(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 December 2012 (13.12.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/168183 A1

(51) International Patent Classification:
B01J 31/22 (2006.01)

(21) International Application Number:
PCT/EP2012/060498

(22) International Filing Date:
4 June 2012 (04.06.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
P.395131 6 June 2011 (06.06.2011) PL

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

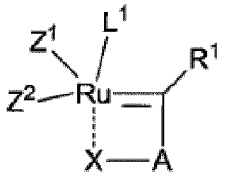
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2012/168183 A1

(54) **Title**: NEW COMPLEXES OF RUTHENIUM, METHOD FOR THEIR PREPARATION, AND THEIR APPLICATION IN OLEFIN METATHESIS REACTIONS



(I)

(57) **Abstract**: The present invention provides new ruthenium complexes of Formula (1), which contain a chelate ring created by a halogen atom X. The invention concerns also a method for the preparation of the new ruthenium complexes and their application in metathesis reactions.

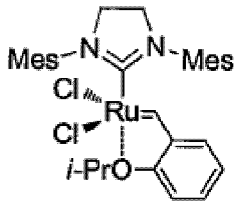
NEW COMPLEXES OF RUTHENIUM, METHOD FOR THEIR PREPARATION, AND THEIR APPLICATION IN OLEFIN METATHESIS REACTIONS

The invention concerns new ruthenium complexes which act as (pre)catalysts, a method for their preparation, and their application in olefin metathesis reactions. This invention is used in organic synthesis in a broad sense.

In applications of olefin metathesis in organic synthesis, significant progress has been made in recent years. In the state of the art, a number of carbene complexes of ruthenium are known which act as (pre)catalysts and which display both high activity in various types of metathesis reaction and broad tolerance of functional groups. The above combination of properties makes this type of (pre)catalyst suitable in organic synthesis.

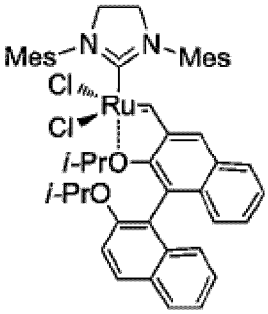
From the point of view of practical application, particularly on an industrial scale, it is highly desirable for such ruthenium complexes to be stable over a long period at an elevated temperature and to be stored and/or purified and/or used without a protective gas atmosphere.

Complexes of ruthenium with such properties are already known (see: J. Am. Chem. Soc. 2000, 122, 8168-8179; Tetrahedron Lett. 2000, 41, 9973-9976), although it has turned out that better stability is linked with reduced catalytic activity. This type of limitation was found in the case of the (pre)catalyst with formula **2**, in which Mes denotes 2,4,6-trimethylphenyl (for a comparison of catalytic activity, see Angew. Chem. Int. Ed. 2002, 114, 832-834).

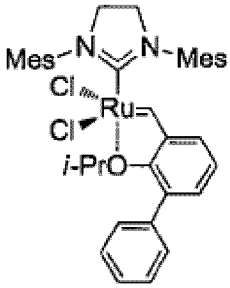


Formula **2**

Then, (pre)catalysts are described with formulae **3** and **4**, which show higher catalytic activity in comparison with the (pre)catalyst of formula **2**.



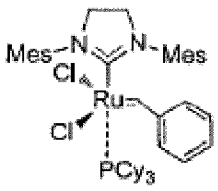
Formula **3**



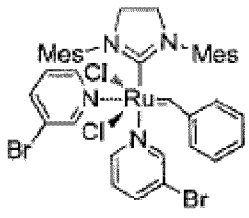
Formula **4**

Catalysts **2**, **3**, and **4** contain an isopropoxyl group which chelates an atom of the metal. The higher activity of arrangements **3** and **4** is explained by the spatial hindrance introduced by the adjacency of the phenyl group or (substituted) naphthyl group in the *ortho* position in relation to the isopropoxyl group (see Angew. Chemie Int. Ed. 2002, 114, 832-834; Angew. Chemie Int. Ed. 2002, 114, 2509-2511).

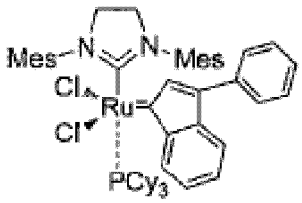
Then, other catalysts are also described with formulae **5a**, **5b**, **6a**, and **6b**, in which Cy denotes cyclohexyl.



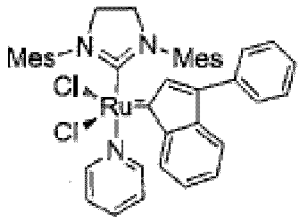
Formula **5a**



Formula **5b**

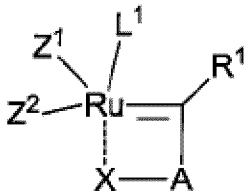


Formula **6a**



Formula **6b**

Unexpectedly, it was found that new complexes of ruthenium in accordance with the invention presented in formula **1**:



Formula **1**

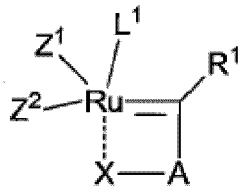
which contain a chelate ring created by a halogen atom are thermally stable and display good catalytic activity. In addition, these compounds display significant changes in activity as a function of temperature, which may be applied to control catalytic processes by changing the temperature of a reaction mixture. Known catalytic arrangements have not shown significant changes in catalytic activity as a function of temperature.

Complexes with formula **1**, in accordance with the invention, are applied broadly. With a good result, numerous reactions can be carried out consisting not only in ring-closing metathesis but also in homometathesis, cross metathesis and metathesis of the alkene-alkyne (ene-yne) type, and ring-opening metathesis polymerisation (ROMP).

Thus, the synthesis of compounds that contain the double C=C bond and other functional groups, when the new catalysts in accordance with the invention are applied, proceeds with a very good result.

When such new complexes are applied in accordance with the invention as (pre)catalysts, the temperature of the reaction can be increased and/or, at the same time, the duration of the reaction can be increased in comparison with those conditions necessary when other known catalysts are used. In this way, there is an improvement both in yield and in the technical opportunity for carrying out the reaction.

One of the objects of the present invention is to provide new complexes of ruthenium with formula **1**:



Formula **1**

in which:

L^1 denotes an inert ligand;

Z^1 and Z^2 denote, independently, an anion ligand;

X denotes a halogen atom;

R^1 denotes an atom of hydrogen, a halogen atom, C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_2-C_{12} alkenyl, C_3-C_{12} cycloalkenyl C_2-C_{12} alkynyl, C_3-C_{12} cycloalkynyl, C_1-C_{12} alkoxyl, C_5-C_{20} aryl, C_5-C_{20} heteroaryl, or 3-12-membered heterocycle;

A denotes a bivalent radical selected from a group comprising C_1-C_{12} alkylene, C_2-C_{12} alkenylene, C_2-C_{12} alkynylene, C_5-C_{20} arylene, or C_5-C_{20} heteroarylene, in which the C_1-C_{12} alkylene, the C_2-C_{12} alkenylene, the C_2-C_{12} alkynylene, the C_5-C_{20} arylene, and the C_5-C_{20} heteroarylene may be optionally substituted with at least one functional group R^2;

each R^2 functional group denotes, independently, a halogen atom, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_2-C_{12} alkynyl, $-OR^3$, $-SR^3$, $-S(O)_mR^3$, $-SO_2NR^3R^4$, $-S(O)_2OR^3$, $-NO_2$, $-NO$, $-SCN$, $-NR^3R^4$, $-CN$, $-C(O)R^3$, $-OC(O)R^3$, $-O(CR^3R^4)_nR^5$, $-$

$NR^3C(O)R^4$, $-(CR^3R^4)_nC(O)OR^5$, $-(CR^3R^4)_nOR^5$, $-C(=NR^3)NR^4R^5$, $-NR^3C(O)NR^4R^5$, $-NR^3S(O)_pR^4$, $-NC(=O)R^3C(=O)R^4$, $-NR^3P(=O)R^4R^5$, $-NR^3As(=O)R^4R^5$, $-PR^3R^4$, $-POR^3R^4$, $-POR^3OR^4$, $-P(=O)R^3R^4$, $-P(=O)OR^3R^4$, $-P(=O)OR^3OR^4$, $-AsR^3R^4$, $-AsOR^3R^4$, $-AsOR^3OR^4$, $-As(=O)R^3R^4$, $-As(=O)OR^3R^4$, $-As(=O)OR^3OR^4$, $-NR^3-C(=NR^4)NR^5R^6$, $-C(=O)R^3$, $-C(=O)OR^3$, $-C(=S)OR^3$, $-C(=O)SR^3$, $-C(=S)SR^3$, $-C(=S)NR^3R^4$, $-SiR^3R^4R^5$, $-SiOR^3R^4R^5$, $-SiOR^3OR^4R^5$, $-SiOR^3OR^4OR^5$, $-(CR^3R^4)_n$(3-12-membered heterocycle), $-(CR^3R^4)_n$(C_3-C_{12} cycloalkyl), $-(CR^3R^4)_n$(C_5-C_{20} aryl), $-(CR^3R^4)_n$(5-12-membered heteroaryl), $-(CR^3R^4)_nC(O)NR^5R^6$, or $-(CR^3R^4)_nC(O)R^5$;

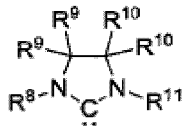
and/or R^2 groups with adjacent atoms may bond together, creating C_5-C_{20} aryl or 3-12-membered heterocycle;

and/or R^2 groups with adjacent atoms may bond with the R^1 group, creating C_5-C_{20} aryl, indenylene, heteroindenylene, 3-12-membered heterocycle, and polycyclic or heteropolycyclic arrangements, whilst the C_5-C_{20} aryl, indenylene, heteroindenylene, 3-12-membered heterocycle, and polycyclic or heteropolycyclic arrangements may be substituted with at least one functional group selected from the group comprising a halogen atom, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_2-C_{12} alkynyl, $-OR^3$, $-SR^3$, $-S(O)_mR^3$, $-SO_2NR^3R^4$, $-S(O)_2OR^3$, $-NO_2$, $-NO$, $-SCN$, $-NR^3R^4$, $-CN$, $-C(O)R^3$, $-OC(O)R^3$, $-O(CR^3R^4)_nR^5$, $-NR^3C(O)R^4$, $-(CR^3R^4)_nC(O)OR^5$, $-(CR^3R^4)_nOR^5$, $-C(=NR^3)NR^4R^5$, $-NR^3C(O)NR^4R^5$, $-NR^3S(O)_pR^4$, $-NC(=O)R^3C(=O)R^4$, $-NR^3P(=O)R^4R^5$, $-NR^3As(=O)R^4R^5$, $-PR^3R^4$, $-POR^3R^4$, $-POR^3OR^4$, $-P(=O)R^3R^4$, $-P(=O)OR^3R^4$, $-P(=O)OR^3OR^4$, $-AsR^3R^4$, $-AsOR^3R^4$, $-AsOR^3OR^4$, $-As(=O)R^3R^4$, $-As(=O)OR^3R^4$, $-As(=O)OR^3OR^4$, $-NR^3-C(=NR^4)NR^5R^6$, $-C(=O)R^3$, $-C(=O)OR^3$, $-C(=S)OR^3$, $-C(=O)SR^3$, $-C(=S)SR^3$, $-C(=S)NR^3R^4$, $-SiR^3R^4R^5$, $-SiOR^3R^4R^5$, $-SiOR^3OR^4R^5$, $-SiOR^3OR^4OR^5$, $-(CR^3R^4)_n$(3-12-membered heterocycle), $-(CR^3R^4)_n$(C_3-C_{12} cycloalkyl), $-(CR^3R^4)_n$(C_5-C_{20} aryl), $-(CR^3R^4)_n$(5-12-membered heteroaryl), $-(CR^3R^4)_nC(O)NR^5R^6$, or $-(CR^3R^4)_nC(O)R^5$;

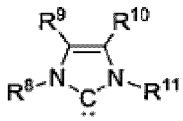
each functional group R^3, R^4, R^5, and R^6 denotes, independently, an atom of hydrogen, a halogen atom, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_2-C_{12} alkynyl, C_3-C_{12} cycloalkyl, C_5-C_{20} aryl, 5-12-membered heterocycle;

each m denotes, independently, 0, 1, or 2;
each n denotes, independently, 0, 1, 2, 3, or 4;
each p denotes, independently, 1 or 2.

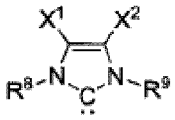
In one embodiment of the invention, R^1 in formula **1** denotes an atom of hydrogen, whilst
anion ligands Z^1 and Z^2 denote, independently, a halogen atom, the group -CN, -SCN, $-OR^{13}$, $-SR^{13}$, $-O(C=O)R^{13}$, $-O(SO_2)R^{13}$, $-OSiR_3{}^{13}$, where R^{13} denotes C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_2-C_{12} alkenyl, or C_5-C_{20} aryl, which may be optionally substituted with at least one C_1-C_{12} alkyl, C_1-C_{12} perhalogenalkyl, C_1-C_{12} alkoxyl, or a halogen atom; and
the inert ligand L^1 is selected from a group comprising $-P(R^7)_3$, $-P(OR^7)_3$, or an N-heterocyclic carbene ligand with formula **7a**, **7b**, **7c**, **7d**, **7e**, **7f**, **7g**, **7h**, **7i**, **7j**, **7k**, **7l**, **7m**, **7n**, **7o**, or **7p**:



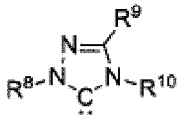
Formula **7a**



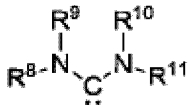
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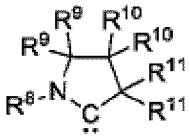
Formula **7c**



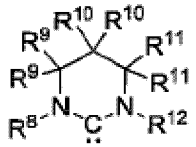
Formula **7d**



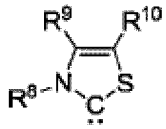
Formula **7e**



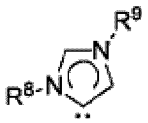
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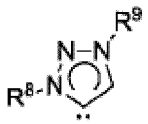
Formula **7g**



Formula **7h**



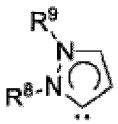
Formula **7i**



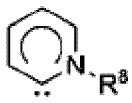
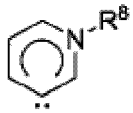
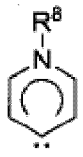
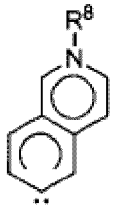
Formula **7j**



Formula **7k**



Formula **7l**

Formula **7m** Formula **7n** Formula **7o** Formula **7p**

where:

each R^7 denotes, independently, C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_5-C_{20} aryl, or 5-12-membered heteroaryl;

each R^8, R^9, R^{10}, R^{11}, and R^{12} denote, independently, an atom of hydrogen, C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_2-C_{12} alkenyl, or C_5-C_{20} aryl, which may be optionally substituted with at least one C_1-C_{12} alkyl, C_1-C_{12} perhalogenalkyl, C_1-C_{12} alkoxyl, or a halogen atom;

the groups R^8, R^9, R^{10}, R^{11}, and R^{12} may optionally bond with each other and

X^1 and X^2 denote, independently, a halogen atom.

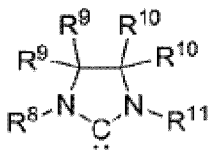
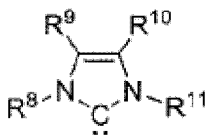
The carbene ligands may be coordinated classically, as in structures **7a-7h**, or non-classically ('abnormal carbenes', see Chem. Rev. 2009, 109, 3445), as in structures **7i-7p**.

In a further embodiment of the invention, the anion ligands Z^1 and Z^2 in formula **1** denote an atom of chlorine; and

X denotes an atom of bromine or iodine; and

A denotes 1,2-phenylene, 1,2-naphthylene, 2,3-naphthylene or 1,8-naphthylene, which may be substituted with at least one functional group selected from a group comprising $-NO_2$, $-NMe_2$; and

the inert ligand L^1 denotes a ligand with formula **7a** or **7b**;

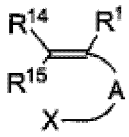



Formula **7a** Formula **7b**

in which the functional groups R^8, R^9, R^{10}, and R^{11} may have the meaning described above.

In a still further embodiment of the invention, the anion ligands Z^1 and Z^2 in formula **1** denote an atom of chlorine; and X denotes an atom of bromine or iodine; and A denotes 1,2-phenylene, 1,2-naphthylene, 2,3-naphthylene or 1,8-naphthylene, which may be substituted with at least one functional group selected from a group comprising –OMe, Me and the inert ligand L^1 denotes a ligand with formula **7a** or **7b** as listed above.

An object of the invention is also to provide a method of preparing ruthenium complexes with formula **1**, which comprises the reaction of the compound of formula **9**



Formula **9**

in which R^{14} and R^{15} denote, independently, an atom of hydrogen or the alkyl group C_1-C_{12};
R^1 denotes hydrogen, a halogen atom, C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_2-C_{12} alkenyl, C_3-C_{12} cycloalkenyl, C_2-C_{12} alkynyl, C_3-C_{12} cycloalkynyl, C_1-C_{12} alkoxyl, C_5-C_{20} aryl, C_5-C_{20} heteroaryl, or 3-12-membered heterocycle;
X denotes a halogen atom;
A denotes a bivalent radical selected from a group comprising C_1-C_{12} alkylene, C_2-C_{12} alkenylene, C_2-C_{12} alkynylene, C_5-C_{20} arylene, or C_5-C_{20} heteroarylene, in which the C_1-C_{12} alkylene, the C_2-C_{12} alkenylene, the C_2-C_{12} alkynylene, the C_5-C_{20} arylene, and the C_5-C_{20} heteroarylene may be optionally substituted with at least one functional group R^2;
each R^2 functional group denotes, independently, a halogen atom, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_2-C_{12} alkynyl, $-OR^3$, $-SR^3$, $-S(O)_mR^3$, $-SO_2NR^3R^4$, $-S(O)_2OR^3$, $-NO_2$, $-NO$, -

SCN, $-NR^3R^4$, -CN, $-C(O)R^3$, $-OC(O)R^3$, $-O(CR^3R^4)_nR^5$, $-NR^3C(O)R^4$, $-(CR^3R^4)_nC(O)OR^5$, $-(CR^3R^4)_nOR^5$, $-C(=NR^3)NR^4R^5$, $-NR^3C(O)NR^4R^5$, $-NR^3S(O)_pR^4$, $-NC(=O)R^3C(=O)R^4$, $-NR^3P(=O)R^4R^5$, $-NR^3As(=O)R^4R^5$, $-PR^3R^4$, $-POR^3R^4$, $-POR^3OR^4$, $-P(=O)R^3R^4$, $-P(=O)OR^3R^4$, $-P(=O)OR^3OR^4$, $-AsR^3R^4$, $-AsOR^3R^4$, $-AsOR^3OR^4$, $-As(=O)R^3R^4$, $-As(=O)OR^3R^4$, $-As(=O)OR^3OR^4$, $-NR^3-C(=NR^4)NR^5R^6$, $-C(=O)R^3$, $-C(=O)OR^3$, $-C(=S)OR^3$, $-C(=O)SR^3$, $-C(=S)SR^3$, $-C(=S)NR^3R^4$, $-SiR^3R^4R^5$, $-SiOR^3R^4R^5$, $-SiOR^3OR^4R^5$, $-SiOR^3OR^4OR^5$, $-(CR^3R^4)_n$(3-12-membered heterocycle), $-(CR^3R^4)_n$(C_3-C_{12} cycloalkyl), $-(CR^3R^4)_n$(C_5-C_{20} aryl), $-(CR^3R^4)_n$(5-12-membered heteroaryl), $-(CR^3R^4)_nC(O)NR^5R^6$, or $-(CR^3R^4)_nC(O)R^5$;

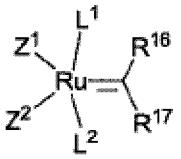
and/or R^2 groups with adjacent atoms may bond together, creating C_5-C_{20} aryl or 3-12-membered heterocycle;

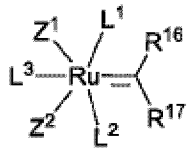
and/or R^2 groups with adjacent atoms may bond with the R^1 group, creating C_5-C_{20} aryl, indenylene, heteroindenylene, 3-12-membered heterocycle, and polycyclic or heteropolycyclic arrangements, whilst the C_5-C_{20} aryl, indenylene, heteroindenylene, 3-12-membered heterocycle, and polycyclic or heteropolycyclic arrangements may be substituted with at least one functional group selected from the group comprising a halogen atom, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_2-C_{12} alkynyl, $-OR^3$, $-SR^3$, $-S(O)_mR^3$, $-SO_2NR^3R^4$, $-S(O)_2OR^3$, $-NO_2$, -NO, -SCN, $-NR^3R^4$, -CN, $-C(O)R^3$, $-OC(O)R^3$, $-O(CR^3R^4)_nR^5$, $-NR^3C(O)R^4$, $-(CR^3R^4)_nC(O)OR^5$, $-(CR^3R^4)_nOR^5$, $-C(=NR^3)NR^4R^5$, $-NR^3C(O)NR^4R^5$, $-NR^3S(O)_pR^4$, $-NC(=O)R^3C(=O)R^4$, $-NR^3P(=O)R^4R^5$, $-NR^3As(=O)R^4R^5$, $-PR^3R^4$, $-POR^3R^4$, $-POR^3OR^4$, $-P(=O)R^3R^4$, $-P(=O)OR^3R^4$, $-P(=O)OR^3OR^4$, $-AsR^3R^4$, $-AsOR^3R^4$, $-AsOR^3OR^4$, $-As(=O)R^3R^4$, $-As(=O)OR^3R^4$, $-As(=O)OR^3OR^4$, $-NR^3-C(=NR^4)NR^5R^6$, $-C(=O)R^3$, $-C(=O)OR^3$, $-C(=S)OR^3$, $-C(=O)SR^3$, $-C(=S)SR^3$, $-C(=S)NR^3R^4$, $-SiR^3R^4R^5$, $-SiOR^3R^4R^5$, $-SiOR^3OR^4R^5$, $-SiOR^3OR^4OR^5$, $-(CR^3R^4)_n$(3-12-membered heterocycle), $-(CR^3R^4)_n$(C_3-C_{12} cycloalkyl), $-(CR^3R^4)_n$(C_5-C_{20} aryl), $-(CR^3R^4)_n$(5-12-membered heteroaryl), $-(CR^3R^4)_nC(O)NR^5R^6$, or $-(CR^3R^4)_nC(O)R^5$;

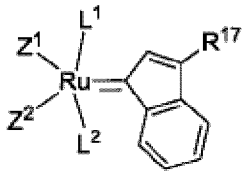
each functional group R^3, R^4, R^5, and R^6 denotes, independently, an atom of hydrogen, a halogen atom, C_1-

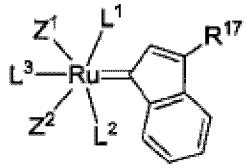
C_{12} alkyl, C_2-C_{12} alkenyl, C_2-C_{12} alkynyl, C_3-C_{12} cycloalkyl, C_5-C_{20} aryl, 5-12-membered heterocycle;
each m denotes, independently, 0, 1, or 2;
each n denotes, independently, 0, 1, 2, 3, or 4;
each p denotes, independently, 1 or 2;

with a ruthenium carbene complex of formula **11a**, **11b**, **11c**, or **11d**:









Formula **11a** Formula **11b** Formula **11c** Formula **11d**

in which
L^1, L^2, and L^3 denote, independently, an inert ligand;
Z^1 and Z^2 denote, independently, an anion ligand;
R^{16} has the same meaning as R^1 in formula **9**;
R^{17} denotes an atom of hydrogen, C_5-C_{20} aryl, C_5-C_{20} heteroaryl, vinyl, or allenyl.

Advantageously, the reaction between the compound of formula **9** and the ruthenium complex of formula **11a**, **11b**, **11c**, or **11d** is carried out in the presence of anhydrous halogen salts of copper(I) such as CuCl or CuBr, or in the presence of Brønsted acids such as H_2SO_4, HCl, HNO_3, H_3PO_4, sulphonated polymers (Nafion-H), or other acids bonded with a fixed substrate, in a solvent.

Advantageously, the reaction is carried out at a temperature in the range of 0-120°C.

Advantageously, the reaction is carried out in a chlorinated solvent or in aromatic hydrocarbons or in protic or aprotic solvents such as alcohol or ketone or in mixtures thereof.

Advantageously, the reaction is carried out in a solvent such as methylene chloride and/or toluene.

The invention also concerns the application and use of the ruthenium complexes defined in formula **1** as (pre)catalysts in metathesis reactions.

Advantageously, ruthenium complexes with formula **1** are used as (pre)catalysts in ring-opening metathesis reactions, homometathesis, cross-metathesis, alkene-alkyne (ene-yne) type metathesis, ring-closing metathesis and ROMP-type polymerisation reactions.

The term *halogen atom* denotes an element selected from F, Cl, Br, and I.

The term *carbene* denotes a molecule containing an inert atom of carbon with a valence number of two and two unpaired valence electrons. The term *carbene* also denotes carbene analogues in which the carbon atom is replaced with another chemical element such as boron, silicon, germanium, tin, lead, nitrogen, phosphorus, sulphur, selenium, and tellurium.

The term *alkyl* relates to a saturated, linear, or branched functional hydrocarbon group with an indicated number of atoms of carbon. Examples of an alkyl functional group are -methyl, -ethyl, -n-propyl, -n-butyl, -n-pentyl, -n-hexyl, -n-heptyl, -n-octyl, -n-nonyl, and -n-decyl. Representative branched -(C_1-C_{10}) alkyls include -iso-propyl, -sec-butyl, -iso-butyl, -tert-butyl, -iso-pentyl, -neopentyl, -1-methylbutyl, -2-methylbutyl, -3-methylbutyl, -1,1-dimethylpropyl, -1,2-dimethylpropyl, -1-methylpentyl, -2-methylpentyl, -3-methylpentyl, -4-methylpentyl, -1-ethylbutyl, -2-ethylbutyl, -3-ethylbutyl, -1,1-dimethylbutyl, -1,2-dimethylbutyl, -1,3-dimethylbutyl, -2,2-dimethylbutyl, -2,3-dimethylbutyl, -3,3-dimethylbutyl, -1-methylhexyl, -2-methylhexyl, -3-methylhexyl, -4-methylhexyl, -5-methylhexyl, -1,2-dimethylpentyl, -1,3-dimethylpentyl, -1,2-dimethylhexyl, -1,3-dimethylhexyl, -3,3-dimethylhexyl, -1,2-dimethylheptyl, -1,3-dimethylheptyl, and -3,3-dimethylheptyl, and similar.

The term *alkoxyl* refers to an alkyl functional group as defined above connected using an oxygen atom.

The term *perfluoroalkyl* denotes an alkyl group as defined above in which all atoms of hydrogen are replaced with the same or different halogen atoms.

The term *cycloalkyl* refers to a saturated monocyclic or polycyclic functional hydrocarbon group with an indicated number of carbon atoms. Examples of a cycloalkyl functional group are -cyclopropyl, -cyclobutyl, -cyclopentyl, -cyclohexyl, -cycloheptyl, -cyclooctyl, -cyclononyl, -cyclodecyl, and similar.

The term *alkenyl* refers to a saturated, linear, or branched non-cyclic functional hydrocarbon group with an indicated number of atoms of carbon and containing at least one double carbon-carbon bond. Examples of an alkenyl functional group are -vinyl, -allyl, 1-butenyl -2-butenyl, -iso-butylenyl, -1-pentenyl, -2-pentenyl, -3-methyl-1-butenyl, -2-methyl-2-butenyl, -2,3-dimethyl-2-butenyl, -1-hexenyl, -2-hexenyl, -3-hexenyl, -1-heptenyl, -2-heptenyl, -3-heptenyl, -1-octenyl, -2-octenyl, -3-octenyl, -1-nonenyl, -2-nonenyl, -3-nonenyl, -1-decenyl, -2-decenyl, -3-decenyl, and similar.

The term *cycloalkenyl* refers to a saturated monocyclic or polycyclic functional hydrocarbon group with an indicated number of atoms of carbon and containing at least one double carbon-carbon bond. Examples of the cycloalkenyl functional group are -cyclopentenyl, -cyclopentadienyl, -cyclohexenyl, -cyclohexadienyl, -cycloheptenyl, -cycloheptadienyl, -cycloheptatrienyl, -cyclooctenyl, -cyclooctadienyl, -cyclooctatrienyl, -cyclooctatetraenyl, -cyclononenyl, -cyclononadienyl, -cyclodecenyl, -cyclodecadienyl, and similar.

The term *alkynyl* refers to a saturated, linear, or branched non-cyclic functional hydrocarbon group with an indicated number of atoms of carbon and containing at least one triple carbon-carbon bond. Examples of an alkynyl functional group are -acetylenyl, -propynyl, -1-butynyl, -2-butynyl, -1-pentynyl, -2-pentynyl, -3-

methyl-1-butynyl, -4- pentynyl, -1-hexynyl, -2-hexynyl, -5-hexynyl, and similar.

The term *cycloalkynyl* refers to a saturated monocyclic or polycyclic functional hydrocarbon group with an indicated number of atoms of carbon and containing at least one triple carbon-carbon bond. Examples of a cycloalkynyl functional group are -cyclohexynyl, -cycloheptynyl, -cyclooctynyl, and similar.

The term *aryl* refers to an aromatic monocyclic or polycyclic functional hydrocarbon group with an indicated number of atoms of carbons. Examples of an aryl functional group are -phenyl, -tolyl, -xylyl, -naphthyl, and similar.

The term *heteroaryl* refers to an aromatic monocyclic or polycyclic functional hydrocarbon group with an indicated number of atoms of carbon with at least one atom of carbon replaced with a heteroatom selected from O, N, and S. Examples of a heteroaryl functional group are -furyl, -thienyl, -imidazolyl, -oxazolyl, -thiazolyl, -isoxazolyl, -triazolyl, -oxadiazolyl, -thiadiazolyl, -tetrazolyl, -pirydyl, -pyrimidyl, -triazynyl, -indolyl, -benzo[b]furyl, -benzo[b]thienyl, -indazolyl, -benzoimidazolyl, -azaindolyl, -chinolyl, -isochinolyl, -carbazolyl, and similar.

The term *heterocycle* refers to a saturated or partly saturated monocyclic or polycyclic functional hydrocarbon group, with an indicated number of atoms with at least one atom of carbon replaced with a heteroatom selected from O, N, and S. Examples of a heterocyclic functional group are -furyl, -thiophenyl, -pyrrolyl, -oxazolyl, -imidazolyl, -thiazolyl, -isoxazolyl, -pyrazolyl, -isothiazolyl, -triazynyl, -pyrrolidinolyl, -pyrrolidinyl, -hydrantoinyl, -oxyranil, -oxetanyl, -tetrahydrofuranyl, -tetrahydrothiophenyl, -quinolinyl, -isoquinolinyl, -chromonyl, -coumarinyl, -indolyl, -indolizinyl, -benzo[b]furanyl, -benzo[b]thiophenyl -indazolyl, -

purinyl, -4H-quinolizinyl, -isoquinolyl, -quinolyl, -phthalazinyl, -naphthyridinyl, -carbazolyl, -β-carbolinyl, and similar.

The term *inert ligand* refers to a functional group without a charge capable of coordinating with the metallic centre (the ruthenium atom). Examples of such ligands are: amines, phosphines and oxides thereof, aryl and alkyl phosphoranes and phosphorines, arsines and oxides thereof, ethers, aryl and alkyl sulphides, coordinated hydrocarbons, and aryl and alkyl halides.

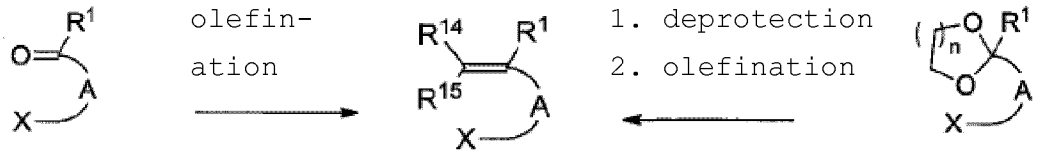
The term *indenylene* refers to an unsaturated functional hydrocarbon with an indene skeleton (benzocyclopentadiene).

The term *heteroindenylene* refers to an indenylene functional group, defined above, in which at least one atom of carbon has been replaced with a heteroatom from a group comprising: nitrogen, oxygen, and sulphur.

The term *anion ligand* refers to a functional group capable of coordination with the metallic centre (the ruthenium atom) with a charge capable of partial or full compensation of the metallic centre charge. Examples of such ligands may be: fluoride, chloride, bromide, iodide, cyanide, cyanate, and thiocyanate, carboxylic acid anions, alcohol anions, phenol anions, thiol and thiophenol anions, hydrocarbon anions with a delocalised charge (e.g. cyclopentadiene), (organo)sulphuric and (organo)phosphoric acid anions and their esters (e.g. alkyl sulphonic and aryl sulphonic acid anions, alkyl phosphoric and aryl phosphoric acid anions, sulphuric acid alkyl and aryl ester anions, phosphoric acid alkyl and aryl ester anions, alkyl phosphoric and aryl phosphoric acid alkyl and aryl ester anions). An anion ligand may have a group L^1, L^2, or L^3 linked like a catechol anion, an acetylacetone anion, or a salicylic aldehyde anion. Anion ligands (Z^1 and Z^2) and inert ligands (L^1, L^2, and L^3) may be linked with each other, creating polydentate ligands, e.g.: the bidentate ligand (Z^1, Z^2), the tridentate ligand (Z^1, Z^2, L^1), the tetradentate ligand

(Z^1, Z^2, L^1, L^2), the bidentate ligand (Z^1, L^1), the tridentate ligand (Z^1, L^1, L^2), the tetradentate ligand (Z^1, L^1, L^2, L^3), the bidentate ligand (L^1, L^2), and the tridentate ligand (L^1, L^2, L^3). Examples of such ligands are: catechol anion, acetylacetone anion, and salicylic aldehyde anion.

The stages of synthesis which are generally used in producing ligands with formula **9** are presented in general in Diagram I, in accordance with which the synthesis of the compounds with formulae **21**, **23**, and **25** is carried out (Examples I-III).



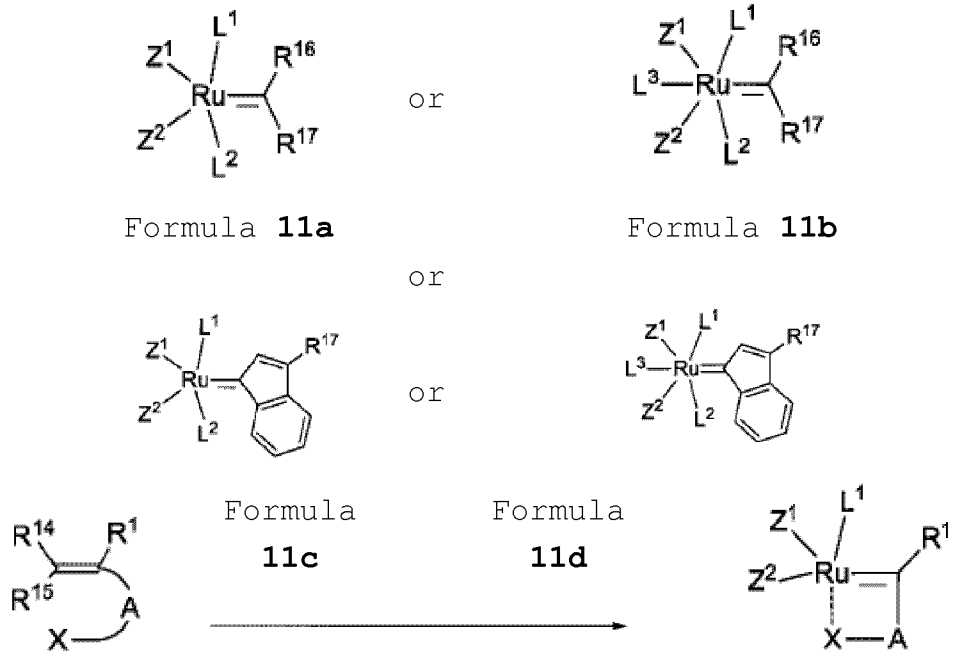
Formula **8** Formula **9** Formula **10**
n = 1, 2

Diagram I

The olefination reaction of substituted aromatic and heteroaromatic halogen aldehyde derivatives with formula **8**, where R^1 has the meaning given above, is advantageously carried out in accordance with Tebbe's method with Tebbe's titanium reagent or in accordance with Wittig's method with Wittig's reagent, or in accordance with Peterson's method. The reaction is carried out in solvents such as alcohol and glycol ethers or cyclic ethers, advantageously THF, aromatic and aliphatic hydrocarbons, and mixtures of all of the above. Compounds with the general formula **9** are also beneficially obtained from the protected aldehyde **10** without generation and purification of the halogen aldehyde with the general formula **8** (Diagram I, experimental data Examples I-III).

In the method in accordance with the invention, the complex with formula **1** is obtained as presented in Diagram II (for experimental data, see Examples IV-XI)

in a reaction between the substituted compound with formula **9** and the ruthenium complex **11a**, **11b**, **11c**, or **11d**, where the functional group has the meaning given above, possibly in the presence of an anhydrous halogen salt of copper(I), such as CuCl or CuBr. The reaction is carried out advantageously in chlorinated solvents, e.g. methylene chloride, or in aromatic hydrocarbons, or in mixtures thereof, over 1-24 hours at a temperature of 0-120°C. Furthermore, protic and aprotic solvents may be used, such as alcohols or ketones. The reaction may be carried out also in the presence of Brønsted acids such as H_2SO_4, HCl, HNO_3, H_3PO_4, sulphonated polymers (Nafion-H), or other acids bonded with a fixed substrate, in the solvent described above.



Formula **11a** Formula **11b**

Formula **9** Formula **1**

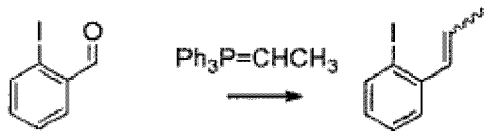
Diagram II

The examples above explain the production and use of the new complexes. The comparative examples with the use of known complexes confirm that the complexes in accordance with the invention of formula **1** are thermally more stable than complexes known from the

state of the art and furthermore display higher catalytic activity.

Example I:

Synthesis of a ligand with formula **23** (in accordance with Diagram I).



Formula **22** Formula **23**

1-iodo-2-(prop-1-enyl)benzene. To the suspension of ethyl triphenyl phosphonium bromide (6.72 g, 18.3 mmol) in THF (30 ml), a solution is added by drops of *tert*-amylate (8.5 ml, 14.5 mmol, 1.7 M solution in toluene) at room temperature. After 1 hour, the reaction mixture is cooled to a temperature of 0°C, an aldehyde solution with formula **22** is added (2.80 g, 12.1 mmol) in THF (10 ml), the cooling bath is removed, and the mixing is continued for 3 hours at room temperature. This is followed by the addition of water (0.5 ml), dilution with *n*-hexane (30 ml), drying using $MgSO_4$, and the solvent is evaporated at reduced pressure. The residue is chromatographed on silica gel (cyclohexane), obtaining a styrene derivative with formula **23** in the form of a colourless oil as a mixture of isomers E:Z = 1.83:1 (2.69 g, 91%).

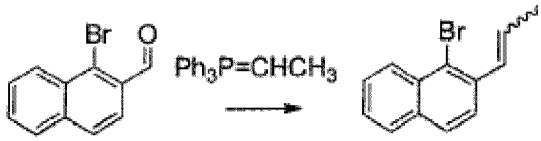
^{1}H NMR (200 MHz): 7.80-7.70 (m, 1H), 7.45-7.18 (m, 1H), 6.96-6.78 (m, 1H), 6.62-6.26 (m, 1H), 1.90 (dd, J = 6.6 Hz, 1.6 Hz, 0.35 x 3H), 1.73 (dd, J = 7.0 Hz, 1.6 Hz, 0.65 x 1H). ^{13}C NMR (50 MHz): 140.8, 139.3, 139.0, 134.7, 133.7, 129.8, 129.0, 128.3, 128.2, 128.2, 127.7, 127.6, 126.3, 100.2, 99.2, 18.6, 14.1.

The compound described in Synlett 2007, 929-933, and J. Am. Chem. Soc. 2003, 125, 4804-4807 without spectral data.

Example II:

Synthesis of a ligand with formula **21** (in accordance with Diagram I).

method a



Formula **20** Formula **21**

1-bromo-2-(prop-1-enyl)naphthalene. To the suspension of ethyl triphenyl phosphonium bromide (3.72 g, 10.0 mmol) in anhydrous THF (8 ml), a solution is added by drops of potassium *tert*-amylate (5.5 ml, 9.3 mmol, 1.7 M solution in toluene) using a syringe at room temperature. After 1 hour, the reaction mixture is cooled to a temperature of 0°C, a solution is added of aldehyde with formula **20** (1.68 g, 7.16 mmol), the cooling bath is removed, and mixing is carried out for 3 hours at room temperature. Then, the reaction mixture is diluted with cyclohexane (30 ml), the sediment is filtered off, and the solvent is evaporated at reduced pressure. The residue is chromatographed on silica gel (cyclohexane), obtaining a naphthalene derivative with formula **21** in the form of an oil as a mixture of isomers E:Z = 1.82:1 (1.66 g, 94%).

^{1}H NMR (200 MHz): 8.44-8.32 (m, 1H), 7.88-7.40 (m, 5H), 7.18-7.02 (m, 0.65 x 1H), 6.76 (dd, *J* = 11.4, 1.6 Hz, 0.35 x 1H), 6.35 (dq, *J* = 15.8, 6.6 Hz, 0.65 x 1H), 6.00 (dq, *J* = 11.4, 7.0 Hz, 0.35 x 1H), 2.03 (dd, *J* = 6.6, 1.6 Hz, 0.65 x 3H), 1.88-1.82 (m, 0.35 x 3H).

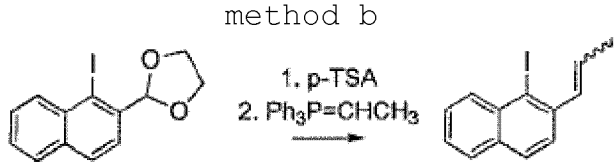
^{13}C NMR (50 MHz): 135.7, 135.1, 133.5, 133.3, 132.6, 131.0, 130.6, 129.7, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 127.3, 127.2, 126.8, 126.2, 126.1, 124.2, 123.6, 122.5, 18.9, 14.6.

HR MS was calculated for $C_{13}H_{11}Br$: 246.0044. Found: 246.0054.

Spectroscopy data in accordance with the literature: Daiichi Sankyo Company, Ltd. Patent application: EP 1 914 229 A1, 2008.

Example III:

Synthesis of a ligand with formula **25** (in accordance with Diagram I).



Formula **24** Formula **25**

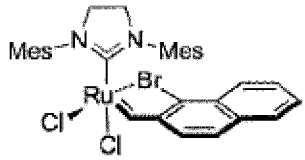
1-Iodo-2-(prop-1-enyl)naphthalene. To the solution of ketal with formula **24** (4.63 g, 14.3 mmol) in a mixture of 1,4-dioxane (40 ml) and water (5 ml), *p*-toluenesulfonic acid (1.36 g, 7.15 mmol) is added and mixed for 16 hours at room temperature. Then, the reaction mixture is diluted with water (100 ml) and a saturated hydrous solution K_2CO_3 (10 ml), and EtOAc (3 x 20 ml) is extracted. The combined organic extracts are rinsed with a saturated solution of NaCl (2 x 30 ml) and dried using $MgSO_4$, and the solvent is evaporated at reduced pressure, obtaining aldehyde in the form of a yellow solid (3.99 g, 99%). The aldehyde obtained is used for the subsequent reaction without further purification.

To the suspension of ethyl triphenyl phosphonium bromide (5.69 g, 15.3 mmol) in anhydrous THF (30 ml), a solution is added by drops of potassium *tert*-amylate (8.7 ml, 14.7 mmol, 1.7 M solution in toluene) using a syringe at room temperature. After 1 hour, the reaction mixture is cooled to a temperature of 0°C, the solution of crude aldehyde previously obtained is added (3.32 g, 11.79 mmol) in THF (10 ml), and mixing is continued for 16 hours at room temperature. Then, water (1 ml) is

added, and dilution takes place with *n*-hexane (30 ml). The sediment created is filtered, and the residue is chromatographed on silica gel (cyclohexane), obtaining naphthalene derivative with formula **25** in the form of a yellow oil (3.12 g, 90%).

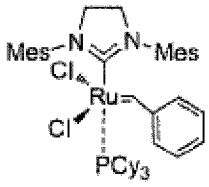
Example IV:

Synthesis of a catalyst with formula **12**, in which Mes denotes 2,4,6-trimethylphenyl (in accordance with Diagram II).



Formula **12**

Procedure A: using a protective atmosphere of argon, in a Schlenk flask are placed anhydrous CuCl (0.0208 g, 0.21 mmol, 1.05 equivalent), bromonaphthalene equivalent with formula **21** (0.0544 g, 0.22 mmol, 1.10 equivalent), dry, deoxygenated CH_2Cl_2 (10 ml), and solid carbene ruthenium complex with formula **5a** (in which Mes denotes 2,4,6-trimethylphenyl, and Cy denotes cyclohexyl):

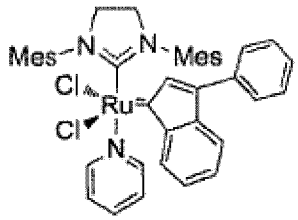


Formula **5a**

('Grubbs' II generation catalyst, 0.170 g, 0.20 mmol) in the sequence indicated. The suspension obtained is mixed at boiling point for 2 hours. From this moment, all subsequent operations are carried out without the use of a protective atmosphere of argon. The reaction mixture is concentrated in a rotary evaporator, and the

residue obtained is chromatographed on silica gel (20 ml), using as eluent 20% ethyl acetate in CH_2Cl_2. Then, solvents are evaporated at reduced pressure, obtaining a catalyst with Formula **12** as a green solid (0.094 g, 68%).

Procedure B: using a protective atmosphere of argon, in a Schlenk flask are placed bromonaphthalene derivative with formula **21** (0.741 g, 3.0 mmol, 1.10 equivalent), dry, deoxygenated toluene (67 ml), and solid carbene ruthenium complex with formula **6b**:



Formula **6b**

('catalyst M31', Umicore AG & Co KG, 1.52 g, 2.0 mmol) in the sequence indicated. The suspension obtained is mixed at a temperature of 80°C for 2 hours. From that moment, all operations are carried out without the use of a protective atmosphere of argon. The product suspension obtained is filtered off using a Büchner funnel, rinsed with *n*-pentane (2 x 8 ml), and dried for 16 hours, obtaining a catalyst with formula **12** as a dark green solid (1.05 g, 75%).

^{1}H NMR (500 MHz, CD_2Cl_2): 17.97 (s, 1H), 8.22 (dd, J = 8.5, 1.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.75 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.64 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.18 (2 s ovl, 2H), 7.10 (d, J = 8.5 Hz, 1H), 6.97 (s, 1H), 5.73 (s, 1H), 4.26-4.19 (m, 1H), 4.12-4.04 (m, 2H), 3.87-3.80 (m, 1H), 2.64 (s, 3H), 2.53 (s, 3H), 2.46 (s, 3H), 2.43 (s, 3H), 2.17 (s, 3H), 1.34 (s, 3H).

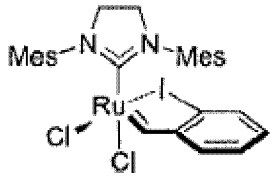
^{13}C NMR (125 MHz, CD_2Cl_2): 278.1, 214.1, 149.4, 141.0, 140.6, 139.1, 138.1, 137.1, 135.7, 135.4, 134.4, 131.9, 131.7, 131.3, 130.4, 130.0, 129.7, 129.5, 129.4, 129.3,

128.3, 127.4, 126.7, 124.8, 52.0, 51.9, 21.6, 21.2, 20.4, 19.5, 18.8, 17.3.

Elemental analysis for $C_{32}H_{34}Cl_2BrN_2Ru$: calculated: C 55.02, H 4.91, N 4.01. Found: C 56.11, H 5.16, N 3.88.

Example V:

Synthesis of a catalyst with formula **14** (in accordance with Diagram II).



Formula **14**

Using a protective atmosphere of argon, in a Schlenk flask are placed iodostyrene with formula **23** (0.549 g, 2.25 mmol, 1.10 equivalent), dry, deoxygenated toluene (50 ml) and solid carbene ruthenium complex with formula **6b** ('catalyst M31', Umicore AG & Co KG, 1.14 g, 1.50 mmol), in the sequence indicated. The suspension obtained is mixed at a temperature of 80°C for 2 hours. From this moment, all subsequent operations are carried out in air, without the use of a protective atmosphere of argon. The reaction mixture is cooled to room temperature, diluted with *n*-pentane (50 ml), filtered off using a Büchner funnel, rinsed with *n*-pentane (2 x 4 ml), and dried for 16 hours, obtaining [a catalyst] with formula **14** as a dark green solid (0.823 g, 70%, solvate with toluene 1:1, in accordance with ^{1}H NMR).

^{1}H NMR (500 MHz, CD_2Cl_2): 18.06 (d, J = 1.0 Hz, 1H), 7.61-7.57 (m, 1H), 7.35 (ddd, J = 9.0, 7.5, 1.5 Hz, 1H), 7.29 (ddd, J = 8.5, 7.0, 1.0 Hz, 1H), 7.17 (s, 1H), 7.04 (s, 1H), 6.94 (s, 1H), 6.91 (dd, J = 7.2, 3.7 Hz, 1H), 6.01 (s, 1H), 4.25-4.17 (m, 1H), 4.10-3.96 (m, 2H), 3.91-3.84 (m, 1H), 2.71 (s, 3H), 2.50 (s, 3H),

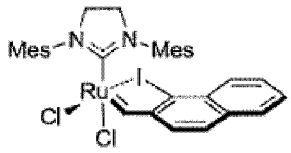
2.41 (s, 3H), 2.38 (s, 3H), 2.16 (s, 3H), 1.62 (s, 3H). Signals of toluene omitted.

^{13}C NMR (125 MHz, CD_2Cl_2): 281.7, 214.7, 157.7, 141.0, 140.5, 139.0, 138.2, 136.5, 136.0, 135.7, 134.3, 132.0, 131.4, 130.8, 130.3, 130.0, 129.5, 129.3, 128.1, 100.7, 52.1, 51.8, 21.5, 21.2, 20.6, 20.3, 19.0, 18.2. Signals of toluene omitted.

Elemental analysis for $C_{35}H_{40}Cl_2In_2Ru$: calculated: C 53.38, H 5.12, N 3.56. Found: C 53.32, H 5.10, N 3.90.

Example VI:

Synthesis of a catalyst with formula **15** (in accordance with Diagram II).

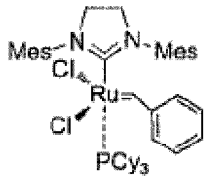


Formula **15**

Procedure A: using a protective atmosphere of argon, in a Schlenk flask are placed iodonaphthalene derivative with formula **25** (0.706 g, 2.4 mmol, 1.10 equivalent), dry, deoxygenated toluene (50 ml), and solid carbene ruthenium complex with formula **6b** ('M31 catalyst', Umicore AG & Co KG, 1.52 g, 2.0 mmol), in the sequence indicated. The suspension obtained is mixed at a temperature of 80°C for 45 minutes. From this moment, all operations are carried out in air, without the use of a protective atmosphere of argon. The reaction mixture is cooled to room temperature, diluted with *n*-pentane (50 ml), filtered off using a Büchner funnel, rinsed with *n*-pentane (2 x 20 ml), and dried for 16 hours, obtaining a catalyst with formula **15** as a dark green solid (1.385 g, 93%).

Procedure B: using a protective atmosphere of argon, in a Schlenk flask are placed anhydrous CuCl (0.0156 mg,

0.158 mmol, 1.05 equivalent), iodonaphthalene derivative with formula **25** (0.0485 g, 0.165 mmol, 1.10 equivalent), dry, deoxygenated CH_2Cl_2 (7.5 ml), and solid carbene ruthenium complex with formula **5a**:



Formula **5a**

('Grubbs II generation catalyst', 0.127 g, 0.150 mmol), in the sequence indicated. The suspension obtained is mixed at boiling point for 10 minutes. From this moment, all operations are carried out in air, without the use of a protective atmosphere of argon. The reaction mixture is concentrated in a rotary evaporator, and the residue obtained is chromatographed on silica gel (20 ml), using, as eluent, 10% ethyl acetate in CH_2Cl_2. Then, the solvents are evaporated at reduced pressure, obtaining a catalyst with formula **15** as an olive green solid (0.0923 g, 83%).

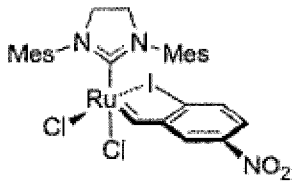
^{1}H NMR (500 MHz, CD_2Cl_2): 18.26 (s, =CH, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.76-7.71 (m, 2H), 7.63-7.58 (m, 1H), 7.19 (s, 1H), 7.09 (s, 1H), 6.97 (s, 1H), 6.96 (d, J = 8.0 Hz, 1H), 5.76 (s, 1H), 4.26-4.17 (m, 1H), 4.10-3.95 (m, 2H), 3.88-3.80 (m, 1H), 2.74 (s, 3H), 2.54 (s, 3H), 2.48 (s, 3H), 2.41 (s, 3H), 2.16 (s, 3H), 1.39 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2): 281.2, 214.3, 156.3, 141.0, 140.5, 139.0, 138.2, 136.5, 135.8, 135.5, 134.6, 133.9, 132.1, 131.4, 130.9, 130.4, 130.1, 129.8, 129.5, 129.4, 128.4, 126.4, 105.8, 52.2, 51.8, 21.5, 21.2, 20.6, 19.1, 18.1.

Elemental analysis for $C_{32}H_{34}Cl_2IN_2Ru$: calculated: C 51.55, H 4.60, N 3.76. Found: C 52.26, H 4.61, N 3.59.

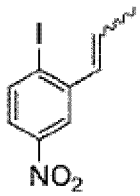
Example VII:

Synthesis of a catalyst with formula **17** (in accordance with Diagram II).



Formula **17**

Procedure: using a protective atmosphere of argon, in a Schlenk flask are placed iodostyrene derivative with formula **28** (0.433 g, 1.5 mmol):



Formula **28**

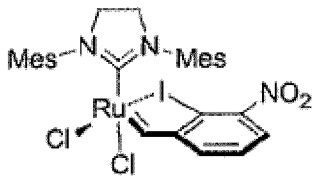
and dry, deoxygenated toluene (20 ml), and solid, carbene complex of ruthenium with formula **6b** ('M31 catalyst', Umicore AG & Co KG, 0.761 g, 1.0 mmol), in the sequence indicated. The suspension obtained is mixed at a temperature of 80°C for 1 hour. From this moment, all operations are carried out in air, without the use of a protective atmosphere of argon. The reaction mixture is cooled to room temperature, diluted with *n*-pentane (20 ml), filtered using a Schott filter, rinsed with *n*-pentane (3 x 10 ml), and dried under pressure, obtaining a compound with formula **17** as a light green solid (0.659 g, 79%, solvate with toluene 1:1 in accordance with ^{1}H NMR).

^{1}H NMR (200 MHz, CD_2Cl_2): 18.11 (d, J = 1.0 Hz, =CH, 1H), 8.19, (dd, J = 8.5, 2.5 Hz, 1H), 7.79 (dd, J = 8.5, 1.0 Hz, 1H), 7.72 (d, J = 2.5 Hz, 1H), 7.27-7.12 (m, 1H + toluene), 7.05 (s, 1H), 7.02 (s, 1H), 6.05 (s,

1H), 4.27-4.20 (m, 1H), 4.13-3.97 (m, 2H), 3.93-3.85 (m, 1H), 2.69 (s, 3H), 2.50 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.34 (s, toluene), 2.08 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): 276.9, 212.9, 157.7, 149.5, 141.2, 140.5, 139.8, 138.4, 136.2, 135.8, 135.6, 134.7, 131.39, 131.37, 130.22, 130.20, 129.4, 129.0, 128.6, 125.6, 123.5, 120.9, 107.6, 52.0, 51.7, 21.5, 21.4, 20.7, 20.4, 20.1, 18.8, 18.1. Signals of toluene were omitted.

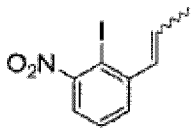
Example VIII:

Synthesis of a catalyst with formula **18** (in accordance with Diagram II).



Formula **18**

Procedure: using a protective atmosphere of argon, in a Schlenk flask are placed an iodostyrene derivative with formula **29** (0.453 g, 1.56 mmol):



Formula **29**

dry, deoxygenated toluene (20 ml) and solid carbene ruthenium complex with formula **6b** ('catalyst M31', Umicore AG & Co KG, 0.787 g, 1.04 mmol). The suspension obtained is mixed at a temperature of 80°C for 1 hour. From this moment, all operations are carried out in air, without the use of a protective atmosphere of argon. The reaction mixture is cooled to room

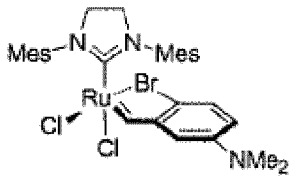
temperature, diluted with *n*-pentane (20 ml), filtered using a Schott filter, rinsed with *n*-pentane (3 x 15 ml), and dried under pressure, obtaining a catalyst with formula **18** as a bronze-coloured solid (0.745 g, 86%, solvate with toluene 1:1, in accordance with ^{1}H NMR).

^{1}H NMR (500 MHz, CD_2Cl_2): 18.12 (s, =CH, 1H), 8.41 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.52 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.26-7.12 (m, 2H + toluene), 7.08 (s, 1H), 6.96 (s, 1H), 5.97 (s, 1H), 4.25-4.18 (m, 1H), 4.11-3.95 (m, 2H), 3.92-3.84 (m, 1H), 2.69 (s, 3H), 2.51 (s, 3H), 2.47 (s, 3H), 2.39 (s, 3H), 2.34 (s, toluene), 2.14 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2): 279.0, 212.9, 158.7, 150.7, 141.1, 140.4, 139.1, 138.4, 138.3, 136.1, 135.7, 135.5, 132.2, 131.4, 131.3, 131.1, 130.22, 130.17, 129.4, 129.1, 128.6, 125.6, 125.4, 93.1, 51.9, 51.8, 21.4, 21.1, 20.4, 20.1, 18.8, 18.2. Signals of toluene are omitted.

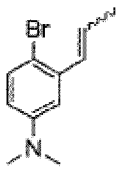
Example IX:

Synthesis of a catalyst with formula **13** (in accordance with Diagram II):



formula **13**

Procedure: using a protective atmosphere of argon, in a Schlenk flask are placed a bromostyrene derivative with formula **26** (0.371 g, 1.55 mmol):



Formula **26**

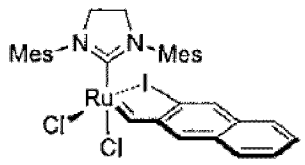
dry, deoxygenated toluene (20 ml), and solid carbene ruthenium complex with formula **6b** ('catalyst M31', Umicore AG & Co KG, 0.780 g, 1.03 mmol), in the sequence indicated. The suspension obtained is mixed at a temperature of 80°C for 30 minutes. From that moment, all operations are carried out in air, without the use of a protective atmosphere of argon. The reaction mixture is cooled to room temperature, diluted with *n*-pentane (20 ml), filtered using a Schott filter, rinsed with *n*-pentane (2 x 10 ml), and dried under pressure, obtaining a catalyst with formula **13** as a dark green solid (0.408 g, 57%).

^{1}H NMR (500 MHz, CD_2Cl_2): 17.75 (s, =CH, 1H), 7.28 (d, *J* = 10.2 Hz, 1H), 7.16 (s, 1H), 7.11 (s, 1H) 6.94 (s, 1H), 6.80 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.41 (d, *J* = 3.0 Hz, 1H), 6.19 (s, 1H), 4.24-4.16 (m, 1H), 4.11-4.02 (m, 1H), 4.02-3.92 (m, 1H), 3.92-3.81 (m, 1H), 2.97 (s, 6H, $N(CH_3)_2$), 2.63 (s, 3H), 2.42 (2s ovl, 6H), 2.40 (s, 3H), 2.17 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2): 280.9, 214.8, 152.5, 151.3, 140.6, 140.2, 138.5, 137.8, 136.9, 136.2, 135.5, 131.8, 131.0, 130.0, 129.7, 129.3, 128.5, 113.7, 114.4, 110.7, 51.9, 51.6, 40.6, 21.3, 20.9, 20.1, 19.1, 18.6, 17.2.

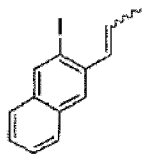
Example X:

The synthesis of a catalyst with formula **16** (in accordance with Diagram II).



Formula **16**

Procedure: using a protective atmosphere of argon, in a Schlenk flask are placed iodonaphthalene derivative with formula **27** (0.137 g, 0.466 mmol):



Formula **27**

dry, deoxygenated toluene (6 ml), and a solid carbene ruthenium complex with formula **6b** ('catalyst M31', Umicore AG & Co KG, 0.239 g, 0.316 mmol), in the sequence indicated. The suspension obtained is mixed at a temperature of 80°C for 1 hour. From this moment, all operations are carried out in air, without the use of a protective atmosphere of argon. The reaction mixture is cooled to room temperature, diluted with *n*-pentane (1 ml), filtered using a Schott filter, rinsed with *n*-pentane (2 x 10 ml), and dried under pressure, obtaining a catalyst with formula **16** as a dark green solid (0.183 g, 78%).

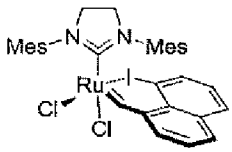
^{1}H NMR (500 MHz, CD_2Cl_2): 18.08 (d, J = 1.0 Hz, =CH, 1H), 8.12 (s, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.77-7.70 (m, 2H), 7.56 (ddd, J = 7.5, 6.0, 2.0 Hz, 1H), 7.42 (s, 1H), 7.17 (s, 1H), 7.06 (s, 1H), 6.95 (s, 1H), 5.59 (s, 1H), 4.25-4.18 (m, 1H), 4.11-3.95 (m, 2H), 3.91-3.84

(m, 1H), 2.70 (s, 3H), 2.50 (s, 3H), 2.44 (s, 3H), 2.39 (s, 3H), 1.88 (s, 3H), 1.63 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2): 280.6, 215.0, 154.7, 140.8, 140.5, 138.9, 138.2, 136.4, 136.1, 135.7, 134.2, 133.49, 133.47, 131.9, 131.2, 130.11, 130.10, 129.8, 129.0, 128.7, 128.4, 127.7, 126.5, 95.8, 51.9, 51.6, 21.4, 21.0, 20.4, 20.2, 18.9, 18.1.

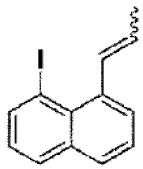
Example XI:

Synthesis of a catalyst with formula **19** (in accordance with Diagram II).



Formula **19**

Procedure: using a protective atmosphere of argon, in the Schlenk flask are placed iodonaphthalene derivative with formula **30** (0.138 g, 0.469 mmol).



Formula **30**,

dry, deoxygenated toluene (6 ml), and solid carbene ruthenium complex with formula **6b** ('catalyst M31', Umicore AG & Co KG, 0.237 mg, 0.313 mmol), in the sequence referred to. The suspension obtained is mixed at a temperature of 80°C for 1 hour. From that moment, all subsequent operations are carried out in air, without the use of a protective atmosphere of argon. The reaction mixture is cooled to room temperature, diluted with *n*-pentane (6 ml), filtered using a Schott filter, rinsed with *n*-pentane (2 x 10 ml), and dried

under pressure, obtaining a catalyst with formula **19**, as a dark green solid (0.113 mg, 48%).

^{1}H NMR (500 MHz, CD_2Cl_2): 18.69 (s, =CH, 1H), 7.99-7.94 (m ovl, 2H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.32-7.22 (m, 2H), 7.18 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.13 (s, 1H), 7.02 (s, 1H), 6.83 (s, 1H), 5.63 (s, 1H), 4.32-4.22 (m, 1H), 4.15-4.04 (m, 2H), 3.97-3.88 (m, 1H), 2.75 (s, 3H), 2.57 (s, 3H), 2.47 (s, 3H), 2.37 (s, 3H), 2.02 (s, 3H), 1.50 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2): 284.2, 216.3, 144.6, 140.7, 140.0, 138.6, 138.5, 138.1, 136.9, 136.3, 136.1, 135.7, 134.9, 133.0, 132.9, 132.4, 131.3, 131.2, 130.04, 130.00, 128.8, 127.4, 127.2, 87.6, 52.1, 51.5, 21.3, 21.1, 20.4 (ovl), 19.1, 18.0.

Example XII:

Testing the catalytic activity for cyclisation of diethyl diallylmalonate using ^{1}H-NMR methods (in accordance with diagram III).

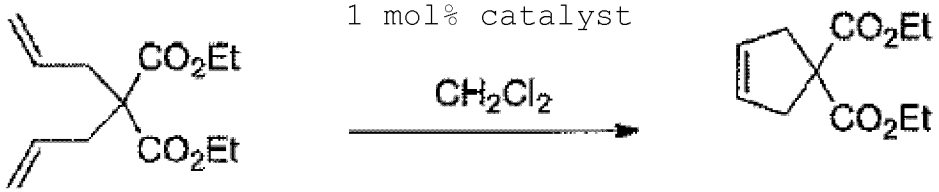


Diagram III

Solution A:

To the 5 ml measurement flask is added diethyl diallylmalonate (0.2882 g, 0.12 mmol), and CD_2Cl_2 is added up to the nominal value.

Solution B:

To a 1.5 ml vial is added a catalyst in accordance with the invention (**12-19**, 0.012 mmol), and 1 ml of CD_2Cl_2 is added.

Reaction profile measurements:

To an NMR tube is added 0.5 ml of solution A, and a micro-syringe is used to add 0.1 ml of solution B. The tube is closed with a cork, and, simultaneously, the time starts to be calculated and the content is mixed and placed in an NMR thermostatic device (at a temperature of 25°C, unless otherwise indicated), with successive ^{1}H NMR spectra being recorded over a total period of 75 minutes. In an identical manner, the activity is studied of the commercially available catalysts **5a** and **6a**. On the basis of the integration of signals δ 2.6-2.9 ppm, conversions are determined, and the results are presented in **Figure 1**, which shows progress during the course of the diethyl diallylmalonate cyclisation reaction in relation to various catalysts (^{1}H NMR).

On the basis of data obtained from tests of the catalytic activity of the complexes in accordance with the invention, it can be found that, at a temperature of 25°C, they are much more active than the commercially available catalyst of formula **6a**.

Example XIII:

Test of the effect of temperature on the catalytic activity of complexes with formulae **15** and **18** in diethyl diallylmalonate cyclisation using ^{1}H NMR methods (in accordance with Diagram III).

The test was carried out in accordance with the procedure described in example XII at temperatures of 25, 40, and 55°C. The reactions carried out at a temperature of 55°C were carried out in an NMR Wilmad pressure tube. The results obtained are presented in **Figure 2** and **Figure 3**, which show progress during the course of the diethyl diallylmalonate cyclisation reaction at various temperatures (by ^{1}H NMR).

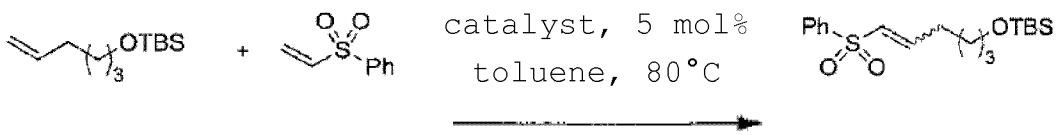
The results obtained show that the catalysts in accordance with the invention show thermal stability

(and can also act at an elevated temperature), and, thanks to changes in activity as a function of temperature, the course of catalytic processes can be easily controlled.

Example XIV:

Examples of application

Tests were carried out into catalytic activity with various substrates in accordance with Diagrams IV–X (the results are shown in tables 1–7 respectively).

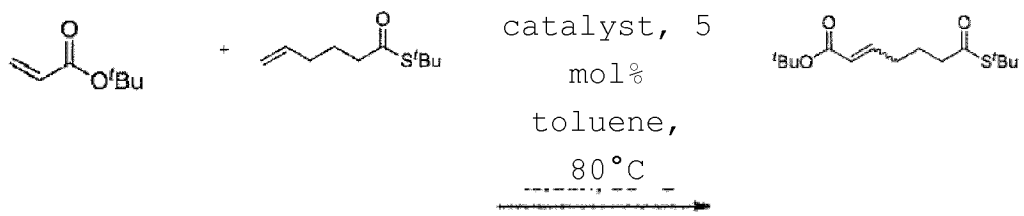


1 mol 2 mol

Diagram IV

Table 1: Results of reactions on a model substrate in accordance with Diagram IV

Catalyst	Duration of the reaction	Product yield
15	30 minutes	78%
12	16 hours	74%
14	16 hours	83%

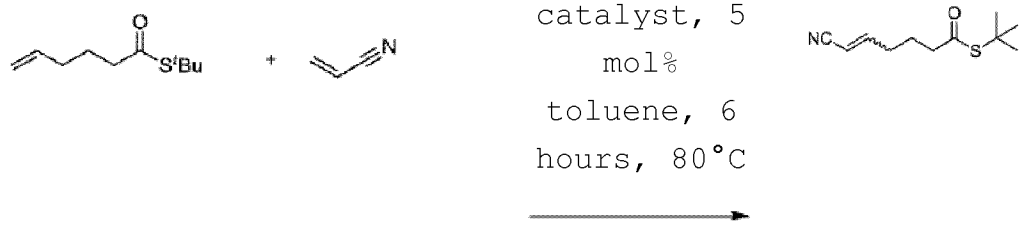


1 mol 2 mol

Diagram V

Table 2: Results of reactions on a model substrate in accordance with Diagram V

Catalyst	Duration of the reaction	Product yield
15	6 hours	80%
12	12 hours	68%
14	8 hours	84%

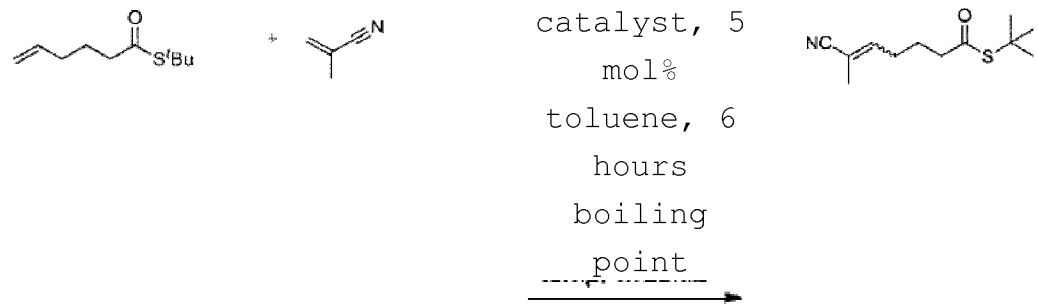


1 mol 2 mol

Diagram VI

Table 3: Results of reactions on a model substrate in accordance with Diagram VI

Catalyst	Product yield
15	72%
12	69%
14	70%
6A (known from the state of the art)	22%

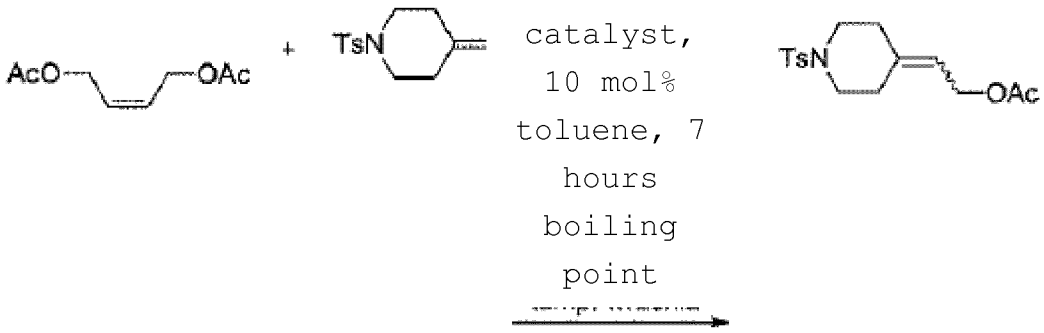


1 mol 6 mol

Diagram VII

Table 4: Results of reactions on a model substrate in accordance with Diagram VII

Catalyst	Product yield
15	41% (23% at 80°C)
12	48%
14	38%
6A (known from the state of the art)	11%

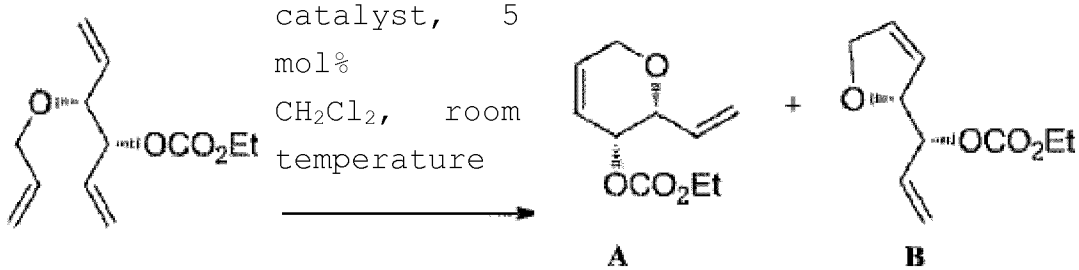


6 mol 1 mol

Diagram VIII

Table 5: Results of reactions on a model substrate in accordance with Diagram VIII

Catalyst	Product yield
15	62%
12	45%
14	63%



A B

Diagram IX

Table 6: Results of reactions on a model substrate in accordance with Diagram IX

Catalyst	Product yield	Proportions of isomers A:B
12	88%	2:1
14	74%	3:1

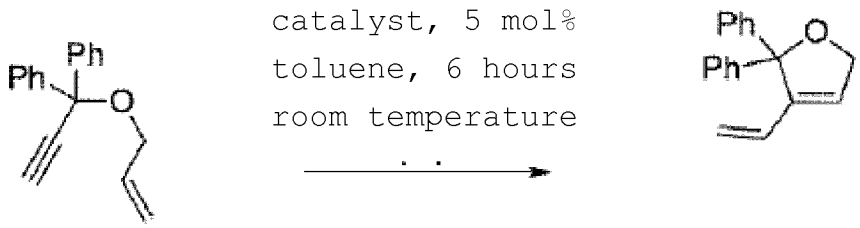


Diagram X

Table 7: Results of reactions on a model substrate in accordance with Diagram X

Catalyst	Duration of reaction	Product yield
15	2.5 hours	56%
12	20 minutes	97%
14	20 minutes	93%
6a (known from the state of the art)	12 hours	92%

The results presented in tables 3, 4, and 7 show clearly that the complexes in accordance with the invention are much more active than the catalyst **6a**, which is known from the state of the art.

Example XV:

An example of the application of new ruthenium complexes in accordance with the invention as ROMP-type (ring-opening metathesis polymerisation-type) polymerisation catalysts.

Obtaining the polydicyclopentadiene:

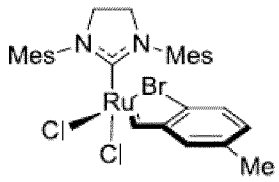
To the flask is added dicyclopentadiene (0.132 g, 1.0 mmol) in CH_2Cl_2 (5 ml), and mixing takes place at room temperature. Then, solution is added of the catalyst with formula **14** (0.0000025 g, 0.0003 mol%), and the contents of the flask are mixed at the same temperature for 1 minute. The contents of the flask are poured into another vessel containing 15 ml of methyl alcohol, and a solid precipitates, which is separated by filtration and dried at reduced pressure with the use of a pressure pump. Polydicyclopentadiene is obtained as an elastic white solid.

This example demonstrates that complexes in accordance with the invention may successfully be applied in a ROMP-type polymerisation reaction.

On the basis of the examples of embodiment presented above, it can be found that ruthenium complexes in accordance with the invention show high catalytic activity in comparison with complexes known from the state of the art. In addition, complexes in accordance with the invention are stable at an elevated temperature and may be stored without a protective gas atmosphere.

Example XVI:

Synthesis of a catalyst with formula **31** (in accordance with Diagram II).



Formula **31**

Procedure: using a protective atmosphere of argon, the styrene derivative 1-bromo-2-(1-propenyl)-4-methyl-benzene (254 mg, 1.2 mmol) and the solid carbene ruthenium complex with formula **6b** ('catalyst M31', Umicore AG & Co KG; 749 mg, 1 mmol) are combined in a Schlenk flask and 20 ml of dry, deoxygenated toluene is added. The suspension obtained is stirred at a temperature of 80°C for 15 minutes under argon. In the course of the reaction, the M31 complex dissolves within 3-5 minutes, while in 5-10 minutes a green precipitate is observed. The reaction mixture is cooled to room temperature, filtered on a Schott filter, washed with toluene and dried under vacuum obtaining catalyst with formula **31** as green powder (89 mg, 0.13 mmol, 13%).

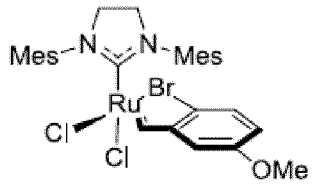
^{1}H NMR (500 MHz, CD_2Cl_2): 17.75 (d, *J*=1.0 Hz, Ru=CH, 1H), 7.40 (d, *J*=8.0 Hz, 1H), 7.32 (dd, *J*=0.5, 8.0Hz, 1H), 7.16 (s, 1H), 7.11 (s, 1H), 6.98 (s, 1H), 6.86 (d, *J*=0.5 Hz, 1H), 6.11 (s, 1H), 4.24-4.15 (m, 1H), 4.11-4.02 (m, 1H), 4.01-3.92 (m, 1H), 3.90-3.82 (m, 1H), 2.62 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H), 2.22 (s, 3H), 1.54 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2): 279.0, 214.5, 151.8, 140.8, 140.3, 139.8, 138.9, 138.0, 136.9, 136.1, 135.5, 131.7, 131.2, 131.0, 130.1, 129.7, 129.2, 128.5, 127.3, 123.0, 51.9, 51.6, 21.4, 21.2, 20.9, 20.2, 19.2, 18.6, 17.2.

Trace signals of the solvent (toluene) were not listed.

Example XVII:

Synthesis of a catalyst with formula **32** (in accordance with Diagram II).



Formula **32**

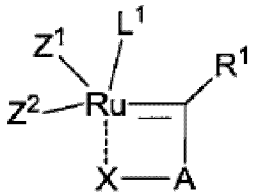
Procedure: using a protective atmosphere of argon, the styrene derivative 1-bromo-2-(1-propenyl)-4-methoxy-benzene (545 mg, 2.4 mmol) and the solid carbene ruthenium complex with formula **6b** ('catalyst M31', Umicore AG & Co KG; 1497 mg, 2 mmol) are combined in a Schlenk flask and 40 ml of dry, deoxygenated toluene is added. The suspension obtained is stirred at a temperature of 80°C for 15 minutes under argon. In the course of the reaction, the M31 complex dissolves within 3-5 minutes, while in 5-10 minutes a green precipitate is observed. The reaction mixture is cooled to room temperature, filtered on a Schott filter, washed with toluene and dried under vacuum obtaining a catalyst with formula **32**, as a green powder (396 mg, 0.58 mmol, 29%).

^{1}H NMR (500 MHz, CD_2Cl_2): 17.76 (d, *J*=1.0 Hz, Ru=CH, 1H), 7.40 (dd, *J*=1.0, 6.7 Hz, 1H), 7.16 (s, 1H), 7.12 (s, 1H), 7.06 (dd, *J*=3.0, 8.6Hz, 1H), 6.96 (s, 1H), 6.60 (d, *J*=3.0 Hz, 1H), 6.15 (s, 1H), 4.25-4.15 (m, 1H), 4.11-4.04 (m, 1H), 4.01-3.94 (m, 1H), 3.90-3.83 (m, 1H), 3.81 (s, OCH3, 3H), 2.61 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H), 2.20 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2): 278.2, 214.3, 160.9, 152.7, 140.8, 140.3, 138.9, 137.9, 136.8, 136.0, 135.4, 131.6, 131.0, 130.1, 129.7, 129.2, 129.0, 116.2, 116.0, 111.5, 56.2, 51.9, 51.6, 21.3, 20.9, 20.2, 19.1, 18.5, 17.3. Trace signals of the solvent (toluene) were not listed.

Patent claims

1. New complexes of ruthenium with formula **1**,



formula **1**

wherein

L^1 denotes an inert ligand;

Z^1 and Z^2 denote, independently, an anion ligand;

X denotes a halogen atom;

R^1 denotes an atom of hydrogen, a halogen atom, C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_2-C_{12} alkenyl, C_3-C_{12} cycloalkenyl, C_2-C_{12} alkynyl, C_3-C_{12} cycloalkynyl, C_1-C_{12} alkoxyl, C_5-C_{20} aryl, C_5-C_{20} heteroaryl, or 3-12-membered heterocycle;

A denotes a bivalent radical selected from a group comprising C_1-C_{12} alkylene, C_2-C_{12} alkenylene, C_2-C_{12} alkynylene, C_5-C_{20} arylene, or C_5-C_{20} heteroarylene, in which the C_1-C_{12} alkylene, the C_2-C_{12} alkenylene, the C_2-C_{12} alkynylene, the C_5-C_{20} arylene, and the C_5-C_{20} heteroarylene may be optionally substituted with at least one functional group R^2;

each R^2 functional group denotes, independently, a halogen atom, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_2-C_{12} alkynyl, $-OR^3$, $-SR^3$, $-S(O)_mR^3$, $-SO_2NR^3R^4$, $-S(O)_2OR^3$, $-NO_2$, $-NO$, $-SCN$, $-NR^3R^4$, $-CN$, $-C(O)R^3$, $-OC(O)R^3$, $-O(CR^3R^4)_nR^5$, $-NR^3C(O)R^4$, $-(CR^3R^4)_nC(O)OR^5$, $-(CR^3R^4)_nOR^5$, $-C(=NR^3)NR^4R^5$, $-NR^3C(O)NR^4R^5$, $-NR^3S(O)_pR^4$, $-NC(=O)R^3C(=O)R^4$, $-NR^3P(=O)R^4R^5$, $-NR^3As(=O)R^4R^5$, $-PR^3R^4$, $-POR^3R^4$, $-POR^3OR^4$, $-P(=O)R^3R^4$, $-P(=O)OR^3R^4$, $-P(=O)OR^3OR^4$, $-AsR^3R^4$, $-AsOR^3R^4$, $-AsOR^3OR^4$, $-As(=O)R^3R^4$, $-As(=O)OR^3R^4$, $-As(=O)OR^3OR^4$, $-NR^3-C(=NR^4)NR^5R^6$, $-$

$C(=O)R^3$, $-C(=O)OR^3$, $-C(=S)OR^3$, $-C(=O)SR^3$, $-C(=S)SR^3$, $-C(=S)NR^3R^4$, $-SiR^3R^4R^5$, $-SiOR^3R^4R^5$, $-SiOR^3OR^4R^5$, $-SiOR^3OR^4OR^5$, $-(CR^3R^4)_n$(3-12-membered heterocycle), $-(CR^3R^4)_n(C_3\text{-}C_{12}$ cycloalkyl), $-(CR^3R^4)_n(C_5\text{-}C_{20}$ aryl), $-(CR^3R^4)_n$(5-12-membered heteroaryl), $-(CR^3R^4)_nC(O)NR^5R^6$, or $-(CR^3R^4)_nC(O)R^5$;

and/or R^2 groups with adjacent atoms may bond together, creating $C_5\text{-}C_{20}$ aryl or 3-12-membered heterocycle;

and/or R^2 groups with adjacent atoms may bond with the R^1 group, creating $C_5\text{-}C_{20}$ aryl, indenylene, heteroindenylene, 3-12-membered heterocycle, and polycyclic or heteropolycyclic arrangements, whilst the $C_5\text{-}C_{20}$ aryl, indenylene, heteroindenylene, 3-12-membered heterocycle, and polycyclic or heteropolycyclic arrangements may be substituted with at least one functional group selected from the group comprising a halogen atom, $C_1\text{-}C_{12}$ alkyl, $C_2\text{-}C_{12}$ alkenyl, $C_2\text{-}C_{12}$ alkynyl, $-OR^3$, $-SR^3$, $-S(O)_mR^3$, $-SO_2NR^3R^4$, $-S(O)_2OR^3$, $-NO_2$, $-NO$, $-SCN$, $-NR^3R^4$, $-CN$, $-C(O)R^3$, $-OC(O)R^3$, $-O(CR^3R^4)_nR^5$, $-NR^3C(O)R^4$, $-(CR^3R^4)_nC(O)OR^5$, $-(CR^3R^4)_nOR^5$, $-C(=NR^3)NR^45^4$, $-NR^3C(O)NR^4R^5$, $-NR^3S(O)_pR^4$, $-NC(=O)R^3C(=O)R^4$, $-NR^3P(=O)R^4R^5$, $-NR^3As(=O)R^4R^5$, $-PR^3R^4$, $-POR^3R^4$, $-POR^3OR^4$, $-P(=O)R^3R^4$, $-P(=O)OR^3R^4$, $-P(=O)OR^3OR^4$, $-AsR^3R^4$, $-AsOR^3R^4$, $-AsOR^3OR^4$, $-As(=O)R^3R^4$, $-As(=O)OR^3R^4$, $-As(=O)OR^3OR^4$, $-NR^3\text{-}C(=NR^4)NR^5R^6$, $-C(=O)R^3$, $-C(=O)OR^3$, $-C(=S)OR^3$, $-C(=O)SR^3$, $-C(=S)SR^3$, $-C(=S)NR^3R^4$, $-SiR^3R^4R^5$, $-SiOR^3R^4R^5$, $-SiOR^3OR^4R^5$, $-SiOR^3OR^4OR^5$, $-(CR^3R^4)_n$(3-12-membered heterocycle), $-(CR^3R^4)_n(C_3\text{-}C_{12}$ cycloalkyl), $-(CR^3R^4)_n(C_5\text{-}C_{20}$ aryl), $-(CR^3R^4)_n$(5-12-membered heteroaryl), $-(CR^3R^4)_nC(O)NR^5R^6$, or $-(CR^3R^4)_nC(O)R^5$;

each functional group R^3, R^4, R^5, and R^6 denotes, independently, an atom of hydrogen, a halogen atom, $C_1\text{-}C_{12}$ alkyl, $C_2\text{-}C_{12}$ alkenyl, $C_2\text{-}C_{12}$ alkynyl, $C_3\text{-}C_{12}$ cycloalkyl, $C_5\text{-}C_{20}$ aryl, 5-12-membered heterocycle;

each m denotes, independently, 0, 1, or 2;

each n denotes, independently, 0, 1, 2, 3, or 4;

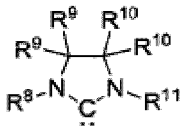
each p denotes, independently, 1 or 2.

2. Complexes according to Claim 1, characterised in that

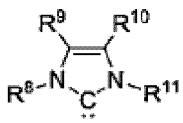
anion ligands Z^1 and Z^2 denote, independently, a halogen atom, the group -CN, -SCN, $-OR^{13}$, $-SR^{13}$, $-O(C=O)R^{13}$, $-O(SO_2)R^{13}$, $-OSiR_3^{13}$, where R^{13} denotes C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_2-C_{12} alkenyl, or C_5-C_{20} aryl, which may be optionally substituted with at least one C_1-C_{12} alkyl, C_1-C_{12} perhalogenalkyl, C_1-C_{12} alkoxyl, or a halogen atom; and

R^1 denotes an atom of hydrogen,

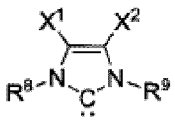
the inert ligand L^1 is selected from a group comprising $-P(R^7)_3$, $-P(OR^7)_3$, or a N-heterocyclic carbene ligand with formula **7a**, **7b**, **7c**, **7d**, **7e**, **7f**, **7g**, **7h**, **7i**, **7j**, **7k**, **7l**, **7m**, **7n**, **7o**, or **7p**:



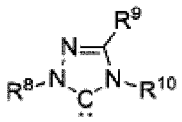
formula **7a**



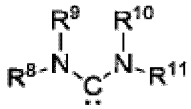
formula **7b**



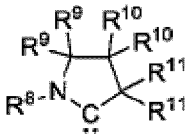
formula **7c**



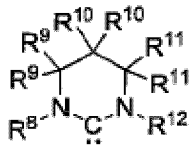
formula **7d**



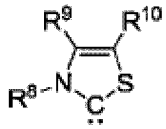
formula **7e**



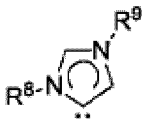
formula **7f**



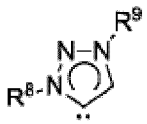
formula **7g**



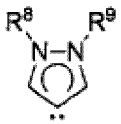
formula **7h**



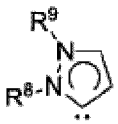
formula **7i**



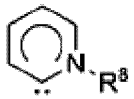
formula **7j**



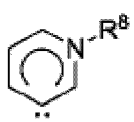
formula **7k**



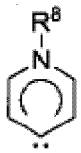
formula **7l**



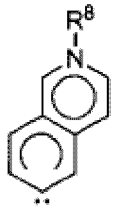
formula **7m**



formula **7n**



formula **7o**



formula **7p**

wherein

each R^7 denotes, independently, C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_5-C_{20} aryl, or 5-12-membered heteroaryl;

each R^8, R^9, R^{10}, R^{11}, and R^{12} denote, independently, an atom of hydrogen, C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_2-C_{12} alkenyl, or C_5-C_{20} aryl, which may be optionally substituted with at least one C_1-C_{12} alkyl, C_1-C_{12} perhalogenalkyl, C_1-C_{12} alkoxyl, or a halogen atom, and the groups R^8, R^9, R^{10}, R^{11}, and R^{12} may optionally bond with each other,

X^1 and X^2 denote, independently, a halogen atom.

3. Complexes according to Claim 1 or 2, characterised in that

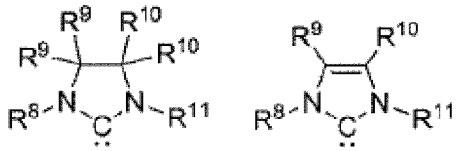
Z^1 and Z^2 each denote an atom of chlorine;

X denotes an atom of bromine or iodine; and

R_1 denotes an atom of hydrogen,

A denotes -1,2-phenylene, -1,2-naphthylene, -2,3-naphthylene or -1,8-naphthylene, which may be substituted with at least one functional group selected from a group comprising $-NO_2$, $-NMe_2$; and

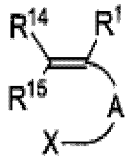
the inert ligand L^1 denotes a ligand with formula **7a** or **7b**;



formula **7a** formula **7b**

in which the functional groups R^8, R^9, R^{10}, and R^{11} may have the meaning described above.

4. Method of producing the ruthenium complexes according to Claim 1, characterised in that the compound with formula **9**



formula **9**

in which R^{14} and R^{15} denote, independently, an atom of hydrogen or the alkyl group C_1-C_{12};

R^1 denotes hydrogen, a halogen atom, C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_2-C_{12} alkenyl, C_3-C_{12} cycloalkenyl, C_2-C_{12} alkynyl, C_3-C_{12} cycloalkynyl, C_1-C_{12} alkoxyl, C_5-C_{20} aryl, C_5-C_{20} heteroaryl, or 3-12-membered heterocycle;

X denotes a halogen atom;

A denotes a bivalent radical selected from a group comprising C_1-C_{12} alkylene, C_2-C_{12} alkenylene, C_2-C_{12} alkynylene, C_5-C_{20} arylene, or C_5-C_{20} heteroarylene, in which the C_1-C_{12} alkylene, the C_2-C_{12} alkenylene, the C_2-C_{12} alkynylene, the C_5-C_{20} arylene, and the C_5-C_{20} heteroarylene may be optionally substituted with at least one functional group R^2;

where each R^2 functional group denotes, independently, a halogen atom, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_2-C_{12} alkynyl, $-OR^3$, $-SR^3$, $-S(O)_mR^3$, $-SO_2NR^3R^4$, $-S(O)_2OR^3$, $-NO_2$, $-NO$, $-SCN$, $-NR^3R^4$, $-CN$, $-C(O)R^3$, $-OC(O)R^3$, $-O(CR^3R^4)_nR^5$, $-NR^3C(O)R^4$, $-(CR^3R^4)_nC(O)OR^5$, $-(CR^3R^4)_nOR^5$, $-C(=NR^3)NR^45^4$, $-NR^3C(O)NR^4R^5$, $-NR^3S(O)_pR^4$, $-NC(=O)R^3C(=O)R^4$, $-NR^3P(=O)R^4R^5$, $-NR^3As(=O)R^4R^5$, $-PR^3R^4$, $-POR^3R^4$, $-POR^3OR^4$, $-P(=O)R^3R^4$, $-P(=O)OR^3R^4$, $-P(=O)OR^3OR^4$, $-AsR^3R^4$, $-AsOR^3R^4$, $-AsOR^3OR^4$, $-As(=O)R^3R^4$, $-As(=O)OR^3R^4$, $-As(=O)OR^3OR^4$, $-NR^3-C(=NR^4)NR^5R^6$, $-C(=O)R^3$, $-C(=O)OR^3$, $-C(=S)OR^3$, $-C(=O)SR^3$, $-C(=S)SR^3$, $-C(=S)NR^3R^4$, $-SiR^3R^4R^5$, $-SiOR^3R^4R^5$, $-SiOR^3OR^4R^5$, $-SiOR^3OR^4OR^5$, $-(CR^3R^4)_n$(3-12-membered heterocycle), $-(CR^3R^4)_n$(C_3-C_{12} cycloalkyl), $-(CR^3R^4)_n$(C_5-C_{20} aryl), $-(CR^3R^4)_n$(5-12-membered heteroaryl), $-(CR^3R^4)_nC(O)NR^5R^6$, or $-(CR^3R^4)_nC(O)R^5$;

and/or R^2 groups with adjacent atoms may bond together, creating C_5-C_{20} aryl or 3-12-membered heterocycle;

and/or R^2 groups with adjacent atoms may bond with the R^1 group, creating C_5-C_{20} aryl, indenylene, heteroindenylene, 3-12-membered heterocycle, and polycyclic or heteropolycyclic arrangements, whilst the C_5-C_{20} aryl, indenylene, heteroindenylene, 3-12-membered heterocycle, and polycyclic or heteropolycyclic arrangements may be substituted with at least one functional group selected from the group comprising a halogen atom, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_2-C_{12} alkynyl, $-OR^3$, $-SR^3$, $-S(O)_mR^3$, $-SO_2NR^3R^4$, $-S(O)_2OR^3$, $-NO_2$, $-NO$, $-SCN$, $-NR^3R^4$, $-CN$, $-C(O)R^3$, $-OC(O)R^3$, $-O(CR^3R^4)_nR^5$, $-NR^3C(O)R^4$, $-(CR^3R^4)_nC(O)OR^5$, $-(CR^3R^4)_nOR^5$, $-C(=NR^3)NR^4R^5$, $-NR^3C(O)NR^4R^5$, $-NR^3S(O)_pR^4$, $-NC(=O)R^3C(=O)R^4$, $-NR^3P(=O)R^4R^5$, $-NR^3As(=O)R^4R^5$, $-PR^3R^4$, $-POR^3R^4$, $-POR^3OR^4$, $-P(=O)R^3R^4$, $-P(=O)OR^3R^4$, $-P(=O)OR^3OR^4$, $-AsR^3R^4$, $-AsOR^3R^4$, $-AsOR^3OR^4$, $-As(=O)R^3R^4$, $-As(=O)OR^3R^4$, $-As(=O)OR^3OR^4$, $-NR^3-C(=NR^4)NR^5R^6$, $-C(=O)R^3$, $-C(=O)OR^3$, $-C(=S)OR^3$, $-C(=O)SR^3$, $-C(=S)SR^3$, $-C(=S)NR^3R^4$, $-SiR^3R^4R^5$, $-SiOR^3R^4R^5$, $-SiOR^3OR^4R^5$, $-SiOR^3OR^4OR^5$, $-(CR^3R^4)_n$(3-12-membered heterocycle), $-(CR^3R^4)_n$(C_3-C_{12} cycloalkyl), $-(CR^3R^4)_n$(C_5-C_{20} aryl), $-(CR^3R^4)_n$(5-12-membered heteroaryl), $-(CR^3R^4)_nC(O)NR^5R^6$, or $-(CR^3R^4)_nC(O)R^5$;

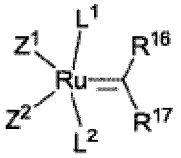
each functional group R^3, R^4, R^5, and R^6 denotes, independently, an atom of hydrogen, a halogen atom, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_2-C_{12} alkynyl, C_3-C_{12} cycloalkyl, C_5-C_{20} aryl, 5-12-membered heterocycle;

each m denotes, independently, 0, 1, or 2;

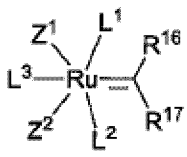
each n denotes, independently, 0, 1, 2, 3, or 4;

each p denotes, independently, 1 or 2;

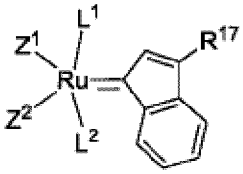
undergoes a reaction with a carbene ruthenium complex with formula **11a**, **11b**, **11c**, or **11d**:



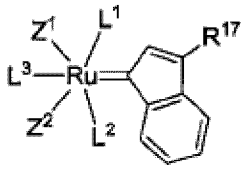
formula **11a**



formula **11b**



formula **11c**



formula **11d**

in which

L^1, L^2, and L^3 denote, independently, an inert ligand;

Z^1 and Z^2 denote, independently, an anion ligand;

R^{16} has the same meaning as R^1 in formula **9**;

R^{17} denotes an atom of hydrogen, C_5-C_{20} aryl, C_5-C_{20} heteroaryl, vinyl, or allenyl.

5. Method according to Claim 4, characterised in that the reaction is carried out in the presence of anhydrous halogen salts of copper(I) such as CuBr or CuCl in the presence of Brønsted acids such as H_2SO_4, HCl, HNO_3, H_3PO_4, sulphonated polymers (Nafion-H), or other acids bonded with a fixed substrate, in a solvent.

6. Method according to Claim 4 or 5, characterised in that the reaction is carried out at a temperature in the range of 0-120°C.

7. Method according to Claim 4 or 5 or 6, characterised in that the reaction is carried out in a protic or aprotic solvent or a chlorinated solvent or in an aromatic hydrocarbon solvent, or in mixtures thereof.

8. Method according to any one of Claims 4 to 7, characterised in that the reaction is carried out in a solvent such as methylene chloride and/or toluene.

9. Use of the ruthenium complexes of formula 1 as (pre)catalysts in metathesis processes.

10. Use according to Claim 9, characterised in that the ruthenium complexes are used as (pre)catalysts in ring-opening metathesis reactions, homometathesis, cross-metathesis, metathesis of the alkene-alkyne (ene-yne) type, ring-closing metathesis or ROMP-type polymerisation reactions.

11. Complexes according to Claim 1 or 2, characterised in that

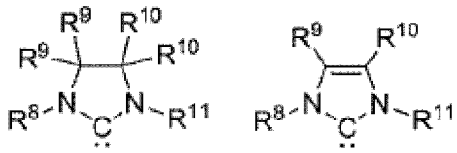
Z^1 and Z^2 each denote an atom of chlorine;

X denotes an atom of bromine or iodine; and

R_1 denotes an atom of hydrogen,

A denotes -1,2-phenylene, -1,2-naphthylene, -2,3-naphthylene or -1,8-naphthylene, which may be substituted with at least one functional group selected from a group comprising -OMe, -Me and

the inert ligand L^1 denotes a ligand with formula **7a** or **7b**;



formula **7a** formula **7b**

in which the functional groups R^8, R^9, R^{10}, and R^{11} may have the meaning described above.

Figure 1

Catalytic activity in cyclisation of diethyl diallylmalonate for the catalysts of the invention (^{1}H-NMR methods; Kinetic profiles of the course of the reaction)

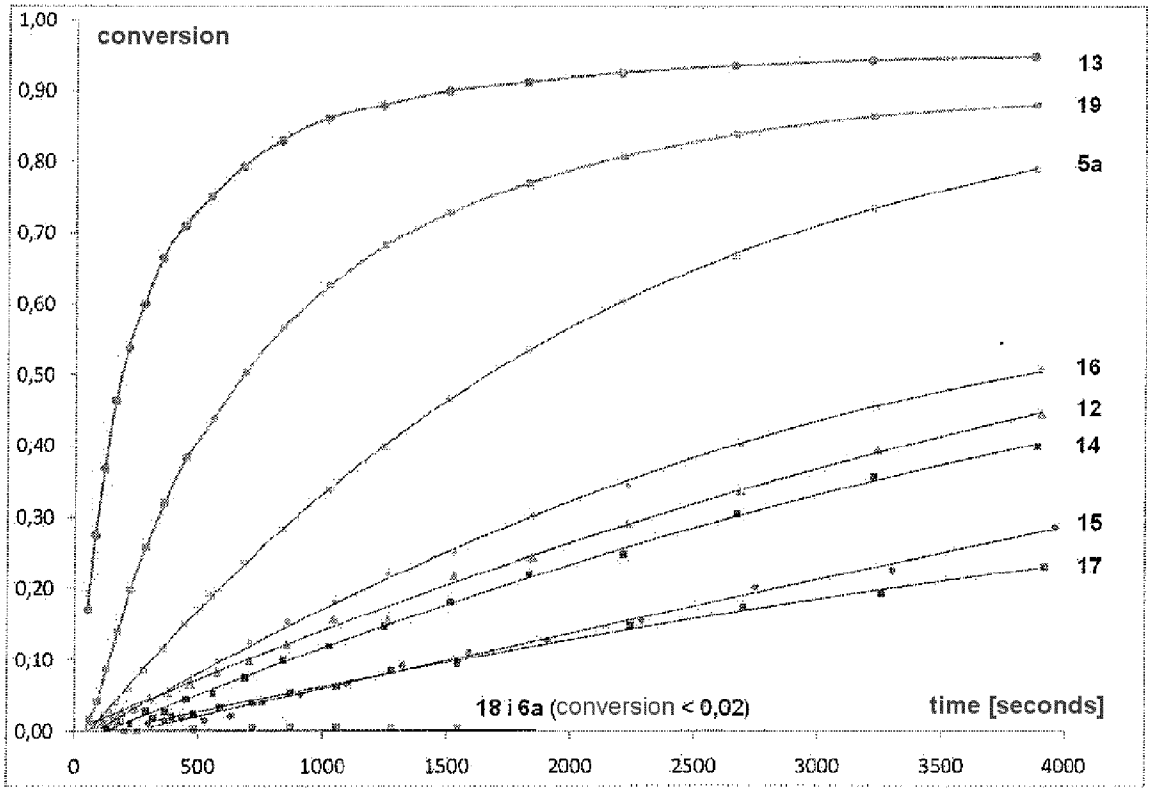


Figure 2

Kinetic profiles of the course of reactions with the catalyst of formula **18** at temperatures of 25, 40, and 55°C

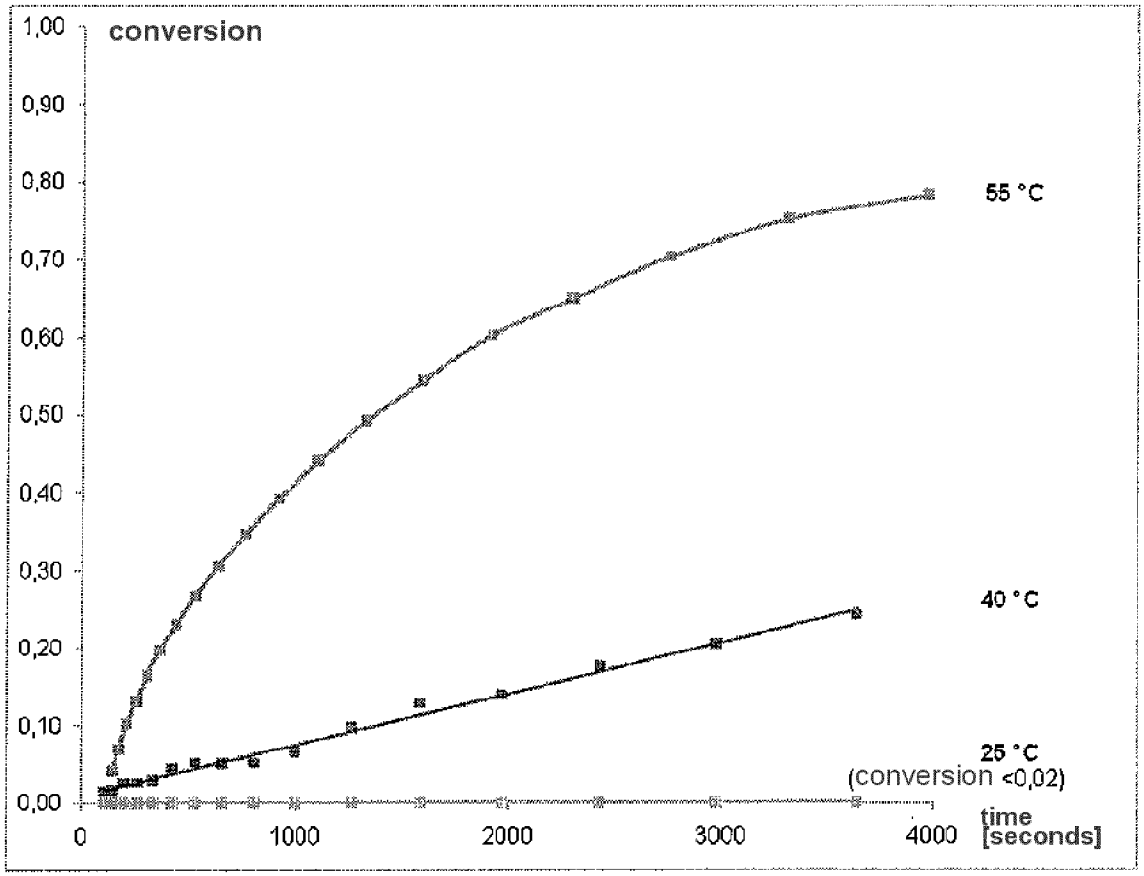
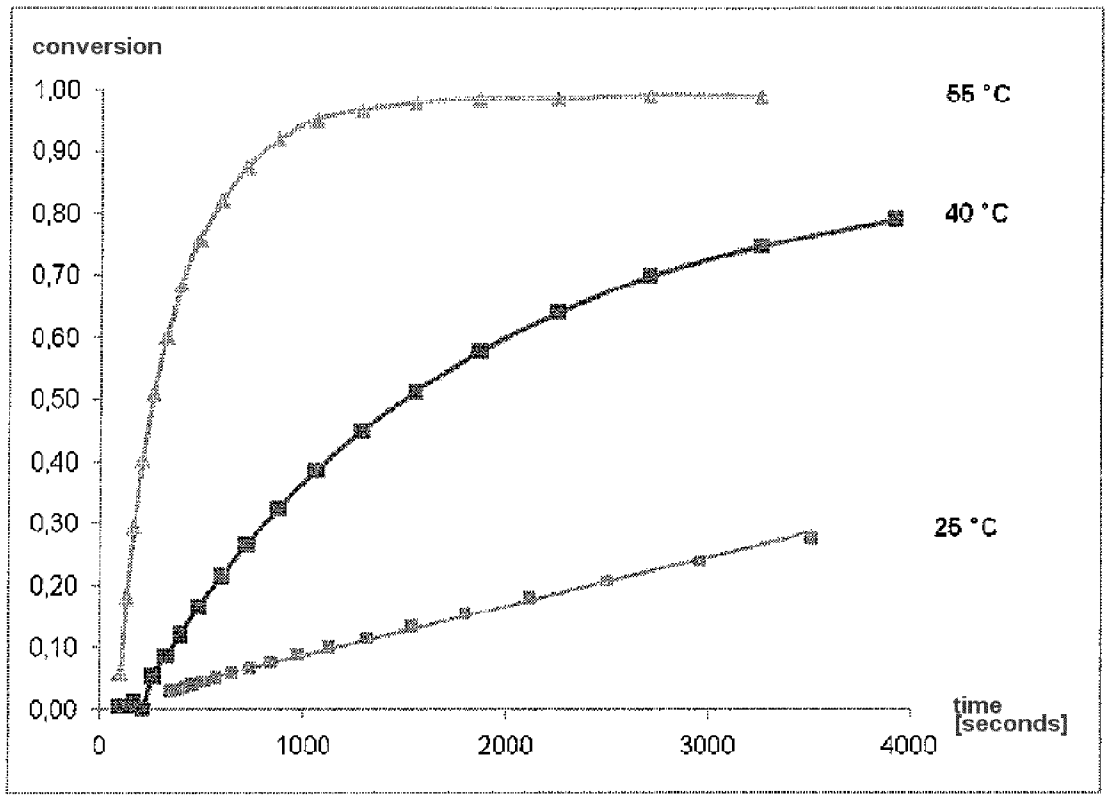


Figure 3

Kinetic profiles of the course of reactions with the catalyst of formula **15** at temperatures of 25, 40, and 55°C



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/060498

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J31/22
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2008/275247 A1 (KADYROV RENAT [DE] ET AL) 6 November 2008 (2008-11-06) paragraphs [0008], [0009] - [0017], [0018] - [0025] paragraphs [0064] - [0079] -----	1,2,4-10 3,11
A	HEJL AA ET AL: "Latent Olefin Metathesis Catalysts Featuring Chelating Alkylidenes", ORGANOMETALLICS, ACS, WASHINGTON, DC, US, vol. 25, no. 26, 1 January 2006 (2006-01-01), pages 6149-6154, XP002496195, ISSN: 0276-7333, DOI: 10.1021/OM060620U [retrieved on 2006-11-14] page 6153, last paragraph; compounds 9,15,17 -----	1-11
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
20 September 2012	27/09/2012

Name and mailing address of the ISA/	Authorized officer
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3

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/043180 A1 (ZHAN ZHENG-YUN J [CN] ZHAN ZHENG-YUN JAMES [CN]) 22 February 2007 (2007-02-22) paragraphs [0004] - [0015]; examples 45,46 -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/060498

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		DE 102007020694 A1	06-11-2008
		EP 1990348 A2	12-11-2008
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		CN 102643175 A	22-08-2012
		EP 1905777 A1	02-04-2008
		JP 2008546846 A	25-12-2008
		KR 20080037009 A	29-04-2008
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		US 2012016093 A1	19-01-2012
		WO 2007003135 A1	11-01-2007