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(21) International Application Number: PCT/EP98/01092 (22) International Filing Date: 26 February 1998 (26.02.98) (30) Priority Data: 0527/97 6 March 1997 (06.03.97) CH (71) Applicant: CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH). (72) Inventors: VAN DER SCHAAF, Paul, Adriaan; Impasse du Castel 9, CH-1700 Fribourg (CH). HAFNER, Andreas; Bendenweg 3, CH-3177 Laupen (CH). MÜHLEBACH, Andreas; Les Grands Esserts 7, CH-1782 Belfaux (CH).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: NEW CATALYSTS (57) Abstract <p>The invention relates to hexacoordinated ruthenium and osmium carbene catalysts for the synthesis of custom-tailored polymers and for the ring-closing metathesis of olefins. It also relates to compositions consisting of dicyclopentadiene or dicyclopentadiene in a mixture with a strained cycloolefin and the ruthenium and osmium carbene catalysts, to processes for preparing metathesis polymers, and to the polymers obtainable in accordance with the processes.</p>		

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New catalysts

The present invention relates to hexacoordinated ruthenium and osmium carbene catalysts, to their preparation and use for synthesizing polymers, for ring-closing metathesis of olefins, for cross-metathesis and for isomerizing olefins.

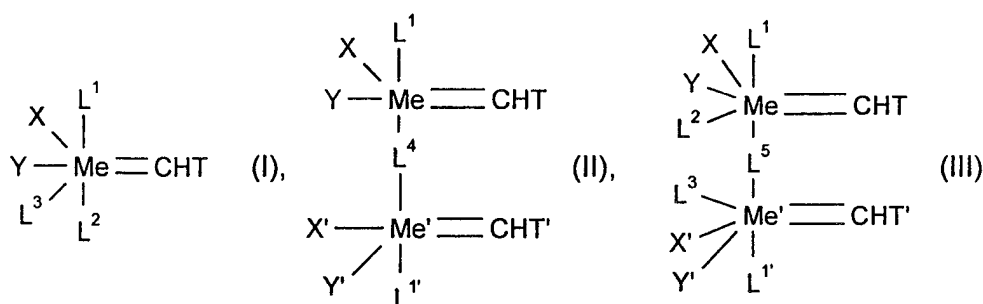
The thermal metathesis polymerization of cycloolefins which are under ring strain, which has in recent times acquired great importance, requires appropriate catalysts. Whereas use was made first of all of systems comprising catalyst and co-catalyst - see, for example, *U.S. Patent 4 060 468* and *International Patent Application WO 93/13171* - one-component catalysts have also been disclosed [*H.H.Thoi et al., J. Mol. Catal. 15:245-270 (1982)*].

Catalysts of particular interest for the application are so-called metal carbenes, i.e. transition metal compounds, for example ruthenium and osmium compounds, having a group $=CR^*R''$ attached to the metal atoms [*WO 93/20111*; *S. Kanaoka et al., Macromolecules 28: 4707-4713 (1995)*; *C. Fraser et al., Polym. Prepr. 36: 237-238 (1995)*; *P. Schwab et al., Angew. Chem. 107: 2179-2181 (1995)*]. This type of compound is also suitable for catalyzing ring closure in dienes [*WO 96/04289*].

The known catalysts are pentacoordinated and contain attached to the metal atoms, in addition to the group $=CR^*R''$, two identical tertiary phosphines as neutral e^- donor ligands [*WO 93/20111*; *WO 96/04289*].

It has surprisingly been found that hexacoordinated ruthenium and osmium carbenes are excellent catalysts for ring-opening metathesis polymerizations, for other metathesis reactions and for the ring closure of dienes. By an appropriate choice of neutral ligands it is possible to exercise close control over the reactivity, for example the latency, over a wide range.

The invention provides compounds of the formulae



in which

Me and Me' independently of one another are ruthenium or osmium;

X, X', Y and Y' independently of one another are anionic ligands, or X and Y and X' and Y' in each case together are bis-anionic ligands;

L¹ and L^{1'} independently of one another are tertiary phosphine;

L² and L³ independently of one another are monodentate, or L² and L³ together are bidentate, neutral e⁻ donor ligands;

L⁴ is a tetradentate, neutral e⁻ donor ligand;

L⁵ is a bidentate, neutral e⁻ donor ligand; and

T and T' independently of one another are H, C₁-C₂₀alkyl, C₃-C₈cycloalkyl, C₃-C₇-heterocycloalkyl, C₆-C₁₄aryl or C₄-C₁₅heteroaryl, where alkyl, cycloalkyl, heterocycloalkyl, aryl and heteroaryl are unsubstituted or substituted by a substituent from the group consisting of C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₆-C₁₀aryl, C₆-C₁₀aryloxy, -NO₂ and halogen.

Me and Me' are preferably ruthenium.

The compounds of the invention have the advantage that dicyclopentadiene (DCPD) is made accessible to thermal metathesis polymerization with a one-component catalyst. It has additionally been found that even linear polybicyclopentadiene can be prepared if the polymerization is conducted in appropriate solvents. Crosslinked polymers are obtained if the polymerization is conducted in bulk. It has also been found that the polymerization takes place even in the presence of polymer additives, such as fillers, for example, and that mouldings, sheets (films) or coatings having excellent physical and mechanical properties are obtained. It was observed, as well, that the compositions comprising DCPD and the compounds of the invention are stable to air and moisture, and thus have high stability on storage. No special protective measures are necessary for the polymerization, which offers

considerable advantages in terms of processing. It has also been found that on using these catalysts DCPD can be copolymerized together with other strained cycloolefins as co-monomers. This enables properties to be modified specifically and adapted to the desired purpose of use.

Anionic ligands which are suitable in the context of the present invention are hydride (H^-), or are derived, for example, from inorganic or organic acids, examples being halide (F^- , Cl^- , Br^- and I^-), anions of oxygen acids, BF_4^- , PF_6^- , SbF_6^- or AsF_6^- .

The anions of oxygen acids can, for example, be sulfate, phosphate, perchlorate, perbromate, periodate, antimonate, arsenate, nitrate, carbonate, the anion of a C_1 - C_8 -carboxylic acid, such as formate, acetate, propionate, butyrate, benzoate, phenylacetate, mono-, di- or trichloro- or -fluoroacetate, sulfonates, such as methylsulfonate, ethylsulfonate, propylsulfonate, butylsulfonate, trifluoromethylsulfonate (triflate), benzylsulfonate or phenylsulfonate unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy or halogen, especially fluorine, chlorine or bromine, for example tosylate, mesylate, brosylate, p-methoxy- or p-ethoxyphenylsulfonate, pentafluorophenylsulfonate or 2,4,6-triisopropylsulfonate.

Other suitable anions are C_1 - C_{12} -, preferably C_1 - C_6 - and, with particular preference, C_1 - C_4 alcoholates, which in particular are branched, for example of the formula $\text{R}_x\text{R}_y\text{R}_z\text{C}-\text{O}^-$, in which R_x is H or C_1 - C_{10} alkyl, R_y is C_1 - C_{10} alkyl and R_z is C_1 - C_{10} alkyl or phenyl, and the sum of the carbon atoms of R_x , R_y and R_z is at least 2, preferably at least 3 and up to 10. Particular examples are i-propoxy and t-butoxy.

Other suitable anions are C_3 - C_{18} -, preferably C_5 - C_{14} - and, with particular preference, C_5 - C_{12} acetylides, which may have the formula $\text{R}_w-\text{C}\equiv\text{C}^-$, in which R_w is C_1 - C_{16} alkyl, preferably α -branched C_3 - C_{12} alkyl, for example of the formula $\text{R}_x\text{R}_y\text{R}_z\text{C}-$, or is benzyl or phenyl unsubstituted or substituted by from one to 3 C_1 - C_4 alkyl or C_1 - C_4 alkoxy substituents. 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.

Further anionic ligands are organic radicals bearing negative charges, such as C₁-C₁₂alkyl, e.g. methyl or aralkyl, e.g. benzyl.

Particular preferred anionic ligands are 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⁻). Cl⁻ is particularly preferred.

Examples of bis-anionic ligands are the bis-anions of diols, diamines and hydroxy amines, such as catechol, N,N'-dimethyl-1,2-benzenediamine, 2-(methylamino)phenol, 3-(methylamino)-2-butanol and N,N'-bis(1,1-dimethylethyl)-1,2-ethanediamine.

The tertiary phosphines contain preferably 3 to 40, more preferably 3 to 30 and, with particular preference, 3 to 18 carbon atoms. They are preferably of the formula:



in which R¹, R² and R³ independently of one another are C₁-C₂₀alkyl, C₄-C₁₂cycloalkyl, C₂-C₁₁heterocycloalkyl, C₆-C₁₆aryl, C₂-C₁₅heteroaryl or C₇-C₁₆aralkyl, where alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl and aralkyl are unsubstituted or substituted by one or more substituents selected from the group consisting of C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₆-C₁₆aryl, -NO₂, SO₃⁻, ammonium or halogen; the radicals R¹ and R² together are tetra- or pentamethylene unsubstituted or substituted by C₁-C₆alkyl, C₁-C₆haloalkyl, -NO₂ or C₁-C₆alkoxy and are possibly fused with 1 or 2 bivalent 1,2-phenylene radicals, and R³ is as defined above.

Examples of alkyl are methyl, ethyl and the isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. An example of aryl-substituted alkyl is benzyl. Examples of alkoxy are methoxy, ethoxy and the isomers of propoxy and butoxy.

Some examples of cycloalkyl are cyclobutyl, cycloheptyl, cyclooctyl and, in particular, cyclopentyl and cyclohexyl. Examples of substituted cycloalkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl and tris-trifluoromethyl-substituted cyclopentyl and cyclohexyl.

Examples of aryl are phenyl and naphthyl. Examples of aryloxy are phenoxy and naphthyloxy. Examples of substituted aryl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- or tristrifluoromethyl-substituted phenyl. An example of aralkyl is benzyl. Examples of substituted aralkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- or tristrifluoromethyl-substituted benzyl.

In the context of the present invention heterocycloalkyl comprises one or two and heteroaryl one to four heteroatoms, the heteroatoms being selected from the group consisting of oxygen, sulfur and nitrogen. Some examples of heterocycloalkyl are tetrahydrofuryl, pyrrolidinyl, piperazinyl and tetrahydrothienyl. Some examples of heteroaryl are furyl, thienyl, pyrrolyl, pyridyl and pyrimidinyl.

Preference is given to compounds of the formula I, II or III in which L^1 and $L^{1'}$ independently of one another are tertiary phosphine of the formula IV in which R^1 , R^2 and R^3 are identical. Particular preference is given, furthermore, to the radicals R^1 , R^2 and R^3 which are sterically bulky, for example cyclic or branched, especially α,α -di-branched and, very particularly, α -branched alkyl groups.

Another group of preferred compounds of the formula I, II or III is formed by those in which L^1 and $L^{1'}$ independently of one another are tertiary phosphine of the formula IV in which R^1 , R^2 and R^3 independently of one another are C_1 - C_{12} alkyl, C_5 - C_8 cycloalkyl, C_6 - C_{12} aryl or C_7 - C_{13} aralkyl, where alkyl, cycloalkyl, aryl and aralkyl are unsubstituted or substituted by one or more substituents selected from the group consisting of C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 -haloalkyl, SO_3^- and ammonium.

Within this group, particular preference is given to those in which R^1 , R^2 and R^3 independently of one another are C_1 - C_8 alkyl, C_5 - or C_6 cycloalkyl, C_6 - C_{10} aryl or C_7 aralkyl, where alkyl, cycloalkyl, aryl and aralkyl are unsubstituted or substituted by one to three substituents selected from the group consisting of methyl, methoxy, ethyl, ethoxy and trifluoromethyl.

Special preference is given to those compounds in which R^1 , R^2 and R^3 are methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, 1-, 2- or 3-pentyl, 1-, 2-, 3- or 4-hexyl, cyclopentyl, cyclohexyl, phenyl, naphthyl or benzyl, e.g. $(i-C_3H_7)_3P$, $(C_5H_9)_3P$ and $(C_6H_{11})_3P$.

Appropriate monodentate, bidentate and tetradentate neutral e^- donor ligands are derived, for example, from unsubstituted or substituted heteroarenes such as furan, thiophene, pyrrole, pyridine, bipyridine, picolylimine, γ -pyran, γ -thiopyran, phenanthroline, pyrimidine, bipyrimidine, pyrazine, indole, coumarone, thionaphthene, carbazole, dibenzofuran, dibenzothiophene, pyrazole, imidazole, benzimidazole, oxazole, thiazole, dithiazole, isoxazole, isothiazole, quinoline, bisquinoline, isoquinoline, bisisoquinoline, acridine, chromene, phenazine, phenoxazine, phenothiazine, triazine, thianthrene, purine, bisimidazole and bisoxazole.

Examples of substituents are OH, halogen, $C(O)OR_{s1}$, $OC(O)R_{s4}$, $C(O)R_{s2}$, nitro, NH_2 , cyano, SO_3M_y , OSO_3M_y , $NR_{20}SO_3M_y$, $N=N-R_{s2}$, $C_1-C_{12}alkyl$, $C_2-C_{12}alkenyl$, $C_1-C_{12}alkoxy$, $C_3-C_{12}cycloalkyl$, $C_3-C_{12}cycloalkenyl$, $C_2-C_{11}heterocycloalkyl$, $C_2-C_{11}heterocycloalkenyl$, $C_6-C_{10}aryl$, $C_6-C_{10}aryloxy$, $C_5-C_9heteroaryl$, $C_5-C_9heteroaryloxy$, $C_7-C_{11}aralkyl$, $C_7-C_{11}aralkyloxy$, $C_6-C_{10}heteroaralkyl$, $C_8-C_{11}aralkenyl$, $C_7-C_{10}heteroaralkenyl$, monoamino, diamino, sulfonyl, sulfonamide, carbamide, carbamate, sulfohydrazide, carbohydrazide, carbohydroxamic acid residue and aminocarbonylamide, in which R_{s1} is hydrogen, M_y , $C_1-C_{12}alkyl$, $C_2-C_{12}alkenyl$, $C_3-C_{12}cycloalkyl$, $C_2-C_{11}heterocycloalkyl$, $C_6-C_{10}aryl$, $C_5-C_9heteroaryl$, $C_7-C_{11}aralkyl$ or $C_6-C_{10}heteroaralkyl$, R_{s4} is hydrogen, $C_1-C_{12}alkyl$, $C_2-C_{12}alkenyl$, $C_3-C_{12}cycloalkyl$, $C_2-C_{11}heterocycloalkyl$, $C_6-C_{10}aryl$, $C_5-C_9heteroaryl$, $C_7-C_{11}aralkyl$ or $C_6-C_{10}heteroaralkyl$, and R_{s2} and R_{20} are hydrogen, $C_1-C_{12}alkyl$, $C_2-C_{12}alkenyl$, $C_3-C_{12}cycloalkyl$, $C_3-C_{12}cycloalkenyl$, $C_2-C_{11}heterocycloalkyl$, $C_2-C_{11}heterocycloalkenyl$, $C_6-C_{10}aryl$, $C_5-C_9heteroaryl$, $C_7-C_{11}aralkyl$, $C_6-C_{10}heteroaralkyl$, $C_8-C_{11}aralkenyl$ or $C_7-C_{10}heteroaralkenyl$, and alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, heterocycloalkyl, heterocycloalkenyl, aryl, aryloxy, heteroaryl, heteroaryloxy, aralkyl, aralkyloxy, heteroaralkyl, aralkenyl and heteroaralkenyl in turn are unsubstituted or substituted by one of the abovementioned substituents; and y is 1 and M is a monovalent metal or y is 1/2 and M is a divalent metal.

In the context of the description of the present invention, the terms metal and corresponding cations refer to an alkali metal, for example Li, Na or K, an alkaline earth metal, for example

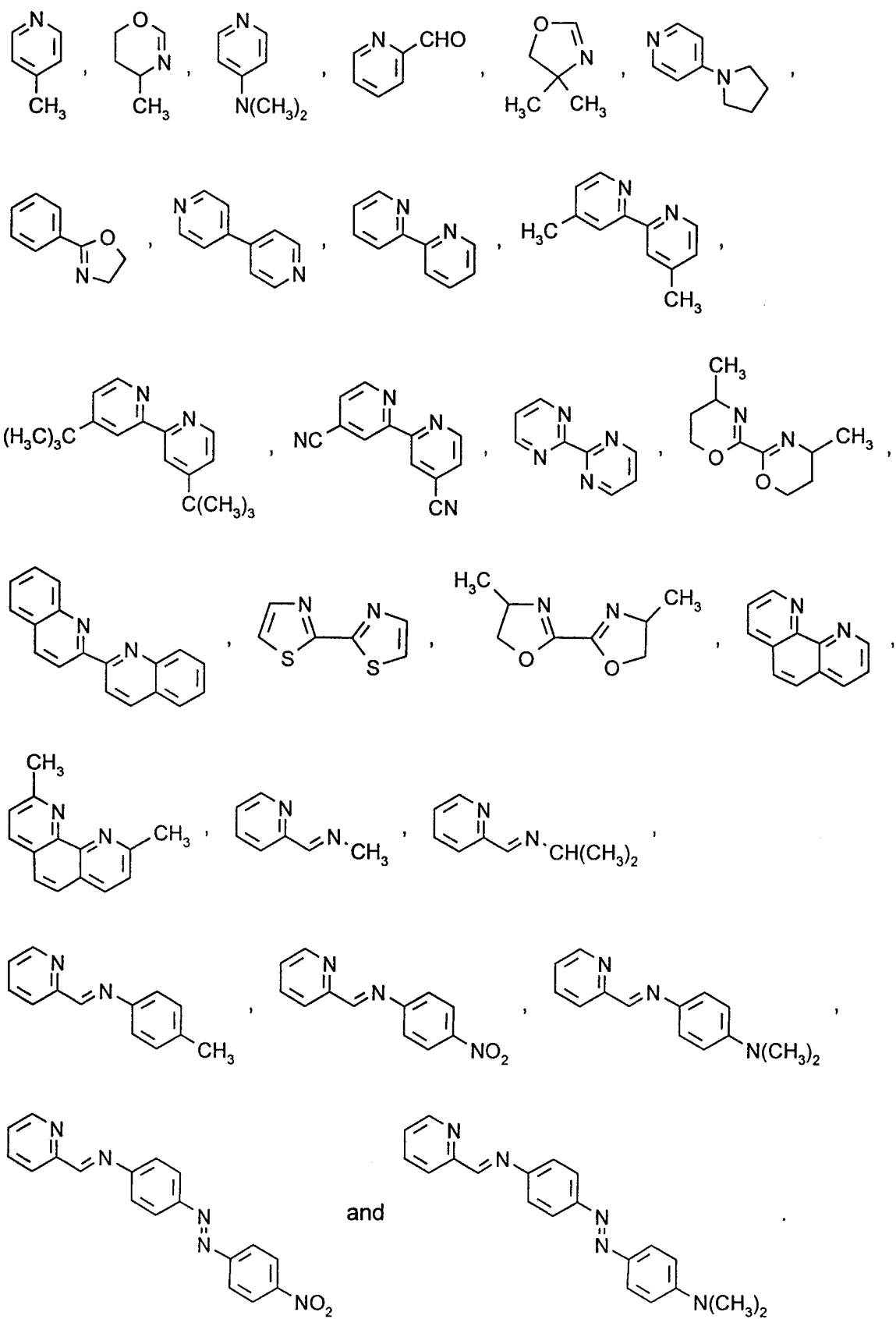
Mg, Ca or Sr, or Mn, Fe, Zn or Ag, and corresponding cations. Lithium, sodium and potassium ions, with their salts, are preferred.

NH₂, monoamino, diamino, carbamide, carbamate, carbohydrazide, sulfonamide, sulfohydrazide and aminocarbonylamide correspond preferably to a group R₈C(O)(NH)_pN(R₉)-, -C(O)(NH)_pNR₈R₉, R₈OC(O)(NH)_pN(R₉)-, R₈R₄₀NC(O)(NH)_pN(R₉)-, -OC(O)(NH)_pNR₈R₉, -N(R₄₀)C(O)(NH)_pNR₈R₉, R₈S(O)₂(NH)_pN(R₉)-; -S(O)₂(NH)_pNR₈R₉; R₈R₄₀NS(O)₂N(R₉)- or -NR₄₀S(O)₂NR₈R₉, in which R₈, R₉ and R₄₀ independently of one another are hydrogen, OH, C₁-C₁₂alkyl, C₁-C₁₂alkenyl, C₃-C₁₂cycloalkyl, C₃-C₁₂-cycloalkenyl, C₂-C₁₁heterocycloalkyl, C₂-C₁₁heterocycloalkenyl, C₆-C₁₀aryl, C₅-C₉heteroaryl, C₇-C₁₆-aralkyl, C₈-C₁₆aralkenyl with C₂-C₆-alkenylene and C₆-C₁₀aryl, C₆-C₁₅heteroaralkyl, C₈-C₁₅-heteroaralkenyl, or di-C₆-C₁₀aryl-C₁-C₆alkyl, or R₈R₉N, in which R₈ and R₉ independently of one another are hydrogen, OH, SO₃M_y, OSO₃M_y, C₁-C₁₂alkyl, C₃-C₁₂cycloalkyl, C₂-C₁₁-heterocycloalkyl, C₆-C₁₀aryl, C₅-C₉heteroaryl, C₇-C₁₁aralkyl, C₆-C₁₀heteroaralkyl, C₈-C₁₆-aralkenyl with C₂-C₆alkenylene and C₆-C₁₀aryl, or di-C₆-C₁₀aryl-C₁-C₆alkyl, which are unsubstituted or substituted by one or more substituents from the group consisting of OH, halogen, C(O)OR_{s1}, OC(O)R_{s4}, C(O)R_{s2}, nitro, NH₂, cyano, SO₃M_y, OSO₃M_y, NR₂₀SO₃M_y, C₁-C₁₂alkyl, C₂-C₁₂alkenyl, C₁-C₁₂alkoxy, C₃-C₁₂cycloalkyl, C₃-C₁₂cycloalkenyl, C₂-C₁₁-heterocycloalkyl, C₂-C₁₁heterocycloalkenyl, C₆-C₁₀aryl, C₆-C₁₀aryloxy, C₅-C₉heteroaryl, C₅-C₉heteroaryloxy, C₇-C₁₁aralkyl, C₇-C₁₁aralkyloxy, C₆-C₁₀heteroaralkyl, C₈-C₁₁aralkenyl, C₇-C₁₀heteroaralkenyl, monoamino, diamino, sulfonyl, sulfonamide, carbamide, carbamate, sulfohydrazide, carbohydrazide, carbohydroxamic acid residue and aminocarbonylamide, in which R_{s1} is hydrogen, M_y, C₁-C₁₂alkyl, C₂-C₁₂alkenyl, C₃-C₁₂cycloalkyl, C₂-C₁₁-heterocycloalkyl, C₆-C₁₀aryl, C₅-C₉heteroaryl, C₇-C₁₁aralkyl or C₆-C₁₀heteroaralkyl, R_{s4} is hydrogen, C₁-C₁₂alkyl, C₂-C₁₂alkenyl, C₃-C₁₂cycloalkyl, C₂-C₁₁heterocycloalkyl, C₆-C₁₀aryl, C₅-C₉heteroaryl, C₇-C₁₁aralkyl or C₆-C₁₀heteroaralkyl, and R_{s2} is hydrogen, C₁-C₁₂alkyl, C₂-C₁₂alkenyl, C₃-C₁₂cycloalkyl, C₃-C₁₂cycloalkenyl, C₂-C₁₁heterocycloalkyl, C₂-C₁₁-heterocycloalkenyl, C₆-C₁₀aryl, C₅-C₉heteroaryl, C₇-C₁₁aralkyl, C₆-C₁₀heteroaralkyl, C₈-C₁₁-aralkenyl or C₇-C₁₀heteroaralkenyl, and alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, heterocycloalkyl, heterocycloalkenyl, aryl, aryloxy, heteroaryl, heteroaryloxy, aralkyl, aralkyloxy, heteroaralkyl, aralkenyl and heteroaralkenyl in turn are unsubstituted or substituted by one of the abovementioned substituents; p is 0 or 1 and y is 1 and M is a monovalent metal or y is 1/2 and M is a divalent metal; or R₈ and R₉ or R₈ and R₉ or R₈ and

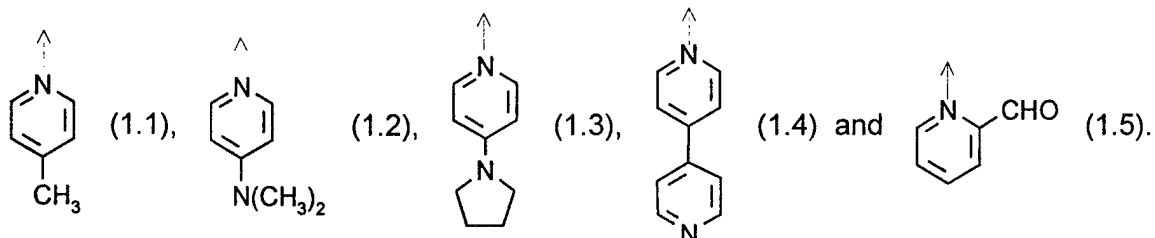
R_{40} in the case of $-NR_8R_9$ or $-NR_8R_9$ or $R_8R_{40}N$ - together are tetramethylene, penta-methylene, $-(CH_2)_2-O-(CH_2)_2-$, $-(CH_2)_2-S-(CH_2)_2-$ or $-(CH_2)_2-NR_7-(CH_2)_2-$, and R_7 is H, C_1-C_6 -alkyl, C_7-C_{11} aralkyl, $C(O)R_{s2}$ or sulfonyl.

The sulfonyl substituent is, for example, of the formula $R_{10}-SO_2-$ in which R_{10} is C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_2-C_{11} heterocycloalkyl, C_6-C_{10} aryl, C_5-C_9 heteroaryl, C_7-C_{11} aralkyl or C_6-C_{10} heteroaralkyl which are unsubstituted or substituted by one or more substituents selected from the group consisting of OH, halogen, $C(O)OR_{s1}$, $OC(O)R_{s4}$, $C(O)R_{s2}$, nitro, NH_2 , cyano, SO_3M_y , OSO_3M_y , $NR_{20}SO_3M_y$, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_1-C_{12} alkoxy, C_3-C_{12} cycloalkyl, C_3-C_{12} cycloalkenyl, C_2-C_{11} heterocycloalkyl, C_2-C_{11} heterocycloalkenyl, C_6-C_{10} aryl, C_6-C_{10} aryloxy, C_5-C_9 heteroaryl, C_5-C_9 heteroaryloxy, C_7-C_{11} aralkyl, C_6-C_{10} heteroaralkyl, C_8-C_{11} aralkenyl, C_7-C_{10} heteroaralkenyl, monoamino, diamino, sulfonyl, sulfonamide, carbamide, carbamate, sulfonylhydrazide, carbohydrazide, carbohydroxamic acid residue and aminocarbonylamide, in which R_{s1} is hydrogen, M_y , C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_3-C_{12} cycloalkyl, C_2-C_{11} heterocycloalkyl, C_6-C_{10} aryl, C_5-C_9 heteroaryl, C_7-C_{11} aralkyl or C_6-C_{10} heteroaralkyl, R_{s4} is hydrogen, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_3-C_{12} cycloalkyl, C_2-C_{11} heterocycloalkyl, C_6-C_{10} aryl, C_5-C_9 heteroaryl, C_7-C_{11} aralkyl or C_6-C_{10} heteroaralkyl, and R_{s2} and R_{20} are hydrogen, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_3-C_{12} cycloalkyl, C_3-C_{12} cycloalkenyl, C_2-C_{11} heterocycloalkyl, C_2-C_{11} heterocycloalkenyl, C_6-C_{10} aryl, C_5-C_9 heteroaryl, C_7-C_{11} aralkyl, C_6-C_{10} heteroaralkyl, C_8-C_{11} aralkenyl or C_7-C_{10} heteroaralkenyl, and alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, heterocycloalkyl, heterocycloalkenyl, aryl, aryloxy, heteroaryl, heteroaryloxy, aralkyl, heteroaralkyl, aralkenyl and heteroaralkenyl in turn are unsubstituted or substituted by one of the abovementioned substituents; and y is 1 and M is a monovalent metal or y is 1/2 and M is a divalent metal.

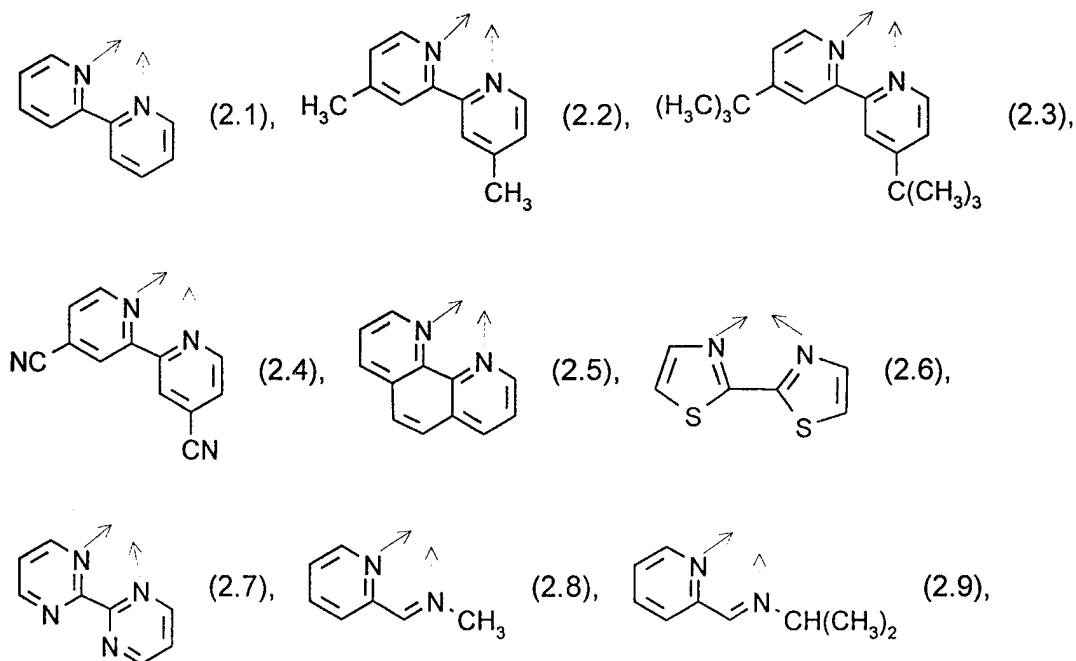
Preferred e^- donor ligands are derived, for example, from heteroarenes of the group

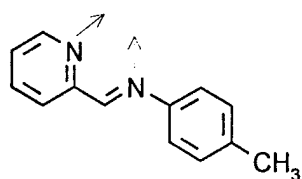


A preferred group of compounds is formed by those compounds of the formula I in which L^2 and L^3 independently of one another are pyridyl which is unsubstituted or substituted by one or more substituents from the group consisting of C_1 - C_{12} alkyl, C_2 - C_{11} heterocycloalkyl, C_5 - C_9 -heteroaryl, monoamino, diamino and $-C(O)H$. Examples are

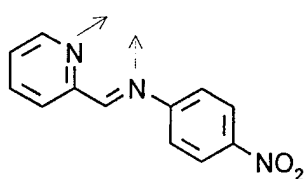


Another preferred group of compounds is formed by those compounds of the formula I in which L^2 and L^3 together are bipyridyl, phenanthrolyl, bithiazolyl, bipyrimidinyl or picolylimine which are unsubstituted or substituted by one or more substituents from the group consisting of C_1 - C_{12} alkyl, C_6 - C_{10} aryl and cyano, the substituents alkyl and aryl being in turn unsubstituted or substituted by one or more substituents from the group consisting of C_1 - C_{12} alkyl, nitro, monoamino, diamino and nitro- or diamino-substituted $-N=N-C_6-C_{10}$ aryl. Examples are

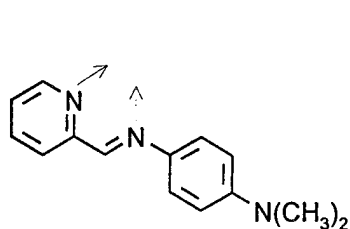




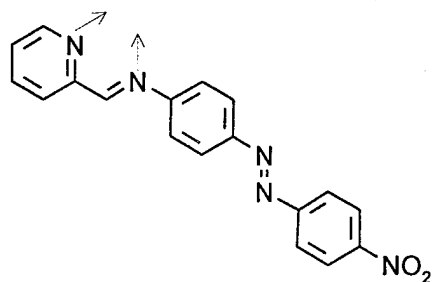
(2.10),



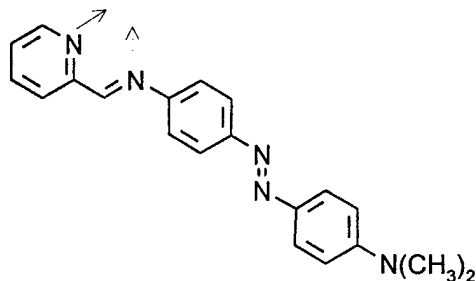
(2.11),



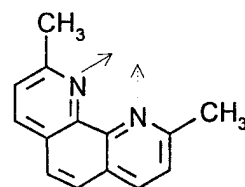
(2.12),



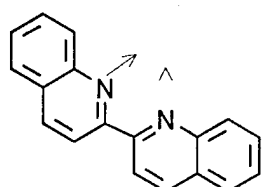
(2.13),



(2.14),

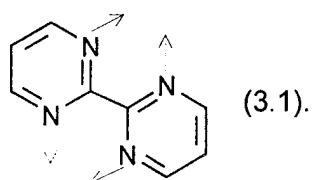


(2.15) and



(2.16).

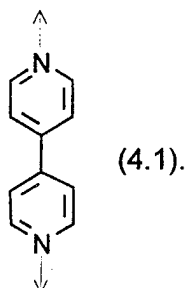
A preferred group of compounds is formed by those compounds of the formula II in which L^4 is bipyrimidinyl which is unsubstituted or substituted by one or more substituents from the group consisting of C_1 - C_{12} alkyl, C_2 - C_{11} heterocycloalkyl, C_5 - C_9 heteroaryl, monoamino, diamino and $-C(O)H$. One example is



(3.1).

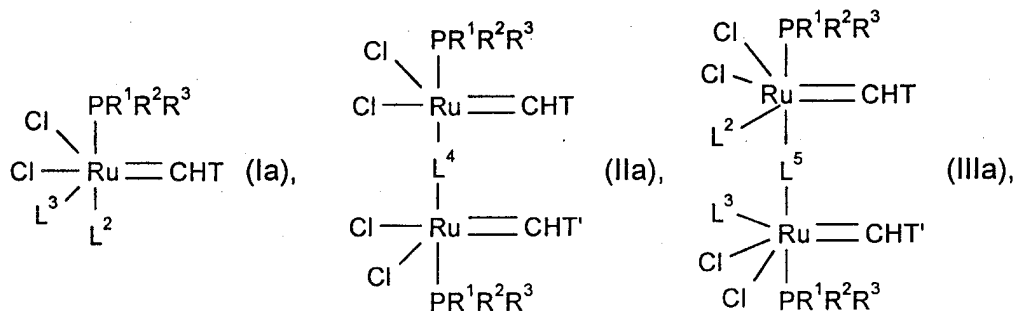
A preferred group of compounds is formed by those compounds of the formula III in which L^2 and L^3 together and L^5 independently thereof are pyridyl which is unsubstituted or

substituted by one or more substituents from the group consisting of C₁-C₁₂alkyl, C₂-C₁₁heterocycloalkyl, C₅-C₉heteroaryl, monoamino, diamino and -C(O)H. One example is



Preference is likewise given to those compounds of the formula I, II or III in which T and T' are unsubstituted or C₁-C₄alkyl-substituted, especially isopropyl-substituted C₆-C₁₄aryl, especially phenyl.

A preferred subgroup of the compounds of the formulae I, II and III comprises those of the formulae Ia, IIa and IIIa:



in which L², L³, L⁴, L⁵, R¹, R², R³, T and T' are as defined.

A further preferred subgroup of the compounds of the formulae I, II and III comprises those of the formulae Ia, IIa and IIIa in which

L² and L³ independently of one another are a monodentate, or L² and L³ together are a bidentate, neutral e⁻ donor ligand;

L⁴ is a tetradentate neutral e⁻ donor ligand;

L⁵ is a bidentate neutral e⁻ donor ligand; and

T and T' independently of one another are H, C₁-C₂₀alkyl, C₃-C₈cycloalkyl, C₃-C₇heterocycloalkyl, C₆-C₁₄aryl or C₄-C₁₅heteroaryl, where alkyl, cycloalkyl, heterocycloalkyl, aryl and heteroaryl are unsubstituted or substituted by one or more substituents from the group

consisting of C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₆-C₁₀aryl, C₆-C₁₀aryloxy, -NO₂ and halogen; and

R¹, R² and R³ independently of one another are C₁-C₂₀alkyl, C₄-C₁₂cycloalkyl, C₂-C₁₁-heterocycloalkyl, C₆-C₁₆aryl, C₂-C₁₅heteroaryl or C₇-C₁₆aralkyl, where alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl and aralkyl are unsubstituted or substituted by one or more substituents selected from the group consisting of C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₆-C₁₆aryl, -NO₂, SO₃⁻, ammonium and halogen; the radicals R¹ and R² together are tetra- or pentamethylene unsubstituted or substituted by C₁-C₆alkyl, C₁-C₆haloalkyl, -NO₂ or C₁-C₆alkoxy and possibly fused with 1 or 2 bivalent 1,2-phenylene radicals, and R³ is as defined above.

Particular preference is given to those compounds of the formula Ia, IIa and IIIa in which L² and L³ independently of one another are pyridyl which is unsubstituted or substituted by one or more substituents from the group consisting of C₁-C₁₂alkyl, C₂-C₁₁heterocycloalkyl, C₅-C₉heteroaryl, monoamino, diamino and -C(O)H; or

L² and L³ together are bipyridyl, phenanthrolyl, bithiazolyl, bipyrimidinyl, bisquinolyl or picolylimine which are unsubstituted or substituted by one or more substituents from the group consisting of C₁-C₁₂alkyl, C₆-C₁₀aryl and cyano and where the substituents alkyl and aryl are in turn unsubstituted or substituted by one or more substituents from the group consisting of C₁-C₁₂alkyl, nitro, monoamino, diamino, nitro and diamino-substituted -N=N-C₆-C₁₀aryl;

L⁴ is bipyrimidinyl; L⁵ is bipyridinyl;

T and T' are unsubstituted or C₁-C₄alkyl-substituted, especially isopropyl- or *t*-butyl-substituted, C₆-C₁₄aryl, especially phenyl; and

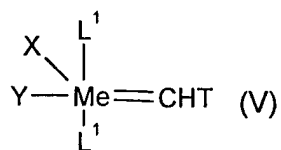
R¹, R² and R³ are isopropyl, cyclopentyl or cyclohexyl.

The present invention additionally provides a process for preparing compounds of the formula I, II or III in which

Me and Me' independently of one another are ruthenium or osmium;

X, X', Y, Y' L¹, L^{1'}, T and T' are as defined, and in order, for example, to prepare compounds in which

- (a) L² and L³ independently of one another are a monodentate or together are a bidentate neutral e⁻ donor ligand, a compound of the formula



in which X, Y, L¹ and T are as defined is reacted with a heteroarene, or

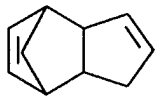
- (b) L⁴ is a tetradentate neutral e⁻ donor ligand, a compound of the formula V in which X, Y, L¹ and T are as defined is reacted with a heteroarene; or
- (c) L² and L³ independently of one another are a monodentate neutral e⁻ donor ligand and L⁵, independently thereof is a bidentate neutral e⁻ donor ligand, a compound of the formula I in which L² and L³ independently of one another are a monodentate neutral e⁻ donor ligand is reacted with a compound of the formula V.

The process of the invention is advantageously carried out such that the compounds of the formula V are dissolved in a solvent and then the desired heteroarenes or a compound of the formula I are or is added. The mass ratio of compounds of the formula V to the heteroarene is generally in the range from 1:1 to 1:100, preference being given to a ratio in the range from 1:1 to 1:5. The mass ratio of compounds of the formula V to compounds of the formula I is generally in the range from 1:1 to 1:10, preference being given to a ratio in the range from 1:1 to 1:2. The reaction takes place advantageously at a temperature in the range from -78°C to 150°C, preferably from 0°C to 100°C and, with particular preference, at from room temperature to 50°C.

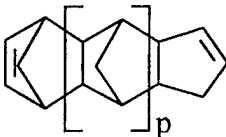
The invention likewise provides a composition comprising

- (α) the individual component dicyclopentadiene, or dicyclopentadiene in a mixture with another strained cycloolefin, and
- (β) a catalytic amount of at least one compound of the formulae I, II or III in which Me, Me', X, X', Y, Y', L¹, L¹', L², L³, L⁴, L⁵, T and T' are as defined, with or without further additives for polymers.

Dicyclopentadiene is the dimer of cyclopentadiene, which is known and commercially

available and has the formula . It is known that, together with further

cyclopentadiene, dicyclopentadiene forms so-called Diels-Alder adducts and hence forms ... oligomers which can likewise be used. In accordance with the invention the composition may comprise pure dicyclopentadiene, oligomers of dicyclopentadiene or mixtures thereof. The

oligomers are of the formula , in which p is a number from 1 to 100,

preferably from 1 to 50, with particular preference from 1 to 20, and with especial preference from 1 to 10.

The cycloolefins known as strained cycloolefins, which may be present as comonomers in the composition of the invention, are known.

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

If the cyclic olefins contain more than one double bond, for example 2 to 4 double bonds, then depending on the reaction conditions, on the chosen monomer and on the amount of catalyst it is also possible for crosslinked polymers to form.

Fused-on alicyclic rings contain preferably 3 to 8, more preferably 4 to 7 and with particular preference 5 or 6 ring carbon atoms.

The cyclic olefins which are present in the composition and can be polymerized with the aid of the catalysts of the invention are known and are described, for example, in WO 96/20235.

The comonomer cycloolefins can be present in an amount of from 0.01 to 99% by weight, preferably 0.1 to 95% by weight, with particular preference from 1 to 90% by weight and, with especial preference, from 5 to 80% by weight, based on the monomers present in the composition. Very particular preference is given to norbornene as comonomer in amounts of, for example, from 20 to 60% by weight.

The dienes which are present in the composition and which can be ring-closed with the aid of the catalysts of the invention are described, for example, in *Miller et al.* [Miller, S.J., Blackwell, H.E., Grubbs, R.H., *J. Am. Chem. Soc.* 118:9606-9614 (1996)] or in *Grubbs et al.* [Grubbs, R.H., Miller, S.J., Fu, G.C., *Acc. Chem. Res.* 28:446-452 (1995)].

The catalysts of the invention can also be used for isomerizing double bonds, as has already been described for ruthenium-based catalysts in *McGrath and Grubbs* [McGrath, D.V., Grubbs, R.H., *Organometallics* 13:224 (1994)].

The composition of the invention can comprise inert solvents. One particular advantage is that in the case of liquid monomers metathesis polymerization can be carried out without the use of a solvent. A further advantage is that the polymerization can even be carried out in water, polar and protic solvents or water/ solvent mixtures. In such cases it is of advantage, in the context of the present invention, to use a surfactant.

Examples of suitable inert solvents are protic polar and aprotic solvents, which can be used alone 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, triethylene glycol dimethyl ether), halogenated hydrocarbons, etc.

Compositions of the invention comprising a DCPD and catalyst with or without a cycloolefin are insensitive to oxygen and moisture, which permits storage and reaction without an inert gas.

Catalytic amounts in the context of the present invention denote preferably an amount from 0.001 to 20 mol-%, with particular preference from 0.01 to 15 mol-% and, with very particular preference, from 0.01 to 10 mol-%, based on the amount of monomer. On the basis of high thermocatalytic activity, very particular preference is given to amounts from 0.001 to 2 mol-%.

The composition of the invention which is used for the polymerization can be prepared directly prior to polymerization or can be used as a preformulated mixture, since the catalysts used are of particularly high stability. The mixture may even be stored for a prolonged period prior to polymerization, as a ready-to-use formulation, which is of advantage for large-scale industrial use.

The composition of the invention can comprise additives suitable for polymers, which additives are preferably used as formulation auxiliaries to improve the chemical and physical properties. The auxiliaries can be present in surprisingly high proportions without adversely affecting the polymerization, for example in amounts of up to 70% by weight, preferably from 1 to 70% by weight, more preferably from 5 to 60% by weight, with particular preference from 10 to 50% by weight and, with especial preference, from 10 to 40% by weight, based on the composition. Such auxiliaries have been disclosed in large numbers and are set out by way of example in the following list of auxiliaries:

1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, linear or sidechain-branched nonylphenols; such as 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-

methylheptadec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl) disulfide.

1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-

4-methylphenyl] terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl 4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl 4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)-amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide, isooctyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl 2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, dioctadecyl 2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, didodecyl mercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, di-[4-(1,1,3,3-tetramethylbutyl)phenyl] 2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.10. Triazine compounds, for example 2,4-bis(octylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl) isocyanurate.

1.11. Benzylphosphonates, for example dimethyl 2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

1.13. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.14. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.15. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)-oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis-(hydroxyethyl)-oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

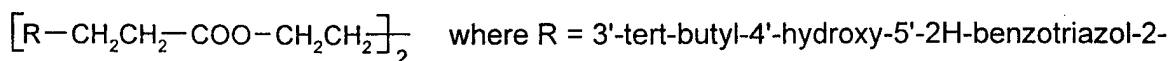
1.17. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazide, N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]-oxamide (Naugard® XL-1 from Uniroyal).

1.18. Ascorbic acid (vitamin C).

1.19. Aminic antioxidants, for example N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethyl-pentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methyl-pentyl)-p-phenylenediamine, N,N'-bis(1-methyl-heptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di-(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethyl-butyl)-N'-phenyl-p-phenylenediamine, N-(1-methyl-heptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfonamido)-diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, di-(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diamino-diphenylmethane, 1,2-di[(2-methyl-phenyl)amino]ethane, 1,2-di(phenylamino)-propane, (o-tolyl)biguanide, di-[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isoheptyl-diphenylamines, mixtures of mono- and dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octyl-phenothiazines, a mixture of mono- and dialkylated tert-octyl-phenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine, bis(2,2,6,6-tetramethylpiperidin-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one and 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilizers

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octoxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis(α,α -dimethylbenzyl)-2'-hydroxyphenyl)-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenyl)benzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazol-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]benzotriazole with polyethylene glycol 300;



2-[2'-hydroxy-3'-(α,α -dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)phenyl]benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-(α,α -dimethylbenzyl)phenyl]-benzotriazole.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octoxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivative.

2.3. Esters of substituted or unsubstituted benzoic acids, for example 4-tert-butyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoylresorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl α -cyano- β,β -diphenylacrylate or isooctyl α -cyano- β,β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxycinnamate or butyl α -cyano- β -methyl-p-methoxycinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of monoalkyl esters, such as of the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenyl undecyl ketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(2,2,6,6-tetramethylpiperidin-4-yl) succinate, bis(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(1,2,2,6,6-pentamethylpiperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl) nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl) 1,2,3,4-butanetetraoate, 1,1'-(1,2-ethanediyl)bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl) malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) succinate, the linear or cyclic condensates of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-di(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis-(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-

hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, the condensate of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine and also 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane, the reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane and epichlorohydrine, 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyl)oxycarbonyl-2-(4-methoxyphenyl) ether, N,N'-bisformyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine, the diester of 4-methoxymethylenemalonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]siloxane, the reaction product of maleic anhydride- α -olefin copolymer and 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine.

2.7. Oxalamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxy-oxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butyloxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butyloxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyloxanilide and mixtures of o- and p-methoxy- and of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-

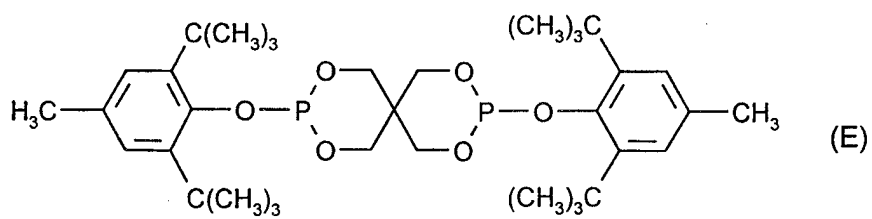
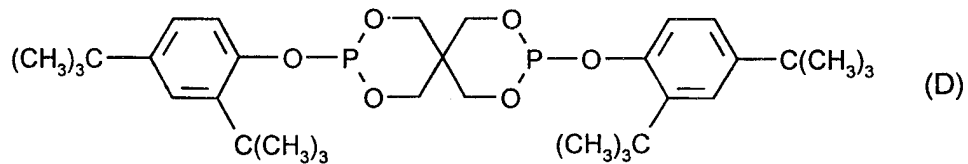
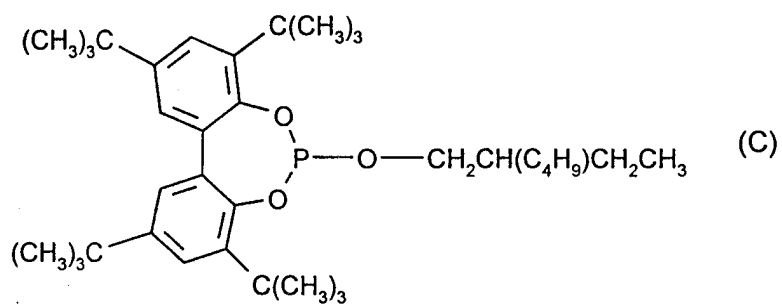
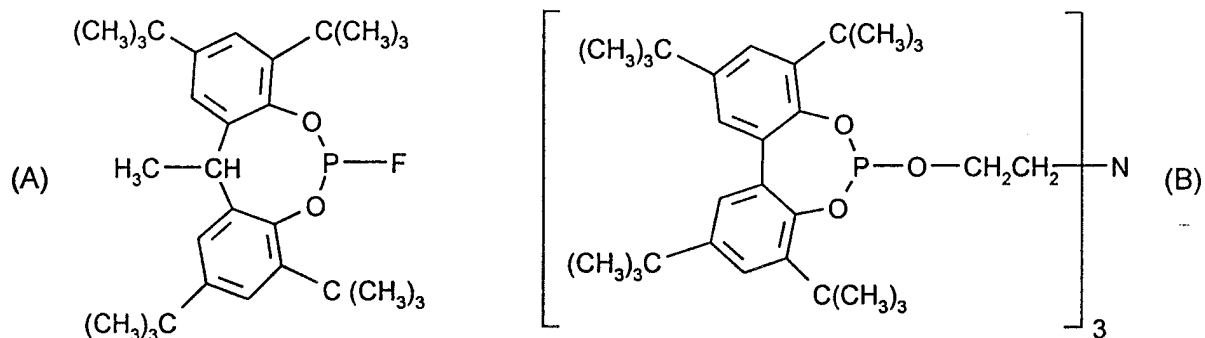
diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxy-propoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine, 2-{2-hydroxy-4-[3-(2-ethylhexyl-1-oxy)-2-hydroxypropyloxy]phenyl}-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

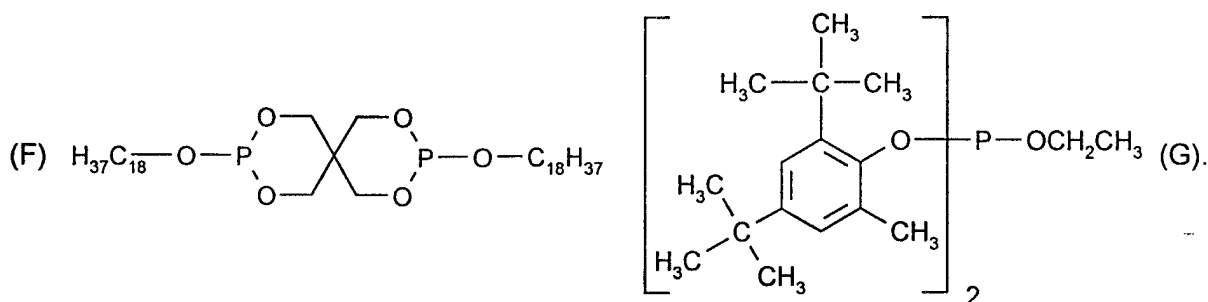
3. Metal deactivators, for example, N,N'-diphenyloxalamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl)hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl-propionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyladi-poyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.

4. Phosphites, phosphines and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, trimethylphosphine, tri-n-butylphosphine, triphenylphosphine, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, bisisodecylloxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tri-tert-butylphenyl)pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosphocin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenzo[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite, 2,2',2''-nitriolo[triethyl-tris(3,3',5,5''tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite], 2-ethylhexyl (3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite.

Particular preference is given to using the following phosphites:

Tris(2,4-di-tert-butylphenyl) phosphite (Irgafos®168, Ciba-Geigy), tris(nonylphenyl) phosphite,





5. Hydroxylamines, for example N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine from hydrogenated tallow fatty amines.

6. Nitrones, for example N-benzyl alpha-phenyl nitrone, N-ethyl alpha-methyl nitrone, N-octyl alpha-heptyl nitrone, N-lauryl alpha-undecyl nitrone, N-tetradecyl alpha-tridecyl nitrone, N-hexadecyl alpha-pentadecyl nitrone, N-octadecyl alpha-heptadecyl nitrone, N-hexadecyl alpha-heptadecyl nitrone, N-octadecyl alpha-pentadecyl nitrone, N-heptadecyl alpha-heptadecyl nitrone, N-octadecyl alpha-hexadecyl-nitron, and nitrones derived from N,N-dialkylhydroxylamines prepared from hydrogenated tallow fatty amines.

7. Thiosynergists, for example dilauryl thiodipropionate or distearyl thiodipropionate.

8. Peroxide scavengers, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole, the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β -dodecylmercapto)propionate.

9. Polyamide stabilizers, for example copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

10. Basic co-stabilizers, for example melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali

metal salts and alkaline earth metal salts of higher fatty acids, for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate, potassium palmitate, antimony pyrocatecholate or zinc pyrocatecholate.

11. Nucleating agents, for example inorganic substances, such as talc, metal oxides such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds such as mono- or polycarboxylic acids and their salts, such as 4-tert-butylbenzoic acid, adipic acid, diphenyl acetic acid, sodium succinate or sodium benzoate; and polymeric compounds, for example ionic copolymers (ionomers).

12. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, glass beads, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibres of other natural products, and synthetic fibres.

13. Other additives, for example plasticizers, lubricants, emulsifiers, pigments, rheological additives, catalysts, levelling assistants, optical brighteners, flameproofing agents, antistatic agents, blowing agents.

14. Benzofuranones and indolinones, as described, for example, in *U.S. 4 325 863*; *U.S. 4 338 244*; *U.S. 5 175 312*, *U.S. 5 216 052*; *U.S. 5 252 643*; *DE-A-4316611*; *DE-A-4316622*; *DE-A-4316876*; *EP-A-0589839* or *EP-A-0591102*, or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butylbenzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-[4-(2-hydroxyethoxy)phenyl]benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(3,4-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(2,3-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one.

The invention provides, furthermore, a process for preparing metathesis polymers, which comprises heating a composition comprising

(α') the individual component dicyclopentadiene, or dicyclopentadiene in the mixture with a strained cycloolefin, and

(β') a catalytic amount of at least one compound of the formulae I, II and III having the above definitions in a mixture with further additives for polymers and, if desired, subjecting the obtainable metathesis polymer to a shaping process.

The process of the invention is preferably carried out at a temperature of at least 0°C. In particular, the process of the invention is conducted at temperatures from 0° to 300°C, preferably at from room temperature to 250°C, with particular preference from room temperature to 200°C and, with especial preference, at from room temperature to 160°C. Following polymerization it may be advantageous to condition the polymers at elevated temperatures, for example from 80 to 200°C. To prepare linear polymers the reaction is preferably carried out in dilute solutions.

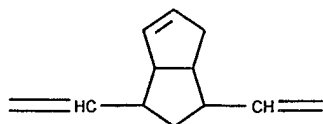
Polymerization can be associated with shaping processes such as calendering, casting, compression moulding, injection moulding or extrusion, for example. With the process of the invention it is possible to produce materials for the machining production of shaped articles or thermoplastically deformable materials for producing mouldings of all kinds and coatings. Advantageously, shaping and polymerization are connected in solvent-free reactive systems, it being possible to employ processing techniques such as injection moulding, extrusion, polymerization in predetermined forms (possibly under superatmospheric pressure), for example.

The invention also provides the polymers obtainable by the process of the invention.

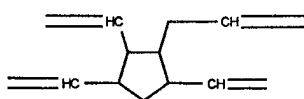
Of the polymers, preference is given to those containing only carbon and hydrogen.

The polymers prepared by the process of the invention can be homopolymers or copolymers with random distribution of the structural units, graft polymers or block polymers, and crosslinked polymers of this kind. They may have an average molecular weight (\overline{M}_w) of, for example, from 500 to 2 million daltons, preferably from 1000 to 1 million daltons (determined by GPC by comparison with polystyrene standards of narrow distribution).

It has surprisingly been found that the polymerization leads in high yields to a polydicyclopentadiene which corresponds to a linear polymer or copolymer having structural units of the formula



and represents a preferred subject of the invention. A further preferred subject of the invention comprises crosslinked copolymers having structural units of the formula



which can be prepared by the process of the invention.

The uncrosslinked or linear polymers comprise oligomers and polymers and can contain, for example, from 5 to 5000, advantageously from 10 to 2000, preferably from 20 to 1000, with particular preference from 20 to 500 and, with especial preference, from 20 to 300 structural units. Where the polymers are processed further preference is given to relatively low molecular weights, and in the case of processing to mouldings use is judiciously made of polymers having relatively high molecular weights.

Depending on the nature and amount of the monomers used, the polymers of the invention may have different properties. Some are notable for very high oxygen permeability, excellent dielectric properties (low dielectric constants, low loss factors or $\tan \delta$ values), good thermal stability (glass transition temperatures above 100°C), good toughnesses (impact and notched impact strength), flexibility and mechanical strengths (fracture resistance), hardness and low water absorption. Others have outstanding optical properties, such as high transparency and low reflective indices, for example. Also deserving of emphasis are the low shrinkage and the excellent surface properties (smoothness, gloss, adhesion). They can therefore be used in a very wide variety of industrial fields.

As coats on the surface of carrier materials, the polymers of the invention are notable for high adhesive strength. In addition, the coated materials are notable for high surface

smoothness and gloss. Among the good mechanical properties particular emphasis should be placed on the low shrinkage and high impact strength, but also the thermal stability. Also deserving of mention are the ease of demoulding and the high solvent resistance. The surfaces can be modified further, for example painted or printed, and the high adhesive strengths of the coatings should be mentioned in this case, too.

The polymers obtainable in accordance with the invention are particularly suitable for producing articles of all kinds, such as mouldings for cars, boats, leisure articles, pallets, pipes, sheets, etc.; as insulating materials for producing electrical and electronic components; as implants; as binders for coating materials; as heat-curable compositions for modelling or as adhesives for bonding substrates having low surface energies (TEFLON, polyethylene or polypropylene). The compositions of the invention can also be used to prepare coatings by thermal polymerization, it being possible to use both clear (transparent) and even pigmented compositions. Both white and colour pigments can be used. The production of mouldings by thermoplastic shaping processes for articles of all kinds should also be mentioned.

The compositions of the invention are also suitable in particular for producing protective coats. The invention also provides a variant of the process of the invention for producing coated materials, in which the composition of the invention is applied with or without solvent as a film to a carrier, for example by dipping, brushing, flow coating, rolling, knife coating or spin coating techniques, the solvent (if used) is removed, and the film is heated for polymerization. With this process it is possible to modify or protect the surfaces of substrates (corrosion protection).

The present invention provides, furthermore, a coated carrier material, wherein a coat of the polymer of the invention is applied to a substrate.

The present invention likewise provides a coated substrate having a cured film of the polymer of the invention.

Examples of suitable substrates (carrier materials) are those of glass, minerals, ceramics, plastics, wood, semi-metals, metals, metal oxides and metal nitrides. The film thicknesses

depend essentially on the desired use and can, for example, be from 0.1 to 1000 μm , preferably from 0.5 to 500 μm and, with particular preference, from 1 to 100 μm . The coated materials are notable for high adhesive strength and good thermal and mechanical properties.

The coated materials of the invention can be prepared by known methods such as brushing, knife coating, flow coating methods such as curtain coating or spin coating.

In the case of coatings, particularly good results are often achieved if the thermal metathesis polymerization is carried out with the additional use of cycloolefins which in addition contain from 1 to three, and preferably one, further double bonds and which in the context of the invention are polycyclic fused ring systems.

The examples which follow illustrate the invention.

A) Preparing the catalysts

Catalysts of the formulae I, II and III are prepared as described in the following examples. The numbers in the definitions of L^2 , L^3 , L^4 and L^5 relate to the examples of neutral e^- donor ligands given above; C_6H_{11} : cyclohexyl; C_5H_9 : cyclopentyl; C_3H_7 : isopropyl. The physical data are collated in Tables 1 - 4. The following text contains preparation instructions for some selected compounds.

Table 1: Compounds of the formula Ia in which L ² and L ³ independently of one another are monodentate ligands										
Comp.No	L ²	L ³	T	PR ¹ R ² R ³	¹ H NMR ^a δ carbene (J _{PH})	Elemental analysis [%]				
						C	H	Cl	N	Ru
1.1	1.1	1.1	Phenyl	P(C ₆ H ₁₁) ₃	20.22 (11.6)	61.14	7.50	9.95	3.98	13.67
1.2	1.2	1.2	Phenyl	P(C ₆ H ₁₁) ₃	19.83 (12.2)	59.71	7.81	9.18	7.33	12.56
1.3	1.2	1.2	4-Isopropylphenyl	P(C ₆ H ₁₁) ₃	19.80 (11.9)	60.61	7.75	8.44	6.51	11.96
1.4	1.2	1.2	Phenyl	P(C ₅ H ₉) ₃	20.10 (12.4)	62.98	6.84	8.75	6.78	12.39
1.5	1.3	1.3	Phenyl	P(C ₆ H ₁₁) ₃	19.95 (12.1)	62.34	6.60	8.41	6.38	12.04
1.6	1.5	1.5	Phenyl	P(C ₆ H ₁₁) ₃	20.21 (11.4)	63.42	6.63	9.51	6.77	11.70
1.7	1.5	1.5	Phenyl	P(C ₆ H ₁₁) ₃	20.75 (n.d.) ^b	58.89	6.65	9.27	3.54	13.19
1.8	1.1	1.1	Phenyl	P(C ₃ H ₇) ₃	20.36 (11.3)	55.42	6.97	11.51	4.73	16.54
1.9	1.2	1.2	Phenyl	P(C ₃ H ₇) ₃	20.25 (11.7)	54.17	7.26	10.60	4.08	15.06

^aNMR in CDCl₃; δ in ppm; J_{PH} in Hz; ^bn.d.: not determined.

Table 2: Compounds of the formula Ia in which L² and L³ together are bidentate ligands

Comp.No.	L ² + L ³	T	PR ¹ R ² R ³	¹ H NMR ^a δ carbene (J _{PH})	Elemental analysis [%]					
					C	H	Cl	N	Ru	
2.1	2.1	Phenyl	P(C ₆ H ₁₁) ₃	19.26 (10.1)	60.32	6.86	10.08	4.14	14.39	
2.2	2.1	4-tert-Butylphenyl	P(C ₆ H ₁₁) ₃	19.52 (12.4)	62.23	7.47	9.35	3.75	13.31	
2.3	2.2	Phenyl	P(C ₆ H ₁₁) ₃	18.67 (15.7)	60.98	6.99	9.81	3.88	13.98	
2.4	2.3	4-tert-Butylphenyl	P(C ₆ H ₁₁) ₃	19.49 (12.2)	65.34	8.07	8.43	3.09	11.51	
2.5	2.4	Phenyl	P(C ₆ H ₁₁) ₃	19.52 (12.1)	59.55	6.23	9.64	7.39	13.32	
2.6	2.5	Phenyl	P(C ₆ H ₁₁) ₃	21.68 (9.5)	61.35	6.76	9.67	3.62	13.81	
2.7	2.5	4-tert-Butylphenyl	P(C ₆ H ₁₁) ₃	21.49 (9.0)	63.41	7.37	9.34	3.84	13.13	
2.8	2.6	Phenyl	P(C ₆ H ₁₁) ₃	19.50 (n.d.) ^b	52.56	6.29	9.83	4.08	14.06	
2.9	2.7	Phenyl	P(C ₆ H ₁₁) ₃	19.52 (12.0)	56.74	6.62	10.01	8.13	14.33	
2.10	2.7	4-Isopropylphenyl	P(C ₆ H ₁₁) ₃	19.26 (11.9)	58.44	7.10	9.73	4.41	13.83	
2.11	2.8	Phenyl	P(C ₆ H ₁₁) ₃	19.68 (n.d.) ^b	58.17	7.25	10.61	4.05	15.13	
2.12	2.9	Phenyl	P(C ₆ H ₁₁) ₃	19.54 (n.d.) ^b	59.17	7.58	10.46	4.27	14.48	
2.13	2.10	Phenyl	P(C ₆ H ₁₁) ₃	18.83 (12.3)	61.94	6.87	9.81	3.86	13.57	
2.14	2.11	4-Isopropylphenyl	P(C ₆ H ₁₁) ₃	18.44 (12.2)	59.67	6.33	8.69	5.42	12.39	
2.15	2.12	4-Isopropylphenyl	P(C ₆ H ₁₁) ₃	18.79 (12.7)	61.95	7.60	8.73	5.16	12.44	

Table 2 (continued)

Comp.No.	L ² + L ³	T	PR ¹ R ² R ³	¹ H NMR ^a δ carbene (J _{PH})	Elemental analysis [%]					
					C	H	Cl	N	Ru	
2.16	2.13	Phenyl	P(C ₆ H ₁₁) ₃	18.82 (12.5)	59.34	6.18	8.35	7.86	11.71	
2.17	2.13	4-isopropylphenyl	P(C ₆ H ₁₁) ₃	18.54 (12.1)	60.52	6.51	7.91	7.85	11.22	
2.18	2.14	4-isopropylphenyl	P(C ₆ H ₁₁) ₃	18.69 (n.d.) ^b	62.93	7.19	7.60	7.51	11.20	
2.19	2.34	Phenyl	P(C ₆ H ₁₁) ₃	19.48 (12.2)	64.93	7.77	8.34	3.25	11.88	
2.20	2.10	Phenyl	P(C ₃ H ₇) ₃	18.94 (12.1)	56.50	6.61	11.28	4.39	16.24	
2.21	2.9	Phenyl	P(C ₃ H ₇) ₃	19.28 (12.2) 18.16 (13.5) ^c	52.51	6.74	12.18	4.78	17.53	
2.22	2.2	4-isopropylphenyl	P(C ₆ H ₁₁) ₃	19.60 (n.d.)	62.32	7.63	9.08	3.47	12.95	
2.23	2.5	Phenyl	P(C ₃ H ₇) ₃	19.95 (14.1)	55.70	8.36	11.93	4.90	16.52	
2.24	2.13	Phenyl	P(C ₃ H ₇) ₃	18.89 (n.d.) ^b	54.34	5.60	9.67	9.14	13.56	
2.25	2.2	Phenyl	P(C ₃ H ₇) ₃	19.80 (11.7)	55.27	6.68	11.53	4.53	16.82	
2.26	2.7	Phenyl	P(C ₆ H ₁₁) ₃	19.30 (12.0)	56.50	6.63	9.89	8.14	14.57	
2.27	2.7	4-isopropylphenyl	P(C ₆ H ₁₁) ₃	19.26 (11.9)	58.41	6.81	9.72	7.42	13.47	
2.28	2.16	4-tert-butylphenyl	P(C ₆ H ₁₁) ₃	19.76 (< 0.3)	66.31	7.15	8.50	3.07	11.61	
2.29	2.15	Phenyl	P(C ₆ H ₁₁) ₃	19.12 (n.d.) ^b	62.18	6.67	9.55	3.50	13.24	

^aNMR in CDCl₃; δ in ppm; J_{PH} in Hz; ^bn.d.: not determined; ^c two isomers

Table 3: Compounds of the formula IIa in which L⁴ is a tetradentate ligand

Comp.No.	L ⁴	T = T'	PR ¹ R ² R ³	¹ H NMR ^a δ carbene (J _{PH})	Elemental analysis [%]				
					C	H	Cl	N	Ru
3.1	3.1	4-Isopropylphenyl	P(C ₆ H ₁₁) ₃	19.50 (n.d.) ^b 19.67 (n.d.) ^b	58.11	7.43	10.53	4.05	15.06
3.2	3.1	4-Phenyl	P(C ₆ H ₁₁) ₃	19.60 (n.d.) ^b 19.80 (n.d.) ^b	56.24	7.04	11.62	4.36	16.04

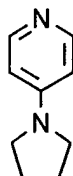
^aNMR in CDCl₃; δ in ppm; J_{PH} in Hz; ^bn.d.: not determinedTable 4: Compounds of the formula IIIa in which L⁵ and L^{5'} independently of one another are bidentate ligands

Comp.No.	L ⁴	T = T'	PR ¹ R ² R ³	¹ H NMR ^a δ carbene (J _{PH})	Elemental analysis [%]				
					C	H	Cl	N	Ru
4.1	4.1	Phenyl	P(C ₆ H ₁₁) ₃	19.80 (n.d.) ^b	60.01	6.92	10.35	4.10	14.58

^aNMR in CDCl₃; δ in ppm; J_{PH} in Hz; ^bn.d.: not determined

Example A1: Preparing the catalyst 1.5

200 mg of $\text{RuCl}_2(\text{=CH-C}_6\text{H}_5)\text{P}(\text{C}_6\text{H}_{11})_3$ are dissolved in 10 ml of CH_2Cl_2 . At room temperature (RT) 5 equivalents of compound No. 1



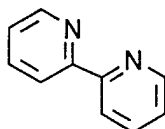
(1)

are added. After stirring at RT for 30 minutes, the reaction mixture is concentrated in vacuo and the residue is washed with hexane (3 x 5 ml each time) and dried in vacuo. The pure product is obtained in virtually quantitative yield.

^1H : 19.95 (d, 1, $J_{\text{PH}} = 12.1$ Hz, carbene-H); 8.30, 8.07, 7.98, 7.56, 7.20, 6.36, 6.12 (d, d, d, m, m, d, d, 13, pyrrolidinopyridine-H and phenyl-H); 3.27 (m, 16, pyrrolidino-H); 2.1-1.2 (m, 33, PCy_3).

Example A2: Preparing catalyst 2.2

200 mg of $\text{RuCl}_2(\text{=CH-C}_6\text{H}_4\text{-4-C}(\text{CH}_3)_3)\text{P}(\text{C}_6\text{H}_{11})_3$ and 5 equivalents of compound No. 2



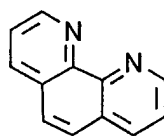
(2)

are used to give, by the method of Example A1, the pure product in virtually quantitative yield.

^1H : 19.52 (d, 1, $J_{\text{PH}} = 12.4$ Hz, carbene-H); 9.90, 8.88, 8.66, 8.51, 8.38, 8.17, 8.01, 7.81, 7.63, 7.49, 7.30, 7.05 (d, d, d, d, d, d, d, t, t, m, d, m, t, 12, phenyl-H and bipyridine-H); 1.8-0.9 (m, 42, t-Bu and PCy_3).

Example A3: Preparing catalyst 2.6

200 mg of $\text{RuCl}_2(\text{=CH-C}_6\text{H}_5)\text{P}(\text{C}_6\text{H}_{11})_3$ and 5 equivalents of compound No. 3



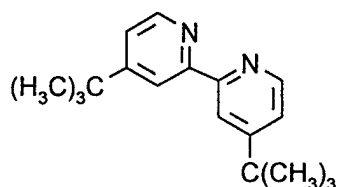
(3)

are used to give, by the method of Example A1, the pure product in virtually quantitative yield.

^1H : 21.68 (d, 1, $J_{\text{PH}} = 9.5$ Hz, carbene-H); 10.0, 9.0, 8.6, 8.46, 8.17, 7.96, 7.87.5, 7.3 (m, 13, phenanthroline-H and phenyl-H); 2.1-1.0 (m, 33, PCy_3).

Example A4: Preparing catalyst 2.4

200 mg of $\text{RuCl}_2(=\text{CH}-\text{C}_6\text{H}_4-4-\text{C}(\text{CH}_3)_3)\text{P}(\text{C}_6\text{H}_{11})_3$ and 5 equivalents of compound No. 4



(4)

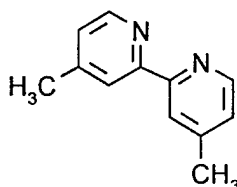
are used to give, by the method of Example A1, the pure product in virtually quantitative yield.

^1H : 19.49 (d, 1, $J_{\text{PH}} = 12.2$ Hz, carbene-H); 9.77, 8.86, 8.31, 8.4, 7.98, 7.65, 7.47, 7.08 (d, d, d, s, s, d, d, d, 10, phenyl-H and bipyridine-H); 1.8-0.9 (m, 60, 3 x t-Bu and PCy_3).

^{31}P : 35.9

Example A5: Preparing catalyst 2.3

200 mg of $\text{RuCl}_2(=\text{CH}-\text{C}_6\text{H}_5)\text{P}(\text{C}_6\text{H}_{11})_3$ and 5 equivalents of compound No. 5



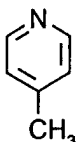
(5)

are used to give, by the method of Example A1, the pure product in virtually quantitative yield.

^1H : 18.67 (d, 1, $J_{\text{PH}} = 15.7$ Hz, carbene-H); 9.5-6.4 (m, 11, phenyl-H and bipyridine-H); 2.7-1.2 (m, 39, PCy_3 and bipyridine-methyl).

Example A6: Preparing catalyst 1.1

200 mg of $\text{RuCl}_2(=\text{CH}-\text{C}_6\text{H}_5)\text{P}(\text{C}_6\text{H}_{11})_3$ and 5 equivalents of compound No. 6



(6)

are used to give, by the method of Example A1, the pure product in virtually quantitative yield.

^1H : 20.22 (d, 1, $J_{\text{PH}} = 11.6$ Hz, carbene-H); 8.91, 8.12, 7.1, 6.75 (4 br s, 8, pyridine-H); 8.03, 7.52, 7.15 (d, t, d, 5, phenyl-H); 2.35-1.15 (m, 39, PCy_3 and pyridine-methyl).

^{31}P : 34.0

B) Practical Examples

B1 Polymerizations of DCPD

0.3% by weight of catalyst is added to DCPD (94% ex Shell, degassed).

Curing conditions: 1 h at 80°C, 1h at 100°C, 2 h at 120°C.

ΔH and T_g measurements by DSC (Differential Scanning Calorimetry), weight loss measurement by TGA (Thermogravimetric Analysis) to 300°C.

Table 5				
Comp. No.	Onset Temperature ^a	ΔH [J/g]	T_g [°C]	Weight loss [%]
1.1	<20	249	135	3.0
1.2	40	334	96	6.4
1.4	50	284	31	13.8
1.5	40	298	82	14.5
1.9	30	376	56	6.9

^a Temperature at which gelling begins.

B2 Polymerizations of norbornene

500 mg of norbornene are dissolved in 10 ml of THF, 1.0% by weight of catalyst is added, and, following the indicated reaction time, reaction is quenched with one drop of vinyltrimethylsilane. The molecular weights and the polydispersity were determined by GPC.

Table 6

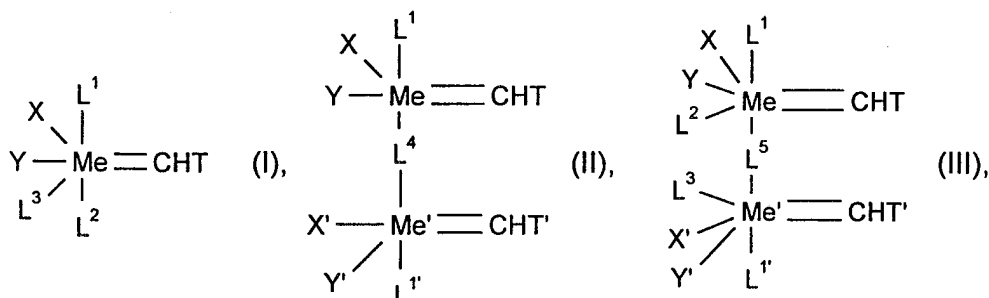
Comp. No.	Reaction time/ temperature	Yield [%]	$M_w [x 10^3]$	M_w/M_n
2.3	5 min./20°C	66	973	2.56
1.8	2 h/20°C	98	154	1.35
1.9	2 h/20°C	98	145	1.74
2.9	5 min./20°C	96	1063	1.98
2.12	5 min./20°C	86	641	2.44
2.13	2 h/20°C	82	389	2.91
2.14	5 min./20°C	88	618	2.33
2.15	2 h/20°C	80	560	2.74
2.20	10 h/60°C	88	356	2.75
2.23	10 h/60°C	14	321	1.99

M_w : ponderal mean of the molecular weight distribution

M_n : numerical mean of the molecular weight distribution

WHAT IS CLAIMED IS:

1. A compound of one of the formulae



in which

Me and Me' independently of one another are ruthenium or osmium;

X, X', Y and Y' independently of one another are anionic ligands, or X and Y and X' and Y' in each case together are bis-anionic ligands;

L¹ and L^{1'} independently of one another are tertiary phosphine;

L² and L³ independently of one another are monodentate, or L² and L³ together are bidentate, neutral e⁻ donor ligands;

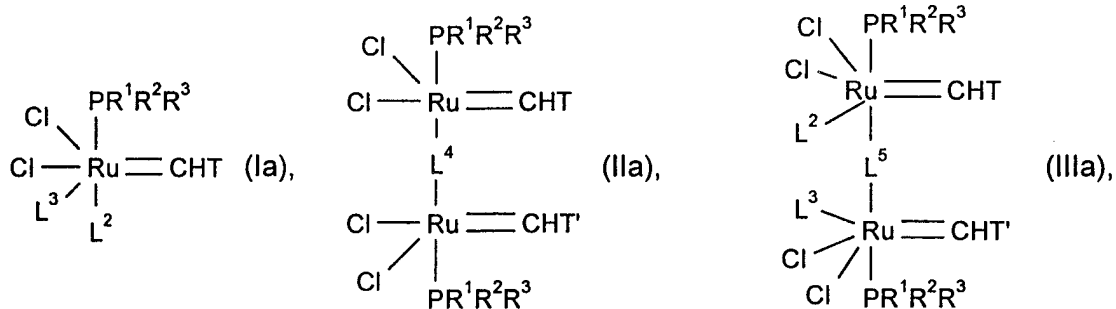
L⁴ is a tetradentate, neutral e⁻ donor ligand;

L⁵ is a bidentate, neutral e⁻ donor ligand; and

T and T' independently of one another are H, C₁-C₂₀alkyl, C₃-C₈cycloalkyl, C₃-C₇-heterocycloalkyl, C₆-C₁₄aryl or C₄-C₁₅heteroaryl, where alkyl, cycloalkyl, heterocycloalkyl, aryl and heteroaryl are unsubstituted or substituted by a substituent from the group consisting of C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₆-C₁₀aryl, C₆-C₁₀aryloxy, -NO₂ and halogen.

2. A compound according to claim 1, wherein Me and Me' are ruthenium.

3. A compound according to claim 1 which is of one of the formulae



in which

L^2 , L^3 , L^4 , L^5 , R^1 , R^2 , R^3 , T and T' are as defined.

4. A compound according to claim 1 which is of one of the formulae Ia, IIa and IIIa in which L^2 and L^3 independently of one another are a monodentate, or L^2 and L^3 together are a bidentate, neutral e^- donor ligand;

L^4 is a tetradentate neutral e^- donor ligand;

L^5 is a bidentate neutral e^- donor ligand; and

T and T' independently of one another are H, $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_8$ cycloalkyl, $\text{C}_3\text{-C}_7$ -heterocycloalkyl, $\text{C}_6\text{-C}_{14}$ aryl or $\text{C}_4\text{-C}_{15}$ heteroaryl, where alkyl, cycloalkyl, heterocycloalkyl, aryl and heteroaryl are unsubstituted or substituted by one or more substituents from the group consisting of $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ haloalkyl, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_6\text{-C}_{10}$ aryl, $\text{C}_6\text{-C}_{10}$ aryloxy, $-\text{NO}_2$ and halogen; and

R^1 , R^2 and R^3 independently of one another are $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_4\text{-C}_{12}$ cycloalkyl, $\text{C}_2\text{-C}_{11}$ -heterocycloalkyl, $\text{C}_6\text{-C}_{16}$ aryl, $\text{C}_2\text{-C}_{15}$ heteroaryl or $\text{C}_7\text{-C}_{16}$ aralkyl, where alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl and aralkyl are unsubstituted or substituted by one or more substituents selected from the group consisting of $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ alkoxy, $\text{C}_1\text{-C}_6$ haloalkyl, $\text{C}_6\text{-C}_{16}$ aryl, $-\text{NO}_2$, SO_3^- , ammonium and halogen; the radicals R^1 and R^2 together are tetra- or pentamethylene unsubstituted or substituted by $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl, $-\text{NO}_2$ or $\text{C}_1\text{-C}_6$ alkoxy and possibly fused with 1 or 2 bivalent 1,2-phenylene radicals, and R^3 is as defined above.

5. A compound according to claim 4, which is of one of the formulae Ia, IIa and IIIa in which L^2 and L^3 independently of one another are pyridyl which is unsubstituted or substituted by one or more substituents from the group consisting of $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_2\text{-C}_{11}$ heterocycloalkyl, $\text{C}_5\text{-C}_9$ heteroaryl, monoamino, diamino and $-\text{C}(\text{O})\text{H}$; or

L^2 and L^3 together are bipyridyl, phenanthrolyl, bithiazolyl, bipyrimidinyl, bisquinolyl or picolylimine which are unsubstituted or substituted by one or more substituents from the group consisting of C_1 - C_{12} alkyl, C_6 - C_{10} aryl and cyano and where the substituents alkyl and aryl are in turn unsubstituted or substituted by one or more substituents from the group consisting of C_1 - C_{12} alkyl, nitro, monoamino, diamino, nitro and diamino-substituted -N=N- C_6 - C_{10} aryl;

L^4 is bipyrimidinyl; L^5 is bipyridinyl;

T and T' are unsubstituted or C_1 - C_4 -alkyl-substituted, especially isopropyl- or *t*-butyl-substituted, C_6 - C_{14} aryl; and

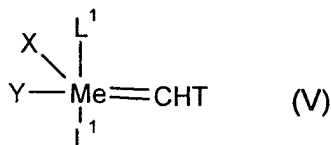
R^1 , R^2 and R^3 are isopropyl, cyclopentyl or cyclohexyl.

6. A process for preparing a compound of the formula I, II or III in which

Me and Me' independently of one another are ruthenium or osmium;

X, X', Y, Y', L^1 , L^1 , T and T' are as defined, which comprises in order to prepare compounds in which

- (a) L^2 and L^3 independently of one another are a monodentate or together are a bidentate neutral e^- donor ligand, reacting a compound of the formula



in which X, Y, L^1 and T are as defined is reacted with a heteroarene, or

- (b) L^4 is a tetradentate neutral e^- donor ligand, reacting a compound of the formula I in which L^2 and L^3 together are a bidentate neutral e^- donor ligand with a compound of the formula V; or
- (c) L^2 and L^3 together and L^5 independently thereof are a bidentate neutral e^- donor ligand, reacting a compound of the formula I in which L^2 and L^3 independently of one another are a monodentate neutral e^- donor ligand with a compound of the formula V.

7. A composition comprising

- (α) the individual component dicyclopentadiene, or dicyclopentadiene in a mixture with another strained cycloolefin, and

(β) a catalytic amount of at least one compound of the formulae I, II or III in which Me, Me', X, X', Y, Y', L¹, L^{1'}, L², L³, L⁴, L⁵, T and T' are as defined, with or without further additives for polymers.

8. A composition according to claim 7, wherein antioxidants are used as additives.

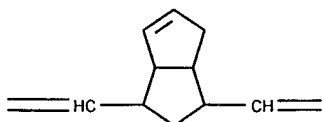
9. A process for preparing a metathesis polymer which comprises heating a composition comprising

(α') the individual component dicyclopentadiene, or dicyclopentadiene in a mixture with another strained cycloolefin, and

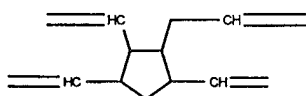
(β') a catalytic amount of at least one compound of the formulae I, II and III having the definitions given in claim 1 with or without further additives for polymers and, if desired, subjecting the obtainable metathesis polymer to a shaping process.

10. A polymer obtainable by a process according to claim 9.

11. A linear polymer or copolymer according to claim 10 having structural units of the formula



or a crosslinked copolymer having structural units of the formula



12. A carrier material, wherein a layer of a compound according to claim 1 has been applied to a substrate.

13. A coated substrate with a cured coat of the composition according to claim 7.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 98/01092

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C07F15/00 C08F32/00 C08G61/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C07F C08F C08G		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 20111 A (E.I. DU PONT DE NEMOURS AND COMPANY) 14 October 1993 cited in the application *Claims*	1-5
A	WO 96 04289 A (CALIFORNIA INSTITUTE OF TECHNOLOGY) 15 February 1996 cited in the application *Claims*	1-5
A	WEBER, BIRGIT ET AL: "Carbyne(dichloro) and carbyne(dichloro)hydrido osmium complexes from alkyne precursors" J. CHEM. SOC., CHEM. COMMUN. (1994), (22), 2595-6 CODEN: JCCCAT; ISSN: 0022-4936, XP002064480	1
<div style="display: flex; justify-content: space-between;"> <input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>^o Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">11 May 1998</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">26/05/1998</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Rinkel, L</div>

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Information on patent family members

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