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(71) Applicant *(for all designated States except US)*: CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: MÜHLEBACH, Andreas [CH/CH]; Les Grands Esserts 7, CH-1782 Belfaux (CH). VAN DER SCHAAF, Paul, Adriaan [NL/CH]; Impasse du Castel 9, CH-1700 Fribourg (CH). HAFNER, Andreas [CH/CH]; Bendenweg 3, CH-3177 Laupen (CH).

(74) Common Representative: CIBA SPECIALTY CHEMICALS HOLDING INC.; Patentabteilung, Klybeckstrasse 141, CH-4057 Basel (CH).

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(54) Title: POLYMERIZABLE COMPOSITION

(57) Abstract

A solvent-free polymerizable composition comprising: a) at least one Diels-Alder adduct of (a1) unsubstituted or substituted cycloolefins and (a2) unsubstituted or substituted 1,3-cyclopentadienes, which adduct has a low content of unsubstituted or substituted cyclopentadienes, and b) a catalytically active amount of a ruthenium catalyst for metathesis polymerization, which composition comprises, based on the Diels-Alder adduct, not more than 0.1 % by weight of cyclopenta-1,3-diene or substituted cyclopenta-1,3-diene and from 0.05 to 0.3 % by weight of ruthenium catalyst; with the exception of dicyclopentadiene in combination with 0.3 % by weight (4-isopropyltolyl)$RuCl_2[P(C_6H_{11})_3]$. The compositions can be used to produce mouldings having very good mechanical properties.

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Polymerizable composition

The present invention relates to a solvent-free composition comprising a) a Diels-Alder adduct of unsubstituted or substituted 1,3-cyclopentadienes and a cycloolefin, which adduct has a low content of unsubstituted or substituted cyclopentadiene, b) if desired, at least one substituted or unsubstituted strained cyclic olefin, and c) a small amount of a ruthenium catalyst for the metathesis polymerization, and to a process, and the use of the composition, for preparing metathesis polymers and mouldings from these polymers.

A. Demonceau et al. in J. Mol. Catal. 76:123-132 (1992) describe ruthenium compounds as suitable metathesis polymerization catalysts of, for example, norbornene, with the possibility of increasing the reactivity by adding diazo esters. Diels-Alder adducts of cyclopentadienes are not among the monomers mentioned.

C. Tanelian et al. in Tetrahedron Letters 52:4589-4592 (1977), describe how the ruthenium compound $RuCl_2[P(C_6H_5)_3]_3$ is deactivated by dicyclopentadiene, and no polymers are formed by thermal metathesis polymerization.

In WO 93/20111, ruthenium compounds having phosphine ligands, for example $[(H_5C_6)_3P]_2Cl_2Ru=CH-CH=C(C_6H_5)_2$, are proposed as thermal catalysts for the ring-opening metathesis polymerization of strained cycloolefins, where cyclodienes, for example dicyclopentadiene, act as catalyst inhibitors and can therefore not be polymerized.

In our own investigations it has been found that dicyclopentadiene can be polymerized with ruthenium catalysts, albeit with the need to use relatively high amounts of catalyst. It has additionally been observed that the polymerization proceeds irregularly in the case of mass polymerizations, and that in many cases different degrees of polymerization occur over the cross-section of a moulding. Even under identical reaction conditions, mouldings with different mechanical properties are often obtained, for example rubber-like products or tough mouldings. Consequently, the resulting mouldings are often unsuitable for industrial use. Useful mouldings can only be obtained by using larger amounts of catalyst, but this is uneconomic. It has additionally been found that oligocyclopentadienes specifically as Diels-Alder adducts, or, more generally, Diels-Alder adducts of 1,3-dicyclopentadienes and cycloolefins, always include a certain amount of 1,3-dicyclopentadienes, the amount being determined by the equilibrium of the Diels-Alder reaction and in general being significantly more than 0.1 % by weight.

It has now surprisingly been found that cyclopentadiene and substituted cyclopentadienes, which are always present in technical-grade and purified Diels-Alder adducts with cycloolefins, inhibit the ruthenium catalysts and are responsible for the variable results of a polymerization. It has also, surprisingly, been found that, even with very small amounts of ruthenium catalyst, hard, elastic and true-to-type mouldings with very good mechanical properties and high glass transition temperatures (T_g) can be obtained even when the content of cyclopentadiene or substituted cyclopentadienes in the Diels-Alder adduct is not more than 0.1 % by weight. The glass transition temperatures (T_g) which can be achieved using, say, dicyclopentadiene may amount to 120 °C or even significantly more.

The invention provides, firstly, a solvent-free polymerizable composition comprising a) at least one Diels-Alder adduct of (a1) unsubstituted or substituted cycloolefins and (a2) unsubstituted or substituted 1,3-cyclopentadienes, which adduct has a low content of unsubstituted or substituted cyclopentadienes, and b) a catalytically active amount of a ruthenium catalyst for metathesis polymerization, which composition comprises, based on the Diels-Alder adduct, not more than 0.1 % by weight of cyclopenta-1,3-diene or substituted cyclopenta-1,3-diene and from 0.05 to 0.3 % by weight of ruthenium catalyst; with the exception of dicyclopentadiene in combination with 0.3 % by weight (p-cumene)$RuCl_2[P(C_6H_{11})_3]$ = (4-isopropyltolyl)$RuCl_2[P(C_6H_{11})_3]$.
The term "p-cumene" in this application is to be understood as referring to "4-isopropyltolyl".

The content of cyclopenta-1,3-diene or substituted cyclopenta-1,3-diene is determined by means of UV spectroscopy in ethanolic solution (for example with 10 or 12 mg of Diels-Alder adduct per ml) at a λ_{max} of 238 nm by comparing the values found for the molar extinction ε with samples of known 1,3-diene content. The content can also be determined in a manner known per se by chromatographic methods (gas chromatography, HPLC [High Pressure Liquid Chromatography]), by comparison with calibration samples of known content.

The Diels-Alder adducts can be substituted in one or more of the rings by one or more radicals, preferably from one to three radicals, more preferably one or two radicals, for example by C_1-C_{18}alkyl, more preferably C_1-C_{12}alkyl, preferably C_1-C_6alkyl and, with particular preference, C_1-C_4alkyl; C_1-C_{12}alkoxy and, preferably C_1-C_4alkoxy; C_1-C_6haloalkyl and, preferably C_1-C_4haloalkyl with halogen preferably as fluorine or chlorine; C_3-C_8cycloalkyl; C_6-C_{12}aryl; C_7-C_{12}aralkyl; =O; halogen, preferably fluorine or chlorine; -CN; -COOM; -COO(M)$_{1/2}$; -C(O)OR$_{01}$; -C(O)NR$_{02}$R$_{03}$; -C(O)-O-C(O)-; -C(O)-NR$_{02}$-C(O)-, in which M is Li, Na or K, (M)$_{1/2}$ Mg, Ca, Ba or Sr, R$_{01}$ is C_1-C_{18}alkyl, C_3-C_{12}alkenyl, C_3-C_{12}cycloalkyl, phenyl or benzyl, and R$_{02}$ and R$_{03}$ independently are H or are as defined for R$_{01}$.

Preferred substituents are C_1-C_6alkyl, C_1-C_4alkoxy, C_5cycloalkyl or C_6cycloalkyl, phenyl, benzyl, $-CH_2F$, $-CHF_2$, $-CF_3$, $-CH_2Cl$, $-CHCl_2$, $-CCl_3$, F, Cl, -CN and -C(O)O-C_1-C_{18}alkyl.

Particular preference is given to alkyl substituents, since then the Diels-Alder adducts are composed entirely of only C and H. Examples of alkyl are methyl, ethyl, n- or i-propyl, n-, i- or t-butyl, and the isomers of pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl.

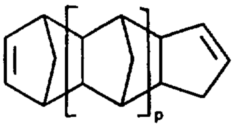
A large number of Diels-Alder adducts of unsubstituted or substituted 1,3-cyclopentadienes with unsubstituted or substituted cycloolefins are known and many are commercially available, or they can be prepared in a known manner by a Diels-Alder reaction of unsubstituted or substituted 1,3-cyclopentadienes with unsubstituted or substituted cycloolefins.

The cycloolefins may be the compounds indicated below under formula II, containing hydrocarbon rings, including the preferences and substitutions indicated.

More preferably, the cycloolefins may be those containing 3 to 12, preferably 5 to 8, ring carbon atoms, and they may be fused ring systems having 2 to 8 and, preferably, 2 to 5 rings, bridged ring systems having 2 to 8 and, preferably, 2 to 5 rings, or fused and bridged ring systems having 2 to 8 and, preferably, 2 to 5 rings. The individual rings can be substituted as indicated above for the Diels-Alder adducts, or aromatic hydrocarbon rings, especially unsubstituted benzene or benzene substituted as indicated above, can be fused onto the individual rings.

Examples of cycloolefins are cyclopropene, cyclobutene, cyclopentene, cyclopentadiene, cyclohexene, cyclohexadiene, cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene, cyclooctatriene, cyclooctatetraene, cyclononene, cyclononadiene, cyclononatriene, cyclodecene, cyclodecadiene, cyclodecatriene, cyclododecene, cyclododecadiene, cyclododecatriene, cyclododecatetraene, bicyclo[3.3.0]oct-6-ene, bicyclo[3.3.0]oct-1,6-diene, bicyclo[3.4.0]non-7-ene, bicyclo[3.4.0]non-2-ene, bicyclo[3.4.0]nona-2,7-diene, bicyclo[4.4.0]dec-2-ene, bicyclo[4.4.0]dec-2-ene, bicyclo[4.4.0]deca-2,7-diene, bicyclo[3.5.0]dec-3-ene, norbornene, norbornadiene, bicyclo[2.2.2]octene and bicyclo[2.2.2]octadiene, which can be substituted by one or more C_1-C_6alkyl groups.

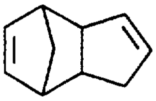
A preferred subgroup comprises Diels-Alder adducts of cyclopentadienes, of which a large number are known and commercially available (they are obtained, for example, in the course of petroleum distillation), or which can be prepared in a known manner by a Diels-Alder reaction of cyclopentadienes with cyclopentadienes, or with Diels-Alder adducts of cyclopentadienes (oligocyclopentadienes). These Diels-Alder adducts may be of the formula I



(I),

in which p is 0 or a number from 1 to 100, preferably 1 to 50, particularly preferably 1 to 20, and especially preferably 1 to 10, it being possible for the adduct to be substituted as indicated above for the Diels-Alder adducts, in particular by C_1-C_6alkyl groups.

Some examples of compounds of the formula I are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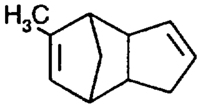

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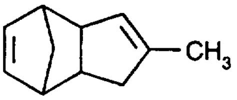

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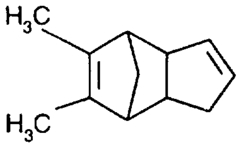

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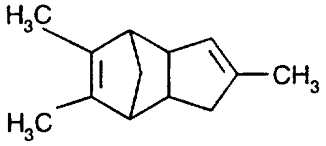

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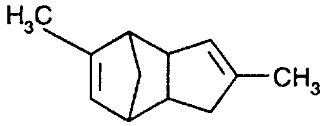

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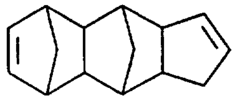
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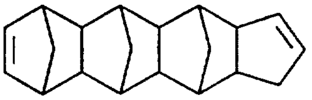
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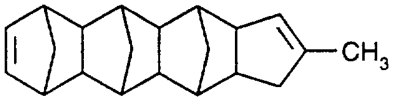

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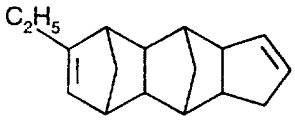

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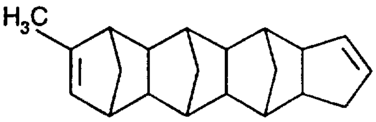

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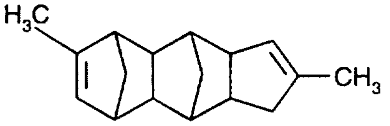

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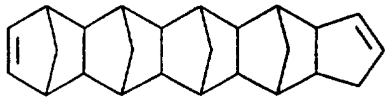
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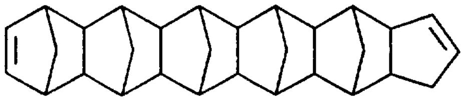
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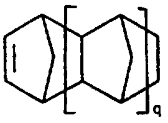
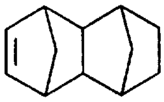
Another preferred subgroup of Diels-Alder adducts comprises those of unsubstituted or substituted norbornenes or norbornadienes with unsubstituted or substituted 1,3-cyclopentadienes. Particular preferred Diels-Alder adducts are those of the formula Ia

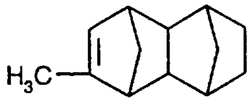


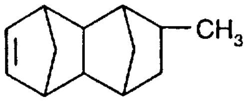
(Ia),

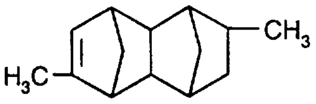
in which q is preferably a number from 1 to 20, more preferably 1 to 10 and, with particular preference, 1 to 5, and the Diels-Alder adducts are unsubstituted or are substituted by, preferably, C_1-C_6alkyl.

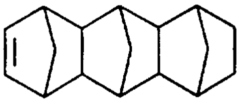
Some examples of the compounds of the formula Ia are

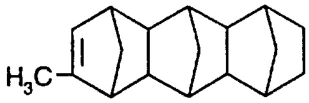


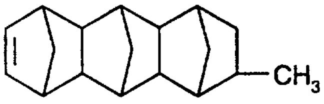


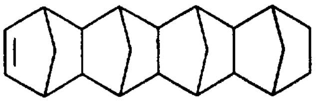


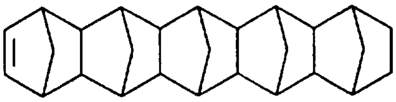










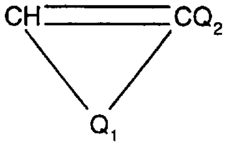


The Diels-Alder adducts can be used alone or together with comonomeric strained cycloolefins which differ from the Diels-Alder adducts and which may be present, for example, in proportions of up to 60 % by weight, preferably up to 40 % by weight and, with particular preference, up to 20 % by weight, based on the overall mixture of monomers. Using the comonomers it is possible to establish desired properties of the metathesis polymers.

The cyclic olefins can be monocyclic or polycyclic fused and/or bridged and/or linked ring systems, for example with from two to four rings, which are unsubstituted or substituted and can contain heteroatoms such as, for example, O, S, N or Si in one or more rings and/or can contain fused aromatic or heteroaromatic rings, for example o-phenylene, o-naphthylene, o-pyridinylene or o-pyrimidinylene. The individual cyclic rings may include 3 to 16, preferably 3 to 12 and, with particular preference, 3 to 8 ring members. The cyclic olefins may include further nonaromatic double bonds, preferably from 2 to 4 such additional double bonds depending on ring size. The ring substituents involved are those which are inert; in other words, those which do not adversely affect the chemical and thermal stability of the ruthenium and osmium catalysts. The cycloolefins are strained rings or ring systems. Particular preference is given to individual rings and ring systems having 5 to 8 carbon atoms in the ring.

If the cyclic olefins contain more than one double bond, for example 2 to 4 double bonds, or mixtures are used of strained cycloolefins having one double bond and strained cycloolefins having at least two double bonds, for example 2 to 4 double bonds, then depending on the reaction conditions, on the chosen monomer and on the amount of catalyst it is also possible for crosslinked polymers to form.

In a preferred embodiment of the novel composition, the cycloolefins are of the formula II



(II), in which

Q_1 is a radical which has at least one carbon atom and which, together with the $-CH=CQ_2-$ group, forms an at least 3-membered alicyclic ring containing, if desired, one or more heteroatoms selected from the group consisting of silicon, phosphorus, oxygen, nitrogen and sulfur, and which is unsubstituted or is substituted by halogen, =O, -CN, $-NO_2$, $R_1R_2R_3Si-(O)_u-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_{20}alkyl, C_1-C_{20}hydroxyalkyl, C_1-C_{20}haloalkyl, C_1-C_6cyanoalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl, C_7-C_{16}aralkyl, C_3-C_6-heterocycloalkyl, C_3-C_{16}heteroaryl, C_4-C_{16}heteroaralkyl or R_4-X-; or in which, if desired, two adjacent carbon atoms are substituted by -CO-O-CO- or $-CO-NR_5-CO-$; or in which, fused onto adjacent carbon atoms of the alicyclic ring, there is an alicyclic, aromatic or heteroaromatic ring which is unsubstituted or is substituted by halogen, -CN, $-NO_2$, $R_6R_7R_8Si-(O)_u-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_1-C_6cyanoalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl, C_7-C_{16}aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{16}heteroaryl, C_4-C_{16}heteroaralkyl or $R_{13}-X_1-$;

X and X_1 independently of one another are -O-, -S-, -CO-, -SO-, $-SO_2-$, -O-C(O)-, -C(O)-O-, $-C(O)-NR_5-$, $-NR_{10}-C(O)-$, $-SO_2-O-$ or $-O-SO_2-$;

R_1, R_2 and R_3 independently of one another are C_1-C_{12}alkyl, C_1-C_{12}perfluoroalkyl, phenyl or benzyl;

R_4 and R_{13} independently are C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl or C_7-C_{16}aralkyl; R_5 and R_{10} independently of one another are hydrogen, C_1-C_{12}alkyl, phenyl or benzyl, the alkyl groups being in turn unsubstituted or substituted by C_1-C_{12}alkoxy or C_3-C_8cycloalkyl;

R_6, R_7 and R_8 independently of one another are C_1-C_{12}alkyl, C_1-C_{12}perfluoroalkyl, phenyl or benzyl;

M is an alkali metal; and

M_1 is an alkaline earth metal; and

u is 0 or 1;

it being possible for the alicyclic ring formed with Q_1 to contain further nonaromatic double bonds;

Q_2 is hydrogen, C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{12}alkoxy, halogen, -CN or R_{11}-X_2-;

R_{11} is C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl or C_7-C_{16}aralkyl;

X_2 is -C(O)-O- or -C(O)-NR_{12}-;

R_{12} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

the abovementioned cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups being unsubstituted or substituted by C_1-C_{12}alkyl, C_1-C_{12}alkoxy, -NO_2, -CN or halogen, and the heteroatoms of the abovementioned heterocycloalkyl, heteroaryl and heteroaralkyl groups being selected from the group consisting of -O-, -S-, -NR_9- and -N=; and

R_9 is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl.

Fused-on alicyclic rings preferably contain 3 to 8, particularly preferably 5 to 8 and, with a special preference, 5 or 6 ring carbon atoms.

If there is an asymmetric centre in the compounds of the formula II, then the consequence of this is that the compounds may exist in optically isomeric forms. Some compounds of the formula I may occur in tautomeric forms (e.g. keto-enol tautomerism). If there is an aliphatic C=C double bond, then geometrical isomerism (E form or Z form) may also occur. Furthermore, exo-endo configurations are also possible. The formula I therefore embraces all possible stereoisomers in the form of enantiomers, tautomers, diastereomers, E/Z isomers or mixtures thereof.

In the definitions of the substituents the alkyl, alkenyl and alkynyl groups can be straight-chain or branched. The same also applies to the alkyl moiety, or each alkyl moiety, of alkoxy, alkylthio, alkoxycarbonyl and other alkyl-containing groups. These alkyl groups contain preferably 1 to 12, more preferably 1 to 8 and, with particular preference, 1 to 4 carbon atoms. These alkenyl and alkynyl groups preferably contain 2 to 12, more preferably 2 to 8 and, with particular preference, 2 to 4 carbon atoms.

Alkyl comprises, for example, methyl, ethyl, i-propyl, n-propyl, n-butyl, i-butyl, t-butyl and the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl radicals.

Hydroxyalkyl comprises, for example, hydroxymethyl, hydroxyethyl, 1-hydroxyisopropyl, 1-hydroxy-n-propyl, 2-hydroxy-n-butyl, 1-hydroxy-iso-butyl, 1-hydroxy-secondary-butyl, 1-hydroxy-tertiary-butyl and the hydroxy derivatives of the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl radicals.

Haloalkyl comprises, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, 2,2,2-trichloroethyl and halogenated, especially fluorinated or chlorinated alkanes, such as, for example, halogen derivatives of the isopropyl, n-propyl, n-butyl, iso-butyl, sec-butyl and tert-butyl radicals and of the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl radicals.

Alkenyl comprises, for example, propenyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, iso-dodecenyl, n-octadec-2-enyl and n-octadec-4-enyl.

Cycloalkyl is preferably C_5-C_8cycloalkyl, especially C_5cycloalkyl or C_6cycloalkyl. Some examples are cyclopropyl, dimethylcyclopropyl, cyclobutyl, cyclopentyl, methylcyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

Cyanoalkyl comprises, for example, cyanomethyl(methylcarbonitrile), cyanoethyl(ethylcarbonitrile), 1-cyanoisopropyl, 1-cyano-n-propyl, 2-cyano-n-butyl, 1-cyano-iso-butyl, 1-cyano-sec-butyl, 1-cyano-tert-butyl and the various isomeric cyanopentyl and cyanohexyl radicals.

Aralkyl contains preferably 7 to 12 carbon atoms and, with particular preference, 7 to 10 carbon atoms and is, for example, phenyl-C_1-C_6alkyl or phenyl-C_1-C_4alkyl. The particular radical may, for example, be benzyl, phenethyl, 3-phenylpropyl, α-methylbenzyl, phenbutyl or α,α-dimethylbenzyl.

Aryl contains preferably 6 to 10 carbon atoms. It may, for example, be phenyl, pentaline, indene, naphthalene, azulene or anthracene.

Heteroaryl contains preferably 4 or 5 carbon atoms and one or two heteroatoms from the group consisting of O, S and N. It may, for example, be pyrrole, furan, thiophene, oxazole, thiazole, pyridine, pyrazine, pyrimidine, pyridazine, indole, purine or quinoline.

Heterocycloalkyl contains preferably 4 or 5 carbon atoms and one or two heteroatoms from the group consisting of O, S and N. It may, for example, be oxiran, azirin, 1,2-oxathiolane, pyrazoline, pyrrolidine, piperidine, piperazine, morpholine, tetrahydrofuran or tetrahydrothiophene.

Alkoxy is, for example, methoxy, ethoxy, propyloxy, i-propyloxy, n-butyloxy, i-butyloxy and t-butyloxy.

Alkali metal in the context of the present invention is to be understood as meaning lithium, sodium, potassium, rubidium or caesium, especially lithium, sodium or potassium.

Alkaline earth metal in the context of the present invention is to be understood as meaning beryllium, magnesium, calcium, strontium or barium, especially magnesium or calcium.

In the above definitions, halogen means fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine.

Particularly suitable compounds of the formula II for the novel composition are those in which Q_2 is hydrogen.

Also preferable for the composition are compounds of the formula II in which the alicyclic ring formed by Q_1 together with the $-CH=CQ_2-$ group has 3 to 16, more preferably 3 to 12, particularly preferably 3 to 8 and, with special preference, 5 to 8 ring atoms and can be a monocyclic, bicyclic, tricyclic or tetracyclic ring system.

With particular advantage, the novel composition comprises compounds of the formula II in which

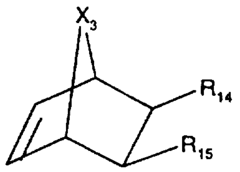
Q_1 is a radical which has at least one carbon atom and which, together with the $-CH=CQ_2-$ group, forms a 3- to 20-membered alicyclic ring possibly containing one or more heteroatoms selected from the group consisting of silicon, oxygen, nitrogen and sulfur, and which is unsubstituted or substituted by halogen, =O, -CN, $-NO_2$, $R_1R_2R_3Si-(O)_u-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}hydroxyalkyl, C_1-C_4cyanoalkyl, C_3-C_6cycloalkyl, C_6-C_{12}aryl, C_7-C_{12}aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{12}heteroaryl, C_4-C_{12}heteroaralkyl or R_4-X-; or in which two adjacent carbon atoms in this radical Q_1 are substituted by -CO-O-CO- or $-CO-NR_5-CO-$; or in which, if desired, fused onto adjacent carbon atoms, there is an alicyclic, aromatic or heteroaromatic ring which is unsubstituted or substituted by halogen, -CN, $-NO_2$, $R_6R_7R_8Si-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}hydroxyalkyl, C_1-C_4cyanoalkyl, C_3-C_6cycloalkyl, C_6-C_{12}aryl, C_7-C_{12}aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{12}heteroaryl, C_4-C_{12}heteroaralkyl or $R_{13}-X_1-$; X and X_1 independently of one another are -O-, -S-, -CO-, -SO-, $-SO_2-$, -O-C(O)-, -C(O)-O-, $-C(O)-NR_5-$, $-NR_{10}-C(O)-$, $-SO_2-O-$ or $-O-SO_2-$; and R_1, R_2 and R_3 independently of one another are C_1-C_6alkyl, C_1-C_6perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M_1 is an alkaline earth metal; R_4 and R_{13} independently of one another are C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{12}aryl or C_7-C_{12}aralkyl; R_5 and R_{10} independently of one another are hydrogen, C_1-C_6alkyl, phenyl or benzyl, the alkyl groups being in turn unsubstituted or substituted by C_1-C_6alkoxy or C_3-C_6cycloalkyl; R_6, R_7 and R_8 independently of one another are C_1-C_6alkyl, C_1-C_6perfluoroalkyl, phenyl or benzyl; u is 0 or 1; and the alicyclic ring formed with Q_1 may contain further nonaromatic double bonds;

Q_2 is hydrogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_6alkoxy, halogen, -CN or $R_{11}-X_2-$; R_{11} is C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}hydroxyalkyl, C_3-C_6cycloalkyl, C_6-C_{12}aryl or C_7-C_{12}aralkyl; X_2 is -C(O)-O- or $-C(O)-NR_{12}-$; and R_{12} is hydrogen, C_1-C_6alkyl, phenyl or benzyl;

and where the cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups are unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6alkoxy, $-NO_2$, -CN or halogen, and where the heteroatoms of the heterocycloalkyl, heteroaryl and heteroaralkyl groups are selected from the group consisting of -O-, -S-, $-NR_9-$ and -N=; and R_9 is hydrogen, C_1-C_6alkyl, phenyl or benzyl.

From this group, preference is given to those compounds of the formula II in which Q_1 is a radical which has at least one carbon atom and which together with the $-CH=CQ_2-$ group forms a 3- to 10-membered alicyclic ring possibly containing a heteroatom selected from the groups consisting of silicon, oxygen, nitrogen and sulfur, and which is unsubstituted or substituted by halogen, -CN, $-NO_2$, $R_1R_2R_3Si-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4cyanoalkyl, C_3-C_6cycloalkyl, phenyl, benzyl or R_4-X-; or in which, if desired, fused onto adjacent carbon atoms, there is an alicyclic, aromatic or heteroaromatic ring which is unsubstituted or substituted by halogen, -CN, $-NO_2$, $R_6R_7R_8Si-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1--C_4cyanoalkyl, C_3-C_6cycloalkyl, phenyl, benzyl or R_{13}-X_1-; R_1, R_2 and R_3 independently of one another are C_1-C_4alkyl, C_1-C_4perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M_1 is an alkaline earth metal; R_4 and R_{13} independently of one another are C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl or C_3-C_6cycloalkyl; X and X_1 independently of one another are -O-, -S-, -CO-, -SO- or $-SO_2-$; R_6, R_7 and R_8 independently of one another are C_1-C_4alkyl, C_1-C_4perfluoroalkyl, phenyl or benzyl; and Q_2 is hydrogen.

In particular, the novel composition comprises norbornene and norbornene derivatives, norbornadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene or cyclododecene. Among the norbornene derivatives, particular preference is given to those which are alternatively of the formula III

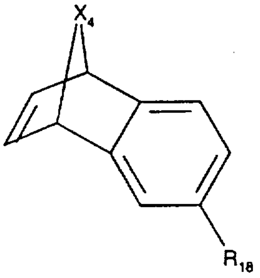


(III), in which

X_3 is $-CHR_{16}-$, oxygen or sulfur;

R_{14} and R_{15} independently of one another are hydrogen, -CN, trifluoromethyl, $(CH_3)_3Si-O-$, $(CH_3)_3Si-$ or $-COOR_{17}$; and

R_{16} and R_{17} independently of one another are hydrogen, C_1-C_{12}alkyl, phenyl or benzyl; or of the formula IV

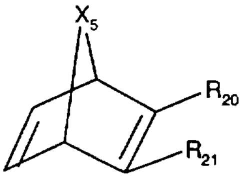


(IV), in which

X_4 is -CHR_{19}-, oxygen or sulfur;

R_{19} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl; and

R_{18} is hydrogen, C_1-C_6alkyl or halogen; or of the formula V



(V), in which

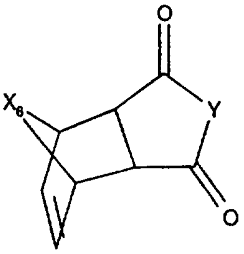
X_5 is -CHR_{22}-, oxygen or sulfur;

R_{22} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

R_{20} and R_{21} independently of one another are hydrogen, CN, trifluoromethyl, $(CH_3)_3Si$-O-, $(CH_3)_3Si$- or -$COOR_{23}$; and

R_{23} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

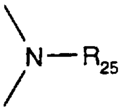
or of the formula VI



(VI), in which

X_6 is -CHR_{24}-, oxygen or sulfur;

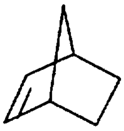
R_{24} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

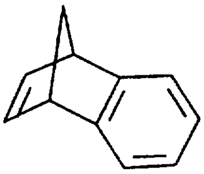
Y is oxygen or  $>N-R_{25}$ and

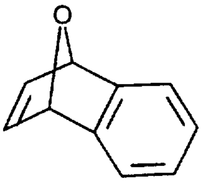
R_{25} is hydrogen, methyl, ethyl or phenyl.

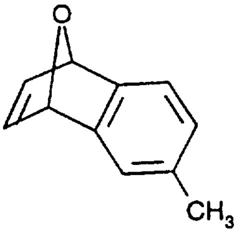
Another preferred subgroup of comonomers comprises those composed only of carbon and hydrogen.

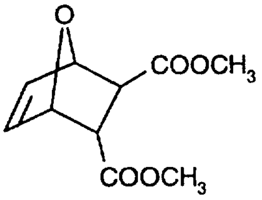
The following compounds of the formula II, which may be preparable by Diels-Alder reactions, are some specific examples, in which the oxanorbornene derivatives may alternatively be norbornene derivatives, and vice versa:

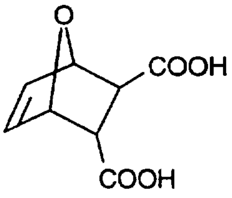


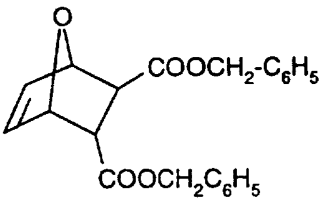


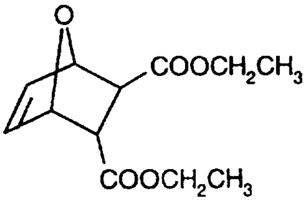


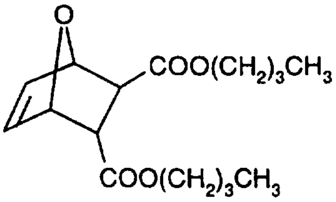


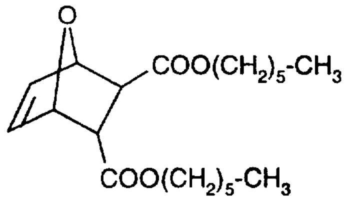


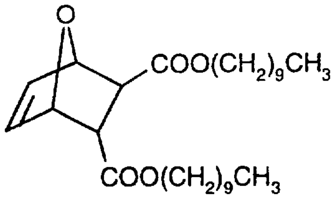


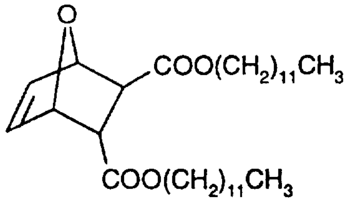


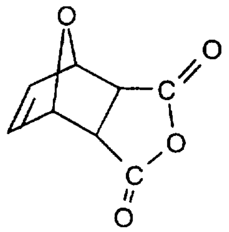


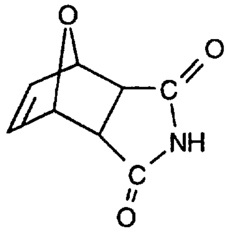


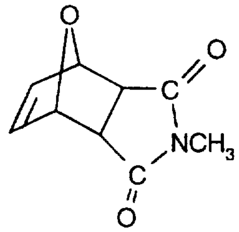

O
COO(CH2)5-CH3
COO(CH2)5-CH3

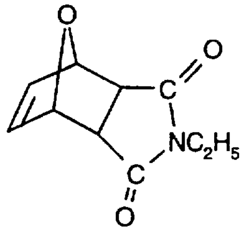

O
COO(CH2)9CH3
COO(CH2)9CH3

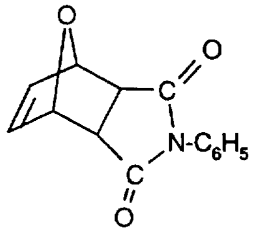

O
COO(CH2)11CH3
COO(CH2)11CH3

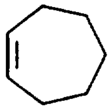

O
C
O
O
C
O

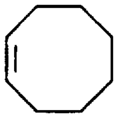

O
C
O
NH
C
O

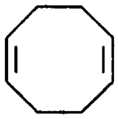

O
C
O
NCH3
C
O

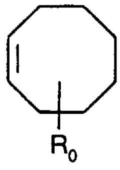

O
C
O
NC2H5
C
O

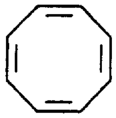

O
C
O
N-C6H5
C
O

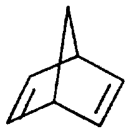


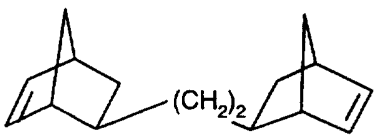


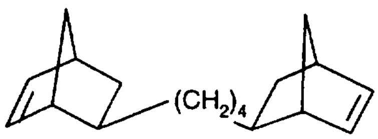


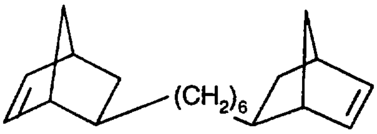

R0

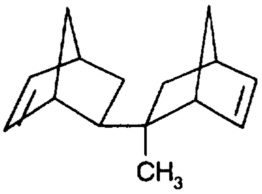


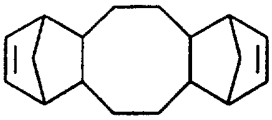


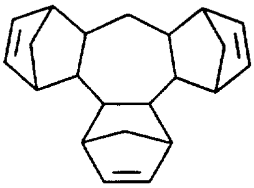

(CH2)2

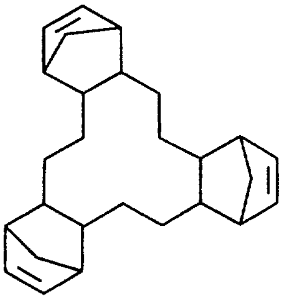

(CH2)4

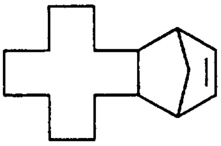

(CH2)6

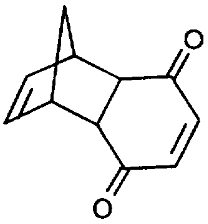

CH3







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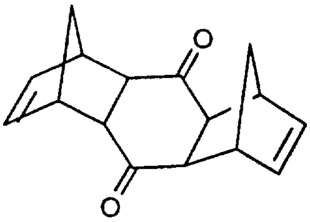
O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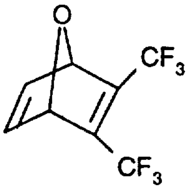
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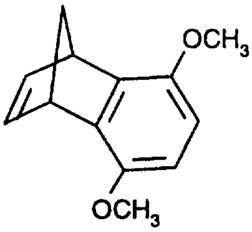
CF3
CF3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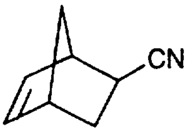
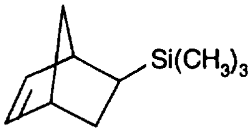
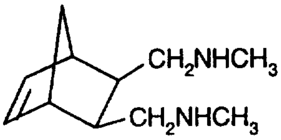
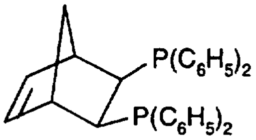
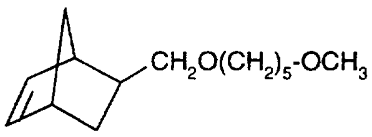
OCH3

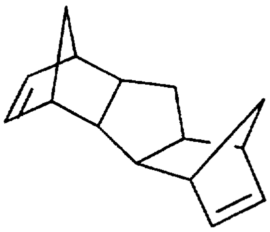

CN

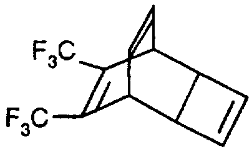

Si(CH3)3

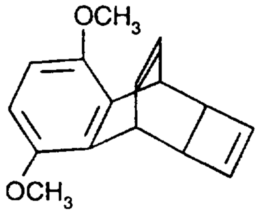

CH2NHCH3
CH2NHCH3


P(C6H5)2
P(C6H5)2









R_0 can, for example, be an epoxide, acrylate or methacrylate group which is attached covalently via a bridge group or directly to the cyclooctene.

Fused and/or bridged and/or linked olefinically unsaturated ring systems are generally prepared by means of Diels-Alder reactions. They should be able to be melted without decomposition, which for the purposes of the invention means that strained cycloolefins can be melted and the catalyst can be dissolved. In the case of thermally unstable strained cycloolefins it may therefore be necessary to dissolve the catalyst under pressure. Where the reaction temperature is above the decomposition point of the strained cycloolefin, it is advisable to employ pressure techniques in order to avoid the monomers decomposing prior to polymerization.

The amount of unsubstituted or substituted 1,3-dicyclopentadiene is preferably not more than 0.08 % by weight, more preferably not more than 0.06 % by weight, particularly preferably not more than 0.04 % by weight and, with special preference, not more than 0.02 % by weight.

The Diels-Alder adducts with a content of 1,3-cyclopentadienes can be purified by methods which are generally known. For instance, the adducts can be treated with basic compounds, for example Grignard compounds, alkali metal hydroxides or alkali metal carbonates, or, preferably, with basic zeolites. The 1,3-cyclopentadienes can also be removed by reaction with dienophiles (see EP-A-0 359 186), for example maleimide. It is additionally possible to bind the 1,3-cyclopentadienes using solid adsorbents, for example carbon, or to flush the

Diels-Alder adducts with inert gas, or to carry out distillation under a high vacuum. If it is intended to use particularly pure Diels-Alder adducts, it is advisable to combine the above methods. It has been found particularly expedient to store the Diels-Alder adducts over adsorbents or zeolites and, before use, to purify them further by distillation in vacuo or by flushing with inert gases.

It has been found that, following the purification of the Diels-Alder adducts, 1,3-cyclopentadienes form again so quickly that, given storage beyond a certain period of time, the requirement made in accordance with the invention regarding the minimum content of 1,3-cyclopentadienes is no longer met. The products must therefore be processed directly after purification. It has also been found that storage of the purified Diels-Alder adducts is possible over a longer period if the purified product is stored over basic zeolites, since these continually bind (remove) the 1,3-cyclopentadienes formed. It is therefore particularly advantageous to purify the Diels-Alder adducts, for example by degassing or distillation under a high vacuum, and to store the purified product over a basic zeolite prior to processing.

The amount of ruthenium catalysts depends essentially on their reactivity. More active catalysts are preferably used in the region of the lower limits, and less active catalysts in the region of the upper limits. The range of amounts is preferably from 0.05 to less than 3 % by weight, more preferably from 0.1 to less than 0.3 % by weight, particularly preferably from 0.1 to 0.25 % by weight, and with special preference from 0.1 to 0.2 % by weight.

Ruthenium catalysts for ring-opening metathesis polymerization are known and can be prepared by known methods. Catalysts of this kind are, for example, disclosed in WO 95/07310, WO 93/20111, or by C. Tanelian et al. in Tetrahedron Letters 52:4589-4592 (1977) and by C. Fraser et al. in Polym. Prepr. 1995, 36, pages 237 to 238. The catalysts are, with particular preference, one-component catalysts with no cocatalysts. The ruthenium catalysts may be mono- or polynuclear and may, for example, include 1, 2 or 3 ruthenium atoms.

The polymerization can be initiated either thermally or by means of actinic radiation, since ruthenium catalysts are known for both methods. Also possible is a combination of photolytic and thermal polymerization. Preference is given, however, to thermal polymerization, especially with regard to the use of casting resins.

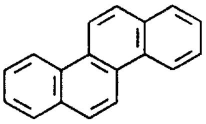
Photocatalysts are described in WO 95/07310. They may be thermally stable ruthenium compounds containing at least one photolabile ligand attached to the ruthenium atom, with the remaining coordination sites being occupied by non-photolabile ligands. Preference is given to ruthenium(II) compounds containing non-nucleophilic anions, for example halides, PF_6, AsF_6, SbF_6, BF_4 and sulfonate anions. Thermally stable denotes that 0.33 % by weight of catalyst in ethanolic solution containing 20 % by weight monomer, at 50 °C in the dark over 96 hours, forms not more than 0.2 % by weight and, preferably, not more than 0.1 % by weight of polymer.

In the context of the invention a photolabile ligand is defined as a ligand which is cleaved off from the catalyst under irradiation with light in the visible or ultraviolet range, and forms a catalytically active species from the ruthenium compound.

Examples of photolabile ligands are N_2, monocyclic, polycyclic or fused arenes or heteroarenes, or aromatic and aliphatic nitriles. Specific examples are benzene, biphenyl, naphthalene, anthracene, pyrene, thiophene, acetonitrile, propionitrile, butyronitrile, benzonitrile and benzylnitrile.

A non-photolabile ligand (also strongly bonding ligand) is not cleaved off in the course of irradiation with light in the visible or ultraviolet range. Examples of such ligands are solvating, organic and inorganic compounds containing heteroatoms selected from the group consisting of O, S and N, or cyclopentadienyls or indenyls, examples being H_2O, H_2S, NH_3, alcohols and thiols, ethers, thioethers, sulfoxides, sulfones, ketones, carboxylates and carboxamides, lactones and lactames, and also amines.

Some examples of photoactive ruthenium catalysts are $Ru(CH_3CN)_6(tosylate)_2$, $Ru(C_6H_6)_2(tosylate)_2$, $[(C_6H_6)(chrysene)]BF_4$, $Ru(benzonitrile)_6(CF_3SO_3)_2$, $Ru(C_6H_6)(CH_3\text{-}CN)_3(PF_6)_2$, $Ru(C_6H_6)(CH_3OH)_3(PF_6)_2$.

Chrysene is 

Among the preferred thermal ruthenium catalysts, those which are particularly suitable contain phosphine ligands. Particular preference is given to divalently cationic ruthenium compounds containing at least one phosphine group and in total from two to five ligands attached to the ruthenium atom, and containing acid anions for charge compensation.

In the ruthenium compounds to be used in accordance with the invention, a monophosphine can be attached once, twice or three times and a diphosphine once to the metal atom. In the ruthenium catalysts there are preferably 1 to 4, more preferably 1 to 3 and, with particular preference, 2 ligands attached. The phosphine ligands are preferably of the formulae VII and VIIa,

$PR_{26}R_{27}R_{28}$ (VII),

$R_{26}R_{27}P\text{-}Z_1\text{-}PR_{26}R_{27}$ (VIIa),

in which R_{26}, R_{27} and R_{28} independently of one another are H, C_1-C_{20}alkyl, C_1-C_{20}alkoxy, unsubstituted or C_1-C_6alkyl-, C_1-C_6haloalkyl- or C_1-C_6alkoxy-substituted C_4-C_{12}cycloalkyl or cycloalkoxy, or unsubstituted or C_1-C_6alkyl-, C_1-C_6haloalkyl- or C_1-C_6alkoxy-substituted C_6-C_{16}aryl or C_6-C_{16}aryloxy, or unsubstituted or C_1-C_6alkyl-, C_1-C_6haloalkyl- or C_1-C_6alkoxy-substituted C_7-C_{16}aralkyl or C_7-C_{16}aralkyloxy; the radicals R_{26} and R_{27} together are unsubstituted or C_1-C_6alkyl-, C_1-C_6haloalkyl- or C_1-C_6alkoxy-substituted tetra- or pentamethylene, or tetra- or pentamethylenedioxyl, or are unsubstituted or C_1-C_6alkyl-, C_1-C_6haloalkyl- or C_1-C_6alkoxy-substituted tetra- or pentamethylene fused with 1 or 2 1,2-phenylene, or tetra- or pentamethylenedioxyl, or are unsubstituted or C_1-C_6alkyl-, C_1-C_6haloalkyl- or C_1-C_6alkoxy-substituted tetramethylenedioxyl which is fused in the 1,2- and 3,4-positions with 1,2-phenylene, and R_{28} is as defined above; and

Z_1 is linear or branched, unsubstituted or C_1-C_4alkoxy-substituted C_2-C_{12}alkylene, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-cycloalkylene of 4 to

8 carbon atoms, or is unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-heterocycloalkylene with 5 or 6 ring members and a heteroatom from the group consisting of O and N.

The radicals R_{26}, R_{27} and R_{28} are preferably identical radicals. Preference is given, furthermore, to sterically bulky radicals, for examples branched alkyl, especially α-branched alkyl, or cyclic radicals. Hydrocarbon radicals are particularly preferred.

Alkyl R_{26}, R_{27} and R_{28} can be linear or branched and contain preferably 1 to 12, more preferably 1 to 8 and, with particular preference, 1 to 6 carbon atoms. Examples of alkyl are methyl, ethyl, n- and i-propyl, n-, i- and t-butyl, the isomers of pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl and eicosyl. Preferred examples are methyl, ethyl, n- and i-propyl, n-, i- and t-butyl, 1-, 2- or 3-pentyl and 1-, 2-, 3- or 4-hexyl.

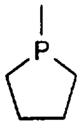
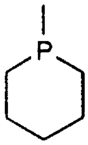
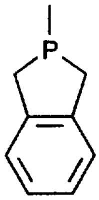
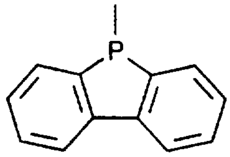
Where R_{26}, R_{27} and R_{28} are substituted, the substituents are preferably C_1-C_4alkyl, C_1-C_4haloalkyl or C_1-C_4alkoxy. Halogen is preferably Cl and, with particular preference, is F. Examples of preferred substituents are methyl, methoxy, ethyl, ethoxy and trifluoromethyl. R_{26}, R_{27} and R_{28} are preferably substituted from one to three times.

Where R_{26}, R_{27} and R_{28} are cycloalkyl, they are preferably C_5-C_8cycloalkyl and, particularly preferably, C_5cycloalkyl or C_6cycloalkyl. Some examples are cyclobutyl, cycloheptyl, cyclooctyl and, in particular, cyclopentyl and cyclohexyl. Examples of substituted cycloalkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tristrifluoromethylcyclopentyl and -cyclohexyl.

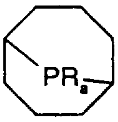
Where R_{26}, R_{27} and R_{28} are aryl, they are preferably C_6-C_{12}aryl and, particularly preferably, phenyl or naphthyl. Examples of substituted aryl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tristrifluoromethylphenyl.

Where R_{26}, R_{27} and R_{28} are aralkyl, they are preferably C_7-C_{13}aralkyl, the alkylene group in the aralkyl preferably being methylene. With particular preference, the aralkyl is benzyl. Examples of substituted aralkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tristrifluoromethylbenzyl.

Examples of unsubstituted or substituted, fused or unfused tetra- and pentamethylene attached to the phosphorus atom are

 ,  ,  ,  .

Other suitable phosphines are cycloaliphatic compounds that have 6 to 8 ring carbon atoms and are bridged with a group $=PR_a$, for example

 ,  ,  ,  ,

in which R_a is C_1-C_6alkyl, cyclohexyl, benzyl or unsubstituted or mono- or di- C_1-C_4alkyl-substituted phenyl.

Z_1 as linear or branched alkylene is preferably 1,2-alkylene or 1,3-alkylene having preferably 2 to 6 carbon atoms, for example ethylene, 1,2-propylene or 1,2-butylene.

Examples of Z_1 as cycloalkylene are 1,2- and 1,3-cyclopentylene and 1,2- or 1,3-cyclohexylene. Examples of Z_1 as heterocycloalkylene are 1,2- and 1,3-pyrrolidine, 1,2- and 1,3-piperidine, and 1,2- and 1,3-tetrahydrofuran.

In a preferred embodiment the phosphine ligands are of the formula VII in which R_{26}, R_{27} and R_{28} independently of one another are H, C_1-C_6alkyl, unsubstituted or C_1-C_4alkyl-substituted cyclopentyl or cyclohexyl, or unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy- or trifluoromethyl-substituted phenyl, or unsubstituted or C_1-C_4alkyl-, C_1-C_4-alkoxy- or trifluoromethyl-substituted benzyl. Particularly preferred examples of phosphine ligands of the formula VII are

$(C_6H_5)H_2P$, $(3-CH_3-6-t-C_4H_9-C_6H_3)_3P$, $(3-CH_3-6-t-C_4H_9-C_6H_3)_3P$, PH_3, $(2,6-di-t-C_4H_9-C_6H_3)_3P$, $(2,3-di-t-C_4H_9-C_6H_3)_3P$, $(2,4-di-t-C_4H_9-C_6H_3)_3P$, $(2,4-di-CH_3-C_6H_3)_3P$, $(2,6-di-CH_3-C_6H_3)_3P$, $(2-CH_3-6-t-C_4H_9-C_6H_3)_3P$, $(CH_3)_3P$, $(2-i-C_3H_7-C_6H_4)_3P$, $(3-i-C_3H_7-C_6H_4)_3P$, $(4-i-C_3H_7-C_6H_4)_3P$, $(2-n-C_4H_9-C_6H_4)_3P$, $(3-n-C_4H_9-C_6H_4)_3P$, $(4-n-C_4H_9-C_6H_4)_3P$, $(2-i-C_4H_9-C_6H_4)_3P$, $(3-i-C_4H_9-C_6H_4)_3P$, $(4-i-C_4H_9-C_6H_4)_3P$, $(2-t-C_4H_9-C_6H_4)_3P$, $(3-t-C_4H_9-C_6H_4)_3P$, $(4-t-C_4H_9-C_6H_4)_3P$, $(4-C_2H_5-C_6H_4)_3P$, $(3-n-C_3H_7-C_6H_4)_3P$, $(2-n-C_3H_7-C_6H_4)_3P$, $(4-n-C_3H_7-C_6H_4)_3P$, $(C_2H_5)_2HP$, $(3-CH_3-C_6H_4)_3P$, $(4-CH_3-C_6H_4)_3P$, $(2-C_2H_5-C_6H_4)_3P$, $(3-C_2H_5-C_6H_4)_3P$, $(i-C_3H_7)H_2P$, $(n-C_4H_9)H_2P$, $(C_6H_5CH_2)_2HP$, $(C_6H_5CH_2)H_2P$, $(2-CH_3-C_6H_4)_3P$, $(C_6H_5)_3P$, $(C_5H_{11})H_2P$, $(C_6H_5CH_2)_3P$, $(n-C_3H_7)_2HP$, $(i-C_3H_7)_2HP$, $(n-C_4H_9)_2HP$, $(n-C_3H_7)H_2P$, $(C_2H_5)H_2P$, $(C_5H_{11})_3P$, $(C_6H_5)_2HP$, $(C_5H_{11})_2HP$, $(n-C_3H_7)_3P$, $(i-C_3H_7)_3P$, $(n-C_4H_9)_3P$, $(CH_3)_2HP$, $(C_2H_5)_3P$, $(C_6H_{11})_3P$, $(C_6H_{11})_2HP$, $(C_5H_9)_3P$, $(C_5H_9)_2HP$ and $(CH_3)H_2P$.

Particularly preferred phosphines are tri-i-propylphosphine, tri-t-butylphosphine, tricyclopentylphosphine and tricyclohexylphosphine.

Ligands for the ruthenium compounds to be used in accordance with the invention are organic or inorganic compounds, atoms or ions which are coordinated to a metal centre.

In the context of the present invention, ligands used with particular advantage are selected, for example, from a group of ligands (A) consisting of nitrogen (N_2); unsubstituted or OH-, C_1-C_4alkyl-, C_1-C_4alkoxy-, C_6-C_{12}aryl- or halo-substituted monocyclic, polycyclic or fused arenes having 6 to 24, preferably 6 to 18 and, with particular preference, 6 to 12 carbon atoms; unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy- or halo-substituted monocyclic heteroarenes; fused heteroarenes; fused arene-heteroarenes having 3 to 22, preferably 4 to 16 and, in particular, 4 to 10 carbon atoms and 1 to 3 heteroatoms selected from the group consisting of O, S and N; and unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy- or halo-substituted aliphatic, cycloaliphatic, aromatic or araliphatic nitriles having 1 to 22, preferably 1 to 18, particularly preferably 1 to 12 and, with very particular preference, 1 to 7 carbon atoms. The preferred substituents are methyl, ethyl, methoxy, ethoxy, fluorine, chlorine and bromine. The arenes and heteroarenes are preferably substituted by from one to three radicals. Among the heteroarenes, the electron-rich heteroarenes are preferred.

Some examples of arenes and heteroarenes are benzene, 4-isopropyltolyl, biphenyl, naphthalene, anthracene, acenaphthene, fluorene, phenanthrene, pyrene, chrysene, fluoroanthrene, furan, thiophene, pyrrole, pyridine, γ-pyran, γ-thiopyran, pyrimidine, pyrazine, indole, coumarone, thionaphthene, carbazole, dibenzofuran, dibenzothiophene, pyrazole, imidazole, benzimidazole, oxazole, thiazole, isoxazole, isothiazole, quinoline, isoquinoline, acridine, chromene, phenazine, phenoxazine, phenothiazine, triazines, thianthrene and purine. Preferred arenes and heteroarenes are unsubstituted or substituted benzene, naphthalene, 4-isopropyltolyl, thiophene and benzothiophene. Very particular preference is given to the arene benzene or a benzene substituted by 1 to 3 C_1-C_4alkyls, for example toluene, xylene, trimethylbenzene, isopropylbenzene, tertiary-butylbenzene or 4-isopropyltolyl. The heteroarene is preferably thiophene.

The nitriles can be substituted, for example, by methoxy, ethoxy, fluorine or chlorine; the nitriles are preferably unsubstituted. The alkyl nitriles are preferably linear. Some examples of nitriles are acetonitrile, propionitrile, butyronitrile, pentylnitrile, hexylnitrile, cyclopentyl- and cyclohexylnitrile, benzonitrile, methylbenzonitrile, benzylnitrile and naphthylnitrile. The nitriles are preferably linear C_1-C_4alkylnitriles or benzonitrile. Among the alkylnitriles, acetonitrile is particularly preferred.

In a preferred subgroup, the ligands of group (A) are N_2, unsubstituted or mono- to tri-C_1-C_4alkyl-substituted benzene, thiophene, benzonitrile or acetonitrile.

Additional ligands may be present, selected for example from the group of ligands (B) consisting of solvating inorganic and organic compounds which contain the heteroatoms O, S or N and which are frequently also used as solvents; and unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy-, $(C_1$-$C_4alkyl)_3Si$- or $(C_1$-$C_4alkyl)_3SiO$-substituted cyclopentadienyl or indenyl. Examples of such compounds are H_2O, H_2S, NH_3; unhalogenated or halogenated, especially fluorinated or chlorinated, aliphatic or cycloaliphatic alcohols or mercaptans having 1 to 18, preferably 1 to 12 and particularly preferably 1 to 6 carbon atoms, aromatic alcohols or thiols having 6 to 18, preferably 6 to 12 carbon atoms, araliphatic alcohols or thiols having 7 to 18, preferably 7 to 12 carbon atoms, open-chain or cyclic and aliphatic, araliphatic or aromatic ethers, thioethers, sulfoxides, sulfones, ketones, aldehydes, carboxylates, lactones, unsubstituted or N-C_1-C_4-mono- or -dialkylated carboxamides having 2 to 20, preferably 2 to 12 and especially 2 to 6 carbon atoms, and unsubstituted or N-C_1-

C_4-alkylated lactams; open-chain or cyclic and aliphatic, araliphatic or aromatic, primary, secondary and tertiary amines having one to 20, preferably 1 to 12 and particularly preferably 1 to 6 carbon atoms; and cyclopentadienyls, for example cyclopentadienyl, indenyl, mono- or poly-methylated or trimethylsilylated cyclopentadienyls or indenyls. Other examples are allyl, methallyl and crotyl.

Further examples of the group of ligands (B) are methanol, ethanol, n- and i-propanol, n-, i- and t-butanol, 1,1,1-trifluoroethanol, bistrifluoromethylmethanol, tristrifluoromethylmethanol, pentanol, hexanol, methyl or ethyl mercaptan, cyclopentanol, cyclohexanol, cyclohexyl mercaptan, phenol, methylphenol, fluorophenol, phenyl mercaptan, benzyl mercaptan, benzyl alcohol, diethyl ether, dimethyl ether, diisopropyl ether, di-n- or di-t-butyl ether, tetrahydrofuran, tetrahydropyran, dioxane, diethyl thioether, tetrahydrothiophene, dimethyl sulfoxide, diethyl sulfoxide, tetra- and pentamethylene sulfoxide, dimethyl sulfone, diethyl sulfone, tetra- and pentamethylene sulfone, acetone, methyl ethyl ketone, diethyl ketone, phenyl methyl ketone, methyl isobutyl ketone, benzyl methyl ketone, acetaldehyde, propionaldehyde, trifluoroacetaldehyde, benzaldehyde, ethyl acetate, butyrolactone, dimethylformamide, dimethylacetamide, pyrrolidone and N-methylpyrrolidone, indenyl, cyclopentadienyl, methyl- or dimethyl- or pentamethylcyclopentadienyl and trimethylsilylcyclopentadienyl.

The primary amines can be of the formula $R_{29}NH_2$, the secondary amines of the formula $R_{29}R_{30}NH$ and the tertiary amines of the formula $R_{29}R_{30}R_{31}N$, in which R_{29} is C_1-C_{18}alkyl, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_5cycloalkyl or C_6cycloalkyl, or unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_6-C_{18}aryl or C_7-C_{12}aralkyl, R_{30} independently is as defined for R_{29}, or R_{29} and R_{30} together are tetramethylene, pentamethylene, 3-oxa-1,5-pentylene or $-CH_2-CH_2-NH-CH_2-CH_2-$ or $-CH_2-CH_2-N(C_1$-C_4alkyl$)-CH_2-CH_2-$, and R_{31} independently is as defined for R_{29}. The alkyl contains preferably 1 to 12 and particularly preferably 1 to 6 carbon atoms. The aryl contains preferably 6 to 12 carbon atoms and the aralkyl contains preferably 7 to 9 carbon atoms. Examples of amines are methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, triethyl-, methyl-ethyl-, dimethyl-ethyl, n-propyl-, di-n-propyl-, tri-n-butyl-, cyclohexyl-, phenyl- and benzylamine, and also pyrrolidine, N-methylpyrrolidine, piperidine, piperazine, morpholine and N-methylmorpholine.

In a preferred subgroup, the ligands of group (B) are H_2O, NH_3, unsubstituted or partially or completely fluorinated C_1-C_4alkanols, or cyclopentadienyl, indenyl, allyl, methallyl or crotyl. Very particular preference is given to H_2O, NH_3, cyclopentadienyl, indenyl, methanol and ethanol.

In a preferred embodiment, the Ru and Os catalysts to be used in accordance with the invention comprises arenes or heteroarenes as ligands, phosphine groups, and anions for charge compensation. With very particular preference they include an arene group as ligand, a tertiary phosphine group, and mono- or divalent anions for charge compensation.

Examples of suitable anions of organic or inorganic acids are hydride (H^-), halide (for example F^-, Cl^-, Br^- and I^-), the anion of an oxygen acid, and BF_4^-, PF_6^-, SbF_6^- or AsF_6^-. It should be noted that the abovementioned ligands cyclopentadienyl, indenyl, allyl, methallyl and crotyl are anionic and thus also serve for charge compensation.

Further suitable anions are C_1-C_{12}-, preferably C_1-C_6- and, with particular preference, C_1-C_4alcoholates, which in particular are branched, and are, for example, of the formula $R_xR_yR_zC$-O^- in which R_x is H or C_1-C_{10}alkyl, R_y is C_1-C_{10}alkyl and R_z is C_1-C_{10}alkyl or phenyl, and the sum of the carbon atoms of R_x, R_y and R_z is at least 2, preferably at least 3, and up to 10. Examples are, in particular, i-propyloxy and t-butyloxy.

Other suitable anions are C_3-C_{18}-, preferably C_5-C_{14}- and, with particular preference, C_5-C_{12}acetylides which can be of the formula R_w-$C\equiv C^-$ in which R_w is C_1-C_{16}alkyl, preferably α-branched C_3-C_{12}alkyl, for example formula $R_xR_yR_zC$-, or unsubstituted or mono- to tri-C_1-C_4alkyl- or C_1-C_1alkoxy-substiuted phenyl or benzyl. Some examples are i-propyl, i- and t-butyl, phenyl, benzyl, 2-methyl-, 2,6-dimethyl-, 2-i-propyl-, 2-i-propyl-6-methyl-, 2-t-butyl-, 2,6-di-t-butyl- and 2-methyl-6-t-butylphenyl acetylide.

The anions of oxygen acids may for example be sulfate, phosphate, perchlorate, perbromate, periodate, antimonate, arsenate, nitrate, carbonate, the anion of a C_1-C_8carboxylic acid, for example formate, acetate, propionate, butyrate, benzoate, phenylacetate, mono-, di- or trichloro- or -fluoroacetate, sulfonates, for example methylsulfonate, ethylsulfonate, propylsulfonate, butylsulfonate, trifluoromethylsulfonate (triflate), unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy or halo-, especially fluoro-, chloro- or bromo-, substituted phenylsulfonate or benzylsulfonate, for example tosylate, mesylate, brosylate, p-methoxy- or p-ethoxyphenylsulfonate, pentafluorophenylsulfonate or 2,4,6-triisopropylsulfonate, and phosphonates, for example methylphosphonate, ethylphosphonate, propylphosphonate, butylphosphonate, phenylphosphonate, p-methylphenylphosphonate or benzylphosphonate.

Particular preference is give to H^-, F^-, Cl^-, Br^-, BF_4^-, PF_6^-, SbF_6^-, AsF_6^-, $CF_3SO_3^-$, C_6H_5-SO_3^-, 4-methyl-C_6H_5-SO_3^-, 3,5-dimethyl-C_6H_5-SO_3^-, 2,4,6-trimethyl-C_6H_5-SO_3^- and 4-CF_3-C_6H_5-SO_3^- and cyclopentadienyl (Cp^-).

In a preferred embodiment, the ruthenium compounds are of one of the formulae VIII to VIIId

$$R_{32}L_1Me^{2+}(Z^{n-})_{2/n} \qquad \text{(VIII)},$$

$$R_{32}L_1L_2Me^{2+}(Z^{n-})_{2/n} \qquad \text{(VIIIa)},$$

$$(R_{32})_2L_1Me^{2+}(Z^{n-})_{2/n} \qquad \text{(VIIIb)},$$

$$(R_{32})_3L_1Me^{2+}(Z^{n-})_{2/n} \qquad \text{(VIIIc)},$$

$$R_{32}(L_1)_2Me^{2+}(Z^{n-})_{2/n} \qquad \text{(VIIId)},$$

in which
R_{32} is a phosphine ligand of the formula VII or VIIa;
Me is Ru;
n is 1, 2 or 3;
Z is the anion of an inorganic or organic acid;
(a) L_1 is a ligand of group A, the ligands L_1 in formula VIId being identical or different, and
(b) L_2 is a ligand of group B.

R_{32}, L_1 and L_2 are subject to the preferences and definitions indicated above for the phosphines of the formulae VII and VIIa.

In the formulae VIII to VIIId, n is preferably 1 or 2, and especially 1. R_{32} is subject to the preferences indicated for the phosphine ligands of the formulae VII and VIIa; in particular, it comprises tertiary phosphines.

With very particular preference, the ruthenium compounds used in the novel process are of one of the formulae IX to IXd

$(R_{26}R_{27}R_{28}P)L_1Me^{2+}(Z_1{}^{1-})Z_2{}^{-1}$ (IX),

$(R_{26}R_{27}R_{28}P)_2L_1Me^{2+}(Z_1{}^{1-})Z_2{}^{-1}$ (IXa),

$(R_{26}R_{27}R_{28}P)L_1L_2Me^{2+}(Z_1{}^{1-})Z_2{}^{-1}$ (IXb),

$(R_{26}R_{27}R_{28}P)_3L_1Me^{2+}(Z_1{}^{1-})Z_2{}^{-1}$ (IXc),

$(R_{26}R_{27}R_{28}P)(L_1)_2Me^{2+}(Z_1{}^{1-})Z_2{}^{-1}$ (IXd),

in which
Me is Ru;
Z_1 and Z_2 independently of one another are H^-, cyclopentadienyl, Cl^-, Br^-, BF_4^-, PF_6^-, SbF_6^-, AsF_6^-, $CF_3SO_3^-$, C_6H_5-SO_3^-, 4-methyl-C_6H_5-SO_3^-, 3,5-dimethyl-C_6H_5-SO_3^-, 2,4,6-trimethyl-C_6H_5-SO_3^- or 4-CF_3-C_6H_5-SO_3^-;
R_{26}, R_{27} and R_{28} independently of one another are C_1-C_6alkyl, unsubstituted or mono- to tri-C_1-C_4alkyl-substituted cyclopentyl or cyclohexyl or cyclopentyloxy or cyclohexyloxy, or unsubstituted or mono- to tri-C_1-C_4alkyl-substituted phenyl or benzyl or phenyloxy or benzyloxy;
L_1 is unsubstituted or mono- to tri-C_1-C_4alkyl-, -C_1-C_4alkoxy-, -OH-, -F- or -Cl-substituted C_6-C_{16}arene or C_5-C_{16}heteroarene or C_1-C_6alkyl-CN, benzonitrile or benzylnitrile, with the ligands L_1 in formula IXd being identical or different; and
L_2 is H_2O or C_1-C_6alkanol.

If the preparation of the ruthenium catalysts is carried out in solvents which are able to coordinate onto a metal atom, for example alkanols, then solvated Ru-cation complexes may be formed, the use of which is included in the context of the novel composition.

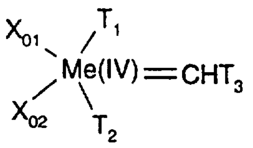
Some examples of ruthenium compounds to be used in accordance with the invention [where Tos is tosylate] are: $(C_6H_{11})_2$HPRu(4-isopropyltolyl)Cl_2, $(C_6H_{11})_3$PRu(4-isopropyltolyl)Cl_2, $(C_6H_{11})_3$PRu(4-isopropyltolyl)$(Tos)_2$, $(C_6H_{11})_3$PRu(4-isopropyltolyl)Br_2, $(C_6H_{11})_3$PRu(4-isopropyltolyl)ClF, $(C_6H_{11})_3PRu(C_6H_6)(Tos)_2$, $(C_6H_{11})_3PRu(CH_3\text{-}C_6H_5)(Tos)_2$, $(C_6H_{11})_3PRu(C_{10}H_8)(Tos)_2$, $(i\text{-}C_3H_7)_3$PRu(4-isopropyltolyl)Cl_2, $(CH_3)_3$PRu(4-isopropyltolyl)Cl_2, $(C_6H_{11})_3PRu(CH_3\text{-}CN)(C_2H_5\text{-}OH)(Tos)_2$, $(C_6H_{11})_3$PRu(4-isopropyltolyl)$(CH_3\text{-}CN)_2(PF_6)_2$, $(C_6H_{11})_3$PRu(4-isopropyltolyl)$(CH_3\text{-}CN)_2(Tos)_2$, $(n\text{-}C_4H_9)_3$PRu(4-isopropyltolyl)$(CH_3\text{-}CN)_2(Tos)_2$, $(C_6H_{11})_3PRu(CH_3CN)Cl_2$, $(C_6H_{11})_3PRu(CH_3\text{-}CN)_2Cl_2$, $(n\text{-}C_4H_9)_3$PRu(4-isopropyltolyl)Cl_2, $(C_6H_{11})_3$PRu(4-isopropyltolyl)$(C_2H_5OH)_2(BF_4)_2$, $(C_6H_{11})_3$PRu(4-isopropyltolyl)$(C_2H_5OH)_2(PF_6)_2$, $[(C_6H_{11})_3P]_3Ru(CH_3\text{-}CN)$, $(C_5H_9)_3$PRu(4-isopropyltolyl)Cl_2, $(C_6H_{11})_3$PRu(4-isopropyltolyl)HCl, $(C_6H_{11})_3PRu[1,2,4,5\text{-}(CH_3)_4C_6H_2]Cl_2$, $(C_6H_{11})_3PRu[1,3,5\text{-}(i\text{-}C_3H_7)_3C_6H_3]Cl_2$, $(C_6H_{11})_3PRu[(C_4H_9)\text{-}C_6H_5]Cl_2$, $(C_6H_5)_3$PRu(4-isopropyltolyl)HCl, $[(C_6H_{11})_3P]_2Ru(CH_3\text{-}CN)(Tos)_2$, $RuCl_2$(4-isopropyltolyl)$[(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2]$, $(C_6H_{11})_3$PRu(4-isopropyltolyl)$(C_2H_5OH)(BF_4)_2$, $(C_6H_{11})_3PRu(C_6H_6)(C_2H_5OH)_2(Tos)_2$, $(C_6H_{11})_3PRu(i\text{-}C_3H_7\text{-}C_6H_5)(Tos\ )_2$, $(C_6H_{11})_3PRu(C_6H_6)$(4-isopropyltolyl)Br_2, $(C_6H_{11})_3$PRu(biphenyl)$(Tos)_2$, $(C_6H_{11})_3$PRu(anthracene)$(Tos)_2$, $(2\text{-}CH_3C_6H_4)_3$PRu(4-isopropyltolyl)Cl_2 and $(C_6H_{11})_3$PRu(chrysene)$(Tos)_2$.

The abovementioned ruthenium catalysts are preferably employed in an amount of from 0.15 to 0.3 % by weight.

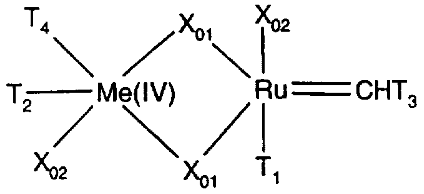
The ruthenium compounds to be used in accordance with the invention are known or can be prepared by known and analogous techniques starting from the metal halides (for example MeX_3 or $[Me\text{-}areneX_2]_2$) by reaction with phosphines and ligand-forming agents.

Another preferred groups of ruthenium compounds are ruthenium carbenes with two phosphine ligands and two halogen atoms.

They can preferably be of the formula X or Xa or mixtures of compounds of the formulae X and Xa



(X),



(Xa),

in which

Me is ruthenium;

T_1 and T_2 independently of one another are a tertiary phosphine, or T_1 and T_2 together are a ditertiary diphosphine;

T_3 is H, C_1-C_{12}alkyl; C_3-C_8cycloalkyl, C_3-C_7heterocycloalkyl with one or two heteroatoms selected from the group consisting of -O-, -S- and -N-, C_6-C_{14}aryl, or C_4-C_{15}heteroaryl with one to three heteroatoms selected from the group consisting of -O-, -S- and -N-, which are unsubstituted or substituted by C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_6-C_{10}aryl, C_6-C_{10}aryloxy, $-NO_2$ or halogen;

T_4 is unsubstituted or mono- to tri-C_1-C_4alkyl-, -C_1-C_4haloalkyl-, -C_1-C_4alkoxy-, -OH-, -F-, -Cl- or -Br-substituted C_6-C_{16}arene or C_4-C_{15}heteroarene, and

X_{01} and X_{02} independently of one another are halogen.

X_{01} and X_{02} in the formulae X and Xa are preferably F, Cl or Br, more preferably Cl or Br, and, with particular preference, are each Cl.

In a preferred embodiment, T_3 is a hydrogen atom or is a hydrocarbon radical defined in the context of the invention, having 1 to 16 carbon atoms, more preferably 1 to 12 carbon atoms.

Alkyl T_3 can preferably contain 1 to 8 and, with particular preference, 1 to 6 carbon atoms. Some examples of alkyl are methyl, ethyl and the isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. With particular preference, T_3 is linear C_1-C_4alkyl.

Cycloalkyl T_3 can preferably contain 5 to 8 carbon atoms. Cyclopentyl and cyclohexyl are particularly preferred.

Heterocycloalkyl T_3 can preferably contain 4 or 5 carbon atoms and preferably one heteroatom selected from the group consisting of -O-, -S- and -N-. Some examples are tetrahydrofuranyl, pyrrolidinyl, piperazinyl and tetrahydrothiophenyl.

Aryl T_3 can preferably contain 6 to 10 carbon atoms. Preferred examples are naphthyl and, in particular phenyl.

Heteroaryl T_3 can preferably contain 4 or 5 carbon atoms and one or two heteroatoms selected from the group consisting of -O-, -S- and -N-. Some examples are furanyl, thiophenyl, pyrrolyl, pyridinyl and pyrimidinyl.

Preferred substituents for T_3 are methyl, ethyl, methoxy, ethoxy, trichloromethyl, trifluoromethyl, phenyl, phenyloxy, F and Cl.

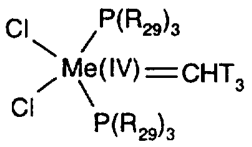
In a preferred embodiment, T_3 is H, C_1-C_4alkyl, cyclopentyl, cyclohexyl, phenyl or naphthyl, which are unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4haloalkyl, phenyl, F or Cl.

T_4 in formula Xa contains as arene preferably 6 to 12 carbon atoms, and as heteroarene preferably 4 to 11 carbon atoms and preferably 1 to 3 heteroatoms from the group consisting of O, S and N. Some examples of substituents of T_4 are methyl, ethyl, n- or i-propyl, n-, i- or t-butyl, methoxy, ethoxy, trifluoromethyl, F and Cl. Preferred arenes and heteroarenes are benzene, toluene, xylene, trimethylbenzene, naphthalene, biphenyl, anthracene, acenaphthene, fluorene, phenanthene, pyrene, chrysene, fluoroanthrene, furan, thiophene, pyrrole, pyridine, γ-pyran, γ-thiopyran, pyrimidine, pyrazine, indole, coumarone, thionaphthene, carbazole, dibenzofuran, dibenzothiophene, pyrazole, imidazole, benzimidazole, oxazole, thiazole, isoxazole, isothiazole, quinoline, isoquinoline, acridine, chromene, phenazine, phenoxazine, phenothiazine, triazine, thianthrene, and purine. More preferred arenes and heteroarenes are benzene, naphthalene, cumene, thiophene and benzthiophene. A very particularly preferred arene is benzene or an C_1-C_4alkyl-substituted benzene, for example toluene, xylene, isopropylbenzene, tertiary-butylbenzene or cumene; a particularly preferred heteroarene is thiophene.

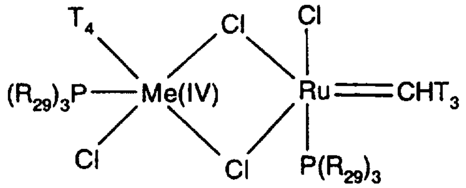
The phosphine group T_1 and T_2 preferably comprises tertiary phosphines, or ditertiary diphosphines having 3 to 40, more preferably 3 to 30 and, particularly preferably, 3 to 24 carbon atoms.

The tertiary phosphine or ditertiary diphosphine groups are subject to the same embodiments and preferences as indicated beforehand under the formulae VII and VIIa.

A preferred subgroup of the compounds of the formulae X and Xa comprises those of the formulae Xb and Xc,



(Xb),



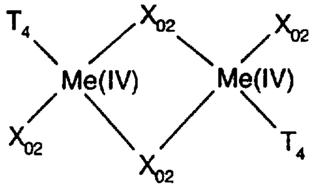
(Xc),

in which Me is Ru, R_{29} is α-branched C_3-C_8alkyl, unsubstituted or C_1-C_4alkyl-, C_1-C_4haloalkyl-, C_1-C_4alkoxy-, halo- or -NO_2-substituted C_5-C_8cycloalkyl, or unsubstituted or C_1-C_4alkyl-, C_1-C_4haloalkyl-, C_1-C_4alkoxy-, halo- or -NO_2-substituted C_6-C_{10}aryl, T_3 is H, C_1-C_6alkyl, unsubstituted or C_1-C_4alkyl-, C_1-C_4haloalkyl-, C_1-C_4-alkoxy-, halo- or -NO_2-substituted C_5-C_8cycloalkyl, or unsubstituted or C_1-C_4alkyl- C_1-C_4haloalkyl-, C_1-C_4alkoxy-, halo- or -NO_2-substituted C_6-C_{10}aryl, and T_4 is phenyl or mono- to tri-C_1-C_4alkyl-substituted phenyl.

Some specific and preferred examples [where Me is Ru(IV)] are: $Cl_2[P(C_6H_{11})_3]_2Me=CH-C_6H_5$, $Cl_2[P(C_5H_9)_3]_2Me=CH-C_6H_5$, $Br_2[P(C_6H_{11})_3]_2Me=CH-C_6H_5$, $Br_2[P(C_5H_9)_3]_2Me=CH-C_6H_5$, $F_2[P(C_6H_{11})_3]_2Me=CH-C_6H_5$, $F_2[P(C_5H_9)_3]_2Me=CH-C_6H_5$, $Cl_2[P(C_6H_{11})_3]_2Me=CH(C_6H_4-Cl)$, $Cl_2[P(C_5H_9)_3]_2Me=CH(C_6H_4-Br)$, $Br_2[P(C_6H_{11})_3]_2Me=CH(C_6H_4-NO_2)$, $Br_2[P(C_5H_9)_3]_2Me=CH(C_6H_4-OC_2H_5)_2$, $Cl_2[P(C_6H_{11})_3]_2Me=CH(C_6H_4-CH_3)$, $F_2[P(C_5H_9)_3]_2Me=CH-[C_6H_3-(CH_3)_2]$, $Cl_2[P(C_6H_{11})_3]_2Me=CH-C_{10}H_9$, $Cl_2[P(C_5H_9)_3]_2Me=CH-CH_3$, $Cl_2[P(C_6H_{11})_3]_2Me=CHCH_3$, $Br_2[P(C_5H_9)_3]_2Me=CH-i-C_3H_7$, $Cl_2[P(C_6H_{11})_3]_2Me=CH-t-C_4H_9$, $Cl_2[P(C_5H_9)_3]_2Me=CH-n-C_4H_9$, $Cl_2[P(C_6H_{11})_3]_2Me=CH-C_6H_4-OCH_3$, $Cl_2[P(C_5H_9)_3]_2Me=CH-C_6H_3-(CH_3)_2$, $Br_2[P(C_6H_{11})_3]_2Me=CH-C_6H_2-(CH_3)_3$, $Br_2[P(C_5H_9)_3]_2Me=CH-CH_2C_6H_5$, $Cl_2[P(t-C_4H_9)_3]_2Me=CH-C_6H_5$, $Cl_2[P(i-C_3H_7)_3]_2Me=CH-C_6H_5$, $Cl_2[P(C_6H_5)_3]_2Me=CH-C_6H_5$, $Cl_2[P(C_6H_3-CH_3)_3]_2Me=CH-C_6H_5$, $Br_2[P(C_5H_4-(CH_3)_2)_3]_2Me=CH-C_6H_5$, $Cl_2[P(C_6H_3-(CH_3)_3]_2Me=CH-C_6H_5$, $Cl_2[P(C_6H_{11})_3-CH_2CH_2-P(C_6H_{11})_3]Me=CH-C_6H_5$, $Cl_2[P(C_5H_9)_3]_2Me=CH-C_6H_{11}$, $Cl_2[P(C_5H_9)_3]_2Me=CH-C_5H_9$, $Cl_2[P(C_5H_9)_3]_2Me=C(C_6H_{11})_2$, $Cl_2[P(C_6H_{11})_3]_2Me=CH_2$, $Cl_2[P(C_5H_9)_3]_2Me=CH_2$, $Cl_2[P(C_6H_{11})_3]_2Me=CH-n$-butyl, $Cl_2[P(C_3H_7)_3]_2Me=CH-C_6H_5$, $CL_2[P(C_3H_7)_3]_2Me=CH-C_5H_{11}$, $Cl_2[P(i-C_3H_7)_3]_2Me=CH-C_6H_5$, $CL_2[P(i-C_3H_7)_3]_2Me=CH-C_5H_{11}$.

The ruthenium carbene catalysts are preferably employed in amounts of from 0.05 to 0.2 % by weight.

The compounds of the formula X are known and their preparation is described by P. Schwab et al. in Angew. Chem. (1995), 107, No. 18, pages 2179 to 2181. The preparation of the dinuclear compounds of the formula Xa, for example, can be carried out by reacting 2 equivalents of a compound of the formula X with one equivalent of a conventional compound of the formula



in which X_{02}, Me and T_4 are as defined for formula Xa, in the presence of an inert solvent.

The novel composition may additionally include further open-chain comonomers which form copolymers with the strained cycloolefins. If, say, dienes are also used, it is possible for crosslinked polymers to be formed. Some examples of such comonomers are olefinically mono- or di-unsaturated compounds, such as olefins and dienes from the group consisting of ethene, propene, butene, pentene, hexene, heptene, octene, decene, dodecylene, cyclohexene (which is known not to form metathesis polymers on its own), acrylic and methacrylic acid, their esters and amides, vinyl ethers, vinyl esters, vinyl chloride, vinylidene chloride, styrene, butadiene, isoprene and chlorobutadiene. If volatile comonomers are used, pressure techniques are frequently necessary. If nonvolatile comonomers are used, therefore, there may be process advantages.

The further open-chain olefins suitable for the copolymerization are present in the novel composition, for example, in an amount of up to 80 % by weight, preferably from 0.1 to 80 % by weight, more preferably from 0.5 to 60 % by weight and, with particular preference, from 5 to 40 % by weight, based on the overall amount of di- and oligocyclopentadienes and other olefins capable of copolymerization.

The novel composition may include formulation auxiliaries. Known auxiliaries are antistats, antioxidants, light stabilizers, plasticizers, dyes, pigments, fillers, reinforcing fillers, lubricants, adhesion promoters, viscosity-increasing agents, and mould release auxiliaries. The fillers can be present in surprisingly high proportions without any adverse effect on the polymerization, for example in amounts of up to 80 % by weight, preferably from 1 to 70 % by weight, more preferably from 5 to 70 % by weight, particularly preferably from 5 to 60 % by weight and, with special preference, from 10 to 60 % by weight, based on the composition. Fillers and reinforcing fillers for improving the optical, physical, mechanical and electrical properties have been disclosed in large numbers. Some examples are glass and quartz in the form of powders, beads and fibres, metal oxides and semimetal oxides, carbonates such as $MgCO_3$, $CaCO_3$, dolomite, metal sulfates, such as gypsum and heavy spar, natural and synthetic silicates, such as talc, zeolites, wollastonite, felspars, aluminas, such as china clay, ground minerals, whiskers, carbon fibres, polymer fibres or polymer powders, and carbon black. Viscosity-increasing agents are, in particular, metathesis polymers which contain olefinically unsaturated groups and which, in the course of the polymerization, can be incorporated into the polymer. Metathesis polymers of this kind are known and are commercially available, for example, under the trade name Vestenamers®.

For the same purpose it is possible to use, for example, poly-1,3-dienes such as polybutadiene, polyisoprene, polychlorobutadiene or copolymers with the underlying dienes and with one or more olefins. Such polymers are likewise commercially available, for example Buna® and Kraton®. The amount of the viscosity-increasing polymers may for example be from 0.1 to 50 % by weight, preferably from 1 to 30 % by weight and, with particular preference, from 1 to 20 % by weight, based on all of the monomers present in the composition. The viscosity-increasing agents serve at the same time to improve the toughness properties of the polymers. The viscosity of the composition can be adjusted to the desired applications over a broad range.

The novel compositions are outstandingly suitable for the direct production of shaped articles. Despite the in some cases high catalyst activity, the individual components can be mixed and brought into the desired shape, since the catalysts dissolve even at room temperature, or with gentle heating, in nonpolar and polar monomers, and therefore permit a sufficient time for processing.

The invention additionally provides a process for preparing polymers by metathesis polymerization, which comprises heating or irradiating a solvent-free novel composition, or first irradiating and then heating such a composition.

Of greater preference is a process for preparing polymers by metathesis polymerization, comprising the steps of

1) purifying at least one solvent-free Diels-Alder adduct of (a) an unsubstituted or substituted 1,3-cyclopentadiene and (b) an unsubstituted or substituted cycloolefin down to a residual content of not more than 0.1 % by weight of cyclopenta-1,3-diene or substituted cyclopenta-1,3-diene,

2) mixing the adduct with from 0.05 to 0.3 % by weight, based on the Diels-Alder adduct, of ruthenium catalyst for the metathesis polymerization, directly after purification or after storage over a basic zeolite,

3) polymerizing the mixture by irradiation or heating, or first irradiation and then heating.

The novel process is subject to the same preferences as for the novel composition.

The novel compositions are not very stable on storage, and it is expedient to mix monomers and catalyst not until just before processing. The novel process is expediently conducted such that the mixing operation is associated, prior to polymerization, with a shaping operation, for example a coating or a shaped article. It is possible in principle to employ all known shaping techniques, for example extrusion, injection moulding and compression. The novel compositions are particularly suitable as casting resins with or without the use of pressure, as for example in the RIM (Reaction Injection Moulding) technique.

Irradiation can be carried out with light having a wavelength ranging from the UV region through the visible region into the near infrared region.

Heating can mean a temperature from 0 °C to 300 °C, preferably from room temperature to 300 °C, more preferably from room temperature to 250 °C, particularly preferably from room temperature to 200 °C, and, with particular preference, from 30 to 200 °C. The polymerization times depend essentially on the catalyst activity, and they can range from seconds through minutes up to a number of hours. Polymerization can also be carried out in stages at ascending temperatures.

Using the novel process it is possible to produce materials (semi-finished products) for the machining of shaped articles, or, directly, to produce mouldings of all kinds, films, sheets and coatings. The invention also provides for the use of the novel composition for producing semi-finished products, mouldings and sheets. The invention additionally provides mouldings from the novel compositions.

Depending on the monomer used, the polymers prepared in accordance with the invention may have very different properties. Some are notable for very high oxygen permeability, low dielectric constants, good thermal stability and low water absorption. Others have outstanding optical properties, such as high transparency and low refractive indices. A further quality to be emphasized, in particular, is the low shrinkage. The polymers can therefore be used in widely differing industrial fields. The avoidance of solvents ensures the production of bubble-free mouldings and coatings even at relatively high polymerization temperatures.

The novel compositions are notable, as coats on the surface of substrate materials, especially apolar substrate materials, for a high bonding strength. A physical (for example plasma treatment) or chemical treatment (application of adhesion promoters) may further increase the bonding strength. In addition, the coated materials are notable for very high surface gloss and surface smoothness. Among the good mechanical properties, particular mention should be made of the low shrinkage and the high impact resistance, but also of the thermal stability. Also deserving a mention are the ease of demoulding, in the case of processing in moulds, and the high solvent resistance. Through the choice of monomers it is possible to tailor the desired properties for the end use. In addition to hard or elastic thermoplastic mouldings, crosslinked thermosetting or elastomeric polymers are obtainable. It is particularly noteworthy that, despite lower amounts of catalyst, polymers with higher glass transition temperatures and better mechanical properties (toughnesses, tensile strength) are obtained than when higher amounts of catalyst and dicyclopentadienes with a relatively high cyclopentene content are used.

These polymers are suitable for producing medical implements, implants or contact lenses; for producing electronic components; as binders for coating materials; as photocurable compositions for constructing models, or as adhesives for bonding substrates having low surface energies (for example Teflon, polyethylene and polypropylene).

The novel compositions are particularly suitable for producing protective coats on substrate materials, and for producing relief images. The invention also provides a variant of the novel process for producing coatings on substrate materials, in which a novel composition is applied as a coat on a substrate, for example by dipping, spreading, flow coating, rolling, knife or spin coating techniques, and the coat is heated for polymerization. This may be followed by further heat treatment. Using this process it is possible to modify or to protect surfaces of substrates.

The present invention likewise provides a composition comprising (a) a substrate material, and (b) a coat of a novel composition, which is applied at least to one surface.

Also provided by the invention is a substrate material which is coated on at least one surface with a novel composition.

The present invention similarly provides a composition comprising (a) a substrate material, and (b) a polymer coat of a novel composition which is applied at least to one surface.

Examples of suitable substrates (substrate materials) are those of glass, minerals, ceramics, plastics, wood, semimetals, metals, metal oxides and metal nitrides. The coat thicknesses are guided essentially by the desired use and may, for example, be from 0.1 to 1000 μm, preferably from 0.5 to 500 μm, and, with particular preference, from 1 to 100 μm. The coated materials are notable for a high bonding strength and good thermal and mechanical properties.

The novel coated materials can be prepared by known methods, for example spreading, knife coating, flow-coating techniques, such as curtain coating, or spin coating.

The novel compositions are also suitable for preparing rubber-like or thermoplastic polymers which can be crosslinked still further. To this end the strained cyclopentadienes can include reactive groups, for example (meth)acrylate or epoxide groups, which are attached covalently via a bridge group or directly to the cycloolefin.

The novel compositions can also be used as heat-curable adhesives for the firm bonding of a wide variety of materials, in which case outstanding peel strengths can be obtained.

In addition to their high bonding strengths, outstanding ease of processing, good surface properties (smoothness, gloss), high crosslinking density and resistance to solvents and other liquids, the novel polymers are particularly notable, in addition, for very good physico-mechanical properties, for example high temperature resistance, breaking strength and flexural strength, and impact resistance, and outstanding electrical properties, for example low conductivities, dielectric constants and loss factors ε and tan δ. Also deserving a mention are the high oxygen permeability and the low water uptake. Polymers composed only of carbon and hydrogen are particularly valuable ecologically, since they can, for example, be completely recycled by pyrolysis or harmlessly incinerated.

The Examples which follow illustrate the invention in more detail.

A) USE EXAMPLES

The following catalysts are employed:

[1-Methyl-4-isopropylbenzene][$PC_6H_{11})_3$]Ru(II)Cl_2 (catalyst A).

$Cl_2[PC_6H_{11})_3]_2$Ru(IV)=CH-C_6H_5 (catalyst B).

Abbreviations:

CPD: 1,3-Cyclopentadiene
DCPD: Dicyclopentadiene
T_g: Glass transition temperature

Example A1:

180 g of DCPD (technical grade) is stored over 18 g of molecular sieve (Union Carbide, type 5A, supplied by Fluka, No. 69849) for one week, occasionally shaking it. Following decantation, the content of CPD is determined as being 0.06 % by weight. 0.3 % by weight of catalyst A is added, the solid is dissolved with gentle heating, and polymerization is carried out in an aluminium mould in a hot-air oven for 1h at 80° C, 1h at 100° C and 2h at 120° C, to give a yellow, transparent, firm plate 4 mm thick and of good impact resistance with a T_g of 100° C.

Comparison Example 1:

The procedure of Example A1 is repeated but without storage of the DCPD. The CPD content is 0.2 % by weight. A soft, black, rubber-like moulding with a T_g < room temperature is obtained.

Comparison Example 2:

The procedure of Comparison Example 1 is repeated but with 0.5 % by weight of catalyst A, to give, despite the higher catalyst content, a firm, yellowish brown plate with a T_g of only 80° C.

Example A2:

180 g of technical-grade DCPD is devolatilized at room temperature under a high vacuum and at a pressure of 5 kPa for 5 minutes. The CPD content is 0.04 % by weight. Then 0.3 % by weight of catalyst A is dissolved and polymerization is carried out as in Example A1, to give a yellow, transparent plate 4 mm thick of good impact resistance with a T_g of 115° C.

Example A3:

The procedure of Example A2 is repeated but the DCPD, prior to devolatilization, is stored over a molecular sieve (amount and molecular sieve as in Example A1). The CPD content is 0.02 % by weight. A yellow, transparent plate 4 mm thick of good impact resistance with a T_g of 127° C is obtained.

Example A4:

Technical-grade DCPD is distilled under vacuum (7 kPa) at 50° C, and 10 g of a middle fraction with a CPD content of 0.03 % by weight are mixed with 0.3 % by weight of catalyst A. Polymerization is carried out as in Example A1, to give a yellow, transparent plate 4 mm thick of good impact resistance with a T_g of 120° C.

Example A5:

5 g of technical-grade DCPD are devolatilized as in Example A2, and 0.2 % by weight of catalyst B is added. The CPD content is 0.04 % by weight. Polymerization is carried out as in Example A1, to give a yellow, transparent plate 4 mm thick of good impact resistance with a T_g of 135° C.

Comparison Example 3:

30 mg of CPD are added to the mixture from Example A5, and polymerization is then carried out as in Example A1, to give a rubber-like product with a strong odour of DCPD, indicating incomplete conversion.

Comparison Example 4:

The procedure for Example A5 is repeated but without devolatilization. The CPD content is 0.2 % by weight. Polymerization is carried out as in Example A1, to give a yellowish brown plate 4 mm thick with a T_g of only 60° C.

WHAT IS CLAIMED IS:

1. A solvent-free polymerizable composition comprising a) at least one Diels-Alder adduct of (a1) unsubstituted or substituted cycloolefins and (a2) unsubstituted or substituted 1,3-cyclopentadienes, which adduct has a low content of unsubstituted or substituted cyclopentadienes, and b) a catalytically active amount of a ruthenium catalyst for metathesis polymerization, which composition comprises, based on the Diels-Alder adduct, not more than 0.1 % by weight of cyclopenta-1,3-diene or substituted cyclopenta-1,3-diene and from 0.05 to 0.3 % by weight of ruthenium catalyst; with the exception of dicyclopentadiene in combination with 0.3 % by weight (4-isopropyltolyl)$RuCl_2[P(C_6H_{11})_3]$.

2. A composition according to claim 1, wherein the Diels-Alder adducts are unsubstituted or substituted in one or more rings by one or more radicals, the substituents being selected from the group consisting of C_1-C_{18}alkyl; C_1-C_{12}alkoxy, C_1-C_6haloalkyl, C_3-C_8cycloalkyl, C_6-C_{12}aryl, C_7-C_{12}aralkyl, =O, halogen, -CN, -COOM, $-COO(M)_{1/2}$, $-C(O)OR_{01}$, $-C(O)NR_{02}R_{03}$, -C(O)-O-C(O)-, $-C(O)-NR_{02}-C(O)-$, in which

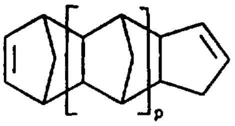
M is Li, Na or K;

$\mathbf{(M)_{1/2}}$ is Mg, Ca, Ba or Sr;

$\mathbf{R_{01}}$ is C_1-C_{18}alkyl, C_3-C_{12}alkenyl, C_3-C_{12}cycloalkyl, phenyl or benzyl; and

$\mathbf{R_{02}}$ and $\mathbf{R_{03}}$ independently of one another are H or are as defined for R_{01}.

3. A composition according to claim 1, wherein the Diels-Alder adducts are of the formula I



(I), in which

p is 0 or a number from 1 to 100;

it being possible for the adduct to be unsubstituted or substituted by C_1-C_{18}alkyl, C_1-C_{12}alkoxy, C_1-C_6haloalkyl, C_3-C_8cycloalkyl, C_6-C_{12}aryl, C_7-C_{12}aralkyl, =O, halogen, -CN, -COOM, $-COO(M)_{1/2}$, $-C(O)OR_{01}$, $-C(O)NR_{02}R_{03}$, -C(O)-O-C(O)- or $-C(O)-NR_{02}-C(O)-$;

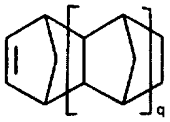
M is Li, Na or K;

$\mathbf{(M)_{1/2}}$ is Mg, Ca, Ba or Sr;

$\mathbf{R_{01}}$ is C_1-C_{18}alkyl, C_3-C_{12}alkenyl, C_3-C_{12}cycloalkyl, phenyl or benzyl; and

R_{02} and **R_{03}** independently of one another are H or are as defined for R_{01}.

4. A composition according to claim 1, wherein the Diels-Alder adducts are of the formula Ia



(Ia), in which

q is a number from 1 to 20;

and the Diels-Alder adducts are unsubstituted or are substituted by C_1-C_6alkyl.

5. A composition according to claim 1, which additionally comprises comonomeric strained cyclic olefins.

6. A composition according to claim 1, wherein the amount of 1,3-cyclopentadiene is not more than 0.08% by weight.

7. A composition according to claim 1, wherein the amount of ruthenium catalyst is from 0.05 to less than 0.3 % by weight.

8. A composition according to claim 1, wherein the ruthenium catalyst is selected from divalently cationic ruthenium compounds containing at least one phosphine group and total from two to five ligands attached to the ruthenium atom, and containing acid anions for charge compensation.

9. A composition according to claim 1, wherein the ruthenium compounds are of one of the formulae VIII to VIIId

$$R_{32}L_1Me^{2+}(Z^{n-})_{2/n} \quad \text{(VIII)},$$

$$R_{32}L_1L_2Me^{2+}(Z^{n-})_{2/n} \quad \text{(VIIIa)},$$

$$(R_{32})_2L_1Me^{2+}(Z^{n-})_{2/n} \quad \text{(VIIIb)},$$

$$(R_{32})_3L_1Me^{2+}(Z^{n-})_{2/n} \quad \text{(VIIIc)},$$

$R_{32}(L_1)_2Me^{2+}(Z^{n-})_{2/n}$ (VIIId), in which

R_{32} is a phosphine ligand of the formula VII or VIIa

$PR_{26}R_{27}R_{28}$ (VII),

$R_{26}R_{27}P\text{-}Z_1\text{-}PR_{26}R_{27}$ (VIIa),

R_{26}, R_{27} and **R_{28}** independently of one another are H, C_1-C_{20}alkyl, C_1-C_{20}alkoxy, C_4-C_{12}cycloalkyl or cycloalkoxy, the C_4-C_{12}cycloalkyl and cycloalkoxy being unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy, or R_{26}, R_{27} and R_{28} are C_6-C_{16}aryl or C_6-C_{16}aryloxy, the radicals C_6-C_{16}aryl and C_6-C_{16}aryloxy being unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy, or R_{26}, R_{27} and R_{28} are C_7-C_{16}aralkyl or C_7-C_{16}aralkyloxy, the radical C_7-C_{16}aralkyl or C_7-C_{16}aralkyloxy being unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy; or the radicals R_{26} and R_{27} together are tetra- or pentamethylene, or are tetra- or pentamethylenedioxyl, the radicals tetra- or pentamethylene or tetra- or pentamethylenedioxyl being unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy, or the radicals R_{26} and R_{27} together form tetra- or pentamethylene, or tetra- or pentamethylenedioxyl, fused with one or two 1,2-phenylene, the 1,2-phenylene-fused radicals tetra- or pentamethylene, or tetra- or pentamethylenedioxyl, being unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy, or the radicals R_{26} and R_{27} together are unsubstituted or C_1-C_6alkyl-, C_1-C_6haloalkyl- or C_1-C_6alkoxy-substituted tetramethylenedioxyl which is fused in the 1,2- and 3,4-positions with 1,2-phenylene; and R_{28} is as defined above; and

Z_1 is linear or branched, unsubstituted or C_1-C_4alkoxy-substituted C_2-C_{12}alkylene, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-cycloalkylene of 4 to 8 carbon atoms, or is unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-heterocycloalkylene having 5 or 6 ring members and one heteroatom from the group consisting of O and N;

Me is Ru;

n is 1, 2 or 3;

Z is the anion of an inorganic or organic acid;

L_1 is a ligand from the group consisting of nitrogen; unsubstituted or OH-, C_1-C_4alkyl-, C_1-C_4alkoxy-, C_6-C_{12}aryl- or halo-substituted monocyclic, polycyclic or fused arenes having 6 to 24 carbon atoms, unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy- or halo-substituted monocyclic heteroarenes, fused heteroarenes, fused arene-heteroarenes having 3 to 22 carbon atoms and 1 to 3 heteroatoms selected from the group consisting of O, S and N, and unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy- or halo-substituted aliphatic, cycloaliphatic, aromatic or araliphatic nitriles having 1 to 22 carbon atoms;
the ligands L_1 in formula VIId being identical or different, and
L_2 is a ligand from the group consisting of solvating inorganic or organic compounds containing the heteroatoms O, S or N, and cyclopentadienyl or indenyl, the radicals cyclopentadienyl and indenyl being unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, $(C_1$-$C_4alkyl)_3Si$ or $(C_1$-$C_4alkyl)_3SiO$-.

10. A composition according to claim 1, wherein the ruthenium compounds are of one of the formulae IX to IXd

$(R_{26}R_{27}R_{28}P)L_1Me^{2+}(Z_1{}^{1-})Z_2{}^{-1}$ (IX),

$(R_{26}R_{27}R_{28}P)_2L_1Me^{2+}(Z_1{}^{1-})Z_2{}^{-1}$ (IXa),

$(R_{26}R_{27}R_{28}P)L_1L_2Me^{2+}(Z_1{}^{1-})Z_2{}^{-1}$ (IXb),

$(R_{26}R_{27}R_{28}P)_3L_1Me^{2+}(Z_1{}^{1-})Z_2{}^{-1}$ (IXc),

$(R_{26}R_{27}R_{28}P)(L_1)_2Me^{2+}(Z_1{}^{1-})Z_2{}^{-1}$ (IXd), in which

Me is Ru;
Z_1 and **Z_2** independently of one another are H^-, cyclopentadienyl, Cl^-, Br^-, BF_4^-, PF_6^-, SbF_6^-, AsF_6^-, $CF_3SO_3^-$, C_6H_5-SO_3^-, 4-methyl-C_6H_5-SO_3^-, 3,5-dimethyl-C_6H_5-SO_3^-, 2,4,6-trimethyl-C_6H_5-SO_3^- or 4-CF_3-C_6H_5-SO_3^-;
R_{26}, **R_{27}** and **R_{28}** independently of one another are C_1-C_6alkyl, cyclopentyl, cyclohexyl, cyclopentyloxy or cyclohexyloxy, the radicals cyclopentyl, cyclohexyl, cyclopentyloxy and cyclohexyloxy being unsubstituted or mono- to tri-C_1-C_4alkyl-substituted, or R_{26}, R_{27} and R_{28}

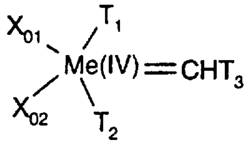
are phenyl, benzyl, phenyloxy or benzyloxy, the radicals phenyl, benzyl, phenyloxy or benzyloxy being unsubstituted or mono- to tri-C_1-C_4alkyl-substituted;

L_1 is C_6-C_{16}arene, C_5-C_{16}heteroarene, C_1-C_6alkyl-CN, benzonitrile or benzylnitrile, the radicals C_6-C_{16}arene, C_5-C_{16}heteroarene, C_1-C_6alkyl-CN, benzonitrile or benzylnitrile being unsubstituted or mono- to tri-substituted by C_1-C_4alkyl, C_1-C_4alkoxy, -OH, -F or Cl, and where the ligands L_1 in formula IXd are identical or different; and

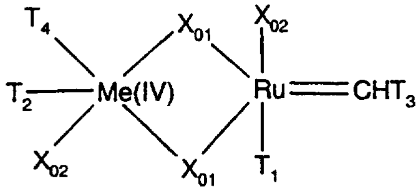
L_2 is H_2O or C_1-C_6alkanol.

11. A composition according to claim 1, wherein the ruthenium compounds are ruthenium carbenes having two phosphine ligands and two halogen atoms.

12. A composition according to claim 1, wherein the ruthenium carbenes are of the formula X or Xa or are mixtures of compounds of the formulae X and Xa



(X),



(Xa), in which

Me is ruthenium;

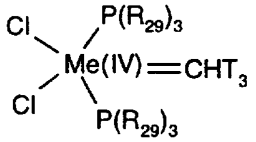
T_1 and **T_2** independently of one another are a tertiary phosphine, or T_1 and T_2 together are a ditertiary diphosphine;

T_3 is H, C_1-C_{12}alkyl; C_3-C_8cycloalkyl, C_3-C_7heterocycloalkyl having one or two heteroatoms selected from the group consisting of -O-, -S- and -N-, or is C_6-C_{14}aryl, or is C_4-C_{15}heteroaryl with one to three heteroatoms selected from the group consisting of -O-, -S- and -N-, the radicals C_3-C_7heterocycloalkyl, C_6-C_{14}aryl and C_4-C_{15}heteroaryl being unsubstituted or substituted by C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_6-C_{10}aryl, C_6-C_{10}aryloxy, $-NO_2$ or halogen;

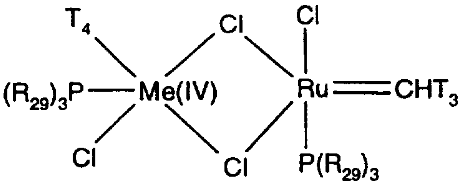
T_4 is C_6-C_{16}arene or C_4-C_{15}heteroarene, the radicals C_6-C_{16}arene and C_4-C_{15}heteroarene being unsubstituted or mono- to tri-substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, -OH, F, Cl or Br; and

X_{01} and **X_{02}** independently of one another are halogen.

13. A composition according to claim 1, wherein the ruthenium compounds are of the formulae Xb and Xc



(Xb),



(Xc), in which

Me is Ru;

R_{29} is α-branched C_3-C_8alkyl, unsubstituted or C_1-C_4alkyl-, C_1-C_4haloalkyl-, C_1-C_4alkoxy-, halo- or -NO_2-substituted C_5-C_8cycloalkyl, or is unsubstituted or C_1-C_4alkyl-, C_1-C_4haloalkyl-, C_1-C_4alkoxy-, halo- or -NO_2-substituted C_6-C_{10}aryl;

T_3 is H, C_1-C_6alkyl, unsubstituted or C_1-C_4alkyl-, C_1-C_4haloalkyl-, C_1-C_4alkoxy-, halo- or -NO_2-substituted C_5-C_8cycloalkyl or unsubstituted or C_1-C_4alkyl-, C_1-C_4haloalkyl-, C_1-C_4alkoxy-, halo- or -NO_2-substituted C_6-C_{10}aryl; and

T_4 is phenyl or mono- to tri-C_1-C_4alkyl-substituted phenyl.

14. A composition according to claim 1, which comprises a filler.

15. A composition according to claim 1, which comprises a viscosity-increasing agent.

16. A process for preparing polymers by thermal metathesis polymerization, which comprises subjecting a solvent-free composition according to claim 1 to irradiation or heating, or first to irradiation and then to heating.

17. A process according to claim 16, comprising the steps of
1) Purifying at least one solvent-free Diels-Alder adduct of (a) an unsubstituted or substituted 1,3-cyclopentadiene and (b) an unsubstituted or substituted cycloolefin down to a residual content of not more than 0.1 % by weight of cyclopenta-1,3-diene or substituted cyclopenta-1,3-diene,
2) Mixing the adduct with from 0.05 to 0.3 % by weight, based on the Diels-Alder adduct, of ruthenium catalyst for the metathesis polymerization, directly after purification or after storage over a basic zeolite,
3) Polymerizing the mixture by irradiation or heating, or first irradiation and then heating.

18. A substrate material which is coated on at least one surface with a composition according to claim 1.

19. The use of a composition according to claim 1 for producing semi-finished products, mouldings and sheets.

20. A moulding from a polymerized composition according to claim 1.

21. A process according to claim 17 for producing semi-finished products, mouldings and sheets.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/00816

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G61/08

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 296 566 A (BROWN-WENSLEY KATHERINE A ET AL) 22 March 1994 see column 6, line 42 - column 7, line 39 see claims 1-18 ---	1-21
P,X	WO 96 20235 A (CIBA GEIGY AG ;HAFNER ANDREAS (CH); SCHAAF PAUL ADRIAAN V D (CH);) 4 July 1996 see claims 1-49 --- -/--	1-21

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search 27 June 1997	Date of mailing of the international search report 28. 07. 97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Stienon, P

Inter ional Application No
PCı/EP 97/00816

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS, no. 11, 7 June 1995, LETCHWORTH GB, pages 1127-1128, XP002033934 A.W.STUMPF ET ALL.: "Ruthenium-based Catalyst for the Ring Opening Metathesis Polymerization of Low-strain Cyclic Olefins and of Functionalised Derivatives of Norbornen and Cyclooctene" see abstract -----	1-21

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INTERNATIONAL SEARCH REPORT

Information on patent family members

In' ational Application No
PCT/EP 97/00816

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US 5491206 A	13-02-96
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		EP 0617720 A	05-10-94
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WO 9620235 A	04-07-96	AU 4342696 A	19-07-96