



Process for the telomerization of acyclic olefins

The present invention relates to a process for the telomerization of acyclic olefins having at least two
5 conjugated double bonds (I) by means of nucleophiles (II) using a palladium complex as catalyst.

For the purposes of the present invention, telomerization is the reaction of olefins having
10 conjugated double bonds (conjugated dienes) in the presence of a nucleophile (telogen). Main products obtained are compounds made up of two equivalents of the diene and one equivalent of the nucleophile.

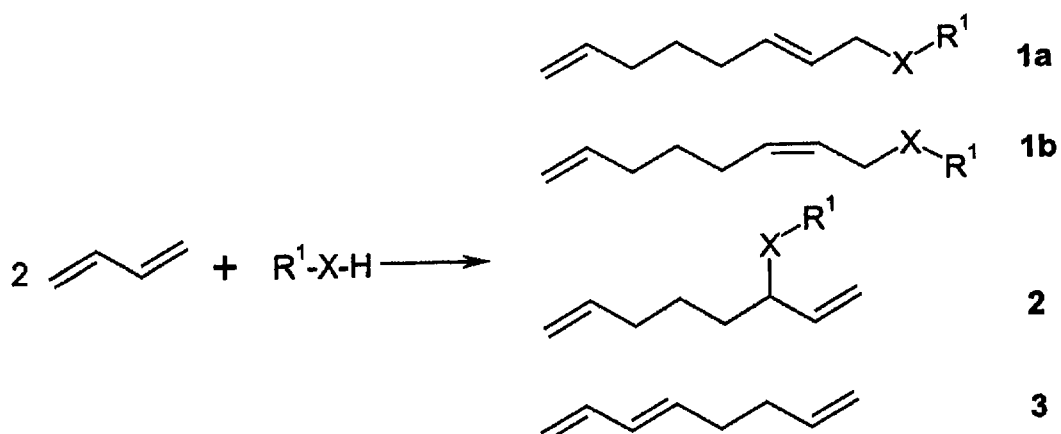
15 The products of the telomerization reaction have industrial importance as versatile precursors for solvents, plasticizers, fine chemicals and intermediates for active compounds. The compounds octadienol, octadienyl ether and octadienyl esters
20 obtainable from butadiene are potential intermediates in processes for preparing corresponding alkenes.

The telomerization of dienes by means of nucleophiles is an industrially interesting method of upgrading
25 inexpensive, industrially available dienes. Owing to their ready availability, the use of butadiene, isoprene or cracker fractions comprising these dienes is of particular interest. However, up to the present time, the telomerization of butadiene has been employed
30 in practice only by the company Kuraray in the fine chemicals field for the synthesis of 1-octanol. Reasons why telomerization processes have not been used more widely include unsatisfactory catalyst activities, catalyst productivities and selectivity problems
35 associated with telomerization catalysts. Thus, the known telomerization processes lead to high catalyst costs and/or by-products which prevent industrial implementation.



Halogen-free palladium(0) and palladium(II) compounds have been found to be effective catalysts for telomerization (A. Behr, in "Aspects of Homogeneous Catalysis", editor: R. Ugo, D. Reidel Publishing Company, Doordrecht/Boston/Lancaster, **1984**, Vol. 5, 3). In addition, compounds of other transition metals, e.g. cobalt (R. Baker, A. Onions, R.J. Popplestone, T.N. Smith, *J. Chem. Soc., Perkin Trans. II* **1975**, 1133-1138), rhodium, nickel (R. Baker, D.E. Halliday, T.N. Smith, *J. Organomet. Chem.* **1972**, 35, C61-C63; R. Baker, *Chem. Rev.* **1973**, 73, 487-530; R. Baker, A.H. Cook, T.N. Smith, *J. Chem. Soc., Perkin Trans. II* **1974**, 1517-1524) and platinum have also been used as catalysts. However, the latter systems are inferior to palladium complexes in respect of activity and selectivity.

Telomerization has been comprehensively described in the technical literature. The abovementioned known catalysts generally give, for example in the telomerization of butadiene by means of methanol, mixtures of the products **1a**, **1b**, **2**, **3** shown, where $X = O$, $R^1 = Me$. Main products are the desired industrially important linear telomers **1a** and **1b**. However, significant proportions of the branched telomer **2** and of 1,3,7-octatriene **3** are formed.



Variable yields of 4-vinyl-1-cyclohexene (Diels-Alder

product of butadiene) are also formed, as are, generally in only small amounts, further by-products. This product spectrum is generally also found when using other nucleophiles having active H atoms, with
5 the methoxy group being replaced by the corresponding radicals of the respective nucleophile.

Significant formation of the by-products mentioned is a further reason for implementation of an economical and environmentally friendly process being extraordinarily
10 difficult. Thus, the abovementioned problems cannot be solved satisfactorily despite the fact that the telomerization of butadiene by means of methanol has been intensively researched and patented by a number of
15 companies.

In a continuous process which has been described by Dow Chemical in WO 91/09822 in 1989 and uses palladium acetylacetonate/2 equivalents of triphenylphosphine as
20 catalyst, catalyst productivities (turnover numbers) up to 44 000 were achieved. However, the chemo-selectivities to the target product 1 at such catalyst turnover numbers are < 85%.

25 In 1987, National Distillers and Chem. Corp. (US 4,642,392, US 4,831,183) described a batch process for preparing octadienyl ethers. In this process, the product mixture was separated by distillation from the catalyst (palladium acetate/5 equivalents of
30 triphenylphosphine) which remained as a solution in tetraglyme. The catalyst can then be reused up to twelve times, with supplementary phosphine being added each time. However, the starting batch gave the linear ether in a yield of only 57% (corresponds to a TON of
35 2 000). The n/iso ratio of product 1 to product 2 was in this case only 3.75:1. In a further patent by National Distillers, the product mixture was separated from the reaction solution by extraction with hexane.

The telomerization was carried out in dimethylformamide or sulfolane using a catalyst mixture of palladium(II) acetate/3 equivalents of triphenylphosphinemonosulfonate. The first batch gave the linear telomer with
5 a TON of 900. The selectivity to the linear alcohol was a low 40%.

Longer-chain primary alcohols such as ethanol, propanol and butanol (J. Beger, H. Reichel, *J. Prakt. Chem.*
10 **1973**, 315, 1067) also form the corresponding telomers with butadiene. However, the catalyst activity of the known catalysts is in these cases even lower than in those mentioned above. Thus, identical reaction
15 conditions [Pd(acetylacetonate)₂/PPh₃/butadiene/alcohol = 1:2:2 000:5 000; 60°C/10 h] result in formation of the telomers of methanol in a yield of 88%, those of propanol in a yield of 65% and those of nonanol in a yield of only 21%.

20 In summary, it can be said that the known palladium-phosphine catalysts for telomerization reactions of butadiene with alcohols do not give satisfactory catalytic turnover numbers (= TONs). TONs of > 100 000 as are sought in industry have rarely been described
25 for known systems. At the same time, it is desirable to achieve high selectivities of > 95% chemoselectivity and regioselectivity in order to obtain an ecologically advantageous process.

30 Like alcohols, carboxylic acids are suitable nucleophiles in telomerization reactions. Acetic acid and butadiene give good yields of the corresponding octadienyl derivatives **1a**, **1b** and **2** in which R = Me-CO, X = O (DE 2 137 291). The ratio of the products **1/2** can
35 be influenced via the ligands on the palladium (D. Rose, H. Lepper, *J. Organomet. Chem.* **1973**, 49, 473). Use of triphenylphosphine as ligand gave a ratio of 4/1, while use of tris(o-methylphenyl) phosphite

enabled the ratio to be increased to 17/1. Other carboxylic acids such as pivalic acid, benzoic acid or methacrylic acid, and also dicarboxylic acids, can likewise be reacted with butadiene.

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In US 5 030 792, Shell Oil has described a process for preparing α -olefins which is based on the telomerization of conjugated dienes by means of carboxylic acids.

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Telomerization reactions in which water is used as nucleophile have been intensively studied by, inter alia, Kuraray (US 4 334 117, US 4 356 333, US 5 057 631). Here, phosphines, mostly water-soluble phosphines, or phosphonium salts (EP 0 296 550) are used as ligands. The use of water-soluble diphosphines as ligands is described in WO 98 08 794, while DE 195 23 335 claims the reaction of alkadienes with water in the presence of phosphonite or phosphinite ligands.

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The telomerization of butadiene by means of nucleophiles such as formaldehyde, aldehydes, ketones, carbon dioxide, sulfur dioxide, sulfinic acids, β -keto esters, β -diketones, malonic esters, α -formylketones and silanes has likewise been described.

25

The major part of the work on telomerization has been carried out using butadiene. However, the reaction is also applicable to other dienes having conjugated double bonds. These can formally be regarded as derivatives of butadiene in which the hydrogen atoms are replaced by other groups. Isoprene is of particular industrial importance. Since isoprene is, unlike butadiene, an unsymmetrical molecule, telomerization results in the formation of further isomers (J. Beger, Ch. Duschek, H. Reichel, *J. Prakt. Chem.* **1973**, 315, 1077-89). The ratio of these isomers is influenced to a

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considerable extent by the type of nucleophile and the choice of ligands.

Owing to the stated importance of telomerization products and the problems associated with the prior art, there is a great need for new catalyst systems for telomerization reactions, which have inexpensive stable ligands, which do not display the disadvantages of the known catalytic processes, which are suitable for industrial implementation and which give the telomerization products in high yield, with high catalyst productivity and in high purity.

This object is achieved by a process for the telomerization of acyclic olefins having at least two conjugated double bonds (I) or mixtures comprising such olefins by means of nucleophiles (II) using a palladium-carbene complex as catalyst.

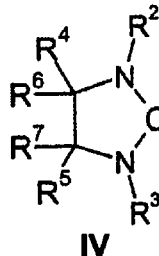
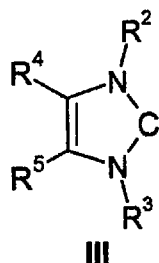
In a preferred embodiment, the nucleophiles (II) used are compounds of the formula (IIa) or (IIb),



where R^1 , $\text{R}^{1'}$ are selected independently from among hydrogen, linear, branched or cyclic $\text{C}_1\text{-C}_{22}$ -alkyl groups, alkenyl groups, alkynyl groups, the carboxyl group and $\text{C}_6\text{-C}_{18}$ -aryl groups, where these groups may bear substituents selected from the group consisting of $-\text{CN}$, $-\text{COOH}$, $-\text{COO-alkyl-(C}_1\text{-C}_8)$, $-\text{CO-alkyl-(C}_1\text{-C}_8)$, $-\text{aryl-(C}_6\text{-C}_{10})$, $-\text{COO-aryl-(C}_6\text{-C}_{10})$, $-\text{CO-aryl-(C}_6\text{-C}_{10})$, $-\text{O-alkyl-(C}_1\text{-C}_8)$, $-\text{O-CO-alkyl-(C}_1\text{-C}_8)$, $-\text{N-alkyl}_2\text{-(C}_1\text{-C}_8)$, $-\text{CHO}$, $-\text{SO}_3\text{H}$, $-\text{NH}_2$, $-\text{F}$, $-\text{Cl}$, $-\text{OH}$, $-\text{CF}_3$, $-\text{NO}_2$,

and the radicals R^1 , $\text{R}^{1'}$ may be joined to one another via covalent bonds.

The catalyst used is preferably a palladium complex comprising carbene ligands of the formula (III) or (IV)



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- where R^2 and R^3 are each, independently of one another, a linear, branched or cyclic C_1 - C_{24} -alkyl or C_5 - C_{18} -aryl group and the alkyl and aryl groups may, independently of one another, bear the substituents -CN, -COOH, COO-alkyl- (C_1 - C_8), -CO-alkyl- (C_1 - C_8), -aryl- (C_5 - C_{18}), -alkyl- (C_1 - C_{24}), -COO-aryl- (C_6 - C_{10}), -CO-aryl- (C_6 - C_{10}), -O-alkyl- (C_1 - C_8), -O-CO-alkyl- (C_1 - C_8), -N-alkyl₂- (C_1 - C_8), -CHO, -SO₃H, -NH₂, -F, -Cl, -OH, -CF₃, -NO₂, ferrocenyl,
- and R^4 to R^7 are each, independently of one another, hydrogen, -CN, -COOH, -COO-alkyl- (C_1 - C_8), -CO-alkyl- (C_1 - C_8), -COO-aryl- (C_6 - C_{10}), -CO-aryl- (C_6 - C_{10}), -O-alkyl- (C_1 - C_8), -O-CO-alkyl- (C_1 - C_8), -N-alkyl₂- (C_1 - C_8), -CHO, -SO₃H, -NH₂, -F, -Cl, -OH, -CF₃, -NO₂ or a linear, branched or cyclic C_1 - C_{24} -alkyl or C_6 - C_{18} -aryl group and the alkyl and aryl groups may, independently of one another, bear the substituents -CN, -COOH, -COO-alkyl- (C_1 - C_8), -CO-alkyl- (C_1 - C_8), -aryl- (C_6 - C_{10}), -COO-aryl- (C_6 - C_{10}), -CO-aryl- (C_6 - C_{10}), -O-alkyl- (C_1 - C_8), -O-CO-alkyl- (C_1 - C_8), -N-alkyl₂- (C_1 - C_8), -CHO, -SO₃H, -NH₂, -F, -Cl, -OH, -CF₃, -NO₂, where the radicals R^4 and R^5 may also be part of a bridging aliphatic or aromatic ring.

In the telomerization, it is in principle possible to use all acyclic olefins having at least two conjugated double bonds. For the purposes of the present invention, the use of 1,3-butadiene and isoprene

(2-methyl-1,3-butadiene) is preferred. It is possible to use both the pure dienes and mixtures in which these dienes are present.

5 As 1,3-butadiene-containing mixtures, preference is given to using mixtures of 1,3-butadiene with other C₄-hydrocarbons and/or C₅-hydrocarbons. Such mixtures are obtained, for example, in cracking processes for the production of ethene, in which refinery gases,
10 naphtha, gas oil, LPG (liquefied petroleum gas), NGL (natural gas liquid), etc., are used as feedstocks. The C₄ fractions obtained as by-product in these processes comprise, depending on the cracking process, variable amounts of 1,3-butadiene. Typical 1,3-butadiene
15 concentrations in the C₄ fraction obtained from a naphtha steam cracker are 20-70% of 1,3-butadiene.

The C₄ components n-butane, i-butane, 1-butene, cis-2-butene, trans-2-butene and i-butene which are
20 likewise present in these fractions do not interfere significantly with the reaction in the telomerization step.

In contrast, dienes having cumulated double bonds
25 (1,2-butadiene, allene, etc.) and alkynes, in particular vinylacetylene, can act as moderators in the telomerization reaction. It is therefore advantageous for the C₄-alkynes and, if appropriate, the 1,2-butadiene to be removed beforehand (DE 195 23 335).
30 This can, if possible, be carried out by means of physical processes such as distillation or extraction. A possible chemical route is selective hydrogenation to convert the alkynes into alkenes or alkanes and the cumulated dienes into monoenes. Processes for such
35 hydrogenations are prior art and are described, for example, in WO 98/12160, EP-A-0 273 900, DE-A-37 44 086 or US 4 704 492.

As nucleophiles, preference is given to using any compounds which have the formula **II**. Examples of telogens of the formula **II** are

- water,
- 5 - monoalcohols and phenols such as methanol, ethanol, n-propanol, isopropanol, allyl alcohol, butanol, octanol, 2-ethylhexanol, isononanol, benzyl alcohol, cyclohexanol, cyclopentanol, 2-methoxyethanol, phenol or 2,7-octadien-1-ol,
- 10 - dialcohols such as ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,2-butanediol, 2,3-butanediol and 1,3-butanediol,
- polyols such as glycerol, glucose, sucrose,
- hydroxy compounds such as α -hydroxyacetic esters,
- 15 - carboxylic acids such as acetic acid, propanoic acid, butanoic acid, isobutanoic acid, benzoic acid, 1,2-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid, 1,2,4-benzenetricarboxylic acid,
- 20 - ammonia,
- primary amines such as methylamine, ethylamine, propylamine, butylamine, octylamine, 2,7-octadienylamine, dodecyclamine [sic], aniline, ethylenediamine or hexamethylenediamine,
- 25 - secondary amines such as dimethylamine, diethylamine, N-methylaniline, bis(2,7-octadienyl)amine, dicyclohexylamine, methylcyclohexylamine, pyrrolidine, piperidine, morpholine, piperazine or hexamethylenimine.

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Telogens which can themselves be obtained via a telomerization reaction can be introduced directly or else formed in situ. Thus, for example, 2,7-octadien-1-ol can be formed in situ from water and butadiene in the presence of the telomerization catalyst, 2,7-octadienylamine can be obtained from ammonia and 1,3-butadiene, etc.

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Particularly preferred telogens are water, methanol, ethanol, n-butanol, allyl alcohol, 2-methoxyethanol, phenol, ethylene glycol, 1,3-propanediol, glycerol, glucose, sucrose, acetic acid, butanoic acid,
5 1,2-benzenedicarboxylic acid, ammonia, dimethylamine and diethylamine.

As solvents, use is generally made of the nucleophile employed in the reaction, provided that it is liquid
10 under the reaction conditions. However, other solvents can also be used. The solvents used should be largely inert. The addition of solvents is preferred when using nucleophiles which are solid under the reaction conditions or in the case of products which would be
15 obtained as solids under the reaction conditions. Suitable solvents include aliphatic, cycloaliphatic and aromatic hydrocarbons such as C₃-C₂₀-alkanes, mixtures of lower alkanes (C₃-C₂₀), cyclohexane, cyclooctane, ethylcyclohexane, alkenes and polyenes,
20 vinylcyclohexene, 1,3,7-octatriene, the C₄-hydrocarbons from C₄ fractions from crackers, benzene, toluene and xylene; polar solvents such as tertiary and secondary alcohols, amides such as acetamide, dimethylacetamide and dimethylformamide, nitriles such as acetonitrile
25 and benzonitrile, ketones such as acetone, methyl isobutyl ketone and diethyl ketone; carboxylic esters such as ethyl acetate, ethers such as dipropyl ether, diethyl ether, dimethyl ether, methyl octyl ether, 3-methoxyoctane, dioxane, tetrahydrofuran, anisole,
30 alkyl and aryl ethers of ethylene glycol, diethylene glycol and polyethylene glycol and other polar solvents such as sulfolane, dimethyl sulfoxide, ethylene carbonate, propylene carbonate and water. Ionic liquids, for example imidazolium or pyridinium salts,
35 can also be used as solvents.

The solvents are used either alone or as mixtures of various solvents.

The temperature at which the telomerization reaction is carried out is in the range from 10 to 180°C, preferably from 30 to 120°C, particularly preferably from 40 to 100°C. The reaction pressure is from 1 to 300 bar, preferably from 1 to 120 bar, particularly preferably from 1 to 64 bar and very particularly preferably from 1 to 20 bar.

An essential feature of the process of the invention is that the telomerization reaction is carried out using catalysts based on palladium complexes comprising carbene ligands.

Examples of carbene ligands of the formula **III** or **IV** and complexes in which such ligands are present have been described in the technical literature (W.A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, 109, 2257; *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 2162; V.P.W. Böhm, C.W.K. Gstöttmayr, T. Weskamp, W.A. Herrmann, *J. Organomet. Chem.* **2000**, 595, 186; DE 44 47 066).

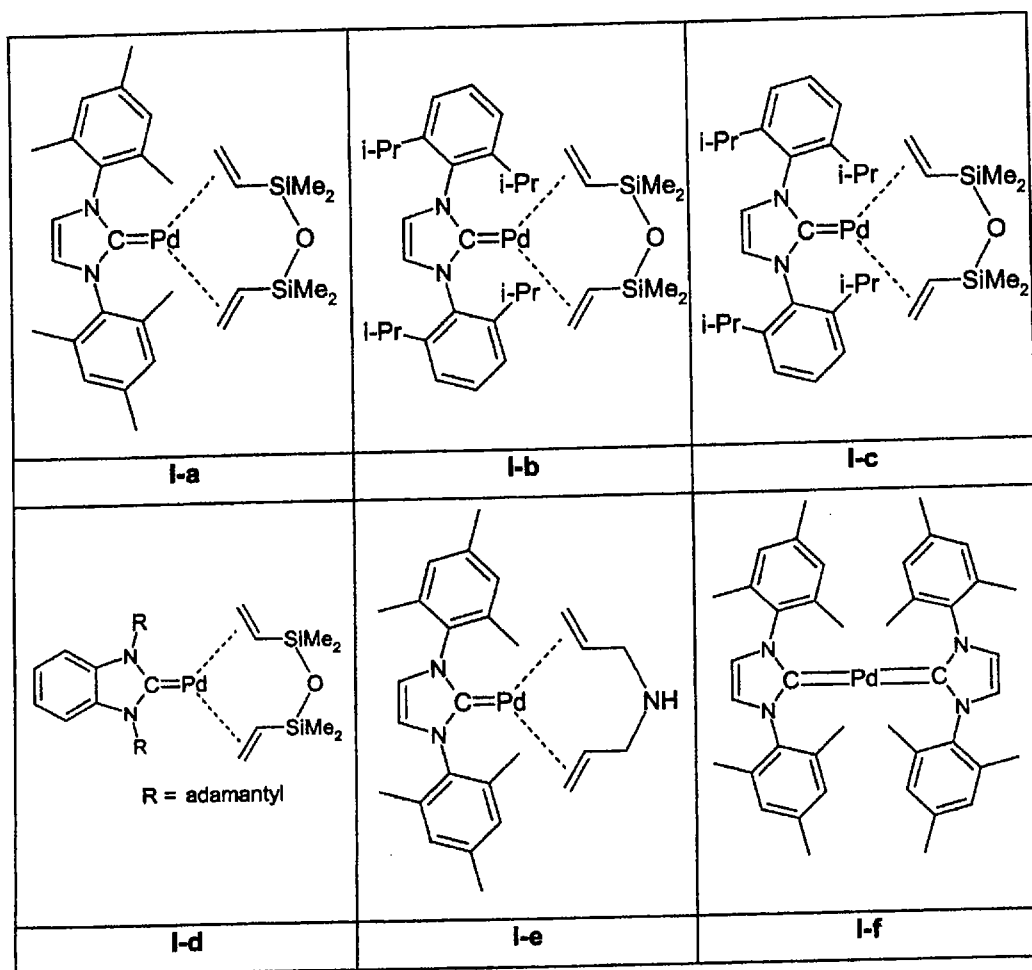
For the purposes of the present invention, the term carbene ligands encompasses both free carbenes which can function as ligand and carbenes coordinated to palladium.

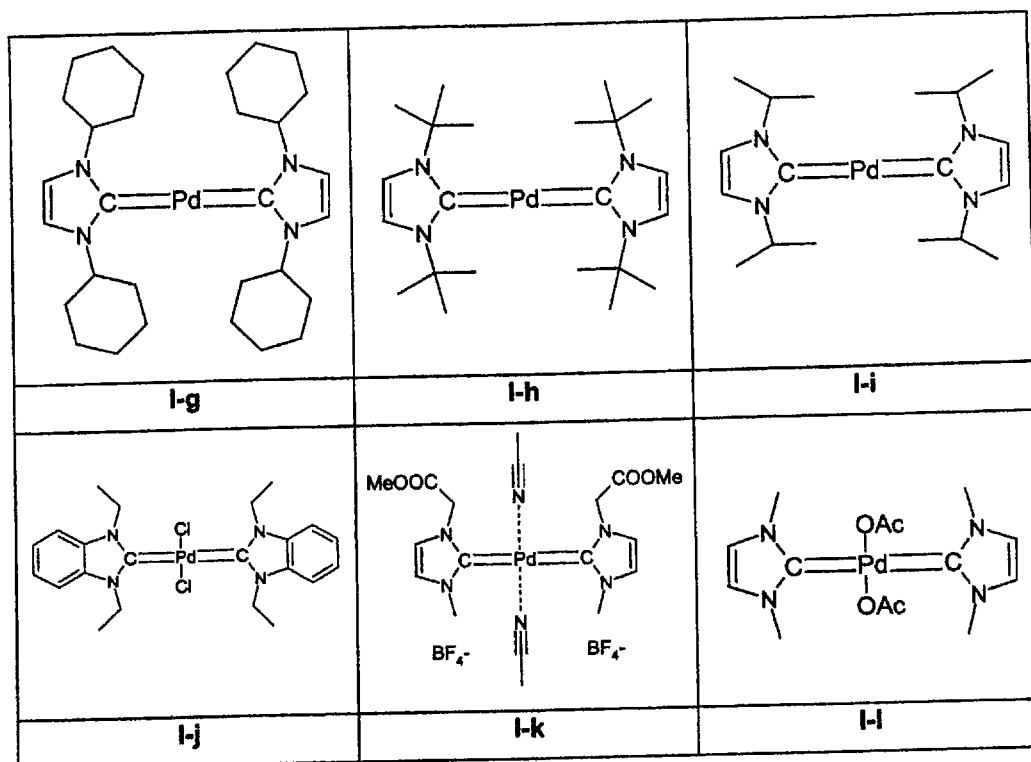
The catalyst metal palladium from which the active catalysts are formed under the reaction conditions can be introduced into the process in various ways.

- a) As palladium-carbene complexes in which the palladium is preferably present in the oxidation state (II) or (0).
- b) In the form of palladium precursors from which the catalysts are formed in situ.

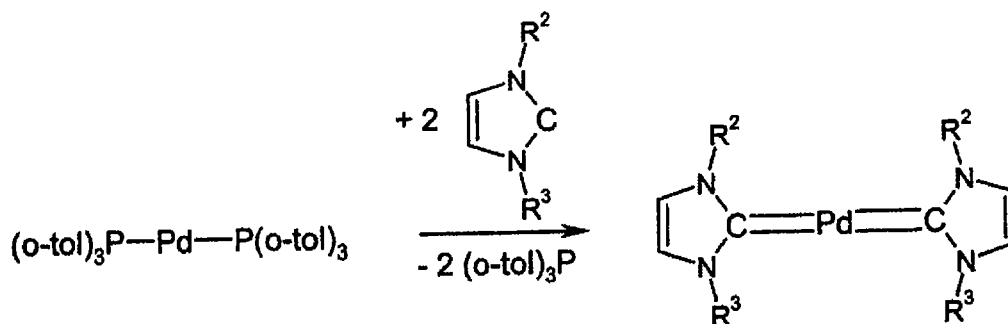
In the case of a):

Examples are palladium(0)-carbene-olefin complexes, palladium(0)-dicarbene complexes and palladium(II)-dicarbene complexes, palladium(0)-carbene-1,6-diene complexes. Compounds which can function as 1,6-diene
 5 are, for example, diallylamine, 1,1'-divinyldisiloxane, 2,7-octadienyl ether or 2,7-octadienylamines. Further examples are shown in the formulae I-a to I-e below.





The carbene complexes of palladium can be prepared in various ways. A simple route is, for example, the addition of carbene ligands or the replacement of ligands on palladium complexes by carbene ligands. Thus, for example, the complexes **I-f** to **I-i** are obtainable by replacement of the phosphorus ligands of the complex bis(tri-*o*-tolylphosphine)palladium(0) (T. Weskamp, W.A. Herrmann, *J. Organomet. Chem.* **2000**, 595, 186).



I-f $\text{R}^2 = \text{R}^3 = \text{mesityl}$

I-g $\text{R}^2 = \text{R}^3 = \text{c-hexyl}$

I-h $\text{R}^2 = \text{R}^3 = \text{t-butyl}$

I-i $\text{R}^2 = \text{R}^3 = \text{i-propyl}$

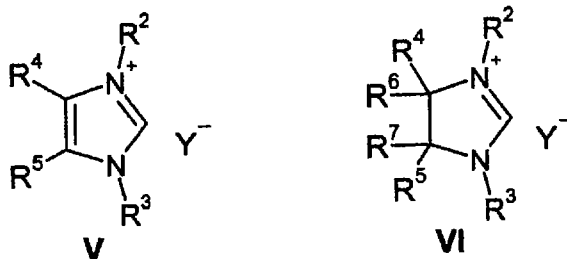
In the case of b):

Palladium precursors which can be used are, for example: palladium(II) acetate, palladium(II) chloride, 5 palladium(II) bromide, lithium tetrachloropalladate, palladium(II) acetylacetonate, palladium(0)-dibenzylideneacetone complexes, palladium(II) propionate, bis(acetonitrile)palladium(II) chloride, bis(triphenylphosphine)palladium(II) dichloride, 10 bis(benzonitrile)palladium(II) chloride, bis(tri-*o*-tolylphosphine)palladium(0) and further palladium(0) and palladium(II) complexes.

The carbenes of the formulae **III** and **IV** are used in the 15 form of free carbenes or as metal complexes or are generated in situ from carbene precursors.

Suitable carbene precursors are, for example, salts of the carbenes which have the formulae **V** and **VI**,

20



where R², R³, R⁴, R⁵, R⁶, R⁷ are as defined in the formulae **III** and **IV** and Y is a singly charged anionic group or a fraction corresponding to the stoichiometry 25 of a multiply charged anionic group.

Examples of Y are halides, hydrogensulfate, sulfate, alkylsulfates, arylsulfates, borates, hydrogen- 30 carbonate, carbonate, alkylcarboxylates, aryl-carboxylates.

The corresponding carbenes can be liberated from the

salts of the carbenes by, for example, reaction with a base.

5 The concentration of the catalyst, indicated formally in ppm (by mass) of palladium metal based on the total mass, is from 0.01 ppm to 1 000 ppm, preferably from 0.5 to 100 ppm, particularly preferably from 1 to 50 ppm.

10 The ratio [mol/mol] of carbene to Pd is from 0.01:1 to 250:1, preferably from 1:1 to 100:1, particularly preferably from 1:1 to 50:1. Apart from the carbene ligands, further ligands such as phosphorus ligands, e.g. triphenylphosphine, may be present in the reaction mixture.

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Due to the catalyst activities and stabilities, it is possible to use extremely small amounts of catalyst in the process of the invention. Apart from a process in which the catalyst is reused, it is therefore also an option not to recycle the catalyst. Both variants have been described in the patent literature (WO 90/13531, US 5254782, US 4642392).

25 It is often advantageous to carry out the telomerization reaction in the presence of bases. Preference is given to using basic components having a pK_b of less than 7, in particular compounds selected from the group consisting of amines, alkali metal salts and alkaline earth metal salts.

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Examples of suitable basic components are amines such as trialkylamines which may be alicyclic or/and open-chain, amides, alkali metal or/and alkaline earth metal salts of aliphatic or/and aromatic carboxylic acids, 35 e.g. acetates, propionates or benzoates, or appropriate carbonates, hydrogen carbonates, alkoxides of alkali metals and/or alkaline earth metals, phosphates, hydrogenphosphates or/and hydroxides, preferably of

lithium, sodium, potassium, calcium, magnesium, cesium, ammonium and phosphonium compounds. Preferred additives are hydroxides of the alkali metals and alkaline earth metals and metal salts of the nucleophile of the
5 formula **II**.

The basic component is generally used in an amount of from 0.01 mol% to 10 mol% (based on the olefin), preferably from 0.1 mol% to 5 mol% and very
10 particularly preferably from 0.2 mol% to 1 mol%.

In the process of the invention, the ratio [mol/mol] of diene used and nucleophile is from 1:100 to 100:1, preferably from 1:50 to 10:1, particularly preferably
15 from 1:10 to 2:1.

The process of the invention can be carried out continuously or batchwise and is not restricted to the use of particular types of reactor. Examples of
20 reactors in which the reaction can be carried out are stirred tank reactors, cascades of stirred tanks, flow tubes and loop reactors. Combinations of various reactors are also possible, for example a stirred tank reactor together with a downstream flow tube.

25 In the process of the invention, carbene ligands are used in telomerization reactions for the first time. Surprisingly, the catalysts used according to the invention are superior to the known palladium-phosphine
30 catalysts both in respect of selectivity and in respect of productivity. In the process of the invention, it is possible, for example, to achieve turnover values for the catalysts (catalyst productivities) in the order of 200 000 and more without problems in the telomerization
35 of butadiene by means of alcohols.

The following examples illustrate the invention without restricting the scope of the patent application.

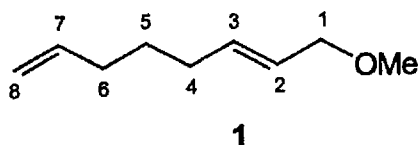
Examples**General procedure for the telomerization of butadiene
by means of methanol:**

In a 100 ml Schlenk tube, an appropriate amount of catalyst (from 0.01 to 0.0001 mol%) is dissolved in 56 g (1.75 mol) of methanol under protective gas. The solution is admixed with 5 mmol of triethylamine or sodium hydroxide. The reaction solution is subsequently drawn into the evacuated autoclave, the autoclave is cooled to $T < -10^{\circ}\text{C}$ and butadiene is condensed in (amount determined by means of the decrease in mass of the butadiene stock bottle). The autoclave is heated to the reaction temperature, and after the reaction is cooled to room temperature. Unreacted butadiene is condensed in a cold trap cooled by means of dry ice. The conversion is determined from the increase in mass of the reaction solution. To isolate the product, the solution is distilled under reduced pressure.

GC analysis: The reaction solution was admixed with 5 ml of isooctane (a) or 5 ml of diethylene glycol dimethyl ether (b) (GC standard).

2,7-Octadien-1-yl methyl ether:

GC (column HP 5/30 m, temp. program: 35°C , 10 min, at $8^{\circ}\text{C min}^{-1}$ to 280°C , inj.: 250°C , const. flow, a). $t_R(\text{vinylcyclohexene}) = 12.3 \text{ min}$, $t_R(\text{octatriene}) = 11.6 \text{ min}$ and 11.7 min , $t_R(\mathbf{1}) = 19 \text{ min}$, $t_R(\text{isooctane}) = 4.5 \text{ min}$.



^1H NMR (CDCl_3 , 400 MHz)

$\delta = 1.39$ (quint, $^3J_{5,4 \text{ and } 6} = 8 \text{ Hz}$, 2H, 5-H), 1.9 (m, 4H,

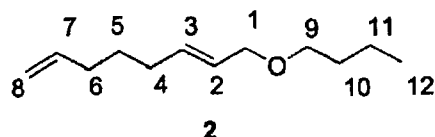
4-H and 6-H), 3.2 (s, 3H, OCH₃), 3.7 (d, ³J_{1,2} = 6 Hz, 2H, 1-H), 4.75-4.9 (m, 2H, 8-H), 5.35-5.45 (m, 1H, 7-H), 5.5-5.7 (m, 2H, 2-H and 3-H).

¹³C NMR (CDCl₃, 100 MHz):

5 δ = 28.6 (C-5), 32.0 (C-4), 33.5 (C-6), 57.9 (OCH₃), 73.5 (C-1), 114.9 (C-8), 126.9 (C-2), 134.8 (C-3), 138.8 (C-7).

2,7-Octadien-1-yl butyl ether:

10 **GC** (column HP 5/30 m, temp. program: 35°C, 10 min, at 8°C min⁻¹ to 280°C, inj.: 250°C, const. flow, b). t_R (vinylcyclohexene) = 12 min, t_R(octatriene) = 11.6 min and 11.7 min, t_R(**2**) 24.1 min, t_R(diglyme) = 17.1 min.



15

1 H NMR (CDCl₃, 400 MHz):

δ = 0.75 (t, J = 7.3 Hz, 3H, 12-H), 1.25 (sext, J = 7.1 Hz, 2H, 11-H), 1.39 (q, ³J_{5,4} and ₆ = 7 Hz, 2H, 5-H), 1.42 (quint, J = 7.1 Hz, 2H, 10-H), 1.9 (m, 4H, 4-H and 6-H), 3.26 (t, J = 6.7 Hz, 2H, 9-H), 3.7 (dd, J = 6 Hz, J = 1 Hz, 2H, 1-H), 4.76-4.9 (m, 2H, 8-H), 5.36-5.45 (m, 1H, 7-H), 5.5-5.7 (m, 2H, 2-H and 3-H).

20

¹³C NMR (CDCl₃, 100 MHz):

25 δ = 13.6 (C-12), 19.1 (C-11), 28.05 (C-5), 31.4 (C-10), 31.6 (C-4), 32.9 (C-6), 69.1 (C-9), 71.3 (C-1), 114.3 (C-8), 126.7 (C-2), 133.5 (C-3), 138.2 (C-7).

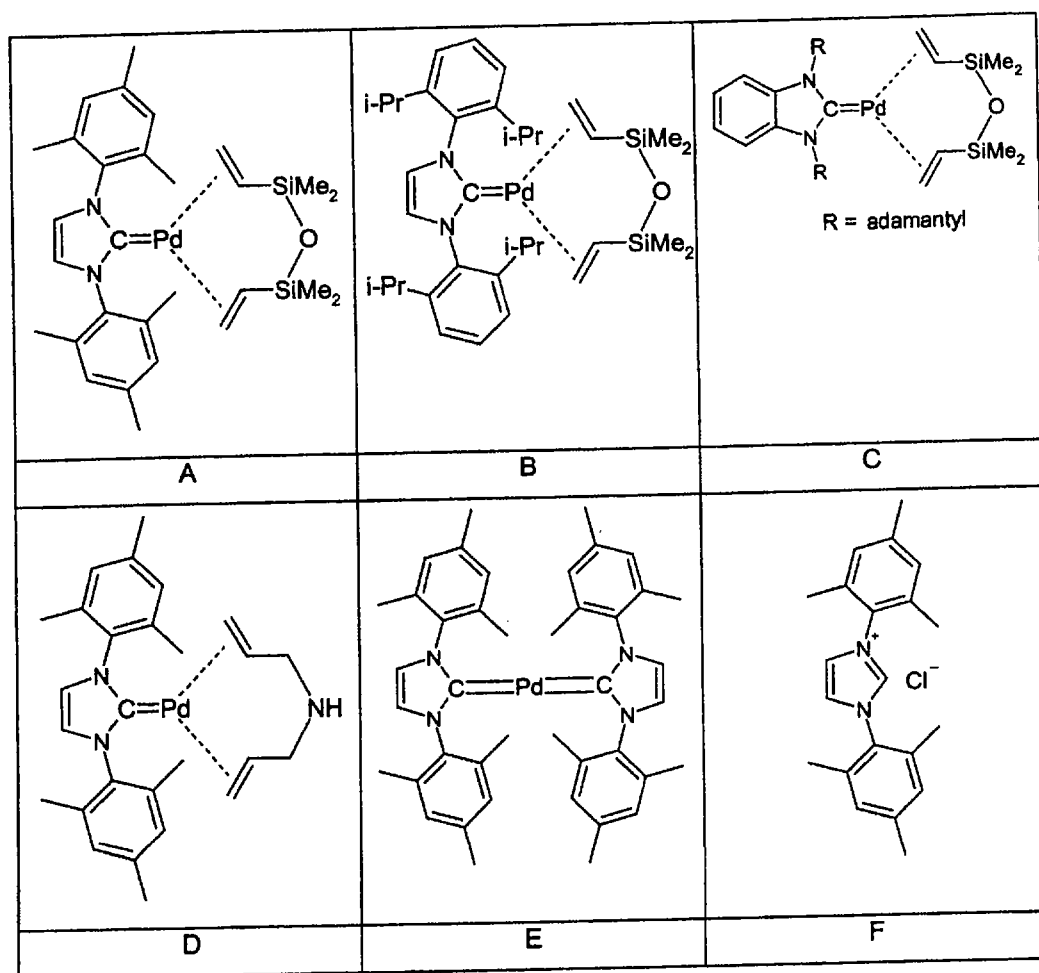
MS m/e (%): 182 [M⁺] (1.4), 139 (4.3), 126 (10.6), 108 (24), 101 (3.9), 97 (11), 93 (27), 82 (35), 67 (72), 57 (100); HRMS: calculated for C₁₂H₂₂O: 182.16707, found: 182.16460

30

Experimental Examples 1-17:

The telomerization was carried out by a method analogous to the general procedure for the telomerization of butadiene using methanol as alcohol. When using other alcohols, the mass of alcohol was maintained and the amounts of butadiene, catalyst, etc., were modified as shown in the table. As palladium compounds, the complexes A-E were added. The base used was sodium hydroxide, and the reaction time was in each case 16 hours.

10



Example 18 - Synthesis of the palladium complex E.

15 A solution of 915 mg of 1,3-dimesitylimidazolin-2-ylidene in 20 ml of toluene is added to a suspension of 1 g of bis(tri-*o*-tolylphosphine)palladium(0) in 20 ml of toluene. The reaction mixture is stirred at

room temperature for one hour and the solvent is subsequently removed under reduced pressure. Washing the residue with hexane (3 x 10 ml) and drying under reduced pressure gives the complex **E** which was used
5 without further purification in the telomerization reactions.

Yield 65%, ^{13}C NMR (C_6D_3 , 100 MHz): $\delta = 186.2$ (Pd-CN₂).

Examples 19-20

10 The catalyst is generated in situ from a palladium precursor and the carbene precursor **F** [$\text{Pd}(\text{OAc})_2$ = palladium(II) acetate, $\text{Pd}_2(\text{dba})_3$ = di(dibenzylidene-acetone)palladium(0)]. The compound **F** can be obtained
15 by known methods (for example WO 0001739) and is also commercially available (Strem). The telomerization was carried out using the general procedure for the telomerization of butadiene by means of methanol. The base used was sodium hydroxide, and the reaction time was in each case 16 hours.

No.	Nucleophile	Nu/butadiene [mol/mol]	Catalyst	Pd [mol%]	Base [mol%]	Temp. [°C]	n+iso telomer [%]	n:iso [%]:[%]	OT+OD+ VCH [%]	TON
1	MeOH	1:2	A	0.01	1	90	≥ 98	96.5:3.5	1.8	>9 800
2	MeOH	1:2	A	0.001	1	90	≥ 98	97.3:2.7	1.2	>98 000
3	MeOH	1:2	A	0.001	1	50	56.5	98.8:1.2	-	56 500
4	MeOH	1:2	A	0.0003	1	90	77	98:2	1.8	256 667
5	BuOH	1:2	A	0.001	1	90	91	98.1:1.9	3.5	91 000
6	BuOH	1:2	A	0.0003	1	90	70	97.2:2.8	4.2	233 333
7	EtOH	1:2	A	0.0003	1	90	75	97:3	2.4	250 000
8	MeOH	1:1	A	0.001	1	70	87	98.2:1.8	0.8	87 000
9	2-EtOH	1:2	A	0.0003	1	90	87	99:1	1.8	290 000
10	MeOH	1:2	B	0.0003	1	90	81	98.2:1.8	1.5	270 000
11	MeOH	1:2	C	0.0003	1	90	90	97.2:2.8	2.2	300 000
12	MeOH	1:2	D	0.0003	1	90	75	97.5:2.5	2.4	250 000
13	MeOH	1:2	Pd(OAc) ₂ /3PPh ₃	0.001	1	90	79	92.2:7.8	9.2	79 000
14	MeOH	1:2	Pd(Oac) ₂ /3PPh ₃	0.0003	1	90	74	93:7	9.5	246 666
15	BuOH	1:2	Pd(OAc) ₂ /3PPh ₃	0.001	1	90	16.7	94:6	31.2	16 700
16	MeOH	1:2	E	0.001	1	90	90	97.4:2.6	1.8	90 000
17	MeOH	1:2	E	0.0003	1	90	76.3	97.6:2.4	2.5	254 000
19	MeOH	1:2	Pd(OAc) ₂ /3 F	0.001	1	90	86	97.3:2.7	1.3	86 000
20	MeOH	1:2	Pd(dba) ₃ /3 F	0.001	1	90	94.7	97.2:2.8	1.5	94 700

Nu = nucleophile

OT = octatriene

n+iso = sum of product 1 + 2

OD = octadiene

n:iso = ratio of product 1 to 2

VCH = vinylcyclohexene

TON = turnover number

Examples 21-22

In a 100 ml Schlenk tube, 70.6 g (0.75 mol) of phenol and the appropriate amount of the catalyst **A** (mol% of Pd based on mol of butadiene) are dissolved in 70 ml of tetrahydrofuran under protective gas. As base, sodium phenoxide is added, 1 mol% based on the amount of phenol used. The reaction solution is subsequently drawn into the evacuated autoclave, the autoclave is cooled to $T < -10^{\circ}\text{C}$ and butadiene is condensed in (amount determined by means of the decrease in mass of the butadiene stock bottle). The molar ratio of phenol to butadiene was 2:1.

The autoclave is heated to 90°C and after 16 hours cooled to room temperature. Unreacted butadiene is condensed in a cold trap cooled by means of dry ice. The conversion is determined from the increase in mass of the reaction solution. To isolate the product, the solution is distilled under reduced pressure.

No.	Base	Pd [mol%]	n+iso telomer [%]	n:iso [%]:[%]	OT+VCH [%]	TON
21	NaOPh	0.005	56	89:11	1.3	11 200
22	NaOPh	0.001	6.4	95:5	3.4	6 400

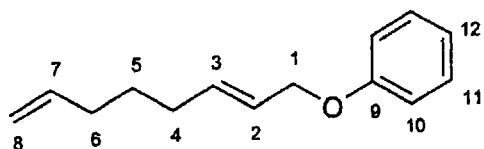
2,7-Octadien-1-yl phenyl ether:¹H NMR (CDCl₃, 400 MHz)

δ = 1.8 (quin, J = 7.5, 5-H), 2.3-2.4 (m, 4H, 4-H and 6-H), 4.74 (d,d, J = 5.5, J = 1, 2H, 1-H), 5.2-5.35 (m, 2H, 8-H), 5.9-6.2 (m, 3H, 7-H, 2-H, 3-H), 7.18-7.21 (m, 3H, 10-H, 12-H), 7.5-7.6 (m, 2H, 11-H)

¹³C NMR (CDCl₃, 100 MHz):

δ = 28.0 (C-5), 31.6 (C-4), 33.0 (C-6), 68.4 (C-1), 114.53 (C-8), 120.5 (C-11), 125.1 (C-2), 129.1 (C-12), 129.2 (C-10), 134.8 (C-3), 138.3 (C-7), 158.5 (C-9)

MS m/e (%): [M^+] 202 (2.5), 108 (9.9), 94 (100), 79 (11), 67 (55), 58 (11), 55 (24), 43 (40), HRMS: calculated for C₁₄H₁₈O: 202.13577, found: 202.13485



Example 23

The telomerization was carried out by a method analogous to the general procedure for the telomerization of butadiene by means of methanol. The complex **A** was added as palladium compound. The base used was sodium isopropoxide, 1 mol%. The reaction time was 16 hours at 90°C, and the molar ratio of i-propanol to butadiene was 2:1.

No.	Catalyst	Pd [mol%]	n+iso telomer [%]	n:iso [%]:[%]	OT+VCH [%]	TON
23	A	0.005	72.5	82:18	26.5	14 500

2,7-Octadien-1-yl isopropyl ether:

GC (column HP 5/30 m, temp. program: 35°C, 10 min, at 8°C min⁻¹ to 280°C, inj.: 250°C, const. flow, b). t_R (vinylcyclohexene) = 12 min, t_R (octatriene) = 11.6 min and 11.7 min, t_R (**2**) = 19.2 min, t_R (**1**) = 16.51, t_R (diglyme) = 17.1 min.

¹H NMR (CDCl₃, 400 MHz)

δ = 1.05 (d of s, 6H, 10-H, 11-H), 1.4 (quint, J = 7.5 Hz, 2H, 10-H), 1.9 (m, 4H, 4-H and 6-H), 3.5 (sept, J = 6.1 Hz, 2H, 9-H), 3.82 (dd, J = 6.2 Hz, J = 1 Hz, 2H, 1-H), 4.76-4.9 (m, 2H, 8-H), 5.36-5.45 (m, 1H, 7-H), 5.5-5.75 (m, 2H, 2-H and 3-H).

¹³C NMR (CDCl₃, 100 MHz):

δ = 21.7 (C-11, C-10), 27.9 (C-5), 31.3 (C-4), 32.9 (C-6), 69.1 (C-9), 70.8 (C-1), 114.8 (C-8), 127.7 (C-2), 133.5 (C-3), 138.7 (C-7).

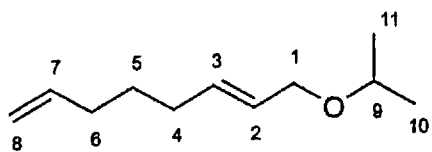
MS m/e (%): [M^+] 168 (0.11), 126 (12.5), 109 (30.6), 97 (13), 93 (25), 82 (68), 67 (95), 55 (76), 43 (100)

EA: calculated for C₁₁H₂₀O: C: 78.51, H: 11.98, found:

O.Z. 5781

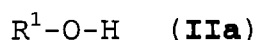
- 24 -

C: 78.56, H: 11.95

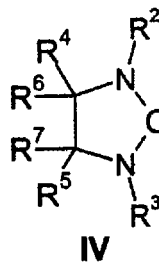


Claims

1. A process for the telomerization of acyclic olefins having at least two conjugated double bonds (**I**) or mixtures comprising such olefins by means of nucleophiles (**II**) using a palladium-carbene complex as catalyst.
2. The process as claimed in claim 1, wherein the nucleophiles used are ones selected from the group consisting of water, alcohols, phenols, polyols, carboxylic acids, ammonia and primary and secondary amines.
3. The process as claimed in claim 1 or 2, wherein the nucleophiles (**II**) used are compounds of the formula (**IIa**) or (**IIb**),



- where R^1 , $R^{1'}$ are selected independently from among hydrogen, linear, branched or cyclic C_1 - C_{22} -alkyl groups, alkenyl groups, alkynyl groups, the carboxyl group and C_5 - C_{18} -aryl groups, where these groups may bear substituents selected from the group consisting of $-CN$, $-COOH$, $-COO$ -alkyl- (C_1 - C_8), $-CO$ -alkyl- (C_1 - C_8), $-aryl$ - (C_5 - C_{10}), $-COO$ -aryl- (C_6 - C_{10}), $-CO$ -aryl- (C_6 - C_{10}), $-O$ -alkyl- (C_1 - C_8), $-O$ - CO -alkyl- (C_1 - C_8), $-N$ -alkyl₂- (C_1 - C_8), $-CHO$, $-SO_3H$, $-NH_2$, $-F$, $-Cl$, $-OH$, $-CF_3$, $-NO_2$, and the radicals R^1 , $R^{1'}$ may be joined to one another via covalent bonds.
4. The process as claimed in claim 1 or 2, wherein the palladium-carbene complex used comprises carbene ligands of the formula (**III**) or (**IV**),



where R^2 and R^3 are each, independently of one
 5 another, a linear, branched or cyclic C_1 - C_{24} -alkyl
 or C_5 - C_{18} -aryl group and the alkyl and aryl groups
 may, independently of one another, bear the
 substituents -CN, -COOH, COO-alkyl- (C_1-C_8) ,
 -CO-alkyl- (C_1-C_8) , -aryl- (C_6-C_{18}) , -alkyl- (C_1-C_{24}) ,
 10 -COO-aryl- (C_6-C_{10}) , -CO-aryl- (C_6-C_{10}) , -O-alkyl-
 (C_1-C_8) , -O-CO-alkyl- (C_1-C_8) , -N-alkyl $_2$ - (C_1-C_8) ,
 -CHO, -SO $_3$ H, -NH $_2$, -F, -Cl, -OH, -CF $_3$, -NO $_2$,
 ferrocenyl,

15 and R^4 to R^7 are each, independently of one
 another, hydrogen, -CN, -COOH, -COO-alkyl- (C_1-C_8) ,
 -CO-alkyl- (C_1-C_8) , -COO-aryl- (C_6-C_{10}) , -CO-
 aryl- (C_6-C_{10}) , -O-alkyl- (C_1-C_8) , -O-CO-alkyl-
 (C_1-C_8) , -N-alkyl $_2$ - (C_1-C_8) , -CHO, -SO $_3$ H, -NH $_2$, -F,
 20 -Cl, -OH, -CF $_3$, -NO $_2$ or a linear, branched or
 cyclic C_1 - C_{24} -alkyl or C_6 - C_{18} -aryl group and the
 alkyl and aryl groups may, independently of one
 another, bear the substituents -CN, -COOH, -COO-
 alkyl- (C_1-C_8) , -CO-alkyl- (C_1-C_8) , -aryl- (C_6-C_{10}) ,
 25 -COO-aryl- (C_6-C_{10}) , -CO-aryl- (C_6-C_{10}) , -O-alkyl-
 (C_1-C_8) , -O-CO-alkyl- (C_1-C_8) , -N-alkyl $_2$ - (C_1-C_8) ,
 -CHO, -SO $_3$ H, -NH $_2$, -F, -Cl, -OH, -CF $_3$, -NO $_2$, where
 the radicals R^4 and R^5 may also be part of a
 bridging aliphatic or aromatic ring.

30

5. The process as claimed in any of claims 1 to 4,
 wherein the acyclic olefin used is 1,3-butadiene

or isoprene.

- 5 6. The process as claimed in any of claims 1 to 5,
wherein 1,3-butadiene is used in admixture with
other C₄-hydrocarbons or C₅-hydrocarbons.
- 10 7. The process as claimed in any of claims 1 to 6,
wherein the nucleophile (**II**) or an inert organic
solvent or a mixture thereof is used as solvent.
- 15 8. The process as claimed in any of claims 1 to 7,
wherein the reaction is carried out at
temperatures of from 10 to 180°C and a pressure of
from 1 to 300 bar.
- 20 9. The process as claimed in any of claims 1 to 8,
wherein the ratio of carbene ligand to Pd
[mol/mol] is from 0.01:1 to 250:1.
- 25 10. The process as claimed in any of claims 1 to 9,
wherein the palladium-carbene complexes are used
as isolated complexes.
- 30 11. The process as claimed in any of claims 1 to 10,
wherein the palladium-carbene complexes are
generated in situ during the telomerization
reaction.
- 35 12. The process as claimed in any of claims 1 to 11,
wherein catalytic amounts of a basic component
having a pK_b of < 7 are added to the reaction.
13. The process as claimed in any of claims 1 to 12,
wherein the basic component used is a compound
selected from the group consisting of amines,
alkali metal salts and alkaline earth metal salts
or a mixture thereof.

14. The process as claimed in any of claims 1 to 13, wherein the basic component is used in an amount of from 0.01 mol% to 10 mol%, based on the olefin compound.
- 5
15. The process as claimed in any of claims 1 to 14, wherein the palladium concentration in the reaction mixture is from 0.01 to 1 000 ppm.