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(54) **CATALYST COMPOSITIONS AND THEIR USE
FOR HYDROGENATION OF NITRILE
RUBBER**

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(57) **ABSTRACT**

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This invention relates to novel catalyst compositions based on ruthenium or osmium carbene-complex catalysts, pref. of the Grubbs-I, -II or -III type or fluorenylidene analogues thereof, and terminal olefins, pref. enol ethers such as ethyl vinyl ether (EVE or VEE) as co-catalysts and to a process for selectively hydrogenating nitrile rubbers in the presence of such catalyst compositions, pref. with a preceding metathesis step using the same complex catalyst as in the hydrogenation step.

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CATALYST COMPOSITIONS AND THEIR USE FOR HYDROGENATION OF NITRILE RUBBER

FIELD OF THE INVENTION

[0001] This invention relates to novel catalyst compositions obtainable from reacting Ruthenium- or Osmium-based complex catalysts with specific co-catalysts and to a process for selectively hydrogenating nitrile rubbers in the presence of such novel catalyst compositions.

BACKGROUND OF THE INVENTION

[0002] The term “acrylonitrile-butadiene rubber” or “nitrile rubber”, also named as “NBR” for short, shall be interpreted broadly and refers to rubbers which are copolymers or terpolymers of at least one α , β -unsaturated nitrile, at least one conjugated diene and, if desired, one or more further copolymerizable monomers.

[0003] Hydrogenated NBR, also referred to as “HNBR” for short, is produced commercially by hydrogenation of NBR. Accordingly, the selective hydrogenation of the carbon-carbon double bonds in the diene-based polymer must be conducted without affecting the nitrile groups and other functional groups (such as carboxyl groups when other copolymerizable monomers were introduced into the polymer chains) in the polymer chains.

[0004] HNBR is a specialty rubber which has very good heat resistance, an excellent resistance to ozone and chemicals and also an excellent oil resistance. The abovementioned physical and chemical properties of HNBR are associated with very good mechanical properties, in particular a high abrasion resistance. For this reason, HNBR has found wide use in a variety of applications. HNBR is used, for example, for seals, hoses, belts and damping elements in the automobile sector, also for stators, oil well seals and valve seals in the field of oil exploration and also for numerous parts in the aircraft industry, the electronics industry, mechanical engineering and shipbuilding. A hydrogenation conversion higher than 95%, or a residual double bond (RDB) content <5%, without cross-linking during the hydrogenation reaction and a gel level of less than about 2.5% in the resultant HNBR is a threshold that ensures high-performance applications of HNBR in these areas and guarantees excellent processability of the final product.

[0005] The degree of hydrogenation of the copolymerized diene units in HNBR may vary in the range from 50 to 100%, however, the desired hydrogenation degree is from about 80 to about 100%, preferably from about 90 to about 99.9%. Commercial grades of HNBR typically have a remaining level of unsaturation below 18% and a content of acrylonitrile of roughly up to about 50%.

[0006] It is possible to carry out the hydrogenation of NBR either with homogeneous or with heterogeneous hydrogenation catalysts. The catalysts used are usually based on rhodium, ruthenium or palladium, but it is also possible to use platinum, iridium, rhenium, osmium, cobalt or copper either as metal or preferably in the form of metal compounds (see e.g. U.S. Pat. No. 3,700,637, DE-A-25 39 132, EP-A-0 134 023, DE-A-35 41 689, DE-A-35 40 918, EP-A-0 298 386, DE-A-35 29 252, DE-A-34 33 392, U.S. Pat. No. 4,464,515 and U.S. Pat. No. 4,503,196). Suitable catalysts and solvents for a hydrogenation in the homogeneous phase are known from DE-A-25 39 132 and EP-A-0 471 250.

[0007] Also for commercial purposes the production of HNBR by hydrogenation of NBR is performed in organic solvents by using either a heterogeneous or a homogeneous transition metal catalyst often based on rhodium or palladium. Such processes suffer from drawbacks such as high prices for the catalyst metals and the cost involved in catalyst metal removal/recycle. This has led to research and development of alternative catalysts based on cheaper noble metals, such as osmium and ruthenium.

[0008] Alternative NBR hydrogenation processes can be performed using Os-based catalysts. One catalyst excellently suited for NBR hydrogenation is $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ as described in Ind. Eng. Chem. Res., 1998, 37(11), 4253-4261. The rates of hydrogenation using this catalyst are superior to those produced by Wilkinson's catalyst ($\text{RhCl}(\text{PPh}_3)_3$) over the entire range of reaction conditions studied.

[0009] Ru-based complexes are also good catalysts for polymer solution hydrogenation, and the price for Ru metal is even cheaper. Ru— PPh_3 complexes and $\text{RuHCl}(\text{CO})\text{L}_2$ (L is a bulky phosphine) catalyst systems lead to quantitative hydrogenation of NBR as disclosed in Journal of Molecular Catalysis A: Chemical, 1997, 126(2-3), 115-131). During such hydrogenation it is not necessary to add a free phosphine ligand to maintain the catalyst activity. However, they are prone to gel formation and may cause a certain degree of cross-linking during hydrogenation.

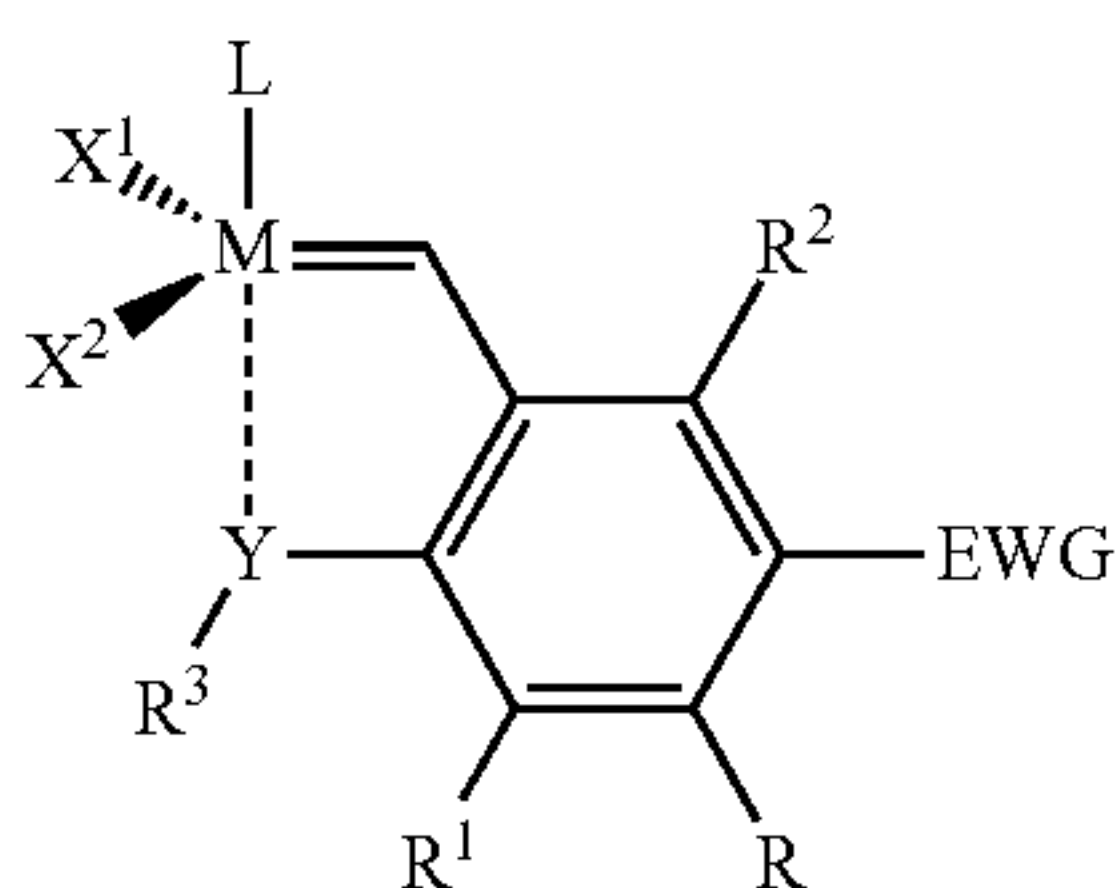
[0010] However, these above mentioned Os or Ru catalysts are active catalysts for hydrogenation only, not for metathesis reactions. Therefore, these types of Os or Ru catalysts cannot be used for NBR metathesis/degradation to produce NBR with reduced molecular weight.

[0011] Another problem of the HNBR production is that HNBR with a low Mooney viscosity is difficult to manufacture by the direct hydrogenation of commercially available NBR. The relatively high Mooney viscosity places restrictions on the processability of HNBR. Many applications would ideally use HNBR grades with a lower molecular weight and a lower Mooney viscosity. This would give a decisive improvement in processability.

[0012] For a long time, it has not been possible to produce HNBR on a large scale having a low molar mass corresponding to a Mooney viscosity (ML1+4 at 100° C.) in the range below 55 or with a weight average molecular weight of about $\text{Mw} < 200000$ g/mol by means of the established direct NBR hydrogenation processes mainly for two reasons: Firstly a sharp increase in the Mooney viscosity occurs during hydrogenation of NBR which means that a HNBR polymer with substantially increased Mooney viscosity is obtained. The Mooney Increase Ratio (MIR) is generally around 2 or even above, depending upon the NBR grade, hydrogenation level and nature of the NBR feedstock. Thus, the Mooney viscosity range of marketed HNBR is limited by the lower limit of the Mooney viscosity of the NBR starting material. Secondly, the molar mass of the NBR feedstock to be used for the hydrogenation cannot be reduced at will since otherwise work-up in the NBR industrial plants available is no longer possible because the rubber becomes too sticky. The lowest Mooney viscosity of an NBR feedstock which can be worked up without difficulties in an established industrial plant is in a range of about 30 Mooney units (ML1+4 at 100° C.). The Mooney viscosity of the hydrogenated nitrile rubber obtained using such an NBR feedstock is in the order of 55 Mooney units (ML1+4 at 100° C.). The Mooney viscosity is determined in accordance with ASTM standard D 1646.

[0013] In the more recent prior art, this problem is solved by reducing the molecular weight of the nitrile rubber before hydrogenation by degradation to a Mooney viscosity (ML1+4 at 100° C.) of less than 30 Mooney units or a weight average molecular weight of $M_w < 200000$ g/mol. The reduction in the molecular weight is achieved by metathesis of the NBR in the presence of metathesis catalysts. WO-A-02/100905 and WO-A-02/100941 describe for example a process which comprises degradation of nitrile rubber starting polymers by olefin metathesis and subsequent hydrogenation. A nitrile rubber is reacted in a first step in the presence of a coolefine and a specific catalyst based on osmium, ruthenium, molybdenum or tungsten complexes and hydrogenated in a second step. The hydrogenated nitrile rubbers obtained may have a weight average molecular weight (M_w) in the range from 30 000 to 250 000, a Mooney viscosity (ML 1+4 at 100° C.) in the range from 3 to 50 and a polydispersity index PDI of less than 2.5. The metathesis reaction is advantageously carried out in the same solvent as the subsequent hydrogenation so that the degraded nitrile rubber does not have to be necessarily isolated from the solvent after the degradation reaction is complete. Well-known for metathesis of nitrile rubber are a number of Ru-based metathesis catalysts like e.g. Grubbs I (benzylidene bis(tricyclohexylphosphine)dichloro ruthenium), Grubbs II (benzylidene [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]tricyclohexylphosphine dichloro ruthenium), Grubbs III (benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-bis(3-bromopyridine)ruthenium), Hoveyda-Grubbs II ([1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(o-isopropoxyphenylmethylene)ruthenium) (see e.g. US-A-2008/0064882) and a number of fluorenyliden-based complex catalysts (see e.g. US-A-2009/0076226)

[0014] EP-A-1 905 777 discloses ruthenium complex catalysts having the general structure



wherein

[0015] M is ruthenium,

[0016] X^1 and X^2 are each chloro or RCOO with R in such RCOO being C_1 - C_{20} alkyl or a derivative thereof,

[0017] L is an electron donating complex ligand, which could be linked or not linked with X^1 to form a cyclic structure

[0018] Y is oxygen, sulfur, nitrogen or phosphorus;

[0019] R is H, halogen atom, nitro, cyano, C_1 - C_{20} alkyl, C_1 - C_{20} alkoxy, C_1 - C_{20} alkylthio, C_1 - C_{20} silanyl, C_1 - C_{20} silanyloxy, C_6 - C_{20} aryl, C_6 - C_{20} aryloxy, C_2 - C_{20} heterocyclic, C_2 - C_{20} heterocyclic aryl, sulfinyl, sulfonyl, formyl, C_1 - C_{20} carbonyl, C_1 - C_{20} ester, C_1 - C_{20} amido, C_1 - C_{20} uramido or derivatives or C_1 - C_{20} sulfonamido group;

[0020] R^1 and R^2 are each H, bromo (Br), iodo (I), C_1 - C_{20} alkyl or derivatives, C_1 - C_{20} alkoxy, C_1 - C_{20} alkylthio, C_1 - C_{20} silanyloxy, C_6 - C_{20} aryloxy, C_6 - C_{20} aryl, C_2 - C_{20}

heterocyclic, C_2 - C_{20} heterocyclic aryl, C_1 - C_{20} ester, C_1 - C_{20} amido, C_1 - C_{20} uramido or derivatives or C_1 - C_{20} sulfonamido group;

[0021] R^3 is H, C_1 - C_{20} alkyl or derivatives, C_1 - C_{20} alkoxy, C_1 - C_{20} alkylthio, C_1 - C_{20} silanyl, C_1 - C_{20} silanyloxy, C_6 - C_{20} aryl, C_6 - C_{20} aryloxy, C_2 - C_{20} heterocyclic, C_2 - C_{20} heterocyclic aryl, sulfinyl, sulfonyl, C_1 - C_{20} carbonyl, C_1 - C_{20} ester, C_1 - C_{20} amido, C_1 - C_{20} uramido or derivatives or C_1 - C_{20} sulfonamido group; and

[0022] EWG is C_1 - C_{20} aminosulfonyl (SO_2NR_2), formyl, C_1 - C_{20} carbonyl, C_1 - C_{20} ester, C_1 - C_{20} aminocarbonyl ($CONR_2$), amido, chloro, fluoro, C_1 - C_{20} uramido or derivatives or C_1 - C_{20} sulfonamido group.

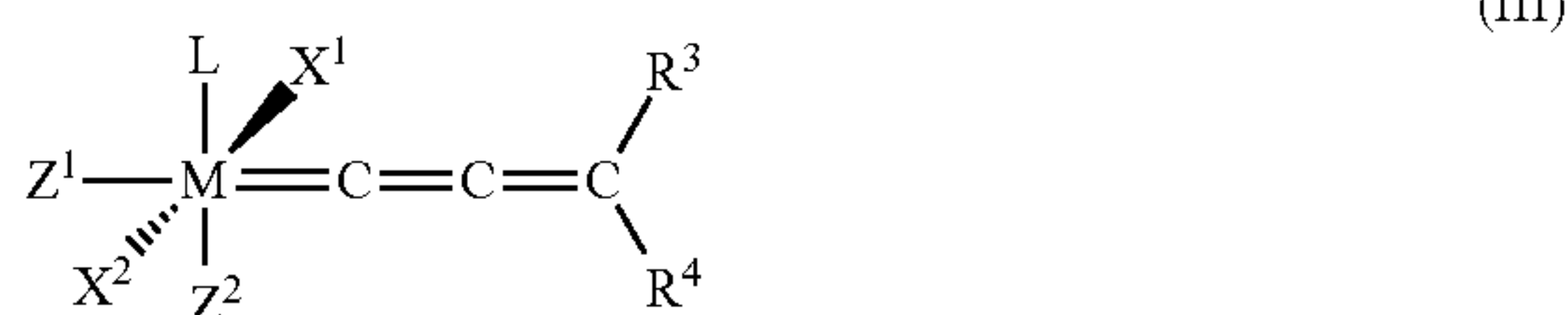
[0023] EP-A-1 905 777 further states that these catalysts can be used in olefin metathesis reactions including ring-closing olefin metathesis reactions, intermolecular olefin metathesis reactions, and olefin metathesis polymerization reactions. The examples show the preparation of low molecular weight substances by intramolecular ring closing metathesis in the presence of certain of the generally disclosed catalysts. EP-A-1 905 777 does neither provide any disclosure that these catalysts can be used to degrade the molecular weight of polymers, in particular nitrile rubbers nor that they show any hydrogenation activity.

[0024] Furtheron processes for simultaneous metathesis and hydrogenation are known from prior art. In WO-A-2005/080456 the preparation of hydrogenated nitrile rubber polymers having low molecular weights and narrower molecular weight distributions than those known in the art is carried out by simultaneously subjecting the nitrile rubber to a metathesis reaction and a hydrogenation reaction. The reaction takes place in the presence of a Ruthenium- or Osmium-based pentacoordinated complex catalyst, in particular 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene (tricyclohexylphosphine) ruthenium (phenylmethylene)dichloride (also called Grubbs 2nd generation catalyst). However, WO-A-2005/080456 does not provide any disclosure or teaching how to influence the two simultaneously occurring reactions, i.e. metathesis and hydrogenation or how to control the activity of the respective catalysts regarding metathesis and hydrogenation.

[0025] WO-A-2011/023788 also discloses a process for subjecting a nitrile rubber in the presence of hydrogen to a combined and simultaneous metathesis and hydrogenation reaction in the presence of specifically defined hexacoordinated Ruthenium-oder Osmium based catalysts in order to prepare hydrogenated nitrile rubbers having lower molecular weights and narrower molecular weight distributions than those known in the art. Such process is performed by using at least one catalyst of general formula (I) to (III)



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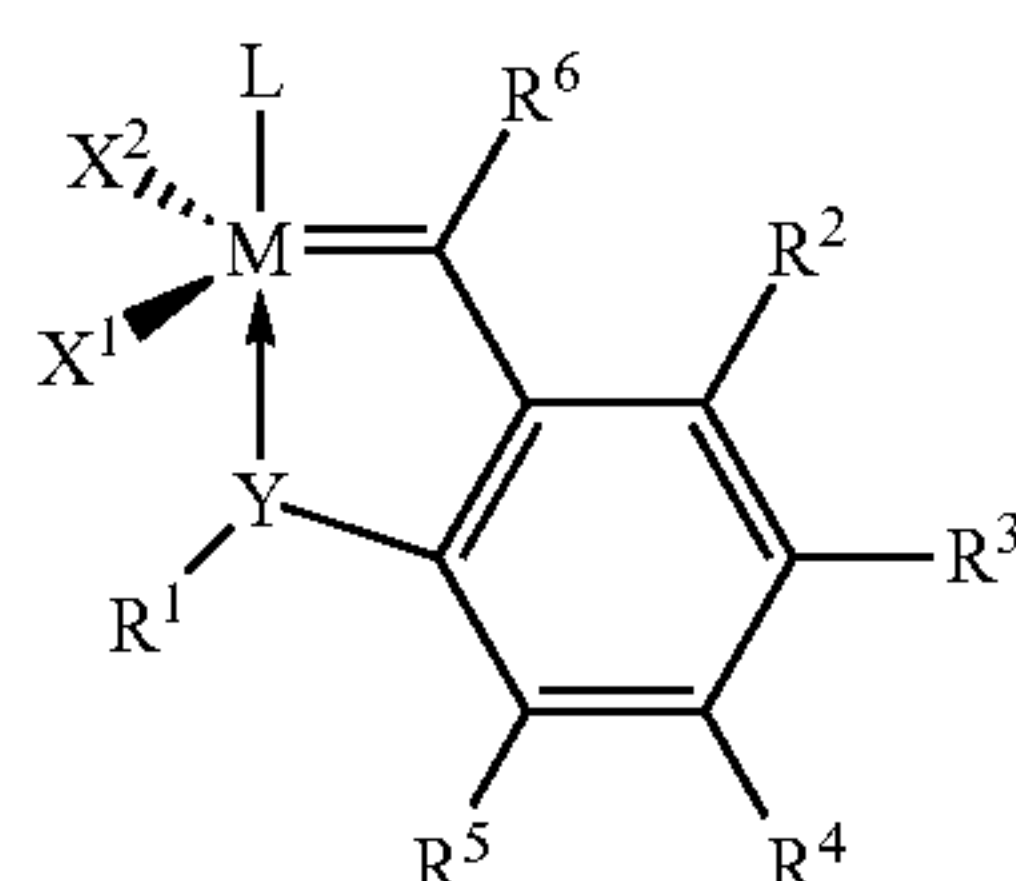
where

[0026] M is ruthenium or osmium,

[0027] X¹ and X² are identical or different ligands, preferably anionic ligands,[0028] Z¹ and Z² are identical or different and neutral electron donor ligands,[0029] R³ and R⁴ are each independently H or a substituent selected from the group consisting of alkyl, cycloalkyl, alkenyl, alkynyl, aryl, carboxylate, alkoxy, alkenyloxy, alkynyl-oxy, aryloxy, alkoxy-carbonyl, alkylamino, alkylthio, arylthio, alkylsulphonyl and alkylsulphinyl radical, each of which may optionally be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl moieties, and

[0030] L is a ligand.

[0031] WO-A-2011/029732 also discloses an alternative process for subjecting a nitrile rubber in the presence of hydrogen to a combined and simultaneous metathesis and hydrogenation reaction in the presence of specifically defined pentacoordinated Ruthenium- or Osmium based catalysts in order to prepare hydrogenated nitrile rubbers having low molecular weights and a narrow molecular weight distribution. Such process is performed in the presence of at least one compound of the general formula (I),



where

[0032] M is ruthenium or osmium,

[0033] Y is oxygen (O), sulphur (S), an N—R¹ radical or a P—R¹ radical,[0034] X¹ and X² are identical or different ligands,[0035] R¹ is an alkyl, cycloalkyl, alkenyl, alkynyl, aryl, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxy-carbonyl, alkylamino, alkylthio, arylthio, alkylsulphonyl, CR¹³C(O)R¹⁴ or alkylsulphinyl moiety, each of which may optionally be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl moiety,[0036] R¹³ is hydrogen or alkyl, cycloalkyl, alkenyl, alkynyl, aryl, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxy-carbonyl, alkylamino, alkylthio, arylthio, alkylsulphonyl or alkylsulphinyl moiety, each of which may optionally be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl moiety;[0037] R¹⁴ is alkyl, cycloalkyl, alkenyl, alkynyl, aryl, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxy-carbonyl, alkylamino, alkylthio, arylthio, alkylsulphonyl or alkylsul-

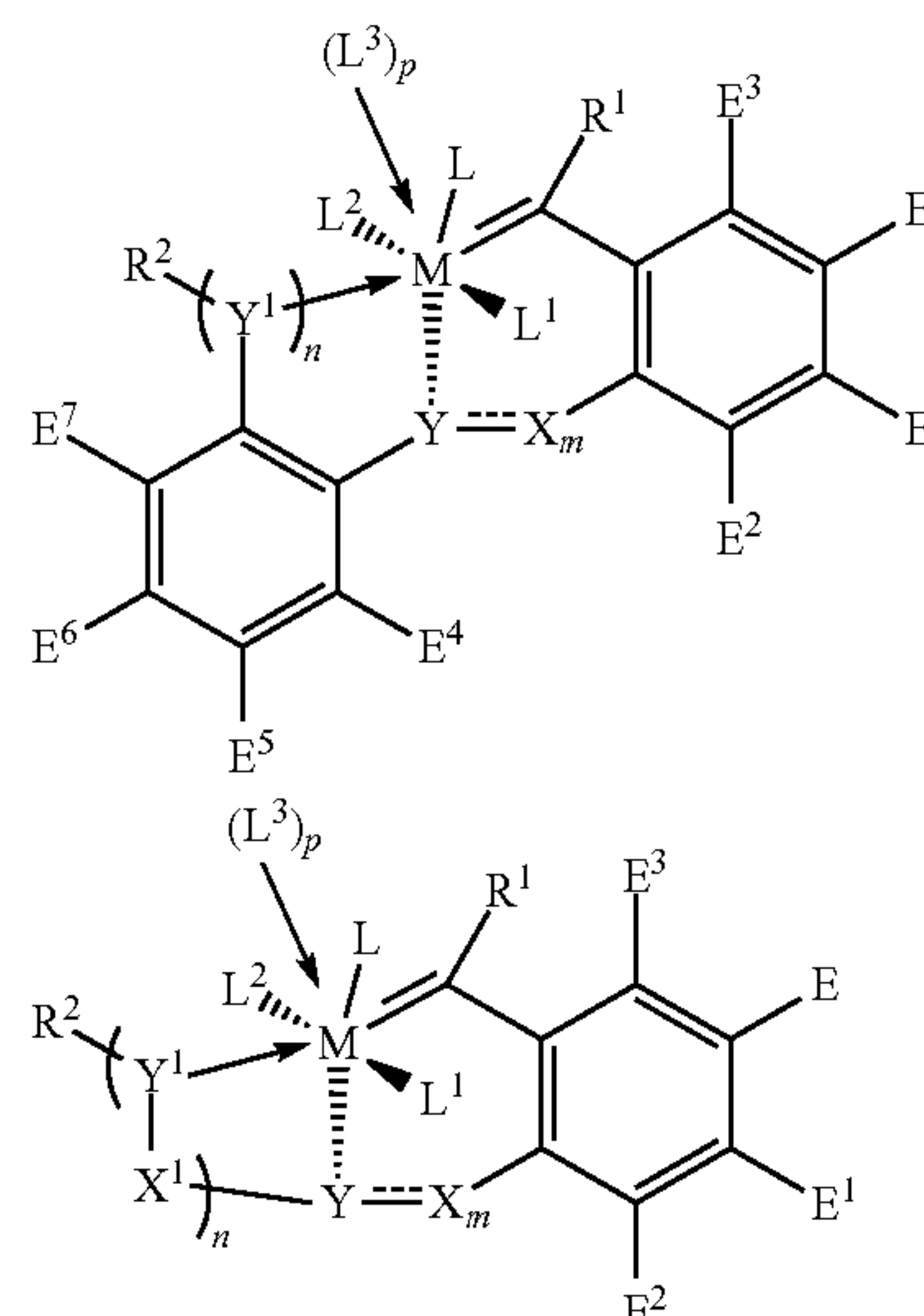
phanyl moiety, each of which may optionally be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl moiety;

[0038] R², R³, R⁴ and R⁵ are identical or different and are each H, organic or inorganic radicals,[0039] R⁶ is H or an alkyl, alkenyl, alkynyl or aryl radical and

[0040] L is a ligand.

[0041] However, neither WO-A-2011/023788 nor WO-A-2011/029732 provide any disclosure or teaching how to influence the two simultaneously occurring reactions, i.e. metathesis and hydrogenation or how to control the two-fold activity of the respective catalysts for metathesis and hydrogenation.

[0042] WO-A-2011/079799 discloses a broad variety of catalysts the general structure of which is shown hereinafter



[0043] It is stated that such catalysts can be used to provide modified nitrile butadiene rubber (NBR) or styrene-butadiene rubber (SBR) by depolymerisation. It is further stated that the catalysts can be used in a method of making a depolymerized HNBR or styrene-butadiene rubber by adding one or more of those catalysts first to carry out depolymerisation of NBR, followed by adding hydrogen into the reactor under high pressure for hydrogenation. In another embodiment it is disclosed to prepare HNBR by adding hydrogen under high pressure first, then followed by adding one or more of the above catalysts. However, WO-A-2011/079799 does not provide any disclosure or teaching how to influence the different catalytic activities of the catalysts for depolymerisation (metathesis) and hydrogenation. It is accepted that while hydrogenation takes place simultaneously metathesis leads to a degradation of the molecular weight in uncontrolled manner.

[0044] A number of references describe the use of metathesis catalysts in two step reactions starting with a ring-opening metathesis polymerisation (ROMP) first which is followed by a hydrogenation reaction (so called "tandem polymerization/hydrogenation reactions").

[0045] According to Organometallics, 2001, 20(26), 5495-5497 the metathesis catalyst Grubbs I can be used for ROMP of cyclooctene or a norbornene derivative first, then followed

by a hydrogenation of the polymers. It is reported that the addition of a base like NEt_3 increases the catalytic activity in the hydrogenation reaction.

[0046] J. Am. Chem. Soc 2007, 129, 4168-9 also relates to tandem ROMP-hydrogenation reactions starting from functionalized norbornenes and compares the use of three Ruthenium-based catalysts, i.e. Grubbs I, Grubbs II and Grubbs III catalysts in such tandem reactions. It is described that the Ruthenium-based catalyst on the end of the polymer backbone is liberated and transformed into a hydrogenation-active species through reaction with H_2 , base (NEt_3), and methanol.

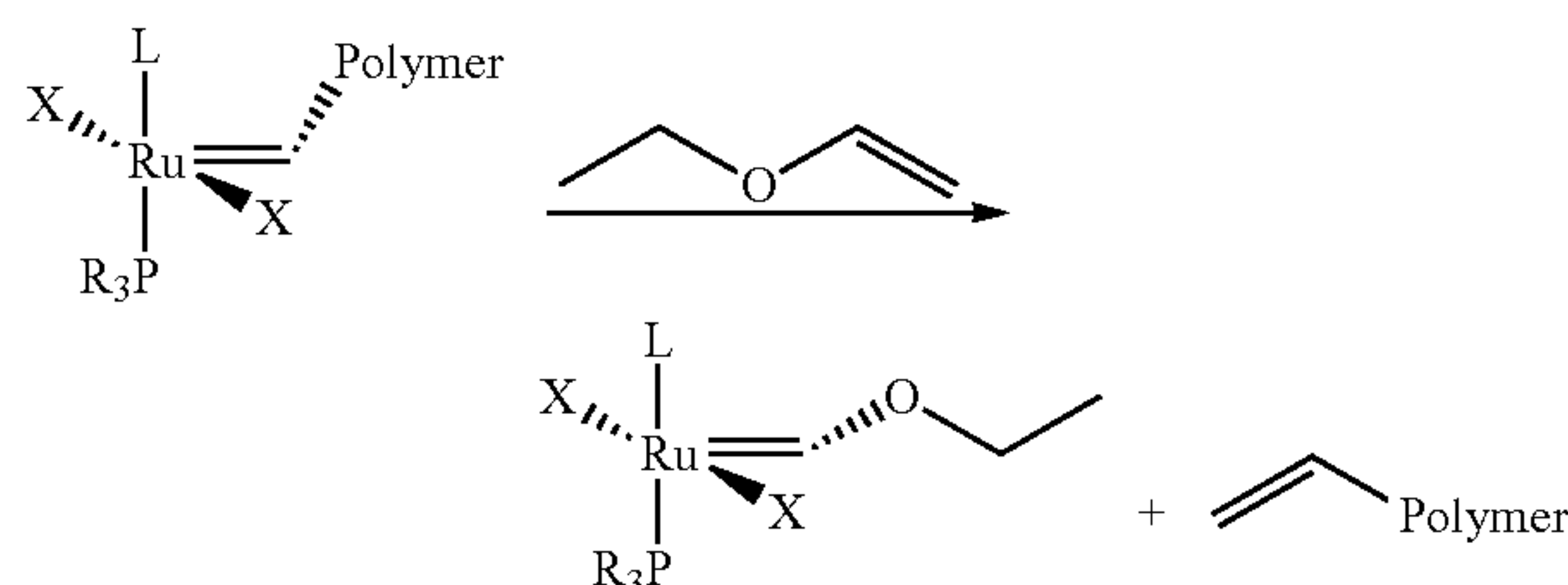
[0047] EP-A-1 197 509 and JP 2005/272572A discloses a process for preparing a hydrogenated polymer by polymerizing a cycloolefine in the presence of an organo ruthenium or osmium compound and subsequently subjecting the unsaturated polymer obtained during polymerization to a hydrogenation under addition of a hydrogenation catalyst. EP-A-1 197 509 does not describe any cross-metathesis and does not relate to any degradation of the polymer via metathesis. JP 2005/272572 A discloses that the polymerisation reaction catalyzed by the metathesis catalyst is stopped by adding alkyl vinyl ether to the reaction system. Thereafter the hydrogenation reaction is performed without adding any further or different catalyst. In Example 1 of JP 2005/272572A Grubbs II catalyst is used in an amount of 0.05 parts by weight and 0.03 parts by weight of ethyl vinyl ether are added after the polymerisation reaction, hence the molar ratio of metathesis catalyst to ethyl vinyl ether is 1:7. In the description of JP 2005/272572A it is further disclosed that the molar ratio of metathesis catalyst to alkyl vinyl ether is generally 1:1 to 1:100, preferably 1:1 to 1:10.

[0048] Inorg. Chem 2000, 39, 5412-14 also explores tandem ROMP polymerization/hydrogenation reactions. The focus lies on the mechanism of the hydrogenolysis of the ruthenium-based metathesis catalyst Grubbs I. It is shown that such catalyst is transformed into dihydride, dihydrogen and hydride species under conditions relevant to hydrogenation chemistry. However, there is no disclosure at all about polymer degradation via metathesis or hydrogenation of unsaturated polymers.

[0049] In further references the quenching of metathesis reactions with vinyl compounds is described: Numerous patent applications, e.g. US-A-2007/0049700, US-A-2008/0064882, US-A-2007/0208206, US-A-2008/0076881, US-A-2009/054597, US-A-2009/0069516, US-A-2009/0076227, US-A-2009/0076226, US-A-2010/0087600, and US-A-2010/0093944, and two not yet published patent applications with the serial numbers EP 11153437.6 and PCT/EP2011/063570 are referring to the molecular weight degradation of nitrile rubbers by a metathesis reaction and contain experiments in which the reaction mixture is treated with vinyl ethylether after the metathesis reaction in order to destroy the metathesis catalyst. The molar ratio of vinyl ethylether to the metathesis catalysts used is very high in order to efficiently stop the metathesis reaction by deactivation of the catalyst. In the aforementioned applications such molar ratio lies in a range of from 567:1 to more than 17.000:1. None of those patent applications provides any disclosure or hint that by choosing lower ratios of the deactivating reagent to the metathesis catalyst a catalyst composition is obtained which is excellently suited for a selective hydrogenation, i.e. without continuing to catalyse the metathetic degradation.

[0050] In J. Am. Chem. Soc. 2001, 123, 6543-54 the mechanism of ruthenium based catalysts for olefin metathesis

is disclosed. Furtheron it is described that the reaction of ruthenium carbenes with ethylvinylether can be utilized as a method for quenching ring opening metathesis polymerization. As shown in the following scheme a so-called Fischer-carbene complex is reported to be built.



[0051] In Tetrahedron Letters 50 (2009), 6103-5 it is disclosed that di (ethylene glycol) vinyl ether and amine derivatives thereof can also be used as deactivating reagents for olefin metathesis catalysts. It is experimentally shown that the use of 4 equivalents of di (ethylene glycol) vinyl ether based on the metathesis catalyst are sufficient to efficiently deactivate the metathesis catalyst. Even 2 equivalents are reported to be sufficient. However, this reference does not deal with hydrogenation processes subsequently to olefin metathesis at all.

[0052] In Macromol. Symp. 2010, 297, 25-32 it is shown that polyisobutylene ("PIB") terminally functionalized with a vinyl ether group may serve to sequester a complex catalyst by conversion of a reactive ruthenium alkylidene complex into a phase-immobilized Fischer carbene complex. Additionally kinetic studies are presented on the reaction of 2 equivalents PIB vinyl ether and 6 as well as 15 equivalents of ethyl vinyl ether with Grubbs II catalyst.

[0053] It can be seen from the above that:

[0054] (1) up to now, hydrogenation catalysts which are very active for the selective hydrogenation of nitrile rubbers are known and Rh- and Pd-based catalysts are already used in industrial hydrogenation processes; however, cheaper Ru-based hydrogenation catalysts are still facing the gel formation problem when used for NBR hydrogenation. Most importantly, only HNBR with high molecular weight can be produced by using these catalysts which can only catalyse the NBR hydrogenation. The molecular weight of the final HNBR is determined by the molecular weight of the raw NBR, not by the hydrogenation catalysts;

[0055] (2) the degradation of nitrile rubber by metathesis is known using ruthenium- or osmium-based metathesis catalysts followed by a hydrogenation of the degraded nitrile rubber to afford hydrogenated nitrile rubber; if the same catalyst is used for metathesis and for hydrogenation, such catalysts are highly active for NBR metathesis while not so active for NBR hydrogenation; and

[0056] (3) catalysts which possess both, i.e. catalytic activity for both, metathesis and hydrogenation, cannot be used in a controlled manner

[0057] Therefore, in current commercial production processes, a separate hydrogenation catalyst is added into the reaction system for the NBR hydrogenation after the NBR metathesis step. In this way, HNBR with controlled molecular weight can be produced, but two catalysts (one for metathesis and one for hydrogenation) are required to achieve high reaction efficiency.

[0058] However, hitherto there is not a single literature reporting the preparation of hydrogenated nitrile rubber with controlled molecular weight and therefore controllable Mooney viscosity only using one kind of ruthenium- or osmium-based catalyst which is otherwise known for its metathetic activity. Also, up to now, there is no hydrogenation catalyst which can be used at a very low concentration for NBR hydrogenation to high conversion. So far the catalyst removal or recycle step is required after the hydrogenation.

[0059] Accordingly it was the object of the present invention to provide an improved catalyst composition allowing a selective hydrogenation of nitrile rubber at low catalyst concentrations and short hydrogenation times. Additionally such improved catalyst composition should be designed in a way to allow an upstream metathesis reaction, if desired, using the same catalyst as contained in the catalyst composition.

SUMMARY OF THE INVENTION

[0060] The present invention relates to novel catalyst compositions which are obtainable by contacting a complex catalyst based on ruthenium or osmium as central metal and bearing at least one ligand which is bound to the ruthenium or osmium central metal in a carbene-like fashion with at least one co-catalyst in a molar ratio of the complex catalyst to the co-catalyst in a range of from 1:(20-550) wherein the co-catalyst must contain at least one vinyl group.

[0061] In a particular embodiment the invention relates to novel catalyst compositions which are obtainable by contacting a complex catalyst based on ruthenium or osmium as central metal and bearing at least one ligand which is bound to the ruthenium or osmium central metal in a carbene-like fashion with at least one co-catalyst must contain at least one vinyl group and wherein the molar ratio of the complex catalyst to the co-catalyst lies in a range of from 1:(20 to below 100), preferably 1:(25 to 99.5), more preferably 1:(30 to 99), even more preferably 1:(35 to 98.5), and most preferably 1:(40 to 70).

[0062] The invention furtheron relates to a process of hydrogenating a nitrile rubber comprising

[0063] a) preparing the catalyst composition according to the invention by contacting a complex catalyst based on ruthenium or osmium as central metal and bearing at least one ligand which is bound to the ruthenium or osmium central metal in a carbene-like fashion with at least one co-catalyst in a molar ratio of the complex catalyst to the co-catalyst in the range of 1:(20-550) wherein the co-catalyst must contain at least one vinyl group and thereafter

[0064] b) hydrogenating the nitrile rubber in the presence of the novel catalyst composition.

[0065] A specific embodiment of the present invention relates to an alternative process which comprises firstly subjecting a nitrile rubber to a molecular weight degradation in a metathesis reaction by contacting the nitrile rubber in the absence or presence of a co-olefin with a complex catalyst based on ruthenium or osmium as central metal and bearing at least one ligand which is bound to the ruthenium or osmium central metal transition metal in a carbene-like fashion, then

[0066] a) preparing the catalyst composition according to the invention by contacting the complex catalyst which is present in the reaction mixture after the metathesis reaction with at least one co-catalyst in a molar ratio of the complex catalyst to the co-catalyst in the range of 1:(20-550) wherein the co-catalyst must contain at least one vinyl group and thereafter

[0067] b) hydrogenating the nitrile rubber in the presence of the novel catalyst composition.

[0068] In a particular embodiment the invention relates to the above processes wherein the molar ratio of the metathesis catalyst to the co-catalyst lies in a range of from 1:(20 to below 100), preferably 1:(25 to 99.5), more preferably 1:(30 to 99), even more preferably 1:(35 to 98.5), and most preferably 1:(40:70).

[0069] While the above described prior art like e.g. WO-A-2011/023788 and WO-A-2011/029732 always disclosed simultaneous and competing metathesis when a catalyst with metathesis activity was used for hydrogenation of nitrile rubbers, the novel process advantageously allows for the first time to perform a hydrogenation of nitrile rubber without a simultaneous metathetic degradation of the nitrile rubber, if a catalyst composition is used which has been obtained by treating the metathesis catalyst with a vinyl compound first. Hence, the present process allows a hydrogenation of nitrile rubbers in a controlled manner, i.e. under formation of hydrogenated nitrile rubber with a tailor-made molecular weight in a commercially attractive fashion. It is possible to keep the molecular weight of the nitrile rubber constant during hydrogenation. In the alternative it is also possible to adjust and regulate the molecular weight of the nitrile rubber in a desired manner by controlling and choosing the molar ratio between the metathesis catalyst and the co-catalyst when preparing the novel catalyst composition. In particular the present process allows in a specific embodiment to take advantage of using one and the same catalyst for a metathesis reaction in a first step, then adding the co-catalyst to the reaction mixture of the metathesis reaction, thereby preparing the novel catalyst composition and thereafter hydrogenating the metathesized nitrile rubber in a second step. The co-catalyst can be added at any degree of metathesis to the reaction mixture containing the transition-metal based metathesis catalyst and therefore allows to prepare tailor-made hydrogenated nitrile rubbers in a commercially attractive fashion. Additionally the hydrogenation process of the present invention allows to use the ruthenium- or osmium-based catalyst in a very low concentration, so that there is no need to remove or recycle the transition metal based catalyst after the hydrogenation.

[0070] The catalyst composition prepared and used according to the present invention is characterized by its high hydrogenation activity. High hydrogenation degrees may be achieved in short reaction times. In particular the hydrogenation activity of the novel catalyst composition is higher than the hydrogenation activity of the corresponding ruthenium- or osmium-based catalyst only used as such for NBR hydrogenation

DETAILED DESCRIPTION OF THE INVENTION

[0071] The term “substituted” used for the purposes of the present patent application means that a hydrogen atom on an indicated radical or atom has been replaced by one of the groups indicated in each case, with the proviso that the valency of the atom indicated is not exceeded and the substitution leads to a stable compound.

[0072] For the purposes of the present patent application and invention, all the definitions of moieties, parameters or explanations given above or below in general terms or in preferred ranges can be combined with one another in any way, i.e. including combinations of the respective ranges and preferred ranges.

Co-Catalyst:

[0073] In a preferred embodiment the co-catalyst has the general formula (1)



in which R and R' are identical or different and shall mean hydrogen,

[0074] OR¹ wherein R¹ shall mean alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or heteroaryl, C(=O)(R²), —C(=O)N(R²)₂, —[(CH₂)_n—X]_mR², —[(CH₂)_n—X]_m—CH=CH₂, or —(CH₂)_p—C(R³)₂R⁴

[0075] wherein

[0076] X is identical or different and means oxygen (O) or NR²

[0077] R² are identical or different and represent H, alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or heteroaryl,

[0078] R³ are identical or different and represent C₁-C₅ alkyl or —(CH₂)_n—O—CH=CH₂,

[0079] R⁴ represents (CH₂)_p—O—CH=CH₂,

[0080] n is in the range of from 1 to 5,

[0081] m is in the range of from 1 to 10,

[0082] p is in the range of from 0 to 5,

[0083] or where in the alternative, if R and R' both represent a group OR¹, both R¹ may be linked to each other and together represent a divalent group —(C(R²)₂)_q— with q being 2, 3 or 4 and

[0084] R² being identical or different and having the above defined meanings,

[0085] SR⁵, SOR⁵, SO₂R⁵

[0086] wherein R⁵ represents alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or heteroaryl,

[0087] N(R⁶R⁷), P(R⁶R⁷)

[0088] wherein R⁶ and R⁷ are identical or different and shall mean alkyl, cycloalkyl, alkenyl, alkynyl, aryl, heteroaryl, —C(=O)(R²), or

[0089] where in the alternative R⁶ and R⁷ may form together with such N or P atom to which they both are linked at the same time a saturated, unsaturated or aromatic cyclic structure with 4 to 7 carbon atoms in the cyclic structure wherein one, two or three of said carbon atoms can be replaced by a moiety selected from oxygen, sulfur, nitrogen, N—R⁸ or P—R⁸ wherein R⁸ shall mean alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or heteroaryl, or

[0090] P(=O)(OR⁹)₂

[0091] in which R⁹ are identical or different and shall mean alkyl, cycloalkyl, alkenyl, alkynyl, aryl, heteroaryl,

[0092] however, under the proviso that R and R' must not both represent hydrogen at the same time.

[0093] In the co-catalysts according to general formula (1) all alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or heteroaryl moieties in R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ or R⁹ may optionally be further substituted by one or more alkyl, halogen, alkoxy, alkenyloxy, aryl or heteroaryl substituents. All aforementioned moieties, in particular the alkyl, alkenyl and/or alkynyl moieties can be either straight chain or branched to the extent chemically plausible. Of course, the above proviso that the valency of the atom indicated is not exceeded and the substitution leads to a stable compound shall be fulfilled.

[0094] If R and R' represent OR¹, both such R¹ can be linked to each other and together represent a divalent group —(C(R²)₂)_q— with q being 2, 3, 4 or 5 and R² being identical or different and having the meanings defined regarding for-

mula (1) above. In such case a cyclic structure is formed by the divalent group together with the two oxygen atoms to which it the divalent group is bound and the adjacent vinylic carbon atom.

[0095] In another embodiment of the present invention the catalyst composition is obtained using at least one, preferably one, co-catalyst having the general formula (1)



in which R is hydrogen and R' shall mean,

[0096] OR¹ wherein R¹ shall mean C₁-C₁₆-alkyl, C₃-C₁₀-cycloalkyl, C₂-C₁₆-alkenyl, C₂-C₂₀-alkynyl, C₆-C₂₄-aryl, C₆-C₂₄-heteroaryl, —C(=O)(R²), —C(=O)N(R²)₂, —[(CH₂)_nX]_mR², —[(CH₂)_nX]_m—CH=CH₂, or —(CH₂)_p—C(R³)₂R⁴,

[0097] wherein

[0098] X is identical or different and oxygen (O) or NR²,

[0099] R² are identical or different and represent H, C₁-C₁₆-alkyl, C₃-C₁₀-cycloalkyl, C₂-C₁₆-alkenyl, C₂-C₂₀-alkynyl, C₆-C₂₄-aryl, or C₃-C₂₀-heteroaryl,

[0100] R³ are identical or different and represent C₁-C₄ alkyl or —(CH₂)_n—O—CH=CH₂,

[0101] R⁴ represents (CH₂)_p—O—CH=CH₂,

[0102] n is in the range of from 1 to 4,

[0103] m is in the range of from 1 to 5,

[0104] p is in the range of from 0 to 5,

[0105] SR⁵, SOR⁵, SO₂R⁵

[0106] wherein R⁵ represents C₁-C₁₆-alkyl, C₃-C₁₀-cycloalkyl, C₂-C₁₆-alkenyl, C₂-C₂₀-alkynyl, C₆-C₂₄-aryl, or C₆-C₂₄-heteroaryl,

[0107] N(R⁶R⁷), P(R⁶R⁷)

[0108] wherein R⁶ and R⁷ are identical or different and shall mean C₁-C₁₆-alkyl, C₃-C₁₀-cycloalkyl, C₂-C₁₆-alkenyl, C₂-C₂₀-alkynyl, C₆-C₂₄-aryl, or C₆-C₂₄-heteroaryl, —C(=O)(R²), or where in the alternative R⁶ and R⁷ may form together with such N or P atom to which they both are linked at the same time a saturated, unsaturated or aromatic cyclic structure with 4 to 7 carbon atoms in the cyclic structure wherein one, two or three of said carbon atoms can be replaced by a moiety selected from oxygen, sulfur, nitrogen, N—R⁸ or P—R⁸ wherein R⁸ shall mean C₁-C₁₆-alkyl, C₃-C₁₀-cycloalkyl, C₂-C₁₆-alkenyl, C₂-C₂₀-alkynyl, C₆-C₂₄-aryl, or C₆-C₂₄-heteroaryl, or

[0109] P(=O)(OR⁹)₂

[0110] in which R⁹ are identical or different and shall mean C₁-C₁₆-alkyl, C₃-C₁₀-cycloalkyl, C₂-C₁₆-alkenyl, C₂-C₂₀-alkynyl, C₆-C₂₄-aryl, or C₆-C₂₄-heteroaryl.

[0111] In another embodiment of the present invention the catalyst composition is obtained using at least one, preferably one, co-catalyst having the general formula (1)



[0112] in which R and R' are identical or different and shall mean

[0113] OR¹ wherein R¹ shall mean C₁-C₁₆-alkyl, C₃-C₁₀-cycloalkyl, C₂-C₁₆-alkenyl, C₂-C₂₀-alkynyl, C₆-C₂₄-aryl, C₆-C₂₄-heteroaryl, —C(=O)(R²), —C(=O)N(R²)₂, —[(CH₂)_nX]_mR², —[(CH₂)_nX]_m—CH=CH₂, or —(CH₂)_p—C(R³)₂R⁴,

[0114] wherein

[0115] X is identical or different and oxygen (O) or NR²,

[0116] R² are identical or different and represent H, C₁-C₁₆-alkyl, C₃-C₁₀-cycloalkyl, C₂-C₁₆-alkenyl, C₂-C₂₀-alkynyl, C₆-C₂₄-aryl, or C₃-C₂₀-heteroaryl,

- [0117] R^3 are identical or different and represent C_1 - C_4 alkyl or $-(CH_2)_n-O-CH=CH_2$,
- [0118] R^4 represents $(CH_2)_p-O-CH=CH_2$,
- [0119] n is in the range of from 1 to 4,
- [0120] m is in the range of from 1 to 5,
- [0121] p is in the range of from 0 to 5,
- [0122] or where in the alternative, if R and R' both represent a group OR^1 , both R^1 may be linked to each other and together represent a divalent group $-(C(R^2))_q-$ with q being 2, 3 or 4 and
- [0123] R^2 being identical or different and having the above defined meanings,
- [0124] SR^5 , SOR^5 , SO_2R^5
- [0125] wherein R^5 represents C_1 - C_{16} -alkyl, C_3 - C_{10} -cycloalkyl, C_2 - C_{16} -alkenyl, C_2 - C_{20} -alkynyl, C_6 - C_{24} -aryl, or C_6 - C_{24} -heteroaryl,
- [0126] $N(R^6R^7)$, $P(R^6R^7)$
- [0127] wherein R^6 and R^7 are identical or different and shall mean C_1 - C_{16} -alkyl, C_3 - C_{10} -cycloalkyl, C_2 - C_{16} -alkenyl, C_2 - C_{20} -alkynyl, C_6 - C_{24} -aryl, or C_6 - C_{24} -heteroaryl, $-C(=O)(R^2)$, or where in the alternative R^6 and R^7 may form together with such N or P atom to which they both are linked at the same time a saturated, unsaturated or aromatic cyclic structure with 4 to 7 carbon atoms in the cyclic structure wherein one, two or three of said carbon atoms can be replaced by a moiety selected from oxygen, sulfur, nitrogen, $N-R^8$ or $P-R^8$ wherein R^8 shall mean C_1 - C_{16} -alkyl, C_3 - C_{10} -cycloalkyl, C_2 - C_{16} -alkenyl, C_2 - C_{20} -alkynyl, C_6 - C_{24} -aryl, or C_6 - C_{24} -heteroaryl, or
- [0128] $P(=O)(OR^9)_2$
- [0129] in which R^9 are identical or different and shall mean C_1 - C_{16} -alkyl, C_3 - C_{10} -cycloalkyl, C_2 - C_{16} -alkenyl, C_2 - C_{20} -alkynyl, C_6 - C_{24} -aryl, or C_6 - C_{24} -heteroaryl.
- [0130] In another preferred embodiment of the present invention the catalyst composition is obtained using at least one, preferably one, co-catalyst having the above depicted general formula (1) wherein
- $$CH_2=CRR' \quad (1)$$
- [0131] in which R is hydrogen and R' shall mean
- [0132] OR^1 wherein R^1 shall mean C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, C_6 - C_{14} -heteroaryl, $-C(=O)(R^2)$, $-C(=O)N(R^2)_2$, $-[(CH_2)_nX]_mR^2$, $-[(CH_2)_nX]_m-CH=CH_2$, or $-(CH_2)_p-C(R^3)_2R^4$,
- [0133] wherein
- [0134] X is identical or different and oxygen (O) or NR^2 ,
- [0135] R^2 are identical or different and represent H , C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, or C_3 - C_{14} -heteroaryl, R^3 are identical or different and represent methyl, ethyl or $-(CH_2)_n-O-CH=CH_2$,
- [0136] R^4 represents $(CH_2)_p-O-CH=CH_2$,
- [0137] n is 1, 2 or 3
- [0138] m is 1, 2, 3, or 4,
- [0139] p is 0, 1, 2, 3 or 4,
- [0140] SR^5 , SOR^5 , SO_2R^5
- [0141] wherein R^5 represents C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, or C_3 - C_{14} -heteroaryl,
- [0142] $N(R^6R^7)$, $P(R^6R^7)$
- [0143] wherein R^6 and R^7 are identical or different and shall mean C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alk-

enyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, or C_6 - C_{14} -heteroaryl, $-C(=O)(R^2)$, or where in the alternative R^6 and R^7 may form together with such N or P atom to which they both are linked at the same time a saturated, unsaturated or aromatic cyclic structure with 4 to 5 carbon atoms in the cyclic structure wherein one or two of said carbon atoms can be replaced by a moiety selected from oxygen, sulfur, nitrogen, $N-R^8$ or $P-R^8$ wherein R^8 shall mean C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, or C_3 - C_{14} -heteroaryl,

[0144] $P(=O)(OR^9)_2$

[0145] in which R^9 are identical or different and shall mean C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, or C_6 - C_{14} -heteroaryl.

[0146] In another preferred embodiment of the present invention the catalyst composition is obtained using at least one, preferably one, co-catalyst having the above depicted general formula (1) wherein



[0147] in which R and R' are identical or different and shall mean

[0148] OR^1 wherein R^1 shall mean C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, C_6 - C_{14} -heteroaryl, $-C(=O)(R^2)$, $-C(=O)N(R^2)_2$, $-[(CH_2)_nX]_mR^2$, $-[(CH_2)_nX]_m-CH=CH_2$, or $-(CH_2)_p-C(R^3)_2R^4$,

[0149] wherein

[0150] X is identical or different and oxygen (O) or NR^2 ,

[0151] R^2 are identical or different and represent H , C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, or C_3 - C_{14} -heteroaryl, R^3 are identical or different and represent methyl, ethyl or $-(CH_2)_n-O-CH=CH_2$,

[0152] R^4 represents $(CH_2)_p-O-CH=CH_2$,

[0153] n is 1, 2 or 3

[0154] m is 1, 2, 3, or 4,

[0155] p is 0, 1, 2, 3 or 4,

[0156] or where in the alternative, if R and R' both represent a group OR^1 , both R^1 may be linked to each other and together represent a divalent group $-(C(R^2))_q-$ with q being 2, or 3 and R^2 being identical or different and representing hydrogen or C_1 - C_4 alkyl,

[0157] SR^5 , SOR^5 , SO_2R^5

[0158] wherein R^5 represents C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, or C_3 - C_{14} -heteroaryl,

[0159] $N(R^6R^7)$, $P(R^6R^7)$

[0160] wherein R^6 and R^7 are identical or different and shall mean C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, or C_6 - C_{14} -heteroaryl, $-C(=O)(R^2)$, or where in the alternative R^6 and R^7 may form together with such N or P atom to which they both are linked at the same time a saturated, unsaturated or aromatic cyclic structure with 4 to 5 carbon atoms in the cyclic structure wherein one or two of said carbon atoms can be replaced by a moiety selected from oxygen, sulfur, nitrogen, $N-R^8$ or $P-R^8$ wherein R^8 shall mean C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, or C_3 - C_{14} -heteroaryl,

[0161] $P(=O)(OR^9)_2$

[0162] in which R^9 are identical or different and shall mean C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_6 - C_{14} -aryl, or C_6 - C_{14} -heteroaryl.

[0163] In another more preferred embodiment of the present invention the catalyst composition is obtained using one co-catalyst having the above depicted general formulae (1) in which

[0164] R is hydrogen and R^1 represents

[0165] OR^1 wherein R^1 shall mean C_1 - C_6 -alkyl, C_5 - C_6 -cycloalkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl, phenyl, imidazolyl, triazolyl, or pyridinyl, $-C(=O)(R^2)$, $-C(=O)N(R^2)_2$, $-[(CH_2)_nO]_mR^2$, $-[(CH_2)_nO]_m-CH=CH_2$, or $-(CH_2)_p-C(R^3)_2R^4$,

[0166] wherein

[0167] R^2 are identical or different and represent H, C_1 - C_6 -alkyl, C_5 - C_8 -cycloalkyl, C_2 - C_8 -alkenyl, C_2 - C_8 -alkynyl, phenyl, imidazolyl, triazolyl, or pyridinyl,

[0168] R^3 are identical or different and represent methyl, ethyl or $-(CH_2)_n-O-CH=CH_2$,

[0169] R^4 represents $(CH_2)_p-O-CH=CH_2$,

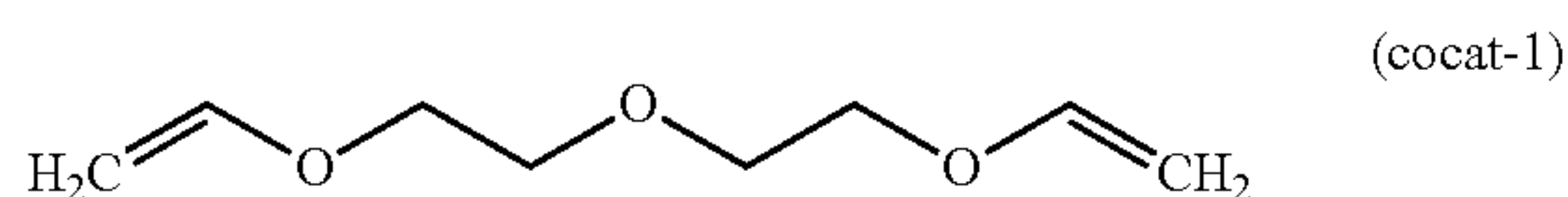
[0170] n is 1, or 2,

[0171] m is 1, 2, or 3, and

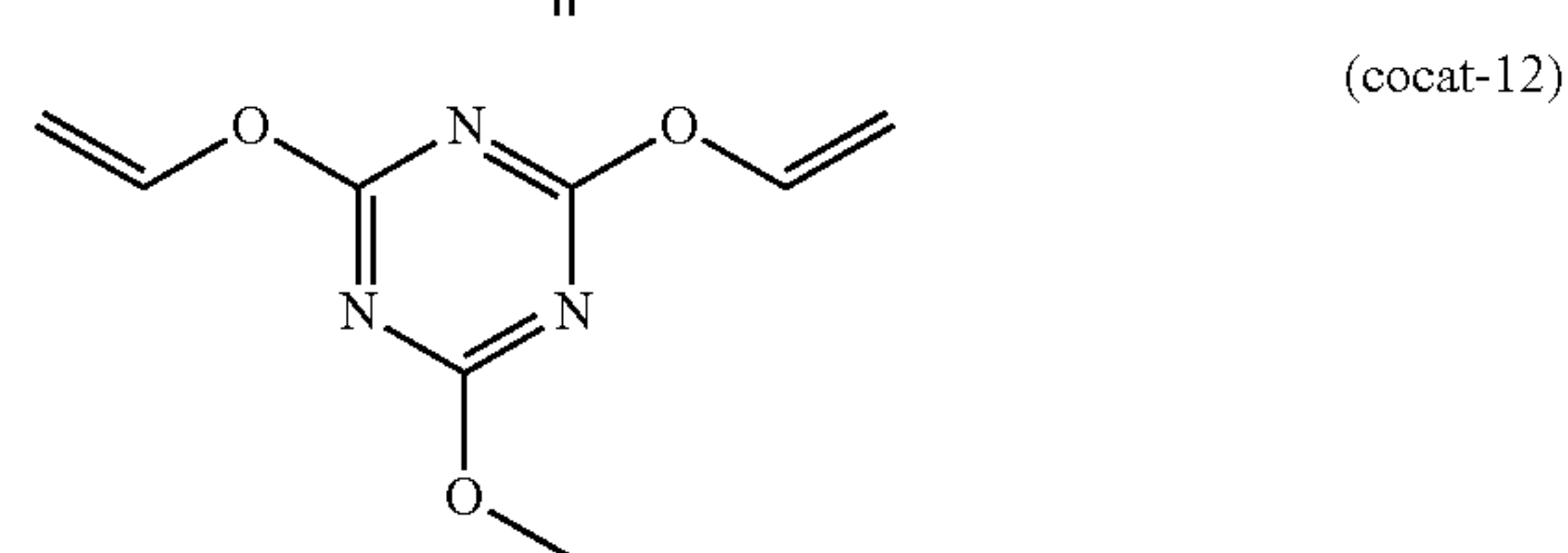
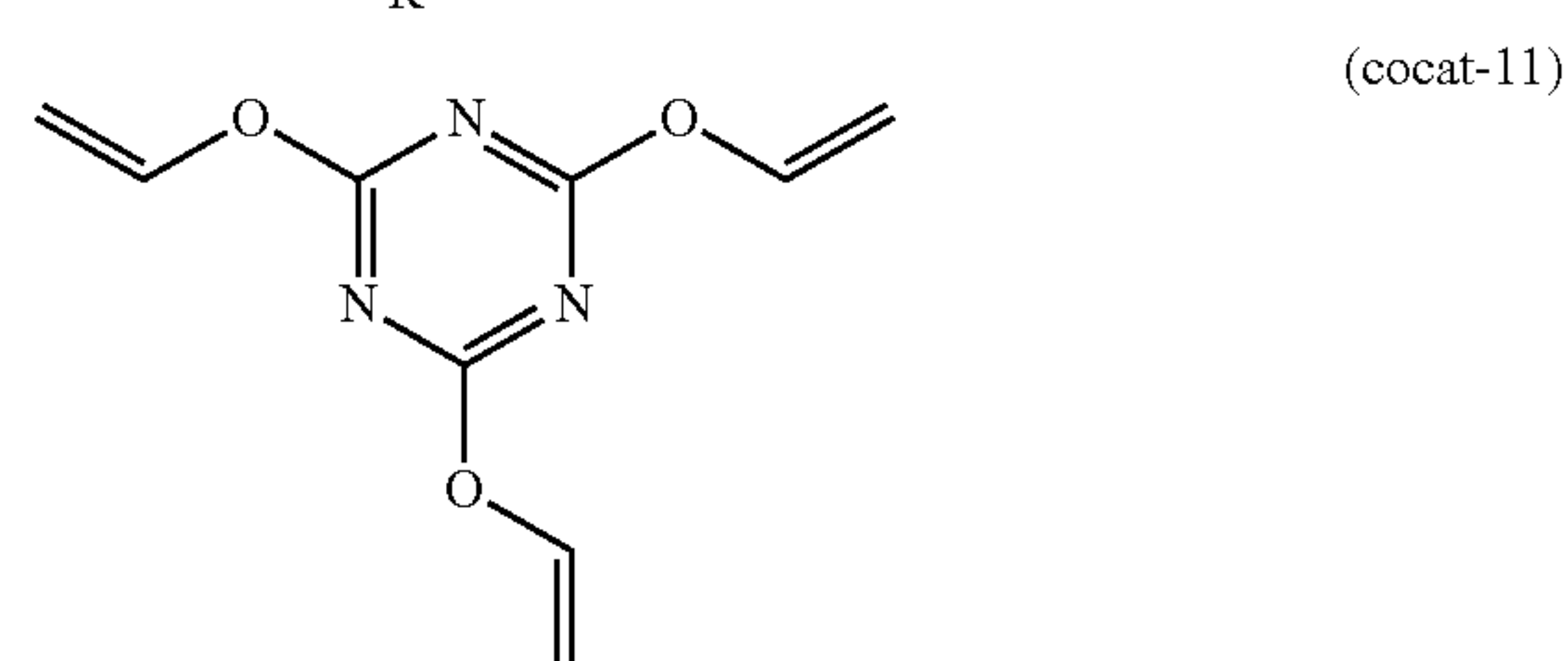
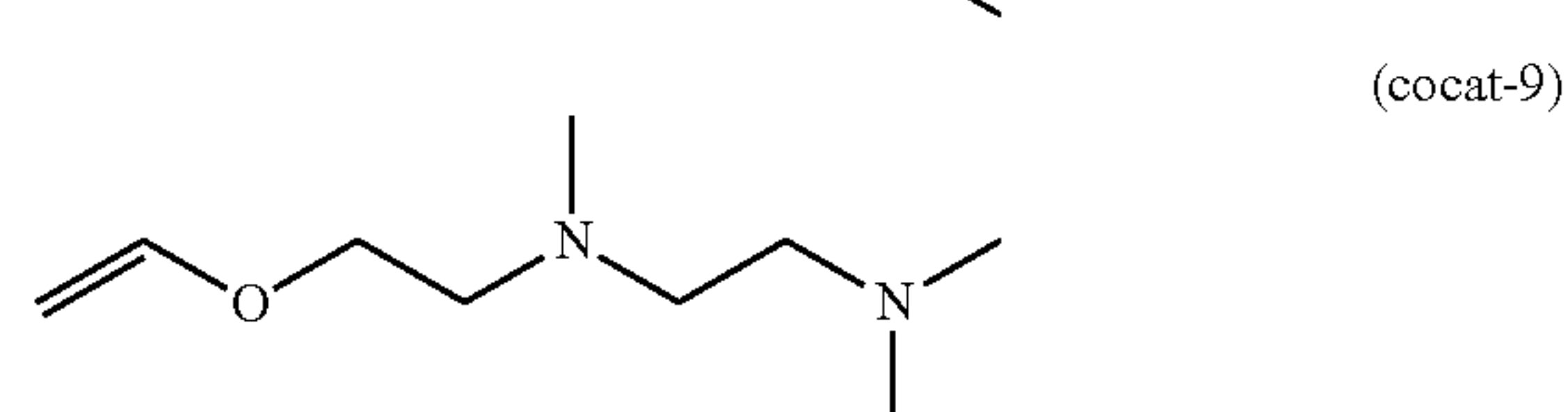
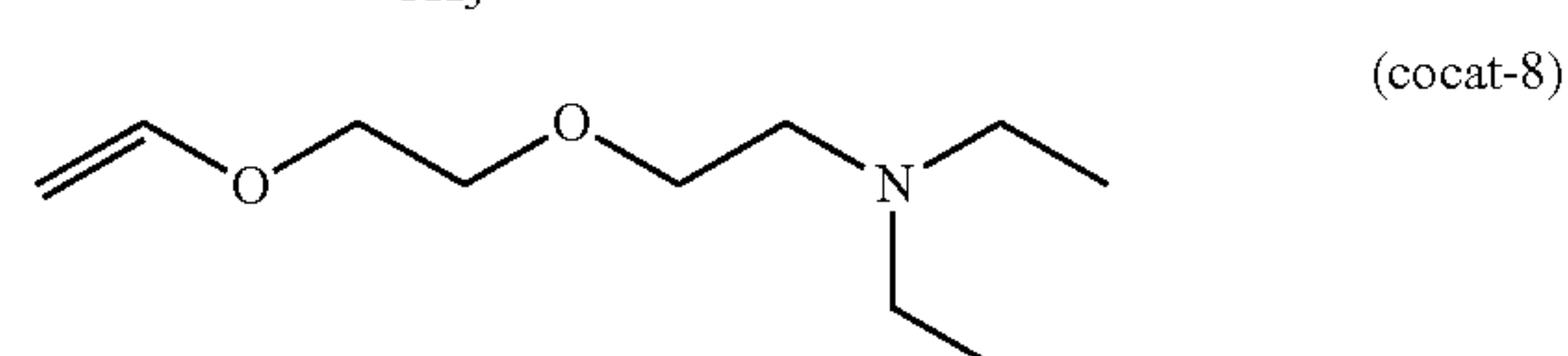
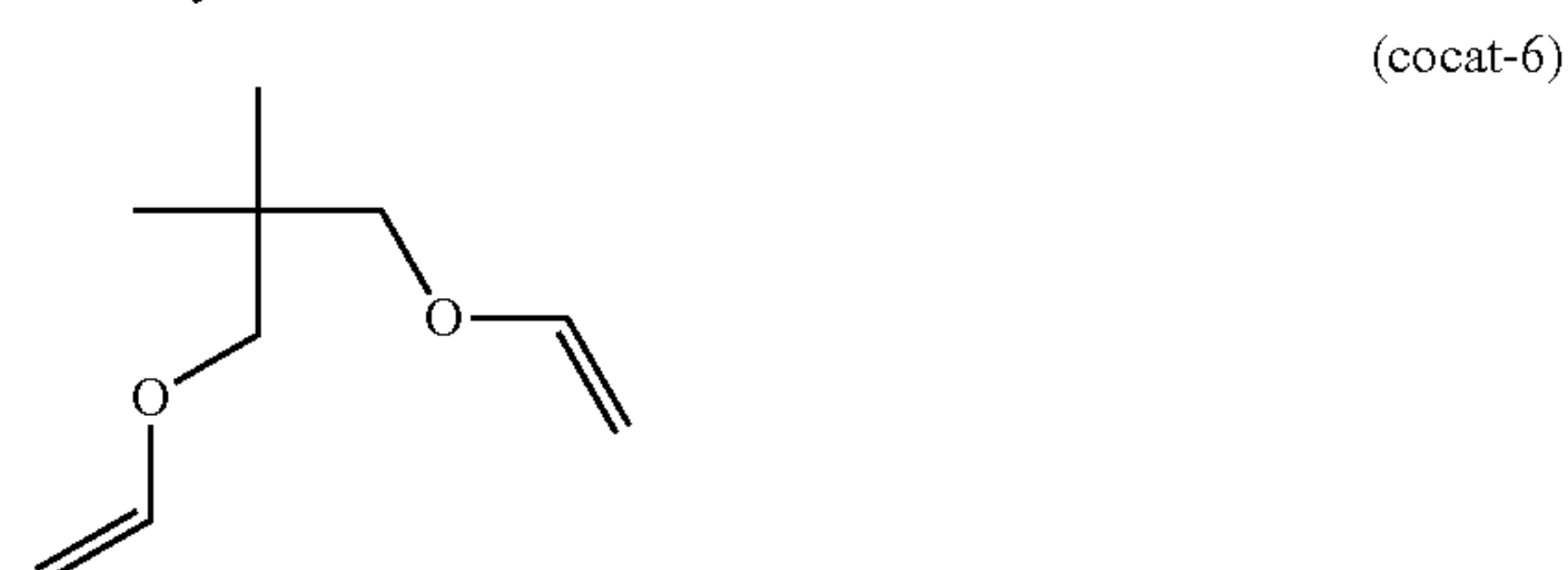
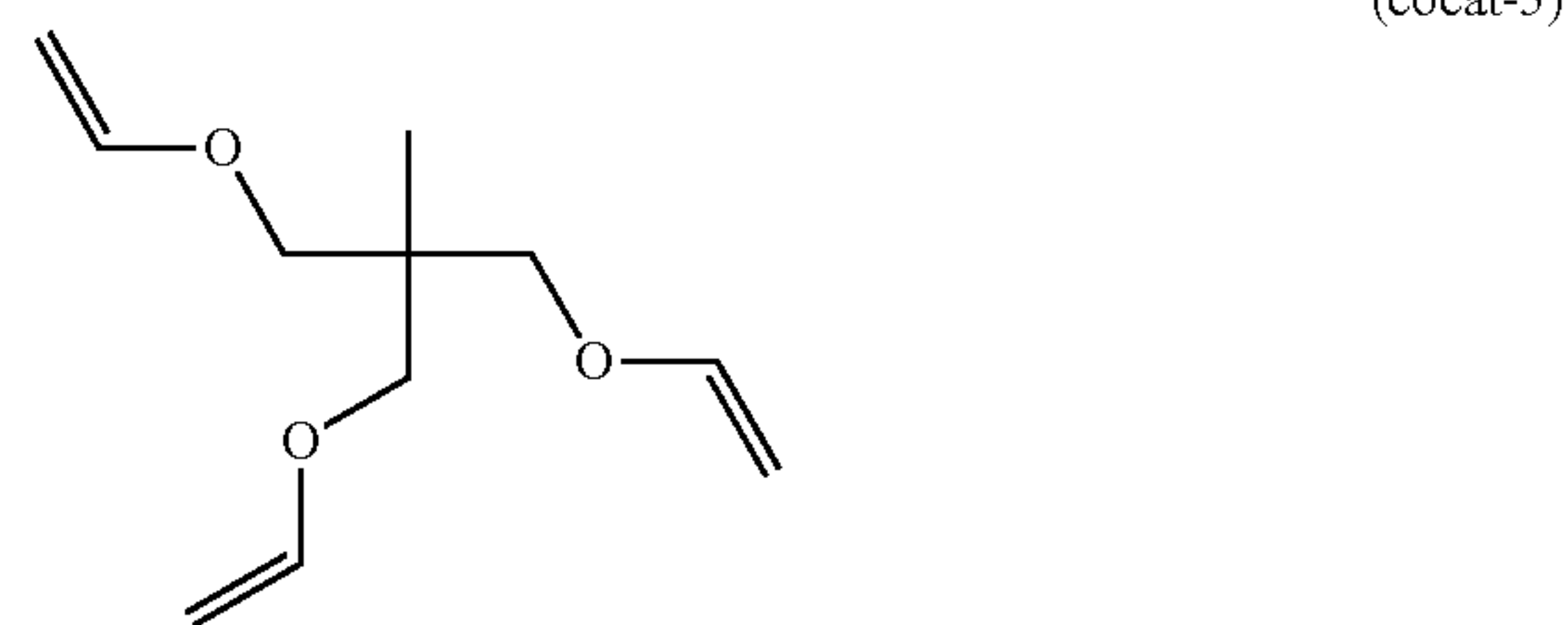
[0172] p is 0, 1, or 3.

[0173] In all the above mentioned preferred, more preferred and most preferred embodiments of the co-catalysts according to general formula (1) the alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or heteroaryl moieties in R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 or R^9 may optionally be further substituted by one or more C_1 - C_6 -alkyl, C_5 - C_6 -cycloalkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl, phenyl, imidazolyl, triazolyl, or pyridinyl moieties. All aforementioned substituents, in particular the alkyl, alkenyl and/or alkynyl moieties can be either straight chain or branched to the extent chemically plausible.

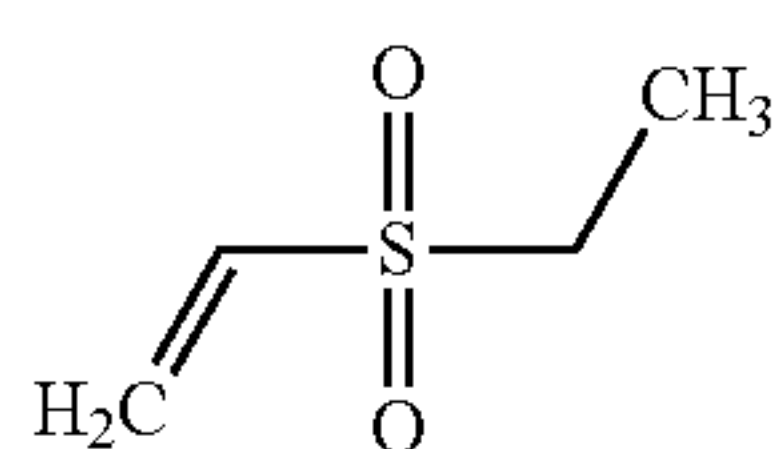
[0174] In an even more preferred embodiment of the present invention one or more co-catalysts are used for the preparation of the novel catalyst compositions which have the following formulae:



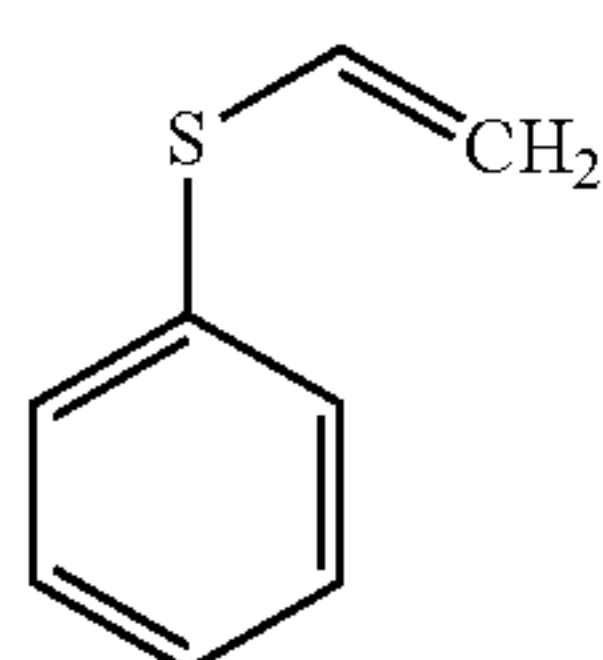
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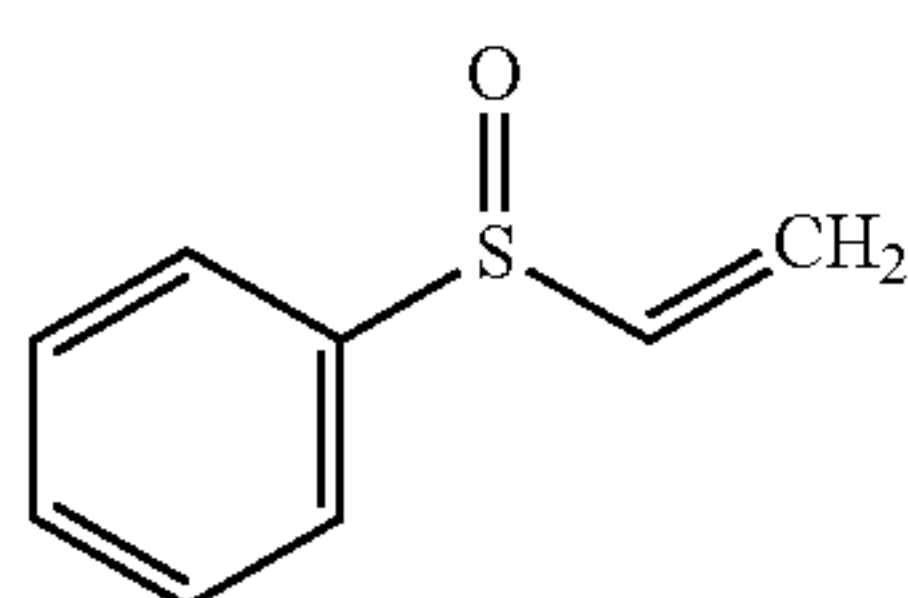
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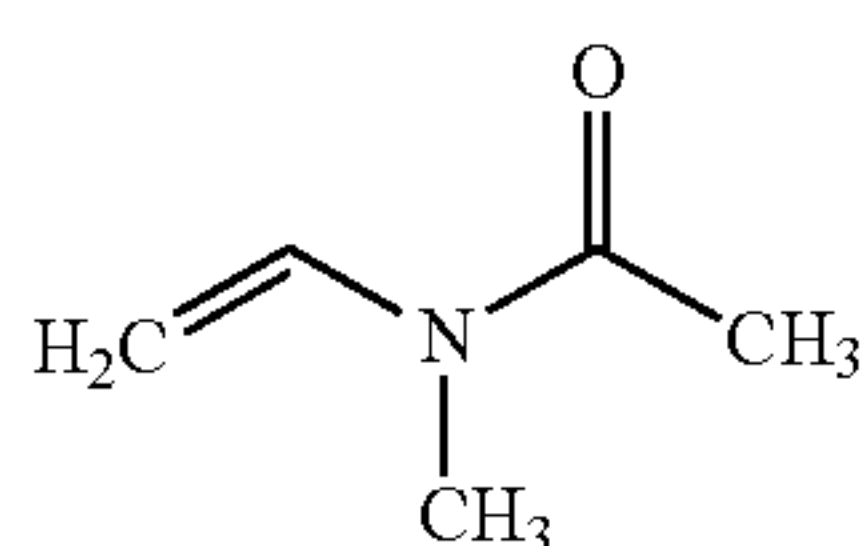
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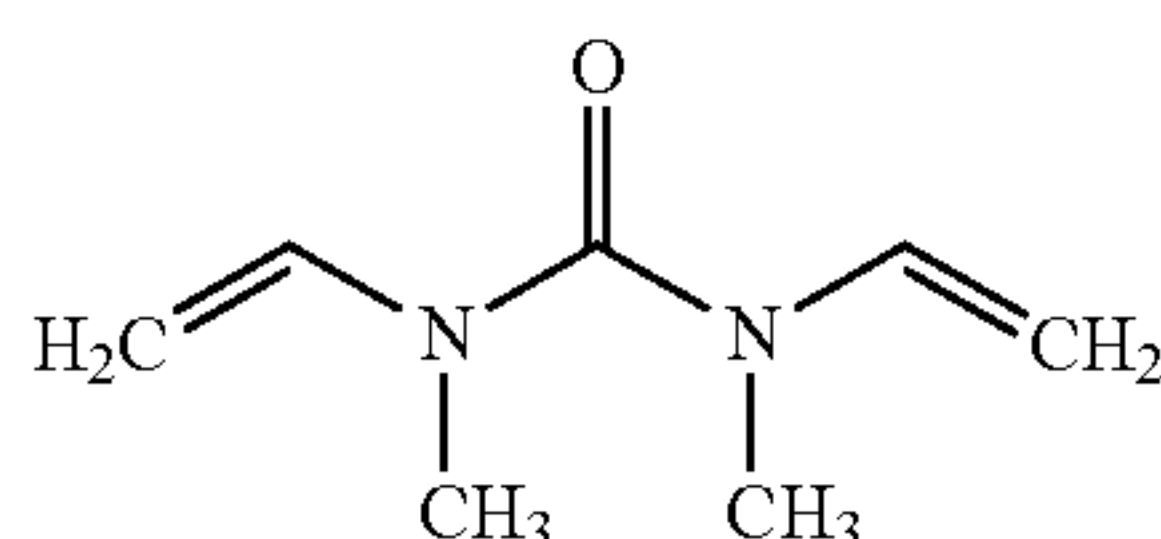
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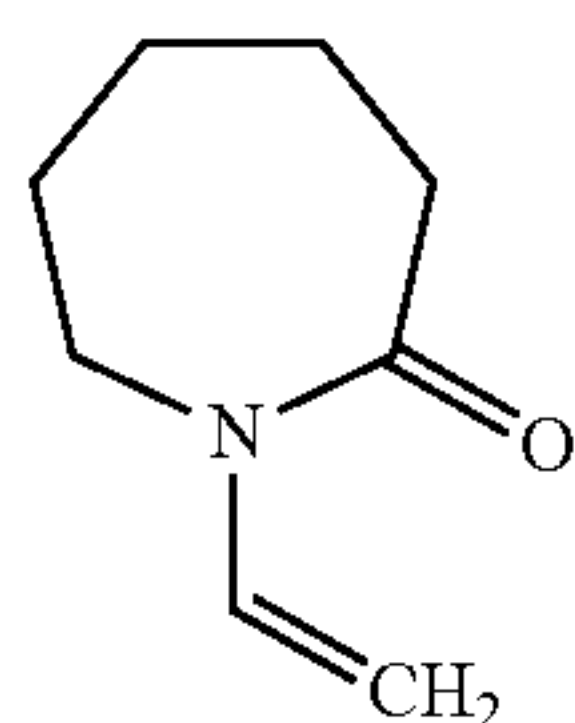
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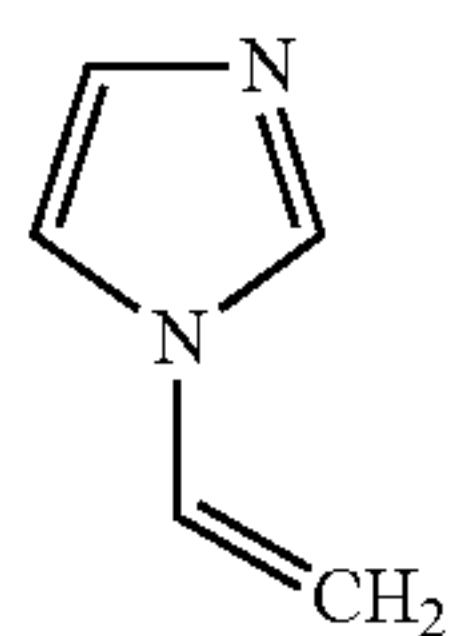
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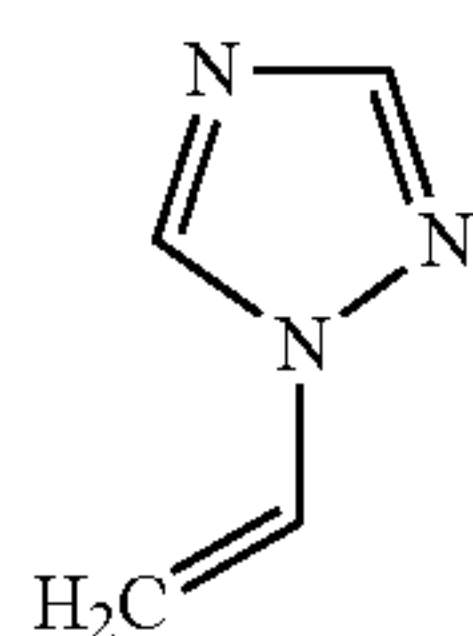
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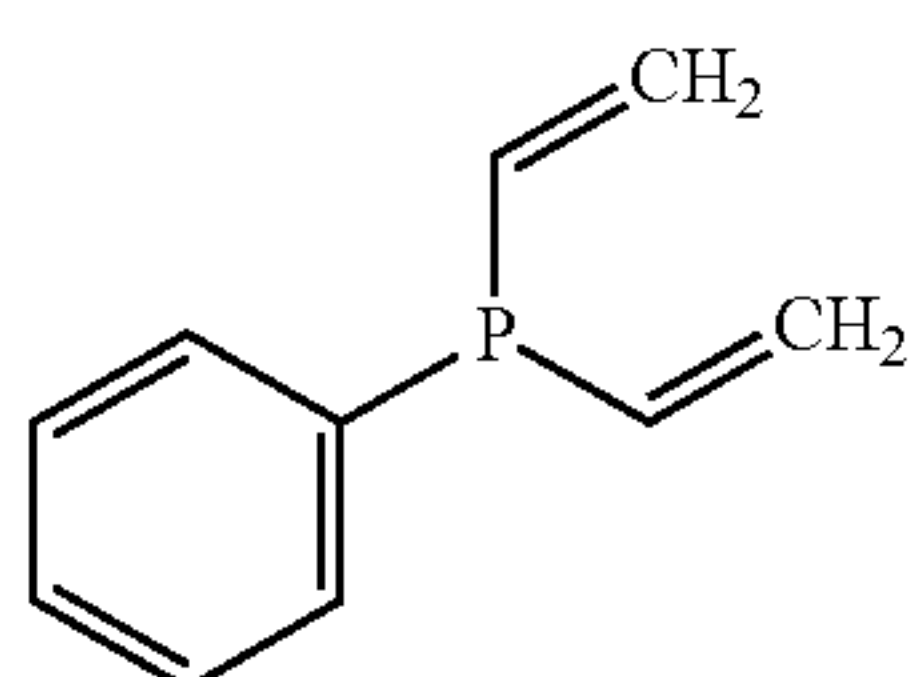
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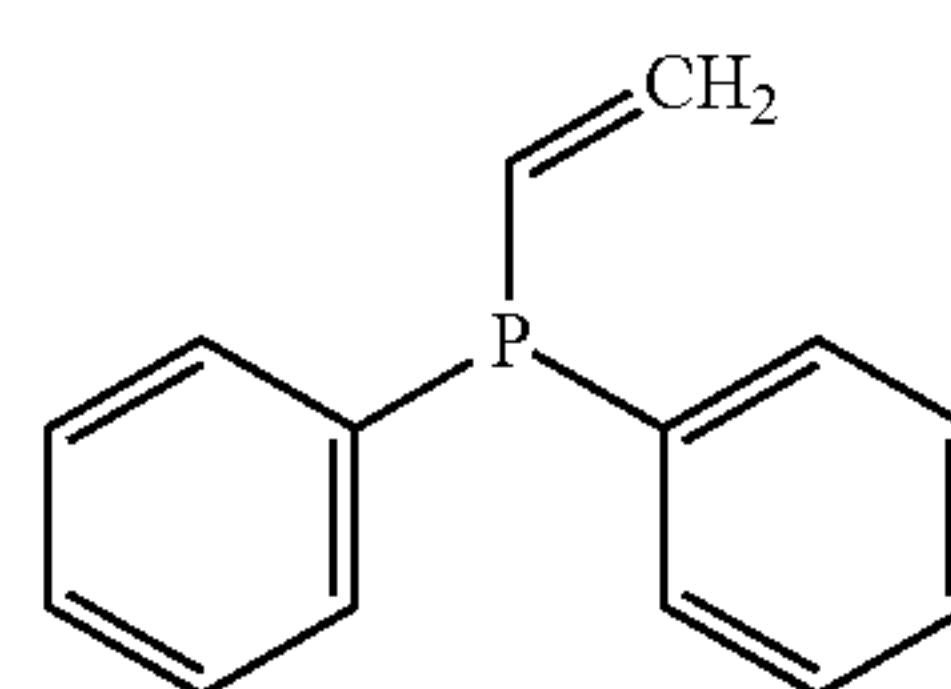


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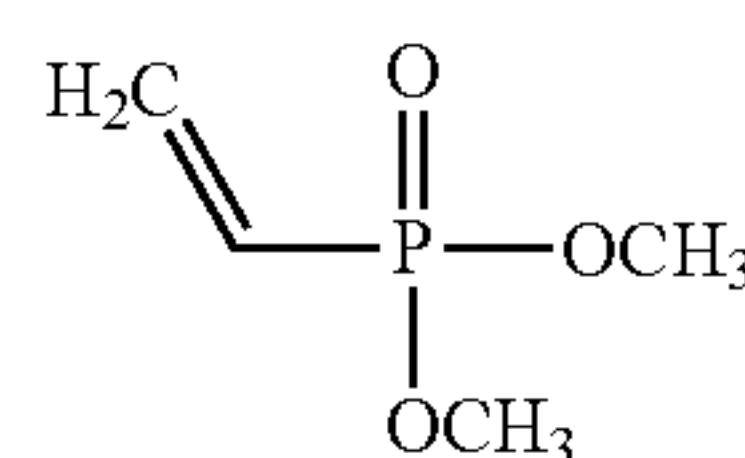


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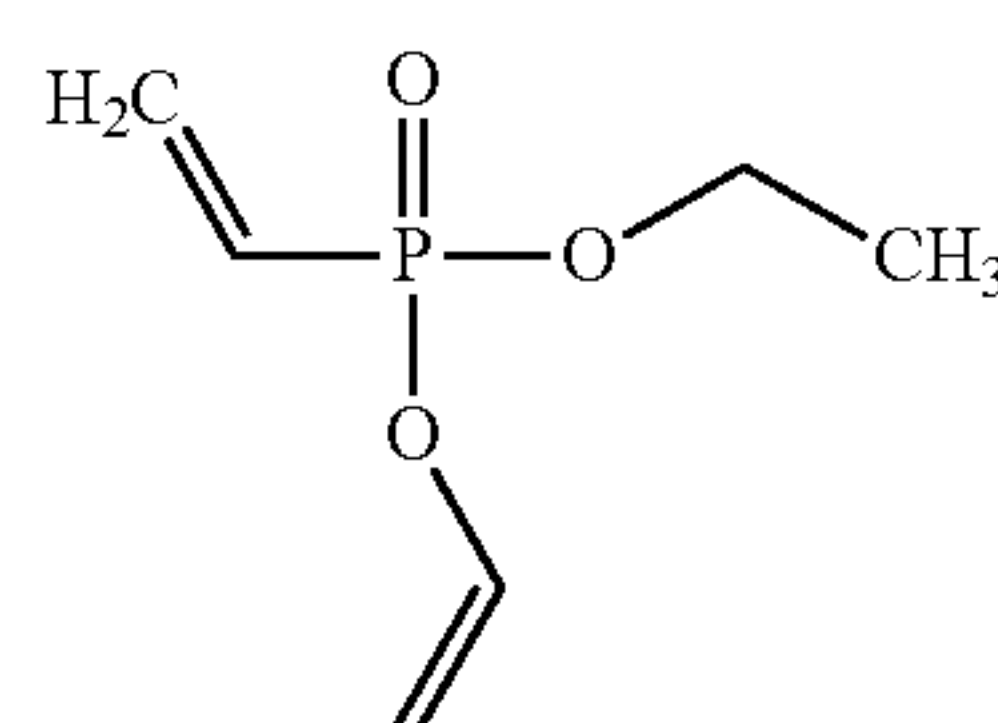
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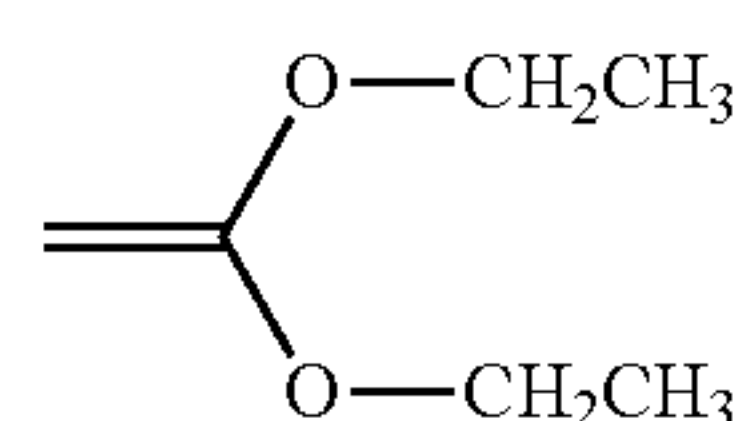
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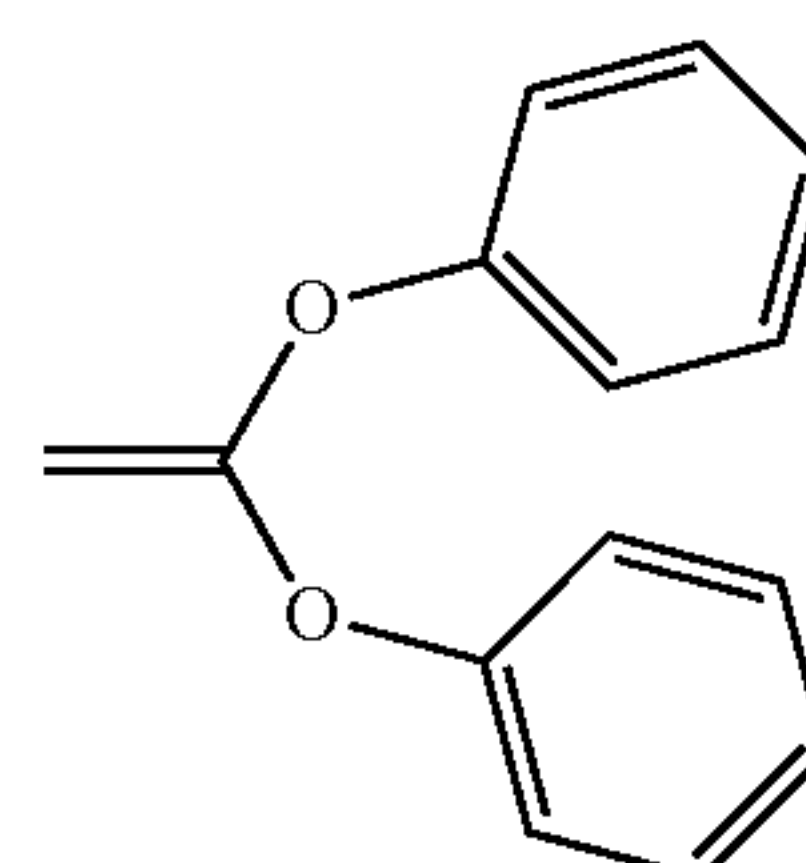
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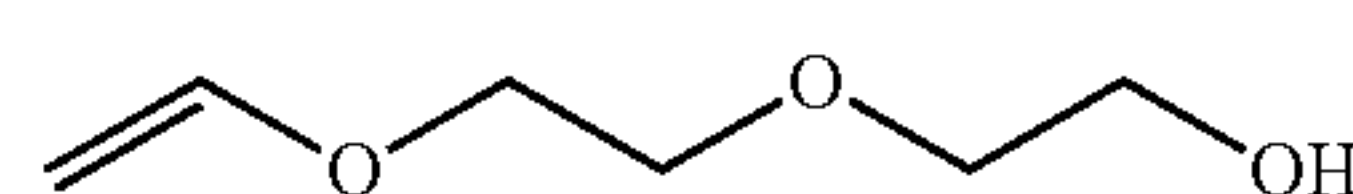
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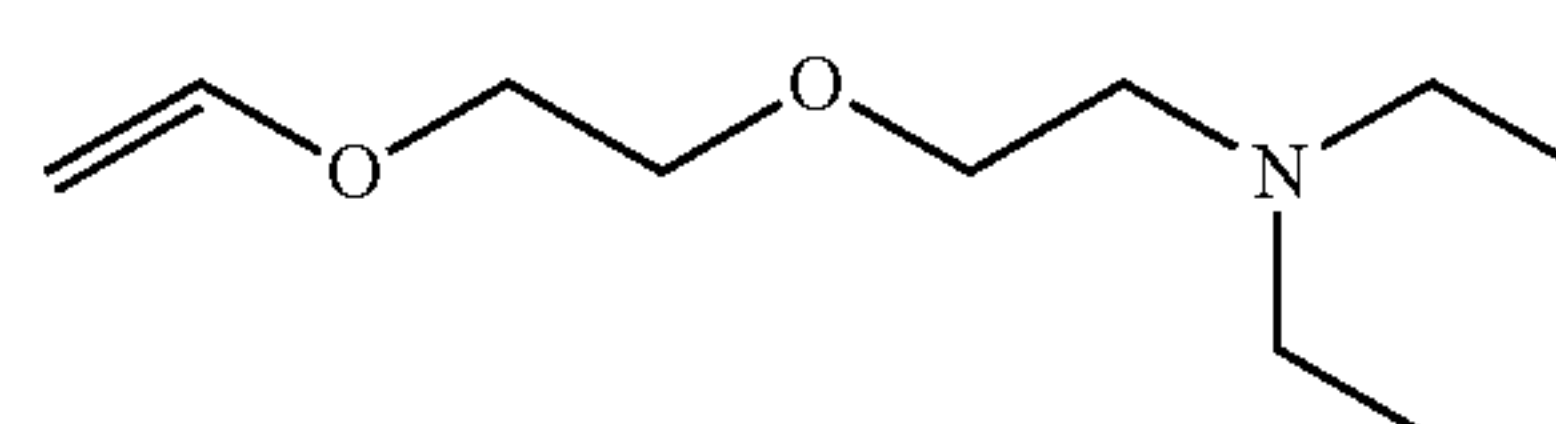
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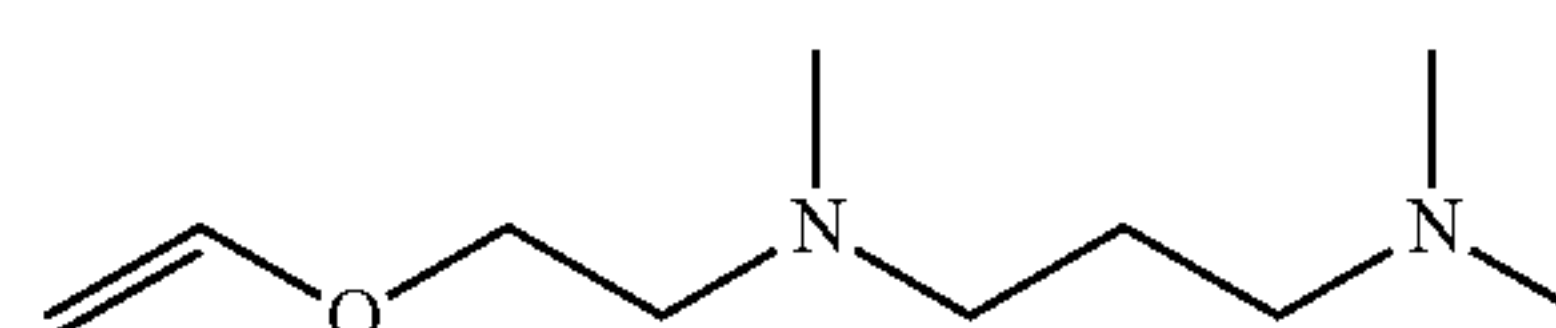
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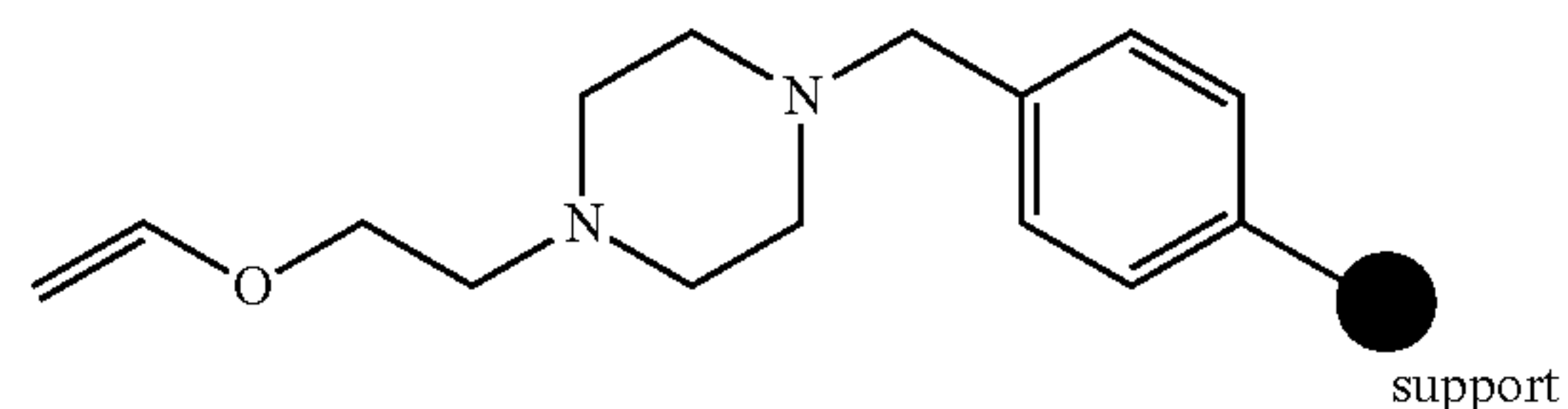
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(cocat-30)



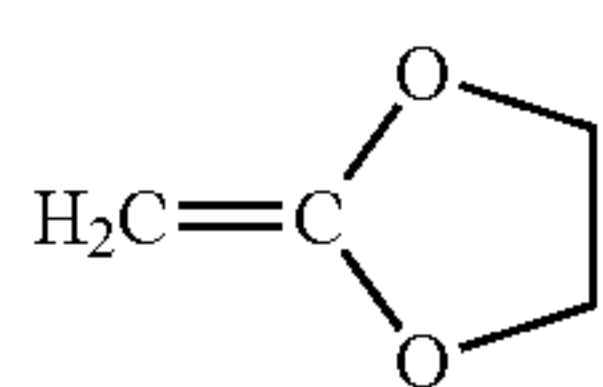
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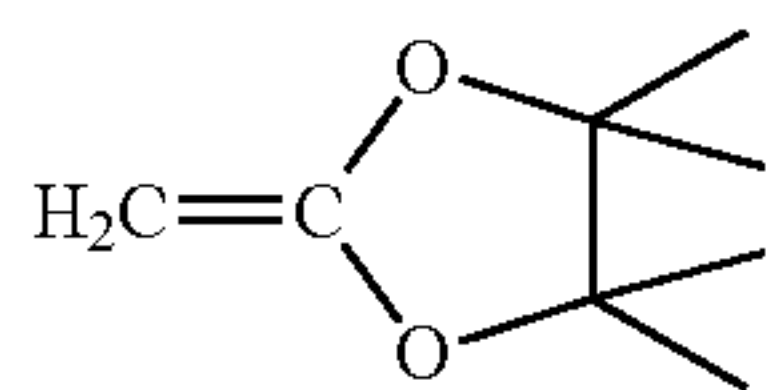
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support

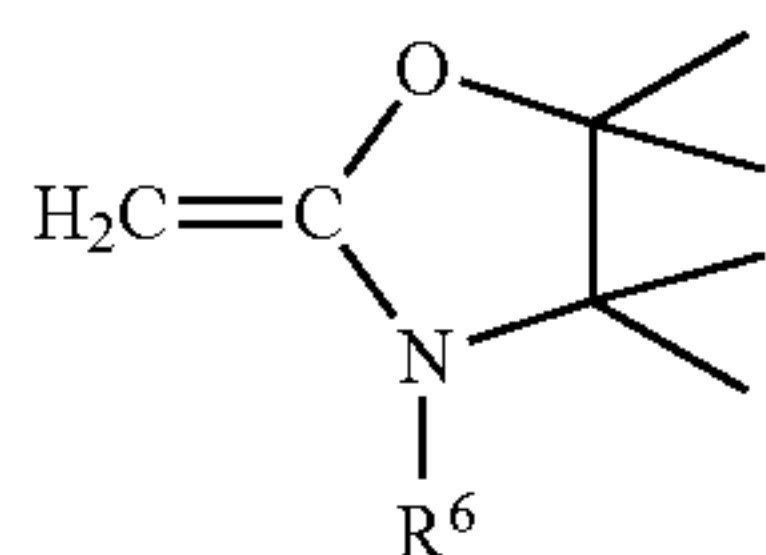
[0175] In another also preferred embodiment of the present invention a co-catalyst is used for the preparation of the novel catalyst compositions in which R and R' both represent OR¹ where such R¹ together form a divalent group as defined above, wherein such specific co-catalysts have the following formulae with R⁶ having the same meaning as outlined for general formula (1).



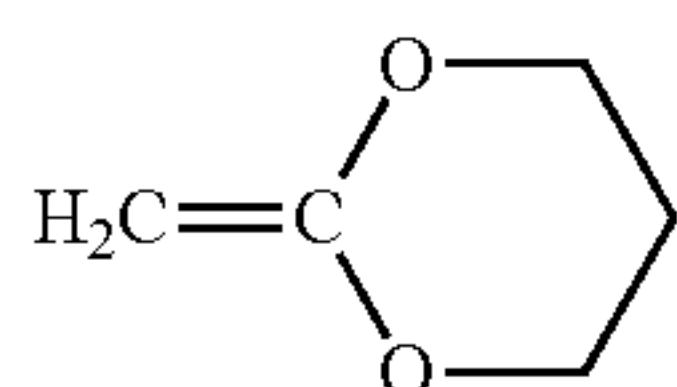
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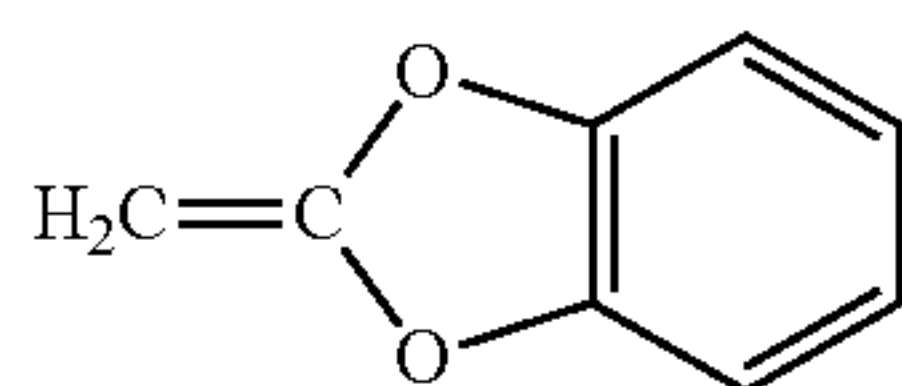
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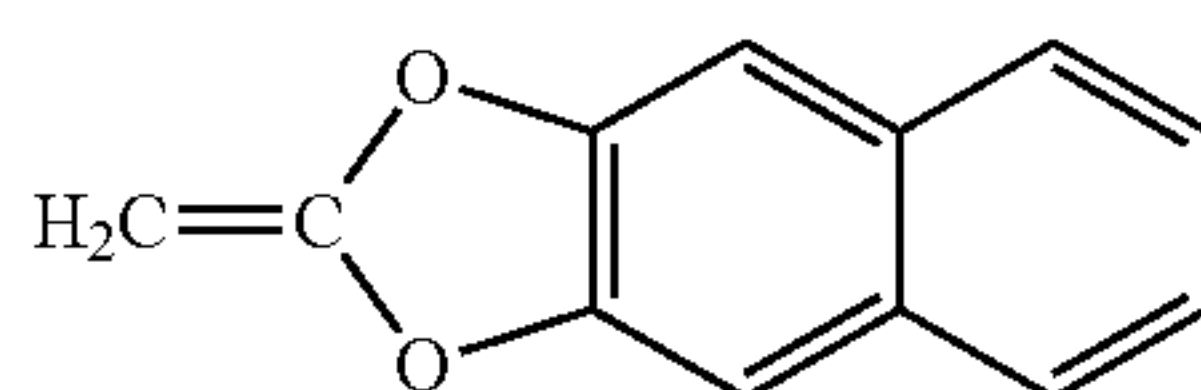
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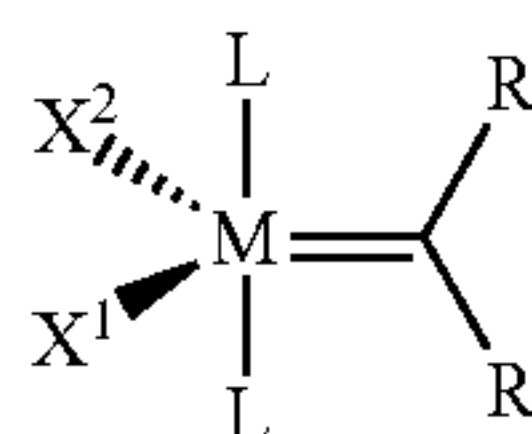


(cocat-38)

Catalysts:

[0176] The catalysts to be used in the process of the invention are complex catalysts based either on ruthenium or osmium. Furtheron, these complex catalysts have the common structural feature that they possess at least one ligand which is bound to ruthenium or osmium in a carbene-like fashion. In a preferred embodiment, the complex catalyst has two carbene ligands, i.e. two ligands which are bound in a carbene-like fashion to the central metal of the complex.

[0177] The novel catalyst composition of the present invention is obtainable using for example a catalyst of the general formula (A),



(A)

where

[0178] M is osmium or ruthenium,

[0179] X¹ and X² are identical or different and are two ligands, preferably anionic ligands,

[0180] L are identical or different ligands, preferably uncharged electron donors,

[0181] R are identical or different and are each hydrogen, alkyl, preferably C₁-C₃₀-alkyl, cycloalkyl, preferably C₃-C₂₀-cycloalkyl, alkenyl, preferably C₂-C₂₀-alkenyl, alkynyl, preferably C₂-C₂₀-alkynyl, aryl, preferably C₆-C₂₄-aryl, carboxylate, preferably C₁-C₂₀-carboxylate, alkoxy, preferably C₁-C₂₀-alkoxy, alkenyloxy, preferably

C₂-C₂₀-alkenyloxy, alkynyloxy, preferably C₂-C₂₀-alkynyloxy, aryloxy, preferably C₆-C₂₄-aryloxy, alkoxycarbonyl, preferably C₂-C₂₀-alkoxycarbonyl, alkylamino, preferably C₁-C₃₀-alkylamino, alkylthio, preferably C₁-C₃₀-alkylthio, arylthio, preferably C₆-C₂₄-arylthio, alkylsulphonyl, preferably C₁-C₂₀-alkylsulphonyl, or alkylsulphinyl, preferably C₁-C₂₀-alkylsulphinyl, where these groups may in each case optionally be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl moieties or, as an alternative, the two groups R together with the common carbon atom to which they are bound are bridged to form a cyclic structure which can be aliphatic or aromatic in nature, may be substituted and may contain one or more heteroatoms.

[0182] Various representatives of the catalysts of the formula (A) are known in principle, e.g. from WO-A-96/04289 and WO-A-97/06185.

[0183] In preferred catalysts of the general formula (A), one group R is hydrogen and the other group R is C₁-C₂₀-alkyl, C₃-C₁₀-cycloalkyl, C₂-C₂₀-alkenyl, C₂-C₂₀-alkynyl, C₆-C₂₄-aryl, C₁-C₂₀-carboxylate, C₁-C₂₀-alkoxy, C₂-C₂₀-alkenyloxy, C₂-C₂₀-alkynyloxy, C₆-C₂₄-aryloxy, C₂-C₂₀-alkoxycarbonyl, C₁-C₃₀-alkylamino, C₁-C₃₀-alkylthio, C₆-C₂₄-arylthio, C₁-C₂₀-alkylsulphonyl or C₁-C₂₀-alkylsulphanyl, where these moiety may in each case be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl groups.

Definition of X^1 and X^2

[0184] In the catalysts of the general formula (A), X^1 and X^2 are identical or different and are two ligands, preferably anionic ligands.

[0185] X^1 and X^2 can be, for example, hydrogen, halogen, pseudohalogen, straight-chain or branched C_1 - C_{30} -alkyl, C_6 - C_{24} -aryl, C_1 - C_{20} -alkoxy, C_6 - C_{24} -aryloxy, C_3 - C_{20} -alkyldiketonate C_6 - C_{24} -aryldiketonate, C_1 - C_{20} -carboxylate, C_1 - C_{20} -alkylsulphonate, C_6 - C_{24} -arylsulphonate, C_1 - C_{20} -alkylthiol, C_6 - C_{24} -arylthiol, C_1 - C_{20} -alkylsulphonyl or C_1 - C_{20} -alkylsulphinyl.

[0186] X¹ and X² can also be substituted by one or more further groups, for example by halogen, preferably fluorine, C₁-C₁₀-alkyl, C₁-C₁₀-alkoxy or C₆-C₂₄-aryl, where these groups, too, may once again be substituted by one or more substituents selected from the group consisting of halogen, preferably fluorine, C₁-C₅-alkyl, C₁-C₅-alkoxy and phenyl.

[0187] In a preferred embodiment, X¹ and X² are identical or different and are each halogen, in particular fluorine, chlorine, bromine or iodine, benzoate, C₁-C₅-carboxylate, C₁-C₅-alkyl, phenoxy, C₁-C₅-alkoxy, C₁-C₅-alkylthiol, C₆-C₂₄-arylthiol, C₆-C₂₄-aryl or C₁-C₅-alkylsulphonate.

[0188] In a particularly preferred embodiment, X¹ and X² are identical and are each halogen, in particular chlorine, CF₃COO, CH₃COO, CFH₂COO, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO (phenoxy), MeO (methoxy), EtO (ethoxy), tosylate (p-CH₃—C₆H₄—SO₃), mesylate (CH₃—SO₃) or CF₃SO₃ (trifluoromethanesulphonate).

Definition of L

[0189] In the general formula (A), the symbols L represent identical or different ligands and are preferably uncharged electron donating ligand.

[0190] The two ligands L can, for example, be, independently of one another, a phosphine, sulphonated phosphine, phosphate, phosphinite, phosphonite, arsine, stibine, ether,

amine, amide, sulfonate, sulfoxide, carboxyl, nitrosyl, pyridine, thioether, imidazoline or imidazolidine (the latter two also being jointly referred to as “Im” ligand(s))

[0191] The term “phosphinite” includes, for example, phenyl diphenylphosphinite, cyclohexyl dicyclohexylphosphinite, isopropyl diisopropylphosphinite and methyl diphenylphosphinite

[0192] The term “phosphite” includes, for example, triphenyl phosphite, tricyclohexyl phosphite, tri-tert-butyl phosphite, triisopropyl phosphite and methyl diphenyl phosphite.

[0193] The term “stibine” includes, for example, triphenylstibine, tricyclohexylstibine and trimethylstibine.

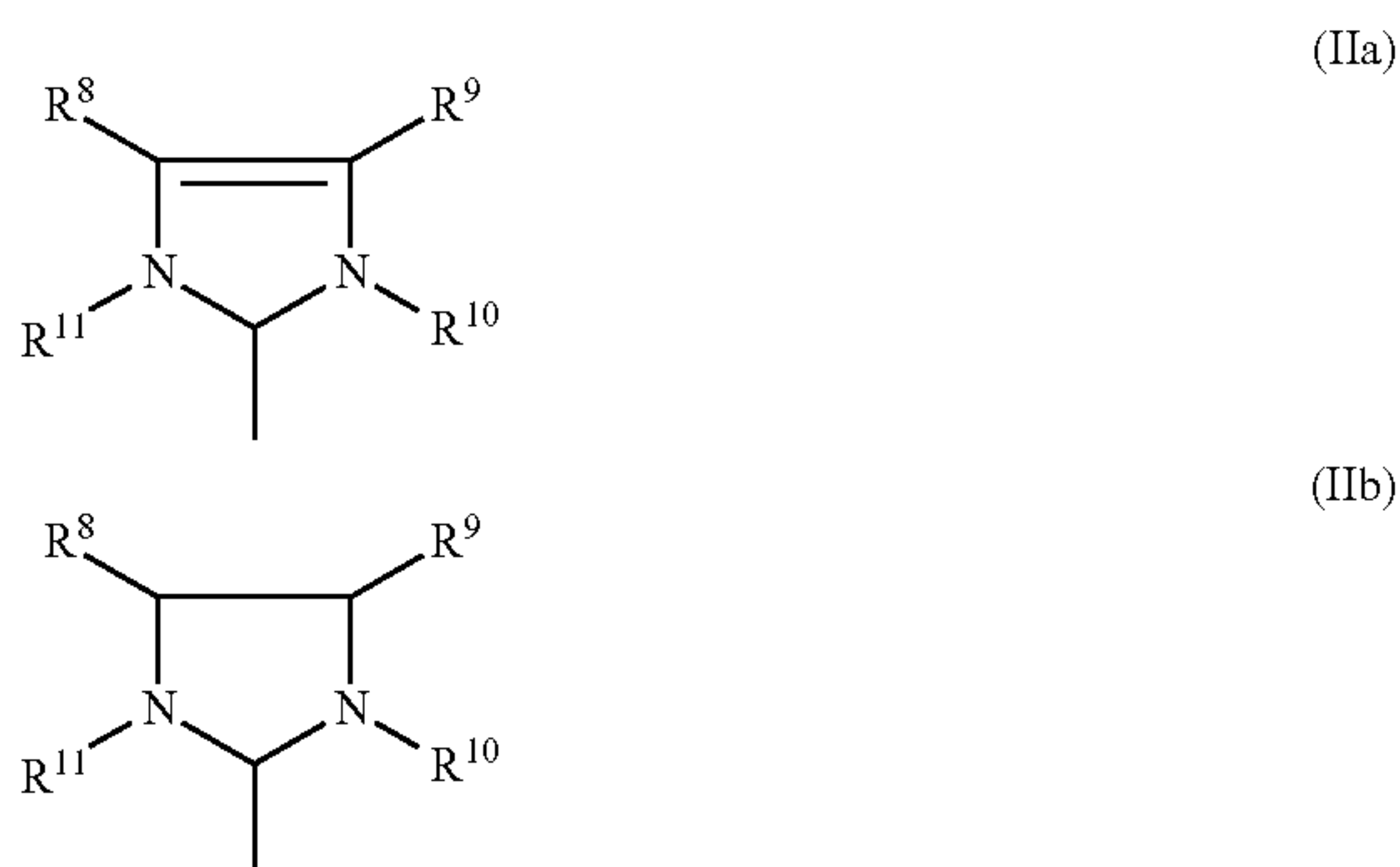
[0194] The term “sulfonate” includes, for example, trifluoromethanesulphonate, tosylate and mesylate.

[0195] The term “sulfoxide” includes, for example, $(\text{CH}_3)_2\text{S}(=\text{O})$ and $(\text{C}_6\text{H}_5)_2\text{S}=\text{O}$.

[0196] The term “thioether” includes, for example, CH_3SCH_3 , $\text{C}_6\text{H}_5\text{SCH}_3$, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{SCH}_3$ and tetrahydrothiophene.

[0197] For the purposes of the present application, the term “pyridine” is used as a collective term for all nitrogen-containing ligands as are mentioned by, for example, Grubbs in WO-A-03/011455. Examples are: pyridine, picolines (including α -, β - and γ -picoline), lutidines (including 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-lutidine), collidine (2,4,6-trimethylpyridine), trifluoromethylpyridine, phenylpyridine, 4-(dimethylamino)pyridine, chloropyridines, bromopyridines, nitropyridines, quinoline, pyrimidine, pyrrole, imidazole and phenylimidazole.

[0198] In a preferred embodiment catalysts of general formula (A) are used in which one or both of ligands L represent an imidazoline or imidazolidine ligand (also jointly referred to as “Im”—ligand in this application unless indicated otherwise), having a structure of general formulae (IIa) or (IIb), wherein the meaning of L can be identical or different in case both ligands L have a structure according to (IIa) or (IIb),



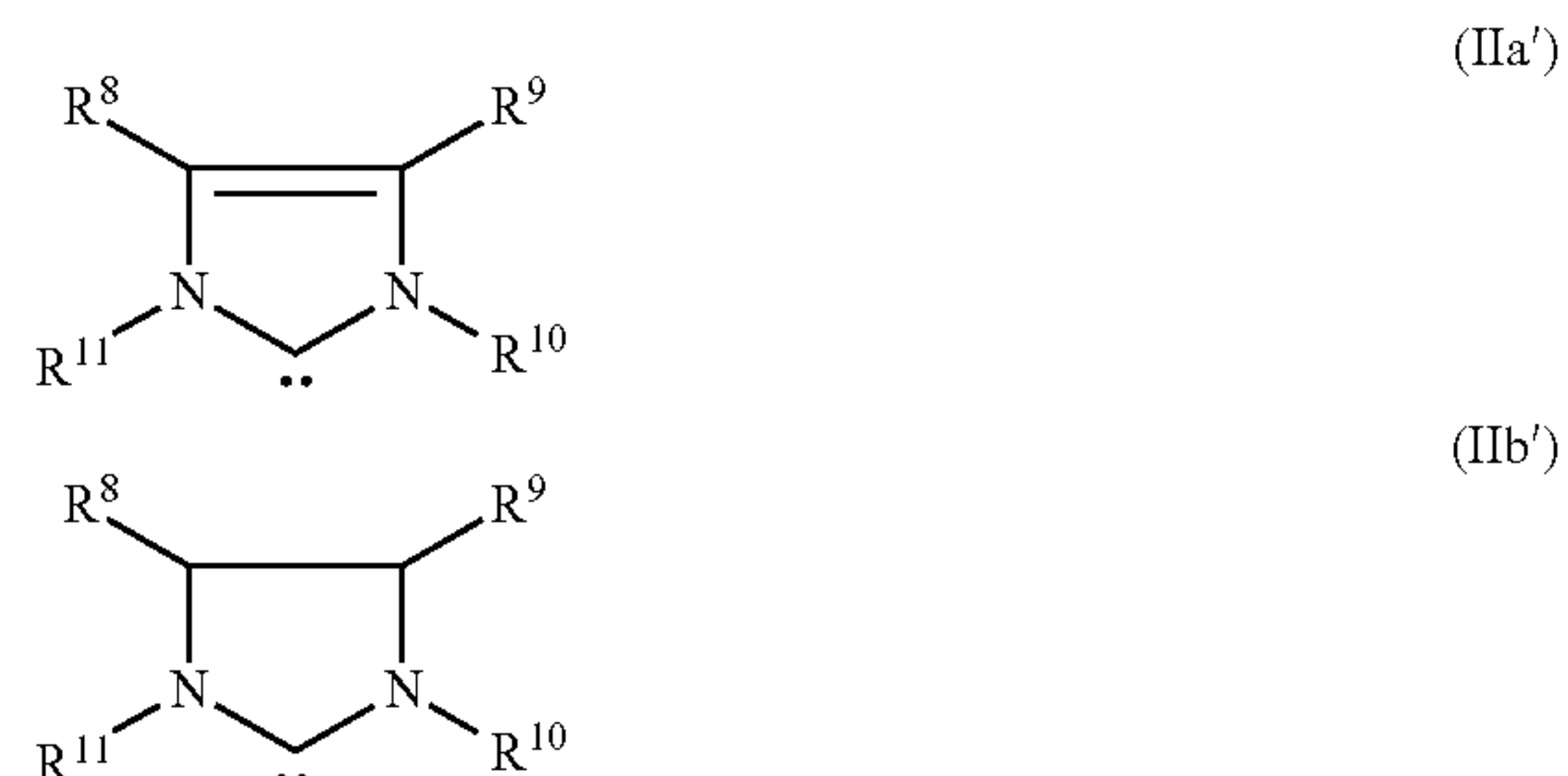
where

[0199] R^8 , R^9 , R^{10} and R^{11} are identical or different and represent hydrogen, straight-chain or branched C_1 - C_{30} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_2 - C_{20} -alkynyl, C_6 - C_{24} -aryl, C_7 - C_{25} -alkaryl, C_2 - C_{20} heteroaryl, C_2 - C_{20} heterocyclyl, C_1 - C_{20} -alkoxy, C_2 - C_{20} -alkenyloxy, C_2 - C_{20} -alkynyloxy, C_6 - C_{20} -aryloxy, C_2 - C_{20} -alkoxycarbonyl, C_1 - C_{20} alkylthio, C_6 - C_{20} -arylthio, $-\text{Si}(\text{R})_3$, $-\text{O}-\text{Si}(\text{R})_3$, $-\text{O}-\text{C}(=\text{O})\text{R}$, $\text{C}(=\text{O})\text{R}$, $-\text{C}(=\text{O})\text{N}(\text{R})_2$, $-\text{NR}-\text{C}(=\text{O})-\text{N}(\text{R})_2$, $-\text{SO}_2\text{N}(\text{R})_2$, $-\text{S}(=\text{O})\text{R}$, $-\text{S}(=\text{O})_2\text{R}$, $-\text{O}-\text{S}(=\text{O})_2\text{R}$, halogen, nitro or cyano, wherein in all above occurrences relating to the meanings of R^8 , R^9 , R^{10}

and R^{11} the group R is identical or different and represents hydrogen, alkyl, cycloalkyl, alkenyl, alkynyl, aryl or heteroaryl.

[0200] If appropriate, one or more of R^8 , R^9 , R^{10} , and R^{11} can independently of one another, be substituted by one or more substituents, preferably straight-chain or branched C_1 - C_{10} -alkyl, C_3 - C_8 -cycloalkyl, C_1 - C_{10} -alkoxy or C_6 - C_{24} -aryl, C_2 - C_{20} heteroaryl, C_2 - C_{20} heterocyclic, and a functional group selected from the group consisting of hydroxy, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulphide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate and halogen, where these abovementioned substituents, to the extent chemically possible, may in turn be substituted by one or more substituents, preferably selected from the group consisting of halogen, in particular chlorine or bromine, C_1 - C_5 -alkyl, C_1 - C_5 -alkoxy and phenyl.

[0201] Merely in the interest of clarity, it may be added that the structures of the imidazoline and imidazolidine ligand depicted in the general formulae (IIa) and (IIb) in the present patent application are equivalent to the structures (IIa') and (IIb') which are frequently also found in the literature for this imidazoline and imidazolidine ligand, respectively, and emphasize the carbene character of the imidazoline and imidazolidine. This applies analogously to the associated preferred structures (IIIa)-(IIIu) depicted below.



[0202] In a preferred embodiment of the catalysts of the general formula (A),

[0203] R^8 and R^9 are each identical or different and represent hydrogen, C_6 - C_{24} -aryl, straight-chain or branched C_1 - C_{10} -alkyl, or form a cycloalkyl or aryl structure together with the carbon atoms to which they are bound.

[0204] More preferably

[0205] R^8 and R^9 are identical and are selected from the group consisting of hydrogen, methyl, propyl, butyl and phenyl.

[0206] The preferred and more preferred meanings of R^8 and R^9 may be substituted by one or more further substituents selected from the group consisting of straight-chain or branched C_1 - C_{10} -alkyl or C_1 - C_{10} -alkoxy, C_3 - C_8 -cycloalkyl, C_6 - C_{24} -aryl, and a functional group selected from the group consisting of hydroxy, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulphide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate and halogen, wherein all these substituents may in turn be substituted by one or more substituents, preferably selected from the group consisting of halogen, in particular chlorine or bromine, C_1 - C_5 -alkyl, C_1 - C_5 -alkoxy and phenyl.

[0207] R^{10} and R^{11} are identical or different and preferably represent straight-chain or branched C_1 - C_{10} -alkyl, C_3 - C_{10} -

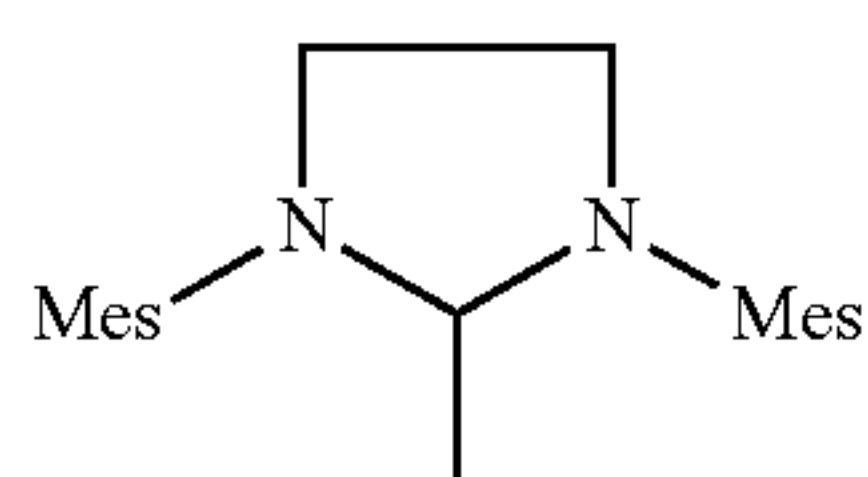
cycloalkyl, C₆-C₂₄-aryl, particularly preferably phenyl, C₁-C₁₀-alkylsulfonate, C₆-C₁₀-arylsulfonate.

[0208] More preferably

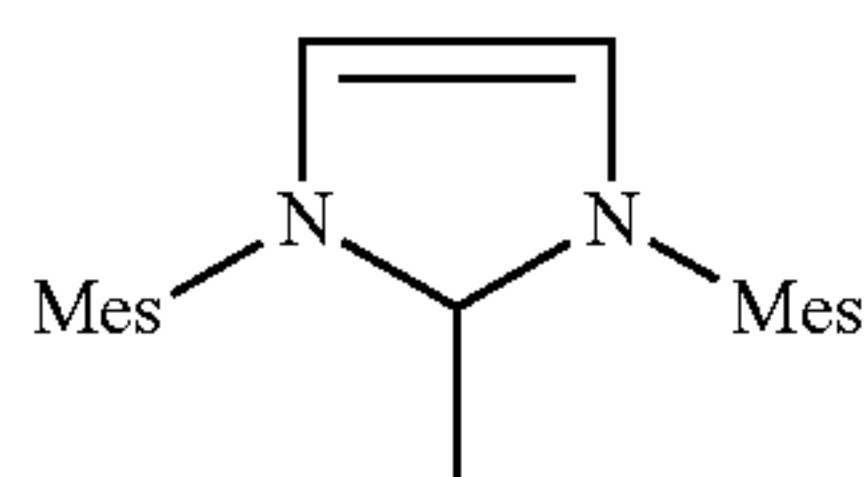
[0209] R¹⁰ and R¹¹ are identical and are selected from the group consisting of i-propyl, neopentyl, adamantyl, phenyl, 2,6-diisopropylphenyl, 2,6-dimethylphenyl, or 2,4,6-trimethylphenyl.

[0210] These preferred meanings of R¹⁰ and R¹¹ may be substituted by one or more further substituents selected from the group consisting of straight-chain or branched C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy, C₃-C₈-cycloalkyl, C₆-C₂₄-aryl, and a functional group selected from the group consisting of hydroxy, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulphide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate and halogen, wherein all these substituents may in turn be substituted by one or more substituents, preferably selected from the group consisting of halogen, in particular chlorine or bromine, C₁-C₅-alkyl, C₁-C₅-alkoxy and phenyl.

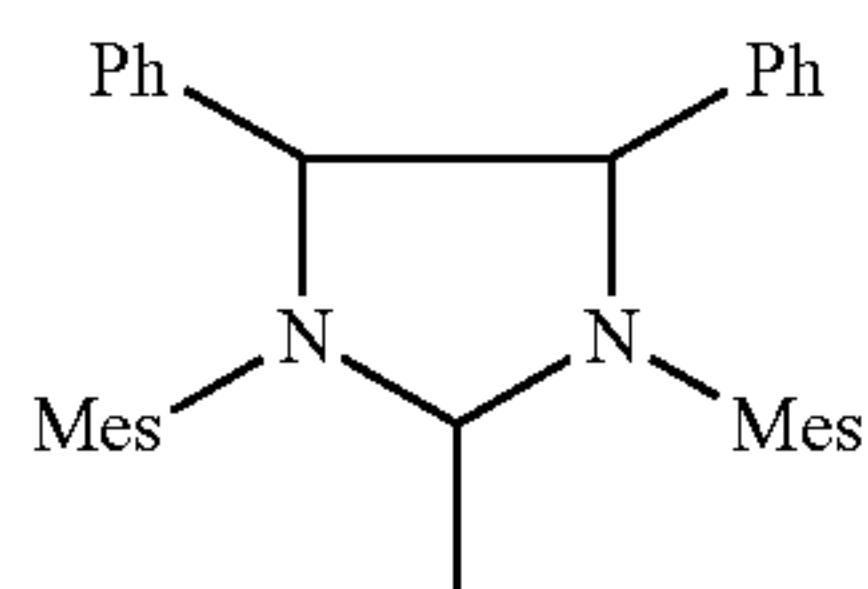
[0211] Particularly preferred are catalysts of general formula (A) in which one or both of ligands L represent imidazoline and imidazolidine ligands having the structures (IIIa) to (IIIu), where “Ph” means in each case phenyl, “Bu” means butyl, “Mes” represents in each case 2,4,6-trimethylphenyl, “Dipp” means in all cases 2,6-diisopropylphenyl and “Dimp” means 2,6-dimethylphenyl, and wherein the meaning of L can be identical or different in case both ligands L in general formula (A) have a structure according to (IIIa) to (IIIu),



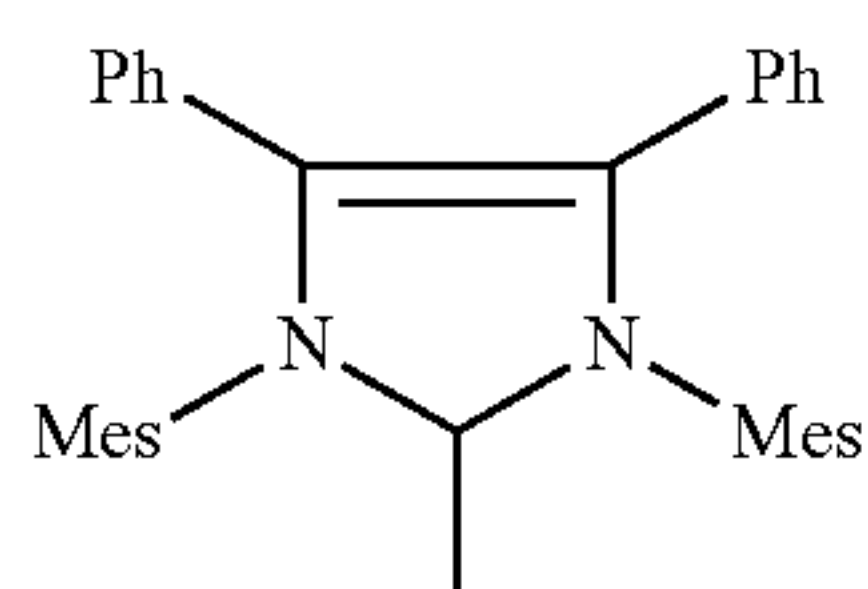
(IIIa)



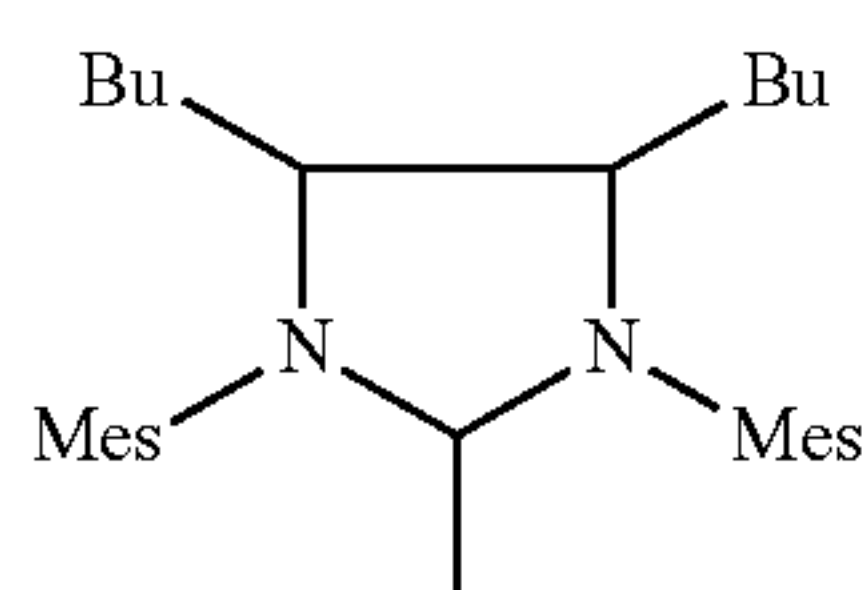
(IIIb)



(IIIc)

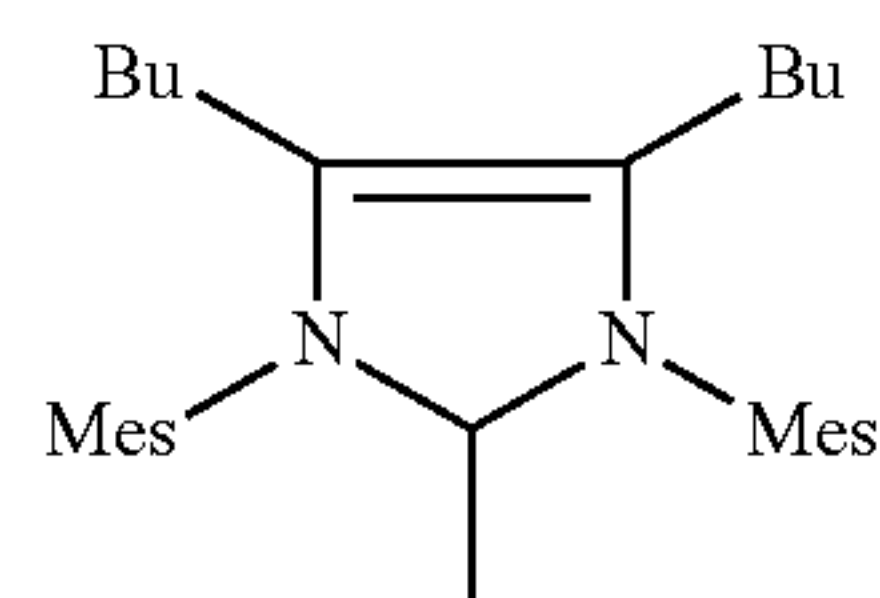


(IIIe)

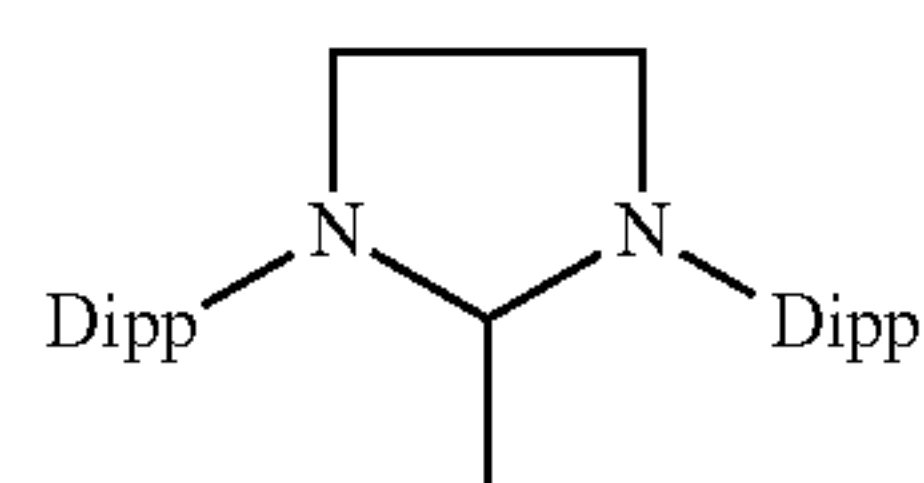


(IIIe)

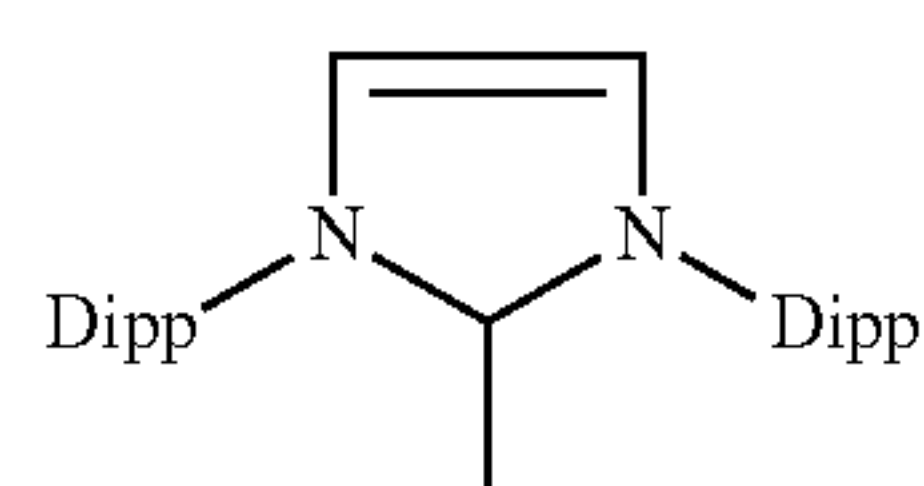
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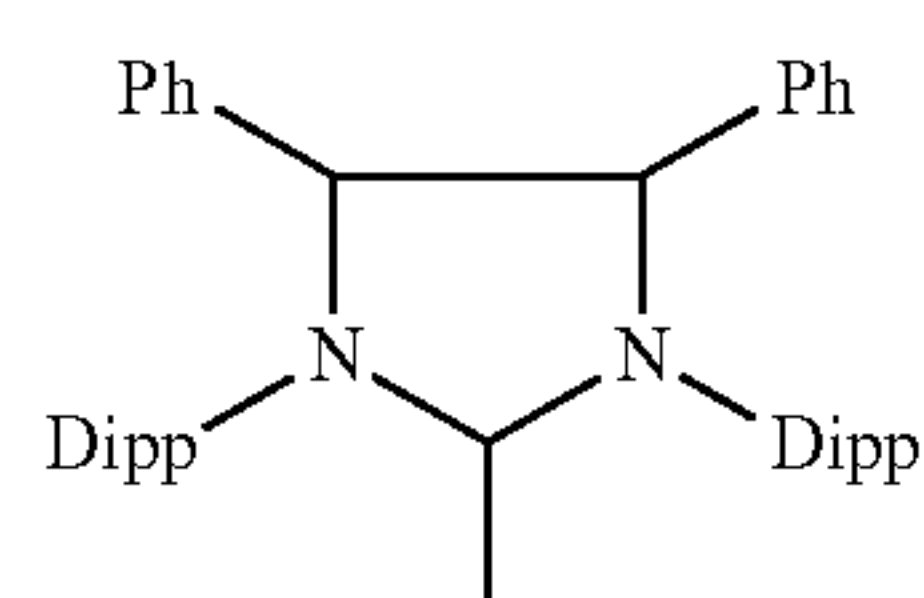
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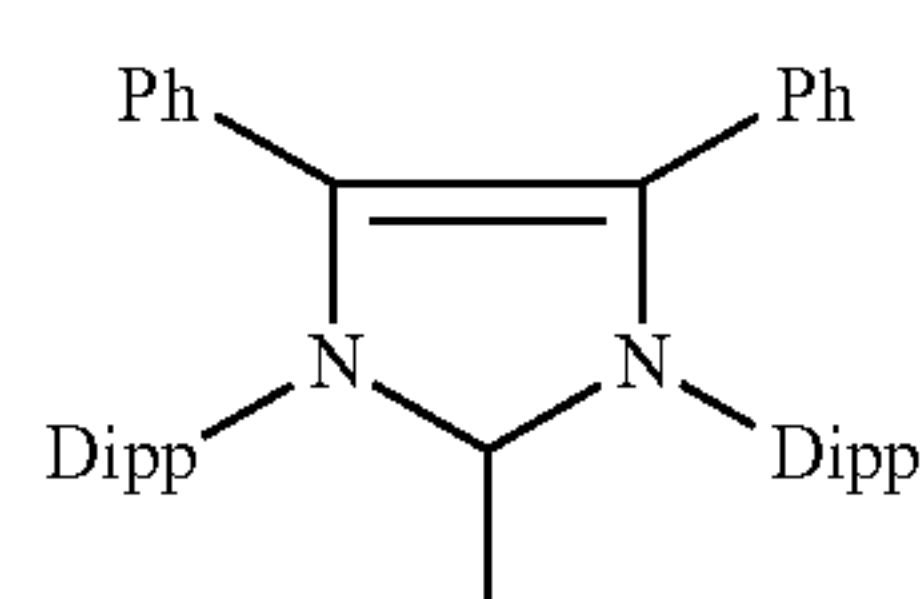
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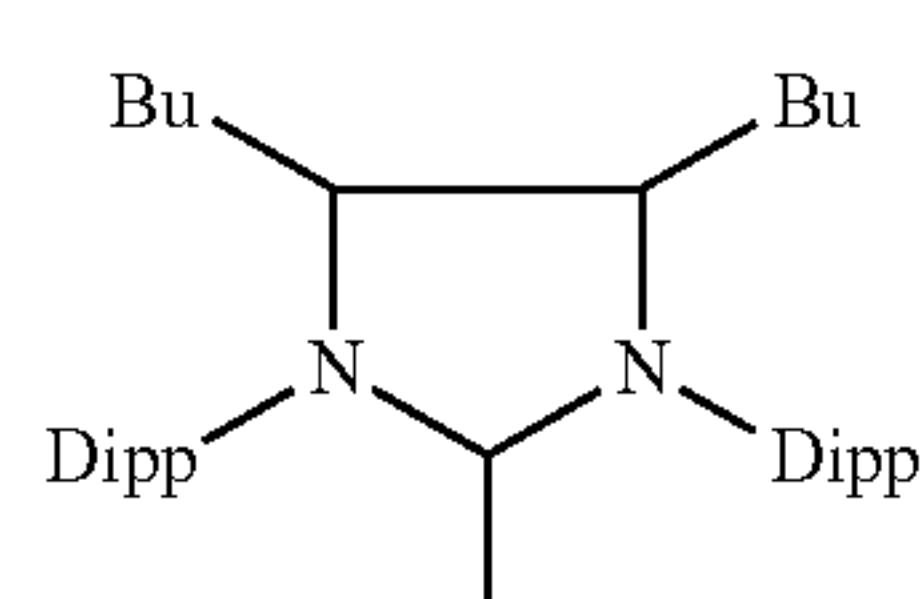
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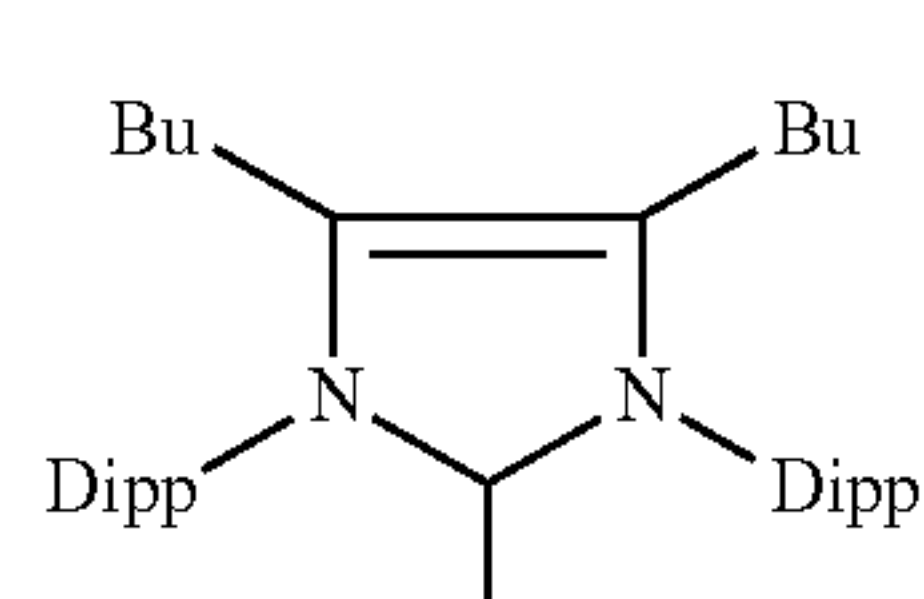
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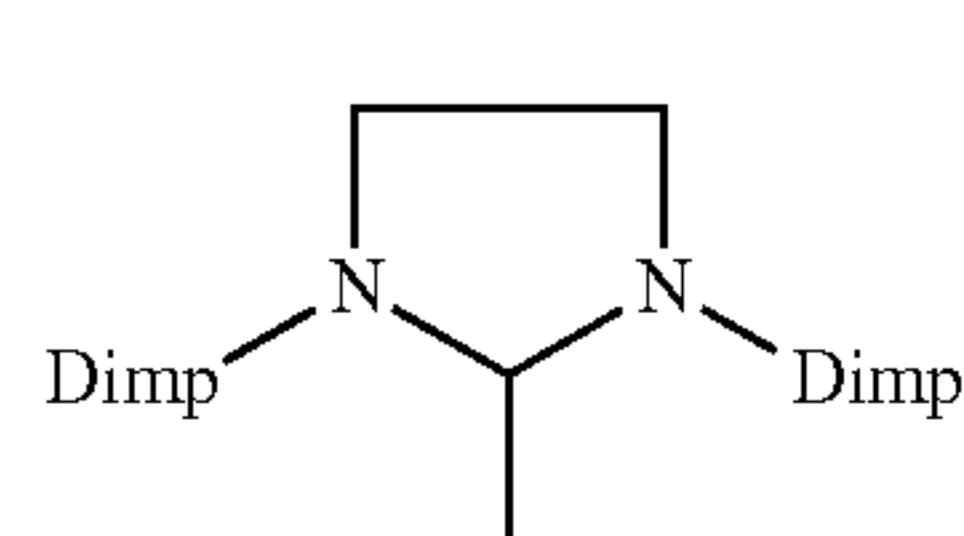
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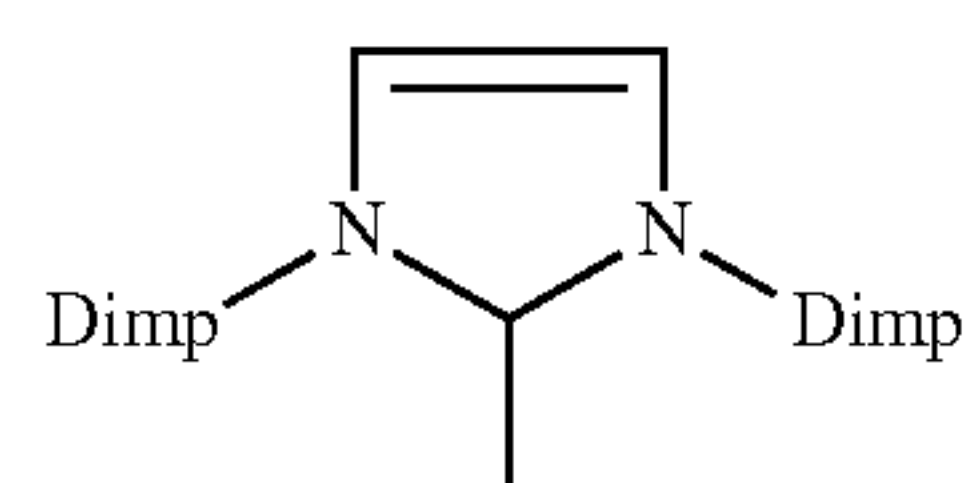
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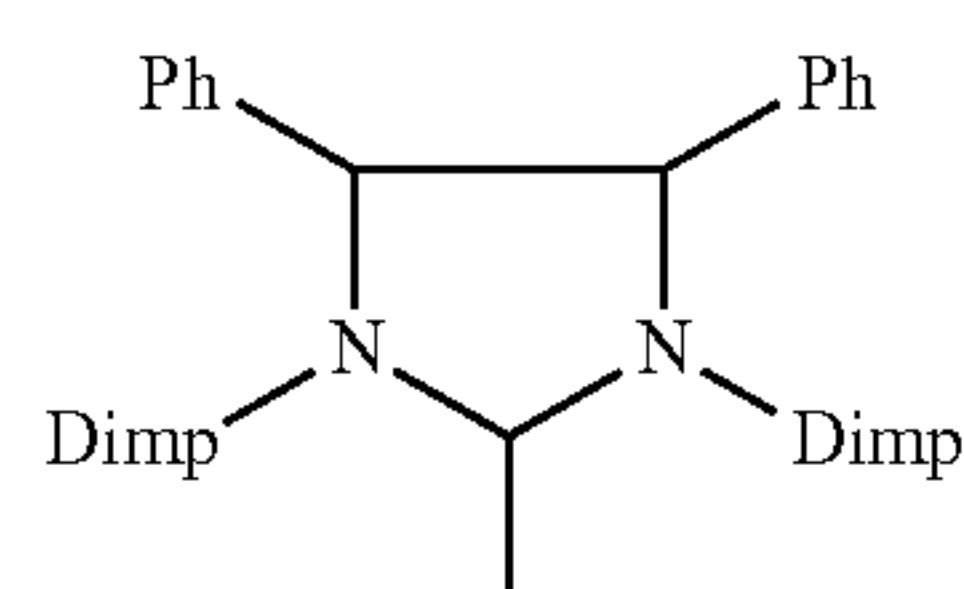
(IIIln)



(IIIpp)

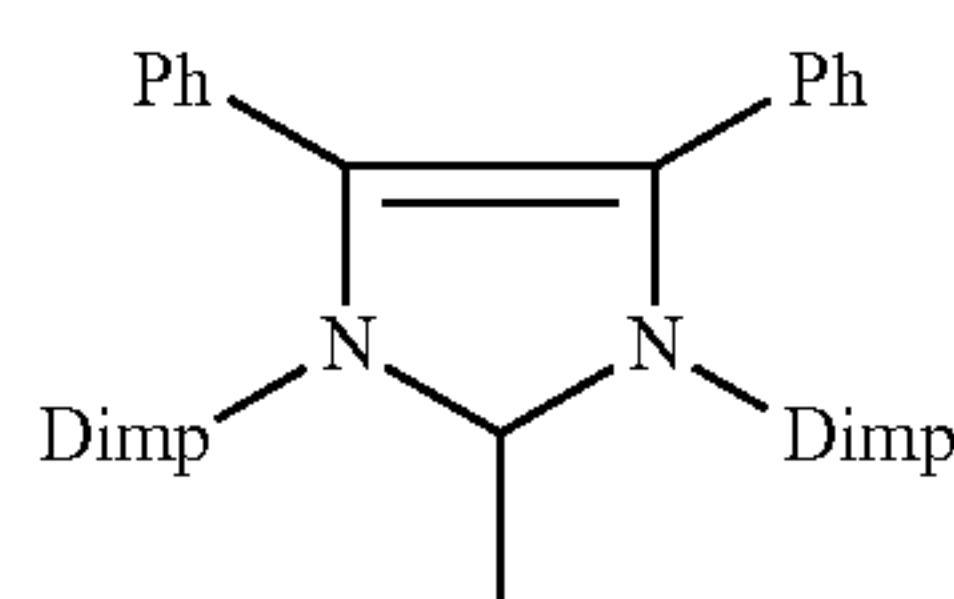


(IIIqq)

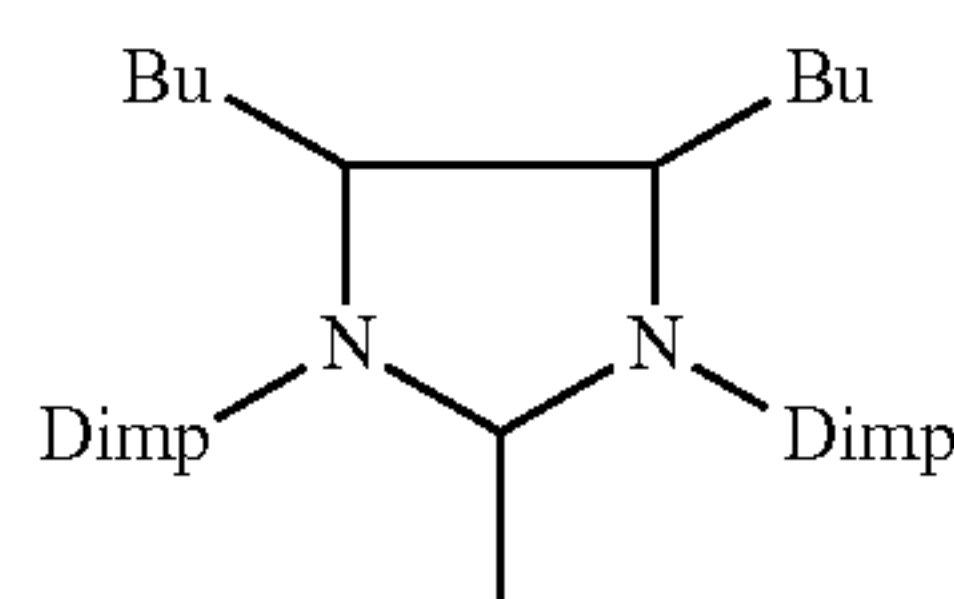


(IIIrr)

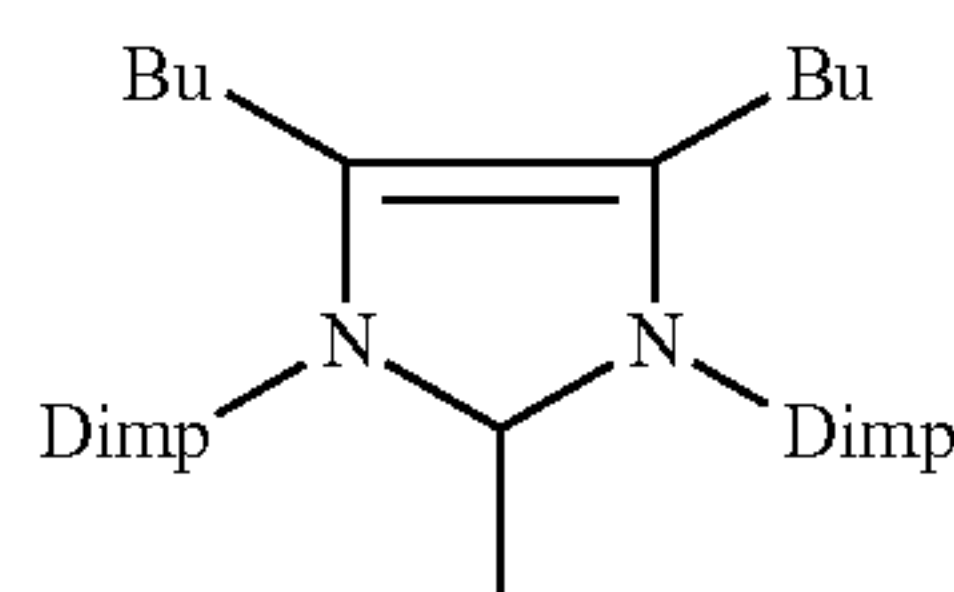
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(IIIIs)

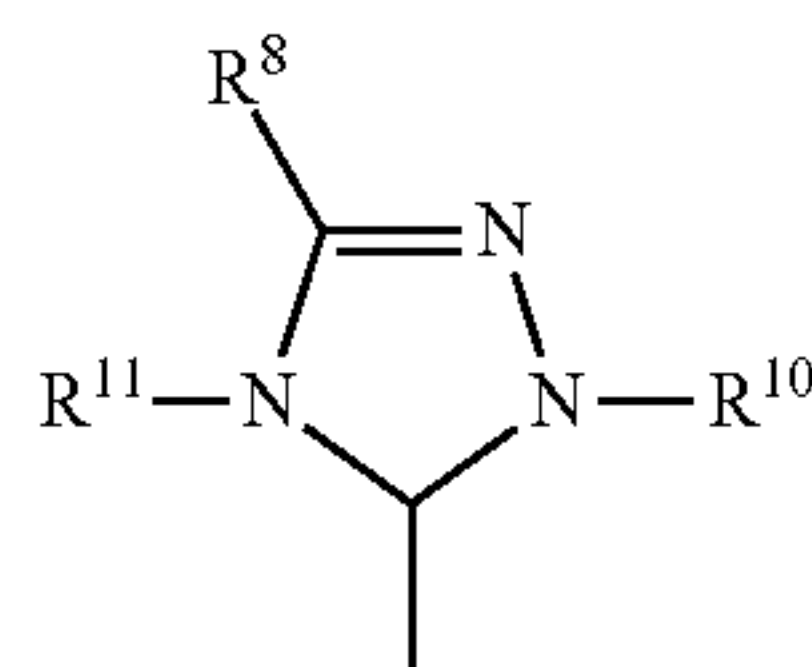


(IIIIt)

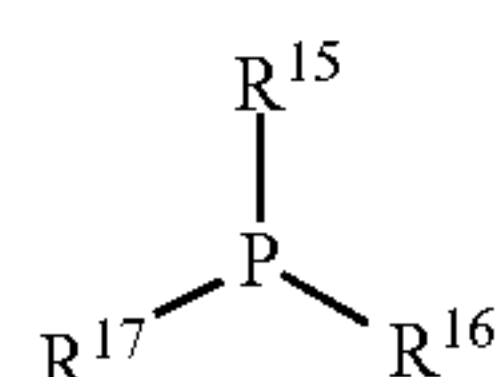


(IIIU)

[0212] In a further preferred embodiment of catalyst (A) one or both of the ligands L may have the meaning of general formulae (IIc) or (IId), wherein the meaning of L can be identical or different in case both ligands L have a structure according to (IIc) or (IId),



(IIc)



(IId)

wherein

[0213] R^8 , R^9 and R^{10} may have all general, preferred, more preferred and most preferred meanings as defined above in relation to general formulae (IIa) and (IIb), and

[0214] R^{15} , R^{16} and R^{17} are identical or different and may represent alkyl, cycloalkyl, alkoxy, aryl, aryloxy, or a heterocyclic group.

[0215] In general formulae (IIc) and (IId) R^8 , R^9 , R^{10} , R^{15} , R^{16} and R^{17} may also be substituted by one or more further, identical or different substituents selected from the group consisting of straight-chain or branched C_1 - C_5 -alkyl, in particular methyl, C_1 - C_5 -alkoxy, aryl and a functional group selected from the group consisting of hydroxy, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulphide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate and halogen.

[0216] In a more preferred embodiment the ligands L has the general formula (IId) wherein

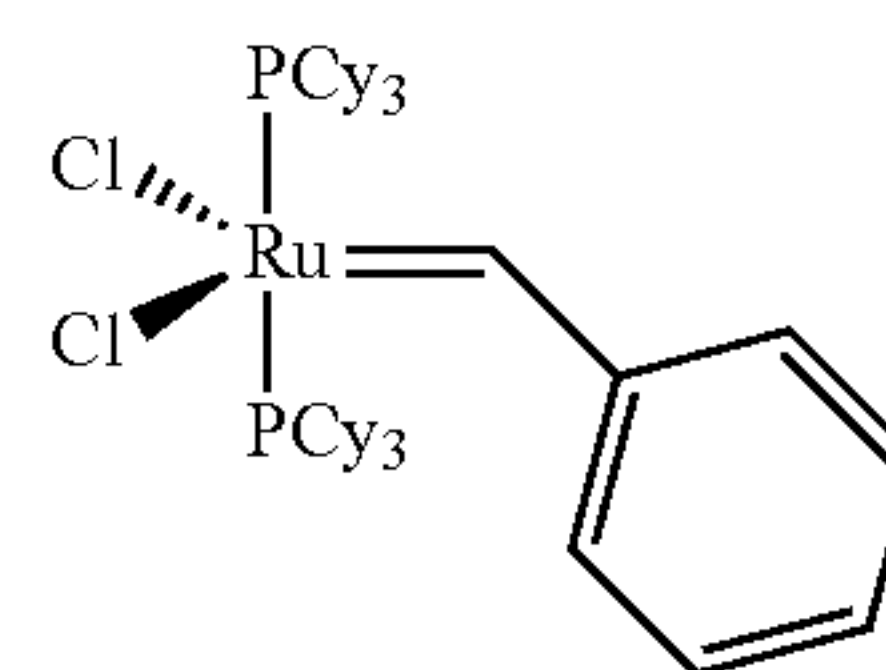
[0217] R^{15} , R^{16} and R^{17} are identical or different, even more preferably identical, and can represent C_1 - C_{20} alkyl, C_3 - C_8 -cycloalkyl, C_1 - C_{20} alkoxy, C_6 - C_{20} aryl, C_6 - C_{20} aryloxy, C_2 - C_{20} heteroaryl or a C_2 - C_{20} heterocyclic group.

[0218] In an even more preferred embodiment the ligand L has the general formula (IId) wherein

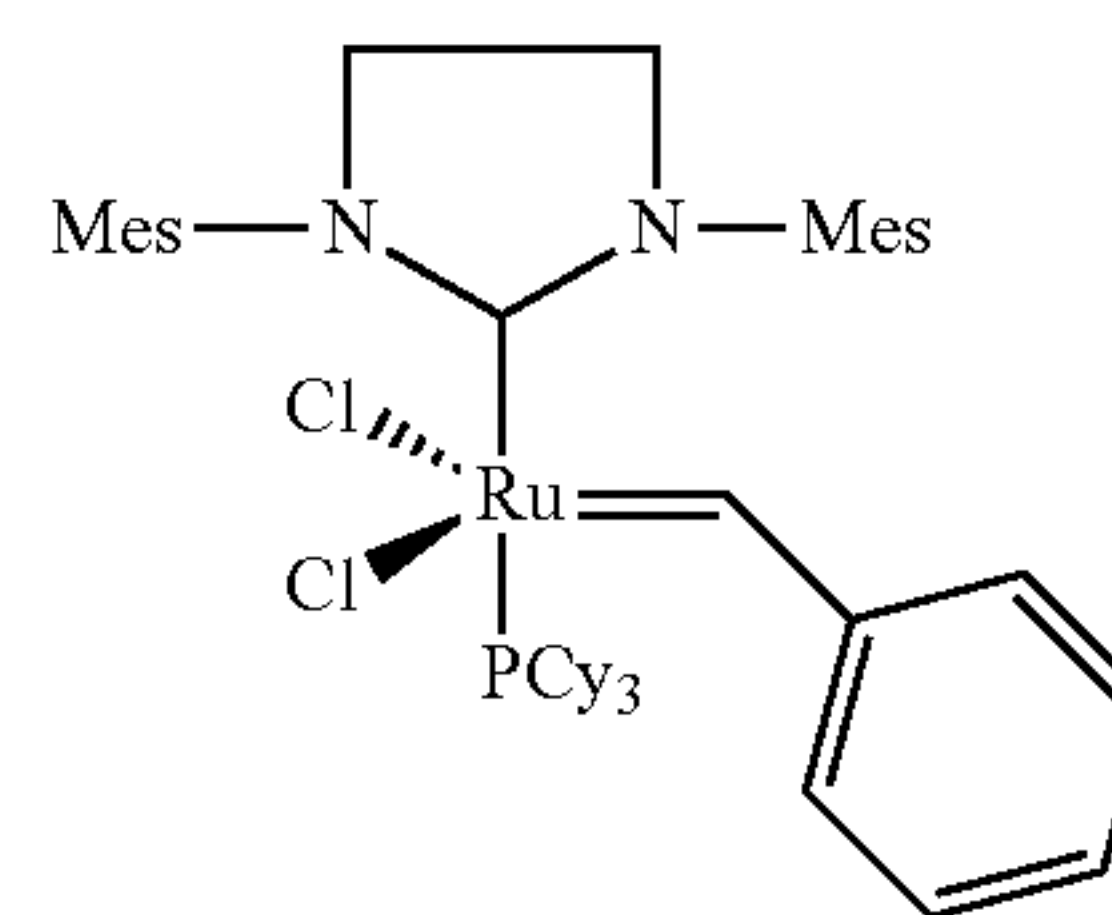
[0219] R^{15} , R^{16} and R^{17} are identical and each selected from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, neopentyl, 1-ethylpropyl, n-hexyl, neophenyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, phenyl, biphenyl, naphthyl, phenanthrenyl, anthracenyl, tolyl, 2,6-dimethylphenyl, and trifluoromethyl.

[0220] In case one or both of the ligand L possess general formula (IId) it most preferably represents PPh_3 , $P(p-Tol)_3$, $P(o-Tol)_3$, $PPh(CH_3)_2$, $P(CF_3)_3$, $P(p-FC_6H_4)_3$, $P(p-CF_3C_6H_4)_3$, $P(C_6H_4-SO_3Na)_3$, $P(CH_2C_6H_4-SO_3Na)_3$, $P(isopropyl)_3$, $P(CHCH_3(CH_2CH_3))_3$, $P(cyclopentyl)_3$, $P(cyclohexyl)_3$, $P(neopentyl)_3$ or $P(neophenyl)_3$.

[0221] Particular preference is given to catalyst systems comprising one of the two catalysts below, which fall under the general formula (A) and have the structures (IV) (Grubbs I catalyst) and (V) (Grubbs II catalyst), where Cy is cyclohexyl.

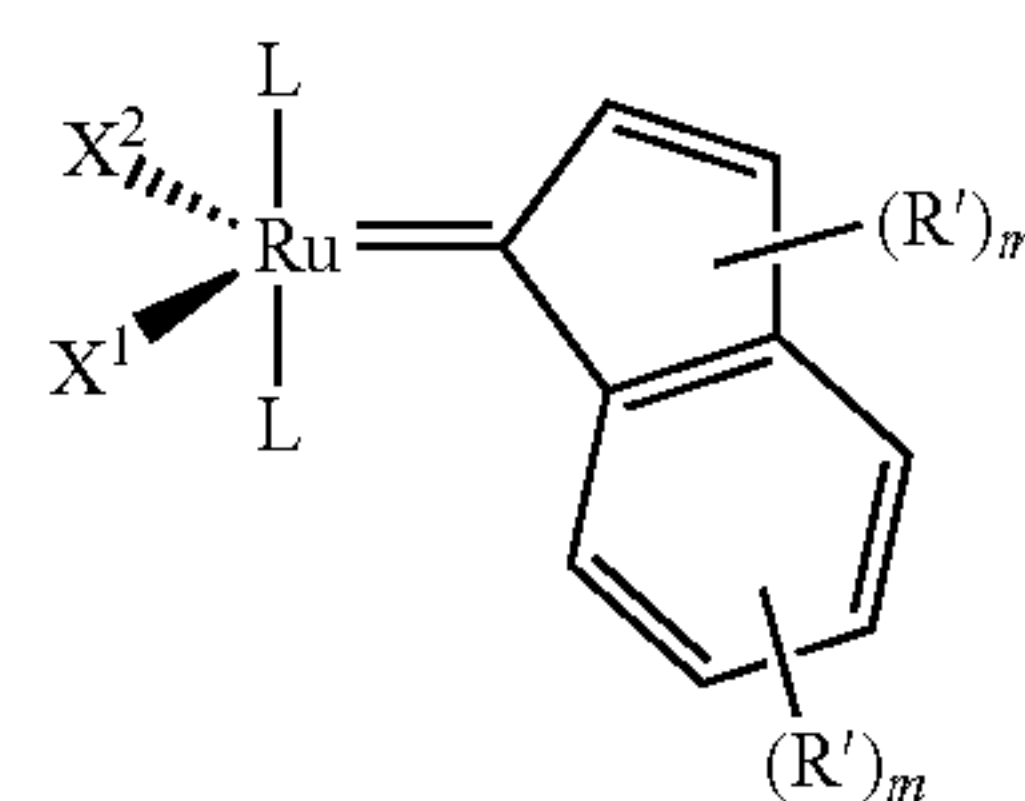


(IV)



(V)

[0222] In a further embodiment, use can be made of a catalyst of the general formula (A1),



(A1)

where

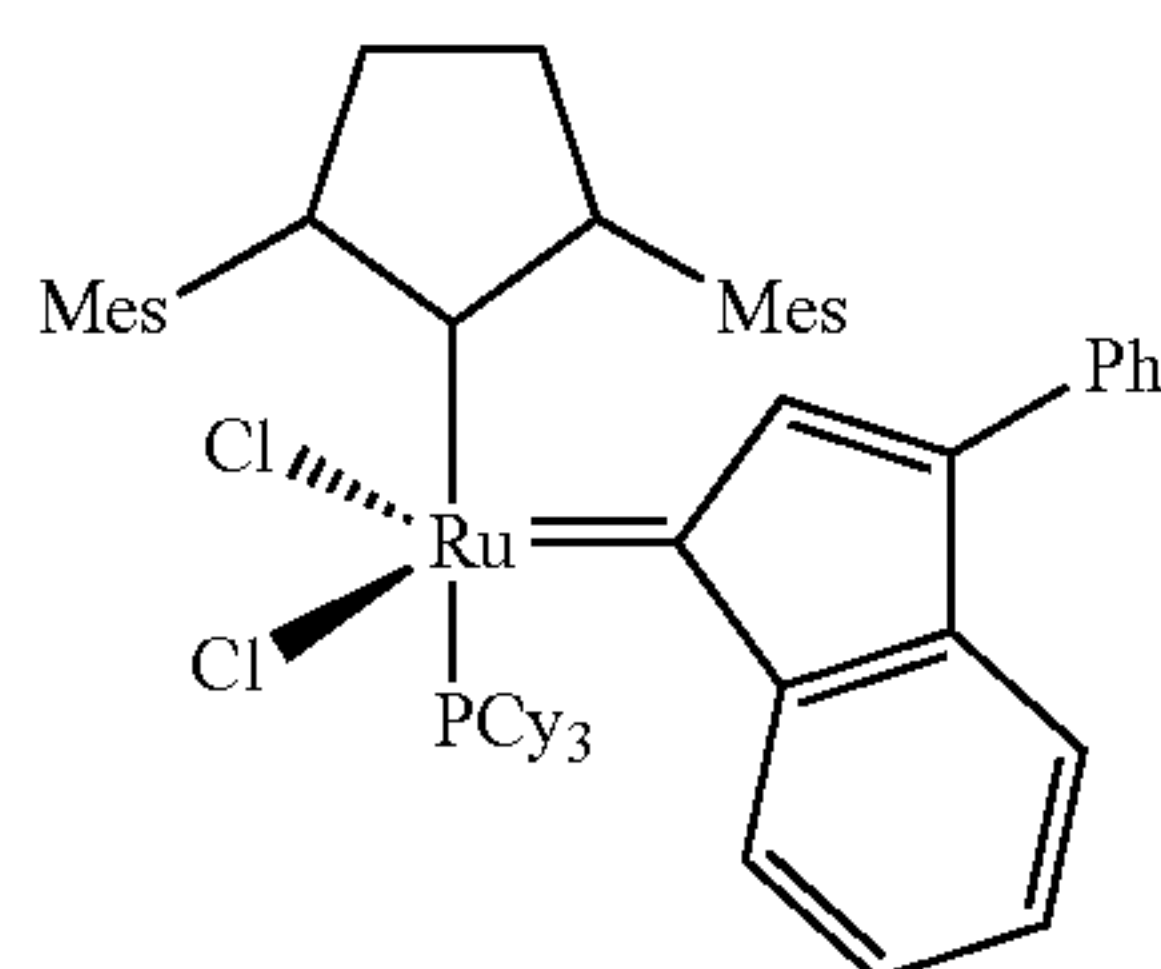
[0223] X^1 , X^2 and L can have the same general, preferred and particularly preferred meanings as in the general formula (A),

[0224] n is 0, 1 or 2,

[0225] m is 0, 1, 2, 3 or 4 and

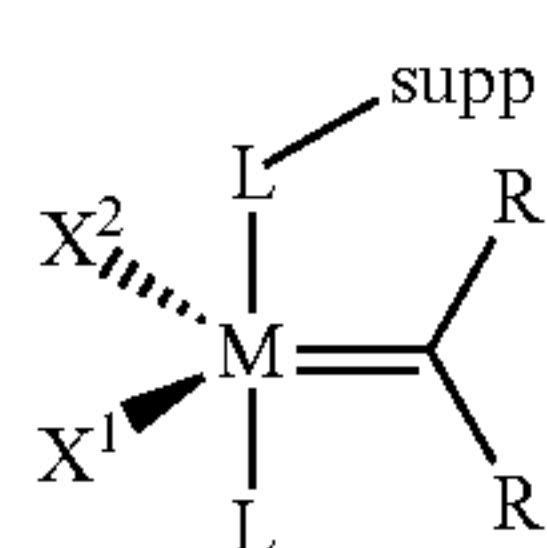
[0226] R' are identical or different and are alkyl, cycloalkyl, alkenyl, alkynyl, aryl, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxycarbonyl, alkylamino, alkylthio, arylthio, alkylsulphonyl or alkylsulphinyl radicals which may in each case be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl.

[0227] As preferred catalyst falling under the general formula (A1), it is possible to use, for example, the catalyst of the formula (VI) below, where Mes is in each case 2,4,6-trimethylphenyl and Ph is phenyl.

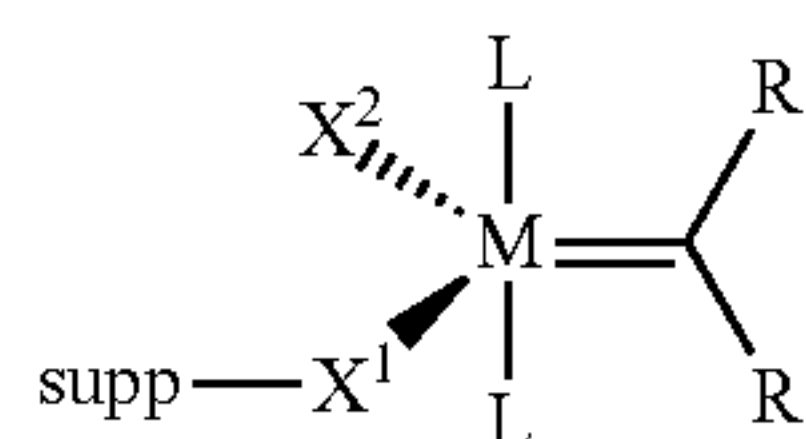


(VI)

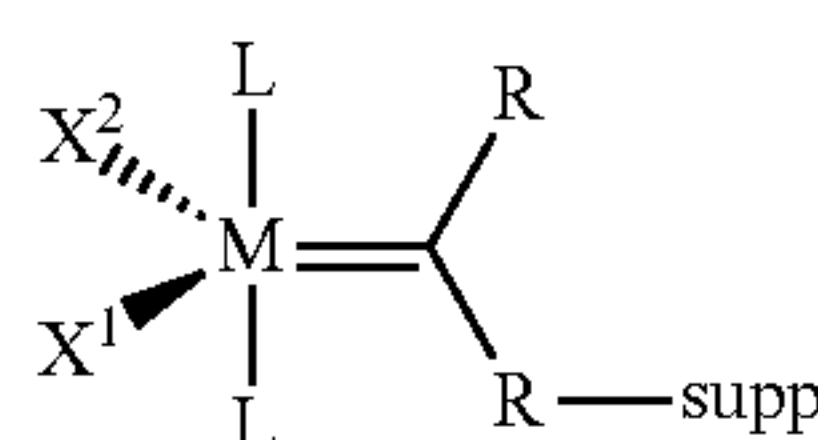
[0228] This catalyst is referred to in literature as “Nolan catalyst” and known from WO-A-2004/112951. The catalysts of general formula (A) as well as the preferred and more preferred embodiments thereof can also be used in immobilized form to prepare the novel catalyst compositions. The immobilization favourably occurs via a chemical bond of the complex catalyst to the surface of a support material. Suited are e.g. complex catalysts having the general formulae (support-1), (support-2), or (support-3), as depicted below, wherein M, Y, L, X¹, X², and R may have all general, preferred, more preferred, particularly preferred and most preferred meanings listed above in this application for general formula (A) and wherein “supp” stands for the support material. Preferably the support material represents a macromolecular material, or silica gels. As macromolecular material synthetic polymers or resins may be used, with polyethylene glycol, polystyrenes or cross-linked polystyrenes (e.g. poly(styrene-divinylbenzene) copolymers (PS-DVB)) being even more preferred. Such support material comprises functional groups on its surface which are able to form covalent bonds to one of the ligands or substituents of the complex catalyst, like e.g. to the ligand L or X¹ or to the substituents R³ or R⁴ as shown in the below depicted formulae.



(support-1)



(support-2)



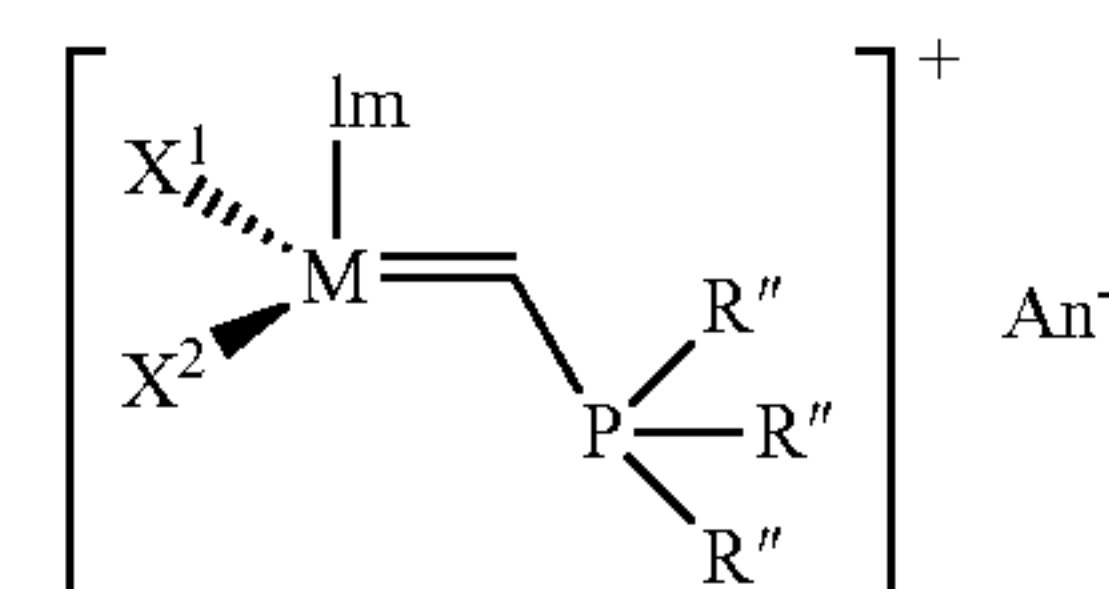
(support-3)

[0229] In such immobilized catalysts of general formulae (support-1), (support-2), or (support-3) “supp” stands more preferably for a polymeric support, a resin, polyethyleneglycole, or silica gels having one or more functional groups “X³” on their surface which are able to form a covalent bond to one of the ligands, like e.g. the L, R or X¹ as shown in

the above formulae. Suitable functional groups “X³” on the surface are hydroxyl, amino, thiol, carboxyl, C₁-C₂₀ alkoxy, C₁-C₂₀ alkylthio, —Si(R)₃, —O—Si(R)₃, C₆-C₁₄ aryloxy, C₂-C₁₄ heterocyclic, sulfinyl, sulfonyl, —C(=O)R, —C(=O)OR, —C(=O)N(R)₂, —NR—C(=O)—N(R)₂, —SO₂N(R)₂, or —N(SO₂—R)₂ wherein in all above occurrences of R in X³ is identical or different and shall mean H, C₁-C₆-alkyl, C₅-C₆-cycloalkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, phenyl, imidazolyl, triazolyl, or pyridinyl moieties.

[0230] Polystyrene or cross-linked polystyrene is the preferred support material, even more preferably with hydroxyl groups on the surface to allow an easy coupling to the catalyst.

[0231] A further embodiment provides catalyst systems obtainable by using a catalyst of the general formula (B),



(B)

where

[0232] M is ruthenium or osmium,

[0233] X¹ and X² are identical or different and are anionic ligands,

[0234] R'' are identical or different and are organic moieties,

[0235] Im is a substituted or unsubstituted imidazoline or imidazolidine ligand and

[0236] An is an anion.

[0237] The catalysts of the general formula (B) are known in principle (see, for example, Angew. Chem. Int. Ed. 2004, 43, 6161-6165).

[0238] X¹ and X² in the general formula (B) can have the same general, preferred and particularly preferred meanings as in the formula (A).

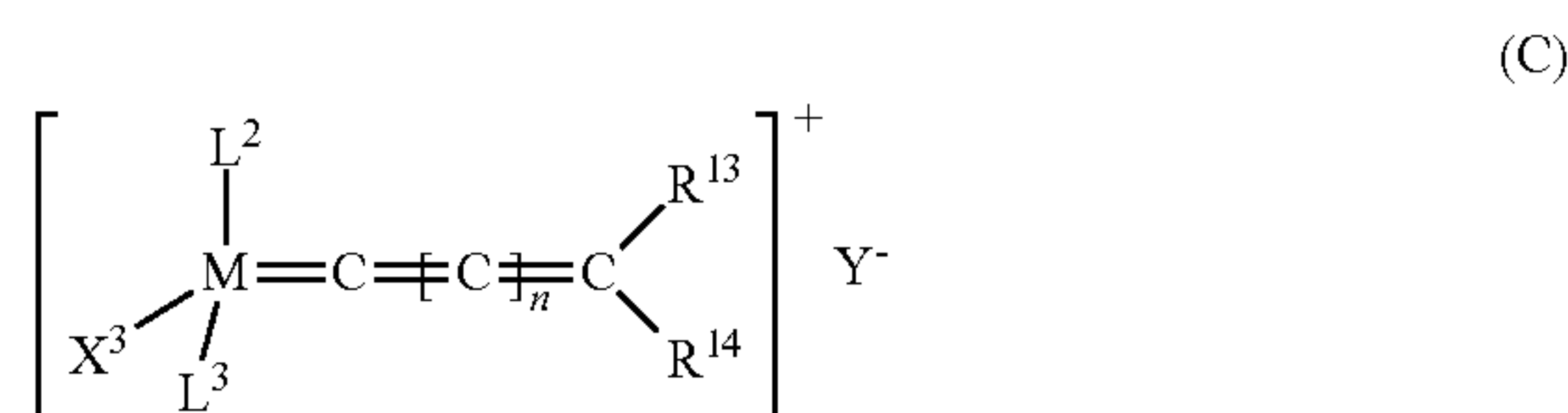
[0239] The imidazoline or imidazolidine ligand usually has a structure of the general formulae (IIa) or (IIb) which have been mentioned above for the catalyst of general formula (A) and can have all the structures mentioned there as preferred, in particular those of the formulae (IIIa)-(IIIu).

[0240] In general formula (B) R'' are identical or different and are each a straight-chain or branched C₁-C₃₀-alkyl, C₅-C₃₀-cycloalkyl or aryl, where the C₁-C₃₀-alkyl moiety may be interrupted by one or more double or triple bonds or one or more heteroatoms, preferably oxygen or nitrogen.

[0241] Aryl is an aromatic radical having from 6 to 24 skeletal carbon atoms. As preferred monocyclic, bicyclic or tricyclic carbocyclic aromatic moieties having from 6 to 10 skeletal carbon atoms, mention may be made by way of example of phenyl, biphenyl, naphthyl, phenanthrenyl or anthracenyl.

[0242] Preference is given to R'' in the general formula (B) being identical and each being phenyl, cyclohexyl, cyclopentyl, isopropyl, o-tolyl, o-xylyl or mesityl.

[0243] A further alternative embodiment provides a catalyst system obtainable by using a catalyst of the general formula (C)



[0244] where

[0245] M is ruthenium or osmium,

[0246] R^{13} and R^{14} are each, independently of one another, hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_2 - C_{20} -alkynyl, C_6 - C_{24} -aryl, C_1 - C_{20} -carboxylate, C_1 - C_{20} -alkoxy, C_2 - C_{20} -alkenyloxy, C_2 - C_{20} -alkynyloxy, C_6 - C_{24} -aryloxy, C_2 - C_{20} -alkoxycarbonyl, C_1 - C_{20} -alkylthio, C_1 - C_{20} -alkylsulphonyl or C_1 - C_{20} -alkylsulphinyl,

[0247] X^3 is an anionic ligand,

[0248] L^2 is an uncharged π -bonded ligand which may either be monocyclic or polycyclic,

[0249] L^3 is a ligand selected from the group consisting of phosphines, sulphonated phosphines, fluorinated phosphines, functionalized phosphines having up to three aminoalkyl, ammonioalkyl, alkoxyalkyl, alkoxycarbonylalkyl, hydrocarbonylalkyl, hydroxyalkyl or ketoalkyl groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines stibines, ethers, amines, amides, imines, sulphoxides, thioethers and pyridines,

[0250] Y^- is a noncoordinating anion and

[0251] n is 0, 1, 2, 3, 4 or 5.

[0252] A further alternative embodiment provides a catalyst system obtainable by using a catalyst of the general formula (D),



where

[0253] M is ruthenium or osmium,

[0254] X^1 and X^2 are identical or different and are anionic ligands which can have all meanings of X^1 and X^2 mentioned in the general formulae (A) and (B),

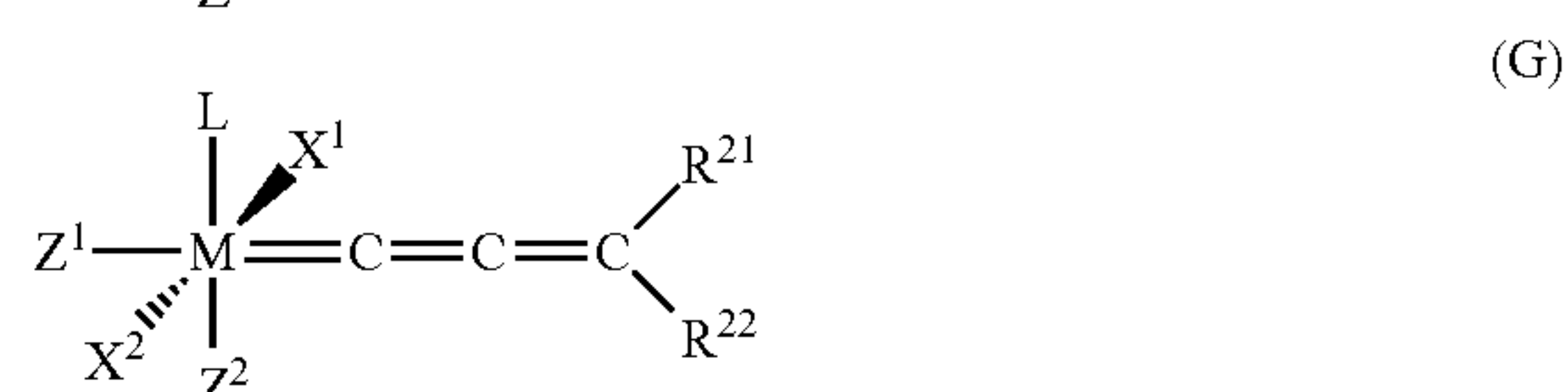
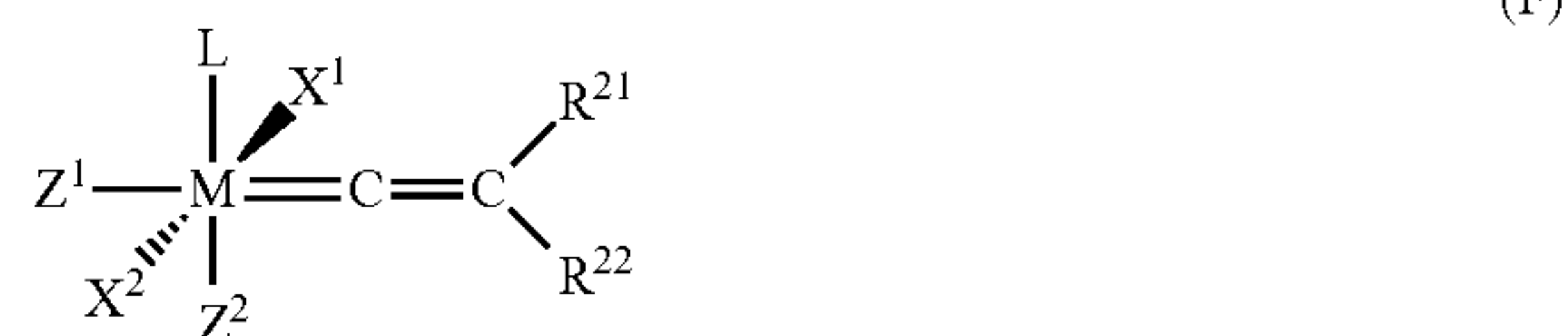
[0255] the symbols L represent identical or different ligands which can have all general and preferred meanings of L mentioned in the general formulae (A) and (B),

[0256] R^{19} and R^{20} are identical or different and are each hydrogen or substituted or unsubstituted alkyl.

[0257] A further alternative embodiment provides a catalyst system according to the invention obtainable by using a catalyst of the general formula (E), (F) or (G),



-continued



where

[0258] M is osmium or ruthenium,

[0259] X^1 and X^2 are identical or different and are two ligands, preferably anionic ligands,

[0260] L is a ligand, preferably an uncharged electron donor,

[0261] Z^1 and Z^2 are identical or different and are uncharged electron donors,

[0262] R^{21} and R^{22} are each, independently of one another, hydrogen alkyl, cycloalkyl, alkenyl, alkynyl, aryl, carboxylate, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxycarbonyl, alkylamino, alkylthio, alkylsulphonyl or alkylsulphinyl which are in each case substituted by one or more substituents selected from among alkyl, halogen, alkoxy, aryl or heteroaryl.

[0263] The catalysts of the general formulae (E), (F), and (G) are known in principle, e.g. from WO 2003/011455 A1, WO 2003/087167 A2, Organometallics 2001, 20, 5314 and Angew. Chem. Int. Ed. 2002, 41, 4038. The catalysts are commercially available or can be synthesized by the preparative methods indicated in the abovementioned literature references.

[0264] In the catalyst systems according to the invention, catalysts of the general formulae (E), (F), and (G) can be used in which Z^1 and Z^2 are identical or different and are uncharged electron donors. These ligands are usually weakly coordinating. The ligands are typically optionally substituted heterocyclic groups. These can be five- or six-membered monocyclic groups having from 1 to 4, preferably from 1 to 3 and particularly preferably 1 or 2, heteroatoms or bicyclic or polycyclic structures made up of 2, 3, 4 or 5 five- or six-membered monocyclic groups of this type, where all the abovementioned groups may in each case optionally be substituted by one or more alkyl, preferably C_1 - C_{10} -alkyl, cycloalkyl, preferably C_3 - C_8 -cycloalkyl, alkoxy, preferably C_1 - C_{10} -alkoxy, halogen, preferably chlorine or bromine, aryl, preferably C_6 - C_{24} -aryl, or heteroaryl, preferably C_5 - C_{23} -heteroaryl, radicals which may in turn each be substituted by one or more moieties, preferably selected from the group consisting of halogen, in particular chlorine or bromine, C_1 - C_5 -alkyl, C_1 - C_5 -alkoxy and phenyl.

[0265] Examples of Z^1 and Z^2 encompass nitrogen-containing heterocycles such as pyridines, pyridazines, bipyridines, pyrimidines, pyrazines, pyrazolidines, pyrrolidines, piperazines, indazoles, quinolines, purines, acridines, bisimidazoles, picolylimines, imidazolines, imidazolidines and pyrroles.

[0266] Z^1 and Z^2 can also be bridged to one another to form a cyclic structure. In this case, Z^1 and Z^2 form a single bidentate ligand.

[0267] In the catalysts of the general formulae (E), (F), and (G) L can have the same general, preferred and particularly preferred meanings as L in the general formula (A) and (B).

[0268] In the catalysts of the general formulae (E), (F), and (G) R^{21} and R^{22} are identical or different and are each alkyl, preferably C_1 - C_{30} -alkyl, particularly preferably C_1 - C_{20} -alkyl, cycloalkyl, preferably C_3 - C_{20} -cycloalkyl, particularly preferably C_3 - C_8 -cycloalkyl, alkenyl, preferably C_2 - C_{20} -alkenyl, particularly preferably C_2 - C_{16} -alkenyl, alkynyl, preferably C_2 - C_{20} -alkynyl, particularly preferably C_2 - C_{16} -alkynyl, aryl, preferably C_6 - C_{24} -aryl, carboxylate, preferably C_1 - C_{20} -carboxylate, alkoxy, preferably C_1 - C_{20} -alkoxy, alkenyloxy, preferably C_2 - C_{20} -alkenyloxy, alkynyloxy, preferably C_2 - C_{20} -alkynyloxy, aryloxy, preferably C_6 - C_{24} -aryloxy, alkoxycarbonyl, preferably C_2 - C_{20} -alkoxycarbonyl, alkylamino, preferably C_1 - C_{30} -alkylamino, alkylthio, preferably C_1 - C_{30} -alkylthio, arylthio, preferably C_6 - C_{24} -arylthio, alkylsulphonyl, preferably C_1 - C_{20} -alkylsulphonyl, or alkylsulphinyl, preferably C_1 - C_{20} -alkylsulphinyl, where the abovementioned substituents may be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl moieties.

[0269] In the catalysts of the general formulae (E), (F), and (G) X^1 and X^2 are identical or different and can have the same general, preferred and particularly preferred meanings as indicated above for X^1 and X^2 in the general formula (A).

[0270] Preference is given to using catalysts of the general formulae (E), (F), and (G) in which

[0271] M is ruthenium,

[0272] X^1 and X^2 are both halogen, in particular chlorine,

[0273] R^1 and R^2 are identical or different and are five- or six-membered monocyclic groups having from 1 to 4, preferably from 1 to 3 and particularly preferably 1 or 2, heteroatoms or bicyclic or polycyclic structures made up of 2, 3, 4 or 5 five- or six-membered monocyclic groups of this type, where all the abovementioned groups may in each case be substituted by one or more moieties selected from the group consisting of alkyl, preferably C_1 - C_{10} -alkyl, cycloalkyl, preferably C_3 - C_8 -cycloalkyl, alkoxy, preferably C_1 - C_{10} -alkoxy, halogen, preferably chlorine or bromine, aryl, preferably C_6 - C_{24} -aryl, or heteroaryl, preferably C_5 - C_{23} -heteroaryl,

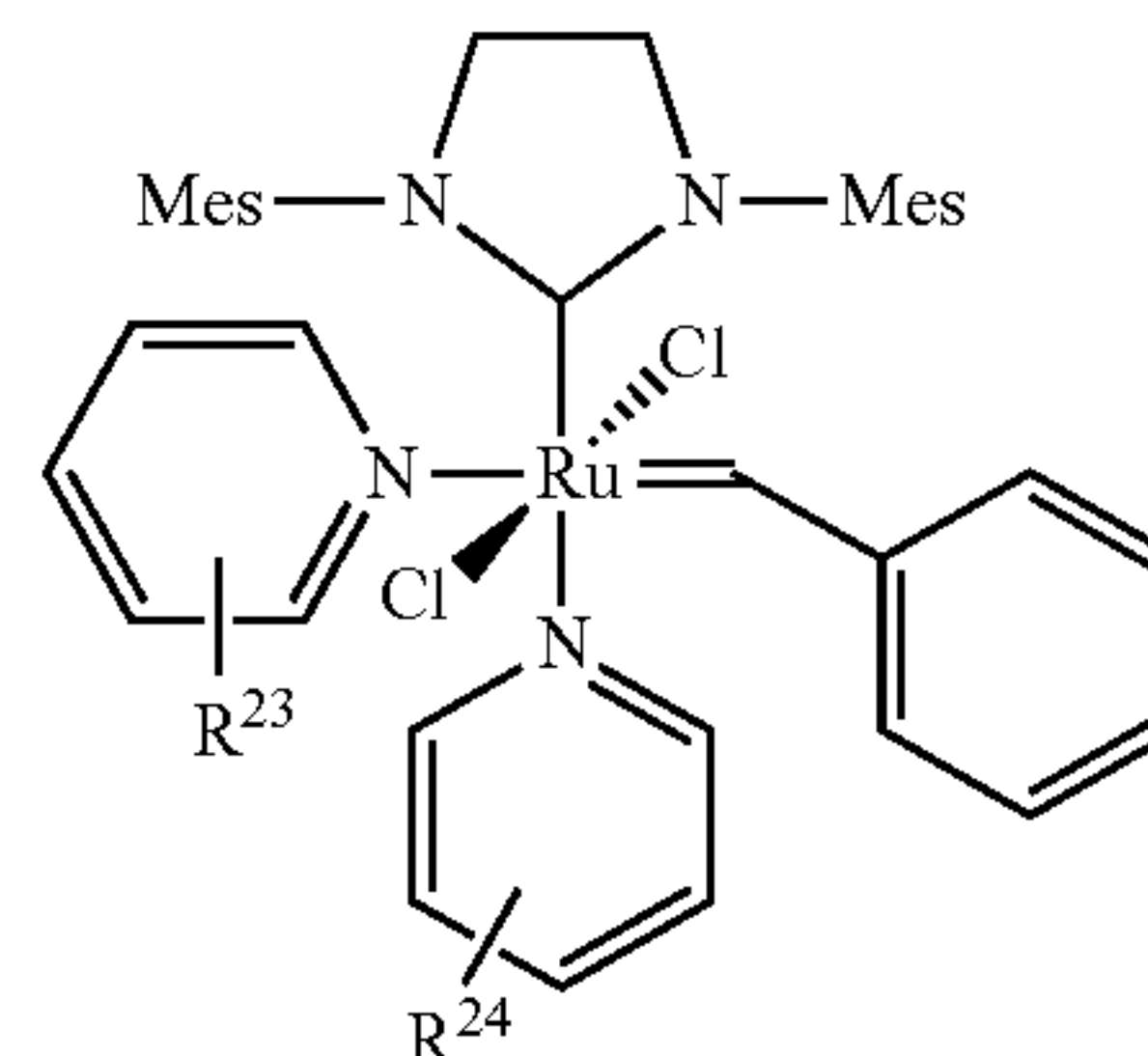
[0274] Z^1 and Z^2 are identical or different and five- or six-membered monocyclic groups having from 1 to 4, preferably from 1 to 3 and particularly preferably 1 or 2, heteroatoms or bicyclic or polycyclic structures made up of 2, 3, 4 or 5 five- or six-membered monocyclic groups of this type, where all these abovementioned groups may in each case optionally be substituted by one or more alkyl, preferably C_1 - C_{10} -alkyl, cycloalkyl, preferably C_3 - C_8 -cycloalkyl, alkoxy, preferably C_1 - C_{10} -alkoxy, halogen, preferably chlorine or bromine, aryl, preferably C_6 - C_{24} -aryl, or heteroaryl, preferably C_5 - C_{23} -heteroaryl, radicals which may in turn each be substituted by one or more moieties, preferably selected from the group consisting of halogen, in particular chlorine or bromine, C_1 - C_5 -alkyl, C_1 - C_5 -alkoxy and phenyl,

[0275] R^{21} and R^{22} are identical or different and are each C_1 - C_{30} -alkyl C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_2 - C_{20} -alkynyl, C_6 - C_{24} -aryl, C_1 - C_{20} -carboxylate, C_1 - C_{20} -alkoxy, C_2 - C_{20} -alkenyloxy, C_2 - C_{20} -alkynyloxy, C_6 - C_{24} -aryloxy, C_2 - C_{20} -alkoxycarbonyl, C_1 - C_{30} -alkylamino, C_1 - C_{30} -alkylthio, C_6 - C_{24} -arylthio, C_1 - C_{20} -alkylsulphonyl, C_1 - C_{20} -alkylsulphinyl, and

[0276] L has a structure of the above-described general formula (IIa) or (IIb), in particular one of the formulae (IIIa) to (IIIu).

[0277] A particularly preferred catalyst coming under general formula (E) has the structure (XIX),

(XIX)

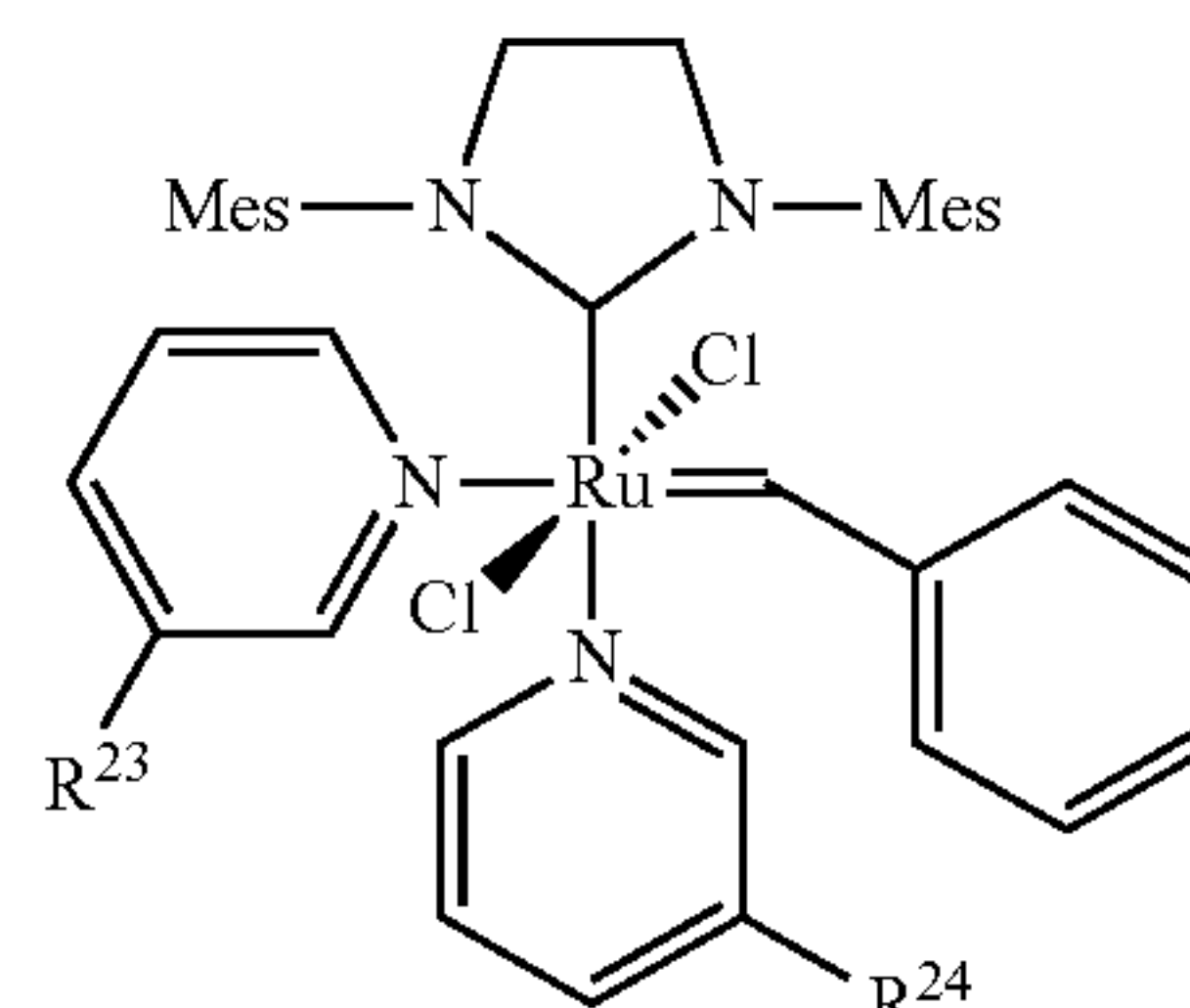


where R^{23} and R^{24} are identical or different and are each halogen, straight-chain or branched C_1 - C_{20} -alkyl, C_1 - C_{20} -heteroalkyl, C_1 - C_{10} -haloalkyl, C_1 - C_{10} -alkoxy, C_6 - C_{24} -aryl, preferably bromine, phenyl, formyl, nitro, a nitrogen heterocycle, preferably pyridine, piperidine or pyrazine, carboxy, alkylcarbonyl, halocarbonyl, carbamoyl, thiocarbamoyl, carbamido, thioformyl, amino, dialkylamino, trialkylsilyl or trialkoxysilyl.

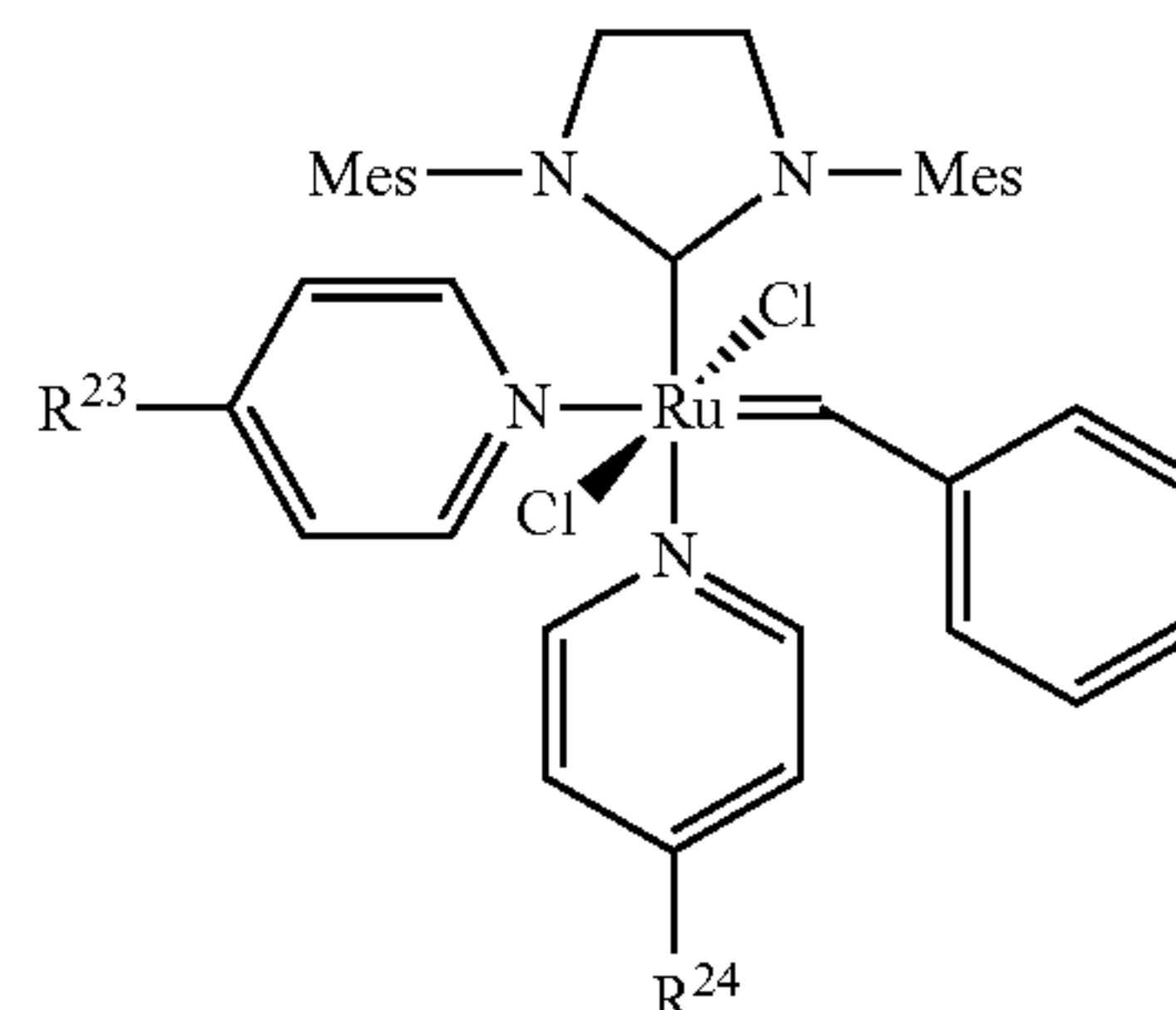
[0278] The abovementioned meanings for R^{23} and R^{24} C_1 - C_{20} -alkyl, C_1 - C_{20} -heteroalkyl, C_1 - C_{10} -haloalkyl, C_1 - C_{10} -alkoxy, C_6 - C_{24} -aryl, preferably phenyl, formyl, nitro, a nitrogen heterocycle, preferably pyridine, piperidine or pyrazine, carboxy, alkylcarbonyl, halocarbonyl, carbamoyl, thiocarbamoyl, carbamido, thioformyl, amino, trialkylsilyl and trialkoxysilyl may in turn each be substituted by one or more halogen, preferably fluorine, chlorine or bromine, C_1 - C_5 -alkyl, C_1 - C_5 -alkoxy or phenyl moieties.

[0279] Particularly preferred embodiments of the catalyst of formula (XIX) have the structure (XIX a) or (XIX b), where R^{23} and R^{24} have the same meanings as indicated in formula (XIX).

(XIXa)

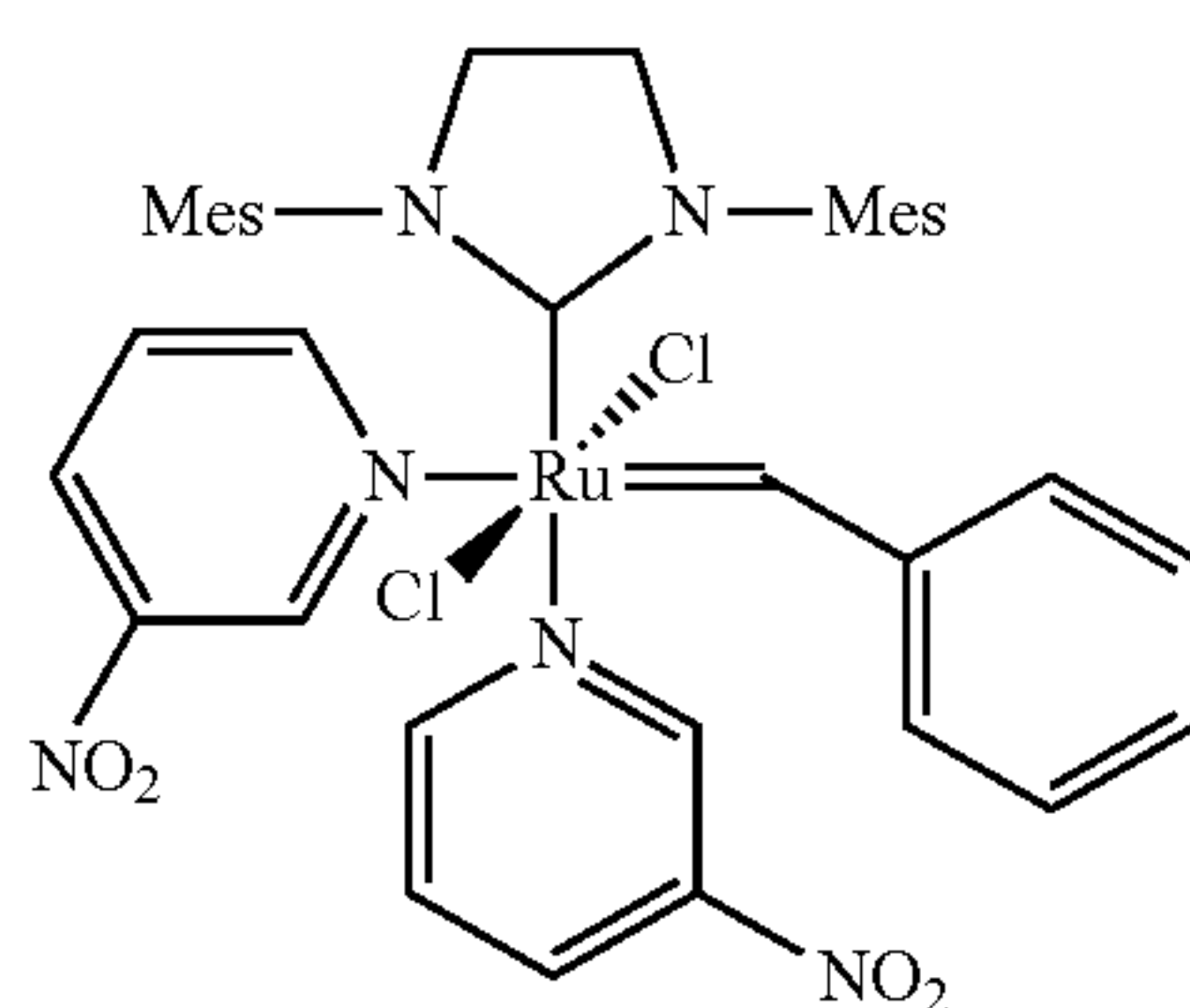
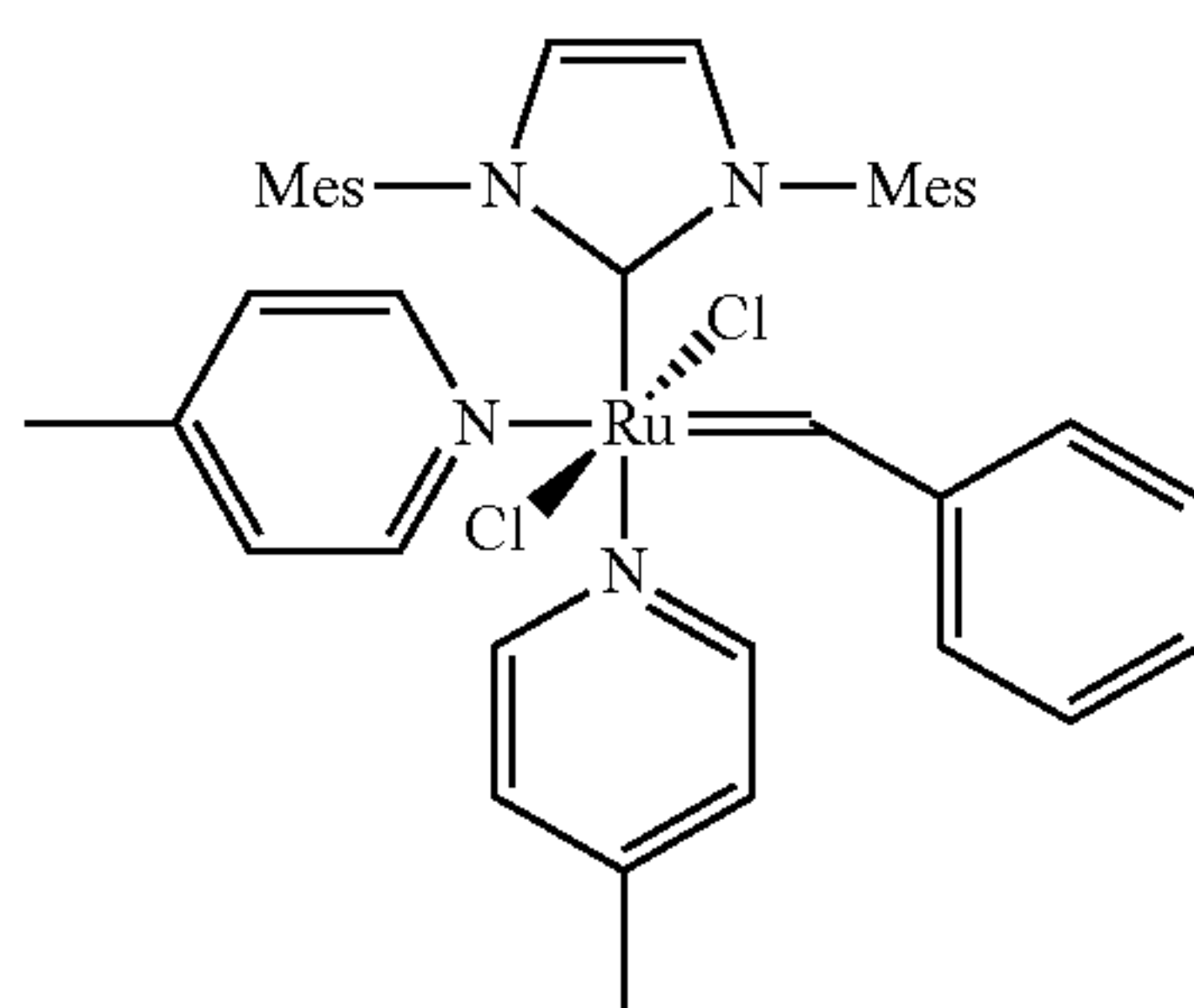
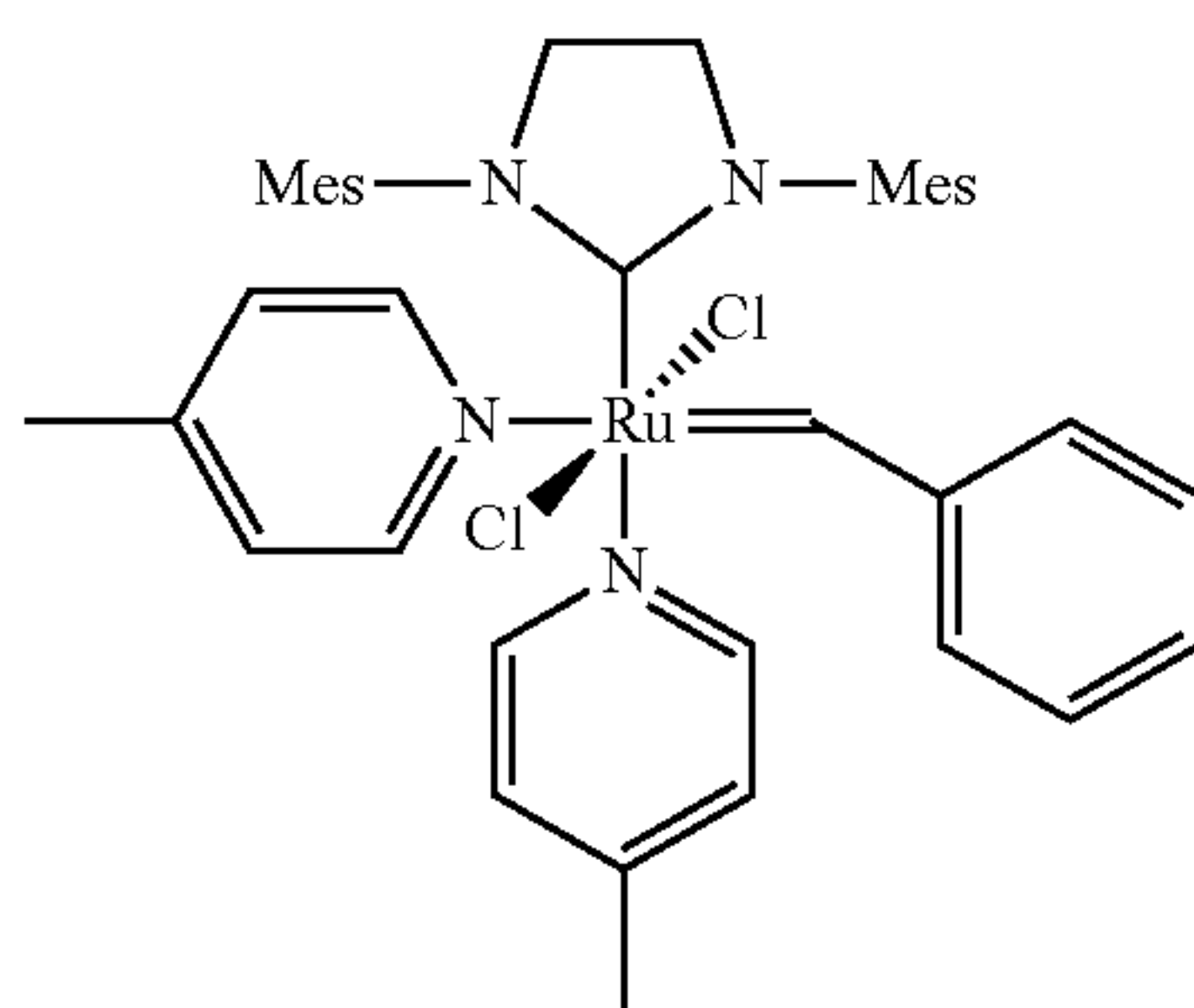
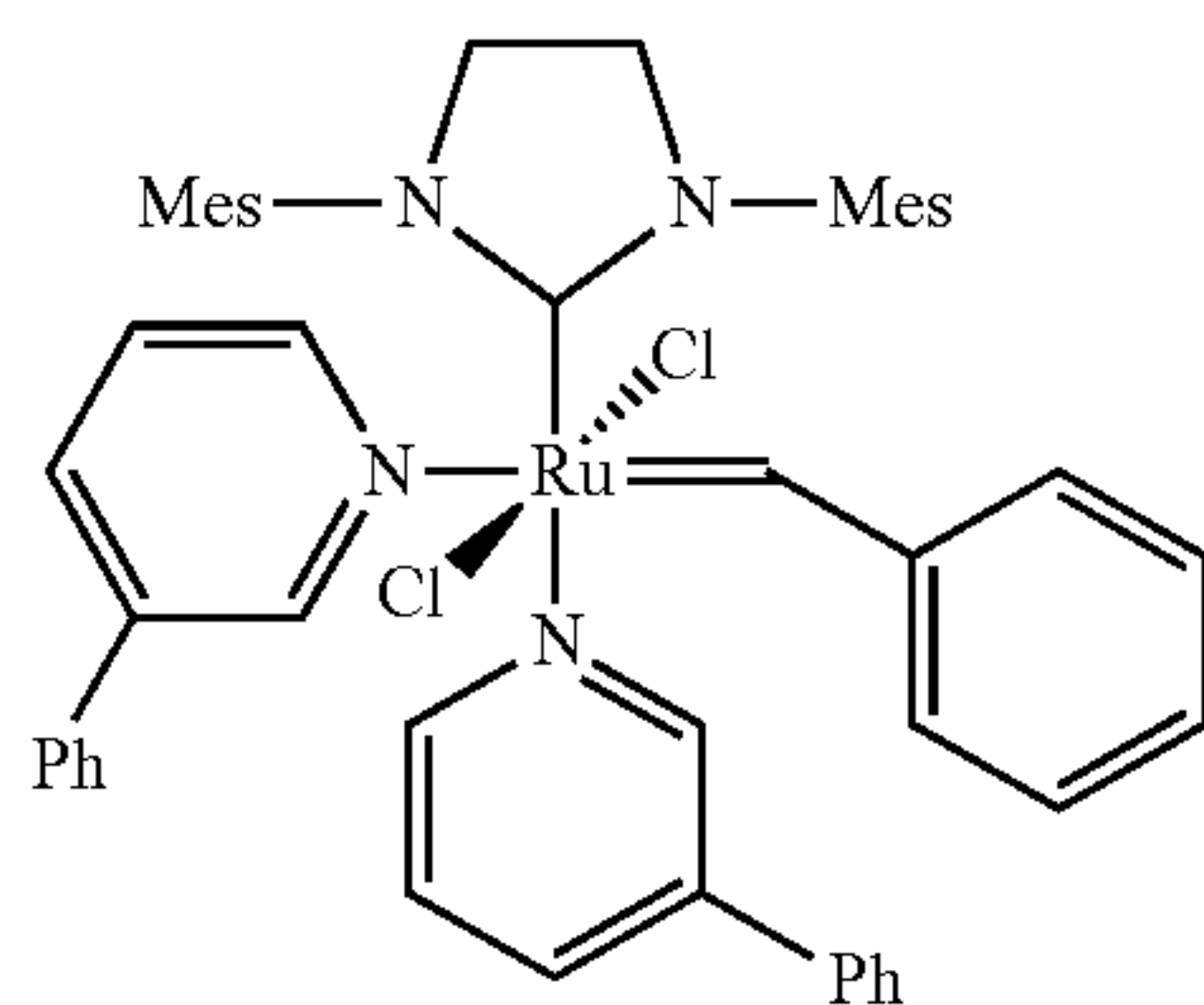
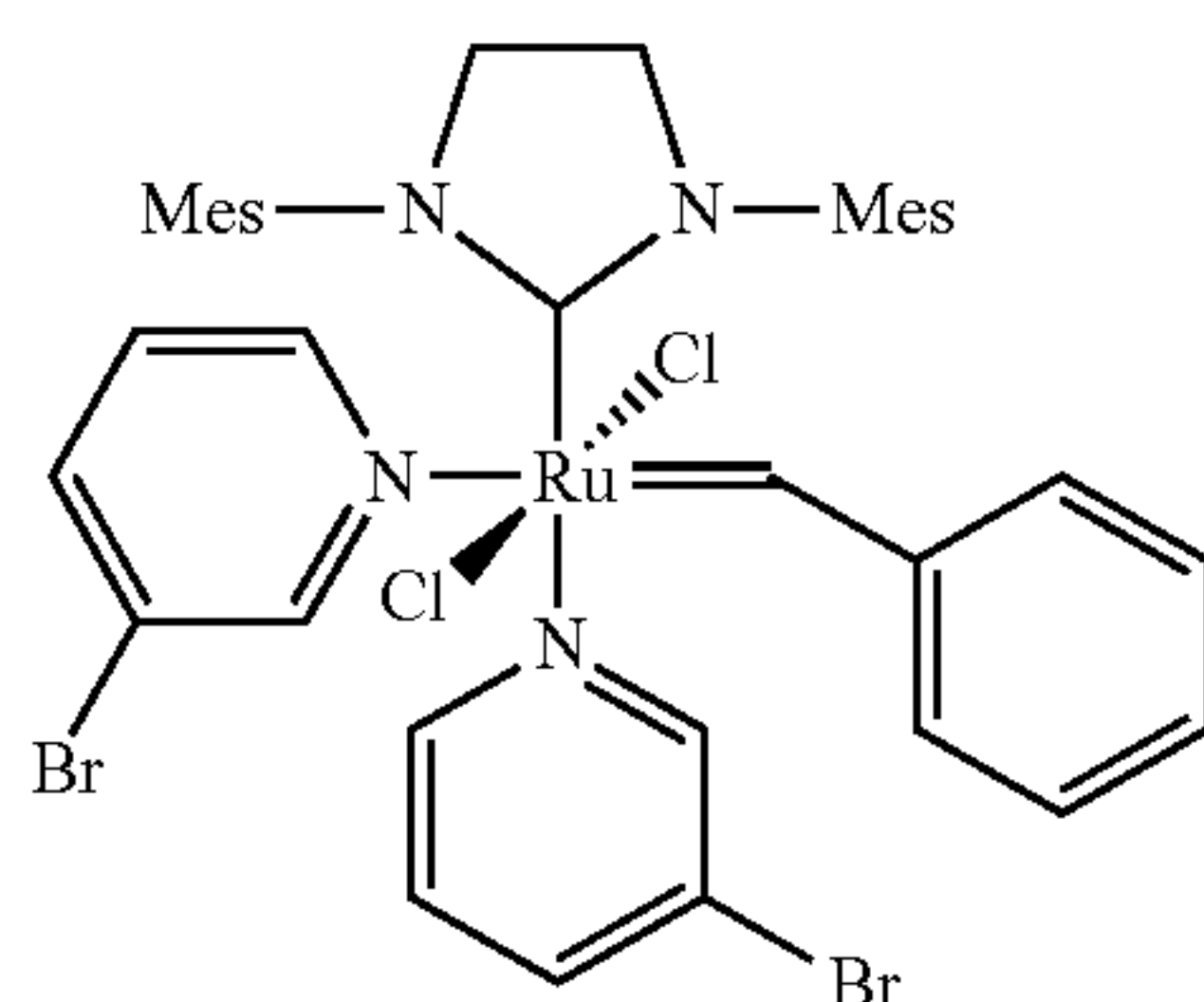


(XIXb)

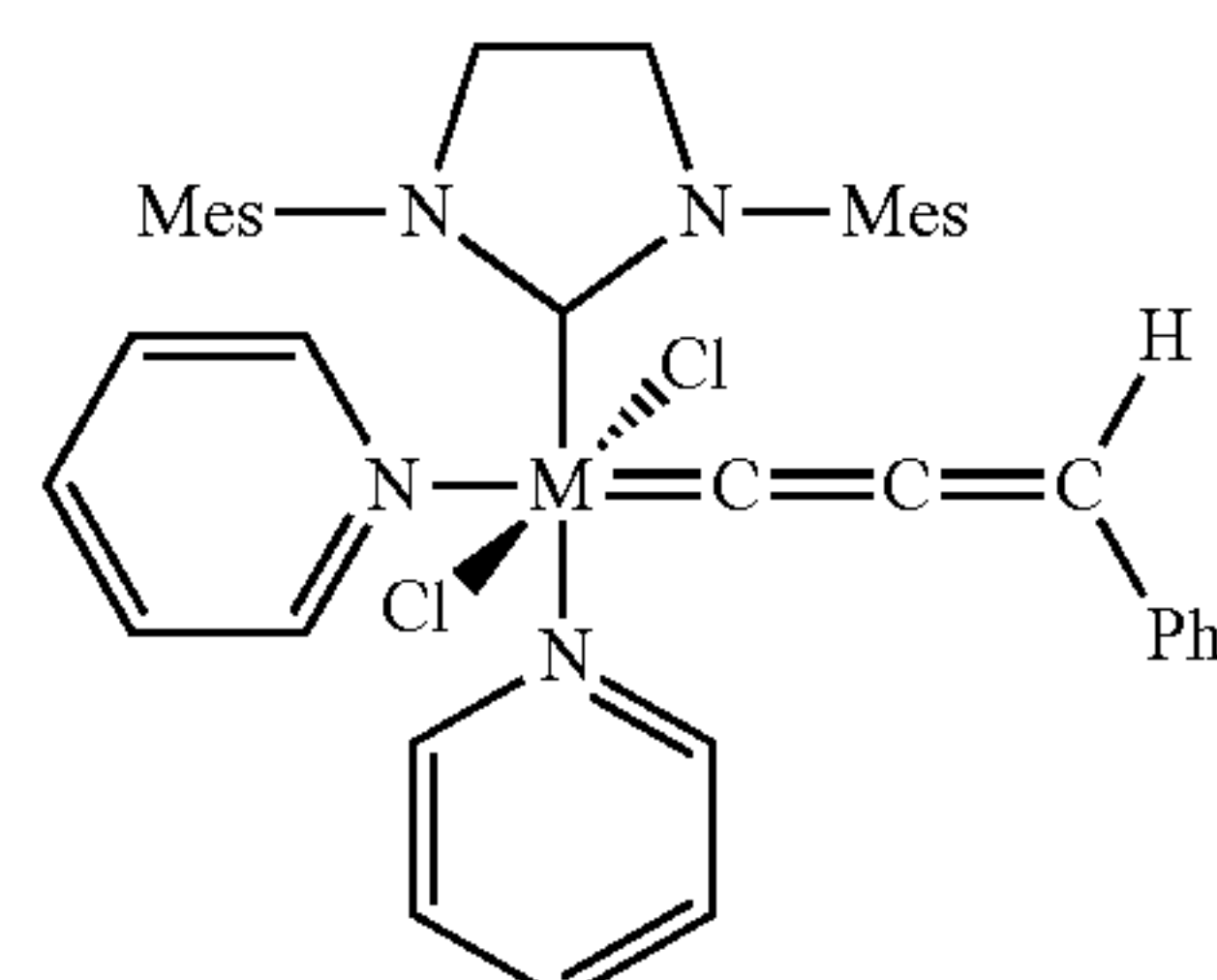
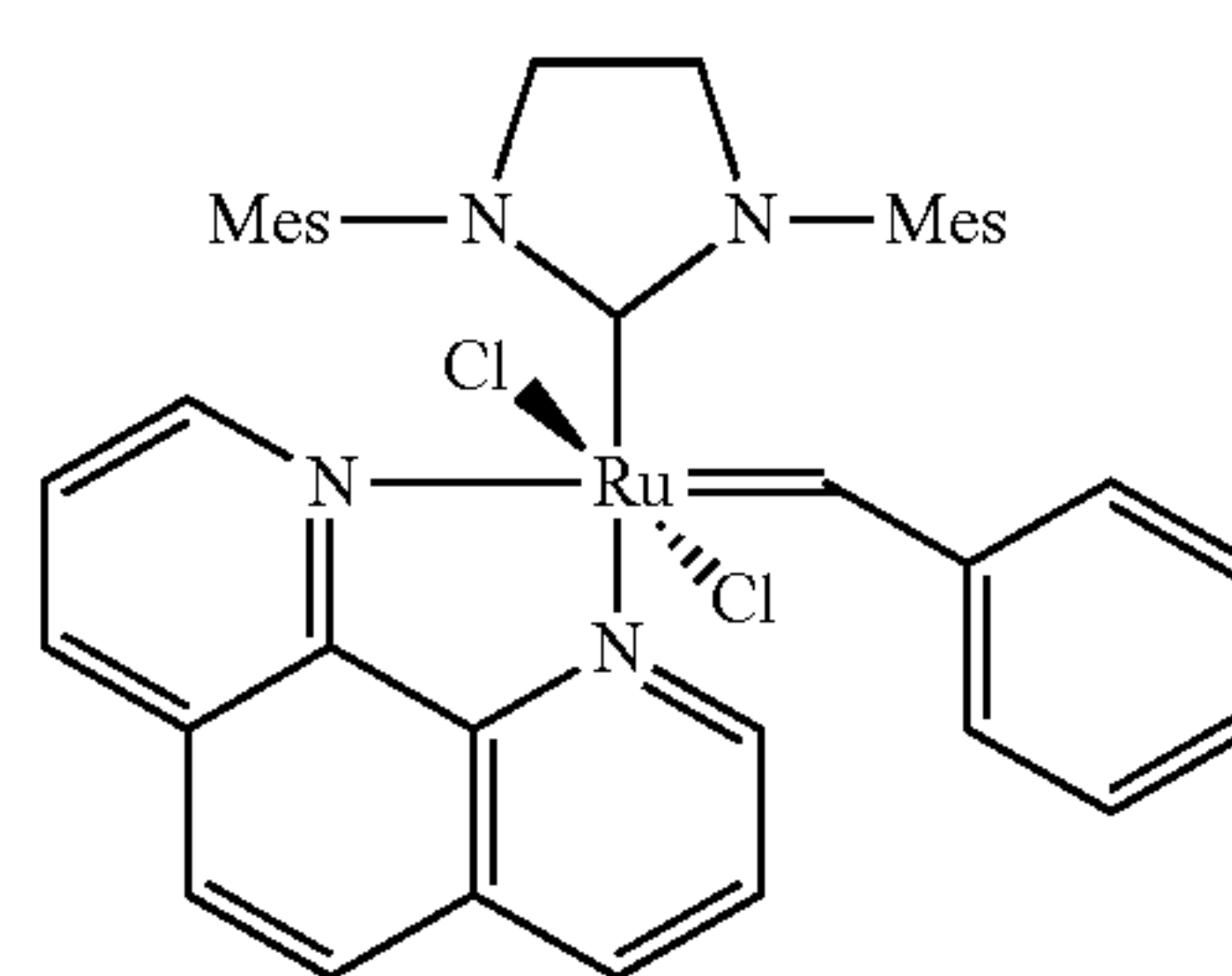
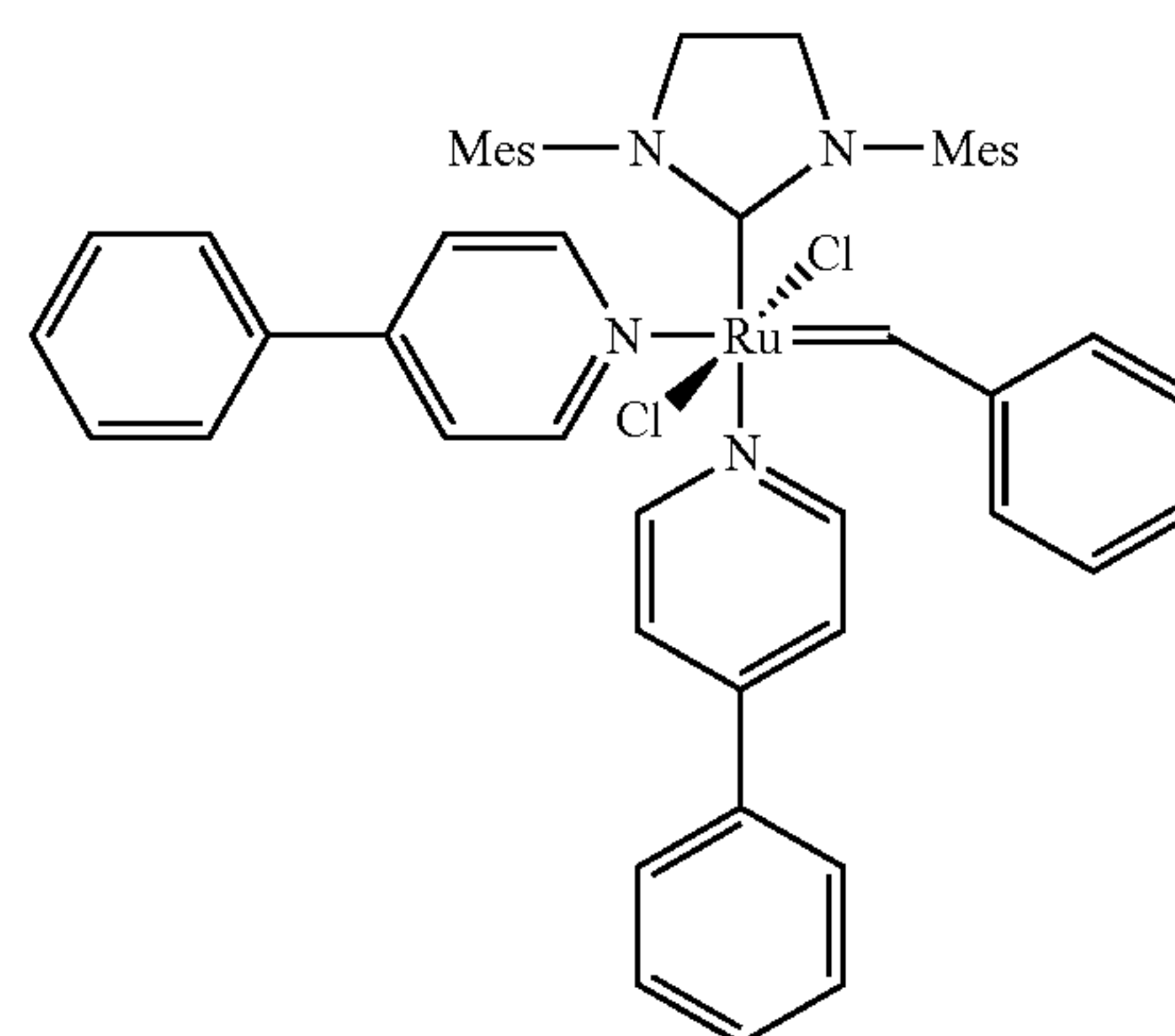
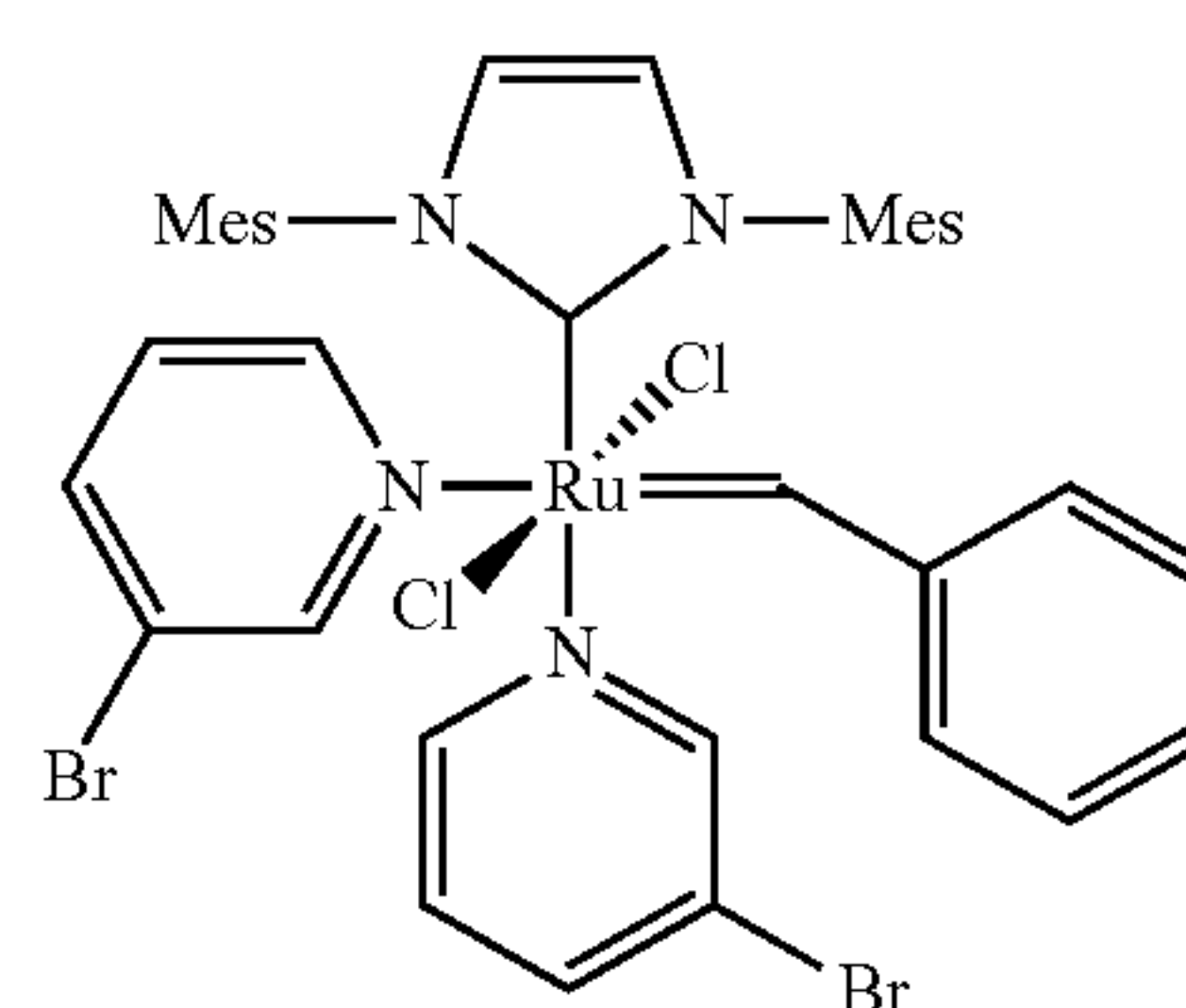
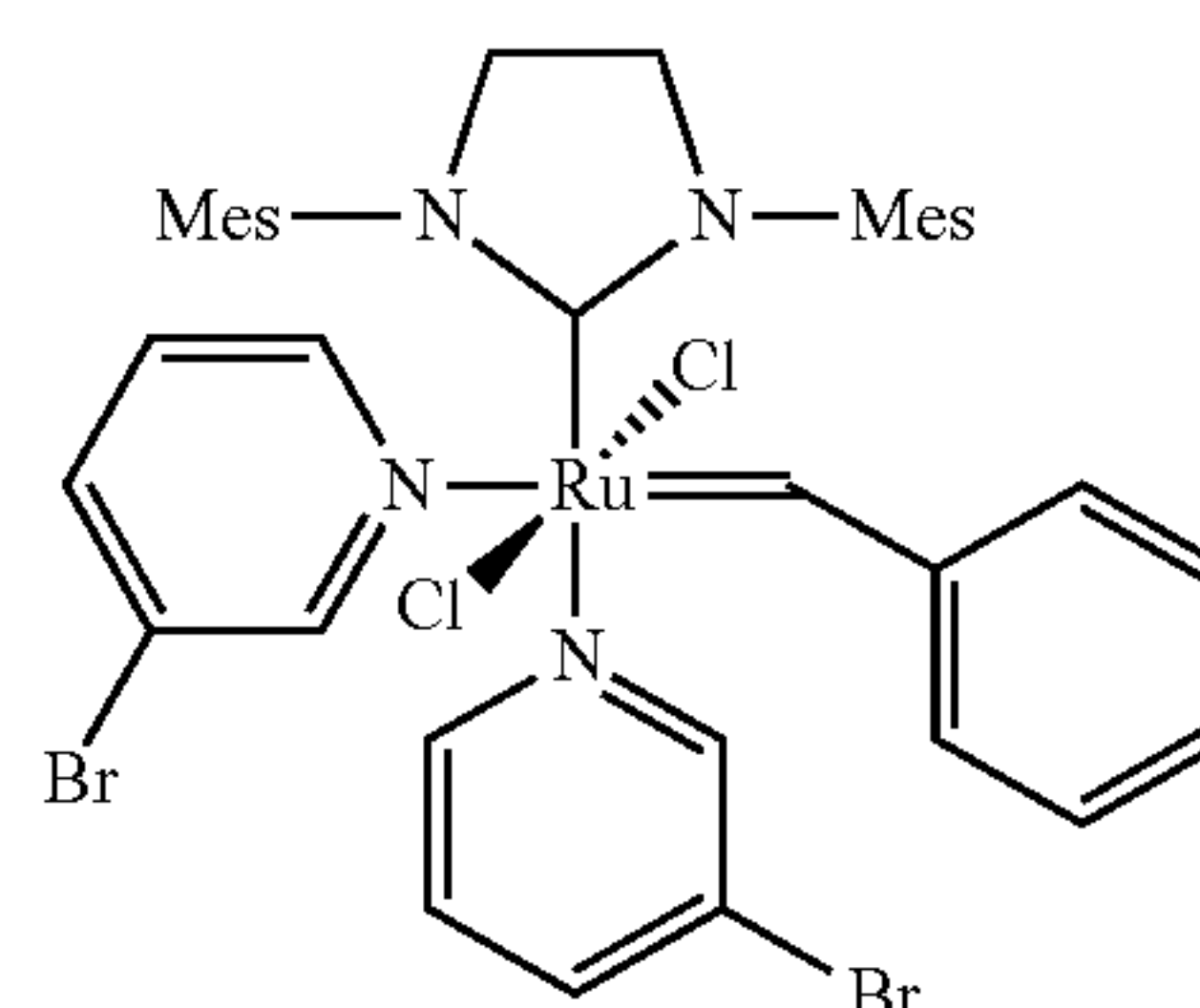


[0280] When R^{23} and R^{24} are each bromine in formula (XIXa), the catalyst is referred to in the literature as the “Grubbs III catalyst”.

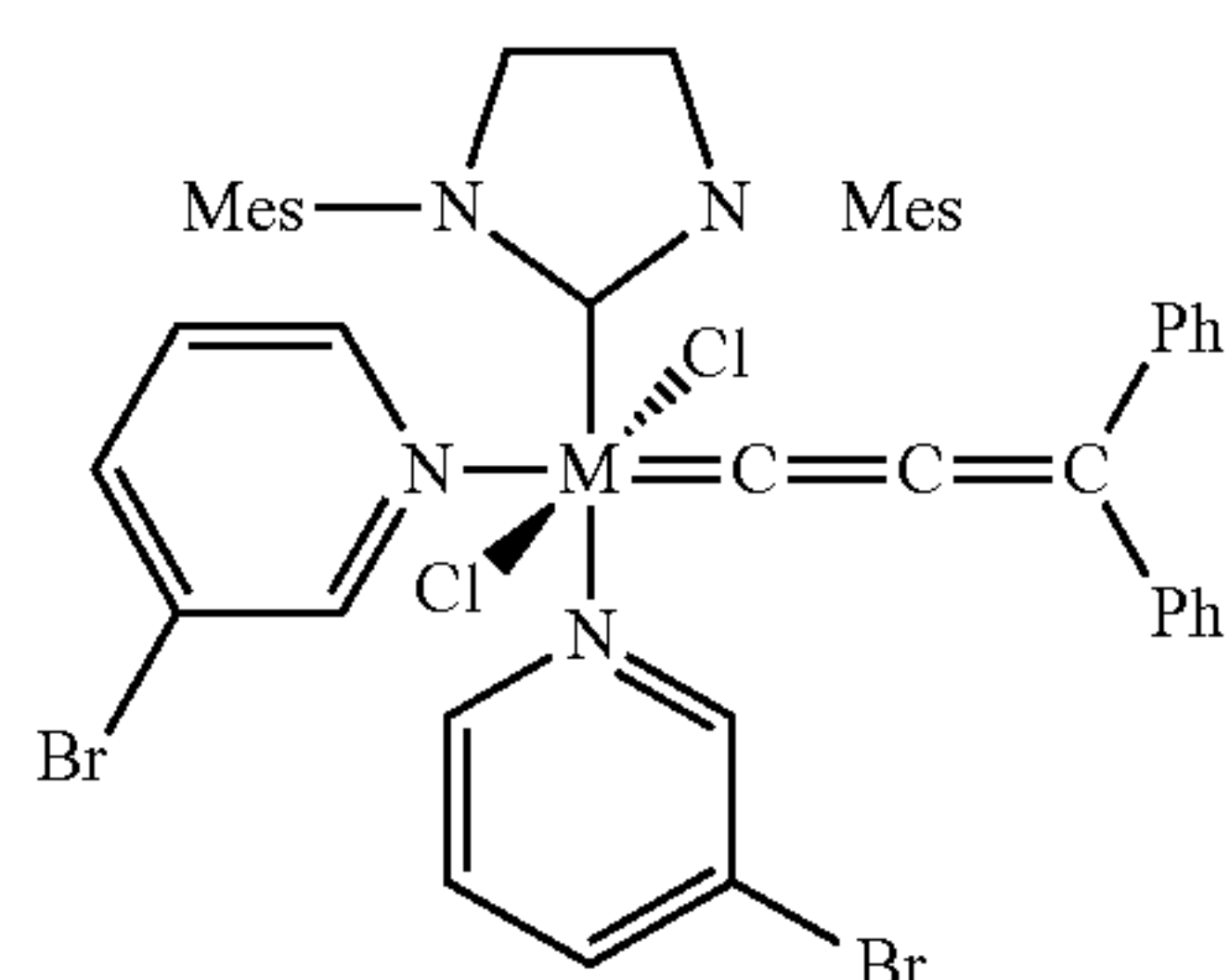
[0281] Further suitable catalysts which come under general formulae (E), (F), and (G) have the structural formulae (XX)-(XXXII), where Mes is in each case 2,4,6-trimethylphenyl.



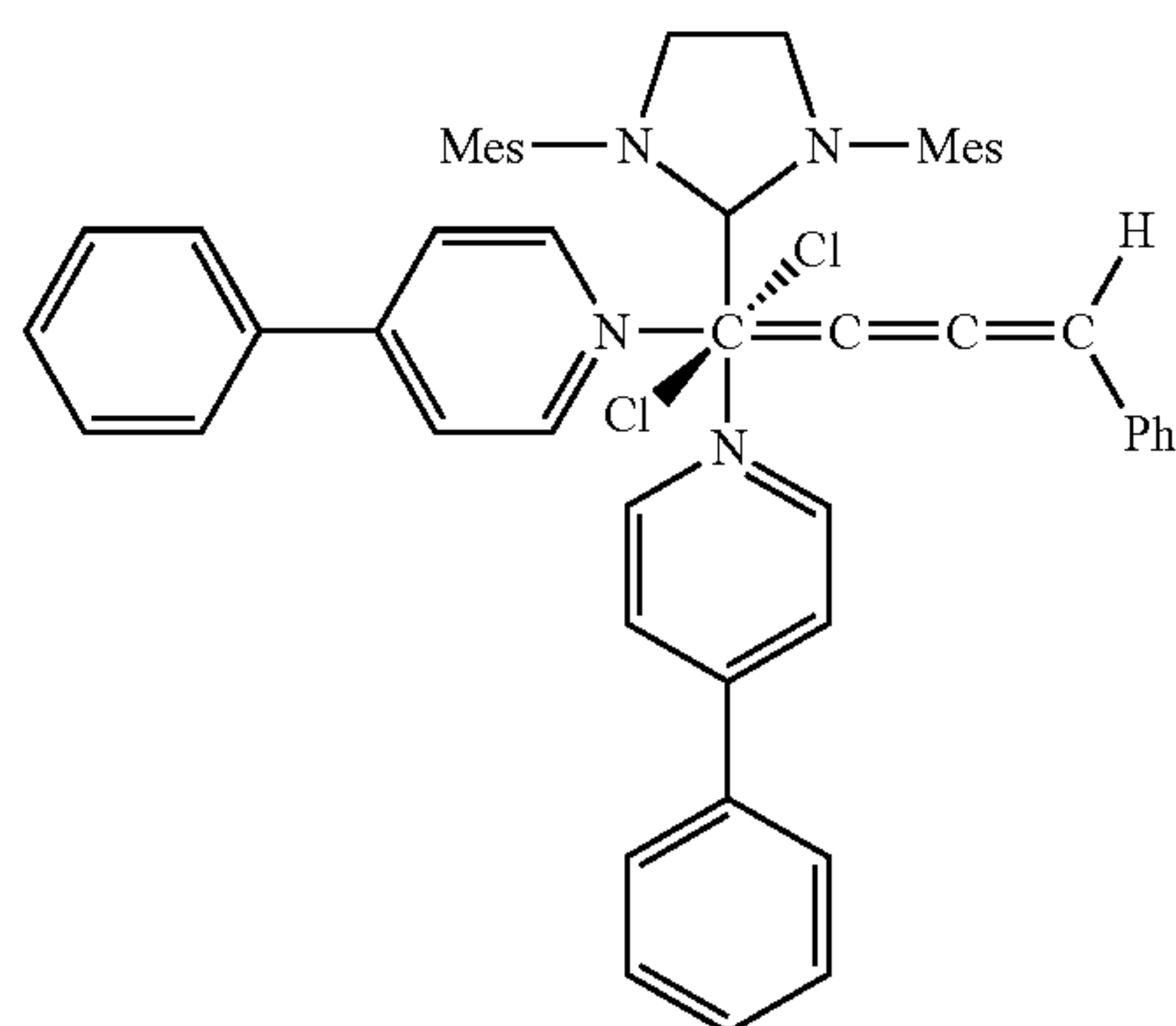
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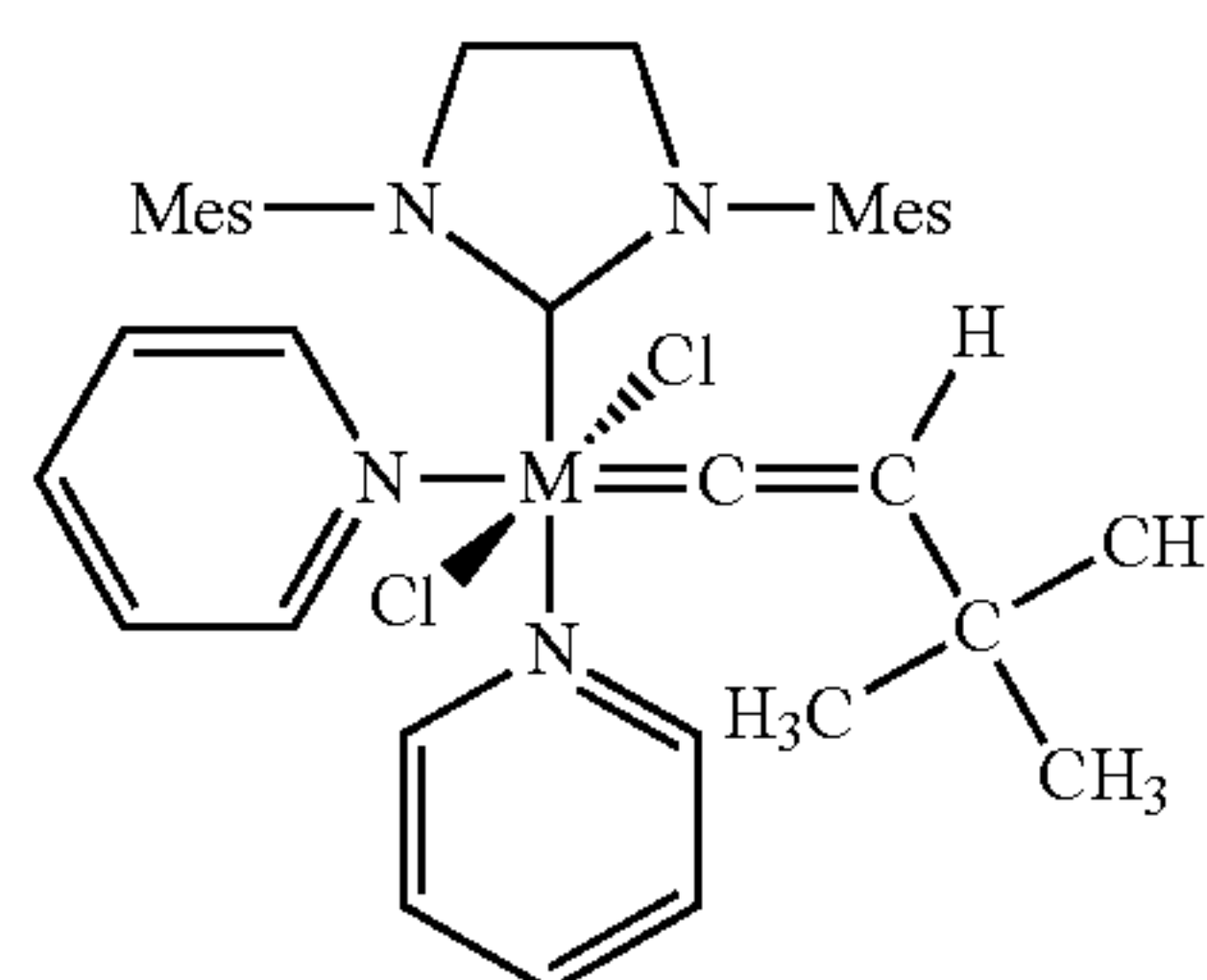
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(XXX)

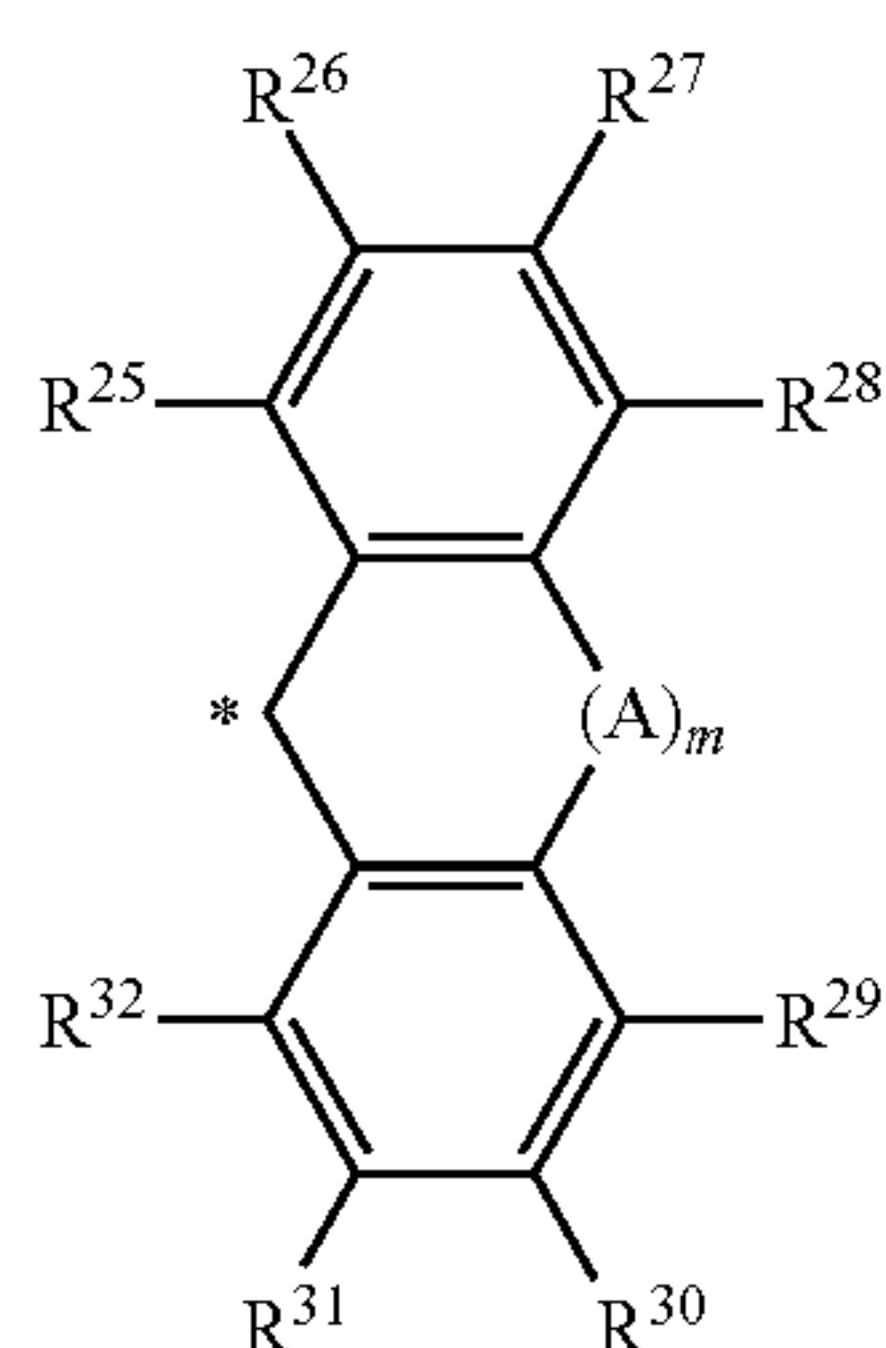


(XXXI)



(XXXII)

[0282] A further embodiment relates to a catalyst system according to the invention obtainable by using a catalyst (N) which has the general structural element (N1), where the carbon atom denoted by “*” is bound via one or more double bonds to the catalyst framework with a ruthenium or osmium central metal,



(N1)

carbamate, thiocarbamate, dithiocarbamate, amino, amido, imino, silyl, sulphonate ($-\text{SO}_3$), $-\text{OSO}_3^-$, $-\text{PO}_3^-$ or OPO_3^- or alkyl, cycloalkyl, alkenyl, alkynyl, aryl, carboxylate, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxycarbonyl, alkylamino, alkylthio, arylthio, alkylsulphonyl, alkylsulphiny, dialkylamino, alkylsilyl or alkoxysilyl, where all these moieties can each optionally be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl substituents, or, as an alternative, two directly adjacent substituents from the group consisting of R^{25} - R^{32} together with the ring carbons to which they are bound form a cyclic group, preferably an aromatic system, by bridging or, as an alternative, R^8 is optionally bridged to another ligand of the ruthenium- or osmium-carbene complex catalyst,

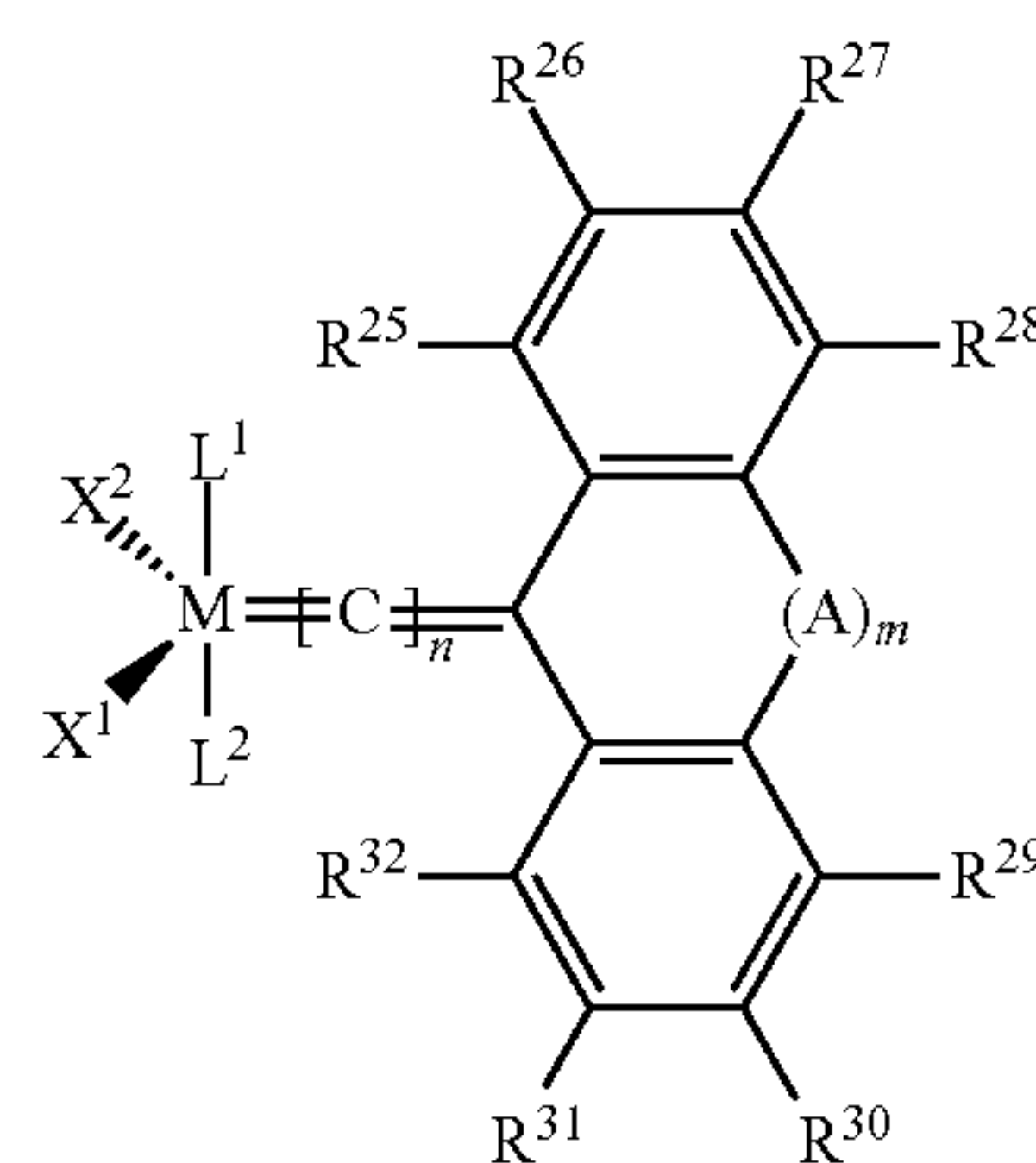
[0284] m is 0 or 1 and

[0285] A is oxygen, sulphur, $\text{C}(\text{R}^{33}\text{R}^{34})$, $\text{N}-\text{R}^{35}$, $-\text{C}(\text{R}^{36})=\text{C}(\text{R}^{37})-$, $-\text{C}(\text{R}^{36})(\text{R}^{38})-\text{C}(\text{R}^{37})(\text{R}^{39})-$, where R^{33} - R^{39} are identical or different and can each have the same meanings as R^{25} - R^{32} .

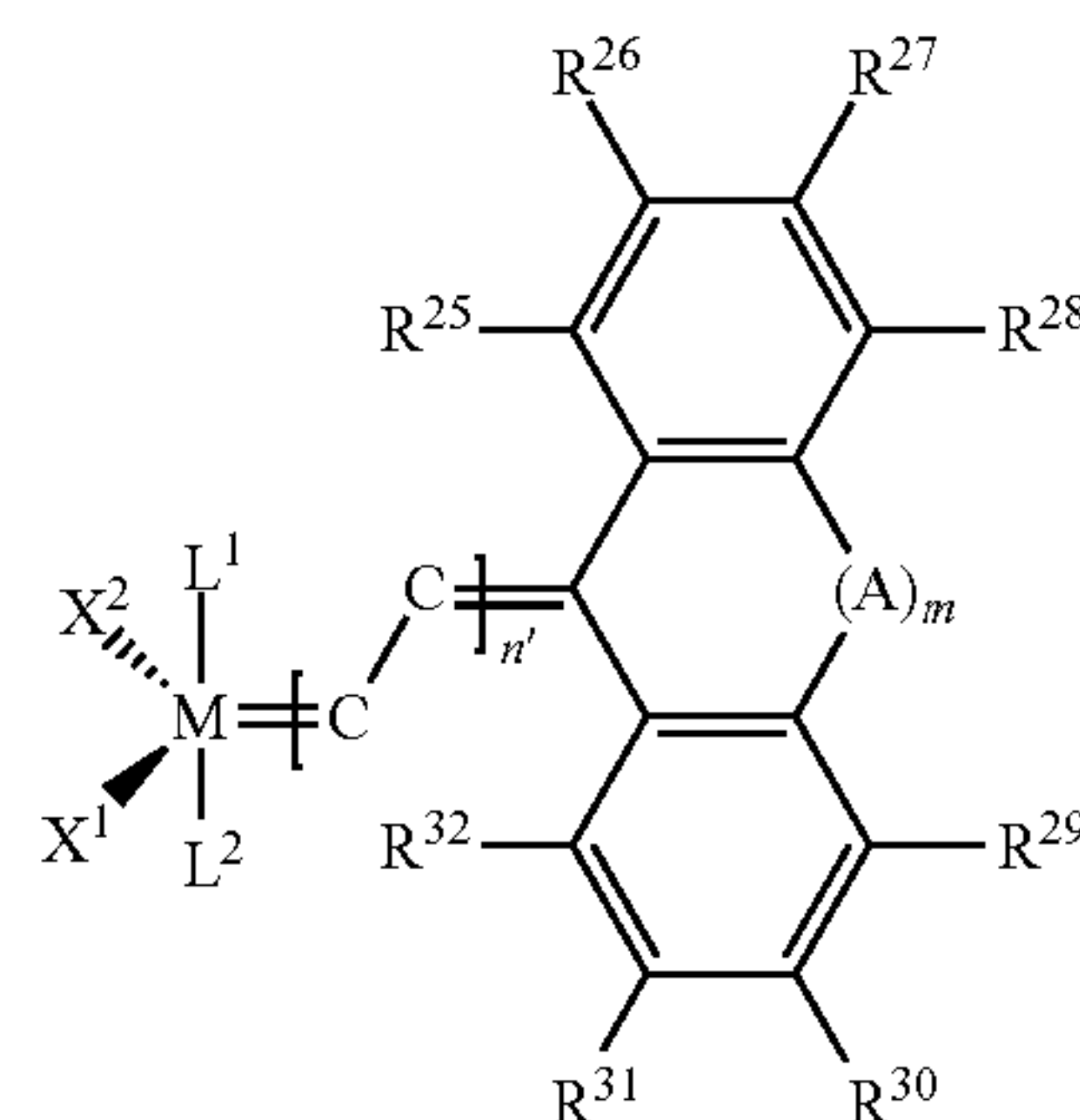
[0286] In the catalysts having the structural element of the general formula (N1) the carbon atom denoted by “*” is bound via one or more double bonds to the catalyst framework. If the carbon atom denoted by “*” is bound via two or more double bonds to the catalyst framework, these double bonds can be cumulated or conjugated.

[0287] Such catalysts (N) have been described in US-A-2009/0076226, which also discloses their preparation.

[0288] The catalysts (N) having a structural element of the general formula (N1) include, for example, catalysts of the general formulae (N2a) and (N2b) below,



(N2a)



(N2b)

and where

[0283] R^{25} - R^{32} are identical or different and are each hydrogen, halogen, hydroxyl, aldehyde, keto, thiol, CF_3 , nitro, nitroso, cyano, thiocyno, isocyanato, carbodiimide,

where

[0289] M is ruthenium or osmium,

[0290] X^1 and X^2 are identical or different and are two ligands, preferably anionic ligands,

[0291] L^1 and L^2 are identical or different ligands, preferably uncharged electron donors, where L^2 can alternatively also be bridged to the radical R^8 ,

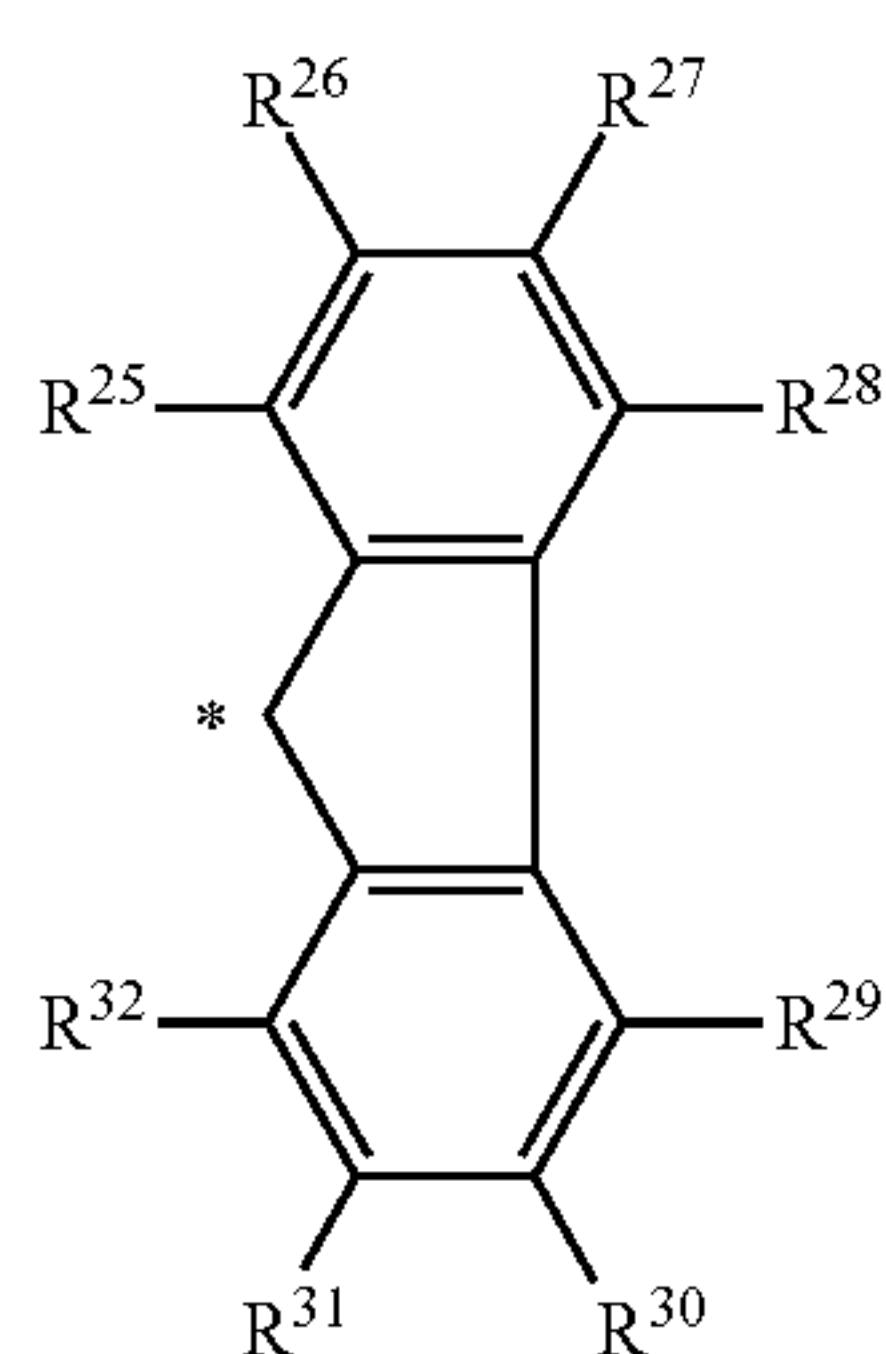
[0292] n is 0, 1, 2 or 3, preferably 0, 1 or 2,

[0293] n' is 1 or 2, preferably 1, and

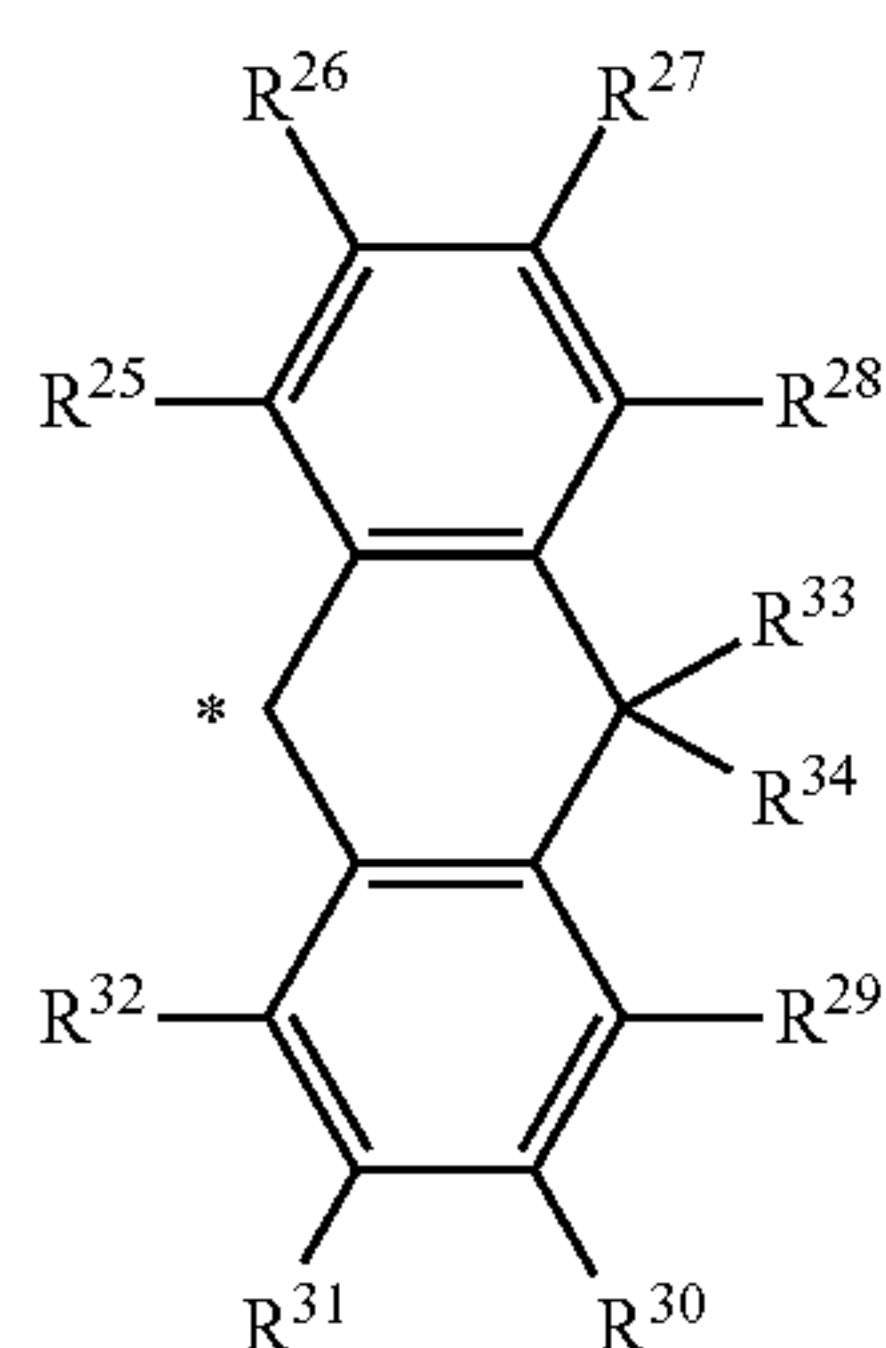
[0294] R^{25} - R^{32} , m and A have the same meanings as in the general formula (N1).

[0295] In the catalysts of the general formula (N2a), the structural element of the general formula (N1) is bound via a double bond ($n=0$) or via 2, 3 or 4 cumulated double bonds (in the case of $n=1, 2$ or 3) to the central metal of the complex catalyst. In the catalysts of the general formula (N2b) suitable to be used for the catalyst systems according to the invention, the structural element of the general formula (N1) is bound via conjugated double bonds to the metal of the complex catalyst. In both cases, the carbon atom denoted by “*” as a double bond in the direction of the central metal of the complex catalyst.

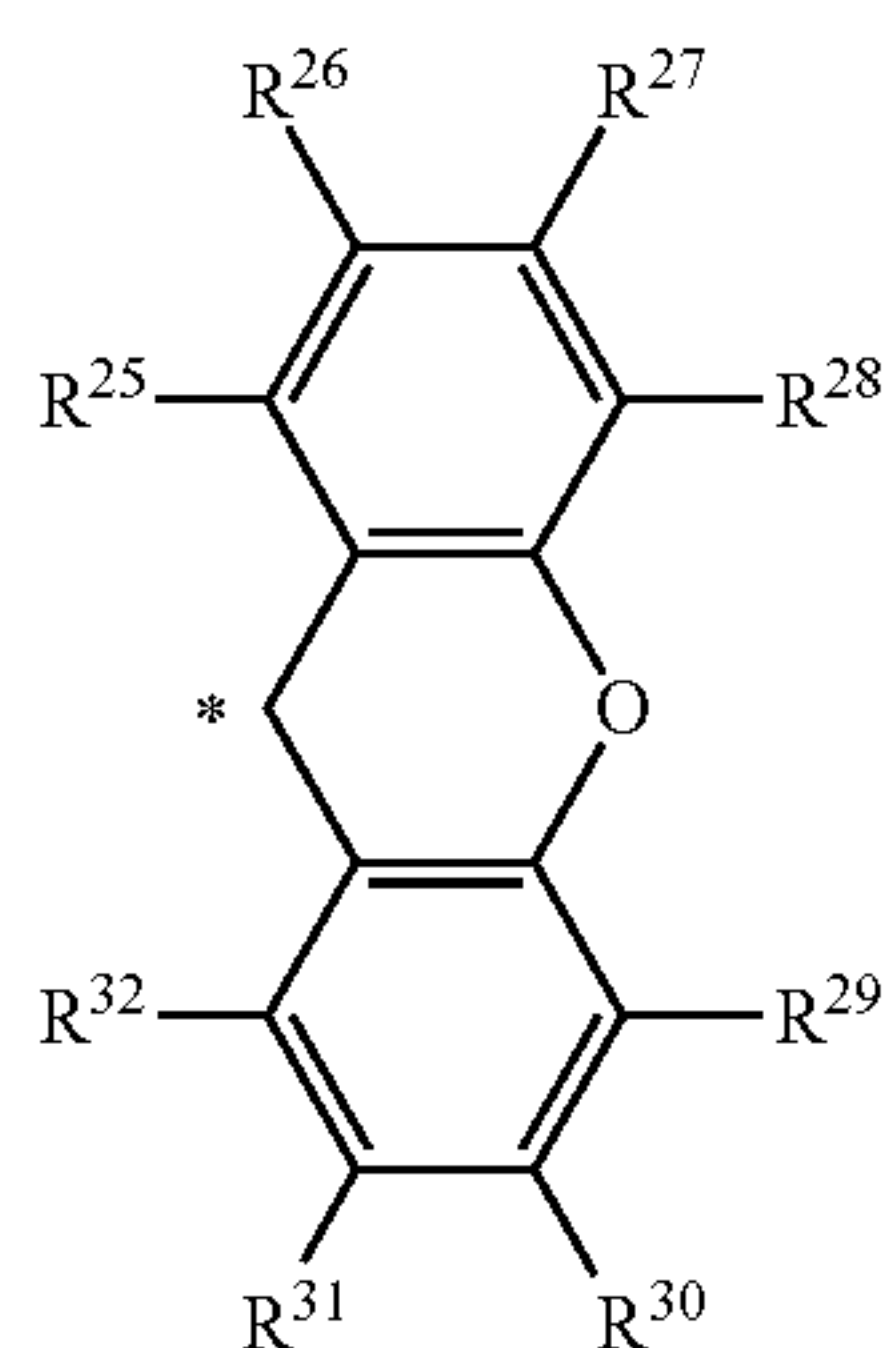
[0296] The catalysts of the general formulae (N2a) and (N2b) thus encompass catalysts in which the general structural elements (N3)-(N9)



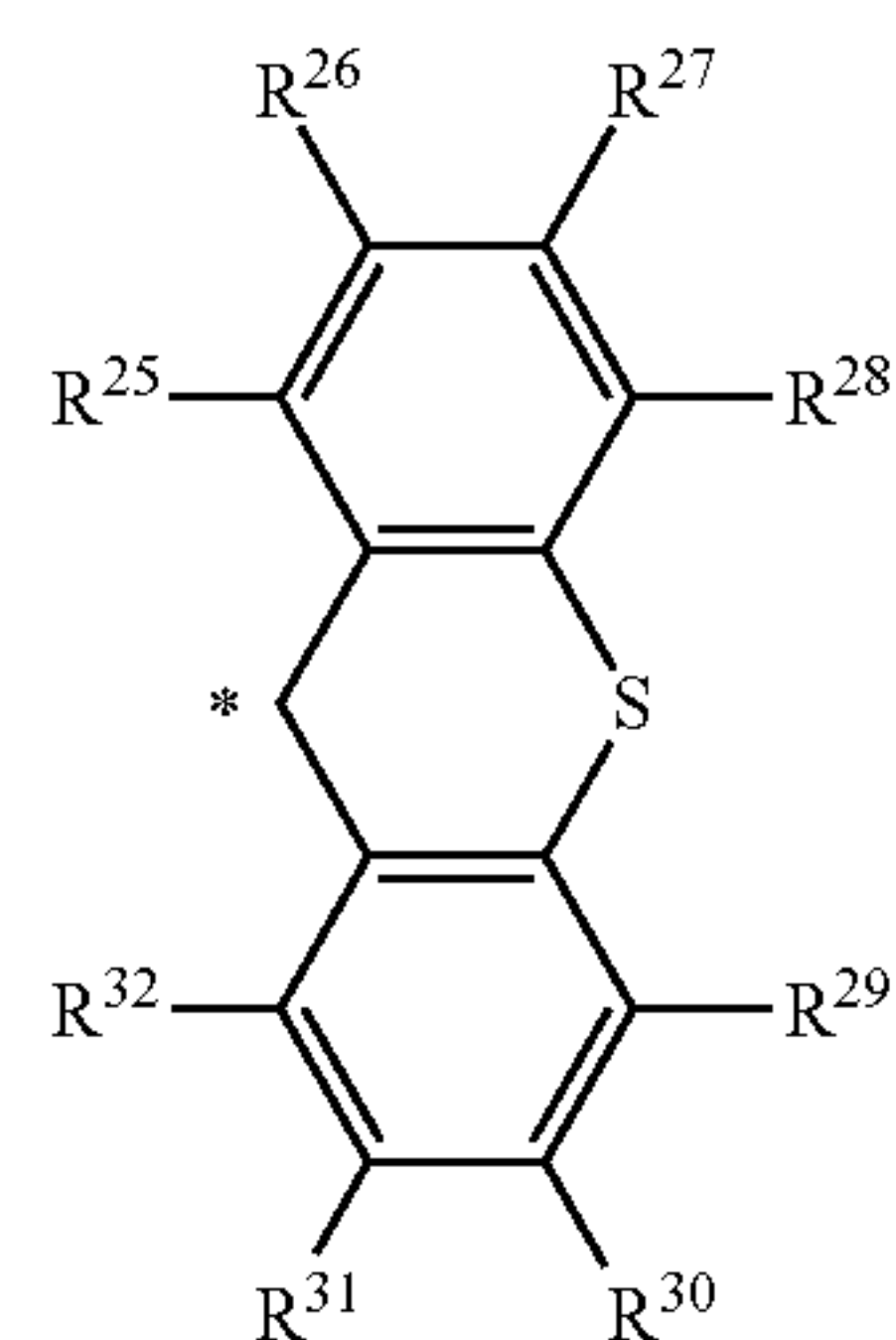
(N3)



(N4)

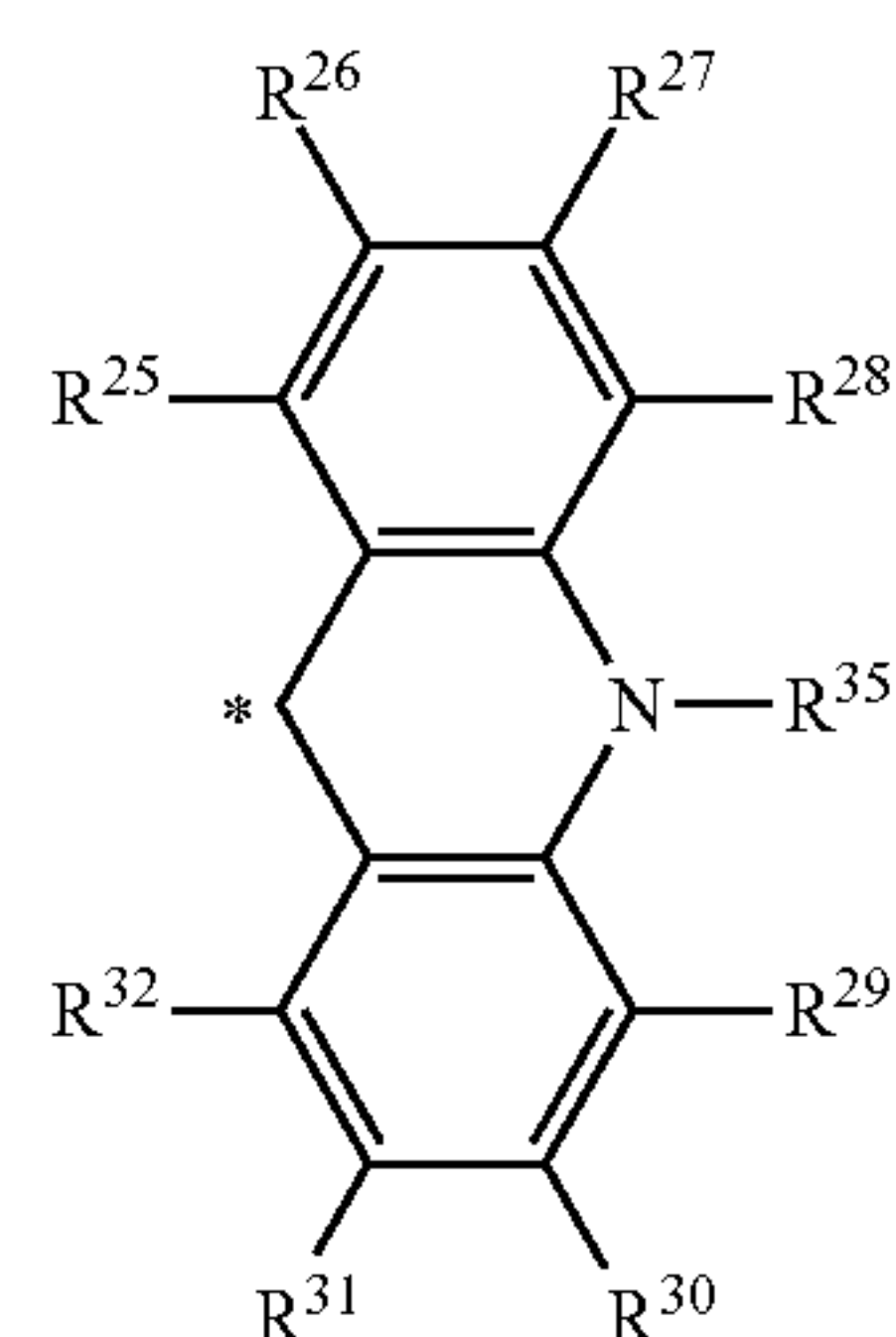


(N5)

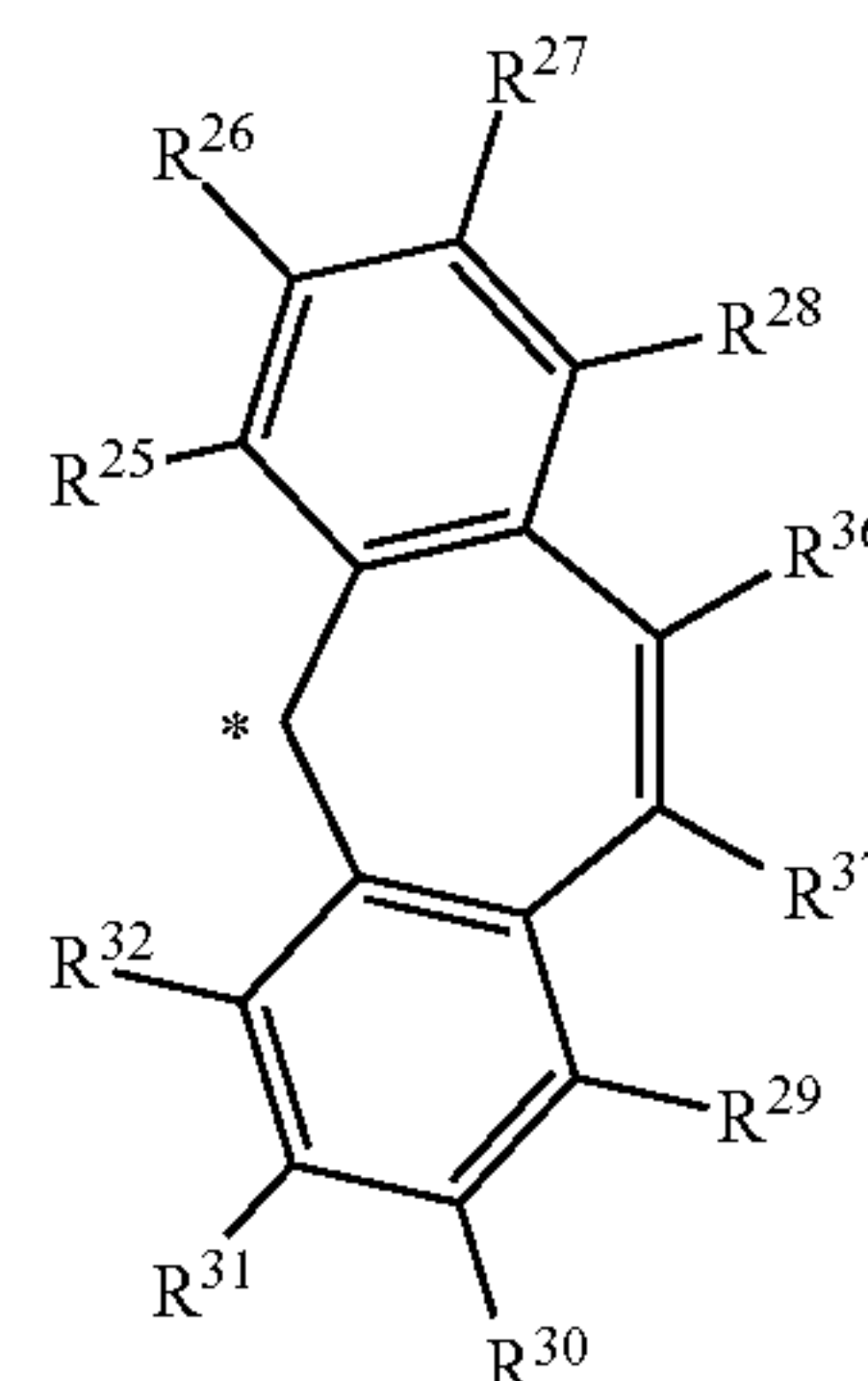


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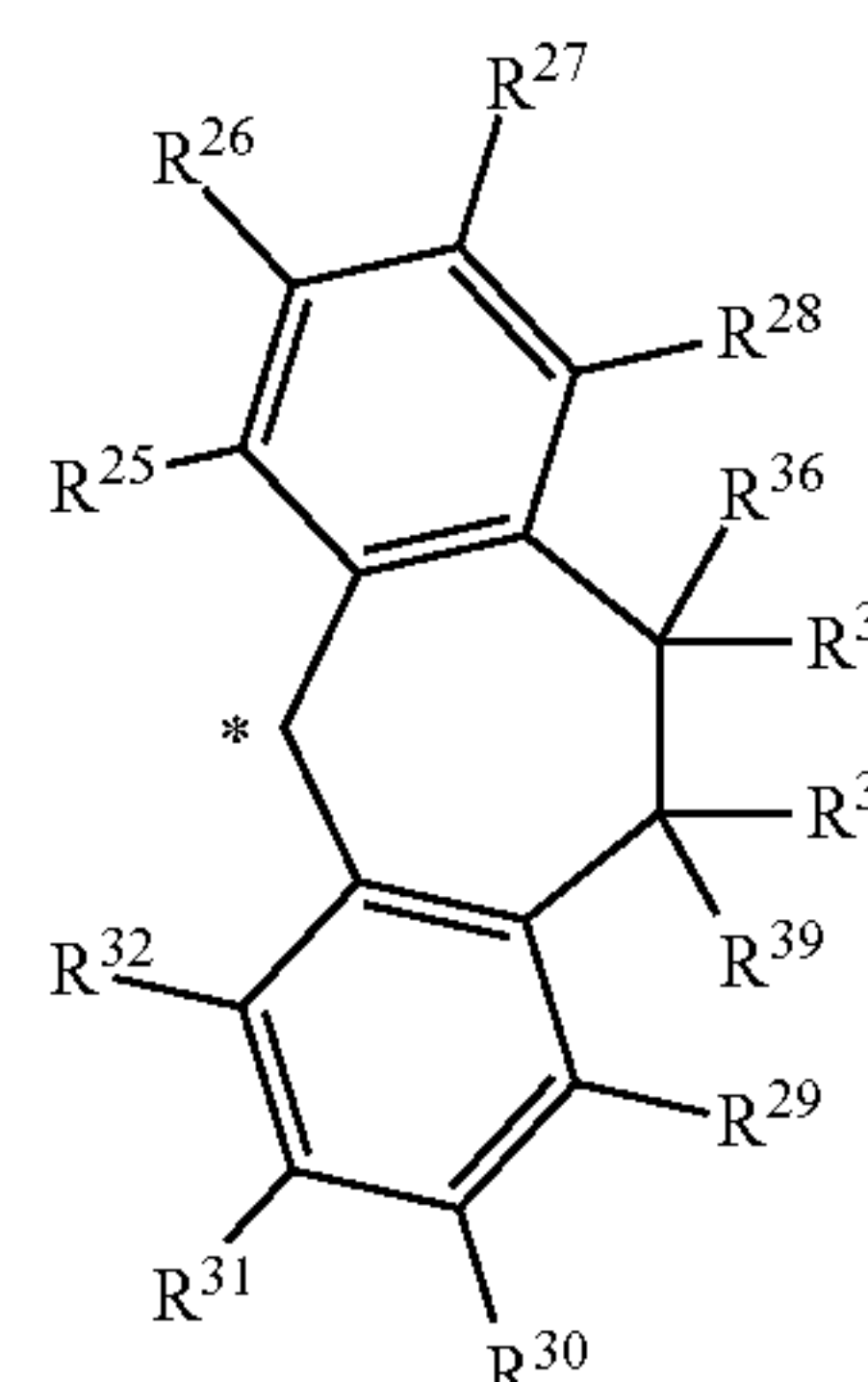
(N6)



(N7)

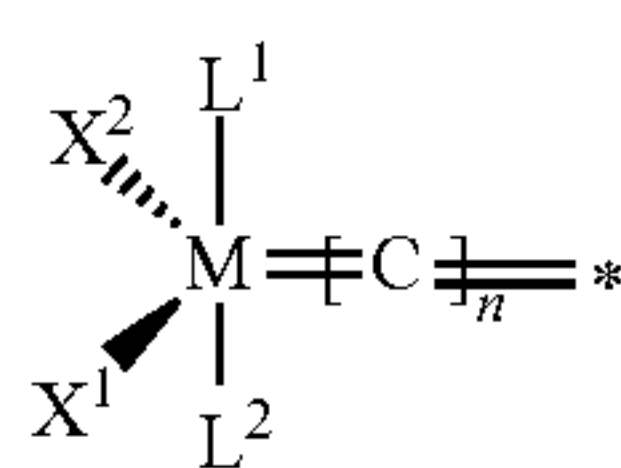


(N8)

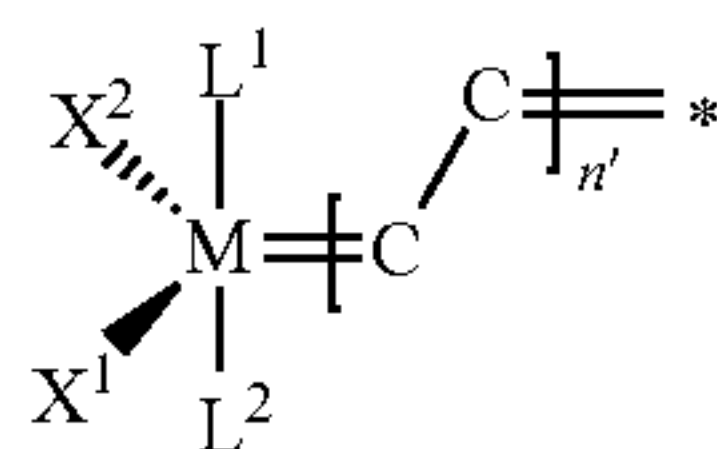


(N9)

are bound via the carbon atom denoted by “*” via one or more double bonds to the catalyst framework of the general formula (N10a) or (N10b)



(N10a)



(N10b)

where X^1 and X^2 , L^1 and L^2 , n , n' and R^{25} - R^{39} have the meanings given for the general formulae (N2a) and (N2b).

[0297] The Ru- or Os-based carbene catalysts resulting thereof typically have five-fold coordination.

[0298] In the structural element of the general formula (N1),

[0299] R^{25} - R^{32} are identical or different and are each hydrogen, halogen, hydroxyl, aldehyde, keto, thiol, CF_3 , nitro, nitroso, cyano, thiocyno, isocyanato, carbodiimide, carbamate, thiocarbamate, dithiocarbamate, amino, amido, imino, silyl, sulphonate ($-SO_3^-$), $-OSO_3^-$, $-PO_3^-$ or OPO_3^- or alkyl, preferably C_1 - C_{20} -alkyl, in particular C_1 - C_6 -alkyl, cycloalkyl, preferably C_3 - C_{20} -cycloalkyl, in particular C_3 - C_8 -cycloalkyl, alkenyl, preferably C_2 - C_{20} -alkenyl, alkynyl, preferably C_2 - C_{20} -alkynyl, aryl, preferably C_6 - C_{24} -aryl, in particular phenyl, carboxylate, preferably C_1 - C_{20} -carboxylate, alkoxy, preferably C_1 - C_{20} -alkoxy, alkenyloxy, preferably C_2 - C_{20} -alkenyloxy, alkynyloxy, preferably C_2 - C_{20} -alkynyloxy, aryloxy, preferably C_6 - C_{24} -aryloxy, alkoxycarbonyl, preferably C_2 - C_{20} -alkoxycarbonyl, alkylamino, preferably C_1 - C_{30} -alkylamino, alkylthio, preferably C_1 - C_{30} -alkylthio, arylthio, preferably C_6 - C_{24} -arylthio, alkylsulphonyl, preferably C_1 - C_{20} -alkylsulphonyl, alkylsulphinyl, preferably C_1 - C_{20} -alkylsulphinyl, dialkylamino, preferably di(C_1 - C_{20} -alkyl)amino, alkylsilyl, preferably C_1 - C_{20} -alkylsilyl, or alkoxysilyl, preferably C_1 - C_{20} -alkoxysilyl, where these moieties can each be optionally substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl substituents, or, as an alternative, in each case two directly adjacent substituents from the group consisting of R^{25} - R^{32} together with the ring carbons to which they are bound may also form a cyclic group, preferably an aromatic system, by bridging or, as an alternative, R^8 is optionally bridged to another ligand of the ruthenium- or osmium-carbene complex catalyst,

[0300] m is 0 or 1 and

[0301] A is oxygen, sulphur, $C(R^{33})(R^{34})$, $N-R^{35}$, $-C(R^{36})=C(R^{37})-$ or $-C(R^{36})(R^{38})-C(R^{37})(R^{39})-$, where R^{33} - R^{39} are identical or different and can each have the same preferred meanings as the radicals R^1 - R^8 .

[0302] C_1 - C_6 -Alkyl in the structural element of the general formula (N1) is, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, neopentyl, 1-ethylpropyl or n-hexyl.

[0303] C_3 - C_8 -Cycloalkyl in the structural element of the general formula (N1) is, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl.

[0304] C_6 - C_{24} -Aryl in the structural element of the general formula (N1) comprises an aromatic radical having from 6 to 24 skeletal carbon atoms. As preferred monocyclic, bicyclic

or tricyclic carbocyclic aromatic radicals having from 6 to 10 skeletal carbon atoms, mention may be made by way of example of phenyl, biphenyl, naphthyl, phenanthrenyl or anthracenyl.

[0305] X^1 and X^2 in the structural element of the general formula (N1) have the same general, preferred and particularly preferred meanings indicated for catalysts of the general formula A.

[0306] In the general formulae (N2a) and (N2b) and analogously in the general formulae (N10a) and (N10b), L^1 and L^2 are identical or different ligands, preferably uncharged electron donors, and can have the same general, preferred and particularly preferred meanings indicated for catalysts of the general formula (A).

[0307] Preference is given to catalysts of the general formulae (N2a) or (N2b) having a general structural unit (N1) in which

[0308] M is ruthenium,

[0309] X^1 and X^2 are both halogen,

[0310] n is 0, 1 or 2 in the general formula (N2a) or

[0311] n' is 1 in the general formula (N2b)

[0312] L^1 and L^2 are identical or different and have the general or preferred meanings indicated for the general formulae (N2a) and (N2b),

[0313] R^{25} - R^{32} are identical or different and have the general or preferred meanings indicated for the general formulae (N2a) and (N2b),

[0314] m is either 0 or 1,

[0315] and, when $m=1$,

[0316] A is oxygen, sulphur, $C(C_1-C_{10}\text{-alkyl})_2$, $-C(C_1-C_{10}\text{-alkyl})_2-C(C_1-C_{10}\text{-alkyl})_2-$, $-C(C_1-C_{10}\text{-alkyl})=C(C_1-C_{10}\text{-alkyl})-$ or $-N(C_1-C_{10}\text{-alkyl})$.

[0317] Very particular preference is given to catalysts of the general formulae (N2a) or (N2b) having a general structural unit (N1) in which

[0318] M is ruthenium,

[0319] X^1 and X^2 are both chlorine,

[0320] n is 0, 1 or 2 in the general formula (N2a) or

[0321] n' is 1 in the general formula (N2b)

[0322] L^1 is an imidazoline or imidazolidine ligand of one of the formulae (IIIa) to (IIIu),

[0323] L^2 is a sulphonated phosphine, phosphate, phosphinite, phosphonite, arsine, stibine, ether, amine, amide, sulphoxide, carboxyl, nitrosyl, pyridine radical, an imidazolidine radical of one of the formulae (XIIa) to (XIIe) or a phosphine ligand, in particular PPh_3 , $P(p\text{-Tol})_3$, $P(o\text{-Tol})_3$, $PPh(CH_3)_2$, $P(CF_3)_3$, $P(p\text{-FC}_6\text{H}_4)_3$, $P(p\text{-CF}_3\text{C}_6\text{H}_4)_3$, $P(C_6\text{H}_4\text{-SO}_3\text{Na})_3$, $P(CH_2\text{C}_6\text{H}_4\text{-SO}_3\text{Na})_3$, $P(\text{isopropyl})_3$, $P(CHCH_3(CH_2CH_3))_3$, $P(\text{cyclopentyl})_3$, $P(\text{cyclohexyl})_3$, $P(\text{neopentyl})_3$ and $P(\text{neophenyl})_3$,

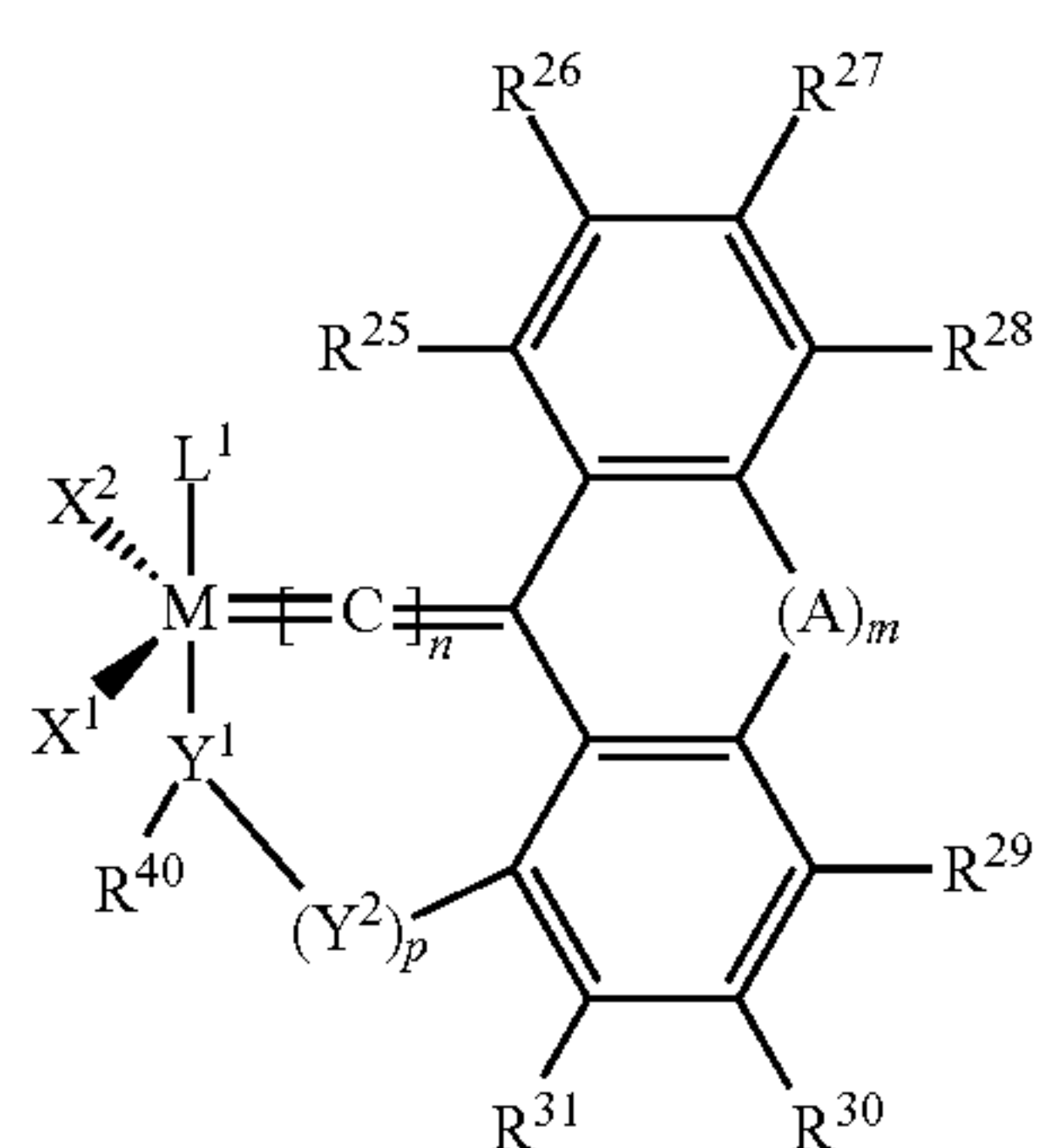
[0324] R^{25} - R^{32} have the general or preferred meanings indicated for the general formulae (N2a) and (N2b),

[0325] m is either 0 or 1

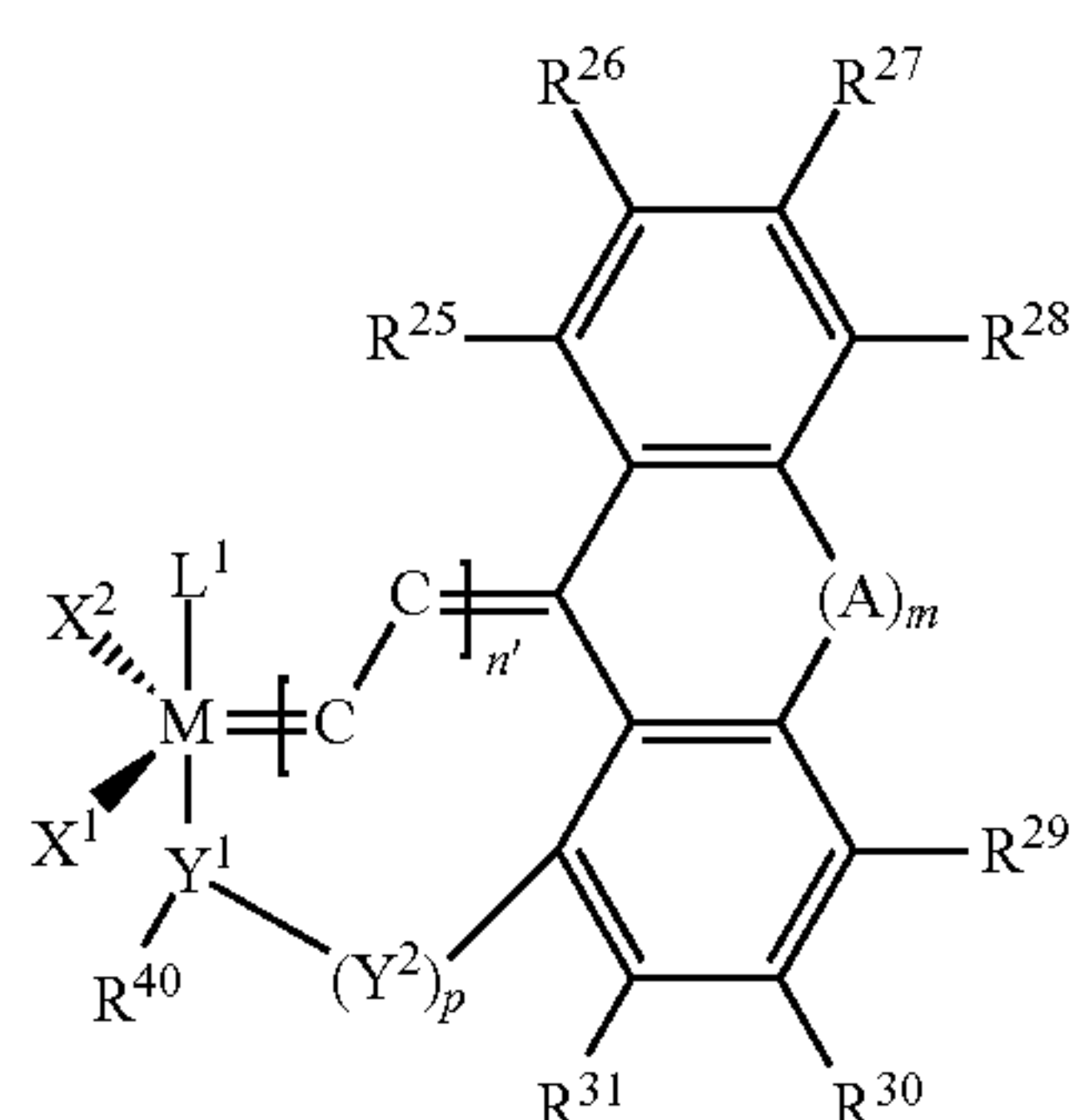
[0326] and, when $m=1$,

[0327] A is oxygen, sulphur, $C(C_1-C_{10}\text{-alkyl})_2$, $-C(C_1-C_{10}\text{-alkyl})_2-C(C_1-C_{10}\text{-alkyl})_2-$, $-C(C_1-C_{10}\text{-alkyl})=C(C_1-C_{10}\text{-alkyl})-$ or $-N(C_1-C_{10}\text{-alkyl})$.

[0328] When R^{25} is bridged to another ligand of the catalyst of the formula N, this results, for example for the catalysts of the general formulae (N2a) and (N2b), in the following structures of the general formulae (N13a) and (N13b)



(N13a)



(N13b)

where

[0329] Y^1 is oxygen, sulphur, $N-R^{41}$ or $P-R^{41}$, where R^{41} has the meanings indicated below,

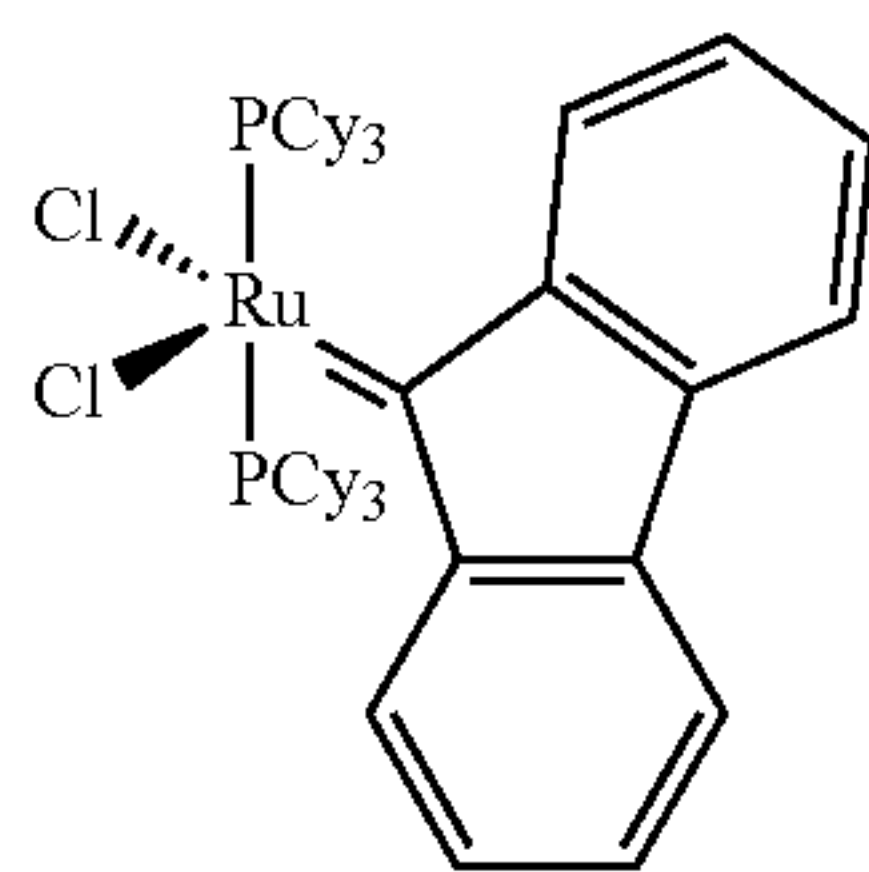
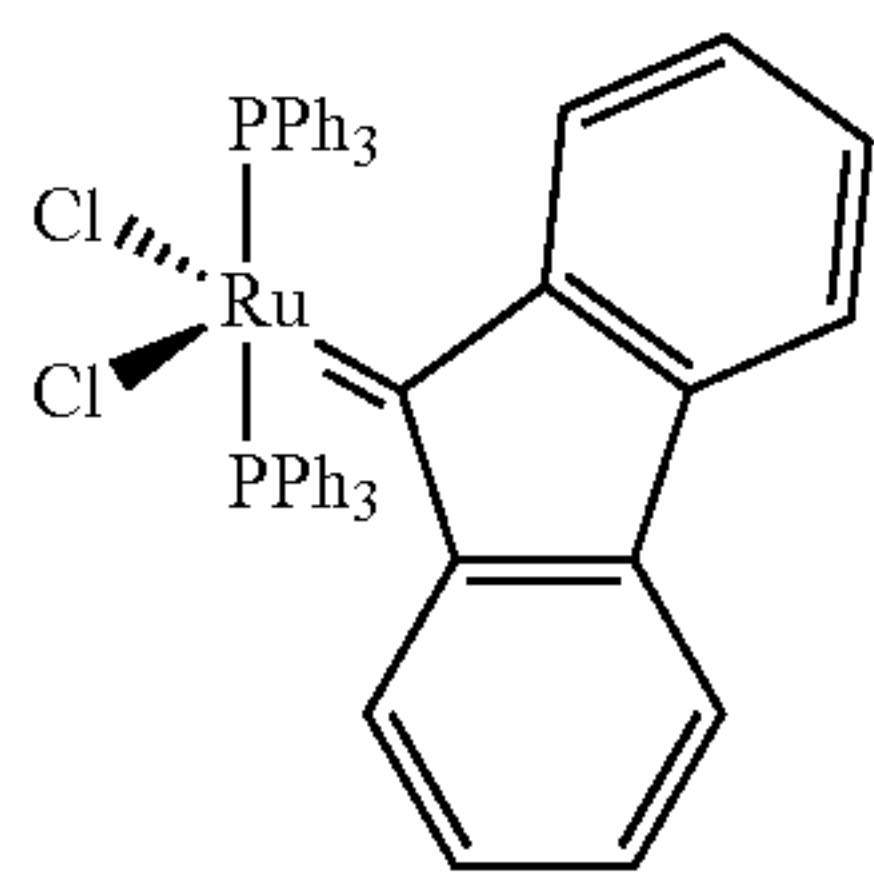
[0330] R^{40} and R^{41} are identical or different and are each alkyl, cycloalkyl, alkenyl, alkynyl, aryl, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxy carbonyl, alkylamino, alkylthio, arylthio, alkylsulphonyl or alkylsulphinyl which may each be optionally substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl substituents,

[0331] p is 0 or 1 and

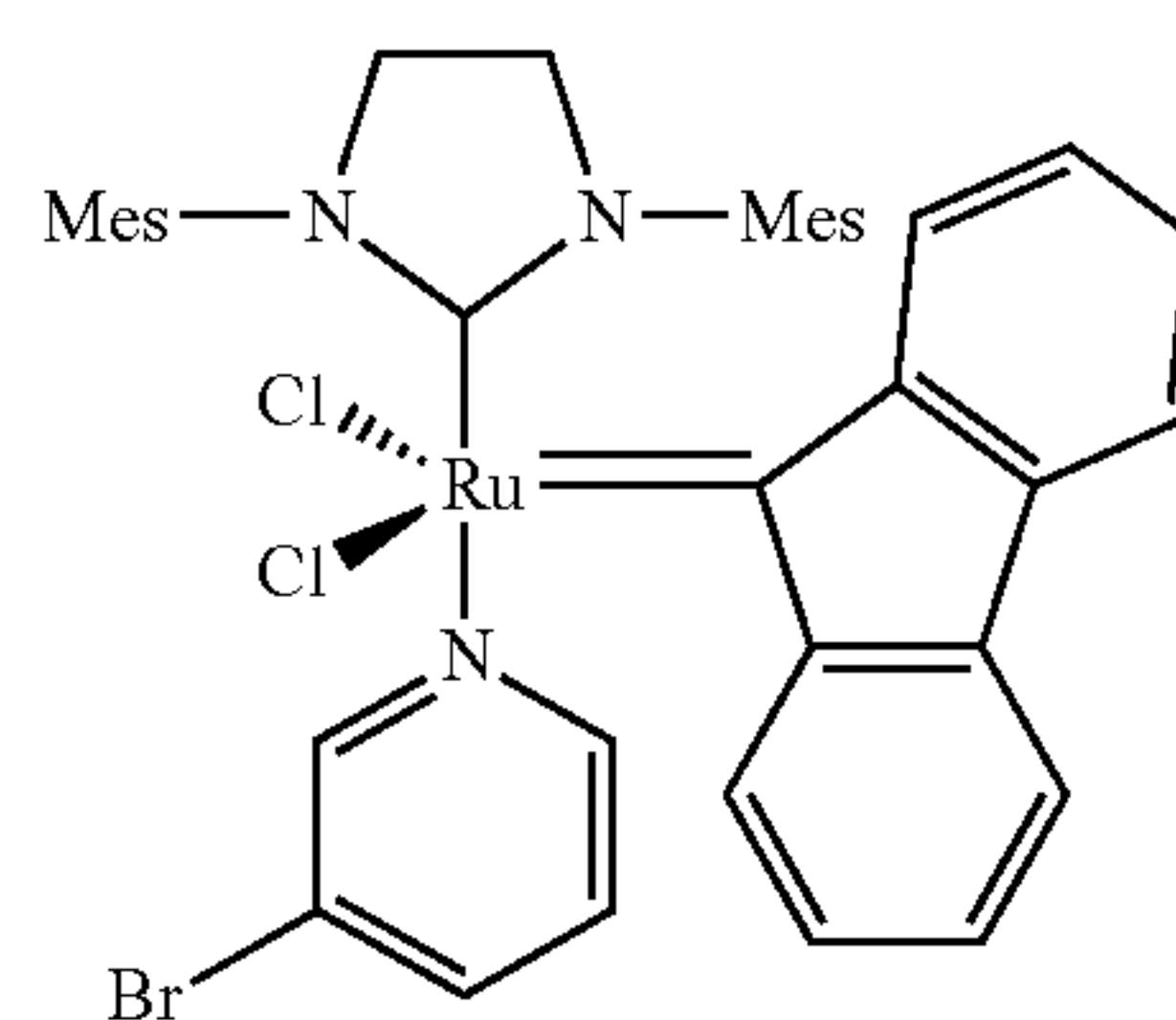
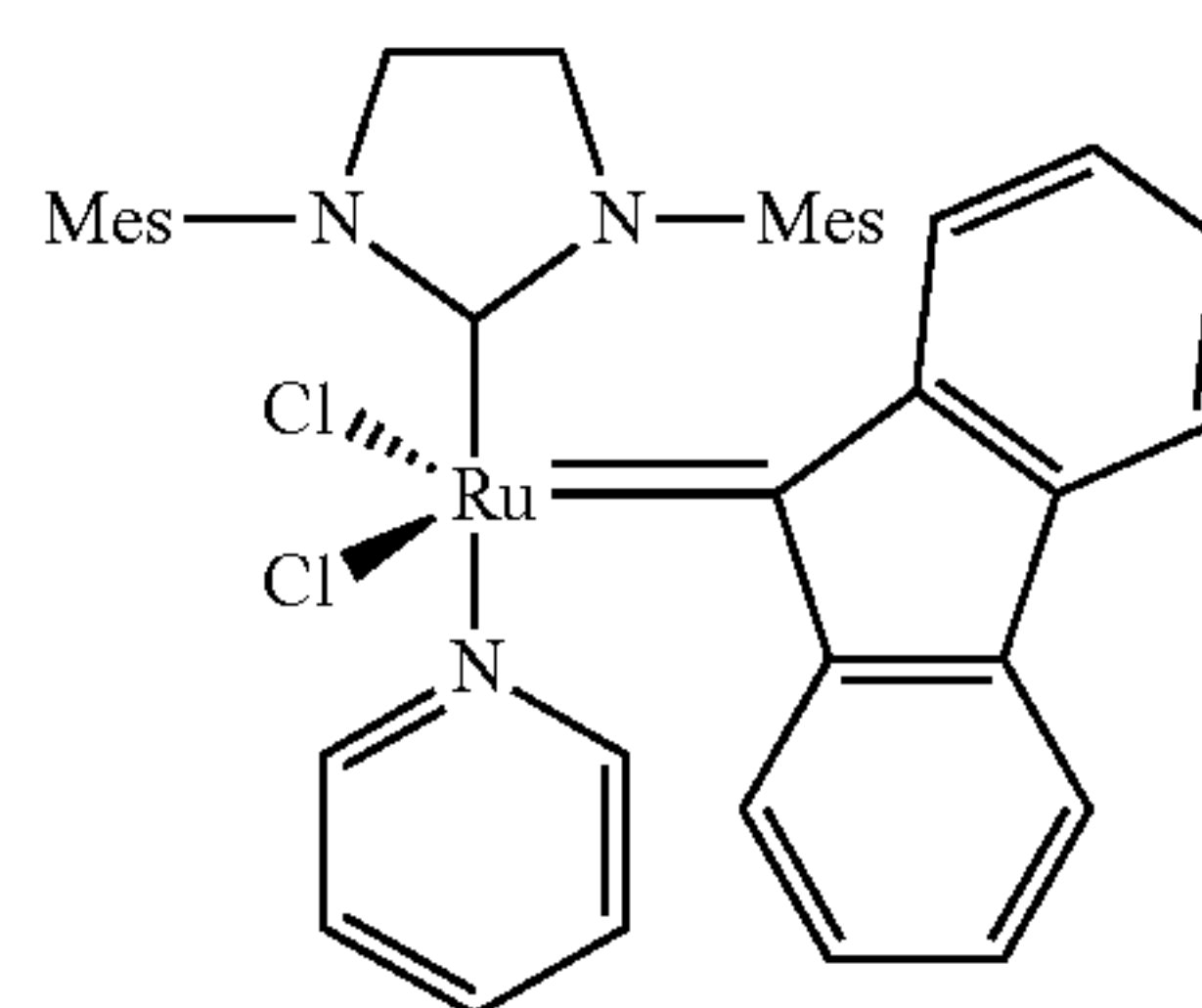
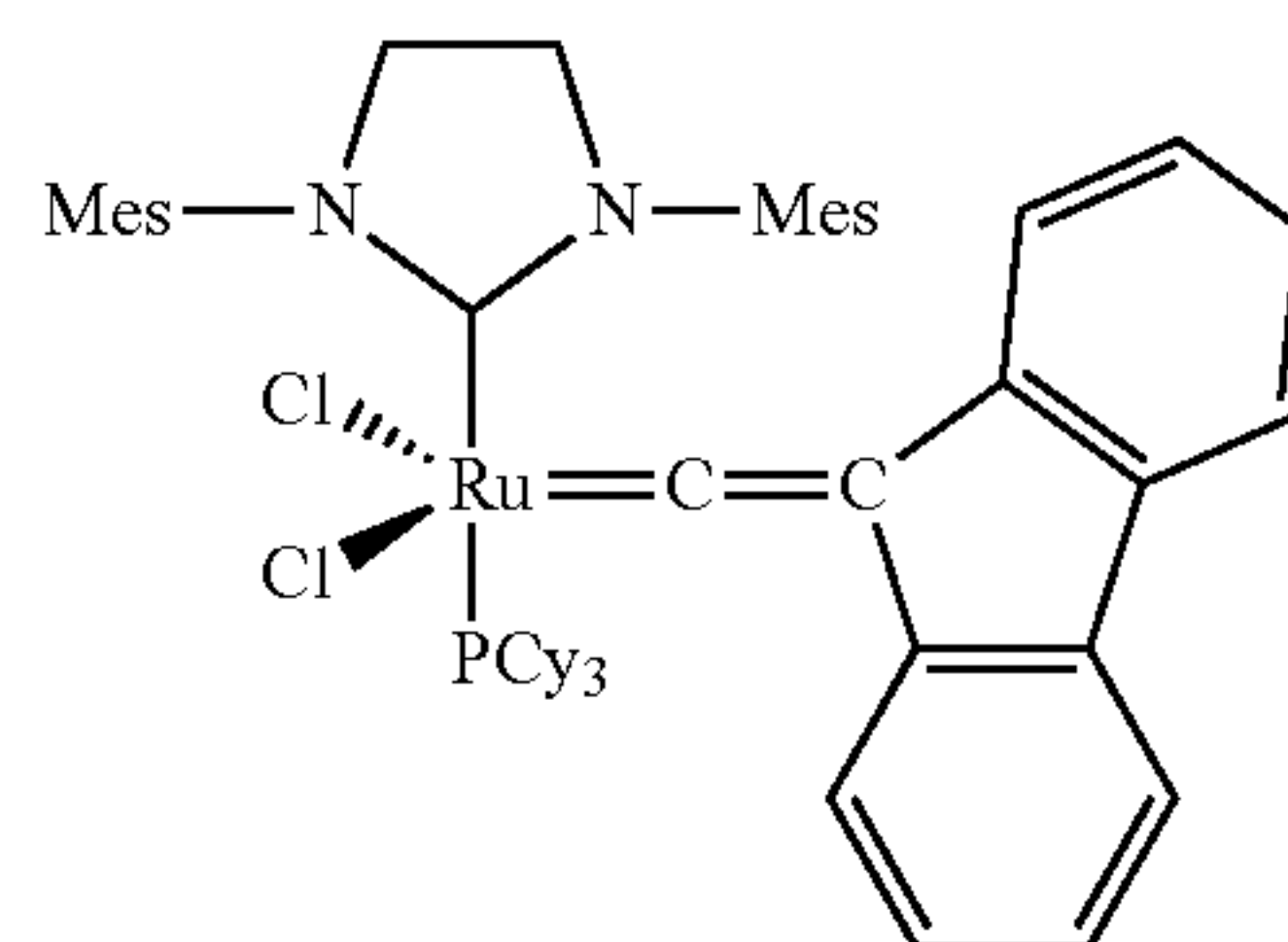
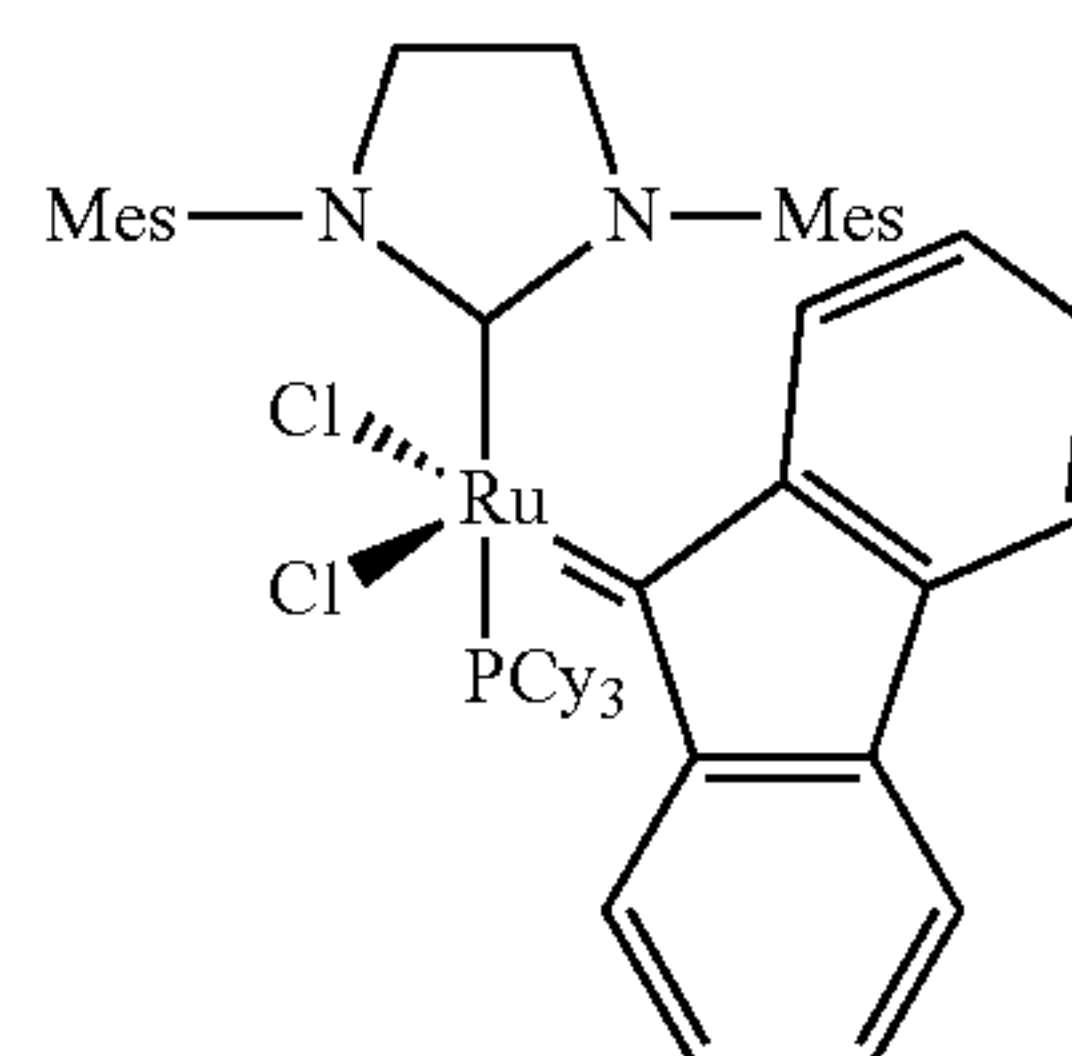
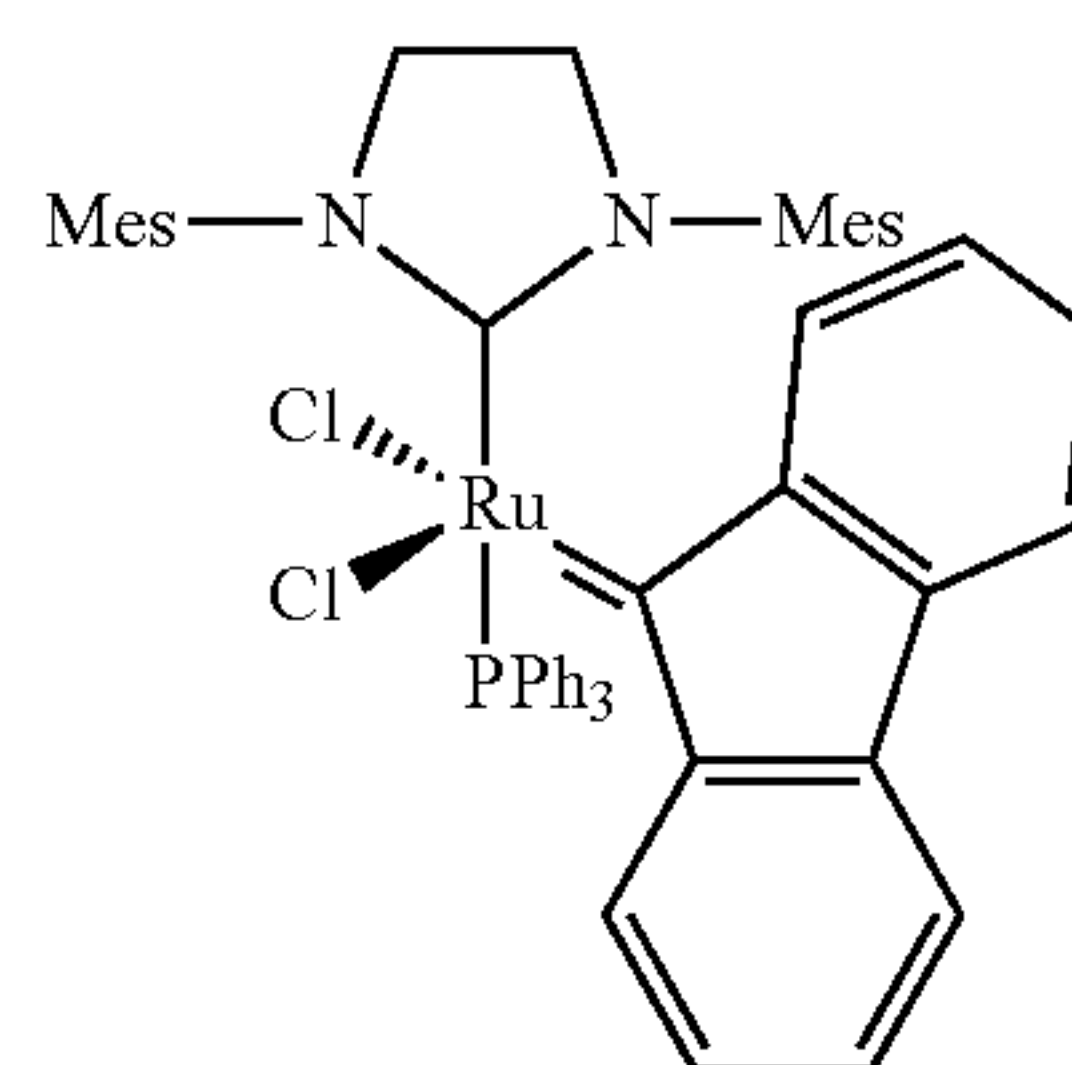
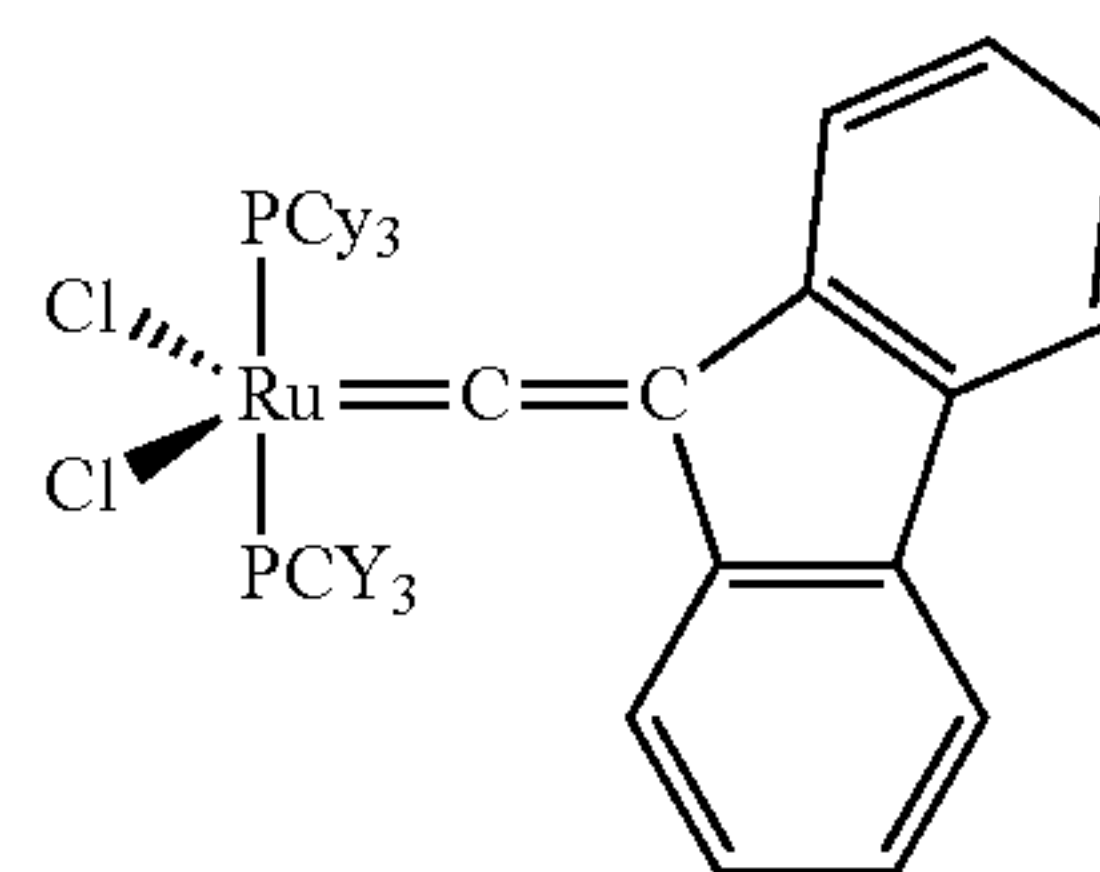
[0332] Y^2 when $p=1$ is $-(CH_2)_r-$ where $r=1, 2$ or 3 , $-C(=O)-CH_2-$, $-C(=O)-$, $-N=CH-$, $-N(H)-C(=O)-$ or, as an alternative, the entire structural unit " $-Y^1(R^{40})-(Y^2)_p$ " is $(-N(R^{40})=CH-CH_2-)$, $(-N(R^{40}, R^{41})=CH-CH_2-)$, and

where M , X^1 , X^2 , L^1 , $R^{25}-R^{32}$, A , m and n have the same meanings as in general formulae (N2a) and (N2b).

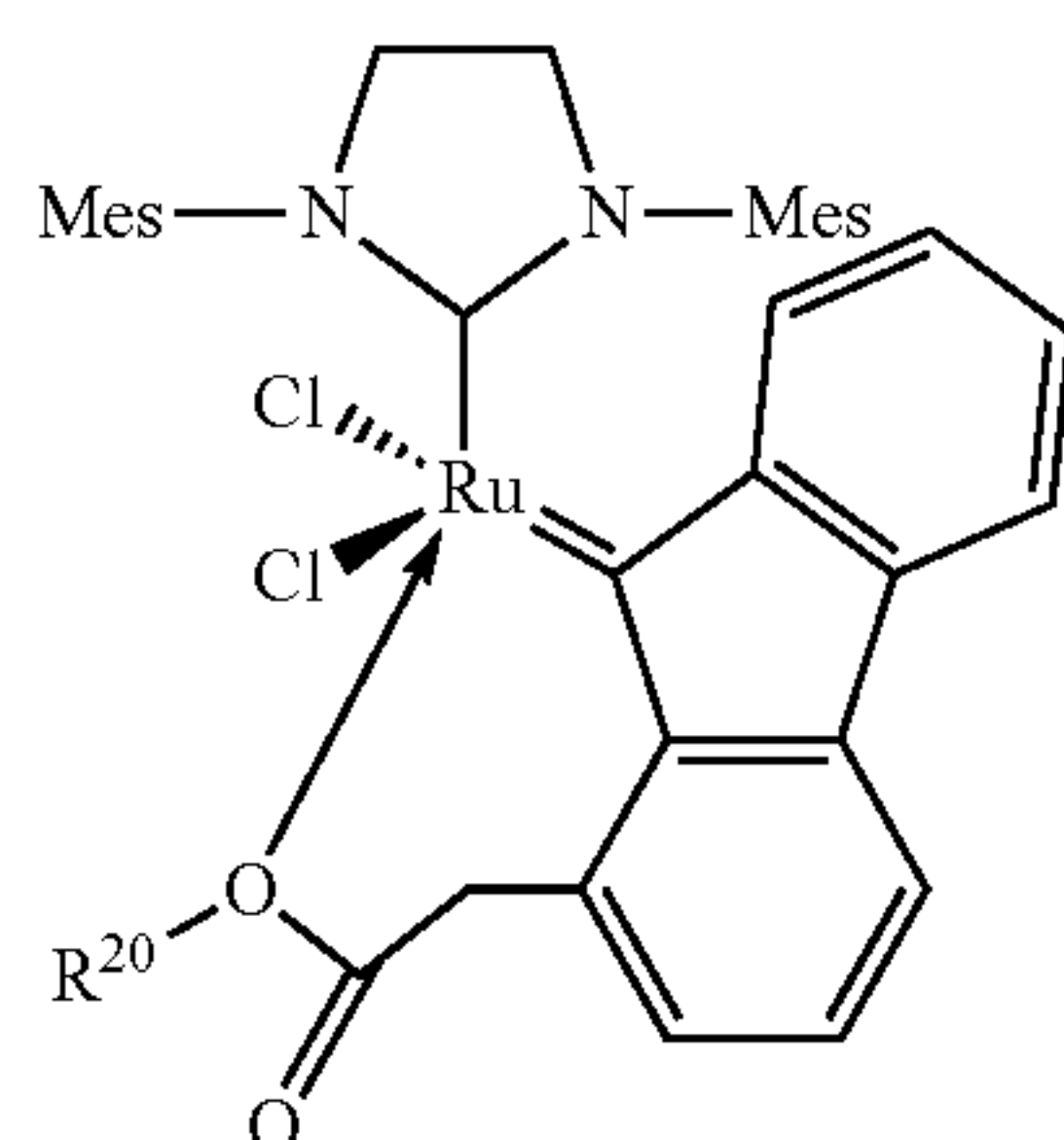
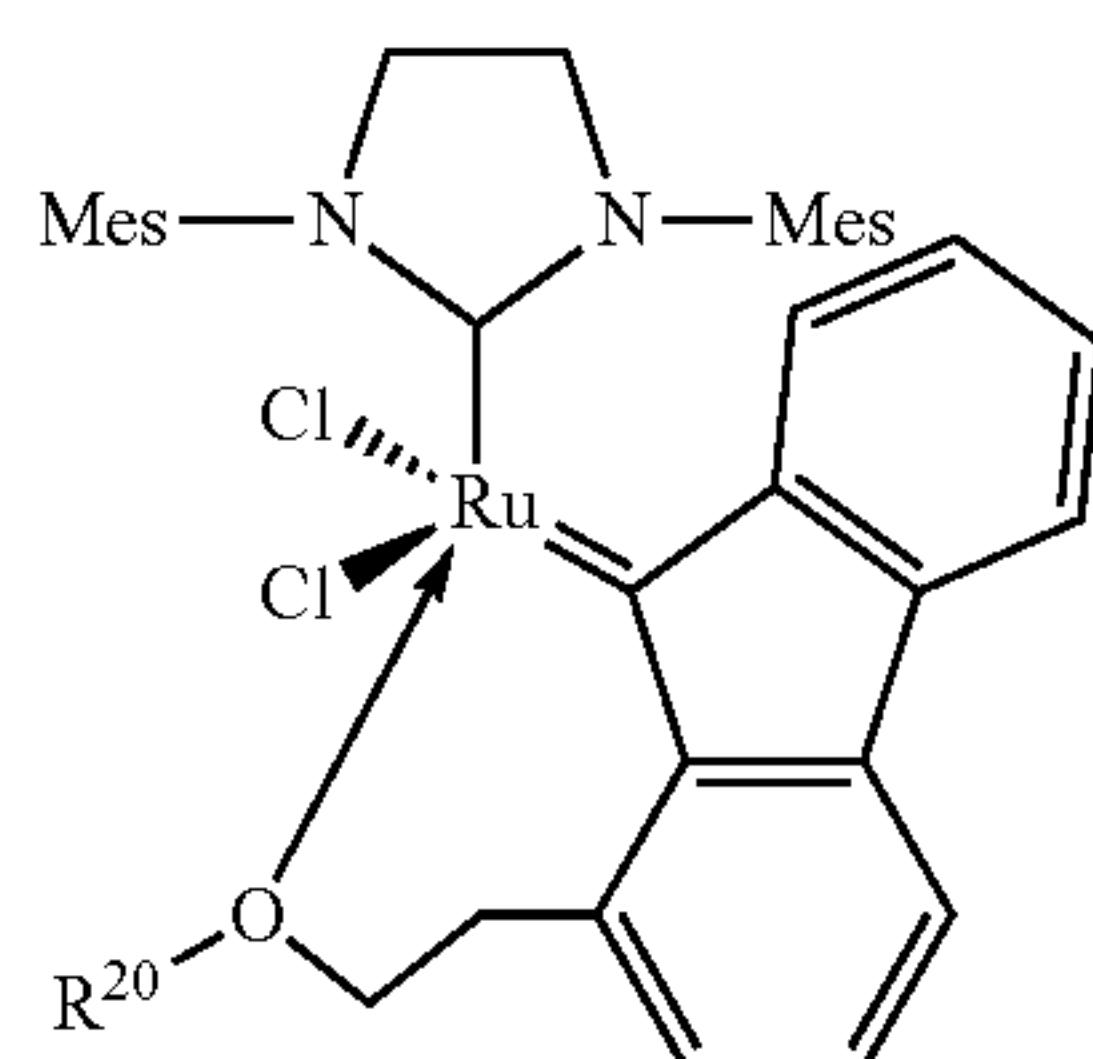
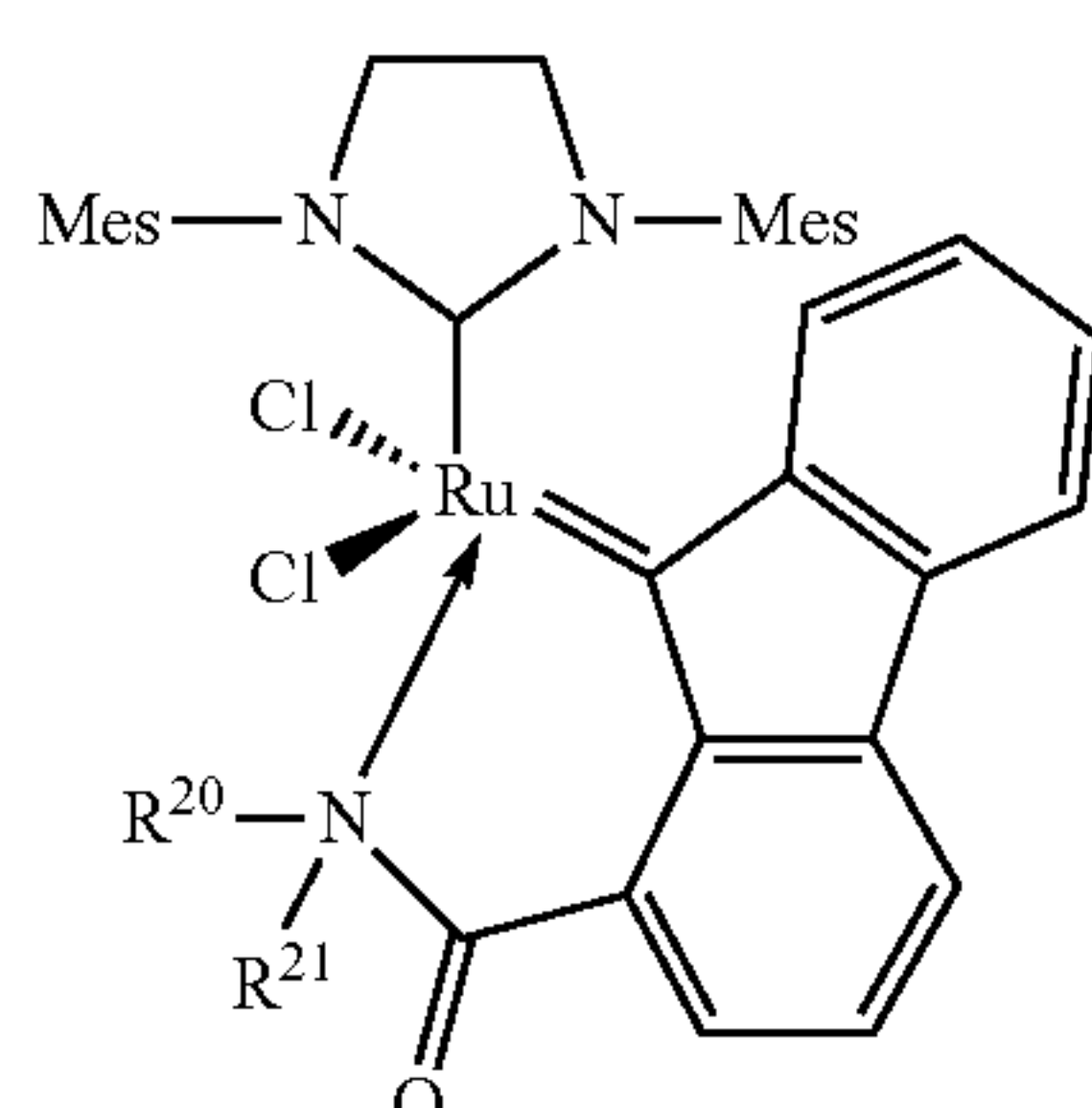
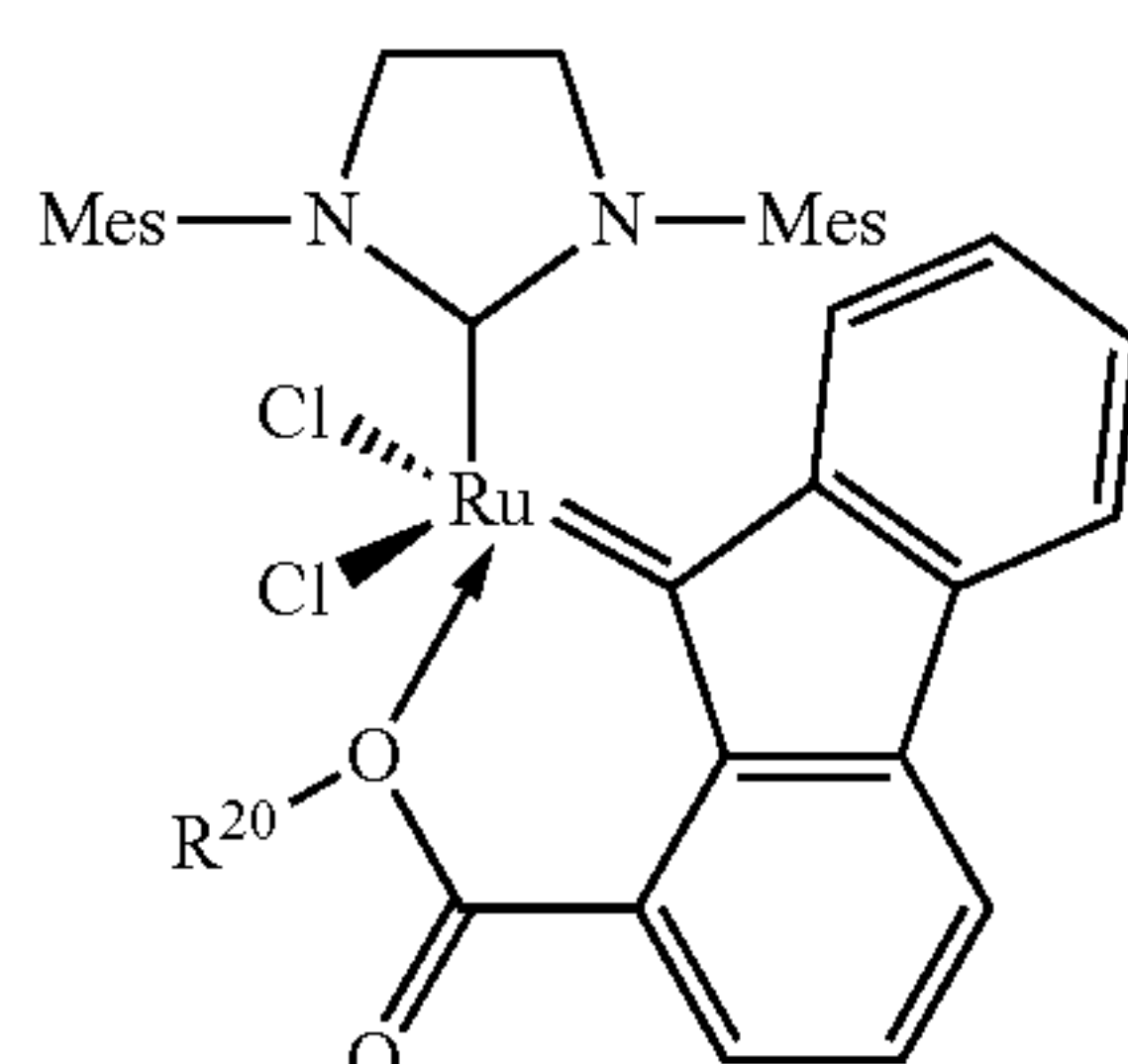
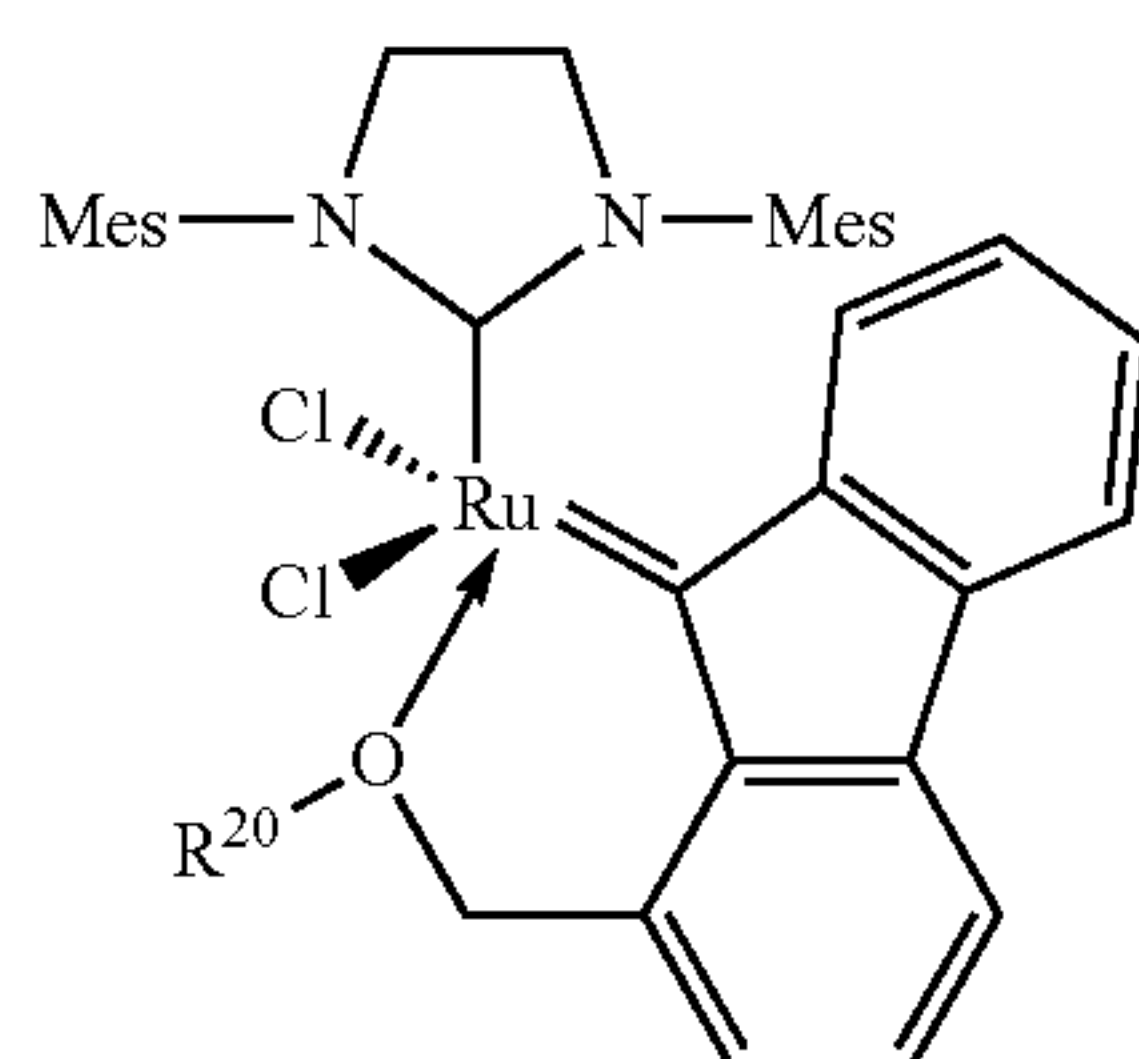
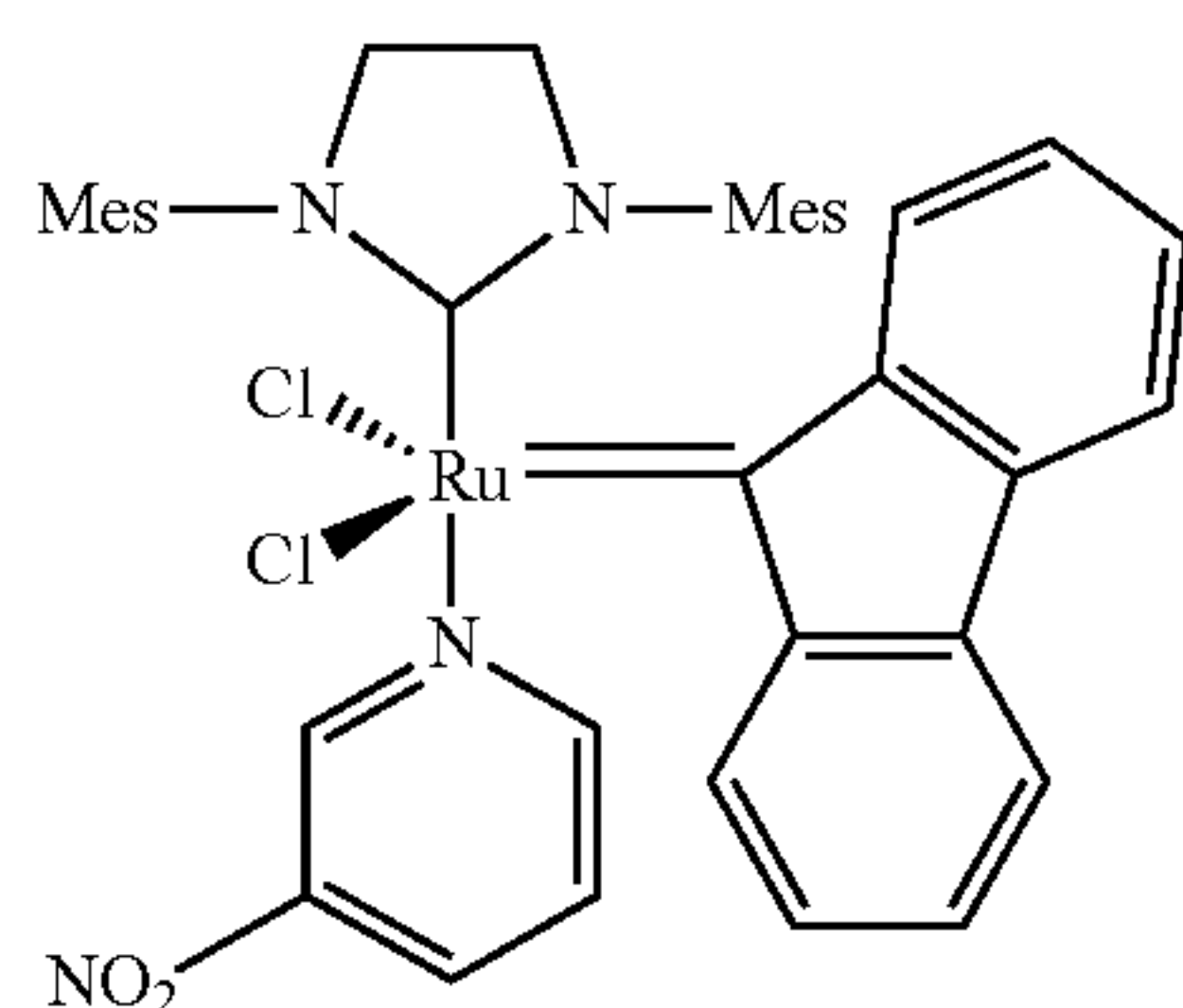
[0333] As examples of catalysts of the formula (N), mention is made of the following structures:



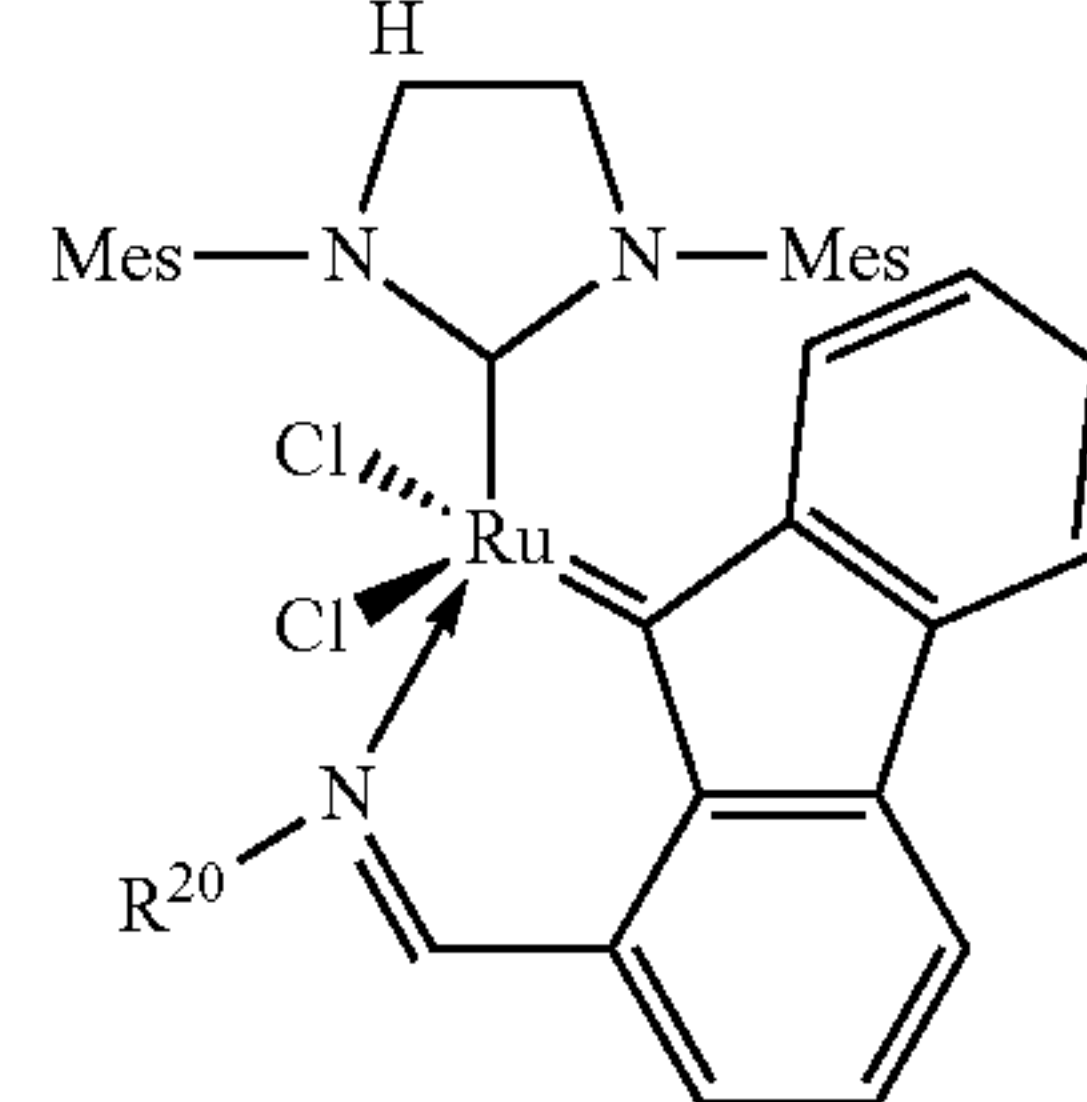
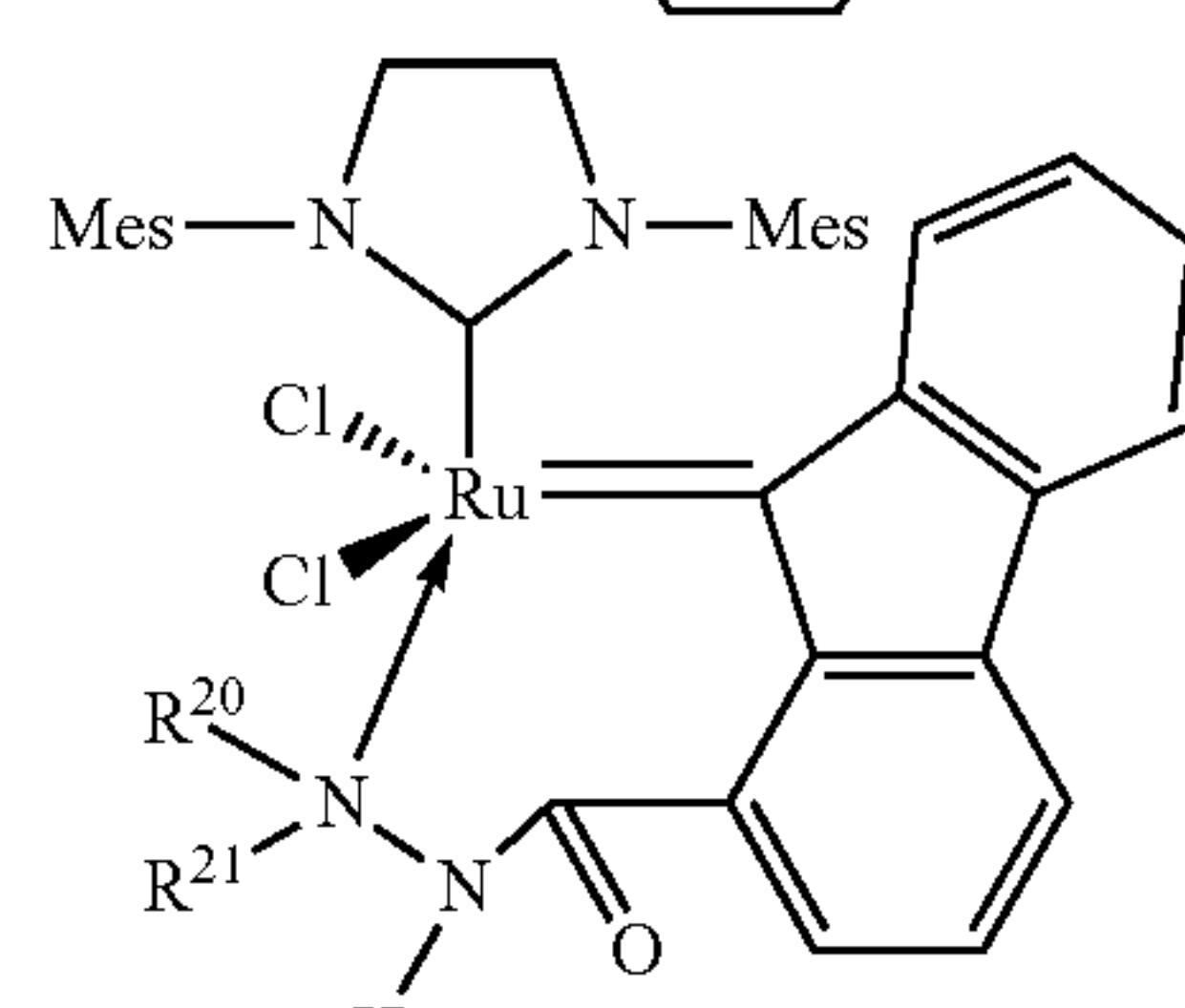
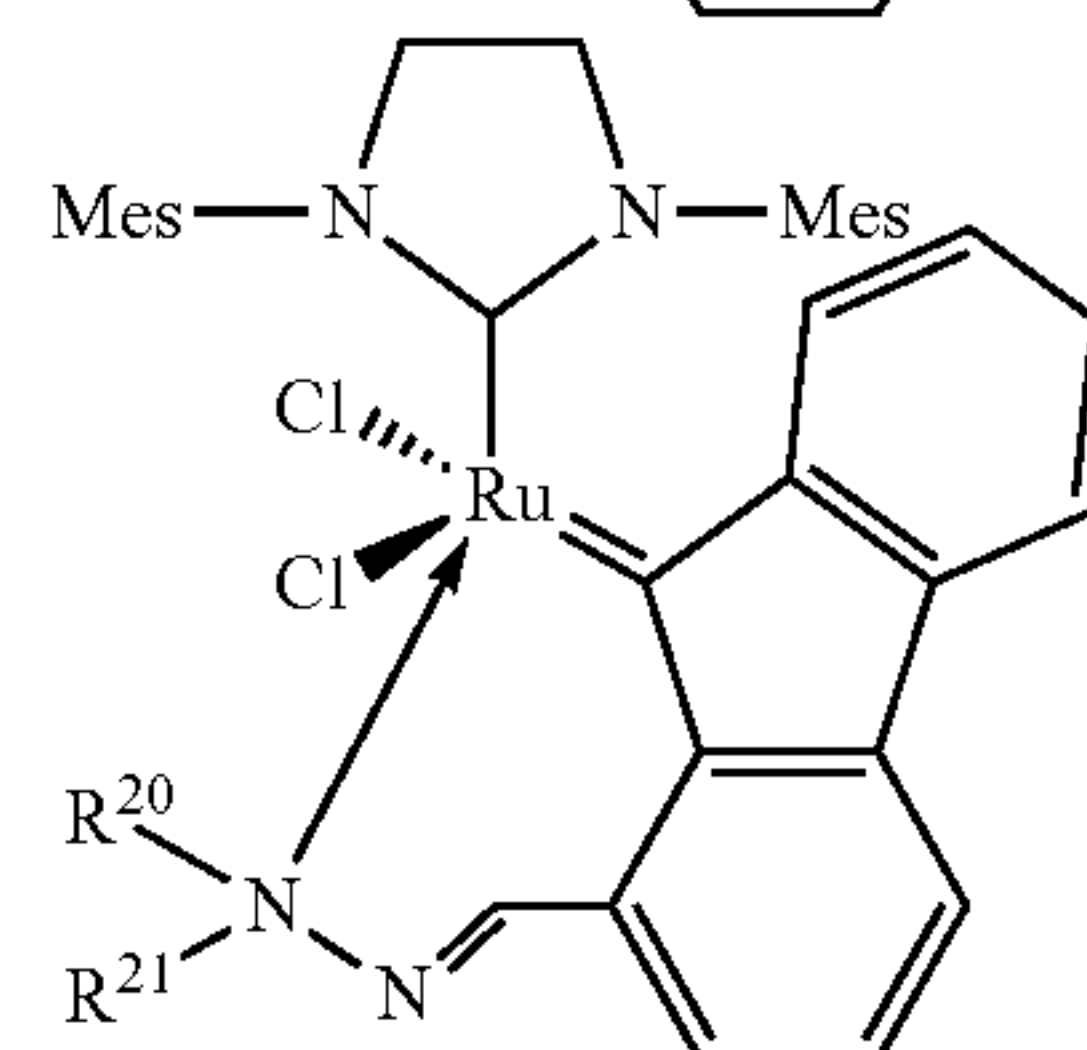
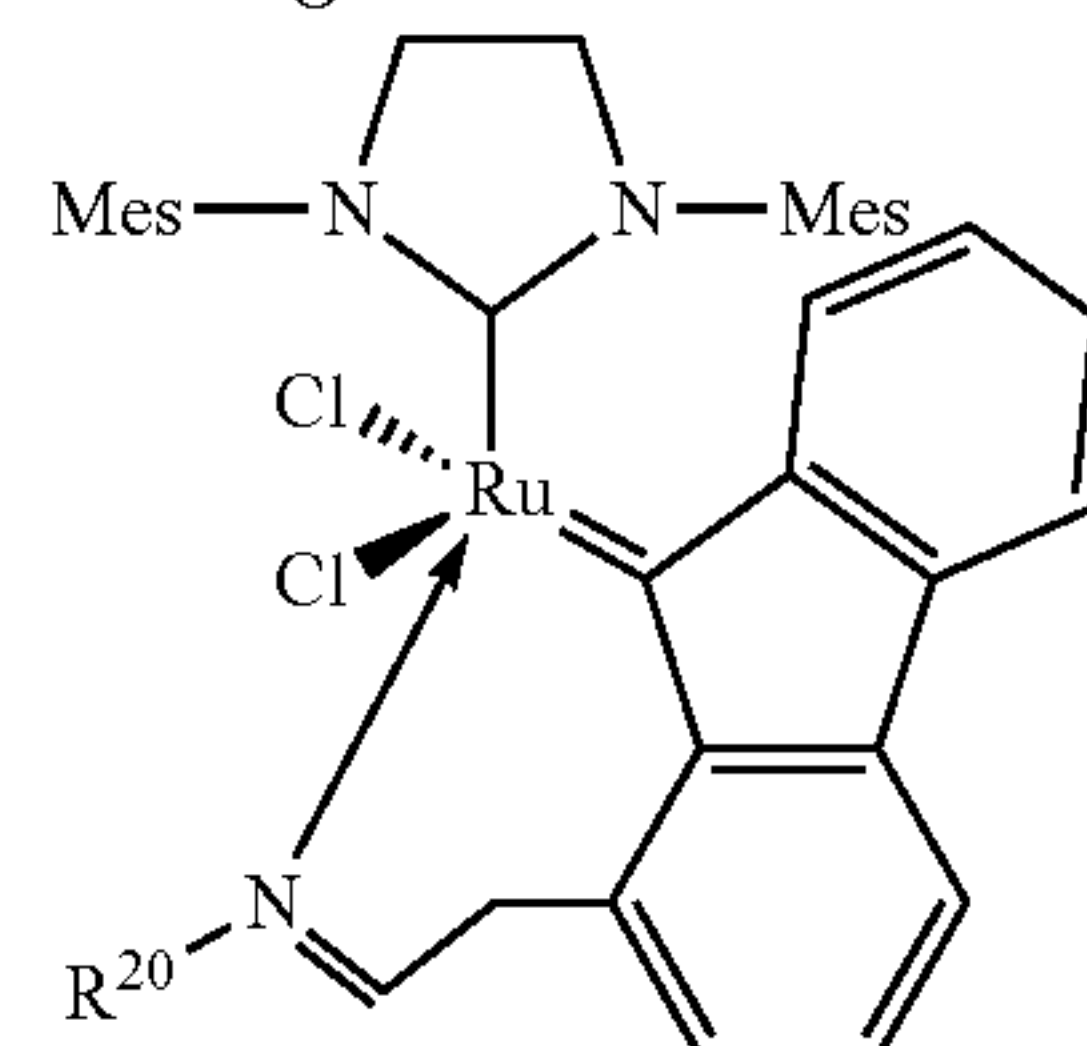
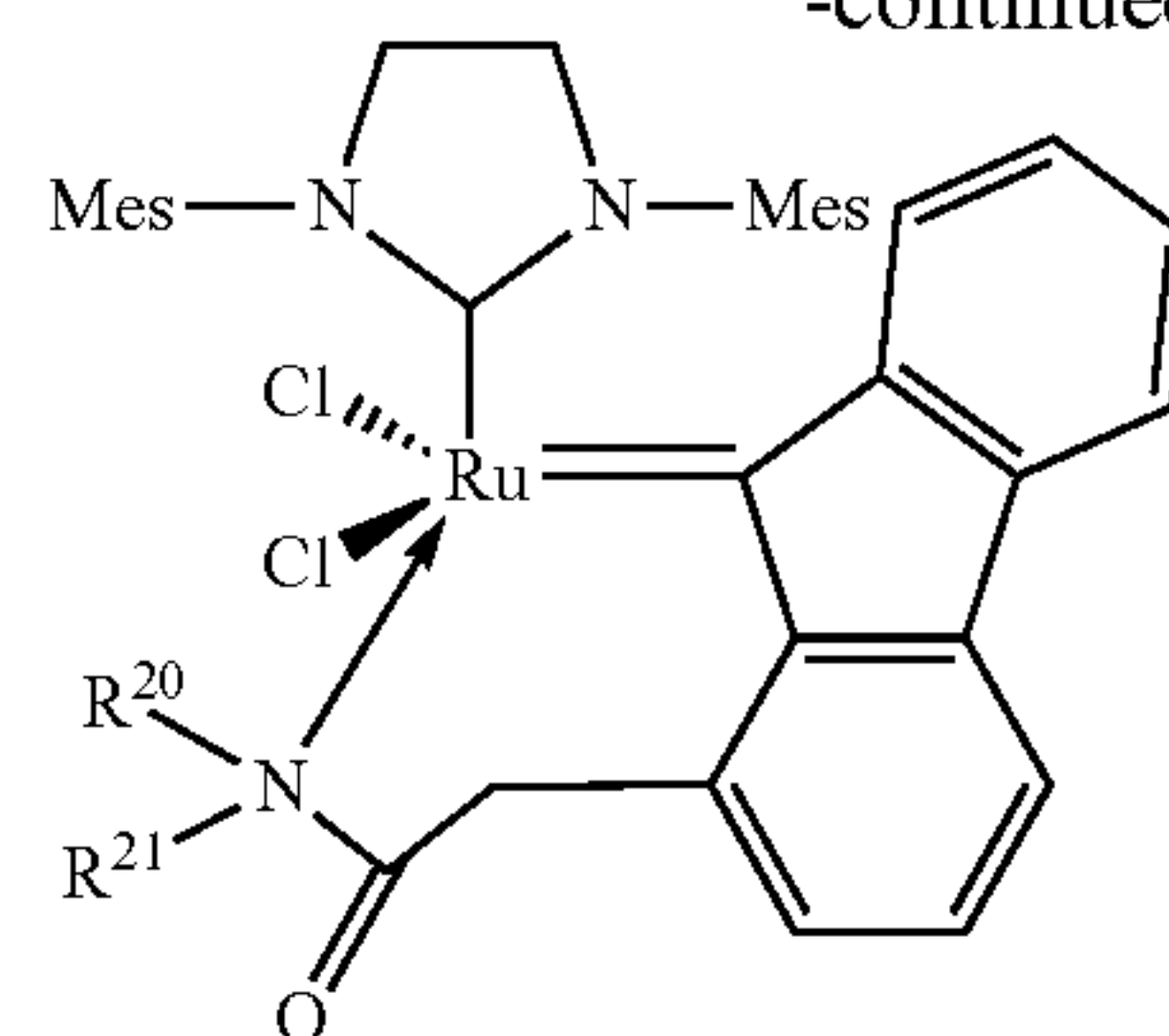
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Step a) of the Process According to the Present Invention:

[0334] The preparation of the novel catalyst composition in step a) of the present process is performed at an appropriate temperature. The choice of the temperature is influenced by the nature of the co-catalyst and the boiling temperature thereof. Typically this preparation step a) is performed at a temperature in the range of from -20°C . to 160°C ., preferably in the range of from 20°C . to 80°C . The suitable time for the catalyst pretreatment using vinyl-containing substance ranges from about 1 minute to 48 hours.

[0335] The ratio of the transition metal catalyst to the co-catalyst is 1:(20-550), preferably 1:(20-500), more preferably 1:(25-475), even more preferably 1:(25-450) and most preferably 1:(30-450).

[0336] In a preferred embodiment the molar ratio of the complex catalyst to the co-catalyst in a range of from 1:(20 to below 100), preferably 1:(25 to 99.5), more preferably 1:(30 to 99), even more preferably 1:(35 to 98.5) and most preferably 1:(40 to 70).

[0337] The preparation of the novel catalyst composition can be carried out in the presence or absence of a suitable solvent which does not deactivate the catalyst used and also does not have an adverse effect on the hydrogenation in any other way. Preferably an organic solvent is used to dissolve the complex catalyst. More preferred solvents include, but are not restricted to, dichloromethane, benzene, toluene, methyl ethyl ketone, acetone, tetrahydrofuran, tetrahydropyran, dioxane, cyclohexane and chlorobenzene. The particularly preferred solvents are chlorobenzene and methyl ethyl ketone. Typically the vinyl compound is added to the solution of the complex catalyst.

[0338] The formation of the novel catalyst composition is performed before hydrogen is brought into the reaction system.

Step b) of the Process According to the Present Invention:

[0339] Thereafter the hydrogenation of the nitrile rubber is carried out by bringing the nitrile rubber into contact with hydrogen and the catalyst composition formed in step a) of the present process.

[0340] The hydrogenation is preferably carried out at a temperature in the range of from 60° C. to 200° C., preferably from 80° C. to 180° C., most preferably from 100° C. to 160° C. and at a hydrogen pressure in the range of 0.5 MPa to 35 MPa, more preferably of 3.0 MPa to 10 MPa.

[0341] Preferably, the hydrogenation time of the nitrile rubber is from 10 minutes to 24 hours, preferably from 15 minutes to 20 hours, more preferably from 30 minutes to 12 hours, even more preferably from 1 hour to 8 hours and most preferably from 1 hour to 4 hours.

[0342] The amount of the catalyst composition which is present in the hydrogenation step b) based on the nitrile rubber can be chosen in a broad range, preferably so that from 1 to 1000 ppm of ruthenium or osmium, preferably from 2 to 500 ppm, in particular from 5 to 250 ppm, are present based on the nitrile rubber used.

[0343] In an alternative embodiment of the present process it is possible to perform a metathesis reaction prior to the preparation of the novel catalyst composition and the subsequent hydrogenation. Such alternative process (hereinafter also referred to as "tandem process") comprises performing a metathesis step before the above described steps a) and b).

[0344] This means that such alternative process comprises firstly subjecting a nitrile rubber to a molecular weight degradation in a metathesis reaction comprising contacting the nitrile rubber in the absence or presence of a co-olefin with a complex catalyst based on ruthenium or osmium as central metal and bearing at least one ligand which is bound to the ruthenium or osmium central metal in a carbene-like fashion, then

[0345] a) contacting the complex catalyst which is present in the reaction mixture obtained after the metathesis reaction with at least one co-catalyst having at least one vinyl group in a molar ratio of the complex catalyst to the co-catalyst in the range of 1:(20-550) to form a catalyst composition and thereafter

[0346] b) hydrogenating the nitrile rubber in the presence of the catalyst composition.

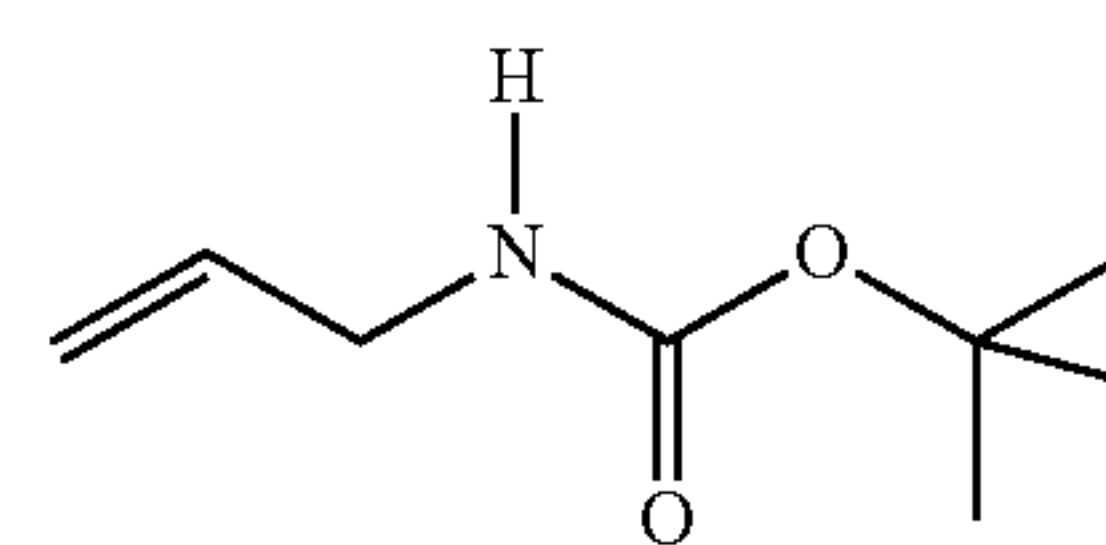
[0347] In a preferred embodiment of this alternative process the molar ratio of the complex catalyst to the co-catalyst in a range of from 1:(20 to below 100), preferably 1:(25 to 99.5), more preferably 1:(30 to 99), even more preferably 1:(35 to 98.5) and most preferably 1:(40 to 70).

Metathesis Step a) of the Tandem Method:

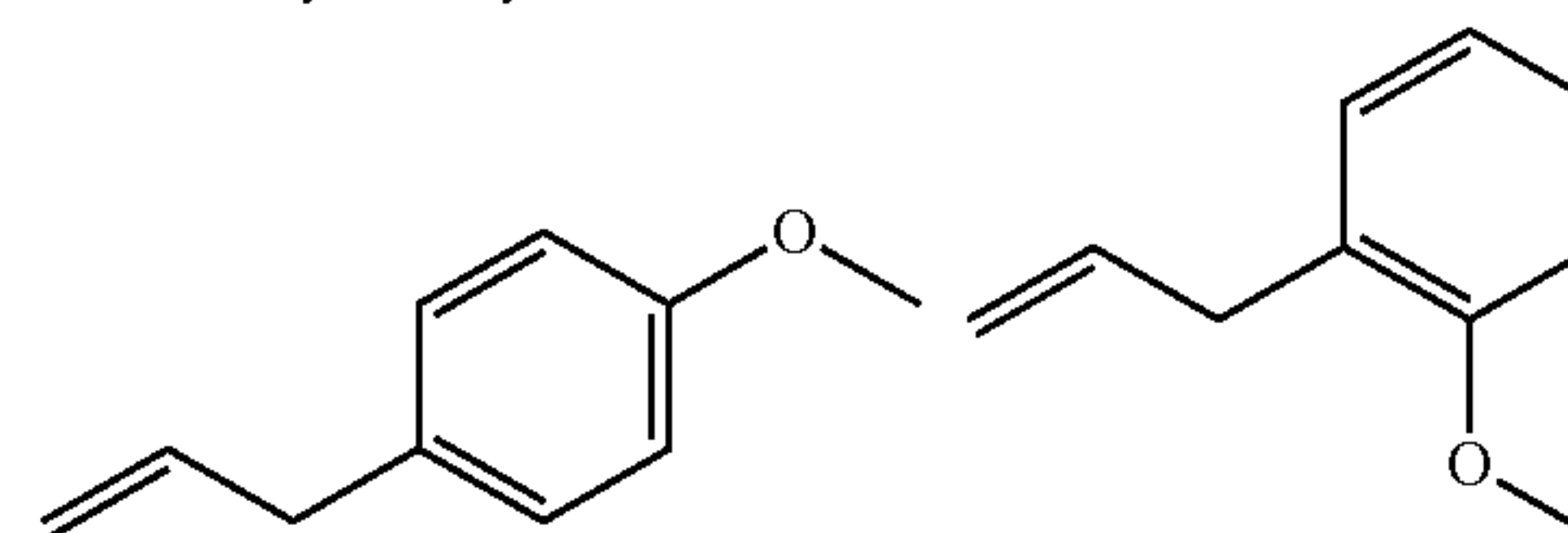
[0348] The NBR metathesis as first step of the tandem method can be carried out in the absence or presence of a co-olefin.

[0349] This co-olefin is preferably a straight-chain or branched C₂-C₁₆-olefin. Suitable co-olefins are, for example, ethylene, propylene, isobutene, styrene, 1-hexene and 1-octene. Particular preference is given to using 1-hexene or 1-octene.

[0350] In the alternative the following functionalized co-olefins can be used:

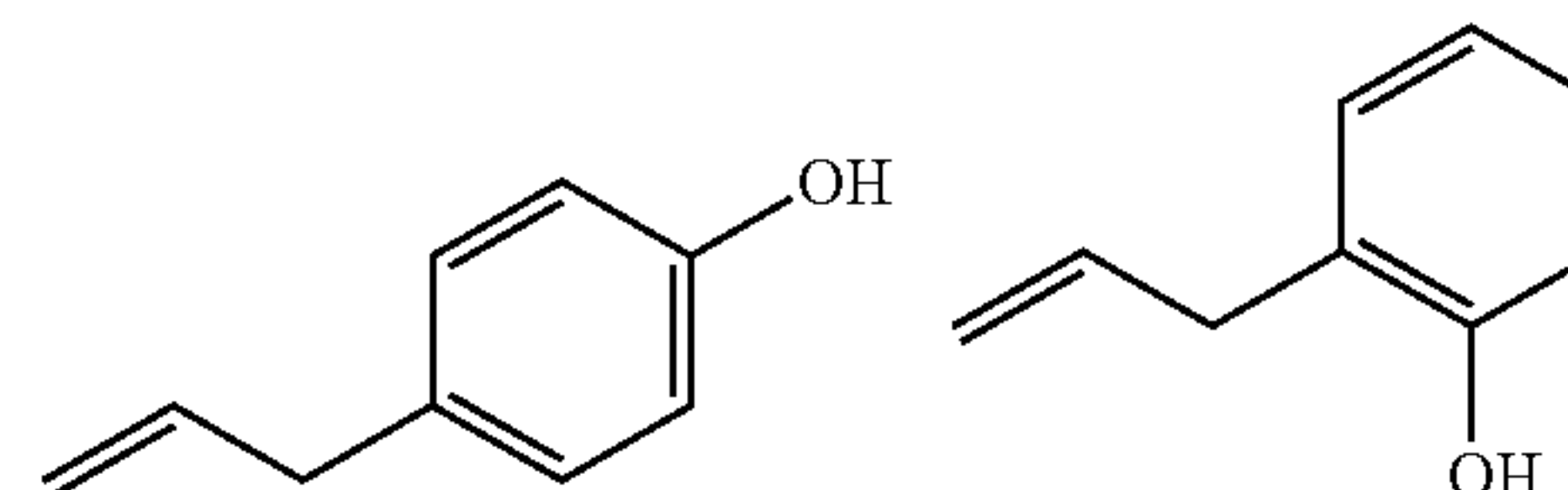


t-butyl-N-allylcarbamate



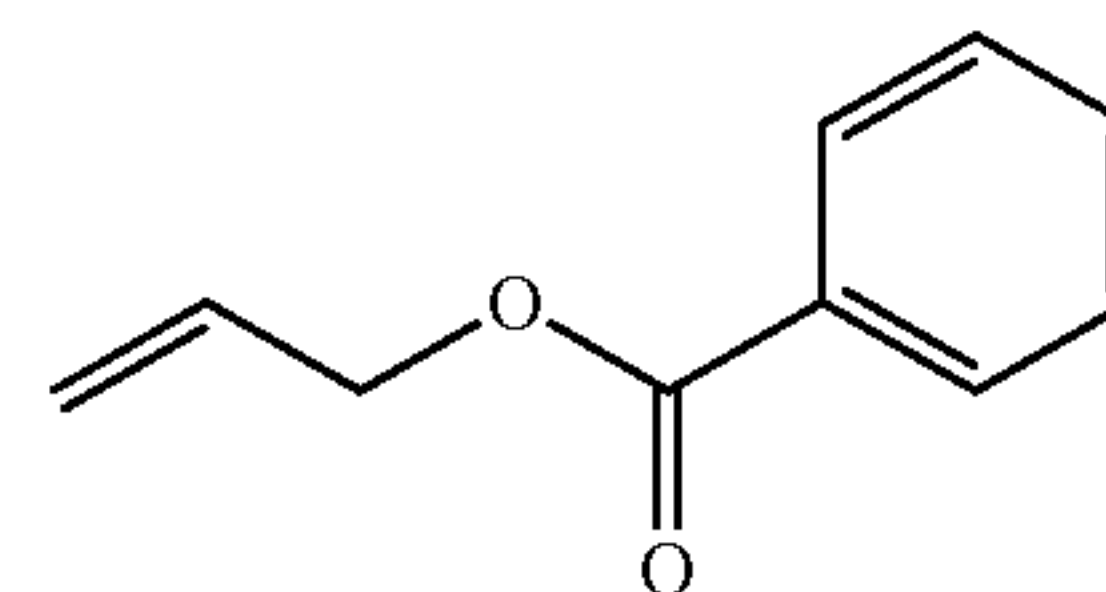
p-allylanisole

o-allylanisole

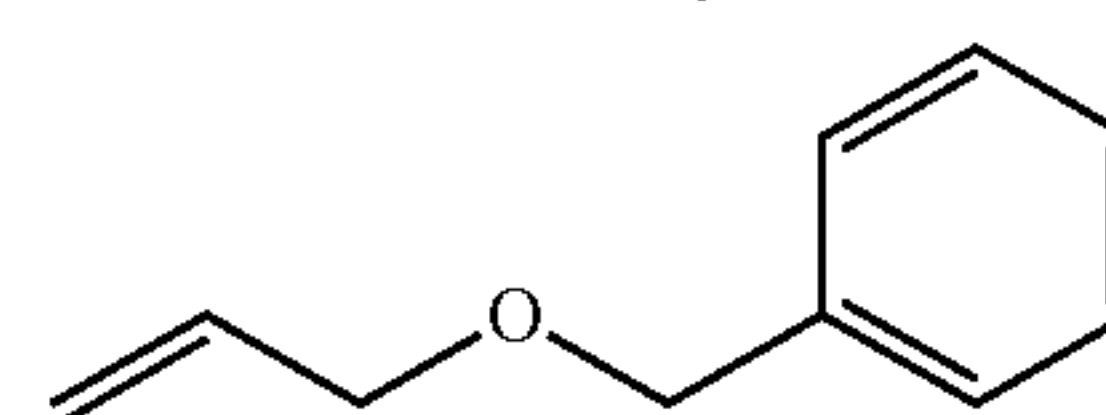


p-allylphenol

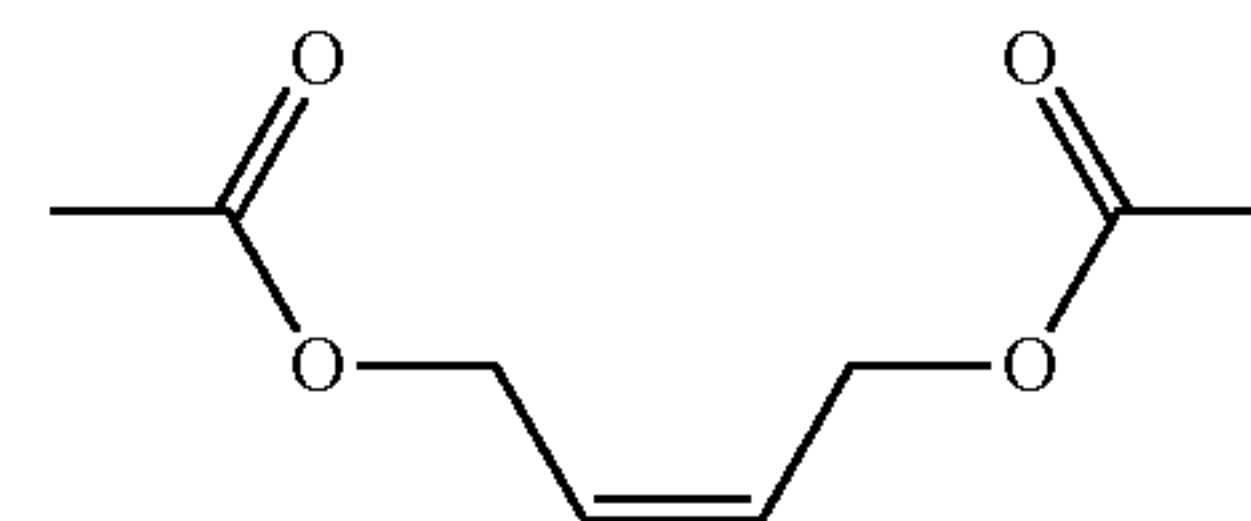
o-allylphenol



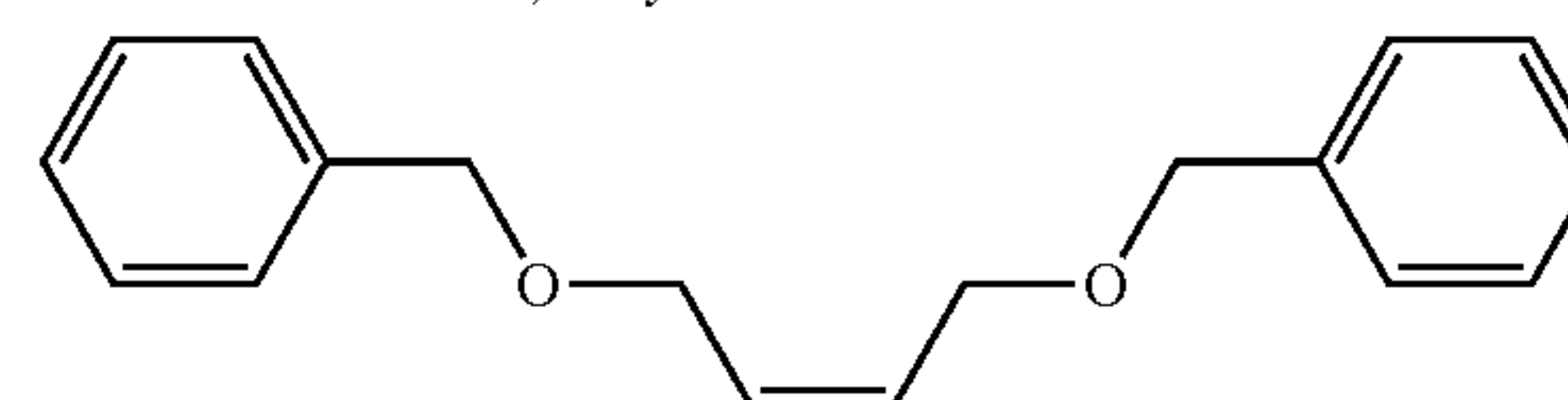
benzoic acid allylic ester



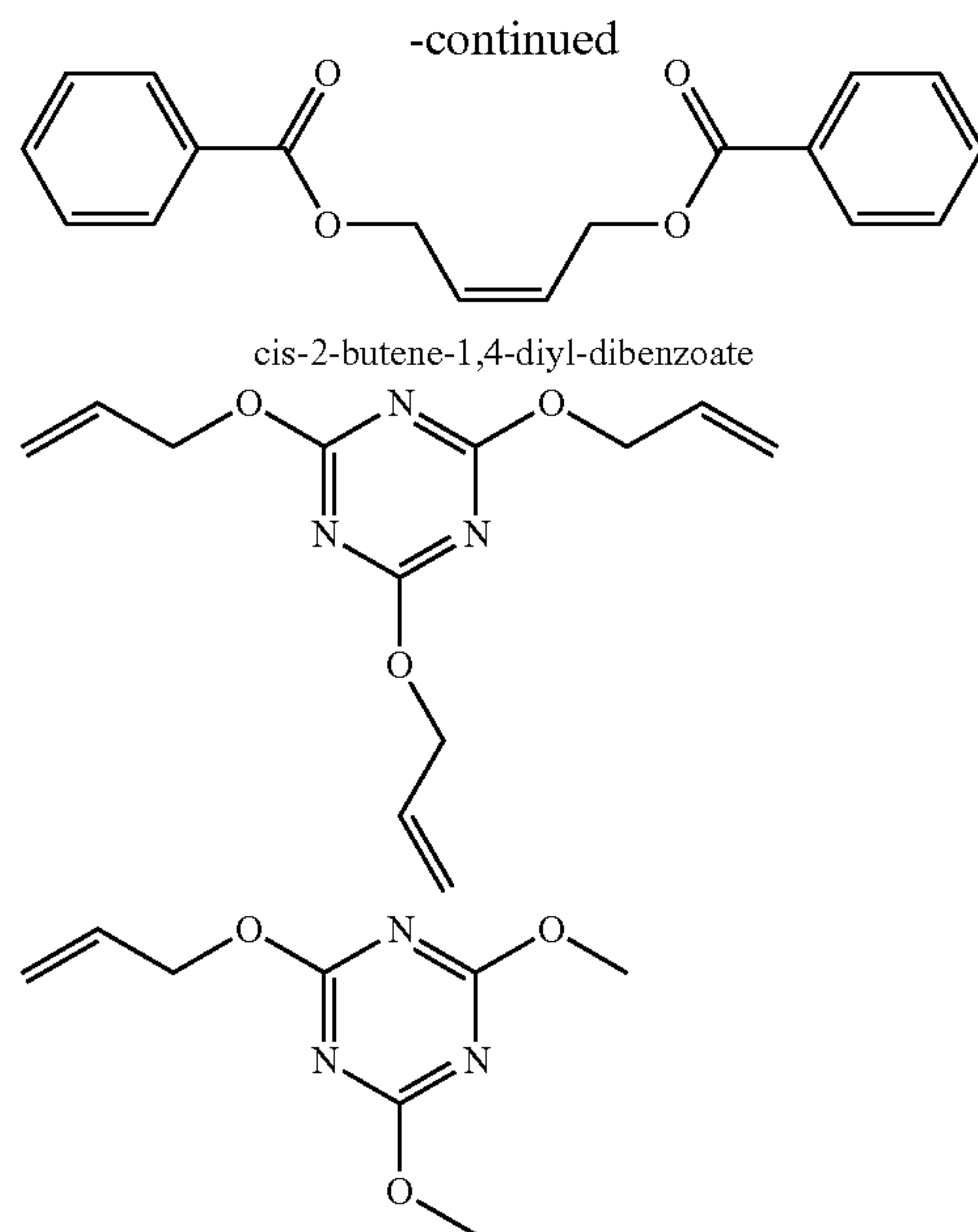
allylic benzyl ether



cis-2-butene-1,4-diyl-diacetate



cis-1,4-bisbenzoyloxy-2-butene



[0351] If the co-olefin is liquid (as in the case of, for example, 1-hexene), the amount of co-olefin is preferably in the range 0.2-20% by weight, based on the nitrile rubber used. If the co-olefin is a gas, as in the case of, for example, ethylene, the amount of co-olefin is selected so that a pressure in the range 1×10^5 Pa- 1×10^7 Pa, preferably a pressure in the range from 5.2×10^5 Pa to 4×10^6 Pa, is established in the reaction vessel at room temperature.

[0352] The metathesis reaction can be carried out in a suitable solvent which does not deactivate the catalyst used and also does not have an adverse effect on the reaction in any other way. Preferred solvents include, but are not restricted to, dichloromethane, benzene, toluene, methyl ethyl ketone, acetone, tetrahydrofuran, tetrahydropyran, dioxane, cyclohexane and chlorobenzene. The particularly preferred solvent is chlorobenzene. In some cases when the co-olefin itself can function as solvent, e.g. in the case of 1-hexene, the addition of a further additional solvent can be dispensed with.

[0353] The amount of catalyst based on the nitrile rubber used in the metathesis step of the tandem method according to the invention depends on the nature and the catalytic activity of the specific complex catalyst. The amount of catalyst used is usually from 1 to 1000 ppm of noble metal, preferably from 2 to 500 ppm, in particular from 5 to 250 ppm, based on the nitrile rubber used.

[0354] The concentration of the nitrile rubber used in the reaction mixture of the metathesis is not critical, but it should naturally be ensured that the reaction is not adversely affected by an excessively high viscosity of the reaction mixture and the associated mixing problems. The concentration of NBR in the reaction mixture is preferably in the range from 1 to 25% by weight, particularly preferably in the range from 5 to 20% by weight, based on the total reaction mixture.

[0355] The metathetic degradation is usually carried out at a temperature in the range from 10° C. to 150° C., preferably at a temperature in the range from 20 to 80° C.

[0356] The metathesis reaction time depends on a number of factors, for example on the type of NBR, the type of catalyst, the catalyst concentration and co-olefin concentration used and the reaction temperature. The progress of the

cross-metathesis can be monitored by standard analytical methods, e.g. by GPC measurements or by determination of the viscosity. The reaction is typically allowed to be conducted for about 15 minutes to six hours under normal conditions. It is also possible to perform the metathesis reaction until the reaction ceases by deactivation of the catalyst.

[0357] After such metathesis step, the reaction mixture containing the metathesis catalyst is taken and brought into contact with the co-catalyst having the general formula (1) or (2). Typically the co-catalyst is simply added to the reaction mixture, preferably in the same solvent in which the metathesis was performed.

[0358] The appropriate temperature for the preparation of the novel catalyst composition after the metathesis in the tandem method can also be chosen in the range of from -20° C. to 160° C., preferably in the range of from 20° C. to 80° C. The suitable time for the preparation of the catalyst composition for the subsequent hydrogenation reaction in such tandem reaction using the vinyl-group containing co-catalyst ranges from about 5 minutes to 48 hours. The preferred time ranges from 10 minutes to 12 hours.

[0359] The subsequent hydrogenation of the nitrile rubber can be carried in the same manner as described above for the hydrogenation reaction.

[0360] One major advantage of the present invention resides in the fact that the catalyst composition used is very active, so that the catalyst residue in the final HNBR products can be low enough to make the catalyst metal removal or recycle step alleviated or even unnecessary. However, to the extent desired, the catalysts used during the process of the present invention may be removed. Such removal can be performed e.g. by using ion-exchange resins as described in EP-A-2 072 532 A1 and EP-A-2 072 533 A1. The reaction mixture obtained after the completion of the hydrogenation reaction can be taken and treated with an ion-exchange resin at e.g. 100° C. for 48 hours under nitrogen and then be precipitated in cold methanol

Nitrile Rubber:

[0361] The nitrile rubber used in the process of the present invention is a copolymer or terpolymer of at least one α,β -unsaturated nitrile, at least one conjugated diene and, if desired, one or more further copolymerizable monomers.

[0362] The conjugated diene can be of any nature. Preference is given to using (C_4 - C_6) conjugated dienes. Particular preference is given to 1,3-butadiene, isoprene, 2,3-dimethylbutadiene, piperylene or mixtures thereof. Very particular preference is given to 1,3-butadiene and isoprene or mixtures thereof. Especial preference is given to 1,3-butadiene.

[0363] As α,β -unsaturated nitrile, it is possible to use any known α,β -unsaturated nitrile, preferably a (C_3 - C_5) α,β -unsaturated nitrile such as acrylonitrile, methacrylonitrile, ethacrylonitrile or mixtures thereof. Particular preference is given to acrylonitrile.

[0364] A particularly preferred nitrile rubber used in the process of this invention is thus a copolymer having repeating units derived from acrylonitrile and 1,3-butadiene.

[0365] Apart from the conjugated diene and the α,β -unsaturated nitrile, the hydrogenated nitrile rubber may comprise repeating units of one or more further copolymerizable monomers known in the art, e.g. α,β -unsaturated (preferably mono-unsaturated) monocarboxylic acids, their esters and amides, α,β -unsaturated (preferably mono-unsaturated)

dicarboxylic acids, their mono- or diesters, as well as the respective anhydrides or amides of said α,β -unsaturated dicarboxylic acids.

[0366] As α,β -unsaturated monocarboxylic acids acrylic acid and methacrylic acid are preferably used.

[0367] Esters of α,β -unsaturated monocarboxylic acids may also be used, in particular alkyl esters, alkoxyalkyl esters, aryl esters, cycloalkylesters, cyanoalkyl esters, hydroxyalkyl esters, and fluoroalkyl esters.

[0368] As alkyl esters C_1 - C_{18} alkyl esters of the α,β -unsaturated monocarboxylic acids are preferably used, more preferably C_1 - C_{18} alkyl esters of acrylic acid or methacrylic acid, such as methylacrylate, ethylacrylate, propylacrylate, n-butylacrylate, tert.-butylacrylate, 2-ethyl-hexylacrylate, n-dodecylacrylate, methylmethacrylate, ethylmethacrylate, propylmethacrylate, n-butylmethacrylate, tert.-butylmethacrylate and 2-ethylhexyl-methacrylate.

[0369] As alkoxyalkyl esters C_2 - C_{18} alkoxyalkyl esters of α,β -unsaturated monocarboxylic acids are preferably used, more preferably alkoxyalkylester of acrylic acid or methacrylic acid such as methoxy methyl(meth)acrylate, methoxy ethyl(meth)acrylate, ethoxyethyl(meth)acrylate and methoxyethyl(meth)acrylate.

[0370] It is also possible to use aryl esters, preferably C_6 - C_{14} -aryl-, more preferably C_6 - C_{10} -aryl esters and most preferably the aforementioned aryl esters of acrylates and methacrylates.

[0371] In another embodiment cycloalkyl esters, preferably C_5 - C_{12} —, more preferably C_6 - C_{12} -cyclo-alkyl and most preferably the aforementioned cycloalkyl acrylates and methacrylates are used.

[0372] It is also possible to use cyanoalkyl esters, in particular cyanoalkyl acrylates or cyanoalkyl methacrylates, with 2 to 12 C atoms in the cyanoalkyl group, preferably α -cyanoethyl acrylate, β -cyanoethyl acrylate or cyanobutyl methacrylate.

[0373] In another embodiment hydroxyalkyl esters are used, in particular hydroxyalkyl acrylates and hydroxyalkyl methacrylates with 1 to 12 C-atoms in the hydroxyalkyl group, preferably 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate or 3-hydroxypropyl acrylate.

[0374] It is also possible to use fluorobenzyl esters, in particular fluorobenzyl acrylates or fluorobenzyl methacrylates, preferably trifluoroethyl acrylate and tetrafluoropropyl methacrylate. Substituted amino group containing acrylates and methacrylates may also be used like dimethylaminomethyl acrylate and diethylaminoethylacrylate.

[0375] Various other esters of the α,β -unsaturated carboxylic acids may also be used, like e.g. poly-ethyleneglycol (meth)acrylate, polypropyleneglycole(meth)acrylate, glycidyl(meth)acrylate, epoxy(meth)acrylate, N-(2-hydroxyethyl)acrylamide, N-(2-hydroxymethyl)acrylamide or urethane(meth)acrylate.

[0376] It is also possible to use mixture of all aforementioned esters of α,β -unsaturated carboxylic acids.

[0377] Further α,β -unsaturated dicarboxylic acids may be used, preferably maleic acid, fumaric acid, crotonic acid, itaconic acid, citraconic acid and mesaconic acid.

[0378] In another embodiment anhydrides of α,β -unsaturated dicarboxylic acids are used, preferably maleic anhydride, itaconic anhydride, itaconic anhydride, citraconic anhydride and mesaconic anhydride.

[0379] In a further embodiment mono- or diesters of α,β -unsaturated dicarboxylic acids can be used. Suitable alkyl

esters are e.g. C_1 - C_{10} -alkyl, preferably ethyl-, n-propyl-, isopropyl, n-butyl-, tert.-butyl, n-pentyl- or n-hexyl mono- or diesters. Suitable alkoxyalkyl esters are e.g. C_2 - C_{12} alkoxyalkyl-, preferably C_3 - C_8 -alkoxyalkyl mono- or diesters. Suitable hydroxyalkyl esters are e.g. C_1 - C_{12} hydroxyalkyl-, preferably C_2 - C_8 -hydroxyalkyl mono- or diesters. Suitable cycloalkyl esters are e.g. C_5 - C_{12} -cycloalkyl-, preferably C_6 - C_{12} -cycloalkyl mono- or diesters. Suitable alkylcycloalkyl esters are e.g. C_6 - C_{12} -alkylcycloalkyl-, preferably C_7 - C_{10} -alkylcycloalkyl mono- or diesters. Suitable aryl esters are e.g. C_6 - C_{14} -aryl, preferably C_6 - C_{10} -aryl mono- or diesters.

[0380] Explicit examples of the α,β -ethylenically unsaturated dicarboxylic acid monoester monomers include

[0381] maleic acid monoalkyl esters, preferably monomethyl maleate, monoethyl maleate, monopropyl maleate, and mono n-butyl maleate;

[0382] maleic acid monocycloalkyl esters, preferably monocyclopentyl maleate, monocyclohexyl maleate, and monocycloheptyl maleate;

[0383] maleic acid monoalkylcycloalkyl esters, preferably monomethylcyclopentyl maleate, and monoethylcyclohexyl maleate;

[0384] maleic acid monoaryl ester, preferably monophenyl maleate;

[0385] maleic acid mono benzyl ester, preferably monobenzyl maleate;

[0386] fumaric acid monoalkyl esters, preferably monomethyl fumarate, monoethyl fumarate, monopropyl fumarate, and mono n-butyl fumarate;

[0387] fumaric acid monocycloalkyl esters, preferably monocyclopentyl fumarate, monocyclohexyl fumarate, and monocycloheptyl fumarate;

[0388] fumaric acid monoalkylcycloalkyl esters, preferably monomethylcyclopentyl fumarate, and monoethylcyclohexyl fumarate;

[0389] fumaric acid monoaryl ester, preferably monophenyl fumarate;

[0390] fumaric acid mono benzyl ester, preferably monobenzyl fumarate;

[0391] citraconic acid monoalkyl esters, preferably monomethyl citraconate, monoethyl citraconate, monopropyl citraconate, and mono n-butyl citraconate;

[0392] citraconic acid monocycloalkyl esters, preferably monocyclopentyl citraconate, monocyclohexyl citraconate, and monocycloheptyl citraconate;

[0393] citraconic acid monoalkylcycloalkyl esters, preferably monomethylcyclopentyl citraconate, and monoethylcyclohexyl citraconate;

[0394] citraconic acid mono aryl ester, preferably monophenyl citraconate;

[0395] citraconic acid mono benzyl ester, preferably monobenzyl citraconate;

[0396] itaconic acid mono alkyl esters, preferably monomethyl itaconate, monoethyl itaconate, monopropyl itaconate, and mono n-butyl itaconate;

[0397] itaconic acid monocycloalkyl esters, preferably monocyclopentyl itaconate, monocyclohexyl itaconate, and monocycloheptyl itaconate;

[0398] itaconic acid monoalkylcycloalkyl esters, preferably monomethylcyclopentyl itaconate, and monoethylcyclohexyl itaconate;

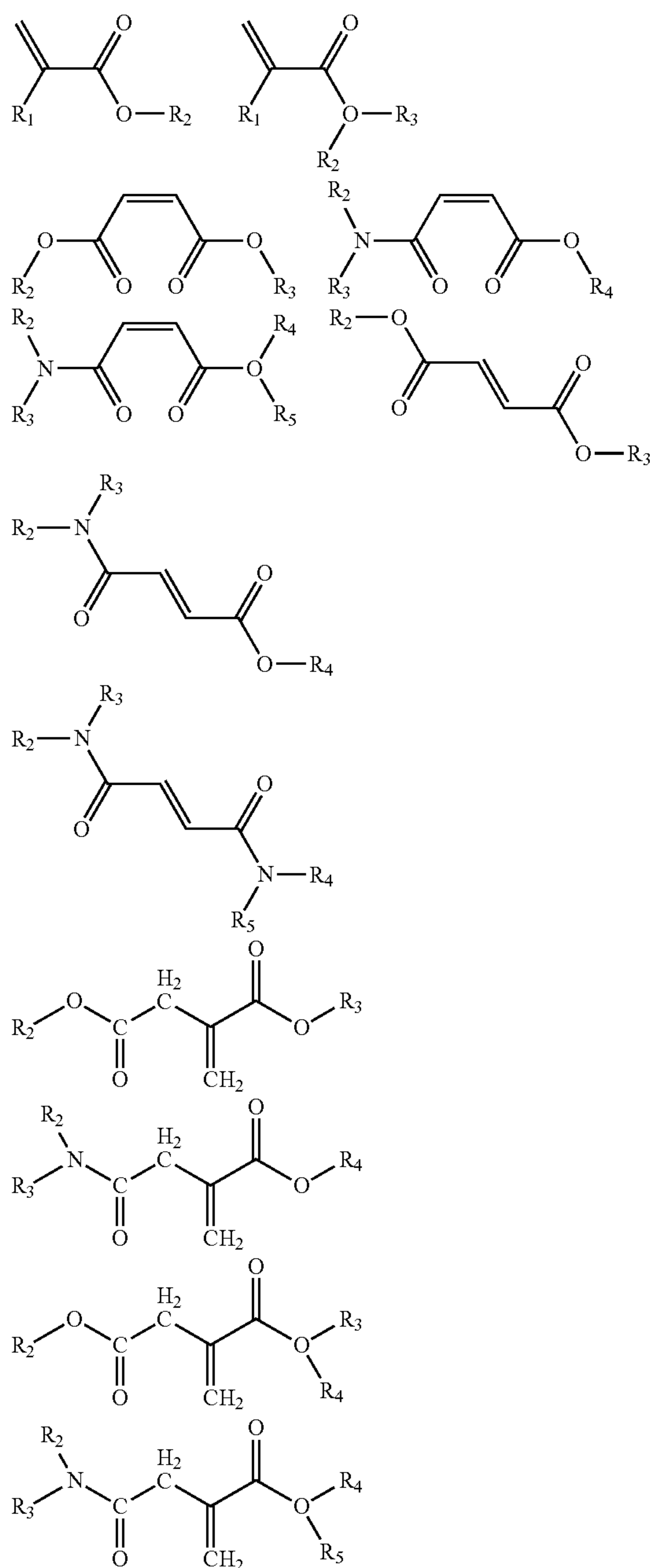
[0399] itaconic acid mono aryl ester, preferably monophenyl itaconate;

[0400] itaconic acid mono benzyl ester, preferably monobenzyl itaconate.

[0401] As α,β -ethylenically unsaturated dicarboxylic acid diester monomers the analogous diesters based on the above explicitly mentioned mono ester monomers may be used, wherein, however, the two organic groups linked to the $C=O$ group via the oxygen atom may be identical or different.

[0402] As further termonomers vinyl aromatic monomers like styrol, α -methylstyrol and vinylpyridine, as well as non-conjugated dienes like 4-cyanocyclohexene and 4-vinylcyclohexene, as well as alkynes like 1- or 2-butine may be used.

[0403] Particularly preferred are termonomers chosen from the below depicted formulae:



where

[0404] R^1 is hydrogen or methyl group, and

[0405] R^2, R^3, R^4, R^5 are identical or different and may represent H, C_1 - C_{12} alkyl, cycloalkyl, alkoxyalkyl, hydroxyalkyl, epoxyalkyl, aryl, heteroaryl.

[0406] The proportions of conjugated diene and α,β -unsaturated nitrile in the NBR polymers to be used can vary within wide ranges. The proportion of the conjugated diene or the sum of conjugated dienes is usually in the range from 40 to 90% by weight, preferably in the range from 60 to 85% by weight, based on the total polymer. The proportion of α,β -unsaturated nitrile or the sum of α,β -unsaturated nitriles is usually from 10 to 60% by weight, preferably from 15 to 40% by weight, based on the total polymer. The proportions of the monomers in each case add up to 100% by weight. The additional monomers can be present in amounts of from 0 to 40% by weight, preferably from 0.1 to 40% by weight, particularly preferably from 1 to 30% by weight, based on the total polymer. In this case, corresponding proportions of the conjugated diene or dienes and/or the α,β -unsaturated nitrile or nitriles are replaced by proportions of the additional monomers, with the proportions of all monomers in each case adding up to 100% by weight.

[0407] The preparation of the nitrile rubbers by polymerization of the abovementioned monomers is adequately known to those skilled in the art and is comprehensively described in the literature. Nitrile rubbers which can be used for the purposes of the invention are also commercially available, e.g. as products from the product range of the Perbunan® and Krynac® grades of Lanxess Deutschland GmbH.

[0408] The nitrile rubbers to be hydrogenated have a Mooney viscosity (ML1+4 at 100° C.), measured in accordance with ASTM standard D 1646, in the range from 1 to 75, and preferably from 5 to 50. The weight average molecular weight M_w is in the range 2,000-500,000 g/mol, preferably in the range 20,000-400,000. The nitrile rubbers have a polydispersity $PDI=M_w/M_n$, where M_w is the weight average molecular weight and M_n is the number average molecular weight, in the range 1-5. The determination of the Mooney viscosity is carried out in accordance with ASTM Standard D 1646.

[0409] As the metathesis activity of the ruthenium- or osmium-based catalyst used to prepare the catalyst composition according to this invention is not existing in the catalyst composition of the present invention the molecular weight of the hydrogenated nitrile rubber obtained after the hydrogenation is comparable to the original NBR feedstock and not further reduced during hydrogenation.

[0410] Hence, a hydrogenated nitrile rubber with a weight average molecular weight M_w in the range 2,000-500,000 g/mol, preferably in the range 20,000-400,000 is obtained. The Mooney viscosity (ML1+4 at 100° C.), measured in accordance with ASTM standard D 1646, of the hydrogenated nitrile rubbers is in the range from 1 to 150, preferably from 10 to 100. The polydispersity $PDI=M_w/M_n$, where M_w is the weight average molecular weight and M_n is the number average molecular weight, in the range 1-5 and preferably in the range 1.5-4.

[0411] For the purposes of the present invention, hydrogenation is a reaction of the double bonds present in the starting

nitrile rubber to an extent of at least 50%, preferably 70-100%, more preferably 80-100%; even more preferably 90-100%

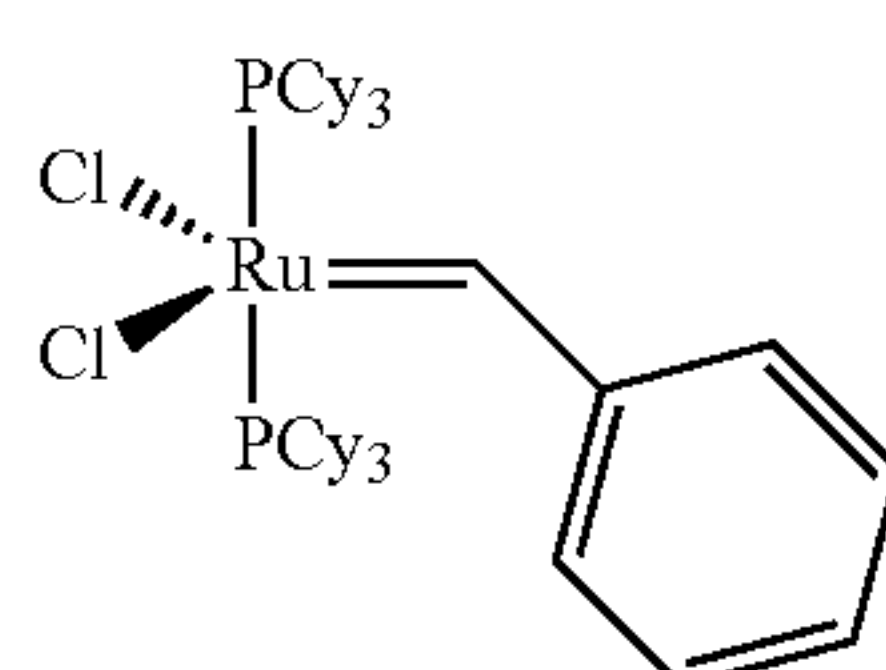
[0412] In the tandem method, the nitrile rubber is firstly degraded using at least one ruthenium- or osmium-based catalyst in the absence or in the presence of a co-olefin. The vinyl compound of general formula (1) is either added when the metathesis reaction has ceased or gone to completion or added before in order to stop the metathesis at a certain degree. Thereafter, the hydrogenation can be carried out to afford hydrogenated nitrile rubber by introducing hydrogen gas. In the sequence of metathesis, catalyst composition formation and hydrogenation, the metathesis degree can be fully controlled and the molecular weight of the final hydrogenated nitrile rubber is adjustable as desired. The nitrile rubbers subjected to metathesis in the tandem method may typically have a Mooney viscosity (ML1+4 at 100° C.), measured in accordance with ASTM standard D 1646, in the range from 30 to 75, and preferably from 30 to 50. The weight average molecular weight Mw is in the range 150,000-500,000 g/mol, preferably in the range 180,000-400,000. These nitrile rubbers have a polydispersity $PDI = Mw/Mn$, where Mw is the weight average molecular weight and Mn is the number average molecular weight, in the range 2 to 6. The determination of the Mooney viscosity is carried out in accordance with ASTM Standard D 1646.

[0413] The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

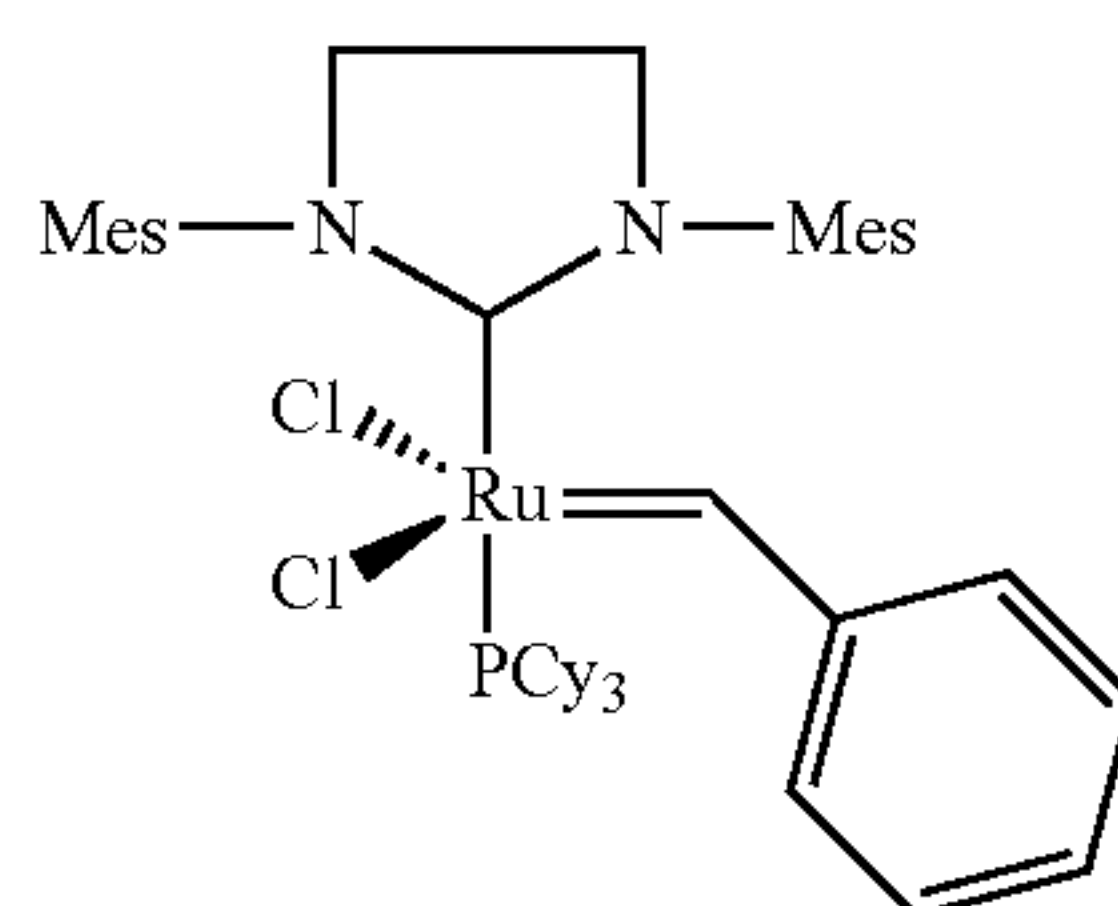
EXAMPLES

Catalysts Used in the Examples

[0414] Catalysts (1) to (3) were purchased from Sigma Aldrich or Strem Chemicals Inc. Catalyst (4) was purchased from Xian Kaili Co. (China). The structures of these catalysts are shown below, wherein “Mes” means mesityl (2,4,6-trimethylphenyl) and “Cy” means cyclohexyl:



(Grubbs I)

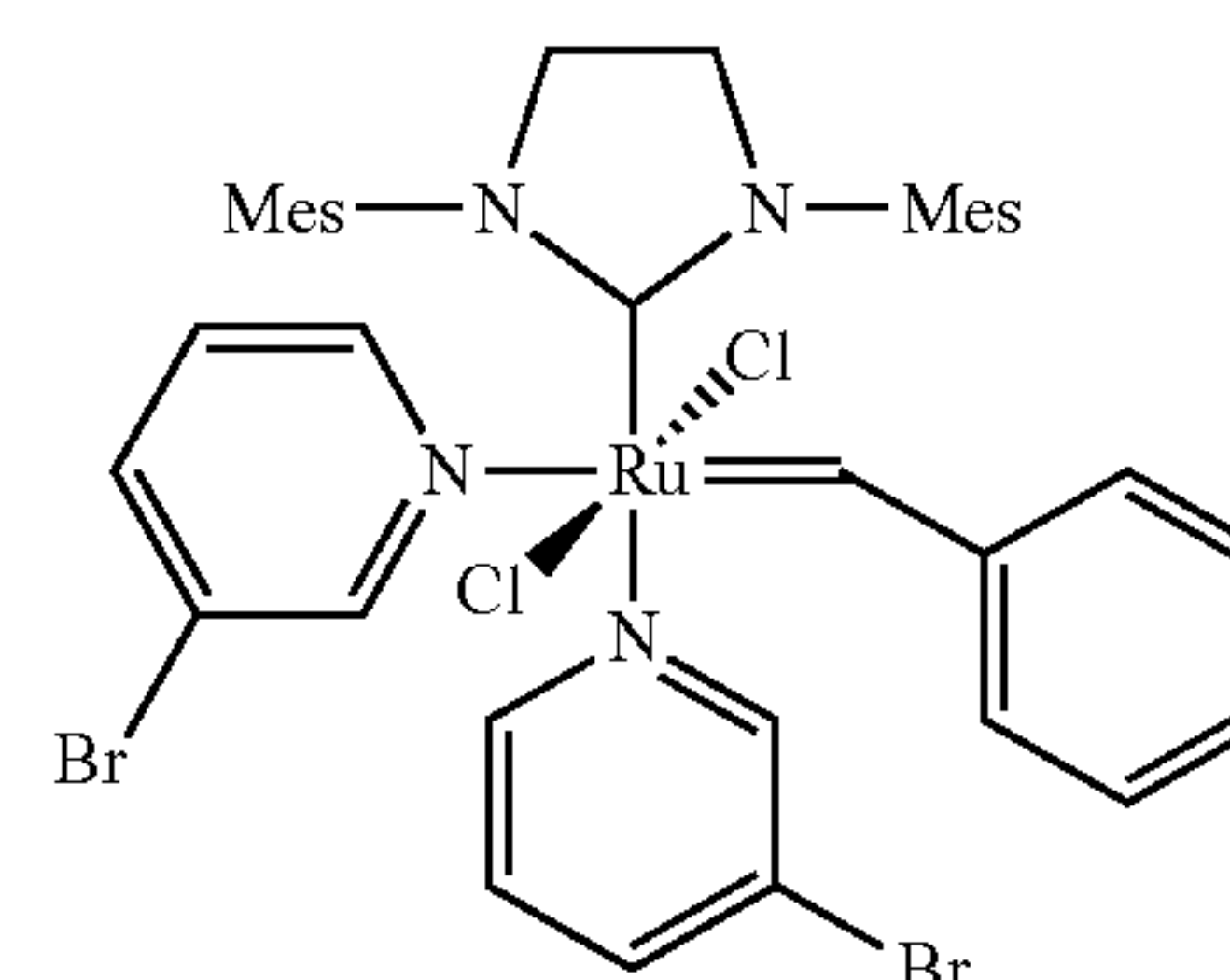


(Grubbs II)

(Catalyst 1)

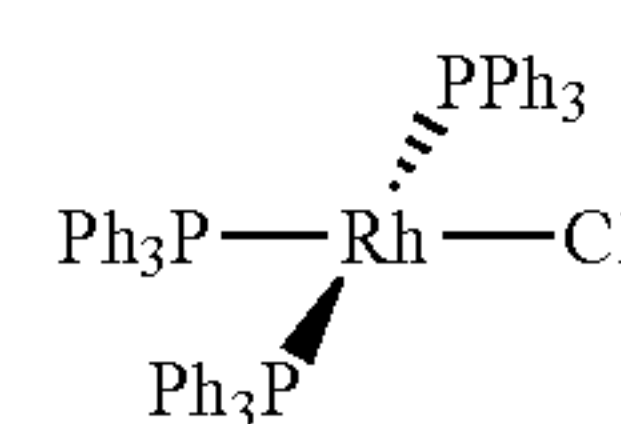
(Catalyst 2)

-continued



(Grubbs III)

(Catalyst 3)



(Wilkinson)

(Catalyst 4)

[0415] These catalysts have the following molecular weights:

catalyst	molecular weight [g/mol]
(1)	822.96
(2)	848.97
(3)	885.55
(4)	925.22

Nitrile Butadiene Rubbers Used in the Examples:

[0416] The nitrile butadiene rubbers used in the examples had the properties outlined in Table 1.

TABLE 1

Nitrile Butadiene Rubbers (NBR) used (“ACN” means acrylonitrile)					
NBR	ACN content % by weight	Mooney viscosity ML(1 + 4) 100° C.	Mn	Mw	PDI
Perbunan® 3431 VP	34	29	77,101	255,395	3.31
NBR-5	34	34	73,711	243,671	3.31
NBR-6	34	34	74,698	249,935	3.35
NBR-7	34	34	70,674	251,292	3.56

[0417] Vinyl ethyl ether (VEE) was purchased from Sigma-Aldrich.

Analytical Tests:

GPC Test:

[0418] The apparent molecular weight Mn and Mw were determined by a Waters GPC system equipped with a Waters 1515 high performance liquid chromatography pump, a Waters 717plus autosampler, a PL gel 10 μm mixed B column and a Waters 2414 RI detector. The GPC test was carried out at 40° C. at 1 mL/min of flow rate with THF as the eluent, and the GPC column was calibrated with narrow PS standard samples.

FT-IR Test:

[0419] The spectrum of nitrile rubber before, during and after the hydrogenation reaction was recorded on a Perkin Elmer spectrum 100 FT-IR spectrometer. The solution of the nitrile butadiene rubber in MCB was cast onto a KBr disk and dried to form a film for the test. The hydrogenation conversion is determined by the FT-IR analysis according to the ASTM D 5670-95 method.

Abbreviations:

[0420] phr: per hundred rubber (weight)
 rpm: revolution per minute
 Mn: number-average molecular weight
 Mw: weight-average molecular weight
 PDI: polydispersity index, defined as Mw/Mn
 PPh₃: triphenylphosphine
 MCB: monochlorobenzene
 VEE: vinyl ethyl ether
 RT: room temperature (22+/-2° C.)

Example 1

Comparison Example, Using Catalyst (4)

[0421] A solution of 18 g Perbunan® 3431VP in 282 g MCB (Perbunan® 3431VP concentration of 6 wt %) was bubbled with nitrogen in a 600 mL Parr autoclave for 30 minutes, and then heated to 120° C. Wilkinson's catalyst (15 mg) and PPh₃ (18 mg) was dissolved in another 22 g of degassed MCB and then added into the reactor. Hydrogenation was conducted under 4.137 MPa of hydrogen pressure and 800 rpm of agitation speed. Samples were taken from the reactor at intervals for FT-IR analysis to determine the hydrogenation degree. After 5 hours of hydrogenation, the hydrogenation degree reached 90.3%, the reactor was cooled to room temperature and the pressure was released. The final molecular weights and PDI were: Mn=76,286, Mw=260,572, PDI=3.42.

Examples 2

Inventive Example; Perbunan 3431VP; Catalyst (1);
VEE as Co-Catalyst

[0422] Catalyst (1) (9 mg) was dissolved in 22 g degassed MCB in a flask. Vinyl ethyl ether (100 μ L) was injected into the flask and the solution was stirred for 12 hours. A solution of 18 g Perbunan® 3431VP in 282 g MCB (Perbunan®3431VP concentration of 6 wt %) was bubbled

with nitrogen in a 600 mL Parr autoclave for 30 minutes, and then heated to 120° C. The catalyst solution in the flask was transferred into the reactor via syringe. Hydrogenation was conducted under 4.137 Mpa of hydrogen pressure and 800 rpm of agitation speed. Samples were taken from the reactor at intervals for FT-IR analysis to determine the hydrogenation degree. After 3 hours of hydrogenation, the hydrogenation degree reached 93%. The final molecular weights and the PDI were: Mn=75,844, Mw=223,863, PDI=2.95.

Example 3

Inventive Example; Perbunan 3431VP; Catalyst (2);
VEE as Co-Catalyst

[0423] All the conditions and operation were the same as in Example 5 except that Catalyst (2) was used (18 mg). The hydrogenation degree at 1 hour was 99%. The final molecular weights and the PDI were: Mn=71,762, Mw=221,604, PDI=3.09.

Example 4

Inventive Example; Perbunan 3431VP; Catalyst (2);
VEE as Co-Catalyst

[0424] All the conditions and operation were the same as in Example 5 except that Catalyst (2) was used (9 mg). The hydrogenation degree at 2 hours was 95%. The final molecular weights and the PDI were: Mn=71,274, Mw=208,575, PDI=2.93.

Example 5

Inventive Example; Perbunan 3431VP; Catalyst (3);
VEE as Co-Catalyst

[0425] All the conditions and operation were the same as in Example 5 except that Catalyst (3) was used (9 mg). The hydrogenation degree at 3 hours was 98%. The final molecular weights and the PDI were: Mn=88,070, Mw=267,466, PDI=3.04.

[0426] The conditions and the results for Example 1-5 are shown in Table 2. In such Table 2 the comparative examples are marked with an asterisk. Furtheron the abbreviation P3431 VP stands for Perbunan® 3431VP. Only for comparison reasons the number and weight average molecular weights as well as PDI has been included at the bottom of Table 2 with regard to the starting nitrile rubber then subjected to hydrogenation in Examples 1 to 5.

TABLE 2

Examples 1 to 5 (for all examples: hydrogenation temperature: 120° C. and pressure: 4.137 MPa)															
Ex	NBR Perbunan® 3431 VP*	MCB (used to dissolve NBR +	catalyst		co-catalyst			Molar ratio	Time	hydrogenation					
	amount	catalyst)	amount		amount			co-catalyst	of pretreatment	time	degree	Mn	Mw	PDI	
	[g]	[g]	no.	[mg]	[mmol]	type	[mg]	[mmol]	to catalyst	[h]	[h]	[%]	[g/mol]	[g/mol]	
													HNBR		
1*	18	282 + 22	(4)	15	0.0162	PPh ₃	18			0	5	90.3	76,286	260,572	3.42
2	18	282 + 22	(1)	18	0.0219	VEE	75	1.04	47.5	12	3	93	75,844	223,863	2.95
3	18	282 + 22	(2)	18	0.0212	VEE	75	1.04	49.1	12	1	99	71,762	221,604	3.09

TABLE 2-continued

Examples 1 to 5 (for all examples: hydrogenation temperature: 120° C. and pressure: 4.137 MPa)															
Ex	NBR Perbunan ® 3431 VP*	MCB (used to dissolve NBR + catalyst)	catalyst			co-catalyst			Molar ratio	Time	hydrogenation			Mn	Mw
	amount		amount			amount			co-catalyst	of pretreatment	time	degree			
	[g]	[g]	no.	[mg]	[mmol]	type	[mg]	[mmol]	to catalyst	[h]	[h]	[%]	[g/mol]	[g/mol]	PDI
4	18	282 + 22	(2)	9	0.0106	VEE	75	1.04	98.1	12	2	95	71,274	208,575	2.93
5	18	282 + 22	(3)	9	0.0102	VEE	75	1.04	102.3	12	3	98	88,070	267,466	3.04
													*Perbunan ® 3431 VP		
													77,101	255,395	3.31

Example 6

Comparison Example: NBR-5; Catalyst (2); First Metathesis, No Additional Treatment with a Co-Catalyst, then Hydrogenation

[0427] A solution of 270 g NBR-5 in 4,350 g MCB was bubbled with nitrogen in a 10 L Parr autoclave for 30 minutes. 11.1 g 1-hexene dissolved in 50 g degassed MCB were added into the reactor and the mixture was stirred for 1 hour. Catalyst (2) (135 mg) was dissolved in another 100 g of degassed MCB, added into the reactor and metathesis was conducted for 1 hour. Then the reactor was heated to 140° C. and hydrogenation was conducted under 8.4 MPa of hydrogen pressure and 600 rpm of agitation speed. Samples were taken from the reactor at intervals for FT-IR analysis to determine the hydrogenation degree. After 2 hours of hydrogenation, the hydrogenation degree reached 99.5%. The final molecular weights and the PDI were: Mn=4,648, Mw=9,952, PDI=2.14.

Example 7

Inventive; NBR-6; Catalyst (2); Treatment with VEE as Co-Catalyst; Thereafter Hydrogenation

[0428] Catalyst (2) (135 mg) was dissolved in 100 g degassed MCB in a flask. Vinyl ethyl ether (0.75 g) was injected into the flask and the solution was stirred under nitrogen for 12 hours at room temperature. A solution of 270 g NBR-6 in 4,350 g MCB was bubbled with nitrogen in 10 L Parr autoclave for 30 minutes, and then heated to 140° C. The catalyst solution in the flask was transferred into the reactor and 11.1 g 1-hexene dissolved in 50 g degassed MCB were added into the reactor. Hydrogenation was conducted under 8.4 MPa of hydrogen pressure and 600 rpm of agitation speed. Samples were taken from the reactor at intervals for FT-IR analysis to determine the hydrogenation degree. After 3 hours of hydrogenation, the hydrogenation degree reached 99.4%. The final molecular weights and the PDI were: Mn=92,462, Mw=258,405, PDI=2.79.

Examples 8-10

Inventive, NBR-6, Catalyst (2); Metathesis, Treatment with VEE as Co-Catalyst and Subsequent Hydrogenation

[0429] A solution of 560 g NBR-6 in 4,516 g MCB (NBR-6 concentration of 11 wt %) was bubbled with nitrogen in a 10 L Parr autoclave for 30 minutes. 23.1 g 1-hexene dissolved in 50 mL degassed MCB were added into the reactor and the mix-

ture was stirred for 1 hour. Catalyst (2) (280 mg) was dissolved in 100 g of degassed MCB at room temperature and then added into the reactor. The metathesis was allowed to conduct for 15 min at room temperature. Then 1.55 g of VEE dissolved in 200 g degassed MCB was added into the autoclave. After stirring for 1 hour, a sample was taken from the reactor for GPC analysis. The temperature of the autoclave was elevated to 140° C. Then the hydrogen gas was introduced into the autoclave. Hydrogenation was conducted under 8.4 MPa of hydrogen pressure and 600 rpm of agitation speed. Samples were taken from the reactor at intervals for FT-IR analysis to determine the hydrogenation degree. The molecular weights and the PDI after the addition of VEE are given in the following Table 4. After 2 hours of hydrogenation, the hydrogenation degree reached 99.8% and 99.7% respectively as shown in Table 4. The final molecular weights and the PDI are given in the following Table 3.

Example 11

Comparison Example; NBR-7; Using Catalyst (2) without Pre-Treatment

[0430] Catalyst (2) (363 mg) was dissolved in 100 g degassed MCB in a cylinder. A solution of 518 g NBR-7 dissolved in MCB (a solid concentration of 13 wt % of NBR solution) was bubbled with nitrogen in a 10 L autoclave for 30 minutes, and then heated to 140° C. The catalyst solution in the cylinder was pressured into the reactor with hydrogen gas. Hydrogenation was conducted under 8.4 MPa of hydrogen pressure and 600 rpm of agitation speed. Samples were taken from the reactor at intervals for FT-IR analysis to determine the hydrogenation degree. After 4 hours of hydrogenation, the hydrogenation degree reached >99%. The final molecular weights and the PDI were: Mn=48,564, Mw=127,044, PDI=2.60.

Example 12

Inventive Example; NBR-7; Catalyst (2); VEE as Co-Catalyst

[0431] Catalyst (2) (259 mg) was dissolved in 100 g degassed MCB in a cylinder. Vinyl ethyl ether (1.41 g) was injected into the cylinder and the solution was stirred at room temperature for 1 hour. A solution of 518 g NBR-7 dissolved in MCB (a solid concentration of 13 wt % of NBR solution) was bubbled with nitrogen in a 10 L autoclave for 30 minutes, and then heated to 140° C. The pre-treated catalyst solution in the cylinder was pressured into the reactor with hydrogen gas.

Hydrogenation was conducted under 8.4 Mpa of hydrogen pressure and 600 rpm of agitation speed. Samples were taken from the reactor at intervals for FT-IR analysis to determine the hydrogenation degree. After 4 hours of hydrogenation, the hydrogenation degree reached >99%. The final molecular weights and the PDI were: Mn=82,973, Mw=261,751, PDI=3.20.

[0432] The examples in this section show that HNBR can be prepared by hydrogenation of NBR in the presence of a catalyst composition which is obtained by contacting a metathesis catalyst with a specific co-catalyst wherein such contacting or pretreatment of the catalyst with the co-catalyst is conducted either separately (see Ex. 2-5 and Ex. 7) or following a metathesis reaction in-situ in the reaction mixture before the addition of hydrogen (see Ex. 8 to 10). The metathesis activity of the catalyst is controlled by contacting the catalyst with the co-catalyst and thereby preparing the catalyst composition according to the invention. Thus the molecular

weight of the HNBR obtained by the hydrogenation using the catalyst composition according to the invention is comparable to the original NBR feedstock. This is clearly shown e.g. by Ex. 7 in which 1-hexene which is known as typical co-olefine to enhance metathesis reactions was added to the hydrogenation reaction, but nevertheless no methathesis occurred and the average molecular weights Mn and Mw of the HNBR obtained are nearly identical to the respective values of the starting NBR. Further, the non-inventive Ex. 11* and the inventive Ex. 12 show that, with the catalyst composition which is obtained by contacting a metathesis catalyst with a specific co-catalyst, the same hydrogenation rate can be achieved by using lower loading of the metathesis catalyst (Ex. 12: 259 mg Grubbs II catalyst vs. Ex 11*: 363 mg Grubbs II catalyst). Therefore, besides controlling the metathesis activity of the metathesis catalyst, it is surprisingly found that, by using such catalyst composition, the hydrogenation activity of the catalyst also be promoted/improved.

TABLE 3

Reaction conditions and results of Examples 6 to 10 (1-hexene as co-catalyst for metathesis: 4.0 phr, hydrogenation pressure: 8.4 MPa, hydrogenation temperature: 140° C., hydrogenation time: 2 h)									
Ex	NBR	MCB to solve NBR, catalyst and co-catalyst	Catalyst (2)		Step 1: Metathesis	Co-catalyst for pretreating the catalyst			Molar ratio co-catalyst to
	amount	amount	amount		time	amount			catalyst
	[g]	[g]	[mg]	[mmol]	[h]	type	[g]	[mmol]	
6*	270 NBR-5	4500	135	0.1590	1	—	—	—	—
7	270 NBR-6	4500	135	0.1590	—	VEE	0.75	10.34	65
8	560 NBR-6	4666	280	0.3298	0.25	VEE	1.55	21.49	65
9	560 NBR-6	4666	280	0.3298	0.25	VEE	2.38	33.01	100
10	560 NBR-6	4666	280	0.3298	0.25	VEE	0.95	13.17	40
11*	518 NBR-7	3567	363	0.4276	—	—	—	—	—
12	518 NBR-7	3567	259	0.3051	—	—	—	—	64

Ex	Pretreatment Catalyst time [h]		Mn [g/mol]	Mw [g/mol]	PDI	Hydrogenation degree [%]
HNBR						
6*	—	after metathesis	14,360	34,287	2.39	0
		after hydrogenation	4,648	9,952	2.14	99.5
7	12	after hydrogenation	74,698	258,405	2.79	99.4
8	1	after metathesis and VEE addition	54,576	147,365	2.70	0
		after hydrogenation	61,976	168,310	2.72	99.8
9	1	after metathesis and VEE addition	56,499	138,269	2.45	0
		after hydrogenation	62,402	155,444	2.49	99.7
10	1	after metathesis and VEE addition	56,127	137,659	2.45	0
		after hydrogenation	64,608	163,139	2.52	99.7
11*	—	after hydrogenation	48,564	127,044	2.60	>99
12	1	after hydrogenation	82,973	261,751	3.20	>99

TABLE 3-continued

Reaction conditions and results of Examples 6 to 10 (1-hexene as co-catalyst for metathesis: 4.0 phr, hydrogenation pressure: 8.4 MPa, hydrogenation temperature: 140° C., hydrogenation time: 2 h)				
	NBR			
NBR-5	73,711	243,671	3.31	
NBR-6	74,698	249,935	3.35	
NBR-7	70,674	251,292	3.56	

What is claimed is:

1. A catalyst composition obtainable by contacting a complex catalyst based on ruthenium or osmium as central metal and bearing at least one ligand which is bound to the ruthenium or osmium central metal in a carbene-like fashion with at least one co-catalyst in a molar ratio of the complex catalyst to the co-catalyst in a range of from 1:(20-550) wherein the co-catalyst must contain at least one vinyl group.

2. The catalyst composition according to claim 1 wherein the co-catalyst has the general formula (1)



in which R and R' are identical or different and shall mean hydrogen or

OR¹ wherein R¹ shall mean alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or heteroaryl, C(=O)(R²), —C(=O)N(R²)₂, —[(CH₂)_n—X]_mR², —[(CH₂)_n—X]_m—CH=CH₂, or —(CH₂)_n—C(R³)₂R⁴

wherein

X is identical or different and means oxygen (O) or NR²

R² are identical or different and represent H, alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or heteroaryl,

R^3 are identical or different and represent C_1 - C_5 alkyl or $-(CH_2)_n-O-CH=CH_2$,

R^4 represents $(CH_2)_p-O-CH=CH_2$,

n is in the range of from 1 to 5,

m is in the range of from 1 to 10,

p is in the range of from 0 to 5,

where in the alternative, if R and R' both represent a group OR¹, both R¹ may be linked to each other and together represent a divalent group —(C(R²)₂)_q— with q being 2, 3 or 4 and R² being identical or different and having the above defined meanings, or

SR⁵, SOR⁵, SO₂R⁵ wherein R⁵ represents alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or heteroaryl, or

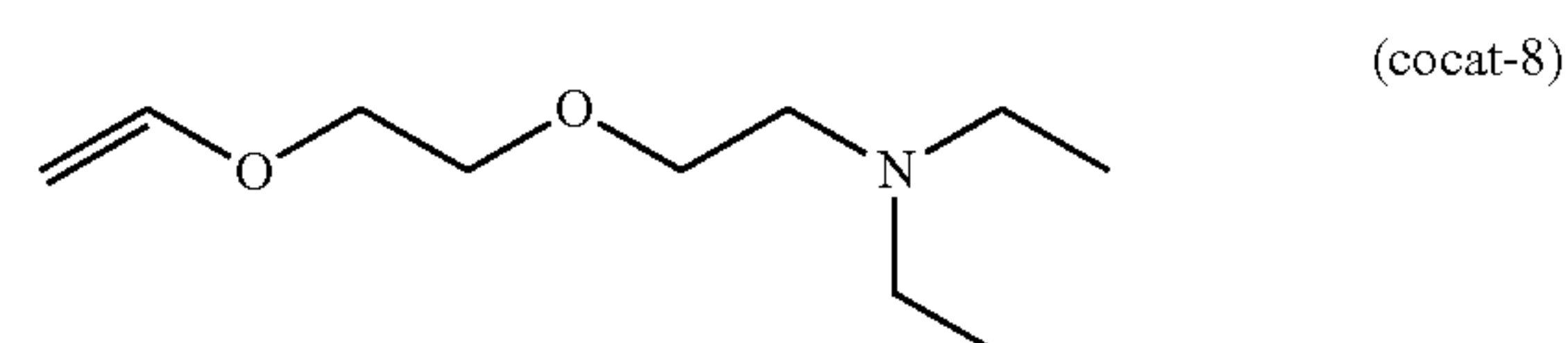
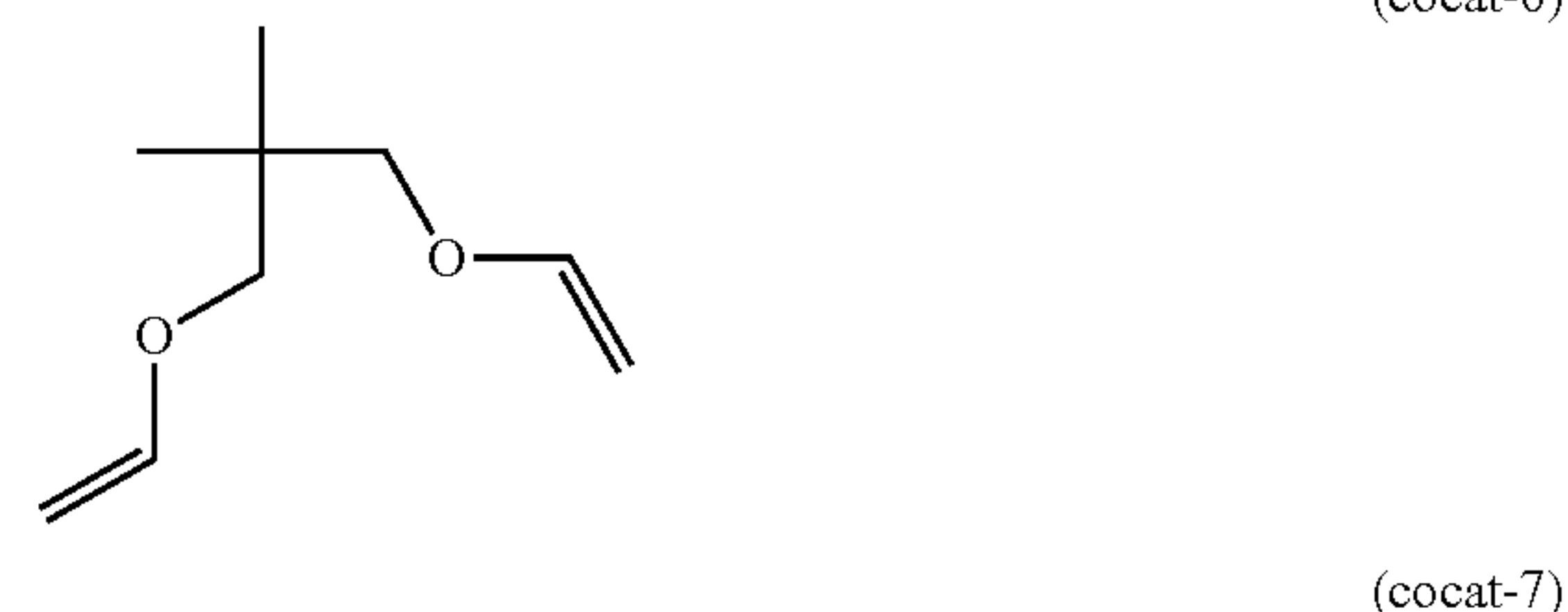
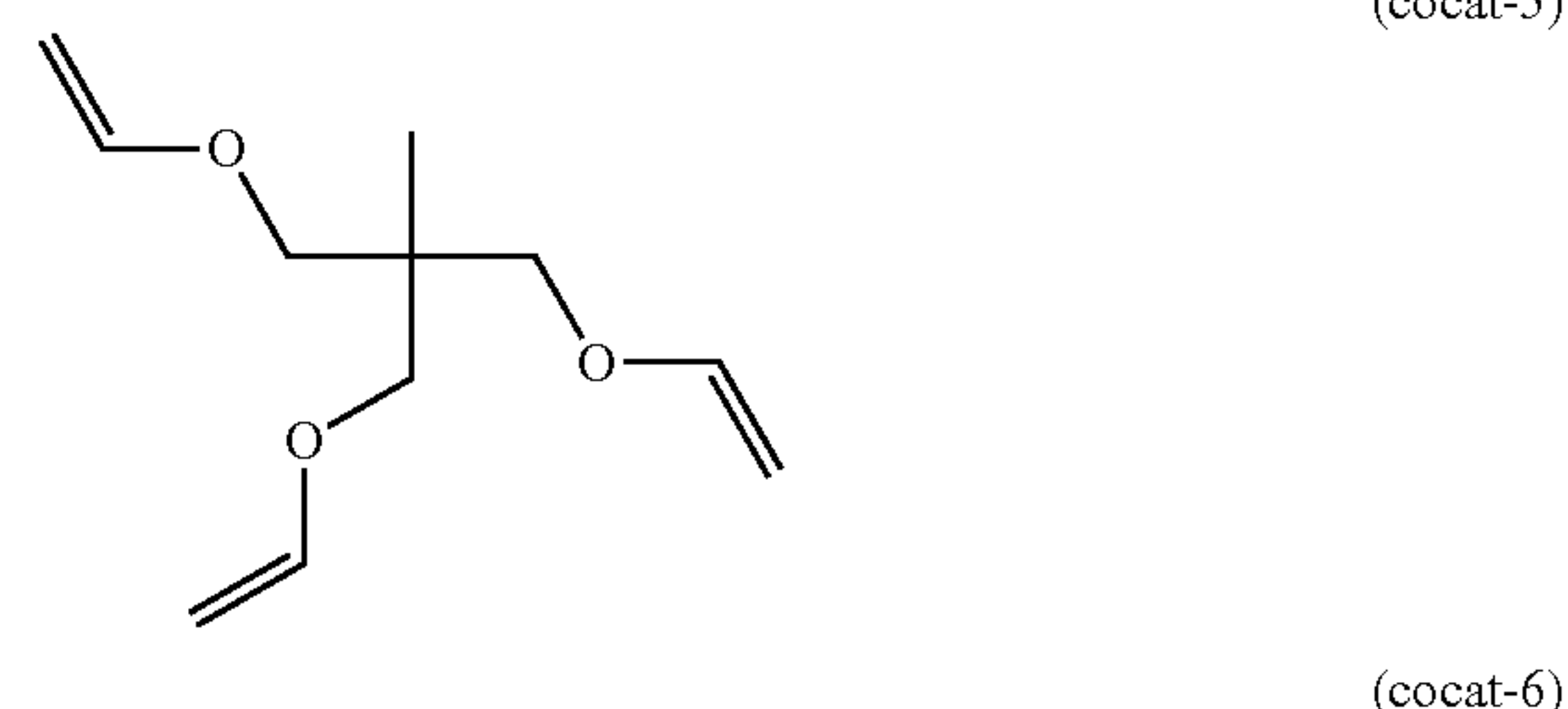
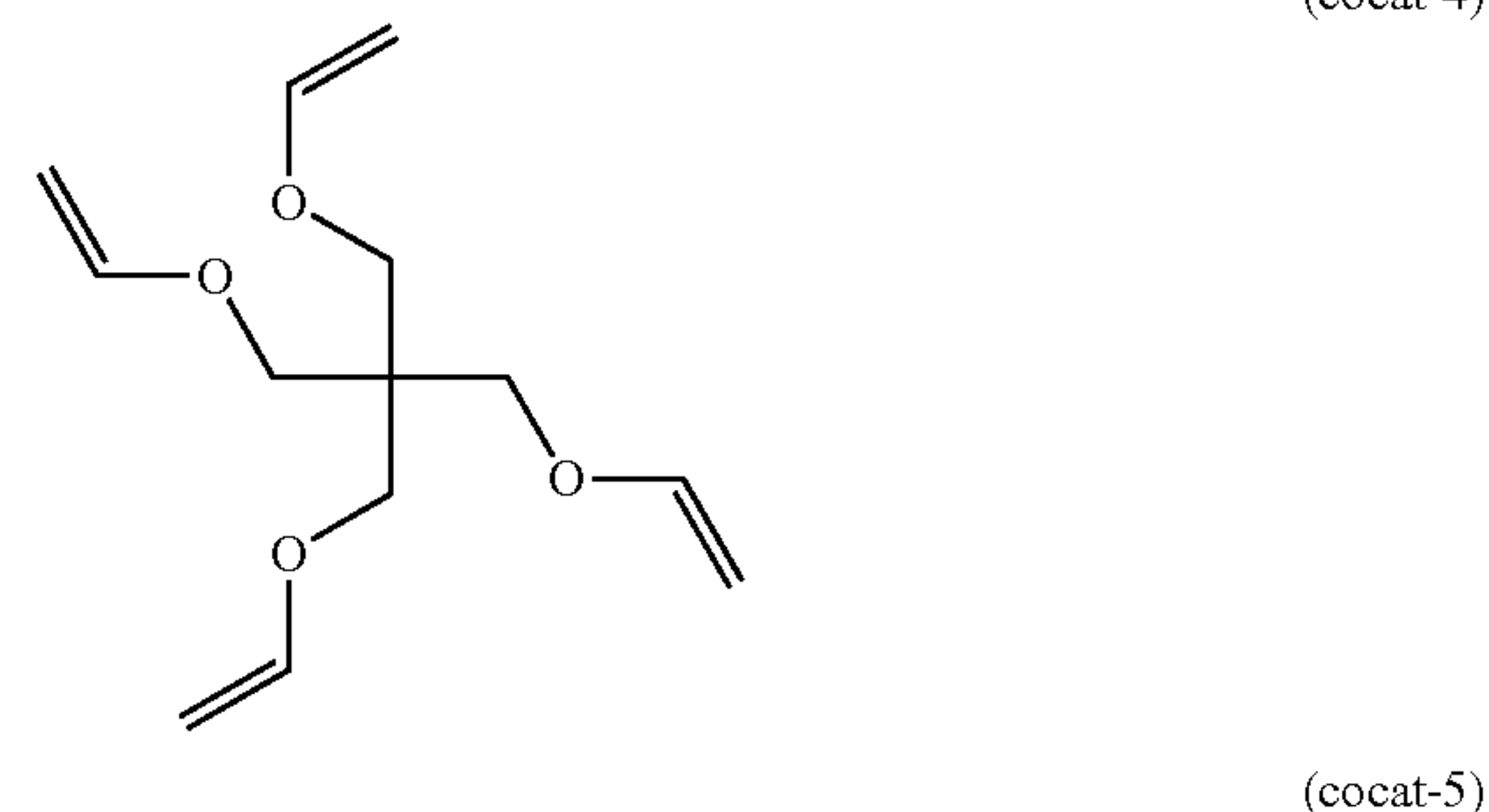
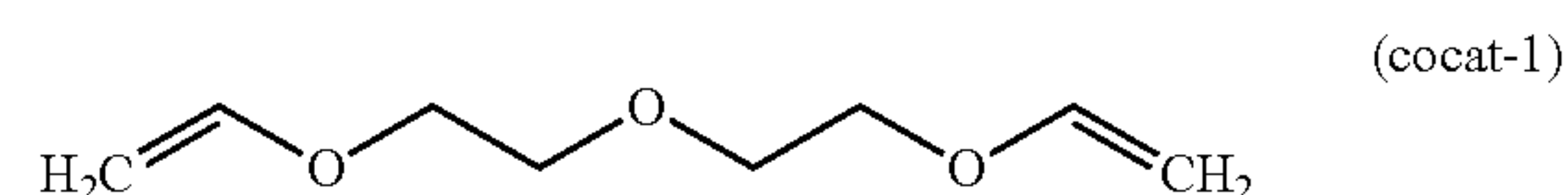
N(R⁶R⁷), P(R⁶R⁷) wherein R⁶ and R⁷ are identical or different and shall mean alkyl, cycloalkyl, alkenyl, alkynyl, aryl, heteroaryl, —C(=O)(R²), or

where in the alternative R⁶ and R⁷ may form together with such N or P atom to which they both are linked at the same time a saturated, unsaturated or aromatic cyclic structure with 4 to 7 carbon atoms in the cyclic structure wherein one, two or three of said carbon atoms can be replaced by a moiety selected from oxygen, sulfur, nitrogen, N—R⁸ or P—R⁸ wherein R⁸ shall mean alkyl, cycloalkyl, alkenyl, alkynyl, aryl, or heteroaryl; or

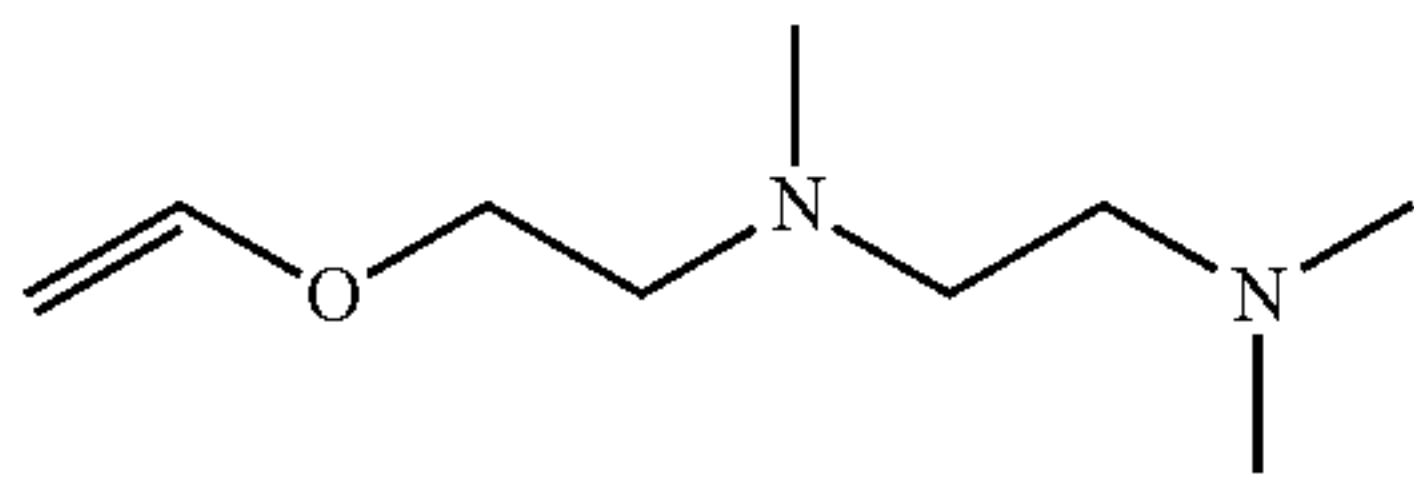
P(=O)(OR⁹)₂ in which R⁹ are identical or different and shall mean alkyl, cycloalkyl, alkenyl, alkynyl, aryl, heteroaryl.

however, under the proviso that R and R' must not both represent hydrogen in formula (1) at the same time.

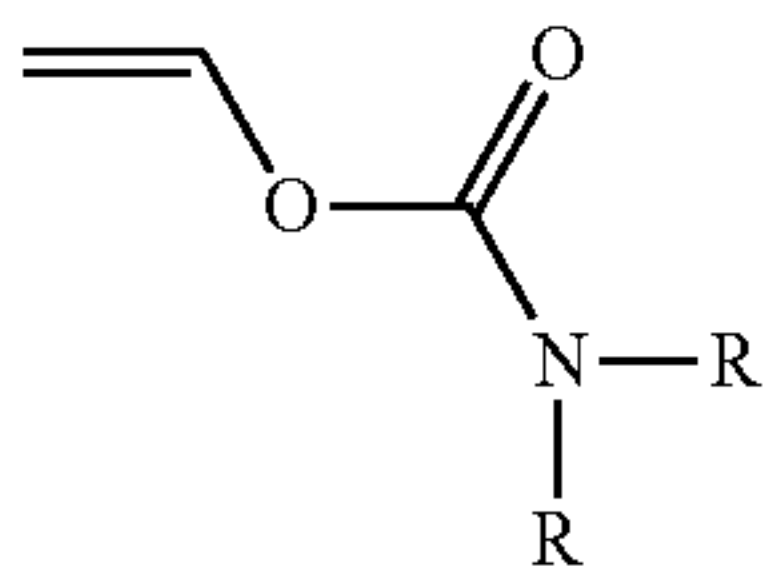
3. The catalyst composition according to claim 1 wherein the co-catalyst is selected from the group consisting of formulae (cocat-1) to (cocat-38).



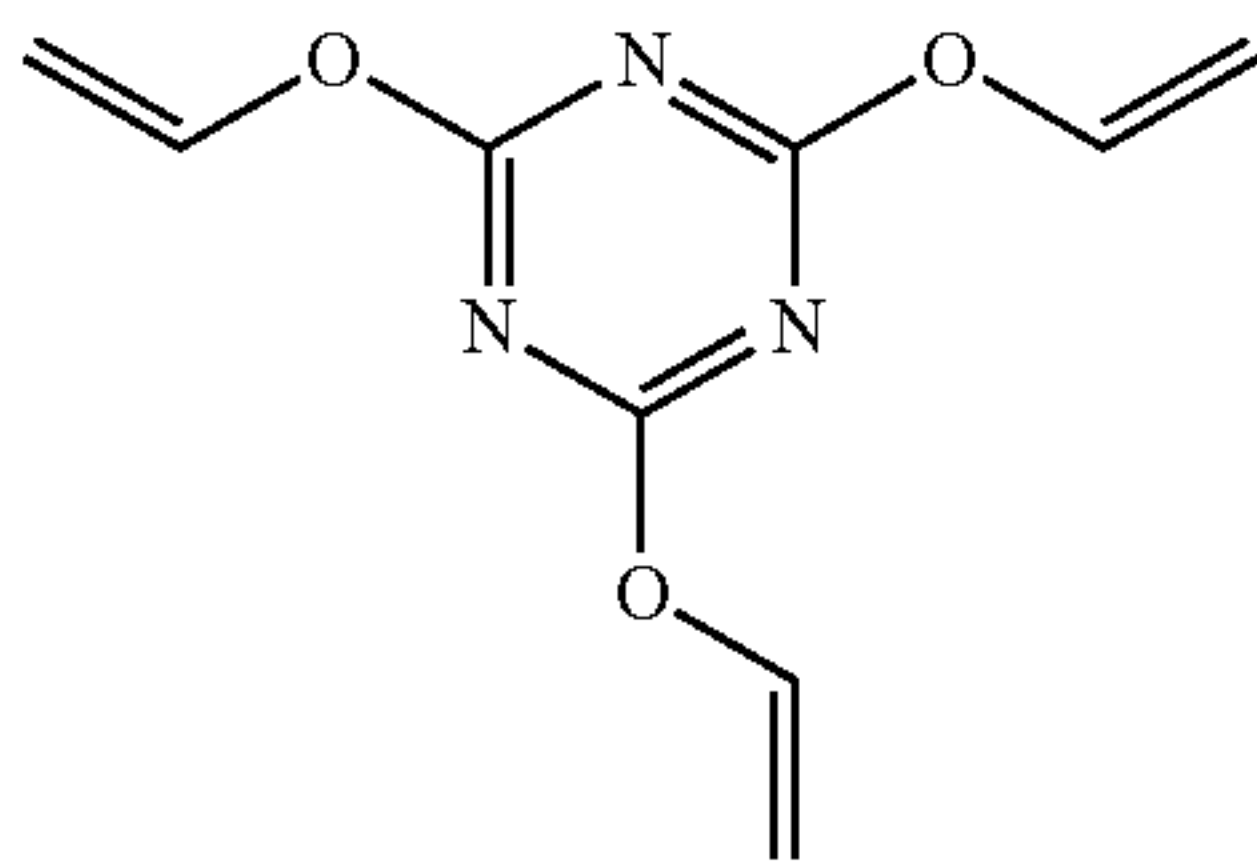
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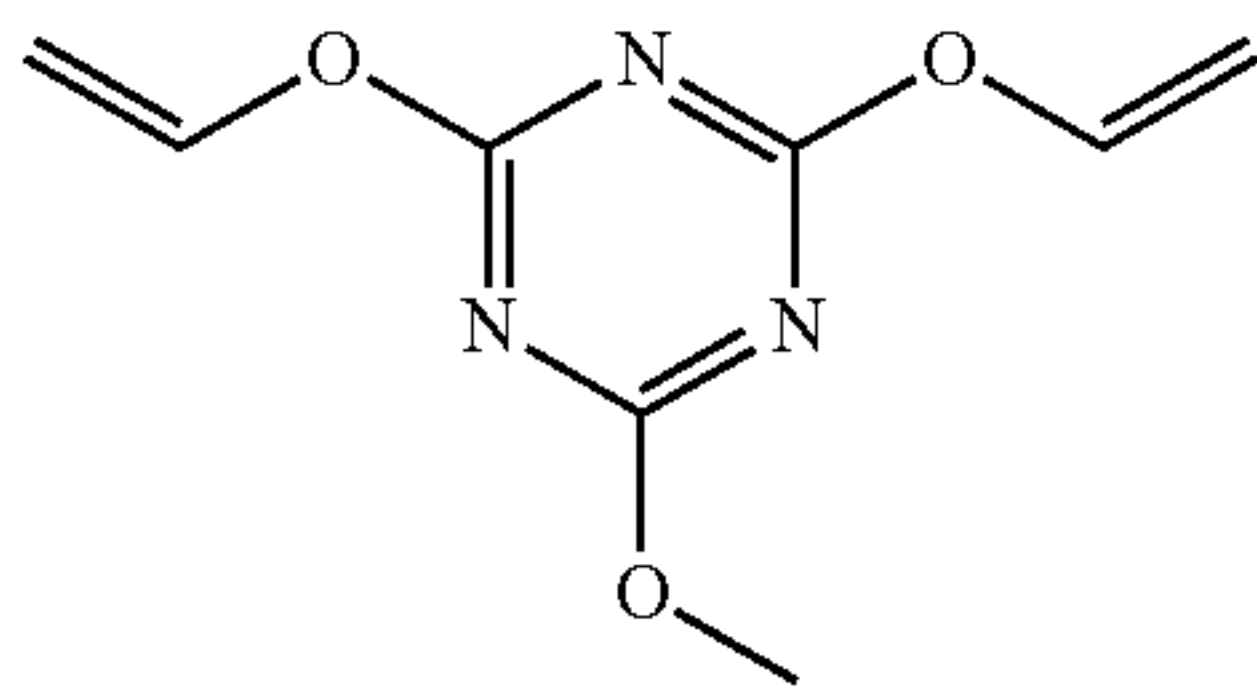
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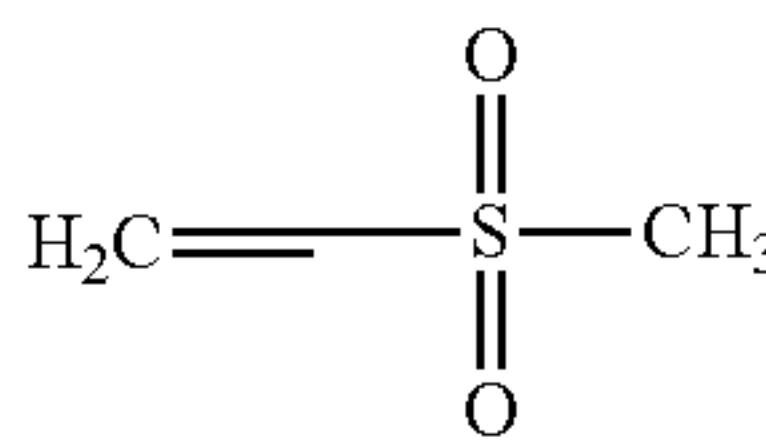
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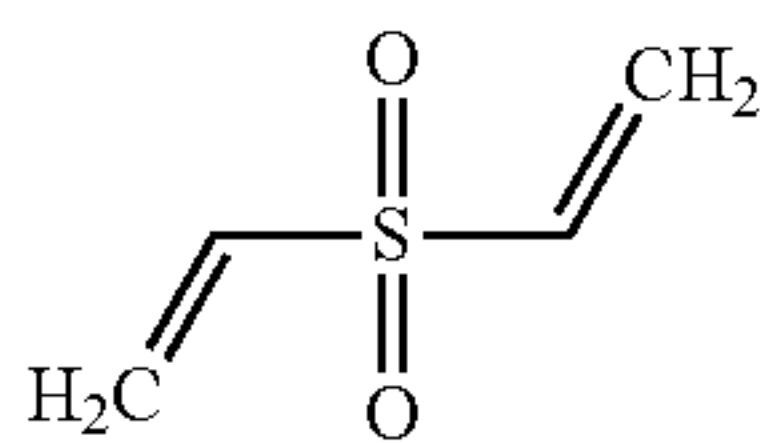
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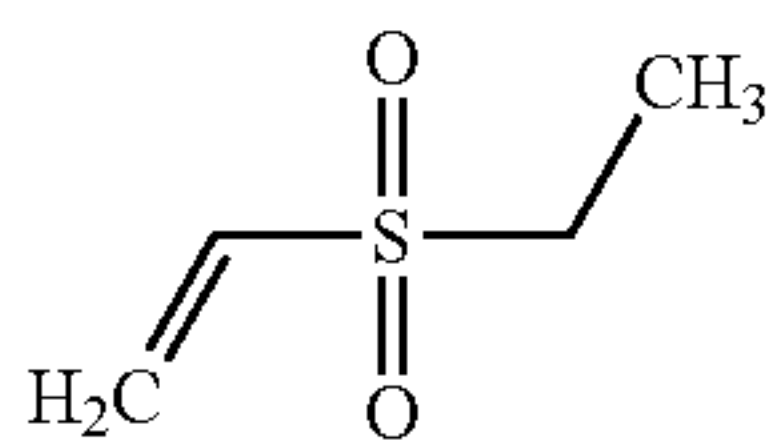
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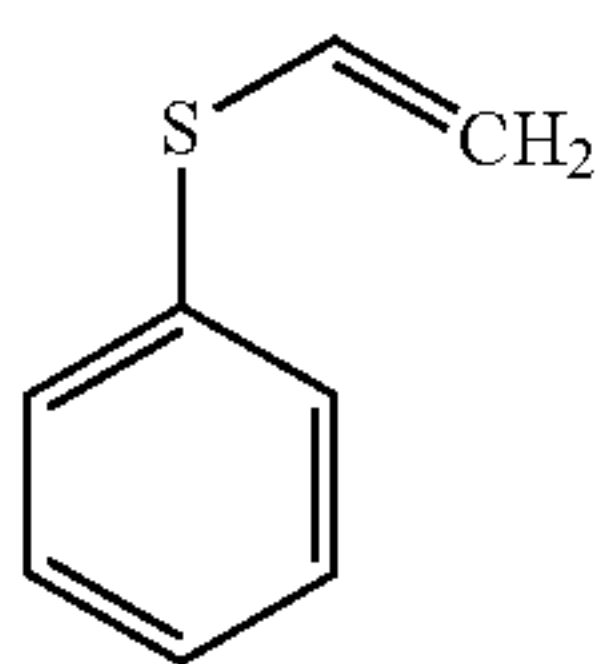
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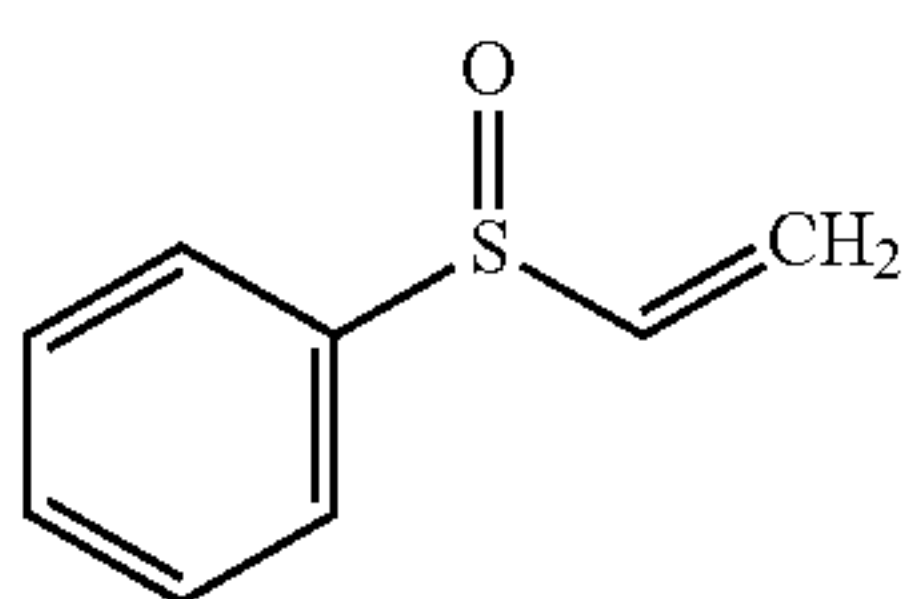
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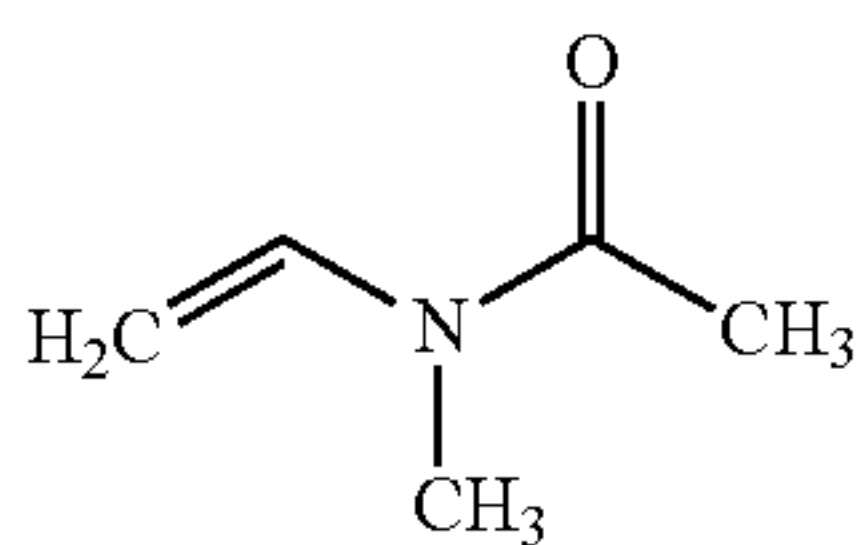
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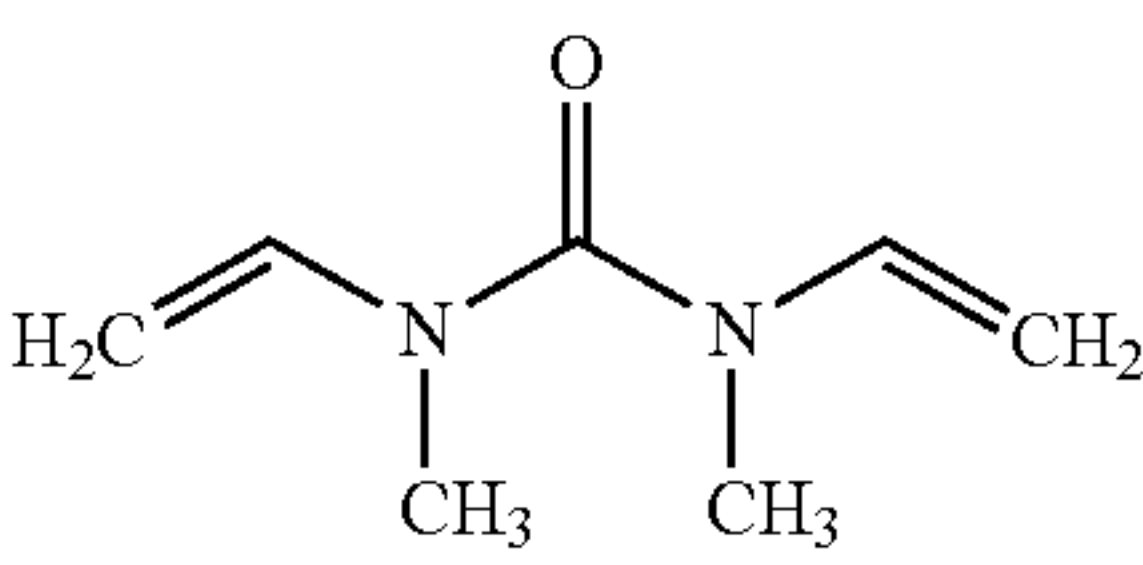


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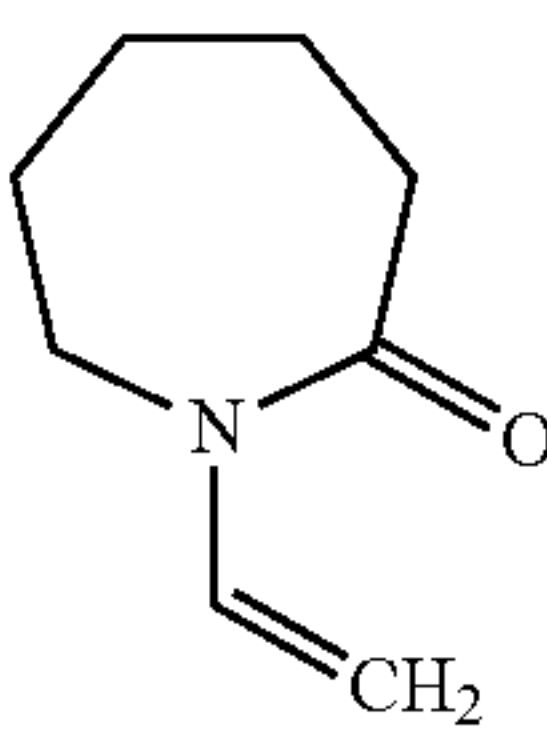


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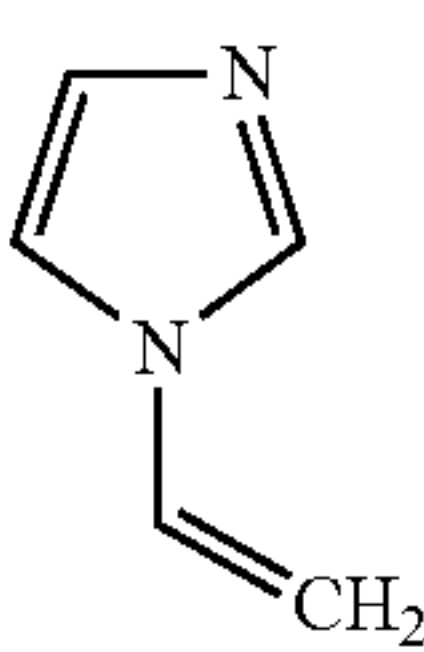
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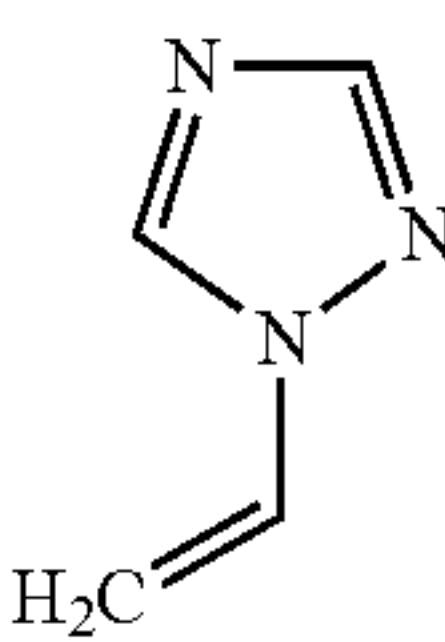
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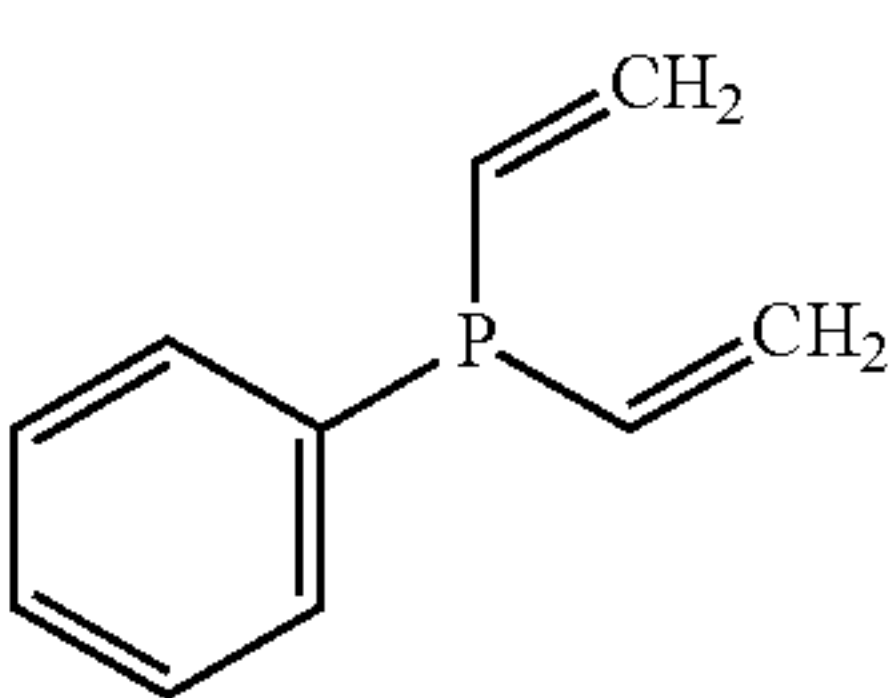
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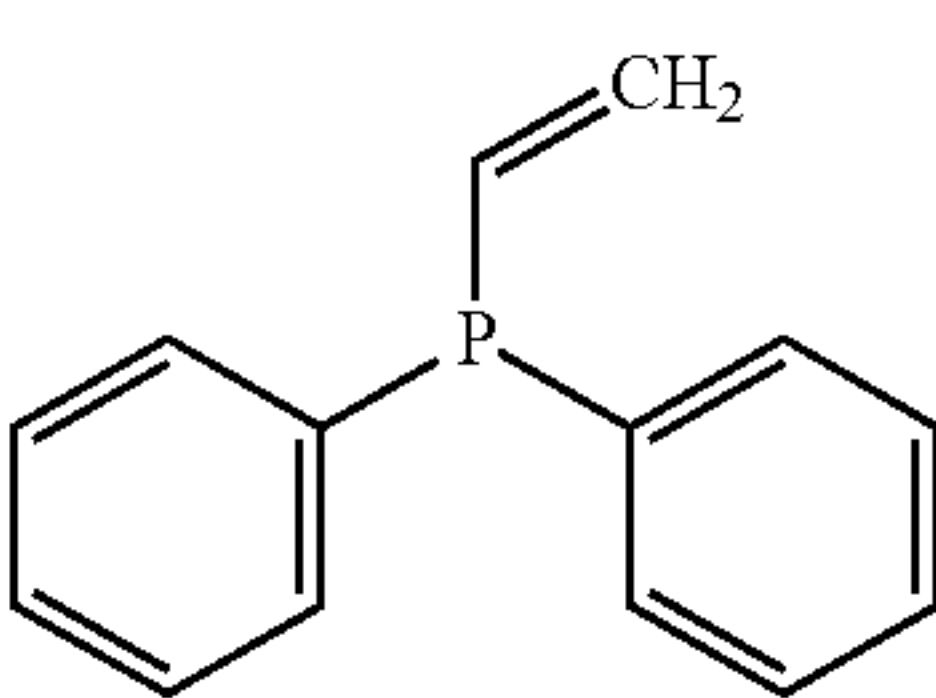
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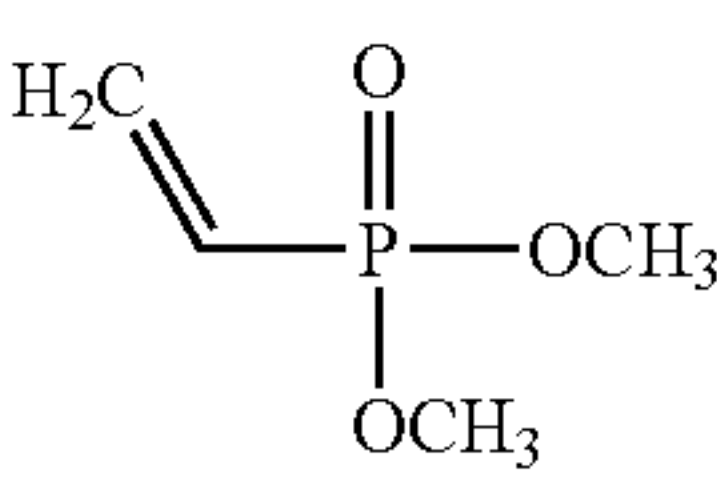
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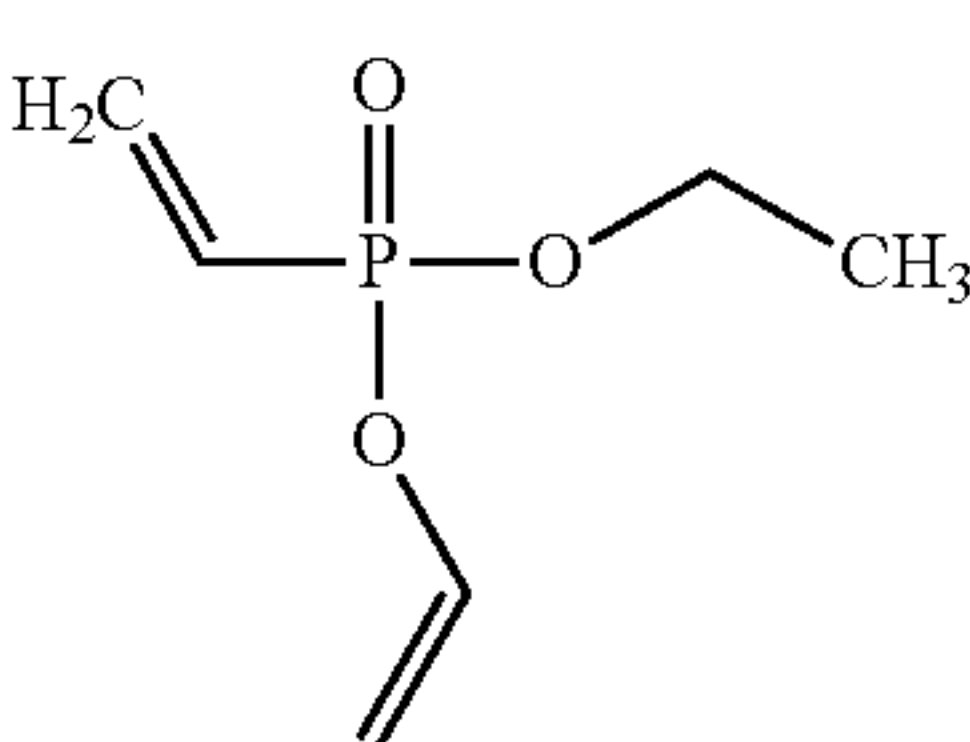
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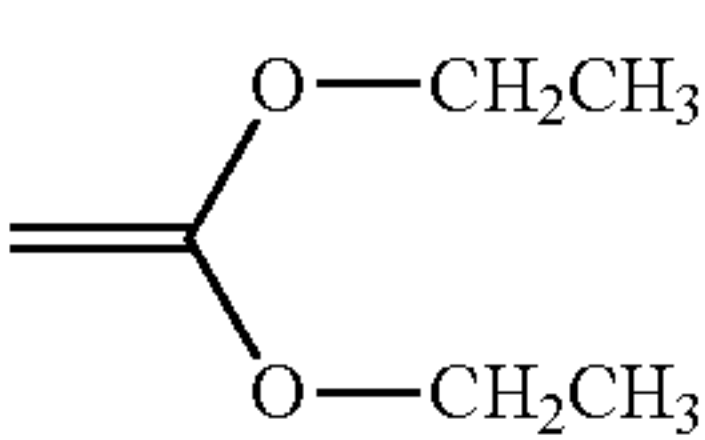
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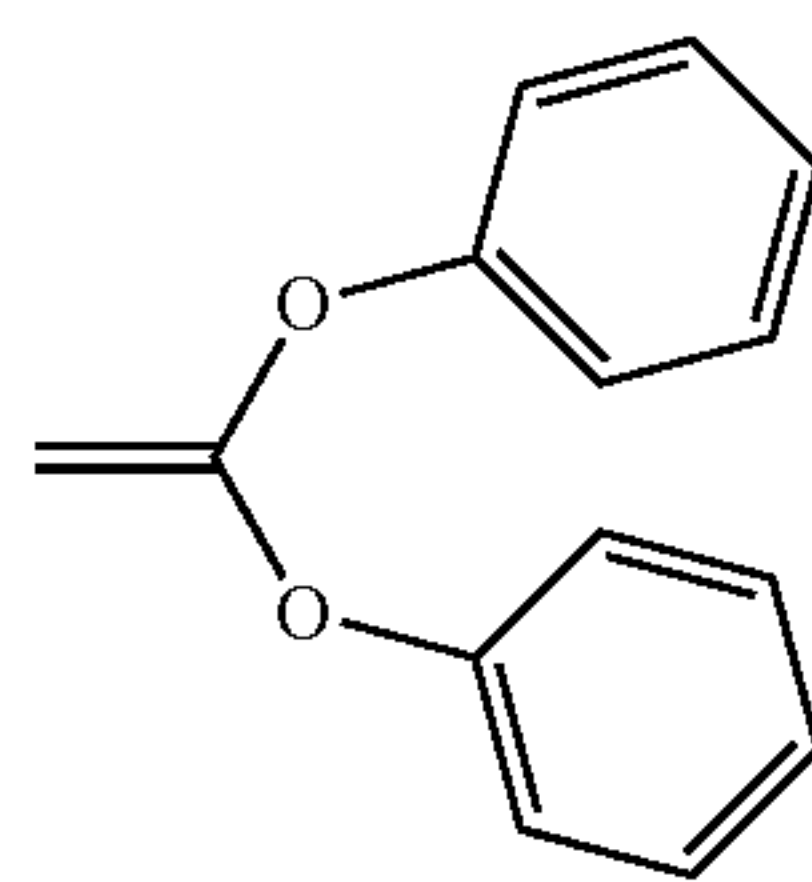


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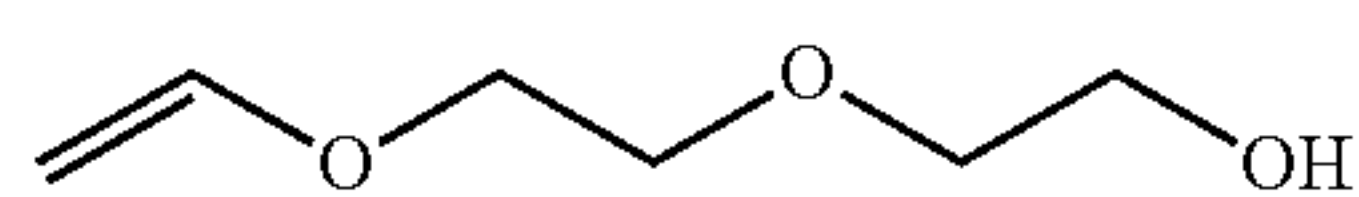


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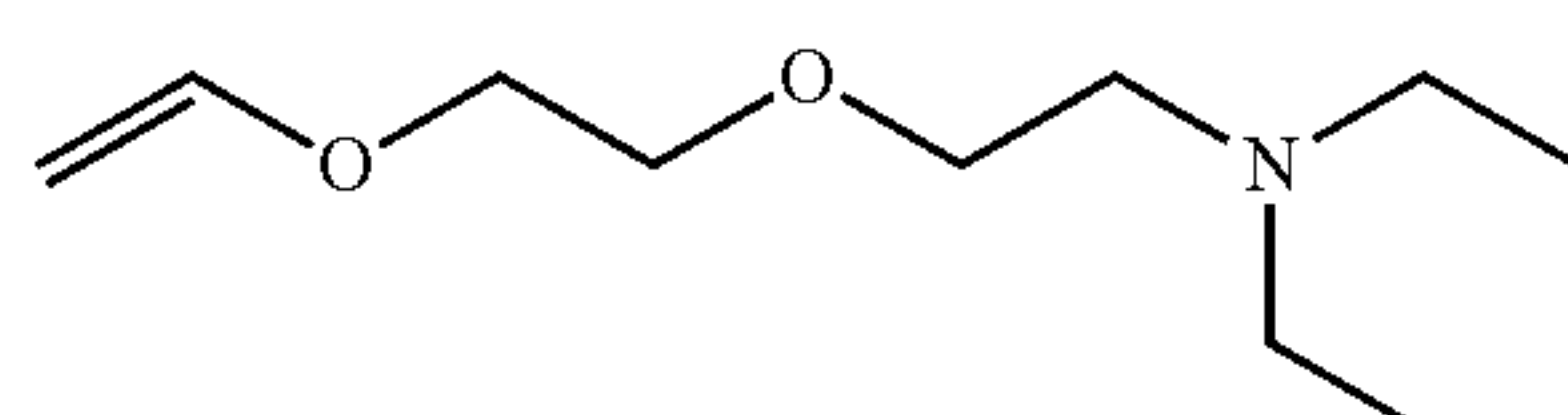
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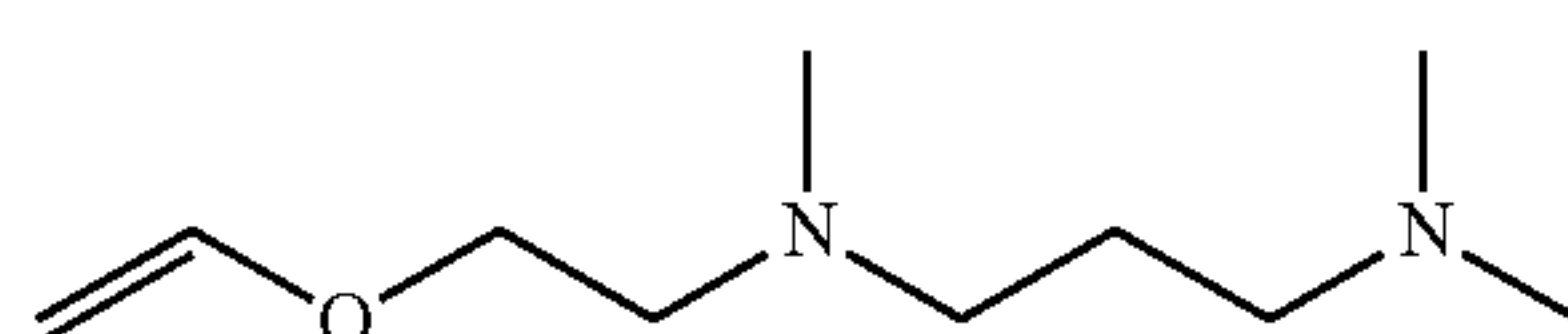
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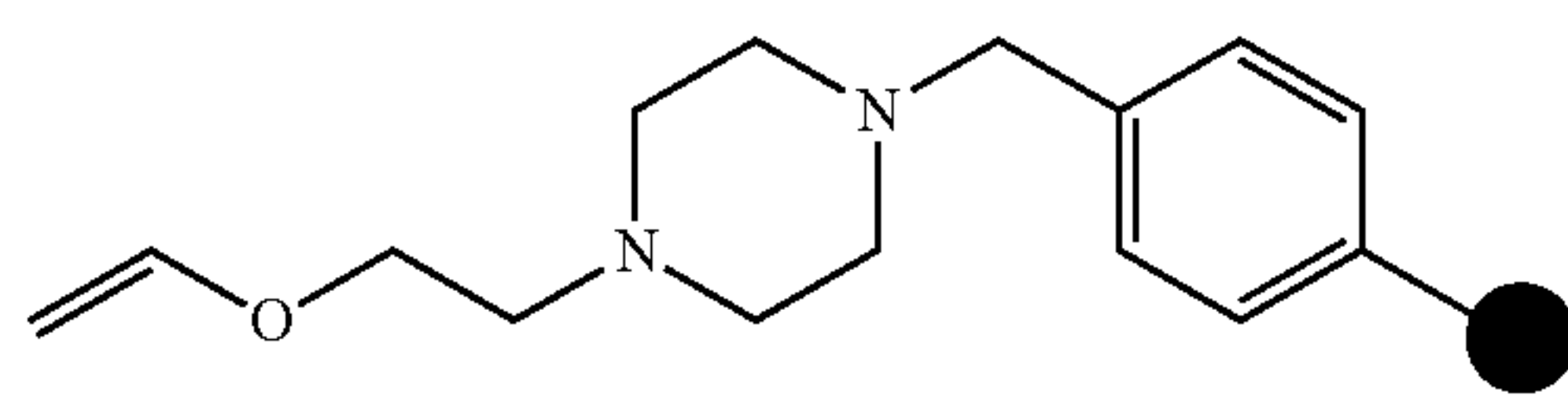
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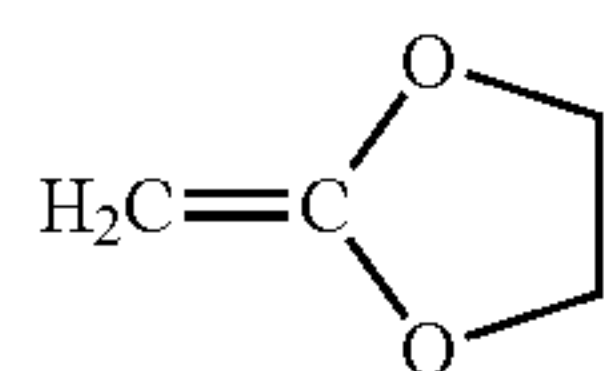
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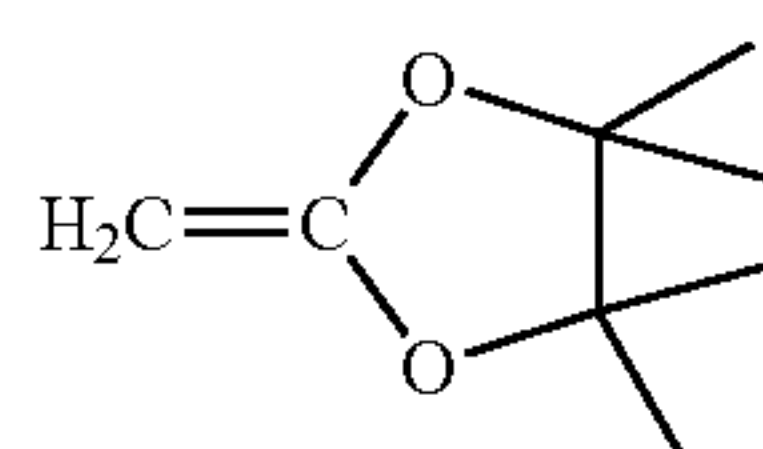
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support

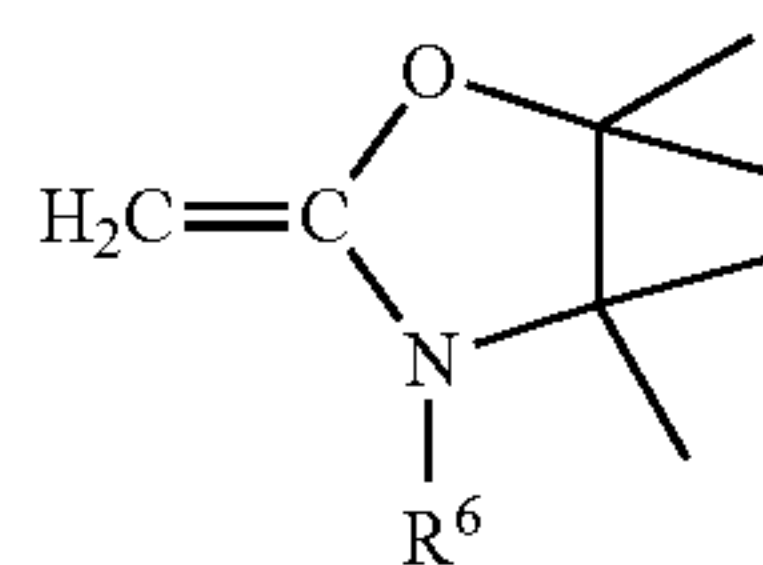
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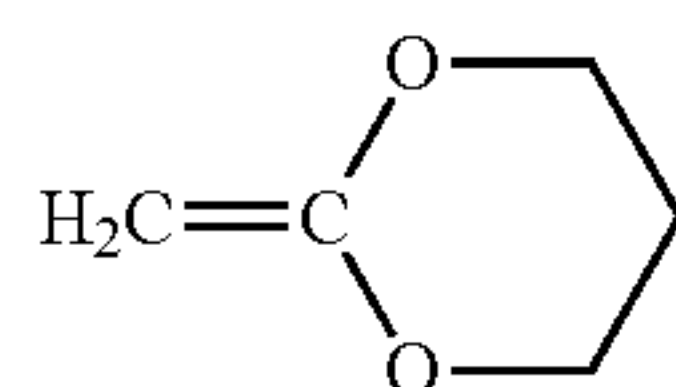
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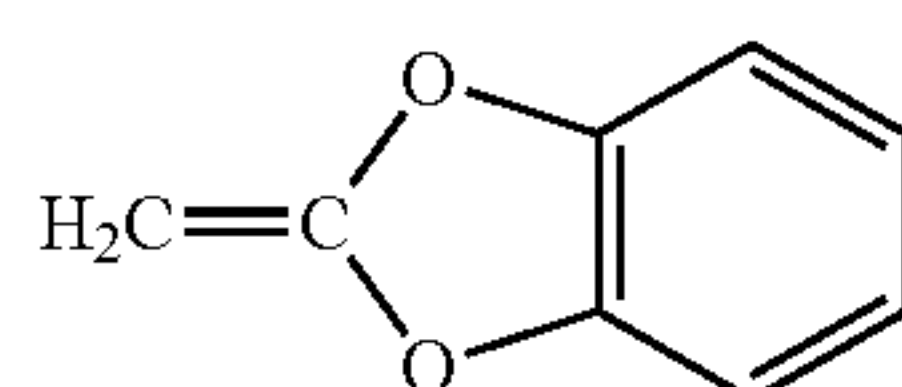
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(cocat-36)



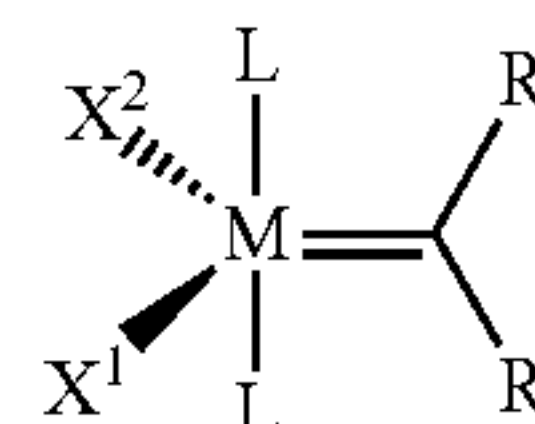
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(cocat-38)

4. The catalyst composition according to any one claims 1 to 3 wherein the complex catalyst is selected from the group consisting of

(i) catalysts of general formula (A),



(A)

where

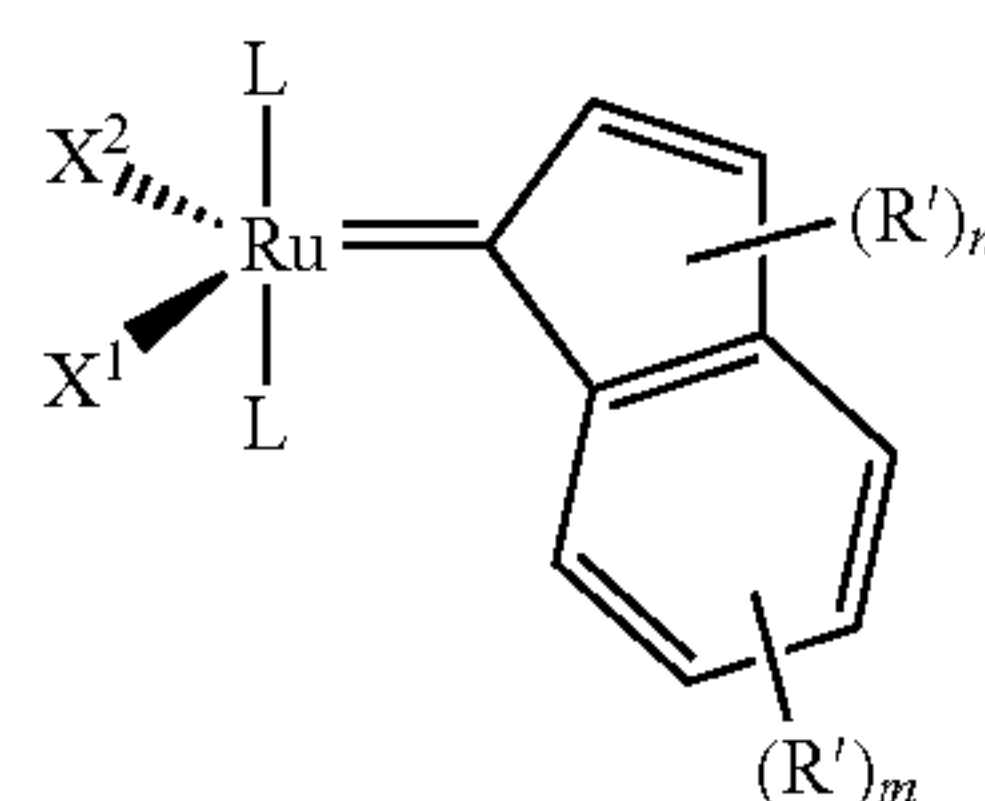
M is osmium or ruthenium,

X¹ and X² are identical or different and are two ligands, preferably anionic ligands,

L are identical or different ligands, preferably uncharged electron donors,

R are identical or different and are each hydrogen, alkyl, preferably C₁-C₃₀-alkyl, cycloalkyl, preferably C₃-C₂₀-cycloalkyl, alkenyl, preferably C₂-C₂₀-alkenyl, alkynyl, preferably C₂-C₂₀-alkynyl, aryl, preferably C₆-C₂₄-aryl, carboxylate, preferably C₁-C₂₀-carboxylate, alkoxy, preferably C₁-C₂₀-alkoxy, alkenyloxy, preferably C₂-C₂₀-alkenyloxy, alkynyloxy, preferably C₂-C₂₀-alkynyloxy, aryloxy, preferably C₆-C₂₄-aryloxy, alkoxy carbonyl, preferably C₂-C₂₀-alkoxy carbonyl, alkylamino, preferably C₁-C₃₀-alkylamino, alkylthio, preferably C₁-C₃₀-alkylthio, arylthio, preferably C₆-C₂₄-arylthio, alkylsulphonyl, preferably C₁-C₂₀-alkylsulphonyl, or alkylsulphinyl, preferably C₁-C₂₀-alkylsulphinyl, where these groups may in each case optionally be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl moieties or, as an alternative, the two groups R together with the common carbon atom to which they are bound are bridged to form a cyclic structure which can be aliphatic or aromatic in nature, may be substituted and may contain one or more heteroatoms,

(ii) catalysts of general formula (A1),



(A1)

where

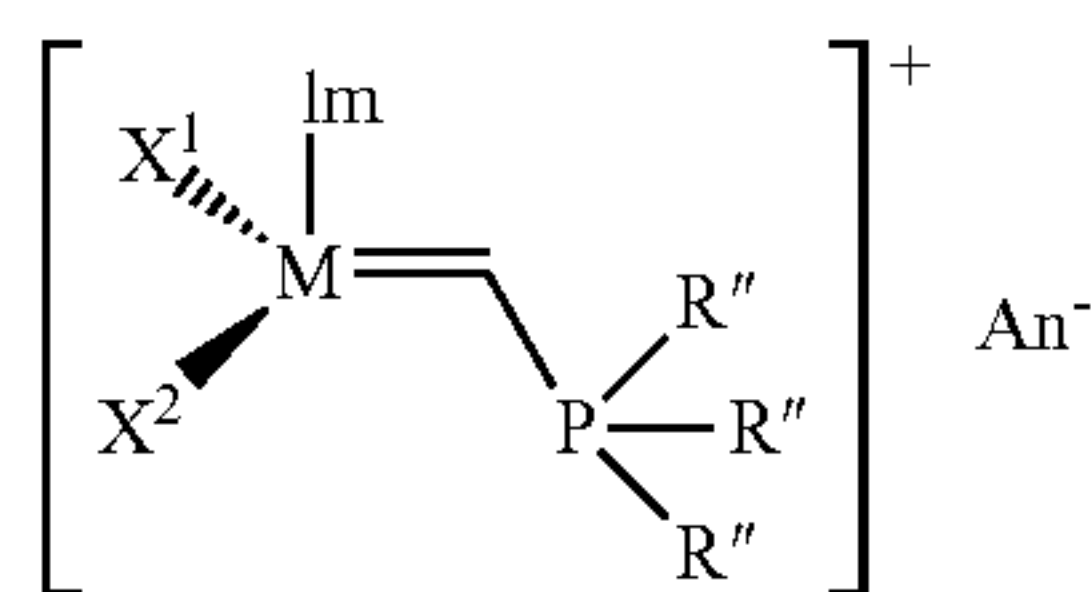
X¹, X² and L can have the same general, preferred and particularly preferred meanings as in the general formula (A),

n is 0, 1 or 2,

m is 0, 1, 2, 3 or 4 and

R' are identical or different and are alkyl, cycloalkyl, alkenyl, alkynyl, aryl, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxy carbonyl, alkylamino, alkylthio, arylthio, alkylsulphonyl or alkylsulphinyl radicals which may in each case be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl,

(iii) catalysts of general formula (B),



(B)

where

M is ruthenium or osmium,

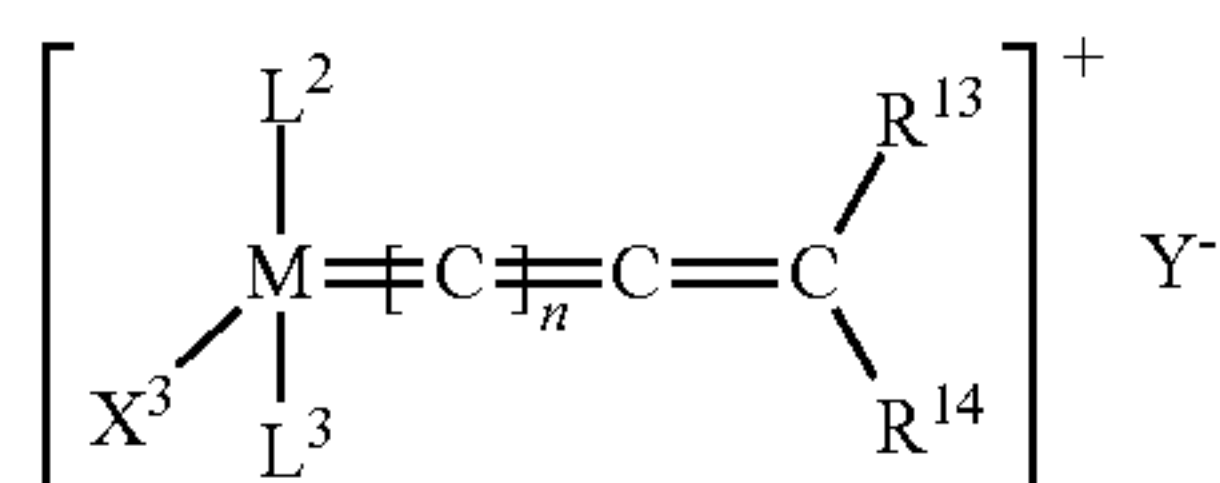
X¹ and X² are identical or different and are anionic ligands,

R'' are identical or different and are organic moieties,

Im is a substituted or unsubstituted imidazoline or imidazolidine ligand and

An is an anion,

(iv) catalysts of general formula (C)



(C)

where

M is ruthenium or osmium,

R¹³ and R¹⁴ are each, independently of one another, hydrogen, C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₂-C₂₀-alkynyl, C₆-C₂₄-aryl, C₁-C₂₀-carboxylate, C₁-C₂₀-alkoxy, C₂-C₂₀-alkenyloxy, C₂-C₂₀-alkynyloxy, C₆-C₂₄-aryloxy, C₂-C₂₀-alkoxycarbonyl, C₁-C₂₀-alkylthio, C₁-C₂₀-alkylsulphonyl or C₁-C₂₀-alkylsulphanyl,

X³ is an anionic ligand,

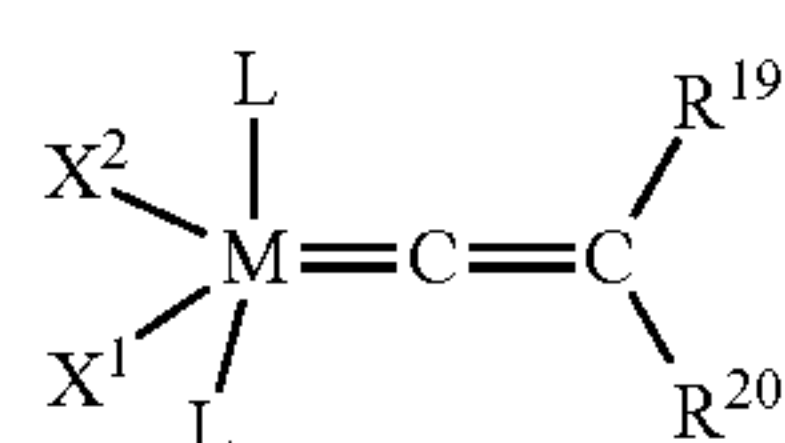
L² is an uncharged π-bonded ligand which may either be monocyclic or polycyclic,

L³ is a ligand selected from the group consisting of phosphines, sulphonated phosphines, fluorinated phosphines, functionalized phosphines having up to three aminoalkyl, ammonioalkyl, alkoxyalkyl, alkoxycarbonylalkyl, hydrocarbonylalkyl, hydroxyalkyl or ketoalkyl groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines stibines, ethers, amines, amides, imines, sulphoxides, thioethers and pyridines,

Y⁻ is a noncoordinating anion and

n is 0, 1, 2, 3, 4 or 5,

(v) catalysts of general formula (D),



(D)

where

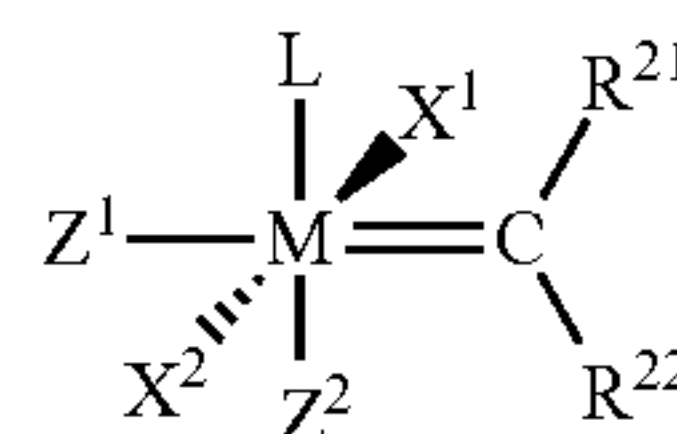
M is ruthenium or osmium,

X¹ and X² are identical or different and are anionic ligands which can have all meanings of X¹ and X² mentioned in the general formulae (A) and (B),

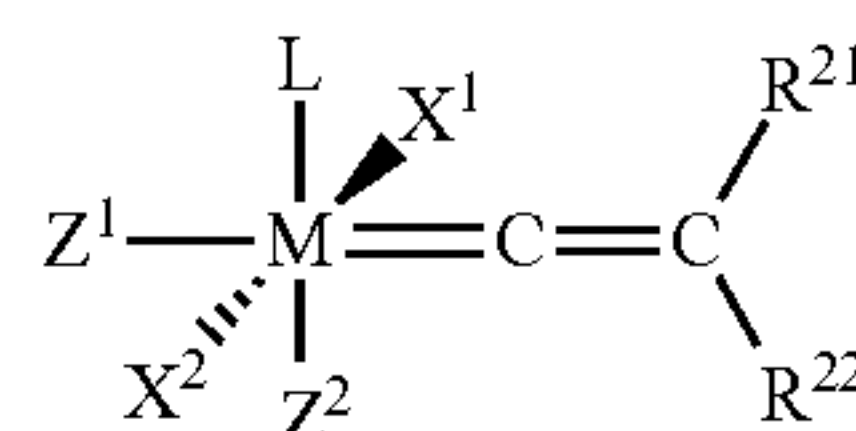
L represent identical or different ligands which can have all general and preferred meanings of L mentioned in the general formulae (A) and (B),

R¹⁹ and R²⁰ are identical or different and are each hydrogen or substituted or unsubstituted alkyl,

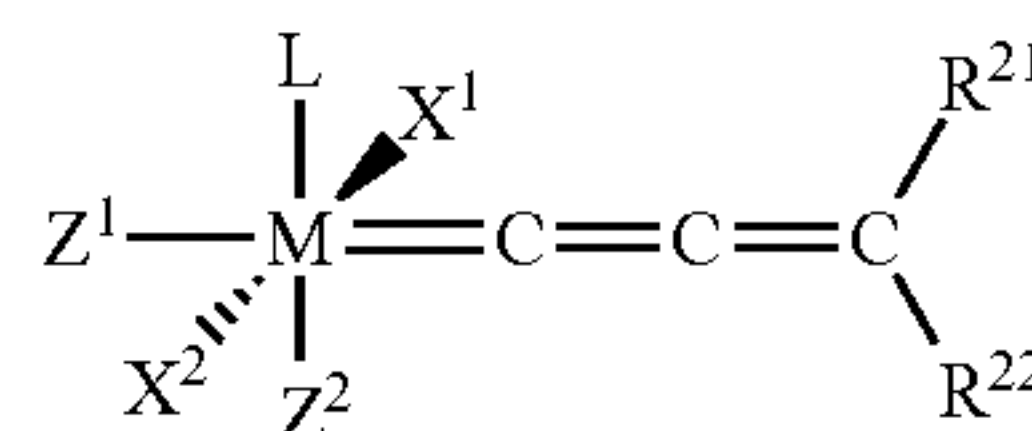
(vi) catalysts of general formula (E), (F) or (G),



(E)



(F)



(G)

where

M is osmium or ruthenium,

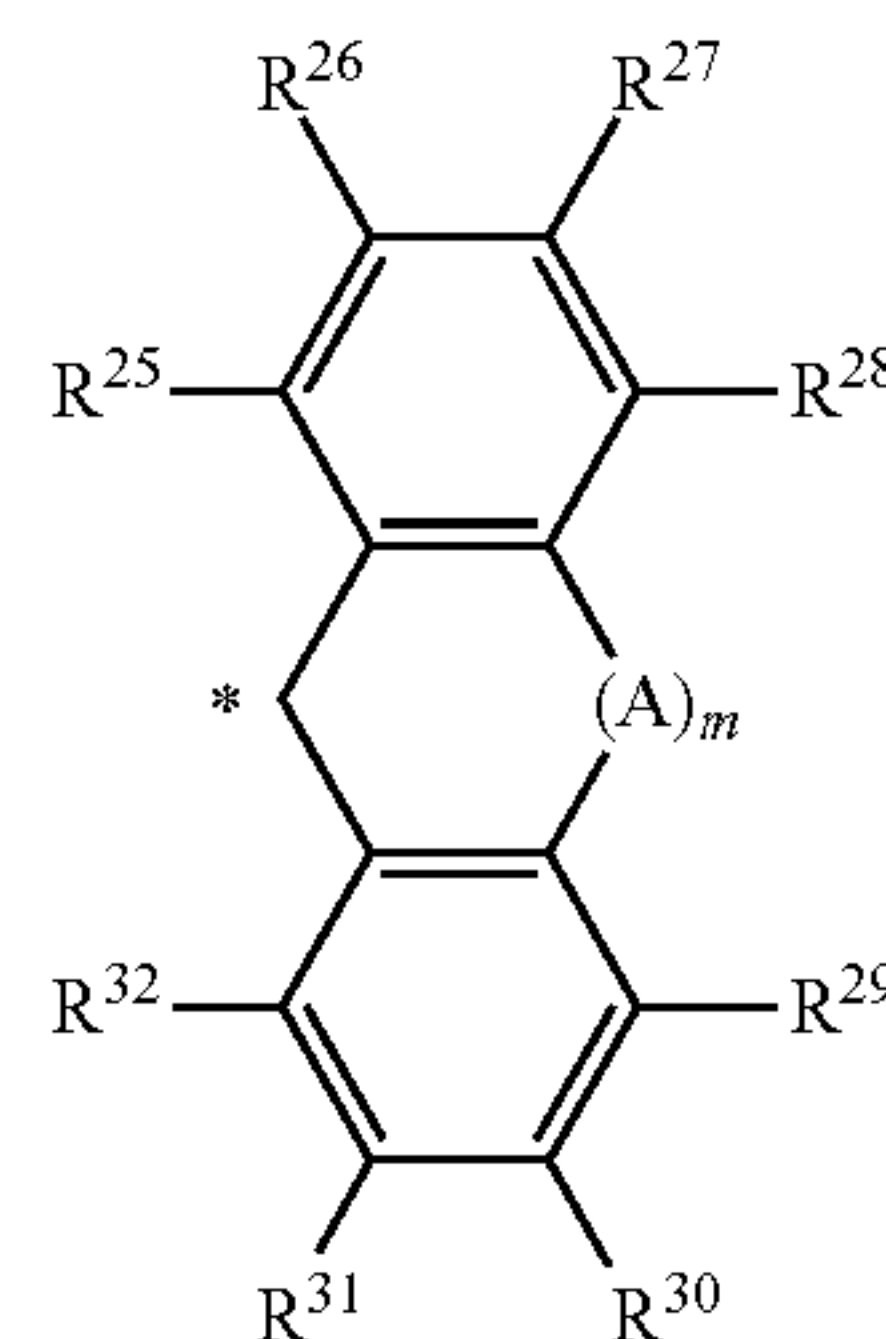
X¹ and X² are identical or different and are two ligands, preferably anionic ligands,

L is a ligand, preferably an uncharged electron donor,

Z¹ and Z² are identical or different and are uncharged electron donors,

R²¹ and R²² are each, independently of one another, hydrogen alkyl, cycloalkyl, alkenyl, alkynyl, aryl, carboxylate, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxycarbonyl, alkylamino, alkylthio, alkylsulphonyl or alkylsulphanyl which are in each case substituted by one or more substituents selected from among alkyl, halogen, alkoxy, aryl or heteroaryl.

(vii) catalysts (N) comprising the general structural element (N1), where the carbon atom denoted by "*" is bound via one or more double bonds to the catalyst framework having a ruthenium or osmium central metal,



(N1)

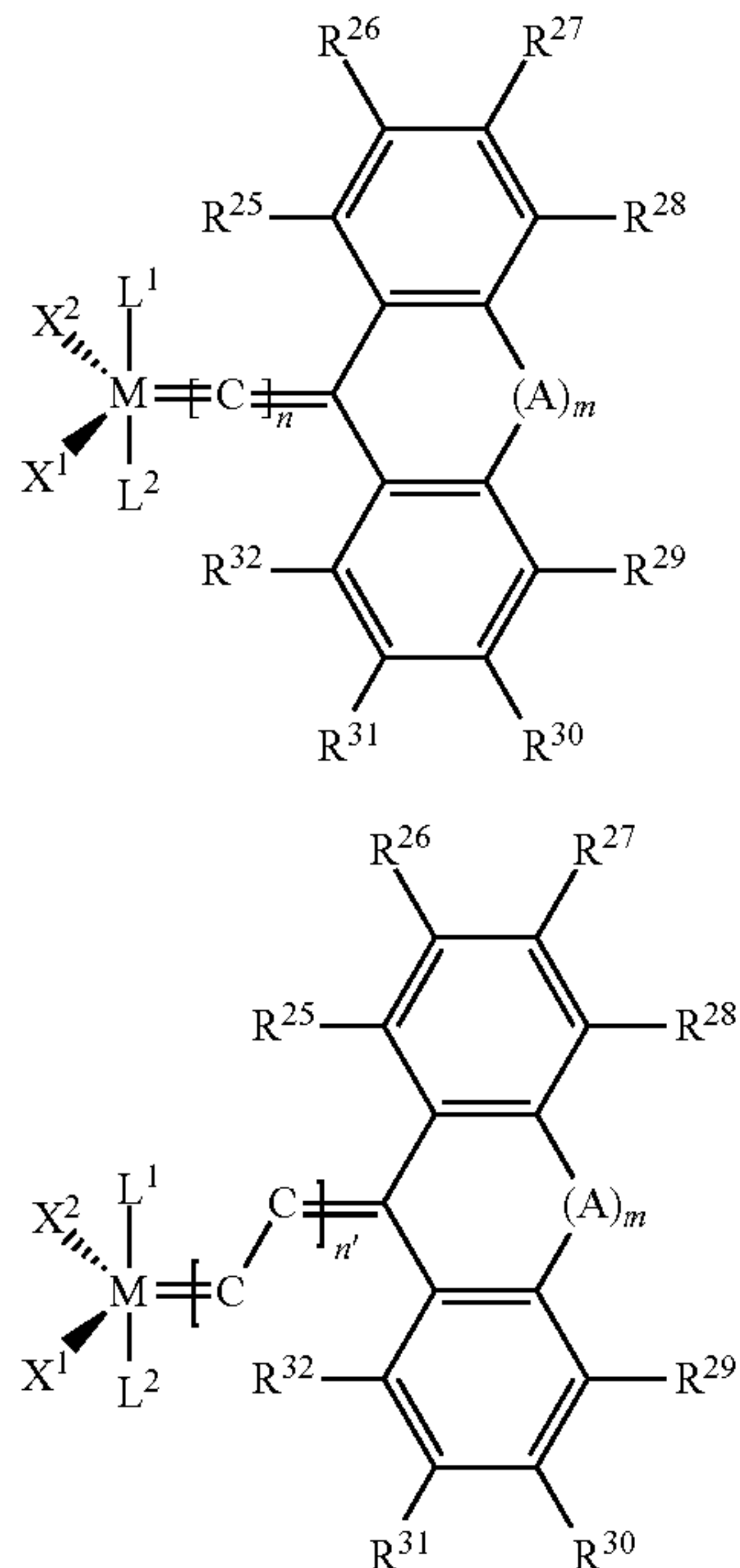
and where

R^{25} - R^{32} are identical or different and are each hydrogen, halogen, hydroxyl, aldehyde, keto, thiol, CF_3 , nitro, nitroso, cyano, thiocyanato, isocyanato, carbodiimide, carbamate, thiocarbamate, dithiocarbamate, amino, amido, imino, silyl, sulphonate ($-SO_3^-$), $-OSO_3^-$, $-PO_3^-$ or OPO_3^- or alkyl, cycloalkyl, alkenyl, alkynyl, aryl, carboxylate, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxy-carbonyl, alkylamino, alkylthio, arylthio, alkylsulphonyl, alkylsulphiny, dialkylamino, alkylsilyl or alkoxy-silyl, where all these moieties can each optionally be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl substituents, or, as an alternative, two directly adjacent substituents from the group consisting of R^{25} - R^{32} together with the ring carbons to which they are bound form a cyclic group, preferably an aromatic system, by bridging or, as an alternative, R^8 is optionally bridged to another ligand of the ruthenium- or osmium-carbene complex catalyst,

m is 0 or 1 and

A is oxygen, sulphur, $C(R^{33}R^{34})$, $N-R^{35}$, $-C(R^{36})=C(R^{37})-$, $-C(R^{36})(R^{38})-C(R^{37})(R^{39})-$, where R^{33} - R^{39} are identical or different and can each have the same meanings as R^{25} - R^{32} , and

(viii) catalysts of general formulae (N2a) or (N2b),



where

M is ruthenium or osmium,

X^1 and X^2 are identical or different and are two ligands, preferably anionic ligands,

L^1 and L^2 are identical or different ligands, preferably uncharged electron donors, where L^2 can alternatively also be bridged to the radical R^8 ,

n is 0, 1, 2 or 3, preferably 0, 1 or 2,

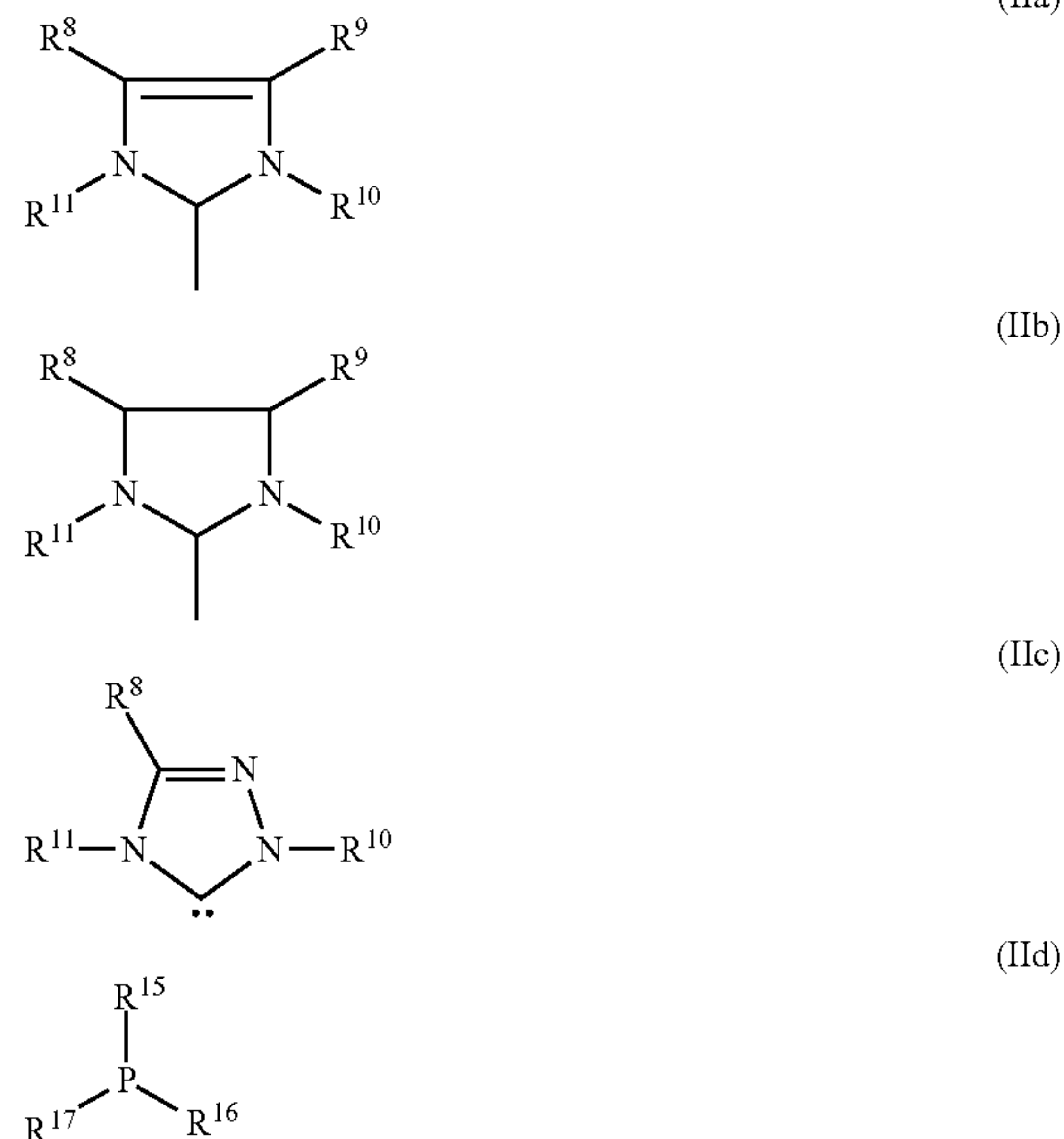
n' is 1 or 2, preferably 1, and

R^{25} - R^{32} , m and A have the same meanings as given in general formula (N1).

5. The catalyst composition according to claim 4 wherein a complex catalyst of general formula (A) is used in which one group R is hydrogen and the other group R is C_1 - C_{20} -alkyl, C_3 - C_{10} -cycloalkyl, C_2 - C_{20} -alkenyl, C_2 - C_{20} -alkynyl, C_6 - C_{24} -aryl, C_1 - C_{20} -carboxylate, C_1 - C_{20} -alkoxy, C_2 - C_{20} -alkenyloxy, C_2 - C_{20} -alkynyloxy, C_6 - C_{24} -aryloxy, C_2 - C_{20} -alkoxy-carbonyl, C_1 - C_{30} -alkylamino, C_1 - C_{30} -alkylthio, C_6 - C_{24} -arylthio, C_1 - C_{20} -alkylsulphonyl or C_1 - C_{20} -alkylsulphiny, where these moieties may in each case be substituted by one or more alkyl, halogen, alkoxy, aryl or heteroaryl groups.

6. The catalyst composition according to claim 4 or 5 wherein a complex catalyst of general formula (A) is used in which X^1 and X^2 are identical and are each halogen, in particular chlorine, CF_3COO , CH_3COO , CFH_2COO , $(CH_3)_3CO$, $(CF_3)_2(CH_3)CO$, $(CF_3)(CH_3)_2CO$, PhO (phenoxy), MeO (methoxy), EtO (ethoxy), tosylate ($p-CH_3-C_6H_4-SO_3$), mesylate (CH_3-SO_3) or CF_3SO_3 (trifluoromethane-sulphonate).

7. The catalyst composition according to any one of claims 4 to 6 wherein a complex catalyst of general formula (A) is used in which one or both of the ligands L have a structure according to general formulae (IIa)-(IIId), wherein the meaning of L can be identical or different in case both ligands L have a structure according to (IIa) to (IIId),



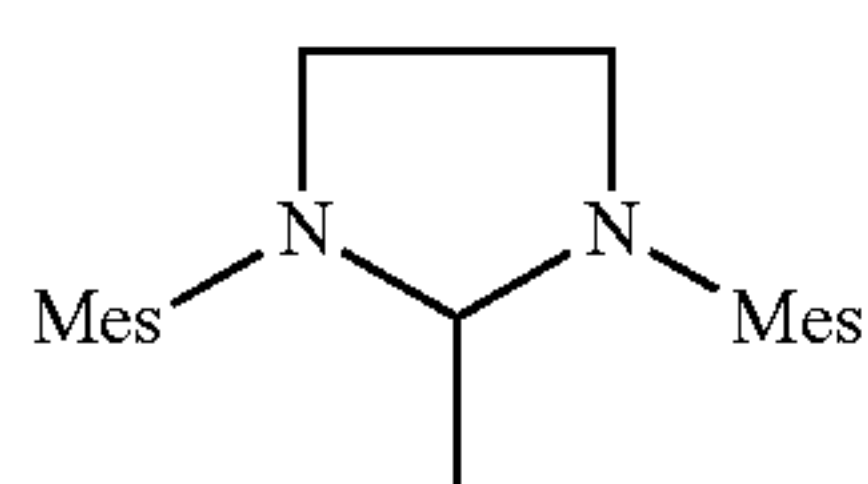
where

R^8 , R^9 , R^{10} and R^{11} are identical or different and represent hydrogen, straight-chain or branched C_1 - C_{30} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_2 - C_{20} -alkynyl, C_6 - C_{24} -aryl, C_7 - C_{25} -alkaryl, C_2 - C_{20} heteroaryl, C_2 - C_{20} heterocyclyl, C_1 - C_{20} -alkoxy, C_2 - C_{20} -alkenyloxy, C_2 - C_{20} -alkynyloxy, C_6 - C_{20} -aryloxy, C_2 - C_{20} -alkoxy-carbonyl, C_1 - C_{20} -alkylthio, C_6 - C_{20} -arylthio, $-Si(R)_3$, $-O-Si(R)_3$, $-O-C(=O)R$, $C(=O)R$, $-C(=O)N(R)_2$, $-NR-C(=O)-N(R)_2$, $-SO_2N(R)_2$, $-S(=O)R$, $-S(=O)_2R$, $-O-S(=O)_2R$, halogen, nitro or cyano, wherein in all above occurrences relating to the

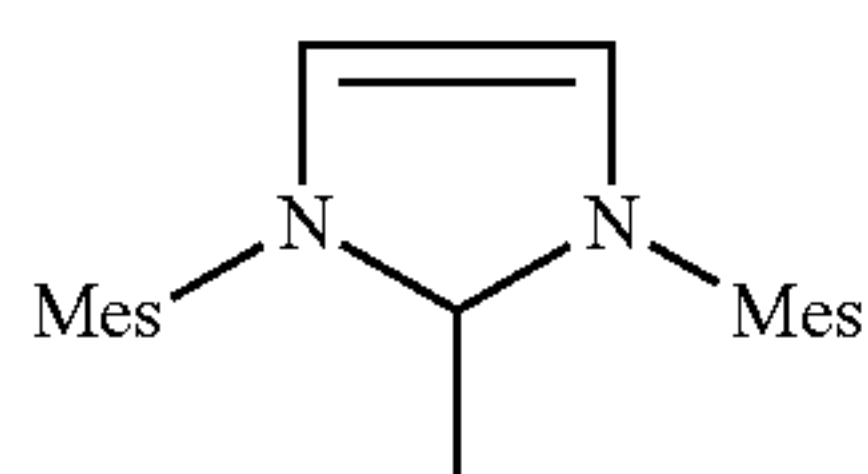
meanings of R^8 , R^9 , R^{10} and R^{11} the group R is identical or different and represents hydrogen, alkyl, cycloalkyl, alkenyl, alkynyl, aryl or heteroaryl, and

R^{15} , R^{16} and R^{17} are identical or different and may represent alkyl, cycloalkyl, alkoxy, aryl, aryloxy, or a heterocyclic group.

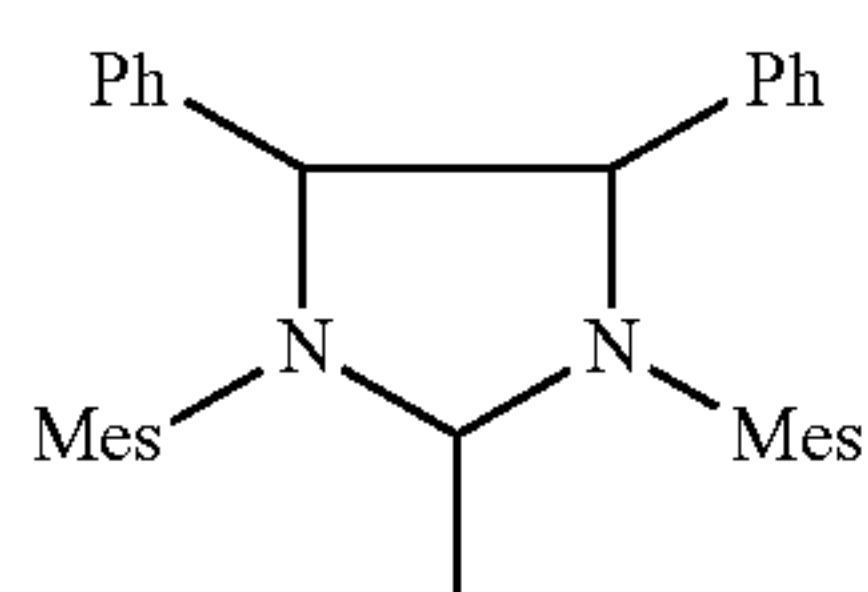
8. The catalyst composition according to any one of claims 4 to 6 wherein a complex catalyst of general formula (A) is used in which one or both of the ligands L may have a structure (IIIa) to (IIIu), where in all cases “Ph” means phenyl, “Bu” butyl, “Mes” 2,4,6-trimethylphenyl, “Dipp” 2,6-diisopropylphenyl, and “Dimp” 2,6-dimethylphenyl, and wherein the meaning of L can be identical or different in case both ligands L have a structure according to (IIIa) to (IIIu),



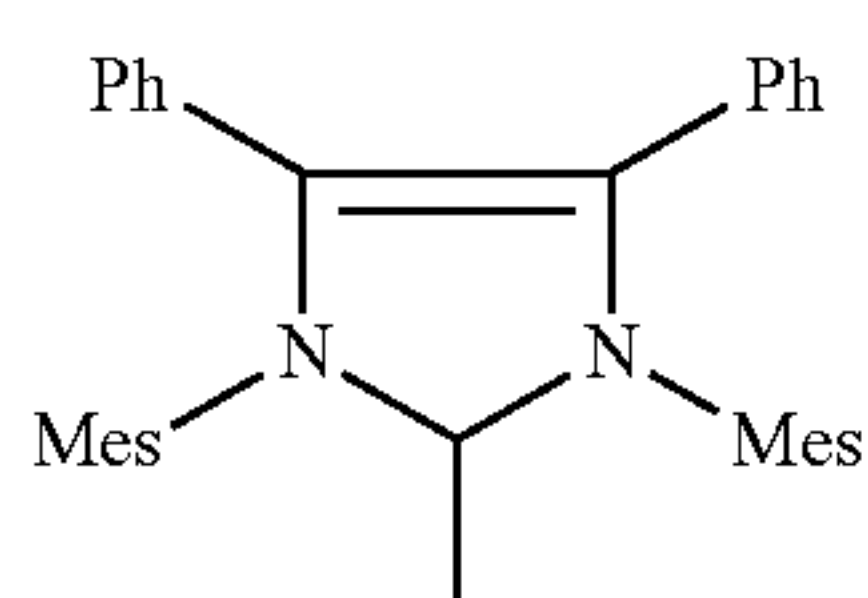
(IIIa)



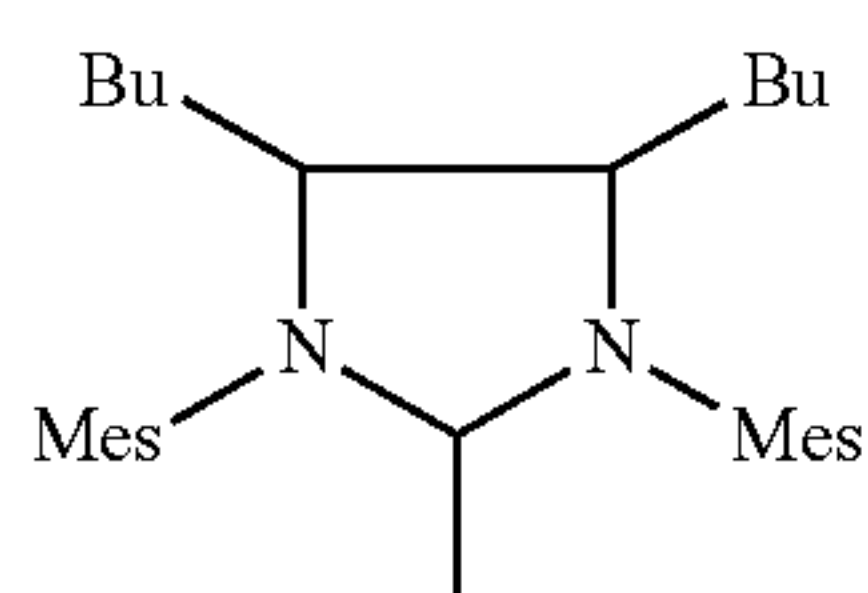
(IIIb)



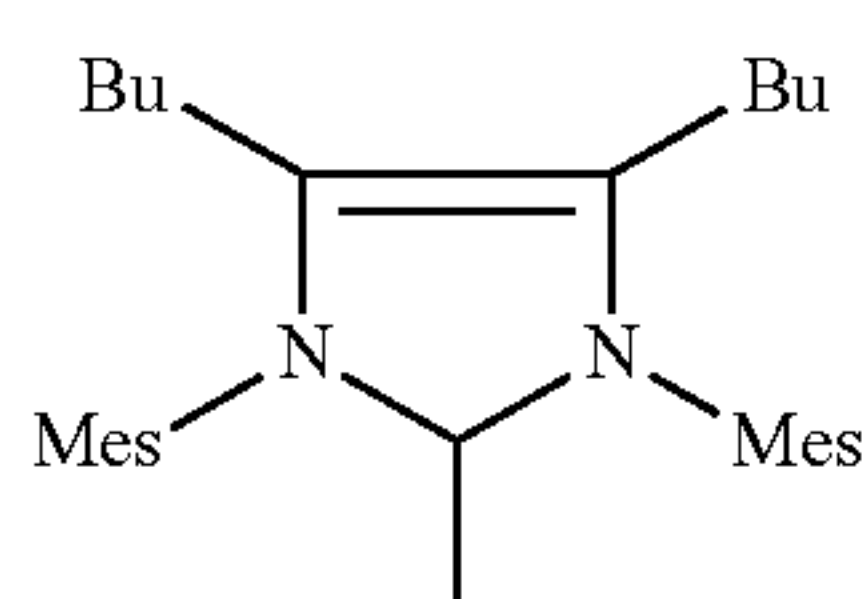
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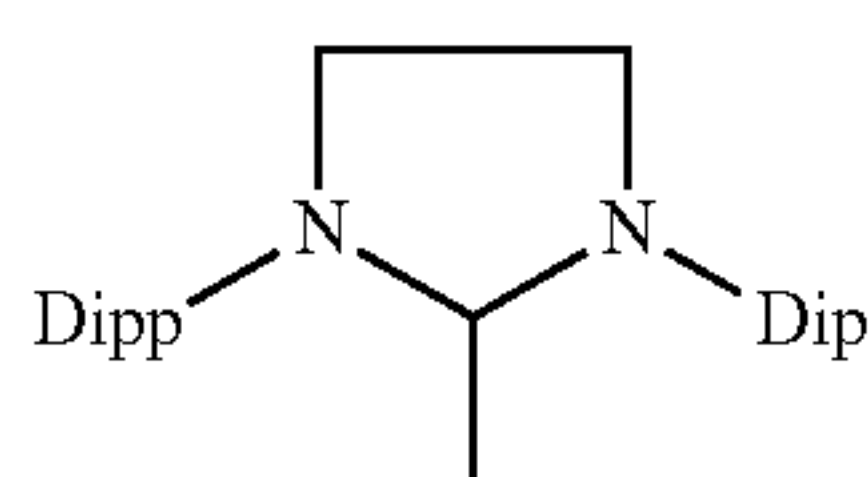
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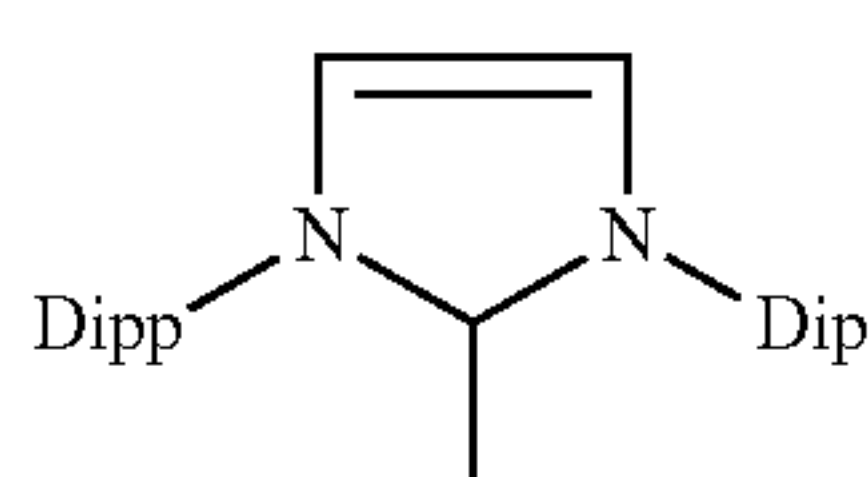
(IIIg)



(IIIh)

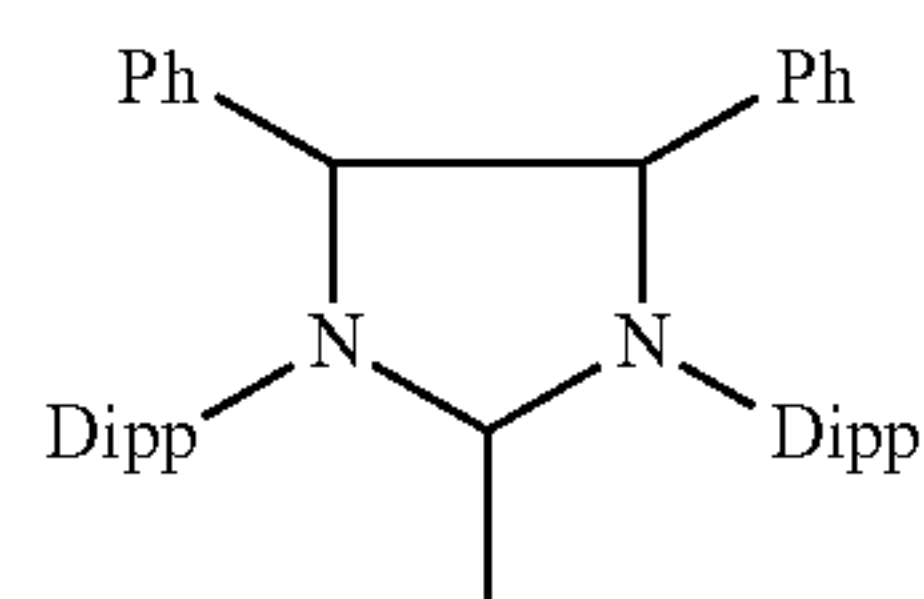


(IIIi)

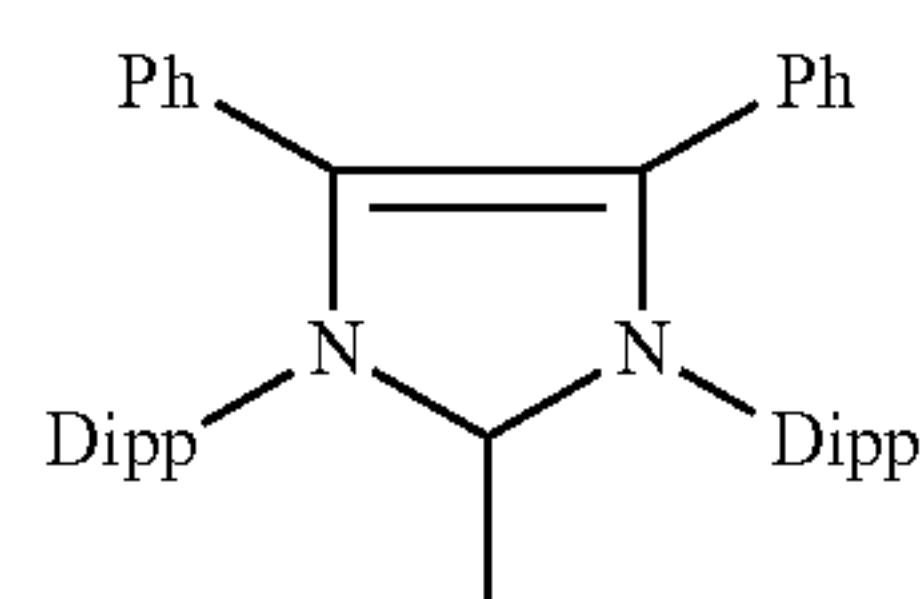


(IIIj)

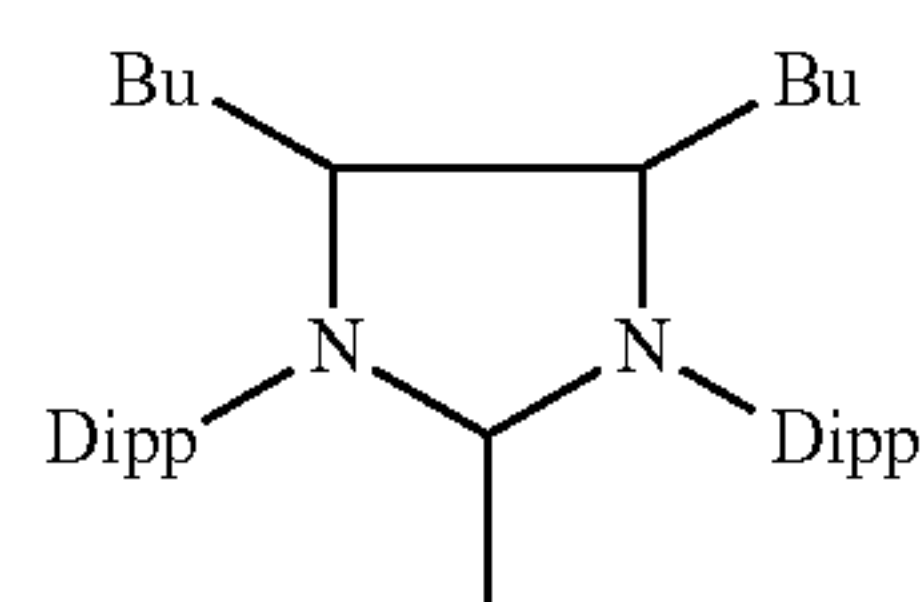
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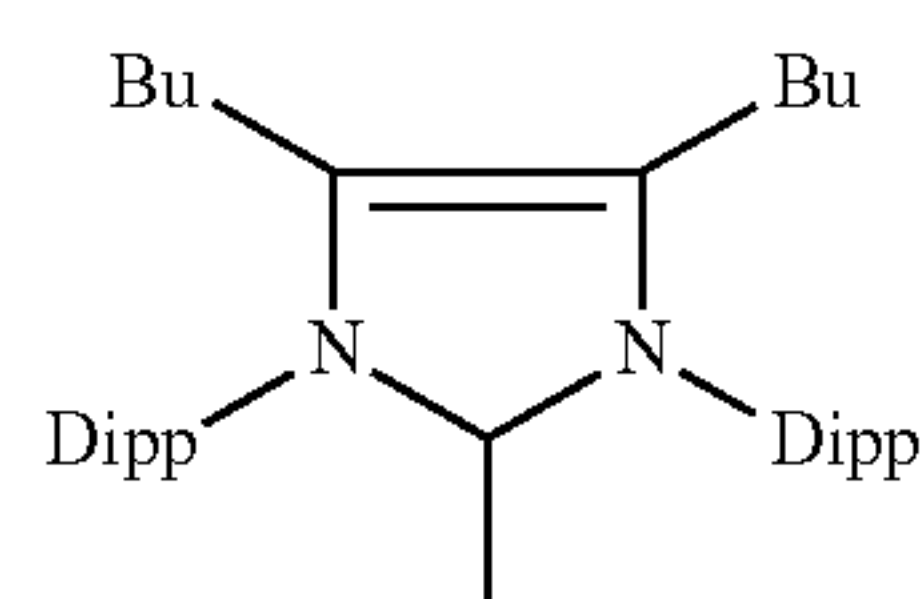
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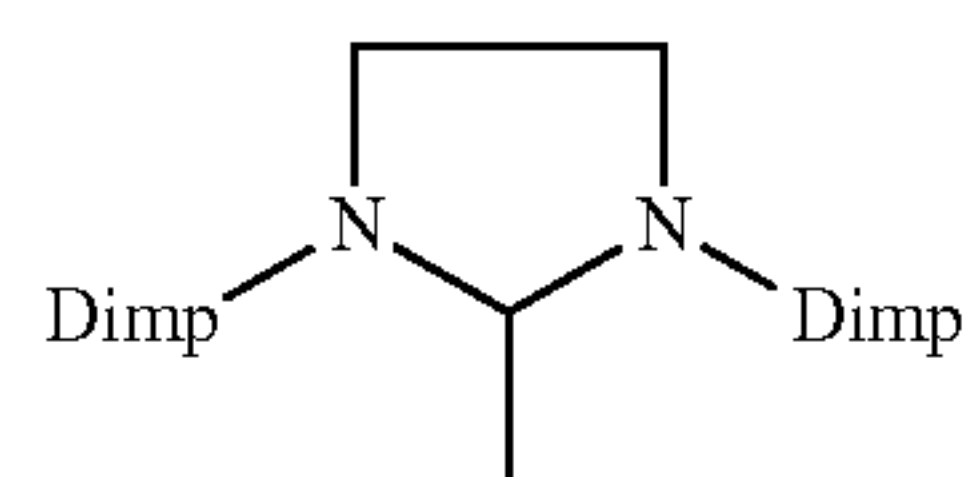
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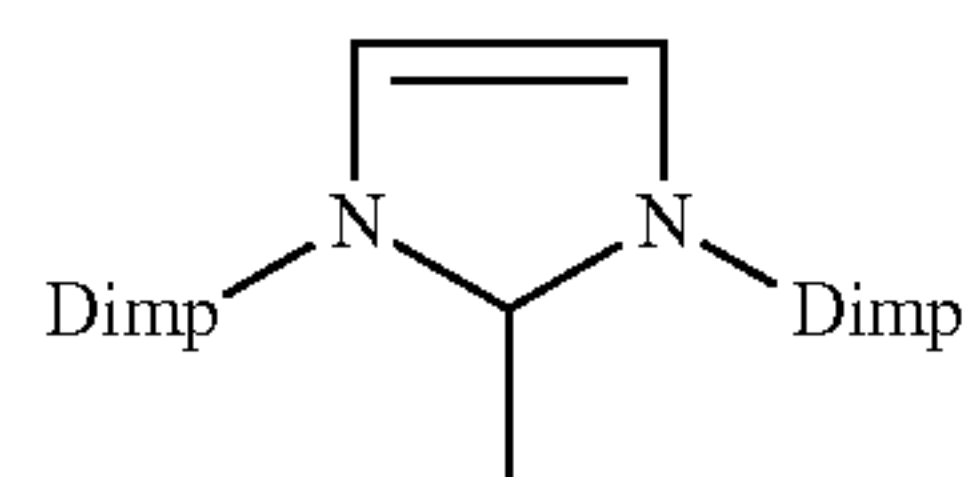
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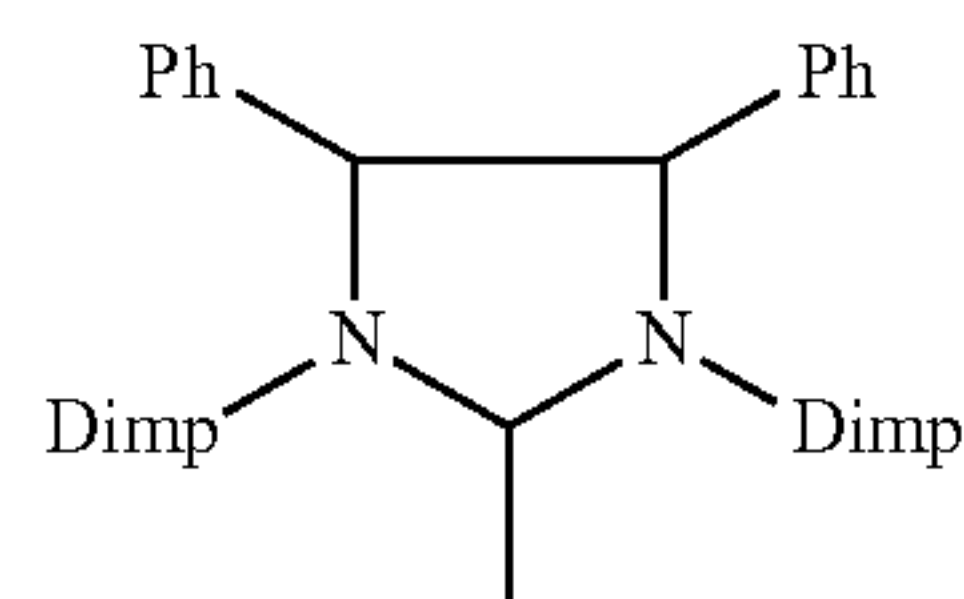
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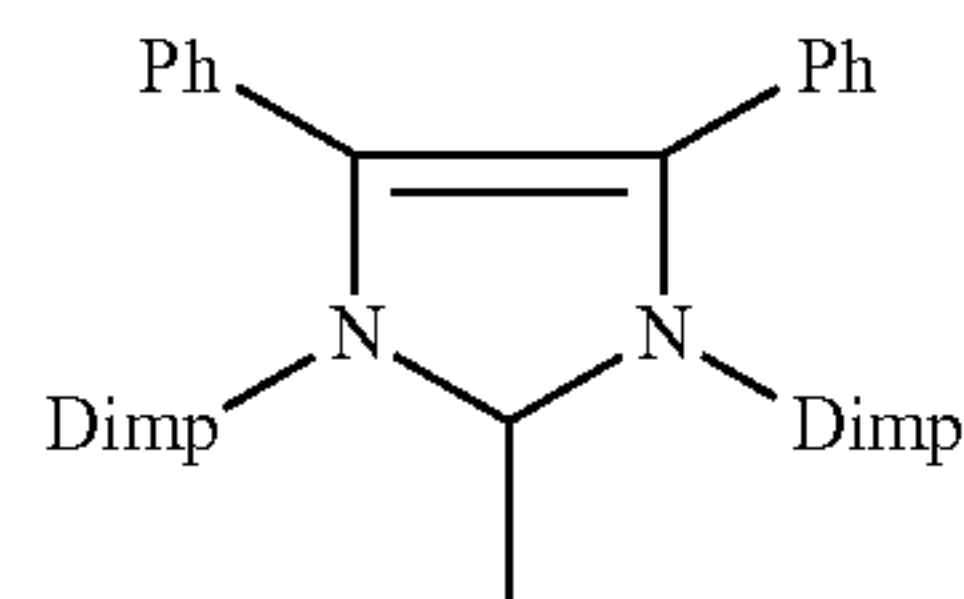
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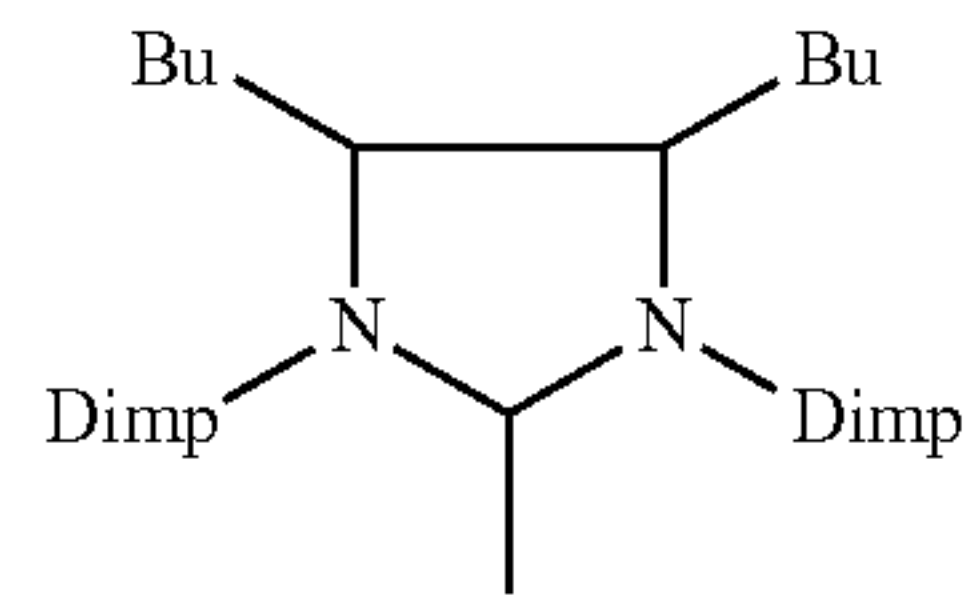
(IIIq)



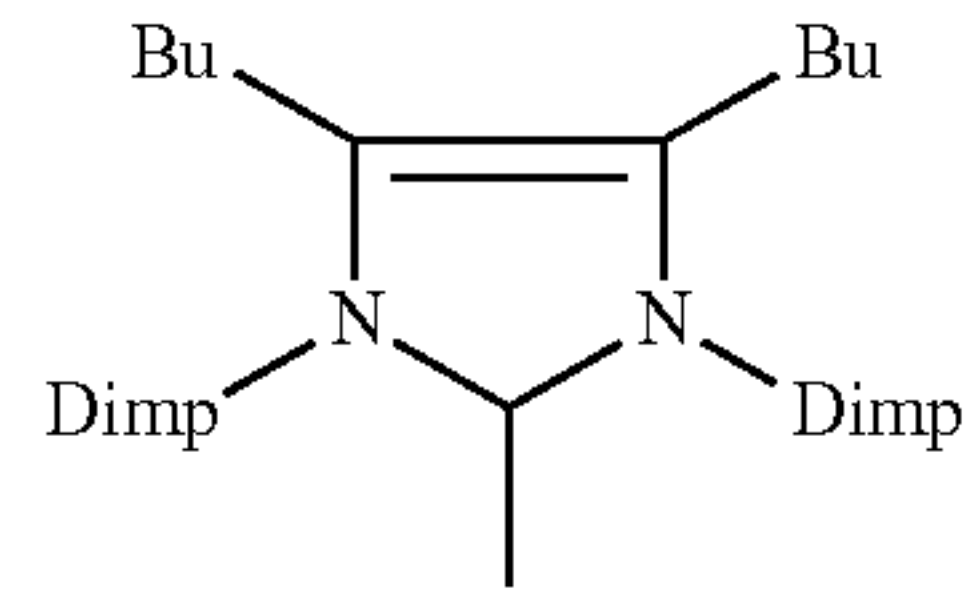
(IIIr)



(IIIs)



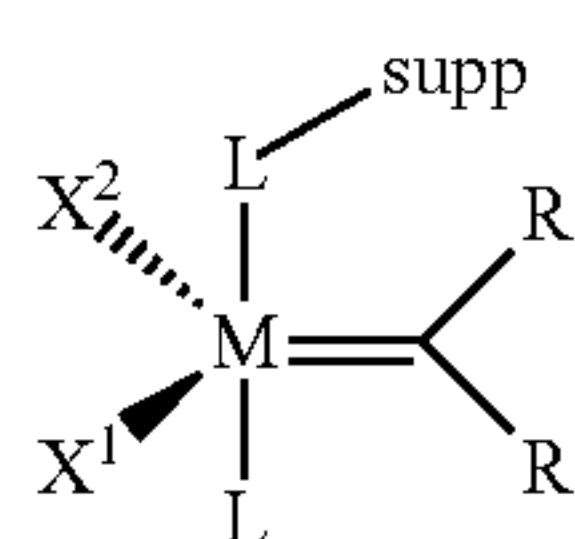
(IIIu)



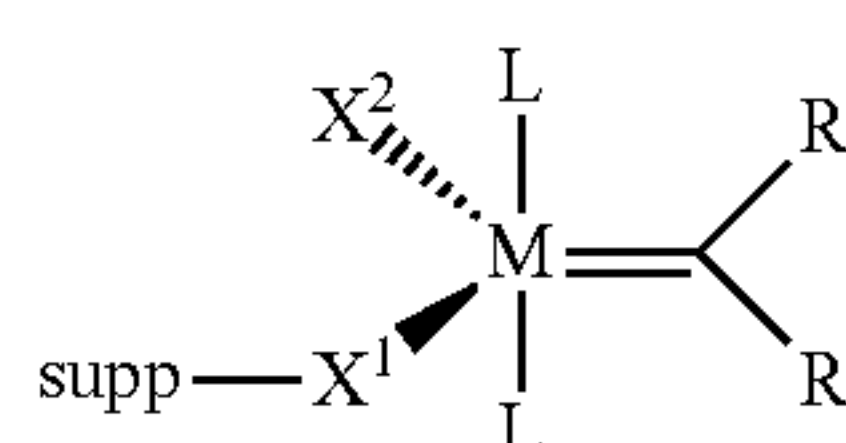
(IIIv)

9. The catalyst composition according to any one of claims 4 to 8 wherein in step a) a catalyst of general formula (A) is

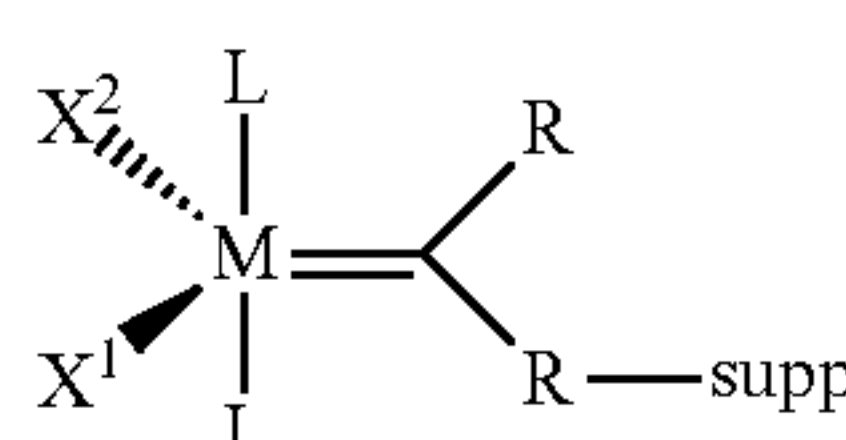
used in immobilized form on a support material, preferably as immobilized catalyst having the general formulae (support-1), (support-2), or (support-3),



(support-1)



(support-2)



(support-3)

wherein M, Y, L, X¹, X², and R may have the meanings given for general formula (A) and wherein “supp” stands for the support material, preferably silica gels or a macromolecular material, more preferably synthetic polymers, most preferably polyethylene glycol, polystyrenes or cross-linked polystyrenes.

10. The catalyst composition according to claim 4 wherein in step a) a catalyst of the general formulae (E), (F), and (G) is used in which

M is ruthenium,

X¹ and X² are both halogen, in particular chlorine,

R¹ and R² are identical or different and are five- or six-membered monocyclic groups having from 1 to 4, preferably from 1 to 3 and particularly preferably 1 or 2, heteroatoms or bicyclic or polycyclic structures made up of 2, 3, 4 or 5 five- or six-membered monocyclic groups of this type, where all the abovementioned groups may in each case be substituted by one or more moieties selected from the group consisting of alkyl, preferably C₁-C₁₀-alkyl, cycloalkyl, preferably C₃-C₈-cycloalkyl, alkoxy, preferably C₁-C₁₀-alkoxy, halogen, preferably chlorine or bromine, aryl, preferably C₆-C₂₄-aryl, or heteroaryl, preferably C₅-C₂₃-heteroaryl,

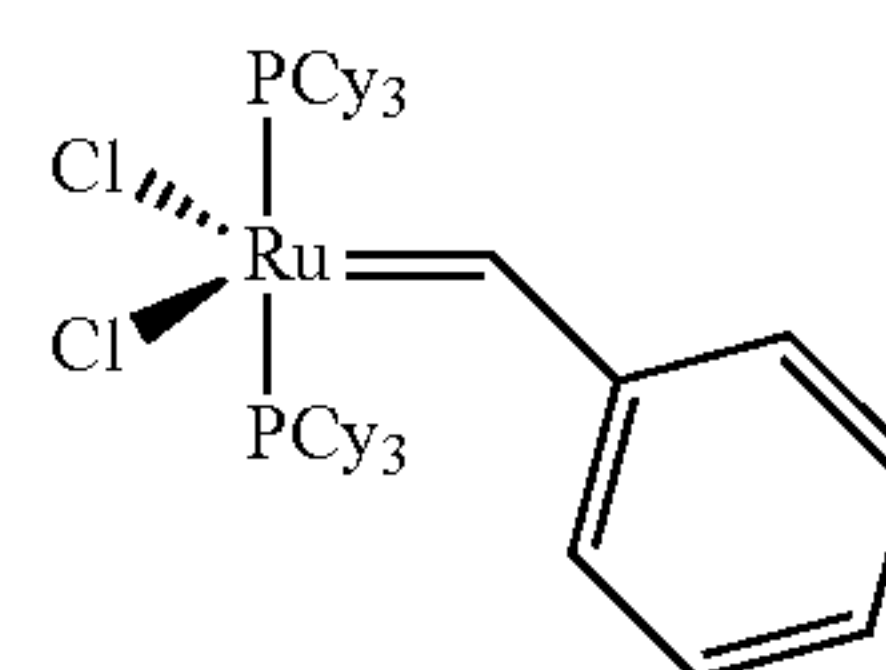
Z¹ and Z² are identical or different and five- or six-membered monocyclic groups having from 1 to 4, preferably from 1 to 3 and particularly preferably 1 or 2, heteroatoms or bicyclic or polycyclic structures made up of 2, 3, 4 or 5 five- or six-membered monocyclic groups of this type, where all these abovementioned groups may in each case optionally be substituted by one or more alkyl, preferably C₁-C₁₀-alkyl, cycloalkyl, preferably C₃-C₈-cycloalkyl, alkoxy, preferably C₁-C₁₀-alkoxy, halogen, preferably chlorine or bromine, aryl, preferably C₆-C₂₄-aryl, or heteroaryl, preferably C₅-C₂₃-heteroaryl, radicals which may in turn each be substituted by one or more moieties, preferably selected from the group consisting of halogen, in particular chlorine or bromine, C₁-C₅-alkyl, C₁-C₅-alkoxy and phenyl.

R²¹ and R²² are identical or different and are each C₁-C₃₀-alkyl C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₂-C₂₀-alkynyl, C₆-C₂₄-aryl, C₁-C₂₀-carboxylate, C₁-C₂₀-alkoxy, C₂-C₂₀-alkenyloxy, C₂-C₂₀-alkynyloxy, C₆-C₂₄-aryloxy, C₂-C₂₀-alkoxycarbonyl, C₁-C₃₀-alkylamino,

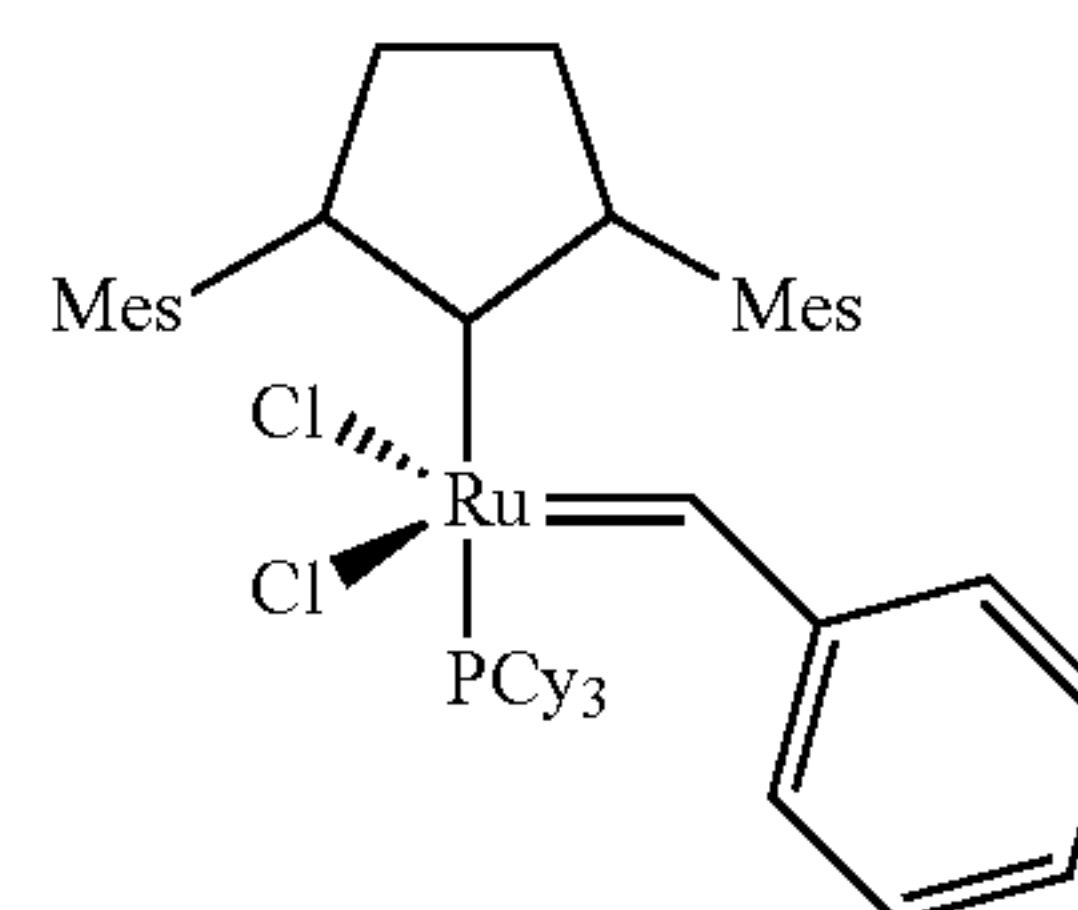
C₁-C₃₀-alkylthio, C₆-C₂₄-arylthio, C₁-C₂₀-alkylsulphonyl, C₁-C₂₀-alkylsulphinyl, and

L has a structure of the above-described general formula (IIa) or (IIb), in particular one of the formulae (IIIa) to (IIIu).

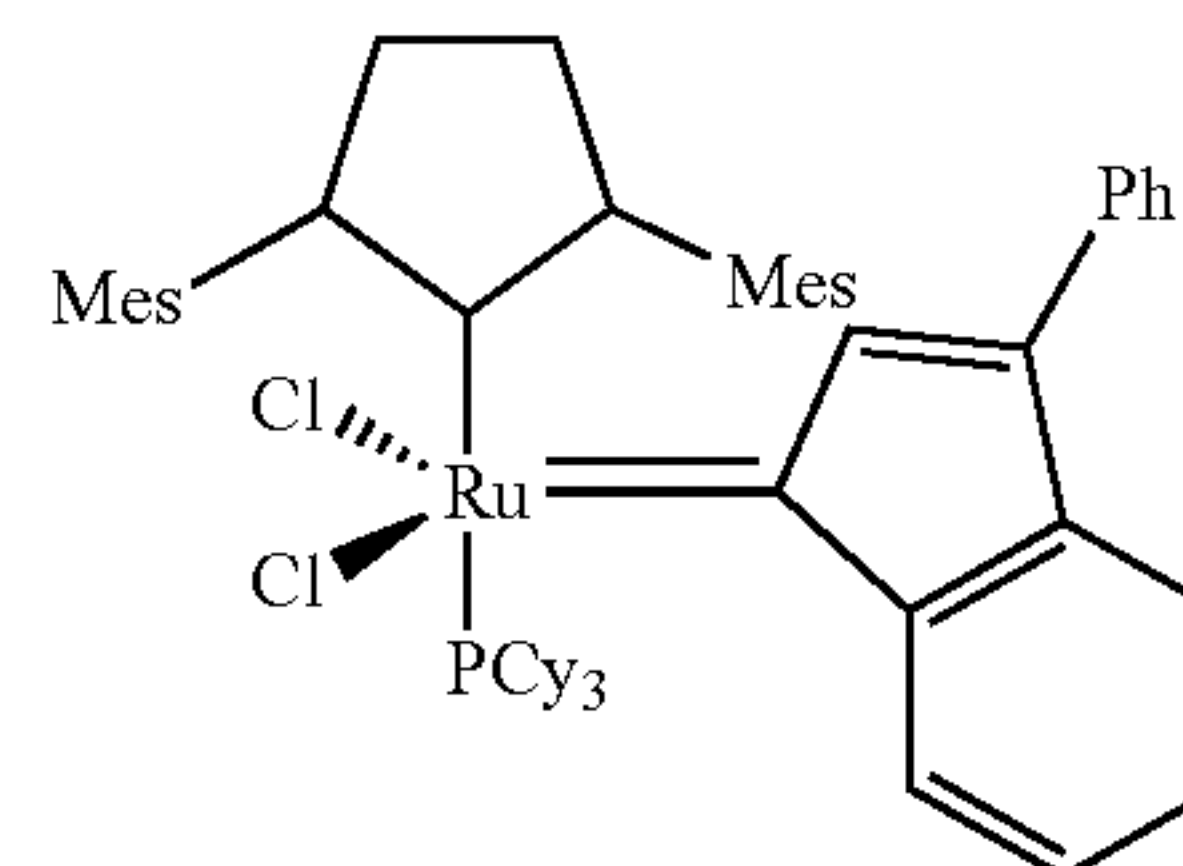
11. The catalyst composition according to any one of claims 1 to 3, wherein in step a) a complex catalyst is used selected from the catalysts shown in the following formulae, wherein in each case “Cy” is cyclohexyl, “Mes” is 2,4,6-trimethylphenyl and “Ph” is phenyl.



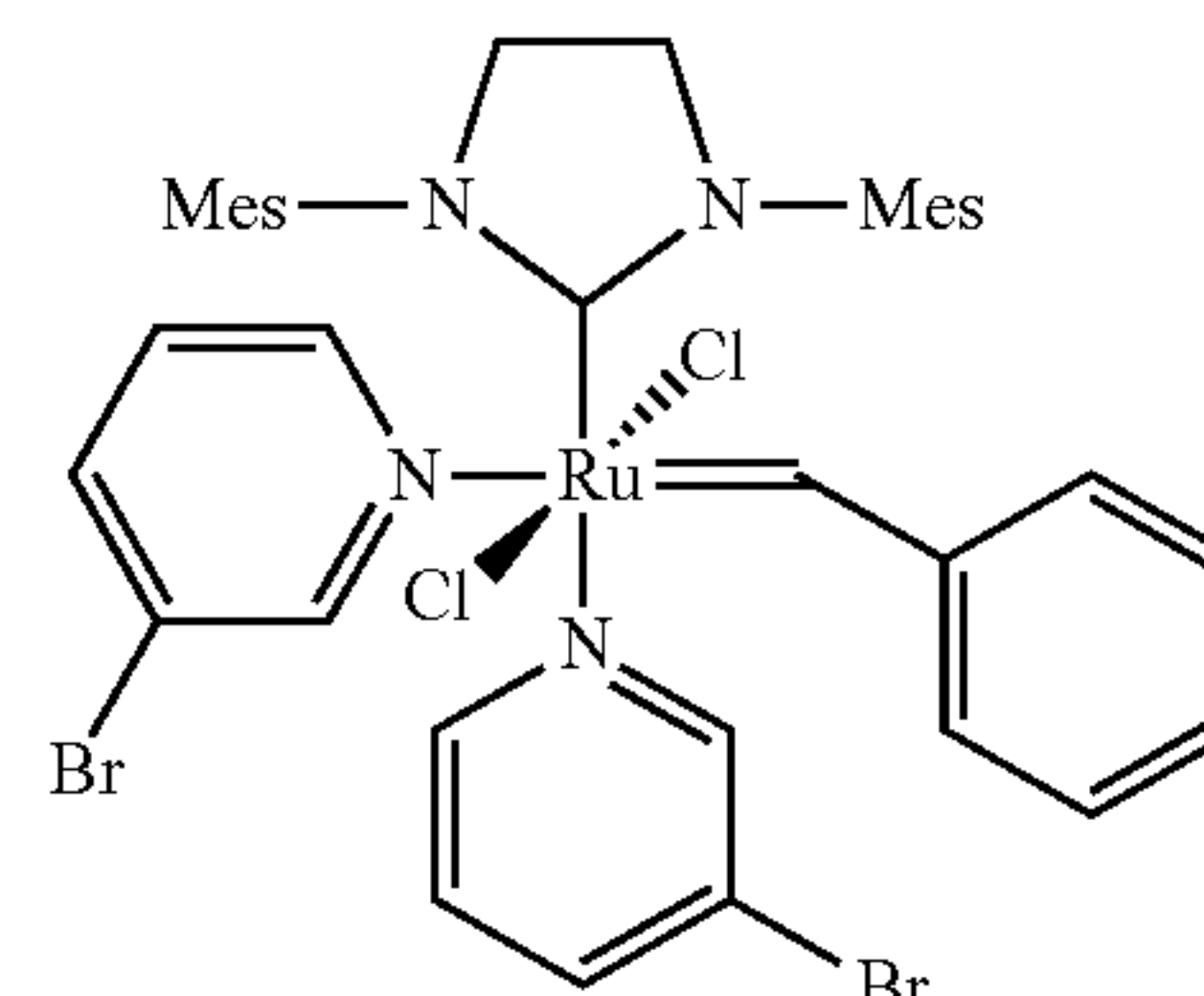
(IV)



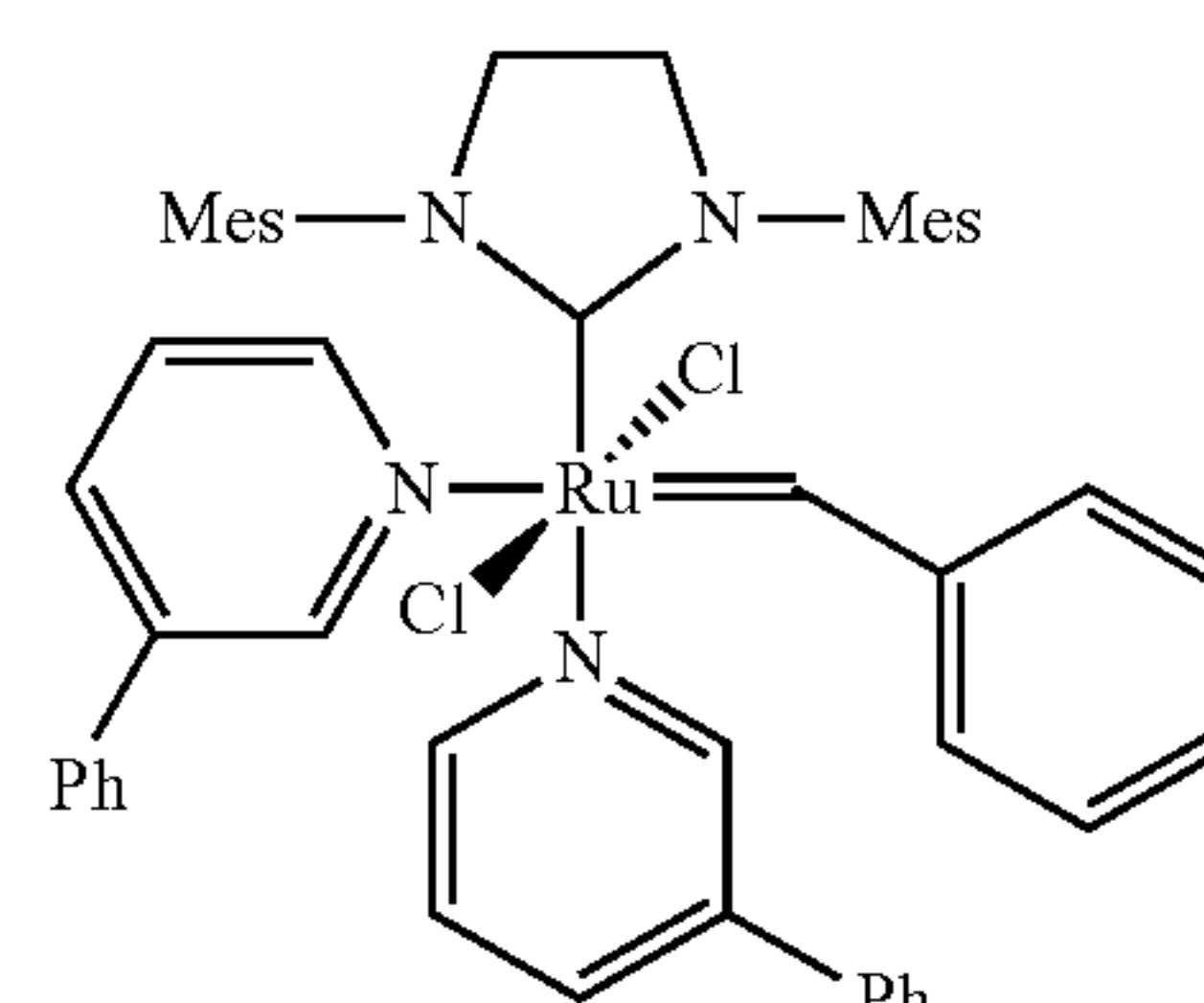
(V)



(VI)

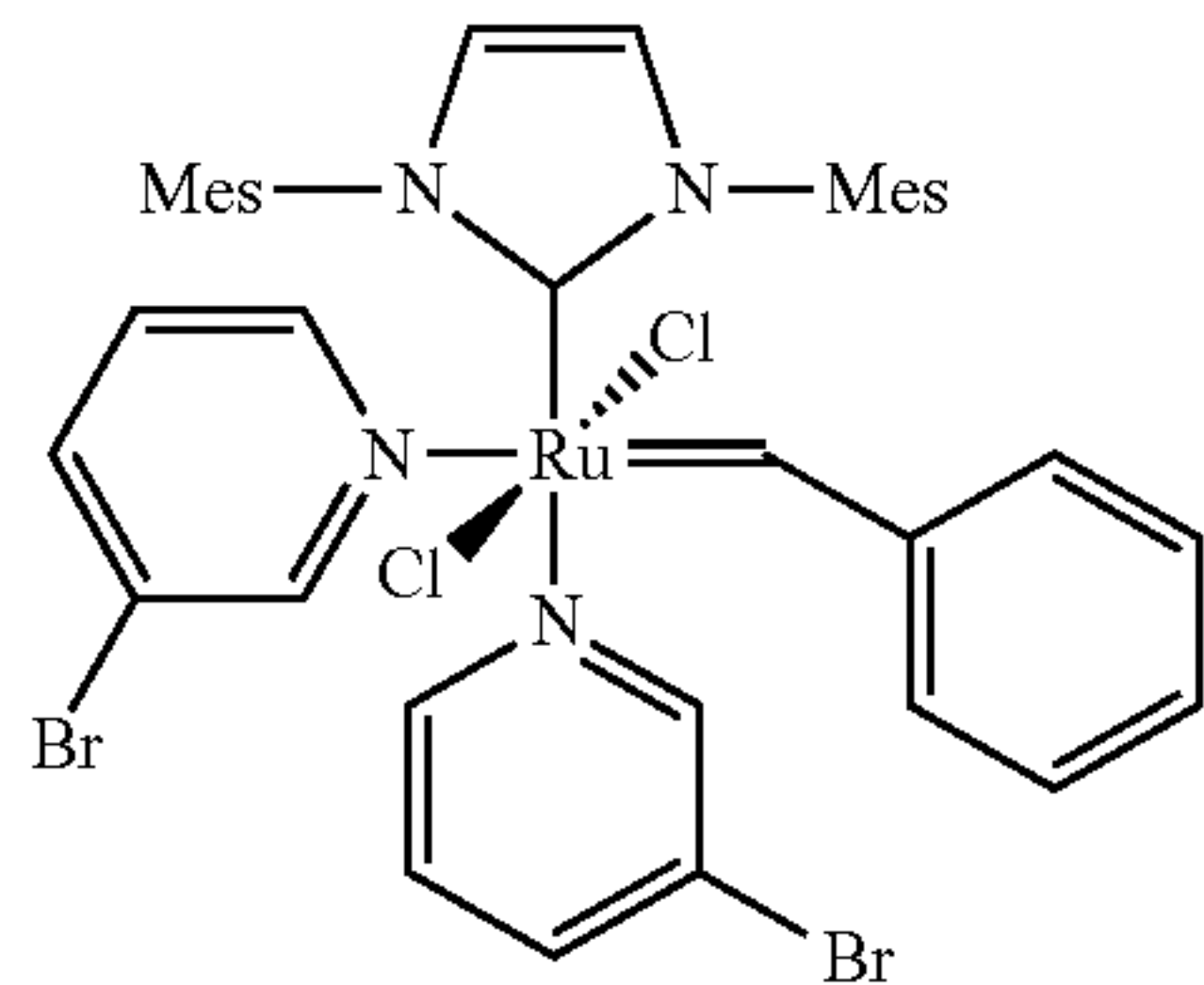
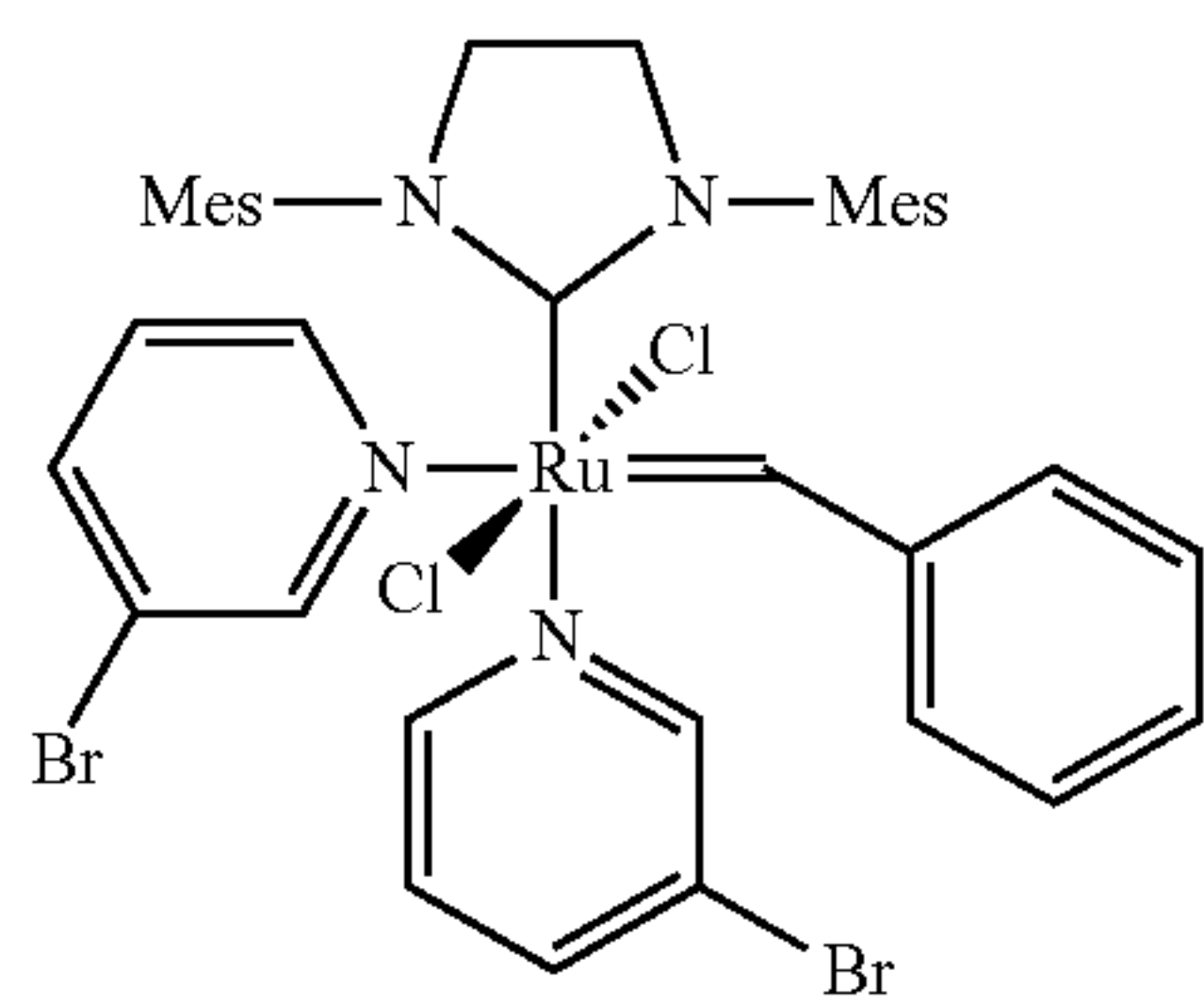
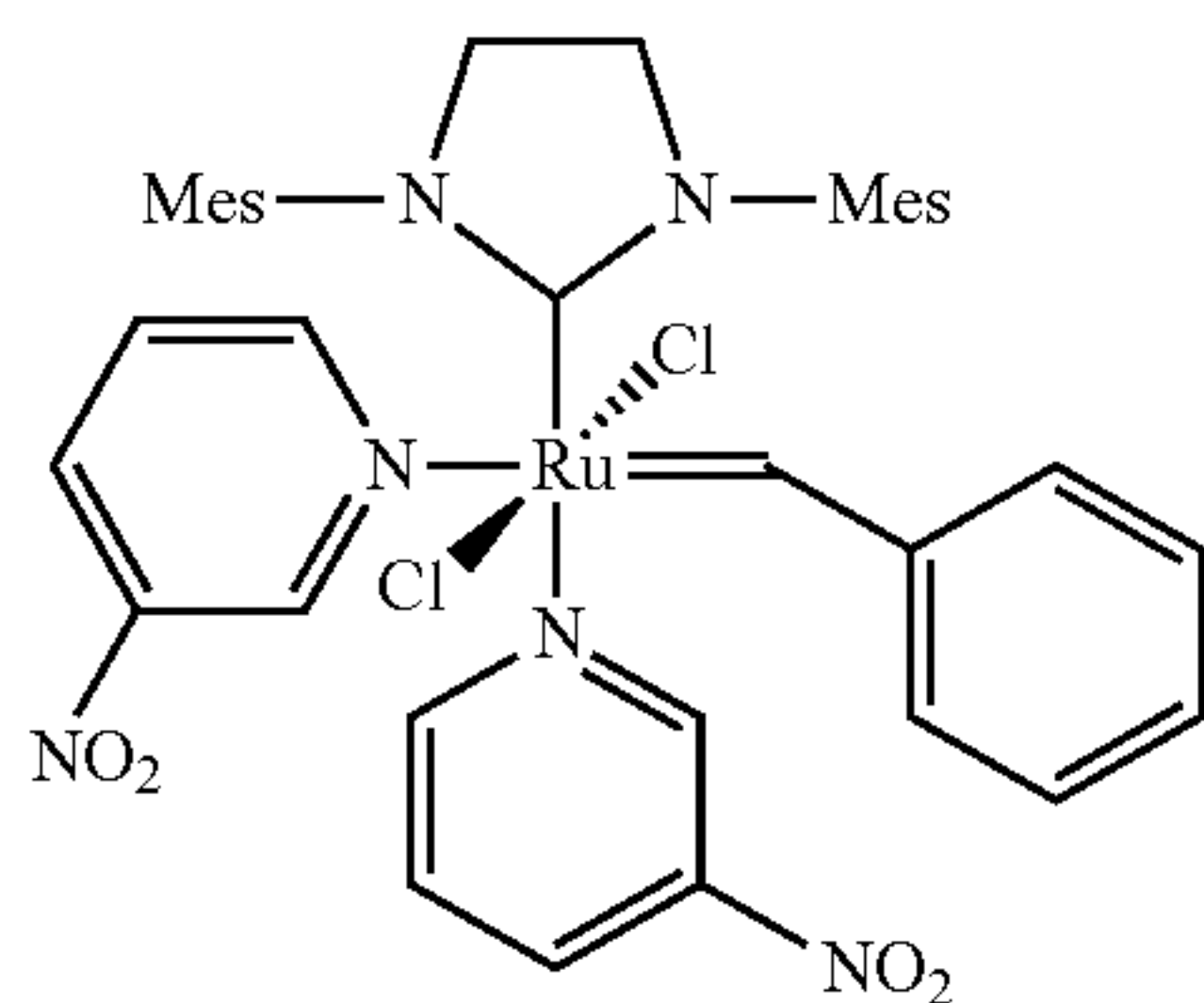
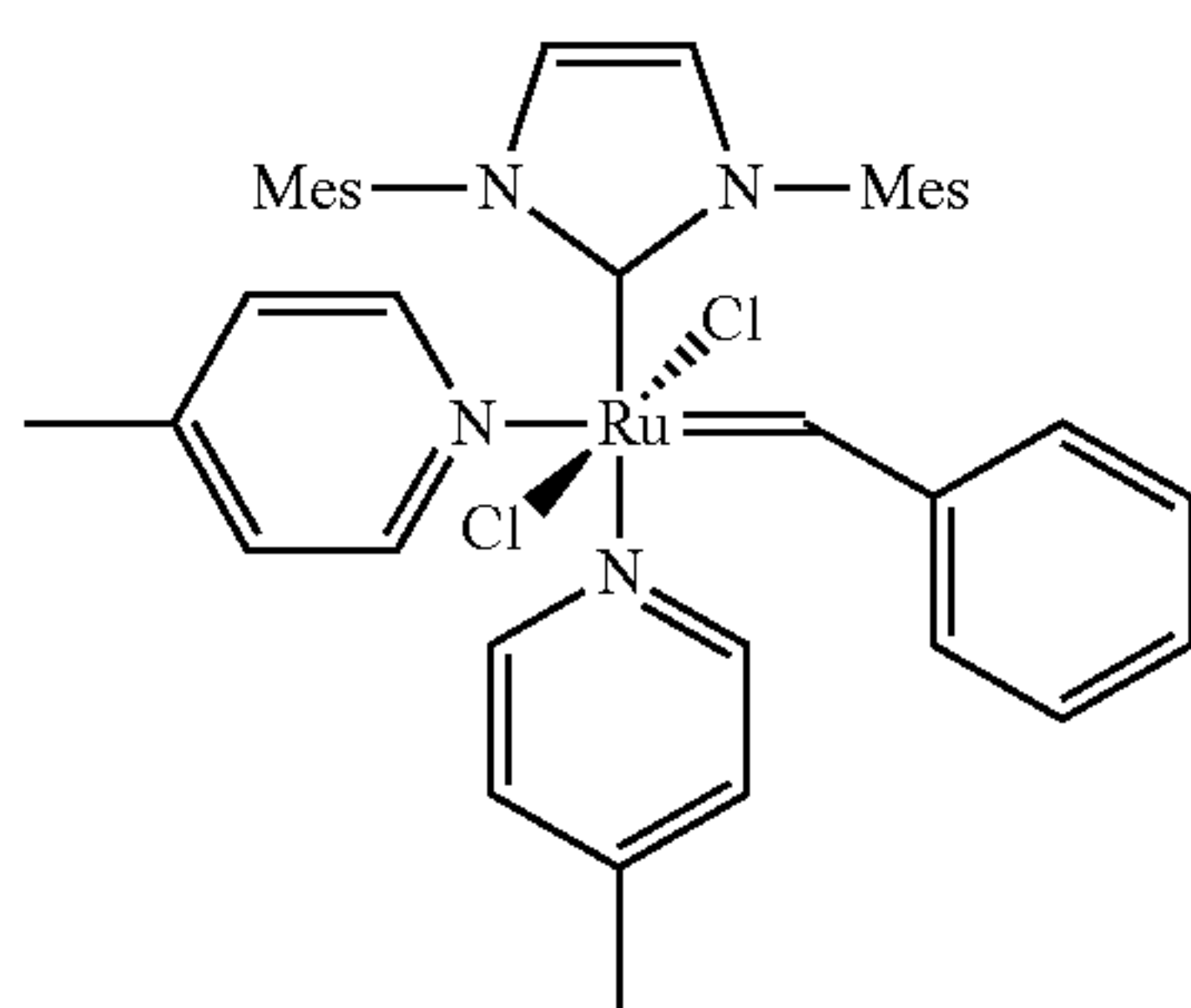
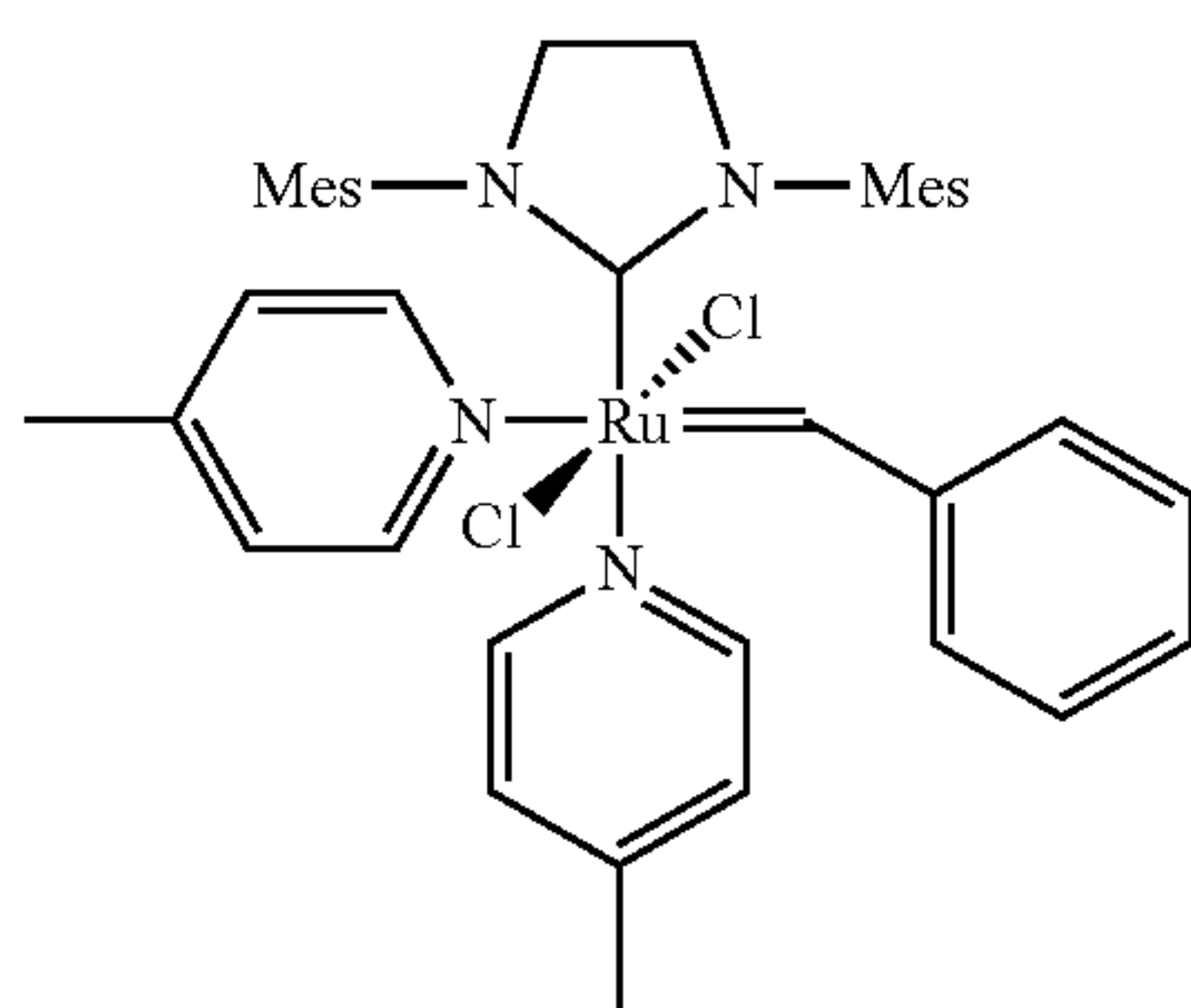


(XX)



(XXI)

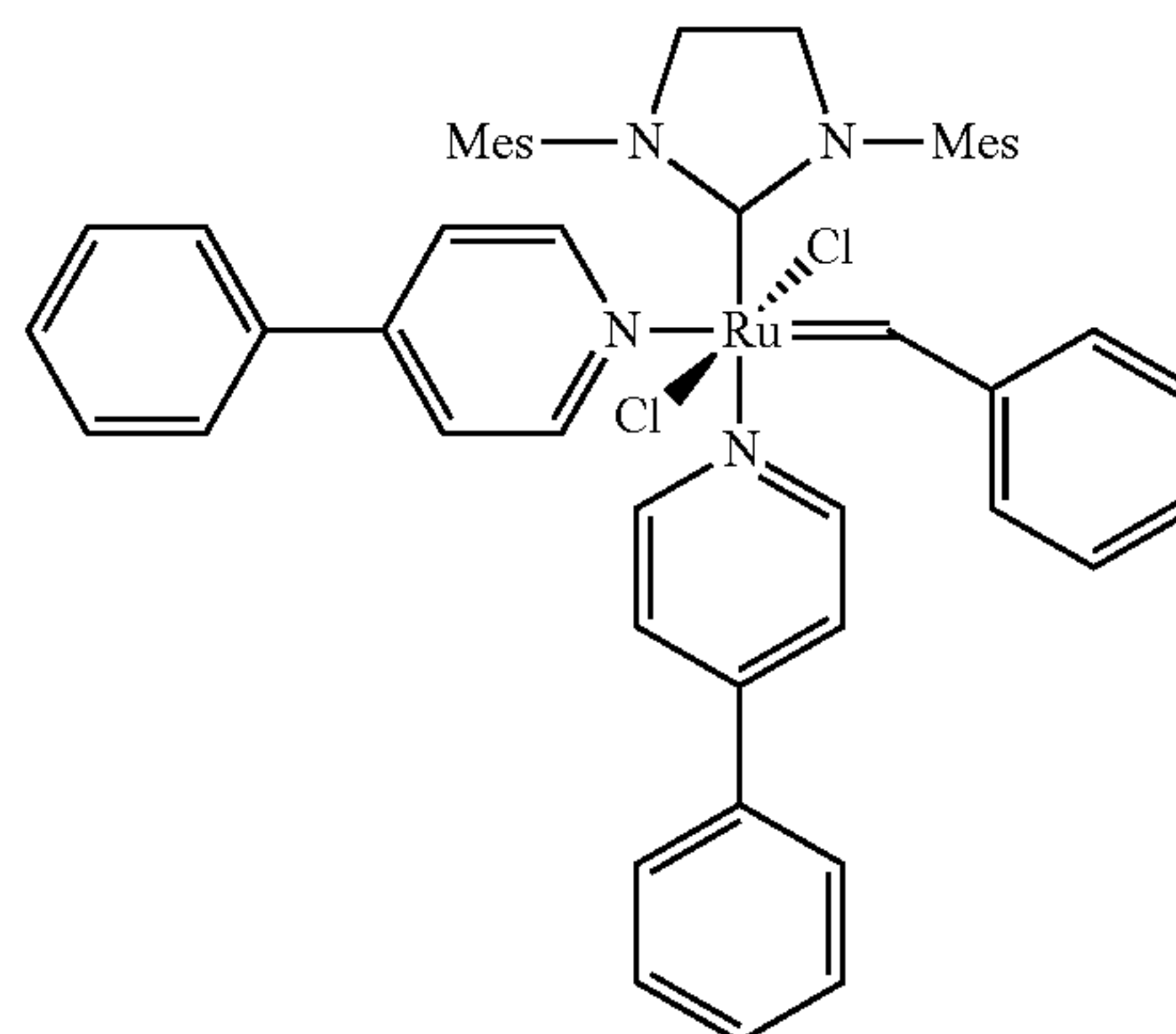
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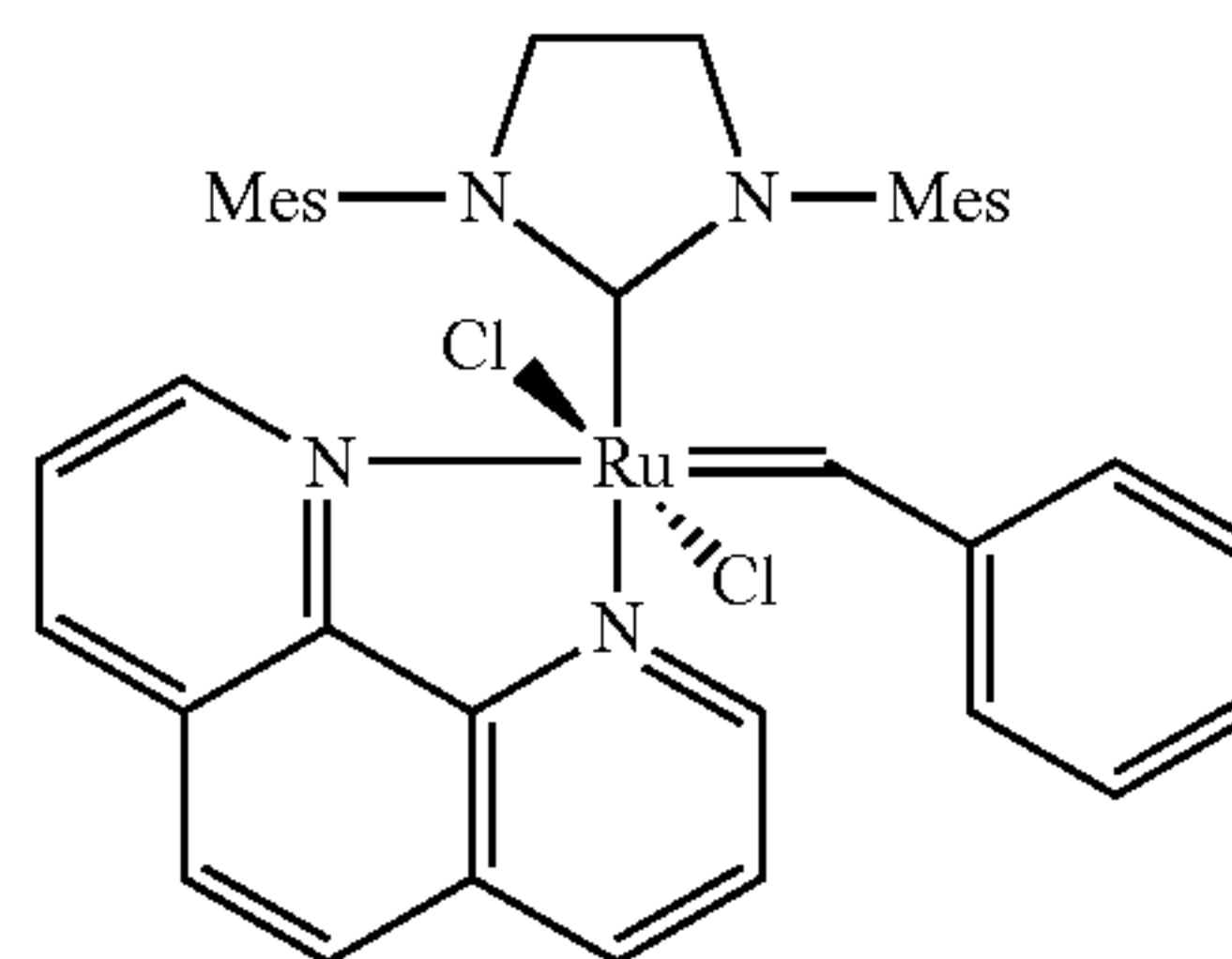
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(XXII)

(XXVII)



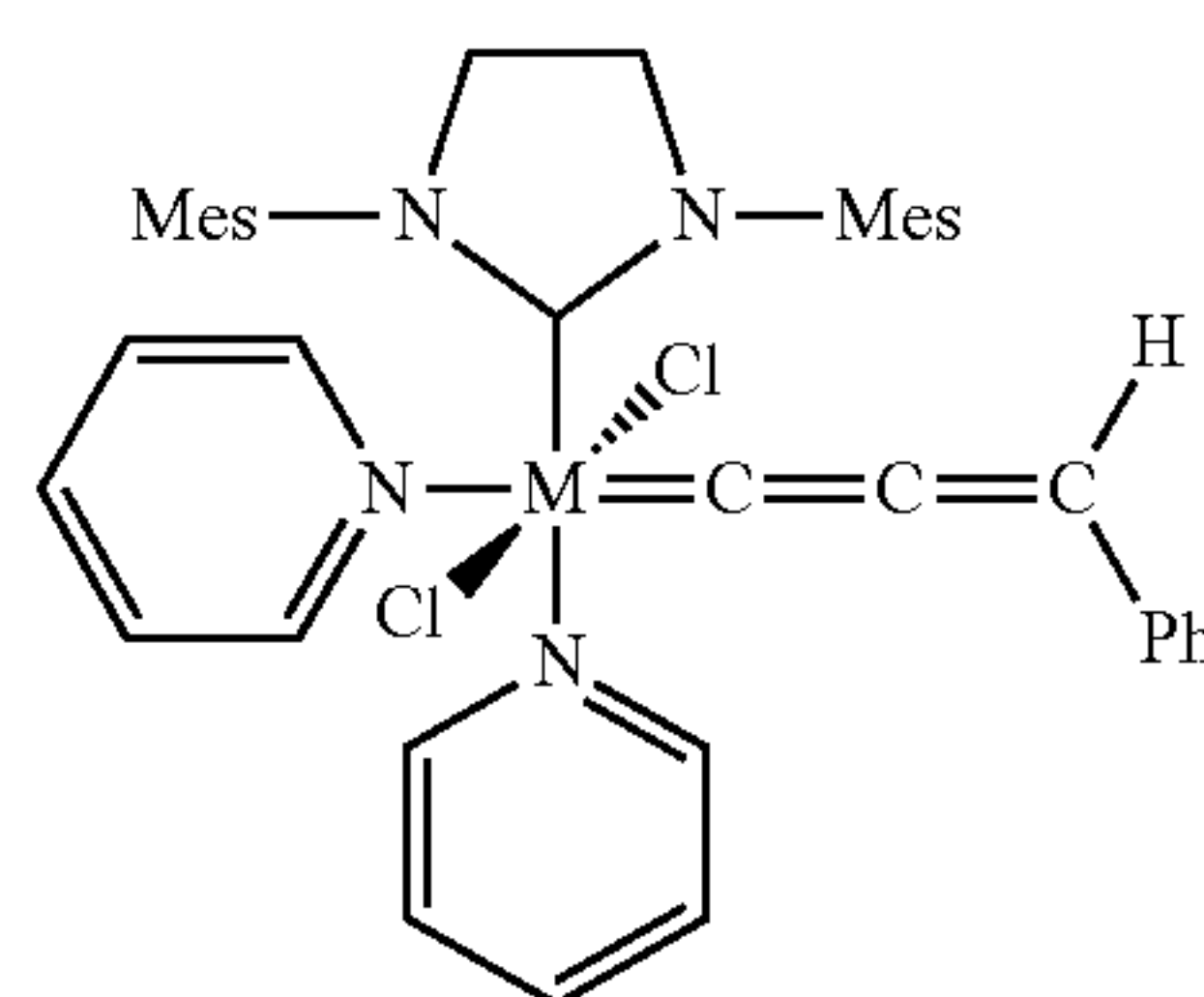
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(XXVIII)

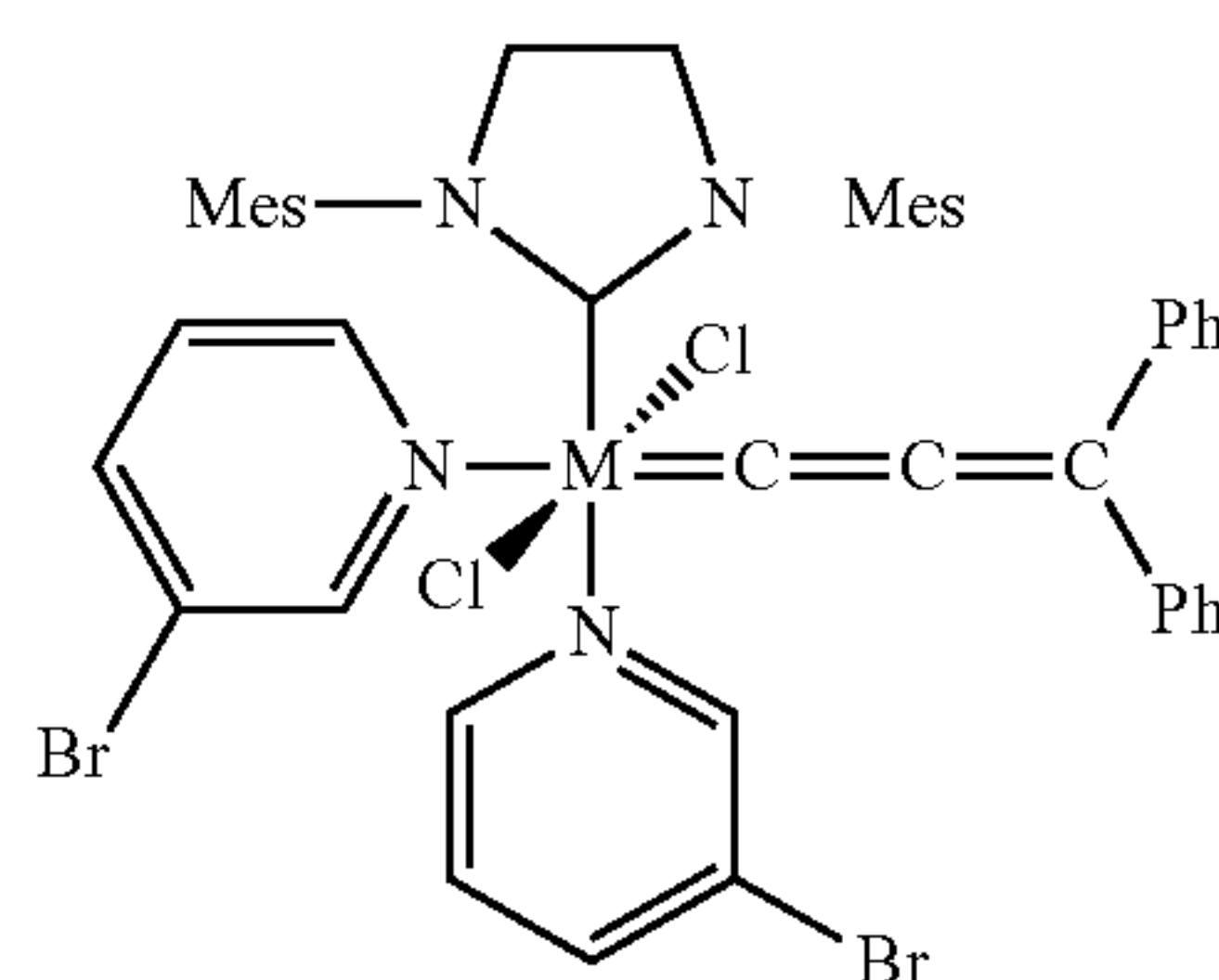
(XXIV)

(XXIX)



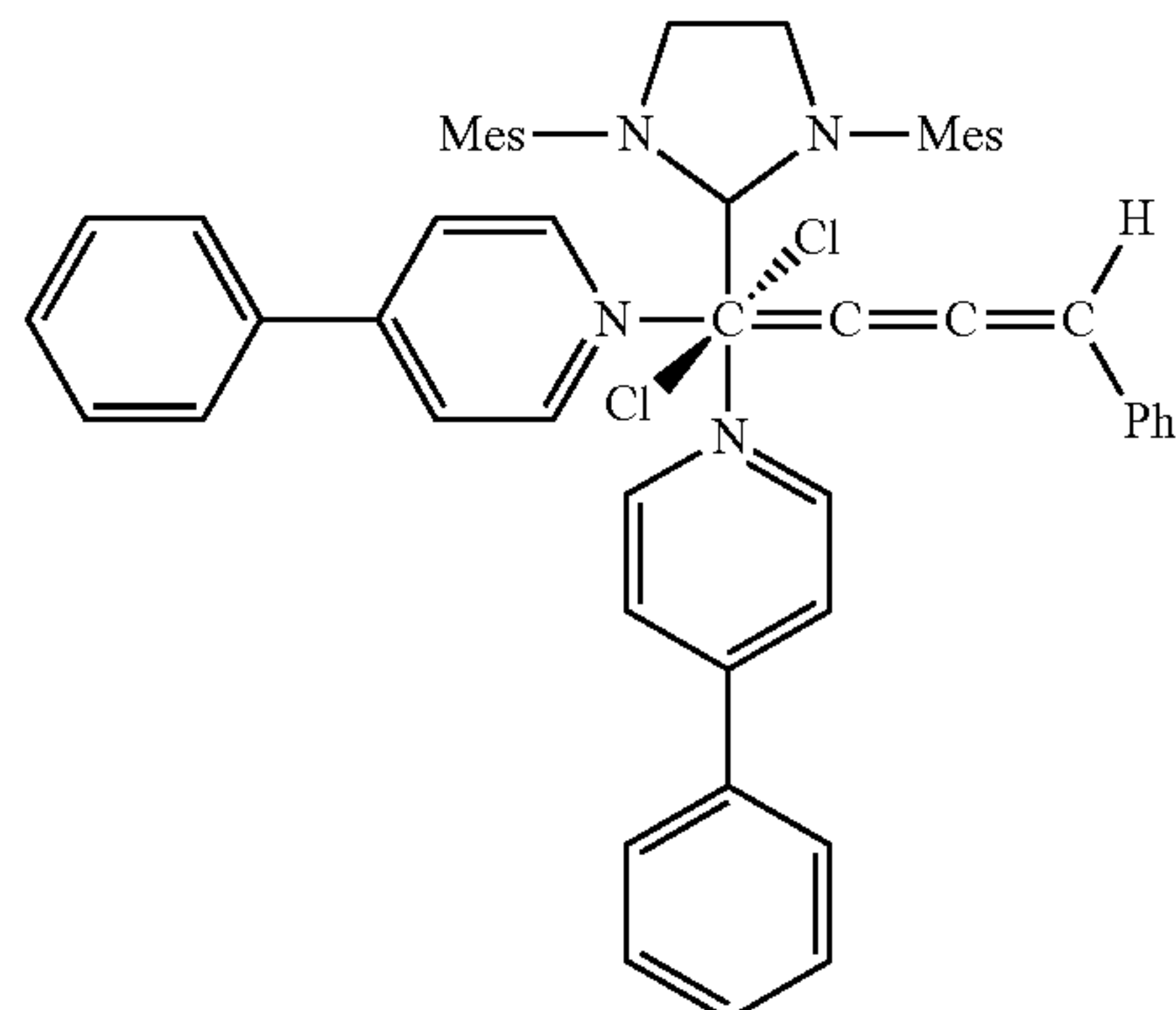
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(XXV)



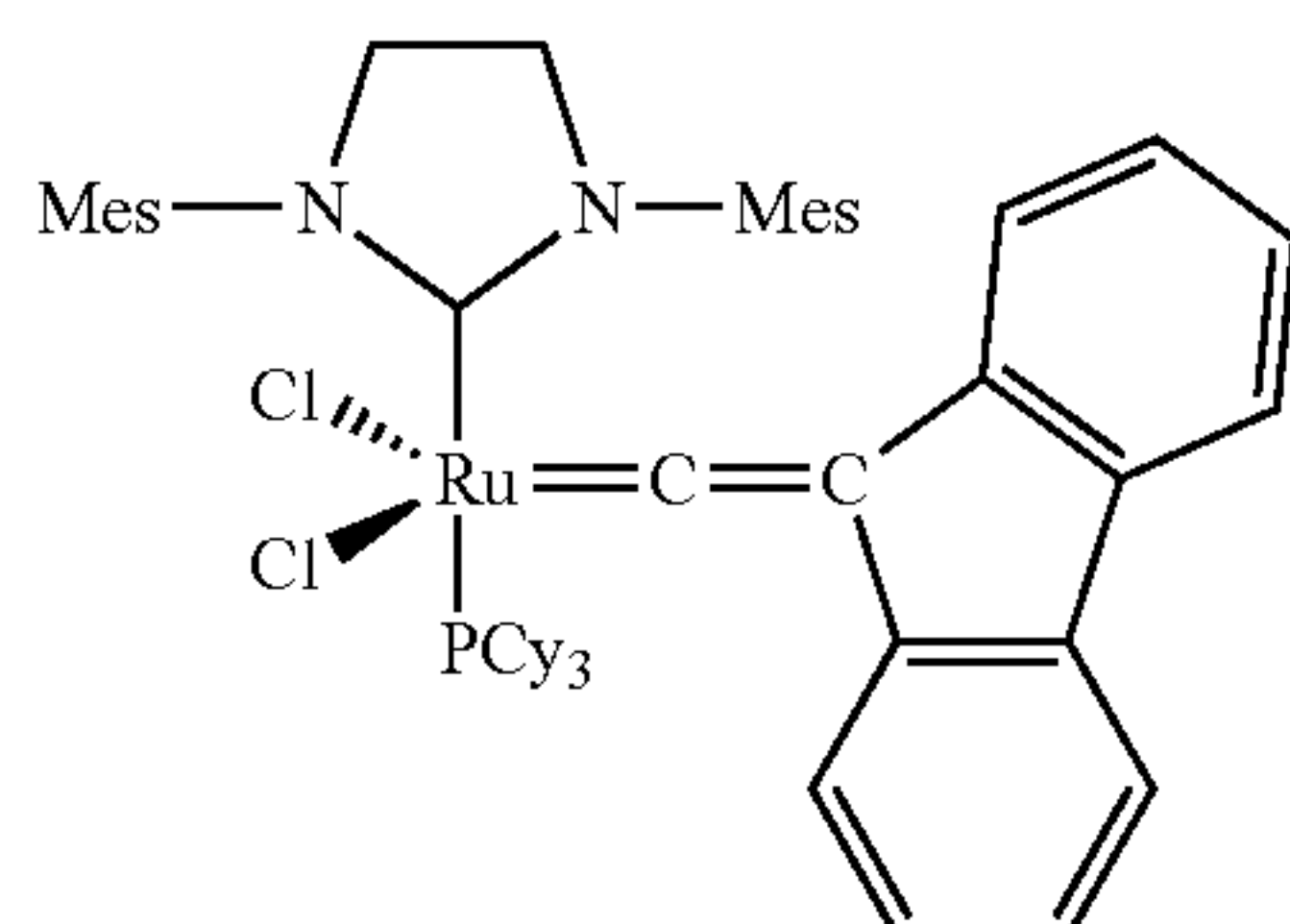
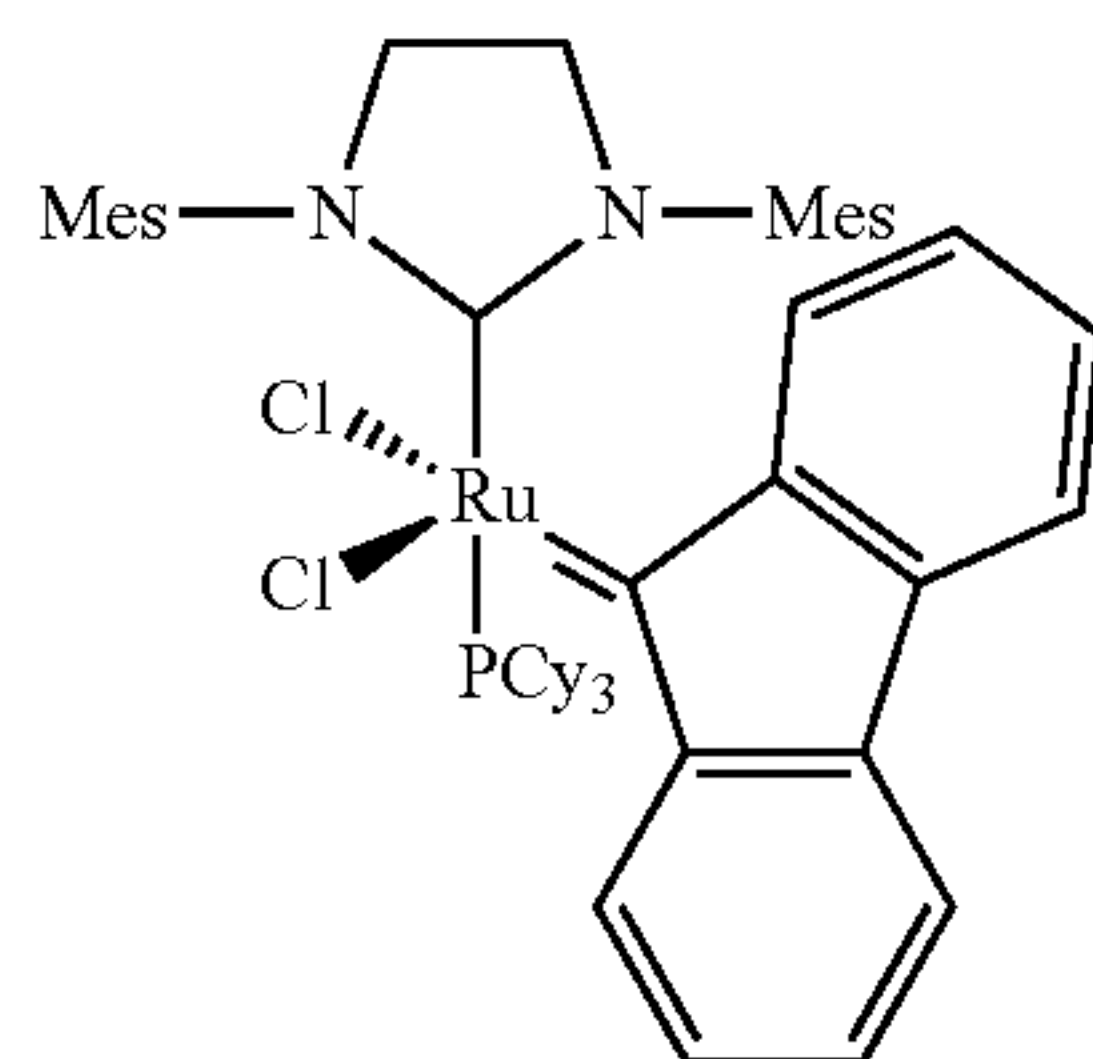
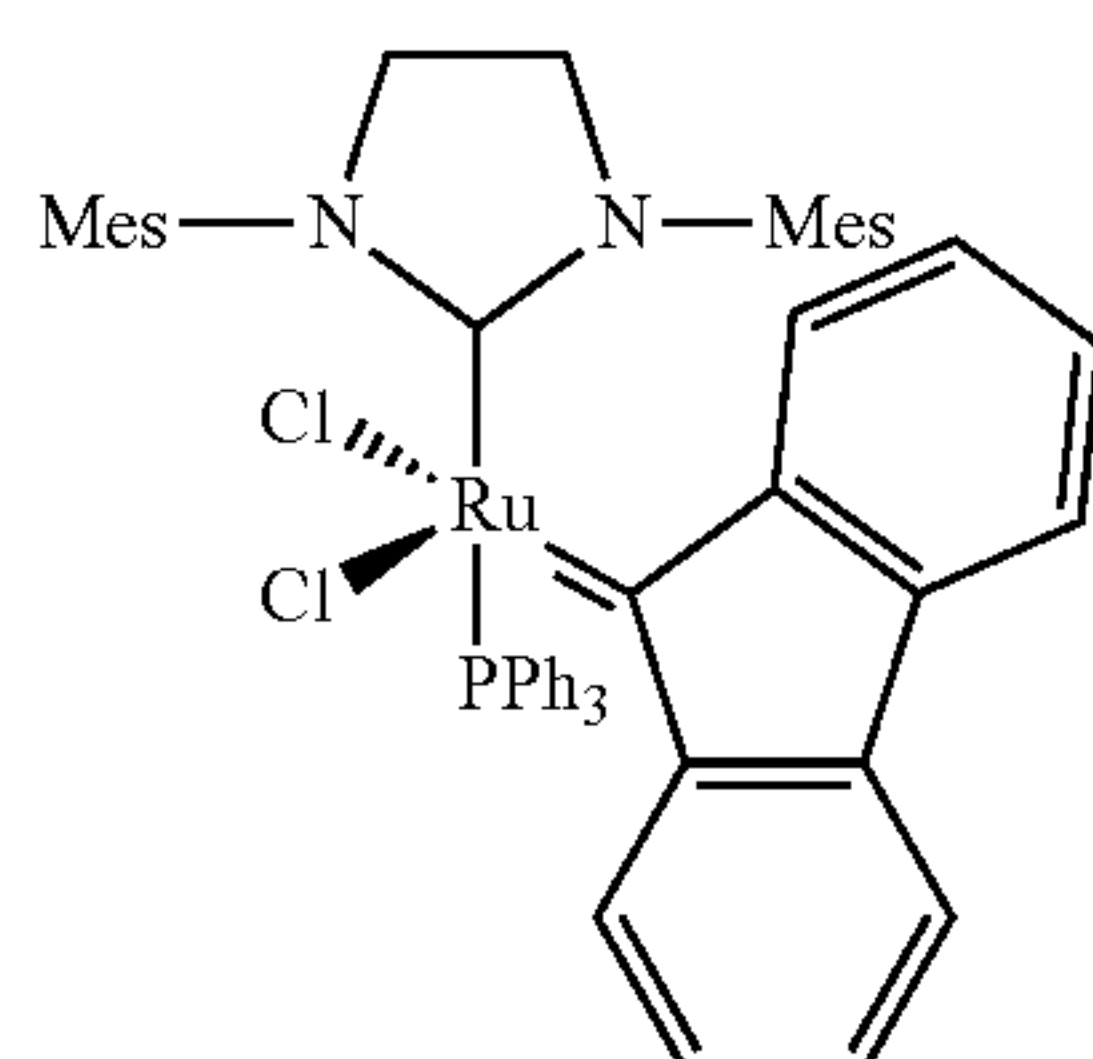
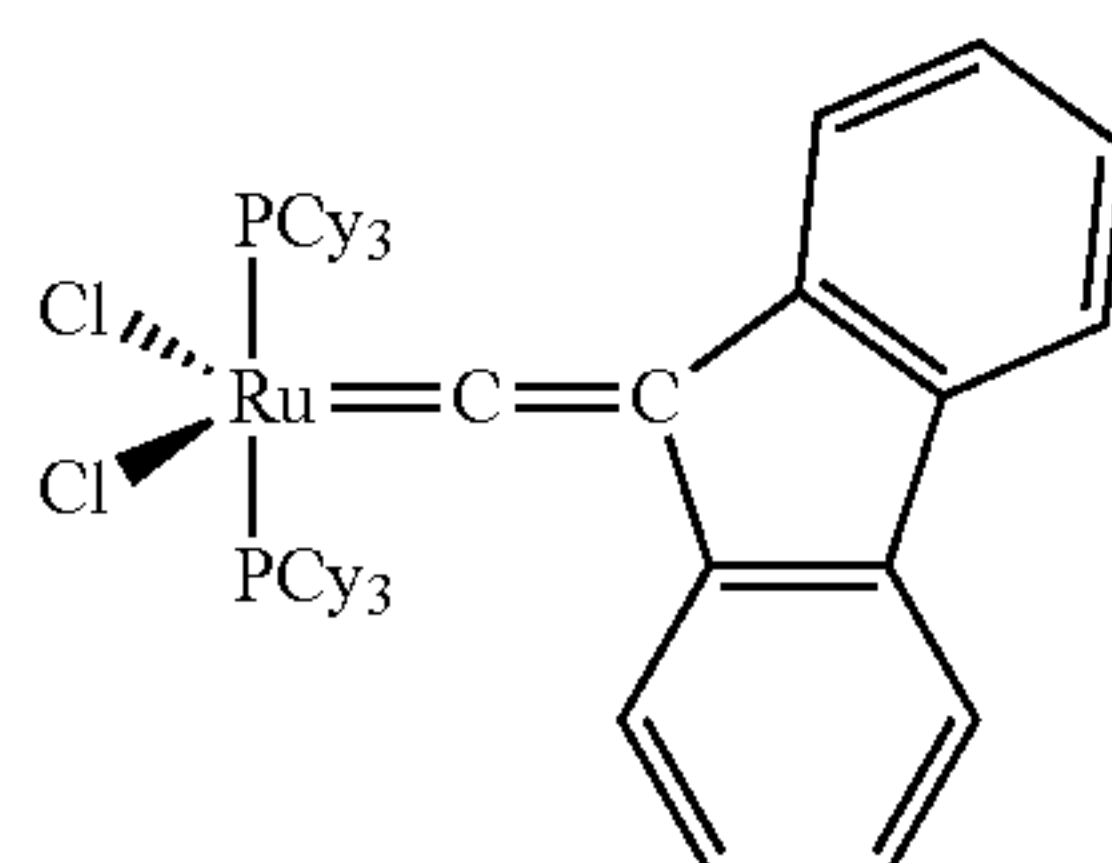
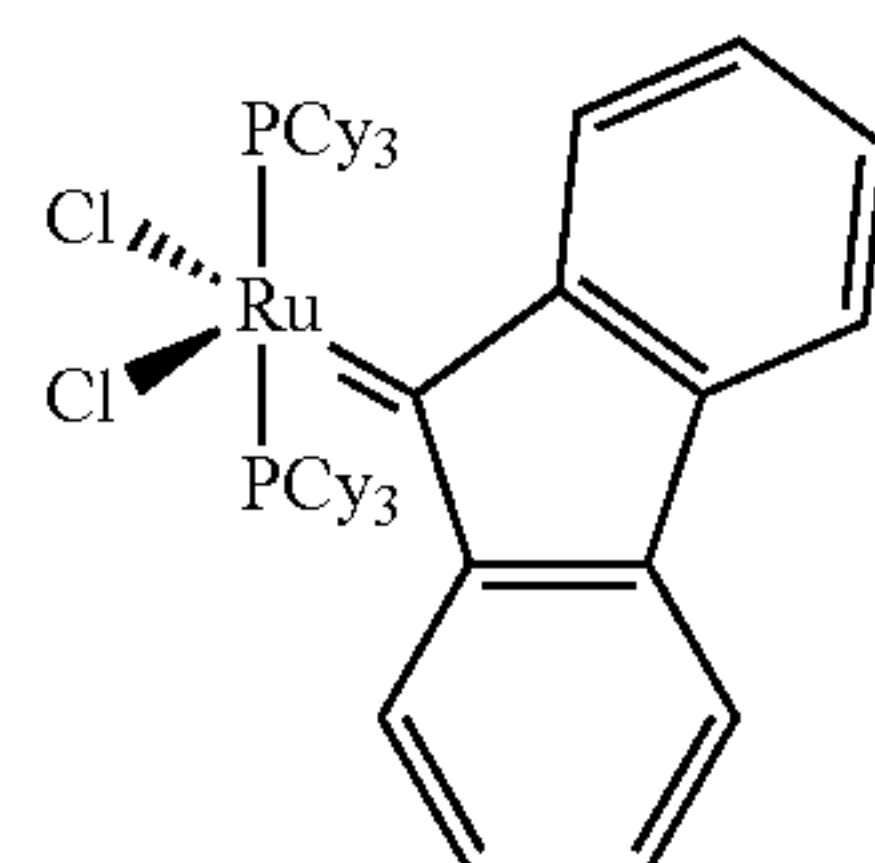
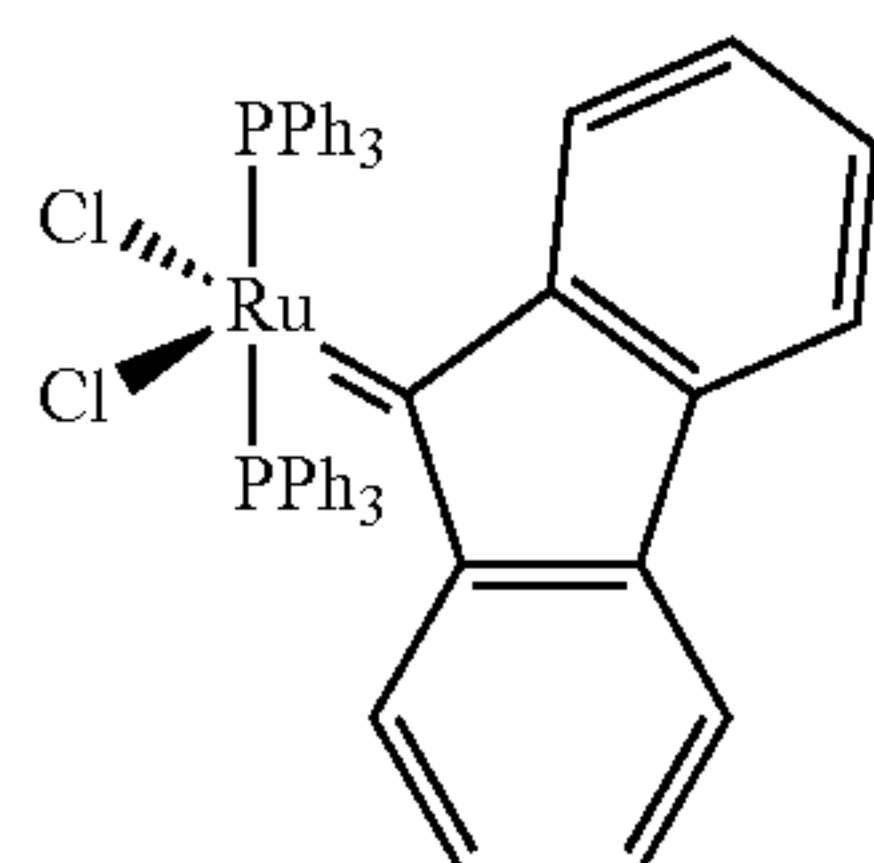
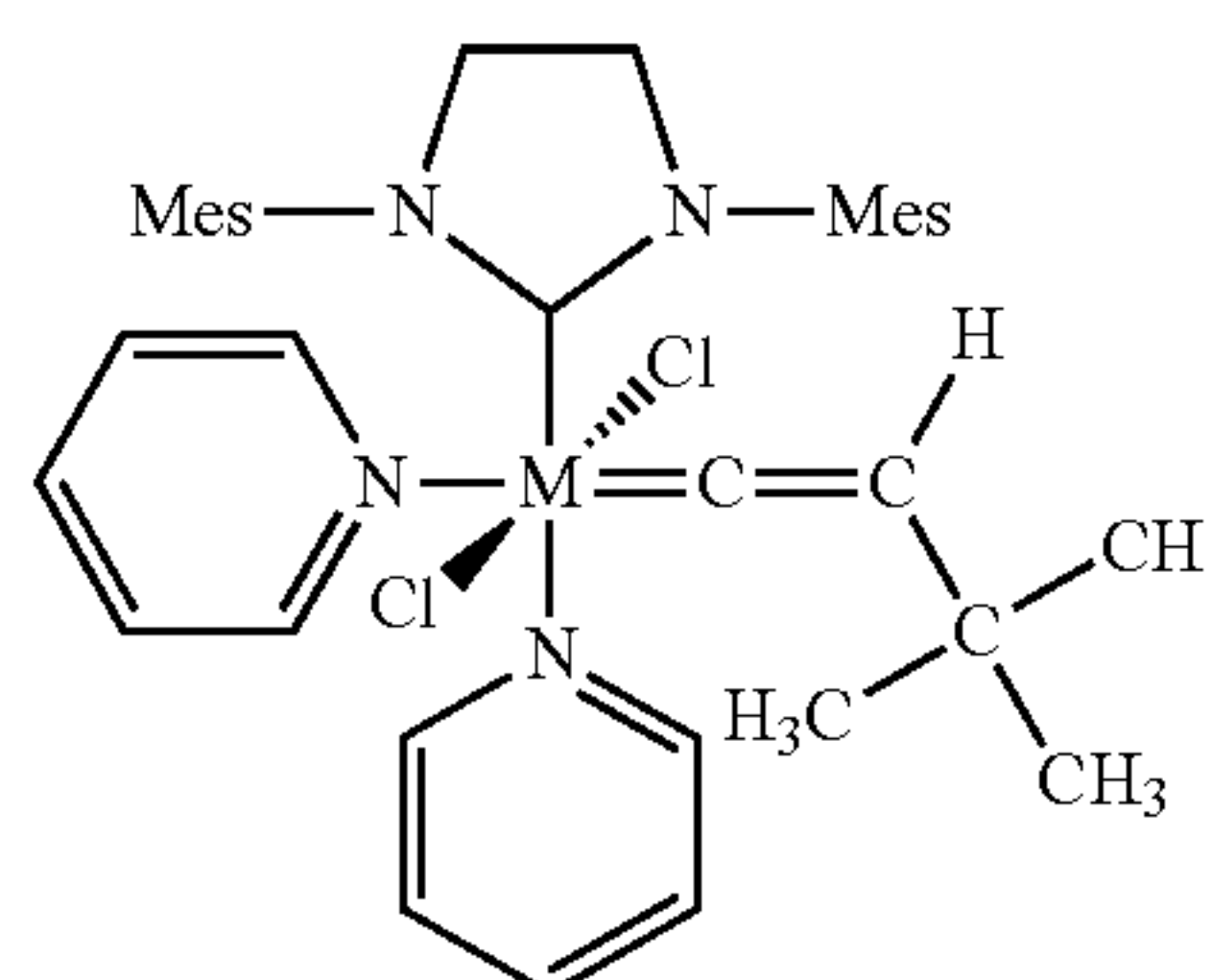
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(XXVI)

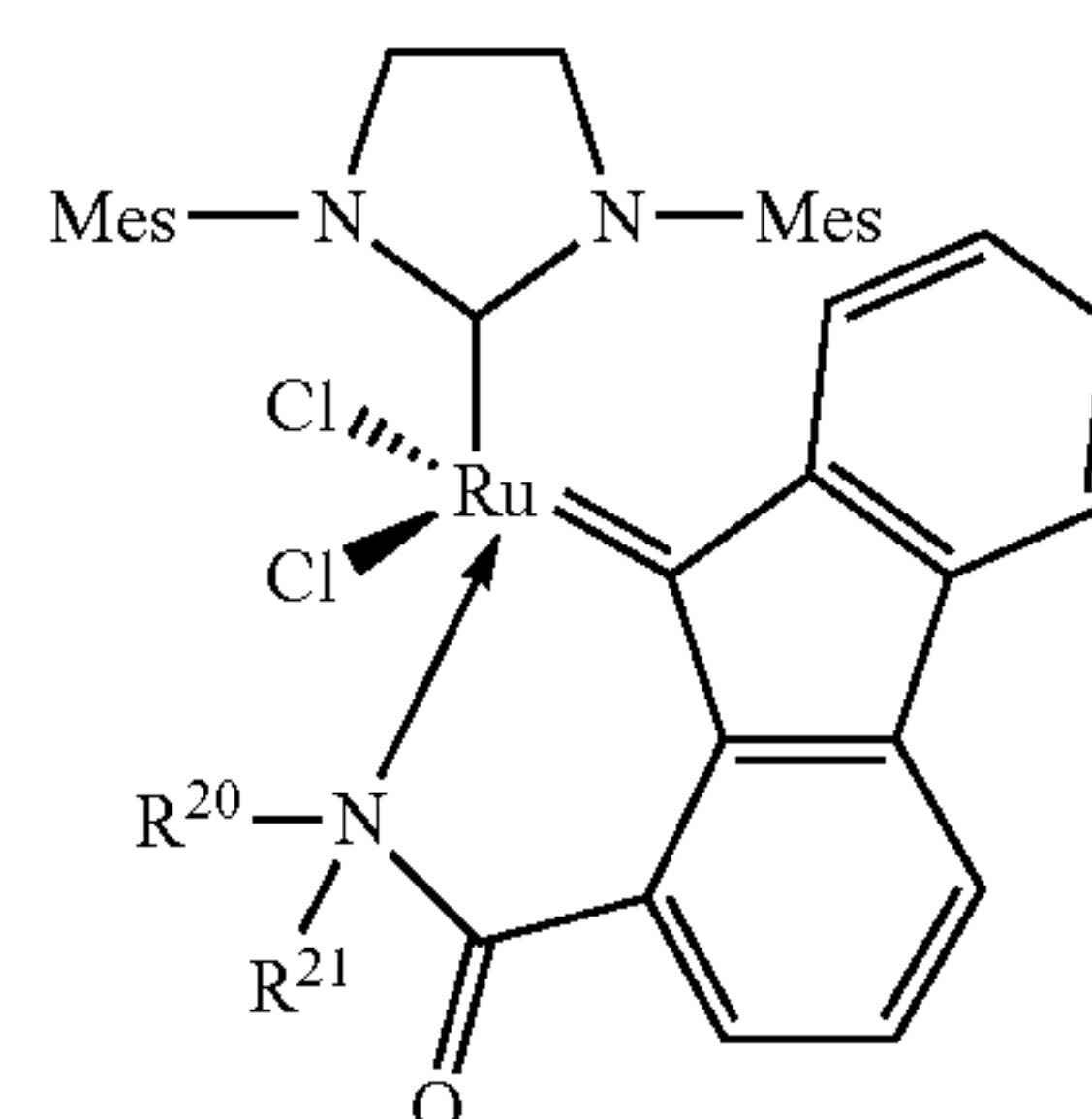
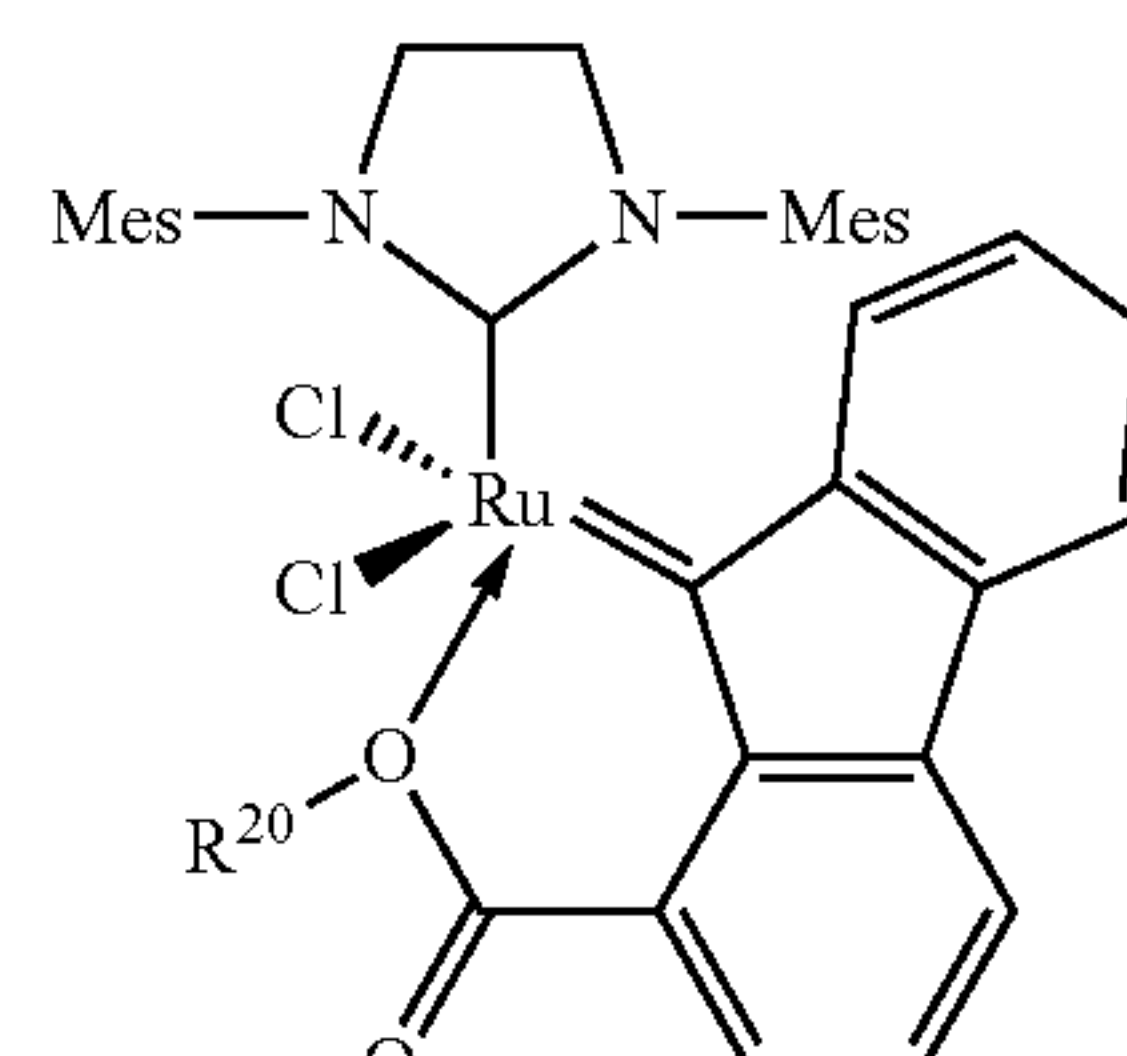
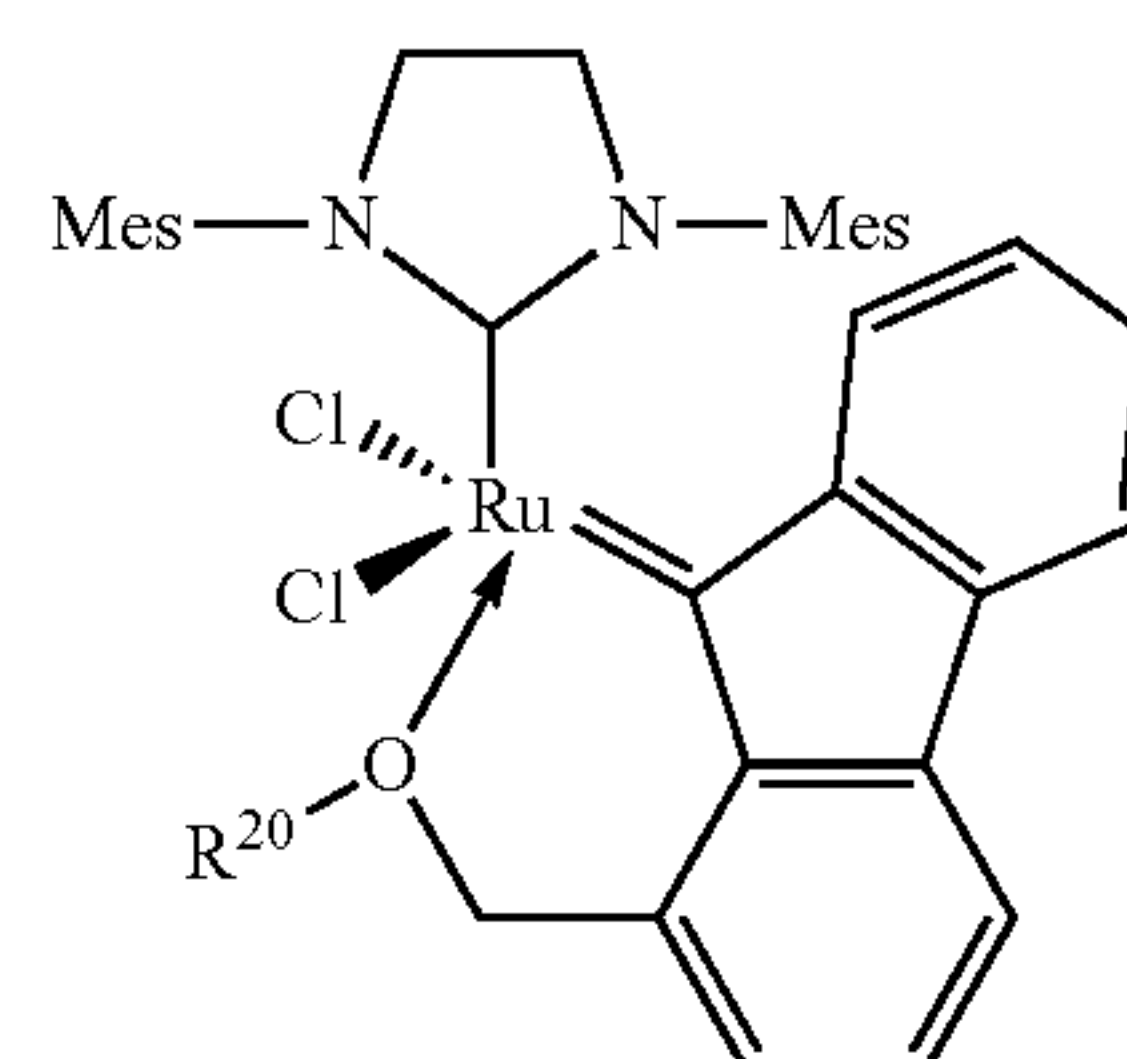
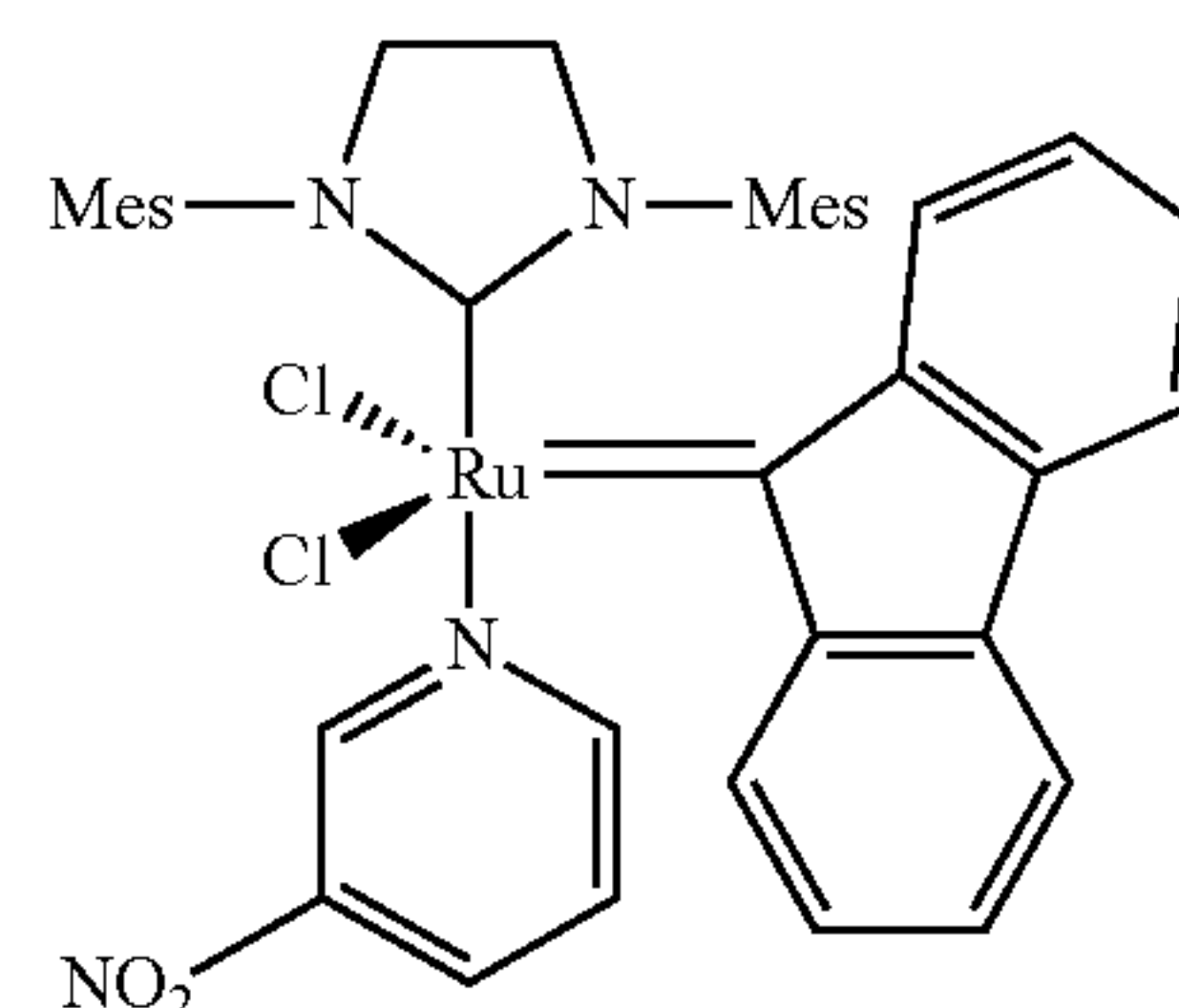
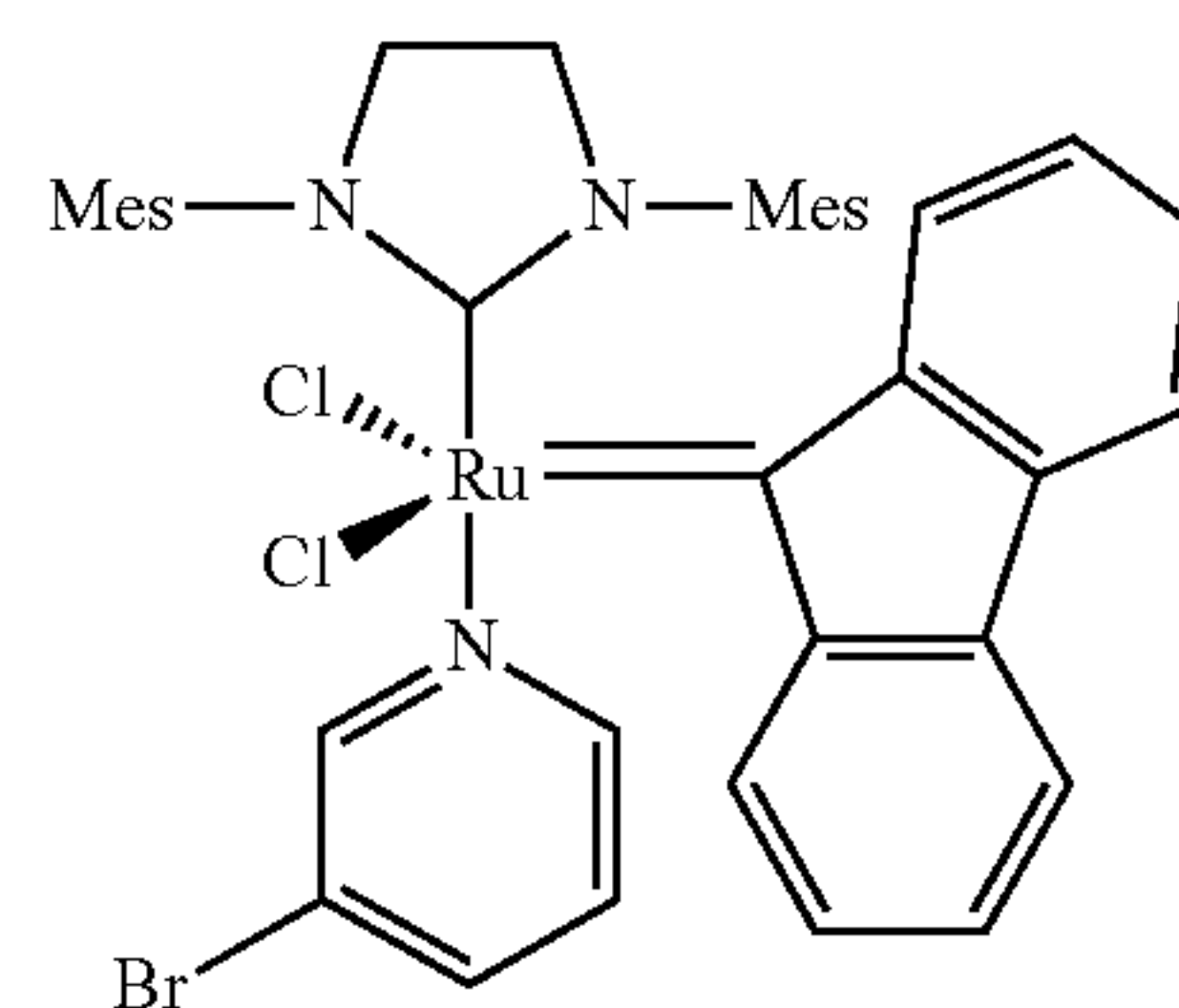
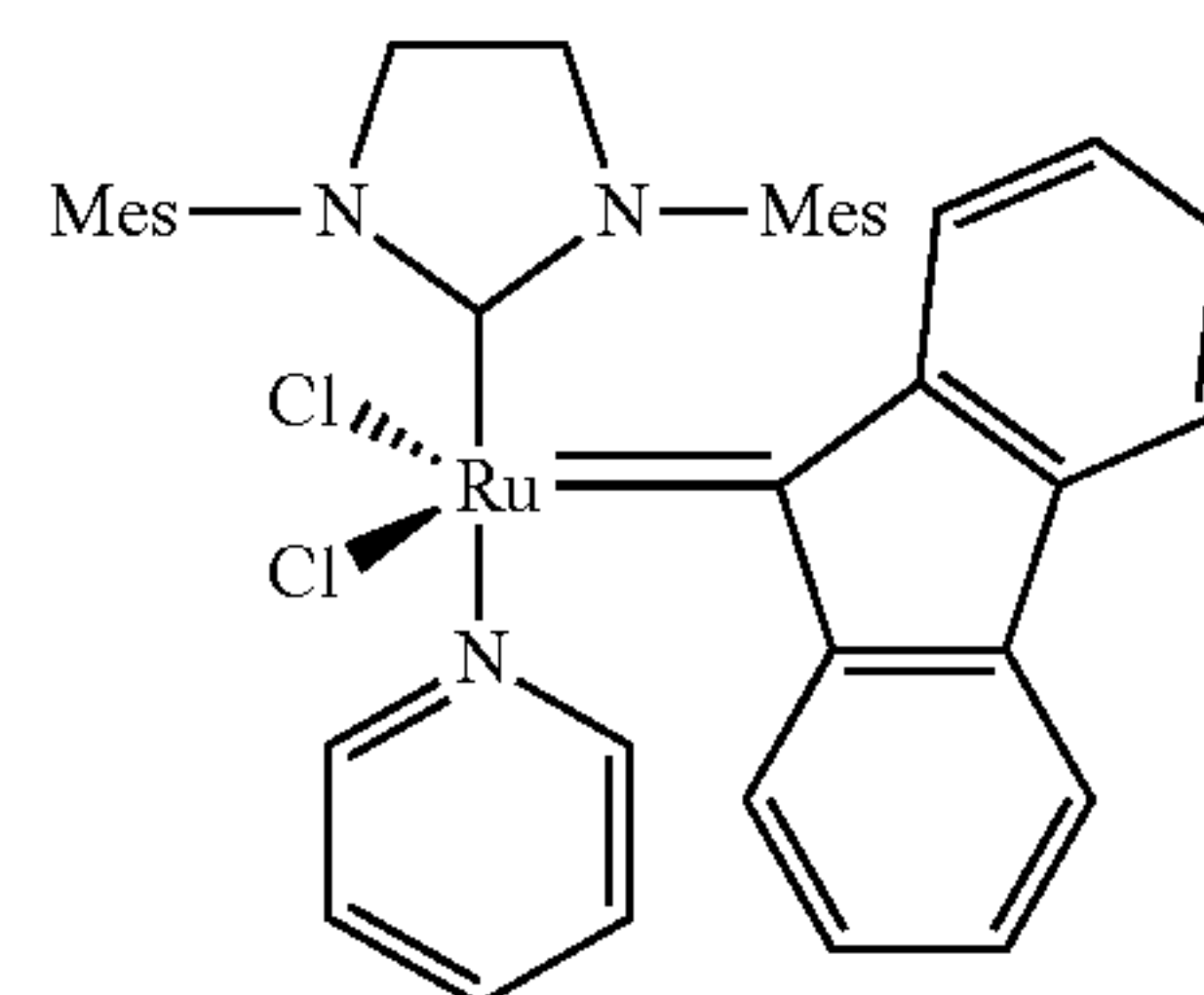


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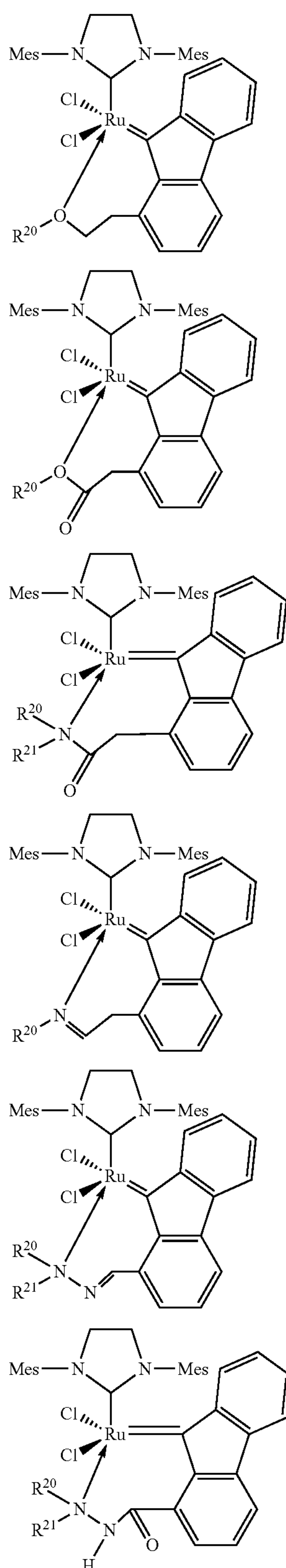
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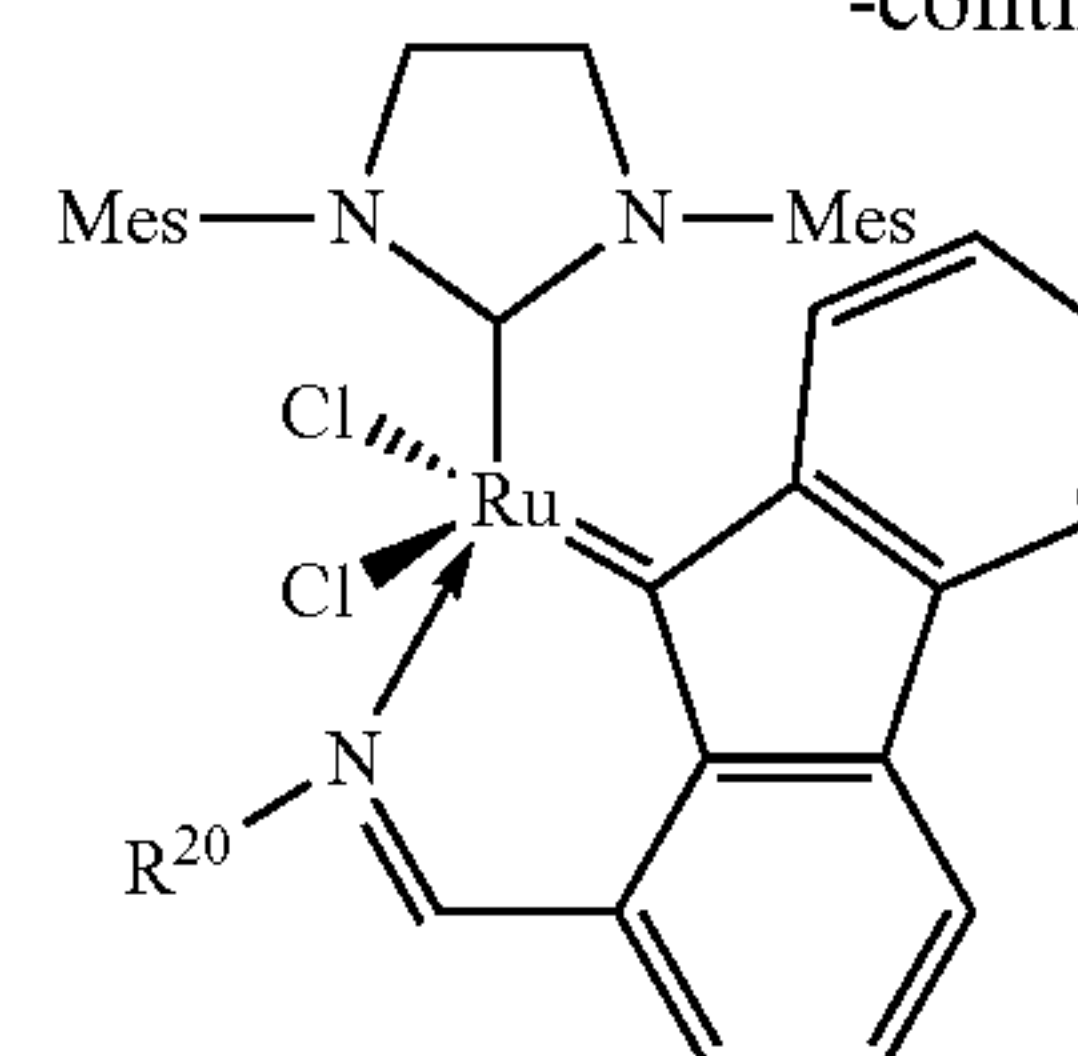
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12. The catalyst composition according to any one of claims **1** to **11** wherein the molar ratio of the complex catalyst to the co-catalyst in a range of from 1:(20 to below 100), preferably 1:(25 to 99.5), more preferably 1:(30 to 99), even more preferably 1:(35 to 98.5) and most preferably 1:(40 to 70).

13. A process for hydrogenating a nitrile rubber comprising

a) preparing the catalyst composition by contacting a complex catalyst based on ruthenium or osmium as central metal and bearing at least one ligand which is bound to the ruthenium or osmium central metal in a carbene-like fashion with at least one co-catalyst in a molar ratio of the complex catalyst to the co-catalyst in the range of 1:(20-550) wherein the co-catalyst must contain at least one vinyl group and thereafter

b) hydrogenating the nitrile rubber in the presence of the catalyst composition formed in step a).

14. The process for hydrogenating a nitrile rubber according to claim **13**, wherein step a) is performed at a temperature in the range of from -20°C . to 160°C . and preferably in the range of from 20°C . to 80°C .

15. The process for hydrogenating a nitrile rubber according to claim **13** or **14**, wherein the ratio of complex catalyst to co-catalyst in step a) is 1:(20-500), preferably 1:(25-475), more preferably 1:(25-450) and most preferably 1:(30-450).

16. The process for hydrogenating a nitrile rubber according to claim **13** or **14**, wherein the molar ratio of the complex catalyst to the co-catalyst in a range of from 1:(20 to below 100), preferably 1:(25 to 99.5), more preferably 1:(30 to 99), even more preferably 1:(35 to 98.5) and most preferably 1:(40 to 70).

17. The process for hydrogenating a nitrile rubber according to any one of claims **13** to **16**, wherein the hydrogenation in step b) is carried out at a temperature in the range of from 60°C . to 200°C ., preferably from 80°C . to 180°C ., most preferably from 100°C . to 160°C . and at a hydrogen pressure in the range of 0.5 MPa to 35 MPa, more preferably of 3.0 MPa to 10 MPa.

18. The process for preparing a hydrogenated nitrile rubber according to any one of claims **13** to **17**, wherein the nitrile rubber prior to being hydrogenated is subjected to a molecular weight degradation in a metathesis reaction first comprising contacting the said nitrile rubber in the absence or presence of a co-olefin with a complex catalyst based on ruthenium or osmium as central metal and bearing at least one ligand which is bound to the ruthenium or osmium central metal in a carbene-like fashion, then

c) contacting the complex catalyst which is present in the reaction mixture obtained after the metathesis reaction with at least one co-catalyst having at least one vinyl

group in a molar ratio of the complex catalyst to the co-catalyst in the range of 1:(20-550) to form a catalyst composition and thereafter
d) hydrogenating the nitrile rubber in the presence of the catalyst composition.

* * * * *