

Description

The present invention relates to a process for the preparation of dimerization products from low molecular weight aliphatic mono-olefins using a catalyst containing palladium and/or ruthenium in an organic solvent.

It has been suggested that ethene can be dimerized to butenes in a reaction medium consisting of highly concentrated strong mineral acids such as phosphoric acid (concentration 14.0 mol/l, ~85%) and sulphuric acid (concentration 17.0 mol/l, ~95%) using as catalyst a palladium salt with an anion which has little or no interaction with the palladium. This dimerization is not attractive because it combines a highly corrosive reaction medium with a very low conversion rate of ethene to butenes relative to the amount of palladium (cf.: USSR Patent Specification 374930 [Chem. Abstr. 90 22286 h]).

Further, it is known that ethene can be dimerized in chloroform using as catalyst the compound



or the compounds



($n=2, 3$) prepared in situ (cf.: J. Am. Chem. Soc. 103 4627—4629 (1981) and 104 3520—3522 (1982)). These catalysts, however, require strictly anhydrous reaction conditions (cf.: Transition metal catalyzed polymerizations; Alkenes and dienes, Part A, Edited by R. P. Quirk, 1983 pp. 341—354).

Moreover it is known from the examples of the British Patent Specification No. 887,362, to prepare dimerization products from an alkene or alkyne with a catalytic system composed of a palladium compound, hydrochloric acid and aprotic solvent. This dimerization process is not attractive too, because it combines a highly corrosive reaction medium with a low conversion rate and selectivity of ethene propyl acetylene or butyl acetylene, relative to the amount of palladium.

The present invention provides a process for the preparation of dimerization products from aliphatic mono-olefins having 2—12 carbon atoms per molecule in the presence of a catalytic system derivable from a compound of a precious group VIII metal and an acid, characterized in that the aliphatic mono-olefin is contacted in an aprotic organic solvent with a catalytic system formed by combining a palladium and/or ruthenium compound and an acid with a pKa of less than 2, except hydrohalogenic acids.

The presence of an acid as defined above in the catalytic system of the process of the invention may result in very high rates of dimerization by strong activating effects in an aprotic organic solvent.

Aliphatic mono-olefins having 1—12 carbon atoms per molecule which can be used in the process according to the invention are linear or branched alkenes or cycloalkenes, such as for example ethene, propene, 1-butene, 2-butene, the isomeric pentenes, hexenes, octenes and dodecenes, cyclopentene, cyclooctene and cyclododecene. Examples of other aliphatic mono-olefins are substituted alkenes such as allyl alcohol, acrylic acid and alkyl-, aryl-, aralkyl esters of acrylic acid. The preferred olefins are ethene and propene.

The term "dimerization products" as it is employed herein refers to olefin products obtained by reaction of two identical olefins as well as by the reaction of two different olefins and to the alcohol, ether or ester derivatives of these olefin products obtained in-situ by the further presence of water, an alcohol or a carboxylic acid, respectively in the reaction mixture.

According to the invention, both homogeneous and heterogeneous catalysts can be used. The use of homogeneous catalysts is preferred.

The catalyst used in the process of the invention therefore preferably comprises palladium compounds and/or ruthenium compounds which are soluble in the reaction mixture or form in situ soluble compounds therein.

Examples of suitable palladium compounds are palladium nitrate, palladium sulfate, palladium halides and palladium carboxylates, preferably carboxylates of carboxylic acids having not more than 12 carbon atoms per molecule. Also palladium salts of acids with a pKa < 2 as specified hereinafter can be used. Palladium carboxylates, in particular palladium acetate, are preferably used.

Further examples of suitable palladium compounds are palladium complexes such as bis(2,4-pentanedionato)palladium, bis(picolinato)palladium, tetrakis(triphenylphosphine)palladium, tetrakis-acetonitrile palladium tetrafluoroborate, bis(tri-*o*-tolylphosphine)palladium acetate, bis(tri-phenylphosphine)palladium sulfate.

Examples of suitable ruthenium compounds are ruthenium (III) chloride, ruthenium (IV) chloride, ruthenium (III) chloride trihydrate, ruthenium oxides, ruthenium carboxylates such as ruthenium acetate or ruthenium propionate, ruthenium (III) tris acetylacetonate and organo ruthenium complexes with monodentate P and N ligands. Further, ruthenium salts of acids with a pKa of less than 2 as specified hereinafter may be suitable.

The quantity of the palladium and/or ruthenium compound used may vary within wide ranges and is generally in the range between 10^{-6} and 10^{-1} and preferably in the range between 10^{-5} and 10^{-2} mol palladium and/or ruthenium compound per mol olefin starting material.

The acid with a pKa of less than 2 used in the process of the invention may comprise organic acids such as carboxylic acids and organic sulfonic acid as well as inorganic acids, which preferably have a non-coordinating anion by which is meant that little or no interaction takes place between the palladium and the anion. Typical examples of such anions are PF_6^- , SbF_6^- , BF_4^- and ClO_4^- .

Acids preferably used are, for instance, perchloric acid, sulfuric acid, sulfonic acids and those acids that can be formed possibly in situ, by interaction of a Lewis acid such as, for example, BF_3 , AsF_5 , SbF_5 , PF_5 , TaF_5 or NbF_5 with a broensted acid such as, for example, a hydrohalogenic acid, in particular HF, fluorosulfonic acid, phosphoric acid or sulfuric acid. Specific examples of the last-named type of acids are fluorosilicic acid, HPF_4 , HSbF_4 and HBF_4 , which is preferred. Typical sulfonic acids that can be used are fluorosulfonic acid, chlorosulfonic acid and the organic sulfonic acids such as, for example, methanesulfonic acid, 2-hydroxypropanesulfonic acid, p-toluenesulfonic acid and trifluoromethanesulfonic acid, of which the last two acids are preferred.

Carboxylic acids which may be used are for example trifluoroacetic acid, trichloroacetic acid and dichloroacetic acid.

The quantity of the acid with a pKa of less than 2 may be at least 1 equivalent and is preferably at least 10 equivalent acid per gramatom palladium and/or ruthenium.

Further when ligands containing Group Va atoms are used in the catalytic system an excess of the acid relative to the ligands strongly activates the catalytic system. Accordingly in the process of the invention the catalytic system is formed by combining the palladium and/or ruthenium compound, a ligand containing at least one atom of Group Va of the Periodic Table of the Elements as coordinating atom and the acid with a pKa of less than 2 in a quantity of more than 1 equivalent acid per gramatom Group Va atom present in the ligand.

Monodentate ligands which may be used in the process of the invention comprise a compound containing one Group Va atom of the Periodic Table of the Elements, in particular a compound containing one trivalent N or P atom, which is bonded to at least one aromatic hydrocarbon group or a compound containing a trivalent N atom, which is a member of a heterocyclic aromatic ring.

Examples of suitable monodentate ligands comprising a compound which contains a trivalent N or P atom bonded to at least one aromatic hydrocarbon group are N,N' - dialkylanilines and phosphines such as N,N' - dimethylaniline, N,N' - diethylaniline, N,N' - dibutylaniline, 4 - chloro - N,N' - dimethylaniline, 4 - ethoxy - N,N' - dimethylaniline, 4 - dimethylaminobenzenesulfonic acid, 3 - dimethylaminobenzene-sulfonic acid, bis(1,1 - dimethylethyl)phenylphosphine, dimethylphenylphosphine, cyclohexyldiphenylphosphine, dibutylphenylphosphine, methylphenylphosphine, triphenylphosphine, tris(4 - chlorophenyl)phosphine, tris(4 - methoxyphenyl)phosphine, tris(2 - methoxyphenyl)phosphine, tris(4 - butylphenyl)phosphine, tris(4 - trifluorophenyl)phosphine, tris(4 - fluorophenyl)phosphine and 2 - carboxyphenyl diphenylphosphine.

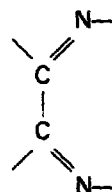
Examples of suitable monodentate ligands comprising a compound which contains a trivalent N atom being part of a heterocyclic aromatic ring are pyridines and quinolines such as pyridine, 2,6 - dimethylpyridine, 4 - ethylpyridine, 2 - methoxypyridine, 2 - chloropyridine, 3 - chloropyridine, 2,6 - dichloropyridine, 2 - pyridine carboxylic acid, 3 - pyridine carboxylic acid, quinoline, 2 - methylquinoline and 2 - chloroquinoline.

The use of a monodentate ligand which comprises N,N' - dimethylaniline, triphenylphosphine, pyridine or the derivatives thereof is preferred.

Chelate ligands which may be used in the process of the invention comprise a compound containing at least two atoms of Group Va of the Periodic Table of the Elements, which are connected through a chain comprising 2-6 carbon atoms.

Examples of suitable chelate ligands comprise compounds containing two phosphorus atoms which are connected through a chain comprising 2 or 3 carbon atoms such as 1,2-ethenediylbis(diphenyl)phosphine, 1,2 - ethanediylbis(diphenyl)phosphine, 1,2 - phenylenebis(diphenyl)phosphine and 1,3 - propanediylbis(diphenyl)phosphine.

Further examples of suitable chelate ligands comprise compounds containing two nitrogen atoms which are connected through a chain comprising 2 carbon atoms, in particular compounds containing in the molecule a group of the formula



such as 1,10 - phenanthroline, 4,7 - dimethyl - 1,10 - phenanthroline, 4,7 - diphenyl - 1,10 phenanthroline - disulfonic acid, 2,2' - bipyridine, 4,4' - dimethyl - 2,2 - bipyridine and 4,4' - dichloro 2,2' - bipyridine.

The quantity of ligand used for the catalyst in the process of the invention is at least 1 mol ligand per gramatom palladium and/or ruthenium.

The process according to the invention is carried out in an aprotic organic solvent. Examples of suitable solvents are hydrocarbons such as hexane, cyclohexane, octane, cyclo-octene, benzene, toluene, the three xylenes, ethylbenzene and cumene, halogenated hydrocarbons such as chloroform, 1,2-dichloroethane, perfluoroalkanes, chlorobenzene and the three dichlorobenzenes, ethers such as tetrahydrofuran, dimethylether of diethylene glycol (diglyme), methylt-butyl ether and dioxane, and nitro compounds such as nitromethane and nitrobenzene.

Reactant olefins may also function as an aprotic solvent especially when higher olefins or substituted olefins such as for example esters of acrylic acid are used.

The use of aromatic hydrocarbons and halogenated aliphatic hydrocarbons as solvent is preferred.

As mentioned earlier the dimerization products of the process of the invention may comprise an alcohol, ether or ester obtained in-situ by the presence of water, an alcohol or carboxylic acid, respectively. The alcohols or carboxylic acids which may be present are preferably lower aliphatic alcohols and carboxylic acids such as methanol, ethanol, propanol, acetic acid, propionic acid or caproic acid. The quantity of water, alcohol or carboxylic acid present should be such that the aprotic properties of the reaction medium dominates, i.e. a quantity below 50 %v and preferably below 20 %v calculated on the quantity of the aprotic solvent.

The process according to the present invention can be carried out at temperatures of up to 200°C and preferably in the range between 20°C and 135°C. The pressure lies between 1 and 100, in particular between 20 and 75 bar gauge.

The process according to the invention can be carried out batchwise, semi-continuously or continuously.

The following examples further illustrate the invention.

Example I

A 300 ml magnetically stirred Hastelloy C autoclave ("Hastelloy" is a trade mark) was charged with 50 ml solvent, 0.1 mmol palladium acetate or ruthenium (acetylacetonate) and an acid with a pKa of less than 2 as catalytic system. The autoclave was flushed with ethene, filled with ethene at a pressure of 40 bar, sealed and heated to a specified temperature. After a specified reaction time the contents of the autoclave were analyzed by gas/liquid chromatography.

The conversion of ethene to products (dimers, trimers, etc.) was calculated as mol ethene per gramatom palladium or ruthenium per hour. The selectivity to the butenes is given as % mol butenes in the products formed.

Data and results of the experiments 1—6 carried out according to the above are indicated in Table I.

In an experiment not according to the invention a glass-lined autoclave was charged with 50 ml toluene and 5 mmol trifluoromethane sulfonic acid. The autoclave was flushed with ethene and filled with ethene at a pressure of 40 bar and heated to 70°C. After a reaction time of 5 hours only traces of dimers appeared to be formed on analysis by gas/liquid chromatography. This experiment shows that under comparable reaction conditions dimerization is not effected by the presence of an acid with a pKa of less than 2 without the presence of a palladium or ruthenium compound.

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TABLE I

Experiment No.	Catalyst	Acid with pKa <2 (mmol)	Solvent	Reaction temperature °C	Reaction time, h	Conversion mol C ₂ H ₄ /gramatom Pd or Ru/h	Selectivity, % mol
1	Pd-acetate	CF ₃ SO ₃ H (5)	toluene	75	1	4600	93
2	Pd-acetate	CF ₃ SO ₃ H (5)	toluene	room temperature	3	900	94
3	Pd-acetate	CF ₃ SO ₃ H (5)	dichloro-benzene	75	1	4500	93
4	Pd-acetate	CF ₃ SO ₃ H (5)	diglyme	70	5	350	93 (1-butene 69%)
5	Pd-acetate	p-toluene-sulfonic acid (5)	toluene	70	5	600	96
6	Pd-acetate	CF ₃ SO ₃ H (4)	hexane	70	0.5	5000	95
7	Ru-(acetyl-acetonate)	CF ₃ SO ₃ H (5)	toluene	60	0.7	8000	95

Example II

A 300 ml magnetically stirred Hastelloy C autoclave ("Hastelloy" is a trade mark) was charged with 50 ml solvent and 0.1 mmol palladium acetate, a ligand, and an acid with a pKa of less than 2 as catalytic system. The autoclave was flushed with ethene, filled with ethene at a specified pressure, sealed and heated to a specified temperature. After a specified reaction time the contents of the autoclave were analyzed by gas/liquid chromatography.

The conversion of ethene to products (dimers, trimers, etc.) was calculated as mol ethene per gramatom palladium per hour.

Data and results of the experiments 1—9 carried out according to the above are indicated in Table II. In experiment 2 the composition of the formed butenes was analyzed as: 1-butene 24%, trans-2-butene 47.7%, cis-2-butene 38.3%. In experiment 9 the composition of the formed butenes was analyzed as: 1-butene 6.3%, trans-2-butene 63.3%, cis-2-butene 30.7%. The experiments 4, 6 and 8 are not according to the invention and show that an excess of the acid with a pKa of less than 2 relative to the ligand is required for a high conversion.

TABLE II

Exp. No.	Catalyst 0.1 mmol Pd-acetate + ligand (mmol)	Acid with Pka <2 (mmol)	Solvent	Ethene, bar	Reaction temperature, °C	Reaction time, h	Conversion, mol C ₂ H ₄ /gram-atom Pd/hour	Selectivity % mol
1	triphenylphosphine (0.1)	p-toluenesulphonic acid (10)	toluene	40	70	1	900	96
2	pyridine (3)	CF ₃ SO ₃ H (5)	toluene	40	80	1	900	94
3	2,2'-bipyridine (1)	CF ₃ SO ₃ H (4)	toluene	40	70	1	5000	93
4	2,2'-bipyridine (2)	CF ₃ SO ₃ H (4)	toluene	40	75	1	traces	
5	triphenylphosphine (3)	CF ₃ SO ₃ H (4)	toluene	40	95	1	5000	97
6	triphenylphosphine (3)	CF ₃ SO ₃ H (2)	toluene	40	105	5	80	100
7	2-carboxyphenyl-di-phenylphosphine (1.5)	HBFe ₄ (4)	chloroform	20	110	0.5	3000	98
8	2-carboxyphenyl-di-phenylphosphine (1.5)	HBFe ₄ (1)	chloroform	20	100	5	60	98
9	N,N'-dimethylaniline (3)	CF ₃ SO ₃ H (5)	toluene	40	75	0.7	7000	93



mple III

A 300 ml magnetically stirred Hastelloy C autoclave ("Hastelloy" is a trade mark) was charged with a solvent and palladium acetate a monodentate ligand and an acid with a pKa of less than 2 as catalytic system. The autoclave was flushed with propene, filled with 40 ml liquid propene, sealed and heated to a specified temperature. After a specified reaction time the contents of the autoclave were analyzed by gas/liquid chromatography.

The conversion of propene to products (dimers, trimers, etc.) was calculated as mol of propene per gramatom palladium per hour. The selectivity to the dimer hexenes is given as % mol dimers in the products formed.

Data and results of the experiments 1 and 2 carried out according to the above are mentioned in Table III.

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TABLE III

Exp. No.	Pd acetate (mmol)	Monodentate ligand (mmol)	Acid with pKa <2 (mmol)	Solvent (ml)	Reaction temperature, °C	Reaction time, h	Conversion, mol C ₃ H ₆ /gram-atom Pd/hr.	Selectivity, % mol
1	0.1	triphenylphosphine (3)	CF ₃ SO ₃ H (4)	toluene (50)	90	5	30	98
2	0.1	2-carboxyphenyl-diphenylphosphine (1.5)	HF ₄ (4)	chloroform (50)	100	5	20	95

Example IV

- A 300 ml magnetically stirred Hastelloy C autoclave ("Hastelloy" is a trade mark) was charged with 40 ml toluene, 10 ml acetic acid and 0.1 mmol palladium acetate and 4 mmol $\text{CF}_3\text{SO}_3\text{H}$ as catalytic system. The autoclave was flushed with ethene and filled with ethene at a pressure of 40 bar, sealed and heated to 70°C.
- After a reaction time of 1 hour the contents of the autoclave were analyzed by gas/liquid chromatography. The conversion of ethene to dimerization products was 4800 mol ethene per gramatom palladium per hour. The conversion of acetic acid to sec-butyl acetate was 78 %mol.

Example V

- A 300 ml magnetically stirred Hastelloy C autoclave ("Hastelloy" is a trade mark) was charged with 50 ml methyl acrylate and 0.5 mmol ruthenium acetylacetonate, 0.5 mmol 1,3-propanediylbis(diphenylphosphine) and 3 mmol trifluoromethanesulfonic acid as catalytic system. The autoclave was flushed with ethene and filled with ethene at a pressure of 40 bar, sealed and heated to 90°C. After a reaction time of 5 hours the contents were analyzed by gas/liquid chromatography.

The conversion of methyl acrylate was 40% mol. The composition of the product mixture was:

	methyl pentenoates	30% mol,
	butenes	30% mol,
	acrylate dimers	40% mol.

Example VI

- A 300 ml magnetically stirred Hastelloy C autoclave ("Hastelloy" is a trade mark) was charged with 50 ml methyl acrylate and 0.5 mmol palladium acetate, 1 mmol triphenylphosphine and 3 mmol trifluoromethanesulfonic acid as catalytic system. The autoclave was flushed with ethene and filled with ethene at a pressure of 40 bar, sealed and heated to 70°C. After a reaction time of 1 hour the contents were analyzed by gas/liquid chromatography.

The conversion of methyl acrylate was 30% mol. The composition of the product mixture was:

	methyl pentenoates	43% mol,
	butenes	46% mol,
	acrylate dimers	11% mol.

Claims

1. A process for the preparation of dimerization products from aliphatic mono-olefins having 2—12 carbon atoms per molecule in the presence of a catalytic system derivable from a compound of a precious Group VIII metal and an acid, characterized in that the aliphatic mono-olefin is contacted in an aprotic organic solvent with a catalytic system formed by combining a palladium and/or ruthenium compound and an acid with a pKa of less than 2, except hydrohalogenic acids.
2. A process as claimed in claim 1, characterized in that the acid with a pKa of less than 2 is HBF_4 .
3. A process as claimed in claim 1, characterized in that the acid with a pKa of less than 2 is a sulphonic acid.
4. A process as claimed in claim 3, characterized in that the acid with a pKa of less than 2 is trifluoromethanesulphonic acid or p-toluenesulphonic acid.
5. A process as claimed in any one of the preceding claims, characterized in that the catalytic system is formed by combining the palladium and/or ruthenium compound, a ligand containing at least one atom of Group Va of the Periodic Table of the Elements as coordinating atom and the acid with a pKa of less than 2 in a quantity of more than 1 equivalent acid per gramatom Group Va atom present in the ligand.
6. A process as claimed in any one of the preceding claims, characterized in that the ligand is a monodentate ligand which comprises a compound containing one trivalent N or P atom which is bonded to at least one aromatic hydrocarbon group.
7. A process as claimed in any one of the preceding claims, characterized in that the monodentate ligand comprises N,N'-dimethylaniline or a derivative thereof.
8. A process as claimed in any one of claims 1 to 6, characterized in that the monodentate ligand comprises triphenylphosphine or a derivative thereof.
9. A process as claimed in any one of claims 1 to 5, characterized in that the monodentate ligand comprises a compound containing a trivalent N atom, which is a member of a heterocyclic aromatic ring.
10. A process as claimed in any one of claims 1 to 5 and 9, characterized in that the monodentate ligand comprises pyridine or a derivative thereof.
11. A process as claimed in any one of claims 1 to 5, characterized in that the ligand is a chelate ligand which comprises a compound containing at least two atoms of Group Va of the Periodic Table of the Elements, which are connected through a chain comprising 2—6 carbon atoms.
12. A process as claimed in any one of claims 1 to 5 and 11, characterized in that the chelate ligand comprises a compound which contains in the molecule a group of the formula



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Example IV

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- 5 After a reaction time of 1 hour the contents of the autoclave were analyzed by gas/liquid chromatography. The conversion of ethene to dimerization products was 4800 mol ethene per gramatom palladium per hour. The conversion of acetic acid to sec-butyl acetate was 78 %mol.

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hours the contents were analyzed by gas/liquid chromatography. The conversion of methyl acrylate was 40% mol. The composition of the product mixture was:

	methyl pentenoates	30% mol,
	butenes	30% mol,
20	acrylate dimers	40% mol.

Example VI

- A 300 ml magnetically stirred Hastelloy C autoclave ("Hastelloy" is a trade mark) was charged with 50 ml methyl acrylate and 0.5 mmol palladium acetate, 1 mmol triphenylphosphine and 3 mmol trifluoromethanesulfonic acid as catalytic system. The autoclave was flushed with ethene and filled with ethene at a pressure of 40 bar, sealed and heated to 70°C. After a reaction time of 1 hour the contents were analyzed by

gas/liquid chromatography. The conversion of methyl acrylate was 30% mol. The composition of the product mixture was:

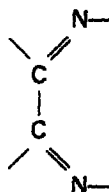
	methyl pentenoates	43% mol,
	butenes	46% mol,
30	acrylate dimers	11% mol.

Claims

- 35 1. A process for the preparation of dimerization products from aliphatic mono-olefins having 2—12 carbon atoms per molecule in the presence of a catalytic system derivable from a compound of a precious Group VIII metal and an acid, characterized in that the aliphatic mono-olefin is contacted in an aprotic organic solvent with a catalytic system formed by combining a palladium and/or ruthenium compound and
- 40 an acid with a pKa of less than 2, except hydrohalogenic acids.
2. A process as claimed in claim 1, characterized in that the acid with a pKa of less than 2 is HBF_4 .
3. A process as claimed in claim 1, characterized in that the acid with a pKa of less than 2 is a sulphonic acid.
4. A process as claimed in claim 3, characterized in that the acid with a pKa of less than 2 is
- 15 trifluoromethanesulphonic acid or p-toluenesulphonic acid.
5. A process as claimed in any one of the preceding claims, characterized in that the catalytic system is formed by combining the palladium and/or ruthenium compound, a ligand containing at least one atom of Group Va of the Periodic Table of the Elements as coordinating atom and the acid with a pKa of less than 2 in a quantity of more than 1 equivalent acid per gramatom Group Va atom present in the ligand.
- 50 6. A process as claimed in any one of the preceding claims, characterized in that the ligand is a monodentate ligand which comprises a compound containing one trivalent N or P atom which is bonded to at least one aromatic hydrocarbon group.
7. A process as claimed in any one of the preceding claims, characterized in that the monodentate ligand comprises N,N'-dimethylaniline or a derivative thereof.
- 55 8. A process as claimed in any one of claims 1 to 6, characterized in that the monodentate ligand comprises triphenylphosphine or a derivative thereof.
9. A process as claimed in any one of claims 1 to 5, characterized in that the monodentate ligand comprises a compound containing a trivalent N atom, which is a member of a heterocyclic aromatic ring.
10. A process as claimed in any one of claims 1 to 5 and 9, characterized in that the monodentate ligand
- 60 comprises pyridine or a derivative thereof.
11. A process as claimed in any one of claims 1 to 5, characterized in that the ligand is a chelate ligand which comprises a compound containing at least two atoms of Group Va of the Periodic Table of the Elements, which are connected through a chain comprising 2—6 carbon atoms.
12. A process as claimed in any one of claims 1 to 5 and 11, characterized in that the chelate ligand
- 65 comprises a compound which contains in the molecule a group of the formula



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13. A process as claimed in any one of the preceding claims, characterized in that the quantity of ligand
10 is at least 1 mol ligand per gramatom palladium and/or ruthenium.

14. A process as claimed in any one of the preceding claims, characterized in that the quantity of the acid with a pKa of less than 2 is at least 10 equivalent acid per gramatom palladium and/or ruthenium.

15. A process as claimed in any one of the preceding claims, characterized in that the aliphatic mono-olefin is ethene.

16. A process as claimed in any one of claims 1 to 14, characterized in that the aliphatic mono-olefin is propene.

Patentansprüche

20 1. Verfahren zur Herstellung von Dimerisationsprodukten aus aliphatischen Monoolefinen mit 2 bis 12 Kohlenstoffatomen je Molekül in Gegenwart eines von einer Verbindung eines Gruppe VIII-Edelmetalles und einer Säure herleitbaren katalytischen Systems, dadurch gekennzeichnet, daß das aliphatische Monoolefin in einem aprotischen organischen Lösungsmittel mit einem katalytischen System, das durch
25 Kombinieren einer Palladium- und/oder Rutheniumverbindung und einer Säure mit einem pKa-Wert von kleiner als 2, ausgenommen Halogenwasserstoffsäuren, gebildet worden ist, in Berührung gebracht wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Säure mit einem pKa-Wert von kleiner als 2 HBF₄ ist.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Säure mit einem pKa-Wert von kleiner als 2 eine Sulfonsäure ist.

30 4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß die Säure mit einem pKa-Wert von kleiner als 2 Trifluoromethansulfonsäure oder para-Toluolsulfonsäure ist.

5. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das katalytische System durch Kombinieren der Palladium- und/oder Rutheniumverbindung, eines Liganden, der
35 wenigstens ein Atom der Gruppe Va des Periodensystems der Elemente als koordinierendes Atom enthält, und der Säure mit einem pKa-Wert von kleiner als 2, in einer Menge von mehr als ein Äquivalent Säure je Grammatom des im Liganden vorliegenden Gruppe Va-Atoms gebildet wird.

6. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß der Ligand ein Monodentatligand ist, der eine Verbindung umfaßt, die ein dreiwertiges N- oder P-Atom enthält, das an
40 wenigstens eine aromatische Kohlenwasserstoffgruppe gebunden ist.

7. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß der Monodentatligand N,N'-Dimethylanilin oder ein Derivat hiervon umfaßt.

8. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß der Monodentatligand Triphenylphosphin oder ein Derivat hiervon umfaßt.

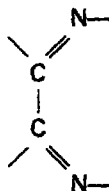
9. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß der Monodentatligand
45 eine Verbindung umfaßt, die ein dreiwertiges Stickstoffatom enthält, das Teil eines heterozyklischen aromatischen Ringes ist.

10. Verfahren nach einem der Ansprüche 1 bis 5 und 9, dadurch gekennzeichnet, daß der Monodentatligand Pyridin oder ein Derivat hiervon umfaßt.

11. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß der Ligand ein
50 Chelatligand ist, der eine Gruppe umfaßt, die wenigstens zwei Gruppe-Va-Atome des Periodensystems der Elemente enthält, die über eine 2 bis 6 Kohlenstoffatome umfassende Kette verbunden sind.

12. Verfahren nach einem der Ansprüche 1 bis 5 und 11, dadurch gekennzeichnet, daß der Chelatligand eine Verbindung umfaßt, die in dem Molekül eine Gruppe der Formel

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enthält.

13. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Menge des
65 Liganden wenigstens ein Mol Ligand je Grammatom Palladium und/oder Ruthenium beträgt.

14. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Menge der Säure mit einem pKa-Wert von kleiner als 2 wenigstens 10 Säureäquivalente je Grammatom Palladium und/oder Ruthenium ausmacht.

15. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das aliphatische Monoolefin Ethen ist.

16. Verfahren nach einem der Ansprüche 1 bis 14, dadurch gekennzeichnet, daß das aliphatische Monoolefin Propen ist.

Revendications

1. Procédé pour la préparation de produits de dimérisation à partir de monooléfines aliphatiques ayant de 2 à 12 atomes de carbone par molécule, en présence d'un système catalytique qui provient d'un composé d'un métal précieux du groupe VIII et d'un acide, caractérisé en ce que l'on met la monooléfine aliphatique, en contact, dans un solvant organique aprotique, avec un système catalytique formé par la combinaison d'un composé du palladium et/ou du ruthénium et d'un acide avec un pKa inférieur à 2, à l'exclusion des acides halogénhydriques.

2. Procédé selon la revendication 1, caractérisé en ce que l'acide avec un pKa inférieur à 2 est HBF_4 .

3. Procédé selon la revendication 1, caractérisé en ce que l'acide avec un pKa inférieur à 2 est un acide sulfonique.

4. Procédé selon la revendication 3, caractérisé en ce que l'acide avec un pKa inférieur à 2 est l'acide trifluorométhanesulfonique ou l'acide p-toluènesulfonique.

5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le système catalytique est formé par la combinaison du composé de palladium et/ou de ruthénium, d'un ligand contenant au moins un atome du groupe Vb du tableau périodique des éléments à titre d'atome de coordination et de l'acide avec un pKa inférieur à 2 en une quantité supérieure à un équivalent d'acide par atome-gramme d'atome du groupe Va présent dans le ligand.

6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le ligand est un ligand monodenté qui comprend un composé contenant un atome trivalent de N ou de P qui est lié à au moins un groupe hydrocarbure aromatique.

7. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le ligand monodenté comprend la N,N'-dimethylaniline ou un de ses dérivés.

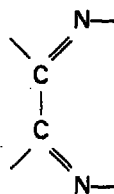
8. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que le ligand monodenté comprend la triphénylphosphine ou un de ses dérivés.

9. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que le ligand monodenté comprend un composé contenant un atome trivalent de N qui est un élément d'un noyau aromatique hétérocyclique.

10. Procédé selon l'une quelconque des revendications 1 à 5 et 9, caractérisé en ce que le ligand monodenté englobe la pyridine ou un de ses dérivés.

11. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que le ligand est un ligand chélate qui comprend un composé contenant au moins deux atomes du groupe Vb du tableau périodique des éléments qui sont reliés par l'intermédiaire d'une chaîne comprenant de 2 à 6 atomes de carbone.

12. Procédé selon l'une quelconque des revendications 1 à 5 et 11, caractérisé en ce que le ligand chélate comprend un composé qui contient dans la molécule un groupe de formule



13. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la quantité de ligand est d'au moins une mole de ligand par atome-gramme de palladium et/ou de ruthénium.

14. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la quantité de l'acide avec un pKa inférieur à 2 est d'au moins 10 équivalents d'acide par atome-gramme de palladium et/ou de ruthénium.

15. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la monooléfine aliphatique est l'éthène.

16. Procédé selon l'une quelconque des revendications 1 à 14, caractérisé en ce que la monooléfine aliphatique est le propène.

