

Peroxo-containing metal complexes having amine oxide, phosphine oxide, arsine oxide, pyridine N-oxide or pyridine ligands as epoxidation catalysts

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The present invention relates to novel catalysts in the form of peroxo-containing metal complexes having amine oxide, phosphine oxide, arsine oxide, pyridine N-oxide or pyridine ligands, which catalysts are suitable for the epoxidation of olefins using
10 aqueous hydrogen peroxide. Furthermore, the invention relates to a process for preparing these catalysts and a corresponding epoxidation process.

The epoxidation of olefins using aqueous hydrogen peroxide (H_2O_2)
15 is only successful in the presence of organic or inorganic activators or catalysts. The transfer of the oxygen atom from H_2O_2 to the substrate can occur in a stoichiometric or catalytic reaction. However, in the case of the use of hydrogen peroxide, the disadvantage of the necessity of an activator or catalyst is more
20 than compensated for by the ecological potential of hydrogen peroxide. In contrast to other oxidates, oxidation using H_2O_2 gives only water as by-product. A further advantage is the high active oxygen content of hydrogen peroxide which, at 47%, is far above that of all other customary oxidates (except for O_2).

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Hydrogen peroxide has hitherto been used industrially mainly as an unselective oxidizing agent, for example for the bleaching of paper, textiles and cellulose or in wastewater treatment. A significant proportion of the world production of H_2O_2 goes into the
30 manufacture of inorganic peroxo compounds for detergents. Only about 10% are used for the preparation of organic chemicals such as percarboxylic acids or N-oxides, which is attributed not least to the lack of suitable selective activators or catalysts.

35 One of the most common methods for the stoichiometric activation of hydrogen peroxide is the reaction with carboxylic acids to give percarboxylic acids which can epoxidize a variety of olefins. However, a problem here is the acid-sensitivity of many epoxides, particularly in aqueous medium, and also the liability
40 of the percarboxylic acids which leads to losses in yield.

Peroxo-containing transition metal complexes such as $MO(O_2)_2L_2$ ($M = Mo$ or W , $L = H_2O$, DMF (dimethylformamide) or HMPA (hexamethylphosphoramide)), which can easily be prepared from H_2O_2 and the
45 corresponding metal oxide MO_3 are also able to epoxidize olefins, which corresponds to a stoichiometric activation of H_2O_2 . Com-

pounds of this specific type have the advantage of being readily available.

For catalytic activation in the epoxidation of olefins using H_2O_2 , use is made, for example, of catalysts derived from the above-mentioned peroxy-containing transition metal complexes $MO(O_2)_2L_2$. Thus, US-A 3 953 362 (1) describes molybdenum complexes obtainable from MoO_3 , H_2O_2 and tertiary amines whose three organic radicals are each C_1 - C_{10} -alkyl or C_6 - C_{10} -aryl groups, or the N-oxides of such tertiary amines, as catalysts for epoxidations using H_2O_2 .

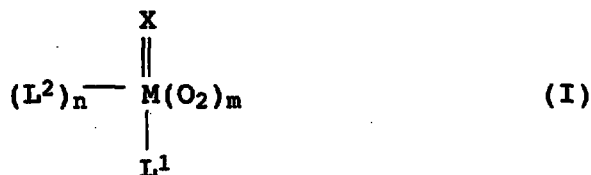
EP-A 215 415 (2) relates to an oxidation process for converting olefins into aldehydes or ketones by means of oxodiperoxo-molybdenum or tungsten complexes having phosphoramidate and, inter alia, also amine oxide or phosphine oxide ligands. Examples of amine oxides mentioned are pyridine N-oxide, 4-picoline N-oxide, trioctylamine N-oxide and phenylpropylpyridine N-oxide; trimethylphosphine oxide is mentioned as an example of a phosphine oxide.

EP-A 097 551 (3) discloses the use of vanadium, niobium or tantalum complexes of the formula $MO(O_2)_2L_2$ having phosphoramidate and also amine oxide or phosphine oxide ligands as epoxidation catalysts for olefins. Examples of amine oxides which are mentioned are trimethylamine N-oxide, N-methylmorpholine N-oxide, pyridine N-oxide, 2-, 3- or 4-picoline N-oxide, quinoline N-oxide and 2,2'-bipyridine N-oxide; examples of phosphine oxides which are mentioned are triphenylphosphine oxide, trimethylphosphine oxide, methyldiphenylphosphine oxide, diethylphenylphosphine oxide and trimorpholinophosphine oxide.

However, disadvantages of the complexes described in the documents (1) to (3) are the comparatively low activities, epoxide selectivities and olefin conversions in the case of olefin epoxidations using aqueous H_2O_2 .

It is an object of the present invention to provide metal complex catalysts, in particular for olefin epoxidations using aqueous H_2O_2 , which are simple and economical to prepare and also have a high effectiveness and efficiency.

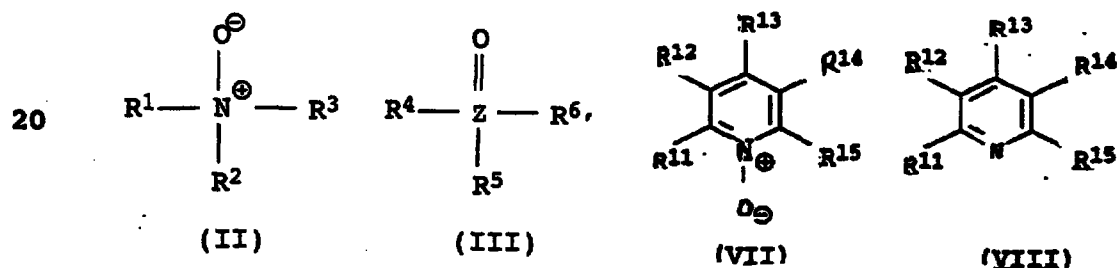
We have found that this object is achieved by catalysts of the general formula I



where

M is a metal from the 4th to 7th transition group of the Periodic Table of the Elements,

L¹ is an amine oxide ligand of the formula II, a phosphine oxide or arsine oxide ligand of the formula III, a pyridine N-oxide ligand of the formula VII or a pyridine ligand of the formula VIII



where

R¹ to R³ are identical or different C₁-C₃₀-alkyl, C₇-C₃₀-aralkyl or C₆-C₃₀-aryl radicals which can additionally contain ether oxygen atoms, carbonyl groups, hydroxyl groups, alkoxy groups, carboxyl groups, cyano groups, carboxylic ester groups, sulfo groups, phosphonic acid groups, nitro groups, halogen atoms and/or unsubstituted or C₁-C₄-alkyl-substituted amino groups as functional groups, where at least one of the radicals R¹ to R³ has to have at least 11 carbon atoms and the two other radicals can be linked to form a ring, and

R⁴ to R⁶ are identical or different C₄-C₃₀-alkyl, C₇-C₃₀-aralkyl or C₁₀-C₃₀-aryl radicals which can additionally contain ether oxygen atoms, carbonyl groups, hydroxyl groups, alkoxy groups, carboxyl groups, cyano groups, carboxylic ester groups, sulfo groups, phosphonic acid groups, nitro groups, halogen atoms and/or unsubstituted or C₁-C₄-alkyl-substituted amino groups as functional groups, and

5 R^{11} to R^{15} are, independently of one another, hydrogen or identical or different C_1 - C_{30} -alkyl radicals, C_7 - C_{30} -aralkyl radicals or C_6 - C_{30} -aryl radicals or C_7 - C_{30} -alkoxy groups, C_7 - C_{30} -aralkoxy groups, C_6 - C_{30} -arlyoxy groups or
 10 dihydrocarbylamino groups having identical or different C_1 - C_{30} -alkyl radicals, C_7 - C_{30} -aralkyl radicals and/or C_6 - C_{30} -aryl radicals as hydrocarbyl radicals which can additionally contain ethyloxygen atoms, carbonyl groups, hydroxyl groups, alkoxy groups, carboxyl groups, cyano
 15 groups, carboxylic ester groups, sulfo groups, phosphonic acid groups, nitro groups, halogen atoms and/or unsubstituted or C_1 - C_4 -alkyl-substituted amino groups as functional groups, where at least one of the radicals R^{11} or R^{15} has to be hydrogen, the sum of the carbon atoms in the radicals R^{11} to R^{15} has to be at least 8 and the radicals R^{11} to R^{15} can be linked in pairs to form rings,

20 L^2 is an auxiliary ligand selected from the group consisting of oxo, halides, pseudohalides, carboxylates, phenoxides, alkoxides, enolates, ketones, ethers, amines, amides, urea, urea derivatives and water or a further ligand L^1 or a free coordination site,

25 X is oxo oxygen or an unsubstituted or C_1 - C_4 -alkyl-substituted imido ligand,

Z is phosphorus or arsenic,

30 m is 1 or 2 and

n is 1, 2 or 3.

The catalysts I of the present invention differ from those known from the prior art in that they have longer-chain or bulkier radicals in the ligands L^1 than is the case in the amine oxide or
 35 phosphine oxide systems previously described for this purpose. In the case of the amine oxide ligands II, at least one of the three radicals R^1 to R^3 has to contain at least 11, preferably at least 12, in particular at least 14, carbon atoms. This radical is preferably a linear or branched alkyl group. In the case of the
 40 phosphine oxide or arsine oxide ligands III, the lower limit for the size of linear or branched alkyl radicals R^4 to R^6 is 4, preferably 6, in particular 8, carbon atoms, the lower limit for the size of aralkyl radicals R^4 to R^6 is 7, preferably 9, in particular
 45 12, carbon atoms, and the lower limit for the size of aryl radicals R^4 to R^6 is 10, preferably 12, in particular 14, carbon atoms. For the pyridine N-oxide and pyridine ligands VII or VIII,

the sum of the carbon atoms of the ring substituents has to be at least 8, preferably at least 9; in particular, one of the radicals R^{11} to R^{15} is a long-chain linear or branched alkyl radical having at least 8, especially at least 9, carbon atoms.

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Suitable transition metals for the catalyst complexes of the present invention are, in particular, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese and rhenium. Particular preference is given to 10 molybdenum and tungsten.

Typical examples of amine N-oxide ligands II are:

- dimethyl-n-undecylamine oxide,
- 15 dimethyl-n-dodecylamine oxide,
- dimethyl-n-tetradecylamine oxide,
- dimethyl-n-hexadecylamine oxide,
- dimethyl-n-octadecylamine oxide,
- dimethyl-n-eicosylamine oxide,
- 20 methyldi(n-dodecyl)amine oxide,
- methyldi(n-octadecyl)amine oxide,
- tri(n-dodecyl)amine oxide,
- tri(n-octadecyl)amine oxide,
- benzyldi(n-dodecyl)amine oxide,
- 25 diphenyl-n-octadecylamine oxide,
- N-undecylmorpholine oxide,
- N-dodecylpiperidine oxide,
- dimethyl(6-phenylhexyl)amine oxide,
- dimethylbisphenylamine oxide and
- 30 methyl-n-dodecyl(6-phenylhexyl)amine oxide.

Typical examples of phosphine oxide and arsine oxide ligands III are:

- 35 tri-n-butylphosphine oxide and tri-n-butylarsine oxide,
- tri-tert-butylphosphine oxide and tri-tert-butylarsine oxide,
- tri-n-hexylphosphine oxide and tri-n-hexylarsine oxide,
- tri-n-octylphosphine oxide and tri-n-octylarsine oxide,
- tri(2-ethylhexyl)phosphine oxide and tri(2-ethylhexyl)arsine
- 40 oxide,
- tri-n-dodecylphosphine oxide and tri-n-dodecylarsine oxide,
- tri-n-octadecylphosphine oxide and tri-n-octadecylarsine oxide,
- di-n-butyl-n-octylphosphine oxide and di-n-butyl-n-octylarsine oxide,
- 45 n-butyldi-n-octylphosphine oxide and n-butyldi-n-octylarsine oxide,
- tribenzylphosphine oxide and tribenzylarsine oxide,

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benzyldi-n-octylphosphine oxide and benzyldi-n-octylarsine oxide, naphthyldi-n-octylphosphine oxide and naphthyldi-n-octylarsine oxide and di-n-butyl-naphthylphosphine oxide and di-n-butyl-naphthylarsine oxide.

Typical examples of pyridine N-oxide and pyridine ligands VII and VIII are:

- 10 4-(1-octyl)pyridine and the corresponding N-oxide,
- 4-[1-(2-ethylhexyl)]pyridine and the corresponding N-oxide,
- 4-(1-nonyl)pyridine and the corresponding N-oxide,
- 4-(5-nonyl)pyridine and the corresponding N-oxide,
- 4-(1-decyl)pyridine and the corresponding N-oxide,
- 15 4-(1-dodecyl)pyridine and the corresponding N-oxide,
- 4-(n-octoxy)pyridine and the corresponding N-oxide,
- 4-(2-ethylhexoxy)pyridine and the corresponding N-oxide,
- 4-(n-nonoxo)pyridine and the corresponding N-oxide,
- 4-(di-n-octylamino)pyridine and the corresponding N-oxide and
- 20 4-(di-2-ethylhexylamino)pyridine and the corresponding N-oxide.

If the radicals R^1 to R^6 and R^{11} to R^{15} contain additional ether oxygen atoms, then such radicals are derived, in particular, from corresponding ethylene oxide, propylene oxide, butylene oxide or tetrahydrofuran reaction products.

Alkoxy substituents and carboxylic ester substituents on R^1 to R^6 and R^{11} to R^{15} preferably bear C_1 - C_4 -alkyl radicals, in particular methyl or ethyl. Halogen atoms on R^1 to R^6 and R^{11} to R^{15} are, in particular, chlorine or bromine. The number of the listed functional groups on R^1 to R^6 and R^{11} to R^{15} is, if any are present, usually from 1 to 3, in the case of ether oxygen atoms from 1 to 14, depending on chain length.

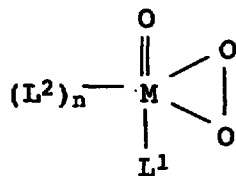
The auxiliary ligands L^2 are those which are customarily used and with which those skilled in the art are therefore familiar.

Preferred catalysts of the present invention are those of the general formula I [sic] or Ib

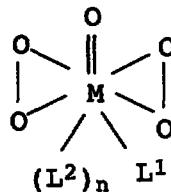
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(Ia)



(Ib)

where L^2 is water and the variables M, L^1 and n are as defined
10 above.

In the case of M = chromium, molybdenum or tungsten, the number n
of the ligands L^2 is preferably 1.

15 A preferred embodiment comprises catalysts of the present invention I or Ia or Ib in which L^1 is an amine oxide ligand II bearing C_1 - C_{20} alkyl groups as radicals R^1 to R^3 , where at least one of the radicals R^1 to R^3 has to be a C_{12} - C_{20} -alkyl group and the two
20 other radicals can be linked to form a saturated 5- or 6-membered ring which can contain further hetero atoms selected from the group consisting of oxygen and nitrogen.

A further preferred embodiment comprises catalysts of the present invention I or Ia or Ib in which L^1 is a phosphine oxide or arsine
25 oxide ligand III bearing C_4 - C_{20} -alkyl groups as radicals R^4 to R^6 .

The catalyst complexes I of the present invention are advantageously prepared from another complex of the metal M and hydrogen peroxide.

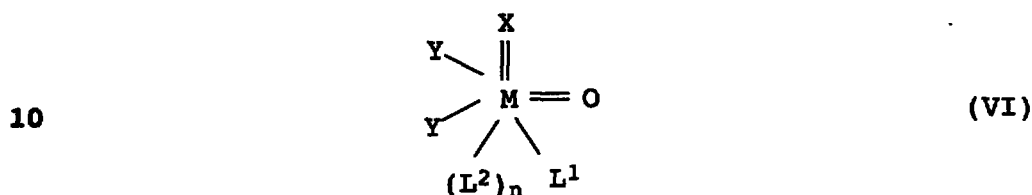
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The complexes I are usually obtained by replacing the ligands L in the abovementioned peroxo-containing transition metal complexes $\text{MX}(\text{O}_2)_m(\text{L}^2)_{n+1}$, where M, X, m and n are as defined above and L is, in particular, H_2O , DMF or HMPA, by amine oxides II or phosphine oxides III. These precursor complexes themselves can usually
35 be prepared very simply from inexpensive starting materials (metal oxide, H_2O_2 and ligand or ligand precursor).

Advantageously, the catalysts I are prepared in situ either by
40 dissolving metal oxides in an excess of aqueous H_2O_2 or from readily available precursors such as $\text{MO}_2\text{Cl}_2(\text{dme})$ (dme = dimethoxyethane), and activation by adding the necessary amount of amine oxide II, phosphine or arsine oxide III, pyridine N-oxide VII or pyridine VIII. In place of the amine N-oxides or phosphine
45 or arsine oxides, it is also possible to directly add the corresponding amines or phosphines or arsines, since they are oxidized in situ by H_2O_2 to give the desired amine N-oxides or phosphine

oxides. The catalysts can be generated in situ or can also be prepared separately, isolated and characterized.

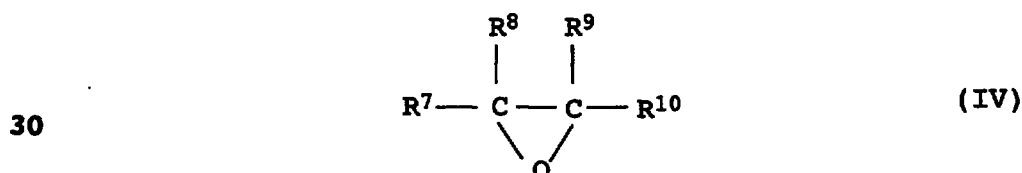
Other suitable precursors for the catalyst complexes I of the present invention are complexes of the formula VI



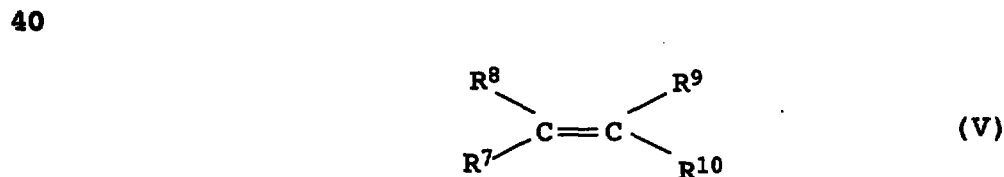
where Y is halide, eg. chloride, or pseudohalide, eg. thio-
 15 cyanate, and the variables M, X, L¹, L² and n are as defined above. The complexes VI are easily converted into the complexes I in the presence of H₂O₂.

The catalysts I of the present invention are very suitable for
 20 the catalytic activation of oxidation reactions, in particular for the epoxidation of olefins, especially using aqueous hydrogen peroxide as epoxidizing agent.

Accordingly, the present invention also provides a process for
 25 preparing epoxides of the general formula IV



where R⁷ to R¹⁰ are identical or different and are hydrogen or un-
 35 substituted or substituted alkyl, alkenyl, heteroalkyl, cycloalkyl, aryl or heteroaryl radicals, where the radicals R⁷ to R¹⁰ can also be linked to form rings, or substituents based on elements of the 4th to 7th main group of the Periodic Table of the Elements, from olefins of the general formula V



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using aqueous hydrogen peroxide, wherein the epoxidation of the olefins V is carried out in the presence of the catalysts I of the present invention.

- 5 For the olefins which can be used, there is no restriction in respect of the type and number of substituents. Typical examples of olefins which can be epoxidized by the process of the present invention are ethylene, propene, 1-butene, 2-butene, isobutene, 1,3-butadiene, 1-pentene, 2-pentene, isoprene, cyclopentene, 10 1-hexene, cyclohexene, C₈-C₂₄- α -monoolefins, styrene, indene, norbornene, cyclopentadiene, dicyclopentadiene and also alkene oligomers having reactive double bonds, eg. polypropene and polyisobutene.

- 15 The olefins V can also bear substituents based on elements of the 4th to 7th main group on the olefinic double bond. Examples are vinylsilicones, vinylamines, vinylphosphines, vinyl ethers, vinyl sulfides and halogenated alkenes such as vinyl chloride, vinylidene chloride or trichloroethylene.

20

To carry out the epoxidation according to the present invention, it is usual to initially charge the catalyst I and to add the necessary amount of aqueous H₂O₂ and olefin, if desired dissolved in a suitable inert organic solvent. The concentration range of

- 25 the aqueous H₂O₂ can be from 2 to 70% by weight, in particular from 5 to 50% by weight. Suitable inert organic solvents are, for example, chloroform, dichloromethane, ethers, carboxylic esters or aromatics. This usually gives a two-phase reaction mixture. When solvents miscible with water, for example methanol, acetone, 30 dimethoxyethane or dioxane, are used, the reaction can also be carried out homogeneously.

- The reaction conditions of the epoxidation according to the present invention are very mild, which is an advantage because of the 35 high reactivity of the epoxides formed. Typically, the reaction is carried out at from -20 to 160°C, in particular from 20 to 100°C, especially from 50 to 80°C, ie. in a temperature range which is likewise favorable for removing the heat of reaction. Increased pressure is necessary only in the case of highly volatile olefins such as propene or butene; the reaction is normally 40 carried out at atmospheric pressure.

- Use of the ligands II, III, VII or VIII having lipophilic substituents in the form of long-chain or bulky radicals generally 45 gives interphase-active catalysts so that the epoxidation can also advantageously be carried out in a two-phase system, ie. in two liquid phases which are not completely miscible with one

another. This procedure has the advantage that, on the one hand, lipophilic, water-insoluble olefins can also be oxidized and that, on the other hand, the epoxides formed remain in the organic phase and the formation of undesired by-products is thus suppressed. In addition, the separation of the product is made easier by the two-phase procedure.

In a preferred embodiment, propene is epoxidized to propylene oxide by the process of the present invention, in particular in a two-phase system.

In a further preferred embodiment, 1,3-butadiene is epoxidized to vinylloxirane by the process of the present invention, in particular in a two-phase system.

Using the highly active catalysts I of the present invention, epoxides are obtained with high selectivities and at high conversion rates from olefins by means of aqueous hydrogen peroxide in a simple and economical procedure under mild and gentle conditions.

Examples

Example 1:

Preparation of the catalyst stock solutions

a) Preparation of an aqueous stock solution of $[\text{Mo}(\text{O})(\text{O}_2)(\text{H}_2\text{O})_2]$

6.00 g (41.7 mmol) of $[\text{MoO}_3]$ were suspended with vigorous stirring in 24.0 g (212 mmol) of 30% strength by weight H_2O_2 solution. The colorless suspension was stirred for 4 hours at 40°C , forming a clear, light yellow solution which was stored at 4°C . $[\text{Mo}(\text{O})(\text{O}_2)(\text{H}_2\text{O})_2]$ content: 1.39 mmol/g.

b) Preparation of an aqueous stock solution of $[\text{W}(\text{O})(\text{O}_2)(\text{H}_2\text{O})_2]$

8.00 g (32.0 mmol) of $[\text{WO}_3 \cdot \text{H}_2\text{O}]$ were suspended with vigorous stirring in 24.0 g (212 mmol) of 30% strength by weight H_2O_2 solution. The yellow suspension was stirred for 6 hours at 40°C , forming a milky, turbid solution. After removal of the insoluble residue (25 mg) by centrifugation, the clear, colorless solution was stored at 4°C . $[\text{W}(\text{O})(\text{O}_2)(\text{H}_2\text{O})_2]$ content: 1.01 mmol/g.

Example 2:

Preparation of the catalysts $[M(O)(O_2)_2L^1]$ a) Preparation of $[Mo(O)(O_2)_2\{OP(n-Oct)_3\}]$

5 4 ml of tetrahydrofuran (THF) were first added to 1.86 g
(2.58 mmol) of Mo stock solution (Example 1a). While
stirring, 500 mg (1.29 mmol) of tri-n-octylphosphine oxide
[OP(n-Oct)₃] were added at 25°C. After vigorous stirring for
2 hours, the yellow solution was evaporated under reduced
10 pressure to about 3 ml, with a yellow oil separating out. The
reaction mixture was extracted with CH₂Cl₂ (3 times, 5 ml each
time). The combined extracts were completely evaporated under
reduced pressure. The light yellow, waxy residue was washed
with water (2 times, 2 ml each time) and dried for 6 hours at
15 25°C/10⁻⁵ mbar.

Yield: 675 mg (93%) of light yellow wax

DTA: 81°C (exothermic decomposition)

CHN analysis: C₂₄H₅₁PO₆Mo (562.6) calc. C 51.24 H 9.14

20 found C 51.68 H 9.45

a) [sic] Preparation of $[W(O)(O_2)_2\{OP(n-Oct)_3\}]$

25 12 ml of THF were first added to 6.00 g (6.06 mmol) of W
stock solution (Example 1b). While stirring, 1.50 g
(3.87 mmol) of [OP(n-Oct)₃] were added to the solution at
25°C. After vigorous stirring for 4 hours, the colorless
solution was evaporated under reduced pressure to about 5 ml,
with a colorless oil separating out. The reaction mixture was
30 extracted with CH₂Cl₂ (3 times, 10 ml each time). The combined
extracts were completely evaporated under reduced pressure.
The colorless, oily residue was washed with water (3 times,
15 ml each time) and dried for 6 hours at 25°C/10⁻⁵ mbar.

35 Yield: 2.40 g (95 %) of colorless oil

DTA: 98°C (exothermic decomposition)

CHN analysis: C₂₄H₅₁PO₆W (650.0) calc. C 44.35 H 7.91

found C 45.14 H 8.53

40 c) Preparation of $[Mo(O)(O_2)_2\{ONMe_2(n-C_{18}H_{37})\}]$

6.00 g (5.74 mmol) of dimethyl-n-octadecylamine oxide
[ONMe₂(n-C₁₈H₃₇)] (30% by weight in water) were added at 25°C
while stirring to 5.00 g (6.95 mmol) of Mo stock solution
45 (Example 1a), with a pale yellow precipitate being
spontaneously formed. After vigorous stirring for 2 hours,
the precipitate was filtered off, washed with water (3 times,

50 ml each time) and dried under reduced pressure for 6 hours at 25°C/10⁻⁵ mbar.

Yield: 2.00 g (71%) of pale yellow, amorphous solid
 5 DTA: 78°C (exothermic decomposition)
 CHN analysis: C₂₀H₄₃MoNO₆ (489.5) calc. C 49.07 H 8.85 N 2.86
 found C 49.07 H 8.88 N 2.82

10 d) Preparation of [Mo(O)(O₂)₂{ON(dodec)₃}]

1.20 g (2.23 mmol) of tri-n-dodecylamine oxide [ON(dodec)₃] dissolved in 5 ml of CH₂Cl₂ were added at 25°C while stirring to 2.00 g (2.87 mmol) of Mo stock solution (Example 1a). After vigorous stirring for 5 hours at 25°C, the organic
 15 phase was separated off, washed with water (3 times, 5 ml each time) and completely evaporated under reduced pressure. The pale yellow, amorphous residue was dried for 6 hours at 25°C/10⁻⁵ mbar.

20 Yield: 2.81 g (95%) of pale yellow, amorphous solid
 DTA: 75°C (exothermic decomposition)
 CHN analysis: C₃₆H₇₅MoNO₆ (713.9) calc. C 60.57 H 10.59 N 1.96
 found C 60.62 H 10.72 N 1.95

25 d) [sic] Preparation of [W(O)(O₂)₂{ON(dodec)₃}]

1.30 g (2.42 mmol) of [ON(dodec)₃] dissolved in 5 ml of CH₂CH₂ [sic] were added at 25°C while stirring to 3.00 g (3.03 mmol) of W stock solution (Example 1b). After vigorous stirring for
 30 5 hours at 25°C, the organic phase was separated off, washed with water (3 times, 5 ml each time) and completely evaporated under reduced pressure. The colorless, sticky residue was dried for 6 hours at 25°C/10⁻⁵ mbar.

35 Yield: 1.84 g (95%) of colorless, sticky wax
 DTA: 68°C (exothermic decomposition)
 CHN analysis: C₃₆H₇₅WNO₆ (801.8) calc. C 53.93 H 9.43 N 1.75
 found C 53.88 H 9.29 N 1.67

40 Example 3

Catalytic oxidation of cyclooctene and 1-octene by 30% strength by weight H₂O₂ using catalysts of the type MO(O₂)₂L¹(H₂O) generated in situ

13

36 mmol of 30% strength by weight H_2O_2 and 9 mmol of olefin were added at 25°C to an aliquot ($0.36 \text{ mmol} \triangleq 4 \text{ mol\%}$) of the catalyst stock solution described in Example 1. The reaction solution was subsequently admixed with 0.36 mmol of phosphine oxide or amine N-oxide ligand dissolved in 4 ml of CHCl_3 and stirred for 24 hours at 60°C . The olefin conversion and the epoxide selectivity were determined by gas chromatography.

The results of the experiments are summarized in Table 1.

10

The same results are also obtained in principle using the analogous, separately prepared catalysts described under Example 2 (in each case using 0.36 mmol dissolved in 4 ml of CHCl_3).

15 Examples 4 and 5

Epoxidation using $\text{L}^1 = \text{tri}(\text{n-dodecyl})\text{arsine oxide}$

A glass autoclave was charged with 1-octene (500 mg, 4.45 mmol), MO_3 (0.17 mmol, 4.0 mol% based on 1-octene, as a 0.5 M solution in 30% strength by weight H_2O_2) and tri-(n-dodecyl)arsine oxide (0.17 mmol dissolved in 3 ml of chloroform). H_2O_2 (17.8 mmol, as 30% strength by weight aqueous solution) was then added and the mixture was stirred at 60°C . Octene epoxide was the only product attempted. The octene oxide yields at various reaction times are summarized in Table 2.

Table 2

30

Yield A of octene oxide (%)				
Example	MO_3	A after t = 4 h	A after t = 24 h	A after t = 48 h
4	MoO_3	26	71	90
5	WO_3	37	42	40

35

Examples 6 and 7

Epoxidation using $\text{L}^1 = 4\text{-(5-nonyl)pyridine}$

40

A glass autoclave was charged with 1-octene (500 mg, 4.45 mmol), MO_3 (0.17 mmol, 4.0 mol% based on 1-octene, as a 0.5 M solution in 30% strength by weight H_2O_2) and 4-(5-nonyl)pyridine (0.17 mmol dissolved in 3 ml of chloroform). H_2O_2 (17.8 mmol, as 30% strength by weight aqueous solution) was then added and the mixture was stirred at 60°C . Octene epoxide was the only product attempted.

45

The octene oxide yields at various reaction times are summarized in Table 3.

Table 3

5

Yield A of octene oxide (%)			
Example	MO ₃	A after t = 4 h	A after t = 24 h
6	MoO ₃	7	23
7	WO ₃	7	11

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Examples 8 and 9

Epoxidation using L¹ = 4-(5-nonyl)pyridine N-oxide

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A glass autoclave was charged with 1-octene (500 mg, 4.45 mmol), MO₃ (0.17 mmol, 4.0 mol% based on 1-octene, as a 0.5 M solution in 30% strength by weight H₂O₂) and 4-(5-nonyl)pyridine N-oxide (0.17 mmol dissolved in 3 ml of chloroform). H₂O₂ (17.8 mmol, as 30% strength by weight aqueous solution) was then added and the mixture was stirred at 60°C. Octene epoxide was the only product attempted. The octene oxide yields at various reaction times are summarized in Table 4.

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Table 4

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Yield A of octene oxide (%)			
Example	MO ₃	A after t = 4 h	A after t = 24 h
8	MoO ₃	7	12
9	WO ₃	3	6

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Examples 10 and 11

35 Epoxidation using L¹ = 4-(dioctylamino)pyridine

A glass autoclave was charged with 1-octene (500 mg, 4.45 mmol), MO₃ (0.17 mmol, 4.0 mol% based on 1-octene, as a 0.5 M solution in 30% strength by weight H₂O₂) and 4-(dioctylamino)pyridine (0.17 mmol dissolved in 3 ml of chloroform). H₂O₂ (17.8 mmol, as 30% strength by weight aqueous solution) was then added and the mixture was stirred at 60°C. Octene epoxide was the only product attempted. The octene oxide yields at various reaction times are summarized in Table 5.

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Table 5

Yield A of octene oxide (%)					
Example	MO ₃	A after t = 4 h	A after t = 24 h	A after t = 48 h	
5	10	MoO ₃	24	32	37
	11	WO ₃	11	16	16

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Table 1

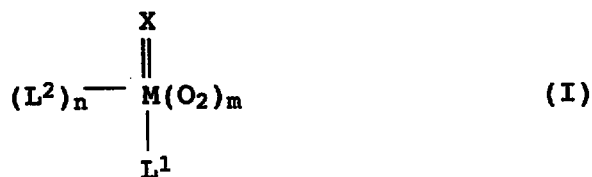
Olefin	Catalyst	Ligand L ¹	Olefin conversion (mol%)	Epoxide selectivity (mol%)	Remarks
Cyclooctene	MoO(O ₂) ₂ L ¹ (H ₂ O)	H ₂ O	2		for comparison
		OP(NMe ₂) ₃	30		for comparison
		OP(t-Bu) ₃	85	>98	
		OP(n-C ₈ H ₁₇) ₃	100	>98	after 20 h
		ONMe ₂ (n-C ₁₈ H ₃₇)	100	>98	after 3 h
		ON(n-C ₁₂ H ₂₅) ₃	100	95	after 2 h
	WO(O ₂) ₂ L ¹ (H ₂ O)	OP(n-C ₈ H ₁₇) ₃	36	>98	
		ONMe ₂ (n-C ₁₈ H ₃₇)	98	>98	
1-Octene	MoO(O ₂) ₂ L ¹ (H ₂ O)	OP(n-C ₈ H ₁₇) ₃	46	97	15 equivalents of L ¹
		ONMe ₂ (n-C ₁₈ H ₃₇)	63	>98	
		ON(n-C ₁₂ H ₂₅) ₃	91	>98	



We claim:

1. A catalyst of the general formula I

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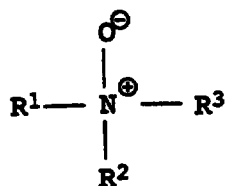
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where

- 15 M is a metal from the 4th to 7th transition group of the Periodic Table of the Elements,

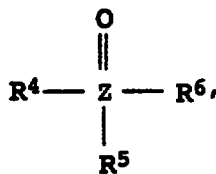
- 20 L¹ is an amine oxide ligand of the formula II, a phosphine oxide or arsine oxide ligand of the formula III, a pyridine N-oxide ligand of the formula VII or a pyridine ligand of the formula VIII

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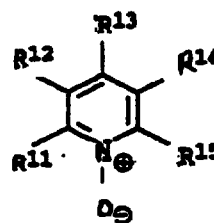


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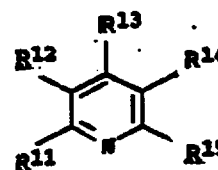
(II)



(III)



(VII)



(VIII)

where

- 35 R¹ to R³ are identical or different C₁-C₃₀-alkyl, C₇-C₃₀-aralkyl or C₆-C₃₀-aryl radicals which can additionally contain ether oxygen atoms, carbonyl groups, hydroxyl groups, alkoxy groups, carboxyl groups, cyano groups, carboxylic ester groups, sulfo groups, phosphonic acid groups, nitro groups, halogen atoms and/or unsubstituted or C₁-C₄-alkyl-substituted amino groups as functional groups, where at least one of the radicals R¹ to R³ has to have at least 11 carbon atoms and the two other radicals can be linked to form a ring, and

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- R⁴ to R⁶ are identical or different C₄-C₃₀-alkyl, C₇-C₃₀-aralkyl or C₁₀-C₃₀-aryl radicals which can additionally contain ether oxygen atoms, carbonyl groups,



5 hydroxyl groups, alkoxy groups, carboxyl groups, cyano groups, carboxylic ester groups, sulfo groups, phosphonic acid groups, nitro groups, halogen atoms and/or unsubstituted or C₁-C₄-alkyl-substituted amino groups as functional groups, and

10 R¹¹ to R¹⁵ are, independently of one another, hydrogen or identical or different C₁-C₃₀-alkyl radicals, C₇-C₃₀-aralkyl radicals or C₆-C₃₀-aryl radicals or C₁-C₃₀-alkoxy groups, C₇-C₃₀-aralkoxy groups, C₆-C₃₀-aralkoxy groups or dihydrocarbylamino groups having identical or different C₁-C₃₀-alkyl radicals, C₇-C₃₀-aralkyl radicals and/or C₆-C₃₀-aryl radicals as hydrocarbyl radicals which can additionally contain ethyl oxygen atoms, carbonyl groups, 15 hydroxyl groups, alkoxy groups, carboxyl groups, cyano groups, carboxylic ester groups, sulfo groups, phosphonic acid groups, nitro groups, halogen atoms and/or unsubstituted or C₁-C₄-alkyl-substituted amino groups as functional groups, where at least one of the radicals R¹¹ or 20 R¹⁵ has to be hydrogen, the sum of the carbon atoms in the radicals R¹¹ to R¹⁵ has to be at least 8 and the radicals R¹¹ to R¹⁵ can be linked in pairs to form rings.

25 L² is an auxiliary ligand selected from the group consisting of oxo, halides, pseudohalides, carboxylates, phenoxides, alkoxides, enolates, ketones, ethers, amines, amides, urea, urea derivatives and water or a further ligand L¹ or a free coordination site,

30 X is oxo oxygen or an unsubstituted or C₁-C₄-alkyl-substituted imido ligand,

Z is phosphorus or arsenic,

35 m is 1 or 2 and

n is 1, 2 or 3.

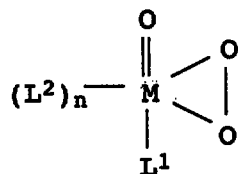
40 2. A catalyst I as claimed in claim 1 in which M is molybdenum or tungsten.

3. A catalyst of the general formula Ia or Ib as claimed in claim 1 or 2

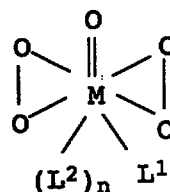
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(Ia)



(Ib)

where L^2 is water and the variables M, L^1 and n are as defined above.

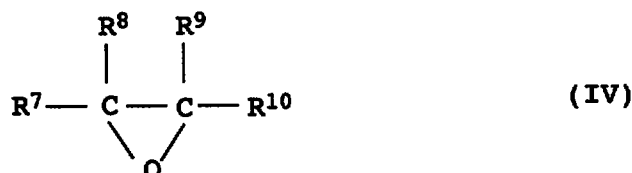
4. A catalyst I as claimed in any of claims 1 to 3, where L^1 is an amine oxide ligand II bearing C_1 - C_{20} -alkyl groups as radicals R^1 to R^3 , where at least one of the radicals R^1 to R^3 has to be a C_{12} - C_{20} -alkyl group and the two other radicals can be linked to form a saturated 5- or 6-membered ring which can contain further hetero atoms selected from the group consisting of oxygen and nitrogen.

5. A catalyst I as claimed in any of claims 1 to 3 in which L^1 is a phosphine oxide or arsine oxide ligand III bearing C_4 - C_{20} -alkyl groups as radicals R^4 to R^6 .

6. A process for preparing a catalyst I as claimed in any of claims 1 to 5, which comprises preparing the catalytically active complex of the general formula I from another complex of the metal M and hydrogen peroxide.

7. Use of a catalyst I as claimed in any of claims 1 to 5 for the epoxidation of olefins.

8. A process for preparing epoxides of the general formula IV



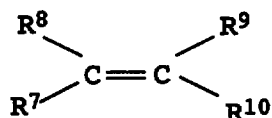
where R^7 to R^{10} are identical or different and are hydrogen or unsubstituted or substituted alkyl, alkenyl, heteroalkyl, cycloalkyl, aryl or heteroaryl radicals, where the radicals R^7 to R^{10} can also be linked to form rings, or substituents based on elements of the 4th to 7th main group of the



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Periodic Table of the Elements, from olefins of the general formula V

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(V)

10 using aqueous hydrogen peroxide, wherein the epoxidation of the olefins V is carried out in the presence of a catalyst I as claimed in any of claims 1 to 5.

9. A process for preparing epoxides IV as claimed in claim 8, wherein the epoxidation of the olefins V is carried out using
15 aqueous hydrogen peroxide in two liquid phases which are not completely miscible with one another.

10. A process for preparing propylene oxide from propene as claimed in claim 8 or 9.

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11. A process for preparing vinyloxirane from 1,3-butadiene as claimed in claim 8 or 9.

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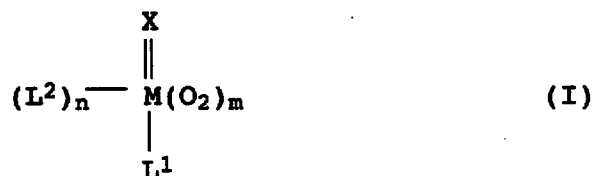
Peroxo-containing metal complexes having amine oxide or phosphine oxide, arsine oxide, pyridine N-oxide or pyridine ligands as epoxidation catalysts

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Abstract

Olefins can be epoxidized using catalysts I

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where

M is a metal of the 4th to 7th transition group of the Periodic Table of the Elements,

L¹ is an amine oxide, phosphine oxide, arsine oxide, pyridine N-oxide or pyridine ligand of the formula II, III, VII or VIII,

25 L² is a customary auxiliary ligand or a further ligand L¹ or a free coordination site,

X is oxo oxygen or an imido ligand,

30 m is 1 or 2, and

n is 1, 2 or 3.

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