

Polymerizable compound and a polymerization process

The present invention relates to a composition of dicyclopentadiene (DCPD), by itself or mixed with at least one stretched cycloolefin, and a single-component catalyst from the group consisting of ruthenium- and osmiumphosphine; a process for the thermal metathesis polymerization of dicyclopentadiene; coated materials; and linear or crosslinked copolymers of dicyclopentadiene and at least one stretched cycloolefin.

Thermally induced ring-opening metathesis polymerization using catalytic amounts of metal compounds has already been known for a relatively long time and is described in many instances in the literature [cf., for example, Ivin, K.J., Olefin Metathesis 1-12, Academic Press, London (1983)]. Such polymers are prepared industrially and are commercially obtainable, for example as Vestenamer®.

Feldman et al. [Feldman, J., Schrock, R.R., in: Lippard, S.J. (editor), Progress in Inorganic Chemistry 39:1-74 (1991)] describe molybdenum- and tungsten-alkylidene complexes which by themselves are only weak but together with Lewis acids are active thermal catalysts for the polymerization of cycloolefins.

WO 93/13171 describes air- and water-stable single-component and two-component catalysts based on carbonyl group-containing molybdenum and tungsten compounds and ruthenium and osmium compounds having at least one polyene ligand for thermal metathesis polymerization, and a photoactivated metathesis polymerization of stretched cycloolefins, in particular norbornene and norbornene derivatives. Other polycyclic - in particular non-fused polycyclic - cycloolefins are not mentioned. The single-component catalysts of the ruthenium compounds used, namely $[\text{Ru}(\text{cumene})\text{Cl}_2]_2$ and $[(\text{C}_6\text{H}_6)\text{Ru}(\text{CH}_3\text{CN})_2\text{Cl}]^+\text{PF}_6^-$, can indeed be activated by UV irradiation; however, the storage stability of the compositions with norbornene are [sic] completely inadequate. These catalysts are capable of replacing the known two-component catalysts only inadequately.

Demonceau et al. [Demonceau, A., Noels, A.F., Saive, E., Hubert, A.J., J. Mol. Catal. 76:123-132 (1992)] describe $(C_6H_5)_3PRuCl_2$, $(C_6H_5)_3PRuHCl$ and $(p\text{-cumene})RuCl_2P(C_6H_{11})_3$ as thermal catalysts for ring-opening metathesis polymerization of norbornene, a fused polycycloolefin. These catalysts have not been able to find acceptance in industrial preparations because their activity is too low. It is therefore proposed to increase the activity by addition of diazo esters. It is also mentioned that only $(p\text{-cumene})RuCl_2P(C_6H_{11})_3$ is capable of polymerizing norbornene at 60°C within a relatively short time. Cyclooctene is also mentioned as a further monomer. Other cycloolefins for metathesis polymerization are not mentioned.

WO 93/20111 describes osmium- and ruthenium-carbene compounds with phosphine ligands, for example $[(H_5C_6)_3P]_2Cl_2=CH-CH=C(C_6H_5)_2$, as purely thermal catalysts for ring-opening metathesis polymerization of stretched cycloolefins, in which cycloienes, such as dicyclopentadiene, act as catalyst inhibitors and cannot be polymerized. These catalysts are difficult to prepare and are moderately stable towards moisture, so that particular protective measures must be taken for storage and processing of compositions comprising these catalysts.

Tanielan et al. [Tanielan, C., Kieffer, R., Harfouch, A., Tetrahedron Letters 52:4589-4592 (1977)] report that the ruthenium compound $RuCl_2[P(C_6H_5)_3]_3$ is deactivated by dicyclopentadiene and no polymers are formed by thermal metathesis polymerization.

It has now been found, surprisingly, that dicyclopentadiene is accessible to thermal metathesis polymerization with a single-component catalyst if carbene-free ruthenium(II)- or osmium(II)-phosphine catalysts are used. It has furthermore been found that even linear polycyclopentadiene can be prepared if the polymerization is carried out in suitable solvents, and crosslinked polymers are obtained if the polymerization is carried out in bulk. It has also been found that the polymerization takes place even in the presence of plastics additives, for example fillers, and shaped articles, foils (films) or coatings with excellent physical and mechanical properties are obtained. It has also been observed that the

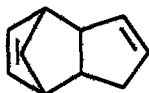
compositions of DCPD and carbene-free ruthenium(II)- or osmium(II)-phosphine catalysts are stable to air and moisture, and therefore both have a high storage stability, if appropriate with exclusion of light, and also necessitate no particular protective measures for the polymerization, which offers considerable advantages during processing. It has also additionally been found that, using these catalysts, DCPD can be copolymerized together with stretched cycloolefins as comonomers. As a result, properties can be modified in a controlled manner and adapted to suit the desired intended use.

The invention relates to a composition of (a) dicyclopentadiene by itself or as a mixture with a stretched cycloolefin and (b) a catalytic amount of at least one carbene-free, divalent-cationic ruthenium or osmium compound, as a single-component catalyst, which contains at least one phosphine group and a total of 2 to 5 ligands bonded to the metal atom and which contains acid anions for charge balancing.

In the context of the invention, total means the sum of the phosphine groups and the ligands. The ruthenium and osmium compounds preferably contain a total of 2 or 3 ligands.

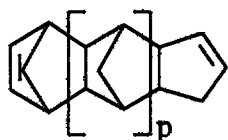
The phosphine group is preferably tertiary phosphines and phosphites, in particular phosphines having 3 to 40, preferably 3 to 30, and particularly preferably 3 to 24 C atoms.

Dicyclopentadiene of the formula



is a dimer of cyclopentadiene,

which is known and commercially obtainable. However, it is known that dicyclopentadiene forms further Diels-Alder adducts with cyclopentadiene and thus forms oligomers, which can also be used. Pure dicyclopentadiene, oligomers of dicyclopentadiene or mixtures thereof can thus be used according to the invention in the composition. The oligomers can correspond to the formula



, in which p is a number from 1 to 100, preferably 1 to 50,

particularly preferably 1 to 20, and especially preferably 1 to 10.

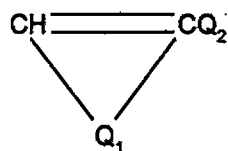
A very large number of stretched cycloolefins which the composition according to the invention can comprise as comonomers are known.

The cyclic olefins can be monocyclic or polycyclic fused and/or bridged ring systems, for example with two to four rings, which are unsubstituted or substituted and can contain heteroatoms, for example O, S, N or Si, in one or more rings and/or fused aromatic or heteroaromatic rings, for example o-phenylene, o-naphthylene, o-pyridinylene or o-pyrimidinylene. The individual cyclic rings can contain 3 to 16, preferably 3 to 12, and particularly preferably 3 to 8 ring members. The cyclic olefins can contain further nonaromatic double bonds, preferably 2 to 4 such additional double bonds, depending on the ring size. The ring substituents are those which are inert, i.e. which do not impair the chemical stability of ruthenium and osmium compounds. The cycloolefins are stretched rings or ring systems.

If the cyclic olefins contain more than one double bond, for example 2 to 4 double bonds, crosslinked polymers can also be formed, depending on the reaction conditions, the monomer chosen and the amount of catalyst.

Fused-on alicyclic rings preferably contain 3 to 8, particularly preferably 4 to 7, and especially preferably 5 or 6 ring C atoms.

In a preferred embodiment of the process according to the invention, the cycloolefins correspond to the formula I



(I),

wherein

Q_1 is a radical having at least one carbon atom which, together with the $-CH=CQ_2$ -group, forms an alicyclic ring which has at least 3 members and which optionally contains one or more heteroatoms chosen from the group consisting of silicon, phosphorus, 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_{20} alkyl, C_1 - C_{20} hydroxyalkyl, C_1 - C_{20} haloalkyl, C_1 - C_6 cyanoalkyl, C_3 - C_8 cycloalkyl, 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 two adjacent C atoms are substituted by $-CO-O-CO-$ or $-CO-NR_5-CO-$; or in which an alicyclic, aromatic or heteroaromatic ring, which is unsubstituted or 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_6 cyanoalkyl, C_3 - C_8 cycloalkyl, 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 $R_{13}-X_1$, is optionally fused onto adjacent carbon atoms of the alicyclic ring;

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 of one another are C_1 - C_{20} alkyl, C_1 - C_{20} haloalkyl, C_1 - C_{20} hydroxyalkyl, C_3 - C_8 cycloalkyl, 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, where the alkyl groups in their turn are unsubstituted or substituted by C_1 - C_{12} alkoxy or C_3 - C_8 cycloalkyl;

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 M₁ is an alkaline earth metal; and

u is 0 or 1;

in which the alicyclic ring formed with Q₁ optionally contains further non-aromatic double bonds;

Q₂ is hydrogen, C₁-C₂₀alkyl, C₁-C₂₀haloalkyl, C₁-C₁₂alkoxy, halogen, -CN or R₁₁-X₂;

R₁₁ is C₁-C₂₀alkyl, C₁-C₂₀haloalkyl, C₁-C₂₀hydroxyalkyl, C₃-C₈cycloalkyl, C₆-C₁₆aryl or C₇-C₁₆aralkyl;

X₂ is -C(O)-O- or -C(O)-NR₁₂;

R₁₂ is hydrogen, C₁-C₁₂alkyl, phenyl or benzyl;

wherein the abovementioned cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups are unsubstituted or substituted by C₁-C₁₂alkyl, C₁-C₁₂alkoxy, -NO₂, -CN or halogen, and where the heteroatoms of the abovementioned heterocycloalkyl, heteroaryl and heteroaralkyl groups are chosen from the group consisting of -O-, -S-, -NR₉- and -N=; and R₉ is hydrogen, C₁-C₁₂alkyl, phenyl or benzyl.

Fused-on alicyclic rings preferably contain 3 to 8, particularly preferably 4 to 7 and especially preferably 5 or 6 ring C atoms.

If an asymmetric center is present in the compounds of the formula I, this means that the compounds can occur in optically isomeric forms. Some compounds of the formula I can occur in tautomeric forms (for example keto-enol tautomerism). If an aliphatic C=C double bond is present, geometric isomerism (E form or Z form) can also occur. Exo-endo configurations are furthermore also possible. The formula I thus includes all the possible stereoisomers which are present 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 moieties of alkoxy, alkylthio, alkoxycarbonyl and other alkyl-containing groups. These alkyl groups preferably contain 1 to 12, more preferably 1 to 8 and particularly preferably 1 to

4 C atoms. These alkenyl and alkynyl groups preferably contain 2 to 12, more preferably 2 to 8 and particularly preferably 2 to 4 C atoms.

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

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

Halogenoalkyl includes, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, 2,2,2-trichloroethyl and halogenated, in particular fluorinated or chlorinated, alkanes, for example the isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl, tert-butyl, and the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl radicals.

Alkenyl includes, 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, isododecenyl, n-octadec-2-enyl and n-octadec-4-enyl.

Cycloalkyl is preferably C₅-C₈cycloalkyl, in particular C₅- or C₆cycloalkyl. Some examples are cyclopropyl, dimethylcyclopropyl, cyclobutyl, cyclopentyl, methylcyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

Cyanoalkyl includes, for example, cyanomethyl (methylnitrile [sic]), cyanoethyl (ethylnitrile [sic]), 1-cyanoisopropyl, 1-cyano-n-propyl, 2-cyano-n-butyl,

1-cyanoisobutyl, 1-cyano-sec-butyl, 1-cyano-tert-butyl and the various isomeric cyanopentyl and -hexyl radicals.

Aralkyl preferably contains 7 to 12 C atoms, and particularly preferably 7 to 10 C atoms. It can be, for example, benzyl, phenethyl, 3-phenylpropyl, α -methylbenzyl, phenbutyl or α,α -dimethylbenzyl.

Aryl preferably contains 6 to 10 C atoms. It can be, for example, phenyl, pentalin, indene, naphthalene, azulene [sic] or anthracene.

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

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

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

Alkali metal in the context of the present invention is to be understood as meaning lithium, sodium, potassium, rubidium and cesium, in particular lithium, sodium and potassium.

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

In the above definitions, halogen is to be understood as meaning fluorine, chlorine, bromine and iodine, preferably fluorine, chlorine and bromine.

Compounds of the formula I which are particularly suitable for the process according to the invention are those in which Q_2 is hydrogen.

Compounds of the formula I which are furthermore preferred for the polymerization are those in which the alicyclic ring which Q_1 forms together with the $-\text{CH}=\text{CQ}_2-$ group contains 3 to 16, more preferably 3 to 12 and particularly preferably 3 to 8 ring atoms, it being possible for this ring to be a monocyclic, bicyclic, tricyclic or tetracyclic ring system.

The process according to the invention can be carried out particularly advantageously with those compounds of the formula I in which Q_1 is a radical having at least one carbon atom, which, together with the $-\text{CH}=\text{CQ}_2-$ group, forms an alicyclic ring which has 3 to 20 members and optionally contains one or more heteroatoms chosen from the group consisting of silicon, oxygen, nitrogen and sulfur; and which is unsubstituted or substituted by halogen, $=\text{O}$, $-\text{CN}$, $-\text{NO}_2$, $\text{R}_1\text{R}_2\text{R}_3\text{Si}-(\text{O})_n-$, $-\text{COOM}$, $-\text{SO}_3\text{M}$, $-\text{PO}_3\text{M}$, $-\text{COO}(\text{M}_1)_{1/2}$, $-\text{SO}_3(\text{M}_1)_{1/2}$, $-\text{PO}_3(\text{M}_1)_{1/2}$, C_1-C_{12} alkyl, C_1-C_{12} haloalkyl, C_1-C_{12} hydroxyalkyl, C_1-C_4 cyanoalkyl, C_3-C_6 cycloalkyl, C_6-C_{12} aryl, C_7-C_{12} aralkyl, C_3-C_6 heterocycloalkyl, C_3-C_{12} heteroaryl, C_4-C_{12} heteroaralkyl or $\text{R}_4-\text{X}-$; or in which two adjacent C atoms in this radical Q_1 are substituted by $-\text{CO}-\text{O}-\text{CO}-$ or $-\text{CO}-\text{NR}_5-\text{CO}-$; or in which an alicyclic, aromatic or heteroaromatic ring, which is unsubstituted or substituted by halogen, $-\text{CN}$, $-\text{NO}_2$, $\text{R}_6\text{R}_7\text{R}_8\text{Si}-$, $-\text{COOM}$, $-\text{SO}_3\text{M}$, $-\text{PO}_3\text{M}$, $-\text{COO}(\text{M}_1)_{1/2}$, $-\text{SO}_3(\text{M}_1)_{1/2}$, $-\text{PO}_3(\text{M}_1)_{1/2}$, C_1-C_{12} alkyl, C_1-C_{12} haloalkyl, C_1-C_{12} hydroxyalkyl, C_1-C_4 cyanoalkyl, C_3-C_6 cycloalkyl, C_6-C_{12} aryl, C_7-C_{12} aralkyl, C_3-C_6 heterocycloalkyl, C_3-C_{12} heteroaryl, C_4-C_{12} heteroaralkyl or $\text{R}_{13}-\text{X}_1-$, is optionally fused onto adjacent carbon atoms; X and X_1 independently of one another are $-\text{O}-$, $-\text{S}-$, $-\text{CO}-$, $-\text{SO}-$, $-\text{SO}_2-$, $-\text{O}-\text{C}(\text{O})-$, $-\text{C}(\text{O})-\text{O}-$, $-\text{C}(\text{O})-\text{NR}_5-$, $-\text{NR}_{10}-\text{C}(\text{O})-$, $-\text{SO}_2-\text{O}-$ or $-\text{O}-\text{SO}_2-$; R_1 , R_2 and R_3 independently of one another are C_1-C_6 alkyl, C_1-C_6 perfluoroalkyl, 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_6 cycloalkyl, 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_6 alkyl, phenyl or benzyl, where the alkyl groups in their turn are unsubstituted or substituted by C_1-C_6 alkoxy or C_3-C_6 cycloalkyl; R_6 , R_7 and R_8 independently of

one another are C₁-C₈alkyl, C₁-C₈perfluoroalkyl, phenyl or benzyl; u is 0 or 1; wherein the alicyclic ring formed with Q₁ optionally contains further nonaromatic double bonds; Q₂ is hydrogen, C₁-C₁₂alkyl, C₁-C₁₂haloalkyl, C₁-C₈alkoxy, halogen, -CN or R₁₁-X₂-; R₁₁ is C₁-C₁₂alkyl, C₁-C₁₂haloalkyl, C₁-C₁₂hydroxyalkyl, C₃-C₆cycloalkyl, C₆-C₁₂aryl or C₇-C₁₂aralkyl; X₂ is -C(O)-O- or -C(O)-NR₁₂-; and R₁₂ is hydrogen, C₁-C₈alkyl, phenyl or benzyl; wherein the cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups are unsubstituted or substituted by C₁-C₈alkyl, C₁-C₈alkoxy, -NO₂, -CN or halogen, and wherein the heteroatoms of the heterocycloalkyl, heteroaryl and heteroaralkyl groups are chosen from the group consisting of -O-, -S-, -NR₉- and -N=; and R₉ is hydrogen, C₁-C₈alkyl, phenyl or benzyl.

Preferred compounds from this group are those compounds of the formula I in which Q₁ is a radical having at least one carbon atom, which, together with the -CH=CQ₂-group, forms an alicyclic ring which has 3 to 10 members and optionally contains a heteroatom chosen from the group consisting of silicon, oxygen, nitrogen and sulfur, and which is unsubstituted or substituted by halogen, -CN, -NO₂, R₁R₂R₃Si-, -COOM, -SO₃M, -PO₃M, -COO(M₁)_{1/2}, -SO₃(M₁)_{1/2}, -PO₃(M₁)_{1/2}, C₁-C₈alkyl, C₁-C₈haloalkyl, C₁-C₈hydroxyalkyl, C₁-C₄cyanoalkyl, C₃-C₆cycloalkyl, phenyl, benzyl or R₄-X-; or in which an alicyclic, aromatic or heteroaromatic ring, which is unsubstituted or substituted by halogen, -CN, -NO₂, R₆R₇R₈Si-, -COOM, -SO₃M, -PO₃M, -COO(M₁)_{1/2}, -SO₃(M₁)_{1/2}, -PO₃(M₁)_{1/2}, C₁-C₈Alkyl, C₁-C₈haloalkyl, C₁-C₈hydroxyalkyl, C₁-C₄cyanoalkyl, C₃-C₆cycloalkyl, phenyl, benzyl or R₁₃-X₁-, is optionally fused onto adjacent carbon atoms; R₁, R₂ and R₃ independently of one another are C₁-C₄alkyl, C₁-C₄perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M₁ is an alkaline earth metal; R₄ and R₁₃ independently of one another are C₁-C₈alkyl, C₁-C₈haloalkyl, C₁-C₈hydroxyalkyl or C₃-C₆cycloalkyl; X and X₁ independently of one another are -O-, -S-, -CO-, -SO- or -SO₂-; R₆, R₇ and R₈ independently of one another are C₁-C₄alkyl, C₁-C₄perfluoroalkyl, phenyl or benzyl; and Q₂ is hydrogen.

The process according to the invention is particularly suitable for the polymerization of norbornene and norbornene derivatives. Particularly preferred

derivatives among these norbornene derivatives are those which correspond alternatively to the formula II



wherein

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 to the formula III



wherein

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_6 alkyl or halogen;

or to the formula IV



wherein

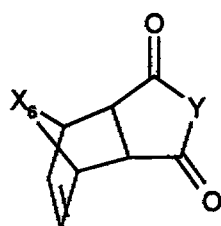
X_5 is $-CHR_{22}-$, oxygen or sulfur;

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 to the formula V



(V),

wherein

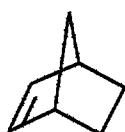
X_6 is $-CHR_{24}-$, oxygen or sulfur;

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

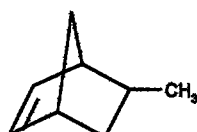
Y is oxygen or $\begin{array}{c} \diagup \\ N-R_{25} \\ \diagdown \end{array}$; and

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

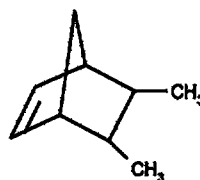
The following compounds of the formula I are particularly suitable for the polymerization process according to the invention, bi- and polycyclic systems being accessible by Diels-Alder reactions:



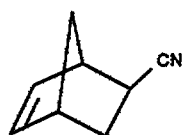
(1),



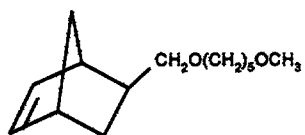
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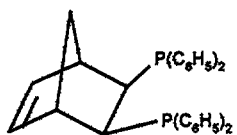
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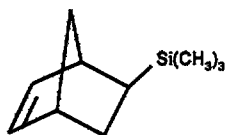
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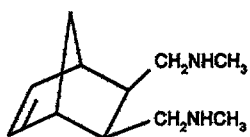
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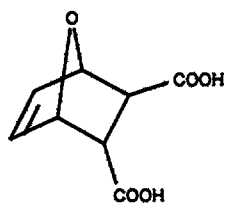
(6),



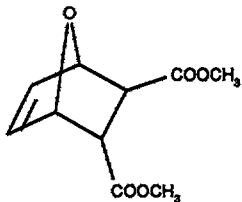
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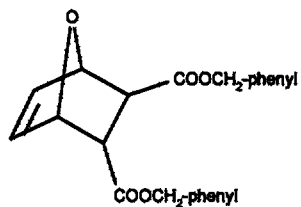
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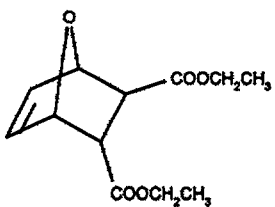
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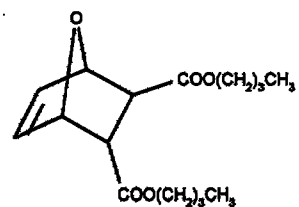
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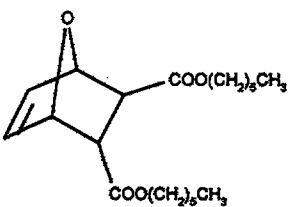
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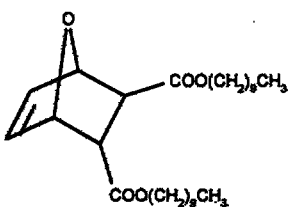
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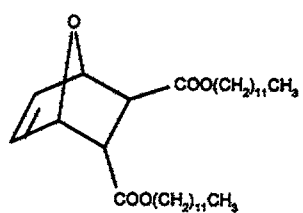
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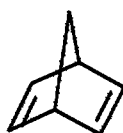
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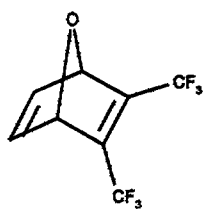
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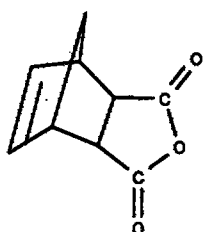
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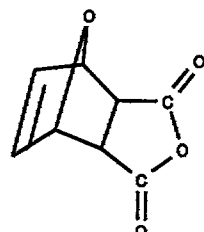
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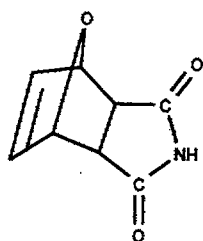
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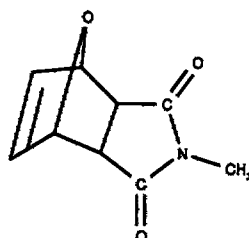
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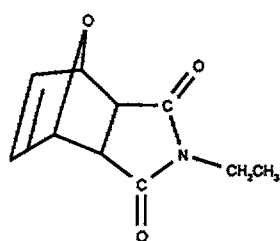
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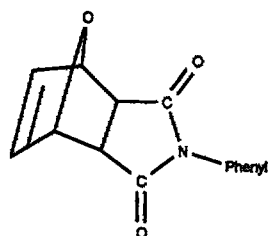
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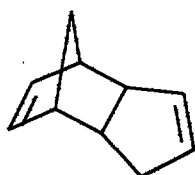
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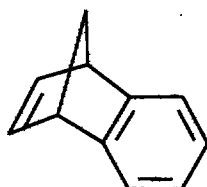
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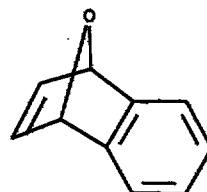
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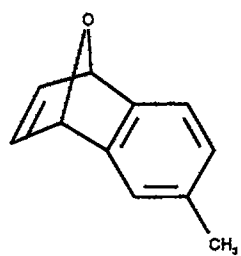
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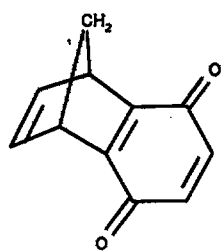
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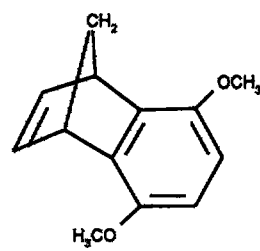
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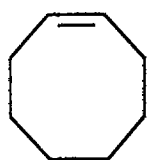
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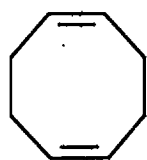
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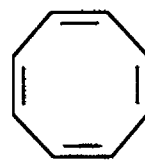
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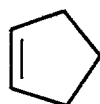
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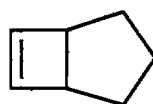
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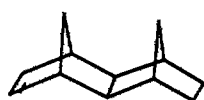
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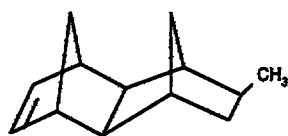
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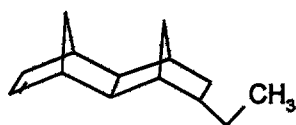
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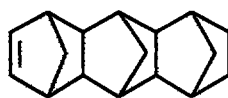
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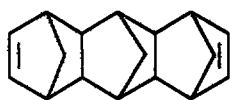
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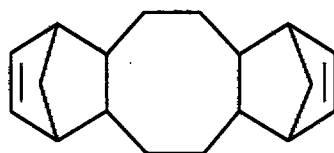
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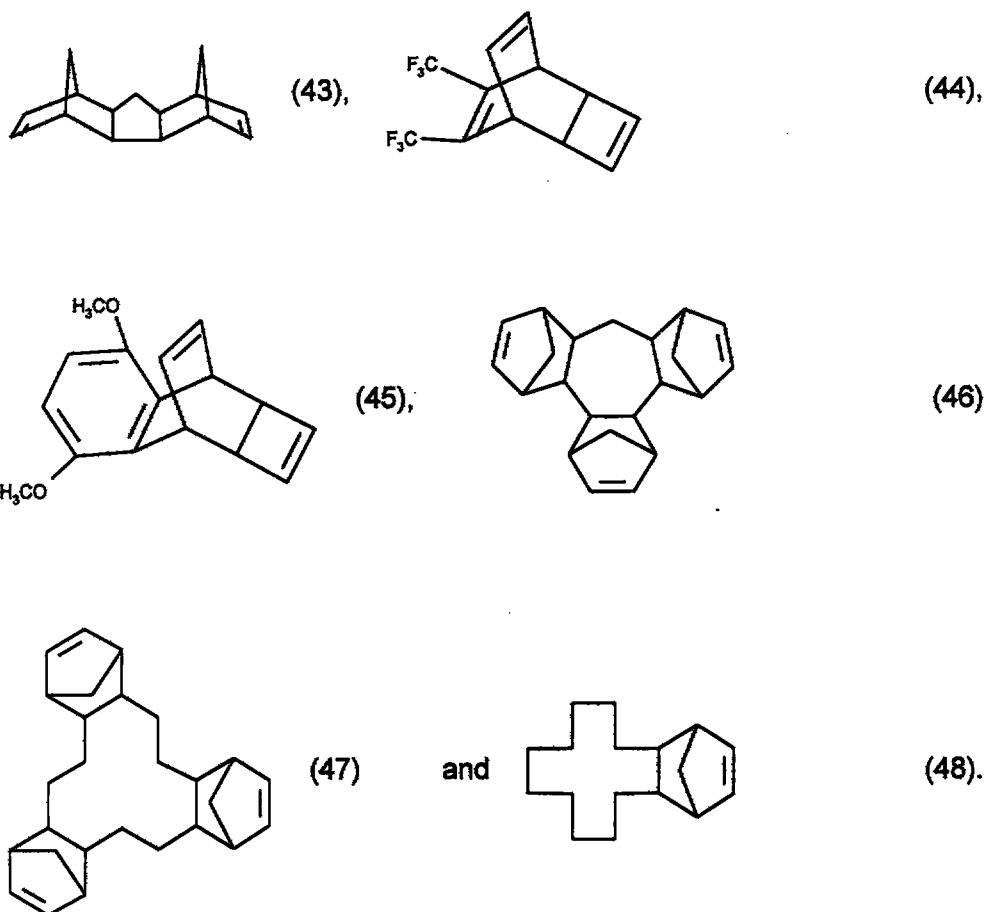
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(41),



(42),



Monomers and comonomers which contain only carbon and hydrogen are particularly preferably used according to the invention.

The composition can comprise the comonomeric cycloolefins in an amount of 0.01 to 99% by weight, preferably 0.1 to 95% by weight, particularly preferably 1 to 90% by weight, and especially preferably 5 to 80% by weight, based on the monomers present in the composition. The composition especially preferably comprises norbornene as the comonomer in amounts of, for example, 20 to 60% by weight.

In the ruthenium and osmium compounds to be used according to the invention, the monophosphine can be bonded to the metal atom once, twice or three times and a diphosphine can be bonded once. Preferably 1 to 4, more preferably 1 to 3,

and especially preferably 2 ligands are bonded in the ruthenium and osmium catalysts. The phosphine ligands preferably correspond to the formulae VI and VIa



wherein R_{26} , R_{27} and R_{28} independently of one another are H, $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_1\text{-C}_{20}$ alkoxy, $\text{C}_4\text{-C}_{12}$ cycloalkyl or cycloalkoxy which are unsubstituted or substituted by $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl or $\text{C}_1\text{-C}_6$ alkoxy, or $\text{C}_6\text{-C}_{16}$ aryl or $\text{C}_6\text{-C}_{16}$ aryloxy which are unsubstituted or substituted by $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl or $\text{C}_1\text{-C}_6$ alkoxy, or $\text{C}_7\text{-C}_{16}$ aralkyl or $\text{C}_7\text{-C}_{16}$ aralkyloxy which are unsubstituted or substituted by $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl or $\text{C}_1\text{-C}_6$ alkoxy; the radicals R_{26} and R_{27} together are tetra- or pentamethylene or tetra- or pentamethylenedioxy, which are unsubstituted or substituted by $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl or $\text{C}_1\text{-C}_6$ alkoxy, or tetra- or pentamethylene or tetra- or pentamethylenedioxy which are unsubstituted or substituted by $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl or $\text{C}_1\text{-C}_6$ alkoxy and fused with 1 or 2 1,2-phenylene, or tetramethylenedioxy which is unsubstituted or substituted by $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl or $\text{C}_1\text{-C}_6$ alkoxy and fused in the 1,2- and 3,4-positions with 1,2-phenylene, and R_{28} has the abovementioned meaning; and Z_1 is linear or branched $\text{C}_2\text{-C}_{12}$ alkylene which is unsubstituted or substituted by $\text{C}_1\text{-C}_4$ alkoxy, 1,2- or 1,3-cycloalkylene which has 4 to 8 C atoms and is unsubstituted or substituted by $\text{C}_1\text{-C}_4$ alkyl or $\text{C}_1\text{-C}_4$ alkoxy, or 1,2- or 1,3-heterocycloalkylene which has 5 or 6 ring members and a heteroatom from the group consisting of O and N and is unsubstituted or substituted by $\text{C}_1\text{-C}_4$ alkyl or $\text{C}_1\text{-C}_4$ alkoxy.

The radicals R_{26} , R_{27} and R_{28} are preferably identical radicals. Sterically bulky radicals, for example branched, in particular α -branched alkyl or alkoxy, or cyclic radicals, are furthermore preferred.

Alkyl R_{26} , R_{27} and R_{28} can be linear or branched and can preferably contain 1 to 12, more preferably 1 to 8, and particularly preferably 1 to 6 C atoms. Examples of

alkyl are methyl, ethyl, n- and i-propyl, n-, i- and t-butyl and 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.

Alkoxy R_{26} , R_{27} and R_{28} can be linear or branched and can preferably contain 1 to 12, more preferably 1 to 8, and particularly preferably 1 to 6 C atoms. Examples of alkoxy are methoxy, ethoxy, n- and i-propyloxy, n-, i- and t-butyloxy and the isomers of pentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tridecyloxy, tetradecyloxy, pentadecyloxy, hexadecyloxy, heptadecyloxy, octadecyloxy and eicosyloxy. Preferred examples are methoxy, ethoxy, n- and i-propyloxy, n-, i- and t-butyloxy, 1-, 2- or 3-pentyloxy and 1-, 2-, 3- or 4-hexyloxy.

If R_{26} , R_{27} and R_{28} are substituted, the substituents are preferably C_1 - C_4 alkyl, C_1 - C_4 haloalkyl or C_1 - C_4 alkoxy. Halogen is preferably Cl, and particularly preferably F. Examples of preferred substituents are methyl, methoxy, ethyl, ethoxy and trifluoromethyl. R_{26} , R_{27} and R_{28} are preferably mono- to trisubstituted.

Cycloalkyl R_{26} , R_{27} and R_{28} is preferably C_5 - C_8 cycloalkyl, and particularly preferably C_5 - or C_6 cycloalkyl. 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 [sic] and tristrifluoromethylcyclopentyl and -cyclohexyl.

Cycloalkyloxy R_{26} , R_{27} and R_{28} is preferably C_5 - C_6 cycloalkyloxy, and particularly preferably C_5 - or C_6 cycloalkyloxy. Some examples are cyclobutyloxy, cycloheptyloxy, cyclooctyloxy and, in particular, cyclopentyloxy and cyclohexyloxy. Examples of substituted cycloalkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl [sic] and tristrifluoromethylcyclopentyloxy and -cyclohexyloxy.

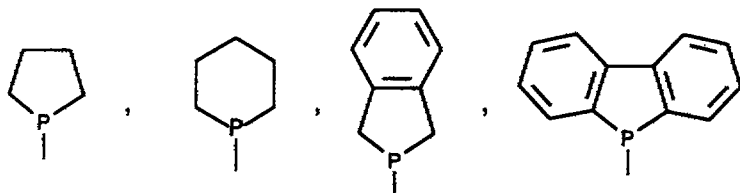
Aryl R_{26} , R_{27} and R_{28} is preferably C_6 - C_{12} aryl, and particularly preferably phenyl or naphthyl. Examples of substituted aryl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tris(trifluoromethyl)phenyl.

Aryloxy R_{26} , R_{27} and R_{28} is preferably C_6 - C_{12} aryloxy and particularly preferably unsubstituted or substituted phenyloxy or naphthyloxy. Examples of substituted aryloxy are methyl-, dimethyl-, trimethyl-, methylisopropyl-, isopropyl-, diisopropyl-, triisopropyl-, tert-butyl-, methyltert-butyl-, di-tert-butyl-, tritert-butyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tris(trifluoromethyl)phenyloxy.

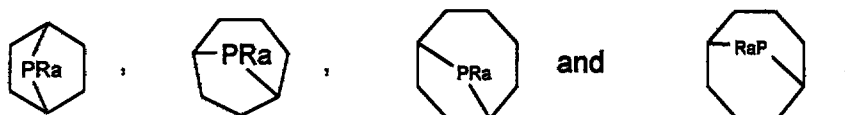
Aralkyl R_{26} , R_{27} and R_{28} is preferably C_7 - C_{13} aralkyl, the alkylene group in the aralkyl preferably being methylene. The aralkyl is particularly preferably benzyl. Examples of substituted aralkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tris(trifluoromethyl)benzyl.

Aralkyloxy R_{26} , R_{27} and R_{28} is preferably unsubstituted or substituted C_7 - C_{13} aralkyloxy, the alkylene group in the aralkyloxy preferably being methylene. The aralkyloxy is particularly preferably unsubstituted or substituted benzyloxy. Examples of substituted aralkyloxy are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tris(trifluoromethyl)benzyloxy.

Examples of optionally substituted or fused tetra- and pentamethylene which are bonded to the P atom are



Other suitable phosphines are cycloaliphatics which have 6 to 8 ring carbon atoms and are bridged with a =PRa group, for example



wherein Ra is C₁-C₆alkyl, cyclohexyl, benzyl, or phenyl which is unsubstituted or substituted by 1 or 2 C₁-C₄alkyl.

Linear or branched alkylene Z₁ is preferably 1,2-alkylene or 1,3-alkylene having preferably 2 to 6 C atoms, for example ethylene, 1,2-propylene or 1,2-butylene.

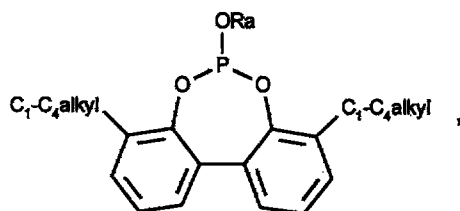
Examples of cycloalkylene Z₁ are 1,2- and 1,3-cyclopentylene and 1,2- or 1,3-cyclohexylene. Examples of heterocycloalkylene Z₁ are 1,2- and 1,3-pyrrolidine, 1,2- and 1,3-piperidine, and 1,2- and 1,3-tetrahydrofuran.

In a preferred embodiment, the phosphine ligands correspond to the formula VI wherein R₂₆, R₂₇ and R₂₈ independently of one another are H, C₁-C₆alkyl, cyclopentyl or cyclohexyl which are unsubstituted or substituted by C₁-C₄alkyl, or phenyl or phenyl [sic] which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkyl [sic] C₁-C₄alkoxy or trifluoromethyl, or benzyl which is unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy or trifluoromethyl. Particularly preferred examples of phosphine ligands of the formula VI are (C₆H₅)₂P, (3-CH₃-6-t-C₄H₉-C₆H₃)₃P, (3-CH₃-6-t-C₄H₉-C₆H₃)₃P, PH₃, (2,6-di-t-C₄H₉-C₆H₃)₃P, (2,3-di-t-C₄H₉-C₆H₃)₃P, (2,4-di-t-C₄H₉-C₆H₃)₃P, (2,4-di-CH₃-C₆H₃)₃P, (2,6-di-CH₃-C₆H₃)₃P, (2-CH₃-6-t-C₄H₉-C₆H₃)₃P, (CH₃)₃P, (2-i-C₃H₇-C₆H₄)₃P, (3-i-C₃H₇-C₆H₄)₃P, (4-i-C₃H₇-C₆H₄)₃P, (2-n-C₄H₉-C₆H₄)₃P, (3-n-C₄H₉-C₆H₄)₃P, (4-n-C₄H₉-C₆H₄)₃P, (2-i-C₄H₉-C₆H₄)₃P, (3-i-C₄H₉-C₆H₄)₃P, (4-i-C₄H₉-C₆H₄)₃P, (2-t-C₄H₉-C₆H₄)₃P, (3-t-C₄H₉-C₆H₄)₃P, (4-t-C₄H₉-C₆H₄)₃P, (4-C₂H₅-C₆H₄)₃P, (3-n-C₃H₇-C₆H₄)₃P, (2-n-C₃H₇-C₆H₄)₃P, (4-n-C₃H₇-C₆H₄)₃P, (C₂H₅)₂HP, (3-CH₃-C₆H₄)₃P, (4-CH₃-C₆H₄)₃P, (2-C₂H₅-C₆H₄)₃P, (3-C₂H₅-C₆H₄)₃P, (i-C₃H₇)₂P, (n-C₄H₉)₂P, (C₆H₅CH₂)₂HP, (C₆H₅CH₂)₂HP, (2-CH₃-C₆H₄)₃P,

$(C_6H_5)_3P$, $(C_5H_{11})_2P$, $(C_6H_5CH_2)_3P$, $(n-C_3H_7)_2HP$, $(i-C_3H_7)_2HP$, $(n-C_4H_9)_2HP$, $(n-C_3H_7)H_2P$, $(C_2H_5)H_2P$, $(C_5H_{11})_3P$, $(C_6H_5)_2HP$, $(C_5H_{11})_2HP$, $(n-C_3H_7)_3P$, $(i-C_3H_7)_3P$, $(n-C_4H_9)_3P$, $(CH_3)_2HP$, $(C_2H_5)_3P$, $(C_6H_{11})_3P$, $(C_6H_{11})_2HP$, $(C_5H_9)_3P$, $(C_5H_9)_2HP$ and $(CH_3)H_2P$.

In another preferred embodiment, the phosphine ligands correspond to the formula VI wherein R_{26} , R_{27} and R_{28} independently of one another are H, C_1 - C_6 alkoxy, cyclopentyloxy or cyclohexyloxy which are unsubstituted or substituted by C_1 - C_4 alkyl, or phenoxy or phenyl which are unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy or trifluoromethyl, or benzyloxy which is unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkyl [sic], C_1 - C_4 alkoxy or trifluoromethyl.

Examples of phosphites are $(CH_3O)_3P$, $(C_2H_5O)_3P$, $(n-C_3H_7O)_3P$, $(i-C_3H_7O)_3P$, $(n-C_4H_9O)_3P$, $(i-C_4H_9O)_3P$, $(t-C_4H_9O)_3P$, $(C_6H_5O)_3P$, $(2,4-di-CH_3-C_6H_3O)_3P$, $(2,6-di-CH_3-C_6H_3O)_3P$, $(2-C_2H_5-C_6H_4O)_3P$, $(3-C_2H_5-C_6H_4O)_3P$, $(4-C_2H_5-C_6H_4O)_3P$, $(2-n-C_3H_7-C_6H_4O)_3P$, $(3-n-C_3H_7-C_6H_4O)_3P$, $(4-n-C_3H_7-C_6H_4O)_3P$, $(2-i-C_3H_7-C_6H_4O)_3P$, $(3-i-C_3H_7-C_6H_4O)_3P$, $(4-i-C_3H_7-C_6H_4O)_3P$, $(2-n-C_4H_9-C_6H_4O)_3P$, $(3-n-C_4H_9-C_6H_4O)_3P$, $(4-n-C_4H_9-C_6H_4O)_3P$, $(2-i-C_4H_9-C_6H_4O)_3P$, $(3-i-C_4H_9-C_6H_4O)_3P$, $(4-i-C_4H_9-C_6H_4O)_3P$, $(2-t-C_4H_9-C_6H_4O)_3P$, $(3-t-C_4H_9-C_6H_4O)_3P$, $(4-t-C_4H_9-C_6H_4O)_3P$, $(2-CH_3-C_6H_4O)_3P$, $(3-CH_3-C_6H_4O)_3P$, $(2-CH_3-6-t-C_4H_9-C_6H_3O)_3P$, $(3-CH_3-6-t-C_4H_9-C_6H_3O)_3P$, $(3-CH_3-6-t-C_4H_9-C_6H_3O)_3P$, $(2,6-Di-t-C_4H_9-C_6H_3O)_3P$, $(2,3-di-t-C_4H_9-C_6H_3O)_3P$, $(2,4-di-t-C_4H_9-C_6H_3O)_3P$, $(4-CH_3-C_6H_4O)_3P$, and phosphites of the formula



wherein Ra is C_1 - C_6 alkyl, cyclohexyl, benzyl, or phenyl which is unsubstituted or substituted by 1 or 2 C_1 - C_4 alkyl.

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

Organic or inorganic compounds, atoms or ions coordinated to a metal center are designated as ligands for the ruthenium and osmium compounds to be used according to the invention.

Ligands which are particularly advantageously used in the context of the present invention are, for example, chosen from the group consisting of ligands (A) consisting of nitrogen (N_2); monocyclic, polycyclic or fused arenes which have 6 to 24, preferably 6 to 18, and particularly preferably 6 to 12 C atoms and are unsubstituted or substituted by OH, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_6 - C_{12} aryl or halogen; monocyclic heteroarenes which are unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy or halogen; fused heteroarenes; fused arene-heteroarenes having 3 to 22, preferably 4 to 16, and in particular 4 to 10 C atoms and 1 to 3 heteroatoms chosen from the group consisting of O, S and N; and aliphatic, cycloaliphatic, aromatic or araliphatic nitriles which have 1 to 22, preferably 1 to 18, particularly preferably 1 to 12, and especially preferably 1 to 7 C atoms and are unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy or halogen. The preferred substituents are methyl, ethyl, methoxy, ethoxy, fluorine, chlorine and bromine. The arenes and heteroarenes are preferably substituted by 1 to 3 radicals. Among the heteroarenes, the electron-rich heteroarenes are preferred.

Some examples of arenes and heteroarenes are benzene, cumene, 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, cumene, thiophene and benzothiophene. The arene is especially preferably benzene or a benzene substituted by 1 to 3 C_1 - C_4 alkyl, for example toluene, xylene,

trimethylbenzene, isopropylbenzene, tert-butylbenzene or cumene. 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, pentynitrile, hexynitrile, cyclopentyl- and cyclohexynitrile, benzonitrile, methylbenzonitrile, benzylnitrile and naphthynitrile. The nitriles are preferably linear C₁-C₄alkynitriles or benzonitrile. Of the alkynitriles, acetonitrile is particularly preferred.

In a preferred sub-group, the ligands of group (A) are N₂, benzene which is unsubstituted or substituted by one to three C₁-C₄alkyl, thiophene, benzonitrile or acetonitrile.

If appropriate, further ligands are present, for example chosen from the group consisting of ligands (B) consisting of solvating inorganic and organic compounds which contain the heteroatoms O, S or N and are often also used as solvents; and cyclopentadienyl or indenyl which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, (C₁-C₄alkyl)₃Si or (C₁-C₄alkyl)₃SiO. Examples of such compounds are H₂O, H₂S and NH₃; optionally halogenated, in particular fluorinated or chlorinated, aliphatic or cycloaliphatic alcohols or mercaptans having 1 to 18, preferably 1 to 12, and particularly preferably 1 to 6 C atoms, aromatic alcohols or thiols having 6 to 18, preferably 6 to 12 C atoms, or araliphatic alcohols or thiols having 7 to 18, preferably 7 to 12 C atoms; open-chain or cyclic and aliphatic, araliphatic or aromatic ethers, thioethers, sulfoxides, sulfones, ketones, aldehydes, carboxylic acid esters, lactones, optionally N-C₁-C₄-mono- or -dialkylated carboxylic acid amides having 2 to 20, preferably 2 to 12, and in particular 2 to 6 C atoms, and optionally N-C₁-C₄alkylated lactams; open-chain or cyclic and aliphatic, araliphatic or aromatic, primary, secondary and tertiary amines having 1 to 20, preferably 1 to 12, and particularly preferably 1 to 6 C atoms; and cyclopentadienyls, for example cyclopentadienyl, indenyl and mono- or polymethylated or -trimethylsilylated cyclopentadienyls or indenyls. Examples are also allyl, metallyl [sic] 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 ethylmercaptan, cyclopentanol, cyclohexanol, cyclohexylmercaptan, phenol, methylphenol, fluorophenol, phenylmercaptan, benzylmercaptan, 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 correspond to the formula $R_{29}NH_2$, the secondary amines can correspond to the formula $R_{29}R_{30}NH$ and the tertiary amines can correspond to the formula $R_{29}R_{30}R_{31}N$, wherein R_{29} is C_1 - C_{18} alkyl, C_5 - or C_6 cycloalkyl which is unsubstituted or substituted by C_1 - C_4 alkyl or C_1 - C_4 alkoxy, or C_6 - C_{18} aryl or C_7 - C_{12} aralkyl which is unsubstituted or substituted by C_1 - C_4 alkyl or C_1 - C_4 alkoxy, R_{30} independently has the meaning of 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 has the meaning of R_{29} . The alkyl preferably contains 1 to 12, and particularly preferably 1 to 6 C atoms. The aryl preferably contains 6 to 12 C atoms and the aralkyl preferably contains 7 to 9 C atoms. Examples of amines are methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, triethyl-, methylethyl-, dimethylethyl-, n-propyl-, di-n-propyl-, tri-n-butyl-, cyclohexyl-, phenyl- and benzylamine, and pyrrolidine, N-methylpyrrolidine, piperidine, piperazine, morpholine and N-methylmorpholine.

In a preferred sub-group, the ligands of group (B) are H_2O , NH_3 , unsubstituted or partly or completely fluorinated C_1 - C_4 alkanols or cyclopentadienyl, indenyl, allyl,

metallyl [sic] or crotyl. H_2O , NH_3 , cyclopentadienyl, indenyl, methanol and ethanol are especially preferred.

In a preferred embodiment, the Ru and Os catalysts to be used according to the invention contain arenes or heteroarenes as ligands, phosphine groups and anions for charge balancing. They especially preferably contain an arene group as a ligand, a tertiary phosphine group and mono- or divalent anions for charge balancing.

Suitable anions of inorganic or organic acids are, for example, hydride ($\text{H}^\ominus$), halide

(for example $\text{F}^\ominus$, $\text{Cl}^\ominus$, $\text{Br}^\ominus$ and $\text{I}^\ominus$), the anion of an oxygen acid, and $\text{BF}_4^\ominus$, $\text{PF}_6^\ominus$,

$\text{SbF}_6^\ominus$ or $\text{AsF}_6^\ominus$. It should be mentioned that the abovementioned ligands

cyclopentadienyl, indenyl, allyl, metallyl [sic] and crotyl are anionic and thus also serve for charge balancing.

Other suitable anions are $\text{C}_1\text{-C}_{12}^-$, preferably $\text{C}_1\text{-C}_6^-$, and particularly preferably $\text{C}_1\text{-C}_4$ alcoholates, which, in particular, are branched and, for example, correspond

to the formula $\text{R}_x\text{R}_y\text{R}_z\text{C-O}^\ominus$, wherein R_x is H or $\text{C}_1\text{-C}_{10}$ alkyl, R_y is $\text{C}_1\text{-C}_{10}$ alkyl and R_z is $\text{C}_1\text{-C}_{10}$ alkyl or phenyl, and the sum of the C atoms of R_x , R_y and R_z is 11.

Examples are, in particular, i-propyloxy and t-butyloxy.

Other suitable anions are $\text{C}_3\text{-C}_{18}^-$, preferably $\text{C}_5\text{-C}_{14}^-$, and particularly preferably

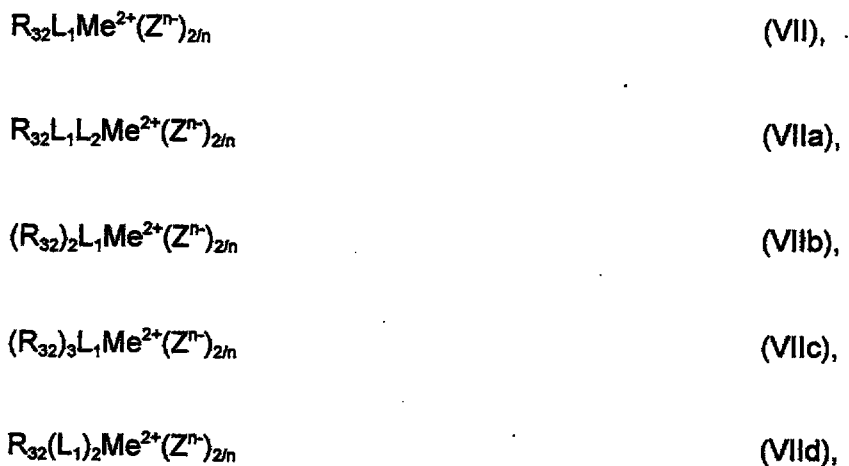
$\text{C}_5\text{-C}_{12}$ acetylides, which can correspond to the formula $\text{R}_w\text{-C}\equiv\text{C}^\ominus$ wherein R_w is

$\text{C}_1\text{-C}_{16}$ alkyl, preferably α -branched $\text{C}_3\text{-C}_{12}$ alkyl, for example formula $\text{R}_x\text{R}_y\text{R}_z\text{C-}$, or are phenyl or benzyl which are unsubstituted or substituted by 1 to 3 $\text{C}_1\text{-C}_4$ alkyl or $\text{C}_1\text{-C}_4$ alkoxy. 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-butylphenylacetylide.

The anions of oxygen atoms can be, for example, sulfate, phosphate, perchlorate, perbromate, periodate, antimonate, arsenate, nitrate, carbonate, the anion of a C₁-C₈carboxylic acid, for example formate, acetate, propionate, butyrate, benzoate, phenyl acetate or mono, di- or trichloro- or -fluoroacetate, sulfonates, for example methylsulfonate, ethylsulfonate, propylsulfonate, butylsulfonate, trifluoromethylsulfonate (triflate) or phenylsulfonate or benzylsulfonate which are optionally substituted by C₁-C₄alkyl, C₁-C₄alkoxy or halogen, in particular fluorine, chlorine or bromine, for example tosylate, mesylate, brosylate, p-methoxy- or p-ethoxyphenylsulfonate, pentafluorophenylsulfonate or 2,4,6-triisopropylsulfonate [sic], and phosphonates, for example methylphosphonate, ethylphosphonate, propylphosphonate [sic], butylphosphonate, phenylphosphonate, p-methylphenylphosphonate or benzyphosphonate.

H[⊖], F[⊖], Cl[⊖], Br[⊖], BF₄[⊖], PF₆[⊖], SbF₆[⊖], AsF₆[⊖], CF₃SO₃[⊖], C₆H₅-SO₃[⊖], 4-methyl-C₆H₅-SO₃[⊖], 3,5-dimethyl-C₆H₅-SO₃[⊖], 2,4,6-trimethyl-C₆H₅-SO₃[⊖] and 4-CF₃-C₆H₅-SO₃[⊖] and cyclopentadienyl (Cp[⊖]) are particularly preferred.

In a preferred embodiment, the ruthenium and osmium compounds correspond to one of the formulae VII to VIId



wherein

R_{32} is a phosphine ligand of the formula VI or VIa;

Me is Ru or Os;

n is the numbers 1, 2 or 3;

Z is the anion of an inorganic or organic acid;

(a) L_1 is a ligand of group A, wherein the L_1 in formula VIId are optionally different,
and

(b) L_2 is a ligand of group B.

The preference is stated above for the individual meanings applied to R_{32} , L_1 and L_2 .

In the formulae VII to VIId, n is preferably 1 or 2, and especially 1. The preferences stated for the phosphine ligands of the formulae VI and VIa applied to R_{32} , and in particular these are tertiary phosphines.

Ruthenium or osmium compounds which are especially preferably used in the process according to the invention are those of one of the formulae VIII to VIId



wherein

Me is Ru or Os;

Z_1 and Z_2 independently of one another are $H^\ominus$, cyclopentadienyl, $Cl^\ominus$, $Br^\ominus$, $BF_4^\ominus$,

$PF_6^\ominus$,

$SbF_6^\ominus$, $AsF_6^\ominus$, $CF_3SO_3^\ominus$, $C_6H_5-SO_3^\ominus$, 4-methyl- $C_6H_5-SO_3^\ominus$, 3,5-dimethyl- $C_6H_5-SO_3^\ominus$,

2,4,6-trimethyl- $C_6H_5-SO_3^\ominus$ or 4- $CF_3-C_6H_5-SO_3^\ominus$;

R_{26} , R_{27} and R_{28} independently of one another are C_1 - C_6 alkyl, cyclopentyl or cyclohexyl or cyclopentyloxy or cyclohexyloxy which are unsubstituted or substituted by 1 to 3 C_1 - C_4 alkyl, or phenyl or benzyl or phenyloxy or benzyloxy which are unsubstituted or substituted by 1 to 3 C_1 - C_4 alkyl;

L_1 is C_6 - C_{16} -arene or C_5 - C_{16} heteroarene which are unsubstituted or substituted by 1 to 3 C_1 - C_4 alkyl, C_1 - C_4 alkoxy, -OH, -F or Cl, or C_1 - C_6 alkyl-CN, benzonitrile or benzylnitrile, wherein the L_1 in formula VIII d are optionally different; and

L_2 is H_2O or C_1 - C_6 alkanol.

If the preparation of the ruthenium and osmium catalysts is carried out in solvents which can coordinate to a metal atom, for example alkanols, solvated Ru/Os cation complexes can be formed, and are also included in the context of the use according to the invention.

Some examples of ruthenium and osmium compounds to be used according to the invention are [tos is tosylate]: $(C_6H_{11})_2HPRu(p\text{-cumene})Cl_2$, $(C_6H_{11})_3PRu(p\text{-cumene})Cl_2$, $(C_6H_{11})_3PRu(p\text{-cumene})(tos)_2$, $(C_6H_{11})_3PRu(p\text{-cumene})Br_2$, $(C_6H_{11})_3PRu(p\text{-cumene})ClF$, $(C_6H_{11})_3PRu(C_6H_6)(tos)_2$, $(C_6H_{11})_3PRu(CH_3-C_6H_5)(tos)_2$, $(C_6H_{11})_3PRu(C_{10}H_8)(tos)_2$, $(i\text{-}C_3H_7)_3PRu(p\text{-cumene})Cl_2$, $(CH_3)_3PRu(p\text{-cumene})Cl_2$, $(C_6H_{11})_3PRu(CH_3-CN)(C_2H_5-OH)(tos)_2$, $(C_6H_{11})_3PRu(p\text{-cumene})(CH_3-CN)_2(PF_6)_2$, $(C_6H_{11})_3PRu(p\text{-cumene})(CH_3-CN)_2(tos)_2$, $(n\text{-}C_4H_9)_3PRu(p\text{-cumene})(CH_3-CN)_2(tos)_2$, $(C_6H_{11})_3PRu(CH_3CN)Cl_2$, $(C_6H_{11})_3PRu(CH_3-CN)_2Cl_2$, $(n\text{-}C_4H_9)_3PRu(p\text{-cumene})Cl_2$, $(C_6H_{11})_3PRu(p\text{-cumene})(C_2H_5OH)_2(BF_4)_2$, $(C_6H_{11})_3PRu(p\text{-cumene})(C_2H_5OH)_2(PF_6)_2$, $(i\text{-}C_3H_7)_3POs(p\text{-cumene})Cl_2$, $(CH_3)_3POs(p\text{-cumene})Cl_2$, $(C_6H_5)_3POs(p\text{-cumene})Cl_2$, $[(C_6H_{11})_3P]_3Ru(CH_3-CN)$, $(C_5H_9)_3PRu(p\text{-cumene})Cl_2$, $(C_6H_{11})_3PRu(p\text{-cumene})HCl$, $(C_6H_{11})_3PRu[1,2,4,5\text{-(}CH_3)_4C_6H_2]Cl_2$, $(C_6H_{11})_3PRu[1,3,5\text{-(}i\text{-}C_3H_7)_3C_6H_3]Cl_2$, $(C_6H_{11})_3PRu[(C_4H_9)\text{-}C_6H_5]Cl_2$, $(C_6H_{11})_3POs(p\text{-cumene})Cl_2$, $(C_6H_5)_3PRu(p\text{-cumene})HCl$, $[(C_6H_{11})_3P]_2Ru(CH_3-CN)(tos)_2$, $RuCl_2(p\text{-cumene})[(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2]$, $(C_6H_{11})_3PRu(p\text{-cumene})(C_2H_5OH)(BF_4)_2$, $(C_6H_{11})_3PRu(C_6H_6)(C_2H_5OH)_2(tos)_2$, $(C_6H_{11})_3PRu(i\text{-}C_3H_7\text{-}C_6H_5)(tos)_2$, $(C_6H_{11})_3PRu(C_6H_6)(p\text{-cumene})Br_2$, $(C_6H_{11})_3PRu(biphenyl)(tos)_2$, $(C_6H_{11})_3PRu(anthracene)(tos)_2$, $(2\text{-}CH_3C_6H_4)_3POs(p\text{-cumene})Cl_2$ and $(C_6H_{11})_3PRu(chrysene)(tos)_2$.

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

The composition according to the invention can comprise inert solvents. It is a particular advantage that in the case of liquid monomers, a metathesis polymerization can be carried out without the use of a solvent. Another advantage is that the polymerization itself can be carried out in water, polar and protic solvents or water/solvent mixtures. In these cases, it is advantageous in the context of the present invention to use a surfactant.

Suitable inert solvents are, for example, protic-polar and aprotic solvents, which can be used by themselves or in mixtures of at least two solvents. Examples are: ethers (dibutyl ether, tetrahydrofuran, dioxane, ethylene glycol monomethyl or dimethyl ether, ethylene glycol monoethyl or diethyl ether, diethylene glycol diethyl ether and triethylene glycol dimethyl ether), halogenated hydrocarbons (methylene chloride, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane), carboxylic acid esters and lactones (ethyl acetate, methyl propionate, ethyl benzoate, 2-methoxyethyl acetate, γ -butyrolactone, δ -valerolactone and pivalolactone), carboxylic acid amides and lactams (N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, tetramethylurea, hexamethylphosphoric acid triamide, γ -butyrolactam, ϵ -caprolactam, N-methylpyrrolidone, N-acetylpyrrolidone and N-methylcaprolactam), sulfoxides (dimethyl sulfoxide), sulfones (dimethyl sulfone, diethyl sulfone, trimethylene sulfone and tetramethylene sulfone), tertiary amines (N-methylpiperidine and N-methylmorpholine), aliphatic and aromatic hydrocarbons, for example petroleum ether, pentane, hexane, cyclohexane, methylcyclohexane, benzene or substituted benzenes (chlorobenzene, o-dichlorobenzene, 1,2,4-trichlorobenzene, nitrobenzene, toluene and xylene), and nitriles (acetonitrile, propionitrile, benzonitrile and phenylacetonitrile). Preferred solvents are aprotic polar and non-polar solvents.

Preferred solvents are aliphatic and aromatic hydrocarbons and mixtures of such solvents.

It is to be particularly emphasized that the composition according to the invention comprising a DCPD, if appropriate a cycloolefin and a catalyst is often insensitive to oxygen and moisture, which allows storage and a reaction procedure without an inert gas.

Catalytic amounts in the context of the present invention preferably means an amount of 0.001 to 20 mol%, particularly preferably 0.01 to 15 mol%, and especially preferably 0.01 to 10 mol%, based on the amount of monomer. Amounts of 0.001 to 2 mol% are especially preferred because of the high thermocatalytic activity.

The composition according to the invention used for the polymerization can be prepared directly before the polymerization or used as a preformulated mixture, since the catalysts used have a particularly high stability. The mixture can even be stored for a relatively long time as a ready-to-use formulation before the polymerization, which is of advantage for use on a large industrial scale.

The composition according to the invention can comprise formulation auxiliaries. Known auxiliaries are antistatics, antioxidants, light stabilizers, plasticizers, dyes, pigments, fillers, reinforcing fillers, lubricants, adhesion promoters, viscosity-increasing agents and mold release auxiliaries. The auxiliaries can be present in surprisingly high proportions without adversely influencing the polymerization, for example in amounts of up to 70% by weight, preferably 1 to 70% by weight, more preferably 5 to 60% by weight, particularly preferably 10 to 50% by weight, and especially preferably 10 to 40% by weight, based on the composition. A very large number of auxiliaries for improving the optical, physical, mechanical and electrical properties have been disclosed. Some examples are glass and quartz in the form of powders, beads and fibers, metal and semimetal oxides, carbonates, such as MgCO_3 , CaCO_3 and dolomite, metal sulfates, such as gypsum and barite, naturally

occurring and synthetic silicates, such as talc, zeolites, wollastonite and feldspars, aluminas, such as china clay, rock powders, whiskers, carbon fibers, fibers or powders of plastics and carbon black. Viscosity-increasing agents are, in particular, metathesis polymers which contain olefinically unsaturated groups and can be incorporated into the polymer during the polymerization. Such metathesis polymers are known and are commercially obtainable, for example, under the trade name Vestenamere®. Other viscosity-increasing agents are polybutadiene, polyisoprene or polychlorobutadiene, as well as copolymers of butadiene, isoprene and chloroprene with olefins.

The invention furthermore relates to a process for the preparation of metathesis polymers, which is characterized in that a composition of (a) dicyclopentadiene, by itself or in a mixture with a stretched cycloolefin, and (b) a catalytic amount of at least one carbene-free, divalent-cationic ruthenium or osmium compound as a single-component catalyst which contains at least one phosphine group and a total of 2 to 5 ligands bonded to the metal atom, and which contains acid anions for charge balancing, is heated.

The process according to the invention is preferably carried out at a temperature of at least 50°C, and more preferably at least 60°C. In particular, the process according to the invention is carried out at temperatures of 60 to 300°C, preferably 60 to 250°C, particularly preferably 60 to 200°C, and especially preferably 70 to 160°C. After the polymerization, it may be advantageous to after-heat the polymers at elevated temperatures, for example 80 to 200°C.

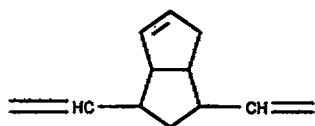
To prepare linear polymers, the reaction is preferably carried out in dilute solutions.

The polymerization can be combined with shaping processes, for example calendaring, casting, compression molding, injection molding or extrusion processes. Materials for production of shaped articles by cutting or thermoplastically deformable materials for production of all types of shaped articles, and coatings can be prepared using the process according to the invention. The shaping and polymerization are advantageously combined in

solvent-free reactive systems, it being possible to use processing processes such as, for example, injection molding, extrusion and polymerization in predetermined molds (if appropriate under pressure).

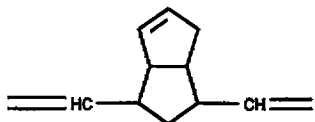
The polymers prepared according to the invention by the ... [sic] can be homopolymers or copolymers with random distribution of the structural units, graft polymers or block polymers, as well as crosslinked polymers of this type. They can have an average molecular weight ($\overline{M}_w$) of, for example, 500 to 2 million dalton, preferably 1000 to 1 million dalton (determined by GPC by comparison with polystyrene standards of narrow distribution).

It has been found, surprisingly, that the polymerization in a solvent leads in high yields to a linear polydicyclopentadiene, a polymer having structural elements of the formula IX

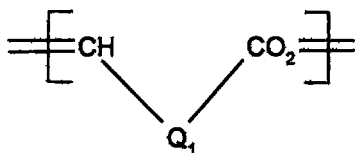


(IX).

The invention furthermore relates to linear copolymers with structural elements of the formula IX and structural elements of the formula X



(IX),



(X),

and crosslinked copolymers, in particular with structural elements of the formulae IX, X and XI



wherein

Q_1 and Q_2 have the abovementioned meanings, including the preferences. The non-crosslinked or linear polymers include oligomers and polymers and can contain, for example, 5 to 5000, advantageously 10 to 2000, preferably 20 to 1000, particularly preferably 20 to 500, and especially preferably 20 to 300 structural units. If the polymers are processed further, lower molecular weights are preferred, and polymers with high molecular weights are advantageously used for processing to moldings.

The invention also relates to polymers which are obtainable by the process according to the invention.

Among the polymers, those which contain only carbon and hydrogen are preferred.

The polymers according to the invention can have very different properties, depending on the nature and amount of monomers used. Some are distinguished by a very high permeability to oxygen, outstanding dielectric properties (low dielectric constants, low loss factors or $\tan\delta$ values) good heat stability (glass transition temperatures above 100°C), high toughnesses (impact strength and notched impact strength), flexibility and mechanical strength (breaking strength), hardness and low absorption of water. Others have outstanding optical properties, for example a high transparency and low refractive indices. The low shrinkage and the excellent surface properties (smoothness, gloss, adhesion) are furthermore to be singled out in particular. They can therefore be used in very different industrial fields.

The compositions according to the invention are distinguished by a high adhesive strength as coats on the surfaces of carrier materials. The coated materials are furthermore distinguished by a very high surface smoothness and gloss. Among the good mechanical properties, the low shrinkage and the high impact strength are to be singled out in particular, as well as the heat resistance. The easy removal from the mold and the high resistance to solvents are furthermore to be mentioned. The surfaces can be modified further, for example painted or printed on, and the high adhesive strength of the paints should also be mentioned here.

The polymers obtainable according to the invention are suitable for the production of medical equipment, implants or contact lenses; for the production of electrical (coil embedding) and electronic components; as binders for paints; as thermosetting compositions for model construction or as adhesives for gluing substrates with low surface energies (for example Teflon, polyethylene and polypropylene), and as a thermopolymerizable composition in stereolithography. The compositions according to the invention can also be used for the preparation of paints by thermopolymerization, it being possible to use on the one hand clear (transparent) and even pigmented compositions. Both white and colored pigments can be used. The production of shaped articles by thermoplastic shaping processes for all types of articles of daily use is furthermore to be mentioned.

The compositions according to the invention are particularly suitable for the production of protective layers. The invention furthermore relates to a variant of the process according to the invention for the production of coated materials in which a composition of (a) dicyclopentadiene, by itself or in a mixture with a stretched cycloolefin, (b) catalyst and, if appropriate, solvent is applied as a layer to a carrier, for example by dipping, brushing, pouring, rolling, knife-coating or whirler-coating processes, the solvent is removed, if appropriate, and the layer is heated for polymerization. Surfaces of substrates can be modified or protected with this process (corrosion protection).

The present invention furthermore relates to a carrier material which is coated with an oligomer or polymer according to the invention and comprises a crosslinking agent. These materials are suitable for the production of protective layers or relief images by heating and subsequent development with a solvent. Suitable crosslinking agents, which the materials may comprise, for example, in an amount of 0.01 to 20% by weight, are, in particular, organic bisazides, in particular commercially obtainable 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone.

The present invention furthermore relates to a coated carrier material, which is characterized in that a layer of a composition according to the invention is applied to a substrate.

The present invention also relates to a coated substrate with a hardened layer of the composition according to the invention.

Suitable substrates (carrier materials) are, for example, those of glass, minerals, ceramics, plastics, wood, semimetals, metals, metal oxides and metal nitrides. The layer thicknesses essentially depend on the desired use and can be, for example, 0.1 to 1000 μm , preferably 0.5 to 500 μm , particularly preferably 1 to 100 μm . The coated materials are distinguished by a high adhesive strength and good thermal and mechanical properties.

The coated materials according to the invention can be produced by known methods, for example brushing, knife-coating and casting processes, such as curtain coating or whirler coating.

Particularly good results are often achieved in coatings if cycloolefins which additionally contain 1 to 3, and preferably 1 further double bond and which are polycyclic condensed ring systems in the context of the invention are additionally used for the thermal metathesis polymerization.

The following examples illustrate the invention further.

Examples 1 to 12:

Dicyclopentadiene (distilled or technical grade) and, if appropriate, a comonomer (additive) are mixed, and (p-cumene)RuCl₂[P(C₆H₁₁)₃] as the catalyst, is dissolved, with gentle heating. If appropriate, Vestenamer® or di-t-butyl-p-cresol (BHT) is added and the mixture is degassed in vacuo at 50-60°C. The mixture is poured into molds and cured by means of heat. The glass transition temperature is determined by differential scanning analysis. The swelling in toluene is stated in percent of the weight uptake of toluene. Further data are found in Table 1.

Table 1

Exp.	DCPD	Additive	Catalyst	Curing	T _g	Swelling
1	dist.		0.5	a, b, c	119	105
2	dist. 90 %	10 2-N	0.5	a, b, c	90	107
3	dist. 50 %	50 2-N	0.5	a, b, c	70	156
4	dist. 99 %	1 BHT	0.5	a, b, c	111	100
5	dist.		0.3	a, b, c	120	102
6	dist. 90.9 %	9.1 PO	0.5	a, b, c	11	128
7	dist. 83 %	17 PO	0.5	a, b, c, d	125	170
8	95.2 %	4.8 PN	0.5	a, b, c	94	109
9	90 %	10 2-N	0.5	a, b, c	90	107
10	50 %	50 2-N	0.5	a, b, c	70	156
11	n.dist.		0.5	a, b, c	110	76
12	n.dist.		0.3	a, b, c	98	88
13	n.dist.		0.3	a, b, c, d	110	70

n.dist.: not distilled; additive: amount in %; BHT: di-t-butyl-p-cresol; PO: Vestenamer®; PN: polynorbornene; 2-N: 2-norbornene; ND: norbornadiene; catalyst: amount (%) based on DCPD; curing: a: 1 hour/80°C; b: 1 hour/100°C; c: 2 hours/120°C; d: 2 hours/150°C; T_g: °C; swelling: (%)

Examples 14 to 21:

The procedure is as in Example 1, and the filler stated in Table 2 is additionally co-used. Curing is carried out for 1 hour at 80°C, followed by 1 hour at 100°C and 2 hours at 120°C. The amount of catalyst is 0.5 % by weight, based on DCPD. Further data are found in Table 2.

Table 2:

Exp.	DCPD	Additive	Filler	T _g	Swelling
14	dist. 95%		5 Aerosil 380 (SiO ₂)	---	---
15	dist. 57%	3 PN	40 Al ₂ O ₃ powder	92	52
16	dist. 48.5%	1.5 PN	50 aluminum hydroxide	---	---
17	dist. 48.5%	1.5 PN	50 talc	103	52
18	dist. 48.5%	1.5 PN	50 aluminum grit	92	60
19	dist. 30 %	1.5 PN	70 quartz flour K8	90	43
20	n.dist. 25%		75 DT 082	101	42
21	n.dist. 99.5%		0.5 Aerosil 350	---	---

n.dist.: not distilled; additive: amount in %; PN: polynorbornene; filler: amount (%); aluminum hydroxide: (DT 082); T_g: °C; swelling: (%)

Example 22:

190 g of technical grade dicyclopentadiene (Shell) and 950 mg of (C₆H₁₁)₃PRu(p-cumene)Cl₂ are mixed and the mixture is heated at 90°C for 4 hours, followed by 120°C for 1 hour and then 150°C for 4 hours. The resulting polymer has the following properties:

T_g: 119°C; weight loss at 300°C: 5.3 %; flexural strength: 102.6 Nmm⁻²; edge fiber elongation: 6.7%; E modulus: 2100 Nmm⁻²; K_{IC}: 3.62 Jm⁻²; G_{IC}: 5320 Jm⁻²; impact strength: 83.5 kJm⁻²; ε (45 Hz, room temperature): 2.4; ε (45 Hz, 200°C): 2.4; ε (1 kHz, room temperature): 2.4; ε (1 kHz, 200°C): 2.4; tanδ (% , 45 Hz, room temperature): 0.1; tanδ (% , 45 Hz, 200°C): 1.0; tanδ (% , 1 kHz, room temperature): 0.1; tanδ (% , 1 kHz, 200°C): 0.7; water uptake (14 days, 70°C): <0.5%; electrical breakdown voltage: 41.6 kVmm⁻²

Example 23:

170 g of technical grade dicyclopentadiene (Shell), 5.1 g of poly(norbornene) and 850 mg of $(C_6H_{11})_3PRu(p\text{-cumene})Cl_2$ are mixed and the mixture is heated at 90°C for 4 hours, followed by 120°C for 1 hour and then at 150°C for 4 hours. The resulting polymer has the following properties:

T_g : 119°C; weight loss at 300°C: 5.3%; flexural strength: 102.3 Nmm⁻²; edge fiber elongation: 6.2%; E modulus: 2200 Nmm⁻²; K_{IC} : 3.11 Jm⁻²; G_{IC} : 3800 Jm⁻²; impact strength: 84.4 kJm⁻²

Example 24:

150 g of technical grade dicyclopentadiene (Shell), 4.5 g of poly(norbornene), 225 g of quartz flour W12 and 750 mg of $(C_6H_{11})_3PRu(p\text{-cumene})Cl_2$ are mixed and the mixture is heated at 90°C for 4 hours, followed by 120°C for 1 hour and then 150°C for 4 hours. The resulting polymer has the following properties:

T_g : 118°C; flexural strength: 41.5 Nmm⁻²; edge fiber elongation: 1.3%; E modulus: 6800 Nmm⁻²; K_{IC} : 2.51 Jm⁻²; G_{IC} : 847 Jm⁻²; ϵ (45 Hz, room temperature): 3.2; ϵ (45 Hz, 200°C): 7.5; ϵ (1 kHz, room temperature): 3.2; ϵ (1 kHz, 200°C): 4.3; $\tan\delta$ (% , 45 Hz, room temperature): 0.4; $\tan\delta$ (% , 45 Hz, 200°C): >20; $\tan\delta$ (% , 1 kHz, room temperature): 0.1; $\tan\delta$ (% , 1 kHz, 200°C): >20; water uptake (14 days, 70°C): about 0.2 %

Example 25:

150 g of technical grade dicyclopentadiene (Shell), 4.5 g of poly(norbornene), 279 g of quartz flour W12 and 750 mg of $(C_6H_{11})_3PRu(p\text{-cumene})Cl_2$ are mixed and the mixture is heated at 90°C for 4 hours, followed by 120°C for 1 hour and then 150°C for 4 hours. The resulting polymer has the following properties:

T_g : 121°C; flexural strength: 46.0 Nmm⁻²; edge fiber elongation: 1.1%; E modulus: 7800 Nmm⁻²; K_{IC} : 3.45 Jm⁻²; G_{IC} : 1380 Jm⁻²

Example 26:

170 g of technical grade dicyclopentadiene (Shell), 5.1 g of poly(butadiene) and 850 mg of $(C_6H_{11})_3PRu(p\text{-cumene})Cl_2$ are mixed and the mixture is heated at 90°C

for 4 hours, followed by 120°C for 1 hour and then 150°C for 4 hours. The resulting polymer has the following properties:

T_g : 109°C; weight loss at 300°C: 4.9%; Flexural strength: 87.3 Nmm⁻²; edge fiber elongation: 6.3%; E modulus: 1900 Nmm⁻²; K_{IC} : 3.36 Jm⁻²; G_{IC} : 5050 Jm⁻²; impact strength: 75,2 kJm⁻²

Example 27:

150 g of technical grade dicyclopentadiene (Shell), 4.5 g of poly(butadiene), 225 g of quartz flour W12 and 750 mg of (C₆H₁₁)₃PRu(p-cumene)Cl₂ are mixed and the mixture is heated at 90°C for 4 hours, followed by 120°C for 1 hour and then 150°C for 4 hours. The resulting polymer has the following properties:

T_g : 117°C; flexural strength: 44.6 Nmm⁻²; edge fiber elongation: 1.7 %; E modulus: 6050 Nmm⁻²; K_{IC} : 3.52 Jm⁻²; G_{IC} : 1870 Jm⁻²; impact strength: 4.60 kJm⁻²

Example 28:

80 ml of water are initially introduced into a 250 ml sulfonating flask with a thermometer, N₂ inlet and dropping funnel, and the flask is flushed with N₂. A solution of 0.5% by weight of (C₆H₁₁)₃PRu(p-cumene)Cl₂ in 30 ml of dicyclopentadiene is now added from the dropping funnel in the course of 30 seconds, with vigorous stirring, and at the same time the sulfonating flask is placed in an oil bath preheated to 120°C (internal temperature rising to 100°C). After 1.5 hours, the polymer formed is filtered off and dried in vacuo (0.1 mbar) at 50°C for 24 hours. Yield: 11.0 g (36.7%).

Example 29:

12 ml of water, 160 mg of Dresinate 731 (surfactant), 8.0 g of dicyclopentadiene and 80 mg of (C₆H₁₁)₃PRu(p-cumene)Cl₂ are mixed. After the mixture has been stirred at 150°C (bath temperature; internal temperature rising to 140°C) for 2 hours, it is cooled and the polymer formed is precipitated in 300 ml of acetone. Yield: 1.50 g (18.8%); T_g = 117°C

Example 30:

12 ml of water, 8.0 g of dicyclopentadiene and 40 mg of $(C_6H_{11})_3PRu(p\text{-cumene})Cl_2$ are mixed. After the mixture has been stirred at 150°C (bath temperature) for 4 hours, it is cooled and the polymer formed is precipitated in 300 ml of acetone. Yield: 5.28 g (66%); $T_g = 59^\circ C$; elemental analysis: C 90.85 (calculated); 88.80 (found); H 9.14 (calculated); 9.15 (found)

Example 31:

12 ml of water, 160 mg of Triton X-100 (Fluka) (surfactant), 8.0 g of dicyclopentadiene and 40 mg of $(C_6H_{11})_3PRu(p\text{-cumene})Cl_2$ are mixed. After the mixture has been stirred at 150°C (bath temperature) for 4 hours, it is cooled and the polymer formed is precipitated in 300 ml of acetone. Yield: 7.2 g (90%); $T_g = 143^\circ C$; elemental analysis: C 90.85 (calculated); 88.70 (found); H 9.14 (calculated); 9.26 (found)

Example 32:

12 ml of water, 160 mg of Disponil APE-256 (Henkel) (surfactant), 8.0 g of dicyclopentadiene and 40 mg of $(C_6H_{11})_3PRu(p\text{-cumene})Cl_2$ are mixed. After the mixture has been stirred at 150°C (bath temperature) for 4 hours, it is cooled and the polymer formed is precipitated in 300 ml of acetone. Yield: 7.3 g (91%); $T_g = 92^\circ C$; elemental analysis: C 90.85 (calculated); 89.08 (found); H 9.14 (calculated); 9.21 (found)

Example 33:

24 ml of water, 320 mg of Triton X-100 (Fluka) (surfactant), 16.0 g of dicyclopentadiene and 80 mg of $(C_6H_{11})_3PRu(p\text{-cumene})Cl_2$ are mixed. After the mixture has been stirred vigorously at 120°C (bath temperature; internal temperature rising to a maximum of 90°C) for 4 hours, it is cooled and the polymer formed is precipitated in 300 ml of acetone. Yield: 12.54 g (78.4%); $T_g = 131^\circ C$; elemental analysis: C 90.85 (calculated); 87.95 (found); H 9.14 (calculated); 8.95 (found)

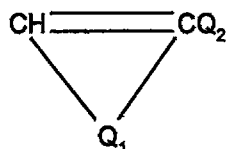


PATENT CLAIMS:

1. Composition of (a) dicyclopentadiene, by itself or in a mixture with a stretched cycloolefin, and (b) a catalytic amount of at least one carbene-free, divalent-cationic ruthenium or osmium compound as a single-component catalyst, which contains at least one phosphine group and a total of 2 to 5 ligands bonded to the metal atom, and which contains acid anions for charge balancing.
2. Composition according to claim 1, characterized in that the ruthenium or osmium compounds contain a total of 2 or 3 ligands.
3. Composition according to claim 1, characterized in that the phosphine group is a tertiary phosphine or phosphite having 3 to 40 C atoms.
4. Composition according to claim 1, characterized in that the cyclic olefins are monocyclic rings or polycyclic, bridged or fused ring systems having 2 to 4 rings, which are unsubstituted or substituted, which contain one or more heteroatoms from the group consisting of O, S, N and Si in one or more rings, and which contain fused aromatic or heteroaromatic rings.
5. Composition according to claim 1, characterized in that the cyclic rings contain 3 to 16 ring members.
6. Composition according to claim 4, characterized in that the cyclic olefins contain further non-aromatic double bonds.
7. Composition according to claim 1, characterized in that the cycloolefins correspond to the formula I

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(I)

wherein

Q_1 is a radical having at least one carbon atom which, together with the $-\text{CH}=\text{CQ}_2$ -group, forms an alicyclic ring which has at least 3 members and which optionally contains one or more heteroatoms chosen from the group consisting of silicon, phosphorus, oxygen, nitrogen and sulfur; and which is unsubstituted or substituted by halogen, $=\text{O}$, $-\text{CN}$, $-\text{NO}_2$, $\text{R}_1\text{R}_2\text{R}_3\text{Si}(\text{O})_{\text{u}-}$, $-\text{COOM}$, $-\text{SO}_3\text{M}$, $-\text{PO}_3\text{M}$, $-\text{COO}(\text{M}_1)_{1/2}$, $-\text{SO}_3(\text{M}_1)_{1/2}$, $-\text{PO}_3(\text{M}_1)_{1/2}$, $\text{C}_1\text{-C}_{20}\text{alkyl}$, $\text{C}_1\text{-C}_{20}\text{hydroxyalkyl}$, $\text{C}_1\text{-C}_{20}\text{haloalkyl}$, $\text{C}_1\text{-C}_6\text{cyanoalkyl}$, $\text{C}_3\text{-C}_8\text{cycloalkyl}$, $\text{C}_6\text{-C}_{16}\text{aryl}$, $\text{C}_7\text{-C}_{16}\text{aralkyl}$, $\text{C}_3\text{-C}_6\text{heterocycloalkyl}$, $\text{C}_3\text{-C}_{16}\text{heteroaryl}$, $\text{C}_4\text{-C}_{16}\text{heteroaralkyl}$ or $\text{R}_4\text{-X-}$; or in which two adjacent C atoms are substituted by $-\text{CO-O-CO-}$ or $-\text{CO-NR}_5\text{-CO-}$; or in which an alicyclic, aromatic or heteroaromatic ring, which is unsubstituted or substituted by halogen, $-\text{CN}$, $-\text{NO}_2$, $\text{R}_6\text{R}_7\text{R}_8\text{Si}(\text{O})_{\text{u}-}$, $-\text{COOM}$, $-\text{SO}_3\text{M}$, $-\text{PO}_3\text{M}$, $-\text{COO}(\text{M}_1)_{1/2}$, $-\text{SO}_3(\text{M}_1)_{1/2}$, $-\text{PO}_3(\text{M}_1)_{1/2}$, $\text{C}_1\text{-C}_{20}\text{alkyl}$, $\text{C}_1\text{-C}_{20}\text{haloalkyl}$, $\text{C}_1\text{-C}_{20}\text{hydroxyalkyl}$, $\text{C}_1\text{-C}_6\text{cyanoalkyl}$, $\text{C}_3\text{-C}_8\text{cycloalkyl}$, $\text{C}_6\text{-C}_{16}\text{aryl}$, $\text{C}_7\text{-C}_{16}\text{aralkyl}$, $\text{C}_3\text{-C}_6\text{heterocycloalkyl}$, $\text{C}_3\text{-C}_{16}\text{heteroaryl}$, $\text{C}_4\text{-C}_{16}\text{heteroaralkyl}$ or $\text{R}_{13}\text{-X}_1\text{-}$, is optionally fused onto adjacent carbon atoms of the alicyclic ring;

X and X_1 independently of one another are $-\text{O-}$, $-\text{S-}$, $-\text{CO-}$, $-\text{SO-}$, $-\text{SO}_2\text{-}$, $-\text{O-C(O)-}$, $-\text{C(O)-O-}$, $-\text{C(O)-NR}_5\text{-}$, $-\text{NR}_{10}\text{-C(O)-}$, $-\text{SO}_2\text{-O-}$ or $-\text{O-SO}_2\text{-}$;

R_1 , R_2 and R_3 independently of one another are $\text{C}_1\text{-C}_{12}\text{alkyl}$, $\text{C}_1\text{-C}_{12}\text{perfluoroalkyl}$, phenyl or benzyl;

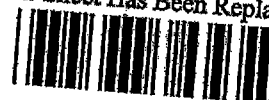
R_4 and R_{13} independently of one another are $\text{C}_1\text{-C}_{20}\text{alkyl}$, $\text{C}_1\text{-C}_{20}\text{haloalkyl}$, $\text{C}_1\text{-C}_{20}\text{hydroxyalkyl}$, $\text{C}_3\text{-C}_8\text{cycloalkyl}$, $\text{C}_6\text{-C}_{16}\text{aryl}$ or $\text{C}_7\text{-C}_{16}\text{aralkyl}$;

R_5 and R_{10} independently of one another are hydrogen, $\text{C}_1\text{-C}_{12}\text{alkyl}$, phenyl or benzyl, where the alkyl groups in their turn are unsubstituted or substituted by $\text{C}_1\text{-C}_{12}\text{alkoxy}$ or $\text{C}_3\text{-C}_8\text{cycloalkyl}$;

R_6 , R_7 and R_8 independently of one another are $\text{C}_1\text{-C}_{12}\text{alkyl}$, $\text{C}_1\text{-C}_{12}\text{perfluoroalkyl}$, phenyl or benzyl;

M is an alkali metal and M_1 is an alkaline earth metal; and

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u is 0 or 1;

in which the alicyclic ring formed with Q_1 optionally contains further non-aromatic 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_8 cycloalkyl, 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;

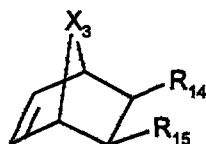
wherein the abovementioned cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups are unsubstituted or substituted by C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy, -NO₂, -CN or halogen, and where the heteroatoms of the abovementioned heterocycloalkyl, heteroaryl and heteroaralkyl groups are chosen from the group consisting of -O-, -S-, -NR₉- and -N=; and R_9 is hydrogen, C_1 - C_{12} alkyl, phenyl or benzyl.

8. Composition according to claim 7, characterized in that the alicyclic ring which Q_1 forms together with the -CH=C Q_2 -group contains 3 to 16 ring atoms, and wherein this is a monocyclic, bicyclic, tricyclic or tetracyclic ring system.

9. Process according to claim 7, characterized in that Q_2 in formula I is hydrogen.

10. Composition according to claim 1, characterized in that the cyclic olefins are norbornene or norbornene derivatives.

11. Composition according to claim 10, characterized in that the norbornene derivatives are those of the formula II



(II),

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wherein

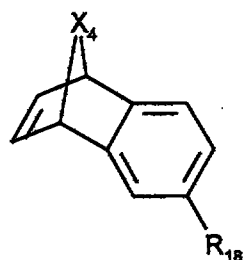
X_3 is $-\text{CHR}_{16}-$, oxygen or sulfur;

R_{14} and R_{15} independently of one another are hydrogen, $-\text{CN}$, trifluoromethyl,

$(\text{CH}_3)_3\text{Si}-\text{O}-$, $(\text{CH}_3)_3\text{Si}-$ or $-\text{COOR}_{17}$; and

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

or to the formula III



(III)

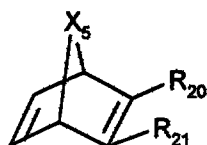
wherein

X_4 is $-\text{CHR}_{19}-$, oxygen or sulfur;

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

R_{18} is hydrogen, C_1-C_6 alkyl or halogen;

or to the formula IV



(IV),

wherein

X_5 is $-\text{CHR}_{22}-$, oxygen or sulfur;

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

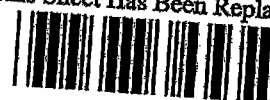
R_{20} and R_{21} independently of one another are hydrogen, CN , trifluoromethyl,

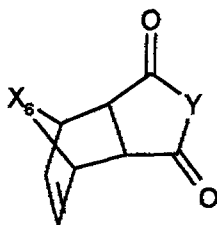
$(\text{CH}_3)_3\text{Si}-\text{O}-$, $(\text{CH}_3)_3\text{Si}-$ or $-\text{COOR}_{23}$; and

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

or to the formula V

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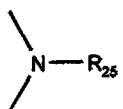


(V),

wherein

X_6 is $-\text{CHR}_{24}-$, oxygen or sulfur;

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

Y is oxygen or ; and

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

12. Composition according to claim 1, characterized in that the cycloolefin contains only carbon and hydrogen.

13. Composition according to claim 1, characterized in that it comprises the comonomeric cycloolefin in an amount of 0.01 to 99% by weight, based on the monomers present in the composition.

14. Composition according to claim 1, characterized in that a monophosphine is bonded to the metal atom one to three times or a diphosphine is bonded once.

15. Composition according to claim 1, characterized in that the phosphine ligands correspond to the formulae VI or VIa





wherein 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 which are unsubstituted or substituted by C_1 - C_6 alkyl, C_1 - C_6 haloalkyl or C_1 - C_6 alkoxy, or C_6 - C_{16} aryl or C_6 - C_{16} aryloxy which are unsubstituted or substituted by C_1 - C_6 alkyl, C_1 - C_6 haloalkyl or C_1 - C_6 alkoxy, or C_7 - C_{16} aralkyl or C_7 - C_{16} aralkyloxy which are unsubstituted or substituted by C_1 - C_6 alkyl, C_1 - C_6 haloalkyl or C_1 - C_6 alkoxy; the radicals R_{26} and R_{27} together are tetra- or pentamethylene or tetra- or pentamethylenedioxy, which are unsubstituted or substituted by C_1 - C_6 alkyl, C_1 - C_6 haloalkyl or C_1 - C_6 alkoxy, or tetra- or pentamethylene or tetra- or pentamethylenedioxy which are unsubstituted or substituted by C_1 - C_6 alkyl, C_1 - C_6 haloalkyl or C_1 - C_6 alkoxy and fused with 1 or 2 1,2-phenylene, or tetramethylenedioxy which is unsubstituted or substituted by C_1 - C_6 alkyl, C_1 - C_6 haloalkyl or C_1 - C_6 alkoxy and fused in the 1,2- and 3,4-positions with 1,2-phenylene, and R_{28} has the abovementioned meaning; and Z_1 is linear or branched C_2 - C_{12} alkylene which is unsubstituted or substituted by C_1 - C_4 alkoxy, 1,2- or 1,3-cycloalkylene which has 4 to 8 C atoms and is unsubstituted or substituted by C_1 - C_4 alkyl or C_1 - C_4 alkoxy, or 1,2- or 1,3-heterocycloalkylene which has 5 or 6 ring members and a heteroatom from the group consisting of O and N and is unsubstituted or substituted by C_1 - C_4 alkyl or C_1 - C_4 alkoxy.

16. Composition according to claim 15, characterized in that the radicals R_{26} , R_{27} and R_{28} are identical radicals.

17. Composition according to claim 15, characterized in that the phosphine ligands correspond to the formula VI wherein R_{26} , R_{27} and R_{28} independently of one another are H, C_1 - C_6 alkyl, cyclopentyl or cyclohexyl which are unsubstituted or substituted by C_1 - C_4 alkyl, or phenyl which is unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy or trifluoromethyl, or benzyl which is unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy or trifluoromethyl.

18. Process [sic] according to claim 15, characterized in that the phosphine ligands of the formula VI are $(C_6H_5)_3P$, $(C_6H_5CH_2)_3P$, $(C_6H_{11})_3P$, $(CH_3)_3P$, $(C_2H_5)_3P$, $(n-C_3H_7)_3P$, $(i-C_3H_7)_3P$, $(n-C_4H_9)_3P$, $(C_6H_5)_2HP$, $(C_6H_5CH_2)_2HP$, $(C_5H_{11})_2HP$,

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$(\text{CH}_3)_2\text{HP}$, $(\text{C}_2\text{H}_5)_2\text{HP}$, $(\text{n-C}_3\text{H}_7)_2\text{HP}$, $(\text{i-C}_3\text{H}_7)_2\text{HP}$, $(\text{n-C}_4\text{H}_9)_2\text{HP}$, $(\text{C}_6\text{H}_5)_2\text{HP}$,
 $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{HP}$, $(\text{C}_6\text{H}_{11})_2\text{HP}$, $(\text{CH}_3)_2\text{HP}$, $(\text{C}_2\text{H}_5)_2\text{HP}$, $(\text{n-C}_3\text{H}_7)_2\text{HP}$, $(\text{i-C}_3\text{H}_7)_2\text{HP}$, $(\text{n-C}_4\text{H}_9)_2\text{HP}$, PH_3 , $(2\text{-methyl-C}_6\text{H}_4)_3\text{P}$, $(3\text{-CH}_3\text{-C}_6\text{H}_4)_3\text{P}$, $(4\text{-CH}_3\text{-C}_6\text{H}_4)_3\text{P}$, $(2,4\text{-di-CH}_3\text{-C}_6\text{H}_3)_3\text{P}$, $(2,6\text{-di-CH}_3\text{-C}_6\text{H}_3)_3\text{P}$, $(2\text{-C}_2\text{H}_5\text{-C}_6\text{H}_4)_3\text{P}$, $(3\text{-C}_2\text{H}_5\text{-C}_6\text{H}_4)_3\text{P}$, $(4\text{-C}_2\text{H}_5\text{-C}_6\text{H}_4)_3\text{P}$,
 $(2\text{-n-C}_3\text{H}_7\text{-C}_6\text{H}_4)_3\text{P}$, $(3\text{-n-C}_3\text{H}_7\text{-C}_6\text{H}_4)_3\text{P}$, $(4\text{-n-C}_3\text{H}_7\text{-C}_6\text{H}_4)_3\text{P}$, $(2\text{-i-C}_3\text{H}_7\text{-C}_6\text{H}_4)_3\text{P}$, $(3\text{-i-C}_3\text{H}_7\text{-C}_6\text{H}_4)_3\text{P}$, $(4\text{-i-C}_3\text{H}_7\text{-C}_6\text{H}_4)_3\text{P}$, $(2\text{-n-C}_4\text{H}_9\text{-C}_6\text{H}_4)_3\text{P}$, $(3\text{-n-C}_4\text{H}_9\text{-C}_6\text{H}_4)_3\text{P}$, $(4\text{-n-C}_4\text{H}_9\text{-C}_6\text{H}_4)_3\text{P}$, $(2\text{-i-C}_4\text{H}_9\text{-C}_6\text{H}_4)_3\text{P}$, $(3\text{-i-C}_4\text{H}_9\text{-C}_6\text{H}_4)_3\text{P}$, $(4\text{-i-C}_4\text{H}_9\text{-C}_6\text{H}_4)_3\text{P}$, $(2\text{-t-C}_4\text{H}_9\text{-C}_6\text{H}_4)_3\text{P}$,
 $(3\text{-t-C}_4\text{H}_9\text{-C}_6\text{H}_4)_3\text{P}$, $(4\text{-t-C}_4\text{H}_9\text{-C}_6\text{H}_4)_3\text{P}$, $(2\text{-CH}_3\text{-6-t-C}_4\text{H}_9\text{-C}_6\text{H}_3)_3\text{P}$, $(3\text{-CH}_3\text{-6-t-C}_4\text{H}_9\text{-C}_6\text{H}_3)_3\text{P}$, $(3\text{-CH}_3\text{-6-t-C}_4\text{H}_9\text{-C}_6\text{H}_3)_3\text{P}$, $(2,6\text{-di-t-C}_4\text{H}_9\text{-C}_6\text{H}_3)_3\text{P}$, $(2,3\text{-di-t-C}_4\text{H}_9\text{-C}_6\text{H}_3)_3\text{P}$,
 $(\text{C}_6\text{H}_{11})_3\text{P}$, $(\text{C}_6\text{H}_{11})_2\text{HP}$, $(\text{C}_5\text{H}_9)_3\text{P}$, $(\text{C}_5\text{H}_9)_2\text{HP}$ or $(2,4\text{-di-t-C}_4\text{H}_9\text{-C}_6\text{H}_3)_3\text{P}$.

19. Composition according to claim 1, characterized in that the ligands are those which are chosen from the group consisting of ligands (A) consisting of nitrogen (N_2); monocyclic, polycyclic or fused arenes which have 6 to 24 C atoms and are unsubstituted or substituted by OH, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_6\text{-C}_{12}$ aryl or halogen; monocyclic heteroarenes which are unsubstituted or substituted by $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy or halogen; fused heteroarenes; fused arene-heteroarenes having 3 to 22 C atoms and 1 to 3 heteroatoms chosen from the group consisting of O, S and N; and aliphatic, cycloaliphatic, aromatic or araliphatic nitriles which have 1 to 22 C atoms and are unsubstituted or substituted by $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy or halogen.

20. Composition according to claim 19, characterized in that the ligands are benzene which is unsubstituted or substituted by one to three $\text{C}_1\text{-C}_4$ alkyl, or thiophene, benzonitrile or acetonitrile.

21. Composition according to claim 20, characterized in that the ligands are benzene which is unsubstituted or substituted by 1 to 3 $\text{C}_1\text{-C}_4$ alkyl.

22. Composition according to claim 19, characterized in that the arenes and heteroarenes are benzene, cumene, 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 or purine.

23. Composition according to claim 1, characterized in that the ruthenium or osmium compound additionally contains a ligand chosen from the group consisting of ligands (B) consisting of solvating inorganic and organic compounds which contain the heteroatoms O, S or N; and cyclopentadienyl or indenyl which are unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, (C₁-C₄alkyl)₃Si or (C₁-C₄alkyl)₃SiO.

24. Composition according to claim 23, characterized in that the ligands are chosen from the group consisting of H₂O, H₂S and NH₃; optionally halogenated, aliphatic or cycloaliphatic alcohols or mercaptans having 1 to 18 C atoms, aromatic alcohols or thiols having 6 to 18 C atoms, or araliphatic alcohols or thiols having 7 to 18 C atoms; open-chain or cyclic and aliphatic, araliphatic or aromatic ethers, thioethers, sulfoxides, sulfones, ketones, aldehydes, carboxylic acid esters, lactones, optionally N-C₁-C₄-mono- or -dialkylated carboxylic acid amides having 2 to 20 C atoms, and optionally N-C₁-C₄alkylated lactams; open-chain or cyclic and aliphatic, araliphatic or aromatic, primary, secondary and tertiary amines having 1 to 20 C atoms, and cyclopentadienyls.

25. Composition according to claim 24, characterized in that the ligands are H₂O, NH₃, unsubstituted or partly or completely fluorinated C₁-C₄alkanols or cyclopentadienyl.

26. Composition according to claim 1, characterized in that the anions of inorganic or organic acids are chosen from the group consisting of hydride, halide, the anion of an oxygen acid, BF₄, PF₆, SbF₆ and AsF₆.

27. Composition according to claim 26, characterized in that the anion of an oxygen acid is sulfate, phosphate, perchlorate, perbromate, periodate,





antimonate, arsenate, nitrate, carbonate, the anion of a C₁-C₈carboxylic acid, sulfonate, phenylsulfonate or benzyisulfonate which are optionally substituted by C₁-C₄alkyl, C₁-C₄alkoxy or halogen, or phosphonate.

28. Composition according to claim 1, characterized in that the acid anions are H[⊖],

F[⊖], Cl[⊖], Br[⊖], BF₄[⊖], PF₆[⊖], SbF₆[⊖], AsF₆[⊖], CF₃SO₃[⊖], 4-CF₃-C₆H₅-SO₃[⊖], C₆H₅-SO₃[⊖], 4-methyl-C₆H₅-SO₃[⊖], 3,5-dimethyl-C₆H₅-SO₃[⊖], 2,4,6-trimethyl-C₆H₅-SO₃[⊖] or cyclopentadienyl (Cp[⊖]).

29. Composition according to claim 1, characterized in that the ruthenium and osmium compounds correspond to one of the formulae VII to VIId



wherein

R₃₂ is a phosphine ligand of the formula VI or VIa according to claim 15;

Me is Ru or Os;

n is the numbers 1, 2 or 3;

Z is the anion of an inorganic or organic acid;

L₁ is a ligand of group A according to claim 19, wherein the L₁ in formula VIId are optionally different, and

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L₂ is a ligand of group B according to claim 23.

30. Composition according to claim 1, characterized in that the ruthenium and osmium compounds correspond to one of the formulae VIII to VIId



wherein

Me is Ru or Os;

Z₁ and Z₂ independently of one another are H[⊖], cyclopentadienyl, Cl[⊖], Br[⊖], BF₄[⊖],

PF₆[⊖], SbF₆[⊖], AsF₆[⊖], CF₃SO₃[⊖], C₆H₅-SO₃[⊖], 4-methyl-C₆H₅-SO₃[⊖],

3,5-dimethyl-C₆H₅-SO₃[⊖], 2,4,6-trimethyl-C₆H₅-SO₃[⊖] or 4-CF₃-C₆H₅-SO₃[⊖];

R₂₆, R₂₇ and R₂₈ independently of one another are C₁-C₆alkyl, cyclopentyl or cyclohexyl or cyclopentyloxy or cyclohexyloxy which are unsubstituted or substituted by 1 to 3 C₁-C₄alkyl, or phenyl or benzyl or phenyloxy or benzyloxy which are unsubstituted or substituted by 1 to 3 C₁-C₄alkyl;

L₁ is C₆-C₁₆-arene or C₅-C₁₆heteroarene which are unsubstituted or substituted by 1 to 3 C₁-C₄alkyl, C₁-C₄alkoxy, -OH, -F or Cl, or C₁-C₆alkyl-CN, benzonitrile or benzylnitrile, wherein the L₁ in formula VIId are optionally different; and

L₂ is H₂O or C₁-C₆alkanol.

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31. Composition according to claim 1, characterized in that the ruthenium and osmium compounds are chosen from the group consisting of [tos is tosylate]:

$(C_6H_{11})_3PRu(i-C_3H_7-C_6H_5)(tos)_2$, $(C_6H_{11})_3PRu(C_6H_5)(C_2H_5OH)_2(tos)_2$,
 $(CH_3)_3PRu(p-cumene)Cl_2$, $(C_6H_{11})_3PRu(anthracene)(tos)_2$, $(C_6H_5)_3PRu(p-cumene)HCl$,
 $[(C_6H_{11})_3P]_3Ru(CH_3-CN)$, $(C_5H_9)_3PRu(p-cumene)Cl_2$, $(C_6H_{11})_3PRu[(C_4H_9)-C_6H_5]Cl_2$,
 $(C_6H_{11})_3POs(p-cumene)Cl_2$, $(C_6H_5)_3POs(p-cumene)Cl_2$, $(2-CH_3C_6H_4)_3POs(p-cumene)Cl_2$,
 $(C_6H_{11})_3PRu(C_6H_5)(p-cumene)Br_2$, $(C_6H_{11})_3PRu(CH_3CN)Cl_2$, $(CH_3)_3POs(p-cumene)Cl_2$,
 $(C_6H_{11})_3PRu[1,2,4,5-(CH_3)_4C_6H_2]Cl_2$, $RuCl_2(p-cumene)[(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2]$,
 $(C_6H_{11})_3PRu(p-cumene)(CH_3-CN)_2(PF_6)_2$, $(C_6H_{11})_3PRu(p-cumene)(CH_3-CN)_2(tos)_2$,
 $(C_6H_{11})_3PRu(p-cumene)(C_2H_5OH)_2(BF_4)_2$, $(C_6H_{11})_3PRu(p-cumene)(C_2H_5OH)_2(PF_6)_2$,
 $(C_6H_{11})_3PRu[1,3,5-(i-C_3H_7)_3C_6H_3]Cl_2$, $(n-C_4H_9)_3PRu(p-cumene)(CH_3-CN)_2(tos)_2$,
 $(i-C_3H_7)_3PRu(p-cumene)Cl_2$, $(n-C_4H_9)_3PRu(p-cumene)Cl_2$, $(i-C_3H_7)_3POs(p-cumene)Cl_2$,
 $(C_6H_{11})_3PRu(chrysene)(tos)_2$, $(C_6H_{11})_3PRu(p-cumene)Cl_2$, $(C_6H_{11})_3PRu(p-cumene)Br_2$,
 $(C_6H_{11})_3PRu(p-cumene)(tos)_2$, $(C_6H_{11})_3PRu(p-cumene)ClF$,
 $(C_6H_{11})_3PRu(C_6H_5)(tos)_2$,
 $(C_6H_{11})_3PRu(CH_3-C_6H_5)(tos)_2$, $(C_6H_{11})_3PRu(CH_3-CN)_2Cl_2$, $(C_6H_{11})_3PRu(p-cumene)HCl$,
 $(C_6H_{11})_2HPRu(p-cumene)Cl_2$, $(C_6H_{11})_3PRu(CH_3-CN)(C_2H_5-OH)(tos)_2$,
 $(C_6H_{11})_3PRu(C_{10}H_8)(tos)_2$, $(C_6H_{11})_3PRu(p-cumene)(C_2H_5OH)(BF_4)_2$,
 $(C_6H_{11})_3PRu(biphenyl)(tos)_2$ and $[(C_6H_{11})_3P]_2Ru(CH_3-CN)(tos)_2$.

32. Composition according to claim 31, characterized in that the single-component catalyst is $(C_6H_{11})_3PRu(p-cumene)Cl_2$, $(C_5H_9)_3PRu(p-cumene)Cl_2$ or $[CH(CH_3)_2]_3PRu(p-cumene)Cl_2$.

33. Composition according to claim 1, characterized in that it additionally comprises a solvent.

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34. Composition according to claim 1, characterized in that it comprises a single-component catalyst in an amount of 0.001 to 20 mol%, based on the amount of the monomer.

35. Composition according to claim 34, characterized in that it comprises the single-component catalyst in an amount of 0.01 to 15 mol%.

36. Composition according to claim 35, characterized in that it comprises the single-component catalyst in an amount of 0.01 to 10 mol%.

37. Composition according to claim 36, characterized in that it comprises the single-component catalyst in an amount of 0.001 to 2 mol%.

38. Composition according to claim 1, characterized in that it comprises formulation auxiliaries.

39. Composition according to claim 38, characterized in that it comprises the formulation auxiliaries in an amount of 0.1 to 70% by weight.

40. Process for the preparation of metathesis polymers, which is characterized in that a composition of (a) dicyclopentadiene, by itself or in a mixture with a stretched cycloolefin, and (b) a catalytic amount of at least one carbene-free, divalent-cationic ruthenium or osmium compound as a single-component catalyst, which contains at least one phosphine group and a total of 2 to 5 ligands bonded to the metal atom, and which contains acid anions for charge balancing, is heated.

41. Process according to claim 40, characterized in that it is carried out in dilute solution.

42. Process according to claim 40, characterized in that it is carried out at a temperature of at least 50°C.





43. Process according to claim 40, characterized in that the temperature is from 60 to 300°C.

44. Linear copolymers with structural elements of the formula IX and structural elements of the formula X



and crosslinked copolymers with structural elements of the formulae IX, X and XI



wherein Q₁ and Q₂ have the meanings according to claim 7.

45. Polymers which are obtainable by the process according to claim 40.

46. Process for the preparation of coated materials, in which a composition of (a) dicyclopentadien, by itself or in a mixture with a stretched cycloolefin and (b) a catalytic amount of at least one carbene-free, bivalent-cationic ruthenium or osmium compound as a one-component catalyst, which contains at least one phosphine group and a total of 2 to 5 ligands bonded to the metal atom, and which contains acid anions for charge balancing, and if appropriate a solvent are applied as a layer to a carrier, the solvent is removed, if appropriate, and the layer is heated for polymerization.

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47. Carrier material, characterized in that a layer of a composition according to claim 1 is applied to a substrate.

48. Coated substrate with a hardened layer of the composition according to claim 1.

49. Shaped articles of a composition according to claim 1.

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