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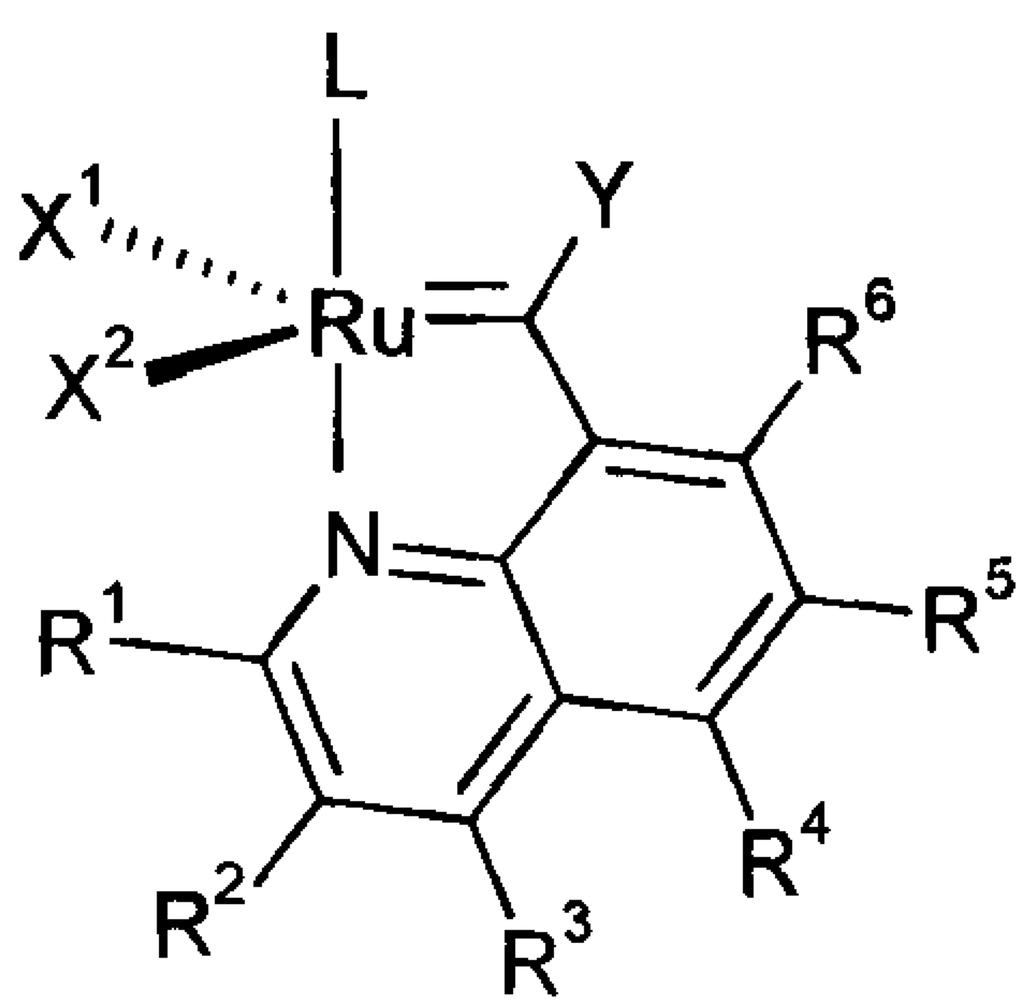
(54) Titre : NOUVEAUX COMPLEXES DU RUTHENIUM COMME CATALYSEURS POUR DES REACTIONS DE METATHESE

(54) Title: NEW RUTHENIUM COMPLEXES AS CATALYSTS FOR METATHESIS REACTIONS



I

(57) Abrégé/Abstract:
Disclosed are novel metathesis catalysts of the formula (I), a process for making the same and their use in metathesis reactions such as ring closing or cross metathesis.

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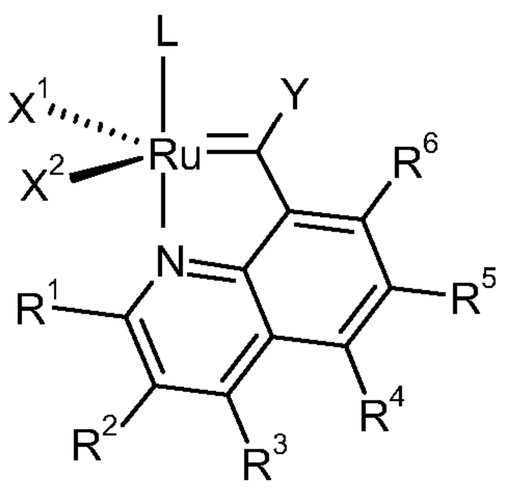
(54) Title: NEW RUTHENIUM COMPLEXES AS CATALYSTS FOR METAHESIS REACTIONS

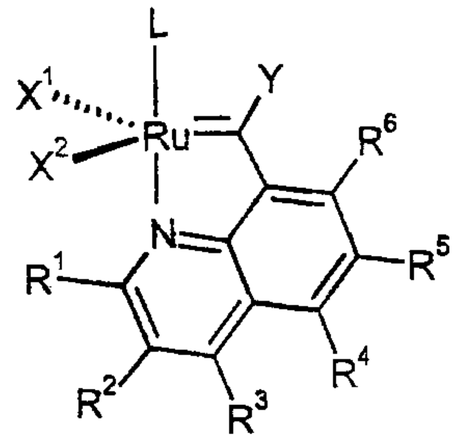


(I)

(57) Abstract: Disclosed are novel metathesis catalysts of the formula (I), a process for making the same and their use in metathesis reactions such as ring closing or cross metathesis.

NEW RUTHENIUM COMPLEXES AS CATALYSTS FOR METATHESIS REACTIONS

The invention relates to novel metathesis catalysts of the formula

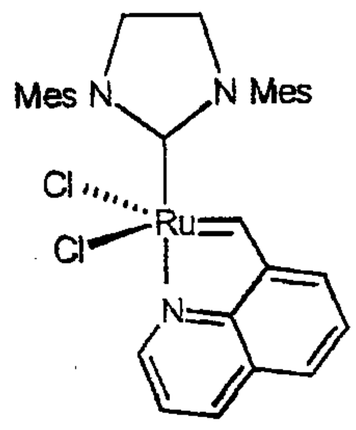


I

a process for making the same and their use in metathesis reactions such as ring closing or cross metathesis.

Metathesis reactions using ruthenium or other transition metal complexes as catalysts are meanwhile well known and have been widely applied in organic synthesis (see e.g. WO 2004/035596, WO 2002/14376 or EP-A 1180108).

A metathesis catalyst of the formula



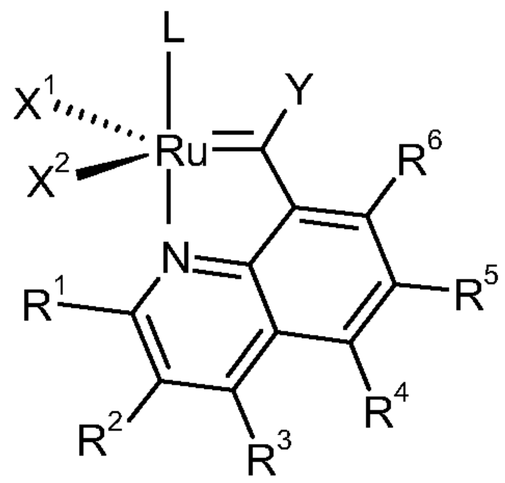
is described by Barbasiewicz et al in *Organometallics*, published on Web June 17, 2006. The authors have shown that applying this catalyst in a ring closing metathesis reaction of *N*,*N*-diallyl-4-methylbenzenesulfonamide in dichloromethane at room temperature 41% of 1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole was formed after a reaction time of 24h. Upon reworking under the same conditions, the conversion was very poor (<3%) affording less than 1% of 1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole and even at a higher reaction temperature (110°C in toluene) the activity of this catalyst remained poor.

Object of the present invention therefore was to provide superior metathesis catalysts.

It was surprisingly found that a substitution in alpha position of the nitrogen atom significantly improved the activity of the catalysts.

It could be shown that the ruthenium complexes of formula I have the potential to be useful catalysts in metathesis reactions such as in the ring closing or cross metathesis reactions.

The compounds of the present invention are characterized by the formula



I

wherein L is a neutral ligand;

X^1 and X^2 independently of each other are anionic ligands;

R^1 is C_{1-6}-alkyl, halogen-C_{1-6}-alkyl, C_{1-6}-alkoxy, C_{1-6}-alkylcarbonyl, aryl, hydroxy, aryloxy, nitro, amino, mono-C_{1-6}-alkyl-or di-C_{1-6}-alkylamino, halogen, thio, C_{1-6}-alkylthio or SO_2-C_{1-6}-alkyl, SO_2-aryl, SO_3H, SO_3-C_{1-6}-alkyl or $OSi(C_{1-6}\text{-alkyl})_3$ and SO_2-N R'R" wherein R' and R" independently of each other have the meaning of hydrogen or C_{1-6}-alkyl or R' and R" together with the N atom form a carbocycle;

R^2, R^3, R^4, R^5 and R^6 independently of each other have the meaning of hydrogen, C_{1-6}-alkyl, halogen-C_{1-6}-alkyl, C_{1-6}-alkoxy, C_{1-6}-alkylcarbonyl, aryl, hydroxy, aryloxy, nitro, amino, mono-C_{1-6}-alkyl-or di-C_{1-6}-alkylamino, halogen, thio, C_{1-6}-alkylthio or SO_2-C_{1-6}-alkyl, SO_2-aryl, SO_3H, SO_3-C_{1-6}-alkyl or $OSi(C_{1-6}\text{-alkyl})_3$ and SO_2-N R'R" wherein R' and R" independently of each other have the meaning of hydrogen or C_{1-6}-alkyl or R' and R" together with the N atom form a carbocycle,

Y is hydrogen, C_{1-6}-alkyl, C_{2-6}- alkenyl or aryl, or Y and R^6 taken together to form a (CH=CR) - or a $-(CH_2)_n$- bridge with n having the meaning of 2 or 3 and R as defined for R^2.

The present invention further includes a process for the preparation of the compounds of formula I and its use in metathesis reactions.

The following definitions are set forth to illustrate and define the meaning and scope of the various terms used to describe the invention herein.

The term “alkyl”, alone or in combination with other groups, refers to a branched or straight-chain monovalent saturated aliphatic hydrocarbon radical of one to six carbon atoms, preferably one to four carbon atoms. This term is further exemplified by radicals as methyl, ethyl, n-propyl, isopropyl, n-butyl, s-butyl, t-butyl, 1-adamantyl and the groups specifically exemplified herein.

The term “alkenyl”, alone or in combination with other groups, refers to a branched or straight-chain monovalent unsaturated aliphatic hydrocarbon radical of two to six carbon atoms, preferably two to four carbon atoms. This term is further exemplified by radicals as vinyl and propenyl, butenyl, pentenyl and hexenyl and their isomers. Preferred alkenyl radical is vinyl.

The term “halogen” refers to fluorine, chlorine, bromine and iodine. Preferred halogen is chlorine.

The term “halogen-C_{1-6}-alkyl” refers to a halogen substituted C_{1-6}-alkyl radical wherein halogen has the meaning as above. Preferred “halogen-C_{1-6}-alkyl” radicals are the fluorinated C_{1-6}-alkyl radicals such as CF_3, CH_2CF_3, $CH(CF_3)_2$, C_4F_9.

The term “alkoxy” refers to a branched or straight-chain monovalent saturated aliphatic hydrocarbon radical of one to six carbon atoms, preferably 1 to four carbon atoms attached to an oxygen atom. Examples of “alkoxy” are methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy and hexyloxy. Preferred are the alkoxy groups specifically exemplified herein.
The alkyl chain of the alkoxy group can optionally be substituted, particularly mono-, di- or tri-substituted by alkoxy groups as defined above, preferably methoxy, or ethoxy or by aryl groups, preferably phenyl.
Preferred substituted alkoxy group is the benzyloxy group.

The term “alkyl carbonyl” refers to a C_{1-6}-alkycarbonyl group preferably to a C_{1-4}-alkycarbonyl group. It includes for example acetyl, propanoyl, butanoyl or pivaloyl. Preferred alkyl carbonyl group is acetyl.

The term "alkylthio" refers to the group R'-S-, wherein R' is C_{1-6}-alkyl, preferably C_{1-4}-alkyl e.g. methylthio or ethylthio. Preferred are the alkylthio groups specifically exemplified herein.

The term "SO_2- C_{1-6}-alkyl" refers to a sulfonyl substituted C_{1-6}-alkyl radical. Preferred SO_2-C_{1-6}-alkyl radical is SO_2-methyl.

The term "SO_2- aryl" refers to a sulfonyl substituted aryl radical. Preferred SO_2-aryl radical is SO_2-phenyl.

The term "SO_2-N R'R" " refers to a sulfonyl substituted amino group N R'R" wherein R' and R" independently of each other have the meaning of hydrogen or C_{1-6}-alkyl or R' and R" together with the N atom form a carbocycle. Preferred SO_2-N R'R" radicals is SO_2-N(methyl)$_2$.

The term "OSi(C_{1-6}-alkyl)$_3$ " refers to a tri- C_{1-6}-alkyl-substituted silyloxy group . Preferred meaning of OSi(C_{1-6}-alkyl)$_3$ are trimethylsilyloxy, triethylsilyloxy and t-butyldimethylsilyloxy.

The term "mono- or di-alkyl-amino" refers to an amino group, which is mono- or disubstituted with C_{1-6}-alkyl, preferably C_{1-4}-alkyl. A mono-C_{1-6}-alkyl-amino group includes for example methylamino or ethylamino. The term "di-C_{1-6}-alkyl-amino" includes for example dimethylamino, diethylamino or ethylmethylamino. Preferred are the mono- or di-C_{1-4}-alkylamino groups specifically exemplified herein. It is hereby understood that the term "di-C_{1-6}-alkyl-amino" includes ring systems wherein the two alkyl groups together with the nitrogen atom to which they are attached form a 4 to 7 membered heterocycle which also may carry one further hetero atom selected from nitrogen, oxygen or sulfur.

The terms "amino" and "mono- or di-alkyl-amino" also encompass a group of the formula –NR'R"H^+Z^- wherein R' and R" are as above and Z^- is an anion such as a halogenide, particularly chloride or a sulfonate, particularly methansulfonate or p-toluenesulfonate.

The term "cycloalkyl" denotes a "C_{3-7}-cycloalkyl" group containing from 3 to 7 carbon atoms, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or cycloheptyl.

The term "aryl" relates to the phenyl or naphthyl group, preferably the phenyl group, which can optionally be mono-, di-, tri- or multiply-substituted by halogen, hydroxy, CN, CF_3, NO_2, NH_2, N(H,alkyl), N(alkyl)$_2$, carboxy, aminocarbonyl, alkyl,

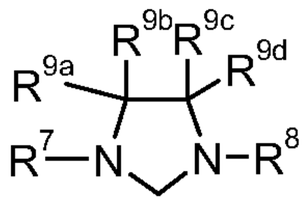
alkoxy, alkylcarbonyl, SO_2-alkyl, SO_2-aryl, SO_3H, SO_3-alkyl, SO_2-NR'R'', aryl and/or aryloxy. Preferred aryl group is phenyl.

The term "aryloxy" relates to an aryl radical attached to an oxygen atom. The term "aryl" has the meaning as defined above. Preferred aryloxy group is phenyloxy.

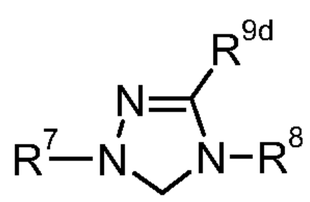
The term "heteroaryl" relates to a heterocyclic aryl radical containing 1 to 3 heteroatoms in the ring with the remainder being carbon atoms. Suitable heteroatoms include, without limitation, oxygen, sulfur, and nitrogen. Exemplary heteroaryl groups include furanyl, thienyl, pyridyl, pyrrolyl, N-alkyl pyrrolo, pyrimidyl, pyrazinyl, imidazolyl, benzofuranyl, quinolinyl, and indolyl. Like the aryl group the heteroaryl group can optionally be mono-, di-, tri- or multiply-substituted by halogen, hydroxy, CN, CF_3, NO_2, NH_2, N(H,alkyl), $N(alkyl)_2$, carboxy, aminocarbonyl, alkyl, alkoxy, alkylcarbonyl, SO_2-alkyl, SO_2-aryl, SO_3H, SO_3-alkyl, SO_2-NR'R'', aryl and/or aryloxy.

The ligand L is a neutral ligand preferably selected from

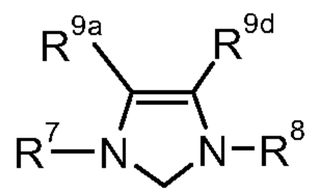
$-P(R^{10})_3$;



IIa ;



IIb ;



IIc

wherein R^7 and R^8 independently of each other are C_{1-6}-alkyl, aryl, C_{2-6}- alkenyl or 1-adamantyl and

R^{9a-d} are independently of each other hydrogen, C_{1-6}-alkyl, C_{2-6}- alkenyl or aryl, or R^{9b} and R^{9c} or R^{9a} and R^{9d} taken together form a-$(CH_2)_4$-bridge;

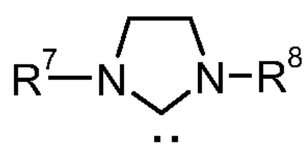
R^{10} is independently of each other C_{1-6}-alkyl, C_{3-7}-cycloalkyl, aryl or heteroaryl

In a preferred embodiment R^7 and R^8 are C_{1-6}-alkyl or a phenyl group which is di- or tri-substituted with C_{1-6}-alkyl.
R^7 and R^8 more preferably have the meaning of t-butyl, 1-adamantyl, isopropyl, 2, 6-diisopropylphenyl or 2, 4, 6-trimethylphenyl most preferably 2, 4, 6-trimethylphenyl.

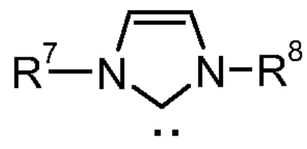
In a preferred embodiment R^{9a} and R^{9c} are methyl or phenyl and R^{9b} and R^{9d} are hydrogen, or R^{9a} and R^{9c} or R^{9b} and R^{9d} are taken together to form a -$(CH_2)_n$- bridge with n having the meaning of 5 or 6. Its herby understood that if chiral carbon atoms are present, both the racemic and the enantiomerically pure form are comprised.

In a further preferred embodiment R^{9a-d} is hydrogen.

In a further preferred embodiment L is



IId



IIe

wherein R^7 and R^8 are as described above.

In a further preferred embodiment R^{10} is cyclohexyl.

As anionic ligand X^1 and X^2 a halogenide or a pseudo halogenide such as cyanide, a rhodanide, a cyanate, an isocycanate, acetate or trifluoroacetate may be selected. Preferred anionic ligand for X^1 and X^2 is a halogenide, whereas chloro is the most preferred anionic ligand.

In a further preferred embodiment R^1 is C_{1-6}- alkyl, halogen-C_{1-6}-alkyl or aryl. R^1 more preferably is methyl, trifluoromethyl, phenyl, ortho-tolyl or 2,6-dimethylphenyl.

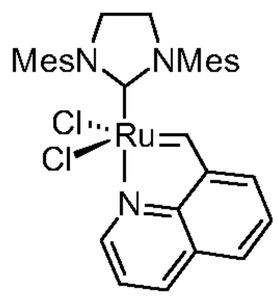
In a further preferred embodiment R^2, R^4, R^5 and R^6 are hydrogen.

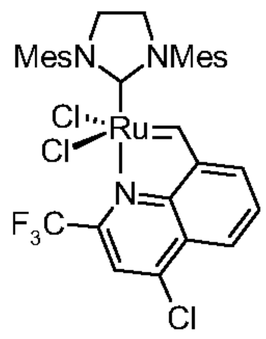
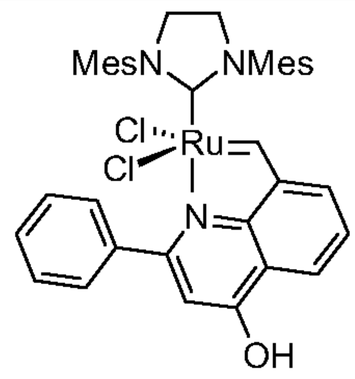
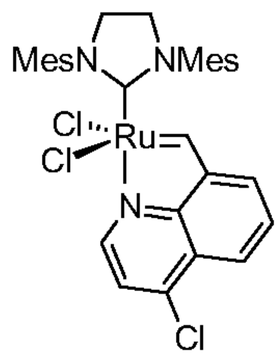
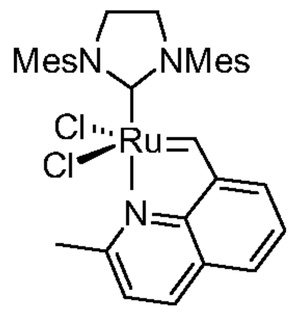
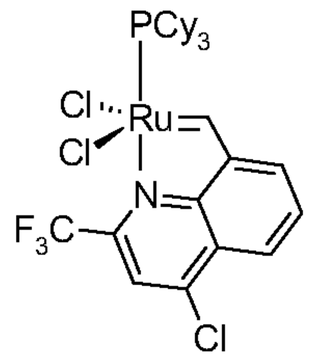
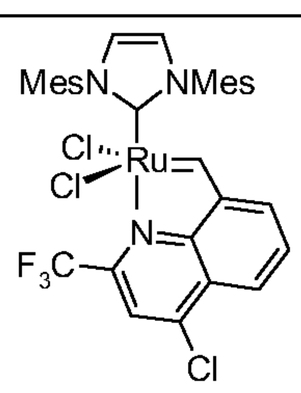
R^3 preferably is hydrogen, hydroxy, C_{1-6}-alkoxy, C_{1-6}-alkoxycarbonyl, nitro, amino and halogen. More preferred R^3 stands for chloro, hydroxy, benzyloxy, amino, nitro and acetyl.

The following compounds represent the most preferred representatives of the present invention.

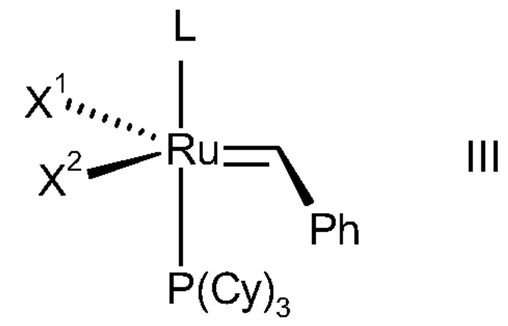
Abbreviations: ImH_2Mes = 1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene; ImMes = 1,3-bis-(2,4,6-trimethylphenyl)-2-imidazoylidene

Table of catalysts tested:

Catalyst Structure	Chemical Name
	$[RuCl_2(ImH_2Mes)$(8-quinolinylmethylene)] (Comparison example)

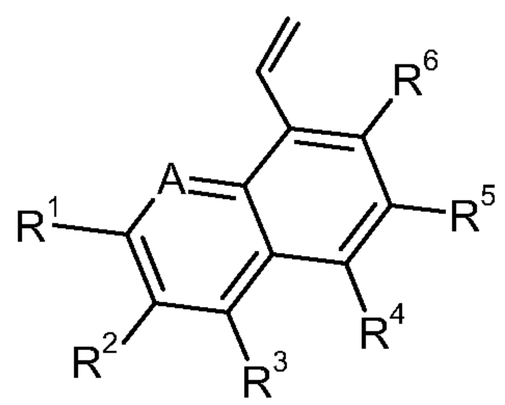
	[$RuCl_2(ImH_2Mes)$((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)]
	[$RuCl_2(ImH_2Mes)$((4-hydroxy-2-phenyl-8-quinolinyl)methylene)]
	[$RuCl_2(ImH_2Mes)$((4-chloro-8-quinolinyl)methylene)] (Comparison example)
	[$RuCl_2(ImH_2Mes)$((2-methyl-8-quinolinyl)methylene)]
	[$RuCl_2$(tricyclohexylphosphine)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)]
	[$RuCl_2(ImMes)$((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)]

The present invention also comprises a process for the preparation of a compound of the formula I which comprises the transformation of a Ru-precursor compound of the formula III



III

wherein X^1 and X^2 are as defined, Cy has the meaning of cyclohexyl and Ph is phenyl with a compound of formula IV

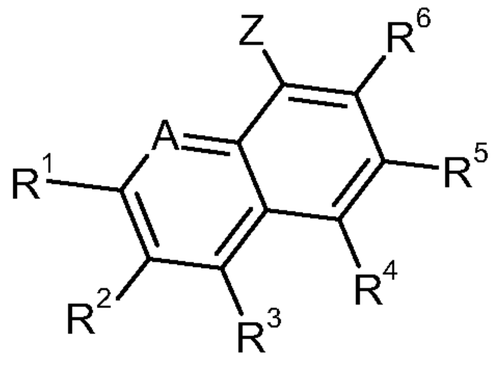


IV

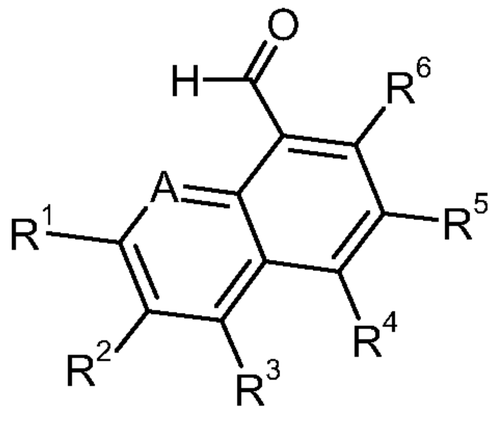
wherein R^1 to R^6 have the meaning as above.

The conversion as a rule takes place in an organic solvent like toluene, benzene, tetrahydrofuran or dichloromethane in the presence of a copper salt, preferably copper chloride at a temperature of about 0°C to 60°C.

The compounds of formula IV can be prepared by several well known cross-coupling reactions which are e.g. described in F. Diederich and P. J. Stang in `Metal-catalyzed cross-coupling reactions` Wiley-VCH, 1998 or J. March in `Advanced organic chemistry ` Wiley-VCH, 1992 starting from commercially available or easy accessible compounds of formula V with e.g. vinylstannanes, ethylene, vinylboronates ,vinylboranes, vinyl Grignard reagents or under Wittig, Wittig-Horner, Wittig-Horner-Emmons, Tebbe or Peterson conditions starting from commercially available aldehydes of formula VI.



V



VI

wherein Z is halogen or trifluoromethansulfonyloxy and R^1 to R^6 have the meaning as above.

The compounds of the present invention can be used in metathesis reactions particularly in ring closing or cross metathesis reactions. Though it is apparent for the skilled in the art that reaction conditions have to be adapted for each substrate, the following conditions can as a rule be applied.

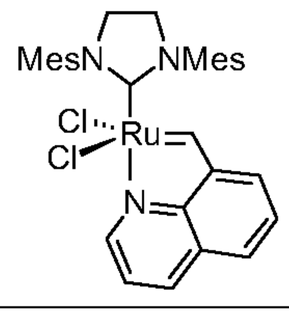
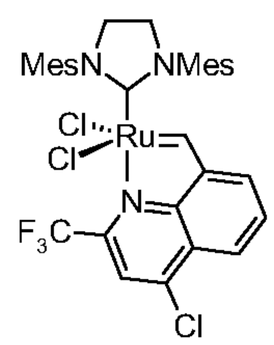
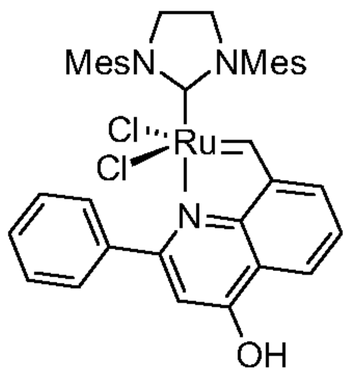
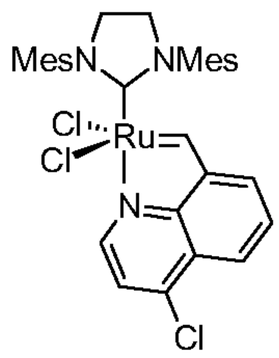
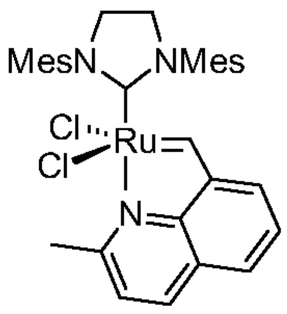
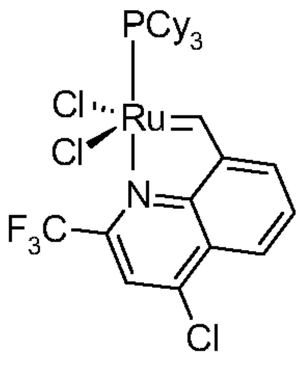
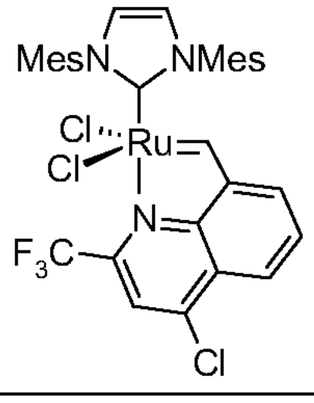
Ring closing and cross metathesis reactions are usually performed in an inert organic solvent such as in toluene, xylene, mesitylene, and dichloromethane and at reaction temperatures from 20°C to 180°C. Catalyst concentration is commonly selected between 0.1 mol% and 10 mol%.

The following examples illustrate the invention without limiting it.

Examples

Abbreviations: ImH_2Mes = 1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene; ImMes = 1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolylidene

Table of Catalysts tested:

Catalyst Structure	Chemical Name
	[$RuCl_2$(ImH2Mes)(8-quinolinylmethylene)] (Comparison example)
	[$RuCl_2$(ImH2Mes)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)]
	[$RuCl_2$(ImH2Mes)((4-hydroxy-2-phenyl-8-quinolinyl)methylene)]
	[$RuCl_2$(ImH_2Mes)((4-chloro-8-quinolinyl)methylene)] (Comparison example)
	[$RuCl_2$(ImH_2Mes)((2-methyl-8-quinolinyl)methylene)]
	[$RuCl_2$(tricyclohexylphosphine)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)]
	[$RuCl_2$(ImH2Mes)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)]

Synthesis of Catalysts: Examples 1-11

Example 1

[$RuCl_2(ImH_2Mes)$(8-quinolinylmethylene)]

A suspension of 500 mg (0.59 mmol) of [$RuCl_2(PCy_3)(ImH_2Mes)$(phenylmethylene)] (commercially available from Sigma-Aldrich Inc., St. Louis, USA), 60 mg (0.61 mmol) copper chloride and 100 mg (0.64 mmol) 8-vinylquinoline (prepared according to G.T. Crisp, S. Papadopoulos, *Aust. J. Chem.* 1989, *42*, 279-285) in 40 ml methylene chloride was stirred at room temperature for 90 min. The reaction mixture was evaporated to dryness and the isolated crude product purified by silica gel chromatography (hexane / ethyl acetat 2:1) to yield 255 mg (70%) of the title compound as green crystals. MS: 584.4 ($M\text{-}Cl^+$). ^{1}H-NMR (300 MHz, CD_2Cl_2): 2.36 (s, 6H); 2.40 (s, 12H); 4.04 (s, 4H); 7.01 (s, 4H); 7.19 (dd, J=8.4, 4.9Hz, 1H); 7.34 (t, J=7.7Hz, 1H); 7.51 (d, J=7.1Hz, 1H); 8.08-8.18 (m, 2H); 8.26 (dd, J=4.8, 1.3Hz, 1H); 16.95 (s, 1H). Anal. calcd. for $C_{31}H_{33}N_3Cl_2Ru$: C, 60.09; H, 5.37; N, 6.78; Cl, 11.44. Found: C, 60.06; H, 5.75; N, 6.16; Cl, 10.90.

Example 2

4-Chloro-2-trifluoromethyl-8-vinyl-quinoline

A suspension of 2.00 g (6.25 mmol) 8-bromo-4-chloro-2-trifluoromethylquinoline (commercially available from Maybridge, Cornwall, UK), 258 mg (0.31 mmol) $PdCl_2dppf{\cdot}CH_2Cl_2$, 1.29 g (9.37 mmol) potassium vinyl tetrafluoroborate and 0.88 ml (6.28 mmol) triethylamine in 40 ml ethanol was heated at reflux for 3 h. The resulting yellow suspension was filtered and the filtrate evaporated to dryness. The residue was suspended in ethyl acetate, filtered and the filtrate extracted with water. The organic layer was evaporated to dryness and the isolated crude product purified by silica gel chromatography (hexane) to yield 1.17 g (72%) of the title compound as white crystals. MS: 257.1 (M^+). ^{1}H-NMR (300 MHz, $CDCl_3$): 5.58 (dd, J=11.1, 1.1Hz, 1H); 6.07 (dd, J=17.8, 1.1Hz, 1H); 7.75 (t, J=7.7Hz, 1H); 7.81 (s, 1H); 7.99 (dd, J=17.8, 11.1Hz, 1H); 8.09 (d, J=7.2Hz, 1H); 8.23 (d, J=8.4Hz, 1H).

Example 3

[$RuCl_2(ImH_2Mes)$((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)]

A suspension of 1.39 g (1.64 mmol) of [$RuCl_2(PCy_3)(ImH_2Mes)$(phenylmethylene)], 0.17 g (1.80 mmol) copper chloride and 464 mg (1.69 mmol) 4-chloro-2-trifluoromethyl-8-vinyl-quinoline in 100 ml methylene chloride was stirred at 30°C for 90

min. The reaction mixture was evaporated to dryness and the isolated crude product purified by silica gel chromatography (hexane / ethyl acetate 5:2) to yield 278 mg (24%) of the title compound as green crystals. MS: 721.2 (M^+). ^{1}H-NMR (300 MHz, CD_2Cl_2): 2.85 (s, 6H); 2.40 (s, 12H); 4.05 (s, 4H); 7.01 (s, 4H); 7.54 (s, 1H); 7.56 (t, J=7.7Hz, 1H); 7.65 (d, J=6.8Hz, 1H); 8.51 (d, J=8.4Hz, 1H); 16.70-17.10 (br, 1H).

Example 4

2-Phenyl-8-vinyl-quinoline-4-ol

A suspension of 500 mg (1.67 mmol) 8-bromo-2-phenyl-quinoline-4-ol (commercially available from Ubichem Research Ltd, Budapest, Hungary), 97 mg (0.09 mmol) $Pd(PPh_3)_4$, 71 mg (1.67 mmol) lithium chloride and 528 mg (1.67 mmol) tributylvinyl stannane in 20 ml dioxane was heated at 90°C for 16 h. The resulting yellow suspension was filtered and the filtrate evaporated to dryness. The residue was suspended in ethyl acetate, filtered and the filtrate extracted with water. The organic layer was evaporated to dryness and the isolated crude product purified by silica gel chromatography (ethyl acetate) to yield 178 mg (43%) of the title compound as yellowish crystals. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.59 (d, J=11.1Hz, 1H); 5.75 (d, J=17.4Hz, 1H); 6.42(s, 1H); 7.04 (dd, J=17.4, 11.1Hz, 1H); 7.23 (t, J=8.1Hz, 1H); 7.40-7.60 (m, 6H); 8.21 (d, J=8.1Hz, 1H); 8.70 (br, 1H).

Example 5

[$RuCl_2$(ImH_2Mes)((4-hydroxy-2-phenyl-8-quinolinyl)methylene)]

A suspension of 100 mg (0.12 mmol) of [$RuCl_2(PCy_3)(ImH_2Mes)$(phenylmethylene)], 12 mg (0.12 mmol) copper chloride and 100 mg (0.12 mmol) 2-phenyl-8-vinyl-quinoline-4-ol in 11 ml methylene chloride was stirred at 40°C for 1 h. The reaction mixture was evaporated to dryness and the isolated crude product purified by silica gel chromatography (hexane / ethyl acetat 2:1) to yield 51 mg (61%) of the title compound as green crystals. MS: 711.1 (M^+). ^{1}H-NMR (300 MHz, CD_2Cl_2): 2.32 (s, 12H); 2.41 (s, 6H); 3.90 (s, 4H); 6.12-6.28 (br, 1H); 6.80-6.92 (m, 2H); 6.98 (s, 4H); 7.04-7.14 (m, 1H); 7.19 (t, J=7.1Hz, 1H); 7.29 (d, J=6.9Hz, 1H); 7.35 (d, J=7.5Hz, 2H); 7.49 (d, J=7.1Hz, 1H); 7.80-8.00 (br, 1H); 17.34 (s, 1H).

Example 6

4-Chloro-8-vinyl-quinoline

A suspension of 975 mg (4.02 mmol) 8-bromo-4-chloroquinoline (commercially available from Ubichem Research Ltd, Budapest, Hungary), 166 mg (0.20 mmol)

$PdCl_2dppf{\cdot}CH_2Cl_2$, 833 mg (6.00 mmol) potassium vinyl tetrafluoroborate and 0.57 ml (4.10 mmol) triethylamine in 20 ml ethanol was heated at reflux for 3 h. The resulting yellow suspension was filtered and the filtrate evaporated to dryness. The residue was suspended in ethyl acetate, filtered and the filtrate extracted with water. The organic layer was evaporated to dryness and the isolated crude product purified by silica gel chromatography (hexane / ethyl acetate 9:1) to yield 207 mg (27%) of the title compound as white crystals. MS: 189.1 (M^+). ^{1}H-NMR (300 MHz, $CDCl_3$): 5.53 (d, J=11.1Hz, 1H); 5.95 (d, J=17.7Hz, 1H); 7.51 (d, J=4.6Hz. 1H); 7.63 (t, J=7.9Hz, 1H); 7.96 (dd, J=17.7, 11.1 Hz, 1H); 7.97 (d, J=7.1Hz, 1H); 8.19 (d, J=8.5Hz, 1H); 8.80 (d, J=4.6 Hz, 1H).

Example 7 (for comparison)

[$RuCl_2$(ImH_2Mes)((4-chloro-8-quinolinyl)methylene)]

A suspension of 790 mg (0.93 mmol) of [$RuCl_2(PCy_3)(ImH_2Mes)$(phenylmethylene)], 95 mg (0.96 mmol) copper chloride and 196 mg (1.03 mmol) 4-chloro-8-vinyl-quinoline in 70 ml methylene chloride was stirred at 30°C for 90 min. The reaction mixture was evaporated to dryness and the isolated crude product purified by silica gel chromatography (hexane / ethyl acetat 5:2) and finally digested in 20 ml pentane at room temperature for 30 min to yield 311 mg (51%) of the title compound as green crystals. MS: 655.0 (M^+). ^{1}H-NMR (300 MHz, CD_2Cl_2): 2.35 (s, 6H); 2.39 (s, 12H); 4.04 (s, 4H); 7.00 (s, 4H); 7.25 (d, J=5.3Hz, 1H); 7.43 (dd, J=8.2, 7.3Hz, 1H); 7.56 (dd, J=7.1, 0.7Hz, 1H); 8.13 (d, J=5.3Hz, 1H); 8.41 (dd, J=8.2, 0.7Hz, 1H); 16.95 (s, 1H). Anal. calcd. for $C_{31}H_{32}N_3Cl_3Ru$: C, 56.93; H, 4.93; N, 6.42; Cl, 16.26. Found: C, 56.59; H, 5.04; N, 6.02; Cl, 15.49.

Example 8

2-Methyl-8-vinyl-quinoline

A suspension of 4.80 g (21.60 mmol) 8-bromo-2-methylquinoline (commercially available from ACB Block Ltd, Moscow, Russia), 0.89 g (1.10 mmol) $PdCl_2dppf{\cdot}CH_2Cl_2$, 4.48 g (32.40 mmol) potassium vinyl tetrafluoroborate and 3.10 ml (22.10 mmol) triethylamine in 150 ml ethanol was heated at reflux for 3 h. The resulting yellow suspension was filtered and the filtrate evaporated to dryness. The residue was suspended in ethyl acetate, filtered and the filtrate extracted with water. The organic layer was evaporated to dryness and the isolated crude product purified by silica gel chromatography (CH_2Cl_2 / ethyl acetate 98:2) to yield 2.68 g (73%) of the title compound as a colorless oil. MS: 169.1 (M^+). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.74 (s, 1H); 5.47 (dd, J=11.1, 1.6Hz, 1H); 5.97 (dd, 17.9, 1.6 Hz, 1H); 7.24 (d, J=8.4Hz, 1H); 7.43 (t, J=7.7Hz,

1H); 7.66 (dd, J=8.1,1.2Hz, 1H); 7.87 (dd, J=7.3, 1.2Hz, 1H); 7.97 (d, J=8.4Hz, 1H); 8.05 (dd, J=17.9, 11.1Hz, 1H).

Example 9

[$RuCl_2$(ImH_2Mes)((2-methyl-8-quinolinyl)methylene)]

A suspension of 218 mg (0.26 mmol) of [$RuCl_2(PCy_3)$(ImH_2Mes)(phenylmethylene)], 26 mg (0.26 mmol) copper chloride and 49 mg (0.29 mmol) 2-methyl-8-vinyl-quinoline in 17 ml methylene chloride was stirred at 30°C for 90 min. The reaction mixture was evaporated to dryness and the isolated crude product purified by silica gel chromatography (hexane / ethyl acetat 7:3) and finally digested in 15 ml hexane at room temperature for 30 min to yield 157 mg (96%) of the title compound as green crystals. MS: 632.9 (M^+). ^{1}H-NMR (300 MHz, C_6D_6): 2.15 (s, 3H); 2.29 (s, 6H); 2.64 (s, 12H); 3.49 (s, 4H); 6.30 (d, J=8.4Hz, 1H); 6.80 (t, J=7.3Hz, 1H); 6.98 (s, 4H); 7.10 (d, J=8.4Hz, 1H); 7.40 (d, J=8.1Hz, 1H); 7.52 (d, J=7.0Hz, 1H), 17.15-17.32 (br, 1H). Anal. calcd. for $C_{32}H_{35}N_3Cl_2Ru$: C, 60.66; H, 5.57; N, 6.63; Cl, 11.19. Found: C, 60.33; H, 5.58; N, 6.27; Cl, 10.90.

Example 10

[$RuCl_2$(tricyclohexylphosphine)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)]

A suspension of 3.07 g (3.73 mmol) of [$RuCl_2(PCy_3)_2$(phenylmethylene)] (commercial available from Sigma-Aldrich Inc., St. Louis, USA), 380 mg (3.84 mmol) copper chloride and 1.06 g (4.10 mmol) 4-chloro-2-trifluoromethyl-8-vinyl-quinoline in 135 ml methylene chloride was stirred at 30°C for 90 min. The reaction mixture was evaporated to dryness and the isolated crude product purified by silica gel chromatography (hexane / ethyl acetat 2:1) and finally digested in 50 ml pentane at room temperature for 30 min to yield 429 mg (17%) of the title compound as dark green crystals. MS: 697.0 (M^+). ^{31}P-NMR (121 MHz, C_6D_6): 54.2 ppm. ^{1}H-NMR (300 MHz, C_6D_6): 1.18-2.35 (m, 30H); 2.60 (q, J=12.0Hz, 3H); 6.82 (t, J=6.0Hz, 1H); 7.01 (d, J=3.0Hz, 1H); 7.55 (d, J= 6.0Hz, 1H); 7.89 (d, J=6.0Hz, 1H); 17.80-17.90 (m, 1H).

Example 11

[$RuCl_2$(ImMes)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)]

A suspension of 1.30 g (1.54 mmol) of [$RuCl_2(PCy_3)$(ImMes)(phenylmethylene)] (prepared according to J. Huang, E. Stevens, S. Nolan, J. Petersen, *J. Am. Chem. Soc.* 1999, *121*, 2674-2678), 0.15 g (1.54 mmol) copper chloride and 435 mg (1.68 mmol) 4-chloro-

2-trifluoromethyl-8-vinyl-quinoline in 100 ml methylene chloride was stirred at 30°C for 90 min. The reaction mixture was evaporated to dryness and the isolated crude product purified by silica gel chromatography (hexane / ethyl acetate 5:2) to yield 260 mg (24%) of the title compound as orange crystals. MS: 719.0 (M^+). ^{1}H-NMR (300 MHz, C_6D_6): 2.33 (s, 6H); 2.46 (s, 12H); 6.30 (s, 2H); 6.76 (dd, J=9.0, 6.0Hz, 1H); 6.83 (s, 1H); 6.97 (s, 4H); 7.58 (d, J=6.0Hz, 1H); 7.85 (d, J=9.0Hz, 1H); 17.31-17.36 (m, 1H).

Application of Catalysts in Ring Closing Metathesis: Examples 12-18

Example 12

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole

A solution of 257 mg (1.02 mmol) *N*,*N*-diallyl 4-methylbenzenesulfonamide (prepared according to S. Varray, R. Lazaro., J. Matinez, F. Lamaty, *Organometallics* 2003, *22*, 2426-2435) and 19 mg (0.03 mmol) [$RuCl_2$(ImH_2Mes)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] in 5 ml toluene was stirred at 110°C. To monitor the conversion and selectivity, 0.2-ml samples were taken were after 1 h and 4 h. Each sample was filtered over a silica gel pad, the filtrate was evaporated to dryness and analyzed by GC (column: DB-1701; injector: 260°C; detector: 260°; oven: 70 to 250°C / 5°C per min; carrier gas: H_2 (60 kPa); retention times: 15.5 min *N*,*N*-diallyl 4-methylbenzenesulfonamide, 24.5 min 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole, 25.5 min 1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole). After 1 h (98% conversion), 96 % of the title compound and 2 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole and after 4 h (100% conversion) 92% of the title compound and 8% of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole were formed. ^{1}H-NMR of 1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole (300 MHz, C_6D_6): 2.43 (s, 3H); 4.12 (s, 4H); 5.65 (s, 2H); 7.32 (d, J=8.3Hz, 2H); 7.73 (d, J=8.3Hz, 2H). ^{1}H-NMR of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole (300 MHz, C_6D_6): 2.40-2.55 (m, 2H); 2.43 (s, 3H); 3.48 (t, J=8.9Hz, 2H); 5.10-5.15 (m, 1H); 8.35-8.40 (m, 1H); 7.32 (d, J=8.3Hz, 2H); 7.67 (d, J=8.3Hz, 2H).

Example 13 (for comparison)

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole

In an analogous manner to Example 12 but in the presence of 17 mg (0.03 mmol) [$RuCl_2$(ImH_2Mes)((4-chloro-8-quinolinyl)methylene)] instead of [$RuCl_2$(ImH_2Mes)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] as catalyst, after 1 h (7% conversion), 7 % of the title compound and after 4 h (15% conversion), 14% of the title compound and 1 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole were formed.

Example 14 (for comparison)

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole

a) In an analogous manner to Example 12 but in the presence of 16 mg (0.03 mmol) [$RuCl_2(ImH_2Mes)$(8-quinolinylmethylene)] instead of [$RuCl_2(ImH_2Mes)$((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] as catalyst, after 1 h (7% conversion), 7 % of the title compound and after 4 h (31% conversion), 28% of the title compound and 3 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole were formed.

b) According to Barbasiewicz et al. (*Organometallics*, published on Web June 17, 2006), a solution of 88 mg (0.35 mmol) *N*,*N*-diallyl 4-methylbenzenesulfonamide and 11.2 mg (0.018 mmol) [$RuCl_2(ImH_2Mes)$(8-quinolinylmethylene)] in 17.5 ml dichloromethane was stirred at room temperature. To monitor the conversion and selectivity, 0.2-ml samples were taken were after 4 h and 24 h. Each sample was filtered over a silica gel pad, the filtrate was evaporated to dryness and analyzed by GC as described in Example 12. After 4 h (2% conversion), 0.6 % of the title compound and 0.3 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole and after 24 h (3% conversion) 1.5% of the title compound and 0.5% of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole were formed.

Example 15

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole

In an analogous manner to Example 12 but in the presence of 18 mg (0.03 mmol) [$RuCl_2(ImH_2Mes)$((4-hydroxy-2-phenyl-8-quinolinyl)methylene)] instead of [$RuCl_2(ImH_2Mes)$((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] as catalyst, after 1 h (99% conversion) 98 % of the title compound and 1 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole and after 4 h (100% conversion), 99 % of the title compound and 1 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole were formed.

Example 16

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole

In an analogous manner to Example 12 but in the presence of 18 mg (0.03 mmol) [$RuCl_2(ImH_2Mes)$((2-methyl-8-quinolinyl)methylene)] instead of [$RuCl_2(ImH_2Mes)$((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] as catalyst, after 1 h (22%

conversion) 11 % of the title compound and after 4 h (66% conversion), 22 % of the title compound and 5 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole were formed.

Example 17

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole

In an analogous manner to Example 12 but in the presence of 16 mg (0.03 mmol) [$RuCl_2$(tricyclohexylphosphine)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] instead of [$RuCl_2$(ImH_2Mes)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] as catalyst, after 1 h (11% conversion) 7 % of the title compound and 1 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole and after 4 h (42% conversion), 25 % of the title compound and 1 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole were formed.

Example 18

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole

In an analogous manner to Example 12 but in the presence of 20 mg (0.03 mmol) [$RuCl_2$(ImMes)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] instead of [$RuCl_2$(ImH_2Mes)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] as catalyst, after 1 h (53% conversion) 11 % of the title compound and 11 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole, after 4 h (100% conversion), 54 % of the title compound and 2 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole and after 20 h (100% conversion), 1 % of the title compound and 64 % of 1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrole were formed.

Application of Catalysts in Cross Metathesis: Examples 19-20

Example 19

(*E*)/(*Z*)-Diethyl 2-[3-cyano-2-propenyl]malonate

A solution of 100.0 mg (0.48 mmol) diethyl allylmalonate, 77.4 mg (1.45 mmol) acrylonitrile and 35.0 mg (0.05 mmol) [$RuCl_2$(ImH_2Mes)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] in 5 ml toluene was stirred at 110°C. To monitor the conversion and selectivity, 0.05-ml samples were taken were taken after 3h and 40 h. Each sample was filtered over a silica gel pad, the filtrate was evaporated to dryness and analyzed by GC (column: HP-5, 5% phenyl methyl siloxan (Agilent™ 19091-413); injector: 250°C; detector: 250°C; oven: 100 to 150°C / 5°C per min, 5 min at 150°C, 150 to 200°C / 5°C per min and 200 to 300°C / 20°C per min; carrier gas: He (0.46 bar); retention times: 9.2 min diethyl allylmalonate, 17.5 min (*Z*)-diethyl 2-[3-cyano-2-propenyl]malonate and 18.8 min (*E*)-

diethyl 2-[3-cyano-2-propenyl]malonate). After 3 h (66% conversion), 57 % of the title compound and after 40 h (94% conversion) 83% of the title compound as an (*E*):(*Z*) mixture of 1:2 was formed. After evaporation of the solvent under reduced pressure, the crude product was purified by silica gel chromatography (cyclohexane / ethyl acetate 8:2) to yield 65.1 mg (60%) of the title compound as a (*E*):(*Z*) mixture of 1:2. MS: 226.3 (M^+). ^{1}H-NMR of diethyl 2-[3-cyano-2-propenyl]malonate (300 MHz, C_6D_6): (*Z*)-isomer: 1.29 (t, J=7.1Hz, 6H); 2.99 (td, J=7.1, 1.5Hz, 2H); 3.51 (t, J=7.0 Hz, 1H); 4.20-4.24 (m, 4H); 5.40-5.42 (m, 1H); 6.54 (m, 1H). (*E*)-isomer: 1.28 (t, J=7.1Hz, 6H); 2.79 (td, J=7.1, 1.5Hz, 2H); 3.46 (t, J=7.1 Hz, 1H); 4.20-4.24 (m, 4H); 5.40-5.42 (m, 1H); 6.68 (m,1H).

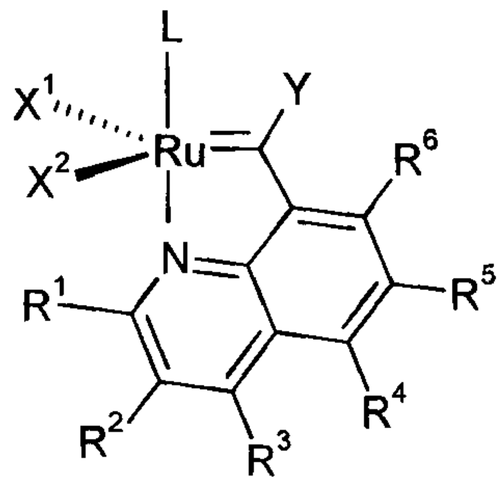
Example 20

(*E*)/(*Z*)-Diethyl 2-[3-cyano-2-propenyl]malonate

In an analogous manner to Example 19 but in the presence of 34.9 mg (0.05 mmol) [$RuCl_2$(ImMes)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] instead of [$RuCl_2$(ImH_2Mes)((4-chloro-2-trifluoromethyl-8-quinolinyl)methylene)] as catalyst, after 19 h (80% conversion), 48 % of the title compound and after 40 h (87% conversion) 49% of the title compound as an (*E*):(*Z*) mixture of 1:2 was formed.

Claims

1. A compound of the formula I



I

wherein L is a neutral ligand;

X^1 and X^2 independently of each other are anionic ligands;

R^1 is C_{1-6}-alkyl, halogen-C_{1-6}-alkyl, C_{1-6}-alkoxy, C_{1-6}-alkylcarbonyl, aryl, hydroxy, aryloxy, nitro, amino, mono-C_{1-6}-alkylamino, di-C_{1-6}-alkylamino, halogen, thio, C_{1-6}-alkylthio, SO_2-C_{1-6}-alkyl, SO_2-aryl, SO_3H, SO_3-C_{1-6}-alkyl, $OSi(C_{1-6}\text{-alkyl})_3$ or SO_2-N R'R'', wherein R' and R'' independently of each other have the meaning of hydrogen or C_{1-6}-alkyl, or R' and R'' together with the N atom form a carbocycle;

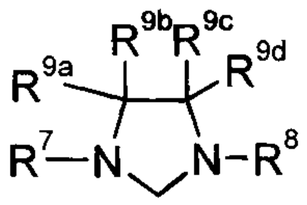
R^2, R^3, R^4, R^5 and R^6 independently of each other have the meaning of hydrogen, C_{1-6}-alkyl, halogen-C_{1-6}-alkyl, C_{1-6}-alkoxy, C_{1-6}-alkylcarbonyl, aryl, hydroxy, aryloxy, nitro, amino, mono-C_{1-6}-alkylamino, di-C_{1-6}-alkylamino, halogen, thio, C_{1-6}-alkylthio, SO_2-C_{1-6}-alkyl, SO_2-aryl, SO_3H, SO_3-C_{1-6}-alkyl, $OSi(C_{1-6}\text{-alkyl})_3$, or SO_2-N R'R'', wherein R' and R'' independently of each other have the meaning of hydrogen or C_{1-6}-alkyl, or R' and R'' together with the N atom form a carbocycle; and

Y is hydrogen, C_{1-6}-alkyl, C_{2-6}- alkenyl or aryl, or Y and R^6 taken together to form a (CH=CR) - or a -$(CH_2)_n$- bridge with n having the meaning of 2 or 3 and R is as defined for R^2.

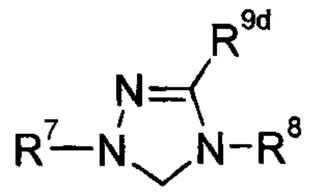
2. A compound according to claim 1 wherein

L is a neutral ligand represented by

$-P(R^{10})_3$;

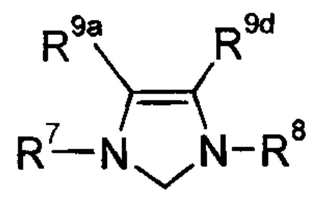


IIa



IIb

; or



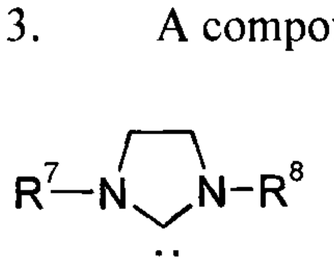
IIc

wherein R^7 and R^8 independently of each other are C_{1-6}-alkyl, aryl, C_{2-6}-alkenyl or 1-adamantyl; and

R^{9a-d} are independently of each other hydrogen, C_{1-6}-alkyl, C_{2-6}- alkenyl or aryl, or R^{9b} and R^{9c} or R^{9a} and R^{9d} taken together form a $-(CH_2)_4$-bridge;

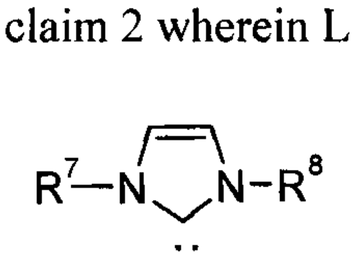
R^{10} is independently of each other C_{1-6}-alkyl, C_{3-7}-cycloalkyl, aryl or heteroaryl.

3. A compound according to claim 2 wherein L is represented by



IId

or



IIe

wherein R^7 and R^8 are as defined in claim 2.

4. A compound according to claim 2 or 3 wherein R^7 and R^8 are 2, 4, 6-trimethylphenyl.

5. A compound according to any one of claims 1 to 4 wherein X^1 and X^2 independently of each other are a halogen.

6. A compound according to claim 5 wherein X^1 and X^2 are chloro.

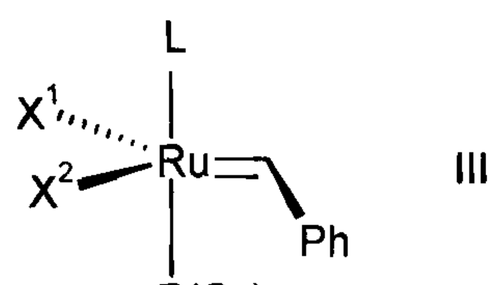
7. A compound according to any one of claims 1 to 6 wherein R^1 is C_{1-6}-alkyl, halogen C_{1-6}-alkyl or aryl.

8. A compound according to claim 7 wherein R^1 is methyl, trifluoromethyl, ortho-tolyl, 2,6-dimethylphenyl or phenyl.

9. A compound according to any one of claims 1 to 8 wherein R^3 is hydrogen, hydroxy, C_{1-6}-alkoxy, nitro, amino or halogen.

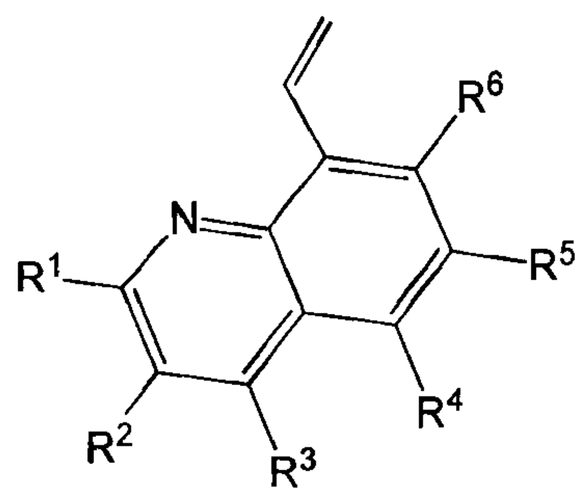
10. A compound according to any one of claims 1 to 9 wherein R^2, R^4, R^5 and R^6 are hydrogen.

11. A process for the preparation of a compound of the formula I according to any one of claims 1 to 10 which comprises the transformation of a Ru-precursor compound of the formula



III

wherein X^1 and X^2 are as defined in claim 1, Cy has the meaning of cyclohexyl and Ph is phenyl with a compound of formula IV



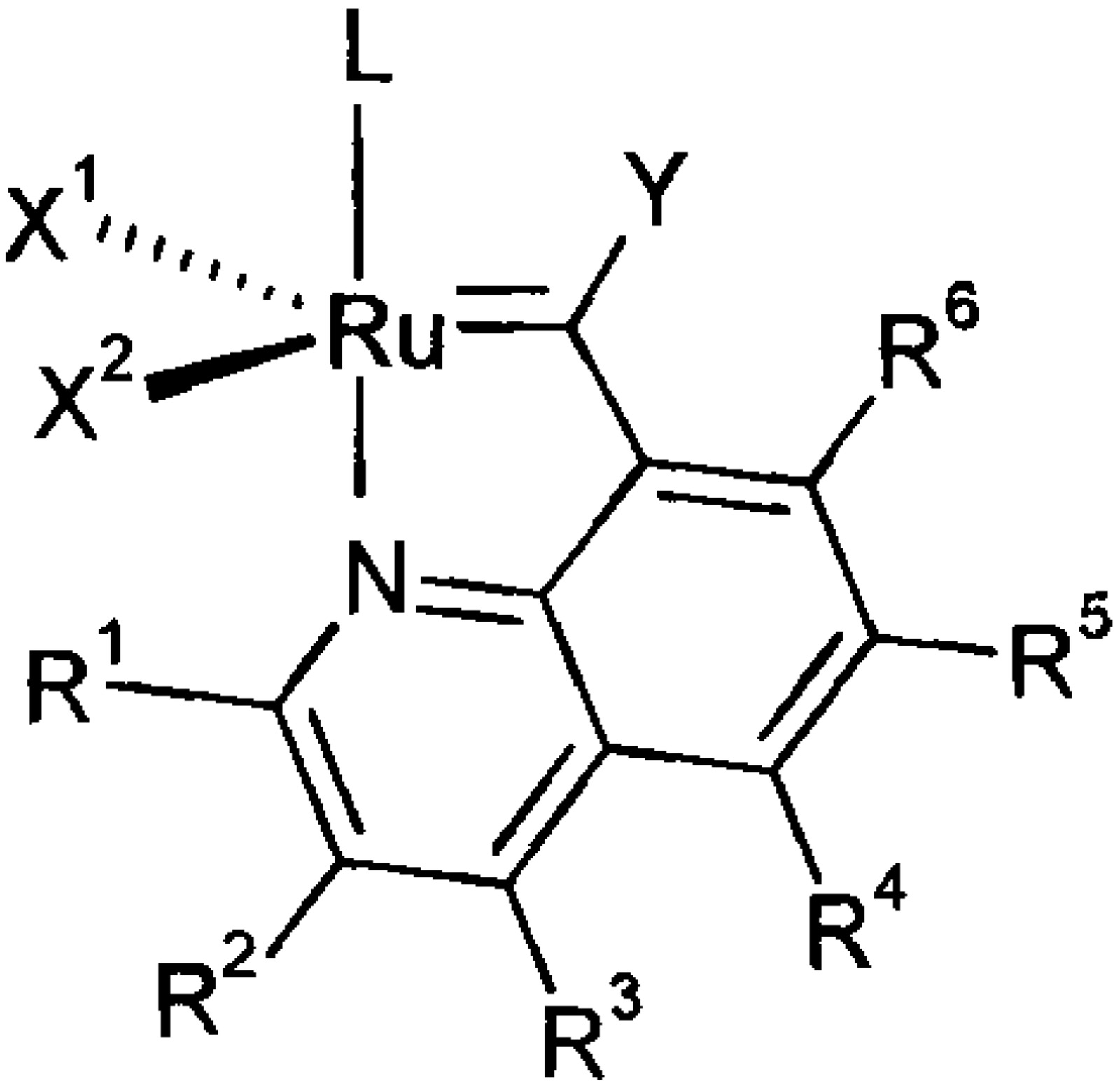
IV

wherein R^1 to R^6 are as defined in claim 1.

12. The use of a compound of the formula I according to any one of claims 1 to 10 in metathesis reactions.

13. The use of a compound of the formula I according to claim 12, in ring closing metathesis reactions.

14. The use of a compound of the formula I according to claim 12, in cross metathesis reactions.



I