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(54) Title: CROSS-METATHESIS OF OLEFINS DIRECTLY SUBSTITUTED WITH AN ELECTRON-WITHDRAWING GROUP USING TRANSITION METAL CARBENE CATALYSTS

(57) Abstract: The invention pertains to the use of Group 8 transition metal alkylidene complexes as catalysts for olefin cross-metathesis reactions. In particular, ruthenium and osmium alkylidene complexes substituted with an N-heterocyclic carbene ligand and at least one electron donor ligand in the form of a heterocyclic group are used to catalyze cross-metathesis reactions to provide a olefin products that are directly substituted with an electron-withdrawing group.

CROSS-METATHESIS OF OLEFINS DIRECTLY SUBSTITUTED WITH AN ELECTRON-WITHDRAWING GROUP USING TRANSITION METAL CARBENE CATALYSTS

TECHNICAL FIELD

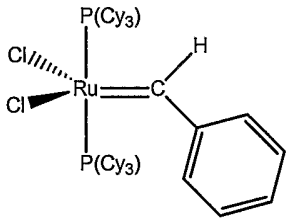
[0001] This invention relates generally to a method for carrying out an olefin metathesis reaction using a Group 8 transition metal complex as a catalyst, and more particularly relates to a method for carrying out cross-metathesis reactions using such a catalyst. The invention enables the synthesis of olefins that are directly substituted with an electron-withdrawing group via a cross-metathesis reaction. as reactants to synthesize acrylonitriles as reactants to synthesize disubstituted cyano-olefins. The invention has utility in the fields of catalysis, organic synthesis, and organometallic chemistry.

BACKGROUND OF THE INVENTION

[0002] To the synthetic organic or polymer chemist, simple methods for forming carbon-carbon bonds are extremely important and valuable tools. One method of C-C bond formation that has proved particularly useful is transition-metal catalyzed olefin metathesis. "Olefin metathesis," as is understood in the art, refers to the metal-catalyzed redistribution of carbon-carbon bonds. See Trnka and Grubbs (2001) *Acc. Chem. Res.* 34:18-29. Over two decades of intensive research effort has culminated in the discovery of well-defined transition metal alkylidene complexes that are highly active olefin metathesis catalysts and stable in the presence of a variety of functional groups.

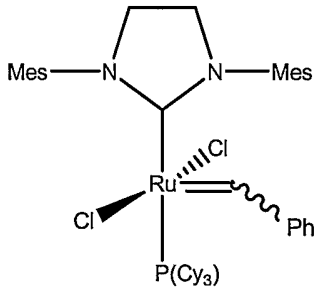
[0003] Examples of these transition metal alkylidene complexes are described in U.S. Patent Nos. 5,312,940, 5,342,909, 5,831,108, 5,969,170, 6,111,121, and 6,211,391 to Grubbs et al., assigned to the California Institute of Technology. The complexes disclosed in these patents all possess metal centers that are formally in the +2 oxidation state, have an electron count of 16, and are penta-coordinated. These catalysts are of the general formula XX′M(LL′)=CRR′ wherein M is a Group 8 transition metal such as ruthenium or osmium, X and X′ are anionic ligands, L and L′ are neutral electron donors, and R and R′ are specific substituents, e.g., one may be H and the other may be a substituted or unsubstituted hydrocarbyl group such as phenyl or $C=C(CH_3)_2$. Such complexes have been disclosed as useful in catalyzing a variety of olefin metathesis reactions, including ring-opening metathesis polymerization ("ROMP"), ring closing metathesis ("RCM"), acyclic diene metathesis polymerization ("ADMET"), ring-opening metathesis ("ROM"), and cross-metathesis ("CM" or "XMET") reactions.

[0004] Such metathesis catalysts include those that have been prepared with phosphine ligands, e.g., triphenylphosphine or dimethylphenylphospine, exemplified by phenylmethylene-bis(tricyclohexylphosphine)ruthenium dichloride



[0005] wherein "Cy" is cyclohexyl. See U.S. Patent No. 5,917,071 to Grubbs et al. and Trnka and Grubbs (2001), cited *supra*. These compounds are highly reactive catalysts useful for catalyzing a variety of olefin metathesis reactions, and are tolerant of many different functional groups. See Schwab et al. (1995) *Angew. Chem, Int. Ed. Engl.* 34:2039-2041 and Schwab et al. (1996) *J. Am. Chem. Soc.* 118:100-110. However, as has been recognized by those in the field, the compounds display low thermal stability, decomposing at relatively low temperatures. Jafarpour and Nolan (2000) *Organometallics* 19(11):2055-2057.

[0006] More recently, significant interest has focused on such transition metal alkylidene catalysts wherein one of the phosphine ligands is replaced with an N-heterocyclic carbene ligand. See, e.g., Trnka and Grubbs, *supra*; Bourissou et al. (2000) *Chem. Rev.* 100:39-91; Scholl et al. (1999) *Tetrahedron Lett.* 40:2247-2250; Scholl et al. (1999) *Organic Lett.* 1(6):953-956; and Huang et al. (1999) *J. Am. Chem. Soc.* 121:2674-2678. N-heterocyclic carbene ligands offer many advantages, including readily tunable steric bulk, vastly increased electron donor character, compatibility with a variety of metal species, and improved thermal stability. See Scholl et al. (1999) *Tetrahedron Lett.* 40:2247-2250; Scholl et al. (1999) *Org. Lett.* 1:953-956; Chatterjee et al. (2000) *J. Am. Chem. Soc.* 122:3783-3784; and Bielawski et al. (2000) *Angew. Chem. Int. Ed.* 39:2903-2906, A representative of these second generation catalysts is the ruthenium complex $(IMesH_2)(PCy_3)(Cl)_2Ru{=}CHPh$



[0007] wherein Cy is cyclohexyl, Ph is phenyl, and Mes represents mesityl (2,4,6-trimethylphenyl).

[0008] These transition metal carbene complexes have been found to address a number of previously unsolved problems in olefin metathesis reactions, particularly cross-metathesis reactions. However, metathesis reactions with directly functionalized olefins, particularly olefins that are directly substituted with an electron-withdrawing substituent, remain a formidable challenge.

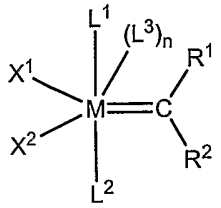
[0009] For example, acrylonitriles are unusually difficult substrates to use in olefin metathesis reactions, and only one single-component catalyst system, based on molybdenum, has been described as active for cyano-olefin cross-metathesis (Crowe et al. (1995) *J. Am. Chem. Soc.* 117:5162-5163; Brümmer et al. (1997) *Chem. Eur. J.* 3:441-446). This is in part due to the fact that these olefins are directly substituted with an electron-withdrawing group, and in part a result of the metal-coordinating ability of the cyano group. See Randl et al. (2001) *Synlett*, pp. 430-432, Blanco et al. (1999) *Synlett*, pp. 557-558, Gessler et al. (2000) *Tetrahedron Lett.* 41:9973-9976, and Cossy et al. (2001) *J. Organomet. Chem.* 634:216-221.

[00010] Accordingly, there is a need in the art for an effective and efficient method of carrying out an olefin metathesis reaction using olefins substituted with an electron-withdrawing group, e.g., a cyano-substituted olefin.

SUMMARY OF THE INVENTION

[00011] The present invention is addressed to the aforementioned needs in the art, and provides a novel process for using certain Group 8 transition metal complexes to catalyze olefin metathesis reactions, primarily cross-metathesis reactions, wherein the olefins are substituted with an electron-withdrawing group. The complexes used are metal alkylidene complexes comprised of a Group 8 transition metal, e.g., ruthenium or osmium. These complexes contain, in addition to the functional alkylidene ligand, two anionic ligands and two or three neutral electron donor ligands. One of the neutral electron donor ligands is strongly binding, i.e., selected so as to remain bound to the metal center of the complex throughout the metathesis reaction, while the remaining neutral electron donor ligand(s) are more weakly binding, and thus dissociate from the metal center during reaction, prior to olefin binding. In contrast to previous catalysts used in olefin cross-metathesis, the present complexes allow an olefinic reactant to be substituted with an electron-withdrawing group without significantly compromising the efficiency or selectivity of a metathesis reaction involving that olefin.

[00012] These cross-metathesis reactions are carried out with a catalyst having the structure of formula (I)

(I) 

in which:

[00013] L^1 is a strongly coordinating neutral electron donor ligand;

[00014] n is zero or 1;

[00015] L^2 and L^3 are weakly coordinating neutral electron donor ligands;

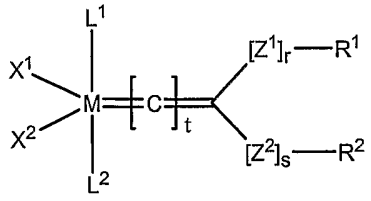
[00016] X^1 and X^2 are anionic ligands; and

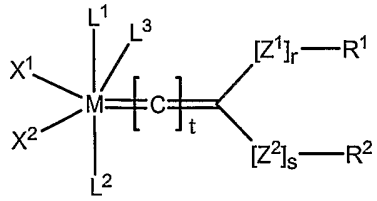
[00017] R^1 and R^2 are independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups, or may be taken together to form a vinylidene moiety,

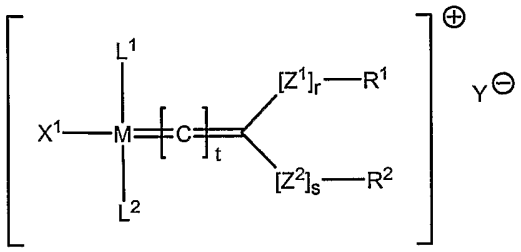
[00018] wherein any two or more of X^1, X^2, L^1, L^2, L^3, R^1, and R^2 can be taken together to form a cyclic group, and further wherein any one or more of X^1, X^2, L^1, L^2, L^3, R^1, and R^2 may be attached to a support.

[00019] Preferred catalysts contain Ru or Os as the Group 8 transition metal, with Ru particularly preferred.

[00020] The metal centers of these complexes are formally in the +2 oxidation state. It will be appreciated that when n is zero, the metal center has an electron count of 16 and is penta-coordinated, while when n is 1, the metal center has an electron count of 18 and is hexacoordinated. The complexes may also be modified so as to be cationic (in which case one of the anionic ligands dissociates), such that the metal center has an electron count of 14 and is tetracoordinated. These complexes are represented by structures (II), (III), and (IV), respectively:

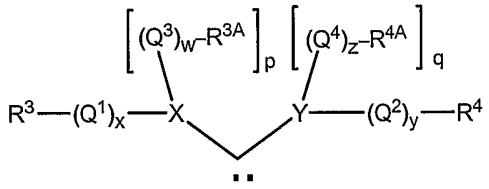
(II) 

(III) 

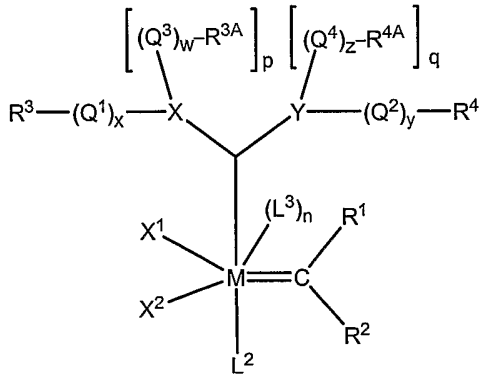
(IV) 

[00021] In the foregoing structures, X^1, X^2, L^1, L^2, L^3, R^1, and R^2 are as defined previously, r and s are independently zero or 1, t is an integer in the range of zero to 5, Y is any noncoordinating anion, Z^1 and Z^2 are linkages containing 1 to about 6 spacer atoms, any two or more of X^1, X^2, L^1, L^2, L^3, Z^1, Z^2, R^1, and R^2 may be taken together to form a cyclic group, e.g., a multidentate ligand, and any one or more of X^1, X^2, L^1, L^2, L^3, Z^1, Z^2, R^1, and R^2 may be attached to a support.

[00022] Exemplary catalysts are transition metal carbene complexes wherein L^2 and L^3 are optionally substituted heterocyclic ligands and L^1 is a carbene having the structure of formula (V)

(V)  ,

such that the complex has the structure of formula (VI)

(VI)  ,

wherein:

[00023] X^1, X^2, L^1, L^2, L^3, n, R^1, and R^2 are as defined above;

[00024] X and Y are heteroatoms selected from N, O, S, and P;

[00025] p is zero when X is O or S, and p is 1 when X is N or P;

[00026] q is zero when Y is O or S, and q is 1 when Y is N or P;

[00027] Q^1, Q^2, Q^3, and Q^4 are independently selected from hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, and -(CO)-, and further wherein two or more substituents on adjacent atoms within Q may be linked to form an additional cyclic group;

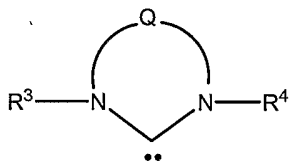
[00028] w, x, y, and z are independently zero or 1; and

[00029] 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,

[00030] wherein any two or more of X^1, X^2, 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, and further wherein any one or more of X^1, X^2, L^2, L^3, R^1, R^2, R^3, R^{3A}, R^4, and R^{4A} may be attached to a support.

[00031] In a preferred embodiment, L^1 is an N-heterocyclic carbene having the structure of formula (VII)

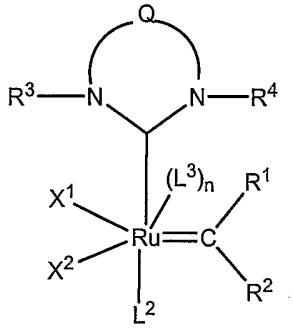
(VII)



wherein R^3 and R^4 are defined above, with preferably at least one of R^3 and R^4, and more preferably both R^3 and R^4, being alicyclic or aromatic of one to about five rings, and optionally containing one or more heteroatoms and/or substituents. 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.

[00032] A preferred metal carbene complex of formula (VI) is a ruthenium complex having the structure of formula (VIII)

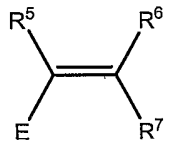
(VIII)



[00033] wherein X^1, X^2, L^1, L^2, L^3, n, Q, R^1, R^2, R^3, and R^4 are as defined previously.

[00034] In one embodiment, then, a method is provided for synthesizing an olefin that is substituted with an electron-withdrawing group and at least one other substitutent, wherein the electron-withdrawing group is directly bound to an olefinic carbon atom. The method involves using a transition metal carbene complex as described above to catalyze a cross-metathesis reaction between two olefinic reactants, or "cross partners," wherein at least one of the olefinic reactants is directly substituted with an electron-withdrawing group E. Generally, such reactants have the structure of formula (IX)

(IX)



wherein:

[00035] E is the electron-withdrawing group;

[00036] R^5, R^6, and R^7 are independently selected from the group consisting of hydrogen,

[00037] $-(Z)_m-Fn$, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, and substituted heteroatom-containing hydrocarbyl, and, if substituted hydrocarbyl or substituted heteroatom-containing hydrocarbyl, wherein one or more of the substituents may be $-(Z)_n-Fn$;

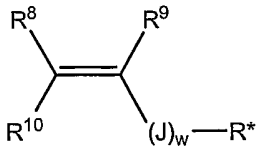
[00038] Fn is a functional group;

[00039] m is zero or 1; and

[00040] Z is a hydrocarbylene or a substituted and/or heteroatom-containing hydrocarbylene linking group such as an alkylene, substituted alkylene, heteroalkylene, substituted heteroalkene, arylene, substituted arylene, heteroarylene, or substituted heteroarylene linkage

[00041] The reaction partner, i.e., the second olefinic reactant, has a molecular structure given by formula (X)

(X)



wherein w is zero or 1, J is a linking group, R* is a nonhydrogen substituent, e.g., hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, or Fn, and R^8, R^9, and R^{10} are hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, $-(Z)_m-Fn$, or

$-(J)_w-R^*$.

DETAILED DESCRIPTION OF THE INVENTION

I. DEFINITIONS AND NOMENCLATURE

[00042] It is to be understood that unless otherwise indicated this invention is not limited to specific reactants, reaction conditions, ligands, 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 intended to be limiting.

[00043] 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 "a compound" encompasses a combination or mixture of different compounds as well as a single compound, reference to "a substituent" includes a single substituent as well as two or more substituents that may or may not be the same, and the like.

[00044] 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:

[00045] As used herein, the phrase "having the formula" or "having the structure" is not intended to be limiting and is used in the same way that the term "comprising" is commonly used.

[00046] The term "alkyl" as used herein refers to a linear, branched, or cyclic saturated hydrocarbon group typically although not necessarily containing 1 to about 20 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.

[00047] The term "alkylene" as used herein refers to a difunctional linear, branched, or cyclic alkyl group, where "alkyl" is as defined above.

[00048] The term "alkenyl" as used herein refers to a linear, branched, or cyclic hydrocarbon group of 2 to about 20 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.

[00049] The term "alkenylene" as used herein refers to a difunctional linear, branched, or cyclic alkenyl group, where "alkenyl" is as defined above.

[00050] The term "alkynyl" as used herein refers to a linear or branched hydrocarbon group of 2 to about 20 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.

[00051] 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.

[00052] 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 substituent, in which at least one carbon atom is replaced with a heteroatom, as will be described in further detail *infra*.

[00053] 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 20 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.

[00054] 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. 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.

[00055] The term "cyclic" refers to alicyclic or aromatic substituents 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.

[00056] The terms "halo" and "halogen" are used in the conventional sense to refer to a chloro, bromo, fluoro or iodo substituent.

[00057] "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.

[00058] 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."

[00059] 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_{20} alkoxy, C_2-C_{20} alkenyloxy, C_2-C_{20} alkynyloxy, C_5-C_{24} aryloxy, C_6-C_{24} aralkyloxy, C_6-C_{24} alkaryloxy, acyl (including C_2-C_{20} alkylcarbonyl (-CO-alkyl) and C_6-C_{24} arylcarbonyl (-CO-aryl)), acyloxy (-O-acyl, including C_2-C_{20} alkylcarbonyloxy (-O-CO-alkyl) and C_6-C_{24} arylcarbonyloxy (-O-CO-aryl)), C_2-C_{20} alkoxycarbonyl (-(CO)-O-alkyl), C_6-C_{24} aryloxycarbonyl (-(CO)-O-aryl), halocarbonyl (-CO)-X where X is halo), C_2-C_{20} 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_{20} alkyl)-substituted carbamoyl (-(CO)-NH(C_1-C_{20} alkyl)), di-(C_1-C_{20} alkyl)-substituted carbamoyl (-(CO)-N(C_1-C_{20} 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_{20} alkyl),N-(C_5-C_{24} aryl)-substituted carbamoyl, thiocarbamoyl (-(CS)-NH_2), mono-(C_1-C_{20} alkyl)-substituted thiocarbamoyl (-(CO)-NH(C_1-C_{20} alkyl)), di-(C_1-C_{20} alkyl)-substituted thiocarbamoyl (-(CO)-N(C_1-C_{20} 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_{20} 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_{20} alkyl)-substituted amino, di-(C_1-C_{20} alkyl)-substituted amino, mono-(C_5-C_{24} aryl)-

substituted amino, di-(C_5-C_{24} aryl)-substituted amino, C_2-C_{20} alkylamido (-NH-(CO)-alkyl), C_6-C_{24} arylamido (-NH-(CO)-aryl), imino (-CR=NH where R = hydrogen, C_1-C_{20} 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_{20} 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_{20} alkylsulfanyl (-S-alkyl; also termed "alkylthio"), C_5-C_{24} arylsulfanyl (-S-aryl; also termed "arylthio"), C_1-C_{20} alkylsulfinyl (-(SO)-alkyl), C_5-C_{24} arylsulfinyl (-(SO)-aryl), C_1-C_{20} alkylsulfonyl (-SO_2-alkyl), 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_{20} alkyl (preferably C_1-C_{12} alkyl, more preferably C_1-C_6 alkyl), C_2-C_{20} alkenyl (preferably C_2-C_{12} alkenyl, more preferably C_2-C_6 alkenyl), C_2-C_{20} 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).

[00060] 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.

[00061] When the term "substituted" appears prior to a list of possible substituted groups, it is intended that the term apply to every member of that group. For example, the phrase "substituted alkyl, alkenyl, and aryl" is to be interpreted as "substituted alkyl, substituted alkenyl, and substituted aryl." Analogously, when the term "heteroatom-containing" appears prior to a list of possible heteroatom-containing groups, it is intended that the term apply to every member of that group. For example, the phrase "heteroatom-containing alkyl, alkenyl, and aryl" is to be interpreted as "heteroatom-containing alkyl, substituted alkenyl, and substituted aryl."

[00062] "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.

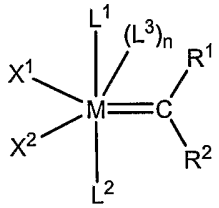
[00063] In the molecular structures herein, the use of bold and dashed lines to denote particular conformation of groups follows the IUPAC convention. A bond indicated by a broken line indicates that the group in question is below the general plane of the molecule as drawn (the

"α" configuration), and a bond indicated by a bold line indicates that the group at the position in question is above the general plane of the molecule as drawn (the "β" configuration).

II. THE CATALYST

[00064] The cross-metathesis reactions of the invention are carried out catalytically, using a Group 8 transition metal complex having the structure of formula (I)

(I)



in which the various substituents are as follows.

[00065] M, which serves as the transition metal center in the +2 oxidation state, is a Group 8 transition metal, particularly ruthenium or osmium. In a particularly preferred embodiment, M is ruthenium.

[00066] L^1 is a strongly coordinating neutral electron donor ligand, as will be discussed in detail *infra*.

[00067] L^2 and L^3 are weakly coordinating neutral electron donor ligands in the form of optionally substituted heterocyclic groups, and n is zero or 1, such that L^3 may or may not be present. Generally, 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 polycylic 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. Examples of L^2 and L^3 include, without limitation:

[00068] nitrogen-containing heterocycles such as pyridine, bipyridine, pyridazine, pyrimidine, bipyridamine, pyrazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, pyrrole, 2H-pyrrole, 3H-pyrrole, pyrazole, 2H-imidazole, 1,2,3-triazole, 1,2,4-triazole, indole, 3H-indole, 1H-isoindole, cyclopenta(b)pyridine, indazole, quinoline, bisquinoline, isoquinoline, bisisoquinoline, cinnoline, quinazoline, naphthyridine, piperidine, piperazine, pyrrolidine, pyrazolidine, quinuclidine, imidazolidine, picolylimine, purine, benzimidazole, bisimidazole, phenazine, acridine, and carbazole;

[00069] sulfur-containing heterocycles such as thiophene, 1,2-dithiole, 1,3-dithiole, thiepin, benzo(b)thiophene, benzo(c)thiophene, thionaphthene, dibenzothiophene, 2H-thiopyran, 4H-thiopyran, and thioanthrene;

[00070] oxygen-containing heterocycles such as 2H-pyran, 4H-pyran, 2-pyrone, 4-pyrone, 1,2-dioxin, 1,3-dioxin, oxepin, furan, 2H-1-benzopyran, coumarin, coumarone, chromene, chroman-4-one, isochromen-1-one, isochromen-3-one, xanthene, tetrahydrofuran, 1,4-dioxan, and dibenzofuran; and

[00071] mixed heterocycles such as isoxazole, oxazole, thiazole, isothiazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,3,4-oxadiazole, 1,2,3,4-oxatriazole, 1,2,3,5-oxatriazole, 3H-1,2,3-dioxazole, 3H-1,2-oxathiole, 1,3-oxathiole, 4H-1,2-oxazine, 2H-1,3-oxazine, 1,4-oxazine, 1,2,5-oxathiazine, o-isooxazine, phenoxazine, phenothiazine, pyrano[3,4-b]pyrrole, indoxazine, benzoxazole, anthranil, and morpholine.

[00072] Preferred L^2 and L^3 ligands are aromatic nitrogen-containing and oxygen-containing heterocycles, and particularly preferred L^2 and L^3 ligands are monocyclic N-heteroaryl ligands that are optionally substituted with 1 to 3, preferably 1 or 2, substituents. Specific examples of particularly preferred L^2 and L^3 ligands are pyridine and substituted pyridines, such as 3-bromopyridine, 4-bromopyridine, 3,5-dibromopyridine, 2,4,6-tribromopyridine, 2,6-dibromopyridine, 3-chloropyridine, 4-chloropyridine, 3,5-dichloropyridine, 2,4,6-trichloropyridine, 2,6-dichloropyridine, 4-iodopyridine, 3,5-diiodopyridine, 3,5-dibromo-4-methylpyridine, 3,5-dichloro-4-methylpyridine, 3,5-dimethyl-4-bromopyridine, 3,5-dimethylpyridine, 4-methylpyridine, 3,5-diisopropylpyridine, 2,4,6-trimethylpyridine, 2,4,6-triisopropylpyridine, 4-(*tert*-butyl)pyridine, 4-phenylpyridine, 3,5-diphenylpyridine, 3,5-dichloro-4-phenylpyridine, and the like.

[00073] In general, any substituents present on L^2 and/or L^3 are selected from halo, C_1-C_{20} alkyl, 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, substituted C_5-C_{24} heteroaryl, C_6-C_{24} alkaryl, substituted C_6-C_{24} alkaryl, C_6-C_{24} heteroalkaryl, substituted C_6-C_{24} heteroalkaryl, C_6-C_{24} aralkyl, substituted C_6-C_{24} aralkyl, C_6-C_{24} heteroaralkyl, substituted C_6-C_{24} heteroaralkyl, and functional groups, with suitable functional groups including, without limitation, C_1-C_{20} alkoxy, C_5-C_{24} aryloxy, C_2-C_{20} alkylcarbonyl, C_6-C_{24} arylcarbonyl, C_2-C_{20} alkylcarbonyloxy, C_6-C_{24} arylcarbonyloxy, C_2-C_{20} alkoxycarbonyl, C_6-C_{24} aryloxycarbonyl, halocarbonyl, C_2-C_{20} alkylcarbonato, C_6-C_{24} arylcarbonato, carboxy, carboxylato, carbamoyl, mono-(C_1-C_{20} alkyl)-substituted carbamoyl, di-(C_1-C_{20} alkyl)-substituted carbamoyl, di-N-(C_1-C_{20} alkyl), N-(C_5-C_{24} aryl)-substituted carbamoyl, mono-(C_5-C_{24} aryl)-substituted carbamoyl, di-(C_6-C_{24} aryl)-substituted carbamoyl, thiocarbamoyl, mono-(C_1-C_{20} alkyl)-substituted thiocarbamoyl, di-(C_1-C_{20} alkyl)-substituted thiocarbamoyl, di-N-(C_1-C_{20} alkyl)-N-(C_6-C_{24} aryl)-substituted thiocarbamoyl, mono-(C_6-C_{24} aryl)-substituted thiocarbamoyl, di-(C_6-C_{24} aryl)-substituted thiocarbamoyl, carbamido, formyl, thioformyl, amino, mono-(C_1-C_{20} alkyl)-substituted amino, di-(C_1-C_{20} alkyl)-substituted amino, mono-(C_5-C_{24} aryl)-substituted amino, di-(C_5-C_{24} aryl)-substituted amino, di-N-(C_1-C_{20} alkyl),N-(C_5-C_{24} aryl)-

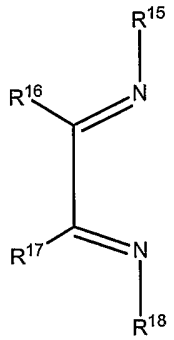
substituted amino, C_2-C_{20} alkylamido, C_6-C_{24} arylamido, imino, C_1-C_{20} alkylimino, C_5-C_{24} arylimino, nitro, and nitroso. In addition, two adjacent substituents may be taken together to form a ring, generally a five- or six-membered alicyclic or aryl ring, optionally containing 1 to 3 heteroatoms and 1 to 3 substituents as above.

[00074] Preferred substituents on L^2 and L^3 include, without limitation, halo, C_1-C_{12} alkyl, substituted C_1-C_{12} alkyl, C_1-C_{12} heteroalkyl, substituted C_1-C_{12} heteroalkyl, C_5-C_{14} aryl, substituted C_5-C_{14} aryl, C_5-C_{14} heteroaryl, substituted C_5-C_{14} heteroaryl, C_6-C_{16} alkaryl, substituted C_6-C_{16} alkaryl, C_6-C_{16} heteroalkaryl, substituted C_6-C_{16} heteroalkaryl, C_6-C_{16} aralkyl, substituted C_6-C_{16} aralkyl, C_6-C_{16} heteroaralkyl, substituted C_6-C_{16} heteroaralkyl, C_1-C_{12} alkoxy, C_5-C_{14} aryloxy, C_2-C_{12} alkylcarbonyl, C_6-C_{14} arylcarbonyl, C_2-C_{12} alkylcarbonyloxy, C_6-C_{14} arylcarbonyloxy, C_2-C_{12} alkoxycarbonyl, C_6-C_{14} aryloxycarbonyl, halocarbonyl, formyl, amino, mono-(C_1-C_{12} alkyl)-substituted amino, di-(C_1-C_{12} alkyl)-substituted amino, mono-(C_5-C_{14} aryl)-substituted amino, di-(C_5-C_{14} aryl)-substituted amino, and nitro.

[00075] Of the foregoing, the most preferred substituents are halo, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 alkoxy, phenyl, substituted phenyl, formyl, N,N-diC_1-C_6 alkyl)amino, nitro, and nitrogen heterocycles as described above (including, for example, pyrrolidine, piperidine, piperazine, pyrazine, pyrimidine, pyridine, pyridazine, etc.).

[00076] L^2 and L^3 may also be taken together to form a bidentate or multidentate ligand containing two or more, generally two, coordinating heteroatoms such as N, O, S, or P, with preferred such ligands being diimine ligands of the Brookhart type. One representative bidentate ligand has the structure of formula (XI)

(XI)



wherein R^{15}, R^{16}, R^{17}, and R^{18} 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, or C_6-C_{24} aralkyl), 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, or C_6-C_{24} aralkyl), heteroatom-containing hydrocarbyl (e.g., C_1-C_{20} heteroalkyl, C_5-C_{24} heteroaryl, heteroatom-containing C_6-C_{24} aralkyl, or heteroatom-containing C_6-C_{24} alkaryl), or substituted heteroatom-containing hydrocarbyl (e.g., substituted C_1-C_{20} heteroalkyl, C_5-C_{24} heteroaryl, heteroatom-containing C_6-C_{24} aralkyl, or heteroatom-containing C_6-C_{24} alkaryl), or (1) R^{15} and R^{16}, (2) R^{17} and R^{18}, (3) R^{16} and

R^{17}, or (4) both R^{15} and R^{16}, and R^{17} and R^{18}, may be taken together to form a ring, i.e., an N-heterocycle. Preferred cyclic groups in such a case are five-and six-membered rings, typically aromatic rings.

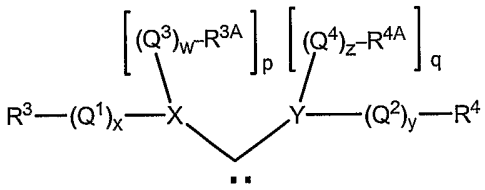
[00077] X^1 and X^2 are anionic ligands, and may be the same or different, or are linked together to form a cyclic group, typically although not necessarily a five- to eight-membered ring. In preferred embodiments, X^1 and X^2 are each independently hydrogen, halide, or one of the following groups: C_1-C_{20} alkyl, C_5-C_{24} aryl, C_1-C_{20} alkoxy, C_5-C_{24} aryloxy, C_2-C_{20} alkoxycarbonyl, C_6-C_{24} aryloxycarbonyl, 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. Optionally, X^1 and X^2 may be substituted with one or more moieties selected from C_1-C_{12} alkyl, C_1-C_{12} alkoxy, C_5-C_{24} aryl, 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_6 alkoxy, and phenyl. In more preferred embodiments, X^1 and X^2 are halide, benzoate, 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. In even more preferred embodiments, X^1 and X^2 are each halide, CF_3CO_2, CH_3CO_2, CFH_2CO_2, $(CH_3)_3CO$, $(CF_3)_2(CH_3)CO$, $(CF_3)(CH_3)_2CO$, PhO, MeO, EtO, tosylate, mesylate, or trifluoromethane-sulfonate. In the most preferred embodiments, X^1 and X^2 are each chloride.

[00078] 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 to 8, ring atoms. R^1 and R^2 may also together form a vinylidene moiety or an analog thereof, as discussed *infra* with respect to catalysts having the structure of formula (II), (III), and (IV).

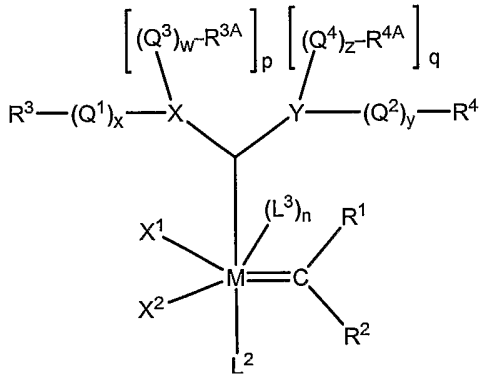
[00079] In preferred catalysts, R^1 is hydrogen and R^2 is selected from C_1-C_{20} alkyl, C_2-C_{20} alkenyl, and C_5-C_{24} aryl, more preferably C_1-C_6 alkyl, C_2-C_6 alkenyl, and C_5-C_{14} aryl. Still more preferably, R^2 is phenyl, vinyl, methyl, isopropyl, or t-butyl, optionally substituted with one or more moieties selected from C_1-C_6 alkyl, C_1-C_6 alkoxy, phenyl, and a functional group Fn as defined earlier herein. 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. Optimally, R^2 is phenyl or $-C{=}C(CH_3)_2$.

[00080] Any two or more (typically two, three, or four) of X^1, X^2, L^1, L^2, L^3, R^1, and R^2 can be taken together to form a cyclic group, as disclosed, for example, in U.S. Patent No. 5,312,940 to Grubbs et al. When any of X^1, X^2, L^1, L^2, L^3, R^1, and R^2 are linked to form cyclic groups, those cyclic groups may be five- or six-membered rings, or may comprise two or three five- or six-membered rings, which may be either fused or linked. The cyclic groups may be aliphatic or aromatic, and may be heteroatom-containing and/or substituted. The cyclic group may, in some cases, form a bidentate ligand or a tridentate ligand. Examples of bidentate ligands include, but are not limited to, bisphosphines, dialkoxides, alkyldiketonates, and aryldiketonates.

[00081] In preferred catalysts, L^1 is a carbene ligand having the structure of formula (V)

(V) 

such that the complex has the structure of formula (VI)

(VI) 

wherein X^1, X^2, L^1, L^2, L^3, n, R^1, and R^2 are as defined previously, and the remaining substituents are as follows:

[00082] 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, and q is necessarily zero when Y is O or S. However, when X is N or P, then p is 1, and when Y is N or P, then q is 1. In a preferred embodiment, both X and Y are N.

[00083] 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. Preferably, w, x, y, and

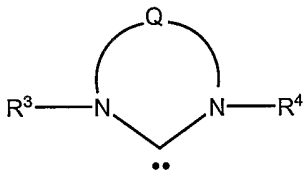
z are all zero. Further, two or more substituents on adjacent atoms within Q may be linked to form an additional cyclic group.

[00084] 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.

[00085] In addition, any two or more of X^1, X^2, 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, and any one or more of X^1, X^2, L^1, L^2, L^3, R^1, R^2, R^3, R^{3A}, R^4, and R^{4A} may be attached to a support.

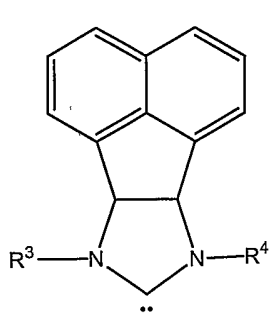
[00086] Preferably, R^{3A} and R^{4A} are linked to form a cyclic group so that the carbene ligand has the structure of formula (VII)

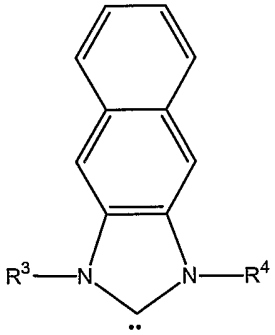
(VII)

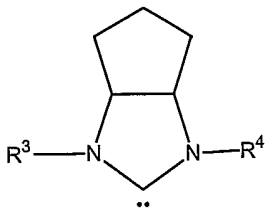


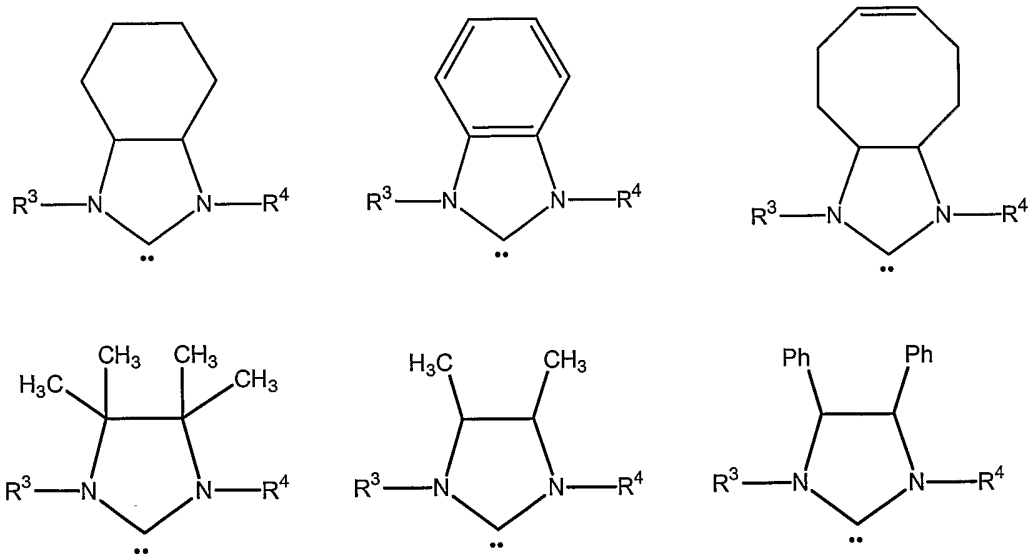
wherein R^3 and R^4 are defined above, with preferably at least one of R^3 and R^4, and more preferably both R^3 and R^4, being alicyclic or aromatic of one to about five rings, and optionally containing one or more heteroatoms and/or substituents. Q is a linker, typically a hydrocarbylene linker, including 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.

[00087] Examples of N-heterocyclic carbene ligands suitable as L^1 thus include, but are not limited to, the following:



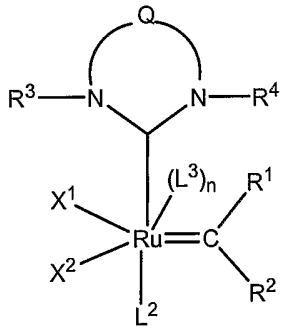






[00088] When M is ruthenium, then, the preferred complexes have the structure of formula (VIII)

(VIII)

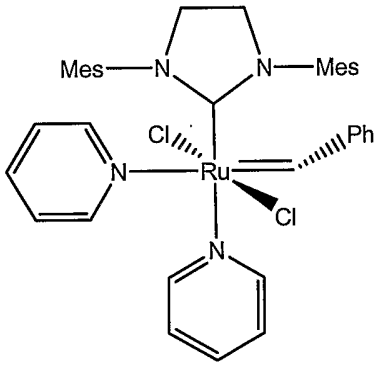


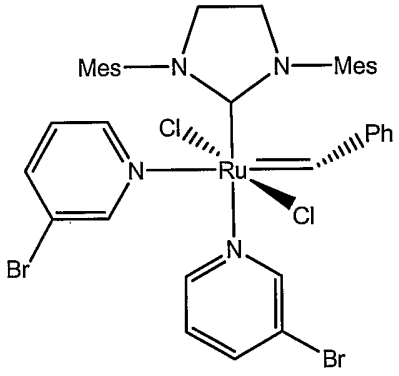
[00089] In a more preferred embodiment, Q is a two-atom linkage having the structure

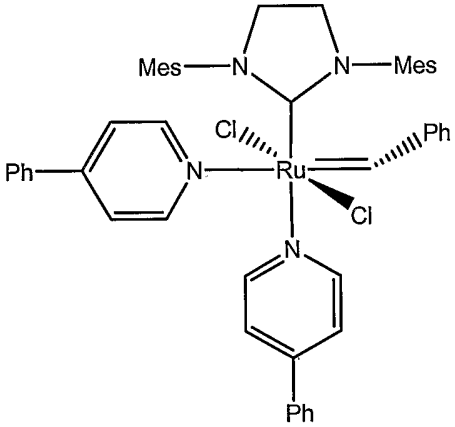
[00090] $-CR^{11}R^{12}-CR^{13}R^{14}-$ or $-CR^{11}=CR^{13}-$, preferably $-CR^{11}R^{12}-CR^{13}R^{14}-$, wherein R^{11}, R^{12}, R^{13}, and R^{14} are independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups. Examples of functional groups here 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.

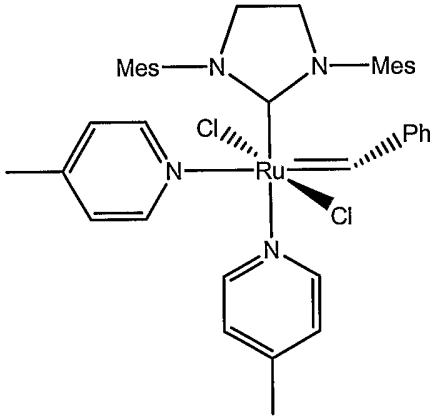
[00091] When R^3 and R^4 are aromatic, they are typically although not necessarily composed of one or two aromatic rings, which may or may not be substituted, e.g., R^3 and R^4 may be phenyl, substituted phenyl, biphenyl, substituted biphenyl, or the like. In one preferred embodiment, R^3 and R^4 are the same and are each unsubstituted phenyl or phenyl substituted with up to three substituents selected from C_1-C_{20} alkyl, 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 preferably, R^3 and R^4 are mesityl.

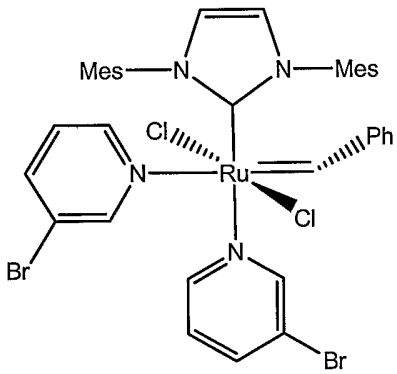
[00092] Examples of such catalysts include, but are not limited to, the following:

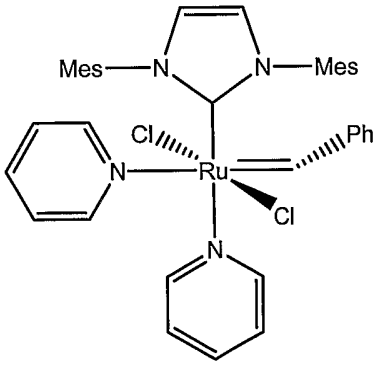

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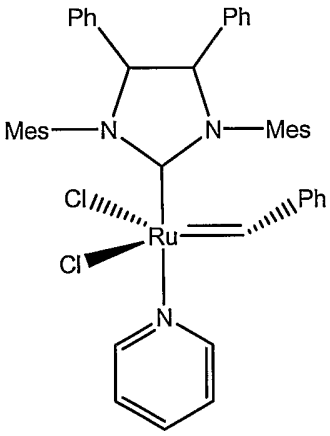

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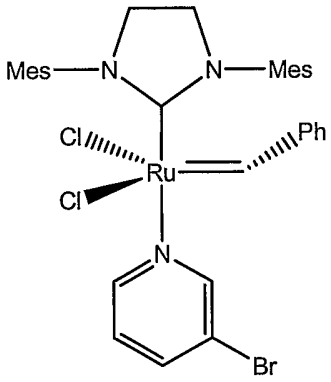

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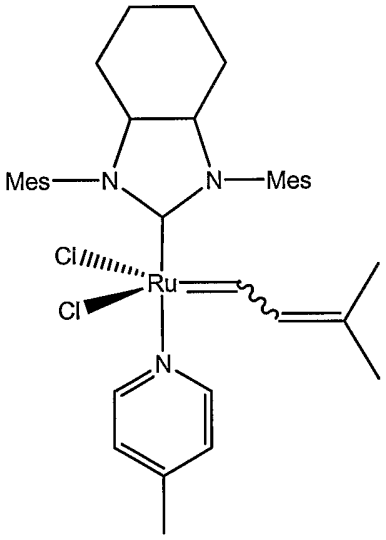

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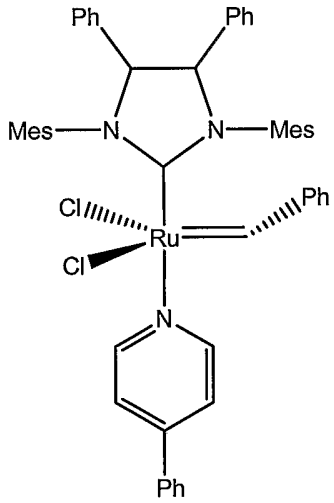

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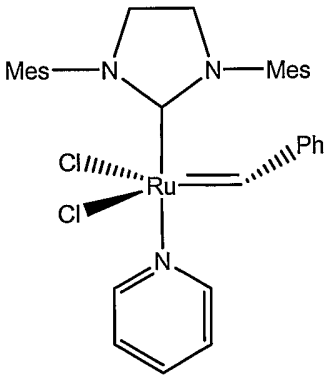

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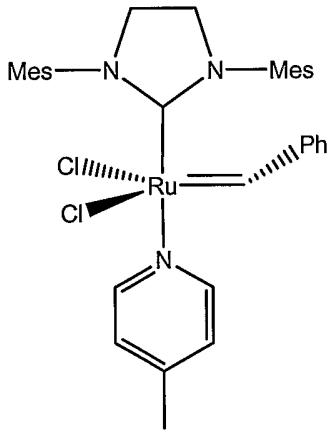

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In the foregoing molecular structures, Ph represents phenyl, and Mes represents mesityl.

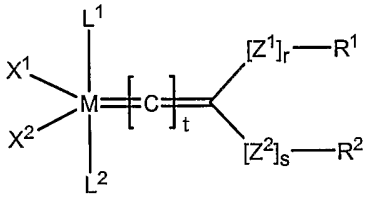
[00093] Additional transition metal carbene complexes include, but are not limited to:

[00094] 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 (II);

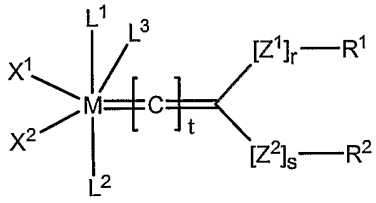
[00095] cationic ruthenium or osmium metal carbene complexes containing metal centers that are formally in the +2 oxidation state, have an electron count of 14, are tetra-coordinated, and are of the general formula (III); and

[00096] 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 (IV)

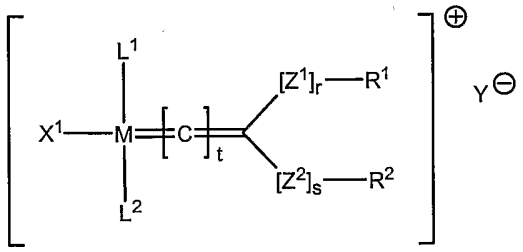
(II)



(III)



(IV)



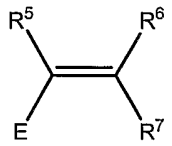
wherein X^1, X^2, L^1, L^2, n, L^3, R^1, and R^2 are as defined previously, r and s are independently zero or 1, t is an integer in the range of zero to 5, Y is any noncoordinating anion (e.g., a halide ion), Z^1 and Z^2 are independently selected from -O-, -S-, $-NR^2-$, $-PR^2-$, $-P(=O)R^2-$, $-P(OR^2)-$, $-P(=O)(OR^2)-$, -C(=O)-, -C(=O)O-, -OC(=O)-, -OC(=O)O-, -S(=O)-, or $-S(=O)_2-$, and any two or more of X^1, X^2, L^1, L^2, L^3, n, Z^1, Z^2, 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, X^2, L^1, L^2, n, L^3, Z^1, Z^2, R^1, and R^2 may

be attached to a support. As understood in the field of catalysis, suitable solid supports may be of synthetic, semi-synthetic, or naturally occurring materials, which may be organic or inorganic, e.g., polymeric, ceramic, or metallic. Attachment to the support will generally, although not necessarily, be covalent, and the covalent linkage may be direct or indirect, if indirect, typically through a functional group on a support surface.

[00097] The transition metal complexes used as catalysts herein can be prepared by several different methods, such as those described by Schwab et al. (1996) *J. Am. Chem. Soc.* 118:100-110, Scholl et al. (1999) *Org. Lett.* 6:953-956, Sanford et al. (2001) *J. Am. Chem. Soc.* 123:749-750, U.S. Patent No. 5,312,940 and U.S. Patent No. 5,342,909. Also see U.S. Patent Publication No. 2003/0055262 to Grubbs et al. for "Group 8 Transition Metal Carbene Complexes as Enantioselective Olefin Metathesis Catalysts," International Patent Publication No. WO 02/079208 to Grubbs et al. for "One-Pot Synthesis of Group 8 Transition Metal Carbene Complexes Useful as Olefin Metathesis Catalysts," commonly assigned herewith to the California Institute of Technology. Preferred synthetic methods are described in International Patent Publication No. WO 03/11455A1 to Grubbs et al. for "Hexacoordinated Ruthenium or Osmium Metal Carbene Metathesis Catalysts," published February 13, 2003.

III. THE CROSS-METATHESIS REACTION

[00098] The transition metal complexes described in the foregoing section are used herein to catalyze an olefin metathesis reaction to synthesize olefins directly substituted with an electron-withdrawing group and substituted with at least one additional substituent. The first olefinic reactant has the structure of formula (IX)

(IX) 

wherein the various substituents are as follows:

[00099] E is an electron-withdrawing group, which, as will be appreciated by those of ordinary skill in the art, is a group that has greater electronegativity than the carbon atom to which it is bound. In general, this means that E is more electron-withdrawing than a hydrogen atom. Accordingly, representative electron-withdrawing substituents include, without limitation, halo, cyano, C_1-C_{20} haloalkyl (preferably C_1-C_{12} haloalkyl, more preferably C_1-C_6 haloalkyl), C_1-C_{20} alkylsulfonyl (preferably C_1-C_{12} alkylsulfonyl, more preferably C_1-C_6 alkylsulfonyl), C_5-C_{24} arylsulfonyl (preferably C_5-C_{14} arylsulfonyl), carboxyl, C_5-C_{24} aryloxy (preferably C_5-C_{14} aryloxy), C_1-C_{20} alkoxy (preferably C_1-C_{12} alkoxy, more preferably C_1-C_6 alkoxy), C_6-C_{24}

aryloxy), C_1-C_{20} alkoxy (preferably C_1-C_{12} alkoxy, more preferably C_1-C_6 alkoxy), C_6-C_{24} aryloxycarbonyl (preferably C_6-C_{14} aryloxycarbonyl), C_1-C_{20} alkoxycarbonyl (preferably C_1-C_{12} alkoxycarbonyl, more preferably C_1-C_6 alkoxycarbonyl), C_6-C_{24} arylcarbonyl (preferably C_6-C_{14} arylcarbonyl), C_1-C_{20} alkylcarbonyl (preferably C_1-C_{12} alkylcarbonyl, more preferably C_1-C_6 alkylcarbonyl), formyl, nitro, quaternary amino (including alkyl- and aryl-substituted amino), sulfhydryl, C_1-C_{20} alkylthio (preferably C_1-C_{12} alkylthio, more preferably C_1-C_6 alkylthio), C_5-C_{24} arylthio (preferably C_5-C_{14} arylthio), hydroxyl, C_5-C_{24} aryl (preferably C_5-C_{14} aryl), C_1-C_{20} alkyl (preferably C_1-C_{12} alkyl, more preferably C_1-C_6 alkyl), any of which may be substituted and/or heteroatom-containing. Cyano groups are of particular interest herein.

[000100] R^5, R^6, and R^7 are independently selected from the group consisting of hydrogen,

[000101] $-(Z)_m$-Fn, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, and substituted heteroatom-containing hydrocarbyl, and, if substituted hydrocarbyl or substituted heteroatom-containing hydrocarbyl, wherein one or more of the substituents may be $-(Z)_m$-Fn. In a preferred embodiment, R^5 is hydrogen or substituted and/or heteroatom-containing C_1-C_{12} hydrocarbyl, e.g., C_1-C_{12} alkyl, substituted C_1-C_{12} alkyl, C_1-C_{12} heteroalkyl, substituted C_1-C_{12} heteroalkyl, C_5-C_{14} aryl, substituted C_5-C_{14} aryl, C_5-C_{14} heteroaryl, substituted C_5-C_{14} heteroaryl, C_6-C_{16} alkaryl, substituted C_6-C_{16} alkaryl, C_6-C_{16} heteroalkaryl, substituted C_6-C_{16} heteroalkaryl, C_6-C_{16} aralkyl, substituted C_6-C_{16} aralkyl, C_6-C_{16} heteroaralkyl, or substituted C_6-C_{16} heteroaralkyl, and R^6 and R^7 are hydrogen. In a more preferred embodiment, R^5 is hydrogen, C_1-C_{12} alkyl, or C_6-C_{16} aralkyl, and, most preferably, R^5 is hydrogen.

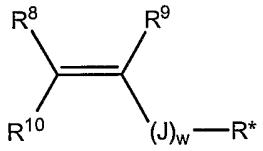
[000102] Fn is a functional group as defined earlier herein, with exemplary Fn groups including, without limitation, halide, hydroxyl, sulfhydryl, C_1-C_{20} alkoxy, C_5-C_{24} aryloxy, C_6-C_{24} aralkyloxy, C_2-C_{20} alkylcarbonyl, C_6-C_{24} arylcarbonyl, C_2-C_{20} alkylcarbonyloxy, C_6-C_{24} arylcarbonyloxy, C_2-C_{20} alkoxycarbonyl, C_6-C_{24} aryloxycarbonyl, halocarbonyl, C_2-C_{20} alkylcarbonato, C_6-C_{24} arylcarbonato, carboxy, carboxylato, carbamoyl, mono-(C_1-C_{20} alkyl)-substituted carbamoyl, di-(C_1-C_{20} alkyl)-substituted carbamoyl, di-N-(C_1-C_{20} alkyl)-N-(C_5-C_{24} aryl)-substituted carbamoyl, mono-(C_5-C_{24} aryl)-substituted carbamoyl, di-(C_6-C_{24} aryl)-substituted carbamoyl, thiocarbamoyl, mono-(C_1-C_{20} alkyl)-substituted thiocarbamoyl, di-(C_1-C_{20} alkyl)-substituted thiocarbamoyl, di-N-(C_1-C_{20} alkyl)-N-(C_6-C_{24} aryl)-substituted thiocarbamoyl, mono-(C_6-C_{24} aryl)-substituted thiocarbamoyl, di- (C_6-C_{24} aryl)-substituted thiocarbamoyl, carbamido, formyl, thioformyl, amino, mono-(C_1-C_{20} alkyl)-substituted amino, di-(C_1-C_{20} alkyl)-substituted amino, mono-(C_5-C_{24} aryl)-substituted amino, di-(C_5-C_{24} aryl)-substituted amino, (C_1-C_{20} alkyl)(C_5-C_{24} aryl)-substituted amino, C_2-C_{20} alkylamido, C_6-C_{24} arylamido, imino, C_2-C_{20} alkylimino, C_6-C_{24} arylimino, nitro, nitroso, sulfo, sulfonato, C_1-C_{20} alkylthio, C_5-C_{24} arylthio, C_1-C_{20} alkylsulfinyl, C_5-C_{24} arylsulfinyl, C_1-C_{20} alkylsulfonyl, C_5-C_{24} arylsulfonyl, boryl, borono, boronato, phosphono, phosphonato, phosphinato, phospho, and phosphino, any of which may be

further substituted, if the functional group allows, with an additional functional group and/or at least one hydrocarbyl moiety generally selected from C_1-C_{20} alkyl (preferably C_1-C_{12} alkyl, more preferably C_1-C_6 alkyl), C_2-C_{20} alkenyl (preferably C_2-C_{12} alkenyl, more preferably C_2-C_6 alkenyl), C_2-C_{20} 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).

[000103] Z is a hydrocarbylene (e.g., C_1-C_{20} alkylene, C_2-C_{20} alkenylene, C_2-C_{20} alkynylene, C_5-C_{24} arylene, C_6-C_{24} alkarylene, or C_6-C_{24} aralkylene), substituted hydrocarbylene (e.g., substituted C_1-C_{20} alkylene, C_2-C_{20} alkenylene, C_2-C_{20} alkynylene, C_5-C_{24} arylene, C_6-C_{24} alkarylene, or C_6-C_{24} aralkylene), heteroatom-containing hydrocarbylene (e.g., C_1-C_{20} heteroalkylene, C_2-C_{20} heteroalkenylene, C_2-C_{20} heteroalkynylene, C_5-C_{24} heteroarylene, heteroatom-containing C_6-C_{24} aralkylene, or heteroatom-containing C_6-C_{24} alkarylene), or substituted heteroatom-containing hydrocarbylene (e.g., substituted C_1-C_{20} heteroalkylene, substituted C_2-C_{20} heteroalkenylene, substituted C_2-C_{20} heteroalkynylene, substituted C_5-C_{24} heteroarylene, substituted heteroatom-containing C_6-C_{24} aralkylene, or substituted heteroatom-containing C_6-C_{24} alkarylene). Preferred Z linkages are C_1-C_{12} alkylene, optionally substituted and/or heteroatom-containing, and particularly preferred Z linkages are C_1-C_6 alkylene. The functional group will generally not be directly bound to the olefinic carbon through a heteroatom containing one or more lone pairs of electrons, e.g., an oxygen, sulfur, nitrogen or phosphorus atom; with such functional groups, there will normally be an intervening linkage Z, i.e., m is 1.

[000104] The reaction partner, i.e., the second olefinic reactant, has a molecular structure given by formula (X)

(X)



[000105] wherein w is zero or 1, J is a linking group and is defined as for Z, R* is a nonhydrogen substituent, e.g., hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, or Fn, and R^8, R^9, and R^{10} are hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, -$(Z)_m$-Fn, or -$(J)_w$-R*.

[000106] In a preferred embodiment:

[000107] either (1) R^8 and R^{10} are hydrogen, or (2) R^8 and R^9 are hydrogen and R^{10} is either hydrogen or -$(J)_w$-R*;

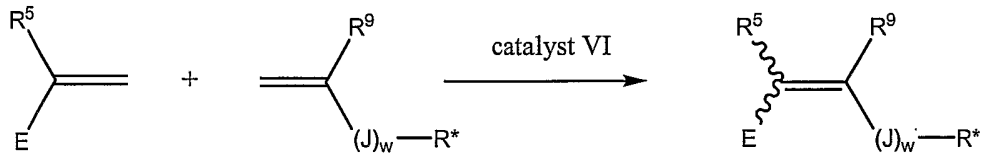
[000108] J is C_1-C_6 alkylene, substituted C_1-C_6 alkylene, C_1-C_6 heteroalkylene, or substituted C_1-C_6 heteroalkylene, and is preferably C_1-C_6 alkylene; and

[000109] R* is selected from C_1-C_{20} alkyl, 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, substituted C_5-C_{24} heteroaryl, C_6-C_{24} aralkyl, substituted C_6-C_{24} aralkyl, C_6-C_{24} heteroaralkyl, and substituted C_6-C_{24} heteroaralkyl, hydroxyl, sulfhydryl, protected hydroxyl, protected sulfhydryl, C_1-C_{20} alkoxy, C_5-C_{24} aryloxy, C_6-C_{24} aralkyloxy, C_2-C_{20} alkylcarbonyl, C_6-C_{24} arylcarbonyl, C_2-C_{20} alkylcarbonyloxy, C_6-C_{24} arylcarbonyloxy, C_2-C_{20} alkoxycarbonyl, C_6-C_{24} aryloxycarbonyl, halocarbonyl, C_2-C_{20} alkylcarbonato, C_6-C_{24} arylcarbonato, carboxy, carboxylato, carbamoyl, mono-(C_1-C_{20} alkyl)-substituted carbamoyl, di-(C_1-C_{20} alkyl)-substituted carbamoyl, di-N-(C_1-C_{20} alkyl)-N-(C_5-C_{24} aryl)-substituted carbamoyl, mono-(C_5-C_{24} aryl)-substituted carbamoyl, di-(C_6-C_{24} aryl)-substituted carbamoyl, thiocarbamoyl, mono-(C_1-C_{20} alkyl)-substituted thiocarbamoyl, di-(C_1-C_{20} alkyl)-substituted thiocarbamoyl, di-N-(C_1-C_{20} alkyl)-N-(C_6-C_{24} aryl)-substituted thiocarbamoyl, mono-(C_6-C_{24} aryl)-substituted thiocarbamoyl, di- (C_6-C_{24} aryl)-substituted thiocarbamoyl, carbamido, formyl, thioformyl, amino, mono-(C_1-C_{20} alkyl)-substituted amino, di-(C_1-C_{20} alkyl)-substituted amino, mono-(C_5-C_{24} aryl)-substituted amino, di-(C_5-C_{24} aryl)-substituted amino, di-N-(C_1-C_{20} alkyl)-N-(C_5-C_{24} aryl)-substituted amino, C_2-C_{20} alkylamido, C_6-C_{24} arylamido, imino, C_2-C_{20} alkylimino, C_6-C_{24} arylimino, nitro, nitroso, sulfo, sulfonato, C_1-C_{20} alkylthio, C_5-C_{24} arylthio, C_1-C_{20} alkylsulfinyl, C_5-C_{24} arylsulfinyl, C_1-C_{20} alkylsulfonyl, C_5-C_{24} arylsulfonyl, boryl, borono, boronato, phosphono, phosphonato, phosphinato, phospho, and phosphino.

[000110] In a more preferred embodiment, J is C_1-C_3 alkylene, e.g., methylene, and R* is selected from hydroxyl, sulfhydryl, protected hydroxyl, protected sulfhydryl, C_1-C_{12} alkoxy, C_5-C_{14} aryloxy, C_6-C_{14} aralkyloxy, C_2-C_{12} alkylcarbonyl, C_6-C_{14} arylcarbonyl, C_2-C_{12} alkylcarbonyloxy, C_6-C_{14} arylcarbonyloxy, C_2-C_{12} alkoxycarbonyl, C_6-C_{14} aryloxycarbonyl, halocarbonyl, di-(C_1-C_{12} alkyl)-substituted carbamoyl, di-N-(C_1-C_{12} alkyl)-N-(C_5-C_{14} aryl)-substituted carbamoyl, mono-(C_5-C_{14} aryl)-substituted carbamoyl, di-(C_6-C_{14} aryl)-substituted carbamoyl, formyl, mono-(C_1-C_{12} alkyl)-substituted amino, di-(C_1-C_{12} alkyl)-substituted amino, mono-(C_5-C_{14} aryl)-substituted amino, di-(C_5-C_{14} aryl)-substituted amino, di-N-(C_1-C_{20} alkyl)-N-(C_5-C_{24} aryl)-substituted amino, C_2-C_{12} alkylamido, C_6-C_{14} arylamido, nitro, C_1-C_{12} alkylthio, and C_5-C_{14} arylthio. Most typical R* substituents are hydroxyl, protected hydroxyl, C_1-C_6 alkoxy, C_5-C_{14} aryloxy, C_6-C_{14} aralkyloxy, C_2-C_6 alkylcarbonyl, C_6-C_{14} arylcarbonyl, halocarbonyl, formyl, di-(C_1-C_6 alkyl)-substituted amino, di-(C_5-C_{14} aryl)-substituted amino, C_1-C_6 alkylthio, and C_5-C_{14} arylthio.

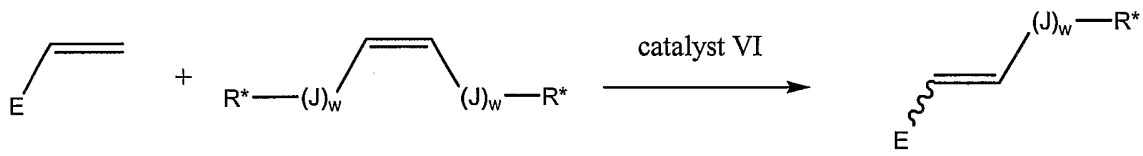
[000111] Accordingly, one representative reaction of the invention, wherein R^6, R^7, R^8, and R^{10} are hydrogen, is illustrated in Scheme 1:

Scheme 1:



[000112] Another representative reaction of the invention, wherein R^5, R^6, R^7, R^8, and R^9 are hydrogen and R^{10} is $-(J)_w-R^*$, is illustrated in Scheme 2:

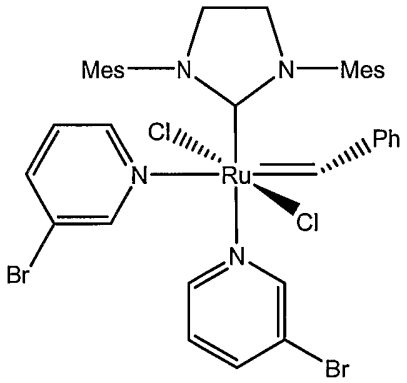
Scheme 2:



(predominantly)

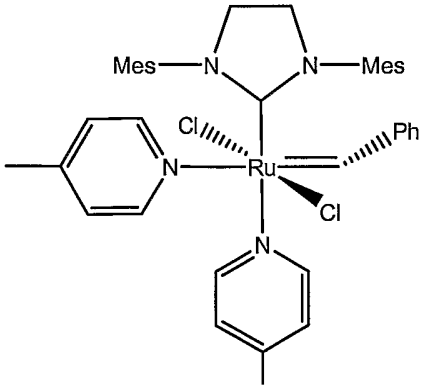
[000113] The capability of the method of the invention with respect to synthesis of such substituted olefins, wherein an electron-withdrawing substituent is directly bound to an olefinic carbon atom, is illustrated in Example 4 using several types of olefinic reactants and the ruthenium catalysts (2), (3), and (4)

(2)



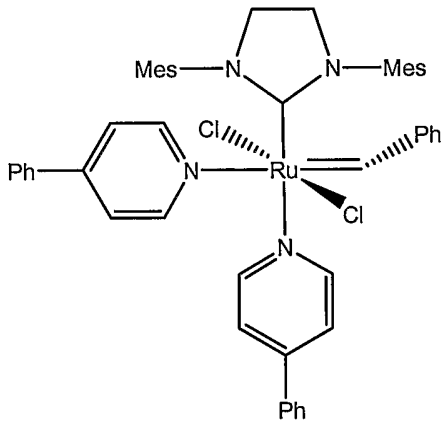
,

(3)



, and

(4)



EXPERIMENTAL:

[000114] Manipulation of organometallic compounds was performed using standard Schlenk techniques under an atmosphere of dry argon or in a nitrogen-filled Vacuum Atmospheres drybox (O_2 < 2ppm). NMR spectra were recorded on a Varian Inova (499.85 MHz for ^1H; 202.34 MHz for ^{31}P; 125.69 MHz for ^{13}C) or a Varian Mercury 300 (299.817 for ^1H; 121.39 MHz for ^{31}P; 74.45 MHz for ^{13}C). ^{31}P NMR spectra were referenced using H_3PO_4 (ò = 0 ppm) as an external standard. UV-vis spectra were recorded on an HP 8452A diode-array spectrophotometer.

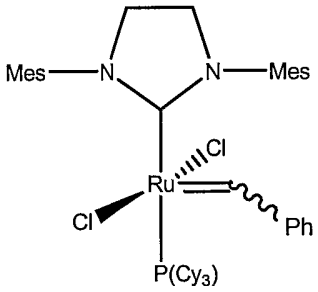
[000115] Materials and methods: All solvents were dried by passage through solvent purification columns. Pyridine was dried by vacuum transfer from CaH_2.

EXAMPLE 1

[000116] Synthesis of $(IMesH_2)(C_5H_4BrN)_2(Cl_2)$=CHPh (2):

[000117] Complex 1 ($(IMesH_2)(PCy_3)_2(Cl_2)$=CHPh) (2.0 g), prepared according to literature procedures,

(1)



was dissolved in toluene (10 mL), and 3-bromopyridine (1.50 grams, 4 mol equivalents) was added. The reaction flask was purged with argon and the reaction mixture was stirred for approximately 12 hours at about 20 °C to about 25 °C during which time a color change from dark

purple to light green was observed. The reaction mixture was transferred into 75 mL of cold (about 0 °C) pentane, and a light green solid precipitated. The precipitate was filtered, washed with 4 x 20 mL of cold pentane, and dried under vacuum to afford $(IMesH_2)(C_5H_4BrN)_2(Cl)_2Ru$=CHPh 6 as a light green powder (1.8 grams, 86% yield).

EXAMPLE 2

[000118] Synthesis of $(IMesH_2)(C_6H_7N)_2(Cl_2)$=CHPh (2) :

[000119] Complex 1 (2.0 grams) was dissolved in toluene (10 mL), and 4-methylpyridine (0.88 grams, 4 mol equivalents) was added. The reaction flask was purged with argon and the reaction mixture was stirred for approximately 12 hours at about 20 °C to about 25 °C during which time a color change from dark purple to light green was observed. The reaction mixture was transferred into 75 mL of cold (about 0 °C) pentane, and a light green solid precipitated. The precipitate was filtered, washed with 4 x 20 mL of cold pentane, and dried under vacuum to afford $(IMesH_2)(C_6H_7N)_2Ru$=CHPh 8 as a light green powder (1.5 grams, 84% yield).INSERT C

EXAMPLE 3

[000120] Synthesis of $(IMesH_2)(C_{11}H_9N)_2(Cl_2)$=CHPh (3):

[000121] Complex 1 (2.0 grams) was dissolved in toluene (10 mL), and 4-phenylpyridine (1.50 grams, 4 mol equivalents) was added. The reaction flask was purged with argon and the reaction mixture was stirred for approximately 12 hours at about 20 °C to about 25 °C during which time a color change from dark purple to dark green was observed. The reaction mixture was transferred into 75 mL of cold (about 0 °C) pentane, and a dark green solid precipitated. The precipitate was filtered, washed with 4 x 20 mL of cold pentane, and dried under vacuum to afford $(IMesH_2)(C_{11}H_9N)_2(Cl)_2Ru$=CHPh 13 as a dark green powder (2.0 grams, 97% yield).

[000122] ^{1}H NMR (500 MHz, CD_2Cl_2): δ 19.23 (s, 1H, C*H*Ph), 8.74 (br. s, 2H, pyridine), 7.91 (br. s, 2H, pyridine), 7.70-7.08 (multiple peaks, 19H, ortho C*H*, para C*H*, meta C*H*, pyridine), 6.93 (br. S, 2H, Mes C*H*) 6.79 (br. s, 2H, Mes C*H*), 4.05 (br. s, 4H, NCH_2CH_2N), 2.62-2.29 (multiple peaks, 18H, Mes C*H*3).

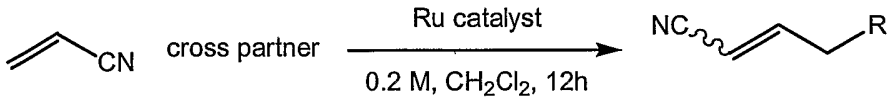
EXAMPLE 4

[000123] Cross-Metathesis (CM) Reactions:

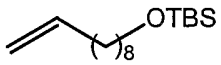
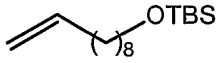
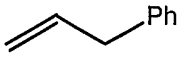
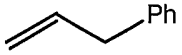
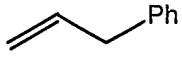
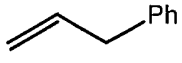
[000124] General procedure: Cross-metathesis reactions were conducted with 1.0 or 2.5 mol% of catalyst (1), (2), or (3) in a reaction with acrylonitrile (1 equivalent) and either an α-terminal olefin or a 1,2-disubstituted olefin (2.5 equivalents) in methylene chloride at room temperature or 40°C for 12 hours to generate the di- or trisubstituted CM product. The specific conditions for each reaction are set forth in Table 1. In general, it should be noted that the CM reaction will

generally be carried out in a solvent at a temperature in the range of about 20°C to about 80°C, optimally about 25°C to about 45°C, with about 0.1 mol% to about 5 mol%, optimally about 0.5 mol% to about 3.5 mol% catalyst. It should be noted that depending on the substitution of the pyridine ligands, high Z-olefin selectivity (> 10:1 *Z*:*E*) also can be achieved.

Table 1. Cross Metathesis of Acrylonitrile



1.0 eq 2.5 eq R = $(CH_2)_7OTBS$, OBn, Ph

cross partner	catalyst	mol % catalyst	temp °C	yield (%)	*E*:*Z*	R
	1	2.5	40 °C	81	1.1:1	OTBS
	1	1	40 °C	76	1:1	OTBS
	1	2.5	40 °C	71	1:1.7	OBn
	1	2.5	40 °C	67	1:1.8	Ph
	1	2.5	rt	36	1:1	Ph
	2	2.5	40 °C	22	1:>10	Ph
	3	2.5	40 °C	29	1:1.8	Ph

CLAIMS:

1. A method for synthesizing an olefin directly substituted with an electron-withdrawing group and substituted with at least one additional substituent, comprising contacting (a) a first olefinic reactant directly substituted with an electron-withdrawing group with (b) a second olefinic reactant substituted with a different substituent in the presence of (c) a catalyst composed of a Group 8 transition metal alkylidene complex under conditions and for a time period effective to allow cross-metathesis to occur, wherein the catalyst contains two anionic ligands, a carbene ligand, and one or two electron-donating heterocyclic ligands.

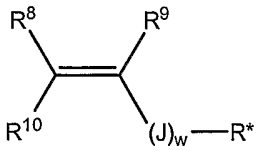
2. The method of claim 1, wherein the electron-withdrawing group is selected from halo, cyano, C_1-C_{20} haloalkyl, C_1-C_{20} alkylsulfonyl, C_5-C_{24} arylsulfonyl, carboxyl,C_5-C_{24} aryloxy, C_1-C_{20} alkoxy, C_6-C_{24} aryloxycarbonyl, C_2-C_{20} alkoxycarbonyl, C_6-C_{24} arylcarbonyl, C_2-C_{20} alkylcarbonyl, formyl, nitro, quaternary amino, sulfhydryl, C_1-C_{20} alkylthio, C_5-C_{24} arylthio, hydroxyl, C_5-C_{24} aryl, and C_1-C_{20} alkyl, any of which may be substituted and/or heteroatom-containing.

3. The method of claim 2, wherein the electron-withdrawing group is selected from halo, cyano, C_1-C_{12} haloalkyl, C_1-C_{12} alkylsulfonyl, C_5-C_{14} arylsulfonyl, carboxyl,C_5-C_{14} aryloxy, C_1-C_{12} alkoxy, C_6-C_{14} aryloxycarbonyl, C_2-C_{12} alkoxycarbonyl, C_6-C_{14} arylcarbonyl, C_2-C_{12} alkylcarbonyl, formyl, nitro, quaternary amino, sulfhydryl, C_1-C_{12} alkylthio, C_5-C_{24} arylthio, hydroxyl, C_5-C_{24} aryl, and C_1-C_{12} alkyl, any of which may be substituted and/or heteroatom-containing.

4. The method of claim 3, wherein the electron-withdrawing group is cyano.

5. The method of claim 1, wherein: the first olefinic reactant has the structure CH_2=CER^5 wherein E is the electron-withdrawing group and R^5 is hydrogen or substituted and/or heteroatom-containing C_1-C_{12} hydrocarbyl; and the second olefinic reactant has the structure

(X)



wherein w is zero or 1, J is a linking group, R* is a nonhydrogen substituent, and R^8, R^9, and R^{10} are hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, or -$(J)_w$-R*.

6. The method of claim 5, wherein R^5, R^8, and R^{10} are hydrogen.

7. The method of claim 6, wherein R^9 is hydrogen.

8. The method of claim 7, wherein E is cyano, w is 1, J is C_1-C_6 alkylene, substituted C_1-C_6 alkylene, heteroatom-containing C_1-C_6 alkylene, and substituted heteroatom-containing C_1-C_6 alkylene, and R* is selected from hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups.

9. The method of claim 8, wherein J is C_1-C_6 alkylene and R* is selected from C_1-C_{20} alkyl, 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, substituted C_5-C_{24} heteroaryl, C_6-C_{24} aralkyl, substituted C_6-C_{24} aralkyl, C_6-C_{24} heteroaralkyl, and substituted C_6-C_{24} heteroaralkyl, hydroxyl, sulfhydryl, protected hydroxyl, protected sulfhydryl, C_1-C_{20} alkoxy, C_5-C_{24} aryloxy, C_6-C_{24} aralkyloxy, C_2-C_{20} alkylcarbonyl, C_6-C_{24} arylcarbonyl, C_2-C_{20} alkylcarbonyloxy, C_6-C_{24} arylcarbonyloxy, C_2-C_{20} alkoxycarbonyl, C_6-C_{24} aryloxycarbonyl, halocarbonyl, C_2-C_{20} alkylcarbonato, C_6-C_{24} arylcarbonato, carboxy, carboxylato, carbamoyl, mono-(C_1-C_{20} alkyl)-substituted carbamoyl, di-(C_1-C_{20} alkyl)-substituted carbamoyl, di-N-(C_1-C_{20} alkyl)-N-(C_5-C_{24} aryl)-substituted carbamoyl, mono-(C_5-C_{24} aryl)-substituted carbamoyl, di-(C_6-C_{24} aryl)-substituted carbamoyl, thiocarbamoyl, mono-(C_1-C_{20} alkyl)-substituted thiocarbamoyl, di-(C_1-C_{20} alkyl)-substituted thiocarbamoyl, di-N-(C_1-C_{20} alkyl)-N-(C_6-C_{24} aryl)-substituted thiocarbamoyl, mono-(C_6-C_{24} aryl)-substituted thiocarbamoyl, di- (C_6-C_{24} aryl)-substituted thiocarbamoyl, carbamido, formyl, thioformyl, amino, mono-(C_1-C_{20} alkyl)-substituted amino, di-(C_1-C_{20} alkyl)-substituted amino, mono-(C_5-C_{24} aryl)-substituted amino, di-(C_5-C_{24} aryl)-substituted amino, di-N-(C_1-C_{20} alkyl)-N-(C_5-C_{24} aryl)-substituted amino, C_2-C_{20} alkylamido, C_6-C_{24} arylamido, imino, C_2-C_{20} alkylimino, C_6-C_{24} arylimino, nitro, nitroso, sulfo, sulfonato, C_1-C_{20} alkylthio, C_5-C_{24} arylthio, C_1-C_{20} alkylsulfinyl, C_5-C_{24} arylsulfinyl, C_1-C_{20} alkylsulfonyl, C_5-C_{24} arylsulfonyl, boryl, borono, boronato, phosphono, phosphonato, phosphinato, phospho, and phosphino.

10. The method of claim 8, wherein J is C_1-C_3 alkylene and R* is selected from hydroxyl, sulfhydryl, protected hydroxyl, protected sulfhydryl, C_1-C_{12} alkoxy, C_5-C_{14} aryloxy, C_6-C_{14} aralkyloxy, C_2-C_{12} alkylcarbonyl, C_6-C_{14} arylcarbonyl, C_2-C_{12} alkylcarbonyloxy, C_6-C_{14} arylcarbonyloxy, C_2-C_{12} alkoxycarbonyl, C_6-C_{14} aryloxycarbonyl, halocarbonyl, di-(C_1-C_{12} alkyl)-substituted carbamoyl, di-N-(C_1-C_{12} alkyl)-N-(C_5-C_{14} aryl)-substituted carbamoyl, mono-(C_5-C_{14} aryl)-substituted carbamoyl, di-(C_6-C_{14} aryl)-substituted carbamoyl, formyl, mono-(C_1-C_{12} alkyl)-

substituted amino, di-(C_1-C_{12} alkyl)-substituted amino, mono-(C_5-C_{14} aryl)-substituted amino, di-(C_5-C_{14} aryl)-substituted amino, di-N-(C_1-C_{20} alkyl)-N-(C_5-C_{24} aryl)-substituted amino, C_2-C_{12} alkylamido, C_6-C_{14} arylamido, nitro, C_1-C_{12} alkylthio, and C_5-C_{14} arylthio.

11. The method of claim 10, wherein J is methylene and R* is selected from hydroxyl, protected hydroxyl, C_1-C_6 alkoxy, C_5-C_{14} aryloxy, C_6-C_{14} aralkyloxy, C_2-C_6 alkylcarbonyl, C_6-C_{14} arylcarbonyl, halocarbonyl, formyl, di-(C_1-C_6 alkyl)-substituted amino, di-(C_5-C_{14} aryl)-substituted amino, C_1-C_6 alkylthio, and C_5-C_{14} arylthio.

12. The method of claim 5, wherein R^5, R^8, and R^9 are hydrogen and R^{10} is -$(J)_w$-R*.

13. The method of claim 12, wherein E is cyano, w is 1, J is C_1-C_6 alkylene, substituted C_1-C_6 alkylene, heteroatom-containing C_1-C_6 alkylene, or substituted heteroatom-containing C_1-C_6 alkylene, and R* is selected from hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups.

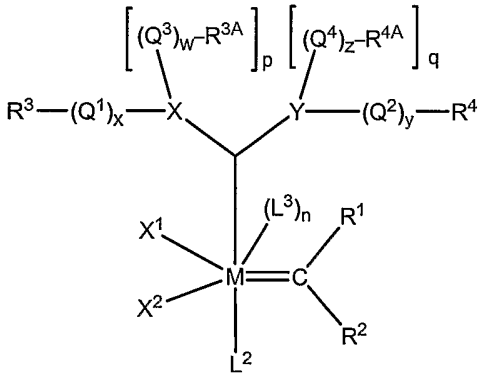
14. The method of claim 13, wherein J is C_1-C_6 alkylene and R* is selected from C_1-C_{20} alkyl, substituted C_1-C_{20} alkyl, C_1-C_{20} heteroalkyl, substituted C_1-C_{20} heteroalkyl, C_5-C_{24} aryl, substituted C_5-C_{24} aryl, C_5-C_{24} heteroaryl, substituted C_5-C_{24} heteroaryl, C_6-C_{24} aralkyl, substituted C_6-C_{24} aralkyl, C_6-C_{24} heteroaralkyl, and substituted C_6-C_{24} heteroaralkyl, hydroxyl, sulfhydryl, protected hydroxyl, protected sulfhydryl, C_1-C_{20} alkoxy, C_5-C_{24} aryloxy, C_6-C_{24} aralkyloxy, C_2-C_{20} alkylcarbonyl, C_6-C_{24} arylcarbonyl, C_2-C_{20} alkylcarbonyloxy, C_6-C_{24} arylcarbonyloxy, C_2-C_{20} alkoxycarbonyl, C_6-C_{24} aryloxycarbonyl, halocarbonyl, C_2-C_{20} alkylcarbonato, C_6-C_{24} arylcarbonato, carboxy, carboxylato, carbamoyl, mono-(C_1-C_{20} alkyl)-substituted carbamoyl, di-(C_1-C_{20} alkyl)-substituted carbamoyl, di-N-(C_1-C_{20} alkyl)-N-(C_5-C_{24} aryl)-substituted carbamoyl, mono-(C_5-C_{24} aryl)-substituted carbamoyl, di-(C_6-C_{24} aryl)-substituted carbamoyl, thiocarbamoyl, mono-(C_1-C_{20} alkyl)-substituted thiocarbamoyl, di-(C_1-C_{20} alkyl)-substituted thiocarbamoyl, di-N-(C_1-C_{20} alkyl)-N-(C_6-C_{24} aryl)-substituted thiocarbamoyl, mono-(C_6-C_{24} aryl)-substituted thiocarbamoyl, di- (C_6-C_{24} aryl)-substituted thiocarbamoyl, carbamido, formyl, thioformyl, amino, mono-(C_1-C_{20} alkyl)-substituted amino, di-(C_1-C_{20} alkyl)-substituted amino, mono-(C_5-C_{24} aryl)-substituted amino, di-(C_5-C_{24} aryl)-substituted amino, di-N-(C_1-C_{20} alkyl)-N-(C_5-C_{24} aryl)-substituted amino, C_2-C_{20} alkylamido, C_6-C_{24} arylamido, imino, C_2-C_{20} alkylimino, C_6-C_{24} arylimino, nitro, nitroso, sulfo, sulfonato, C_1-C_{20} alkylthio, C_5-C_{24} arylthio, C_1-C_{20} alkylsulfinyl, C_5-C_{24} arylsulfinyl, C_1-C_{20} alkylsulfonyl, C_5-C_{24} arylsulfonyl, boryl, borono, boronato, phosphono, phosphonato, phosphinato, phospho, and phosphino.

15. The method of claim 14, wherein J is C_1-C_3 alkylene and R* is selected from hydroxyl, sulfhydryl, protected hydroxyl, protected sulfhydryl, C_1-C_{12} alkoxy, C_5-C_{14} aryloxy, C_6-C_{14} aralkyloxy, C_2-C_{12} alkylcarbonyl, C_6-C_{14} arylcarbonyl, C_2-C_{12} alkylcarbonyloxy, C_6-C_{14} arylcarbonyloxy, C_2-C_{12} alkoxycarbonyl, C_6-C_{14} aryloxycarbonyl, halocarbonyl, di-(C_1-C_{12} alkyl)-substituted carbamoyl, di-N-(C_1-C_{12} alkyl)-N-(C_5-C_{14} aryl)-substituted carbamoyl, mono-(C_5-C_{14} aryl)-substituted carbamoyl, di-(C_6-C_{14} aryl)-substituted carbamoyl, formyl, mono-(C_1-C_{12} alkyl)-substituted amino, di-(C_1-C_{12} alkyl)-substituted amino, mono-(C_5-C_{14} aryl)-substituted amino, di-(C_5-C_{14} aryl)-substituted amino, di-N-(C_1-C_{20} alkyl)-N-(C_5-C_{24} aryl)-substituted amino, C_2-C_{12} alkylamido, C_6-C_{14} arylamido, nitro, C_1-C_{12} alkylthio, and C_5-C_{14} arylthio.

16. The method of claim 15, wherein J is methylene and R* is selected from hydroxyl, protected hydroxyl, C_1-C_6 alkoxy, C_5-C_{14} aryloxy, C_6-C_{14} aralkyloxy, C_2-C_6 alkylcarbonyl, C_6-C_{14} arylcarbonyl, halocarbonyl, formyl, di-(C_1-C_6 alkyl)-substituted amino, di-(C_5-C_{14} aryl)-substituted amino, C_1-C_6 alkylthio, and C_5-C_{14} arylthio.

17. The method of claim 1, wherein the transition metal alkylidene complex has the structure of formula (VI)

(VI)



wherein:

M is the Group 8 transition metal;

n is zero or 1;

X^1 and X^2 are the anionic ligands;

L^2 and L^3 are the electron-donating heterocyclic ligands, or may be taken together to form a single bidentate electron-donating heterocyclic ligand;

R^1 and R^2 are independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups, or may be taken together to form a vinylidene moiety;

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

p is zero when X is O or S, and p is 1 when X is N or P;

q is zero when Y is O or S, and q is 1 when Y is N or P;

Q^1, Q^2, Q^3, and Q^4 are independently selected from hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, and -(CO)- , and further wherein two or more substituents on adjacent atoms within Q may be linked to form an additional cyclic group;

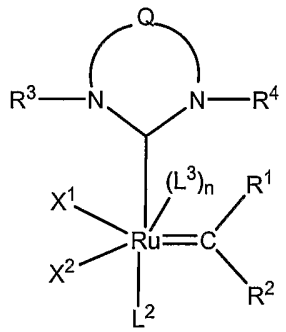
w, x, y, and z are independently zero or 1; and

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,

wherein any two or more of X^1, X^2, L^1, L^2, L^3, R^1, and R^2 can be taken together to form a cyclic group, and further wherein any one or more of X^1, X^2, L^1, L^2, L^3, R^1, and R^2 may be attached to a support.

18. The method of claim 17, wherein M is ruthenium, w, x, y, and z are zero, X and Y are N, and R^{3A} and R^{4A} are linked to form -Q-, such that the complex has the structure of formula (VIII)

(VIII)



wherein Q is a hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, or substituted heteroatom-containing hydrocarbylene linker, and further wherein two or more substituents on adjacent atoms within Q may be linked to form an additional cyclic group.

19. The method of claim 18, wherein:

X^1 and X^2 are halo;

Q is $-CR^{11}R^{12}-CR^{13}R^{14}-$ or $-CR^{11}=CR^{13}-$, 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, or wherein

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; and

R^3 and R^4 are aromatic.

20. The method of claim 19, wherein:

Q is $-CR^{11}R^{12}-CR^{13}R^{14}-$ wherein R^{11}, R^{12}, R^{13}, and R^{14} are 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; and

R^3 and R^4 are unsubstituted phenyl or phenyl substituted with up to three substituents selected from C_1-C_{20} alkyl, 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.

21. The method of claim 20, wherein R^3 and R^4 are mesityl, and R^{11}, R^{12}, R^{13}, and R^{14} are hydrogen.

22. The method of claim 19, wherein one of R^1 and R^2 is hydrogen, and the other is selected from C_1-C_{20} alkyl, C_2-C_{20} alkenyl, and C_5-C_{24} aryl, optionally substituted with one or more moieties selected from C_1-C_6 alkyl, C_1-C_6 alkoxy, and phenyl.

23. The method of claim 20, wherein one of R^1 and R^2 is hydrogen, and the other is selected from C_2-C_6 alkenyl and phenyl.

24. The method of claim 21, wherein R^1 is hydrogen and R^2 is phenyl.

25. The method of any one of claims 19, 20, 21, 22, 23, or 24, wherein L^2 and L^3 are selected from nitrogen-containing heterocycles, sulfur-containing heterocycles, and oxygen-containing heterocycles.

26. The method of claim 25, wherein L^2 and L^3 are nitrogen-containing heterocycles.

27. The method of claim 26, wherein L^2 and L^3 are selected from pyridine, bipyridine, pyridazine, pyrimidine, bipyridamine, pyrazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, pyrrole, 2H-pyrrole, 3H-pyrrole, pyrazole, 2H-imidazole, 1,2,3-triazole, 1,2,4-triazole, indole, 3H-indole, 1H-isoindole, cyclopenta(b)pyridine, indazole, quinoline, bisquinoline, isoquinoline, bisisoquinoline, cinnoline, quinazoline, naphthyridine, piperidine, piperazine, pyrrolidine,

pyrazolidine, quinuclidine, imidazolidine, picolylimine, purine, benzimidazole, bisimidazole, phenazine, acridine, carbazole, any of which is optionally substituted on a non-coordinating heteroatom with a nonhydrogen substituent.

28. The method of claim 27, wherein L^2 and L^3 are selected from pyridine and substituted pyridines.

29. The method of claim 28, wherein L^2 and L^3 are selected from pyridine, 3-halopyridine, 4-methylpyridine, and 4-phenylpyridine.

30. The method of any one of claims 19, 20, 21, 22, 23, or 24, wherein n is zero and L^2 is selected from nitrogen-containing heterocycles, sulfur-containing heterocycles, and oxygen-containing heterocycles.

31. The method of claim 30, wherein L^2 is a nitrogen-containing heterocycle.

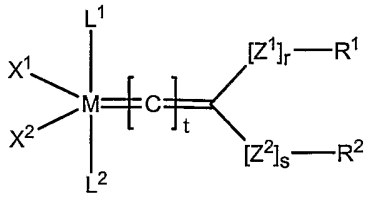
32. The method of claim 31, wherein L^2 is selected from pyridine, bipyridine, pyridazine, pyrimidine, bipyridamine, pyrazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, pyrrole, 2H-pyrrole, 3H-pyrrole, pyrazole, 2H-imidazole, 1,2,3-triazole, 1,2,4-triazole, indole, 3H-indole, 1H-isoindole, cyclopenta(b)pyridine, indazole, quinoline, bisquinoline, isoquinoline, bisisoquinoline, cinnoline, quinazoline, naphthyridine, piperidine, piperazine, pyrrolidine, pyrazolidine, quinuclidine, imidazolidine, picolylimine, purine, benzimidazole, bisimidazole, phenazine, acridine, carbazole, any of which is optionally substituted on a non-coordinating heteroatom with a nonhydrogen substituent.

33. The method of claim 32, wherein L^2 is selected from pyridine and substituted pyridines.

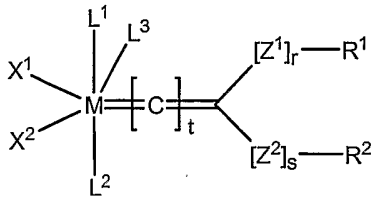
34. The method of claim 33, wherein L^2 is selected from pyridine, 3-halopyridine, 4-methylpyridine, and 4-phenylpyridine.

35. The method of claim 1, wherein the catalyst has the structure of formula (II), (III), or (IV)

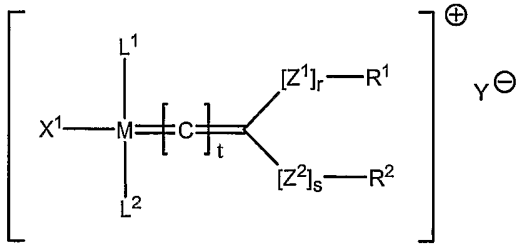
(II)



(III)



(IV)



wherein:

X^1 and X^2 are the anionic ligands;

L^1 is a carbene ligand;

L^2 and L^3 are the electron-donating heterocyclic ligands, or may be taken together to form a single bidentate electron-donating heterocyclic ligand;

R^1 and R^2 are independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups, or may be taken together to form a vinylidene moiety;

r and s are independently zero or 1;

t is an integer in the range of zero to 5,

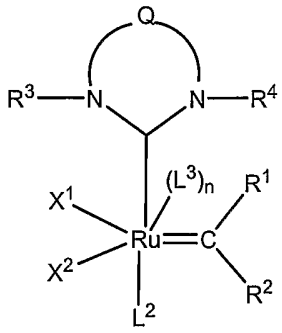
Y is a noncoordinating anion; and

Z^1 and Z^2 are linkages containing 1 to about 6 spacer atoms,

wherein any two or more of X^1, X^2, L^1, L^2, L^3, Z^1, Z^2, R^1, and R^2 may be taken together to form a cyclic group, and any one or more of X^1, X^2, L^1, L^2, L^3, Z^1, Z^2, R^1, and R^2 may be attached to a support.

36. A method for synthesizing a substituted acrylonitrile, comprising contacting acrylonitrile with a substituted olefinic reactant in the presence of a catalyst composed of a Group 8 transition metal alkylidene complex under conditions and for a time period effective to allow cross-metathesis to occur, wherein the catalyst has the structure of formula (VIII)

(VIII)



in which:

X^1 and X^2 are halo;

Q is $-CR^{11}R^{12}-CR^{13}R^{14}-$ wherein R^{11}, R^{12}, R^{13}, and R^{14} are 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; and

one of R^1 and R^2 is hydrogen, and the other is selected from C_2-C_6 alkenyl and phenyl;

R^3 and R^4 are unsubstituted phenyl or phenyl substituted with up to three substituents selected from C_1-C_{20} alkyl, 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;

n is zero or 1; and

L^2 and L^3 are selected from pyridine, 3-substituted pyridine, and 4-substituted pyridine, wherein the substituents are halo, lower alkyl, or phenyl.

37. The method of claim 36, wherein R^{11}, R^{12}, R^{13}, and R^{14} are hydrogen, and R^3 and R^4 are mesityl.

38. The method of claim 36, wherein the substituted olefinic reactant has the structure CH_2=CH(CH_2-R*) or CH(CH_2-R*)=CH(CH_2-R*) wherein R* is selected from hydroxyl, protected hydroxyl, C_1-C_6 alkoxy, C_5-C_{14} aryloxy, C_6-C_{14} aralkyloxy, C_2-C_6 alkylcarbonyl, C_6-C_{14} arylcarbonyl, halocarbonyl, formyl, di-(C_1-C_6 alkyl)-substituted amino, di-(C_5-C_{14} aryl)-substituted amino, C_1-C_6 alkylthio, and C_5-C_{14} arylthio.