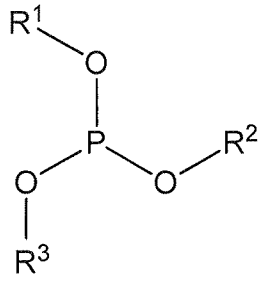
hydroformylation of olefins, with which branched, unbranched, terminal and internal olefins can be terminally hydroformylated with high yields and selectivities, i.e. very substantially linear aldehydes can be prepared.

In addition, the cost/benefit ratio of the ligands being used is to be optimized.

The object is achieved by a mixture ~~according to Claim 1~~of the present disclosure.

~~In a first aspect, t~~There is provided a mixture comprising a compound of the structure **Ia**:



Ia

where

R^1 is selected from:

$-(C_1\text{-}C_{12})$-alkyl, $-(C_3\text{-}C_{12})$-cycloalkyl,

and

R^2, R^3 are each independently selected from:

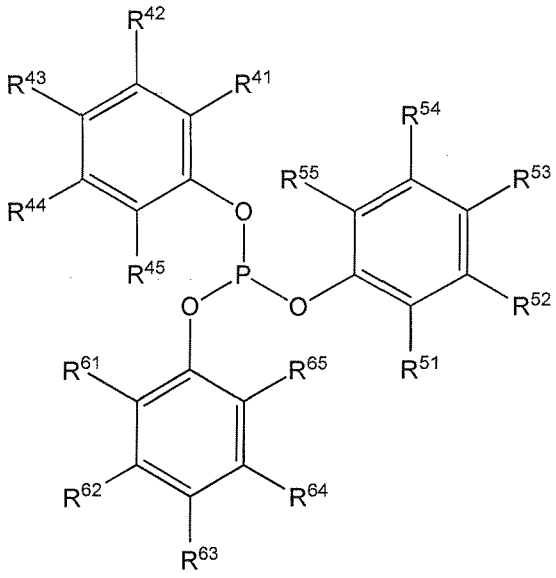
$-(C_1\text{-}C_{12})$-alkyl, $-(C_6\text{-}C_{20})$-aryl, $-(C_3\text{-}C_{12})$-cycloalkyl,

the R^2 and R^3 radicals may also be bridged to one another, and may have a $-(C_6\text{-}C_{20})$-aryl-$(C_6\text{-}C_{20})$-aryl unit,

where the alkyl, cycloalkyl and aryl groups mentioned may be substituted,

and

comprising a compound of the structure **IIb**:



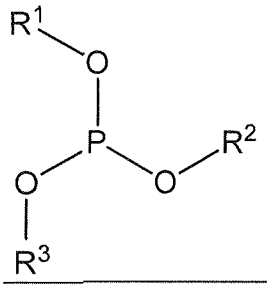
IIb

where

R^{41}, R^{42}, R^{43}, R^{44}, R^{45}, R^{51}, R^{52}, R^{53}, R^{54}, R^{55}, R^{61}, R^{62}, R^{63}, R^{64}, R^{65} are each independently selected from:

-H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -O-(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl, -halogen, -COO-(C_1-C_{12})-alkyl, -CO-(C_1-C_{12})-alkyl, -CO-(C_6-C_{20})-aryl, -COOH, -OH.

In a first aspect, there is provided a mixture comprising a compound of the structure **Ia**:



Ia

where

R^1 is selected from:

-(C_1-C_{12})-alkyl,

and

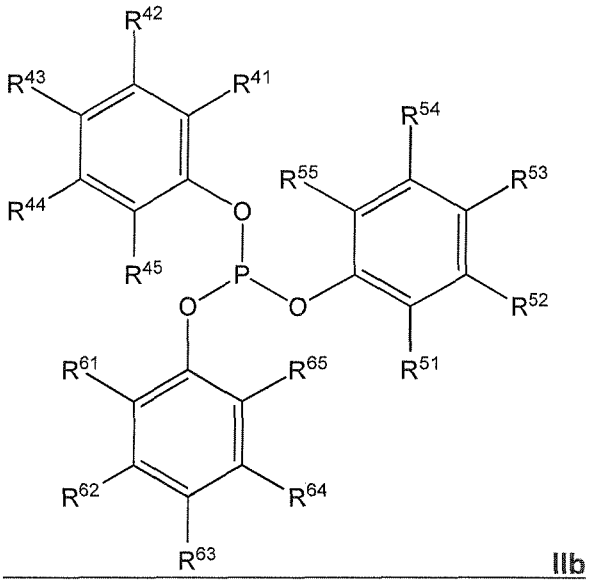
R^2, R^3 are each independently selected from:

-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl, -(C_3-C_{12})-cycloalkyl,

where the alkyl, cycloalkyl and aryl groups mentioned may be substituted,

and

comprising a compound of the structure **IIb**:



IIb

where

R^{41}, R^{42}, R^{43}, R^{44}, R^{45}, R^{51}, R^{52}, R^{53}, R^{54}, R^{55}, R^{61}, R^{62}, R^{63}, R^{64}, R^{65} are each independently selected from:

-H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -O-(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl, -halogen, -COO-(C_1-C_{12})-alkyl, -CO-(C_1-C_{12})-alkyl, -CO-(C_6-C_{20})-aryl, -COOH, -OH.

(C_1-C_{12})-Alkyl may in each case be unsubstituted or substituted by one or more identical or different radicals selected from (C_3-C_{12})-cycloalkyl, (C_3-C_{12})-heterocycloalkyl, (C_6-C_{20})-aryl, fluorine, chlorine, cyano, formyl, acyl and alkoxycarbonyl.

(C_6-C_{20})-Aryl may in each case be unsubstituted or substituted by one or more identical or different radicals selected from -H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -O-(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl, -halogen (such as Cl, F, Br, I), -COO-(C_1-C_{12})-alkyl, -CONH-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl-CON[(C_1-C_{12})-alkyl]$_2$, -CO-(C_1-C_{12})-alkyl, -CO-(C_6-C_{20})-aryl, -COOH, -OH, -SO_3H, -SO_3Na, -NO_2, -CN, -NH_2, -N[(C_1-C_{12})-alkyl]$_2$.

(C_3-C_{12})-Cycloalkyl may in each case be unsubstituted or substituted by one or more identical or different radicals selected from (C_1-C_{12})-alkyl, (C_1-C_{12})-alkoxy, (C_3-C_{12})-cycloalkyl, (C_3-C_{12})-heterocycloalkyl, (C_6-C_{20})-aryl, fluorine, chlorine, cyano, formyl, acyl and alkoxycarbonyl.

In the context of the disclosure, the expression "-(C_1-C_{12})-alkyl" encompasses straight-chain and branched alkyl groups. Preferably, these groups are unsubstituted straight-

In a second aspect, there is provided a complex mixture comprising:
- an above-described mixture,
- a metal atom selected from: Rh, Ru, Co, Ir.

In this regard, see R. Franke, D. Selent, A. Börner, "Applied Hydroformylation", Chem. Rev., 2012, DOI:10.1021/cr3001803; p. 5688, Scheme 12 "General Method for the Preparation of a P-Modified Rh precatalyst" and references cited therein, and also P. W. N. M. van Leeuwen, in Rhodium Catalyzed Hydroformylation, P. W. N. M. van Leeuwen, C. Claver (eds.), Kluwer, Dordrecht, 2000, inter alia p. 48 ff., p. 233 ff. and references cited therein, and also K.D. Wiese and D. Obst in Top. Organomet. Chem. 2006, 18, 1-13; Springer Verlag Berlin Heidelberg 2006 p. 6 ff. and references cited therein.

In the complex mixture, three different cases may exist:

1) The complex has ligands either of the **I** or **II** type, and the mixture is of complex molecules having only ligands of the **I** type with complex molecules having only ligands of the **II** type.

2) A complex in itself already has ligands of the **I** and **II** type.

3) Is a mixed form of 1) and 2).

As well as the mixtures/complex mixtures, also disclosed is the use thereof as complex mixtures for catalysis of a hydroformylation reaction. In this case, the compounds in the mixture are the ligands in the complex. The ligands coordinate to the central metal atom. The ligand-metal complex thus obtained or the complex mixtures thus obtained then catalyse the hydroformylation reaction.

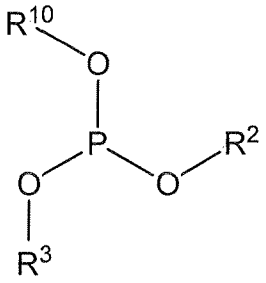
In a third aspect, there is provided the use of an above-described mixture in a complex mixture for catalysis of a hydroformylation reaction.

In addition, also disclosed is the hydroformylation reaction.

~~In a fourth aspect, t~~There is provided a process comprising the process steps of:

a) initially charging an olefin,

b) adding a mixture comprising a compound of the structure **IIIa**:



IIIa

where

R^{10} is selected from:

-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl, -(C_3-C_{12})-cycloalkyl,

and

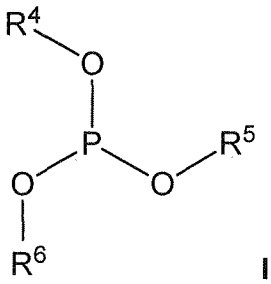
R^2, R^3 are each independently selected from:

-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl, -(C_3-C_{12})-cycloalkyl,

the R^2 and R^3 radicals may also be bridged to one another, and may have a -(C_6-C_{20})-aryl-(C_6-C_{20})-aryl unit,

where the alkyl, cycloalkyl and aryl groups mentioned may be substituted,

and a compound of the structure **IIa**:



IIa

where

R^4, R^5, R^6 are each independently selected from:

-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl, -(C_3-C_{12})-cycloalkyl,

two R^4 and R^5 or R^5 and R^6 or R^6 and R^4 radicals may also be bridged to one another, and may have a -(C_6-C_{20})-aryl-(C_6-C_{20})-aryl unit,

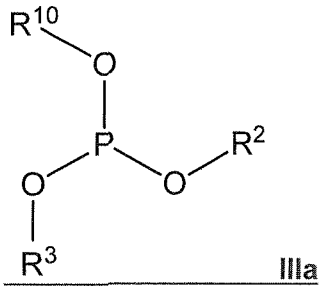
where the alkyl, cycloalkyl and aryl groups mentioned may be substituted;

c) adding a compound comprising one of the following metals: Rh, Ru, Co, Ir,

~~c~~d) feeding in H_2 and CO,

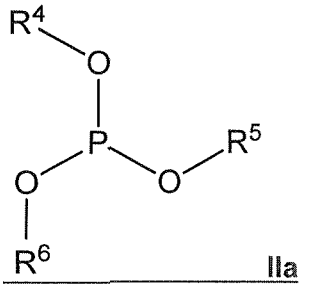
~~d~~e) heating the reaction mixture, with conversion of the olefin to an aldehyde,
where the additions in process steps b) and c) can also be effected in one step through the addition of a corresponding complex mixture.

In a fourth aspect, there is provided a process comprising the process steps of:
a) initially charging an olefin,
b) adding a mixture comprising a compound of the structure **IIIa**:



IIIa

where
R^{10} is selected from:
-(C_1-C_{12})-alkyl,
and
R^2, R^3 are each independently selected from:
-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl, -(C_3-C_{12})-cycloalkyl,
where the alkyl, cycloalkyl and aryl groups mentioned may be substituted,
and a compound of the structure **IIa**:



IIa

where
R^4, R^5, R^6 are each independently selected from:
-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl, -(C_3-C_{12})-cycloalkyl,
two R^4 and R^5 or R^5 and R^6 or R^6 and R^4 radicals may also be bridged to one another, and may have a -(C_6-C_{20})-aryl-(C_6-C_{20})-aryl unit,
where the alkyl, cycloalkyl and aryl groups mentioned may be substituted;

c) adding a compound comprising one of the following metals: Rh, Ru, Co, Ir,
d) feeding in H_2 and CO,
e) heating the reaction mixture, with conversion of the olefin to an aldehyde,
where the additions in process steps b) and c) can also be effected in one step through the addition of a corresponding complex mixture.

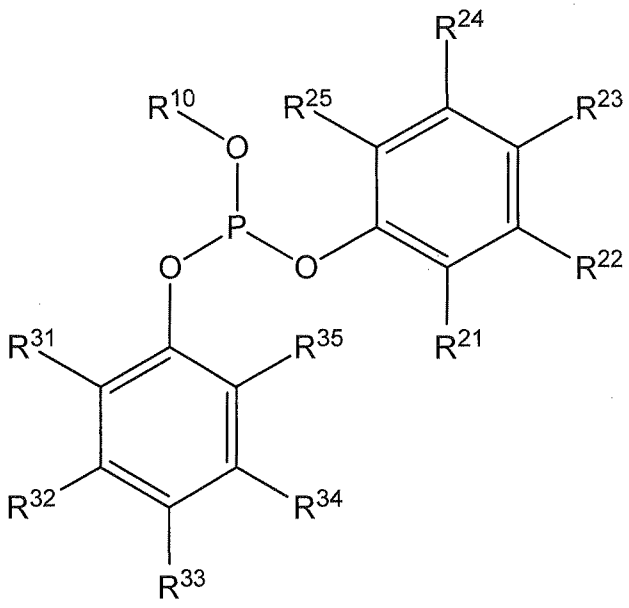
In this process, process steps a) to e) can be effected in any desired sequence.

Preference is given to a temperature of 80°C to 160°C and a pressure of 1 to 300 bar. Particular preference is given to a temperature of 100°C to 160°C and a pressure of 15 to 250 bar.

In one variant of the process, R^{10} is selected from: -(C_1-C_{12})-alkyl, -(C_3-C_{12})-cycloalkyl.

In one variant of the process, R^{10} is selected from: -(C_1-C_{12})-alkyl.

In one variant of the process, the mixture comprises a compound of the structure **IIIb**:



IIIb

where
R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{31}, R^{32}, R^{33}, R^{34}, R^{35} are each independently selected from:
-H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -O-(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl, -halogen, -COO-(C_1-C_{12})-alkyl, -CO-(C_1-C_{12})-alkyl, -CO-(C_6-C_{20})-aryl, -COOH, -OH.

where

R^{41}, R^{42}, R^{43}, R^{44}, R^{45}, R^{51}, R^{52}, R^{53}, R^{54}, R^{55}, R^{61}, R^{62}, R^{63}, R^{64}, R^{65} are each independently selected from:

-H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -O-(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl, -halogen, -COO-(C_1-C_{12})-alkyl, -CO-(C_1-C_{12})-alkyl, -CO-(C_6-C_{20})-aryl, -COOH, -OH.

In one variant of the process, R^{41}, R^{42}, R^{43}, R^{44}, R^{45}, R^{51}, R^{52}, R^{53}, R^{54}, R^{55}, R^{61}, R^{62}, R^{63}, R^{64}, R^{65} are each independently selected from:

-H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -O-(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl.

In one variant of the process, R^{41}, R^{43}, R^{51}, R^{53}, R^{61}, R^{63} are each *tert*-butyl.

In one variant of the process, R^{45}, R^{55}, R^{65} are each -H.

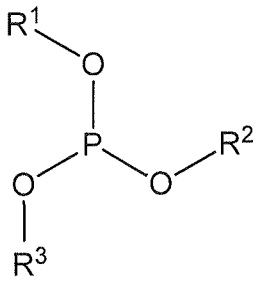
In a preferred embodiment, the metal is Rh.

The reactants for the hydroformylation in the process of the ~~invention~~ present disclosure are olefins or mixtures of olefins, especially monoolefins having 2 to 24, preferably 3 to 16 and more preferably 3 to 12 carbon atoms, having terminal or internal C-C double bonds, for example 1-propene, 1-butene, 2-butene, 1- or 2-pentene, 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene, 1-, 2- or 3-hexene, the C_6 olefin mixture obtained in the dimerization of propene (dipropene), heptenes, 2- or 3-methyl-1-hexenes, octenes, 2-methylheptenes, 3-methylheptenes, 5-methyl-2-heptene, 6-methyl-2-heptene, 2-ethyl-1-hexene, the C_8 olefin mixture obtained in the dimerization of butenes (di-n-butene, diisobutene), nonenes, 2- or 3-methyloctenes, the C_9 olefin mixture obtained in the trimerization of propene (tripropene), decenes, 2-ethyl-1-octene, dodecenes, the C_{12} olefin mixture obtained in the tetramerization of propene or the trimerization of butenes (tetrapropene or tributene), tetradecenes, hexadecenes, the C_{16} olefin mixture obtained in the tetramerization of butenes (tetrabutene), and olefin mixtures prepared by cooligomerization of olefins having different numbers of carbon atoms (preferably 2 to 4).

The process according to the ~~invention~~ present disclosure using the mixtures/complex mixtures according to the ~~invention~~ present disclosure can be used to hydroformylate α-olefins, terminally branched, internal and internally branched olefins. What is remarkable is the high yield of terminally

Claims

1. Mixture comprising a compound of the structure **Ia**:



Ia

where

R^1 is selected from:

-(C_1-C_{12})-alkyl~~, -(C_3-C_{12})-cycloalkyl~~,

and

R^2, R^3 are each independently selected from:

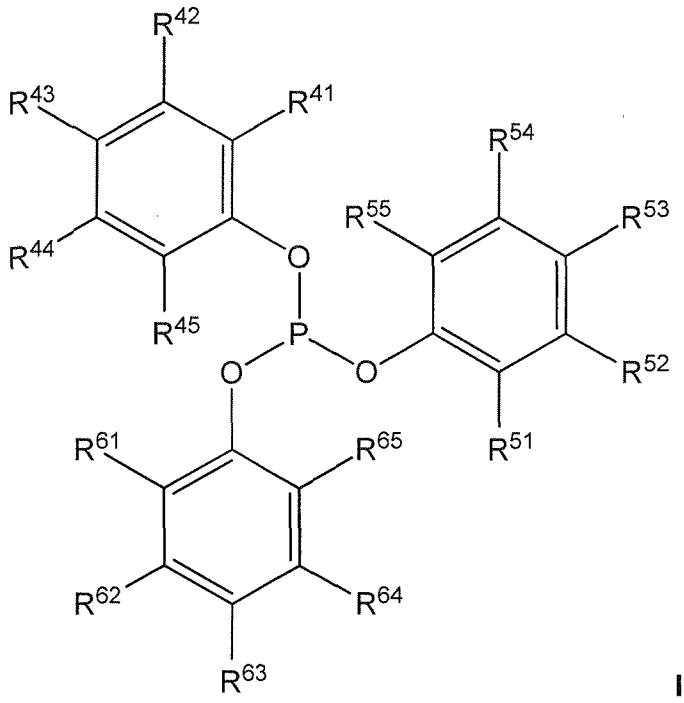
-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl, -(C_3-C_{12})-cycloalkyl,

~~the R^2 and R^3 radicals may also be bridged to one another, and may have a -(C_6-C_{20})-aryl-(C_6-C_{20})-aryl unit,~~

where the alkyl, cycloalkyl and aryl groups mentioned may be substituted,

and

comprising a compound of the structure **IIb**:



IIb

where

R^{41}, R^{42}, R^{43}, R^{44}, R^{45}, R^{51}, R^{52}, R^{53}, R^{54}, R^{55}, R^{61}, R^{62}, R^{63}, R^{64}, R^{65} are each independently selected from:

-H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -O-(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl, -halogen, -COO-(C_1-C_{12})-alkyl, -CO-(C_1-C_{12})-alkyl, -CO-(C_6-C_{20})-aryl, -COOH, -OH.

~~2. Mixture according to Claim 1,~~
~~where R^1 is -(C_1-C_{12})-alkyl.~~

~~3.~~2. Mixture according to ~~either of Claims 1 and 2~~ Claim 1,
where R^1 is not the same as one of the R^2, R^3 radicals.

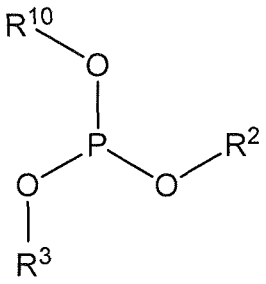
~~4.~~3. Mixture according to ~~any~~ either of Claims 1 ~~to 3~~ and 2,
where R^{41}, R^{42}, R^{43}, R^{44}, R^{45}, R^{51}, R^{52}, R^{53}, R^{54}, R^{55}, R^{61}, R^{62}, R^{63}, R^{64}, R^{65} are each independently selected from:
-H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -O-(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl.

~~5.~~4. Mixture according to any of Claims 1 to ~~4~~ 3,
where R^{41}, R^{43}, R^{51}, R^{53}, R^{61}, R^{63} are each *tert*-butyl.

~~6.~~5. Complex mixture comprising:
- a mixture according to any of Claims 1 to ~~5~~ 4,
- a metal atom selected from: Rh, Ru, Co, Ir.

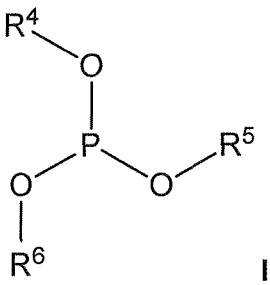
~~7.~~6. Use of a mixture according to any of Claims 1 to ~~5~~ 4
in a complex mixture for catalysis of a hydroformylation reaction.

~~8.~~7. Process comprising the process steps of:
a) initially charging an olefin,
b) adding a mixture comprising a compound of the structure **IIIa**:



IIIa

where
R^{10} is selected from:
$-(C_1-C_{12})$-alkyl, ~~$-(C_6-C_{20})$-aryl, $-(C_3-C_{12})$-cycloalkyl,~~
and
R^2, R^3 are each independently selected from:
$-(C_1-C_{12})$-alkyl, $-(C_6-C_{20})$-aryl, $-(C_3-C_{12})$-cycloalkyl,
~~the R^2 and R^3 radicals may also be bridged to one another, and may have a $-(C_6-C_{20})$-aryl-(C_6-C_{20})-aryl unit,~~
where the alkyl, cycloalkyl and aryl groups mentioned may be substituted,
and a compound of the structure **IIa**:



IIa

where

R^4, R^5, R^6 are each independently selected from:

-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl, -(C_3-C_{12})-cycloalkyl,

two R^4 and R^5 or R^5 and R^6 or R^6 and R^4 radicals may also be bridged to one another, and may have a -(C_6-C_{20})-aryl-(C_6-C_{20})-aryl unit,

where the alkyl, cycloalkyl and aryl groups mentioned may be substituted;

c) adding a compound comprising one of the following metals: Rh, Ru, Co, Ir,

~~c~~d) feeding in H_2 and CO,

~~d~~e) heating the reaction mixture, with conversion of the olefin to an aldehyde,

where the additions in process steps b) and c) can also be effected in one step through the addition of a corresponding complex mixture.

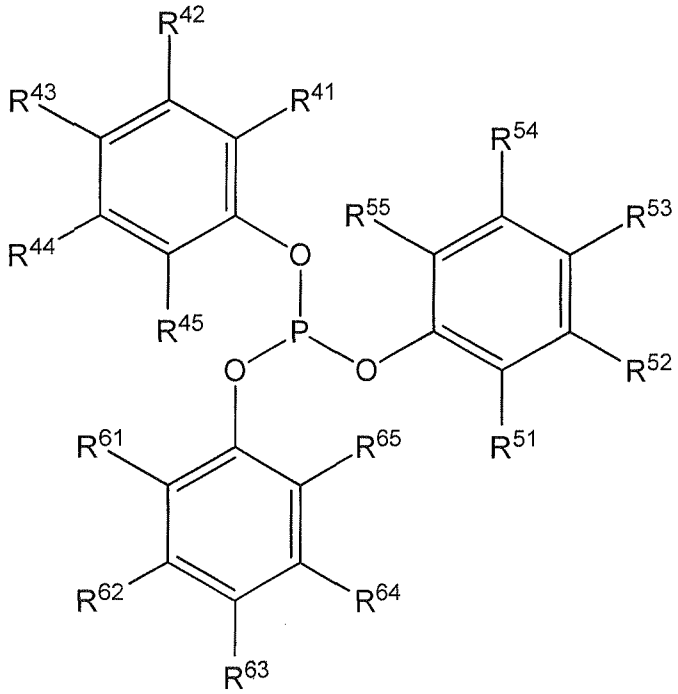
~~9. Process according to Claim 8,~~

~~where R^{10} is selected from: -(C_1-C_{12})-alkyl.~~

~~10.~~8. Process according to ~~either of Claims 8 and 9~~ Claim 7,

wherein, in addition to the compound of the structure **IIIa**,

the mixture in process step b) comprises a compound of the structure **IIb**:



IIb

where

R^{41}, R^{42}, R^{43}, R^{44}, R^{45}, R^{51}, R^{52}, R^{53}, R^{54}, R^{55}, R^{61}, R^{62}, R^{63}, R^{64}, R^{65} are each independently selected from:

-H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -O-(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl, -halogen, -COO-(C_1-C_{12})-alkyl, -CO-(C_1-C_{12})-alkyl, -CO-(C_6-C_{20})-aryl, -COOH, -OH.

~~11.~~9. Process according to Claim ~~10~~ 8,

where R^{41}, R^{42}, R^{43}, R^{44}, R^{45}, R^{51}, R^{52}, R^{53}, R^{54}, R^{55}, R^{61}, R^{62}, R^{63}, R^{64}, R^{65} are each independently selected from:

-H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -O-(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl.

~~12.~~10. Process according to either of Claims ~~10~~ 8 and ~~11~~ 9,

where R^{41}, R^{43}, R^{51}, R^{53}, R^{61}, R^{63} are each *tert*-butyl.