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(54) **Title:** ALKOXYLATION PROCESSES AND CATALYSTS THEREFOR

(57) **Abstract:** A process of contacting an alkylene oxide with 2-methoxy-1-propanol (PM1) in the presence of an oligomeric Schiff base metal complex catalyst is disclosed. Further, a process involving contacting an alkylene oxide with an alkyl alcohol using an oligomeric Schiff base metal complex as a catalyst is also disclosed. Additionally, novel compositions which can be used as catalysts in processes involving the contacting of an alkyl alcohol with an alkylene oxide are also disclosed.

ALKOXYLATION PROCESSES AND CATALYSTS THEREFOR

FIELD OF THE INVENTION

5 This invention relates to novel achiral tetradentate Schiff base compositions. This invention further relates to contacting an alkylene oxide with an alcohol in the presence of a Schiff base catalyst. This invention also relates to the propoxylation of 2-methoxy-1-propanol and 1-methoxy-2-propanol.

BACKGROUND OF THE INVENTION

10 The conversion of propylene oxide using base-catalyzed conditions to produce a mixture of monopropylene glycol methyl ethers (PM), dipropylene glycol methyl ether (DPM), tripropylene glycol methyl ethers (TPM) and heavier molecular weight polypropylene glycol methyl ethers is the current industry standard technology for commercial PM glycol ethers. The mixture of the mono-, di-, tri- and heavier product
15 categories can be controlled by adjusting the methanol-to-propylene oxide feed mole ratio, recycling products back to the reactor for further propylene oxide addition, and adjusting the reactor temperature among other means.

 The monopropylene glycol methyl ether family includes two isomers, 1-methoxy-2-propanol (PM2) and 2-methoxy-1-propanol (PM1). Using industry
20 standard base-catalyzed technology, the PM2/PM1 ratio is ~20/1. Reaction technology giving a selectivity >20/1 is preferable since PM1 is classified as a teratogen and can be present as a component in the commercial PM2 product at <0.5 wt%. In order to achieve this specification, costly distillation is used to separate these similar boiling materials (PM2 bp = 118-119 °C; PM1 bp = 130 °C).

Catalytically propoxylating PM1 to propoxylated adducts with very little reaction of PM2 can provide a mixture that is easily separated by simple distillation yet retains the highly desired PM2 product. Moreover, a catalyst system that selectively propoxylates methanol to monopropylene glycol methyl ether and at the same time further catalyzes the selective propoxylation of the undesired PM1 product to DPM can result in a highly selective process for producing PM2.

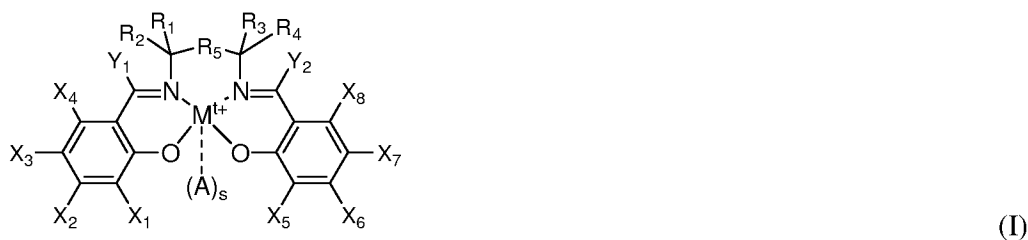
Although the primary hydroxyl group of PM1 is more acidic than the secondary hydroxyl group of PM2, significant propoxylation of both PM1 and PM2 occurs under base-catalyzed (e.g., NaOH or KOH) conditions.

Therefore, novel compositions which can be used as catalysts for the regioselective methanolysis of propylene oxide would also be desirable.

SUMMARY OF THE INVENTION

In accordance with an embodiment of the invention, there is provided a composition comprising, consisting of, or consisting essentially of:

an achiral tetradentate Schiff-base metal complex, wherein a monomer of said Schiff-base metal complex is defined by the formula



wherein R_1 , R_2 , R_3 , R_4 , Y_1 , Y_2 , X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , and X_8 comprise, independently of one another, substituents selected from the group consisting of hydrogen, halogen, alkyl, alkenyl, alkynyl, hydrocarbyl, hydroxyl, amino, nitro, alkoxy,

amide, phosphoryl, phosphonate, phosphine, carbonyl, carboxyl, silyl, ether, thioether, sulfonyl, selenoether, ketone, aldehyde, and ester;

or wherein two or more of R_1 , R_2 , R_3 , R_4 , Y_1 , Y_2 , X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , and X_8 together form a ring selected from the group consisting of a carbocyclic ring and a

5 heterocyclic ring, said ring having from 4 to 10 atoms in the ring;

wherein R_5 group is selected from the group comprising a carbon-carbon bond, a methylene group, an ethylene group, an amine group, an oxygen atom, and a sulfur atom;

wherein one or more of R_1 , R_2 , R_3 , R_4 , Y_1 , Y_2 , X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , and X_8 are
10 capable of providing a complementary interaction to form a component selected from the group consisting of an oligomer, a polymer, and a copolymer;

wherein M^{t+} is a Group 2-15 metal capable of complexing with a ligand to affect catalysis, wherein t is an integer between 2 and 4;

wherein the group A is selected from the group consisting of neutral groups, bound
15 anionic groups, unbound anionic groups, and combinations thereof, wherein s is the number of A groups associated to the metal and is an integer between 0 and 2; and wherein said composition is selected from the group consisting of oligomer, polymer, and copolymer.

In accordance with an embodiment of the invention, a process is provided, the
20 process comprising, consisting of, or consisting essentially of contacting an alkylene oxide with 2-methoxy-1-propanol (PM1) in the presence of a catalyst comprising a tetradentate Schiff-base metal complex in a reaction zone under reaction conditions to produce a reaction product, said reaction product comprising alkoxyated PM1 with less than 10 alkylene oxide equivalents.

In accordance with another embodiment of the invention, there is provided a process comprising, consisting of, or consisting essentially of contacting an alkylene oxide with an alcohol in the presence of a catalyst comprising a tetradentate Schiff base metal complex in a reaction zone under reaction conditions to produce a reaction
5 product comprising a mixture of at least two components selected from the group consisting of mono-alkoxylated alcohol, di-alkoxylated alcohol, tri-alkoxylated alcohol, and heavy molecular weight alkoxylated alcohols containing not more than 10 alkylene oxide equivalents.

10 DETAILED DESCRIPTION OF THE INVENTION

“Chiral” describes an object that is non-superimposable on its mirror image.

“Achiral” describes an object that is superimposable on its mirror image.

“Stereoisomers” are isomeric molecules that have the same molecular formula and sequence of bonded atoms(constitution), but which differ in the three dimensional
15 orientations of their atoms in space.

“Diastereomers” are stereoisomers not related through a reflection operation. They are not mirror images of each other.

“Tetradentate” is a chelating agent which has four groups capable of attachment to a metal ion.

20 A “Schiff base” is a functional group resulting from the condensation of aldehydes or ketones with primary amines.

A “Lewis acid” is a molecule that is an electron-pair acceptor.

In accordance with an embodiment of the invention, there is provided a composition comprising, consisting of, or consisting essentially of an oligomerized,

polymerized or copolymerized achiral tetradentate Schiff-base metal complex. The monomer of the metal complex is defined by formula (I).

$R_1, R_2, R_3, R_4, Y_1, Y_2, X_1, X_2, X_3, X_4, X_5, X_6, X_7,$ and X_8 comprise, independently of one another, substituents selected from the group consisting of
5 hydrogen, halogen, alkyl, alkenyl, alkynyl, hydrocarbyl, hydroxyl, alkoxy, nitro, amide, phosphoryl, phosphonate, phosphine, carbonyl, carboxyl, silyl, ether, thioether, sulfonyl, selenoether, ketone, aldehyde, and ester.

In an embodiment, two or more of $R_1, R_2, R_3, R_4, Y_1, Y_2, X_1, X_2, X_3, X_4, X_5, X_6,$
 $X_7,$ and X_8 can together form a ring selected from the group consisting of a carbocyclic
10 ring and a heterocyclic ring, the ring having from 4 to 10 atoms in the ring.

In an embodiment, R_5 is selected from the group comprising a carbon-carbon bond, a methylene group, an ethylene group, an amine, an oxygen atom, and a sulfur atom;

In an embodiment, one or more of $R_1, R_2, R_3, R_4, Y_1, Y_2, X_1, X_2, X_3, X_4, X_5, X_6,$
15 $X_7,$ and X_8 are capable of providing a complementary interaction to form a component selected from the group consisting of oligomer, polymer, and copolymer;

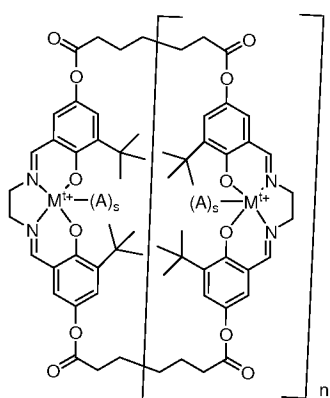
A complementary interaction can include: carbon-carbon coupling, condensation, etherification, amide formation, esterification, ring opening polymerizations, olefin metathesis, olefin polymerization such as cationic
20 polymerization, anionic polymerization, radical polymerization, group transfer polymerization, heterogeneous Ziegler-Natta polymerization, and homogeneous Ziegler-Natta polymerization.

M^{t+} is a Group 2-15 metal capable of complexing with a ligand to affect catalysis, wherein t is an integer between 2 and 4;

A is selected from the group consisting of neutral groups, bound anionic groups, unbound anionic groups, and combinations thereof, wherein s is the number of A groups associated to the metal and is an integer between 0 and 2.

The composition can be present as an oligomer, a polymer, or a co-polymer.

5 In an embodiment of the invention the catalyst is as described in formula II below:



(II)

In an embodiment of the invention, M is cobalt and A is selected from the group consisting of carboxylate, sulfonate, halide, alkoxide, hexafluorophosphate, tetrafluoroborate, hexafluoroantimonate and bis(trialkylsilyl)amide. In an embodiment

10 of the invention, A is 3-nitrobenzenesulfonate and $s = 1$.

In an embodiment of the invention, the composition is present as an oligomer bound to a support wherein the oligomer is 1-20 repeat units of the above defined monomer.

Examples of supports that can be used include, but are not limited to, an organic

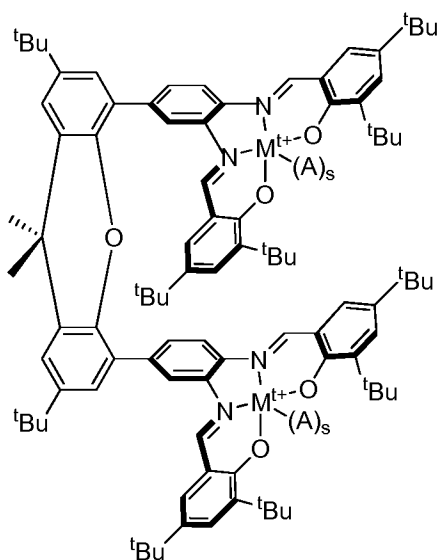
15 polymer, an ion-exchange resin, an inorganic support, a metal organic framework, and carbon. The catalyst can be incorporated into or onto the support by any suitable method known to those skilled in the art including, but not limited to, covalent bonding, ionic bonding, hydrogen bonding, metal complexing, encapsulating, and intercalating.

The following documents provide examples of such supporting techniques and their entire contents are herein disclosed by reference: Baleizo, *et. al. Chemical Reviews* **2006**, 106(9), 3987-4043; Orejón, *et al., Industrial and Engineering Chemical Research* **2008**, 47(21), 8032-8036; Yang, *et al., Journal of Catalysis* **2007**, 248, 204-212; Kim, *et. al., Catalysis Today* **2000**, 63, 537-547.

In an embodiment of the invention, the catalyst can be incorporated into polymeric structures by utilizing any of several different methods. The following documents provide examples of such techniques and their entire contents are herein disclosed by reference. Hu, *et al., Journal of Applied Polymer Science* **2006**, 101, 2431-2436 Song, *et al., Tetrahedron Letters* **2003**, 44, 7081-7085, Kwon, *et al., Catalysis Today* **2003**, 87, 145-151, Gill, *et al., Chemistry – A European Journal* **2008**, 14, 7306-7313, Zheng, *et al., Chemistry – A European Journal* **2006**, 12, 576-583, Zheng, *et al., Advanced Synthesis and Catalysis* **2008**, 350, 255-261.

In an embodiment of the invention, more than one of the composition is present and is joined by a polyfunctional A, wherein A is selected from the group consisting of a polycarboxylate, polysulfonate, and a mixture thereof.

In an embodiment of the invention more than one achiral monomeric composition can be linked with one or more achiral monomers to yield greater catalytic activity than the single monomer. One embodiment of the composition is shown in Formula III below wherein the M^{t+} group(s) independently of one another is(are) a Group 2-15 metal capable of complexing with the ligand to affect catalysis, wherein $t = 2, 3, \text{ or } 4$; and wherein the group(s) A independently of one another is(are) selected from the group consisting of neutral groups, bound and unbound anionic groups and combinations thereof, where s is the number of A groups associated to the metal and is 0, 1, or 2.



(III)

5 In an embodiment of the invention, there is provided a process comprising, consisting of, or consisting essentially of contacting an alkylene oxide with 2-methoxy-1-propanol (PM1) in the presence of a catalyst comprising a tetradentate Schiff-base metal complex in a reaction zone under reaction conditions to produce a reaction product comprising alkoxyated PM1 with less than 10 alkylene oxide equivalents.

10 The catalyst is defined as a Schiff-base metal complex, wherein a monomer of the metal complex is defined by Formula (I). The catalyst can be any catalyst described in the previous embodiments, or any other monomeric catalyst defined by Formula (I).

The catalyst can be either homogenous or heterogeneous. The catalyst can be present as a monomer, oligomer, polymer or copolymer as described above. The
15 catalyst can also be bound to a support, as described above.

In an embodiment, a cocatalyst can optionally be used. Generally, the cocatalyst is a Lewis acid. Examples of Lewis acids that can be used include, but are not limited to metal triflate, metal tosylate, tris-perfluorinated aryl borate, metal halides, and combinations thereof. An example of a metal triflate that can be used is aluminum triflate. When a cocatalyst is used, the mole ratio of the catalyst monomeric unit to the co-catalyst is generally in the range of from about 1:1 to about 20:1.

The alkylene oxide is generally selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, pentylene oxide, hexylene oxide, epihalohydrin and combinations thereof. In an embodiment, the alkylene oxide is propylene oxide.

The alkylene oxide and PM1 are generally present in a mole ratio of from about 0.01/1 to about 100/1. In an embodiment the reaction conditions includes a mole ratio of from 0.25/1 to about 10/1

The reaction conditions in the reaction zone generally include a temperature in the range of from about -10°C to about 200°C. In an embodiment, the reaction conditions include a temperature in the range of from 0°C to 60°C.

The reaction zone can be of the type comprising of a fixed bed, a fluidized bed, a continuous stirred tank reactor (CSTR), batch, semi-batch, continuous types or combinations thereof. Said reaction zone can be operated for example isothermally, adiabatically, or a combination thereof.

A reaction product is produced which comprises alkoxyated PM1 with less than 10 alkylene oxide equivalents. The reaction product generally comprises unreacted 2-methoxy-1-propanol (PM1), unreacted alkylene oxide, mono-alkoxylates of PM1, di-alkoxylates of PM1, and heavy molecular weight alkoxyates of PM1, which are alkoxyates with 3 to 10 alkylene oxide equivalents. The mono-alkoxylates of PM1 are

typically present in the reaction product in an amount in the range of from about 0.1 weight percent to about 100 weight percent, based on the total weight of the reaction product. The di-alkoxylates of PM1 are typically present in the reaction product in an amount in the range of from about 0 weight percent to about 10 weight percent, based
5 on the total weight of the reaction product.

In an embodiment of the invention, there is disclosed a process comprising, consisting of or consisting essentially of contacting an alkylene oxide with an alcohol in the presence of a catalyst comprising a tetradentate Schiff-base metal complex in a reaction zone under reaction conditions to produce a reaction product comprising a
10 mixture of at least two components selected from the group consisting of a mono-alkoxylated alcohol, a di-alkoxylated alcohol, a tri-alkoxylated alcohol, and heavy molecular weight alkoxylated alcohols containing not more than 10 alkylene oxide equivalents.

In an embodiment, the alkoxylated alcohol products from above can optionally
15 be contacted with additional alkylene oxide in the presence of the catalyst in a reaction zone under reaction conditions to produce a second reaction product with a mono-alkoxylated alcohol/di-alkoxylated alcohol product ratio less than in the first reaction product.

The catalyst is defined as an achiral tetradentate Schiff-base metal complex,
20 wherein a monomer of said metal complex is defined by Formula (I). The catalyst can be any composition described in the above embodiments, or any other suitable composition defined by Formula (I) including monomeric forms.

The catalyst can be either homogenous or heterogeneous. The catalyst can be present as a monomer, an oligomer, a polymer or mixture thereof. The catalyst can also be bound to a support, as described above.

In an embodiment, a cocatalyst can also be used. The cocatalyst is a Lewis acid.

5 Examples of Lewis acids that can be used include, but are not limited to metal triflate, metal tosylate, tris-perfluorinated aryl borate, metal halides, alkyl metals and combinations thereof. When a cocatalyst is used, the ratio of the catalyst monomer unit to the cocatalyst is generally in the range of from about 1:1 to about 20:1. In an embodiment, the Lewis acid is aluminum triflate.

10 Generally, alkylene oxide is selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, pentylene oxide, hexylene oxide, epihalohydrin and combinations thereof. In an embodiment, the alkylene oxide is propylene oxide.

Generally, the alcohol is selected from the group consisting of methanol, ethanol, propanol, butanol, pentanol, hexanol, 2-ethylhexanol, propylene glycol, ethylene glycol, glycerol, erythritol, pentaerythritol, trimethylolpropane, sorbitol, 2-
15 methoxy-1-propanol, 1-methoxy-2-propanol, glycol ether, phenol and combinations thereof. In an embodiment, the alcohol is methanol.

In this embodiment, alkylene oxide and the alcohol are typically present in a ratio of from about 0.1/1 to about 10/1.

20 The reaction conditions in the reaction zone generally include a temperature in the range of from about -10 °C to about 200 °C. In an embodiment, reaction conditions can include a temperature in the range of from 0 °C to 60 °C.

The reaction zone can be of the type comprising of fixed bed, fluidized bed, continuous stirred tank reactor (CSTR), batch reactor, semi-batch reactor, continuous

reactor or combination of thereof, said reaction zone can be operated for example isothermally, adiabatically, or a combination thereof.

The reaction zone of the optional secondary reaction step in this embodiment can be in either the same or different vessels as the reaction zone of the first reaction
5 step.

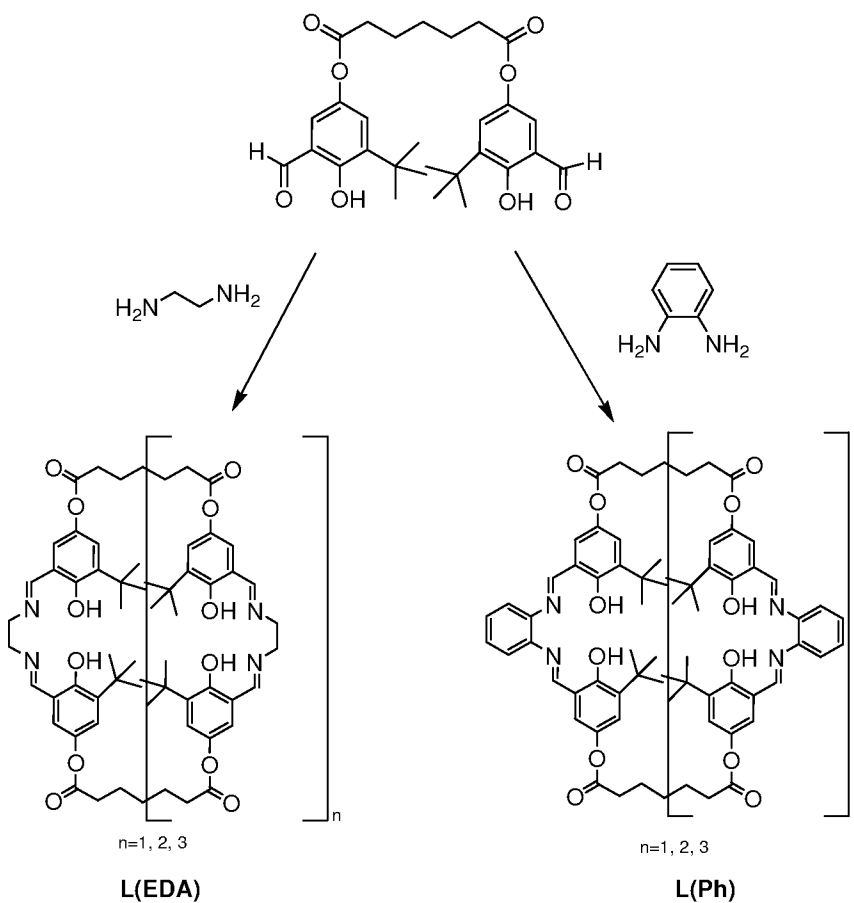
A reaction product is produced which comprises alkoxyated alcohols with less than 10 alkylene oxide equivalents. The reaction product of the first and second reaction zones comprises at least two of monoalkoxyated alcohols (MA), dialkoxyated alcohols (DA), trialkoxyated alcohols (TA) and heavy molecular weight alkoxyated
10 alcohols containing less than 10 alkylene oxide equivalents per molecule. The MA is present in said reaction product in an amount in the range of from about 10 weight percent to about 99.99 weight percent, based on the total weight of said reaction product. The DA is present in said reaction product in an amount in the range of from about 0.01 weight percent to about 80 weight percent, based on the total weight of said
15 reaction product. The TP is present in said reaction product in an amount in the range of from about 0 weight percent to about 1 weight percent, based on the total weight of said reaction product.

The used catalyst can be isolated or concentrated in a process stream and recycled back to the reactor. Prior to recycling the catalyst may optionally be
20 reactivated for example by treatment with acid, a source of oxygen, a metal capable of electron transfer, or a combination thereof.

Examples

The following examples are intended to be illustrative of the present invention and to teach one of ordinary skill in the art to make and use the invention. These examples are not intended to limit the invention in any way.

5 Preparation of achiral Schiff-base ligands:



Preparation of ethylenediamine oligomeric Schiff base ligand (L(EDA))

A round bottom flask (100 mL) with a teflon coated stir bar was charged with bis(3-*t*-butyl-5-formyl-4-hydroxyphenyl) heptanedioate (0.40 g, 0.78 mmol, synthesized as per
5 procedure provided by White, D. E., Harvard University Thesis: "Development and mechanistic studies of a highly active and selective oligomeric (salen)Co(III) catalyst for asymmetric epoxide ring opening reactions" 2005, p. 172), ethane-1,2-diamine (0.047 g, 0.78 mmol) and benzene (50 mL). The round bottom flask was equipped with a Dean-Stark trap and a cold water condenser. The reaction was placed under a N₂
10 atmosphere and was refluxed for 18 hours. The reaction mixture was diluted with diethyl ether (50 mL) and washed with deionized water (50 mL). The organic layer was dried over MgSO₄, filtered and upon rotary evaporation and further drying *in vacuo* (50 °C), afforded 330 mg (39 % yield) of yellow/orange solids.

15 Preparation of phenylenediamine oligomeric Schiff base ligand (L(Ph))

A round bottom flask (100 mL) with a Teflon coated stir bar was charged with bis(3-*t*-butyl-5-formyl-4-hydroxyphenyl) heptanedioate (0.40 g, 0.78 mmol, synthesized as per
procedure provided by White, D. E., Harvard University Thesis: "Development and mechanistic studies of a highly active and selective oligomeric (salen)Co(III) catalyst
20 for asymmetric epoxide ring opening reactions" 2005, p. 172), benzene-1,2-diamine (0.048 g, 0.44 mmol) and benzene (50 mL). *p*-Toluene sulfonic acid (PTSA, 0.035g, 0.19 mmol) was added into the reaction mixture and the round bottom flask was equipped with a Dean-Stark trap and a cold water condenser. The reaction was placed under a N₂ atmosphere, stirred magnetically and refluxed overnight. The following

morning an aliquot of the reaction mixture was concentrated to dryness and dissolved in CDCl_3 for ^1H NMR analysis which showed near complete consumption of the starting dialdehyde. The undissolved PTSA was filtered and the benzene solution was washed with d.i. water and dried over MgSO_4 . Filtration, removal of solvent by rotary
5 evaporation and *in vacuo* drying afforded 0.43 g (94%) of orange solids.

General preparation of Schiff-base Cobalt complexes:

Co(II)acetate tetrahydrate (0.036 g, 0.14 mmol) was made into a solution with 2 mL of methanol in an inert atmosphere box. This solution was added to a toluene (3mL)
10 solution of the schiff base ligand (0.083 mmol) and allowed to stir under anaerobic conditions for 1.5 h. The mixture was concentrated under vacuum leaving a brick red solid residue. To this was added 0.083 mmol of organic acid (3-nitrobenzenesulfonic acid*1H₂O, toluenesulfonic acid, or acetic acid) and the mixture was taken up into 10 mL of methylenechloride and 2 mL of toluene. The mixture was removed from the
15 glovebox and allowed to stir open to air overnight. After solvent removal the brownish/green solid was used without further purification (each complex noted as “**ligand**”-Co(III)-X where X refers to the respective counter ion for the organic acid used in the oxidation, 3-nitrobenzenesulfonate (3NOBS), p-toluenesulfonate (OTs), or acetate (OAc)).

20

General epoxide ring opening procedure: The Co(III)Ligand complex was weighed into a thick-walled vial fitted with a magnetic stir bar. To this was added a pre-mixed mixture of propylene oxide and methanol. The vial was capped and placed into an aluminum block on a stir plate and allowed to stir without added heat. The composition

of the reaction mixture was examined by GC. Results for each of the reactions are summarized in the following table:

Catalyst	rac-PO (g)	MeOH (g)	Catalyst (g)	rxn time (h)	% PO conv	PM2/PM1	PM/DPM + highers
L(EDA)-Co(III)-3NOBS	0.44	0.87	0.011	4	61%	81	219
L(Ph)-Co(III)-3NOBS	0.86	0.65	0.012	4	83%	294	184

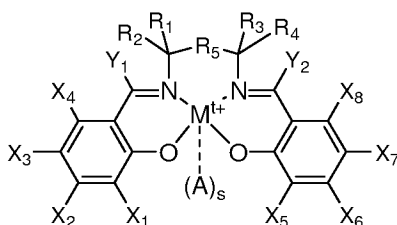
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While this invention has been described in detail for the purpose of illustration, it should not be construed as limited thereby but intended to cover all changes and modifications within the spirit and scope thereof.

THAT WHICH IS CLAIMED:

1. A composition comprising:

an achiral tetradentate Schiff-base metal complex, wherein a monomer of said Schiff-base metal complex is defined by the formula



wherein R_1 , R_2 , R_3 , R_4 , Y_1 , Y_2 , X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , and X_8 comprise, independently of one another, substituents selected from the group consisting of hydrogen, halogen, alkyl, alkenyl, alkynyl, hydrocarbyl, hydroxyl, alkoxy, amino, nitro, amide, phosphoryl, phosphonate, phosphine, carbonyl, carboxyl, silyl, ether, thioether, sulfonyl, selenoether, ketone, aldehyde, and ester;

or wherein two or more of R_1 , R_2 , R_3 , R_4 , Y_1 , Y_2 , X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , and X_8 together form a ring selected from the group consisting of a carbocyclic ring and a heterocyclic ring, said ring having from 4 to 10 atoms in the ring;

wherein R_5 group is selected from the group comprising a carbon-carbon bond, a methylene group, an ethylene group, an amine, an oxygen atom, and a sulfur atom;

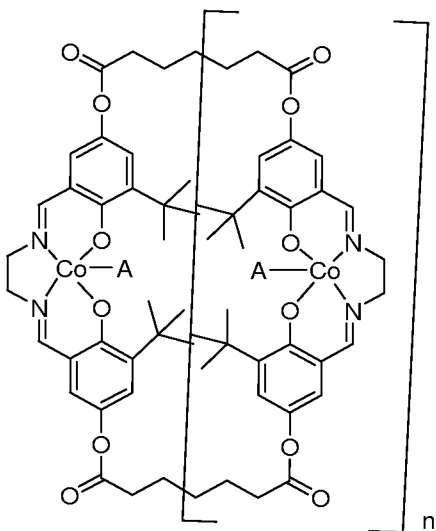
wherein one or more of R_1 , R_2 , R_3 , R_4 , Y_1 , Y_2 , X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , and X_8 are capable of providing a complementary interaction to form a component selected from the group consisting of oligomer, polymer, and copolymer;

wherein M^{t+} is a Group 2-15 metal capable of complexing with a ligand to affect catalysis, wherein t is an integer between 2 and 4;

wherein group A is selected from the group consisting of neutral group, bound anionic group, unbound anionic group, and combinations thereof, wherein s is the number of A groups associated with the metal and is an integer between 0 and 2; and wherein said composition is selected from the group consisting of oligomer, polymer, and copolymer.

2. A composition in accordance with claim 1 wherein M is cobalt.
3. A composition in accordance with claim 1 wherein A is selected from the group consisting of carboxylate, sulfonate, halide, alkoxide, phenoxide, hexafluorophosphate, tetrafluoroborate, hexafluoroantimonate and bis(trialkylsilyl)amide.
4. A composition in accordance with claim 3 where A is 3-nitrobenzenesulfonate and s = 1.
5. A composition in accordance with claim 1 wherein said complementary interaction is selected from the group consisting of carbon-carbon coupling, condensation, etherification, amide formation, esterification, ring-opening polymerizations, olefin metathesis, olefin polymerization, free radical polymerization, cationic polymerization, anionic polymerization, group-transfer polymerization, heterogeneous Ziegler-Natta polymerization, and homogeneous Ziegler-Natta polymerization;
6. A composition in accordance with claim 1 wherein said composition is an oligomer having from 1 to 20 repeat units.
7. A composition in accordance with claim 1 wherein said composition is bound to a support.

8. A composition in accordance with claim 1 wherein said composition is defined by the formula:



wherein A is 3-nitrobenzenesulfonate and n is an integer between 1 and 3.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/025397

A. CLASSIFICATION OF SUBJECT MATTER INV. : B01J31/22 B01J31/16 C07C41/03 ADD.		
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) B01J 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) EPO-Internal; CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	READY J M ET AL: "A practical Oligomeric [(salen)Co] Catalyst for Asymmetric Epoxide Ring-Opening Reactions" ANGEWANDTE CHEMIE., vol. 41, no. 8, 16 April 2002 (2002-04-16), pages 1374-1377, XP002268689 INTERNATIONAL EDITION, WILEY VCH VERLAG, WEINHEIM ISSN: 1433-7851 equations (3) - (5), compounds 1-4	1-6,8
X	BROWN ET AL: "TOTAL SYNTHESIS OF CIS-SYLVATICIN" ORGANIC LETTERS, vol. 10, no. 12, 20 May 2008 (2008-05-20), pages 2489-2492, XP002581170 scheme 2	1-6,8
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.	
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 21 May 2010	Date of mailing of the international search report 28/06/2010	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Klaes, Daphne	

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/025397

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JACOBSEN ET AL: "Highly active oligomeric (salen)co catalysts for asymmetric epoxide ring-opening reactions" J. AM. CHEM. SOC., vol. 123, 23 February 2001 (2001-02-23), pages 2687-2688, XP002585913 scheme 2, table 1	1-6,8
X	SHIMAKOSHI H ET AL: "Synthesis and redox behavior of dialkylated dicobalt complexes having two discrete salen units" TETRAHEDRON LETTERS, vol. 42, no. 10, 4 March 2001 (2001-03-04) , pages 1949-1951, XP004316761 ELSEVIER, AMSTERDAM, NL ISSN: 0040-4039 scheme 1	1,2,5,6
X	DIOOS B M L ET AL: "Heterogenisation of dimeric Cr(salen) with supported ionic liquids" JOURNAL OF CATALYSIS, vol. 243, no. 1, 1 October 2006 (2006-10-01), pages 217-219, XP024913422 ACADEMIC PRESS, DULUTH, MN, US ISSN: 0021-9517 [retrieved on 2006-10-01] passage bridging pages 217 and 218 figure 1	1,3-7
X	JI C ET AL: "Catalytic reduction of 1- and 2-bromooctanes by a dinickel(I) Schiff base complex containing two salen units electrogenerated at carbon cathodes in dimethylformamide" JOURNAL OF ELECTROANALYTICAL CHEMISTRY AND INTERFACIAL ELECTRO CHEMISTRY,, vol. 622, no. 1, 1 October 2008 (2008-10-01), pages 15-21, XP025427983 ELSEVIER, AMSTERDAM, NL ISSN: 0022-0728 [retrieved on 2008-05-04] scheme 2	1,3,5,6
X	HISAEDA ET AL: "Reductive coupling of benzyl bromide catalyzed by a novel dicobalt complex having two salen units" JOURNAL OF THE CHEMICAL SOCIETY, DALTON TRANSACTIONS, vol. 13, 15 June 2001 (2001-06-15), XP002581694 scheme 2	1,2,5,6

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/025397

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	OKAWA ET AL: "Tetranuclear mixed-metal M(II) ₂ Cu(II) ₂ complexes derived from a phenol-based macrocyclic ligand having two N(amine) ₂ O ₂ and two N(imine) ₂ O ₂ metal-binding sites" INORG. CHEM, vol. 40, 21 June 2001 (2001-06-21), pages 3739-3744, XP002581695 scheme 1 -----	1,5,6