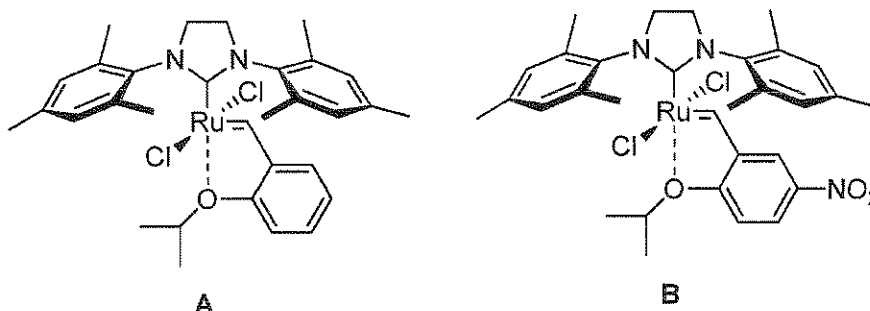


METATHESIS CATALYSTS CONTAINING ONIUM GROUPS

This disclosure relates to a general method for the preparation of complexes containing a quaternary onium group in an inert ligand which complexes are widely used as pre(catalysts) in metathesis reactions. This disclosure also relates to new metal complexes, and their method of preparation and use in metathesis reactions. The disclosure also relates to intermediates used in the preparation of these complexes, and methods of conducting metathesis reactions.

In recent years, tremendous progress has been made in the field of olefin metathesis. The development of new, more stable and active olefin metathesis catalysts (such as **A** and **B**) led to a significant increase in the area of possible applications of this transformation.



A significant problem with using metathesis catalysts in the industry (mainly pharmaceutical) is removal of contamination containing heavy metal from the product. The development of practical, efficient and economically advantageous methods of metal removal can support further implementation of metathesis technology.

There are several classic methods of removing by-products containing heavy metal. Various "scavengers" were used for this purpose, or catalysts were designed with an increased affinity to silica. None of the existing methods appear to be universal either due to too little or too much scavenger activity (resulting in

a prolonged purification stage or side reactions), or insufficient affinity of catalysts for an adsorbent.

In order to develop a simple method of removing metals from the postreaction mixture, catalysts containing polar ammonium groups were synthesized. Although a simple filtration of the postreaction mixture through silica gel can reduce the heavy metal content in the product, the method is not adequate to meet the requirements of the pharmaceutical industry. Additionally, there has been little research activity related to (pre)catalysts having onium groups in an inert ligand, likely because of the difficulty in the synthesis of such complexes. Furthermore, catalysts which contain an onium group in a *N*-heterocyclic carbene ligand (NHC) are known, which may be as a result of unique difficulties occurring during the synthesis by means of classical methods.

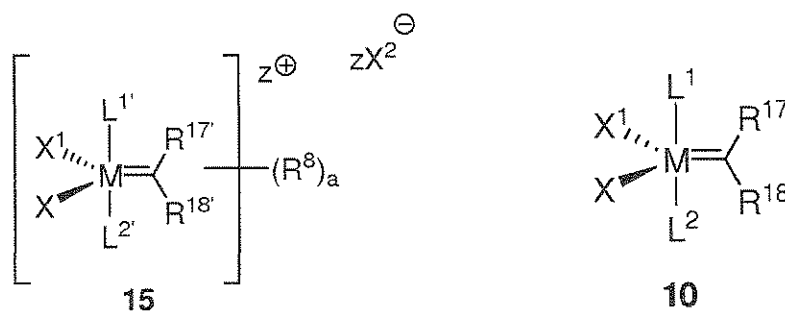
Another significant problem is the lack of effective and active catalysts for a metathesis reaction carried out in water. Such a transformation may be of great importance in the synthesis of compounds of biological activity.

It was surprisingly discovered that complexes containing an quaternary onium group in an inert ligand can be prepared in a simple and efficient manner. Therefore, some embodiments include a method of preparation of complexes containing an quaternary onium group in an inert ligand in the course of a reaction of a relevant complex with an alkylating reagent. Some embodiments include, in addition to new metal complexes acting as pre(catalysts) of a metathesis reaction, a method of their preparation and their use in a metathesis reaction.

The complexes described herein (referred to herein as "the complexes") have an analogous effectiveness and/or activity in metathesis reactions to certain catalysts known in the prior art. The complexes allow products with a very low content of metal to be obtained following the application of simple and

cheap methods for treatment of the postreaction mixture. Furthermore, the complexes are characterized by good solubility and high stability in pure water, and exhibit high activity and/or effectiveness in metathesis reactions carried out in water.

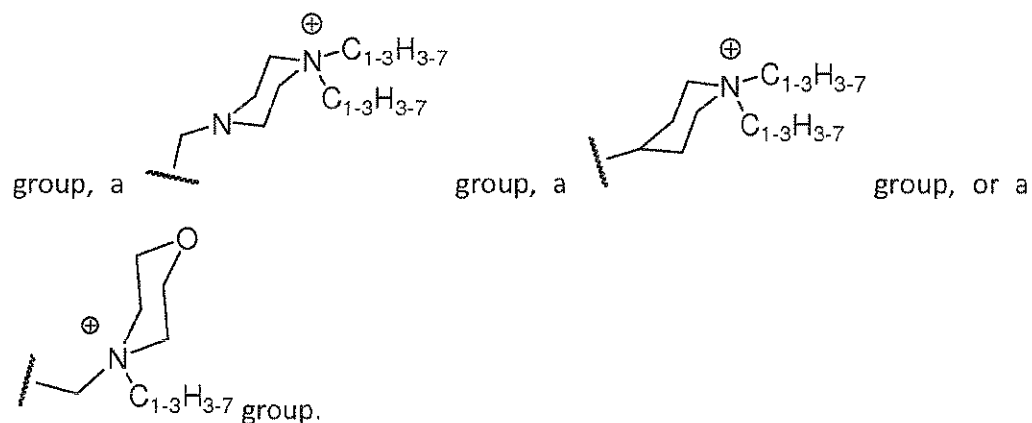
- 5 Some embodiments include a method of synthesis of complexes of formula **15**. In such a method, a complex of formula **10** is subjected to a reaction with an alkylating reagent of formula R^8X^2 .



- 10 With respect to formula **15**, $L^{1'}$ is an inert ligand.

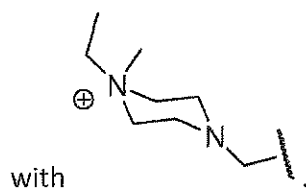
With respect to formula **15**, $L^{2'}$ is an inert ligand.

- With respect to formula **15**, at least one of $L^{1'}$ and $L^{2'}$ is substituted with at least one quaternary ammonium, including a $C_{4-20}N_{1-2}$ quaternary ammonium, a $C_{4-10}N$ quaternary ammonium, a $C_{4-20}N_2$ quaternary ammonium, or a $C_{4-20}NO$ quaternary ammonium, and/or a phosphonium group, such as a $C_{4-20}P_{1-2}$ phosphonium, a $C_{4-10}P$ phosphonium, or a $C_{4-20}P_2$ phosphonium. In some
- 15 embodiments, at least one of $L^{1'}$ and $L^{2'}$ is substituted with a $-(CH_2)_{0-4}N^+(C_{1-3}H_{3-7})_3$

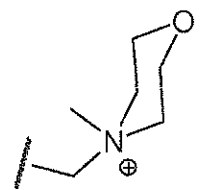


In some embodiments, at least one of $L^{1'}$ and $L^{2'}$ is substituted with a $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$ group.

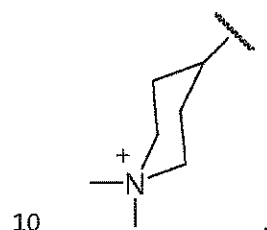
5 In some embodiments, at least one of $L^{1'}$ and $L^{2'}$ is substituted



In some embodiments, at least one of $L^{1'}$ and $L^{2'}$ is substituted with



In some embodiments, at least one of $L^{1'}$ and $L^{2'}$ is substituted with



With respect to formula 10 or 15, M is ruthenium or osmium.

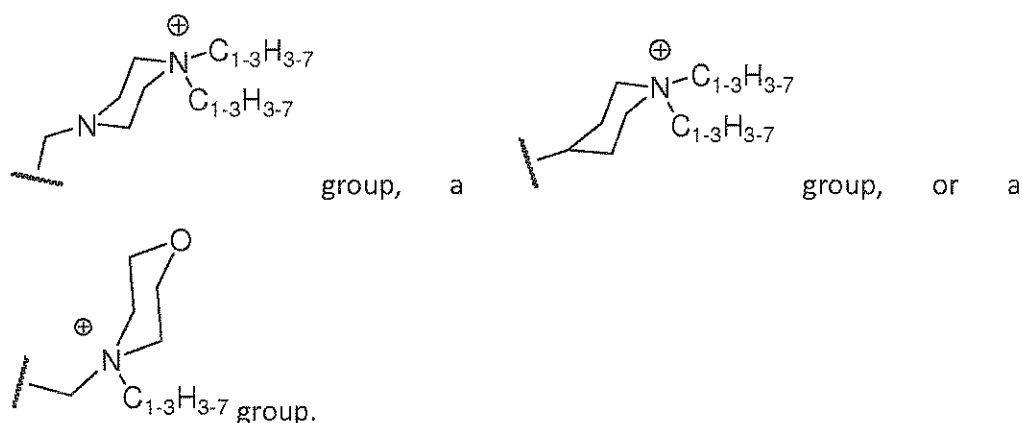
With respect to formula 10 or 15, X is an anionic ligand. In some embodiments, X is F⁻, Cl⁻, Br⁻, or I⁻. In some embodiments, X is Cl⁻.

With respect to formula 10 or 15, X¹ is an anionic ligand. In some embodiments, X¹ is F⁻, Cl⁻, Br⁻, or I⁻. In some embodiments, X¹ is Cl⁻.

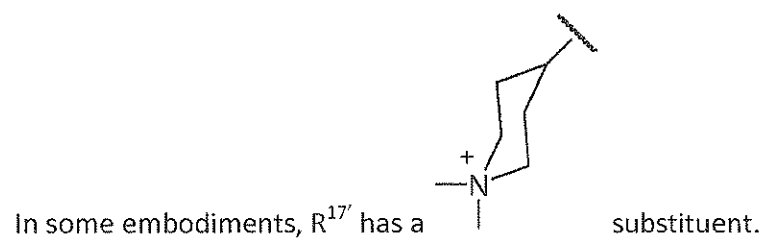
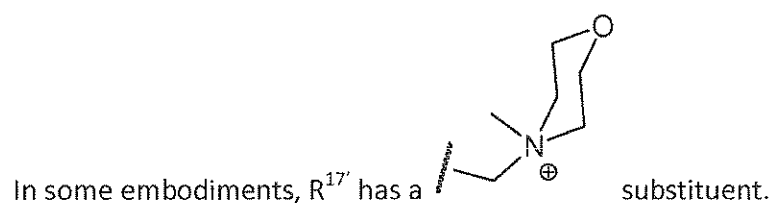
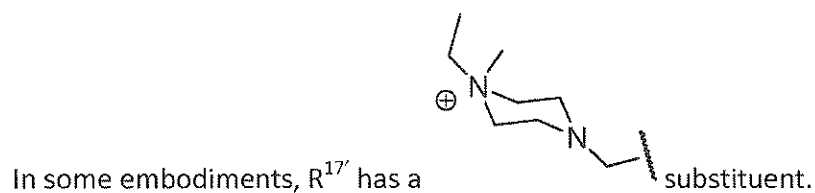
5 With respect to formula 10 or 15, or the alkylating reagent of formula R⁸X², X² is an anionic ligand. In some embodiments, X² is F⁻, Cl⁻, Br⁻, or I⁻. In some embodiments, X² is Cl⁻.

With respect to formula 15, R⁸ is -C₁₋₂₀ alkyl (including C₁₋₃ alkyl, C₁₋₆ alkyl, C₁₋₁₂ alkyl, etc.), -C₃₋₈ cycloalkyl, -C₂₋₂₀ alkenyl, -C₂₋₂₀ alkynyl group. Each of these
 10 groups may be optionally substituted with a group such as a halogen atom, -C₅₋₁₀ aryl (such as phenyl or naphthyl), -C(=O)-C₁₋₆ alkyl (such as acetyl, propionyl, butyryl, etc.),
 -C(=O)-O-C₁₋₆ alkyl, -C(=O)-N(C₁₋₆ alkyl)₂,
 -C(=O)-N-(C₁₋₆ alkyl)-O-C₁₋₆ alkyl, -C(=O)-C₅₋₁₀ aryl, -C(=O)-O-C₅₋₁₀ aryl,
 -C(=O)-N(C₅₋₁₀ aryl)₂, -C(=O)-N-(C₅₋₁₀ aryl)-O-C₅₋₁₀ aryl group, etc. Examples of C₁₋₆
 15 alkyl for any of the groups above include methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl, pentyl groups, hexyl groups, etc.

With respect to formula 15, R^{17'} is H, -C₁₋₂₀ alkyl, -C₂₋₂₀ alkenyl, -C₂₋₂₀ alkynyl or -C₅₋₁₀ aryl group. Each of these groups (except H) may be optionally substituted. In some embodiments, at least one of the substituents is
 20 a quaternary ammonium, including a C₄₋₂₀N₁₋₂ quaternary ammonium, a C₄₋₁₀N quaternary ammonium, a C₄₋₂₀N₂ quaternary ammonium, or a C₄₋₂₀NO quaternary ammonium, and/or a phosphonium group, such as a C₄₋₂₀P₁₋₂ phosphonium, a C₄₋₁₀P phosphonium, or a C₄₋₂₀P₂ phosphonium. In some embodiments, the quaternary ammonium is a -(CH₂)₀₋₄N⁺(C₁₋₃H₃₋₇)₃ group, a

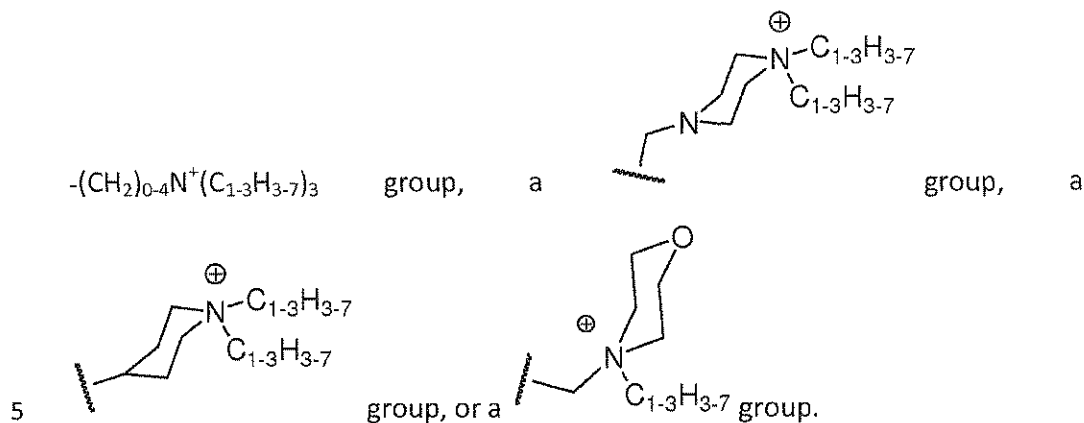


In some embodiments, R^{17'} has a -CH₂N⁺(CH₃)₃ substituent, meaning that -C₁₋₂₀ alkyl, -C₂₋₂₀ alkenyl, -C₂₋₂₀ alkynyl or -C₅₋₁₀ aryl group has a -CH₂N⁺(CH₃)₃ substituent.

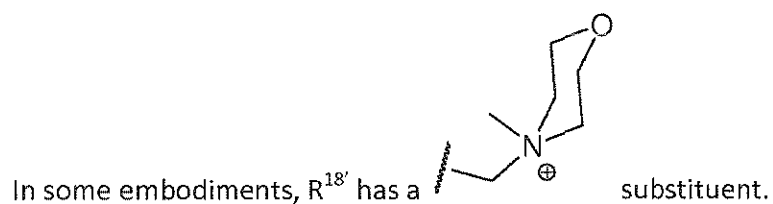
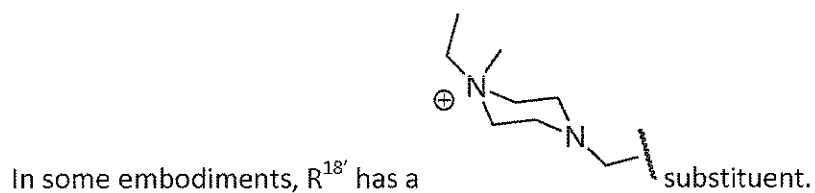


With respect to formula 15, R^{18'} is a phenyl or vinyl substituent, or -C=C(CH₃)₂. Each of these groups may be optionally substituted. In some embodiments, at least one of the substituents is a quaternary ammonium, including a C₄₋₂₀N₁₋₂ quaternary ammonium, a C₄₋₁₀N quaternary ammonium, a

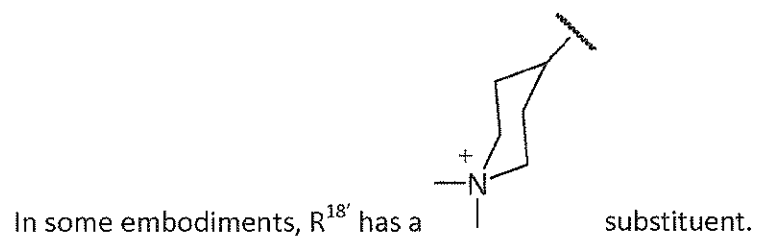
$C_{4-20}N_2$ quaternary ammonium, or a $C_{4-20}NO$ quaternary ammonium, and/or a phosphonium group, such as a $C_{4-20}P_{1-2}$ phosphonium, a $C_{4-10}P$ phosphonium, or a $C_{4-20}P_2$ phosphonium. In some embodiments, the quaternary ammonium is a



In some embodiments, $R^{18'}$ has a $-CH_2N^+(CH_3)_3$ substituent, meaning that a phenyl, vinyl, or $-C=C(CH_3)_2$ has a $-CH_2N^+(CH_3)_3$ substituent.



10



With respect to formula 15, $R^{17'}$ and $R^{18'}$ may be optionally linked together to form a cyclic or polycyclic system that is aliphatic or aromatic.

With respect to formula 15, $R^{17'}$ and $R^{18'}$, together with a carbon atom connecting them, can optionally be a 3-phenyl-1H-indene-1-ylidene substituent.

- 5 With respect to formula 15, $R^{17'}$ and/or $R^{18'}$ may be optionally linked to L^1 or L^2 to form a bidentate ligand.

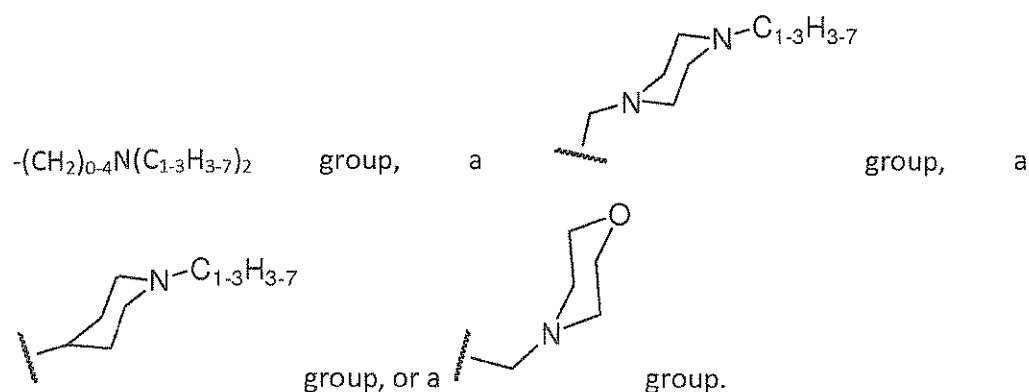
With respect to formula 15, a is 1, 2, 3, 4, 5, 6 or 7.

With respect to formula 15, z is 1, 2, 3, 4, 5, 6 or 7.

With respect to formula 10, L^1 is an inert ligand.

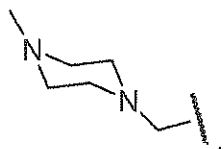
- 10 With respect to formula 10, L^2 is an inert ligand.

With respect to formula 10, at least one of L^1 and L^2 contains independently at least one X^2 substituent or is independently substituted with aliphatic and/or aromatic and/or heterocyclic alkylamino or alkylphosphine. In some embodiments, the alkylamino may include a $C_{3-20}N_{1-2}$ amino, a $C_{3-10}N$ amino, a $C_{3-20}N_2$ amino, or a $C_{3-20}NO$ amino. In some embodiments, the alkylphosphine may include a $C_{3-20}P_{1-2}$ phosphine, a $C_{4-10}P$ phosphine, or a $C_{4-20}P_2$ phosphine. In some embodiments, at least one of L^1 and L^2 is substituted with a

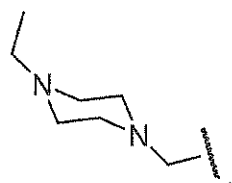


In some embodiments, at least one of L^1 and L^2 is substituted with a $CH_2N(CH_3)_2$ group.

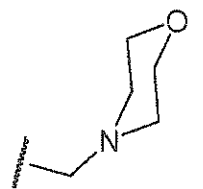
In some embodiments, at least one of L^1 and L^2 is substituted with



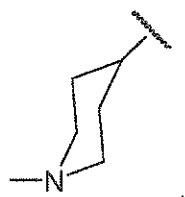
5 In some embodiments, at least one of L^1 and L^2 is substituted with



In some embodiments, at least one of L^1 and L^2 is substituted with



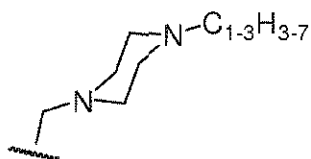
10 In some embodiments, at least one of L^1 and L^2 is substituted with



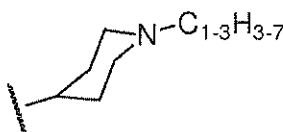
With respect to formula 10, R^{17} is H, $-C_{1-20}$ alkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl or a $-C_{5-10}$ aryl group. Each of these groups, except H, is optionally substituted. In some embodiments, at least one substituent is X^2 or an aliphatic and/or aromatic and/or heterocyclic alkylamino or alkylphosphine. In some
15
embodiments, the alkylamino may include a $C_{3-20}N_{1-2}$ amino, a $C_{3-10}N$ amino, a

C₃₋₂₀N₂ amino, or a C₃₋₂₀NO amino. In some embodiments, the alkylphosphine may include a C₃₋₂₀P₁₋₂ phosphine, a C₄₋₁₀P phosphine, or a C₄₋₂₀P₂ phosphine.

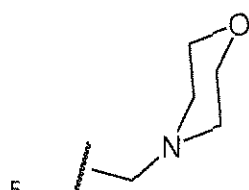
In some embodiments, R¹⁷ has a -(CH₂)₀₋₄N(C₁₋₃H₃₋₇)₂ substituent, a



substituent, a



substituent, or a

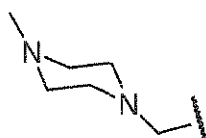


5

substituent, meaning that -C₁₋₂₀ alkyl, -C₂₋₂₀ alkenyl, -C₂₋₂₀ alkynyl or -C₅₋₁₀ aryl has one of these substituents.

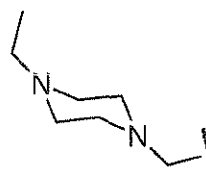
In some embodiments, R¹⁷ has a -CH₂N(CH₃)₂ substituent.

In some embodiments, R¹⁷ has a



substituent.

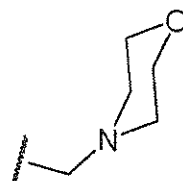
In some embodiments, R¹⁷ has a



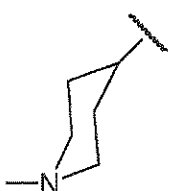
substituent.

10

In some embodiments, R¹⁷ has a

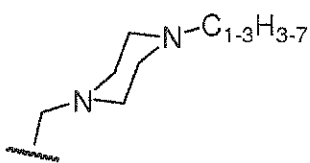
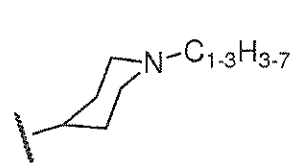


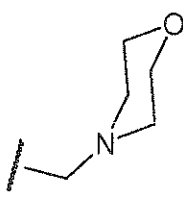
substituent.

In some embodiments, R^{17} has a  substituent.

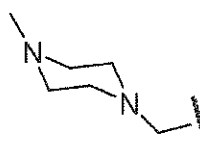
With respect to formula 10, R^{18} is a phenyl, vinyl, or $-C=C(CH_3)_2$. Each of these is optionally substituted. In some embodiments, at least one substituent is X^2 or an aliphatic and/or aromatic and/or heterocyclic alkylamino or
 5 alkylphosphine. In some embodiments, the alkylamino may include a $C_{3-20}N_{1-2}$ amino, a $C_{3-10}N$ amino, a $C_{3-20}N_2$ amino, or a $C_{3-20}NO$ amino. In some embodiments, the alkylphosphine may include a $C_{3-20}P_{1-2}$ phosphine, a $C_{4-10}P$ phosphine, or a $C_{4-20}P_2$ phosphine.

In some embodiments, R^{18} has a $-(CH_2)_{0-4}N(C_{1-3}H_{3-7})_2$ substituent, a

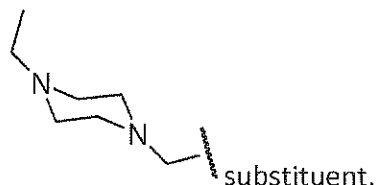
10  substituent, a  substituent, or a

 substituent, meaning that $-C_{1-20}$ alkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl or $-C_{5-10}$ aryl has one of these substituents.

In some embodiments, R^{18} has a $-CH_2N(CH_3)_2$ substituent.

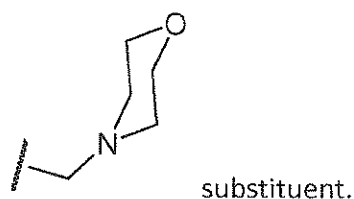
In some embodiments, R^{18} has a  substituent.

In some embodiments, R¹⁸ has a



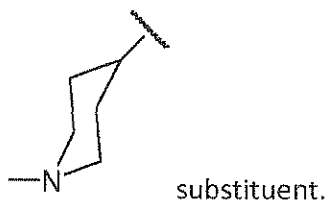
substituent.

In some embodiments, R¹⁸ has a



substituent.

In some embodiments, R¹⁸ has a

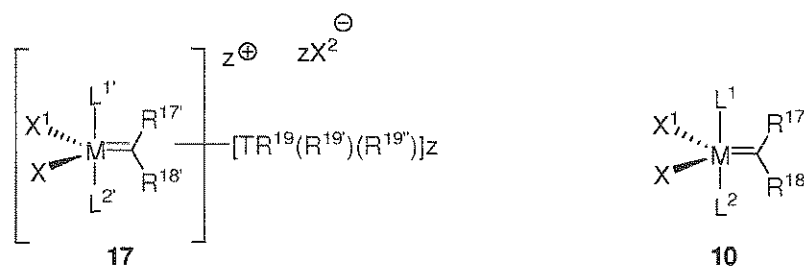


substituent.

- 5 With respect to formula 10, R¹⁷ and R¹⁸ may also be optionally linked together to form a cyclic or polycyclic system that is aliphatic or aromatic; R¹⁷ and/or R¹⁸ may also be optionally linked to L¹ or L² to form a bidentate ligand; and/or R¹⁷ and R¹⁸, together with a carbon atom connecting them, can optionally be a 3-phenyl-1H-indene-1-ylidene substituent.

- 10 With respect to the alkylating reagent of formula R⁸X², R⁸ is -C₁₋₂₀ alkyl (such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl, pentyl groups, hexyl groups, etc.), -C₃₋₈ cycloalkyl, -C₂₋₂₀ alkenyl, -C₂₋₂₀ alkynyl group. Each of these groups are optionally substituted with halogen atoms, -C₅₋₁₀ aryl, -C(=O)-C₁₋₆ alkyl, -C(=O)-O-C₁₋₆ alkyl, -C(=O)-N(C₁₋₆ alkyl)₂,
 15 -C(=O)-N-(C₁₋₆ alkyl)-O-C₁₋₆ alkyl, -C(=O)-C₅₋₁₀ aryl, -C(=O)-O-C₅₋₁₀ aryl, -C(=O)-N(C₅₋₁₀ aryl)₂, or -C(=O)-N-(C₅₋₁₀ aryl)-O-C₅₋₁₀ aryl.

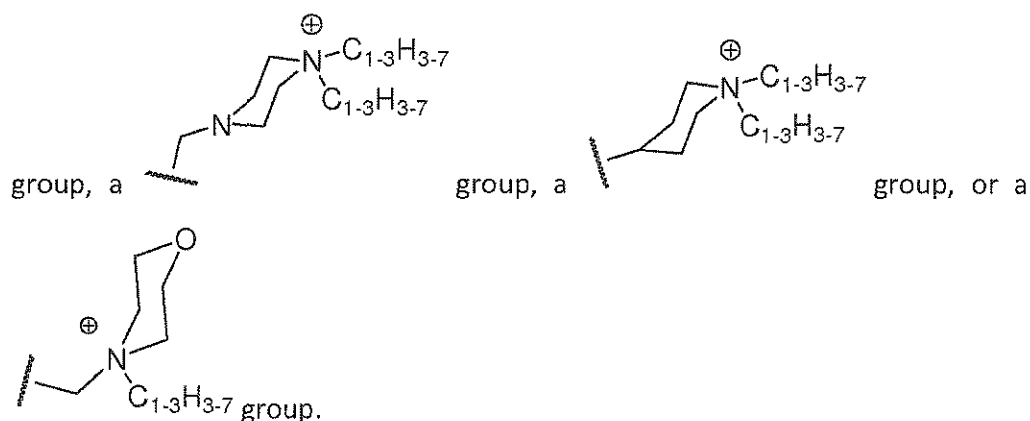
Some embodiments include a method of synthesis of complexes of formula **17**. In this method, a complex of formula **10** is subjected to a reaction with compound $\text{TR}^{19}(\text{R}^{19'}) (\text{R}^{19''})$.



5 With respect to formula **17**, $\text{L}^{1'}$ is an inert ligand.

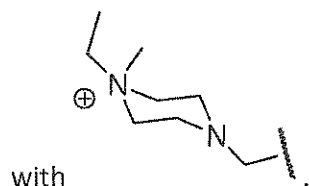
With respect to formula **17**, $\text{L}^{2'}$ is an inert ligand.

With respect to formula **17**, at least one of $\text{L}^{1'}$ and $\text{L}^{2'}$ is substituted with at least one quaternary ammonium, including a $\text{C}_{4-20}\text{N}_{1-2}$ quaternary ammonium, a C_{4-10}N quaternary ammonium, a $\text{C}_{4-20}\text{N}_2$ quaternary ammonium, or a C_{4-20}NO quaternary ammonium, and/or a phosphonium group, such as a $\text{C}_{4-20}\text{P}_{1-2}$ phosphonium, a C_{4-10}P phosphonium, or a $\text{C}_{4-20}\text{P}_2$ phosphonium. In some
 10 embodiments, at least one of $\text{L}^{1'}$ and $\text{L}^{2'}$ is substituted with a $-(\text{CH}_2)_{0-4}\text{N}^+(\text{C}_{1-3}\text{H}_{3-7})_3$

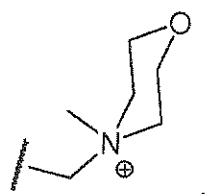


15 In some embodiments, at least one of $\text{L}^{1'}$ and $\text{L}^{2'}$ is substituted with a $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$ group.

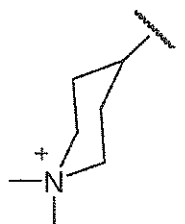
In some embodiments, at least one of $L^{1'}$ and $L^{2'}$ is substituted



In some embodiments, at least one of $L^{1'}$ and $L^{2'}$ is substituted with



5 In some embodiments, at least one of $L^{1'}$ and $L^{2'}$ is substituted with



With respect to formula 10 or 17, M is ruthenium or osmium.

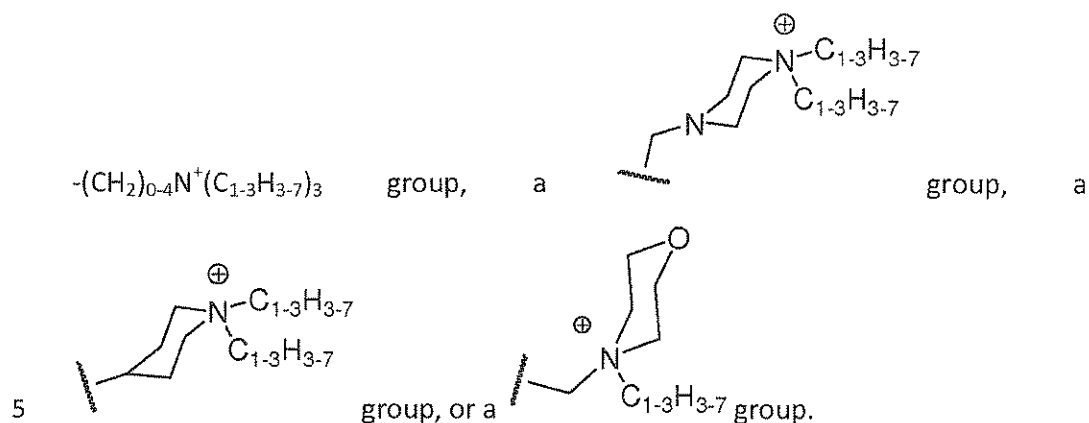
With respect to formula 10 or 17, X is an anionic ligand. In some embodiments, X is F^- , Cl^- , Br^- , or I^- . In some embodiments, X is Cl^- .

10 With respect to formula 10 or 17, X^1 is an anionic ligand. In some embodiments, X^1 is F^- , Cl^- , Br^- , or I^- . In some embodiments, X^1 is Cl^- .

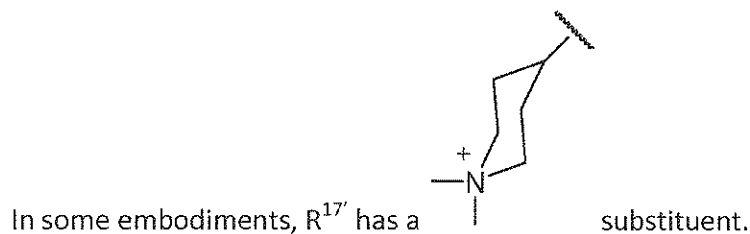
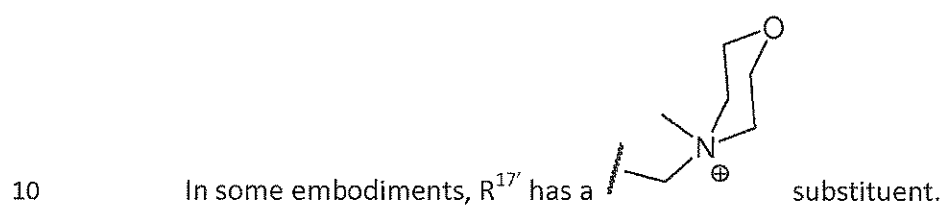
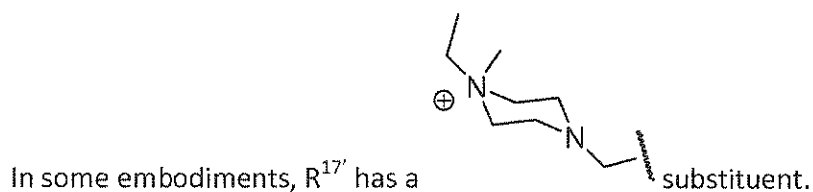
With respect to formula 17, X^2 is an anionic ligand. In some embodiments, X^2 is F^- , Cl^- , Br^- , or I^- . In some embodiments, X^2 is Cl^- .

15 With respect to formula 17, $R^{17'}$ is H, $-C_{1-20}$ alkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl or $-C_{5-10}$ aryl group. Each of these groups (except H) may be optionally substituted with a quaternary ammonium, including a $C_{4-20}N_{1-2}$ quaternary ammonium, a $C_{4-10}N$ quaternary ammonium, a $C_{4-20}N_2$ quaternary

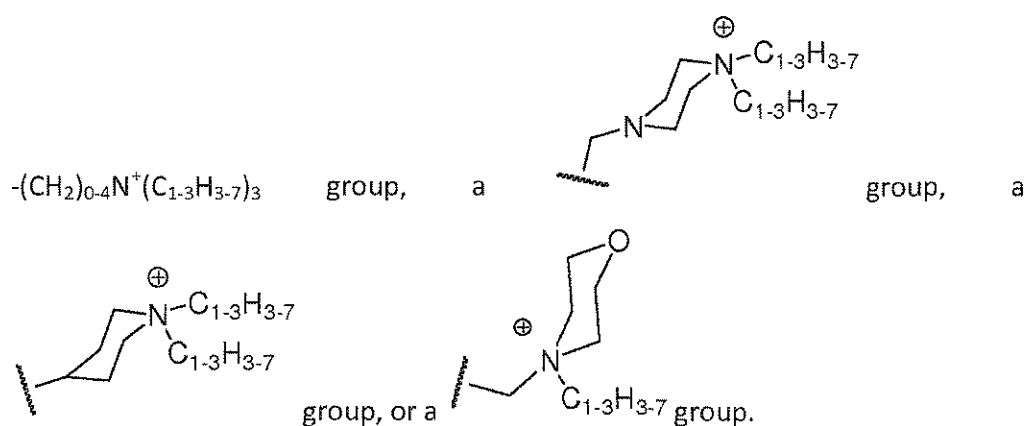
ammonium, or a $C_{4-20}NO$ quaternary ammonium, and/or a phosphonium group, such as a $C_{4-20}P_{1-2}$ phosphonium, a $C_{4-10}P$ phosphonium, or a $C_{4-20}P_2$ phosphonium. In some embodiments, the quaternary ammonium is a



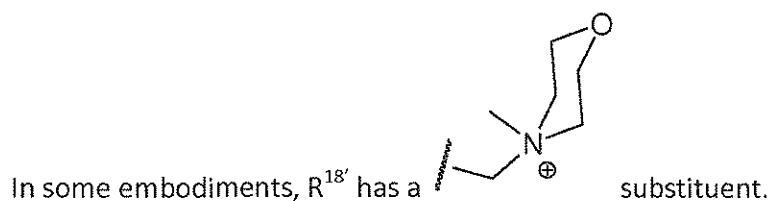
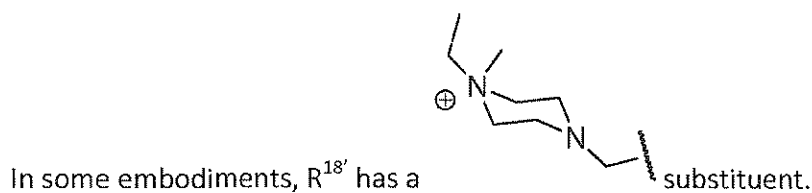
In some embodiments, $R^{17'}$ has a $-CH_2N^+(CH_3)_3$ substituent, meaning that $-C_{1-20}$ alkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl, or $-C_{5-10}$ aryl has a $-CH_2N^+(CH_3)_3$ substituent.

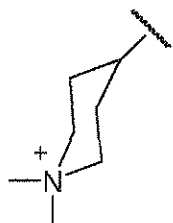


With respect to formula 17, $R^{18'}$ is a phenyl or vinyl substituent, or $-C=C(CH_3)_2$. Each of these groups is optionally substituted. In some embodiments, at least one substituent is a quaternary ammonium, including a $C_{4-20}N_{1-2}$ quaternary ammonium, a $C_{4-10}N$ quaternary ammonium, a $C_{4-20}N_2$ quaternary ammonium, or a $C_{4-20}NO$ quaternary ammonium, and/or a phosphonium group, such as a $C_{4-20}P_{1-2}$ phosphonium, a $C_{4-10}P$ phosphonium, or a $C_{4-20}P_2$ phosphonium. In some embodiments, the quaternary ammonium is a



10 In some embodiments, $R^{18'}$ has a $-CH_2N^+(CH_3)_3$ substituent, meaning that a phenyl, vinyl, or $-C=C(CH_3)_2$ has a $-CH_2N^+(CH_3)_3$ substituent.





In some embodiments, $R^{18'}$ is

With respect to formula 17, $R^{17'}$ and $R^{18'}$ may be optionally linked together to form a cyclic or polycyclic system that is aliphatic or aromatic.

With respect to formula 17, $R^{17'}$ and $R^{18'}$, together with a carbon atom
5 connecting them, can optionally be a 3-phenyl-1H-indene-1-ylidene substituent.

With respect to formula 17, $R^{17'}$ and/or $R^{18'}$ may be optionally linked to L^1 or L^2 to form a bidentate ligand.

With respect to formula 17, a is 1, 2, 3, 4, 5, 6 or 7.

With respect to formula 17, z is 1, 2, 3, 4, 5, 6 or 7.

10 With respect to formula **17** or compound $TR^{19}(R^{19'})(R^{19''})$, T is N or P.

With respect to formula **17** or compound $TR^{19}(R^{19'})(R^{19''})$, R^{19} is H, $-C_{1-6}$ alkyl (such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl, pentyl isomers, hexyl isomers, etc.), $-C_{5-10}$ aryl (such as phenyl, naphthyl, etc.), or a C_{4-10} heterocyclic group.

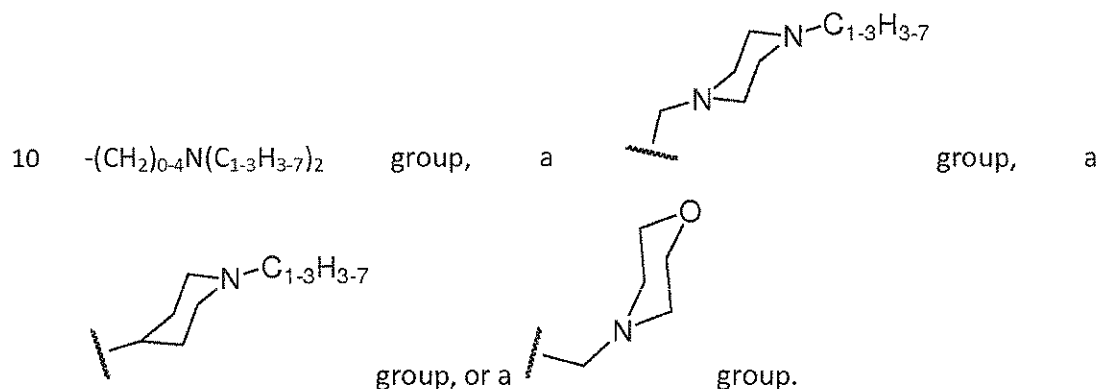
15 With respect to formula **17** or compound $TR^{19}(R^{19'})(R^{19''})$, $R^{19'}$ is H, $-C_{1-6}$ alkyl (such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl, pentyl isomers, hexyl isomers, etc.), $-C_{5-10}$ aryl (such as phenyl, naphthyl, etc.), or a C_{4-10} heterocyclic group.

20 With respect to formula **17** or compound $TR^{19}(R^{19'})(R^{19''})$, $R^{19''}$ is H, $-C_{1-6}$ alkyl (such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl, pentyl isomers, hexyl isomers, etc.), $-C_{5-10}$ aryl (such as phenyl, naphthyl, etc.), or a C_{4-10} heterocyclic group.

With respect to formula 10, L^1 is an inert ligand.

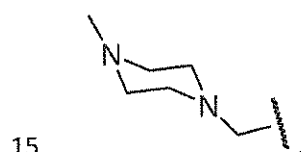
With respect to formula 10, L^2 is an inert ligand.

With respect to formula 10, at least one of L^1 and L^2 contains independently at least one X^2 substituent, or is independently substituted with
 5 aliphatic and/or aromatic and/or heterocyclic alkylamino or alkylphosphine. In some embodiments, the alkylamino may include a $C_{3-20}N_{1-2}$ amino, a $C_{3-10}N$ amino, a $C_{3-20}N_2$ amino, or a $C_{3-20}NO$ amino. In some embodiments, the alkylphosphine may include a $C_{3-20}P_{1-2}$ phosphine, a $C_{4-10}P$ phosphine, or a $C_{4-20}P_2$ phosphine. In some embodiments, at least one of L^1 and L^2 is substituted with a

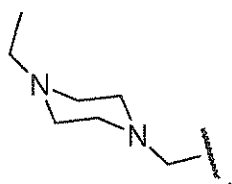


In some embodiments, at least one of L^1 and L^2 is substituted with a $-CH_2N(CH_3)_2$ group.

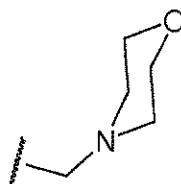
In some embodiments, at least one of L^1 and L^2 is substituted with



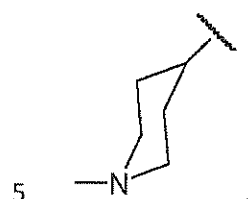
In some embodiments, at least one of L^1 and L^2 is substituted with



In some embodiments, at least one of L^1 and L^2 is substituted with



In some embodiments, at least one of L^1 and L^2 is substituted with

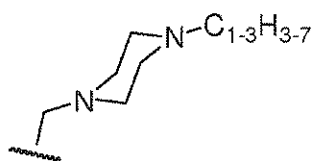


With respect to formula 10, R^{17} is H, $-C_{1-20}$ alkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl or a $-C_{5-10}$ aryl group. Each of these groups, except H, is optionally substituted. In some embodiments, at least one substituent is X^2 or an aliphatic and/or aromatic and/or heterocyclic alkylamino or alkylphosphine. In some

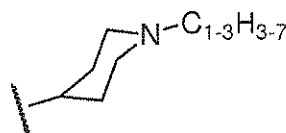
10

embodiments, the alkylamino may include a $C_{3-20}N_{1-2}$ amino, a $C_{3-10}N$ amino, a $C_{3-20}N_2$ amino, or a $C_{3-20}NO$ amino. In some embodiments, the alkylphosphine may include a $C_{3-20}P_{1-2}$ phosphine, a $C_{4-10}P$ phosphine, or a $C_{4-20}P_2$ phosphine.

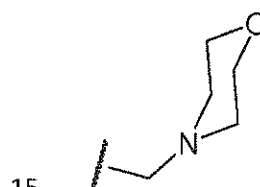
In some embodiments, R^{17} has a $-(CH_2)_{0-4}N(C_{1-3}H_{3-7})_2$ substituent, a



substituent, a

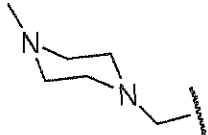


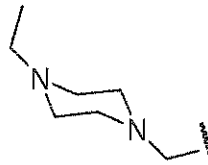
substituent, or a

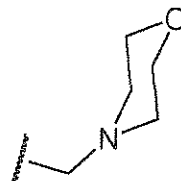


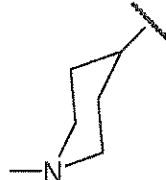
substituent, meaning that $-C_{1-20}$ alkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl or $-C_{5-10}$ aryl has one of these substituents.

In some embodiments, R^{17} has a $-\text{CH}_2\text{N}(\text{CH}_3)_2$ substituent.

In some embodiments, R^{17} has a  substituent.

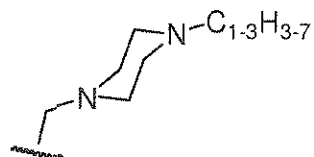
In some embodiments, R^{17} has a  substituent.

5 In some embodiments, R^{17} has a  substituent.

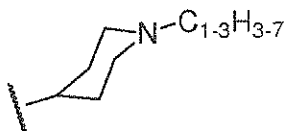
In some embodiments, R^{17} has a  substituent.

10 With respect to formula 10, R^{18} is a phenyl, vinyl, or $-\text{C}=\text{C}(\text{CH}_3)_2$. Each of these groups is optionally substituted. In some embodiments, at least one substituent is X^2 or an aliphatic and/or aromatic and/or heterocyclic alkylamino or alkylphosphine. In some embodiments, the alkylamino may include a $\text{C}_{3-20}\text{N}_{1-2}$ amino, a C_{3-10}N amino, a $\text{C}_{3-20}\text{N}_2$ amino, or a C_{3-20}NO amino. In some embodiments, the alkylphosphine may include a $\text{C}_{3-20}\text{P}_{1-2}$ phosphine, a C_{4-10}P phosphine, or a $\text{C}_{4-20}\text{P}_2$ phosphine.

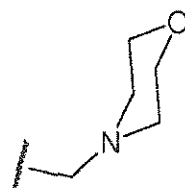
In some embodiments, R^{18} has a $-(CH_2)_{0-4}N(C_{1-3}H_{3-7})_2$ substituent, a



substituent, a



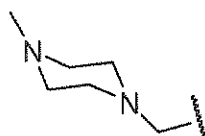
substituent, or a



substituent, meaning that $-C_{1-20}$ alkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl

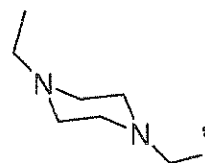
or $-C_{5-10}$ aryl has one of these substituents.

5 In some embodiments, R^{18} has a $-CH_2N(CH_3)_2$ substituent.



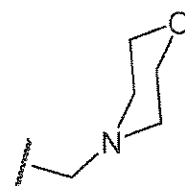
In some embodiments, R^{18} has a

substituent.



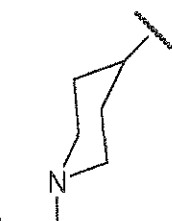
In some embodiments, R^{18} has a

substituent.



In some embodiments, R^{18} has a

substituent.



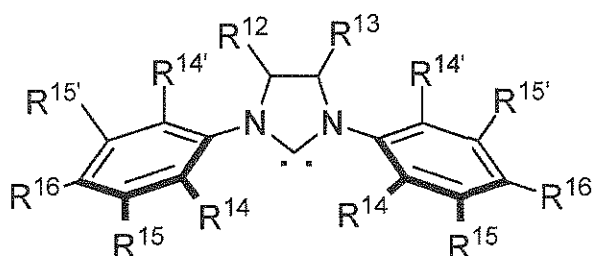
10

In some embodiments, R^{18} has a

substituent.

With respect to formula 10, R^{17} and R^{18} may also be optionally linked together to form a cyclic or polycyclic system that is aliphatic or aromatic; R^{17} and/or R^{18} may also be optionally linked to L^1 or L^2 to form a bidentate ligand; and/or R^{17} and R^{18} , together with a carbon atom connecting them, can optionally
 5 be a 3-phenyl-1H-indene-1-ylidene substituent.

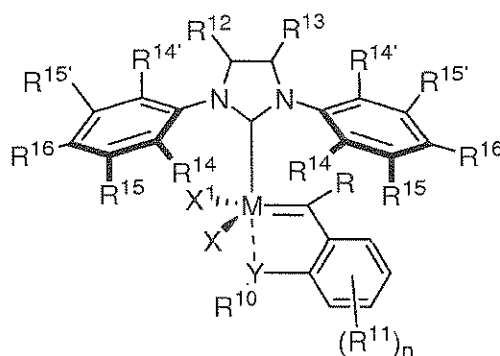
In some embodiments, L^1 in the complex of general formula 10 is defined by formula 9.



9

In some embodiments, L^2 is an inert ligand, wherein group 9 and/or L^2
 10 contain at least one X^2 substituent or are substituted with at least one aliphatic and/or aromatic and/or heterocyclic alkylamino or alkylphosphine.

In some embodiments, a complex of general formula 10 is defined by general formula 14



14

With respect to formula 14, M is ruthenium or osmium. In some embodiments, M is ruthenium.

With respect to formula 14, X and X¹ are, independently, inert ligands.

In some embodiments, X is Cl or I. In some embodiments, X is Cl. In
5 some embodiments, X is I.

In some embodiments, both X and X¹ are Cl or I. In some embodiments, both X and X¹ are Cl. In some embodiments, both X and X¹ are I.

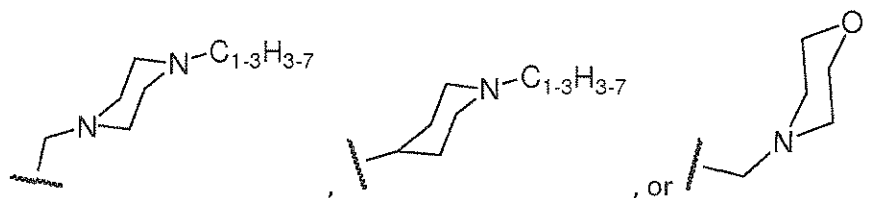
With respect to formula 14, Y is O, S, N or P. In some embodiments, Y is O.

10 With respect to formula 14, R is H, -C₁₋₂₀ alkyl, -C₂₋₂₀ alkenyl, -C₂₋₂₀ alkynyl or -C₃₋₁₀ aryl group. In some embodiments, R is H.

With respect to formula 14, R¹⁰ is -C₁₋₂₀ alkyl, -C₅₋₁₀ aryl, -C₁₋₂₀ alkoxy, -C₅₋₁₀ aryloxy, -C₁₋₂₀ alkylamino, -C₁₋₂₀ protonated alkylamino, -C₁₋₂₀ alkylammonium, -C₁₋₁₂ alkylthiol, -CH₂C(=O)-C₁₋₆ alkyl, -CH₂C(=O)-O-C₁₋₆ alkyl,
15 -CH₂C(=O)-N(C₁₋₆ alkyl)₂, -CH₂C(=O)-N-(C₁₋₆ alkyl)-O-C₁₋₆ alkyl, -CH₂C(=O)-C₅₋₁₀ aryl, -CH₂C(=O)-O-C₅₋₁₀ aryl, -CH₂C(=O)-N(C₅₋₁₀ aryl)₂, -CH₂C(=O)-N-(C₅₋₁₀ aryl)-O-C₅₋₁₀ aryl, -C₁₋₂₀ alkylphosphino, -C₁₋₂₀ alkylphosphonium, -C₄₋₁₀ heterocyclic, -C₄₋₁₀ quaternized heterocyclic group. Each of the groups listed above can be optionally substituted with -C₁₋₂₀ alkyl,
20 -C₅₋₁₀ aryl, or a -C₄₋₁₀ heterocyclic group.

In some embodiments, R¹⁰ is C₁₋₆ alkyl, such as CH₃, C₂H₅, C₃H₇, C₄H₉, etc.; or -C₁₋₂₀ alkylamine, such as C₃₋₂₀N₁₋₂H₈₋₄₄, C₃₋₁₀NH₈₋₂₄, C₃₋₂₀N₂H₈₋₄₄, or C₃₋₂₀NOH₈₋₄₄, etc.

In some embodiments, R^{10} is C_{1-3} alkyl, $-(CH_2)_{0-4}N(C_{1-3}H_{3-7})_2$,



In some embodiments, R^{10} is isopropyl.

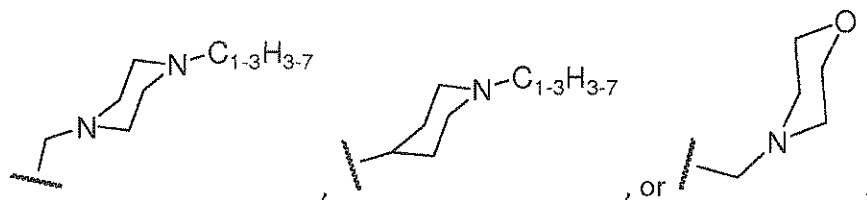


In some embodiments, R^{10} is

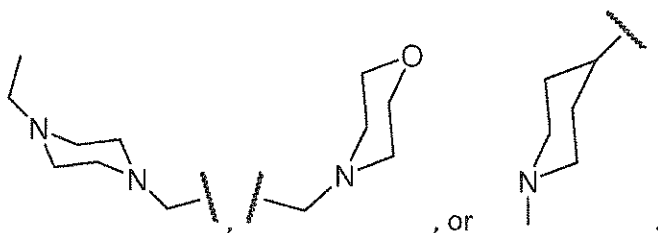
- 5 With respect to formula 14, each R^{11} is independently halogen, $-C_{1-20}$ alkyl, $-C_{1-20}$ haloalkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl, $-C_{5-10}$ aryl, $-C_{1-20}$ alkoxy, $-C_{2-20}$ alkenyloxy, $-C_{2-20}$ alkynyloxy, $-C_{5-10}$ aryloxy, $-C_{1-20}$ alkoxy carbonyl, $-C_{1-20}$ -alkylamino, $-C_{1-20}$ protonated alkylamino, $-C_{1-20}$ alkylammonium, amino, protonated amino, $-C_{4-10}$ heterocyclic, $-C_{4-10}$ quaternized
- 10 heterocyclic, $-C_{1-20}$ alkylphosphino, $-C_{1-20}$ alkylphosphonium, $-C_{1-20}$ alkylthiol, nitro, carboxyl, amido, sulfonamido, or $-C_{1-20}$ perhaloalkyl. Each of the groups listed above, except halogen, nitro, and carboxyl, is optionally substituted with $-C_{1-20}$ alkyl, $-C_{1-20}$ haloalkyl, $-C_{1-20}$ perhaloalkyl, $-C_{5-10}$ aryl, or a $-C_{4-10}$ heterocyclic group.

- 15 In some embodiments, R^{11} is nitro; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylamine, such as $C_{1-20}N_{1-2}H_{3-42}$, $C_{1-10}NH_{3-22}$, $C_{2-20}N_2H_{7-44}$, or $C_{2-20}NOH_{6-44}$, etc.

In some embodiments, R^{11} is nitro, $-(CH_2)_{0-4}N(C_{1-3}H_{3-7})_2$,



In some embodiments, R^{11} is nitro, $-CH_2N(CH_3)_2$, $-NHCOCH_2N(CH_3)_2$,



5 In some embodiments, R^4 is nitro.



In some embodiments, R^{11} is

In some embodiments, R^{11} is $-CH_2N(CH_3)_2$.

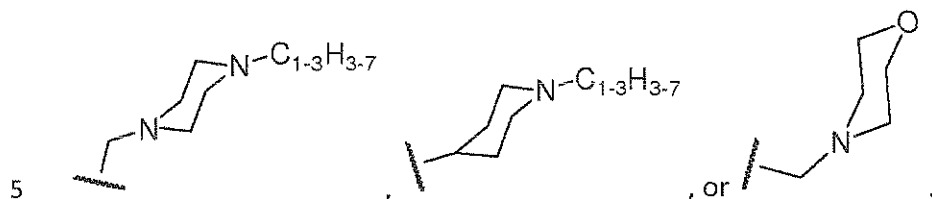
In some embodiments, R^{11} is $-NHCOCH_2N(CH_3)_2$.

10 With respect to formula 14, n is 0, 1, 2, 3, or 4. In some embodiments, n is 0. In some embodiments, n is 1.

With respect to formula 9 or 14, R^{12} is H, $-C_{1-6}$ alkyl, $-C_{1-6}$ haloalkyl, $-C_{5-10}$ aryl, $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, or $-C_{4-10}$ heterocyclic group. Each of the groups above, except H, is optionally substituted with $-C_{1-6}$ alkyl, $-C_{1-6}$ alkylamino or a $-C_{4-10}$ heterocyclic group.

In some embodiments, R^{12} is H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylamine, such as $C_{1-20}N_{1-2}H_{3-42}$, $C_{1-10}NH_{3-22}$, $C_{2-20}N_2H_{7-44}$, or $C_{2-20}NOH_{6-44}$, etc.

In some embodiments, R^{12} is H, C_{1-3} alkyl, $-(CH_2)_{0-4}N(C_{1-3}H_{3-7})_2$,

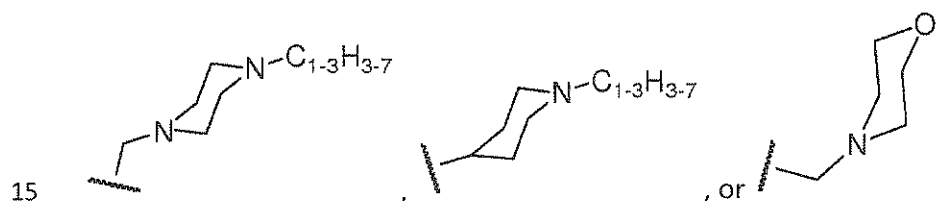


In some embodiments, R^{12} is H.

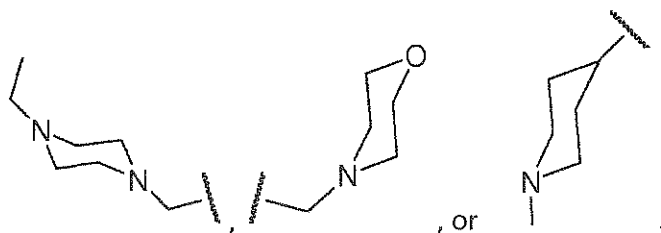
With respect to formula 9 or 14, R^{13} is H, $-C_{1-6}$ alkyl, $-C_{1-6}$ haloalkyl, $-C_{5-10}$ aryl, $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, or $-C_{4-10}$ heterocyclic group. Each of the groups above, except H, is optionally substituted with $-C_{1-6}$ alkyl, $-C_{1-6}$ alkylamino or a $-C_{4-10}$ heterocyclic group.

In some embodiments, R^{13} is H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylamine, such as $C_{1-20}N_{1-2}H_{3-42}$, $C_{1-10}NH_{3-22}$, $C_{2-20}N_2H_{7-44}$, or $C_{2-20}NOH_{6-44}$, etc.

In some embodiments, R^{13} is H, C_{1-3} alkyl, $-(CH_2)_{0-4}N(C_{1-3}H_{3-7})_2$,

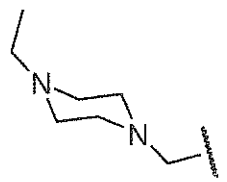


In some embodiments, R^{13} is H, $-CH_2N(CH_3)_2$, $-NHCOCH_2N(CH_3)_2$,



In some embodiments, R^{13} is H.

In some embodiments, R^{13} is $-\text{CH}_2\text{N}(\text{CH}_3)_2$.

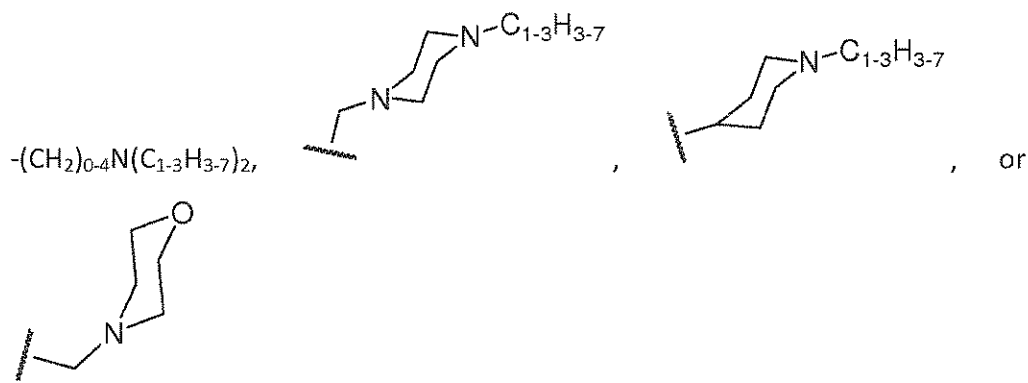


In some embodiments, R^{13} is

With respect to formula 9 or 14, each R^{14} is independently H, $-\text{C}_{1-6}$ alkyl,
 5 $-\text{C}_{1-6}$ haloalkyl, $-\text{C}_{5-10}$ aryl, $-\text{C}_{1-20}$ alkylamino, $-\text{C}_{1-20}$ alkylphosphino, or $-\text{C}_{4-10}$
 heterocyclic group. Each of the groups above, except H, is optionally substituted
 with $-\text{C}_{1-6}$ alkyl, $-\text{C}_{1-6}$ alkylamino or a $-\text{C}_{4-10}$ heterocyclic group.

In some embodiments, each R^{14} is independently H; C_{1-6} alkyl, such as
 CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-\text{C}_{1-20}$ alkylamine, such as $\text{C}_{1-20}\text{N}_{1-2}\text{H}_{3-42}$, $\text{C}_{1-10}\text{NH}_{3-22}$,
 10 $\text{C}_{2-20}\text{N}_2\text{H}_{7-44}$, or $\text{C}_{2-20}\text{NOH}_{6-44}$, etc.

In some embodiments, each R^{14} is independently H, C_{1-4} alkyl,



In some embodiments, at least one R^{14} is methyl.

15 In some embodiments, both R^{14} are methyl.

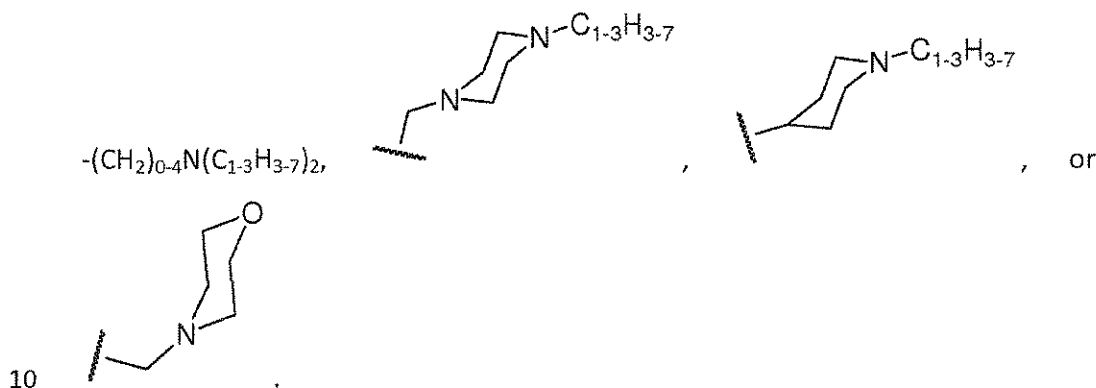
In some embodiments, at least one R^{14} is isopropyl.

In some embodiments, both R^{14} are isopropyl.

With respect to formula 9 or 14, each $R^{14'}$ is independently H, $-C_{1-6}$ alkyl, $-C_{1-6}$ haloalkyl, $-C_{5-10}$ aryl, $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, or $-C_{4-10}$ heterocyclic group. Each of the groups above, except H, is optionally substituted with $-C_{1-6}$ alkyl, $-C_{1-6}$ alkylamino or a $-C_{4-10}$ heterocyclic group.

- 5 In some embodiments, each $R^{14'}$ is independently H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylamine, such as $C_{1-20}N_{1-2}H_{3-42}$, $C_{1-10}NH_{3-22}$, $C_{2-20}N_2H_{7-44}$, or $C_{2-20}NOH_{6-44}$, etc.

In some embodiments, each $R^{14'}$ is independently H, C_{1-4} alkyl,



In some embodiments, at least one $R^{14'}$ is methyl.

In some embodiments, both $R^{14'}$ are methyl.

In some embodiments, at least one $R^{14'}$ is isopropyl.

In some embodiments, both $R^{14'}$ are isopropyl.

- 15 In some embodiments, both R^{14} and both $R^{14'}$ are methyl.

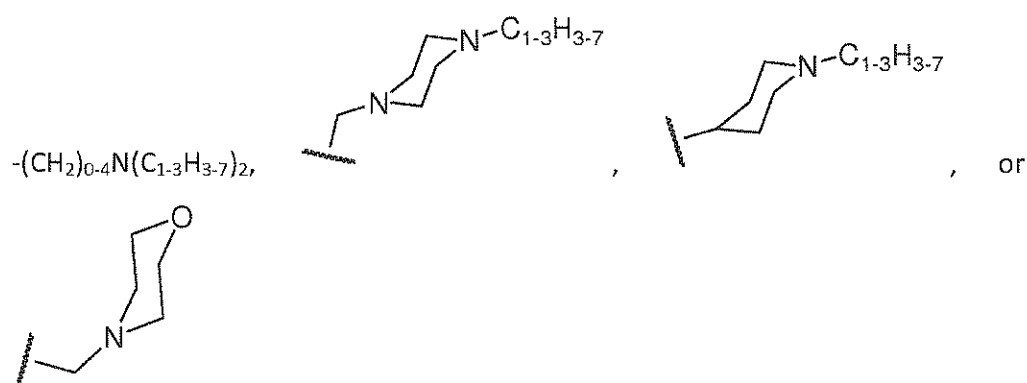
In some embodiments, both R^{14} and both $R^{14'}$ are isopropyl.

With respect to formula 9 or 14, each R^{15} is independently H, $-C_{1-6}$ alkyl, $-C_{1-6}$ haloalkyl, $-C_{5-10}$ aryl, $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, or $-C_{4-10}$

heterocyclic group. Each of the groups above, except H, is optionally substituted with $-C_{1-6}$ alkyl, $-C_{1-6}$ alkylamino or a $-C_{4-10}$ heterocyclic group.

- In some embodiments, each R^{15} is independently H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylamine, such as $C_{1-20}N_{1-2}H_{3-42}$, $C_{1-10}NH_{3-22}$,
 5 $C_{2-20}N_2H_{7-44}$, or $C_{2-20}NOH_{6-44}$, etc.

In some embodiments, each R^{15} is independently H, C_{1-4} alkyl,



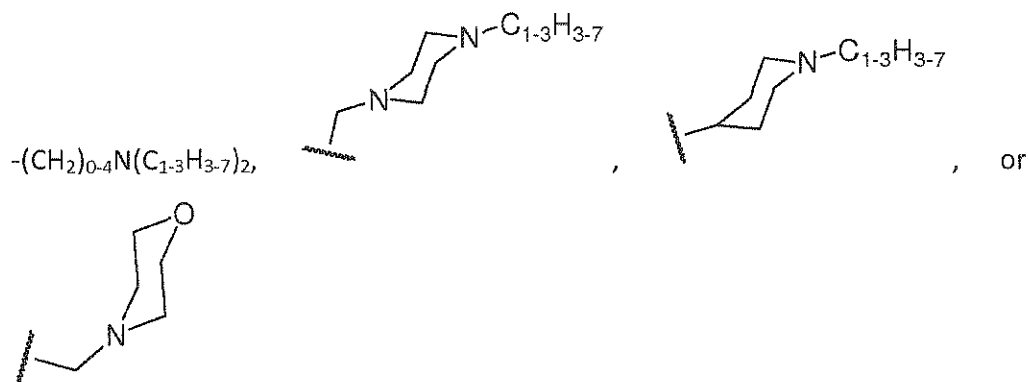
In some embodiments, at least one R^{15} is H.

- 10 In some embodiments, both R^{15} are H.

With respect to formula 9 or 14, each $R^{15'}$ is independently H, $-C_{1-6}$ alkyl, $-C_{1-6}$ haloalkyl, $-C_{5-10}$ aryl, $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, or $-C_{4-10}$ heterocyclic group. Each of the groups above, except H, is optionally substituted with $-C_{1-6}$ alkyl, $-C_{1-6}$ alkylamino or a $-C_{4-10}$ heterocyclic group.

- 15 In some embodiments, each $R^{15'}$ is independently H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylamine, such as $C_{1-20}N_{1-2}H_{3-42}$, $C_{1-10}NH_{3-22}$, $C_{2-20}N_2H_{7-44}$, or $C_{2-20}NOH_{6-44}$, etc.

In some embodiments, each $R^{15'}$ is independently H, C_{1-4} alkyl,



In some embodiments, at least one $R^{15'}$ is H.

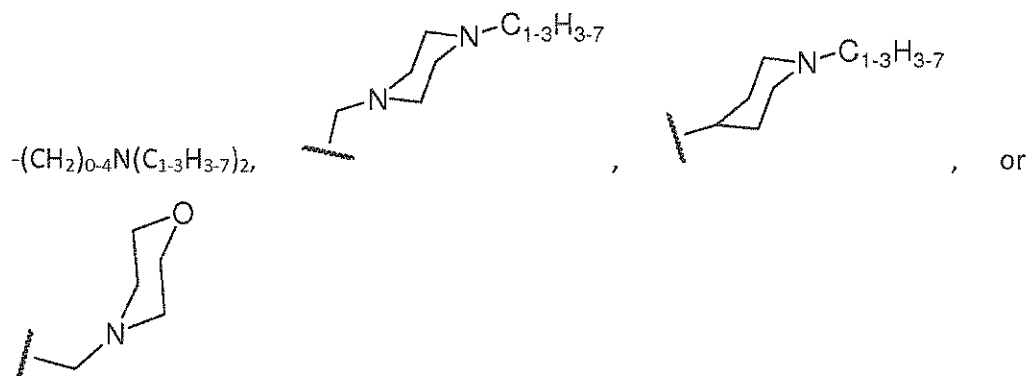
5 In some embodiments, both $R^{15'}$ are H.

In some embodiments, both R^{15} and both $R^{15'}$ are H.

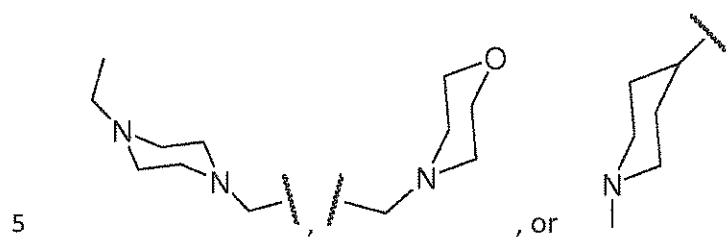
With respect to formula 9 or 14, each R^{16} is independently H, $-C_{1-6}$ alkyl, $-C_{1-6}$ haloalkyl, $-C_{5-10}$ aryl, $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, or $-C_{4-10}$ heterocyclic group. Each of the groups above, except H, is optionally substituted
 10 with $-C_{1-6}$ alkyl, $-C_{1-6}$ alkylamino or a $-C_{4-10}$ heterocyclic group.

In some embodiments, each R^{16} is independently H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylamine, such as $C_{1-20}N_{1-2}H_{3-42}$, $C_{1-10}NH_{3-22}$, $C_{2-20}N_2H_{7-44}$, or $C_{2-20}NOH_{6-44}$, etc.

In some embodiments, each R^{16} is independently H, C_{1-3} alkyl,



In some embodiments, R^{16} is H, C_{1-3} alkyl, $-CH_2N(CH_3)_2$, $-NHCOCH_2N(CH_3)_2$,



In some embodiments, at least one R^{16} is H.

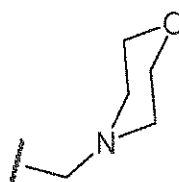
In some embodiments, both R^{16} are H.

In some embodiments, at least one R^{16} is methyl.

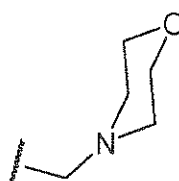
In some embodiments, both R^{16} are methyl.

10

In some embodiments, at least one R^{16} is

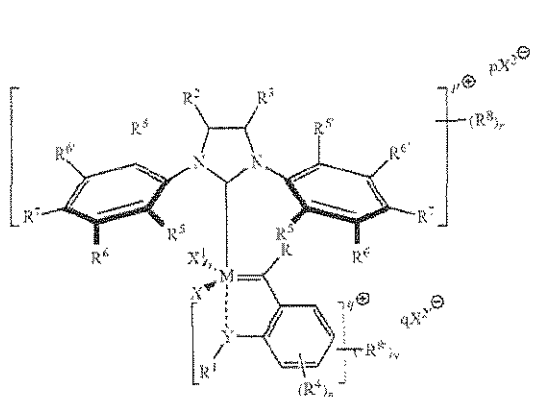


In some embodiments, both R^{16} are



With respect to formula 9 or 14, R^{12} and R^{13} , as well as R^{14} and R^{15} , as well as $R^{14'}$ and $R^{15'}$ may be optionally linked together to form a substituted or unsubstituted, fused -C₄₋₈ carbocyclic ring, or a substituted or unsubstituted, fused aromatic ring.

- 5 In one aspect, there is provided a complex of formula 1



wherein M is ruthenium or osmium;

X, X¹, X² and X^{2'} are, independently, inert ligands;

Y is O, S, N, or P;

- 10 R is H, —C₁₋₂₀ alkyl, —C₂₋₂₀ alkenyl, —C₂₋₂₀ alkynyl, or —C₅₋₁₀ aryl;

- R¹ is optionally substituted —C₁₋₂₀ alkyl, optionally substituted C₃₋₈ cycloalkyl, optionally substituted —C₂₋₂₀ alkenyl, optionally substituted —C₂₋₂₀ alkynyl, optionally substituted —C₅₋₁₀ aryl, optionally substituted —C₁₋₂₀ alkoxy, optionally substituted —C₂₋₂₀ alkenyloxy, optionally substituted —C₂₋₂₀ alkynyloxy, optionally substituted —C₅₋₁₀ aryloxy, optionally substituted —C₁₋₂₀ alkoxycarbonyl, optionally substituted —C₁₋₂₀ alkylamino, optionally substituted —C₁₋₂₀ alkylphosphino, optionally substituted C₁₋₂₀ alkylthiol, optionally substituted —C₁₋₂₀ quaternary alkylammonium, optionally substituted —C₁₋₂₀ alkylphosphonium, optionally substituted —C₁₋₂₀ alkylsulfonyl, optionally substituted —C₁₋₂₀

alkylosulfinyl, optionally substituted $-\text{CH}_2\text{C}(=\text{O})-\text{C}_{1-6}$ alkyl, optionally substituted $-\text{CH}_2\text{C}(=\text{O})-\text{O}-\text{C}_{1-6}$ alkyl, optionally substituted $-\text{CH}_2\text{C}(=\text{O})-\text{N}(\text{C}_{1-6} \text{ alkyl})_2$, optionally substituted $-\text{CH}_2\text{C}(=\text{O})-\text{N}-(\text{C}_{1-6} \text{ alkyl})-\text{O}-\text{C}_{1-6}$ alkyl, optionally substituted $-\text{CH}_2\text{C}(=\text{O})-\text{C}_{5-10}$ aryl, optionally substituted $-\text{CH}_2\text{C}(=\text{O})-\text{O}-\text{C}_{5-10}$ aryl, optionally substituted $-\text{CH}_2\text{C}(=\text{O})-\text{N}(\text{C}_{5-10} \text{ aryl})_2$, optionally substituted $-\text{CH}_2\text{C}(=\text{O})-\text{N}-(\text{C}_{5-10} \text{ aryl})-\text{O}-\text{C}_{5-10}$ aryl, optionally substituted $-\text{C}_{4-10}$ heterocyclic, or optionally substituted $-\text{C}_{4-10}$ quaternized heterocyclic, wherein each substituent is independently $-\text{C}_{1-20}$ alkyl, $-\text{C}_{5-10}$ aryl, or a $-\text{C}_{4-10}$ heterocyclic group;

R^1 may be optionally linked to X or X^1 to form a tridentate ligand;

R^2 and R^3 are, independently, H, optionally substituted $-\text{C}_{1-6}$ alkyl, optionally substituted $-\text{C}_{3-8}$ cycloalkyl, optionally substituted $-\text{C}_{5-10}$ aryl, optionally substituted $-\text{C}_{1-20}$ alkylamino, optionally substituted $-\text{C}_{1-20}$ alkylphosphino, optionally substituted $-\text{C}_{1-20}$ quaternary alkylammonium, or optionally substituted $-\text{C}_{1-20}$ alkylphosphonium, wherein each substituent is independently: $-\text{C}_{5-10}$ aryl, $-\text{C}_{4-10}$ heterocyclic, or a $-\text{C}_{4-10}$ quaternized heterocyclic group, which in turn may be substituted with at least one: nitro, $-\text{C}_{1-6}$ alkyl, $-\text{C}_{1-6}$ alkoxy, $-\text{C}_{5-10}$ aryl group or halogen;

R^2 and R^3 may be optionally linked together to form a substituted or unsubstituted, fused $-\text{C}_{4-8}$ carbocyclic ring, or a substituted or unsubstituted, fused aromatic ring;

R^4 is halogen, optionally substituted $-\text{C}_{1-20}$ alkyl, optionally substituted $-\text{C}_{2-20}$ alkenyl, optionally substituted $-\text{C}_{2-20}$ alkynyl, optionally substituted $-\text{C}_{5-10}$ aryl, optionally substituted $-\text{C}_{1-20}$ alkoxy, optionally substituted $-\text{C}_{2-20}$ alkenyloxy, optionally substituted $-\text{C}_{2-20}$ alkynyloxy, optionally

substituted $-C_{5-10}$ aryloxy, optionally substituted $-C_{1-20}$ alkoxy carbonyl, optionally substituted $-C_{1-20}$ alkylamino, optionally substituted $-C_{1-20}$ protonated alkylamino, optionally substituted amino, optionally substituted protonated amino, optionally substituted $-C_{1-20}$ alkylphosphino, optionally substituted $-C_{1-20}$ alkylthiol, optionally substituted $-C_{1-20}$ quaternary alkylammonium, optionally substituted $-C_{1-20}$ alkylphosphonium, optionally substituted $-C_{4-10}$ quaternized heterocyclic, nitro, carboxyl, optionally substituted amido, optionally substituted sulfonamido, or optionally substituted $-C_{1-20}$ perhaloalkyl; wherein each substituent is independently $-C_{1-20}$ alkyl, $-C_{1-20}$ perhaloalkyl, $-C_{5-10}$ aryl, or a $-C_{4-10}$ quaternized heterocyclic group;

n is 0, 1, 2, 3, or 4;

R^5 , $R^{5'}$, R^6 , $R^{6'}$, and R^7 are, independently, H, optionally substituted $-C_{1-6}$ alkyl, optionally substituted $-C_{1-20}$ alkylamino, optionally substituted $-C_{1-20}$ alkylphosphino, optionally substituted $-C_{1-20}$ quaternary alkylammonium, optionally substituted $-C_{1-20}$ alkylphosphonium, optionally substituted $-C_{4-10}$ heterocyclic, optionally substituted $-C_{4-10}$ quaternized heterocyclic group, wherein each substituent is independently a $-C_{4-10}$ quaternized heterocyclic, $-C_{1-6}$ alkyl, or $-C_{5-10}$ aryl, which in turn may be substituted with nitro, $-C_{1-6}$ alkyl, $-C_{1-6}$ alkoxy, $-C_{5-10}$ aryl group or halogen;

R^5 and R^6 , and $R^{5'}$ and $R^{6'}$ may be optionally linked together to form a substituted or unsubstituted, fused $-C_{4-8}$ carbocyclic ring, or a substituted or unsubstituted, fused aromatic ring;

R^8 is optionally substituted $-C_{1-20}$ alkyl, optionally substituted $-C_{3-8}$ cycloalkyl, optionally substituted $-C_{2-20}$ alkenyl, or optionally substituted $-C_{2-20}$ alkynyl; wherein each substituent is independently a halogen atom, $-C_5-$

aryl , $-\text{C}(=\text{O})-\text{C}_{1-6} \text{ alkyl}$, $-\text{C}(=\text{O})-\text{O}-\text{C}_{1-6} \text{ alkyl}$, $-\text{C}(=\text{O})-\text{N}(\text{C}_{1-6} \text{ alkyl})_2$, $-\text{C}(=\text{O})-\text{N}-(\text{C}_{1-6} \text{ alkyl})-\text{O}-\text{C}_{1-6} \text{ alkyl}$, $-\text{C}(=\text{O})-\text{C}_{5-10} \text{ aryl}$, $-\text{C}(=\text{O})-\text{O}-\text{C}_{5-10} \text{ aryl}$, $-\text{C}(=\text{O})-\text{N}(\text{C}_{5-10} \text{ aryl})_2$, or $-\text{C}(=\text{O})-\text{N}-(\text{C}_{5-10} \text{ aryl})-\text{O}-\text{C}_{5-10} \text{ aryl}$;

5 p is 1, 2, 3, 4, or 5;

r is 0, 1, 2, or 3;

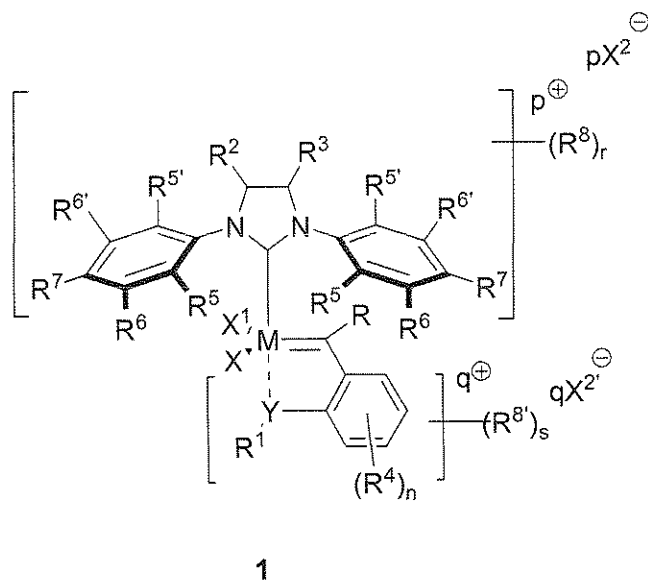
$R^{8'}$ is H, $-\text{C}_{1-20} \text{ alkyl}$, $\text{C}_{3-8} \text{ cycloalkyl}$, $-\text{C}_{2-20} \text{ alkenyl}$, or $-\text{C}_{2-20} \text{ alkynyl}$;

q is 0, 1, 2 or 3;

s is 0, 1, 2, or 3; and

10 wherein at least one substituent among R^2 , R^3 , R^5 , $R^{5'}$, R^6 , $R^{6'}$, and R^7 contains a quaternary onium group.

In some embodiments, a complex of general formula **15** is defined by general formula **1**



With respect to formula **1**, M is ruthenium or osmium. In some
5 embodiments, M is ruthenium.

With respect to formula **1**, X, X¹, X² and X^{2'} are, independently, an inert
ligand.

In some embodiments, X is Cl or I. In some embodiments, X is Cl. In
some embodiments, X is I.

10 In some embodiments, both X and X¹ are Cl or I. In some embodiments,
both X and X¹ are Cl. In some embodiments, both X and X¹ are I.

In some embodiments, X^2 is Cl or I. In some embodiments, X^2 is Cl. In some embodiments, X^2 is I.

In some embodiments, $X^{2'}$ is Cl or I. In some embodiments, $X^{2'}$ is Cl. In some embodiments, $X^{2'}$ is I.

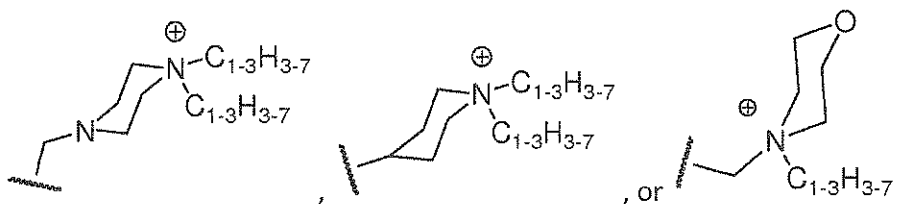
- 5 With respect to formula 1, Y is O, S, N, or P. In some embodiments, Y is O.

With respect to formula 1, R is H, $-C_{1-20}$ alkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl or $-C_{5-10}$ aryl group. In some embodiments, R is H.

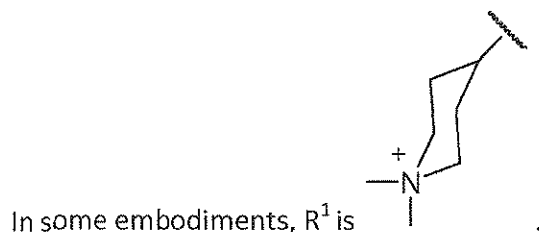
- With respect to formula 1, R^1 is $-C_{1-20}$ alkyl, C_{3-8} cycloalkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl, $-C_{5-10}$ aryl, $-C_{1-20}$ alkoxy, $-C_{2-20}$ alkenyloxy, $-C_{2-20}$ alkynyloxy, $-C_{5-10}$ aryloxy, $-C_{1-20}$ alkoxycarbonyl, $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, $-C_{1-20}$ alkylthiol, $-C_{1-20}$ alkylammonium, $-C_{1-20}$ alkylphosphonium, $-C_{1-20}$ alkylsulfonyl, $-C_{1-20}$ alkylsulfinyl, $-CH_2C(=O)-C_{1-6}$ alkyl, $-CH_2C(=O)-O-C_{1-6}$ alkyl, $-CH_2C(=O)-N(C_{1-6} \text{ alkyl})_2$, $-CH_2C(=O)-N-(C_{1-6} \text{ alkyl})-O-C_{1-6}$ alkyl, $-CH_2C(=O)-C_{5-10}$ aryl, $-CH_2C(=O)-O-C_{5-10}$ aryl, $-CH_2C(=O)-N(C_{5-10} \text{ aryl})_2$, $-CH_2C(=O)-N-(C_{5-10} \text{ aryl})-O-C_{5-10}$ aryl, $-C_{4-10}$ heterocyclic, $-C_{4-10}$ quaternized heterocyclic group. Each of these groups is optionally substituted with $-C_{1-20}$ alkyl, $-C_{5-10}$ aryl, or a $-C_{4-10}$ heterocyclic group.
- 10
- 15

- In some embodiments, R^1 is C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylammonium, such as $(C_{4-20}N_{1-2}H_{12-44})^+$, $(C_{4-10}NH_{12-24})^+$, $(C_{4-20}N_2H_{12-44})^+$, or a $(C_{4-20}NOH_{12-44})^+$, etc.
- 20

In some embodiments, R^1 is C_{1-3} alkyl, $-(CH_2)_{0-4}N^+(C_{1-3}H_{3-7})_3$,



In some embodiments, R^1 is isopropyl.

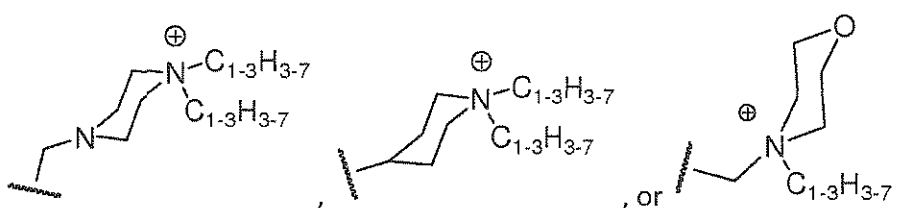


R^1 may be optionally linked to X or X^1 to form a tridentate ligand;

With respect to formula 1, R^2 is H, $-C_{1-6}$ alkyl, $-C_{3-8}$ cycloalkyl, $-C_{5-10}$ aryl,
 5 $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, $-C_{1-20}$ alkylammonium, or $-C_{1-20}$
 alkylphosphonium. Each of these groups, except H, is optionally substituted with
 $-C_{5-10}$ aryl, $-C_{4-10}$ heterocyclic, or a $-C_{4-10}$ quaternized heterocyclic group, which in
 turn may be substituted with at least one nitro, $-C_{1-6}$ alkyl, $-C_{1-6}$ alkoxy, $-C_{5-10}$ aryl
 group or halogen.

10 In some embodiments, R^2 is H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 ,
 etc.; or $-C_{1-20}$ alkylammonium, such as $(C_{4-20}N_{1-2}H_{12-44})^+$, $(C_{4-10}NH_{12-24})^+$,
 $(C_{4-20}N_2H_{12-44})^+$, or a $(C_{4-20}NOH_{12-44})^+$, etc.

In some embodiments, R^2 is H, C_{1-3} alkyl, $-(CH_2)_{0-4}N^+(C_{1-3}H_{3-7})_3$,



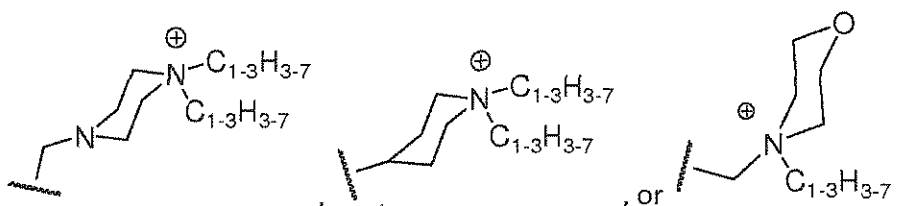
15 In some embodiments, R^2 is H.

With respect to formula 1, R^3 is H, $-C_{1-6}$ alkyl, $-C_{3-8}$ cycloalkyl, $-C_{5-10}$ aryl,
 $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, $-C_{1-20}$ alkylammonium, or $-C_{1-20}$
 alkylphosphonium. Each of these groups, except H, is optionally substituted with
 $-C_{5-10}$ aryl, $-C_{4-10}$ heterocyclic, or a $-C_{4-10}$ quaternized heterocyclic group, which in

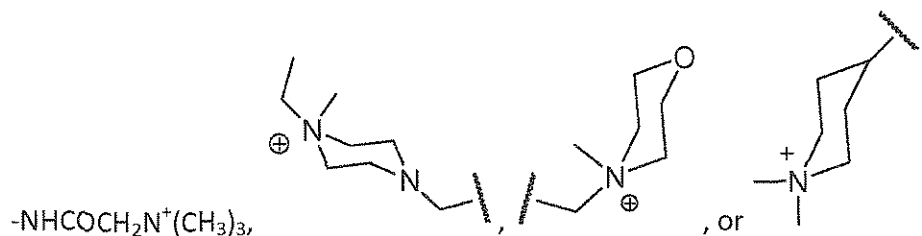
turn may be substituted with at least one nitro, $-C_{1-6}$ alkyl, $-C_{1-6}$ alkoxy, $-C_{5-10}$ aryl group or halogen.

In some embodiments, R^3 is H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylammonium, such as $(C_{4-20}N_{1-2}H_{12-44})^+$, $(C_{4-10}NH_{12-24})^+$,
 5 $(C_{4-20}N_2H_{12-44})^+$, or a $(C_{4-20}NOH_{12-44})^+$, etc.

In some embodiments, R^3 is H, C_{1-3} alkyl, $-(CH_2)_{0-4}N^+(C_{1-3}H_{3-7})_3$,

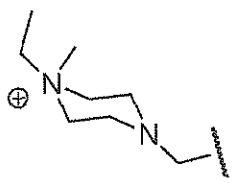


In some embodiments, R^3 is H, C_{1-3} alkyl, $-CH_2N^+(CH_3)_3$,



10 In some embodiments, R^3 is H.

In some embodiments, R^3 is $-CH_2N^+(CH_3)_3$.



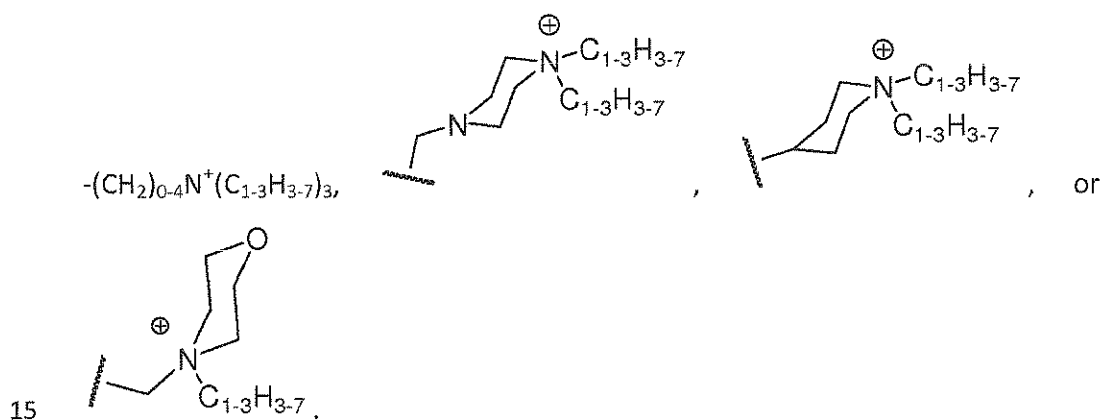
In some embodiments, R^3 is

With respect to formula 1, R^2 and R^3 may be optionally linked together to form a substituted or unsubstituted, fused $-C_{4-8}$ carbocyclic ring, or a substituted
 15 or unsubstituted, fused aromatic ring.

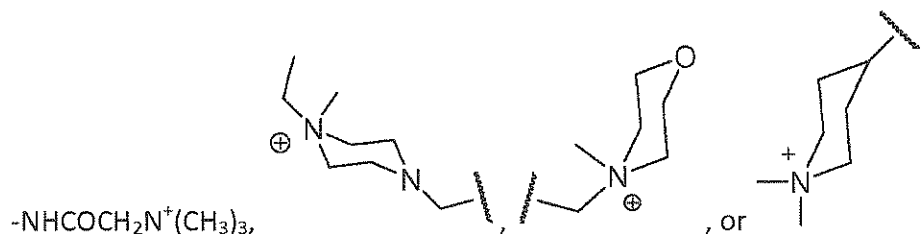
With respect to formula 1, each R^4 is independently halogen, $-C_{1-20}$ alkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl, $-C_{5-10}$ aryl, $-C_{1-20}$ alkoxy, $-C_{2-20}$ alkenyloxy, $-C_{2-20}$ alkynyloxy, $-C_{5-10}$ aryloxy, $-C_{1-20}$ alkoxy carbonyl, $-C_{1-20}$ alkylamino, $-C_{1-20}$ protonated alkylamino, amino, protonated amino, $-C_{1-20}$ alkylphosphino, $-C_{1-20}$ alkylthiol, $-C_{1-20}$ alkylammonium, $-C_{1-20}$ alkylphosphonium, $-C_{4-10}$ quaternized heterocyclic, nitro, carboxyl, amido, sulfonamido, or a $-C_{1-20}$ perhaloalkyl group. Each of these, except halogen, nitro, and carboxyl, is optionally substituted with $-C_{1-20}$ alkyl, $-C_{1-20}$ perhaloalkyl, $-C_{5-10}$ aryl, or a $-C_{4-10}$ quaternized heterocyclic group.

10 In some embodiments, each R^4 is independently nitro; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylammonium, such as $(C_{4-20}N_{1-2}H_{12-44})^+$, $(C_{4-10}NH_{12-24})^+$, $(C_{4-20}N_2H_{12-44})^+$, or a $(C_{4-20}NOH_{12-44})^+$, etc.

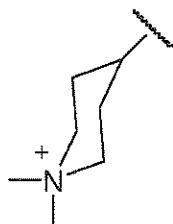
In some embodiments, each R^4 is independently nitro,



In some embodiments, each R^4 is independently nitro, $-CH_2N^+(CH_3)_3$,



In some embodiments, each R^4 is independently nitro.



In some embodiments, R^4 is .

In some embodiments, R^4 is $-\text{CH}_2\text{N}^+(\text{CH}_3)_3$.

In some embodiments, R^4 is $-\text{NHCOCH}_2\text{N}^+(\text{CH}_3)_3$.

With respect to formula 1, n is 0, 1, 2, 3, or 4;

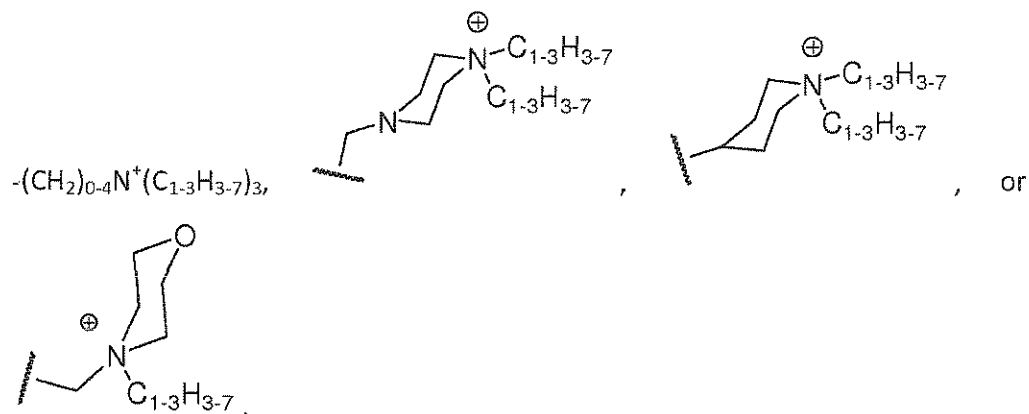
5 In some embodiments, n is 0.

In some embodiments, n is 1.

With respect to formula 1, each R^5 is independently H, $-\text{C}_{1-6}$ alkyl, $-\text{C}_{1-20}$ alkylamino, $-\text{C}_{1-20}$ alkylphosphino, $-\text{C}_{1-20}$ alkylammonium, $-\text{C}_{1-20}$ alkylphosphonium, $-\text{C}_{4-10}$ heterocyclic, or a $-\text{C}_{4-10}$ quaternized heterocyclic group. Each of these groups, except H, is optionally substituted with a
 10 $-\text{C}_{4-10}$ quaternized heterocyclic group, $-\text{C}_{1-6}$ alkyl, or $-\text{C}_{5-10}$ aryl, which in turn may be substituted with nitro, $-\text{C}_{1-6}$ alkyl, $-\text{C}_{1-6}$ alkoxy, $-\text{C}_{5-10}$ aryl group or halogen.

In some embodiments, each R^5 is independently H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-\text{C}_{1-20}$ alkylammonium, such as $(\text{C}_{4-20}\text{N}_{1-2}\text{H}_{12-44})^+$,
 15 $(\text{C}_{4-10}\text{NH}_{12-24})^+$, $(\text{C}_{4-20}\text{N}_2\text{H}_{12-44})^+$, or a $(\text{C}_{4-20}\text{NOH}_{12-44})^+$, etc.

In some embodiments, each R^5 is independently H, C_{1-4} alkyl,



In some embodiments, at least one R^5 is methyl.

5 In some embodiments, both R^5 are methyl.

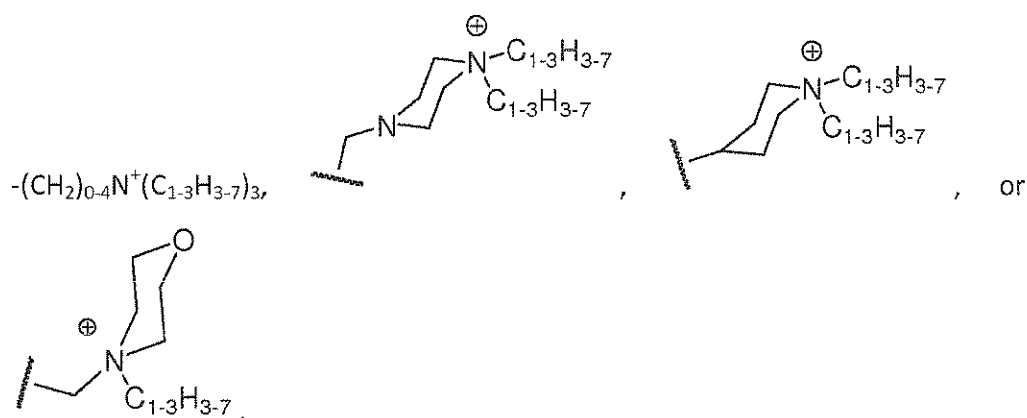
In some embodiments, at least one R^5 is isopropyl.

In some embodiments, both R^5 are isopropyl.

With respect to formula 1, each $R^{5'}$ is independently H, $-C_{1-6}$ alkyl, $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, $-C_{1-20}$ alkylammonium,
 10 $-C_{1-20}$ alkylphosphonium, $-C_{4-10}$ heterocyclic, or a $-C_{4-10}$ quaternized heterocyclic group. Each of these groups, except H, is optionally substituted with a $-C_{4-10}$ quaternized heterocyclic group, $-C_{1-6}$ alkyl, or $-C_{5-10}$ aryl, which in turn may be substituted with nitro, $-C_{1-6}$ alkyl, $-C_{1-6}$ alkoxy, $-C_{5-10}$ aryl group or halogen.

In some embodiments, each $R^{5'}$ is independently H; C_{1-6} alkyl, such as
 15 CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylammonium, such as $(C_{4-20}N_{1-2}H_{12-44})^+$, $(C_{4-10}NH_{12-24})^+$, $(C_{4-20}N_2H_{12-44})^+$, or a $(C_{4-20}NOH_{12-44})^+$, etc.

In some embodiments, each R^{5'} is independently H, C₁₋₄ alkyl,



In some embodiments, at least one R^{5'} is methyl.

5 In some embodiments, both $R^{5'}$ are methyl.

In some embodiments, at least one R^{5'} is isopropyl.

In some embodiments, both R^{5'} are isopropyl.

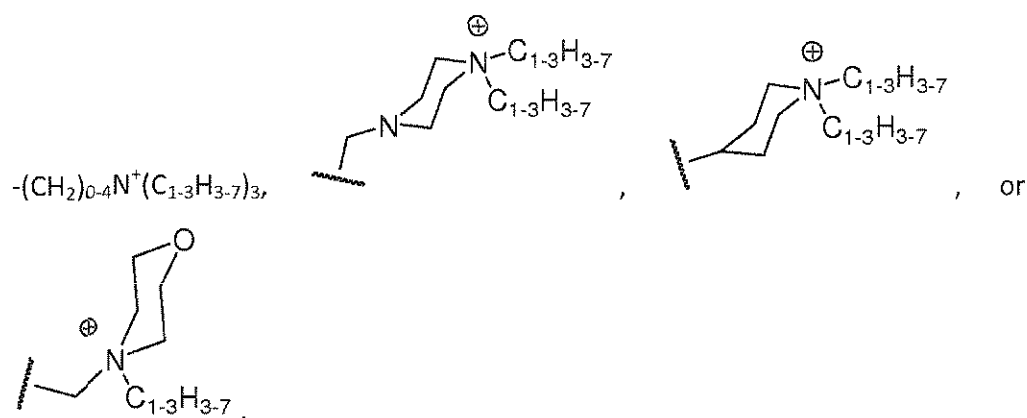
In some embodiments, both R^5 and both $R^{5'}$ are methyl.

In some embodiments, both R^5 and both $R^{5'}$ are isopropyl.

With respect to formula 1, each R⁶ is independently H, -C₁₋₆ alkyl, -C₁₋₂₀ alkylamino, -C₁₋₂₀ alkylphosphino, -C₁₋₂₀ alkylammonium, -C₁₋₂₀ alkylphosphonium, -C₄₋₁₀ heterocyclic, or a -C₄₋₁₀ quaternized heterocyclic group. Each of these groups, except H, is optionally substituted with a -C₄₋₁₀ quaternized heterocyclic group, -C₁₋₆ alkyl, or -C₅₋₁₀ aryl, which in turn may be substituted with nitro, -C₁₋₆ alkyl, -C₁₋₆ alkoxy, -C₅₋₁₀ aryl group or halogen.

In some embodiments, each R^6 is independently H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylammonium, such as $(C_{4-20}N_{1-2}H_{12-44})^+$, $(C_{4-10}NH_{12-24})^+$, $(C_{4-20}N_2H_{12-44})^+$, or a $(C_{4-20}NOH_{12-44})^+$, etc.

In some embodiments, each R^6 is independently H, C_{1-4} alkyl,



In some embodiments, at least one R^6 is H.

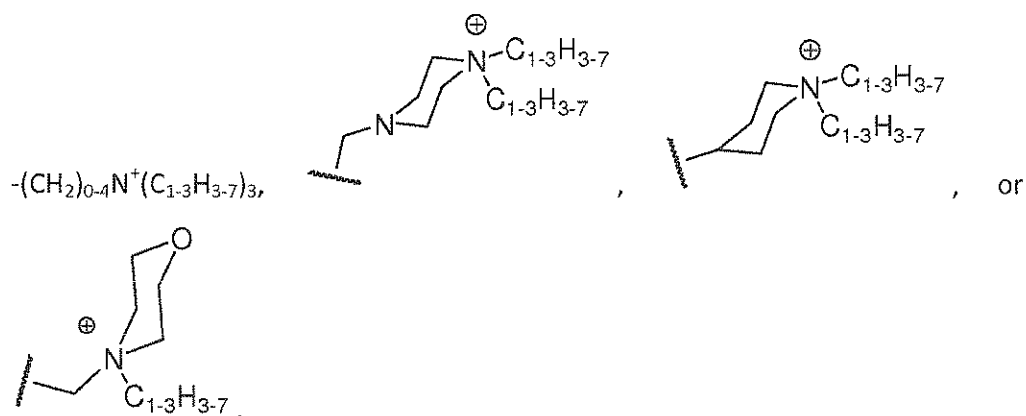
5 In some embodiments, both R^6 are H.

With respect to formula 1, each $R^{6'}$ is independently H, $-C_{1-6}$ alkyl, $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, $-C_{1-20}$ alkylammonium, $-C_{1-20}$ alkylphosphonium, $-C_{4-10}$ heterocyclic, or a $-C_{4-10}$ quaternized heterocyclic group. Each of these groups, except H, is optionally substituted with a

10 $-C_{4-10}$ quaternized heterocyclic group, $-C_{1-6}$ alkyl, or $-C_{5-10}$ aryl, which in turn may be substituted with nitro, $-C_{1-6}$ alkyl, $-C_{1-6}$ alkoxy, $-C_{5-10}$ aryl group or halogen.

In some embodiments, each $R^{6'}$ is independently H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylammonium, such as $(C_{4-20}N_{1-2}H_{12-44})^+$, $(C_{4-10}NH_{12-24})^+$, $(C_{4-20}N_2H_{12-44})^+$, or a $(C_{4-20}NOH_{12-44})^+$, etc.

In some embodiments, each $R^{6'}$ is independently H, C_{1-4} alkyl,



In some embodiments, at least one $R^{6'}$ is H.

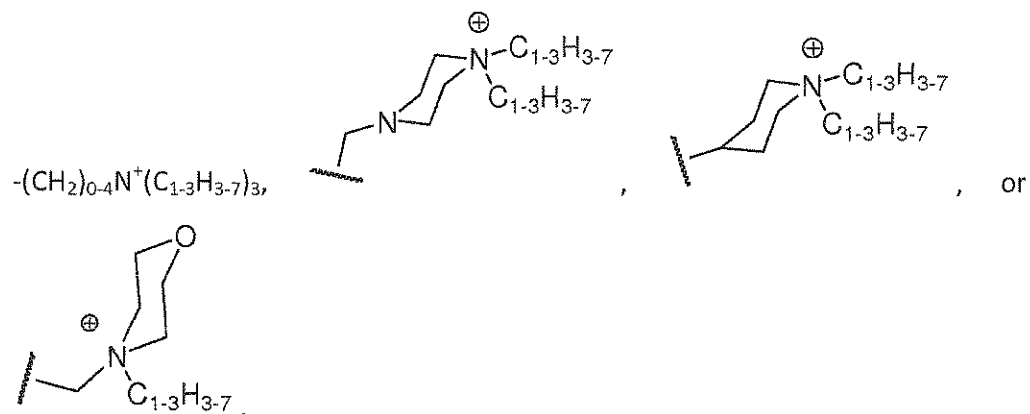
5 In some embodiments, both $R^{6'}$ are H.

In some embodiments, both R^6 and both $R^{6'}$ are H.

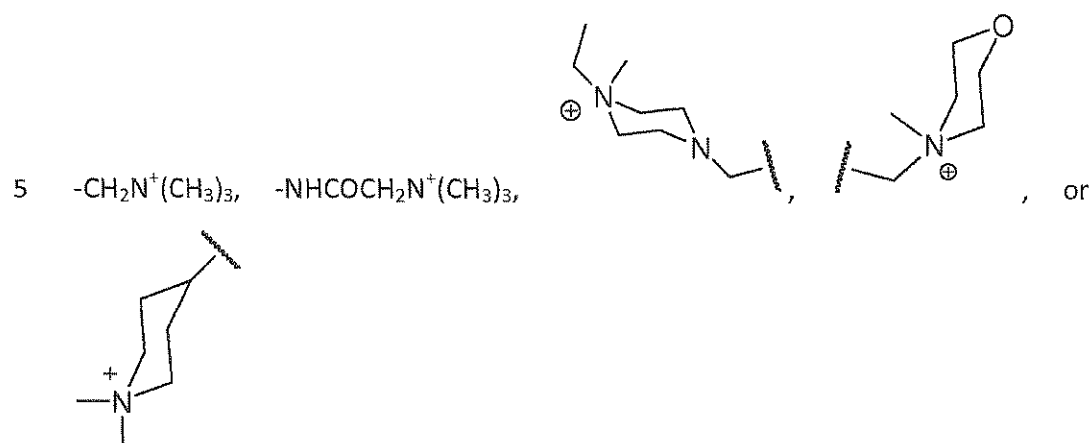
With respect to formula 1, each R^7 is independently H, $-C_{1-6}$ alkyl, $-C_{1-20}$ alkylamino, $-C_{1-20}$ alkylphosphino, $-C_{1-20}$ alkylammonium, $-C_{1-20}$ alkylphosphonium, $-C_{4-10}$ heterocyclic, or a $-C_{4-10}$ quaternized heterocyclic group. Each of these groups, except H, is optionally substituted with a $-C_{4-10}$ quaternized heterocyclic group, $-C_{1-6}$ alkyl, or $-C_{5-10}$ aryl, which in turn may be substituted with nitro, $-C_{1-6}$ alkyl, $-C_{1-6}$ alkoxy, $-C_{5-10}$ aryl group or halogen.

15 In some embodiments, each R^7 is independently H; C_{1-6} alkyl, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , etc.; or $-C_{1-20}$ alkylammonium, such as $(C_{4-20}N_{1-2}H_{12-44})^+$, $(C_{4-10}NH_{12-24})^+$, $(C_{4-20}N_2H_{12-44})^+$, or a $(C_{4-20}NOH_{12-44})^+$, etc.

In some embodiments, each R^7 is independently H, C_{1-3} alkyl,



In some embodiments, each R^7 is independently H, C_{1-3} alkyl,

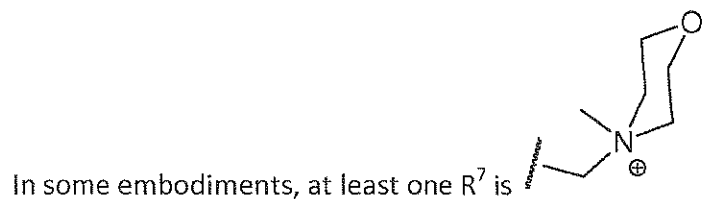


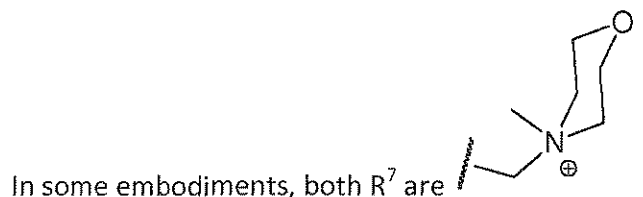
In some embodiments, at least one R^7 is H.

In some embodiments, both R^7 are H.

In some embodiments, at least one R^7 is methyl.

10 In some embodiments, both R^7 are methyl.





With respect to formula 1, R⁵ and R⁶, as well as R^{5'} and R^{6'} may be optionally linked together to form a substituted or unsubstituted, fused -C₄₋₈ carbocyclic ring, or a substituted or unsubstituted, fused aromatic ring.

- 5 With respect to formula 1, each R⁸ is independently -C₁₋₂₀ alkyl, -C₃₋₈ cycloalkyl, -C₂₋₂₀ alkenyl, or -C₂₋₂₀ alkynyl. Each of these is optionally substituted with one or more halogen atoms, -C₅₋₁₀ aryl, -C(=O)-C₁₋₆ alkyl, -C(=O)-O-C₁₋₆ alkyl, -C(=O)-N(C₁₋₆ alkyl)₂, -C(=O)-N-(C₁₋₆ alkyl)-O-C₁₋₆ alkyl, -C(=O)-C₅₋₁₀ aryl, -C(=O)-O-C₅₋₁₀ aryl, -C(=O)-N(C₅₋₁₀ aryl)₂, or
 10 -C(=O)-N-(C₅₋₁₀ aryl)-O-C₅₋₁₀ aryl group;

With respect to formula 1, p is 1, 2, 3, 4, or 5.

With respect to formula 1, r is 0, 1, 2, or 3.

With respect to formula 1, each R^{8'} is independently H, -C₁₋₂₀ alkyl, C₃₋₈ cycloalkyl, -C₂₋₂₀ alkenyl, or -C₂₋₂₀ alkynyl.

- 15 With respect to formula 1, q is 0, 1, 2 or 3.

With respect to formula 1, s is 0, 1, 2, or 3.

With respect to formula 1, at least one substituent among R², R³, R⁵, R^{5'}, R⁶, R^{6'}, R⁷ contains a quaternary onium group.

- In some embodiments, a complex of formula 1, obtained by a method
 20 described herein, may be optionally subjected to a further reaction with a compound of formula R^{8'}X^{2'}, giving a different complex of formula 1, wherein R^{8'} and X^{2'} are as defined above.

In some embodiments, in formula **14** symbol M is ruthenium;

X and X¹ are an inert ligand;

Y is O;

R¹⁰ is -C₁₋₁₂ alkyl, -C₁₋₁₂ haloalkyl, -C₅₋₁₀ aryl, -C₁₋₁₂ alkoxy, -C₅₋₁₀ aryloxy,
5 -C₁₋₁₂ alkoxy carbonyl, -C₁₋₁₂ alkylamino, -C₄₋₁₀ heterocyclic group, each optionally
substituted with -C₁₋₁₂ alkyl, -C₅₋₁₀ aryl or -C₄₋₁₀ heterocyclic group;

R¹¹ is halogen, -C₁₋₁₂ alkyl, -C₁₋₁₂ haloalkyl, aryl, -C₁₋₁₂ alkoxy, -C₅₋₁₀ aryloxy,
-C₁₋₁₂ alkoxy carbonyl, -C₁₋₁₂ alkylamino, amino, -C₁₋₁₂ alkylphosphino, -C₄₋₁₀
heterocyclic, nitro, carboxyl, amido, sulfonamido group; each optionally
10 substituted with -C₁₋₁₂ alkyl, -C₁₋₁₂ haloalkyl, -C₁₋₁₂ perhaloalkyl, -C₅₋₁₀ aryl, -C₄₋₁₀
heterocyclic group;

n is 0, 1 or 2;

R¹², R¹³, R¹⁴, R^{14'}, R¹⁵, R^{15'}, R¹⁶ are, independently, H, -C₁₋₆ alkyl, -C₁₋₆
haloalkyl, -C₅₋₁₀ aryl, -C₁₋₆ alkylamino, -C₁₋₆ alkylphosphino, -C₄₋₁₀ heterocyclic
15 group, each optionally substituted with -C₁₋₆ alkyl or -C₄₋₁₀ heterocyclic group;

R¹² and R¹³ as well as R¹⁴ and R¹⁵ as well as R^{14'} and R^{15'} may be optionally
linked together to form a substituted or unsubstituted, fused -C₄₋₈ carbocyclic
ring, or a substituted or unsubstituted, fused aromatic ring.

In some embodiments related to formula **14** symbol M is ruthenium;

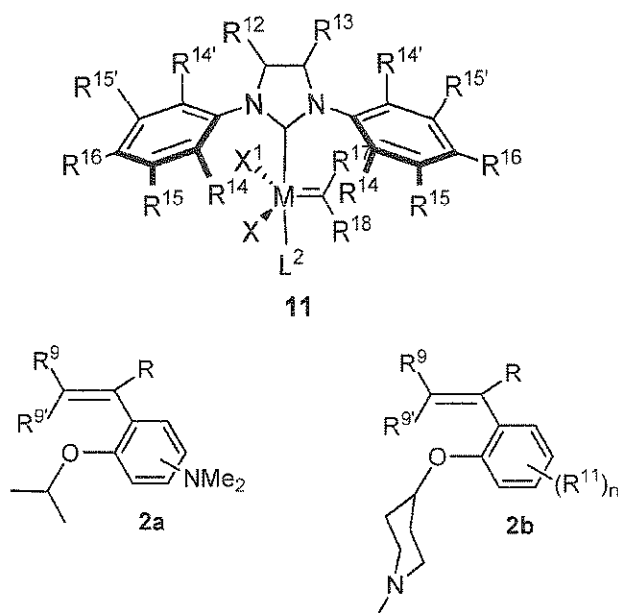
20 X, X¹ are independently Cl, Br or I;

R is H;

R¹⁰ is *iso*-propyl group or 1-methyl-4-piperidinyl group; R¹¹ is a nitro or
-NMe₂ group; and/or

n is 0 or 1.

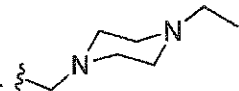
In some embodiments, the compound of formula **14** is obtained by reacting the compound of formula **11** with an intermediate of formula **2a** or **2b**.



5 All groups of formula **11** are as defined above.

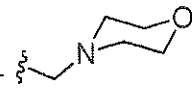
With respect to formula **2a** or formula **2b**, R is H; R^9 , $R^{9'}$ are a methyl or ethyl group; R^{11} is an electron acceptor group; and n is 0 or 1.

In some embodiments, in formula **9**:

substituents R^{12} , R^{13} are, independently, H, $-CH_2NMe_2$, or  ;

10 R^{14} , $R^{14'}$ are a methyl or *iso*-propyl group;

R^{15} , $R^{15'}$ are H; and/or

R^{16} is H, methyl, or .

In some embodiments, the reaction is carried out in R^8X^2 as a solvent. In some embodiments, R^8X^2 is CH_3Cl , CH_3I , CH_3Br , $(CH_3)_2SO_4$.

In some embodiments, the reaction is carried out in a solvent selected from solvents such as methanol, ethanol, ethyl acetate, *iso*-propanol, *tert*-butanol, *sec*-butanol, diethyl ether, *n*-propyl ether, diisopropyl ether, *tert*-butyl-methyl ether, cyclopentyl-methyl ether, 1,2-dioxane, 1,3-dioxane,
5 1,4-dioxane, dimethylformamide, tetrahydrofuran, dichloromethane, dichloroethane, trichloromethane, tetrachloromethane, tetrachloroethane, pentane, hexane, heptane, benzene, toluene, xylene or any mixture thereof. In some embodiments, a solvent is selected from the group consisting of methanol, ethanol, dichloromethane or ethyl acetate or any mixture thereof.

10 In some embodiments, $\text{TR}^{19}(\text{R}^{19'}) (\text{R}^{19''})$ is trimethylamine.

In some embodiments, the reaction is carried out at a temperature in the range from 0°C to 120°C or from 20°C to 80°C.

In some embodiments, the reaction is carried out within the period from 0.1 hour to 96 hours, or from 1 hour to 72 hours.

15 In some embodiments, the reaction is carried out under atmospheric pressure.

In some embodiments, the reaction is carried out under elevated pressure.

Some embodiments relate to compositions of matter comprising, or consisting essentially of, compounds that are complexes of general formula 1, as
20 described above.

With respect to formula 1, in some embodiments:

symbol M is ruthenium;

X, X^1 , X^2 and $\text{X}^{2'}$ are, independently, halogen, -C₁₋₅ carboxyl, -C₁₋₆ alkyl, -C₅₋₁₀ aryl, -C₁₋₆ alkoxy, -C₅₋₁₀ aryloxy, -C₁₋₅ alkylthiol, -C₁₋₅ alkylsulfonyl, -CH₃SO₄, benzoate, or
25 benzoic group;

Y is O, S or N;

R is H, -C₁₋₅ alkyl or -C₅₋₁₀ aryl group;

R¹ is -C₁₋₆ alkyl, C₃₋₈ cycloalkyl, -C₅₋₁₀ aryl, -C₅₋₁₀ aryloxy, -C₁₋₆ alkylamino, -C₁₋₆ alkylammonium, -C₄₋₁₀ heterocyclic, -C₄₋₁₀ quaternized *N*-heterocyclic,
 5 -CH₂C(=O)-C₁₋₆ alkyl, -CH₂C(=O)-O-C₁₋₆ alkyl, -CH₂C(=O)-N(C₁₋₆ alkyl)₂,
 -CH₂C(=O)-N-(C₁₋₆ alkyl)-O-C₁₋₆ alkyl, -CH₂C(=O)-C₅₋₁₀ aryl, -CH₂C(=O)-O-C₅₋₁₀ aryl,
 -CH₂C(=O)-N(C₅₋₁₀ aryl)₂, -CH₂C(=O)-N-(C₅₋₁₀ aryl)-O-C₅₋₁₀ aryl group;

R², R³ are, independently, H, -C₁₋₆ alkyl, -C₁₋₂₀ alkylamino, -C₁₋₂₀ alkylammonium
 group, optionally substituted with -C₅₋₁₀ aryl, -C₄₋₁₀ *N*-heterocyclic, -C₄₋₁₀
 10 quaternized *N*-heterocyclic group, which each in turn may be substituted with
 one or more nitro, -C₁₋₅ alkyl, -C₁₋₅ alkoxy, phenyl group or halogen;

R² and R³ may be optionally linked together to form a substituted or
 unsubstituted, fused -C₄₋₈ carbocyclic ring, or a substituted or unsubstituted,
 fused aromatic ring;

15 R⁴ is halogen, -C₁₋₆ alkyl, -C₅₋₁₀ aryl, -C₁₋₆ alkoxy, -C₅₋₁₀ aryloxy, -C₁₋₆ alkoxy
 carbonyl, -C₁₋₂₀ protonated alkylamino, protonated amino, -C₄₋₁₀ heterocyclic,
 -C₁₋₁₂ alkylammonium, -C₄₋₁₀ quaternized *N*-heterocyclic, nitro, carboxyl, amido,
 sulfonamido, -C₁₋₂₀ perhaloalkyl group, each optionally substituted with
 -C₁₋₆ alkyl, -C₁₋₆ perhaloalkyl, -C₅₋₁₀ aryl, -C₄₋₁₀ quaternized *N*-heterocyclic group;

20 n is 0, 1, 2 or 3;

R⁵, R^{5'}, R⁶, R^{6'}, R⁷ are, independently, H, -C₁₋₆ alkyl, -C₁₋₁₆ alkylammonium,
 -C₄₋₁₀ quaternized *N*-heterocyclic group, each optionally substituted with -C₄₋₁₀
 quaternized heterocyclic group;

R⁸ is -C₁₋₆ alkyl group;

25 p is 1, 2, 3 or 4;

$R^{8'}$ is H, $-C_{1-6}$ alkyl; and/or

q is 0, 1 or 2.

In some embodiments related to formula 1:

M is ruthenium;

- 5 X, X^1 , X^2 and $X^{2'}$ are, independently, halogen, CF_3CO_2 , CH_3CO_2 , MeO, EtO, PhO, $(NO_2)PhO$, CH_3SO_3 , CF_3SO_3 , tosylate, CH_3SO_4 group;

Y is O;

R is H;

- 10 R^1 is $-C_{1-6}$ alkyl, $-C_{5-10}$ aryl, $-C_{1-6}$ alkylammonium, $-C_{4-10}$ quaternized *N*-heterocyclic group;

R^2 , R^3 are, independently, H, $-C_{1-6}$ alkyl, $-C_{1-12}$ alkylammonium group, which may be optionally substituted with $-C_{4-10}$ quaternized *N*-heterocyclic group, which in turn may be substituted with at least one $-C_{1-6}$ alkyl, $-C_{1-5}$ alkoxy, phenyl group or halogen;

- 15 R^4 is halogen, $-C_{5-10}$ aryl, $-C_{1-6}$ alkoxy, $-C_{5-10}$ aryloxy, $-C_{1-12}$ alkylammonium, $-C_{1-12}$ protonated alkylamino, protonated amino, $-C_{4-10}$ quaternized *N*-heterocyclic, nitro, amido, sulfonamido, $-C_{1-20}$ perhaloalkyl group, where each may be optionally substituted with $-C_{1-6}$ alkyl, $-C_{1-6}$ perhaloalkyl, $-C_{5-10}$ aryl, $-C_{4-10}$ quaternized *N*-heterocyclic group;

- 20 n is 0, 1 or 2;

R^5 , $R^{5'}$, R^6 , $R^{6'}$, R^7 are, independently, H, $-C_{1-6}$ alkyl, $-C_{1-12}$ alkylammonium, $-C_{4-10}$ quaternized *N*-heterocyclic group, each optionally substituted with $-C_{4-10}$ quaternized heterocyclic group;

R^8 is $-C_{1-6}$ alkyl group;

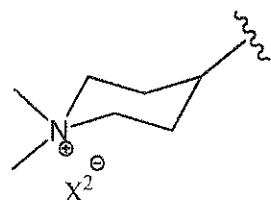
p is 1 or 2;

$R^{8'}$ is H, $-C_{1-6}$ alkyl group; and/or

q is 0 or 1;

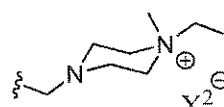
In some embodiments related to formula **1**, X, X^1 , X^2 and $X^{2'}$ are,
 5 independently, halogen; or X, X^1 , X^2 and $X^{2'}$ are, independently, chlorine or iodine.

In some embodiments related to formula **1**, R is H, R^1 is an *iso*-propyl group or



; and/or X^2 is an anionic ligand.

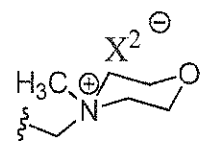
In some embodiments related to formula **1**, substituents R^2 , R^3 are,

10 independently, H, $-\overset{\oplus}{CH_2}NMe_3 X^{2-}$ or  group; and/or X^2 is an anionic ligand.

In some embodiments related to formula **1**, substituent R^4 is a nitro or

$-\overset{\oplus}{N}Me_3 X^{2-}$ or $-\overset{\oplus}{N}Me_3 X^{2-}$ group; X^2 and $X^{2'}$ are independently anionic ligands; and/or n is 0 or 1.

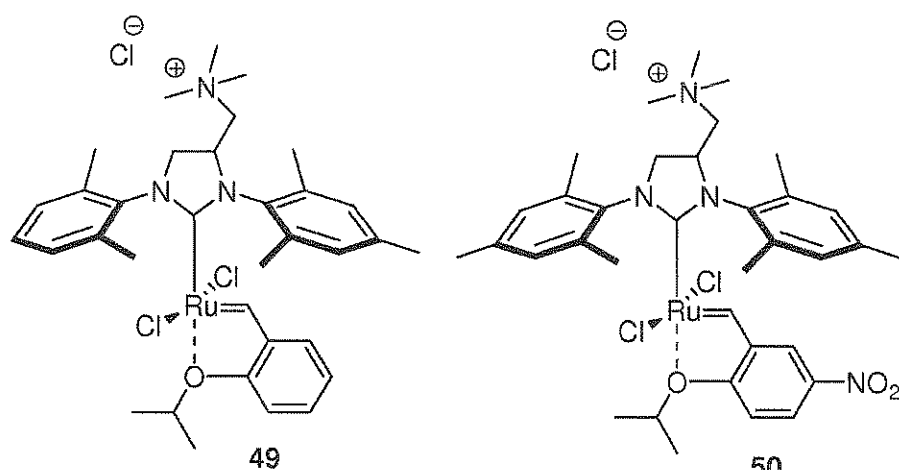
15 In some embodiments related to formula **1**, substituents R^5 and $R^{5'}$ are a methyl or *iso*-propyl group; R^6 and $R^{6'}$ are H; and/or R^7 is H, a methyl group or



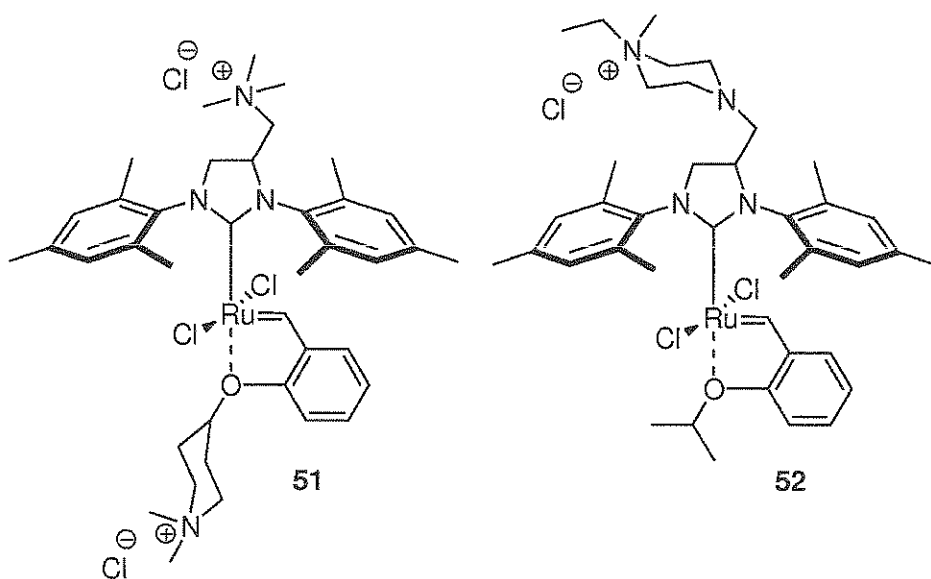
; and X^2 is an anionic ligand.

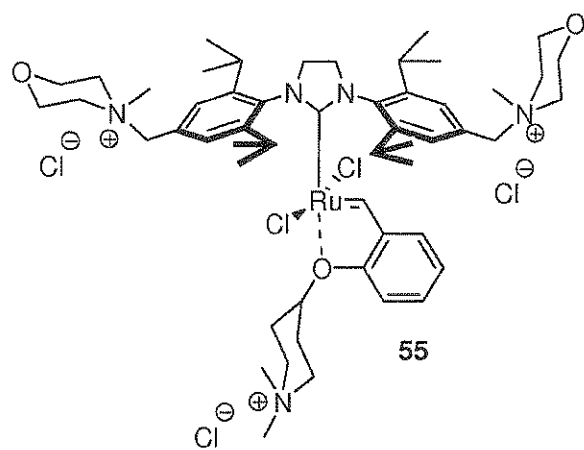
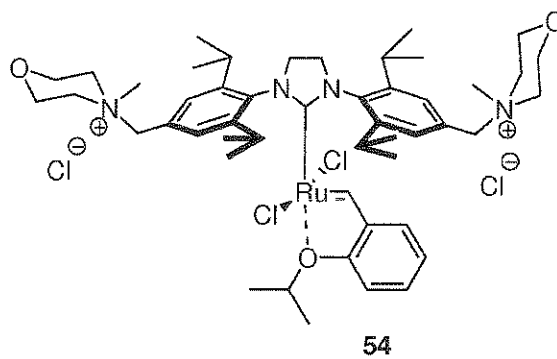
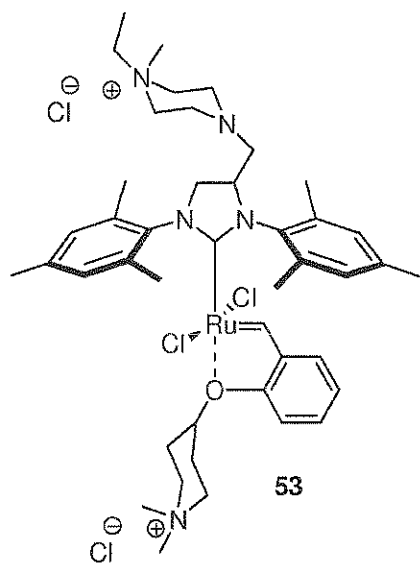
In some embodiments related to formula 1, substituent R^8 is a nitro or methyl group; p is 1 or 2; R^9 is H, a methyl group; q is 0 or 1.

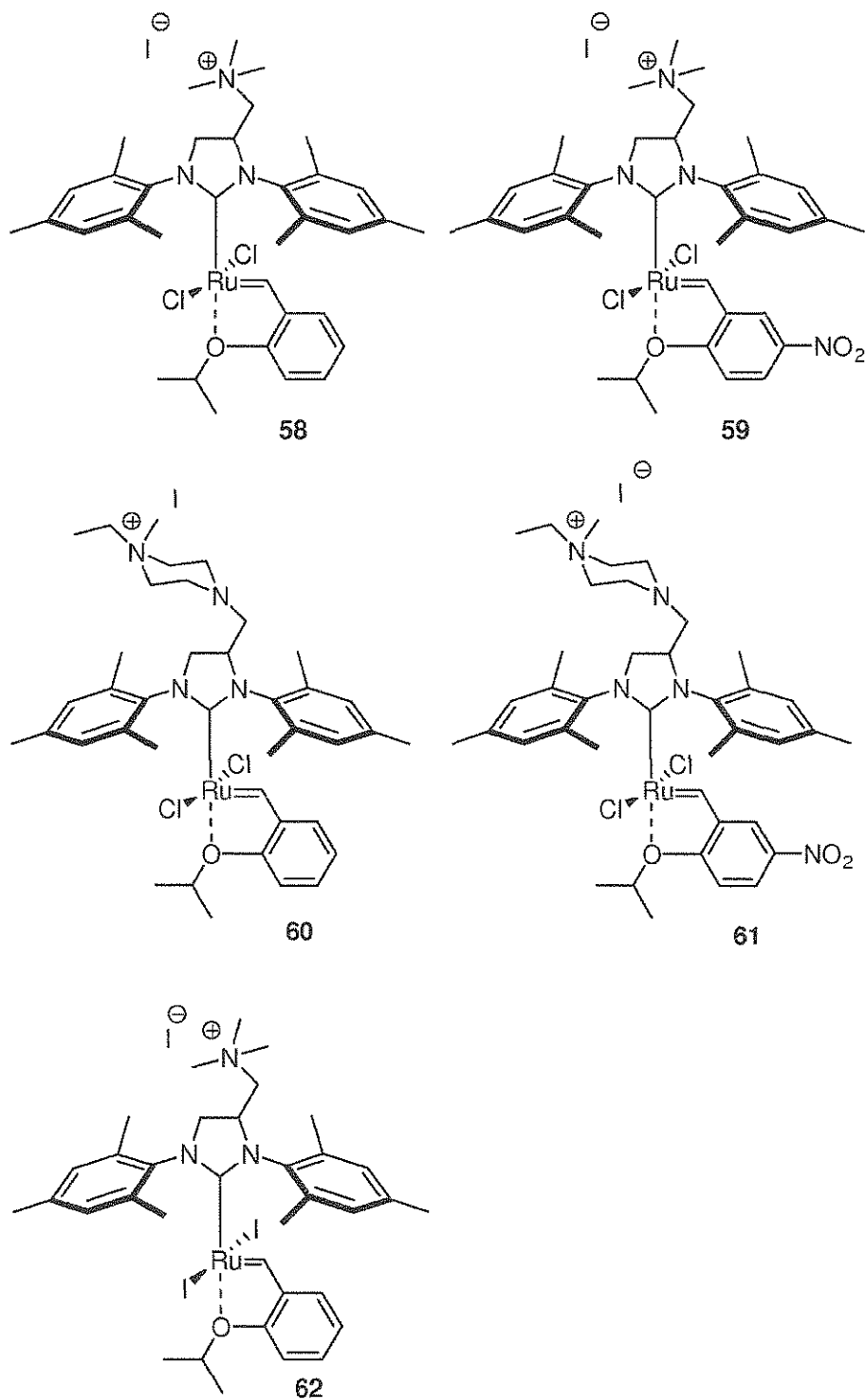
Some embodiments include complexes of any of formulae 49-55 and 58-62



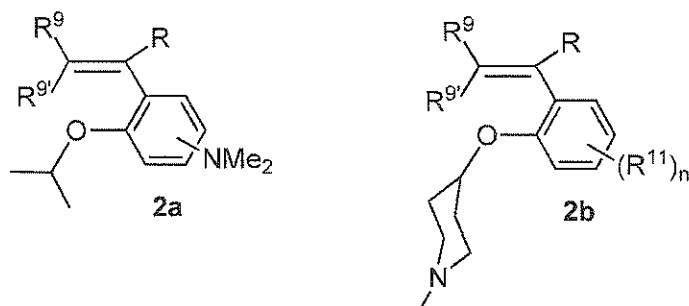
5







5 Some embodiments include intermediates of formulae **2a** and **2b**



wherein R is H;

$R^9, R^{9'}$ are a methyl or ethyl group;

m is 0 or 1; R¹¹ is an electron acceptor group; and/or

5 n is 0 or 1;

Some embodiments include the use of complexes of formula 1 as (pre)catalysts in metathesis reactions, or complexes of formula 1 are used as (pre)catalysts in a ring-closing metathesis (RCM), cross metathesis (CM), homometathesis, alken-alkyn (en-yn) metathesis.

10 In some embodiments, complexes of formula **1** are used as (pre)catalysts in a ring opening metathesis polymerization (ROMP).

Some embodiments include a method of carrying out an olefin metathesis reaction, characterized in that at least one olefin is contacted with a complex of formula **1** as a (pre)catalyst.

15 In some embodiments, the metathesis reaction is carried out in a mixture of water and an alcohol, or the metathesis reaction is carried out in water.

In some embodiments, the metathesis reaction is carried out in an organic solvent.

In some embodiments, a metathesis reaction product is purified from the heavy metal pollutants by filtering the reaction mixture through the adsorbent layer.

In some embodiments, a metathesis reaction product is purified from the heavy metal pollutants by adding an appropriate adsorbent to the reaction mixture and by filtration.

In some embodiments, the adsorbent is selected from the group consisting of silica, alumina, activated alumina, diatomaceous earth and activated carbon. In some embodiments, the adsorbent is silica gel.

In some embodiments, a reaction product is purified from the heavy metal pollutants by extraction with water.

The terms which are not defined below should have the broadest meaning known in the art.

Unless otherwise indicated, when a compound or chemical structural feature is referred to as being "optionally substituted," it includes a feature that has no substituents (i.e. unsubstituted), or a feature that is "substituted," meaning that the feature has one or more substituents, provided that adding the substituent results in a stable compound. The term "substituent" has the broadest meaning known to one of ordinary skill in the art, and includes a moiety that replaces one or more hydrogen atoms attached to a parent compound or structural feature. In some embodiments, a substituent may be an ordinary organic moiety known in the art, which may have a molecular weight (e.g. the sum of the atomic masses of the atoms of the substituent) of 15 g/mol to 50 g/mol, 15 g/mol to 100 g/mol, 15 g/mol to 150 g/mol, 15 g/mol to 200 g/mol, 15 g/mol to 300 g/mol, or 15 g/mol to 500 g/mol. In some embodiments, a substituent comprises, or consists of: 0-30, 0-20, 0-10, or 0-5 carbon atoms; and 0-30, 0-20, 0-10, or 0-5 heteroatoms, wherein each heteroatom may

independently be: N, O, S, Si, F, Cl, Br, or I; provided that the substituent includes one C, N, O, S, Si, F, Cl, Br, or I atom. Examples of substituents include, but are not limited to, alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, aryl, heteroaryl, hydroxy, alkoxy, aryloxy, acyl, acyloxy, alkylcarboxylate, thiol, alkylthio, amino, phosphine, ammonium, phosphonium, cyano, halo, thiocarbonyl, O-carbamyl, N-carbamyl, O-thiocarbamyl, N-thiocarbamyl, C-amido, N-amido, S-sulfonamido, N-sulfonamido, isocyanato, thiocyanato, isothiocyanato, nitro, silyl, sulfenyl, sulfinyl, sulfonyl, haloalkyl, haloalkoxyl, trihalomethanesulfonyl, trihalomethanesulfonamido, etc.

For convenience, the term "molecular weight" is used with respect to a moiety or part of a molecule to indicate the sum of the atomic masses of the atoms in the moiety or part of a molecule, even though it may not be a complete molecule.

The term "aryl group," as used herein, refers to an aromatic mono- or polycyclic hydrocarbon substituent of the indicated number of carbon atoms. The examples of an aryl group include but are not limited to phenyl, tolyl, naphthyl groups.

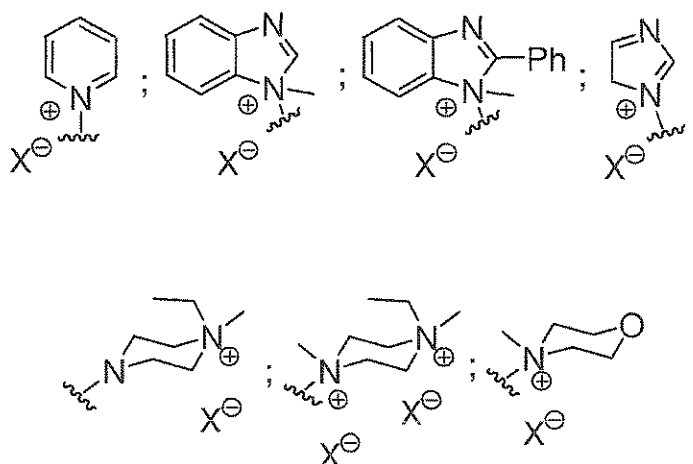
The term "heterocyclic group," as used herein, refers to an aromatic and non-aromatic cyclic substituent of the indicated number of carbon atoms in which any one or more carbon atoms is replaced with a heteroatom such as nitrogen, phosphorus, sulfur, oxygen, with the proviso that the ring of said group does not contain two adjacent oxygen or sulfur atoms. Non-aromatic heterocyclic groups may contain from 4 to 10 atoms in a ring, while aromatic heterocyclic groups must have at least 5 atoms in a ring. The heterocyclic groups include also benzo-fused ring systems. Examples of non-aromatic heterocyclic groups include but are not limited to pyrrolidinyl, tetrahydrofuranyl, dihydrofuranyl, tetrahydrothienyl, tetrahydropyranyl, dihydropyranyl, tetrahydrothiopyranyl, piperidino, morpholino, thiomorpholino, 2-pyrrolinyl,

indolyl groups. Examples of aromatic heterocyclic groups include but are not limited to pyridinyl, imidazolyl, pyrimidinyl, pyrazolyl, triazolyl, pyrazinyl, furyl, thienyl, isoxazolyl, oxazolyl groups. The foregoing groups may be C-attached or N-attached. For example, a substituent derived from attaching pyrrol may be

5 pyrrol-1-yl (N-attached) or pyrrol-3-yl (C-attached).

The term "quaternized heterocyclic group," as used herein, should be understood as the term "heterocyclic group" with the exception that any one or more heteroatoms, such as nitrogen and phosphorus, has four substituents, whereby the heteroatoms are positively charged. Examples of quaternized

10 heterocyclic groups include but are not limited to:



where X is an anionic ligand.

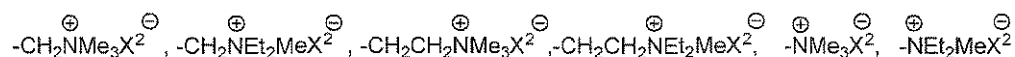
The term "halogen," as used herein, means an element selected from fluorine, chlorine, bromine, and iodine.

15 The term "alkyl group," as used herein, refers to a saturated, linear or branched hydrocarbon substituent of the indicated number of carbon atoms. Examples of alkyl groups include but are not limited to methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, tert-butyl, pentyl, iso-pentyl groups.

The term "alkylamino group," as used herein, should be understood as the term "alkyl group" with the exception that one or more hydrogen atoms have been substituted with a zero-order, first-order or second-order nitrogen atom. Examples of alkylamino groups include but are not limited to: -CH₂NMe₂,
 5 -CH₂NEt₂, -CH₂CH₂NMe₂, -CH₂CH₂NEt₂, -NMe₂, -NEt₂.

The term "alkylphosphine group," as used herein, should be understood as the term "alkylamino group" with the exception that a nitrogen atom has been substituted with a phosphorus atom.

The term "alkylammonium group," as used herein, should be understood
 10 as the term "alkyl group" with the exception that one or more hydrogen atoms have been substituted with a third-order nitrogen atom, whereby a nitrogen atom is positively charged. Examples of alkylammonium groups include but are not limited to:



15 wherein X² is an anionic ligand.

The term "alkylphosphonium group," as used herein, should be understood as the term "alkylamino group" with the exception that a nitrogen atom has been substituted with a phosphorus atom.

The term "alkenyl group," as used herein, refers to a non-cyclic, linear or
 20 branched alkenyl chain of the indicated number of carbon atoms and containing at least one double carbon-carbon bond. Examples of alkenyl groups include but are not limited to vinyl, allyl, 1-butenyl, 2-butenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl groups.

The term "alkynyl group," as used herein, refers to a non-cyclic, linear or
 25 branched alkynyl chain of the indicated number of carbon atoms and containing at least one triple carbon-carbon bond. Examples of alkynyl groups include but

are not limited to: ethynyl, propynyl, 1-butylnyl, 2-butylnyl, 1-hexynyl, 2-hexynyl, 5-hexynyl groups.

The term "cycloalkyl group," as used herein, refers to a saturated mono- or polycyclic hydrocarbon substituent of the indicated number of carbon atoms.

5 Examples of a cycloalkyl group include but are not limited to cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl groups.

The term "electron acceptor group," as used herein, refers to an organic substituent, which causes that the energy of the lowest unoccupied molecular orbital (LUMO) of the molecule substituted with such a group is lower than the LUMO energy of the unsubstituted molecule. An electron acceptor group reduces the electron density in the molecule by the inductive or resonance effect. Examples of an electron acceptor group include but are not limited to amido, aldehyde, ketone, sulfonyl, carboxyl, phenyl, I, Br, Cl, F, cyano, nitro group, aromatic group substituted with halogen atoms, aromatic group substituted with perfluorinated groups.

10
15

The term "inert ligand," as used herein, refers to an uncharged substituent, capable of coordinating with a ruthenium centre. Examples of inert ligands include but are not limited to amines, phosphines and oxides thereof, alkyl and aryl phosphites and phosphates, ethers, alkyl and aryl sulfides, alkyl and aryl halides, coordinated hydrocarbons, *N*-heterocyclic carbenes.

20

The term "anionic ligand," as used herein, refers to a substituent capable of coordinating with a metallic centre, having a charge capable of partial or complete compensation of a metallic centre charge. Examples of anionic ligands include but are not limited to fluoride, chloride, bromide, iodide, cyanide, cyanate, thiocyanate anions, anions of carboxylic acids, anions of alcohols and phenols, anions of thiols and thiophenols, anions of hydrocarbons with a delocalized charge (e.g. a cyclopentadiene anion), anions of (organo)sulfuric

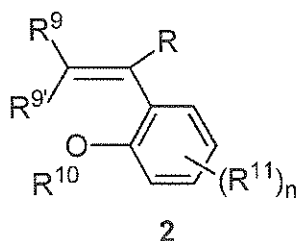
25

acids and of (organo)phosphoric acids and esters thereof (such as e.g. anions of alkylosulfonic acids and of arylosulphonic acids, anions of alkylophosphoric acids and of arylophosphoric acids, anions of alkyl and aryl esters of sulfuric acid, anions of alkyl and aryl esters of phosphoric acids, anions of alkyl and aryl esters of alkylphosphoric and arylphosphoric acids). Alternatively, an anionic ligand may have L^1 , L^2 groups combined like a catechol anion, an acetylacetonate anion, a salicylaldehyde anion. Anionic ligand (X , X^1 , X^2) and inert ligands (L^1 , L^2) may be linked together to form multidentate ligands, for example, bidentate ligand ($X \text{---} X^1$), tridentate ligand ($X \text{---} X^1 \text{---} L^1$), tetradentate ligand ($X \text{---} X^1 \text{---} L^1 \text{---} L^2$), bidentate ligand ($X^1 \text{---} L^1$), tridentate ligand ($X^1 \text{---} L^1 \text{---} L^2$), bidentate ligand ($L^1 \text{---} L^2$). Examples of such ligands include but are not limited to a catechol anion, an acetylacetonate anion, a salicylaldehyde anion.

The term "carbene," as used herein, means a particle containing an inert carbon atom of valency number being two and two unpaired valence electrons. The term "carbene" covers also carbene analogs in which a carbon atom is substituted with another chemical element; examples of such elements include but are not limited to boron, silicon, germanium, tin, lead, nitrogen, phosphorus, sulfur, selenium and tellurium.

The term "onium group," as used herein, refers to aliphatic, aromatic and heterocyclic quaternary ammonium, phosphonium or sulphonium group.

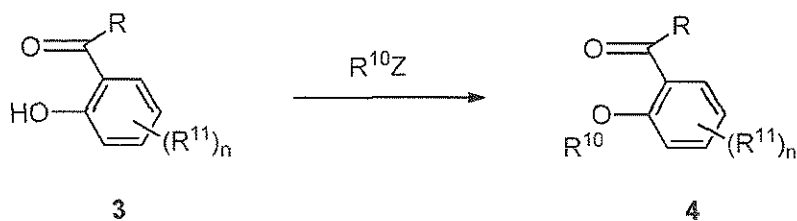
Intermediates in the synthesis of new complexes of formula 1 are alkoxy-styrene derivatives of formula 2:



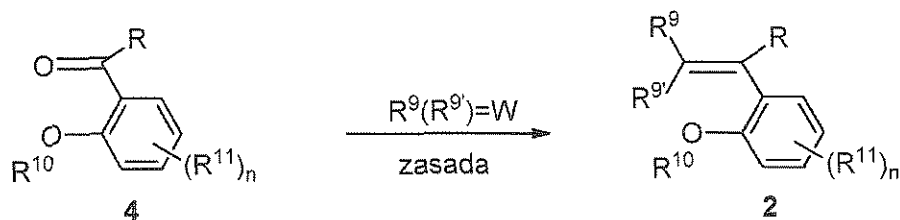
wherein R^{10} is $-C_{1-20}$ alkyl, $-C_{3-8}$ cycloalkyl, $-C_{2-20}$ alkenyl, $-C_{2-20}$ alkynyl, $-C_{5-10}$ aryl, $-C_{1-20}$ alkoxy, $-C_{2-20}$ alkenyloxy, $-C_{2-20}$ alkynyloxy, $-C_{5-10}$ aryloxy, $-C_{1-20}$ alkoxy carbonyl, $-C_{1-20}$ alkylamino, amino, $-C_{1-20}$ alkylphosphine, $-C_{1-20}$ alkylthiol, $-C_{1-20}$ alkylsulfonyl, $-C_{1-20}$ alkylsulfinyl, $-\text{CH}_2\text{C}(=\text{O})-\text{R}$, $-\text{CH}_2\text{C}(=\text{O})-\text{O}-\text{R}$, $-\text{CH}_2\text{C}(=\text{O})-\text{NR}_2$,
 5 $-\text{CH}_2\text{C}(=\text{O})-\text{N}-\text{R}-\text{O}-\text{R}$, $-C_{4-10}$ heterocyclic group, optionally substituted with $-C_{1-20}$ alkyl, $-C_{5-10}$ aryl or $-C_{4-10}$ heterocyclic group;

and the remaining substituents are as defined above.

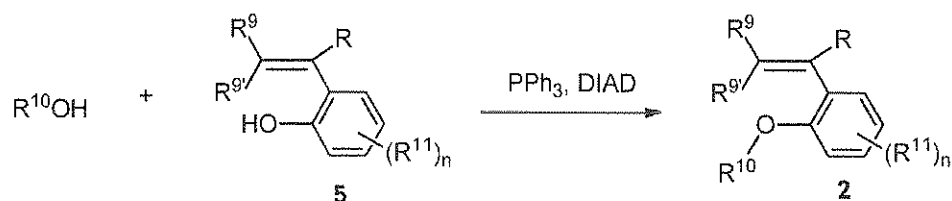
Compounds of formula **2** can be obtained from compounds of formula **3**, wherein R^{11} is as defined above, by reacting with an alkylating reagent $R^{10}\text{Z}$,
 10 wherein R^{10} is as defined above, Z is an iodine or bromine atom, to give compound **4**.



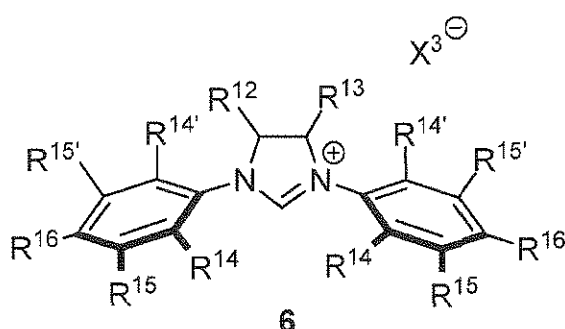
The substituted compound of formula **4**, containing a carbonyl group then reacts with an olefinating reagent of formula $\text{R}^9(\text{R}^{9'})=\text{W}$, wherein R^9 , $\text{R}^{9'}$ is as
 15 defined above, W is a leaving group suitable for an olefination reaction, to give a compound of formula **2**.



In another reaction, the substituted phenol **5** reacts with a compound of formula R^{10}OH in the presence of triphenylphosphine and diisopropyl
 20 azodicarboxylate (DIAD) to give a compound of formula **2**.

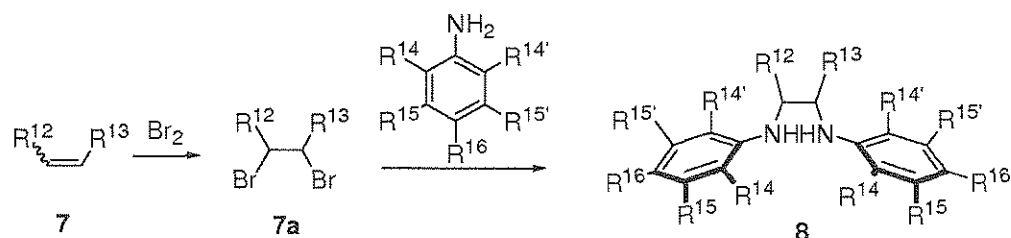


Precursors of *N*-heterocyclic carbene ligands, which are used in the synthesis of complexes of formula 1, are compounds of formula 6



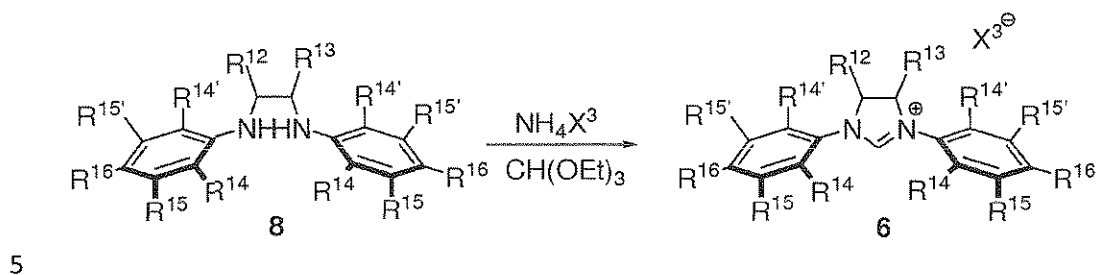
- 5 wherein all substituents are as defined above, and X^3 is a chlorine atom or a BF_4 group.

Compounds of formula 6 can be obtained from an intermediate of formula 7a, which in turn is obtained by the addition of bromine to alkene of formula 7. A compound of formula 7a is heated in the presence of an excess of an aromatic amine to give a compound of formula 8. Compounds of formula 7a and 8 may be carried out into the appropriate hydrochlorides, which facilitates their isolation and purification.

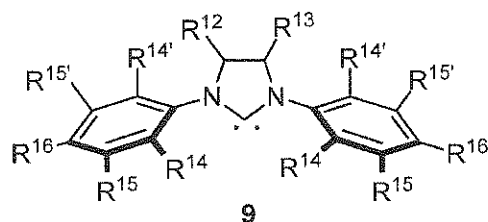


wherein R^{12} , R^{13} , R^{14} , $R^{14'}$, R^{15} , $R^{15'}$ and R^{16} have the meaning as defined above.

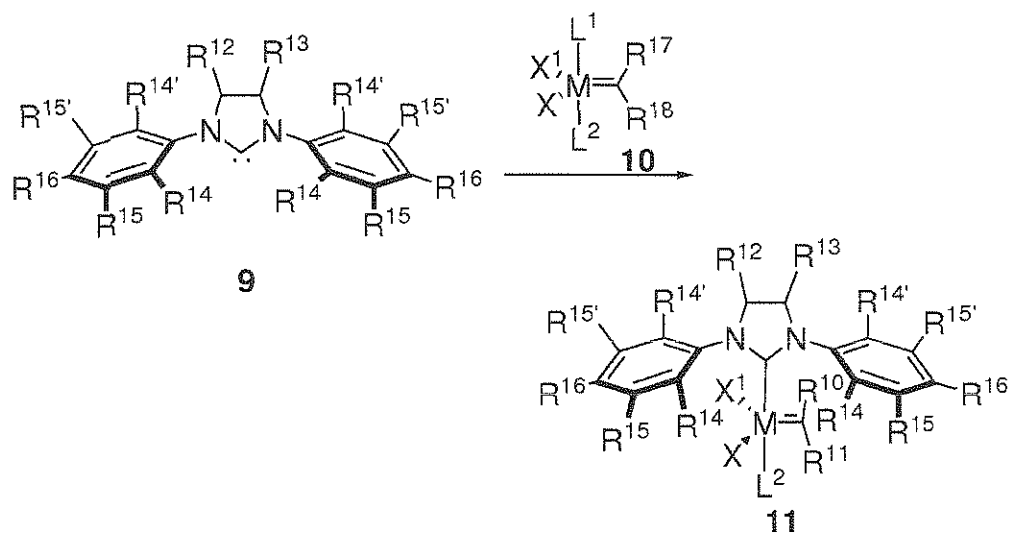
A compound of formula **8** is then heated in triethyl orthoformate in the presence of NH_4X^3 , giving a precursor of a *N*-heterocyclic carbene ligand of formula **6**, directly or by exchange of a counterion X^3 .



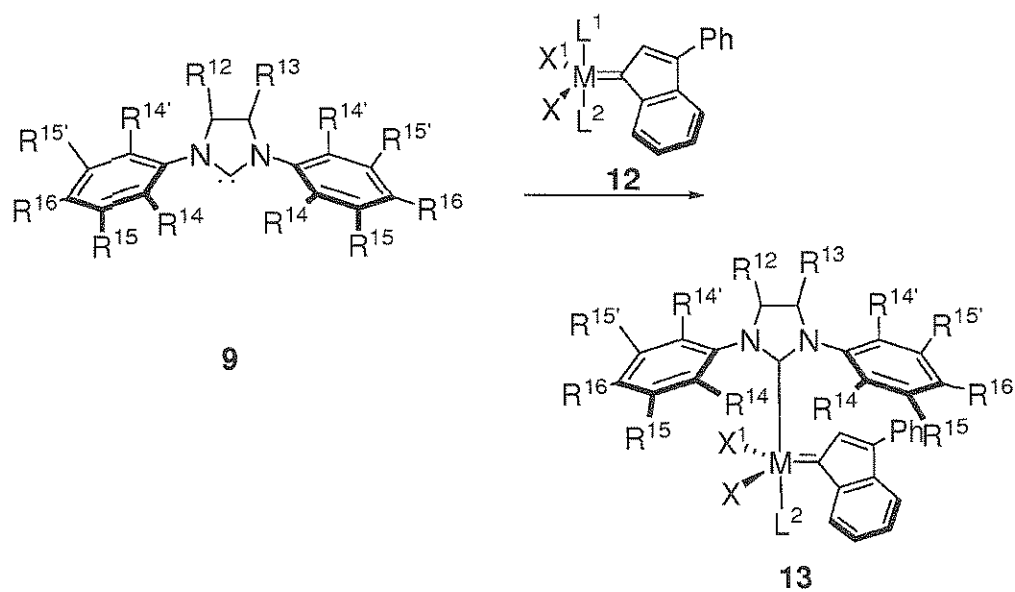
A compound of formula **6** in a reaction with an appropriate base (such as potassium *tert*-amylate) gives *N*-heterocyclic carbene of formula **9**.



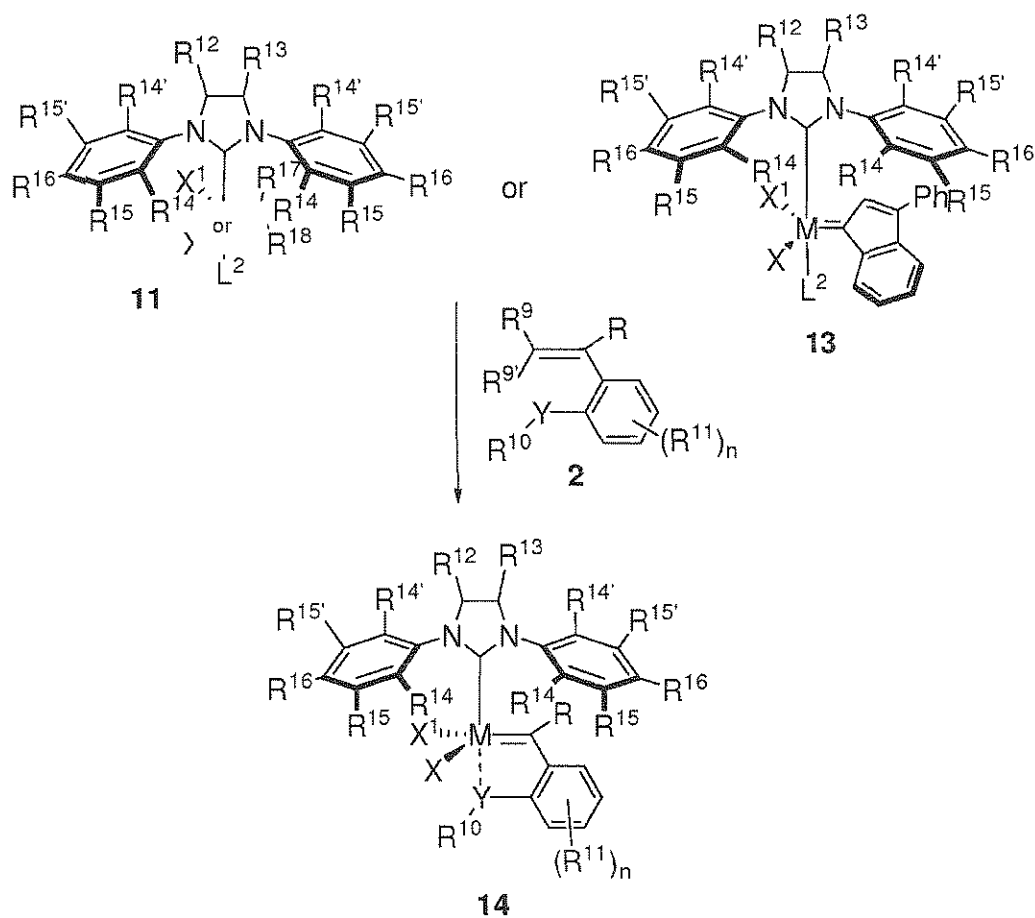
A compound of formula **9** may react *in situ* with a complex of formula **10** (which is a (pre)catalyst of the first generation), where all substituents are as defined above, giving a complex of formula **11**, wherein the substituents are as defined above.



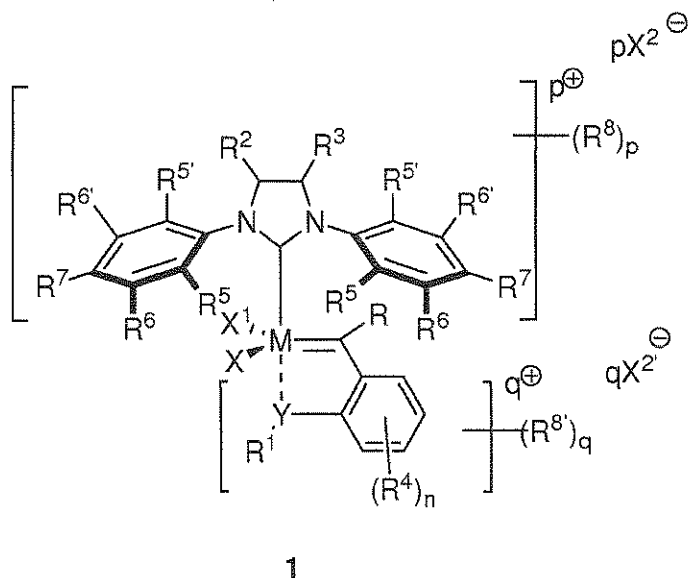
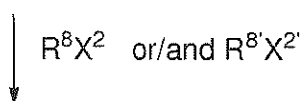
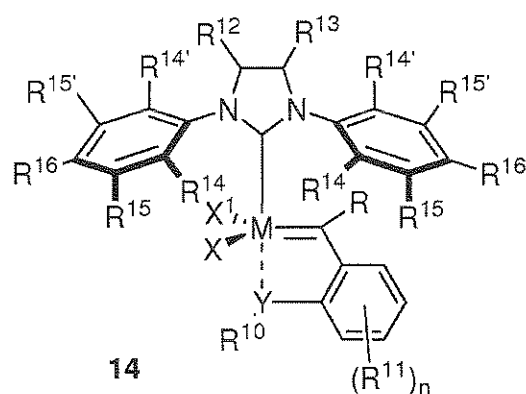
A compound of formula **9** may also react *in situ* with a complex of formula **12**, wherein the substituents are as defined above, giving a compound of formula **13**.



Complexes of formulae **11** and **13** in a reaction with a compound of formula **2** give a complex of formula **14**, where the ligands are as defined above.



A complex of formula **14** can be subjected to a reaction with an alkylating reagent of formula R^8X^2 thus giving a complex of formula **1**. The thus obtained complex of formula **1** may be optionally subjected to a reaction with a reagent of formula $R^{8'}X^{2'}$.



Precursors of *N*-heterocyclic carbene ligands of formula **6** are characterized by the fact that complexes **10**, **12** and **14** can be obtained from them which easily undergo a quaternization reaction giving complexes of formulae **15**, **17** and **1**, respectively.

Complexes of formulae **1**, **15** and **17** containing a quaternary onium group in an inert ligand were not so far obtained by the reaction of an appropriate complex with an alkylating reagent. This method allows to obtain the products in a simple, efficient and cost-effective way. For example, the catalysts obtained by

R.H. Grubbs were purified by a threefold column chromatography under anaerobic conditions, and one of the ligands was obtained using an expensive ion-exchange resin (J.P. Jordan, R.H. Grubbs; *Angew. Chem. Int. Ed.*, **2007**, *46*, 5152-5155).

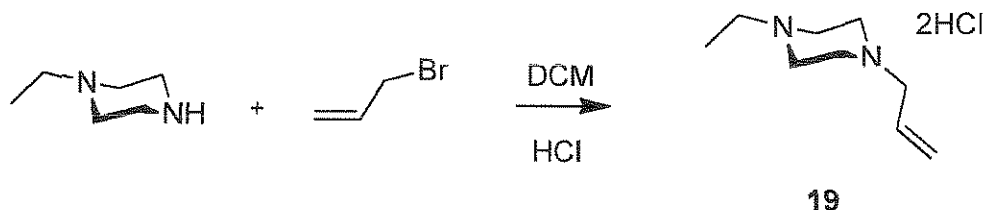
5 The complexes are highly efficient and effective (pre)catalysts for an olefin metathesis reaction and possess the physico-chemical properties which are desirable from the point of view of the purification of products of the metathesis reaction. In the metathesis reaction there is a contact between the complexes and the substrates under conditions appropriate for this type of
10 reaction. Complexes are used in a ring closing metathesis (RCM), cross metathesis (CM), alkene-alkyne (en-yn) reaction, homometathesis (which is a kind of a cross metathesis) and a ring opening metathesis polymerization (ROMP).

 The term "desirable physico-chemical properties" means that the
15 complexes have a high affinity to an adsorbent (in particular, acidic silica gel and alumina) and exhibit good (and in some cases excellent) solubility in pure water. Metathesis reaction conditions for the complexes are comparable to those used for the complexes known in the prior art. The metathesis reaction is normally carried out with an amount of a (pre)catalyst ranging from 0.2 to 5 mol%, at a
20 temperature from 0°C to 120°C, within the period from 0.1 to 96 hours.

 Olefin metathesis reaction products obtained with the use of the complexes contain a very small amount of heavy metal (typically less than 10 ppm), while their purification process is simple, fast and cheap. The simplicity and effectiveness of heavy metal removal from the postreaction mixture is
25 extremely important from the point of view of the application of metathesis technology in the pharmaceutical industry. The complexes are also highly active and effective in an olefin metathesis reaction carried out in pure water, and what, such reactions can be carried out in the presence of oxygen.

The following abbreviations are used in the description of NMR spectra:
s – singlet, bs – broad singlet, d – doublet, dd – doublet of doublet, t – triplet,
q – quartet, sept – septet; J – is a coupling constant between two protons.

Synthesis of compound 19.



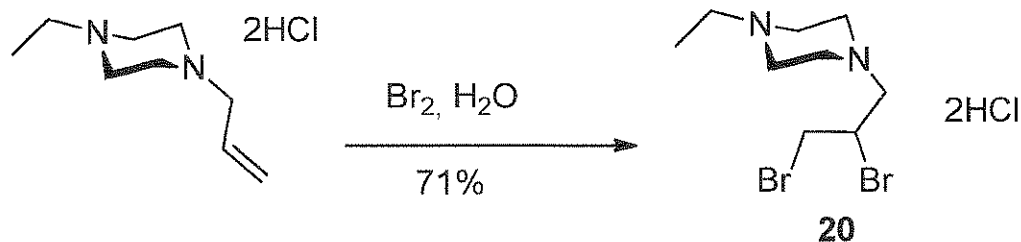
Allyl bromide (68.6 ml, 788 mmol) was slowly added at 0°C to a solution of *N*-ethyl-piperazine (100 ml, 788 mmol) in dichloromethane (500 ml). When the addition was completed reaction mixture was heated to reflux and stirred at this temperature for 1.5 h. Then it was cooled to room temperature, washed with sodium hydroxide aq (10%, 350 ml) and dried with magnesium sulphate. Drying agent was filtered off, dichloromethane was evaporated and the residue was dissolved in methanol (100 ml) and hydrochloric acid aq (36%, 157 ml) was added. Removal of solvent and crystallization of crude product from ethanol/diethyl ether mixture afforded **19** (106 g, 59%) as a colorless crystals.

10

¹H (500 MHz, D₂O). δ ppm: 6.019-5.936 (m, 1H), 5.730-5.690 (m, 2H), 3.956 (d, 2H, J=7.5Hz), 3.930-3.450 (bs, 8H), 3.404 (q, 2H, J=7.5Hz), 1.402 (tr, 3H, J=7.5Hz). ¹³C (125MHz, D₂O). δ ppm: 128.2, 124.7, 59.1, 52.6, 48.4, 48.3, 8.2. HRMS (ESI) calcd for C₉H₁₈N₂ ([M+H]⁺) *m/z* 155.1548 found 155.1553.

15

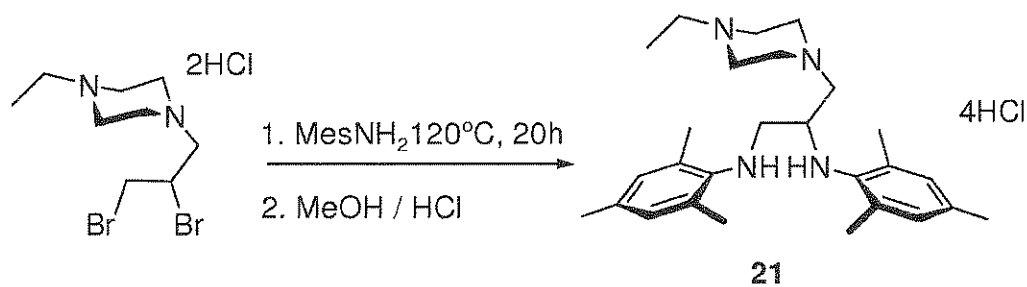
20 Synthesis of compound 20



Bromine (23.9 ml, 462 mmol) was slowly added at 50 °C to a solution of **19** (105 g, 462 mmol) in water (200 ml) at such a rate that the temperature did not exceed 60 °C. When the addition was completed water was evaporated to dryness. Recrystallization of crude product from ethanol afforded **20** (127 g, 71%) as a colorless crystals.

^1H (500 MHz, D_2O). δ ppm: 4.100-3.428 (m, 12H), 3.413-3.399 (m, 3H, $J=7.5\text{Hz}$), 1.405 (tr, 3H, $J=7.5\text{Hz}$). ^{13}C (125MHz, D_2O). δ ppm: 64.6, 61.3, 60.4, 52.6, 48.4, 46.3, 8.8. HRMS (ESI) calcd for $\text{C}_9\text{H}_{18}\text{Br}_2\text{N}_2$ ($[\text{M}+\text{H}]^+$) m/z 314.9946 found 314.9934.

Synthesis of compound 21

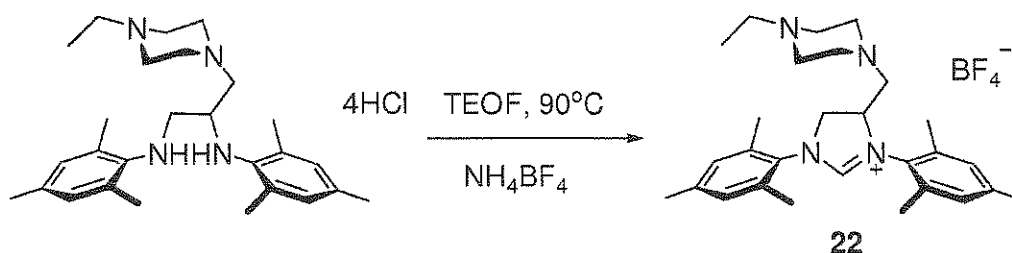


Compound **20** and 2,4,6-trimethylaniline were heated together at 125 °C for 24 h. Reaction mixture was then cooled down to room temperature and alkalized with sodium hydroxide aq (15%, 190 ml). Product was extracted with dichloromethane (300 ml). Organic fraction was washed with water (100 ml) and dried with magnesium sulphate. Drying agent was filtered off and solvent was evaporated. Then excess of 2,4,6-trimethylaniline was removed under reduced

pressure (3 mbar). Crude product was dissolved in methanol (200 ml) and hydrochloric acid aq (36%, 51.3 ml) was added. Removal of solvent and crystallization of crude product from acetone (500 ml) afforded **21** (46.3 g, 62%) as a white solid.

5 ^1H (500 MHz, D_2O). δ ppm: 6.844 (s, 4H), 3.755-3.714 (m, 1H), 3.667-3.624 (m, 2H), 3.600-3.440 (m, 2H), 3.418-3.379 (m, 2H), 3.308-3.262 (m, 2H), 3.216-3.191 (m, 4H), 3.100-2.920 (m, 2H), 2.311-2.183 (m, 20H), 1.367 (tr, 3H, $J=7.5\text{Hz}$). ^{13}C (125MHz, D_2O). δ ppm: 140.3, 136.8, 134.2, 131.1, 131.0, 130.7, 58.4, 52.4, 51.9, 49.9, 49.7, 30.4, 19.9, 18.0, 16.9. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{43}\text{N}_4$ ($[\text{M}+\text{H}]^+$) m/z 423.3488 found 423.3473.

Synthesis of compound 22



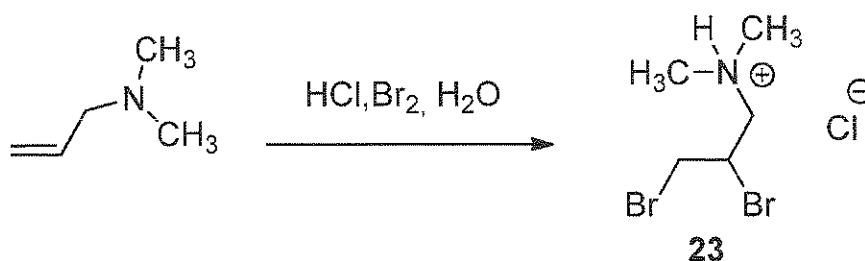
Solution of **21** (72.3 g, 124 mmol) in mixture of triethyl orthoformate (TEOF) (103 ml, 620 mmol) and methanol (170 ml) was stirred at 90°C for 3 h. After evaporation of solvents, crude product was dissolved in water (100 ml) and solution of ammonium tetrafluoroborate (19.5 g, 186 mmol) in water (200 ml) and sodium hydroxide aq (5%, 180 ml) were added. After extraction of product with dichloromethane (300 ml), organic fraction was dried with sodium sulphate.

20 Drying agent was filtered off and solvent was evaporated. Crude product was purified by recrystallization from dichloromethane/tetrachloromethane mixture to afford **22** (50.5 g, 78%) as a white crystals.

^1H (500 MHz, CD_2Cl_2). δ ppm: 8.226 (s, 1H), 7.070-7.067 (d, 4H, $J=1.5\text{Hz}$), 5.115-5.046 (m, 1H), 4.653 (m, 1H), 4.159-4.117 (m, 1H), 2.817-2.800 (m, 2H), 2.517-2.472 (m, 8H), 2.413-2.352 (m, 20H), 1.101 (tr, 3H, $J=7.0\text{Hz}$). ^{13}C (125MHz CD_2Cl_2). δ ppm: 159.4, 141.6, 135.7, 135.5, 130.9, 130.54, 130.5, 61.65, 60.0,

56.3, 52.5, 52.5, 52.4, 21.4, 21.3, 19.0, 18.5, 11.3. HRMS (ESI) calcd for $C_{28}H_{41}N_4$ ($[M+H]^+$) m/z 433.3331 found 433.3342.

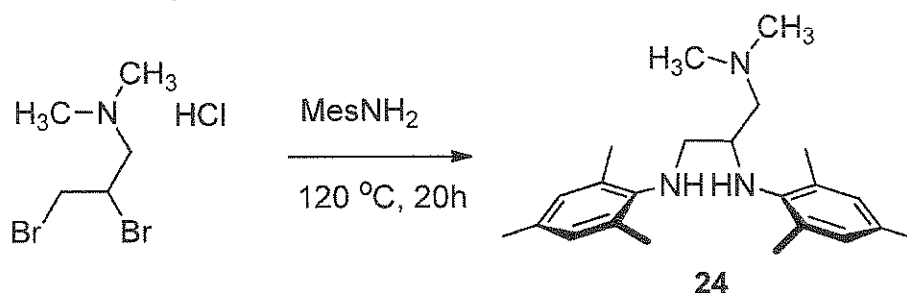
Synthesis of compound 23



5 Hydrochloric acid aq (36%, 22.7 ml) was added at 5°C to a solution of *N,N*-dimethylallylamine (19.4 g, 228 mmol) in water (20 ml). After that reaction mixture was heated to 50°C and bromine (11.9 ml, 228) was added at such a rate that the temperature did not exceed 60°C. When the addition was completed
10 water was evaporated to dryness. Recrystallization of crude product from ethanol afforded **23** (127 g, 71%) as a colorless crystals.

1H (200 MHz, D_2O). δ ppm: 4.133-3.602 (m, 5H), 2.990 (s, 6H). ^{13}C (50 MHz, D_2O). δ ppm: 61.7, 60.8, 45.7, 45.1, 30.0.

Synthesis of compound 24

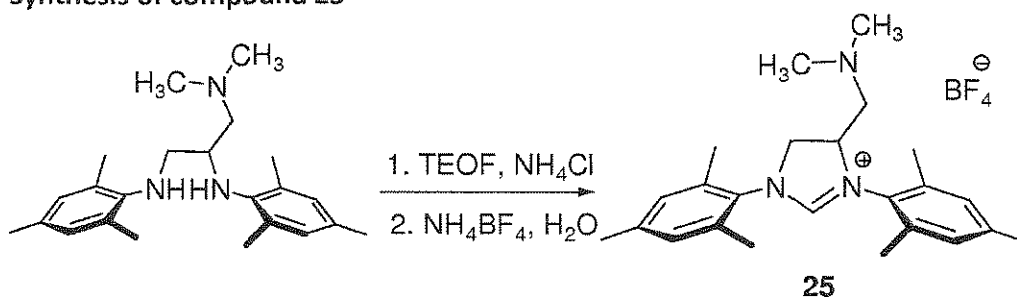


15 Compound **23** and 2,4,6-trimethylaniline was heated together at 125°C for 24 h. Reaction mixture was then cooled down to room temperature and alkalized with sodium hydroxide solution aq (15%, 190 ml). Product was extracted with dichloromethane (300 ml). Organic fraction was washed with water (100 ml) and
20 dried with magnesium sulphate. Drying agent was filtered off and solvent was evaporated. Then excess of 2,4,6-trimethylaniline was removed under reduced

pressure (3 mbar). Purification of the residue by column chromatography (DCM/MeOH 9/1) afforded **24** (17.7 g, 70%) as a brown oil.

¹H (500 MHz, CDCl₃). δ ppm: 6.810-6.775 (m, 4H), 3.606-3.557 (m, 1H), 3.132-3.098 (dd, 1H, J=5.5Hz, J=11.5Hz), 3.031-3.009 (m, 2H), 2.962-2.929 (dd, 1H, J=4.5Hz, J=11.5Hz), 2.380 (s, 6H), 2.254-2.179 (m, 18H), 1.634 (bs, 2H). ¹³C (125MHz, CDCl₃). δ ppm: 144.2, 142.0, 131.4, 129.9, 129.7, 128.9, 65.14, 54.97, 47.19, 46.05, 41.02, 20.80, 18.64, 18.48.

Synthesis of compound 25



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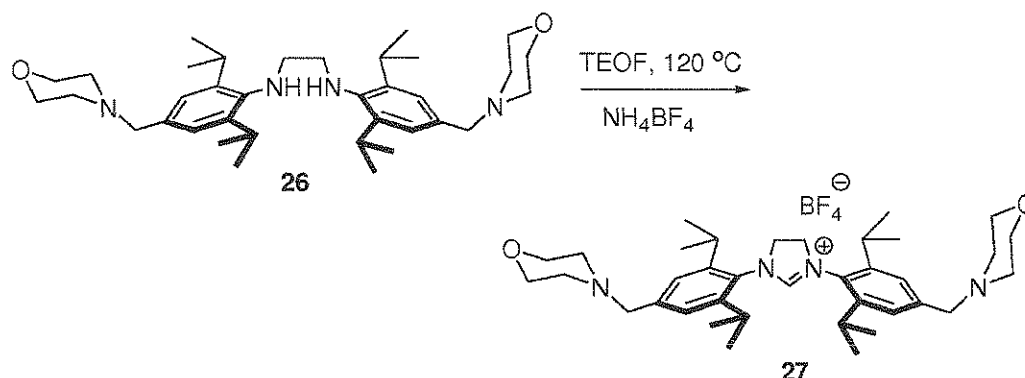
Solution of **24** (13.3 g, 37.6 mmol) and ammonium chloride (2 g, 37.6 mmol) in TEOF was stirred at 120°C for 3 h. After evaporation of solvent, the residue was dissolved in water (100 ml) and solution of ammonium tetrafluoroborate (3.94 g, 37.6 mmol) in water (20 ml) was added. Crude product was filtered off and recrystallized from DCM/CCl₄ mixture to afford **25** (10.5 g, 62%) as a white crystals.

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¹H (500 MHz, CDCl₃). δ ppm: 8.158 (s, 1H), 6.953 (s, 4H), 4.996-4.928 (m, 1H), 4.621-4.573 (m, 1H, J=7.2Hz), 4.125 (dd, 1H, J=8.5, J=12.5Hz), 2.715 (dd, 1H, J=9.5Hz, J=12.0Hz), 2.539 (dd, 1H, J=5.0Hz, J=12.0Hz), 2.396-2.288 (m, 18H), 2.157 (s, 6H). ¹³C (125MHz, CDCl₃). δ ppm: 159.2, 140.8, 135.4, 130.6, 130.3, 129.6, 62.13, 60.97, 56.11, 45.84, 21.31, 21.26, 18.74, 18.30, 17.78.

20

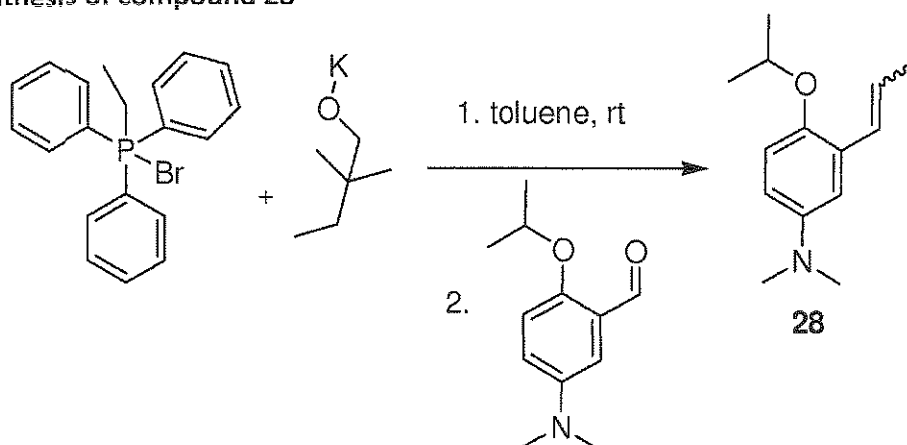
Synthesis of compound 27



Compound **26** (see: Volodymyr Sashuk, Dirk Schoeps, Herbert Plenio, Chem. Commun., **2009**, 770–772) (10.13 g, 17.50 mmol) and ammonium tetrafluoroborate (1.926 g, 18.37 mmol) were dissolved in TEOF (150 ml) and stirred at 120°C for 3 h. Then reaction mixture was cooled to room temperature and hexane (150 ml) was added to precipitate the product. Crude product was filtered and recrystallized from acetone to afford the **27** (4.59 g, 39%) as a white solid.

¹H (200 MHz, CDCl₃) δ ppm: 7.806 (s, 1H), 7.208 (d, 4H, J=4Hz), 4.538 (s, 4H), 3.662-3.618 (m, 8H), 3.472 (s, 4H), 2.918 (m, 4H), 2.413-2.369 (m, 8H), 1.327 (d, 12H, J=6.6Hz), 1.174 (d, 12H, J=6.6Hz).

Synthesis of compound **28**



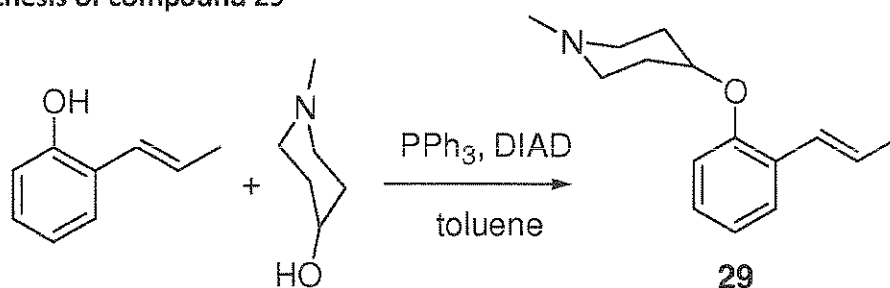
Potassium *tert*-amylate (1.7 M in toluene, 13 ml, 22.1 mmol) was added at 0°C to a suspension of ethyltriphenylphosphonium bromide (8.51 g, 22.9 mmol) in dry toluene (65 ml). After that mixture was warmed to room temperature and stirred

for 1 h. Then it was cooled to -15 °C and solution of 5-dimethylamino-2-isopropoxy-benzaldehyde (3.27 g, 15.8 mmol) in dry toluene (35 ml) was dropped in. Next reaction mixture was slowly warmed to room temperature and stirred overnight. The reaction was quenched with saturated
 5 NH₄Cl aq (30 ml). The organic solvent was removed under reduced pressure and the residue was extracted with *tert*-butyl-methyl ether (4x20 mL). The combined organic layers were dried with magnesium sulphate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (*c*-hexane/EtOAc/Et₃N 19:1:0.1) to give **28** (3.10 g, 89%) as a
 10 yellow oil.

¹H (300 MHz, CDCl₃) δ ppm: 6.864-6.806 (m, 1H), 6.759 (d, 1H, J=3Hz), 6.667-6.628 (m, 1H), 6.582-6.537 (m, 1H), 5.826-5.764 (m, 1H), 4.324 (heptet, 1H, J=6.3Hz), 2.898 (s, 6H), 1.887-1.857 (m, 3H), 1.382-1.282 (d, 6H, J=6Hz). HRMS (ESI) calcd for C₁₄H₂₂NO ([M+H]⁺) *m/z* 220.1701 found 220.1700.

15

Synthesis of compound 29



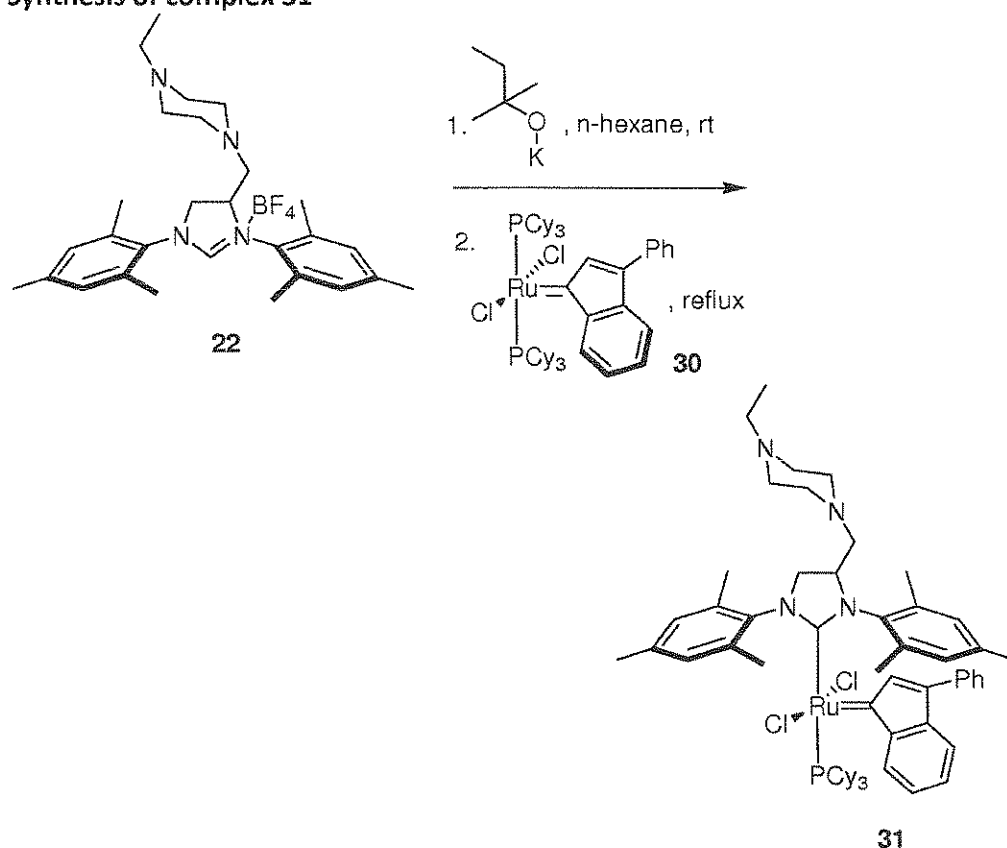
2-Propenyl-phenol was added under argon to a solution of 1-methyl-piperidin-4-ol (2.60 g, 22.6 mmol) and triphenylphosphine (6.52 g, 24.9
 20 mmol) in dry toluene (40 ml). Mixture was cooled to 0°C and diisopropyl azodicarboxylate (4.9 ml, 24.9 mmol) was slowly added. When the addition was completed reaction mixture was warmed to room temperature and stirred for 20 h and then for 4 h at 60°C. Mixture was cooled to room temperature, diluted with ethyl acetate (150 ml) and washed with water (200 ml) and with saturated
 25 potassium carbonate aq (200ml). Product was extracted from organic phase with

hydrochloric acid aq (0.5 M, 240 ml). Water fraction was then alkalinized to pH 10 and product was extracted with dichloromethane (240 ml). Organic phase was washed with water (100 ml), dried with magnesium sulphate, filtered and solvent was evaporated. Crude product was purified by column chromatography (DCM/*c*-hexane/EtOAc/Et₃N 3:3:1:0.1). Evaporation of solvents afforded **29** (4.26 g, 81%) as a yellow oil.

¹H (200 MHz, CDCl₃) δ ppm: 7.725-6.826 (m, 4H), 6.793-6.705 (m, 1H), 6.316-5.727 (m, 1H), 4.381-4.271 (m, 1H), 2.750-2.629 (m, 2H), 2.380-2.104 (m, 2H) 2.309 (s, 3H), 2.080-1.182 (m, 7H).

10

Synthesis of complex **31**



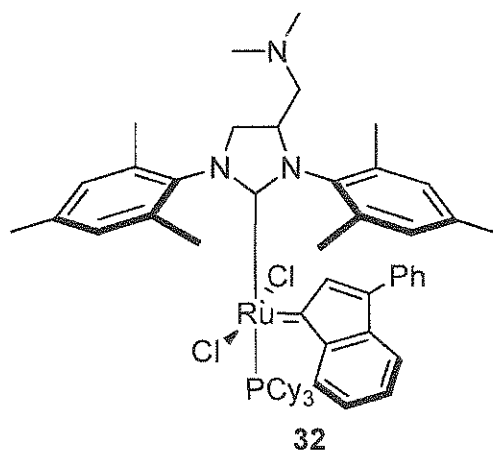
Potassium t-amylate (1.7 M in toluene, 2.26 ml, 3.85 mmol) was added at room temperature to a suspension of **22** (2.00 g, 3.85 mmol) in dry hexane (40 ml) under argon. Reaction mixture was stirred at room temperature for 1 h, then complex **30** was added and stirring was continued at reflux for 1 h. After cooling

15

down, reaction mixture was filtered through a short pad of silica gel (c-hexane/EtOAc 8:2). Solvents were evaporated, catalyst was washed with *n*-pentane and dried under vacuum to afford complex **31** (2.51 g, 85%) as a dark red solid.

- 5 ^1H (300 MHz, CDCl_3) δ ppm: 8.668-8.519 (m, 1H), 7.668-7.392 (m, 2H), 7.525-7.008 (m, 9H), 6.448-6.370 (m, 1H), 6.013-5.945 (m, 1H), 4.146-3.655 (m, 3H), 2.741-2.722 (m, 3H), 2.661-2.624 (m, 4H), 2.556-2.386 (m, 3H), 2.319-1.832 (m, 24H), 1.628-1.362 (m, 7H), 1.340-1.222 (m, 4H), 1.140-0.959 (m, 18H), 0.882 (tr, 3H, $J=7.2\text{Hz}$). ^{31}P (124.5 MHz, CDCl_3) δ ppm: 26.09, 26.47, 24.66. ^{13}C (75,4
- 10 MHz, CDCl_3) δ ppm: 292.6, 219.4-217.7 (m), 144.9, 144.8, 144.7, 140.9, 140.8, 139.1, 138.9, 138.8, 138.4, 138.0, 137.9, 137.6, 137.0, 136.9, 136.7, 136.4, 136.2, 136.9, 135.4, 135.3, 134.8, 134.7, 130.1, 129.9, 129.4, 129.3, 128.9, 128.8, 128.6, 128.1, 128.0, 127.4, 127.1, 127.0, 126.8, 126.4, 126.3, 115.9, 115.8, 62.71, 62.48, 62.14, 61.21, 60.6, 60.50, 60.36, 58.69, 58.49, 57.88, 53.40, 52.27, 33.24, 33.03,
- 15 32.82, 29.30, 29.22, 29.12, 27.89, 27.75, 27.61, 26.26, 21.20, 14.10, 11.90. HRMS (ESI) calcd for $\text{C}_{61}\text{H}_{83}\text{N}_4\text{PClRu}$ ($[\text{M}-\text{Cl}]^+$) m/z 1039.5087 found 1039.5063

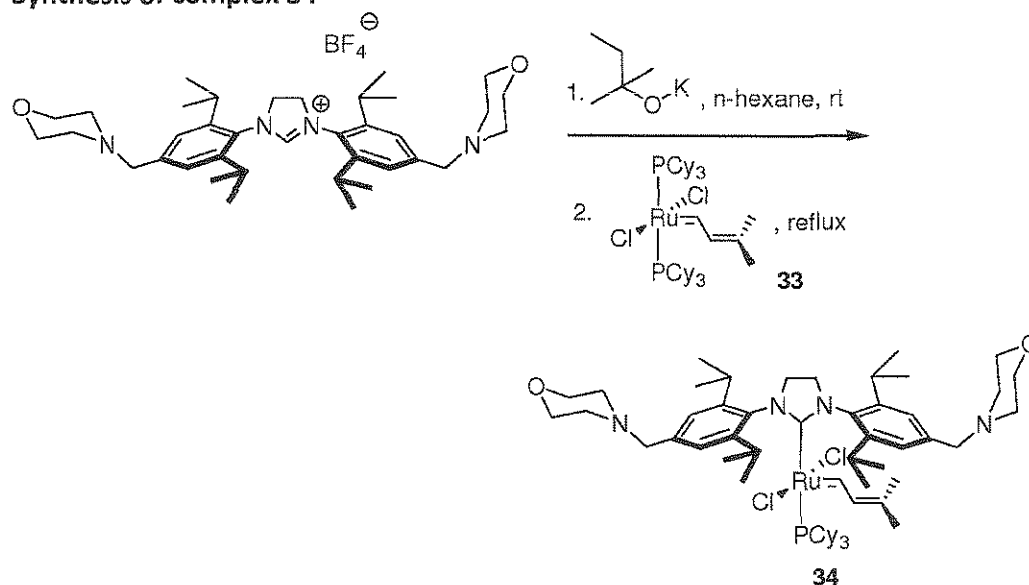
Synthesis of complex **32**



- 20 The same procedure as described for complex **31** was employed to afford the catalyst **32** as a dark red solid in 81% yield.

0.250 g (81 %) – red solid; ^1H (300 MHz, CDCl_3) δ ppm: 8.684-8.537 (m, 1H), 7.746-7.673 (m, 2H), 7.530-7.460 (m, 1H), 7.426-7.353 (m, 2H), 7.227-7.096 (m, 2H), 7.074-7.008 (m, 3H), 6.923-6.779 (m, 1H), 6.444-6.377 (m, 1H), 6.031-5.957 (m, 1H), 4.538-4.288 (m, 1H), 4.231-4.108 (m, 1H), 3.997-3.632 (m, 1H), 2.767-2.720 (m, 2H), 2.677-2.635 (m, 3H), 2.385-2.232 (m, 4H), 2.289-2.255 (m, 5H), 2.234-2.201 (m, 5H), 2.168-2.094 (m, 8H), 2.073-2.019 (m, 3H), 1.979-1.799 (m, 4H), 1.487-1.430 (m, 10H), 1.143-0.863 (m, 15H). ^{31}P (124.5 MHz, CDCl_3) δ ppm: 26.09, 26.47, 24.66. ^{13}C (75,4 MHz, CDCl_3) δ ppm: 292.6-292.3 (m), 219.6-217.6 (m), 164.40, 143.88, 140.97, 140.5, 139.44, 139.24, 138.90, 138.75, 138.33, 138.04, 137.90, 137.60, 137.40, 137.21, 137.12, 137.06, 136.98, 136.85, 137.67, 137.54, 136.42, 136.22, 135.90, 131.13, 130.24, 130.10, 129.95, 129.48, 129.35, 128.60, 128.11, 126.65, 126.38, 126.30, 115.9, 115.83, 62.59, 61.95, 61.84, 57.95, 56.67, 52.52, 46.04, 46.90, 29.31-29.23 (m), 27.9, 26.95, 26.26, 21.2-20.33 (m), 19.19-18.39 (m). HRMS (ESI) obliczono dla $\text{C}_{57}\text{H}_{76}\text{N}_3\text{PClRu}$ ($[\text{M}-\text{Cl}]^+$) m/z 970,4509 oznaczono 970,4512.

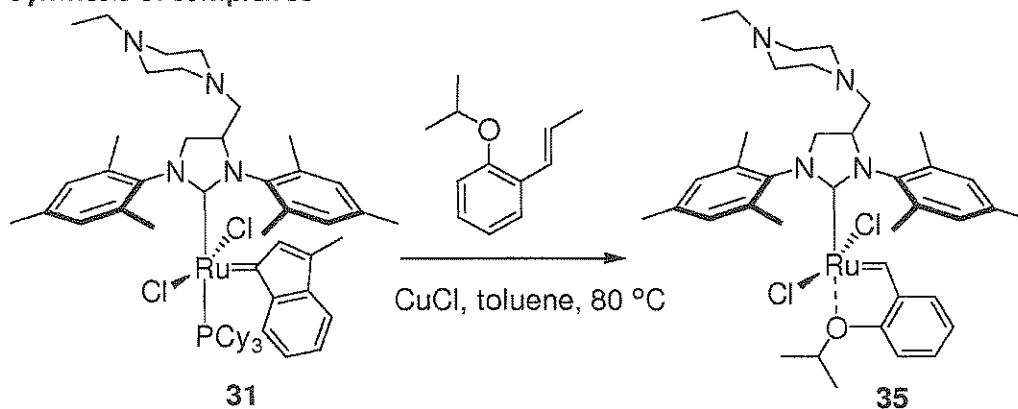
Synthesis of complex 34



Potassium *t*-amylate (1,7 M in toluene , 0.224 ml, 0.381 mmol) was added at room temperature to a suspension of **27** (0.250 g, 0.423 mmol) in dry hexane under argon. Reaction mixture was stirred at room temperature for 1 h, then complex **33** was added and stirring was continued at reflux for 1 h. After cooling down, reaction mixture was directly filtered through a short pad of silica gel (c-hexane/EtOAc 8:2). Solvents were evaporated, catalyst was washed with *n*-pentane and dried under vacuum to afford complex **34** (0.24 g, 77%) as a light brown solid.

^1H (300 MHz, CDCl_3) δ ppm: 18.700 (d, 1H, $J=11.3\text{Hz}$), 7.363 (d, 1H, $J=11.3\text{Hz}$), 7.223 (s, 2H), 7.014 (s, 2H), 4.110-4.044 (m, 2H), 3.959-3.819 (m, 4H), 3.781-3.729 (m, 8H), 3.570-3.444 (m, 6H), 2.518-2.460 (m, 8H), 2.185-2.077 (m, 4H), 1.525-1.497 (m, 10H), 1.466-1.414 (m, 13H), 1.270-1.126 (m, 14H), 1.086-0.948 (m, 22H). ^{31}P (124.5 MHz, CDCl_3) δ ppm: 25.80. ^{13}C (75,4 MHz, CDCl_3) δ ppm: 287.7, 222.5, 149.5, 147.5, 146.1, 138.7, 137.1, 136.9, 128.9, 125.1, 124.7, 67.15, 63.38, 54.57, 54.19, 53.69, 53.63, 31.68, 31.47, 28.93, 28.60, 27.82, 27.70, 27.54, 27.00, 26.69, 26.42, 26.17, 23.94, 23.06, 20.04. HRMS (ESI) calcd for $\text{C}_{60}\text{H}_{97}\text{N}_4\text{O}_2\text{PClRu}$ ($[\text{M}-\text{Cl}]^+$) m/z 1073.6081 found 1073.6084.

Synthesis of complex 35

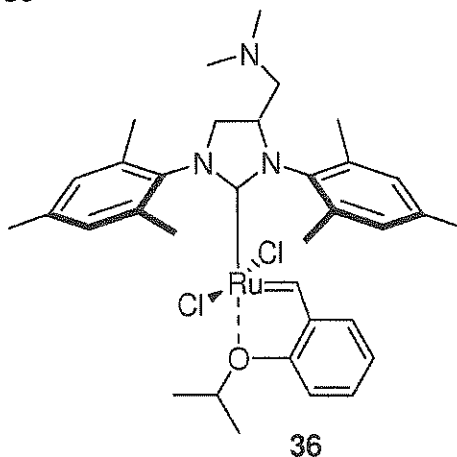


1-Isopropoxy-2-propenyl-benzene (0.143 g, 0.814 mmol) and CuCl (0.121 g, 1.221 mmol) were placed in a Schlenk flask. The flask was filled with argon and then

dry toluene (20 ml) was added. Afterwards complex **31** (0.876 g, 0.814 mmol) was added and the resulting solution was stirred at 80 °C for 20 min. The reaction mixture was cooled to room temperature and concentrated under vacuum. The resulting material was dissolved in a minimum amount of EtOAc and the insoluble white solid filtered through a Pasteur pipette containing cotton wool. The solvent was concentrated again in vacuum, and the crude catalyst was purified by flash chromatography (c-hexane/EtOAc 7:3). Removal of solvents afforded complex **35** (0.42 g, 68%) as a green solid.

¹H (300 MHz, CDCl₃) δ ppm: 16.533 (s, 1H), 7.507-7.450 (m, 1H), 7.075-7.045 (m, 4H), 6.934-6.770 (m, 3H), 4.890 (heptet 1H, J=6.6 Hz), 4.609-4.558 (m, 1H), 4.272 (tr, 1H, J= 10.2 Hz), 4.036-3.973 (m, 1H), 2.762-2.673 (m, 2H), 2.400-2.319 (m, 28H), 1.260 (d, 6H, J=6.6Hz), 1.0457 (tr, 3H, J=7.2Hz). ¹³C (75,4 MHz, CDCl₃) δ ppm: 298.2, 213.2, 152.2, 145.4, 139.4, 138.8, 138.6, 129.6, 129.5, 122.8, 122.3, 112.9, 74.93, 61.35, 57.73, 57.64, 57.33, 57.30, 53.60, 52.76, 52.29, 21.47, 11.97. HRMS (ESI) calcd for C₃₈H₅₂N₄ONaCl₂Ru ([M+Na]⁺) m/z 775.2459 found 775.2436.

Synthesis of complex **36**

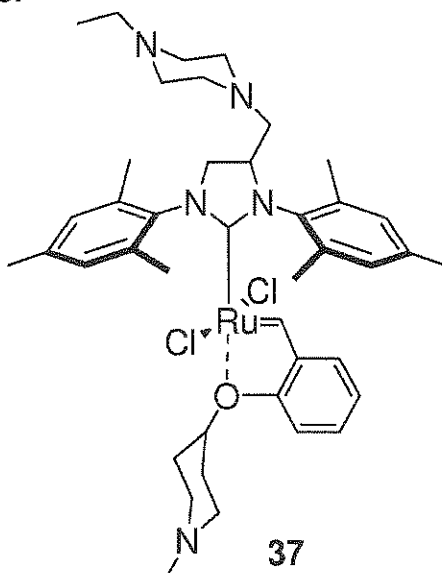


The same procedure as described for complex **35** was employed to afford the catalyst **36** as a green solid in 64% yield.

0.340 g (64%) – green solid, ¹H (300 MHz, CDCl₃) δ ppm: 16.510-16.530 (bs, 1H), 7.486-7.477 (m, 1H), 7.060-7.072 (m, 4H), 6.930-6.940 (m, 1H), 6.848-6.856 (m,

1H), 6.782-6.802 (m, 1H), 4.890 (heptet, 1H, $J=6.3\text{Hz}$), 4.563-4.500 (m, 1H), 4.284 (m, 1H), 4.022 (dd, 1H, $J=8.1\text{Hz}$, $J=10.5\text{Hz}$), 2.757-2.683 (m, 2H), 2.530-2.290 (m, 18H), 2.201 (s, 6H), 1.284-1.258 (m, 6H). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 298.2, 213.2, 145.4, 139.4, 138.8, 138.7, 130.0, 129.7, 129.6, 129.3, 122.8, 122.3, 112.9, 74.93, 62.61, 57.63, 46.13, 21.15. HRMS (ESI) calcd for $\text{C}_{34}\text{H}_{45}\text{N}_3\text{ONaCl}_2\text{Ru}$ ($[\text{M}+\text{Na}]^+$) m/z 706.1881 found 706.1865.

Synthesis of complex 37

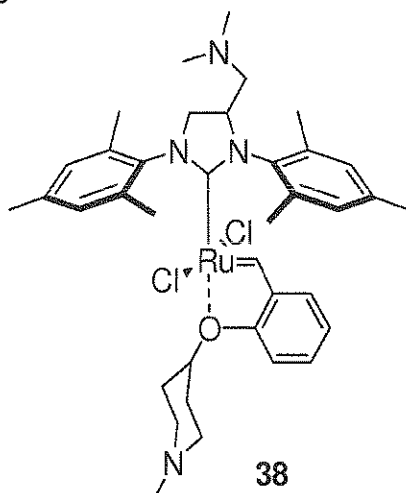


10 The same procedure as described for complex **35** was employed to afford the catalyst **37** as a green solid in 37% yield. Column chromatography was performed using c-hexane/EtOAc 1:1 mixture.

0.280 g (37%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.504 (s, 1H), 7.46 (m, 1H), 7.081-7.063 (m, 4H), 6.953-6.829 (m, 2H), 6.762 (d, 1H, $J=8.1\text{Hz}$), 4.591 (m, 1H), 4.468 (m, 1H), 4.270 (m, 1H), 4.000 (m, 1H), 2.759-2.691 (m, 4H), 2.492-2.315 (m, 26H), 2.238 (s, 3H), 1.970-1.746 (m, 8H), 1.043 (tr, 3H, $J=7.2\text{Hz}$). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 297.9, 213.2, 151.9, 136.6, 138.8, 138.6, 130.0, 129.6, 129.5, 123.00, 122.6, 112.7, 78.91, 61.36, 53.93, 53.59, 52.77, 52.30,

45.59, 30.10, 26.95, 21.20, 11.99. HRMS (ESI) calcd for $C_{41}H_{57}N_5OClRu$ ($[M-Cl]^+$) m/z 772.3295 found 772.3283.

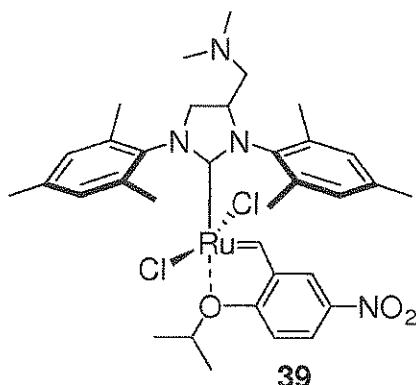
Synthesis of complex 38



- 5 The same procedure as described for complex **35** was employed to afford the catalyst **38** as a green solid in 38% yield. Column chromatography was performed using c-hexane/EtOAc 1:1 mixture.

0.200 g (38%) – green solid; 1H (300 MHz, $CDCl_3$) δ ppm: 16.583–16.303 (bs, 1H),
 10 7.708–7.640 (m, 1H), 7.847–7.436 (m, 2H), 7.090–7.070 (m, 3H), 6.912–6.831 (m, 1H), 6.776–6.748 (d, 1H, $J=8.4$ Hz), 4.570–4.472 (m, 2H), 4.313 (tr, 1H, $J=10.5$ Hz), 4.018–3.983 (m, 1H), 2.766–2.675 (m, 2H), 2.531–2.284 (m, 18H), 2.237 (s, 3H), 2.195 (s, 6H), 1.972–1.746 (m, 8H). ^{13}C (75,4 MHz, $CDCl_3$) δ ppm: 297.6, 212.9, 151.9, 145.2, 139.6, 138.7, 138.6, 132.2, 132.1, 131.97, 129.6, 129.5, 129.4,
 15 128.5, 123.0, 122.6, 112.7, 78.80, 62.60, 53.90, 46.14, 45.58, 30.08, 21.22. HRMS (ESI) calcd for $C_{37}H_{50}N_4OClRu$ ($[M-Cl]^+$) m/z 703.2717 found 703.2717.

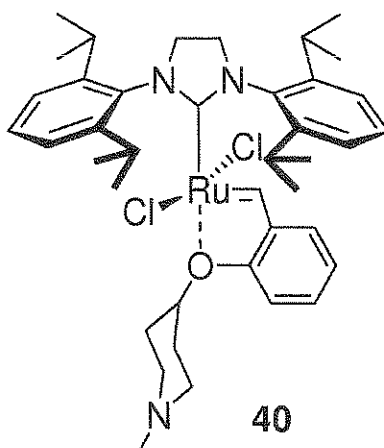
Synthesis of complex 39



The same procedure as described for complex **35** was employed to afford the catalyst **39** as a green solid in 69% yield.

0.300 g (69%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.420 (s, 1H),
 5 8.440-8.401 (dd, 1H, $J=2.7\text{Hz}$, $J=9.0\text{Hz}$), 7.805 (d, 1H, $J=2,7\text{ Hz}$), 7.096-7.081 (m, 4H), 6.885 (d, 1H, $J=9.0\text{Hz}$), 4.968 (heptet, 1H, $J=6.3\text{Hz}$), 4.625-4.514 (m, 1H), 4.306 (m, 1H), 4.005 (dd, 1H, $J=8.4\text{ Hz}$, $J=10.5\text{Hz}$), 2.712 (m, 2H), 2.549-2.448 (m, 18H), 2.204 (s, 6H), 1.306-1.274 (m, 6H). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 292.2, 209,9, 156.4, 144.7, 143.1, 139.4, 139.3, 139.2, 129.7, 129.5, 124.2, 117.5, 112.
 10 80, 62.55, 57.55, 46.11, 26.94. 21.12. HRMS (ESI) calcd for $\text{C}_{34}\text{H}_{40}\text{N}_4\text{O}_3\text{ClRu}$ ($[\text{M}-\text{Cl}]^+$) m/z 689.1832 found 689.1838.

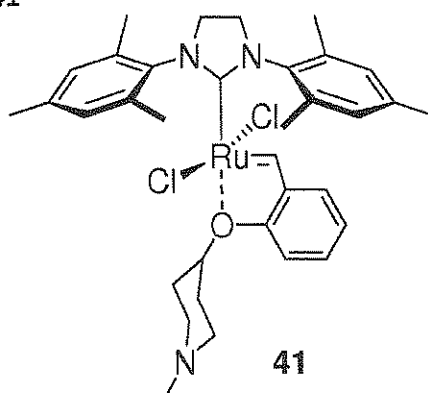
Synthesis of complex **40**



The same procedure as described for complex **35** was employed to afford the catalyst **40** as a green solid in 64% yield.

0.125 g (64%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.395 (s, 1H), 7.566-7.515 (m, 2H), 7.429-7.391 (m, 5H), 6.832-6.766 (m, 3H), 4.508-4.478 (m, 1H), 4.189 (s, 4H), 3.649-3.560 (m, 4H), 2.779-2.761 (m, 2H), 2.203 (s, 3H), 2.104-1.926 (m, 6H), 1.271-1.238 (m, 24H). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 290.1, 213.7, 152.2, 149.2, 144.0, 136.7, 129.8, 129.2, 124.4, 122.5, 122.4, 112.8, 79.09, 54.59, 53.89, 45.56, 30.50, 28.84, 26.66, 23.39. HRMS (ESI) calcd for $\text{C}_{40}\text{H}_{56}\text{N}_3\text{OCl}_2\text{Ru}$ ($[\text{M}+\text{H}]^+$) m/z 766.2844 found 766.2856.

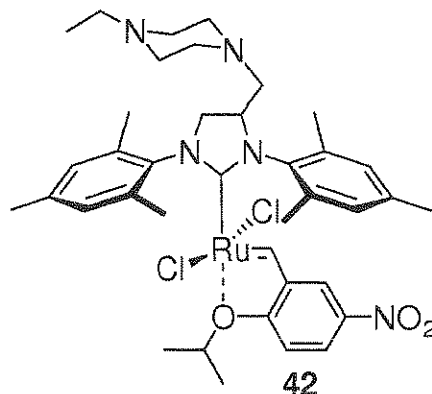
Synthesis of complex 41



The same procedure as described for complex 35 was employed to afford the catalyst 41 as a green solid in 44% yield.

0.224 g (44%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.538 (s, 1H), 7.498-7.442 (m, 1H), 7.088 (s, 4H), 6.953-6.7560 (m, 3H), 4.540-4.445 (m, 1H), 4.178 (s, 4H), 2.776-2.727 (m, 2H), 2.472-2.425 (m, 18H), 2.239 (s, 3H), 2.041-1.754 (m, 6H). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 297.3, 211.3, 151.9, 145.14, 138.80, 129.5, 129.4, 123.0, 122.6, 112.7, 78.65, 53.85, 51.47, 45.47, 30.03, 29.95, 21.21, 19.47. HRMS (ESI) calcd for $\text{C}_{34}\text{H}_{43}\text{N}_3\text{OClRu}$ ($[\text{M}-\text{Cl}]^+$) m/z 646.2138 found 646.2145.

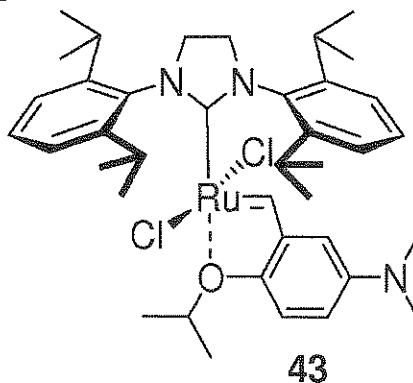
Synthesis of complex 42



The same procedure as described for complex **35** was employed to afford the catalyst **42** as a green solid in 69% yield.

0.51 g (69%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.433 (m, 1H),
 5 8.431-8.386 (m, 1H), 7.805-7.795 (m, 1H), 7.093-7.075 (m, 4H), 6.918-6.868 (m,
 1H), 5.003-4.921 (heptet, 1H, $J=6.3$ Hz), 4.648-4.563 (m, 1H), 4.331-4.260 (m,
 1H), 4.056-3.992 (m, 1H), 2.763-2.698 (m, 2H), 2.656-2.147 (m, 28H), 1.360-1.207
 (d, 6H, $J=6.3$ Hz), 1.091-1.022 (t, 3H, $J=6.9$ Hz). ^{13}C (75,4 MHz, CDCl_3) δ ppm:
 292.1, 210.0, 156.3, 144.7, 143.1, 139.4, 139.3, 130.1, 129.7, 129.5, 129.3, 124.3,
 10 117.4, 112.8, 61.75, 61.62, 61.28, 57.48, 53.52, 52.74, 52.30, 26.94, 22.36, 21.84,
 21.13, 21.11, 20.98, 20.91, 20.48, 19.00, 18.92, 18.57, 17.95, 14.10, 11.93. HRMS
 (ESI) obliczono dla $\text{C}_{38}\text{H}_{51}\text{N}_5\text{O}_3\text{ClRu}$ ($[\text{M}-\text{Cl}]^+$) m/z 762,2724 oznaczono 762,2733.

Synthesis of complex **43**

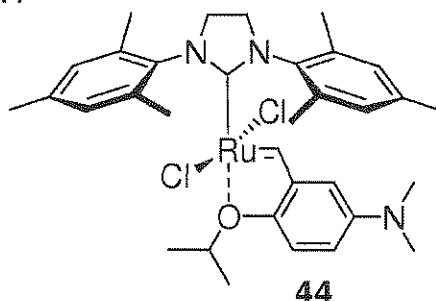


15

The same procedure as described for complex **35** was employed to afford the catalyst **43** as a green solid in 71% yield.

0.211 g (71%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.322 (s, 1H), 7.555-7.504 (m, 2H), 7.393-7.367 (m, 4H), 6.928 (dd, 1H, $J=3.0\text{Hz}$, $J=8.7\text{Hz}$), 6.678 (d, 1H, $J=8.7\text{Hz}$), 6.258 (d, 1H, $J=3\text{Hz}$), 4.829 (heptet, 1H, 6.3Hz), 4.183 (s, 4H), 3.619 (m, 4H), 2.800 (s, 6H), 1.346 (d, 6H, $J=6.3\text{Hz}$), 1.236 (d, 24H, $J=6.9\text{Hz}$). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 291.3, 214.4, 149.3, 146.8, 145.4, 144.3, 136.9, 129.5, 124.4, 114.8, 112.9, 108.0, 74.26, 54.54, 41.9, 28.81, 26.62, 23.47, 21.81. HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{55}\text{N}_3\text{OClRu}$ ($[\text{M}-\text{Cl}]^+$) m/z 718.3077 found 718.3054.

Synthesis of complex 44



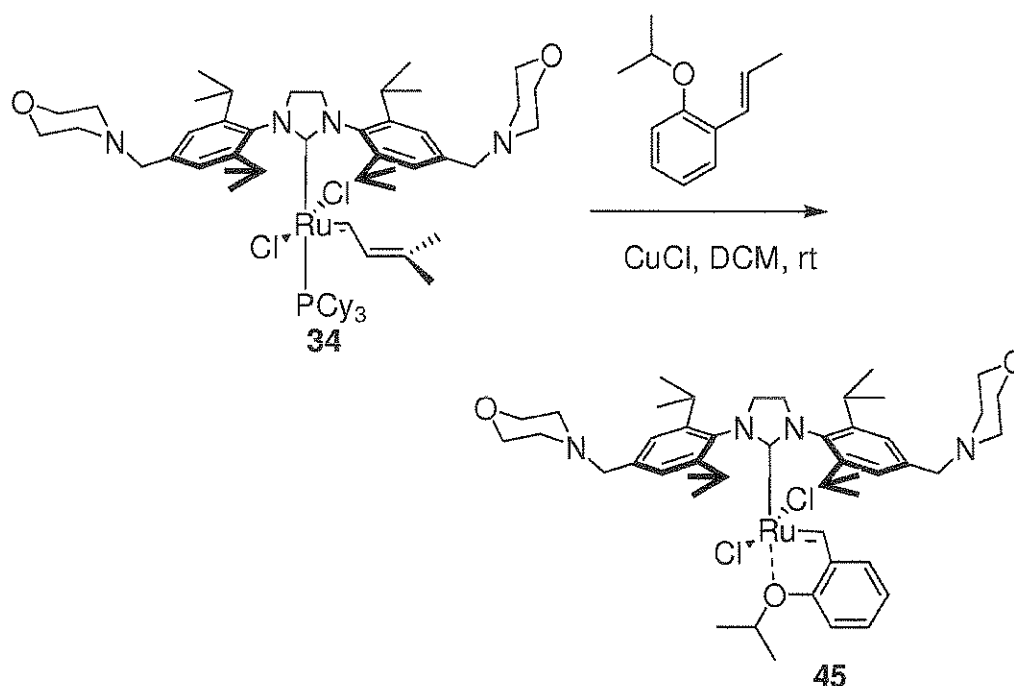
10

The same procedure as described for complex 35 was employed to afford the catalyst **44** as a green solid in 68% yield.

0.486 g (68%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.365-16.390 (bs, 1H), 7.070-7.055 (m, 4H), 6.983 (dd, 1H, $J=3.0\text{ Hz}$, $J=8.7\text{ Hz}$), 6.690 (d, 1H, $J=8.7\text{ Hz}$), 6.370 (d, 1H, $J=3.0\text{ Hz}$), 4.802 (heptet, 1H, $J=6.3\text{ Hz}$), 4.186 (s, 4H), 2.828 (s, 6H), 2.487-2.399 (m, 18H) 1.238 (d, 6H, $J=6.3\text{ Hz}$). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 298.5, 212.3, 146.9, 145.3, 145.1, 139.3, 138.7, 129.4, 115.4, 113.0, 108.3, 74.30, 53.51, 51.47, 41.86, 21.16, 21.09, 19.60. HRMS (ESI) calcd for $\text{C}_{33}\text{H}_{43}\text{N}_3\text{OClRu}$ ($[\text{M}-\text{Cl}]^+$) m/z 634.2138 found 634.2110. HRMS (ESI) calcd for $\text{C}_{33}\text{H}_{43}\text{N}_3\text{OClRu}$ ($[\text{M}-\text{Cl}]^+$) m/z 634.2138 found 634.2110.

20

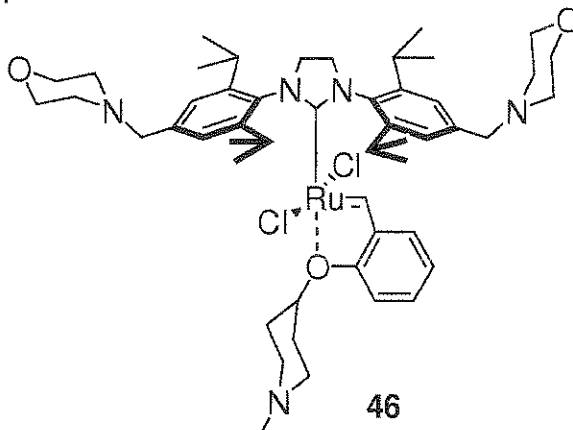
Synthesis of complex 45



1-Isopropoxy-2-propenyl-benzene (0.175 g, 0.991 mmol) and CuCl (0.147 g, 1.486 mmol) were placed in a Schlenk flask. The flask was filled with argon and then dry dichloromethane (20 ml) was added. Afterwards complex **34** (1.10 g, 0.991 mmol) was added and the resulting solution was stirred at room temperature for 30 min. Solvent was evaporated, resulting material was dissolved in a minimum amount of EtOAc and the insoluble white solid filtered through a Pasteur pipette containing cotton wool. The solvent was concentrated again in vacuum, and the crude catalyst was purified by flash chromatography (c-hexane/EtOAc 7:3). Removal of solvents afforded product **45** (0.31 g, 34%) as a green solid.

^1H (300 MHz, CDCl_3) δ ppm: 16.493, (s, 1H), 7.470-7.412 (m, 1H), 7.309 (s, 4H), 6.811-6.776 (m, 3H), 4.910 (heptet, 1H, $J=6.3\text{Hz}$), 4.164 (s, 4H), 3.780-3.750 (m, 8H), 3.643 (s, 4H) 3.622-3.533 (m, 4H), 2.562-2.531 (m, 8H), 1.344 (d, 6H, $J=6.3\text{Hz}$), 1.259 -1.237 (m, 24H). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 289.7, 213.7, 152.4, 149.0, 144.2, 138.9, 129.4, 125.2, 122.1, 113.1, 74.80, 67.14, 63.51, 54.62, 53.59, 28.80, 26.61, 23.41, 21.82. HRMS (ESI) calcd for $\text{C}_{47}\text{H}_{68}\text{N}_4\text{O}_3\text{ClRu}$ ($[\text{M}-\text{Cl}]^+$) m/z 873.4023 found 873.4020.

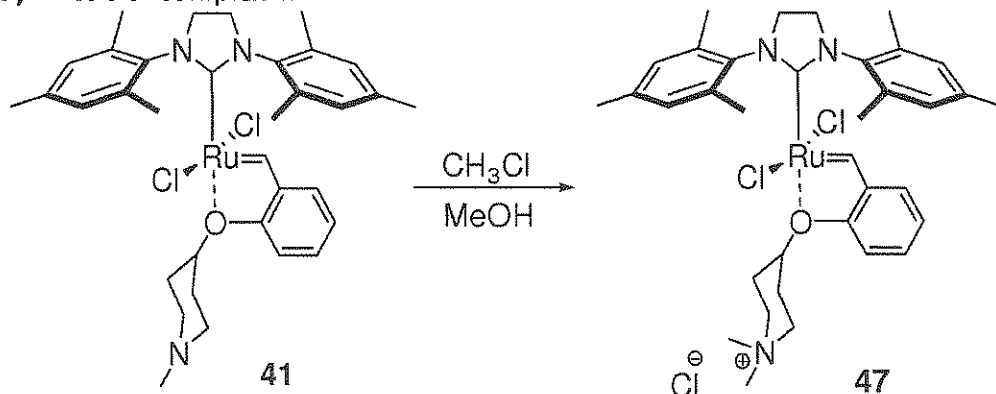
Synthesis of complex 46



The same procedure as described for complex **45** was employed to afford the catalyst **46** as a green solid in 30% yield. Column chromatography was performed using c-hexane/EtOAc 1:1 mixture.

0.450 g (30%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.490 (s, 1H), 7.450-7.393 (m, 1H), 7.311 (s, 4H), 6.792-6.764 (m, 3H), 4.550-4.380 (m, 1H), 4.160 (s, 4H), 3.790-3.760 (m, 8H), 3.637 (s, 4H), 3.613-3.548 (m, 4H), 2.534-2.554 (m, 8H), 2.188 (s, 3H), 2.133-1.859 (m, 8H), 1.245 (d, 24H, $J=6.9\text{Hz}$). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 298.4, 213.5, 152.2, 149.0, 140.1, 139.0, 129.3, 125.0, 122.3, 122.2, 112.9, 79.10, 67.16, 63.47, 54.59, 53.67, 45.67, 30.69, 28.78, 26.65, 23.36. HRMS (ESI) calcd for $\text{C}_{50}\text{H}_{74}\text{N}_5\text{O}_3\text{Cl}_2\text{Ru}$ ($[\text{M}]^+$) m/z 964.4212 found 964.4242.

Synthesis of complex 47

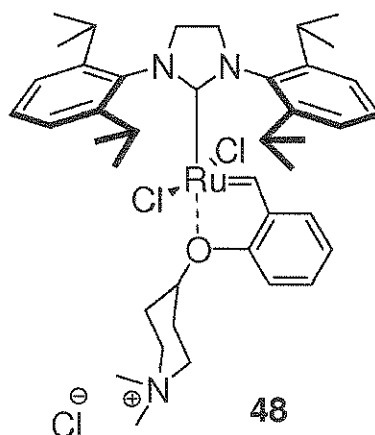


Complex **41** (0.224 g, 0.329 mmol) was placed under argon in pressure flask and dry methanol (3 ml) was added. Mixture was cooled to -30°C and cold liquid chloromethane (ca 3 ml) was added. Mixture was slowly warmed to room temperature, then placed in oil bath heated to 50 °C and stirred for 60 h. After
 5 that time flask was opened carefully to remove chloromethane and mixture was concentrated. Residue was purified by filtration through a short plug of aluminium oxide (neutral, Brockman grade I, ethyl acetate/methanol 19:1). Solvents were evaporated, catalyst was washed with ethyl acetate twice and dried on vacuum to afford complex **47** (0.220 g, 91 %) as a green solid.

10 Water solubility 2 mg/ml.

¹H (300 MHz, MeOD) δ ppm: 16.53 (s, 1H), 7.63-7.57 (m, 1H), 7.14-7.10 (m, 5H), 6.98-6.97 (m, 2H), 5.37-5.35 (m, 1H), 4.19 (s, 4H), 4.13-4.05 (m, 2H), 3.44 (s, 3H), 3.38-3.30 (m, 2H), 3.06 (s, 3H), 2.51-2.42 (m, 18H), 2.35-2.23 (m, 4H). ¹³C (75.4 MHz, MeOD) δ ppm: 296.6, 208.1, 150.7, 144.4, 139.0, 130.1, 129.6, 129.2,
 15 122.3, 113.1, 72.27, 59.56, 52.98, 51.42, 24.58, 19.98, 18.13. HRMS (ESI) calcd for C₃₅H₄₆N₃OCl₂Ru ([M-Cl]⁺) *m/z* 696.2061 found 696.2070. ¹H (300 MHz, CD₂Cl₂) δ ppm: 16.66 (s, 1H), 7.64-7.57 (m, 1H), 7.14-7.10 (m, 5H), 6.98-6.97 (m, 2H), 5.37-5.35 (m, 1H), 4.19 (s, 4H), 4.11-4.02 (m, 2H), 3.44 (s, 3H), 3.38-3.34 (m, 2H), 3.06 (s, 3H), 2.51-2.38 (m, 18H), 2.35-2.24 (m, 4H).

20 Synthesis of complex **48**

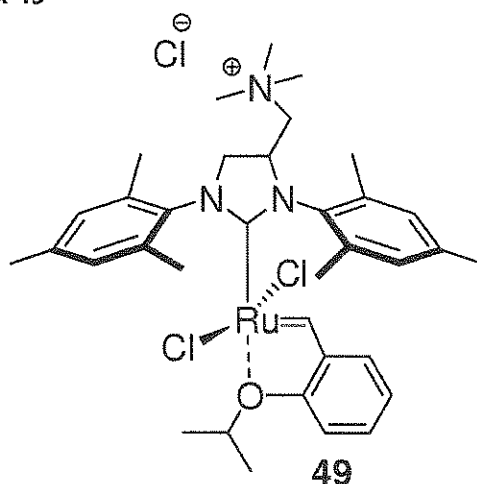


The same procedure as described for complex **47** was employed to afford the catalyst **48** as a green solid in 98% yield.

Insoluble in neat water, excellent solubility in methanol, ethanol and water/alcohol mixture.

0.208 g (98%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.381 (s, 1H), 7.594-7.264 (m, 7H), 6.986-6.832 (m, 3H), 5.370-5.084 (bs, 1H), 4.200 (s, 4H),
 5 4.000-3.720 (bs, 3H), 3.700-3.250 (bs, 8H), 3.114-2.279 (bs, 3H), 2.543-2.100 (bs, 4H), 1.724-0.724 (m, 24H). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 291.2, 212.0, 151.0, 149.5, 143.3, 136.3, 130.4, 130.1, 124.5, 123.4, 122.9, 113.3, 72.08, 59.52, 54.57, 53.81, 50.71, 28.98, 26.63, 25.03, 23.30. HRMS (ESI) calcd for $\text{C}_{41}\text{H}_{58}\text{N}_3\text{OCl}_2\text{Ru}$ ($[\text{M}-\text{Cl}]^+$) m/z 780.3000 found 780.3017

10 Synthesis of complex 49

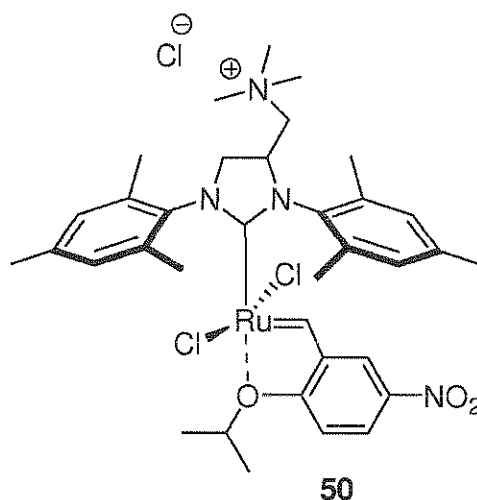


The same procedure as described for complex **47** was employed to afford the catalyst **49** as a green solid in 84% yield.

Water solubility 3 mg/ml.

15 0.218 g (84%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.375 (bs, 1H), 7.483-7.506 (m, 2H), 7.030-6.776 (d, 6H), 5.080-5.060 (bs, 1H), 4.875-4.840 (m, 1H), 4.660-4.640 (bs, 1H), 4.416-4.395 (bs, 1H), 4.230-4.180 (bs, 2H), 3.053-3.015 (bs, 9H), 2.393-2.376 (bs, 18H), 1.222-1.216 (m, 6H). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 298.5, 214.5, 152.4, 145.3, 139.8, 139.0, 130.1, 130.0, 129.5, 129.3, 122.9,
 20 122.4, 113.0, 75.70, 45.88, 21.22, 21.11, 8.70. HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{48}\text{N}_3\text{OCl}_2\text{Ru}$ ($[\text{M}-\text{Cl}]^+$) m/z 698.2218 found 698.2237.

Synthesis of complex 50

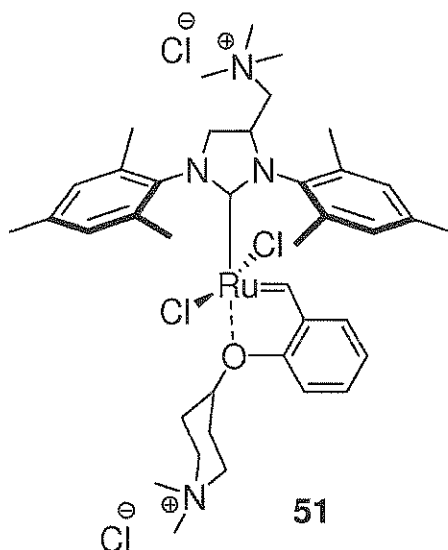


The same procedure as described for complex **47** was employed to afford the catalyst **50** as a green solid in 64% yield.

Water solubility 3 mg/ml.

- 5 0.165 g (64%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.255 (s, 1H), 8.425 (dd, $J=1.8\text{Hz}$, $J=9.0\text{Hz}$, 1H), 7.754 (d, $J=1.8\text{ Hz}$, 1H), 7.120-6.884 (m, 5H), 5.350-5.100 (m, 1H), 5.010-4.928 (m, 1H), 4.855-4.750 (m, 1H), 4.600-4.400 (m, 1H), 3.520-3.435 (m, 2H), 3.325 (s, 9H), 2.573-2.186 (m, 18H), 1.276-1.2746 (m, 6H). HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{47}\text{N}_4\text{O}_3\text{Cl}_2\text{Ru}$ ($[\text{M}-\text{Cl}]^+$) m/z 743.2069 found
- 10 743.2091. ^1H (300 MHz, CD_2Cl_2) δ ppm: 16.26 (s, 1H), 8.47 (dd, $J = 2.4\text{ Hz}$, $J = 9.0\text{ Hz}$, 1H), 7.78 (d, $J = 2.4\text{ Hz}$, 1H), 7.13-6.96 (m, 5H), 5.32-5.21 (m, 1H), 5.00 (heptet, $J = 6.0\text{ Hz}$, 1H), 4.87-4.81 (m, 1H), 4.62-4.47 (m, 2H), 3.31 (s, 9H), 3.13 (d, $J = 12.6\text{ Hz}$, 1H), 2.45 (bs, 18H), 1.28-1.25 (m, 6H). ^{13}C (75.4 MHz, CD_2Cl_2) δ ppm: 291.1, 211.1, 156.3, 144.5, 143.1, 140.2, 139.7, 139.6, 130.6, 130.0, 129.5,
- 15 124.5, 117.0, 113.0, 78.0, 68.0, 58.6, 21.0, 20.9. IR (KBr) ν 3402, 2977, 2920, 1605, 1575, 1520, 1478, 1381, 1341, 1292, 1134, 1092, 948, 916, 855, 828, 746, 657.

20 Synthesis of complex 51

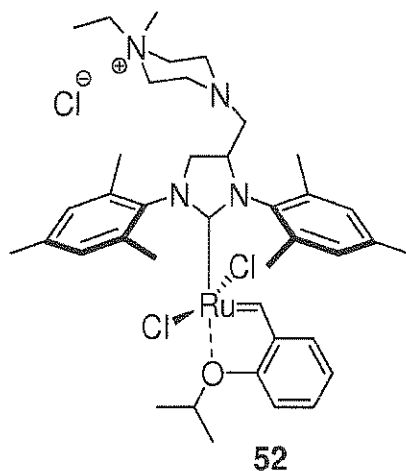


The same procedure as described for complex **47** was employed to afford the catalyst **51** as a green solid in 95% yield.

Water solubility 35 mg/ml.

- 5 0.220 g (95%) – green solid; ^1H (300 MHz, MeOD) δ ppm: 16.404-16.435 (bs, 1H), 7.692-7.641 (m, 1H), 7.203-7.149 (m, 5H), 7.051-7.002 (m, 1H), 6.933-6.908 (m, 1H), 5.239-5.068 (m, 1H), 4.868 (s, 4H), 4.665 (tr, 1H, $J=10.2\text{Hz}$), 4.370 (tr, 1H, $J=10.5\text{Hz}$), 4.172-4.062 (m, 1H), 3.459-3.348 (m, 2H), 3.230 (bs, 3H), 3.156 (s, 9H), 3.052 (s, 3H), 2.520-2.473 (m, 18H), 2.432-2.226 (m, 4H). ^{13}C (75,4 MHz, MeOD) δ
- 10 ppm: 297.3, 212.8, 150.8, 144.43, 140.1, 139.6, 130.6, 130.5, 130.0, 129.4, 129.3, 123.3, 122.4, 113.2, 72.67, 67.43, 59.98, 58.43, 53.76, 52.89, 24.79, 24.70, 20.01, 13.10. LRMS (ESI) calcd for $\text{C}_{39}\text{H}_{56}\text{N}_4\text{OCl}_2\text{Ru}$ ($[\text{M}-2\text{Cl}]^{2+}$) m/z 384.1 found 384.2.

Synthesis of complex 52

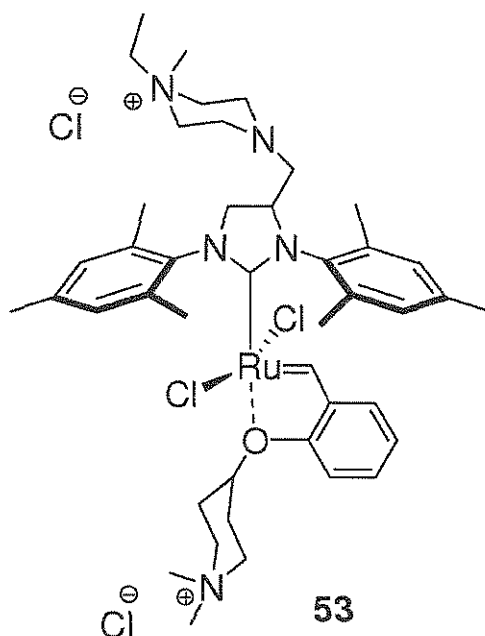


The same procedure as described for complex **47** was employed to afford the catalyst **52** as a green solid in 97% yield.

Water solubility 3 mg/ml.

- 5 0.290 g (97%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm 16.44 (s, 1H), 7.60-7.54 (m, 1H), 7.10-7.08 (m, 4H), 6.97-6.84 (m, 3H), 4.89 (heptet, 1H, $J=6.0\text{Hz}$), 4.70-4.59 (m, 1H), 4.35-4.28 (m, 1H), 3.95-3.88 (m, 1H), 3.78-3.71 (m, 2H), 3.60-3.56 (m, 2H), 3.35-3.22 (m, 5H), 2.86-2.83 (m, 2H), 2.79-2.72 (m, 2H), 2.43-2.36 (m, 18 H), 1.35 (t, 3H, $J=7.1\text{Hz}$), 1.23 (d, 6H, $J=6.0\text{Hz}$). ^{13}C (75.4 MHz, CDCl_3) δ ppm: 298.4, 214.2, 152.3, 145.3, 139.0, 138.1, 130.0, 129.9, 129.4,
- 10 122.8, 122.4, 113.0, 75.05, 60.45, 59.50 59.40, 46.90, 31.01, 22.68, 21.13, 14.16, 7.84. HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{55}\text{N}_4\text{OCl}_2\text{Ru}$ ($[\text{M}-\text{Cl}]^+$) m/z 767.2796 found 767.2802. ^1H NMR (600 MHz, CD_2Cl_2) δ ppm: 16.44 (s, 1H), 7.58-7.55 (m, 1H), 7.10-7.07 (m, 4H), 6.96-6.91 (m, 2H) 6.84 (d, 1H, $J=7.8\text{Hz}$), 4.89 (heptet, 1H, $J=6.0\text{Hz}$), 4.67-4.62 (m, 1H), 4.31 (*pseudot*, 1H, $J=10.2\text{Hz}$), 3.91 (*pseudot*, 1H, $J=9.6\text{Hz}$), 3.70-3.67 (m, 2H, NCH_2CH_3), 3.52 (bs, 2H), 3.29-3.23 (m, 5H), 2.85-2.79 (m, 4H), 2.79-2.74-2.69 (m, 2H), 2.42-2.27 (m, 18 H), 1.34 (t, 3H, $J=6.6\text{Hz}$, NCH_2CH_3), 1.22 (d, 6H, $J=6.0\text{Hz}$).
- 15

Synthesis of complex 53

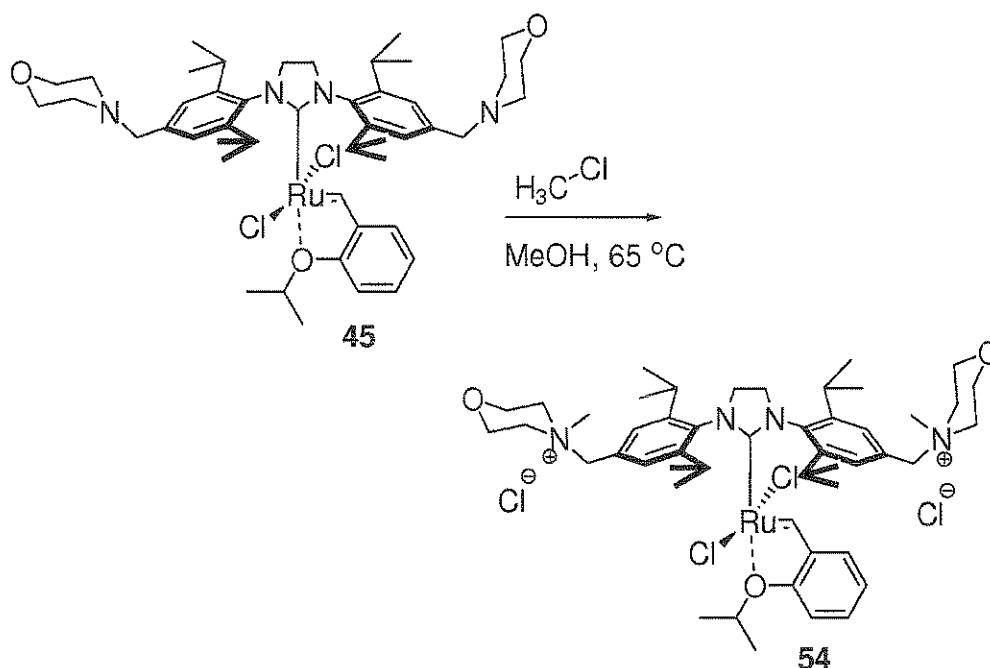


The same procedure as described for complex **47** was employed to afford the catalyst **53** as a green solid in 93% yield.

Water solubility 35 mg/ml.

- 5 0.370 g (93%) – green solid; ^1H (300 MHz, MeOD) δ ppm: 16.590 (s, 1H), 7.670-7.632 (m, 1H), 7.200-7.122 (m, 5H), 7.013 (tr, 1H, $J=7.5\text{Hz}$), 6.940-6.915 (m, 1H), 5.032 (m, 1H), 4.860 (s, 4H), 4.700-4.860 (m, 1H), 4.383 (tr, 1H, $J=10.5\text{Hz}$), 4.00-4.020 (m, 1H), 3.442-3.418 (m, 6H), 3.202 (s, 3H), 3.0310-3.019 (m, 6H), 2.871-2.462 (m, 6H), 2.464-2.011 (m, 22H), 1.334 (tr, 3H, $J=6.9\text{Hz}$). ^{13}C (75,4 MHz, MeOD) δ ppm: 297.2, 211.0, 150.7, 144.5, 139.5, 139.2, 139.0, 130.3, 129.3, 123.3, 122.4, 113.1, 72.37, 61.23, 59.80, 59.73, 59.56, 53.30, 24.77, 24.62, 27.03, 19.96. LRMS (ESI) calcd for $\text{C}_{43}\text{H}_{63}\text{N}_5\text{OCl}_2\text{Ru}$ ($[\text{M}-2\text{Cl}]^{2+}$) m/z 418.7 found 418.6.
- 10

Synthesis of complex 54



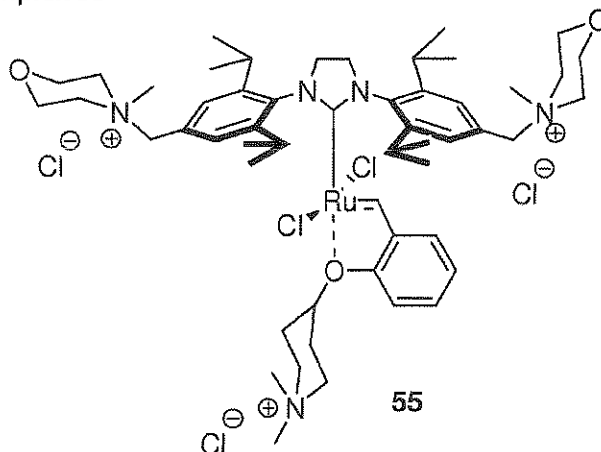
Complex **45** (0.224 g, 0.329 mmol) was placed under argon in pressure flask and dry methanol (3 ml) was added. Mixture was cooled to -30 °C and cold liquid chloromethane (ca 3 ml) was added. Mixture was slowly warmed to room temperature, then placed in oil bath heated to 65 °C and stirred for 72 h. After that time flask was opened carefully to remove chloromethane and mixture was concentrated. The residue was purified by filtration through a short plug of aluminium oxide (neutral, Brockman grade I, ethyl acetate/methanol 19:1). Solvents were evaporated, catalyst was washed with ethyl acetate twice and dried on vacuum to afford complex **54** (0.220 g, 91 %) as a green solid.

Water solubility 2 mg/ml.

¹H (300 MHz, MeOD) δ ppm: 16.577 (s, 1H), 7.653-7.546 (m, 5H), 7.065-7.021 (m, 1H), 6.924-6.875 (m, 1H), 6.820-6.764 (m, 1H), 5.021 (sep, 1H, J=6.3Hz), 4.380-4.020 (m, 12H), 3.917-3.884 (m, 3H), 3.734-3.436 (m, 11H), 3.281-3.175 (m, 8H), 1.413 (d, 6H, J=6.6Hz), 1.373-1.237 (m, 24 H). ¹³C (75,4 MHz, MeOD) δ ppm: 289.2, 212.6, 152.5, 151.0, 150.6, 149.3, 143.8, 143.7, 139.1, 138.7, 137.6, 130.0, 129.9, 129.4, 129.0, 128.2, 128.0, 126.8, 122.1, 122.0, 121.7, 113.2, 113.1, 74.9, 74.8, 69.2, 65.0, 61.5, 60.2, 59.2, 55.1, 54.7, 54.3, 52.3, 46.5, 29.1, 28.8.

28.5, 25.8, 25.4, 25.0, 22.6, 22.3, 22.0, 21.2, 7.85. LRMS (ESI) calcd for $C_{49}H_{74}N_4O_3Cl_2Ru$ ($[M-2Cl]^{2+}$) m/z 469.2 found 469.2.

Synthesis of complex 55



5

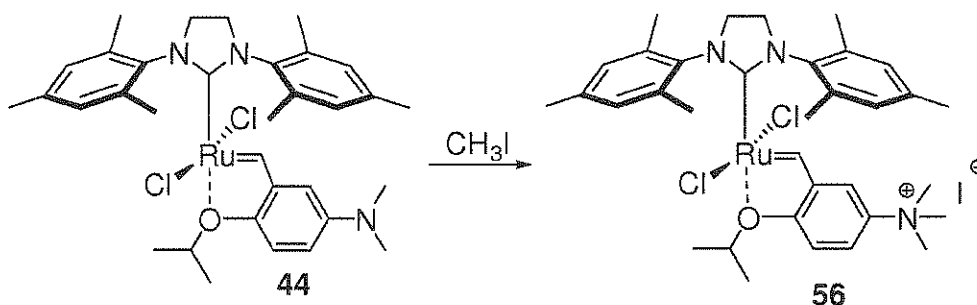
The same procedure as described for complex **54** was employed to afford the catalyst **55** as a green solid in 95% yield.

Water solubility 65 mg/ml.

0.425 g (95%) – green solid; 1H (300 MHz, MeOD) δ ppm: 16.534 (s, 1H), 7.711 (s, 4H), 7.661-7.609 (m, 1H), 7.211-7.183 (s, 1H), 7.025-6.975 (m, 1H), 6.881-6.842 (m, 1H), 5.171-5.050 (bs, 1H), 4.970 (s, 2H), 4.874 (s, 4H), 4.229-4.283 (m, 4H), 4.140-4.109 (m, 9H), 3.747-3.582 (m, 9H), 3.508-3.460 (m, 4H), 3.347-3.262 (m, 4H), 3.065-3.043 (m, 3H), 2.348-2.261 (m, 4H), 2.012 (s, 3H), 1.342-1.213 (m, 26H). ^{13}C (75,4 MHz, MeOD) δ ppm: 287.8, 211.3, 150.7, 150.0, 143.2, 138.8, 130.4, 130.3, 129.4, 128.6, 127.5, 123.3, 122.2, 113.3, 72.82, 69.10, 60.3, 60.16, 60.09, 55.39, 54.86, 45.21, 28.91, 25.49, 25.41, 22.46, 22.27, 13.10. LRMS (ESI) calcd for $C_{53}H_{82}N_5O_3Cl_2Ru$ ($[M-3Cl]^{3+}$) m/z 336.1 found 336.1.

15

Synthesis of complex 56

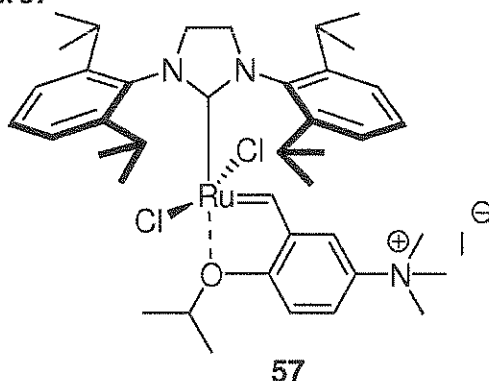


Complex **44** (0.441 g, 0.658 mmol) was placed under argon in a Shlenk flask and iodomethane (8.19 ml, 132 mmol) was added. Mixture was stirred at room temperature for 5 h. Ethyl acetate was added to a reaction mixture and crude product was filtered off. Next complex was washed with ethyl acetate twice then precipitated from dichloromethane/ethyl acetate mixture, filtered and dried on vacuum to afford **56** (491 mg, 92%) as a green solid.

Water solubility 1 mg/ml.

¹H (300 MHz, CDCl₃) δ ppm: 16.386 (s, 1H), 7.050-7.066 (m, 7H), 4.912 (heptet, 1H, J=6 Hz), 4.204 (s, 4H), 3.892 (s, 9H), 2.448-2.389 (m, 18H), 1.232 (d, 6H, J=6 Hz). ¹³C (75,4 MHz, CDCl₃) δ ppm: 289.4, 207.9, 152.5, 144.2, 141.9, 139.1, 138.7, 129.5, 122.1, 115.5, 112.1, 57.99, 51.20, 21.58, 21.54, 21.21, 21.04. LRMS (ESI) calcd for C₃₄H₄₆N₃OCl₂Ru ([M-I]⁺) *m/z* 684.2 found 684.2.

Synthesis of complex 57

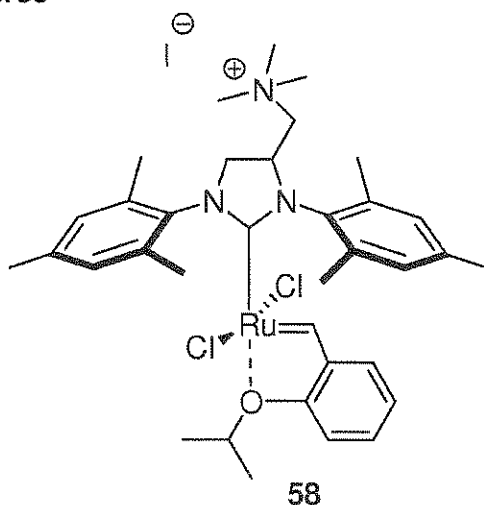


15 **57**
The same procedure as described for complex **56** was employed to afford the catalyst **57** as a green solid in 84% yield.

0.100 g (84%) – green solid; ^1H (300 MHz, CD_2Cl_2) δ ppm: 16.181 (s, 1H), 8.491 (dd, 1H, $J=9.3\text{Hz}$, $J=2.4\text{Hz}$), 7.589-7.538 (m, 2H), 7.400-7.373 (m, 4H), 7.055 (d,

1H, $J=9.3\text{Hz}$), 6.889 (d, 1H, $J=2.4\text{Hz}$), 4.946 (heptet, 1H, $J=6.0\text{Hz}$), 4.208-4.216 (m, 4H), 3.722-3.875 (bs, 9H), 3.553-3.490 (m, 4H), 1.332 (d, 6H, $J=6.0\text{Hz}$), 1.265-1.242 (m, 24H). ^{13}C (75,4 MHz, CD_2Cl_2) δ ppm: 282.0, 210.1, 152.8, 149.2, 143.7, 141.8, 136.3, 129.9, 124.8, 124.5, 121.2, 115.1, 111.2, 57.86, 54.52, 28.89, 26.62, 23.42, 21.67. HRMS (ESI) calcd for $\text{C}_{40}\text{H}_{58}\text{N}_3\text{OCl}_2\text{Ru}$ ($[\text{M}-\text{I}]^+$) m/z 768.3000 found 768.2995.

Synthesis of complex 58



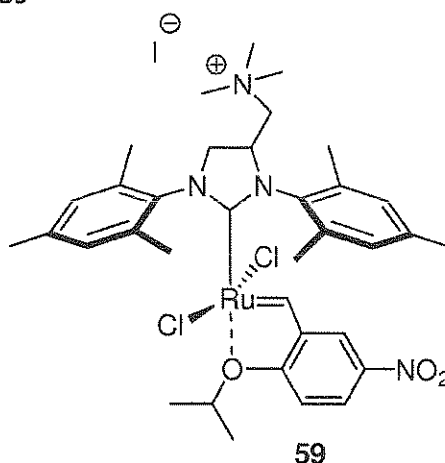
The same procedure as described for complex **56** was employed to afford the catalyst **58** as a green solid in 98% yield.

0.138 g (98%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.356 (s, 1H), 7.506-7.494 (m, 1H), 7.115-6.757 (m, 7H), 5.220-5.030 (bs, 1H), 4.865-4.820 (m, 1H), 4.704-4.680 (m, 1H), 4.500-4.400 (bs, 1H), 3.393-2.951 (m, 11H), 2.640-2.169 (m, 18H), 1.234-1.190 (m, 6H). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 298.5, 214.4, 152.4, 145.2, 139.9, 139.2, 138.6, 131.6, 130.2, 129.5, 128.7, 128.5, 126.5, 122.8, 122.8, 113.1, 75.27, 67.95, 58.30, 54.31, 22.04, 21.10, 19.10, 14.2. HRMS (ESI) calc for $\text{C}_{35}\text{H}_{48}\text{N}_3\text{OCl}_2\text{Ru}$ ($[\text{M}-\text{I}]^+$) m/z 698.2218 found 698.2228.

^1H (300 MHz, CD_2Cl_2) δ ppm: 16.33 (s, 1H), 7.61-7.53 (m, 1H), 7.13-7.05 (m, 4H), 6.94-6.92 (d, $J = 4.5\text{ Hz}$, 2H), 6.87-6.84 (d, $J = 8.4\text{ Hz}$, 2H), 5.26-5.15 (m, 1H), 4.88 (heptet, $J = 6.0\text{ Hz}$, 1H), 4.81-4.74 (m, 1H), 4.63-4.50 (bs, 2H), 3.24 (s, 9H), 3.10 (d, $J = 12.3\text{ Hz}$, 1H), 2.43 (bs, 18H), 1.21 (dd, $J = 2.4\text{ Hz}$, $J = 6.0\text{ Hz}$, 6H). ^{13}C (75.4 MHz, CD_2Cl_2) δ ppm: 296.9,

214.0, 152.2, 145.1, 139.9, 139.7, 139.3, 130.6, 130.1, 129.5, 129.3, 122.5, 122.4, 113.1, 75.4, 67.7, 58.3, 20.9.

Synthesis of complex 59

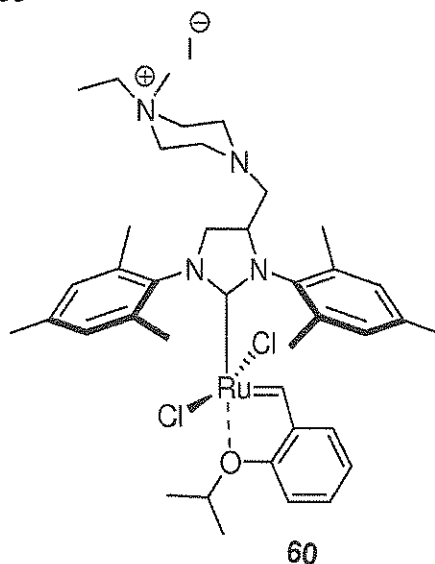


- 5 The same procedure as described for complex **56** was employed to afford the catalyst **59** as a green solid in 86% yield.

0.045 g (86%) – green solid; LRMS (ESI) calcd for $C_{35}H_{47}Cl_2N_4O_3Ru$ ($[M-I]^+$) m/z 743.2 found 743.1. IR (KBr) ν 3434, 2980, 2919, 1605, 1576, 1521, 1478, 1421, 1379, 1343, 1344, 1197, 1136, 1094, 1013, 950, 917, 857, 829, 745, 658.

10

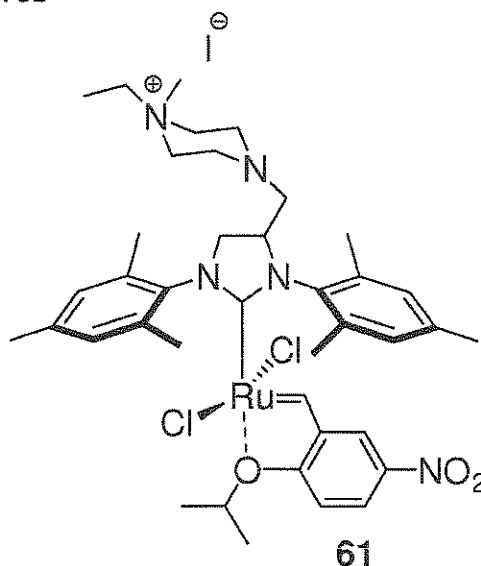
Synthesis of complex 60



The same procedure as described for complex **56** was employed to afford the catalyst **60** as a green solid in 85% yield.

0.385 g (85%) – green solid ^1H (300 MHz, CD_2Cl_2) δ ppm: 16.443 (s, 1H), 7.504-7.446 (m, 1H), 7.108-6.741 (m, 7H), 4.893 (heptet, 1H, $J=6.0\text{Hz}$), 4.677-4.598 (m, 1H), 4.338 (tr, 1H, 10.8Hz), 3.947-3.882 (m, 1H), 3.676-3.204 (m, 6H), 3.204 (s, 3H), 2.903-2.689 (m, 6H) 2.415-2.440 (m, 18H), 1.321-1.266, (m, 3H), 1.247-1.417 (m, 6H). ^{13}C (75,4 MHz, CD_2Cl_2) δ ppm: 296.6, 213.6, 152.0, 145.2, 139.9, 129.9, 129.7, 129.4, 122.4, 122.3, 113.0, 60.72, 60.18, 60.00, 56.98, 46.74, 46.58, 20.91, 7.740. HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{55}\text{N}_4\text{OCl}_2\text{Ru}$ ($[\text{M}-\text{I}]^+$) m/z 767.2796 found 767.2792.

Synthesis of complex 61



10

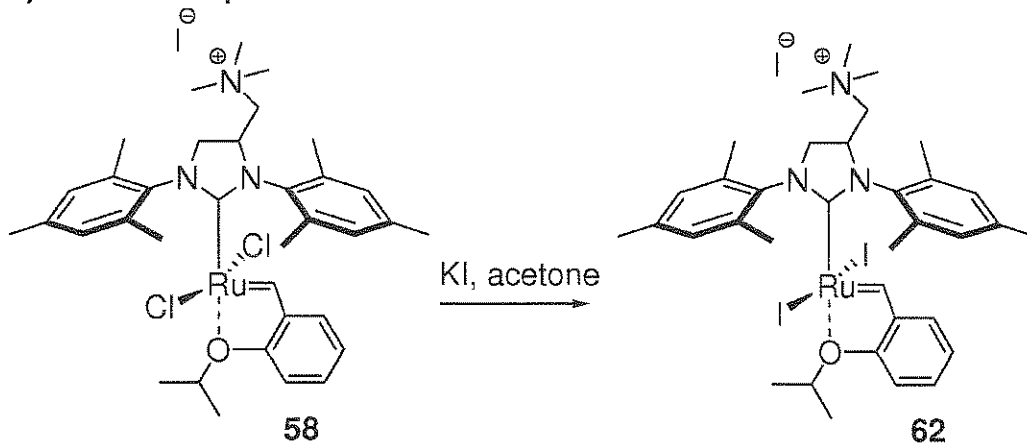
The same procedure as described for complex **56** was employed to afford the catalyst **61** as a green solid in 85% yield.

15

0.180 g (85%) – green solid; ^1H (300 MHz, CDCl_3) δ ppm: 16.360 (s, 1H), 8.452-8.386 (m, 1H), 7.770-7.612 (m, 1H), 7.152-6.876 (m, 5H), 5.001-4.940 (m, 1H) 4.753-4.500 (m, 1H) 4.450-4.200 (m, 1H), 3.931-3.870 (m, 1H), 3.656-3.383 (m, 4H), 3.380-2.990 (m, 5H), 2.850-2.765 (m, 5H) 2.418-2.030 (m, 19H), 1.335-1.270 (m, 9H). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 292.3, 156.4, 144.6, 143.1, 139.4, 139.2, 130.6, 130.2, 129.5, 124.7, 124.4, 117.4, 112.9, 76.7, 67.27, 60.8, 60.3, 60.02, 47.65, 46.83, 31.60, 22.66, 21.83, 21.57, 21.11, 14.13. HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{54}\text{N}_5\text{O}_3\text{Cl}_2\text{Ru}$ ($[\text{M}-\text{I}]^+$) m/z 812.2647 found 812.2655.

20

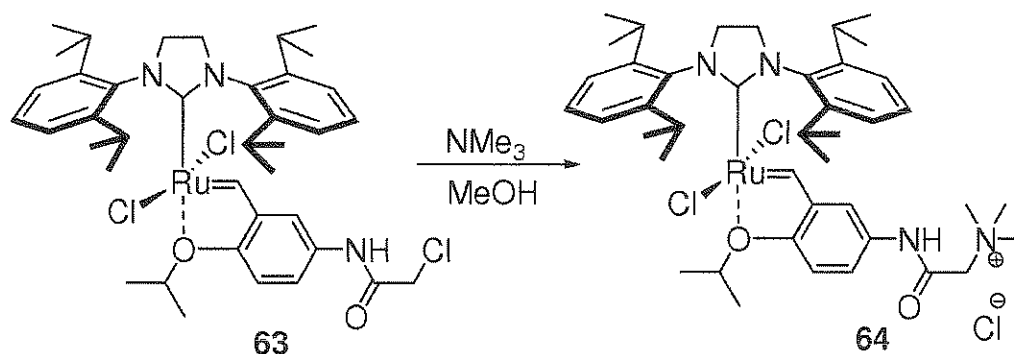
Synthesis of complex 62



- 5 Potassium iodide (0.723 g, 4.35 mmol) was added to a solution of complex **58** (0.120 g, 0.145 mmol) in acetone (5 ml). Mixture was stirred for 1 h and then solvent was evaporated. Catalyst was dissolved in dichloromethane (10 ml) and insoluble material was filtered off. Dichloromethane was evaporated to dryness and above procedure was repeated 3 times. Product was dried on vacuum.
- 10 Complex **62** was obtained as a dark green solid (0.130 g, 89%). Product was obtained as a mixture of rotamers.

^1H (300 MHz, CDCl_3) δ ppm: 15.488-15.328 (m, 1H), 7.564-7.515 (m, 1H), 7.114-6.816 (m, 7H), 5.090-4.973 (m, 2H), 4.743-4.703 (m, 1H), 4.482-4.395 (m, 1H), 3.357 (s, 9H), 3.200-3.0924 (m, 2H), 2.756-2.166 (m, 18H), 1.502-1.254 (m, 6H). ^{13}C (75,4 MHz, CDCl_3) δ ppm: 299.7, 217.8, 216.8, 153.3, 153.1, 145.3, 144.9, 140.0, 139.9, 139.7, 139.2, 138.4, 138.2, 137.7, 137.5, 136.7, 134.6, 132.8, 131.5, 131.3, 131.1, 130.4, 130.1, 129.6, 123.4, 122.0, 113.5, 75.95, 68.6, 67.88, 67.26, 59.71, 58.3, 57.9, 54.4, 25.53, 25.07, 21.90, 21.8, 21.68, 21.52, 21.4, 21.3, 20.80. HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{48}\text{N}_3\text{ORuI}_2$ ($[\text{M-I}]^+$) m/z 882.0930 found 882.0958.

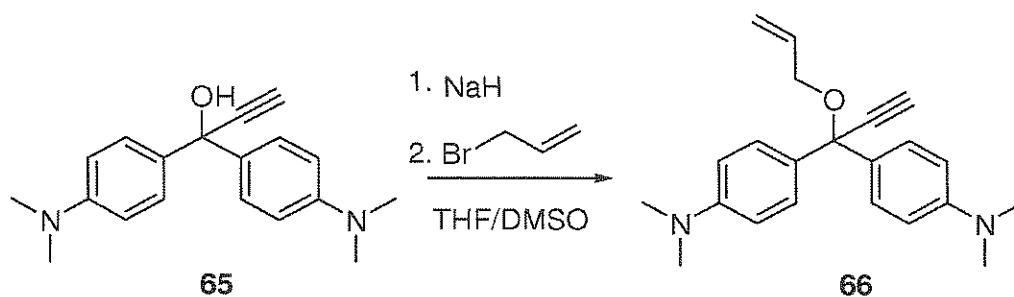
20 **Synthesis of complex 64**



Complex **63** (0.224 g, 0.329 mmol) was placed under argon in pressure flask and dry methanol (3 ml) was added. Mixture was cooled to -10 °C and cold trimethylamine (33% wt in methanol, 3 ml) was added. Mixture was slowly warmed to room temperature, then placed in oil bath heated to 50°C and stirred for 60 h. Reaction mixture was concentrated and the residue was filtered through a short pad of aluminium oxide (neutral, Brockman grade I, ethyl acetate/methanol 19:1). Solvents were evaporated, catalyst was washed with ethyl acetate twice and dried on vacuum to afford **64** (0.220 g, 91%) as a green solid.

¹H (300 MHz, CD₂Cl₂) δ ppm: 16.240 (s, 1H), 11.550-11.350 (bs, 1H) 7.872-7.846 (m, 1H), 7.626 (m, 2H), 7.414-7.389 (m, 5H) 6.808-6.780 (m, 1H), 4.897-4.856 (m, 1H), 4.762-4.600 (m, 2H), 4.202 (s, 4H), 3.594-3.550 (m, 4H), 3.353 (s, 9H), 1.326-1.220 (m, 30H).

Synthesis of compound 66



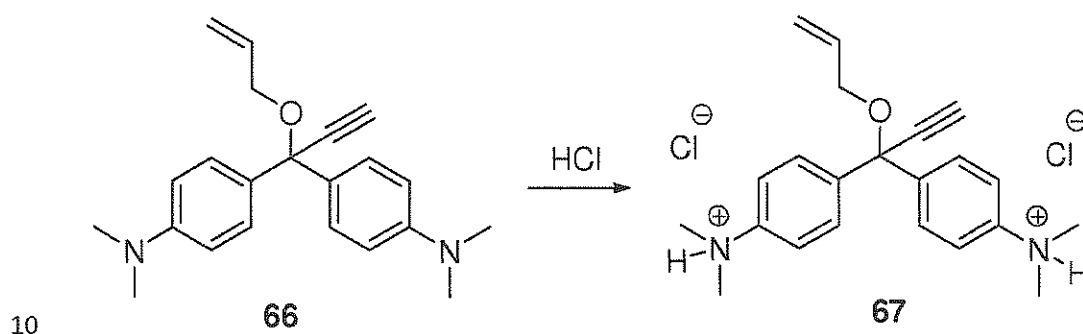
NaH (15 mg, 0.374 mmol) was added at -10°C to a solution of **65** (100 mg, 0.340 mmol) in THF/DMSO mixture (9/1, 4 ml). Reaction mixture was warmed to room

temperature and stirred for 1 h. Then it was cooled down to -10°C and allyl bromide (0,044 ml, 0.510 mmol) was added in one portion. After that, mixture was stirred at room temperature for 1 h. Solvents were evaporated and crude product was purified by column chromatography (c-hexane/EtOAc/Et₃N 8/2/0.1).

5 Solvents were removed to afford **66** (103 mg, 91%) as a light-yellow oil.

¹H (300 MHz, CDCl₃) δ ppm: 7.422-7.392 (m, 4H), 6.701-6.650 (m, 4H), 6.045-5.935 (m, 1H), 5.389-5.319 (m, 1H), 5.159-5.118 (m, 1H), 4.036-4.008 (m, 2H), 2.936 (s, 12 H), 2.827 (s, 1H).

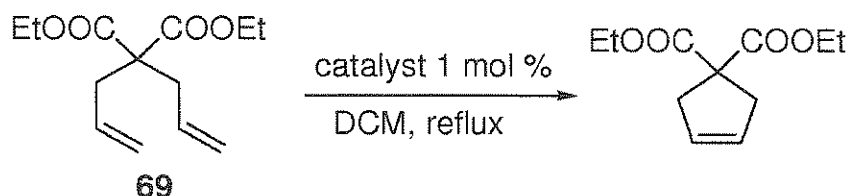
Synthesis of compound 67



HCl (1M in Et₂O, 0.625 ml) was added at 0°C to a solution of **66** (102 mg, 0.305 mmol) in Et₂O (4 ml). White solid was filtered, washed with Et₂O (2x5 ml) and dried on vacuum to afford **67** (114 mg, 92 %) as a green solid (product changed from white to green during work up).

15 ¹H (300 MHz, D₂O) δ ppm: 7.772-7.742 (m, 4H), 7.533-7.503 (m, 4H), 5.988-5.896 (m, 1H), 5.357-5.163 (m, 2H), 4.027-3.999 (m, 2H), 3.475 (s, 1 H), 3.172 (s, 12H).

Example 1 - ring closing metathesis of 2,2-diallyl-malonic acid diethyl ester.



Appropriate amount of catalyst (1 mol%) was added under argon to a solution **69** (165 mg, 0.69 mmol) in dry, degassed dichloromethane. Reaction mixture was stirred at reflux, progress of the reaction was monitored using GC method. After

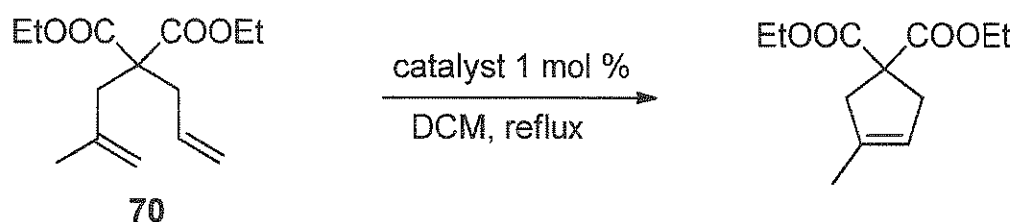
20

completion of the reaction, mixture was filtered through a pad of silica gel. Weight of silica gel used was two hundred times greater than the weight of the catalyst. Product was removed from silica gel with additional amount of dichloromethane. In all cases product was isolated with quantitative yield. GC

5 purity and Ru content (using ICP MS method) was determined.

Entry	Catalyst	Time [min]	GC purity [%]	Ru [ppm]
1	B	30	99	2180
2	57	30	95	73
3	58	240	97	3,8
4	59	60	98	2.6
5	60	240	99	3.1

Example 2 - ring closing metathesis of 2-allyl-2-(2-methyl-allyl)-malonic acid diethyl ester.



10 Appropriate amount of catalyst (1 mol%) was added under argon to a solution of **70** (196 mg, 0.77 mmol) in dry, degassed dichloromethane. Reaction mixture was stirred at reflux, progress of the reaction was monitored using GC method. After completion of the reaction, mixture was filtered through a pad of silica gel. Weight of silica gel used was two hundred times greater than the weight of the

15 catalyst. Product was removed from silica gel with additional amount of dichloromethane. In all cases product was isolated with quantitative yield. GC purity and Ru content (using ICP MS method) was determined.

Entry	Catalyst	Time [min]	GC purity [%]	Ru [ppm]
1	A	120	94	3640
2	A	120	97	658 ^a
3	A	120	89	293 ^b

4	B	50	98	1950
9	50	120	98	11 ^c
5	57	60	92	55
6	58	600	91	0.89
7	58	600	91	9 ^d
8	59	300	97	1
10	60	600	92	2.1
11	61	300	95	1.8
12	62	600	80	ND

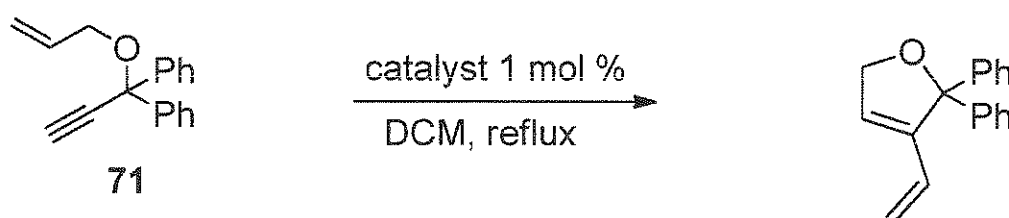
^a – result obtained with commercially available scavenger: *SiliaBond* Thiol, using protocol recommended by SILICYCLE

^b – result obtained with commercially available scavenger: *SiliaBond* DMT, using protocol recommended by SILICYCLE

^c – reaction mixture was washed with water five times

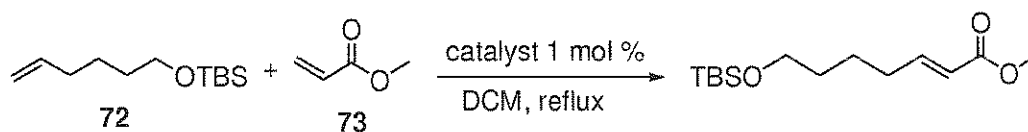
^d – product purification: silica gel was added to the reaction mixture and this was stirred for 10 min; after that reaction mixture was filtered through a Schott funnel.

10 Example 3 - alken-alkyn ring closing metathesis.



Appropriate amount of catalyst (1 mol%) was added under argon to a solution of **71** (196 mg, 0.77 mmol) in dry, degassed dichloromethane. Reaction mixture was stirred at reflux, progress of the reaction was monitored using GC method. After completion of the reaction, mixture was filtered through a pad of silica gel. Weight of silica gel used was two hundred times greater than the weight of the catalyst. Product was removed from silica gel with additional amount of dichloromethane. In all cases product was isolated with quantitative yield. GC purity and Ru content (using ICP MS method) was determined.

Entry	Catalyst	Time [min]	GC purity [%]	Ru [ppm]
1	B	15	>99,5	1430
2	57	15	>99,5	74
3	58	80	96,2	9,2
4	59	30	>99,5	7,8
5	60	80	97,5	3,8

Example 4 - cross metathesis.

Appropriate amount of catalyst (1 mol%) was added under argon to a solution of **72** and **73** (196 mg, 0.77 mmol) in dry, degassed dichloromethane. Reaction mixture was stirred at reflux, progress of the reaction was monitored using GC method. After completion of the reaction, mixture was filtered through a pad of silica gel. Weight of silica gel used was two hundred times greater than the weight of the catalyst. Product was removed from silica gel with additional amount of dichloromethane. GC purity and Ru content (using ICP MS method) was determined.

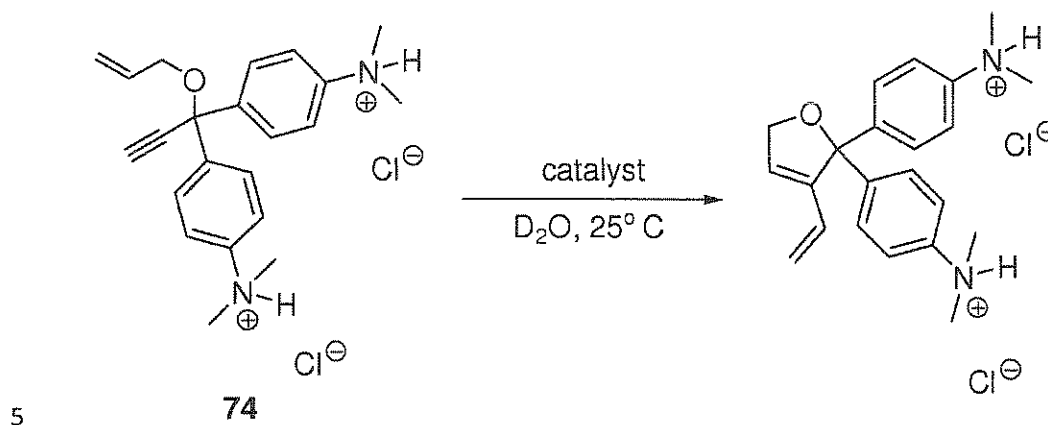
Entry	Catalyst	Time [min]	GC purity [%]	E/Z	Yield [%]	Ru [ppm]
1	A	40	56,5 ^c	21/1	87	2550
2	A	40	95	21/1	89	1310 ^a
3	A	40	91	19/1	99	109 ^b
4	B	15	99	17/1	94	704
5	49	80	92	16/1	93	4,2
6	57	30	95	15/1	94	97
7	58	80	97	18/1	96	1,7
8	59	40	98	17/1	96	0,77
9	60	80	97	18/1	95	10
10	61	40	97	17/1	89	1,5
11	62	260	56	13/1	97	ND

^a – results obtained with commercially available scavenger: SiliaBond Thiol, using protocol recommended by SILICYCLE

^b – results obtained with commercially available scavenger: SiliaBond DMT, using protocol recommended by SILICYCLE

^c – conversion >99% (GC)

Example 5 - alken-alkyn ring closing metathesis in water.

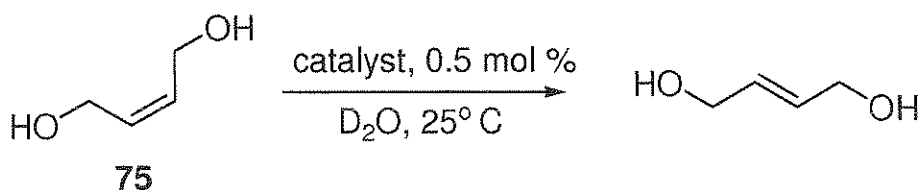


Appropriate amount of catalyst (2.5 or 5 mol%) was added on air to a solution of **74** (61 mg, 0.15 mmol) in D₂O (1,5 ml). Reaction mixture was stirred at 25 °C. 0,7 ml of reaction mixture was transferred to an NMR tube. Conversion and product purity was determined using NMR method.

10 Product: ¹H NMR (500 MHz, D₂O): δ = 3.34 (s, 12H), 4.87 (br s, 2H), 5.26 (d, 1H, J=11 Hz), 5.3 (d, 1H, J=17.5 Hz), 6.34 (dd, 1H, J=18 Hz, J=11.5 Hz), 6.46 (br s, 1H), 7.59-7.61 (m, 4H) 7.65-7.78 (m, 4H) ; ¹³C NMR (50 MHz, D₂O): δ = 46.5, 74.0, 94.0, 118.9, 120.5, 126.9, 128.6, 130.1, 141.0, 141.9, 144.4.

Entry	Catalyst (loading mol %)	Time [h]	Conversion [%]	Purity [%]
1	49 (2,5)	24	94	72
2	52 (5)	24	>98	80
3	53 (2,5)	1,5	59	98
4	54 (5)	24	>98	92

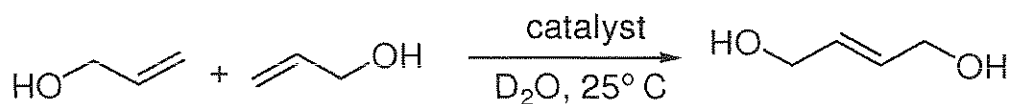
15 **Example 6 - isomerization of *cis*-1,4-butenediol in water.**



Appropriate amount of catalyst (0,5 mol%) was added on air, at 25 °C to a solution of **75** (12 mg, 0.14 mmol) in D₂O (0,7 ml). Reaction mixture was transferred to an NMR tube and conversion and was determined using NMR method.

Entry	Catalyst	Time [min]	Conversion [%]
1	47	8	93
2	49	65	73
3	51	39	92
4	52	64	71
5	53	10	94
6	54	64	52
7	55	16	94
8	56	64	44

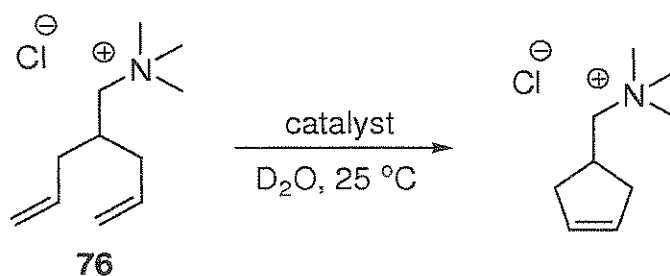
Example 7 - self metathesis of allyl alcohol in water.



Appropriate amount of catalyst (2.5 or 5 mol%) was added on air to a solution of allyl alcohol (12 mg, 0.2 mmol) in D₂O (1 ml). Reaction mixture was stirred at 25 °C. 0,7 ml of reaction mixture was transferred to an NMR tube and conversion was determined using NMR method.

Entry	Catalyst (loading mol %)	Time [h]	Conversion [%]	E/Z
1	49 (2,5)	1,5	82	9,5/1
2	49 (2,5)	24	78	11,9/1
3	49 (5)	1,5	82	11,1/1
4	49 (5)	24	89	-
5	51 (2,5)	1,5	54	6,7/1
6	51 (2,5)	24	53	6,9/1

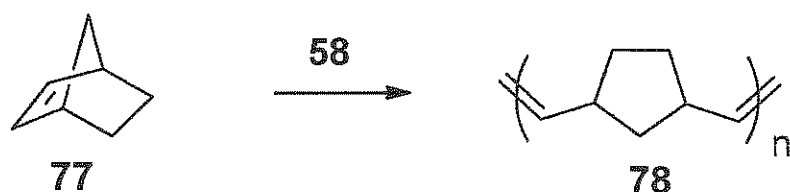
7	51 (5)	1,5	64	6,7/1
8	51 (5)	24	70	8,0/1
9	52 (5)	1,5	77	-
10	52 (5)	24	89	11,2/1
11	53 (2,5)	1,5	59	9,0/1
12	53 (2,5)	24	64	8,3/1
13	53 (5)	1,5	53	8,2/1
14	53 (5)	24	62	8,2/1
15	54 (2,5)	1,5	57	7,7/1
16	54 (2,5)	24	60	9,4/1
17	54 (5)	1,5	72	9,1/1
18	54 (5)	24	86	7,4/1
19	55 (5)	1,5	72	12,1/1
20	56 (2,5)	1,5	68	8,2/1
21	56 (2,5)	24	73	10,8/1

Example 8 - ring closing metathesis in water.

Appropriate amount of catalyst (2.5 or 5 mol%) was added on air to a solution of **76** (41 mg, 0.2 mmol) in D₂O (1 ml). Reaction mixture was stirred at 25 °C. 0,7 ml of reaction mixture was transferred to an NMR tube and conversion was determined using NMR method.

Entry	Catalyst (loading mol %)	Time [h]	Conversion [%]
1	49 (2,5)	2,5	97
2	49 (2,5)	24	>98
3	51 (2,5)	2,5	95
4	51 (2,5)	24	>98
5	52 (2,5)	2,5	96
6	52 (2,5)	24	>98
7	53 (2,5)	2,5	88
8	53 (2,5)	24	89
9	54 (2,5)	2,5	86

10	55 (2,5)	24	86
11	55 (5)	2,5	>98
12	56 (2,5)	2,5	>98

Example 9 - ring opening metathesis polimerization (ROMP)

Appropriate amount of catalyst **58** (0.25 mol%) was added under argon to a solution of **77** (318 mg, 3.38 mmol) in dry, degased dichloromethane. Reaction mixture was stirred at room temperature for 10 minutes. Silica gel (318 mg) was added to the reaction mixture and resulted suspension was stirred for 10 minutes. Next, suspension was filtered through a funnel and colorless viscous filtrate was concentrated on rotavapor to dryness to afford **78** (295 mg, 93%) as a white solid. Ruthenium content in the product (8 ppm) was determined by ICP MS method.

As it is shown in examples 1-9, catalysts described herein are highly active and effective in various metathesis transformation, giving the product with low ruthenium contamination. Moreover catalysts described herein efficiently mediate metathesis reactions in water at relatively low loadings.

The diagram shows a metal complex where a central metal atom M is coordinated by a macrocyclic ligand and a phenyl group. The macrocyclic ligand consists of two benzene rings connected by a five-membered ring containing two nitrogen atoms. The left benzene ring has substituents $R^2, R^5, R^6, R^{6'}$ and is part of a larger structure with R^7 and R^8 . The right benzene ring has substituents $R^3, R^4, R^{4'}, R^{5'}$. The five-membered ring has substituents R^2, R^3 and a nitrogen atom with substituent R^5 . The metal atom M is also coordinated by a phenyl group with substituent R^1 and a group R . The complex is shown with counterions $2X_1^{2-}$ and $4X_2^{2-}$.

R² and R³ are, independently, H, optionally substituted —C₁₋₆ alkyl, optionally substituted —C₃₋₈ cycloalkyl, optionally substituted —C₅₋₁₀ aryl, optionally substituted —C₁₋₂₀ alkylamino, optionally

substituted $-C_{1-20}$ alkylphosphino, optionally substituted $-C_{1-20}$ quaternary alkylammonium, or optionally substituted $-C_{1-20}$ alkylphosphonium, wherein each substituent is independently: $-C_{5-10}$ aryl, $-C_{4-10}$ heterocyclic, or a $-C_{4-10}$ quaternized heterocyclic group, which in turn may be substituted with at least one: nitro, $-C_{1-6}$ alkyl, $-C_{1-6}$ alkoxy, $-C_{5-10}$ aryl group or halogen;

R^2 and R^3 may be optionally linked together to form a substituted or unsubstituted, fused $-C_{4-8}$ carbocyclic ring, or a substituted or unsubstituted, fused aromatic ring;

R^4 is halogen, optionally substituted $-C_{1-20}$ alkyl, optionally substituted $-C_{2-20}$ alkenyl, optionally substituted $-C_{2-20}$ alkynyl, optionally substituted $-C_{5-10}$ aryl, optionally substituted $-C_{1-20}$ alkoxy, optionally substituted $-C_{2-20}$ alkenyloxy, optionally substituted $-C_{2-20}$ alkynyloxy, optionally substituted $-C_{5-10}$ aryloxy, optionally substituted $-C_{1-20}$ alkoxy carbonyl, optionally substituted $-C_{1-20}$ alkylamino, optionally substituted $-C_{1-20}$ protonated alkylamino, optionally substituted amino, optionally substituted protonated amino, optionally substituted $-C_{1-20}$ alkylphosphino, optionally substituted $-C_{1-20}$ alkylthiol, optionally substituted $-C_{1-20}$ quaternary alkylammonium, optionally substituted $-C_{1-20}$ alkylphosphonium, optionally substituted $-C_{4-10}$ quaternized heterocyclic, nitro, carboxyl, optionally substituted amido, optionally substituted sulfonamido, or optionally substituted $-C_{1-20}$ perhaloalkyl; wherein each substituent is independently $-C_{1-20}$ alkyl, $-C_{1-20}$ perhaloalkyl, $-C_{5-10}$ aryl, or a $-C_{4-10}$ quaternized heterocyclic group;

n is 0, 1, 2, 3, or 4;

R^5 , $R^{5'}$, R^6 , $R^{6'}$, and R^7 are, independently, H, optionally substituted $-C_{1-6}$ alkyl, optionally substituted $-C_{1-20}$ alkylamino, optionally substituted $-C_{1-20}$ alkylphosphino, optionally substituted $-C_{1-20}$ quaternary alkylammonium, optionally substituted $-C_{1-20}$ alkylphosphonium, optionally substituted $-C_{4-10}$ heterocyclic, optionally substituted $-C_{4-10}$ quaternized heterocyclic group, wherein each substituent is independently a $-C_{4-10}$ quaternized heterocyclic, $-C_{1-6}$ alkyl, or $-C_{5-10}$ aryl, which in turn may be substituted with nitro, $-C_{1-6}$ alkyl, $-C_{1-6}$ alkoxy, $-C_{5-10}$ aryl group or halogen;

R^5 and R^6 , and $R^{5'}$ and $R^{6'}$ may be optionally linked together to form a substituted or unsubstituted, fused $-C_{4-8}$ carbocyclic ring, or a substituted or unsubstituted, fused aromatic ring;

R^8 is optionally substituted $-C_{1-20}$ alkyl, optionally substituted $-C_{3-8}$ cycloalkyl, optionally substituted $-C_{2-20}$ alkenyl, or optionally substituted $-C_{2-20}$ alkynyl; wherein each substituent is independently a halogen atom, $-C_{5-10}$ aryl, $-C(=O)-C_{1-6}$ alkyl, $-C(=O)-O-C_{1-6}$ alkyl, $-C(=O)-N(C_{1-6} \text{ alkyl})_2$,

—C(=O)—N—(C₁₋₆ alkyl)—O—C₁₋₆ alkyl, —C(=O)—C₅₋₁₀ aryl, —C(=O)—O—C₅₋₁₀ aryl, —(=O)—N(C₅₋₁₀ aryl)₂, or —C(=O)—N—(C₅₋₁₀ aryl)—O—C₅₋₁₀ aryl;

p is 1, 2, 3, 4, or 5;

r is 0, 1, 2, or 3;

R⁸ is H, —C₁₋₂₀ alkyl, C₃₋₈ cycloalkyl, —C₂₋₂₀ alkenyl, or —C₂₋₂₀ alkynyl;

q is 0, 1, 2 or 3;

s is 0, 1, 2, or 3; and

wherein at least one substituent among R², R³, R⁵, R^{5'}, R⁶, R^{6'}, and R⁷ contains a quaternary onium group.

2. The complex of claim 1, wherein

M is ruthenium;

X, X¹, X² and X^{2'} are, independently, halogen, —C₁₋₅ carboxyl, —C₁₋₆ alkyl, —C₅₋₁₀ aryl, —C₁₋₆ alkoxy, —C₅₋₁₀ aryloxy, —C₁₋₅ alkylthiol, —C₁₋₅ alkylsulfonyl, CH₃SO₄, or benzoate;

Y is O, S or N;

R is H, —C₁₋₅ alkyl or —C₅₋₁₀ aryl group;

R¹ is —C₁₋₆ alkyl, C₃₋₈ cycloalkyl, —C₅₋₁₀ aryl, —C₅₋₁₀ aryloxy, —C₁₋₆ alkylamino, —C₁₋₆ alkylammonium, —C₄₋₁₀ heterocyclic, —C₄₋₁₀ quaternized N-heterocyclic, —CH₂C(=O)—C₁₋₆ alkyl, —CH₂C(=O)—O—C₁₋₆ alkyl, —CH₂C(=O)—N(C₁₋₆ alkyl)₂, —CH₂C(=O)—N—(C₁₋₆ alkyl)—O—C₁₋₆ alkyl, —CH₂C(=O)—C₅₋₁₀ aryl, —CH₂C(=O)—O—C₅₋₁₀ aryl, —CH₂C(=O)—N(C₅₋₁₀ aryl)₂, or —CH₂C(=O)—N—(C₅₋₁₀ aryl)—O—C₅₋₁₀ aryl;

R² and R³ are, independently, H, optionally substituted —C₁₋₆ alkyl, optionally substituted —C₁₋₂₀ alkylamino, optionally substituted —C₁₋₂₀ quaternary alkylammonium group, wherein each substituent is independently —C₅₋₁₀ aryl, —C₄₋₁₀ N-heterocyclic, or —C₄₋₁₀ quaternized N-heterocyclic, which each in turn may be substituted with one or more nitro, —C₁₋₅ alkyl, —C₁₋₅ alkoxy, phenyl group or halogen;

R² and R³ may be optionally linked together to form a substituted or unsubstituted, fused —C₄₋₈ carbocyclic ring, or a substituted or unsubstituted, fused aromatic ring;

R⁴ is halogen, optionally substituted —C₁₋₆ alkyl, optionally substituted —C₅₋₁₀ aryl, optionally substituted —C₁₋₆ alkoxy, optionally substituted —C₅₋₁₀ aryloxy, optionally substituted —C₁₋₆ alkoxy carbonyl, optionally substituted —C₁₋₂₀ protonated alkylamino, optionally substituted protonated amino, optionally substituted —C₄₋₁₀ heterocyclic, optionally substituted —C₁₋₁₂ quaternary alkylammonium, optionally substituted —C₄₋₁₀ quaternized N-heterocyclic, nitro, carboxyl,

optionally substituted amido, optionally substituted sulfonamido, optionally substituted ---C_{1-20} perhaloalkyl group, wherein each substituent is independently ---C_{1-6} alkyl, ---C_{1-6} perhaloalkyl, ---C_{5-10} aryl, or a ---C_{4-10} quaternized N-heterocyclic group;

n is 0, 1, 2 or 3;

R^5 , $R^{5'}$, R^6 , $R^{6'}$, and R^7 are, independently, H, optionally substituted ---C_{1-6} alkyl, optionally substituted ---C_{1-16} quaternary alkylammonium, or an optionally substituted ---C_{4-10} quaternized N-heterocyclic group, wherein each substituent is independently a ---C_{4-10} quaternized heterocyclic group;

R^8 is ---C_{1-6} alkyl;

p is 1, 2, 3 or 4;

$R^{8'}$ is H or ---C_{1-6} alkyl; and

q is 0, 1 or 2.

3. The complex of claim 2, wherein

M is ruthenium;

X, X^1 , X^2 and $X^{2'}$ are, independently, halogen, CF_3CO_2 , CH_3CO_2 , MeO, EtO, PhO, $(\text{NO}_2)\text{PhO}$, CH_3SO_3 , CF_3SO_3 , tosylate, CH_3SO_4 group;

Y is O;

R is H;

R^1 is ---C_{1-6} alkyl, ---C_{5-10} aryl, ---C_{1-6} quaternary alkylammonium, or a ---C_{4-10} quaternized N-heterocyclic group;

R^2 , R^3 are, independently, H, optionally substituted ---C_{1-6} alkyl, or an optionally substituted ---C_{1-12} quaternary alkylammonium group, wherein each substituent is independently a ---C_{4-10} quaternized N-heterocyclic group, which in turn may be substituted with at least one ---C_{1-6} alkyl, ---C_{1-5} alkoxy, phenyl group or halogen;

R^4 is halogen, optionally substituted ---C_{5-10} aryl, optionally substituted ---C_{1-6} alkoxy, optionally substituted ---C_{5-10} aryloxy, optionally substituted ---C_{1-12} quaternary alkylammonium, optionally substituted ---C_{1-12} protonated alkylamino, optionally substituted protonated amino, optionally substituted ---C_{4-10} quaternized N-heterocyclic, nitro, optionally substituted amido, optionally substituted sulfonamido, or an optionally substituted ---C_{1-20} perhaloalkyl group, wherein each substituent is independently ---C_{1-6} alkyl, ---C_{1-6} perhaloalkyl, ---C_{5-10} aryl, or a ---C_{4-10} quaternized N-heterocyclic group;

n is 0, 1 or 2;

$R^5, R^{5'}, R^6, R^{6'}, R^7$ are, independently, H, optionally substituted $-C_{1-6}$ alkyl, optionally substituted $-C_{1-12}$ quaternary alkylammonium, or an optionally substituted $-C_{4-10}$ quaternized N-heterocyclic group, wherein each substituent is independently a $-C_{4-10}$ quaternized heterocyclic group;

R^8 is $-C_{1-6}$ alkyl;

p is 1 or 2;

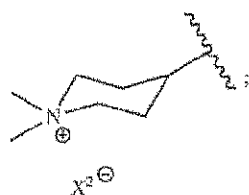
$R^{8'}$ is H or $-C_{1-6}$ alkyl; and

q is 0 or 1.

4. The complex of claim 3, wherein substituents X, X^1 , X^2 and $X^{2'}$ are, independently, halogen.

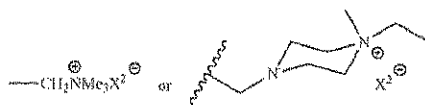
5. The complex of claim 4, wherein substituents X, X^1 , X^2 and $X^{2'}$ are, independently, chlorine or iodine.

6. The complex of claim 1, wherein R is H, R^1 is an iso-propyl group or



X^2 is an anionic ligand.

7. The complex of claim 1, wherein R^2 and R^3 are, independently, H,

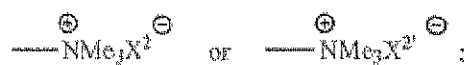


group;

X^2 is an anionic ligand.

8. The complex of claim 1, wherein

R^4 is a nitro group or



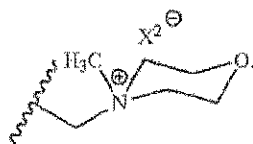
X^2 and $\text{X}^{2'}$ are an anionic ligand; n is 0 or 1.

9. The complex of claim 1, wherein

R^5 and $\text{R}^{5'}$ are a methyl or iso-propyl group;

$\text{R}^6, \text{R}^{6'}$ are H;

R^7 is H, a methyl group or



X^2 is an anionic ligand.

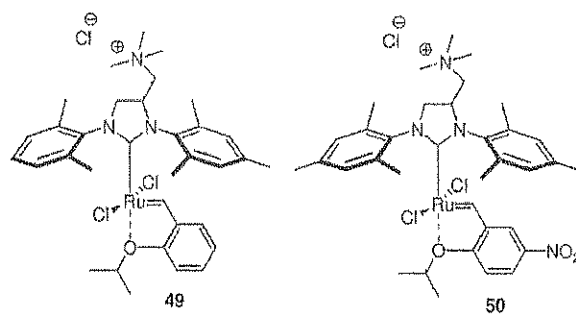
10. The complex of claim 1, wherein R^8 is a methyl group;

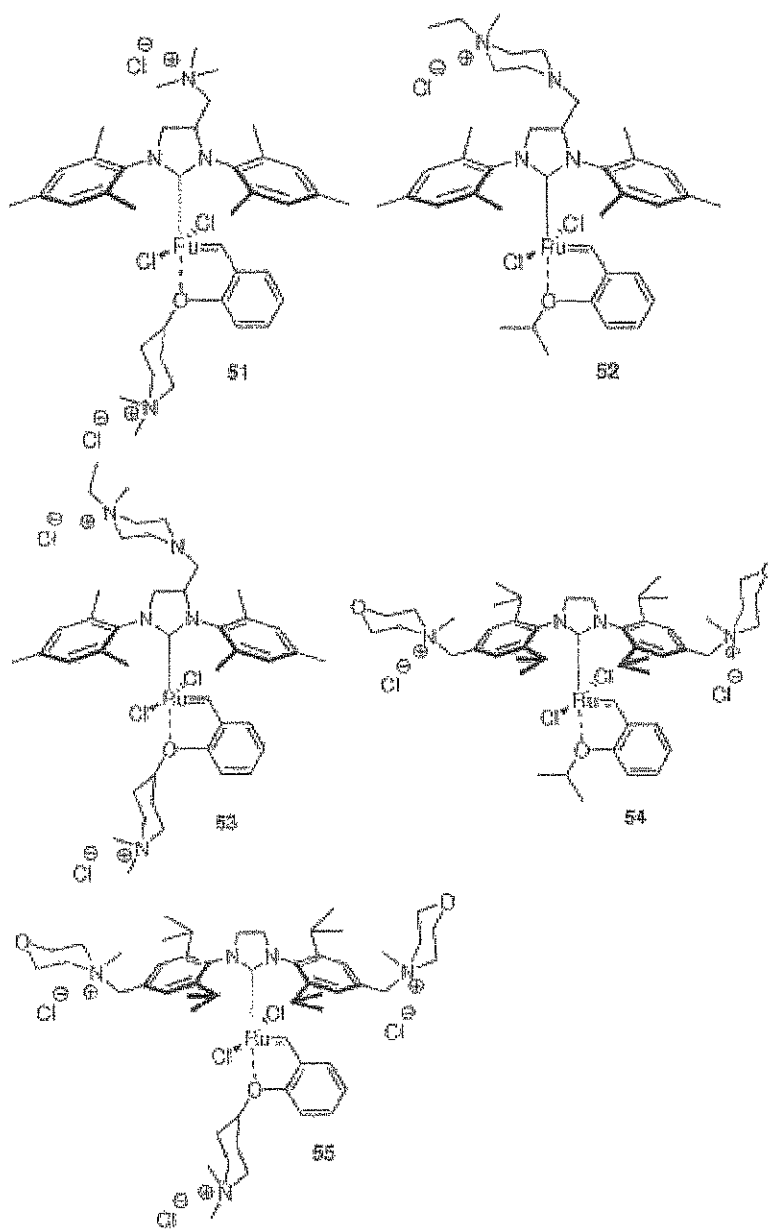
p is 1 or 2;

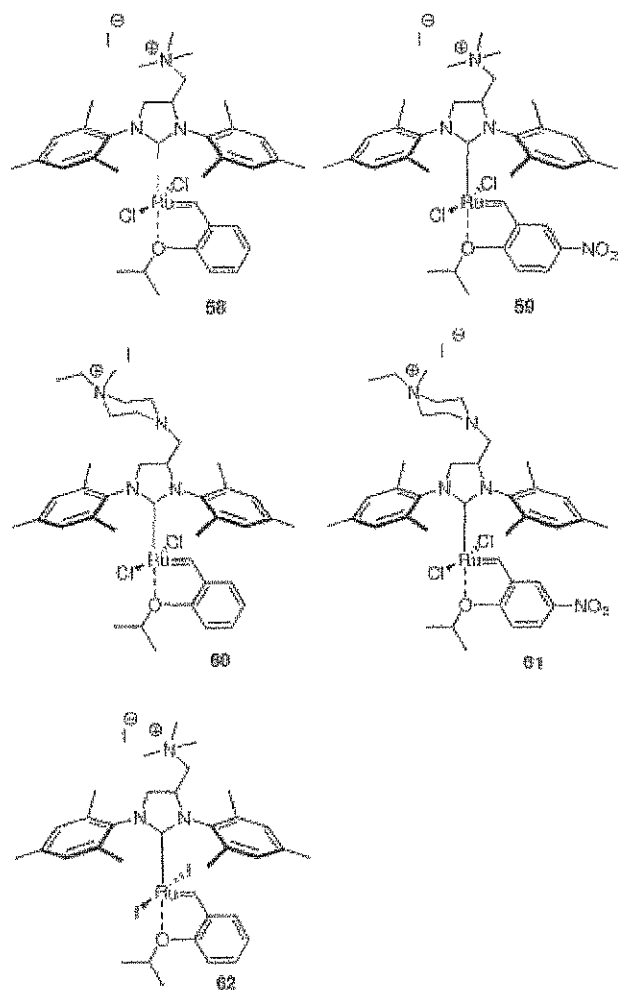
$\text{R}^{8'}$ is H or a methyl group;

q is 0 or 1.

11. The complex of claim 1, wherein they are selected from the following formulas 49-55, 58-62.







12. The complex of claim 1, wherein any $-\text{C}_{1-20}$ quaternary alkylammonium is $-(\text{CH}_2)_{0-4}\text{N}^+(\text{C}_{1-3}\text{H}_{3-7})_3$,

