performance liquid chromatography.

Table 12 lists alkenes epoxidised by Methods E or F, together with respective reaction times (approximate time to discharge of green colour) and enantiomeric excesses.

Method G. Process for catalytic epoxidation of alkenes with Cr(V)oxosalen hexafluorophosphate complexes (II) using iodosylbenzene as oxygen source.

To a solution of alkene (0.2 mmol), donor ligand D (if to be used, 0.02 mmol) and Cr(V)oxosalen hexafluorophosphate complex (II) lacking donor ligand (0.02 mmol) in acetonitrile or dichloromethane (1 ml) is added at room temperature iodosylbenzene (75 mg). The solution becomes green and is allowed to stir overnight or longer when it has turned orange. It is then filtered to remove iodosylbenzene. The solution is then evaporated and the residue subjected to short path chromatography on silica gel (elution with

dichloromethane) or alumina (elution with ether) before being analysed for yield and enantiomeric excess of the resultant epoxide by either chiral gas-liquid chromatography or chiral high performance liquid chromatography.

Method H. Process for catalytic epoxidation of alkenes with Cr(V)oxosalen-donor ligand hexafluorophosphate complexes (II) using iodosylbenzene as oxygen source.

To a solution of alkene (0.2 mmol) and Cr(V)oxosalen-donor ligand hexafluorophosphate complex (II) (0.02 mmol) in acetonitrile or dichloromethane (1 ml) is added at room temperature iodosylbenzene (75mg). The solution becomes green and is allowed to stir overnight or longer when it has turned orange. It is then filtered to remove iodosylbenzene. The solution is then evaporated and the residue subjected to short path chromatography on silica gel (elution with dichloromethane) or alumina (elution with ether) before being analysed for yield and enantiomeric excess of the resultant epoxide by either chiral gas-liquid chromatography or chiral high performance liquid chromatography.

Table 13 lists alkenes epoxidised by Methods G or H, with respective reaction times (approximate time to discharge of green colour) and enantiomeric excesses.

References

1. L.M. Simandi, *Int. Rev. Phys. Chem.*, **1989**, *8*, 21.
2. T. Katsuki and K.B. Sharpless, *J. Am. Chem. Soc.*, **1980**, *102*, 5974; S.S. Woodard, M.G. Finn and K.B. Sharpless, *J. Am. Chem. Soc.*, **1991**, *113*, 106; R.A. Johnson and K.B. Sharpless, Chapter 4.1 in *Catalytic Asymmetric Synthesis*, I. Ojima (ed.), VCH, **1993**, pp 103-158.
3. J.P. Collman, X. Zhang, V.J. Lee, E.S. Uffelman and J.I. Brauman, *Science*, **1993**, *261*, 1404-1411.
4 E.N. Jacobsen, Chapter 4.2 in *Catalytic Asymmetric Synthesis*, I. Ojima (ed.), VCH, 1993, pp 159-202.
5. E.G. Samsel, K. Srinivasan and J.K. Kochi, *J. Am. Chem. Soc.*, **1985**, *107*, 7606.
6. K. Srinivasan, P. Michaud and J.K. Kochi, *J. Am. Chem. Soc.*, **1986**, *108*, 2309.
7. B. Meunier, E. Guilmet, M-E. De Carvalho and R. Poilblanc, *J. Am. Chem. Soc.*, **1984**, *106*, 6668-6676.
8 H. Yoon and C.J. Burrows, *J. Am. Chem. Soc.*, **1988**, *110*, 4087-4089.
9. E. Cesarotti, A. Pasini and R. Ugo, *J. Chem. Soc. Dalton Trans.*, **1981**, 2147-52 and refs cited therein.
10. K. Nakajima, M. Kojima and J. Fujita, *Chem. Lett.*, **1986**, 1483-1486.
11. A. Nishinaga, H. Yamato, T. Abe, K. Maruyama and T. Marsuura, *Tetrahedron Lett.*, **1988**, 6309-6312.
12. (a) W. Zhang, J.L. Loebach, S.R. Wilson and E.N. Jacobsen, *J. Am. Chem. Soc.*, **1990**, *112*, 2801-2803; E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker and L. Deng, *J. Am. Chem. Soc.*, **1991**, *113*, 7063; (b) B.D. Brandes and E.N. Jacobsen, *J. Org. Chem.*, **1994**, *59*, 4378; (c) S. Chang, J.M. Galvin and E.N. Jacobsen, *J. Am. Chem. Soc.*, **1994**, *116*, 6937.

13. (a) R. Irie, K. Noda, Y. Ito, N. Matsumoto and T. Katsuki, *Tetrahedron Lett.*, **1990**, *31*, 7345; (b) R. Irie, Y. Ito and T. Katsuki, *Synlett*, **1991**, 265; (c) T. Hamada, R. Irie and T. Katsuki, *Synlett*, **1994**, 479; (d) N. Hosoya, A. Hatayama, R. Irie, H. Sasaki and T. Katsuki, *Tetrahedron*, **1994**, *50*, 4311-4322.

14. K.J. O'Connor, S-J. Wey and C.J. Burrows, *Tetrahedron Lett.*, **1992**, *33*, 1001-1004; D.R. Reddy and E.R. Thornton, *J. Chem. Soc. Chem. Commun.*, **1992**, 172-173; T. Yamada, K. Imagawa, T. Nagata and T. Mukaiyama, *Chem. Lett.*, **1992**, 2231-2234; M.T. Rispens, A. Meetsma and B.L. Feringa, *Recl. Trav. Chim. Pays-Bas*, **1994**, *113*, 413-15.

15. J.T. Groves, T.E. Nemo and R.S. Myers, *J. Am. Chem. Soc.*, **1979**, *101*, 1032-1033; J.T. Groves and R.S. Myers, *J. Am. Chem. Soc.*, **1983**, *105*, 5791-5796; J.T. Groves, Y. Han and D. Van Engen, *J. Chem. Soc. Chem. Commun.*, **1990**, 436-437.

16. A search of Chemical Abstracts on 4th March 1995 identified 2017 non-alkene or alkyne-substituted, non-metal substituted, non-polymeric salicaldehyde derivatives.

17. H.B. Kagan, Chapter 4.3 in *Catalytic Asymmetric Synthesis*, I. Ojima (ed.), VCH, 1993, pp 203-226.

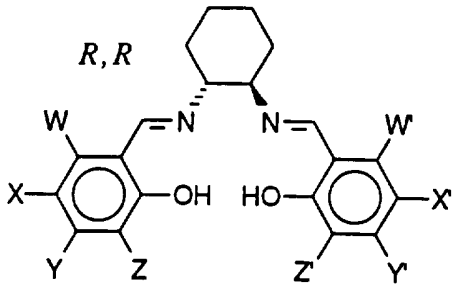
18. P-O. Norrby, C. Linde and B. Akermark, *J.Am.Chem.Soc.*, **1995**, *117*.

19. F. Galsbol, P. Steenbol and B. Sondergaard Sorensen, *Acta. Chem. Scand*, **1972**, *26*, 3605.

TABLE 1

LIST OF SALEN LIGANDS (13) MADE BASED ON THE STRUCTURE BELOW

Where there is no entry in a data column, the compound has been made and its activity examined but it has not yet not yet been fully characterised

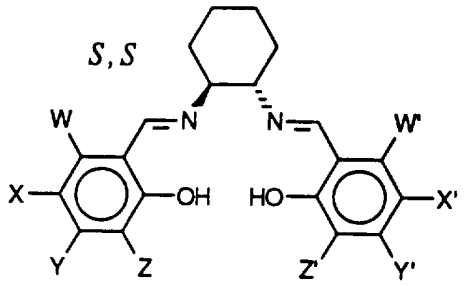


Substituents				Analysis Data (calc in brackets)				Method
W,W'	X,X'	Y,Y'	Z,Z'	%C	%H	%N	%Hal	
H	H	H	H					A
H	Cl	H	H	61.06 (61.39)	5.48 (5.15)	6.98 (7.16)	18.88 (18.12)	A
H	Br	H	H					A
H	Me	H	H	75.66 (75.40)	7.65 (7.48)	8.06 (7.99)		A
H	^{t}Bu	H	H					A
H	OMe	H	H					A
H	H	H	OMe					A
H	Cl	H	Cl	52.13 (52.20)	3.91 (3.94)	6.09 (6.09)	30.44 (30.82)	A
H	Br	H	Br	37.36 (37.65)	2.83 (2.84)	4.43 (4.39)	49.83 (50.10)	A
H	I	H	I					A
H	^{t}Bu	H	^{t}Bu	79.27 (79.07)	9.94 (9.95)	5.20 (5.12)		A/B
H	H	H	F					A
H	H	H	Cl	61.50 (61.39)	5.16 (5.15)	7.22 (7.16)	17.85 (18.12)	A/B
H	H	H	Me					A
H	H	H	^{t}Bu					A
H	H	H	CH_2Ph					A
H	H	H	Ph					A
H	F	H	F					A
H	I	H	I					A
H	H	NEt_2	H					A
Cl	Cl	H	Cl	45.46 (45.39)	3.00 (3.05)	5.32 (5.32)	39.82 (40.20)	A/B
benzo		H	H	79.48 (79.59)	6.22 (6.22	6.54 (6.62)		A

TABLE 2

LIST OF SALEN LIGANDS (13) MADE BASED ON THE STRUCTURE BELOW

Where there is no entry in a data column, the compound has been made and its activity examined but it has not yet not yet been fully characterised

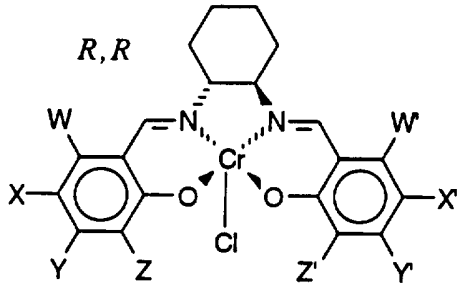


Substituents				Analysis Data (calc)				Method
W,W'	X,X'	Y,Y'	Z,Z'	%C	%H	%N	%Hal	
H	H	H	H					A
H	Cl	H	H					A
H	Cl	H	Cl					A

TABLE 3

LIST OF Cr(III)SALEN INTERMEDIATE COMPLEXES MADE BASED ON THE STRUCTURE BELOW)

Where there is no entry in a data column, the compound has been made and its activity examined but it has not yet not yet been fully characterised

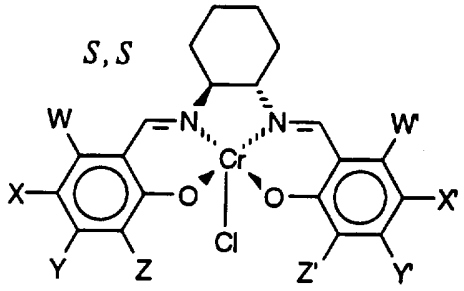


Substituents				Analysis Data (calc)					ir freq
W,W'	X,X'	Y,Y'	Z,Z'	%C	%H	%N	%Cr	%Hal	
H	H	H	H						
H	Cl	H	H						
H	Br	H	H						
H	Me	H	H						
H	^{t}Bu	H	H						
H	OMe	H	H						
H	H	H	OMe						
H	Cl	H	Cl						
H	Br	H	Br						
H	^{t}Bu	H	^{t}Bu						
H	H	H	F						
H	H	H	Cl						
H	H	H	Me						
H	H	H	^{t}Bu						
H	H	H	Bz						
H	H	H	Ph						
H	F	H	F						
H	I	H	I						
H	H	NEt_2	H						
Cl	Cl	H	Cl						
benzo		H	H						

TABLE 4

LIST OF Cr(III)SALEN INTERMEDIATE COMPLEXES MADE BASED ON THE STRUCTURE BELOW)

Where there is no entry in a data column, the compound has been made and its activity examined but it has not yet not yet been fully characterised

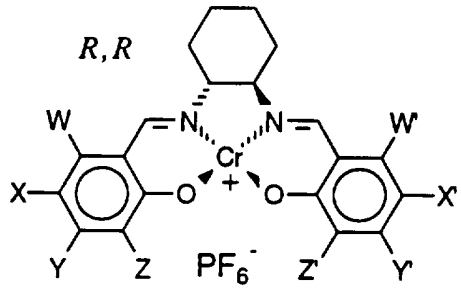


Substituents				Analysis Data (calc)					ir freq
W,W'	X,X'	Y,Y'	Z,Z'	%C	%H	%N	%Cr	%Hal	
H	H	H	H						
H	Cl	H	H						
H	Cl	H	Cl						

TABLE 5

LIST OF Cr(III)SALEN COMPLEXES (I) MADE BASED ON THE STRUCTURE BELOW (i.e D = none and NNA$^-$ = PF_6^-)

All made by Method A except unsubstituted (1st entry) made by both A and B
Where there is no entry in a data column, the compound has been made and its activity examined but it has not yet not yet been fully characterised.

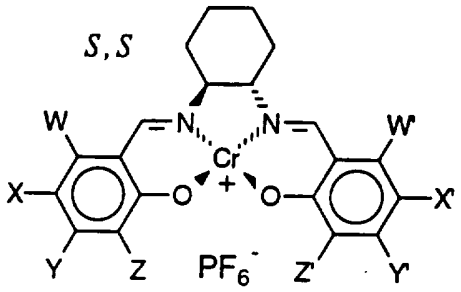


Substituents				Analysis Data on unpurified compds (calc in brackets - not including solvent or water of crystallisation)					ir freq
W,W'	X,X'	Y,Y'	Z,Z'	%C	%H	%N	%Cr	%Hal	
H	H	H	H	39.20 (46.43)	4.97 (3.90)	4.39 (5.41)	8.34 (10.05)	18.28 (22.03)	1630 (C=N) 844 (PF_6^-)
H	Cl	H	H	38.16 (43.53)	4.24 (3.47)	4.42 (5.08)	7.87 (9.42)		
H	Br	H	H	32.73 (40.29)	3.37 (3.21)	3.52 (4.70	6.52 (8.72)		
H	Me	H	H	42.76 (48.36)	5.20 (4.61)	4.30 (5.13)	8.16 (9.52)	18.11 (20.86)	
H	^{t}Bu	H	H						
H	OMe	H	H	42.82 (45.76)	4.75 (4.19)	4.31 (4.85)	8.76 (9.01)	17.97 (19.74)	
H	H	H	OMe	41.52 (45.76)	4.90 (4.19)	4.15 (4.85)	7.58 (9.01)	16.70 (19.74)	
H	Cl	H	Cl	35.25 (36.66)	2.88 (2.46)	2.96 (4.27)	6.65 (7.94)	33.93 (39.04)	1631 (C=N) 844 (PF_6^-)
H	Br	H	Br						
H	^{t}Bu	H	^{t}Bu	54.15 (58.29)	7.35 (7.06)	3.21 (3.77)	6.56 (7.00)	12.07 (15.36)	1621 (C=N) 837 (PF_6^-)
H	H	H	F						
H	H	H	Cl	39.34 (40.98)	3.87 (3.09)	4.17 (4.78)	7.55 (8.87)	24.44 (31.53)	1631 (C=N) 845 (PF_6^-)
H	H	H	Me						
H	H	H	^{t}Bu						1620 (C=N) 847 (PF_6^-)
H	H	H	Bz						
H	H	H	Ph						1626 (C=N) 844 (PF_6^-)
H	F	H	F						1638 (C=N) 843 (PF_6^-)
H	I	H	I	21.56 (22.73)	1.83 (1.91)	2.03 (2.65)	3.67 (4.92)	57.66 (59.19)	1624 (C=N) 841 (PF_6^-)
H	H	NEt_2	H						1591 (C=N) 844 (PF_6^-)
Cl	Cl	H	Cl						1625 (C=N) 849 (PF_6^-)
benzo		H	H	58.74 (54.46)	4.96 (3.92)	4.87 (4.53)	8.38 (8.42)		1619 (C=N) 851 (PF_6^-)

TABLE 6

LIST OF Cr(III)SALEN COMPLEXES (I) MADE (by Method A) BASED ON THE STRUCTURE BELOW (i.e D = none and NNA⁻ = PF_6^-)

Where there is no entry in a data column, the compound has been made and its activity examined but it has not yet not yet been fully characterised

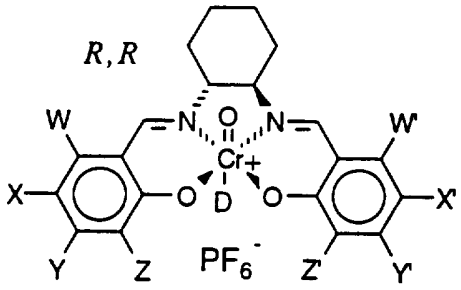


Substituents				Analysis Data (calc in brackets)					ir freq
W,W'	X,X'	Y,Y'	Z,Z'	%C	%H	%N	%Cr	%Hal	
H	H	H	H						
H	Cl	H	H						
H	Cl	H	Cl						

TABLE 7

LIST OF Cr(V)OXOSALEN COMPLEXES (II) MADE ALL BASED ON THE STRUCTURE BELOW ($NNA^- = PF_6^-$)

Where there is no entry in a data column, the compound has been made and its activity examined but it has not yet not yet been fully characterised

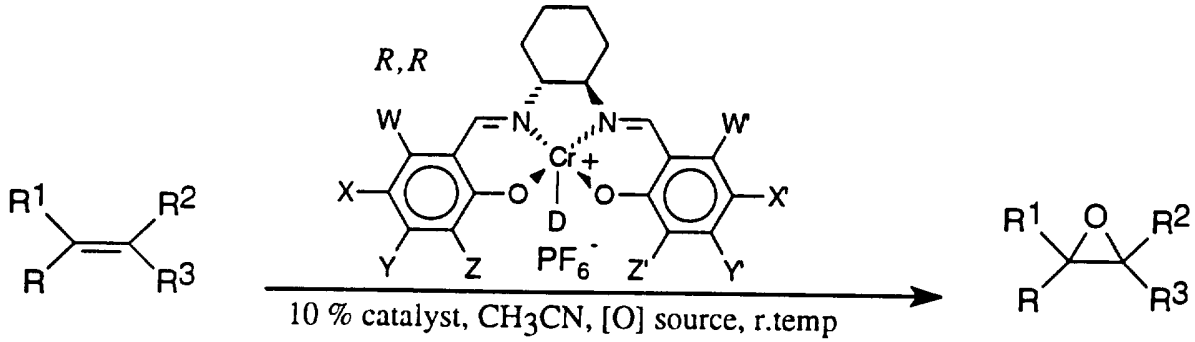


Substituents				D	Analysis Data for unpurified complexes (calc in brackets - excl solvent or water of crystallisation)					ir freq
W,W'	X,X'	Y,Y'	Z,Z'		%C	%H	%N	%Cr	%Hal	
H	H	H	H	none						1601 (C=N) 1010 (Cr=O) 838 (PF_6^-)
H	H	H	H	TPPO						1624 (C=N) 947 (Cr=O) 839 (PF_6^-)
H	Cl	H	H	none						
H	Br	H	H	none						
H	Me	H	H	none						
H	^{t}Bu	H	H	none						
H	OMe	H	H	none						
H	H	H	OMe	none						
H	Cl	H	Cl	none						
H	Br	H	Br	none						
H	^{t}Bu	H	^{t}Bu	none						
H	H	H	F	none						
H	H	H	Cl	none	41.82 (39.89)	3.94 (3.01)	4.97 (4.65)	7.21 (8.63)	24.91 (30.70)	1626 (C=N) 1018 (Cr=O) 843 (PF_6^-)
H	H	H	Cl	TPPO	53.26 (51.83)	4.32 (3.78)	3.12 (3.18)	5.08 (5.91)	18.12 (21.00)	1625 (C=N) 946 (Cr=O) 842 (PF_6^-)
H	H	H	Me	none						
H	H	H	^{t}Bu	none						
H	H	H	Bz	none						
H	H	H	Ph	none						
H	F	H	F	none						
H	I	H	I	none						
H	H	NEt_2	H	none						
Cl	Cl	H	Cl	none						
benzo		H	H	none						

TABLE 8

LIST OF ALKENES EPOXIDISED BY METHODS A-C (CATALYTIC)

%ee: resultant enantiomeric excess in product epoxide;
time: approx time to discharge of green colour;
config: absolute configuration of major product epoxide



METHOD A

W,W'	X,X'	Y,Y'	Z,Z'	D	time	%ee	config	yield
E-β-methylstyrene								
H	H	H	H	none	2 d	38	1*R*,2*R*	28%
H	H	H	H	triphenylphosphine oxide	2 d	50	1*R*,2*R*	31%

METHOD B

W,W'	X,X'	Y,Y'	Z,Z'	D	time	%ee	config	yield
E-β-methylstyrene								
H	H	H	H	none	2 d	38	1*R*,2*R*	28%
H	H	H	H	triphenylphosphine oxide	2 d	56	1*R*,2*R*	31%
H	H	H	H	(±)-naphthylMePhP=O	2 d	52	1*R*,2*R*	54%
H	H	H	H	benzyltertbutylsulphoxide	2 d	48	1*R*,2*R*	36%
H	H	H	H	anisyltoluylsulphoxide	2 d	53	1*R*,2*R*	56%
H	H	H	H	3-picoline-N-oxide	2 d	53	1*R*,2*R*	53%
H	Cl	H	H	triphenylphosphine oxide	1 d	61	1*R*,2*R*	
H	Cl	H	Cl	triphenylphosphine oxide	1 d	73	1*R*,2*R*	79%

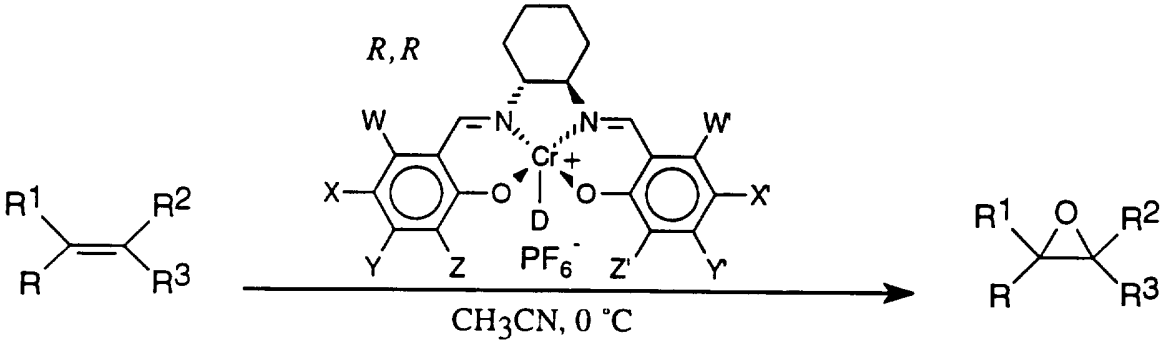
METHOD C

W,W'	X,X'	Y,Y'	Z,Z'	D	time	%ee	config	yield
E-β-methylstyrene								
H	H	H	H	none	2 d	50	1*R*,2*R*	51%
H	H	H	H	triphenylphosphine oxide	2 d	38	1*R*,2*R*	25%

TABLE 9

LIST OF ALKENES EPOXIDISED BY METHOD D (STOICHIOMETRIC) USING R,R-HEXAFLUOROPHOSPHATE COMPLEX

%ee: resultant enantiomeric excess in product epoxide;
time: approx time to discharge of green colour;
config: absolute configuration of major product epoxide



W,W'	X,X'	Y,Y'	Z,Z'	D	time	%ee	config	yield
***E*-β-methylstyrene**								
H	H	H	H	none	12 h	58	1*R*,2*R*	
H	H	H	H	triphenylphosphine oxide	12 h	72	1*R*,2*R*	90%
H	H	H	H	(±)-anisylMePhP=O	12 h	71	1*R*,2*R*	
H	H	H	H	dimethylsulphoxide	12 h	66	1*R*,2*R*	
H	H	H	H	benzyltertbutylsulphoxide	12 h	62	1*R*,2*R*	
H	H	H	H	anisyltoluylsulphoxide	12 h	66	1*R*,2*R*	
H	H	H	H	dimethylformamide	12 h	69	1*R*,2*R*	
H	H	H	H	pyridine-N-oxide	12 h	68	1*R*,2*R*	
H	H	H	H	4-phenylpyridine-N-oxide	12 h	67	1*R*,2*R*	
H	H	H	H	2-picoline-N-oxide	12 h	66	1*R*,2*R*	44%
H	H	H	H	3-picoline-N-oxide	12 h	66	1*R*,2*R*	
H	H	H	H	trimesitylphosphine oxide	12 h	62	1*R*,2*R*	
H	H	H	H	tributylphosphine oxide	12 h	63	1*R*,2*R*	
H	H	H	H	(±)-anisylMePhP=O	12 h	69	1*R*,2*R*	
H	H	H	H	(±)-anisylMePhP-BH_3	12 h	68	1*R*,2*R*	
H	H	H	H	trioctylphosphine oxide	12 h	69	1*R*,2*R*	
H	H	H	H	trihexyl phosphate	12 h	70	1*R*,2*R*	
H	H	H	H	tritolyl phosphate	12 h	65	1*R*,2*R*	
H	H	H	H	tris(2-ethylhexyl) phosphate	12 h	65	1*R*,2*R*	
H	H	H	H	triethyl phosphate	12 h	65	1*R*,2*R*	
H	H	H	H	triphenylphosphine sulphide	12 h	63	1*R*,2*R*	
H	H	H	H	(±)-anisylMePhP=S	12 h	57	1*R*,2*R*	
H	H	H	H	naphthalene	12 h	67	1*R*,2*R*	
H	Br	H	H	none	10 m	58	1*R*,2*R*	
H	Br	H	H	triphenylphosphine oxide	10 m	71	1*R*,2*R*	
H	Br	H	H	dimethylsulphoxide	10 m	69	1*R*,2*R*	
H	Br	H	H	dimethylformamide	10 m	70	1*R*,2*R*	
H	Br	H	H	pyridine-N-oxide	10 m	74	1*R*,2*R*	
H	Br	H	H	4-phenylpyridine-N-oxide	10 m	75	1*R*,2*R*	

W,W'	X,X'	Y,Y'	Z,Z'	D	time	%ee	config	yield
H	Cl	H	H	none	10 m	58	1*R*,2*R*	
H	Cl	H	H	triphenylphosphine oxide	10 m	71	1*R*,2*R*	
H	Cl	H	H	(±)-anisylMePhP=O	10 m	73	1*R*,2*R*	
H	Cl	H	H	(+)-anisylMePhP=O	10 m	74	1*R*,2*R*	
H	Cl	H	H	(-)-anisylMePhP=O	10 m	74	1*R*,2*R*	
H	Cl	H	H	dimethylsulphoxide	10 m	69	1*R*,2*R*	
H	Cl	H	H	dimethylformamide	10 m	70	1*R*,2*R*	
H	Cl	H	H	pyridine-N-oxide	10 m	74	1*R*,2*R*	
H	Cl	H	H	4-phenylpyridine-N-oxide	10 m	75	1*R*,2*R*	
H	Cl	H	H	(+)-menthoxyMePhP=O	10 m	64	1*R*,2*R*	
H	Cl	H	Cl	none	5 m	67	1*R*,2*R*	
H	Cl	H	Cl	triphenylphosphine oxide	5 m	83	1*R*,2*R*	90%
H	Cl	H	Cl	4-phenylpyridine-N-oxide	5 m	50	1*R*,2*R*	
H	^{t}Bu	H	^{t}Bu	triphenylphosphine oxide	1 w	73	1*R*,2*R*	
H	H	H	F	none	5 m	70	1*R*,2*R*	
H	H	H	F	triphenylphosphine oxide	5 m	86	1*R*,2*R*	85%
H	H	H	F	4-phenylpyridine-N-oxide	5 m	85	1*R*,2*R*	
H	H	H	Cl	none	10 m	80	1*R*,2*R*	
H	H	H	Cl	triphenylphosphine oxide	10 m	86	1*R*,2*R*	85%
H	H	H	Cl	dimethylsulphoxide	10 m	78	1*R*,2*R*	
H	H	H	Cl	dimethylformamide	10 m	82	1*R*,2*R*	
H	H	H	Cl	pyridine-N-oxide	10 m	69	1*R*,2*R*	
H	H	H	Cl	4-phenylpyridine-N-oxide	10 m	69	1*R*,2*R*	
H	H	H	Cl	trimesitylphosphine oxide	10 m	78	1*R*,2*R*	
H	H	H	Cl	tributylphosphine oxide	10 m	83	1*R*,2*R*	
H	H	H	Cl	(±)-anisylMePhP=O	10 m	82	1*R*,2*R*	
H	H	H	Cl	(±)-naphthylMePhP=O	10 m	78	1*R*,2*R*	
H	H	H	Cl	(±)-anisylMePhP-BH_3	10 m	1	1*R*,2*R*	
H	H	H	Cl	trioctylphosphine oxide	10 m	81	1*R*,2*R*	
H	H	H	Cl	trihexyl phosphate	10 m	76	1*R*,2*R*	
H	H	H	Cl	tritolyl phosphate	10 m	80	1*R*,2*R*	
H	H	H	Cl	tris(2-ethylhexyl) phosphate	10 m	83	1*R*,2*R*	
H	H	H	Cl	triethyl phosphate	10 m	80	1*R*,2*R*	
H	H	H	Cl	tris(*N*-pyrollidinyl)P=O	10 m	80	1*R*,2*R*	
H	H	H	Cl	diphenylmethylphosphine oxide	10 m	79	1*R*,2*R*	
H	H	H	Cl	acetone	10 m	73	1*R*,2*R*	
H	H	H	Cl	ethyl acetate	10 m	70	1*R*,2*R*	
H	H	H	Cl	sulpholane	10 m	71	1*R*,2*R*	
Cl	Cl	H	Cl	triphenylphosphine oxide	5 m	72	1*R*,2*R*	
Cl	Cl	H	Cl	dimethylsulphoxide	5 m	72	1*R*,2*R*	
Cl	Cl	H	Cl	dimethylformamide	5 m	71	1*R*,2*R*	
Cl	Cl	H	Cl	phosphoryl chloride	5 m	33	1*R*,2*R*	

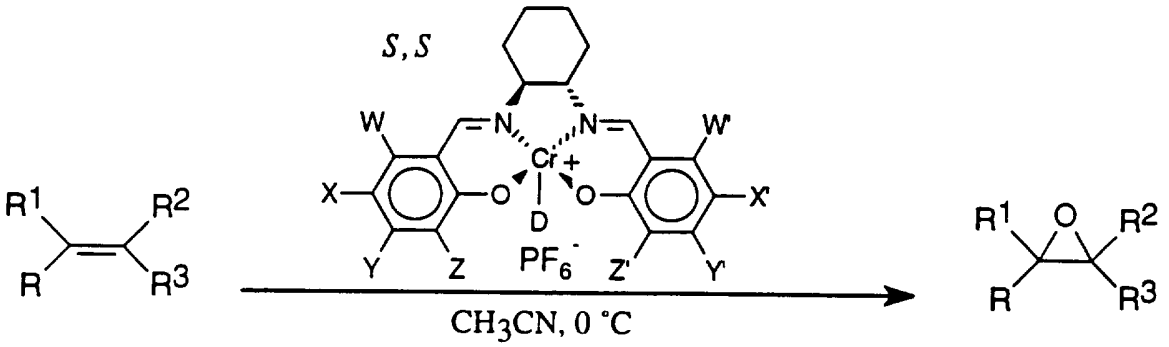
W,W'	X,X'	Y,Y'	Z,Z'	D	time	%ee	config	yield
H	H	H	Me	triphenylphosphine oxide	2 d	82	1*R*,2*R*	
H	H	H	tBu	triphenylphosphine oxide	1 w	79	1*R*,2*R*	
H	H	H	Bz	triphenylphosphine oxide	2 d	86	1*R*,2*R*	
H	H	H	Ph	triphenylphosphine oxide	2 d	80	1*R*,2*R*	
H	H	H	OMe	triphenylphosphine oxide	30 m	66	1*R*,2*R*	
H	F	H	F	triphenylphosphine oxide	5 m	83	1*R*,2*R*	
H	I	H	I	triphenylphosphine oxide	10 m	53	1*R*,2*R*	
H	H	NEt_2	H	triphenylphosphine oxide	1 d	45	1*R*,2*R*	
benzo		H	H	none	2 d	44	1*R*,2*R*	
benzo		H	H	triphenylphosphine oxide	2 d	56	1*R*,2*R*	
benzo		H	H	dimethylsulphoxide	2 d	46	1*R*,2*R*	
benzo		H	H	dimethylformamide	2 d	52	1*R*,2*R*	
benzo		H	H	pyridine-N-oxide	2 d	51	1*R*,2*R*	
benzo		H	H	4-phenylpyridine-N-oxide	2 d	41	1*R*,2*R*	
benzo		H	H	2-picoline-N-oxide	2 d	53	1*R*,2*R*	
anethole								
H	H	H	H	triphenylphosphine oxide	12 h	57		
H	H	H	H	4-phenylpyridine-N-oxide	12 h	63		
H	Cl	H	Cl	triphenylphosphine oxide	5 m	67		
H	Cl	H	Cl	4-phenylpyridine-N-oxide	5 m	40		
***E*-stilbene**								
H	Cl	H	Cl	triphenylphosphine oxide	12 h	42		
H	Cl	H	Cl	4-phenylpyridine-N-oxide	12 h	62		
***E*-3-hexene**								
H	H	H	H	none	12 h	5		
H	H	H	H	triphenylphosphine oxide	12 h	5		
H	H	H	H	4-phenylpyridine-N-oxide	12 h	5		
H	Cl	H	Cl	none	5 m	7		
H	Cl	H	Cl	triphenylphosphine oxide	5 m	12		
H	Cl	H	Cl	4-phenylpyridine-N-oxide	5 m	22		
styrene								
H	H	H	H	none	12 h	3		
H	H	H	H	triphenylphosphine oxide	12 h	-4		
H	H	H	H	4-phenylpyridine-N-oxide	12 h	-3		
H	Cl	H	Cl	triphenylphosphine oxide	5 m	20		
H	Cl	H	Cl	4-phenylpyridine-N-oxide	5 m	0		

W,W'	X,X'	Y,Y'	Z,Z'	D	time	%ee	config	yield
						5		
α-methylstyrene						5		
H	H	H	H	triphenylphosphine oxide	12 h			
H	H	H	H	4-phenylpyridine-N-oxide	12 h			
Z-β-methylstyrene								
H	H	H	H	none	12 h	25	1*S*,2*R*	
H	H	H	H	triphenylphosphine oxide	12 h	27	1*S*,2*R*	
H	H	H	H	dimethylsulphoxide	12 h	38	1*S*,2*R*	
H	H	H	H	dimethylformamide	12 h	28	1*S*,2*R*	
H	H	H	H	pyridine-N-oxide	12 h	31	1*S*,2*R*	
H	H	H	H	4-phenylpyridine-N-oxide	12 h	31	1*S*,2*R*	
H	Cl	H	H	none	10 m	33	1*S*,2*R*	
H	Cl	H	H	triphenylphosphine oxide	10 m	35	1*S*,2*R*	
H	Cl	H	H	dimethylsulphoxide	10 m	35	1*S*,2*R*	
H	Cl	H	H	dimethylformamide	10 m	36	1*S*,2*R*	
H	Cl	H	H	pyridine-N-oxide	10 m	37	1*S*,2*R*	
H	Cl	H	H	4-phenylpyridine-N-oxide	10 m	37	1*S*,2*R*	
H	Br	H	H	none	10 m	33	1*S*,2*R*	
H	Br	H	H	triphenylphosphine oxide	10 m	35	1*S*,2*R*	
H	Br	H	H	dimethylsulphoxide	10 m	35	1*S*,2*R*	
H	Br	H	H	dimethylformamide	10 m	36	1*S*,2*R*	
H	Br	H	H	pyridine-N-oxide	10 m	37	1*S*,2*R*	
H	Br	H	H	4-phenylpyridine-N-oxide	10 m	37	1*S*,2*R*	
H	Cl	H	Cl	none	5 m	43	1*S*,2*R*	
H	Cl	H	Cl	triphenylphosphine oxide	5 m	56	1*S*,2*R*	
H	Cl	H	Cl	dimethylsulphoxide	5 m	50	1*S*,2*R*	
H	Cl	H	Cl	dimethylformamide	5 m	55	1*S*,2*R*	
H	Cl	H	Cl	pyridine-N-oxide	5 m	40	1*S*,2*R*	
H	Cl	H	Cl	4-phenylpyridine-N-oxide	5 m	40	1*S*,2*R*	
H	H	H	F	none	5 m	33	1*S*,2*R*	
H	H	H	F	triphenylphosphine oxide	5 m	36	1*S*,2*R*	
H	H	H	F	4-phenylpyridine-N-oxide	5 m	28	1*S*,2*R*	
1,2-dihydronaphthalene								
H	Cl	H	Cl	none	5 m	20		
H	Cl	H	Cl	triphenylphosphine oxide	5 m	50		
H	Cl	H	Cl	4-phenylpyridine-N-oxide	5 m	65		

TABLE 10

LIST OF ALKENES EPOXIDISED BY METHOD D (STOICHIOMETRIC) USING S,S-HEXAFLUOROPHOSPHATE COMPLEX

%ee: resultant enantiomeric excess in product epoxide;
time: approx time to discharge of green colour;
config: absolute configuration of major product epoxide

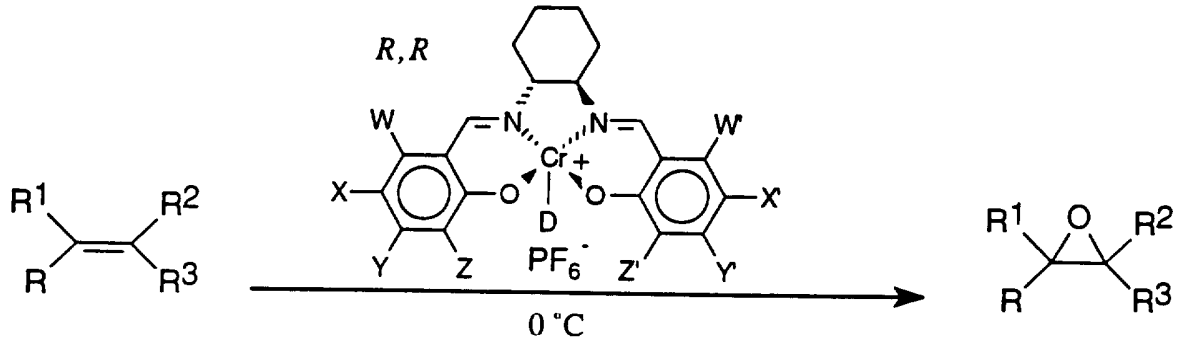


W,W'	X,X'	Y,Y'	Z,Z'	D	time	%ee	config	yield
***E*-β-methylstyrene**								
H	H	H	H	none	12 h	58	1*S*,2*S*	
H	H	H	H	triphenylphosphine oxide	12 h	72	1*S*,2*S*	
H	H	H	H	dimethylsulphoxide	12 h	66	1*S*,2*S*	
H	H	H	H	dimethylformamide	12 h	69	1*S*,2*S*	
H	H	H	H	pyridine-N-oxide	12 h	68	1*S*,2*S*	
H	H	H	H	4-phenylpyridine-N-oxide	12 h	67	1*S*,2*S*	
H	Cl	H	H	triphenylphosphine oxide	10 m	71	1*S*,2*S*	
H	Cl	H	H	(±)-anisylMePhP=O	10 m	73	1*S*,2*S*	
H	Cl	H	H	(+)-anisylMePhP=O	10 m	74	1*S*,2*S*	
H	Cl	H	H	(-)-anisylMePhP=O	10 m	74	1*S*,2*S*	
H	Cl	H	H	dimethylformamide	10 m	69	1*S*,2*S*	
H	Cl	H	H	4-phenylpyridine-N-oxide	10 m	75	1*S*,2*S*	
H	Cl	H	Cl	triphenylphosphine oxide	5 m	83	1*S*,2*S*	

TABLE 11

LIST OF ALKENES EPOXIDISED BY METHOD D (STOICHIOMETRIC) USING R,R-HEXAFLUOROPHOSPHATE COMPLEX WITH TRIPHENYLPHOSPHINE OXIDE AS LIGAND D IN DIFFERENT SOLVENTS

%ee: resultant enantiomeric excess in product epoxide;
time: approx time to discharge of green colour;
config: absolute configuration of major product epoxide

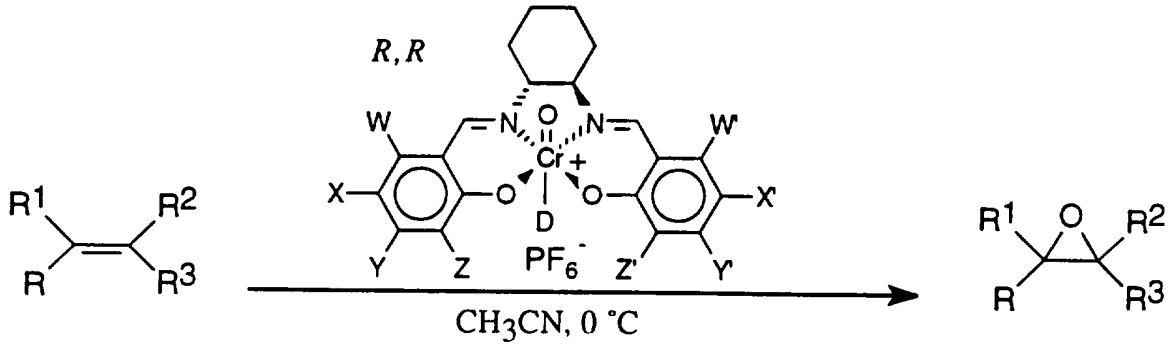


WW'	XX'	YY'	ZZ'	Solvent	time	%ee	config	yield
E-β-methylstyrene								
H	Cl	H	Cl	acetonitrile	5 m	83	1*R*,2*R*	
H	Cl	H	Cl	dichloromethane	5 m	83	1*R*,2*R*	
H	Cl	H	Cl	tetrahydrofuran	5 m	72	1*R*,2*R*	
H	Cl	H	Cl	acetone	5 m	73	1*R*,2*R*	

TABLE 12

LIST OF ALKENES EPOXIDISED BY METHODS E-F (STOICHIOMETRIC)

%ee: resultant enantiomeric excess in product epoxide;
time: approx time to discharge of green colour;
config: absolute configuration of major product epoxide



METHOD E

WW'	XX'	YY'	ZZ'	D	time	%ee	config	yield
E-β-methylstyrene								
H	H	H	H	triphenylphosphine oxide	12 h	72	1*R*,2*R*	

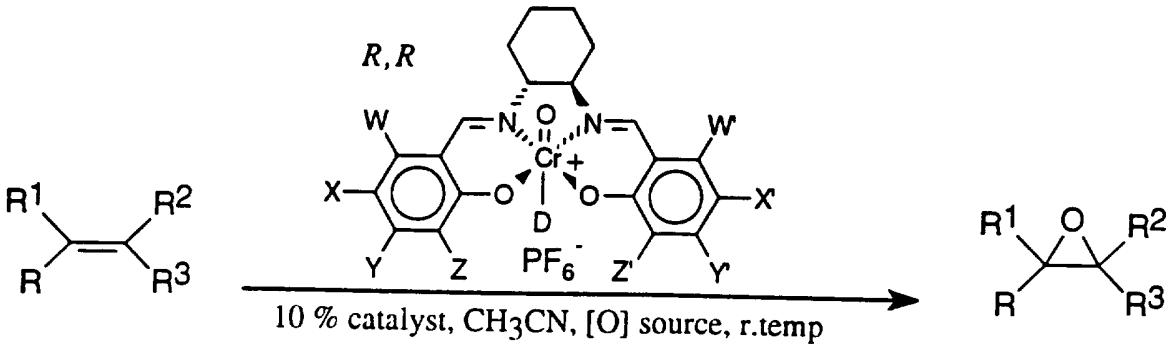
METHOD F

WW'	XX'	YY'	ZZ'	D	time	%ee	config	yield
E-β-methylstyrene								
H	H	H	H	triphenylphosphine oxide	12 h	72	1*R*,2*R*	

TABLE 13

LIST OF ALKENES EPOXIDISED BY METHODS G-H (CATALYTIC)

%ee: resultant enantiomeric excess in product epoxide;
time: approx time to discharge of green colour;
config: absolute configuration of major product epoxide



METHOD G

WW'	XX'	YY'	ZZ'	D	time	%ee	config	yield
***E*-β-methylstyrene**								
H	H	H	H	triphenylphosphine oxide	2 d	56	1*R*,2*R*	

METHOD H

WW'	XX'	YY'	ZZ'	D	time	%ee	config	yield
***E*-β-methylstyrene**								
H	H	H	H	triphenylphosphine oxide	2 d	56	1*R*,2*R*	

CLAIMS:

1. A transition metal cationic chiral non-racemic complex containing a substituted or unsubstituted tetradentate or quinquedentate ligand derived from two salicylaldimine units, the cationic complex including a non-nucleophilic anion NNA and, optionally, an oxygen atom bonded to the transition metal and, optionally, a neutral donor ligand D capable of coordinative bonding to the transition metal, the cationic chiral complex and the cationic chiral oxo-complex having the structural formulae (I) and (II), respectively, given hereinafter, in which:

M is a transition metal atom;

NNA is a non-nucleophilic anion;

D, which may be present or absent, is a neutral donor ligand;

C_n represents a connecting chain of atoms in which is n is 0 to 4, preferably 0, 1 or 2;

A, A', B and B' are each a non-oxidisable group or atom, or A and B' or B and A' together with their respective intermediate carbon atoms, each form a substituted or unsubstituted ring structure, or A and B or A' and B' together form a substituted or unsubstituted spiro ring structure; and

V, V', W, W', X, X', Y, Y', Z and Z' are each a non-oxidisable group or atom or any two of V, W, X, Y and Z and/or any two of V', W', X', Y' and Z' together with their respective intermediate carbon atoms may form a substituted or unsubstituted ring structure or V and V' or W and W' or X and X' or Y and Y' or Z and Z' together with their respective intermediate carbon atoms may form a substituted or unsubstituted ring structure.

2. A complex according to Claim 1, in which the NNA is a non-coordinating species selected from hexafluorophosphate, trifluoromethanesulphonate, tetrahalogenoborates, substituted or unsubstituted arylmethanesulphonates and tetraarylborates, in which aryl is phenyl, toluyl or mesityl, or trifluoroacetate, most preferably, hexafluorophosphate or trifluoromethanesulphonate.

3. A complex according to Claim 1 or 2, in which D is selected from:

a phosphine oxide, preferably selected from triphenylphosphine oxide, diphenylmethylphosphine oxide, triethylphosphine oxide, (RS)- or (R)- or (S)-anisylmethylphenylphosphine oxide, (RS)- or (R)- or(S)-naphthylmethylphenylphosphine oxide, (RS)- or (R)- or (S)-anisylnaphthylphenylphosphine oxide, trimesitylphosphine oxide, trimesitylphenylphosphine oxide, tributylphosphine oxide, trioctylphosphine oxide or trichlorophosphine oxide;
a phosphine sulphide preferably selected from triphenylphosphine sulphide, triethylphosphine sulphide, (RS)- or (R)- or (S)-anisylmethylphenylphosphine sulphide, (RS)- or (R)- or (S)-methylnaphthylphenylphosphine sulphide, (RS)- or (R)- or (S)-anisylnaphthylphenylphosphine sulphide;
a phosphine imine, preferably selected from triphenylphosphine imine or (RS)- or (R)- or (S)-anisylmethylphenylphosphine imine;
an alkyl/aryl phosphonate, preferably selected from methyl diphenylphosphonate, methyl dimethylphosphonate, (RS)- or (R)- or (S)-methyl methylphenylphosphonate or any isomer of menthyl methylphenylphosphonate;
an alkyl/aryl phosphinate, preferably selected from dimethylphenylphosphinate or dimethyl methylphosphinate;
an alkyl/aryl phosphate, preferably selected from trimethyl phosphate, triphenyl phosphate, trihexyl phosphate, tritolyl phosphate, tris(2-ethylhexyl) phosphate or triethyl phosphate;

a phosphoramide, preferably selected from hexamethylphosphoramide or tripyrrollidinylphosphine oxide; a phosphinamide; a phosphonamide; a phosphine borane, preferably selected from triphenylphosphine borane or (RS)- or (R)- or (S)-anisylmethylphenylphosphine borane; an amine oxide preferably selected from pyridine-N-oxide, 4-phenylpyridine-N-oxide, 2-picoline-N-oxide, 3-picoline-N-oxide, 4-picoline-N-oxide or trimethylamine-N-oxide;
a sulphoxide, preferably selected from dimethylsulphoxide, diphenylsulphoxide, benzyltert-butylsulphoxide or anisyltoluylsulphoxide;
a sulphone, preferably selected from dimethylsulphone, diphenylsulphone, benzyltert-butylsulphone, anisyltoluylsulphone or sulpholane;
an amide, preferably selected from dimethylformamide or phenylmethylformamide;
an ester, preferably, ethyl acetate; a ketone, preferably, acetone; urea; a carbamate; a carbonate; an α-aminoamide; an α-aminoester; or an unsaturated system capable of coordinative bonding to the transition metal, preferably selected from benzene or napthalene.

4. A complex according to Claim 3, in which D is selected from triphenylphosphine oxide, (RS)-anisylmethylphenylphosphine oxide, N,N-dimethylformamide, dimethylsulphoxide, trimesitylphosphine oxide, tributylphosphine oxide, trioctylphosphine oxide, trihexyl phosphate, tritolyl phosphate, triethyl phosphate, tris(2-ethylhexyl) phosphate, pyridine-N-oxide or 4-phenylpyridine-N-oxide.

5. A complex according to any one of the preceding claims, in which M is selected from Cr, Ni, Co, Fe, Ti, Mo, W or V, preferably Cr.

6. A complex according to any one of the preceding claims, in which A, A', B, B', V, V', W, W', X, X', Y, Y', Z and Z' are each selected from:

hydrogen, halogen (F, Cl, Br, I),
OH, OR,
SH, SR, S(O)R, $S(O_2)R$, SO_3H, SO_3R,
NH_2, NHR, NRR', NO_2,
PRR', PR(OR'), P(OR)(OR'), P(O)RR', P(O)R(OR'), P(O)(OR)(OR'),
optionally substituted alkyl, alkoxy, cycloalkyl, carboalkoxy,
heterocycle, aryl or carboaryloxy, $CHal_3$, $CHal_2R$, CHalRR',
C(O)R, CO_2H, CO_2R, $C(O)NH_2$, C(O)NHR, C(O)NRR', CN,
SiRR'R'', Si(OR)(OR')(OR''), $OSiR_3$, SiR_3, OSiRR'R",
OSi(OR)(OR')(OR"),
wherein R, R' and R'' are each optionally substituted alkyl, cycloalkyl or aryl; carboalkoxy, carboaryloxy, acyl, carbamyl or halogen (F, Cl, Br, I).

7. A complex according to Claim 6, in which V, V' are each hydrogen; W and W' are each hydrogen or chloride, X and X' are each hydrogen, fluoride, chloride, bromide, iodide, lower alkyl, preferably selected from methyl or tert-butyl, or lower alkoxy, preferably methoxy, or W and X and W' and X' each together with their respective intermediate carbon atoms form a benzo ring; Y and Y' are each hydrogen or diethylamine; and Z and Z' are each hydrogen, fluoride, chloride, bromide, iodide, lower alkyl, preferably selected from methyl or tert-butyl, lower alkoxy, preferably, from methoxy or substituted or unsubstituted aryl, preferably selected from benzyl or phenyl.

8. A complex according to Claim 7, in which V, V', W, W', X, X', Y and Y' are each hydrogen and Z and Z' are selected from fluoride, chloride, methyl, tert-butyl, benzyl or phenyl or, alternatively, V, V', W, W', Y and Y' are each hydrogen and X, X', Z and Z' are selected from fluoride, chloride, methyl or tert-butyl or, alternatively, V, V', Y and Y' are each hydrogen and W, W', X, X', Z and Z' are

selected from fluoride, chloride or tert-butyl or, alternatively, V, V', W, W', Y, Y', Z and Z' are each hydrogen and X and X' are selected from chloride or bromide.

9. A complex according to any one of the preceding claims, in which A and B' or B and A' together comprise cyclohexane and A' = B = H or B' = A = H, respectively, n is 0 and the ligand is a tetradentate salen ligand.

10. A complex according to Claim 9, in which A and B or B and A together comprise cyclohexane and A' and B are each hydrogen or B' and A are each hydrogen, respectively, M is Cr, n is 0 and at least one of V, V', W, W', X, X', Y, Y', Z and Z' is halogen.

11. A complex according to Claim 10, in which V and V' or W and W' or X and X' or Y and Y' or Z and Z' are each halogen, preferably, Z and Z' are each halogen, more preferably, Z and Z' are each F or Cl.

12. A process for preparing a complex of the formula (I), which process comprises:

(i) contacting a complex of the formula (I) in which D is replaced by halide, with a salt of a NNA in a suitable solvent; or

(ii) contacting an appropriate quadridentate or quinquedentate ligand of the formula (13) with either a chromium salt and a salt of a NNA or, alternatively, a chromium NNA salt in a suitable solvent.

13. A process according to Claim 12, in which the complex of formula (I) wherein D is replaced by halide, is prepared by contacting an appropriate quadridentate or quinquedentate ligand with a chromium halide in a suitable solvent.

14. A process according to Claim 12 or 13, in which the chromium salt is a chromium(II)halide, most preferably chromium dichloride and the salt of the NNA is an alkali metal salt of the NNA, most preferably potassium hexafluorophosphate.

15. A process for preparing a complex of the formula (II), which process comprises contacting an appropriate complex of the formula (I) with an oxygen source in a suitable solvent and, optionally, with a donor ligand D.

16. A process for stereoselectively epoxidising an alkene, which process comprises contacting the alkene with a complex of the formula (II) in a suitable solvent, optionally in the presence of an oxygen source.

17. A process according to Claim 16, in which the complex acts as a catalyst and an oxygen source is present.

18. A process according to Claim 17, in which the ratio of complex to alkene is in the range of from about 1:10 to 1:1000, preferably about 1:20.

19. A process according to Claim 16, in which the complex is stoichiometrically consumed in the absence of an oxygen source.

20. A process according to Claim 19, in which the stereoselection is an enantioselection and the ratio of complex to alkene should not exceed about 1 to 1.

21. A process according to Claim 19, in which the stereoselection is a diastereoselection, and the ratio of complex to alkene should not exceed about 1:2.

22. A process according to any one of Claims 16 to 21, in which the alkene is a *E*-1,2-disubstituted alkene, more preferably *E*-ß-methylstyrene or *E*-stilbene or, alternatively, the alkene is selected from anethole, *Z*-ß-methylstyrene, *α*-methylstyrene, styrene, *E*-ß-hexene or 1,2-dihydronaphthalene.

23. A process according to any one of Claims 15 to 22, in which the oxygen source may be any suitable oxygen source selected from iodosylarenes, preferably iodosylbenzene, hypohalites preferably bleach, perhalates, preferably selected from sodium periodate, perbromate or perchlorate, halates, preferably, barium chlorate, electrochemical oxidants, preferably, the iron (II/III) ferricyanide couple, the combination of t-butylhydroperoxide and pyridine, oxone, molecular oxygen in the presence of a suitable sacrificial co-reductant, preferably, an aldehyde, or the combination of N-methylmorpholine-N-oxide and m-chloroperbenzoic acid (MCPBA).

24. A process according to any one of Claims 12 to 23, in which the solvent is an organic solvent selected from dichloromethane, acetonitrile, N,N-dimethylformamide, chloroform, acetone, ethyl acetate, tetrahydrofuran, dimethylsulphoxide, toluene or ether, preferably, dichloromethane or acetonitrile.

25. A process for stereoselectively oxidising a tertiary amine or an organic sulphide, which process comprises contacting the tertiary amine or sulphide with a complex of the formula (II) in a suitable solvent optionally in the presence of an oxygen source.

26. A process for stereoselectively oxidising a racemic tertiary phosphine, which process comprises contacting the tertiary phosphine with a complex of the formula (II) in a suitable solvent.

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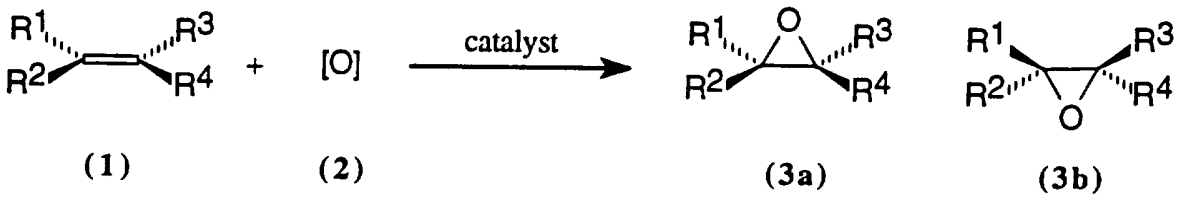
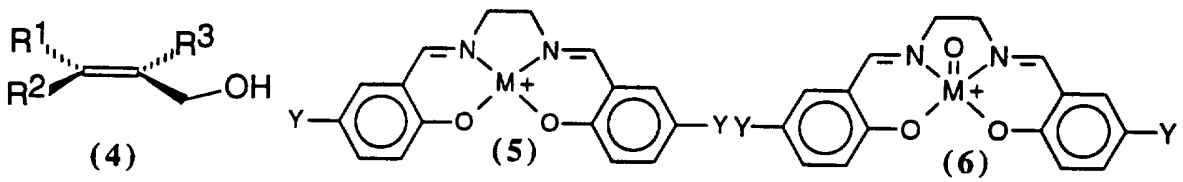


(1) (2) (3a) (3b)



(4) (5) (6)

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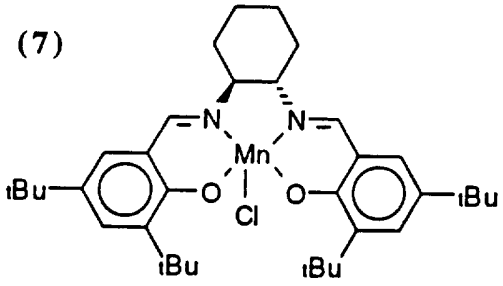

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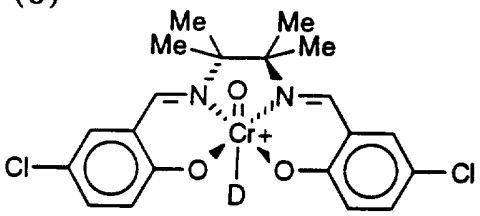
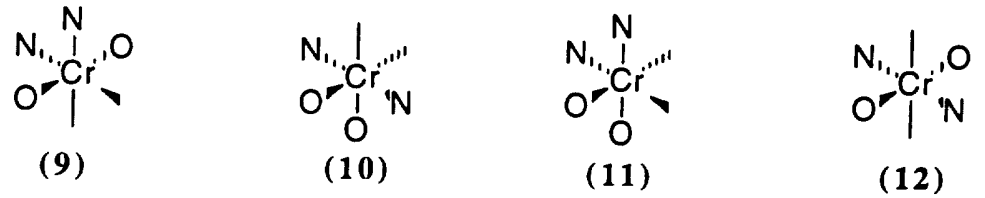




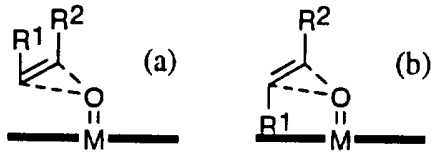
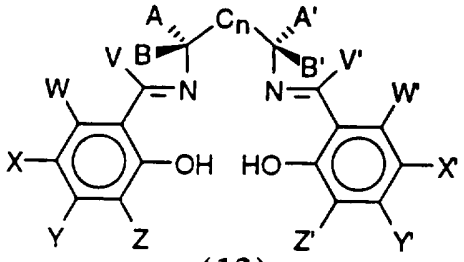


Figure. The side-on approach model for oxygen transfer showing the less-hindered approach for *cis*-alkenes (a) than for *trans*-alkenes (b)



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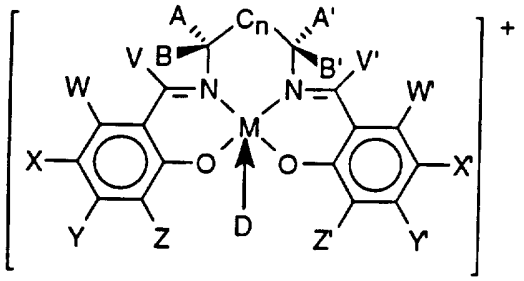

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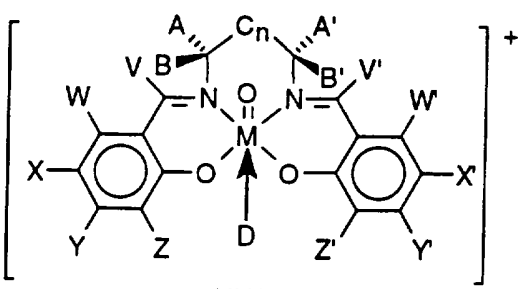

(II)

INTERNATIONAL SEARCH REPORT

Inter nonal Application No
Pc./IE 96/00005

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F11/00 C07F15/00 C07F7/00 C07F9/00 C07C251/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07F C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	TETRAHEDRON LETTERS, vol. 36, no. 42, 1995, pages 7739-7742, XP002001764 BOUSQUET, C. ET AL.: "CHROMIUM CATALYSED ASYMMETRIC ALKENE EPOXIDATION. gREATER SELECTIVITY FOR AN E-ALKENE VERSUS ITS Z-ISOMER" see the whole document ---	1-26
P,X	THE JOURNAL OF ORGANIC CHEMISTRY, vol. 61, no. 1, 1996, pages 389-390, XP002001765 LEIGHTON, J.L. ET AL.: "EFFICIENT SYNTHESIS OF (R)-4-((TRIMETHYLSILYL)OXY)-2-CYCLOPENTENO NE BY ENANTIOSELECTIVE CATALYTIC EPOXIDE RING OPENING" see the whole document ---	1-26
	-/--	

[X] Further documents are listed in the continuation of box C. [ ] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
26 April 1996	30.05.96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer Rinkel, L

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INTERNATIONAL SEARCH REPORT

Inter ional Application No
PC./IE 96/00005

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 117, no. 21, 1995, pages 5897-5898, XP002001766 MARTINEZ, L.E. ET AL.: "HIGHLY ENANTIOSELECTIVE RING OPENING OF EPOXIDES CATALYZED BY (SALEN)CR(III) COMPLEXES" see the whole document	1-26

Form PCT ISA 210 (continuation of second sheet) (July 1992)