Z-SELECTIVE OLEFIN METATHESIS CATALYSTS AND THEIR SYNHETIC PROCEDURE

RELATED APPLICATIONS

[0001] This application claims the benefit of priority to U.S. Provisional Application Ser. No. 61/432,849 (CIT-5776-P), filed January 14, 2011, U.S. Provisional Application Ser. No. 61/433,949 (CIT-5776-P2), filed January 18, 2011, and U.S. Provisional Application Ser. No. 61/515,262 (CIT-5776-P3), filed August 4, 2011, each of which is incorporated herein by reference.

TECHNICAL FIELD

[0002] This invention relates generally to C-H activated olefin metathesis catalyst compounds, to the preparation of such compounds, and the use of such catalysts in the metathesis of olefins and olefin compounds, more particularly, in the use of such catalysts in Z selective olefin metathesis reactions. The invention has utility in the fields of catalysis, organic synthesis, polymer chemistry, and industrial and fine chemicals chemistry.

STATEMENT OF FEDERAL SUPPORT

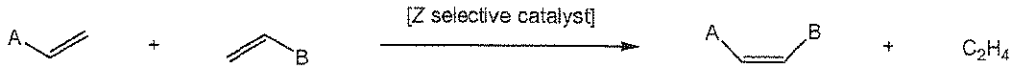
[0003] The U.S. Government has certain rights in this invention pursuant to Grant No. 5R01GM031332-27 awarded by the National Institutes of Health and Grant No. CHE-1048404 awarded by the National Science Foundation.

BACKGROUND

[0004] Since its discovery in the 1950s, olefin metathesis has emerged as a valuable synthetic method for the formation of carbon-carbon double bonds. In particular, its recent advances in applications to organic syntheses and polymer syntheses mostly rely on developments of well-defined catalysts. Among attempts to improve catalyst efficiency over the past decade, one of the most attractive frontiers

has been selective synthesis of stereo-controlled olefin product. Derived from generally accepted their equilibrium reaction mechanisms, most of catalysts give higher proportion of thermodynamically favored *E* isomer of olefin in products. This fundamental nature of olefin metathesis limits its applications to some reactions including natural product synthesis. Thus, a catalyst which selectively gives *Z* isomer of olefin product is expected to open a new convenient route to a value-added product. Especially, use of *Z* selective catalysts in olefin cross metathesis (CM) is promising for outstanding methodology in organic chemistry. In the simplest case of such CM, two different terminal olefin molecules selectively generate one new internal *cis*-olefin molecule and one ethylene molecule (Scheme 1).

Scheme 1



[0005] One of the most important classes of olefin metathesis catalysts is ruthenium-based alkylidene complex represented by the ruthenium catalyst (**1**-**4**) (Figure 1). Because of their high efficiency in catalysis and high tolerance towards various functional groups, they are most widely used in both academic and industrial fields. Typical ruthenium catalysts are known to give more *E* isomer than *Z* isomer in CM and other olefin metathesis reactions (see Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360).

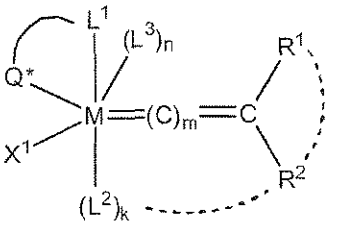
[0006] Bielawski et al. reported that a ruthenium catalyst having acyclic diaminocarbene ligand (**5**) afforded the cross coupled product in a nearly 1 : 1 ratio of its *E* and *Z* isomers at high conversion (~75%) in CM of allylbenzene and *cis*-1,4-diacetoxy-2-butene (see Rosen, E. L.; Sung, D. H.; Chen, Z.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2010**, *29*, 250). Grubbs et al. also demonstrated that a bulky sulfonate ligand substituted 2nd generation catalyst (**6**), which was readily prepared from commercially available reagents, gave the product with *E* isomer / *Z* isomer = 2.9 at very high conversion (~90%) in the same CM reaction (see Teo, P.; Grubbs, R. H. *Organometallics* **2010**, *29*, 6045). Compared to the original

ruthenium catalysts, these catalysts gave much more *Z* isomer of the product; however, their *Z* selectivity were still not satisfactory for precisely stereo-controlled reactions. On the other hand, some of the molybdenum- or tungsten-based catalysts recently developed by Hoveyda and Schrock are outstanding for their *Z* selectivity in metathesis homocoupling of terminal olefins (see Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962). In a particular case, bulky aryloxide substituted tungsten catalyst (7) afforded homocoupled product of 1-hexene with 95% *Z* isomer. Despite the excellent *Z* selectivity, their relatively many synthetic steps and generally required strict reaction conditions for molybdenum and tungsten alkylidene catalysts somewhat restrict their use in common organic syntheses.

[0007] In order to overcome the above mentioned disadvantages of the current catalysts, new highly *Z* selective ruthenium based catalysts are needed. For general use, especially in industry, they should be not only tolerant towards various functional groups and impurities in reaction media but also readily synthesized from common reagents in simple reaction steps. Despite the advances achieved in preparing olefin metathesis catalysts, a continuing need in the art exists for improved catalysts, including catalysts that provide improved Z selectivity.

BRIEF SUMMARY OF THE DISCLOSURE

[0008] The invention is directed to addressing one or more of the aforementioned concerns, and, in one embodiment, provides a C-H activated catalyst compound composed of a Group 8 transition metal complex and a chelating ligand structure formed from the metal center M, a neutral electron donor ligand L^1, and a 2-electron anionic donor bridging moiety, Q*. A general structure of catalyst compounds according to the invention is shown below.



wherein, M is a Group 8 transition metal (e.g., Ru or Os); X^1 is any anionic ligand (e.g., halogen, alkyl, aryl, carboxylate, alkoxy, aryloxy, sulfonate, phosphate, or nitrate); L^1, L^2, and L^3 are, independently, any neutral two electron ligand, where L^2 may connect with R^2; R^1 and R^2 are independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups, and wherein R^1 may connect with R^2 and/or L^2; Q*is a 2-electron anionic donor bridging moiety, (e.g., alkyl, aryl, carboxylate, alkoxy, aryloxy, or sulfonate, etc.); n and k are independently 0 or 1, such that L^3 may or may not be present; and, m is 0, 1, or 2.

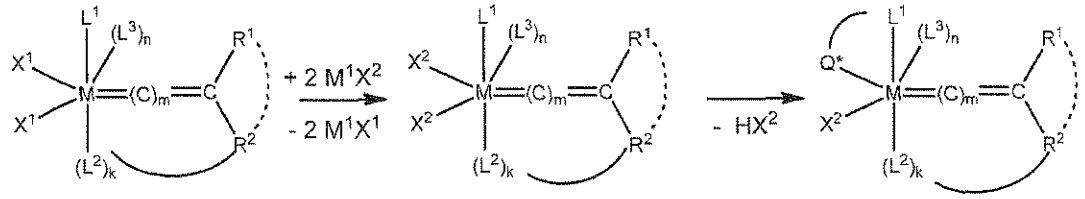
[0009] These complexes comprise a Group 8 metal (M), an alkylidene moiety ($=CR^1R^2$), an anionic ligand (X^1), two or three neutral ligands (L^1, L^2, and L^3) and a 2-electron anionic donor bridging moiety (Q*) which forms a chelate structure in conjunction with L^1 and M. As with other known active ruthenium catalysts (e.g., typical Grubbs' catalysts 1-4 of Figure 1), these group 8 metal-based alkylidene catalysts of the invention are intrinsically tolerant towards various functional groups and impurities in reaction media. Advantageously, the C-H activated catalyst compounds of the invention may be used to catalyze Z selection olefin metathesis reactions.

[0010] In order to synthesize the chelated catalyst compounds of the invention, the following synthetic procedure can be utilized (Scheme 2). In the first step, two anionic ligands (X^1) of Grubbs' 2nd generation type complex are substituted by another anionic ligand (X^2), by contacting the catalyst complex with M^1X^2. Intramolecular C-H bond activation at the substituent of NHC ligand (R^3) and liberation of acid (HX^2) thereafter yield the chelated catalyst of the invention. As shown in scheme 3, an anionic ligand of the chelated catalyst (X^1) can be substituted by another anionic ligand (X^2) by reaction with corresponding Lewis base. For example, in one aspect of the invention, it has now been found that the addition of a nitrate (NO_3^-) group X^2 ligand in place of another X^1 anionic ligand provides catalysts

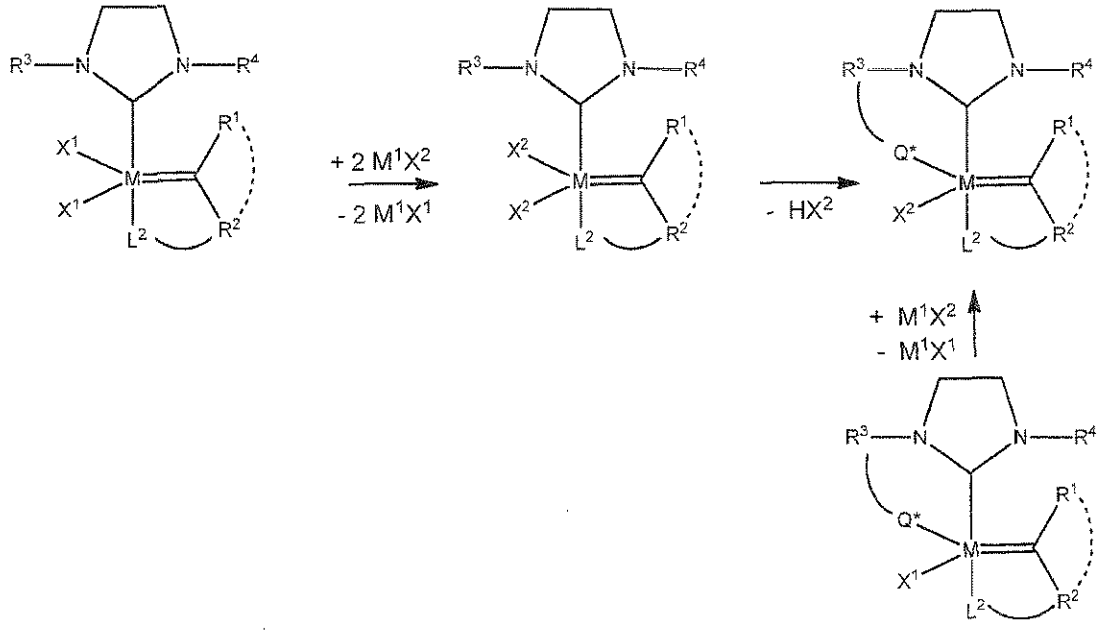
according to the invention that demonstrate certain improvements in catalyzing olefin metathesis reactions,

[0011] It should be noted that a number of Grubbs' 2nd generation catalysts which can be precursors of the chelated catalysts in scheme 2 are now commercially available. In addition, most of reagents used for anion ligand exchange (M^1X^2) are also commercially available or readily prepared by simple reaction step(s). In this procedure X^1 and X^2 are different. Preferably M^1X^1 has lower solubility in the reaction media than M^1X^2.

Scheme 2. General Synthetic Procedure



Scheme 3. Synthetic Procedure



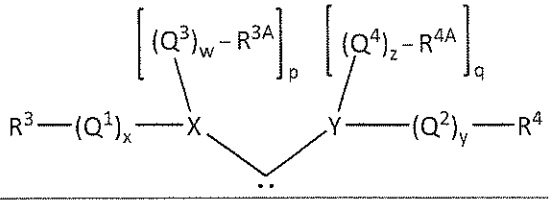
wherein, in each of Schemes 2 and 3, M is a Group 8 transition metal (e.g., Ru or Os); M^1 is a metal such as silver, lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, iron, zinc, or thalium; X^1 and X^2 are independently any anionic ligand (e.g., halogen, alkyl, aryl, carboxylate, alkoxy, aryloxy, sulfonate, phosphate, or nitrate); L^1, L^2, and L^3 are, independently, any neutral two electron ligand, where L^2 may connect with R^2; R^1 and R^2 are independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups, and wherein R^1 may connect with R^2 and/or L^2; Q*is a 2-electron anionic donor bridging moiety, (e.g., alkyl, aryl, carboxylate, alkoxy, aryloxy, or sulfonate, etc.); n and k are independently 0 or 1, such that L^3 may or may not be present; and, m is 0, 1, or 2.

[0011a] In one aspect, there is provided a C-H activated olefin metathesis catalyst compound, wherein the compound has the structure of formula (I):

(I) $X^1(L^3)_n(L^2)_kL^1Q^*M=(C)_mCR^1R^2$

wherein X^1 is any anionic ligand, L^1, L^2, and L^3 are, independently, any neutral electron donor ligand, n and k are, independently, 0 or 1, m is 0, 1, or 2, and R^1 and R^2 are, independently, hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, or functional groups, M is a Group 8 transition metal; Q* is a 2-electron anionic donor bridging moiety linking L^1 and M, forming chelating ligand ring structure having a ring size of 5 or 6 atoms, L^1 is a carbene ligand having the structure of formula (III)

(III)



wherein,

X and Y are heteroatoms selected from N, O, S, and P;

Q^1, Q^2, Q^3, and Q^4 are independently selected from hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, and substituted heteroatom-containing hydrocarbylene;

R^3, R^{3A}, R^4, and R^{4A} are independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, and substituted heteroatom-containing hydrocarbyl;

p and q are zero or 1, such that p is zero when X is O or S, q is zero when Y is O or S, p is 1 when X is N or P, and q is 1 when Y is N or P; and

w, x, y, and z are independently zero or 1.

[0011b] In one aspect, there is provided a method of making a C-H activated olefin metathesis catalyst compound, the method comprising contacting a carboxylate compound of the formula M^1X^2, wherein M^1 is selected from silver, lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, iron, zinc, or thalium, and X^2 is a carboxylate anion, with an olefin metathesis catalyst of the formula $(X^1)_2(L^3)_n(L^2)_kL^1M=(C)_mCR^1R^2$, wherein X^1 is any anionic ligand, L^1, L^2, and L^3 are, independently, any neutral electron donor ligand, n and k are, independently, 0 or 1, m is 0, 1, or 2, M is a Group 8 transition metal, and R^1 and R^2 are, independently, selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, or functional groups; under conditions effective to promote the exchange of X^2 anions for the X^1 anionic ligands, such that a C-H activated olefin metathesis catalyst compound is produced in which M and L^1 are linked together by a 2-electron anionic donor bridging moiety Q* in a M-Q*-L^1 chelating ligand ring-structure having a ring size of 5 or 6 atoms, and the catalyst compound contains an X^2 anionic ligand.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 depicts selected typical Grubbs' catalysts.

[0013] Figure 2 depicts some of the reported olefin metathesis catalysts.

[0014] Figure 3 depicts the general structure of the inventive Z selective olefin metathesis catalyst compounds.

[0015] Figure 4 depicts the X-ray crystal structure of complex **7a** as described in the Examples.

[0016] Figure 5 depicts the X-ray crystal structure of complex **7b** as described in the Examples.

[0017] Figure 6 depicts the X-ray crystal structure of complex **11** as described in the Examples.

[0018] Figure 7 depicts the X-ray crystal structure of complex **18a** as described in the Examples.

[0019] Figure 8 depicts the X-ray crystal structure of complex **18b** as described in the Examples.

[0020] Figure 9 depicts the X-ray crystal structure of complex **18c** as described in the Examples.

[0021] Figure 10 depicts the X-ray crystal structure of complex **19a** as described in the Examples.

[0022] Figure 11 depicts the X-ray crystal structure of complex **21a** as described in the Examples.

[0023] Figure 12 depicts the X-ray crystal structure of complex **22a** as described in the Examples.

[0024] Figure 13 depicts the X-ray crystal structure of complex **24d** as described in the Examples.

DETAILED DESCRIPTION OF THE DISCLOSURE

Terminology and Definitions

[0025] Unless otherwise indicated, the invention is not limited to specific reactants, substituents, catalysts, reaction conditions, or the like, as such may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not to be interpreted as being limiting.

[0026] As used in the specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "an α-olefin" includes a single α-olefin as well as a combination or mixture of two or more α-olefins, reference to "a substituent" encompasses a single substituent as well as two or more substituents, and the like.

[0027] As used in the specification and the appended claims, the terms "for example," "for instance," "such as," or "including" are meant to introduce examples that further clarify more general subject matter. Unless otherwise specified, these examples are provided only as an aid for understanding the invention, and are not meant to be limiting in any fashion.

[0028] In this specification and in the claims that follow, reference will be made to a number of terms, which shall be defined to have the following meanings:

[0029] The term "alkyl" as used herein refers to a linear, branched, or cyclic saturated hydrocarbon group typically although not necessarily containing 1 to about 24 carbon atoms, preferably 1 to about 12 carbon atoms, such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *t*-butyl, octyl, decyl, and the like, as well as cycloalkyl groups such as cyclopentyl, cyclohexyl and the like. Generally, although again not necessarily, alkyl groups herein contain 1 to about 12 carbon atoms. The term "lower alkyl" intends

an alkyl group of 1 to 6 carbon atoms, and the specific term "cycloalkyl" intends a cyclic alkyl group, typically having 4 to 8, preferably 5 to 7, carbon atoms. The term "substituted alkyl" refers to alkyl substituted with one or more substituent groups, and the terms "heteroatom-containing alkyl" and "heteroalkyl" refer to alkyl in which at least one carbon atom is replaced with a heteroatom. If not otherwise indicated, the terms "alkyl" and "lower alkyl" include linear, branched, cyclic, unsubstituted, substituted, and/or heteroatom-containing alkyl and lower alkyl, respectively.

[0030] The term "alkylene" as used herein refers to a difunctional linear, branched, or cyclic alkyl group, where "alkyl" is as defined above.

[0031] The term "alkenyl" as used herein refers to a linear, branched, or cyclic hydrocarbon group of 2 to about 24 carbon atoms containing at least one double bond, such as ethenyl, *n*-propenyl, isopropenyl, *n*-butenyl, isobutenyl, octenyl, decenyl, tetradecenyl, hexadecenyl, eicosenyl, tetracosenyl, and the like. Preferred alkenyl groups herein contain 2 to about 12 carbon atoms. The term "lower alkenyl" intends an alkenyl group of 2 to 6 carbon atoms, and the specific term "cycloalkenyl" intends a cyclic alkenyl group, preferably having 5 to 8 carbon atoms. The term "substituted alkenyl" refers to alkenyl substituted with one or more substituent groups, and the terms "heteroatom-containing alkenyl" and "heteroalkenyl" refer to alkenyl in which at least one carbon atom is replaced with a heteroatom. If not otherwise indicated, the terms "alkenyl" and "lower alkenyl" include linear, branched, cyclic, unsubstituted, substituted, and/or heteroatom-containing alkenyl and lower alkenyl, respectively.

[0032] The term "alkenylene" as used herein refers to a difunctional linear, branched, or cyclic alkenyl group, where "alkenyl" is as defined above.

[0033] The term "alkynyl" as used herein refers to a linear or branched hydrocarbon group of 2 to about 24 carbon atoms containing at least one triple bond, such as ethynyl, *n*-propynyl, and the like. Preferred alkynyl groups herein contain 2 to about 12 carbon atoms. The term "lower alkynyl" intends an alkynyl group of 2 to 6 carbon atoms. The term "substituted alkynyl" refers to alkynyl substituted with

one or more substituent groups, and the terms "heteroatom-containing alkynyl" and "heteroalkynyl" refer to alkynyl in which at least one carbon atom is replaced with a heteroatom. If not otherwise indicated, the terms "alkynyl" and "lower alkynyl" include linear, branched, unsubstituted, substituted, and/or heteroatom-containing alkynyl and lower alkynyl, respectively.

[0034] The term "alkoxy" as used herein intends an alkyl group bound through a single, terminal ether linkage; that is, an "alkoxy" group may be represented as -O-alkyl where alkyl is as defined above. A "lower alkoxy" group intends an alkoxy group containing 1 to 6 carbon atoms. Analogously, "alkenyloxy" and "lower alkenyloxy" respectively refer to an alkenyl and lower alkenyl group bound through a single, terminal ether linkage, and "alkynyloxy" and "lower alkynyloxy" respectively refer to an alkynyl and lower alkynyl group bound through a single, terminal ether linkage.

[0035] The term "aryl" as used herein, and unless otherwise specified, refers to an aromatic substituent containing a single aromatic ring or multiple aromatic rings that are fused together, directly linked, or indirectly linked (such that the different aromatic rings are bound to a common group such as a methylene or ethylene moiety). Preferred aryl groups contain 5 to 24 carbon atoms, and particularly preferred aryl groups contain 5 to 14 carbon atoms. Exemplary aryl groups contain one aromatic ring or two fused or linked aromatic rings, e.g., phenyl, naphthyl, biphenyl, diphenylether, diphenylamine, benzophenone, and the like. "Substituted aryl" refers to an aryl moiety substituted with one or more substituent groups, and the terms "heteroatom-containing aryl" and "heteroaryl" refer to aryl substituents in which at least one carbon atom is replaced with a heteroatom, as will be described in further detail *infra*.

[0036] The term "aryloxy" as used herein refers to an aryl group bound through a single, terminal ether linkage, wherein "aryl" is as defined above. An "aryloxy" group may be represented as -O-aryl where aryl is as defined above. Preferred aryloxy groups contain 5 to 24 carbon atoms, and particularly preferred aryloxy groups contain 5 to 14 carbon atoms. Examples of aryloxy groups include, without

limitation, phenoxy, o-halo-phenoxy, m-halo-phenoxy, p-halo-phenoxy, o-methoxy-phenoxy, m-methoxy-phenoxy, p-methoxy-phenoxy, 2,4-dimethoxy-phenoxy, 3,4,5-trimethoxy-phenoxy, and the like.

[0037] The term "alkaryl" refers to an aryl group with an alkyl substituent, and the term "aralkyl" refers to an alkyl group with an aryl substituent, wherein "aryl" and "alkyl" are as defined above. Preferred alkaryl and aralkyl groups contain 6 to 24 carbon atoms, and particularly preferred alkaryl and aralkyl groups contain 6 to 16 carbon atoms. Alkaryl groups include, for example, p-methylphenyl, 2,4-dimethylphenyl, p-cyclohexylphenyl, 2,7-dimethylnaphthyl, 7-cyclooctylnaphthyl, 3-ethyl-cyclopenta-1,4-diene, and the like. Examples of aralkyl groups include, without limitation, benzyl, 2-phenyl-ethyl, 3-phenyl-propyl, 4-phenyl-butyl, 5-phenyl-pentyl, 4-phenylcyclohexyl, 4-benzylcyclohexyl, 4-phenylcyclohexylmethyl, 4-benzylcyclohexylmethyl, and the like. The terms "alkaryloxy" and "aralkyloxy" refer to substituents of the formula -OR wherein R is alkaryl or aralkyl, respectively, as just defined.

[0038] The term "acyl" refers to substituents having the formula -(CO)-alkyl, -(CO)-aryl, or -(CO)-aralkyl, and the term "acyloxy" refers to substituents having the formula -O(CO)-alkyl, -O(CO)-aryl,or -O(CO)-aralkyl, wherein "alkyl," "aryl, and "aralkyl" are as defined above.

[0039] The terms "cyclic" and "ring" refer to alicyclic or aromatic groups that may or may not be substituted and/or heteroatom containing, and that may be monocyclic, bicyclic, or polycyclic. The term "alicyclic" is used in the conventional sense to refer to an aliphatic cyclic moiety, as opposed to an aromatic cyclic moiety, and may be monocyclic, bicyclic, or polycyclic.

[0040] The terms "halo" and "halogen" are used in the conventional sense to refer to a chloro, bromo, fluoro, or iodo substituent.

[0041] "Hydrocarbyl" refers to univalent hydrocarbyl radicals containing 1 to about 30 carbon atoms, preferably 1 to about 24 carbon atoms, most preferably 1 to about 12 carbon atoms, including linear, branched, cyclic, saturated, and unsaturated species, such as alkyl groups, alkenyl groups, aryl

groups, and the like. The term "lower hydrocarbyl" intends a hydrocarbyl group of 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, and the term "hydrocarbylene" intends a divalent hydrocarbyl moiety containing 1 to about 30 carbon atoms, preferably 1 to about 24 carbon atoms, most preferably 1 to about 12 carbon atoms, including linear, branched, cyclic, saturated and unsaturated species. The term "lower hydrocarbylene" intends a hydrocarbylene group of 1 to 6 carbon atoms. "Substituted hydrocarbyl" refers to hydrocarbyl substituted with one or more substituent groups, and the terms "heteroatom-containing hydrocarbyl" and "heterohydrocarbyl" refer to hydrocarbyl in which at least one carbon atom is replaced with a heteroatom. Similarly, "substituted hydrocarbylene" refers to hydrocarbylene substituted with one or more substituent groups, and the terms "heteroatom-containing hydrocarbylene" and heterohydrocarbylene" refer to hydrocarbylene in which at least one carbon atom is replaced with a heteroatom. Unless otherwise indicated, the term "hydrocarbyl" and "hydrocarbylene" are to be interpreted as including substituted and/or heteroatom-containing hydrocarbyl and hydrocarbylene moieties, respectively.

[0042] The term "heteroatom-containing" as in a "heteroatom-containing hydrocarbyl group" refers to a hydrocarbon molecule or a hydrocarbyl molecular fragment in which one or more carbon atoms is replaced with an atom other than carbon, e.g., nitrogen, oxygen, sulfur, phosphorus or silicon, typically nitrogen, oxygen or sulfur. Similarly, the term "heteroalkyl" refers to an alkyl substituent that is heteroatom-containing, the term "heterocyclic" refers to a cyclic substituent that is heteroatom-containing, the terms "heteroaryl" and heteroaromatic" respectively refer to "aryl" and "aromatic" substituents that are heteroatom-containing, and the like. It should be noted that a "heterocyclic" group or compound may or may not be aromatic, and further that "heterocycles" may be monocyclic, bicyclic, or polycyclic as described above with respect to the term "aryl." Examples of heteroalkyl groups include alkoxyaryl, alkylsulfanyl-substituted alkyl, N-alkylated amino alkyl, and the like. Examples of heteroaryl substituents include pyrrolyl, pyrrolidinyl, pyridinyl, quinolinyl, indolyl, pyrimidinyl, imidazolyl, 1,2,4-

triazolyl, tetrazolyl, etc., and examples of heteroatom-containing alicyclic groups are pyrrolidino, morpholino, piperazino, piperidino, etc.

[0043] By "substituted" as in "substituted hydrocarbyl," "substituted alkyl," "substituted aryl," and the like, as alluded to in some of the aforementioned definitions, is meant that in the hydrocarbyl, alkyl, aryl, or other moiety, at least one hydrogen atom bound to a carbon (or other) atom is replaced with one or more non-hydrogen substituents. Examples of such substituents include, without limitation: functional groups referred to herein as "Fn," such as halo, hydroxyl, sulfhydryl, C_1-C_{24} alkoxy, C_2-C_{24} alkenyloxy, C_2-C_{24} alkynyloxy, C_5-C_{24} aryloxy, C_6-C_{24} aralkyloxy, C_6-C_{24} alkaryloxy, acyl (including C_2-C_{24} alkylcarbonyl (-CO-alkyl) and C_6-C_{24} arylcarbonyl (-CO-aryl)), acyloxy (-O-acyl, including C_2-C_{24} alkylcarbonyloxy (-O-CO-alkyl) and C_6-C_{24} arylcarbonyloxy (-O-CO-aryl)), C_2-C_{24} alkoxycarbonyl (-(CO)-O-alkyl), C_6-C_{24} aryloxycarbonyl (-(CO)-O-aryl), halocarbonyl (-CO)-X where X is halo), C_2-C_{24} alkylcarbonato (-O-(CO)-O-alkyl), C_6-C_{24} arylcarbonato (-O-(CO)-O-aryl), carboxy (-COOH), carboxylato (-COO^-), carbamoyl (-(CO)-NH_2), mono-(C_1-C_{24} alkyl)-substituted carbamoyl (-(CO)-$NH(C_1$-C_{24} alkyl)), di-(C_1-C_{24} alkyl)-substituted carbamoyl (-(CO)-$N(C_1$-C_{24} alkyl)$_2$), mono-(C_1-C_{24} haloalkyl)-substituted carbamoyl (-(CO)-$NH(C_1$-C_{24} alkyl)), di-(C_1-C_{24} haloalkyl)-substituted carbamoyl (-(CO)-$N(C_1$-C_{24} alkyl)$_2$), mono-(C_5-C_{24} aryl)-substituted carbamoyl (-(CO)-NH-aryl), di-(C_5-C_{24} aryl)-substituted carbamoyl (-(CO)-$N(C_5$-C_{24} aryl)$_2$), di-N-(C_1-C_{24} alkyl),N-(C_5-C_{24} aryl)-substituted carbamoyl, thiocarbamoyl (-(CS)-NH_2), mono-(C_1-C_{24} alkyl)-substituted thiocarbamoyl (-(CO)-$NH(C_1$-C_{24} alkyl)), di-(C_1-C_{24} alkyl)-substituted thiocarbamoyl (-(CO)-$N(C_1$-C_{24} alkyl)$_2$), mono-(C_5-C_{24} aryl)-substituted thiocarbamoyl (-(CO)-NH-aryl), di-(C_5-C_{24} aryl)-substituted thiocarbamoyl (-(CO)-$N(C_5$-C_{24} aryl)$_2$), di-N-(C_1-C_{24} alkyl),N-(C_5-C_{24} aryl)-substituted thiocarbamoyl, carbamido (-NH-(CO)-NH_2), cyano(-C=N), cyanato (-O-C=N), thiocyanato (-S-C=N), formyl (-(CO)-H), thioformyl (-(CS)-H), amino (-NH_2), mono-(C_1-C_{24} alkyl)-substituted amino, di-(C_1-C_{24} alkyl)-substituted amino, mono-(C_5-C_{24} aryl)-substituted amino, di-(C_5-C_{24} aryl)-substituted amino, C_2-C_{24} alkylamido (-NH-(CO)-alkyl), C_6-C_{24}

arylamido (-NH-(CO)-aryl), imino (-CR=NH where R = hydrogen, C_1-C_{24} alkyl, C_5-C_{24} aryl, C_6-C_{24} alkaryl, C_6-C_{24} aralkyl, etc.), C_2-C_{20} alkylimino (-CR=N(alkyl), where R = hydrogen, C_1-C_{24} alkyl, C_5-C_{24} aryl, C_6-C_{24} alkaryl, C_6-C_{24} aralkyl, etc.), arylimino (-CR=N(aryl), where R = hydrogen, C_1-C_{20} alkyl, C_5-C_{24} aryl, C_6-C_{24} alkaryl, C_6-C_{24} aralkyl, etc.), nitro ($-NO_2$), nitroso (-NO), sulfo ($-SO_2$-OH), sulfonato ($-SO_2$-O^-), C_1-C_{24} alkylsulfanyl (-S-alkyl; also termed "alkylthio"), C_5-C_{24} arylsulfanyl (-S-aryl; also termed "arylthio"), C_1-C_{24} alkylsulfinyl (-(SO)-alkyl), C_5-C_{24} arylsulfinyl (-(SO)-aryl), C_1-C_{24} alkylsulfonyl ($-SO_2$-alkyl), C_1-C_{24} monoalkylaminosulfonyl $-SO_2$-N(H) alkyl), C_1-C_{24} dialkylaminosulfonyl $-SO_2$-N(alkyl)$_2$, C_5-C_{24} arylsulfonyl ($-SO_2$-aryl), boryl ($-BH_2$), borono ($-B(OH)_2$), boronato ($-B(OR)_2$ where R is alkyl or other hydrocarbyl), phosphono ($-P(O)(OH)_2$), phosphonato ($-P(O)(O^-)_2$), phosphinato ($-P(O)(O^-)$), phospho ($-PO_2$), and phosphino ($-PH_2$); and the hydrocarbyl moieties C_1-C_{24} alkyl (preferably C_1-C_{12} alkyl, more preferably C_1-C_6 alkyl), C_2-C_{24} alkenyl (preferably C_2-C_{12} alkenyl, more preferably C_2-C_6 alkenyl), C_2-C_{24} alkynyl (preferably C_2-C_{12} alkynyl, more preferably C_2-C_6 alkynyl), C_5-C_{24} aryl (preferably C_5-C_{14} aryl), C_6-C_{24} alkaryl (preferably C_6-C_{16} alkaryl), and C_6-C_{24} aralkyl (preferably C_6-C_{16} aralkyl).

[0044] By "functionalized" as in "functionalized hydrocarbyl," "functionalized alkyl," "functionalized olefin," "functionalized cyclic olefin," and the like, is meant that in the hydrocarbyl, alkyl, olefin, cyclic olefin, or other moiety, at least one hydrogen atom bound to a carbon (or other) atom is replaced with one or more functional groups such as those described hereinabove. The term "functional group" is meant to include any functional species that is suitable for the uses described herein. In particular, as used herein, a functional group would necessarily possess the ability to react with or bond to corresponding functional groups on a substrate surface.

[0045] In addition, the aforementioned functional groups may, if a particular group permits, be further substituted with one or more additional functional groups or with one or more hydrocarbyl moieties such as those specifically enumerated above. Analogously, the above-mentioned hydrocarbyl

moieties may be further substituted with one or more functional groups or additional hydrocarbyl moieties such as those specifically enumerated.

[0046] "Optional" or "optionally" means that the subsequently described circumstance may or may not occur, so that the description includes instances where the circumstance occurs and instances where it does not. For example, the phrase "optionally substituted" means that a non-hydrogen substituent may or may not be present on a given atom, and, thus, the description includes structures wherein a non-hydrogen substituent is present and structures wherein a non-hydrogen substituent is not present.

Catalyst Complexes

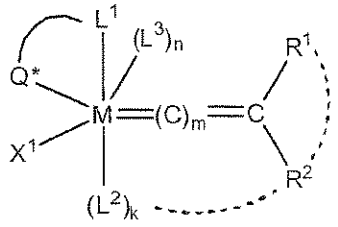
[0047] In general, the catalyst complexes of the invention comprise a Group 8 metal (M), an alkylidene moiety ($=CR^1R^2$), or more generally ($=(C)_mC\ R^1R^2$), an anionic ligand (X^1), two or three neutral ligands (L^1, L^2, and L^3) and a 2-electron anionic donor bridging moiety (Q*) that forms a chelate structure in conjunction with L^1 and M. Suitable catalysts generally have the formula (I)

(I) $$X^1(L^3)_kL^2L^1Q^*M=(C)_mCR^1R^2$$

[0048] wherein X^1 is any anionic ligand, L^1, L^2, and L^3 are, independently, any neural electron donor ligand, k is 0 or 1, m is 0, 1, or 2, Q* is a 2-electron anionic donor bridging moiety linking L^1 and M, M is a Group 8 transition metal, and R^1 and R^2 are, independently, hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, or functional groups.

[0049] The olefin metathesis catalyst complex is preferably a Group 8 transition metal complex having the structure of formula (II)

(II)



in which:

M is a Group 8 transition metal;

L^1, L^2 and L^3 are neutral electron donor ligands;

Q* is a 2-electron anionic donor bridging moiety linking L^1 and M, which can, together with L^1 and M, form one or more cyclic groups;

n is 0 or 1, such that L^3 may or may not be present;

m is 0, 1, or 2; k is 0 or 1;

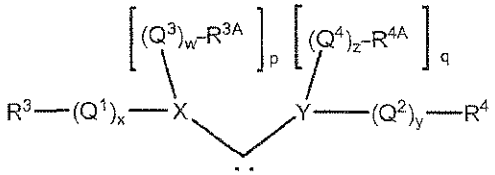
X^1 is an anionic ligand; and

R^1 and R^2 are independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups, wherein any two or more of X^1, Q* , L^1, L^2, L^3, R^1, and R^2 can be taken together to form one or more cyclic groups, and further wherein any one or more of X^1, Q*, L^1, L^2, L^3, R^1, and R^2 may be attached to a support. As shown in formula (II), L^2 may be optionally linked to R^1 or R^2, and R^1 may be optionally linked to R^2.

[0050] Preferred catalysts contain Ru or Os as the Group 8 transition metal, with Ru particularly preferred.

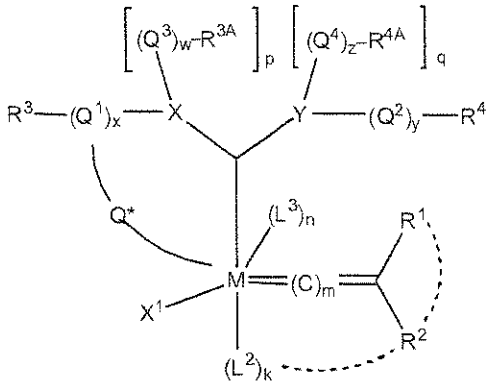
[0051] Catalysts according to formula (II) may be conveniently described according to certain structural features. In a first group of catalysts, commonly referred to as Second Generation Grubbs-type catalysts, L^1 in formula (II) is a carbene ligand having the structure of formula (III)

(III)



such that the complex may have the structure of formula (IV)

(IV)



wherein M, m, n, X^1, L^2, L^3, R^1, and R^2 are as defined for the first group of catalysts, and the remaining substituents are as follows.

[0052] X and Y are heteroatoms typically selected from N, O, S, and P. Since O and S are divalent, p is necessarily zero when X is O or S, q is necessarily zero when Y is O or S, and k is zero or 1. However, when X is N or P, then p is 1, and when Y is N or P, then q is 1. In certain embodiments, both X and Y are N.

[0053] Q* is a 2-electron anionic donor bridging moiety linking L^1 and M, and may be hydrocarbylene (including substituted hydrocarbylene, heteroatom-containing hydrocarbylene, and substituted heteroatom-containing hydrocarbylene, such as substituted and/or heteroatom-containing alkylene) or -(CO)-, and w, x, y, and z are independently zero or 1, meaning that each linker is optional. Although not limited thereto, in one aspect, Q* may link Q^1 to M by a carbon-metal bond.

[0054] Q^1, Q^2, Q^3, and Q^4 are linkers, e.g., hydrocarbylene (including substituted hydrocarbylene, heteroatom-containing hydrocarbylene, and substituted heteroatom-containing hydrocarbylene, such as substituted and/or heteroatom-containing alkylene) or -(CO)-, and w, x, y, and z are independently zero or 1, meaning that each linker is optional. Although not limited thereto, in one aspect, Q^1 may be linked to M by Q* through a carbon-metal bond. Two or more substituents on adjacent atoms within Q^1, Q^2, Q^3, and Q^4 may also be linked to form an additional cyclic group.

[0055] R^3, R^{3A}, R^4, and R^{4A} are independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, and substituted heteroatom-containing, hydrocarbyl (e.g., C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_5-C_{24} aryl, C_6-C_{24} alkaryl, C_6-C_{24} aralkyl, etc.), substituted hydrocarbyl (e.g., substituted C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_5-C_{24} aryl, C_6-C_{24} alkaryl, C_6-C_{24} aralkyl, etc.), heteroatom-containing hydrocarbyl (e.g., heteroatom-containing C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_5-C_{24} aryl, C_6-C_{24} alkaryl, C_6-C_{24} aralkyl, etc.), and substituted heteroatom-containing hydrocarbyl (e.g., substituted heteroatom-containing C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_5-C_{24} aryl, C_6-C_{24} alkaryl, C_6-C_{24} aralkyl, etc.), and functional groups.

[0056] X^1 is an anionic ligand, and, as described below, may be linked together to form a cyclic group, typically although not necessarily a five- to eight-membered ring. Typically, X^1 is hydrogen, halide, nitrate, or one of the following groups: C_1-C_{20} alkyl, C_5-C_{24} aryl, C_1-C_{20} alkoxy, C_1-C_{20} alkylcarboxylate, C_5-C_{24} aryloxy, C_2-C_{20} alkoxycarbonyl, C_6-C_{24} aryloxycarbonyl, C_6-C_{24} arylcarboxylate, C_2-C_{24} acyl, C_2-C_{24} acyloxy, C_1-C_{20} alkylsulfonato, C_5-C_{24} arylsulfonato, C_1-C_{20} alkylsulfanyl, C_5-C_{24} arylsulfanyl, C_1-C_{20} alkylsulfinyl, or C_5-C_{24} arylsulfinyl. X^1 may be optionally substituted with one or more moieties selected from C_1-C_{12} alkyl, C_1-C_{20} alkylcarboxylate, C_1-C_{12} alkoxy, C_5-C_{24} aryl, C_6-C_{24} arylcarboxylate, and halide, which may, in turn, with the exception of halide, be further substituted with one or more groups selected from halide, C_1-C_6 alkyl, C_1-C_{20} alkylcarboxylate, C_1-C_6 alkoxy, and phenyl. In some embodiments, X^1 is benzoate, pivalate, C_2-C_6 acyl, C_2-C_6 alkoxycarbonyl, C_1-C_6 alkyl, phenoxy, C_1-C_6 alkoxy, C_1-C_6 alkylsulfanyl, aryl, or C_1-C_6 alkylsulfonyl. More specifically, X^1 may be is CF_3CO_2, CH_3CO_2, $CH_3CH_2CO_2$,CFH_2CO_2, $(CH_3)_3CO_2$, $(CH_3)_2CHCO_2$, $(CF_3)_2(CH_3)CO_2$, $(CF_3)(CH_3)_2CO_2$, benzoate, naphthylate, tosylate, mesylate, or trifluoromethane-sulfonate. In one more preferred embodiment, X^1 is nitrate (NO_3^-).

[0057] R^1 and R^2 are independently selected from hydrogen, hydrocarbyl (e.g., C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_5-C_{24} aryl, C_6-C_{24} alkaryl, C_6-C_{24} aralkyl, etc.), substituted hydrocarbyl (e.g.,

substituted C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_5-C_{24} aryl, C_6-C_{24} alkaryl, C_6-C_{24} aralkyl, etc.), heteroatom-containing hydrocarbyl (e.g., heteroatom-containing C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_5-C_{24} aryl, C_6-C_{24} alkaryl, C_6-C_{24} aralkyl, etc.), and substituted heteroatom-containing hydrocarbyl (e.g., substituted heteroatom-containing C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_5-C_{24} aryl, C_6-C_{24} alkaryl, C_6-C_{24} aralkyl, etc.), and functional groups. R^1 and R^2 may also be linked to form a cyclic group, which may be aliphatic or aromatic, and may contain substituents and/or heteroatoms. Generally, such a cyclic group will contain 4 to 12, preferably 5, 6, 7, or 8 ring atoms.

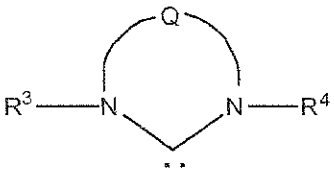
[0058] In certain catalysts, R^1 is hydrogen and R^2 is selected from C_1-C_{20} alkyl, C_2-C_{20} alkenyl, and C_5-C_{24} aryl, more preferably C_1-C_6 alkyl, C_2-C_6 alkenyl, and C_5-C_{14} aryl. Still more preferably, R^2 is phenyl, vinyl, methyl, isopropyl, or t-butyl, optionally substituted with one or more moieties selected from C_1-C_6 alkyl, C_1-C_6 alkoxy, and phenyl. Most preferably, R^2 is phenyl or vinyl substituted with one or more moieties selected from methyl, ethyl, chloro, bromo, iodo, fluoro, nitro, dimethylamino, methyl, methoxy, and phenyl. More specifically, R^2 may be phenyl or $-C{=}C(CH_3)_2$.

[0059] Any two or more (typically two, three, or four) of X^1, Q*, L^1, L^2, L^3, R^1, and R^2 can be taken together to form a cyclic group, including bidentate or multidentate ligands, as disclosed, for example, in U.S. Patent No. 5,312,940 to Grubbs et al. When any of X^1, Q*, L^1, L^2, L^3, R^1, and R^2 are linked to form cyclic groups, those cyclic groups may contain 4 to 12, preferably 4, 5, 6, 7 or 8 atoms, or may comprise two or three of such rings, which may be either fused or linked.

[0060] In addition, any two or more of X^1, Q*, L^1, L^2, L^3, R^1, R^2, R^3, R^{3A}, R^4, and R^{4A} can be taken together to form a cyclic group.

[0061] Preferably, R^{3A} and R^{4A} are linked to form a cyclic group so that the carbene ligand has the structure of formula (V)

(V)

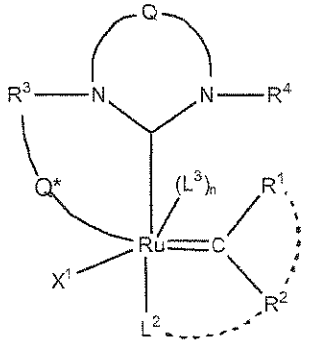


wherein R^3 and R^4 are defined above, with preferably R^3 being alicyclic and R^4 being aromatic.

[0062] Q is a linker, typically a hydrocarbylene linker, including substituted hydrocarbylene, heteroatom-containing hydrocarbylene, and substituted heteroatom-containing hydrocarbylene linkers, wherein two or more substituents on adjacent atoms within Q may also be linked to form an additional cyclic structure, which may be similarly substituted to provide a fused polycyclic structure of two to about five cyclic groups. Q is often, although again not necessarily, a two-atom linkage or a three-atom linkage.

[0063] When M is ruthenium, the complexes have the structure of formula (VI)

(VI)



[0064] In more particular embodiments, Q is a two-atom linkage having the structure $-CR^{11}R^{12}-CR^{13}R^{14}-$ or $-CR^{11}=CR^{13}-$, preferably $-CR^{11}R^{12}-CR^{13}R^{14}-$, wherein R^{11}, R^{12}, R^{13}, and R^{14} are independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups. Examples of suitable functional groups include carboxyl, C_1-C_{20} alkoxy, C_5-C_{24} aryloxy, C_2-C_{20} alkoxycarbonyl, C_5-C_{24} alkoxycarbonyl, C_2-C_{24} acyloxy, C_1-C_{20} alkylthio, C_5-C_{24} arylthio, C_1-C_{20} alkylsulfonyl, and C_1-C_{20} alkylsulfinyl, optionally substituted with one or more moieties selected from C_1-C_{12} alkyl, C_1-C_{12} alkoxy, C_5-C_{14} aryl, hydroxyl, sulfhydryl, formyl, and halide. R^{11}, R^{12}, R^{13}, and R^{14} are preferably independently selected from hydrogen, C_1-C_{12} alkyl, substituted C_1-C_{12} alkyl, C_1-C_{12} heteroalkyl, substituted C_1-C_{12} heteroalkyl, phenyl, and substituted phenyl. Alternatively, any two of R^{11}, R^{12}, R^{13}, and R^{14} may be linked together to form a substituted or unsubstituted, saturated or unsaturated ring structure, e.g., a C_4-C_{12} alicyclic group

or a C_5 or C_6 aryl group, which may itself be substituted, e.g., with linked or fused alicyclic or aromatic groups, or with other substituents. In one further aspect, any one or more of R^{11}, R^{12}, R^{13}, and R^{14} comprises one or more of the linkers.

[0065] In more particular aspects, R^3 and R^4 maybe alkyl or aryl, and may be independently selected from alkyl, aryl, cycloalkyl, heteroalkyl, alkenyl, alkynyl, and halo or halogen- containing groups. More specifically, R^3 and R^4 may be independently selected from C_1-C_{20} alkyl, C_5-C_{14} cycloalkyl, C_1-C_{20} heteroalkyl, or halide. Suitable alkyl groups include, without limitation, methyl, ethyl, n-propyl, isopropyl, isopropyl, n-butyl, isobutyl, t-butyl, octyl, decyl, and the like; suitable cycloalkyl groups include cyclopentyl, cyclohexyl, adamantyl, pinenyl, terpenes and terpenoid derivatives and the like; suitable alkenyl groups include ethenyl, n-propenyl, isopropenyl, n-butenyl, isobutenyl, octenyl, decenyl, tetradecenyl, hexadecenyl, eicosenyl, tetracosenyl, and the like; suitable alkynyl groups include ethynyl, n-propynyl, and the like.

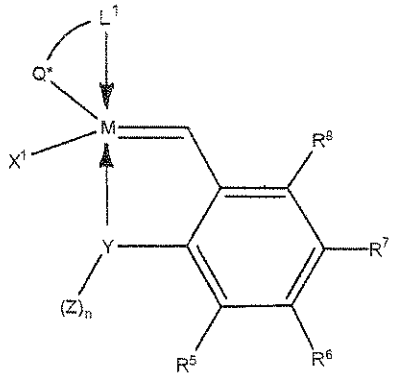
[0066] When R^3 and R^4 are aromatic, each can be independently composed of one or two aromatic rings, which may or may not be substituted, e.g., R^3 and R^4 may be phenyl, substituted phenyl, biphenyl, substituted biphenyl, or the like. In a particular embodiment, R^3 and R^4 are independently an unsubstituted phenyl or phenyl substituted with up to three substituents selected from C_1-C_{20} alkyl, C_1-C_{20} alkylcarboxylate, substituted C_1-C_{20} alkyl, C_1-C_{20} heteroalkyl, substituted C_1-C_{20} heteroalkyl, C_5-C_{24} aryl, substituted C_5-C_{24} aryl, C_5-C_{24} heteroaryl, C_6-C_{24} aralkyl, C_6-C_{24} alkaryl, or halide. Preferably, any substituents present are hydrogen C_1-C_{12} alkyl, C_1-C_{12} alkoxy, C_5-C_{14} aryl, substituted, C_5-C_{14} aryl, or halide. More particularly, R^3 and R^4 may be independently substituted with hydrogen, C_1-C_4 alkyl, C_1-C_4 alkylcarboxylate, C_1-C_4 alkoxy, C_5-C_{14} aryl, substituted C_5-C_{14} aryl, or halide. As an example, R^3 and R^4 are selected from cyclopentyl, cyclohexyl, adamantyl, norbonenyl , pinenyl, terpenes and terpenoid derivatives, mesityl, diisopropylphenyl or, more generally, cycloalkyl substituted with one, two or three C_1-C_4 alkyl or C_1-C_4 alkoxy groups, or a combination thereof.

[0067] In another group of catalysts having the structure of formula (II), M, m, n, X^1, Q*, R^1, and R^2 are as defined for the first group of catalysts, L^1 is a strongly coordinating neutral electron donor ligand such as any of those described for the first and second group of catalysts, and L^2 and L^3 are weakly coordinating neutral electron donor ligands in the form of optionally substituted heterocyclic groups. Again, n is zero or 1, such that L^3 may or may not be present. Generally, in the third group of catalysts, L^2 and L^3 are optionally substituted five- or six-membered monocyclic groups containing 1 to 4, preferably 1 to 3, most preferably 1 to 2 heteroatoms, or are optionally substituted bicyclic or polycyclic structures composed of 2 to 5 such five- or six-membered monocyclic groups. If the heterocyclic group is substituted, it should not be substituted on a coordinating heteroatom, and any one cyclic moiety within a heterocyclic group will generally not be substituted with more than 3 substituents.

[0068] For this group of catalysts, examples of L^2 and L^3 include, without limitation, heterocycles containing nitrogen, sulfur, oxygen, or a mixture thereof.

[0069] Complexes wherein Y is coordinated to the metal are examples of another group of catalysts, and are commonly called "Grubbs-Hoveyda" catalysts. Grubbs-Hoveyda metathesis-active metal carbene complexes may be described by the formula VIII.

(VIII)



wherein,

M is a Group 8 transition metal, particularly Ru or Os, or, more particularly, Ru;

X^1 and L^1 are as previously defined herein;

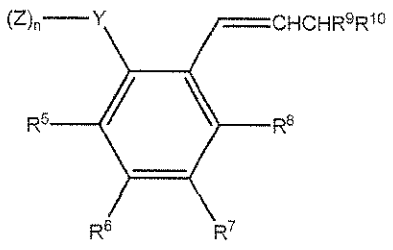
Q* is a 2-electron anionic donor bridging moiety between L^1 and M forming a carbon-metal bond between L^1 and M ;

Y is a heteroatom selected from N, O, S, and P; preferably Y is O or N;

[0070] R^5, R^6, R^7, and R^8 are each, independently, selected from the group consisting of hydrogen, halogen, alkyl, alkenyl, alkynyl, aryl, heteroalkyl, heteroatom containing alkenyl, heteroalkenyl, heteroaryl, alkoxy, alkenyloxy, aryloxy, alkoxycarbonyl, carbonyl, alkylamino, alkylthio, aminosulfonyl, monoalkylaminosulfonyl, dialkylaminosulfonyl, alkylsulfonyl, nitrile, nitro, alkylsulfinyl, trihaloalkyl, perfluoroalkyl, carboxylic acid, ketone, aldehyde, nitrate, cyano, isocyanate, hydroxyl, ester, ether, amine, imine, amide, halogen-substituted amide, trifluoroamide, sulfide, disulfide, sulfonate, carbamate, silane, siloxane, phosphine, phosphate, or borate, wherein any combination of R^5, R^6, R^7, and R^8 can be linked to form one or more cyclic groups; n is 1 or 2, such that n is 1 for the divalent heteroatoms O or S, and n is 2 for the trivalent heteroatoms N or P;

[0071] Z is a group selected from hydrogen, alkyl, aryl, functionalized alkyl, functionalized aryl where the functional group(s) may independently be one or more or the following: alkoxy, aryloxy, halogen, carboxylic acid, ketone, aldehyde, nitrate, cyano, isocyanate, hydroxyl, ester, ether, amine, imine, amide, trifluoroamide, sulfide, disulfide, carbamate, silane, siloxane, phosphine, phosphate, or borate; methyl, isopropyl, sec-butyl, t-butyl, neopentyl, benzyl, phenyl and trimethylsilyl; and wherein any combination or combinations of X^1, Q*, L^1, Y, Z, R^5, R^6, R^7, and R^8 are linked to a support. In general, Grubbs-Hoveyda complexes useful in the invention contain a chelating alkylidene moiety of the formula IX.

(IX)



wherein Y, n, Z, R^5, R^6, R^7, and R^8 are as previously defined herein;

[0072] R^9 and R^{10} are each, independently, selected from hydrogen or a substitutent group selected from alkyl, aryl, alkoxy, aryloxy, C_2-C_{20} alkoxycarbonyl, or C_1-C_{20} trialkylsilyl, wherein each of the substituent groups is substituted or unsubstituted.

[0073] Complexes comprising Grubbs-Hoveyda ligands suitable in the invention wherein, L^1, X^1, X^2, and M are as described for any of the other groups of catalysts. Suitable chelating carbenes and carbene precursors are further described by Pederson et al. (U.S. Pat, Nos. 7026,495; 6,620,955) and Hoveyda et al. (U.S. Pat. No. 6,921,735; WO0214376).

[0074] In addition to the catalysts that have the structure of formula (II), as described above, other transition metal carbene complexes include, but are not limited to:

[0075] neutral ruthenium or osmium metal carbene complexes containing metal centers that are formally in the +2 oxidation state, have an electron count of 16, are penta-coordinated, and are of the general formula (VIII) in which Q* is a 2-electon anionic donor bridging moiety that forms a carbon-metal bond with M;

[0076] neutral ruthenium or osmium metal carbene complexes containing metal centers that are formally in the +2 oxidation state, have an electron count of 18, are hexa-coordinated, and are of the general formula (IX) in which Q* is a 2-electon anionic donor bridging moiety that forms a carbon-metal bond with M;

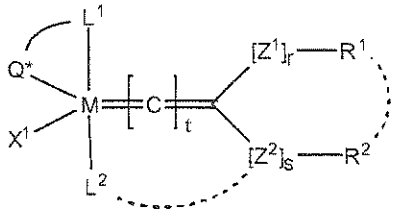
[0077] cationic ruthenium or osmium metal carbene complexes containing metal centers that are formally in the +2 oxidation state, have an electron count of 16, are penta-coordinated, and are of the general formula (X) in which Q* is a 2-electon anionic donor bridging moiety that forms a carbon-metal bond with M;

[0078] cationic ruthenium or osmium metal carbene complexes containing metal centers that are formally in the +2 oxidation state, have an electron count of 18, are tetra-coordinated, and are of the

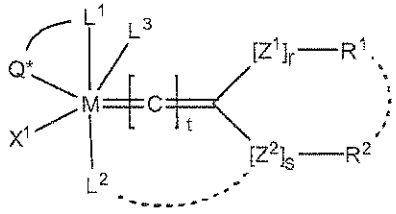
general formula (XI) in which L^2 is a 6-electron neutral arene donor and Q* is a 2-electon anionic donor bridging moiety that forms a carbon-metal bond with M; and

[0079] cationic ruthenium or osmium metal carbene complexes containing metal centers that are formally in the +2 oxidation state, have an electron count of 14, are tetra-coordinated and are of the general formula (XII) in which Q* is a 2-electon anionic donor bridging moiety that forms a carbon-metal bond with M and the alkylidene moiety possesses a formal positive charge.

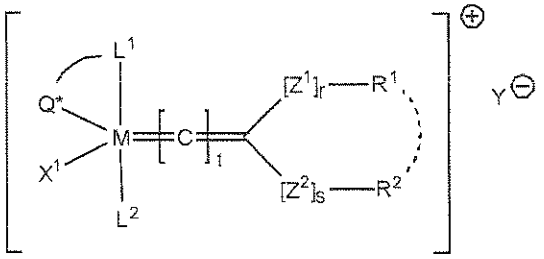
(VIII)



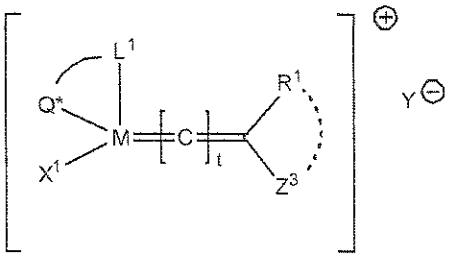
(IX)

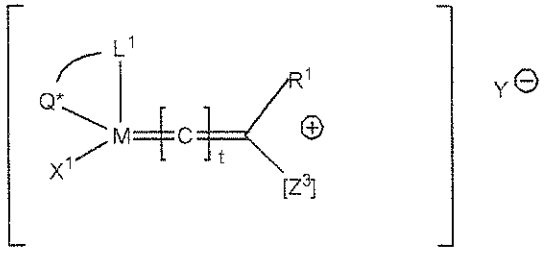


(X)



(XI)



(XII) 

[0080] wherein: X^1, Q*, L^1, L^2, n, L^3, R^1, and R^2 are as defined for any of the previously defined four groups of catalysts; r and s are independently zero or 1; t is an integer in the range of zero to 5; Y is any non-coordinating anion (e.g., a halide ion, BF_4^-, etc.); Z^1 and Z^2 are independently selected from -O-, -S-, $-NR^2-$, $-PR^2-$, $-P(=O)R^2-$, $-P(OR^2)-$, $-P(=O)(OR^2)-$, -C(=O)-, -C(=O)O-, -OC(=O)-, -OC(=O)O-, -S(=O)-, and $-S(=O)_2-$; Z^3 is any cationic moiety such as $-P(R^2)_3^+$ or $-N(R^2)_3^+$; and any two or more of X^1, X^2, L^1, L^2, L^3, n, Z^1, Z^2, Z^3, R^1, and R^2 may be taken together to form a cyclic group, e.g., a multidentate ligand, and wherein any one or more of X^1, Q*, L^1, L^2, n, L^3, Z^1, Z^2, Z^3, R^1, and R^2 may be attached to a support via linker moieties.

[0081] As noted above, the catalyst compounds according to the invention may be prepared using the general procedures of Scheme 2 and 3 previously described. In one embodiment, for example, a C-H activated olefin metathesis catalyst compound may be prepared by contacting a carboxylate compound of the formula M^1X^2, wherein M^1 is selected from silver, lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, iron, zinc, or thalium, and X^2 is a carboxylate anion, with an olefin metathesis catalyst of the formula $(X^1)_2(L^3)_n(L^2)_kL^1M=(C)_mCR^1R^2$, in which, as described previously, X^1 is any anionic ligand, L^1, L^2, and L^3 are, independently, any neutral electron donor ligand, n and k are, independently, 0 or 1, m is 0, 1, or 2, M is a Group 8 transition metal, and R^1 and R^2 are the alkylidene substituents. Such C-H activation reactions may be conducted under conditions effective to promote the exchange of X^2 anions for the X^1 anionic ligands, such that a C-H activated olefin metathesis catalyst compound is produced in which M and L^1 are linked together by a 2-electron anionic bridging moiety Q*in a M-Q*-L^1 chelating ligand ring structure having a ring size of 5, 6, or 7 atoms, and the

catalyst compound contains an X^2 anionic ligand. Typically, M is directly bonded to a carbon atom of Q* in the M-Q*-L^1 chelating ligand ring structure.

[0082] In certain embodiments, M^1 is silver or sodium, and the carboxylate may be of the formula $(R)_3COOM^1$, wherein R is independently selected from hydrogen, C_1-C_{12} alkyl, substituted C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, substituted C_3-C_{12} cycloalkyl, aryl or substituted aryl, wherein at least one R is not hydrogen. The R groups may be more particularly independently selected from hydrogen, C_1-C_{12} alkyl or aryl, such as, e.g., where the $(R)_3$ groups together form *t*-butyl, $PhMe_2C$, Ph_2MeC, or Ph_3C.

[0083] The method of making such C-H activated catalyst compounds may further comprise additional steps, such as anionic ligand exchange reactions. For example, the C-H activated olefin metathesis catalyst compound may be contacted with an anionic ligand exchange compound of the formula M^2X^3, wherein M^2 is a cation and X^3 is an anion; under conditions effective to promote the exchange of X^3 anions for the X^2 anionic ligands, such that the C-H activated olefin metathesis catalyst compound contains a M-Q*-L^1 chelating ligand ring structure having a ring size of 5, 6, or 7 atoms and an X^3 anionic ligand.

[0084] While M^2 and X^3 are not necessarily limited, typically M^2 may be selected from hydrogen, ammonium, silver, lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, iron, zinc, or thalium, and X^3 may be selected from halogen, alkyl, aryl, carboxylate, alkoxy, aryloxy, sulfonate, phosphate, or nitrate.

[0085] It is to be understood that while the invention has been described in conjunction with specific embodiments thereof, that the description above as well as the examples that follow are intended to illustrate and not limit the scope of the invention. Other aspects, advantages, and modifications within the scope of the invention will be apparent to those skilled in the art to which the invention pertains.

Experimental

[0086] In the following examples, efforts have been made to ensure accuracy with respect to numbers used (e.g., amounts, temperature, etc.) but some experimental error and deviation should be accounted for. Unless indicated otherwise, temperature is in degrees C and pressure is at or near atmospheric.

[0087] The following examples are to be considered as not being limiting of the invention as described herein, and are instead provided as representative examples of the catalyst compounds of the invention, the methods that may be used in their preparation, and the methods of using the inventive catalysts.

General Information - materials and methods

[0088] **Atmosphere** All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere unless otherwise specified.

[0089] **Solvents** All solvents were purified by passage through solvent purification columns and further degassed with argon as previously described (Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, 15, 1518). NMR solvents for air-sensitive compounds were dried over CaH_2 and vacuum transferred or distilled into a dry Schlenk flask and subsequently degassed with argon.

[0090] **Materials** Commercially available reagents were used as received unless otherwise noted. Substrates for olefin metathesis reactions were degassed with argon and passed through a plug of neutral alumina (Brockmann I) prior to use.

[0091] **Instrumentation** Standard NMR spectroscopy experiments were conducted on a Varian Inova 400 MHz spectrometer, while kinetic experiments were conducted on a Varian 500 MHz spectrometer equipped with an AutoX probe. Experiments and pulse sequences from Varian's Chempack

4 software were used. Chemical shifts are reported in ppm downfield from Me_4Si by using the residual solvent peak as an internal standard. Spectra were analyzed and processed using MestReNova Ver. 7. Gas chromatography data was obtained using an Agilent 6850 FID gas chromatograph equipped with a DB-Wax Polyethylene Glycol capillary column (J&W Scientific). High-resolution mass spectrometry (HRMS) data was obtained on a JEOL MSRoute mass spectrometer using FAB+ ionization, except where specified.

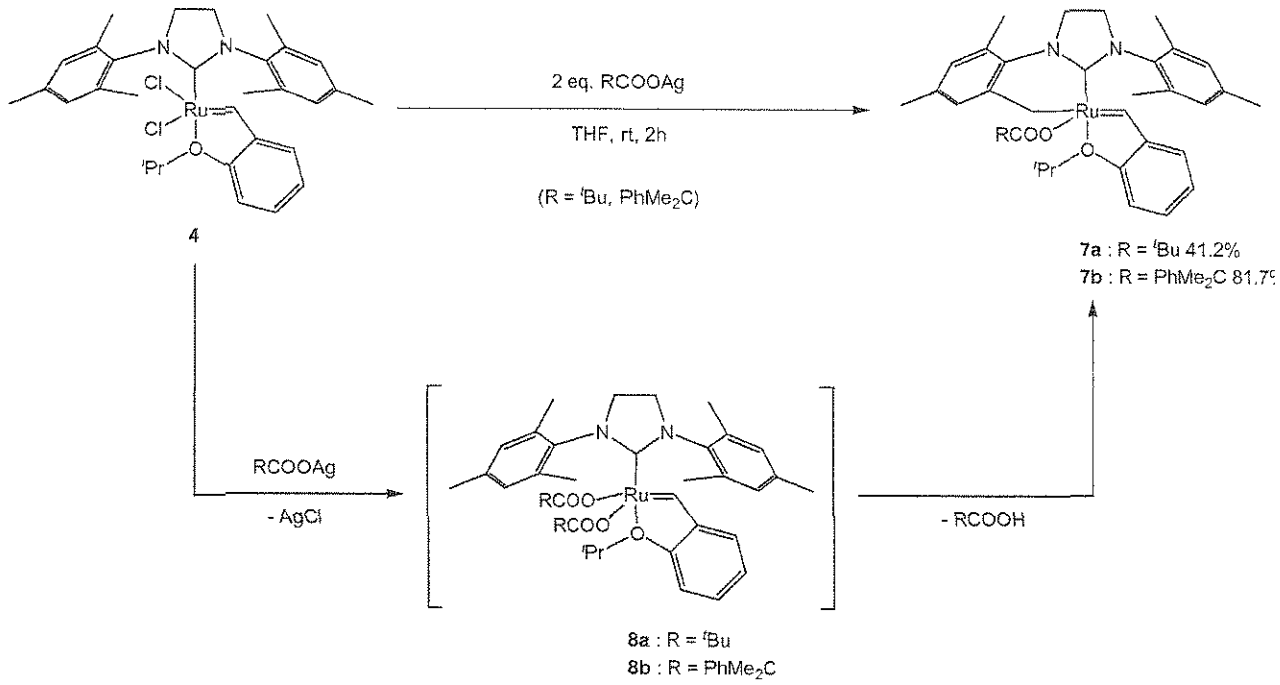
EXAMPLES

Example 1

Preparation of C-H activated catalyst complexes from Ru-complex **4**

[0092] By reaction of $(H_2IMes)RuCl_2[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$ (**4**) and two equivalent of RCOOAg (R = ^{t}Bu, $PhMe_2C$) at room temperature, metallacycle complexes $\{[2\text{-}(CH_2)\text{-}4,6\text{-}Me_2(C_6H_2)](C_3N_2H_4)\text{-}(Mes)\}Ru(OCOR)[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$ (R = ^{t}Bu (**7a**), $PhMe_2C$ (**7b**)) were obtained as an air-stable dark green solids in good yields (Scheme 4). In this reaction, disubstituted complex (**8**) was also observed at early reaction time. Then, C-H bond activation of methyl group of mesityl group in the NHC ligand and formation of corresponding carboxylic acid afforded **7**. The molecular structures of **7a** and **7b** were confirmed by X-ray crystallography. As shown in Figure 4 and 5, both **7a** and **7b** have 6-membered chelates consisting of ruthenium and the NHC ligand.

Scheme 4



[0093] Representative characterization data for complex **7a** is as follows:

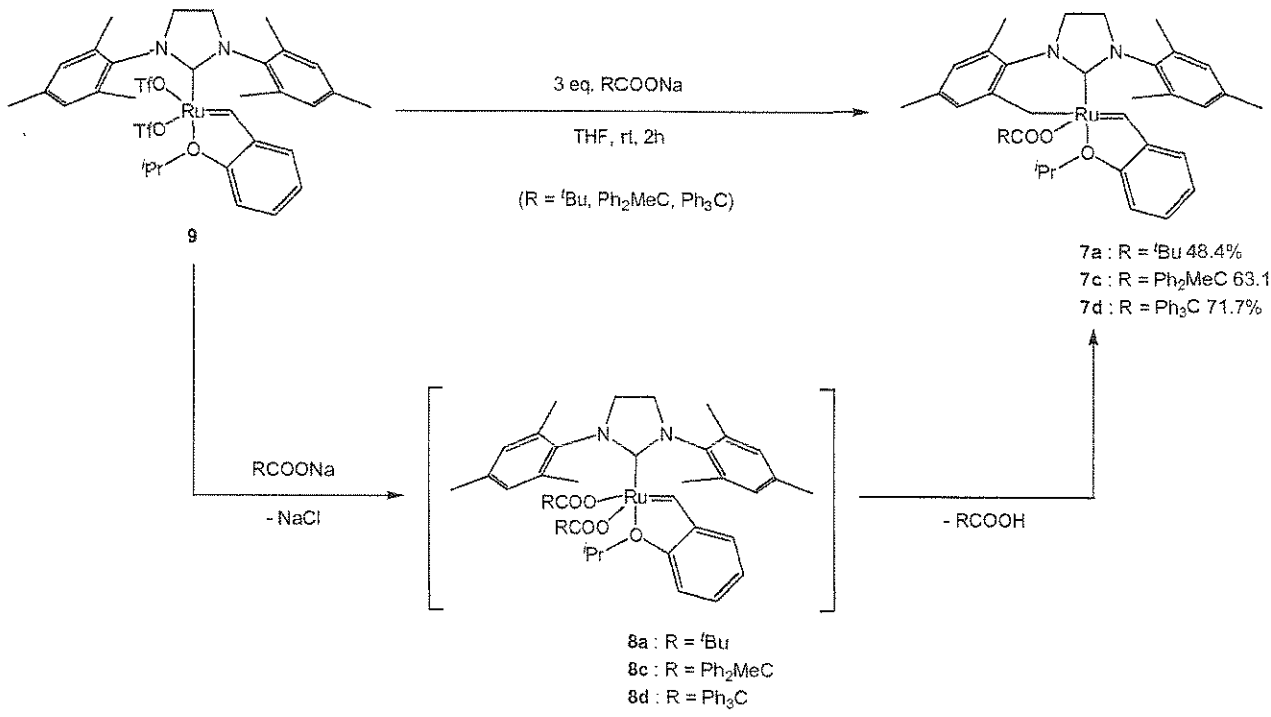
^{1}H NMR (500 MHz, C_6D_6): δ/ppm 15.91 (s, 1H), 7.15-7.11 (m, 2H), 7.06 (s, 1H), 6.95 (s, 1H), 6.92 (s, 1H), 6.73-6.70 (m, 1H), 6.63 (s, 1H), 6.49 (d, J = 8.5 Hz, 1H), 4.68 (sep, J = 6.4 Hz, 1H), 3.87-3.83 (m, 1H), 3.45-3.38 (m, 2H), 3.29 (d, J = 9.8 Hz, 1H), 3.21-3.15 (m, 1H), 2.46 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H), 2.21 (s, 3H), 2.17 (d, J = 9.8 Hz, 1H), 2.12 (s, 3H), 1.48 (d, J = 6.4 Hz, 3H), 1.26 (s, 9H), 1.16 (d, J = 6.4 Hz, 3H). ^{13}C NMR (125.7 MHz, C_6D_6): δ/ppm 280.8, 223.6, 186.6, 154.6, 144.7, 142.7, 142.3, 139.7, 138.4, 137.7, 136.8, 134.5, 130.9, 130.7, 128.8, 128.1, 128.0, 126.9, 123.6, 123.1, 112.7, 54.1, 50.3, 39.5, 28.5, 22.2, 21.7, 21.4, 21.3, 19.9, 18.7, 18.6, 17.9. HRMS (FAB+): Calculated: 656.2552, Found: 656.2548.

Example 2

Preparation of C-H activated catalyst complexes from Ru-complex **9**

[0094] In the same manner as Scheme 4, $(H_2IMes)Ru(OTf)_2[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$ (**9**) (prepared as described in Krause, J. O.; Nuyken, O.; Wurst, K.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 777) gave chelate complexes $\{[2\text{-}(CH_2)\text{-}4,6\text{-}Me_2(C_6H_2)](C_3N_2H_4)(Mes)\}Ru(OCOR)[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$ (R = ^{t}Bu (**7a**), Ph_2MeC (**7c**), Ph_3C (**7d**)) in reactions with corresponding sodium salts (Scheme 5). The products were all air-stable in solid state. In these reactions, formation of disubstituted complexes (**8**) at early stage of reaction and subsequent formation of carboxylic acid were also observed.

Scheme 5

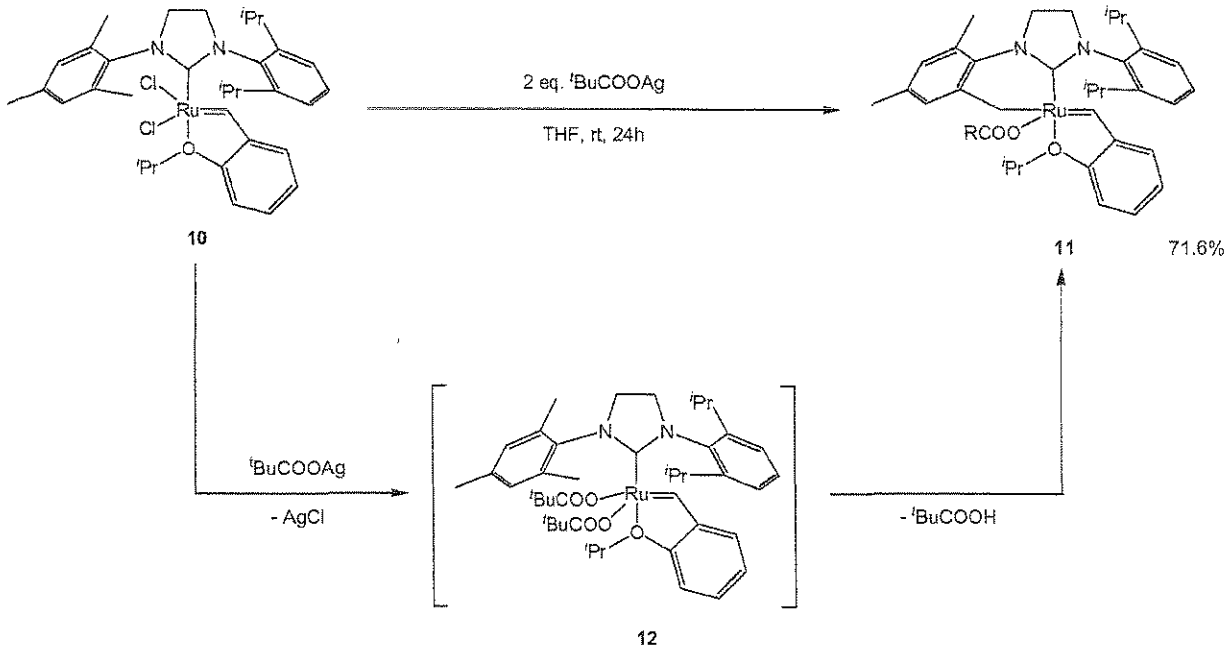


Example 3

Preparation of C-H activated catalyst complexes from Ru-complex **10**

[0095] By reaction of $(H_2IMesDipp)RuCl_2[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$ (**10**), which had an asymmetric NHC ligand containing one 2,6-diisopropylphenyl group instead of mesityl group in **4**, and silver pivalate, $\{[2\text{-}(CH_2)\text{-}4,6\text{-}Me_2(C_6H_2)](C_3N_2H_4)(Dipp)\}Ru(OCO^tBu)[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$ (**11**) was obtained as an air-stable dark green solid in good yield (Scheme 6). During the reaction, disubstituted complex (**12**) was formed and none of the complexes resulting from C-H bond activation in the 2,6-diisopropylphenyl group were observed. The crystal structure of **11** determined by X-ray crystallography (Figure 6) showed a 6-membered chelate and clearly indicated that C-H bond activation had occurred at the methyl group of the mesityl group in the NHC ligand.

Scheme 6

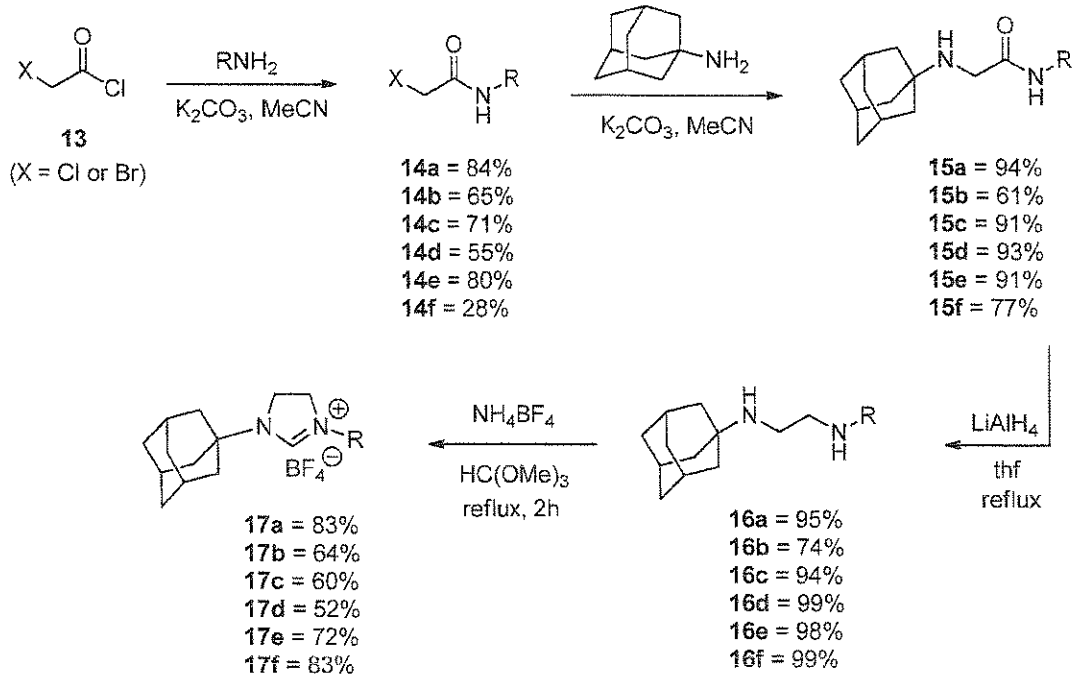


Example 4

Syntheses of $RuCl_2$ complexes comprising an asymmetric NHC ligand that contains an Adamantyl group

[0096] Asymmetric NHC salts **17a-f** containing an adamantyl group were synthesized by modifying a reported procedure (Paczal, A.; Benyei, A. C.; Kotschy, A. *J. Org. Chem.* **2006**, *71*, 5069) as outlined in Scheme 7. All products were obtained in good to excellent yield.

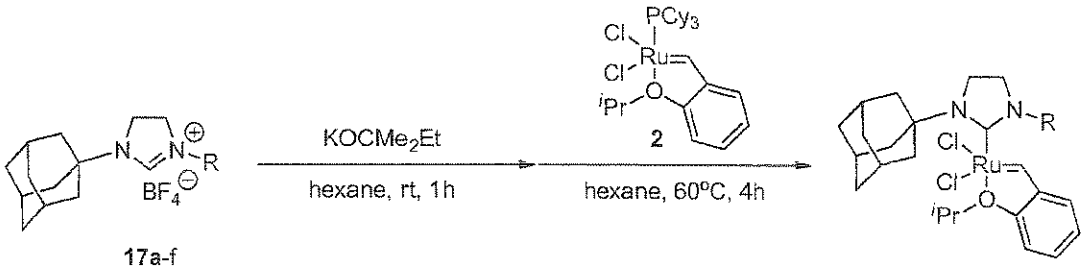
Scheme 7



[0097] Dichloro ruthenium alkylidene catalysts (**18a-f**) having the NHC's **17a-f** were also synthesized by modifying a reported procedure (Jafarpour, L.; Hillier, A. C.; Nolan, S. P. *Organometallics* **2002**, *21*, 442) as outlined in Scheme 8. They were obtained as air-stable green solids in

excellent yield. Structures of **18a-c** were determined by X-ray crystallography and are shown in Figures 7-9.

Scheme 8



[0098] Representative characterization data for complex **18a** is as follows: ^{1}H NMR (500 MHz, C_6D_6): δ/ppm 17.13 (s, 1H), 7.21-7.13 (m, 2H), 6.85 (s, 2H), 6.75-6.73 (m, 1H), 6.46 (d, J = 8.2 Hz, 1H), 4.58 (sep, J = 6.1 Hz, 1H), 3.30-3.28 (m, 4H), 2.95 (br s, 6H), 2.35 (s, 6H), 2.31 (br s, 3H), 2.24 (s, 3H), 1.90 (br d, 3H), 1.69 (br d, 3H), 1.58 (d, J = 6.1 Hz, 6H). ^{13}C NMR (125.7 MHz, C_6D_6): δ/ppm 307.9, 210.4, 153.1, 146.8, 140.7, 138.8, 138.6, 130.3, 130.2, 123.7, 122.8, 113.9, 74.6, 57.5, 51.4, 44.7, 42.6, 36.7, 30.8, 22.8, 21.5, 18.9. HRMS (FAB+): Calculated: 642.1718, Found: 642.1742.

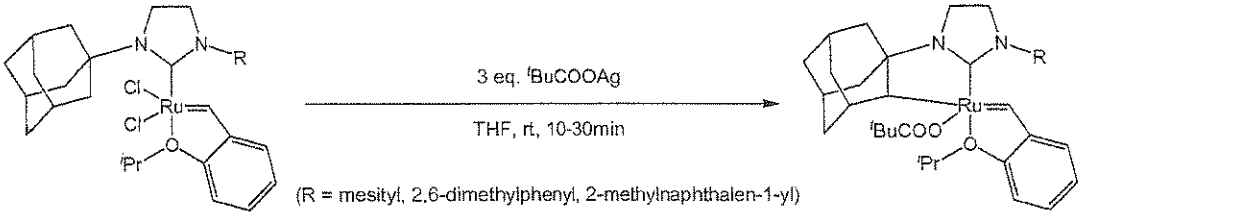
Example 5

Preparation of C-H activated catalyst complexes from Ru-complexes **18a-c**

[0099] A reaction of $(H_2IAdmMes)RuCl_2[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$ (**18a**) and silver pivalate gave $[(C_{10}H_{14})(C_3N_2H_4)(Mes)]Ru(OCO^tBu)[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$ (**19a**) resulting from C-H bond activation at the adamantyl group as an air-stable red-purple solid (Scheme 9). **19a** was easily prepared after a short reaction time and was purified by simply washing and extraction with common organic solvents. Unlike the case of **4** or **10**, products derived from C-H bond activation at mesityl group were not observed. In the

reactions with silver pivalate, {H_2IAdm[2,6-$(CH_3)_2C_6H_3$]}$RuCl_2$[=CH-*o*-(O^iPr)C_6H_4] (**18b**) and {H_2IAdm[2-$(CH_3)C_{10}H_6$]}$RuCl_2$[=CH-*o*-(O^iPr)C_6H_4] (**18c**) also afforded corresponding metallacycle catalysts {$(C_{10}H_{14})(C_3N_2H_4)$[2,6-$(CH_3)_2C_6H_3$]}Ru($OCO^t$Bu)[=CH-*o*-($O^i$Pr)$C_6H_4$] (**19b**) and {$(C_{10}H_{14})(C_3N_2H_4)$-[2-$(CH_3)C_{10}H_6$]}Ru($OCO^t$Bu)[=CH-*o*-($O^i$Pr)$C_6H_4$] (**19c**) which were generated by C-H bond activation at the adamantyl groups as shown in Scheme 9. The structure of **19a** having a 5-membered chelate was determined by X-ray crystallography (Figure 10).

Scheme 9



18a : R = 2,4,6-$(CH_3)_3C_6H_2$
18b : R = 2,6-$(CH_3)_2C_6H_3$
18c : R = 2-$(CH_3)C_{10}H_6$

19a : R = 2,4,6-$(CH_3)_3C_6H_2$ 59.3%
19b : R = 2,6-$(CH_3)_2C_6H_3$ 37.5%
19c : R = 2-$(CH_3)C_{10}H_6$ 52.3%

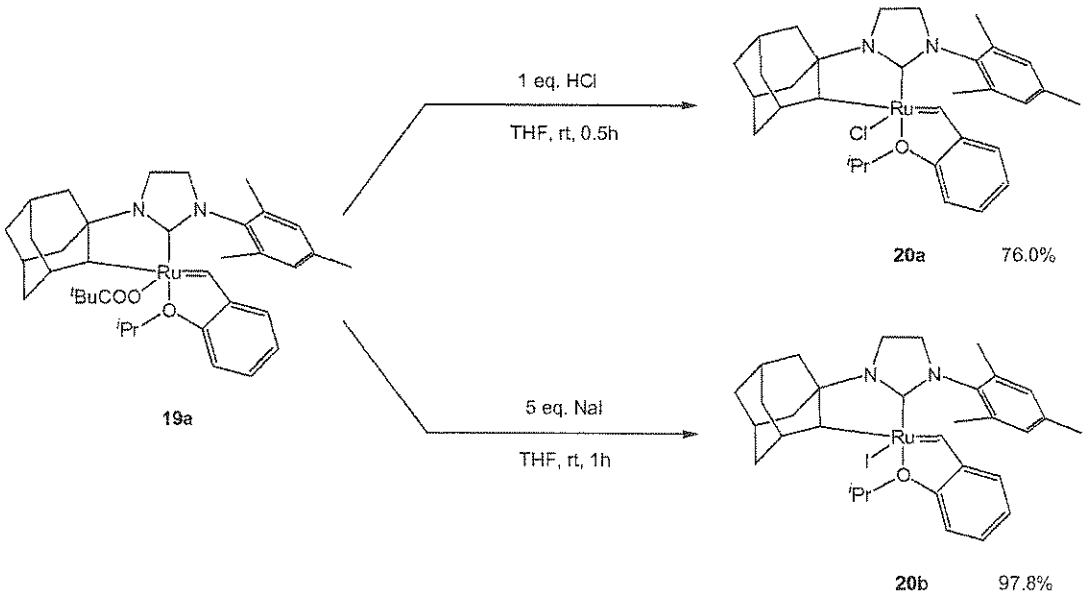
[00100] Representative characterization data for complex **19a** is as follows: ^{1}H NMR (500 MHz, C_6D_6): δ/ppm 14.87 (s, 1H), 7.47 (dd, J = 7.3 Hz, J = 1.2 Hz, 1H), 7.27-7.24 (m, 1H), 6.90 (t, J = 7.3 Hz, 1H), 6.82 (s, 1H), 6,74 (s, 1H), 6.71 (d, J = 8.2 Hz, 1H), 4.80 (sep, J = 6.4 Hz, 1H), 4.19 (s, 1H), 3.46-3.36 (m, 2H), 3.29-3.14 (m, 2H), 2.53 (br s, 1H), 2.43 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H), 2.11-2.08 (br m, 2H), 2.03-2.01 (br m, 1H), 1.95-1.92 (br m, 1H), 1.85-1.81 (br m, 1H), 1.65-1.64 (br m, 1H), 1.56-1.47 (br m, 2H), 1.52 (d, J = 6.4 Hz, 3H), 1.40-1.36 (br m, 1H), 1.25 (s, 9H), 1.21-1.19 (br m, 1H), 1.17 (d, J = 6.4 Hz, 3H), 1.06-1.02 (br m, 1H), 0.68-0.65 (br m, 1H). ^{13}C NMR (125.7 MHz, C_6D_6): δ/ppm 258.9, 216.0, 154.6, 144.2, 138.3, 137.4, 137.1, 136.7, 130.2, 130.0, 125.8, 123.5, 123.5, 114.2, 74.7, 68.9, 63.0, 52.0, 43.7, 41.6, 40.9, 39.9, 38.6, 38.4, 37.2, 34.1, 31.4, 30.3, 28.8, 27.9, 21.9, 21.5, 21.4, 19.5, 19.3. HRMS (FAB+): Calculated: 672.2866, Found: 672.2851.

Example 6

Exchange of the pivalate ligand in complex **19a** with other X-type ligands

[00101] The pivalyl ligand of **19a** was easily replaced by other anionic ligands. As shown in Scheme 10, when **19a** was reacted with hydrogen chloride or sodium iodide, a chloro catalyst $[(C_{10}H_{14})(C_3N_2H_4)$-(Mes)]RuCl[=CH-*o*-($O^iPr$)$C_6H_4$] (**20a**) or an iodo catalyst $[(C_{10}H_{14})(C_3N_2H_4)(Mes)]$RuI[=CH-*o*-($O^iPr$)-$C_6H_4$] (**20b**) were afforded, respectively. Also potassium 2,6-diisopropylphenoxide or potassium pentachlorophenoxide reacted with **19a** and afforded phenoxy substituted catalysts $[(C_{10}H_{14})(C_3N_2H_4)$-(Mes)]Ru[O(2,6-$^iPr_2C_6H_3$)][=CH-*o*-($O^iPr$)$C_6H_4$] (**21a**) or $[(C_{10}H_{14})(C_3N_2H_4)(Mes)]$Ru[$O(C_6Cl_5)$][=CH-*o*-($O^iPr$)$C_6H_4$] (**21b**), respectively as displayed in Scheme 11. **20** and **21** were all air-stable and easy to handle. Complexes **20b**, **21a** and **21b** were purified by simple wash and extraction instead of silica gel chromatography and were obtained in excellent yield. The structure of **21a** was confirmed by X-ray crystallography (Figure 11).

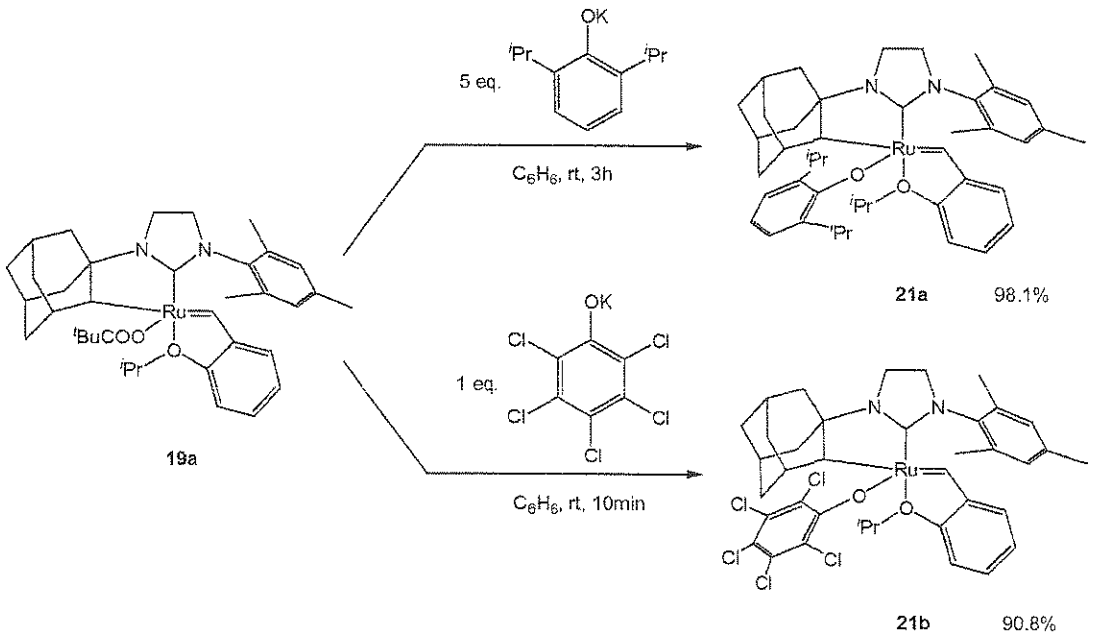
Scheme 10



[00102] Representative characterization data for complex **20b** is as follows:

^{1}H NMR (400 MHz, C_6D_6) δ 13.42 (s, 1H), 7.38 (dd, J = 8, 4 Hz, 1H), 7.15 (m, 1H), 6.97 (br s, 1H), 6.80 (dt, J = 8, 1 Hz, 1H), 6.76 (br s, 1H), 6.64 (d, J = 8 Hz, 1H), 4.81 (sept, J = 4 Hz, 1H), 3.46 (q, J = 8 Hz, 1H), 3.37-3.30 (m, 1H), 3.11-3.06 (m, 2H), 2.61 (br s, 1H), 2.56 (s, 3H), 2.41 (s, 3H), 2.40 (br s, 1H), 2.13 (s, 3H), 2.03 (br s, 1H), 1.91 (d, J = 4 Hz, 3H), 1.86-1.79 (m, 2H), 1.65 (br s, 2H), 1.62 (d, J = 4 Hz, 3H), 1.59-1.57 (m, 1H),1.43-1.37 (m, 3H), 2.30 (br d, J = 8 Hz, 2H), 0.54 (br d, J = 16 Hz, 1H). ^{13}C NMR (126 MHz, C_6D_6) δ 236.56, 215.48, 154.59, 141.54, 139.13, 138.09, 137.45, 135.36, 125.96, 123.47, 122.63, 112.99, 81.52, 75.78, 63.40, 52.52, 42.24, 41.09, 39.39, 38.12, 37.54, 37.25, 33.81, 30.63, 29.64, 22.72, 21.76, 21.16, 20.99, 19.28. HRMS (FAB+): Calculated – 698.1316, Found – 698.1343.

Scheme 11



[00103] Representative characterization data for complex **21b** is as follows:

^{1}H NMR (500 MHz, C_6D_6) δ 14.78 (s, 1H), 7.41 – 7.33 (m, 1H), 7.21 – 7.15 (m, 1H), 6.80 (t, J = 7.4 Hz, 1H), 6.66 (d, J = 1.7 Hz, 1H), 6.46 (d, J = 8.4 Hz, 1H), 6.22 (d, J = 1.6 Hz, 1H), 4.44 (sept, J = 6.2 Hz, 1H), 4.40 (s, 1H), 3.28 – 3.14 (m, 2H), 3.14 – 2.98 (m, 2H), 2.32 (s, 3H), 2.20 (d, J = 3.1 Hz, 1H), 2.15 (s,

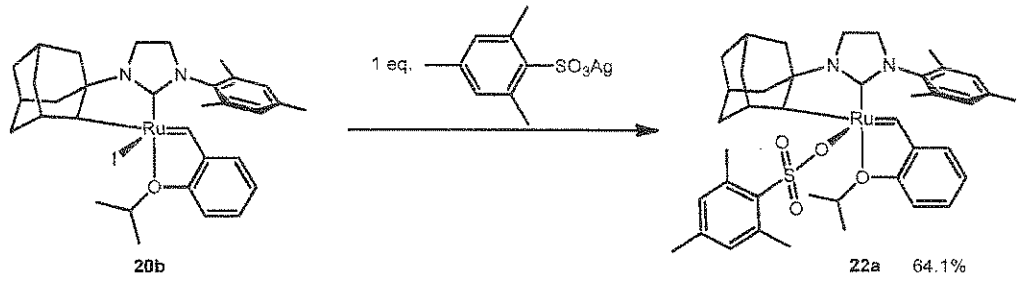
3H), 2.00 (s, 4H), 1.88 (ddt, J = 29.0, 11.0, 2.8 Hz, 2H), 1.77 – 1.62 (m, 2H), 1.57 (s, 1H), 1.50 (d, J = 6.3 Hz, 3H), 1.48 – 1.29 (m, 3H), 1.14 – 0.93 (m, 2H), 0.74 (d, J = 6.1 Hz, 3H), 0.55 (d, J = 12.5, 1H). ^{13}C NMR (126 MHz, C_6D_6) δ 254.34, 214.38, 160.36, 154.03, 144.19, 137.91, 137.60, 136.08, 135.99, 129.10, 128.95, 126.54, 123.34, 123.03, 113.70, 113.05, 74.53, 67.47, 63.08, 51.11, 42.65, 41.41, 39.76, 37.82, 37.80, 36.90, 32.90, 30.77, 29.56, 21.28, 21.09, 20.26, 18.47, 18.17.=

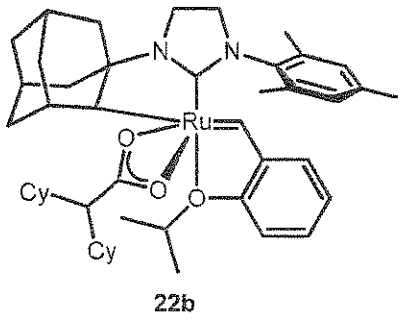
Example 7

Exchange of the iodide ligand in complex **20b** with other X-type ligands

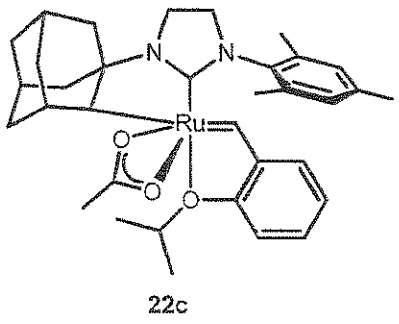
[00104] When **20b** was reacted with silver 2-mesitylenesulfonate, iodo ligand of **20b** was replaced by sulfonate ligand and $[(C_{10}H_{14})(C_3N_2H_4)(Mes)]Ru(SO_3Mes)[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$ (**22a**) was yielded. Compounds **22b-n** (Scheme 12) were synthesized in a similar manner as described for **22a**. An x-ray crystal structure confirming the structure of **22e** is shown in Figure 12.

Scheme 12

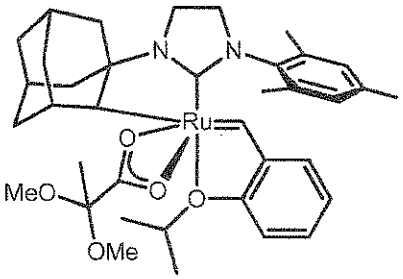




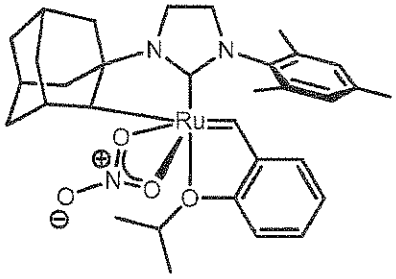
22b



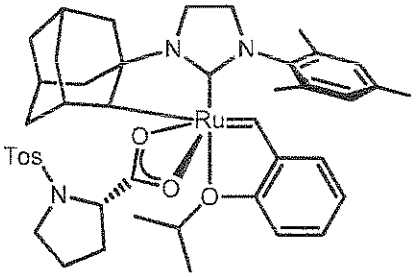
22c



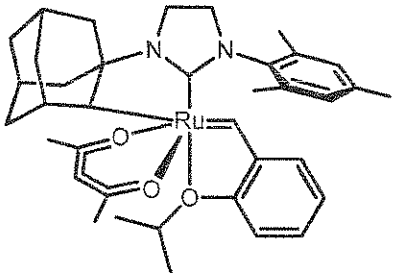
22d



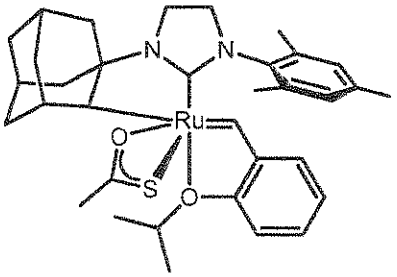
22e



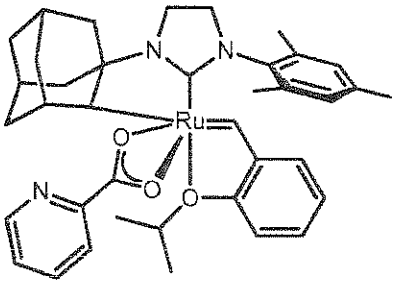
22f



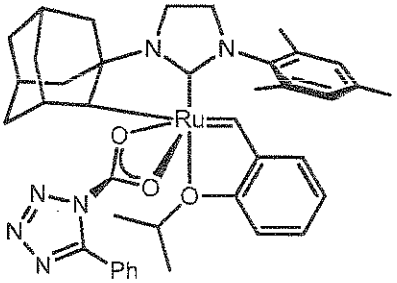
22g



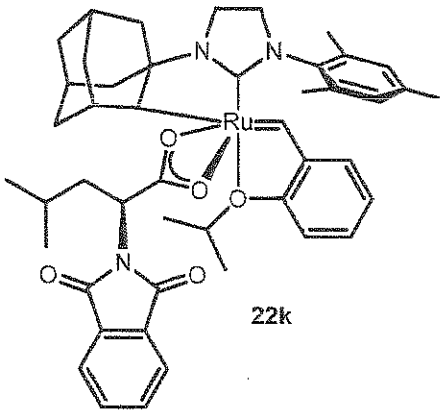
22h



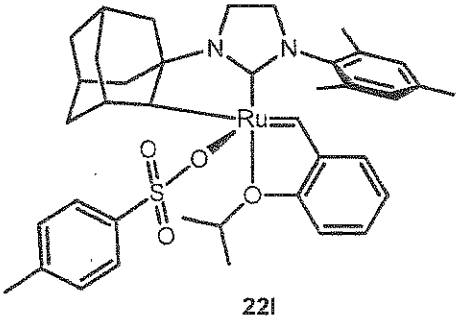
22i



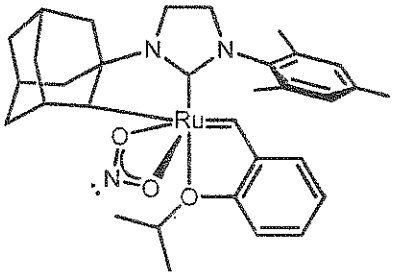
22j



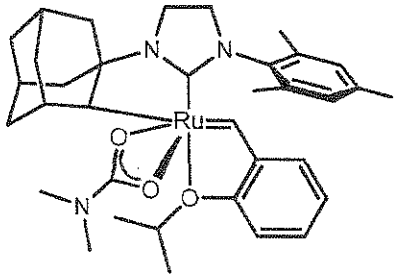
22k



22l



22m



22n

[00105] Representative characterization data for complex **22b** is as follows:

^{1}H NMR (400 MHz, C_6D_6) δ 14.94 (s, 1H), 7.41 (dd, J = 8, 4 Hz, 1H), 7.25 (dt, J = 8, 4 Hz, 1H), 6.87-6.83 (m, 2H), 6.80 (br s, 1H), 6.72 (br d, J = 8 Hz, 1H), 4.78 (sept, J = 8 Hz, 1H), 4.08 (s, 1H), 3.45-3.13 (m, 4H), 2.47 (br s, 1H), 2.44 (s, 3H), 2.33 (s, 1H), 2.25 (s, 1H), 2.10-1.30 (m, 10H), 2.07 (br s, 1H), 1.98 (br d, J = 8 Hz, 3H), 1.88 (br d, J = 8 Hz, 4H), 1.79 (br s, 3H), 1.76 (br s, 2H), 1.64 (br s, 4H), 1.60 (d, J = 4 Hz, 4H), 3.34 (br d, J = 16 Hz, 3H), 1.39 (br s, 1H), 1.36 (d, J = 4 Hz, 5H), 1.17 (br d, J = 8 Hz, 2H), 1.07 (br d, J = 8 Hz, 2H), 0.63 (br d, J = 12 Hz, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 258.83, 214.74, 183.61, 153.90, 143.52, 137.70, 136.58, 136.43, 136.03, 129.47, 129.20, 124.98, 122.86, 122.83, 113.34, 73.83, 67.67, 62.30, 57.15, 51.31, 42.77, 40.96, 40.04, 37.88, 37.58, 36.76, 33.30, 30.71, 29.60, 21.68, 21.35, 20.86, 18.65, 18.49. HRMS (FAB+, (M+H)-H_2): Calculated – 793.3883, Found – 793.3894.

[00106] Representative characterization data for complex **22c** is as follows:

^{1}H NMR (400 MHz, C_6D_6) δ 14.95 (s, 1H), 7.47 (dd, J = 7.6, 1.6 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1H), 6.88 (dt, J = 7.6, 1.2 Hz, 1H), 6.77 (br s, 1H), 6.70 (br s, 1H), 6.65 (br d, J = 8.4 Hz, 1H), 4.76 (sept, J = 6.0 Hz, 1H), 4.06 (s, 1H), 3.47 (q, J = 8.8 Hz, 1H), 3.38-3.21 (m, 4H), 2.43 (s, 3H), 2.40 (br s, 1H), 2.33 (s, 3H), 2.15 (br s, 4H), 2.15-1.04 (m, 2H), 1.98-1.95 (m, 1H), 1.87-1.83 (m, 1H), 1.78 (s, 3H), 1.69 (br s, 1H), 1.57 (d, J = 6.4 Hz, 3H), 1.56-1.53 (m, 2H), 1.22-1.15 (m, 2H), 1.05 (d, J = 6.4 Hz, 3H), 0.73 (br d, J = 12 Hz, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 259.69, 215.65, 180.15, 154.57, 143.79, 137.76, 137.41, 136.81, 136.42, 129.55, 129.24, 125.51, 123.20, 123.19, 112.90, 74.01, 68.79, 67.84, 62.82, 51.44, 43.38,

41.62, 40.64, 38.27, 37.97, 37.72, 33.59, 31.21, 30.03, 25.84, 24.43, 21.35, 21.04, 20.73, 18.75, 18.48. HRMS (FAB+, (M+H)-H_2): Calculated – 629.2318, Found – 629.2345.

[00107] Representative characterization data for complex **22d** is as follows: ^{1}H NMR (600 MHz, C_6D_6) δ 14.88 (s, 1H), 7.43 (br d, J = 12 Hz, 1H), 7.23 (t, J = 6 Hz, 1H), 6.94 (br s, 1H), 6.86 (t, J = 6 Hz, 1H), 6.74-6.71 (m, 2H), 4.87 (br s, 1H), 4.16 (s, 1H), 3.50-3.19 (m, 10H), 2.47 (br s, 1H), 2.45 (s, 3H), 2.40 (s, 3H), 2.20 (s, 3H), 2.13-2.08 (m, 2H), 2.01 (br d, J = 12 Hz, 1H), 1.96 (br d, J = 12 Hz, 1H), 1.82 (br d, J = 12 Hz, 1H), 1.66 (br s, 1H), 1.63 (d, J = 6 Hz, 3H), 1.57-1.54 (m, 1H), 1.50-1.48 (m, 1H), 1.43 (br d, J = 12 Hz, 1H), 1.38 (s, 3H), 1.27 (br d, J = 6 Hz, 3H), 1.17 (br d, J = 12 Hz, 1H), 1.10-1.09 (m, 2H), 0.68 (br d, J = 6 Hz, 1H). ^{13}C NMR (151 MHz, C_6C_6) δ 259.06, 216.37, 177.95, 154.78, 144.04, 138.48, 137.86, 136.61, 136.38, 130.46, 129.48, 125.96, 123.52, 123.39, 113.89, 99.58, 75.37, 69.60, 63.10, 51.94, 43.58, 41.83, 40.83, 38.50, 38.32, 37.63, 33.94, 31.45, 30.30, 21.70, 21.41, 21.17, 20.99, 19.11, 18.88. HRMS (FAB+, (M+H)-H_2): Calculated – 703.2685, Found – 703.2682.

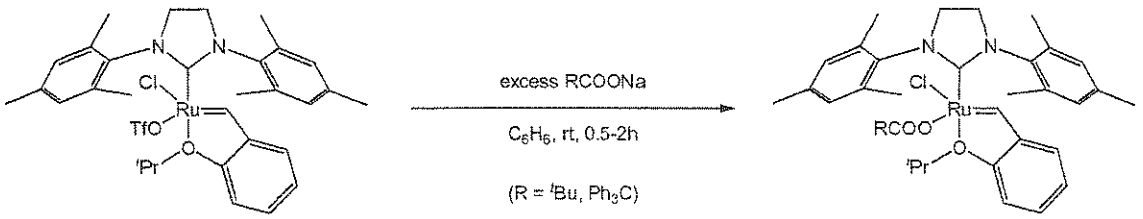
[00108] Representative characterization data for complex **22e** is as follows: ^{1}H NMR (400 MHz, C_6D_6) δ 15.22 (s, 1H), 7.37 (d, J = 7.2 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 6.98 (s, 1H), 6.82 (t, J = 7.6 Hz, 1H), 6.66 (s, 1H), 6.48 (d, J = 8.4 Hz, 1H), 4.57 (sept, J = 6.0 Hz, 1H), 4.17 (s, 1H), 3.43 (q, J = 9.6 Hz, 1H), 3.28 – 3.15 (m, 3H), 2.38 (d, J = 8.4 Hz, 6H), 2.25 (br s, 1H), 2.15 – 2.09 (m, 4H), 2.03 – 1.97 (m, 2H), 1.90 – 1.87 (m, 1H), 1.77 (br d, J = 15.2 Hz, 1H), 1.65 (br s, 1H), 1.55 – 1.47 (m, 2H), 1.42 (d, J = 5.2 Hz, 3H), 1.14 – 1.10 (m, 3H), 0.96 (d, J = 6.0 Hz, 3H), 0.58 (br d, J = 12 Hz, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 265.80, 265.55, 214.16, 154.72, 143.60, 137.69, 137.40, 136.24, 135.45, 130.11, 129.36, 126.83, 123.38, 123.35, 113.00, 74.32, 66.78, 63.05, 51.36, 43.14, 41.84, 40.34, 37.95, 37.81, 37.65, 33.33, 30.98, 29.83, 21.25, 21.09, 20.28, 18.56, 17.44. HRMS (FAB+, M-NO_3): Calculated – 571.2263, Found – 571.2273.

Example 8

Investigations employing complex **23** as a Ru precursor

[00109] When (H_2IMes)RuCl(OTf)[=CH-*o*-(O^{i}Pr)C_6H_4] (**23**) (prepared as described in Krause, J. O.; Nuyken, O.; Wurst, K.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 777) was reacted with RCOONa (R = ^{t}Bu, Ph_3C), the triflate ligand of **23** was selectively substituted by carboxylate ligand and (H_2IMes)RuCl(OCOR)-[=CH-*o*-(O^{i}Pr)C_6H_4] (R = ^{t}Bu (**24a**), Ph_3C (**24d**)) was afforded in an excellent yield (Scheme 13). In this reaction, neither substitution of the chloro ligand of **23** nor C-H bond activation at the mesityl group of **24** was observed. The molecular structure of **24d** determined by X-ray crystallography is shown in Figure 13.

Scheme 13



23

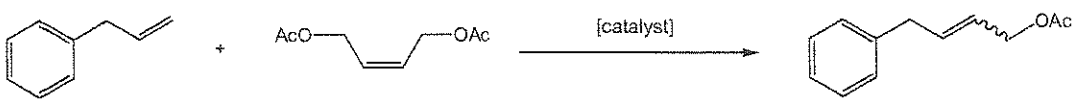
24a : R = ^{t}Bu 93.1%
24d : R = Ph_3C 92.6%

Example 9

Comparative results for the cross-metathesis of allylbenzene and *cis*-1,4-diacetoxy-2-butene with catalysts **1-4** and **7-24**

[00110] Selected data of cross metathesis reaction of allylbenzene (**25**) and *cis*-1,4-diacetoxy-2-butene (**26**) yielding 1-acetoxy- 4-phenyl-2-butene (**27**) (Scheme 14) are summarized in Tables 1-3.

Scheme 14



25 **26** **27**

Table 1. Cross metathesis reactions of allylbenzene (**25**) and *cis*-1,4-diacetoxy-2-butene (**26**) by catalysts {[2-(CH_2)-4,6-$Me_2(C_6H_2)$]($C_3N_2H_4$)(Ar)}Ru(X)[=CH-*o*-(O^iPr)C_6H_4][a]

Entry	Catalyst			Catalyst loading	Solvent	Temperature	Time	conversion[b]	*E*/*Z*[c]	Time	conversion[b]	*E*/*Z*[c]
	No.	Ar	X	mol%	-	°C	min	%	-	*min*	%	-
1	**7a**	Mes	^{t}BuCOO	2.5	C_6H_6	23	10	57.5	1.44	60	57.4	1.44
2	**7b**	Mes	$PhMe_2CCOO$	2.5	C_6H_6	23	10	56.6	1.45	60	57.6	1.46
3	**7c**	Mes	$Ph_2MeCCOO$	2.5	C_6H_6	23	10	62.2	1.82	60	64.4	1.88
4	**7d**	Mes	Ph_3CCOO	2.5	C_6H_6	23	10	50.9	2.16	60	61.9	2.41
5	**11**	Dipp	^{t}BuCOO	2.5	C_6H_6	23	10	69.6	1.11	60	70.6	1.13

[a] All reactions were carried out using 0.20 mmol of allylbenzene (**25**), 0.40 mmol of *cis*-1,4-diacetoxy-2-butene (**26**), 0.10 mmol of tridecane (internal standard for GC analysis) and *0.005 mmol of catalyst in 1.0 ml of solvent.* [b] *Conversion* of allylbenzene (**25**) to 1-aceloxy-4-phenyl-2-butene (**27**) determined by GC analysis. [c] Molar ratio of *E* isomer and *Z* isomer of 1-acetoxy-4-phenyl-2-butene (**27**) determined by GC analysis.

Table 2. Cross metathesis reactions of allylbenzene (**25**) and *cis*-1,4-diacetoxy-2-butene (**26**) by catalysts $[(C_{10}H_{14})(C_3N_2H_4)(Ar)]Ru(X)[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$[a]

Entry	Catalyst			Catalyst loading	Solvent	Temperature	Time	conversion[b]	*E*/*Z*[c]	Time	conversion[b]	*E*/*Z*[c]
	No.	Ar	X	mol%	-	°C	min	%	-	min	%	-
6	**19a**	Mes	^{t}BuCOO	5.0	C_6H_6	70	30	32.5	0.13	120	36.4	0.12
7	**19a**	Mes	^{t}BuCOO	5.0	THF	reflux	240	59.5	0.19	-	-	-
8	**19a**	Mes	^{t}BuCOO	5.0	THF/H_2O[d]	reflux	240	60.9	0.13	-	-	-
9	**19a**	Mes	^{t}BuCOO	5.0	THF/H_2O[e]	reflux	240	64.4	0.14	-	-	-
10	**19b**	2,6-$Me_2C_6H_3$	^{t}BuCOO	5.0	C_6H_6	70	30	1.8	0.13	120	5.5	0.09
11	**19c**	2-$MeC_{10}H_6$	^{t}BuCOO	5.0	C_6H_6	70	30	1.3	0.12	120	2.6	0.11
12	**20a**	Mes	Cl	5.0[f]	C_6H_6	70	30	9.7	2.34	120	11.0	2.30
13	**20b**	Mes	I	5.0	C_6H_6	70	60	0.7	0.23	120	1.0	0.43
14	**21a**	Mes	O(2,6-$^i Pr_2$)C_6H_3	5.0	C_6H_6	70	30	12.3	0.12	120	39.5	0.13
15	**21a**	Mes	O(2,6-$^i Pr_2$)C_6H_3	5.0	THF	reflux	240	50.9	0.16	-	-	-
16	**21b**	Mes	OC_6Cl_5	5.0	C_6H_6	70	120	0.7	0.16	480	2.2	0.21
17	**22**	Mes	SO_3Mes	5.0	C_6H_6	70	30	1.6	0.69	120	1.7	0.65
18	**22**	Mes	SO_3Mes	5.0	Et_2O	reflux	240	8.5	0.85	-	-	-

[a] All reactions were carried out using 0.20 mmol of allylbenzene (**25**), 0.40 mmol of *cis*-1,4-diacetoxy-2-butene (**26**), 0.10 mmol of tridecane (internal standard for GC analysis) and 0.010 mmol of catalyst in 1.0 ml of solvent. [b] Conversion of allylbenzene (**25**) to 1-acetoxy-4-phenyl-2-butene (**27**) determined by GC analysis. [c] Molar ratio of *E* isomer and *Z* isomer of 1-acetoxy-4-phenyl-2-butene (**27**) determined by GC analysis. [d] THF : H_2O = 9 : 1. [e] THF : H_2O = 5 : 5. [f] Contained 0.8 equivalent of pivalic acid.

Table 3. Cross metathesis reactions of allylbenzene (**25**) and *cis*-1,4-diacetoxy-2-butene (**26**) by Grubbs' catalysts[a]

Entry	Catalyst	Catalyst loading	Solvent	Temperature	Time	conversion[b]	*E*/*Z*[c]	Time	conversion[b]	*E*/*Z*[c]
	No.	mol%	-	°C	min	%	-	min	%	-
19	**24a**	2.5	C_6H_6	23	10	60.4	4.44	60	78.8	9.02
20	**24d**	2.5	C_6H_6	23	10	73.4	5.18	60	79.6	9.93
21	**1**	2.5	C_6H_6	23	30	13.0	4.12	120	40.7	3.93
22	**2**	2.5	C_6H_6	23	30	16.6	4.00	120	31.3	3.87
23	**3**	2.5	C_6H_6	23	1	8.1	2.95	30	67.3	9.63
24	**4**	2.5	C_6H_6	23	1	69.7	10.55	30	66.3	10.66
25	**10**	2.5	C_6H_6	23	1	60.0	3.67	30	83.9	9.11
26	**18a**	2.5	C_6H_6	23	1	0.15	3.10	30	0.23	2.90

[a] All reactions were carried out using 0.20 mmol of allylbenzene (**25**), 0.40 mmol of *cis*-1,4-diacetoxy-2-butene (**26**), 0.10 mmol of tridecane (internal standard for GC analysis) and 0.005 mmol of catalyst in 1.0 ml of solvent. [b] Conversion of allylbenzene (**25**) to 1-acetoxy-4-phenyl-2-butene (**27**) determined by GC analysis. [c] Molar ratio of *E* isomer and *Z* isomer of 1-acetoxy-4-phenyl-2-butene (**27**) determined by GC analysis.

[00111] The metallacycle catalysts having carboxylate ligands {[2-(CH_2)-4,6-$Me_2(C_6H_2)$]($C_3N_2H_4$)(Mes)}-Ru(OCOR)[=CH-*o*-(O^iPr)C_6H_4] (R = ^{t}Bu (**7a**), $PhMe_2C$ (**7b**), Ph_2MeC (**7c**), Ph_3C (**7d**)) showed much lower *E*/*Z* ratios of **27** (*E*/*Z* = 1.4-2.3 at ca 60% conversion (Entry 1-4 in Table 1) compared to typical Grubbs' 1st and 2nd generation catalysts (**1**-**4**) (Entry 21-24 in Table 3). On the other hand, non-chelated catalysts (H_2IMes)RuCl(OCOR)[=CH-*o*-(O^iPr)C_6H_4] (R = ^{t}Bu (**24a**), Ph_3C (**24d**)), which also have carboxylate ligands, showed very similar *E*/*Z* ratios of **27** (Entry 19 and 20 in Table 3) compared to the Grubbs' 2nd generation catalysts (**3** and **4**, Entry 23 and 24 in Table 3). Thus, the enhanced *Z* selectivity of **7a-d** is derived from their chelated structures.

[00112] {[2-(CH_2)-4,6-$Me_2(C_6H_2)$]($C_3N_2H_4$)(Dipp)}Ru(OCO^tBu)[=CH-*o*-(O^iPr)C_6H_4] (**11**) with the bulkier diisopropylphenyl group showed increased *Z* selectivity compared to **7a**.

[00113] The catalysts with chelates containing the adamantyl group [($C_{10}H_{14}$)($C_3N_2H_4$)(R)]Ru(OCO^tBu)-[=CH-*o*-(O^iPr)C_6H_4] (R = Mes (**19a**), 2,6-$(CH_3)_2C_6H_3$ (**19b**), 2-$(CH_3)C_{10}H_6$ (**19c**)) showed very high *Z* selectivity in the studied CM reaction (Entry 6, 10 and 11 in Table 2). *E*/*Z* ratios of **27** by these catalysts, which were 0.09-0.12 (ca 90% *Z* isomer) in 120 min, were the lowest among those achieved by ruthenium based olefin metathesis catalysts.

[00114] Ligand substituted catalyst $[(C_{10}H_{14})(C_3N_2H_4)(Mes)]RuX[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$ (X = Cl (**20a**), I (**20b**), $O(2,6\text{-}^iPr_2C_6H_3)$ (**21a**), $O(C_6Cl_5)$ (**21b**), SO_3Mes (**22**)) also showed moderate to excellent *Z* selectivity in the CM reaction (Entry 12-14, 16, 17 in Table 2). When compared to **7a**, **21a** gave **27** with similar *E*/*Z* ratio and better conversion (Entry 14 in Table 2).

[00115] Reaction conditions also affected conversion and stereo-selectivity. When the reactions were carried out at reflux temperatures, improved conversions were observed (Entry 7, 15, 18 in Table 2). In addition, when a mixture of THF and water was used as solvent under reflux, higher conversion and lower *E*/*Z* ratio were achieved than under THF reflux (Entry 8, 9 in Table 2). These results implied not only that water could optimize reaction conditions but also that the chelate catalysts mentioned above are tolerant towards water in organic solvent. Thus, dry solvent is not necessary for these catalysts. This feature enables easy use of the catalysts in common organic synthesis and polymer synthesis.

Example 10

Comparative results for the self-metathesis of allylbenzene with catalysts **4**, **7a**, **11** and **19a**

[00116] Selected data of metathesis homo-coupling of allylbenzene (**25**) yielding 1,4-diphenyl-2-butene (**28**) (Scheme 15) are summarized in Tables 4 and 5.

Scheme 15

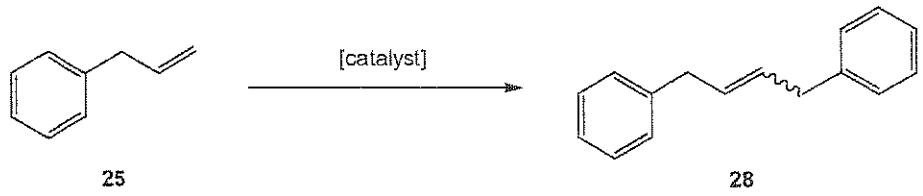


Table 4. Metathesis homocoupling of allylbenzene (**25**) by catalysts [(R)($C_3N_2H_4$)(Ar)]Ru(OCO^{t}Bu)[=CH-o-(O^iPr)C_6H_4][a]

Entry	Catalyst			Catalyst loading	Solvent	Temperature	Time	conversion[b]	*E*/*Z*[c]	Time	conversion[b]	*E*/*Z*[c]
	No.	R	Ar	mol%	-	°C	min	%	-	min	%	-
27	**7a**	Mes[d]	Mes	2.5	C_6H_6	23	30	36.3	1.09	120	41.0	1.37
28	**11**	Mes[d]	Dipp	2.5	C_6H_6	23	30	25.7	0.78	120	37.2	1.14
29	**19a**	Adm[e]	Mes	2.5	C_6H_6	70	30	51.8	0.04	120	65.3	0.17

[a] *All reactions were carried out using* 0.20 mmol of allylbenzene (**25**), 0.10 mmol of tridecane (internal standard for GC analysis) and 0.005 mmol of catalyst in 1.0 ml of solvent. [b] Conversion of allylbenzene (**25**) to 1,4-diphenyl-2-butene (**28**) determined by GC analysis. [c] Molar ratio of *E* isomer and *Z* isomer of 1,4-diphenyl-2-butene (**28**) determined by GC analysis. [d] [2-(CH_2)-4,6-Me_2(C_6H_2)] connecting NHC and ruthenium. [e] ($C_{10}H_{14}$) connecting NHC and ruthenium.

Table 5. Metathesis homocoupling of allylbenzene (**25**) by Grubbs' catalyst[a]

Entry	Catalyst	Catalyst loading	Solvent	Temperature	Time	conversion[b]	*E*/*Z*[c]	Time	conversion[b]	*E*/*Z*[c]
	No.	mol%	-	°C	min	%	-	min	%	-
30	**4**	2.5	C_6H_6	23	1	29.0	5.88	30	27.6	5.43

[a] Reaction was carried out using 0.20 mmol of allylbenzene (**25**), 0.10 mmol of tridecane (internal standard for GC analysis) and 0.005 mmol of catalyst in 1.0 ml of solvent. [b] Conversion of allylbenzene (**25**) to 1,4-diphenyl-2-butene (**28**) determined by GC analysis. [c] Molar ratio of *E* isomer and *Z* isomer of 1,4-diphenyl-2-butene (**28**) determined by GC analysis.

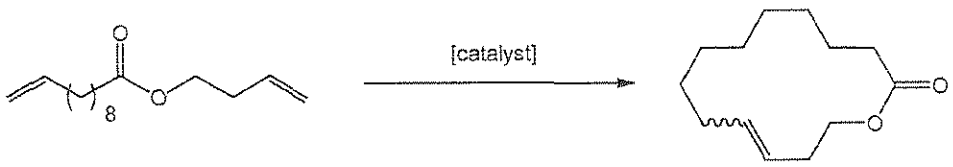
[00117] Compared to typical Grubbs' catalyst $(H_2IMes)RuCl_2[=CH\text{-}o\text{-}(O^iPr)C_6H_4]$ (**4**) (Entry 30 in Table 5), all the chelate catalysts gave much lower *E*/*Z* ratio of **28** (Entry 27-29 in Table 4) and **19a** showed excellent *Z* selectivity of the product.

Example 11

Comparative results for the macrocyclic RCM of **29** with catalysts **4**, **7a**, **11** and **19a**

[00118] Selected data of ring-closing metathesis of diene (**29**) yielding 14-membered lactone (**30**) (Scheme 16) are summarized in Table 6 and 7.

Scheme 16



29 **30**

Table 6. Macrocyclic ring-closing metathesis by catalysts [(R)(C$_3$N$_2$H$_4$)(Ar)]Ru(OCO^{t}Bu)[=CH-o-(O^{i}Pr)C$_6$H$_4$][a]

Entry	Catalyst			Catalyst loading	Solvent	Temperature	Time	conversion[c]	*E*/*Z*[d]	Time	conversion[c]	*E*/*Z*[d]
	No.	R	Ar	mol%	-	°C	min	%	-	min	%	-
31[a]	**7a**	*Mes'*[e]	*Mes*	5.0	C_6H_6	50	30	17.4	1.07	120	24.2	1.12
32[a]	**11**	*Mes'*[e]	Dipp	5.0	C_6H_6	50	30	12.1	0.77	120	19.4	0.83
33[b]	**19a**	*Adm'*[f]	*Mes*	20	C_6H_6	70	120	4.6	0.34	480	7.5	0.26

[a] All reactions were carried out using 0.060 mmol of diene (**29**), 0.10 mmol of tridecane (internal standard for GC analysis) and 0.003 mmol of catalyst in 20 ml of solvent. [b] Reaction was carried out using 0.030 mmol of diene (**29**), 0.10 mmol of tridecane (internal standard for GC analysis) and 0.012 mmol of catalyst in 20 ml of solvent. [c] Conversion of diene (**29**) to 14-membered lactone (**30**) determined by GC analysis. [d] Molar ratio of *E* isomer and *Z* isomer of 14-membered lactone (**30**) determined by GC analysis. [e] [2-(CH$_2$)-4,6-Me$_2$(C$_6$H$_2$)] connecting NHC and ruthenium. [f] ($C_{10}H_{14}$) connecting NHC and ruthenium.

Table 7. Macrocyclic ring-closing metathesis by Grubbs' catalyst[a]

Entry	Catalyst	Catalyst loading	Solvent	Temperature	Time	conversion[b]	*E*/*Z*[c]	Time	conversion[b]	*E*/*Z*[c]
	No.	mol%	-	°C	min	%	-	min	%	-
34	4	5.0	C_6H_6	50	1	46.5	9.98	30	79.5	10.7

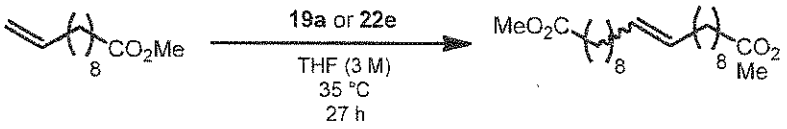
[a] Reaction was carried out using 0.060 mmol of diene (**29**), 0.10 mmol of tridecane (internal standard for GC analysis) and 0.003 mmol of catalyst in 20 ml of solvent. [b] Conversion of diene (**29**) to 14-membered lactone (**30**) determined by GC analysis. [c] Molar ratio of *E* isomer and *Z* isomer of 14-membered lactone (**30**) determined by GC analysis.

[00119] All the metallacycle catalysts showed moderate to very high *Z* selectivity of the product. On the other hand, **4** showed very high *E* selectivity of the product.

Example 12

Comparative results for the self-metathesis of methyl 10-undecenoate with catalysts **19a** and **22e**

Table 8. Comparison of catalysts 19a and 22e for the homodimerization of methyl 10-undecenoate.

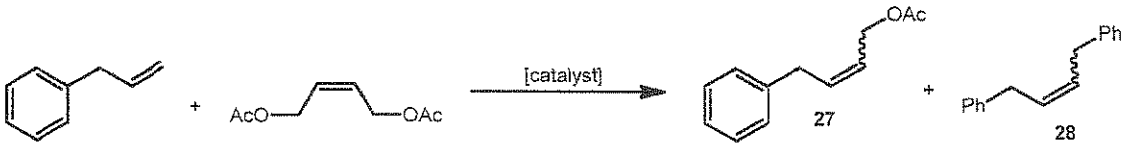


catalyst	cat. load. (mol%)	Z, %	TON
19a	0.5	70	40
22e	0.3	>95	270

Example 13

Comparative results for the cross-metathesis of allylbenzene and *cis*-1,4-diacetoxy-2-butene with catalysts **19a** and **22e**

Table 9. Cross-metathesis reaction of allylbenzene (25) and *cis*-1,4-diacetoxy-2-butene (26) with catalysts 19a and 22e.



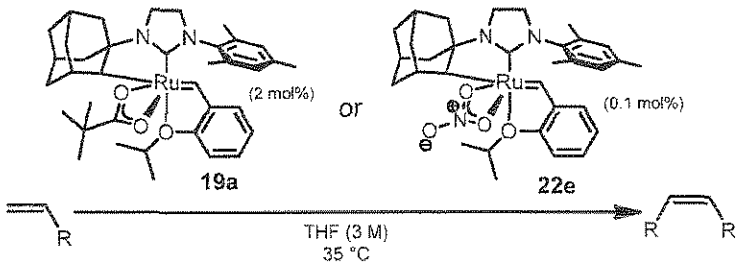
25 **26** **27** **28**

				27		28	
catalyst	cat. load. (mol%)	temp. °C	time, h	conv. %	Z, %	conv. %	Z, %
19a	5	70	4	64	88	29	97
22e	1	35	9	58	91	28	97

Example 14

Comparative results for the self-metathesis of various terminal olefins with catalysts **19a** and **22e**

Table 10. Comparison of catalysts 19a and 22e for the homocoupling of various terminal olefins.



Substrate	Catalyst	cat. loading (mol%)	Time (h)	Conv.[a] (%)	Z[a] (%)	TON[b]
Ph	19a	2	1	>95	92	<50
	22e	0.1	9	88	86	880
TMS	19a	2	3	>95	>95	<50
	22e	0.1	8	13	>95	130
OAc	19a	2	4	>95	89	<50
	22e	0.1	10	5	>95	50
5	19a	2	3	73	69	37
	22e	0.1	10	93	90	930
8 CO_2Me	19a	2	5.5	>95	73	<50
	22e	0.3	27	81	>95	270
3 OH	19a	2	1	>95	72	<50
	22e	0.1	10	70	87	700
B(O)(O)	19a	2	4	>95	>95	<50
	22e	0.1	8	93	89	930
NHPh	19a	2	2	70	71	35
	22e	0.1	8	5	>95	50

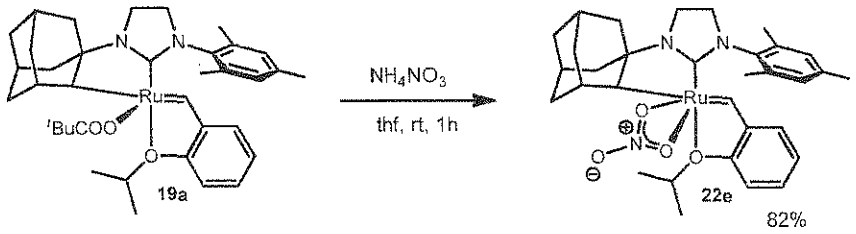
[a] Determined by ^1H NMR spectroscopy. [b] Conversion/Catalyst Loading.

Example 15

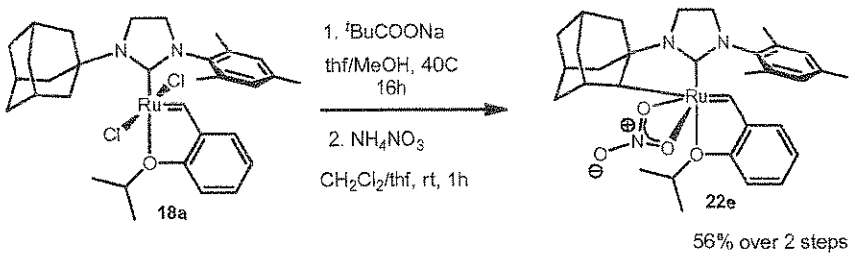
Alternative procedures for the preparation of Ru-catalyst complex **22e**

[00120] Alternative experimental procedures for the synthesis of complex **22e** are presented in Schemes 17 and 18. Scheme 17 describes the synthesis starting from complex **19a** and performing the ligand substitution with NH_4NO_3 in thf. Scheme 18 describes the synthesis starting from the dichloride complex **18a** and performing a two-step sequence with NaOPiv in thf/MeOH and then subsequent ligand substitution with NH_4NO_3 in thf. In both cases, characterization data for **22e** matches that presented previously below Scheme 12.

Scheme 17



Scheme 18



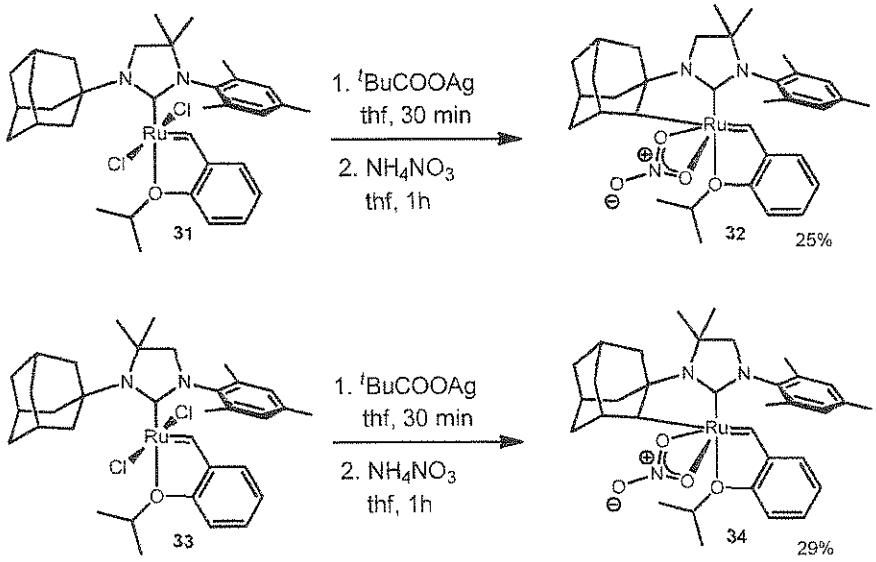
Example 16

Preparation of C-H activated Ru-catalyst complexes **32** and **34**

with methyl substitution on the NHC backbone

[00121] Employing a similar reaction sequences described for the synthesis of **22e** in Schemes 7, 8, 9 and 17, $RuCl_2$ complexes **31** and **33** were synthesized and then converted to the C-H activated nitrate complexes **32** and **34** by the treatment with AgOPiv and subsequent anion exchange with NH_4NO_3.

Scheme 19



[00122] ^{1}H NMR characterization data for complex **32** is as follows:

^{1}H NMR (C_6D_6, 500 MHz) δ 15.29 (s, 1H), 7.40 (dd, 1H, J = 1.5, 7.5 Hz), 7.19 (ddd, 1H, J = 1.7, 7.4, 8.4 Hz), 7.00 (s, 1H), 6.84 (td, 1H, J = 0.8, 7.4 Hz), 6.69 (d, 1H, J = 1.5 Hz), 6.48 (d, 1H, J = 8.5 Hz), 4.56 (hept, 1H, J = 6.3 Hz), 4.24 (s, 1H), 3.16 (d, 1H, J = 9.8 Hz), 3.05 (d, 1H, J = 9.8 Hz), 2.46 (s, 3H), 2.43 (s, 3H), 2.27 (m, 1H), 2.14 (m, 1H), 2.10 (s, 3H), 1.96-2.05 (m, 2H), 1.88-1.93 (m, 1H), 1.79 (dd, 1H, J = 1.7, 12.1 Hz), 1.67 (m, 1H), 1.45-1.58 (m, 3H), 1.43 (d, 3H, J = 6.5 Hz), 1.12 (m, 2H), 1.07 (s, 3H), 1.00 (s, 3H), 0.96 (d, 3H, J = 6.5 Hz), 0.61 (d, 1H, J = 12.0 Hz).

[00123] ^{1}H NMR characterization data for complex **34** is as follows:

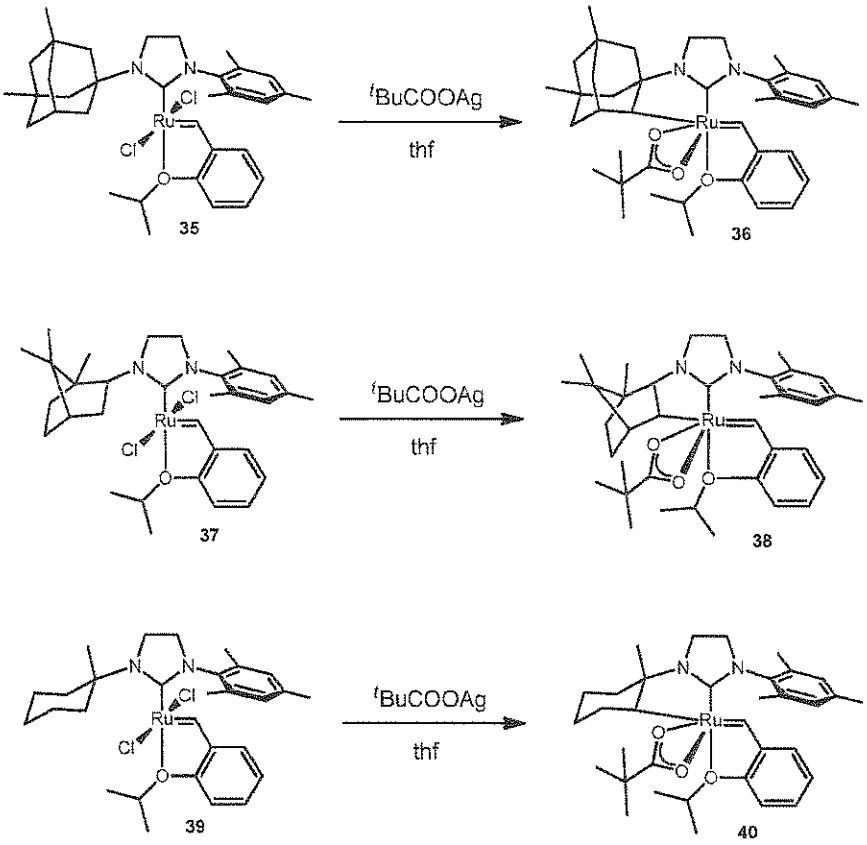
^{1}H NMR (C_6D_6, 500 MHz) δ 15.29 (s, 1H), 7.43 (dd, 1H, J = 1.6, 7.5 Hz), 7.20 (m, 1H), 7.02 (s, 1H), 6.84 (td, 1H, J = 0.7, 7.4 Hz), 6.65 (s, 1H), 6.49 (d, 1H, J = 8.4 Hz), 4.54 (hept, 1H, J = 6.5 Hz), 4.16 (s, 1H), 3.29 (d, 1H, J = 10.0 Hz), 3.10 (d, 1H, J = 10.0 Hz), 2.48 (s, 3H), 2.41 (s, 3H), 2.24 (m, 2H), 2.12 (s, 3H), 2.10 (m, 2H), 2.00 (m, 1H), 1.68-1.78 (m, 2H), 1.60 (s, 1H), 1.49 (q, 2H, J = 12.3 Hz), 1.39 (d, 3H, J = 6.0 Hz), 1.38 (m, 1H), 1.23 (s, 3H), 1.19 (s, 3H), 1.04 (m, 1H), 0.96 (d, 3H, J = 6.5 Hz), 0.61 (d, 1H, J = 12.0 Hz).

Example 17

Preparation of C-H activated Ru-catalyst complexes **36**, **38** and **40** that contain C-H activated moieties different from Adamantyl

[00124] Employing similar reaction procedures to that described in Schemes 8 and 9, Ru-complexes **35**, **37** and **39** were prepared and then converted to C-H activated complexes **36**, **38** and **40** been as outlined in Scheme 20.

Scheme 20



[00125] Representative characterization data for complex **36** is as follows: ^{1}H NMR (400 MHz, C_6D_6) δ 14.83 (s, 1H), 7.46 (dd, J = 7.5, 1.7 Hz, 1H), 7.26 (t, J = 1.2 Hz, 1H), 6.93 (dd, J = 7.4, 0.9 Hz, 1H), 6.85 – 6.81 (m, 1H), 6.77 – 6.74 (m, 1H), 6.70 (d, J = 8.3 Hz, 1H), 4.87 – 4.72 (m, 1H), 3.91 (s, 1H), 3.57 – 3.01 (m, 3H), 2.66 – 2.54 (m, 1H), 2.43 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H), 1.79 – 1.69 (m, 1H), 1.62 – 1.59 (m, 1H), 1.52 (d, J = 6.6 Hz, 3H), 1.43 – 1.39 (m, 2H), 1.26 (s, 13H), 1.17 (d, J = 6.2 Hz, 3H), 1.05 – 1.02 (m, 1H), i0.89 (s, 3H), 0.78 (dt, J = 12.1, 2.8 Hz, 1H), 0.65 – 0.63 (m, 1H), 0.62 (s, 3H), 0.36 – 0.24 (m, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 259.04, 258.78, 214.91, 154.24, 143.78, 137.96, 136.98, 136.83, 136.48, 129.90, 129.67, 125.62, 123.14, 122.79, 113.87, 74.46, 66.54, 64.09, 52.10, 51.72, 48.84, 46.63, 42.65, 41.30, 39.80, 39.10, 38.62, 33.41, 32.12, 30.77, 30.71, 28.92, 27.76, 21.64, 21.19, 21.04, 19.05, 18.97. HRMS (FAB+): Calculated – 700.3178, Found – 700.3181.

Example 18

Results for the self-metathesis of various terminal olefins with catalysts **32** and **34**

[00126] Selected data for the self-metathesis of various terminal olefins employing catalysts **32** and **34** are summarized in Tables 11-12. Experimental conditions were as follows: Catalyst loading: 0.1 mol%; 3M in thf; 35°C.

Table 11. Self-metathesis employing Catalyst **32**

Substrate	Time, h	Conv, %	Z, %
Allyl benzene	1	82	98
	3	94	95
	7	97	90
	12	99	79
Methyl 10-undecenoate	1	35	99
	3	65	98
	7	78	97
	12	82	94
4-penten-1-ol	1	20	96
	3	63	95
	7	71	82
	12	81	63

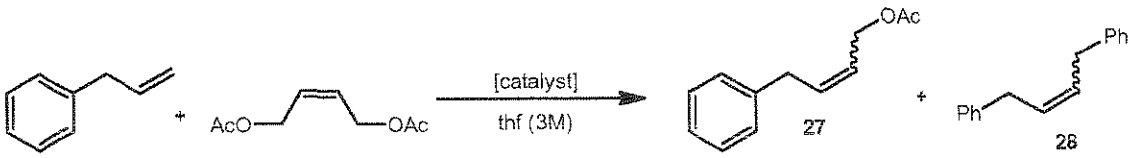
Table 12. Self-metathesis with Catalyst **34**

Substrate	Time, h	Conv, %	Z, %
Allyl benzene	1	72	98
	3	92	95
	7	97	72
	12	98	53
Methyl 10-undecenoate	1	18	99
	3	56	97
	7	79	94
	12	86	91
4-penten-1-ol	1	6	95
	3	55	88
	7	73	78
	12	85	76

Example 19

Comparative results for the cross-metathesis of allylbenzene and *cis*-1,4-diacetoxy-2-butene with catalysts **19a**, **22e** and **36**

Table 13. Comparison of catalysts 19a, 22b, 36 for cross coupling between substrates 25 and 26 for the formation of cross product 27 and homo-coupled product 28.



25 26 27 28

				27		28	
catalyst	cat. load., mol%	temp. °C	time	conv. %	Z, %	conv. %	Z, %
19a	5	35	9 h	37	89	26	96
22b	5	35	20 min	11	77	12	88
			30 min	23	83	19	90
			1.5 h	36	82	26	91
			3 h	43	83	30	92
			6 h	48	82	34	91
36	5	35	5 min	19	89	18	95
			15 min	37	87	29	93
			30 min	42	86	33	92
			1.5 h	47	84	35	91
			4 h	47	82	35	92