Since the 1970s, there have been descriptions of the use of "bulky phosphites" in hydroformylation (see, inter alia, van Leeuwen et al., Journal of Catalysis, 2013, 298, 198-205). These feature good activity, but the n/i selectivity for terminally hydroformylated compounds is in need of improvement.

As well as the use of pure ligands, the use of ligand mixtures has also been described in the literature.

US 20120253080 describes the use of monophosphites with bisphosphites. However, this combination has the disadvantage that the bisphosphites, although having good selectivity, have very low activity in the case of long-chain olefins and are therefore in need of improvement. In an industrial scale process, in addition to the selectivity for the desired product, the space-time yield or the activity of the catalyst system is an important factor with regard to the economic viability thereof. Moreover, the bisphosphites are frequently much more costly to prepare than, for example, the monophosphites.

EP 1 099 678 describes the use of phosphonites with bisphosphites. However, it is disadvantageous here that both ligand types are very costly to produce, and an industrial scale process can therefore hardly be economically viable. Moreover, the addition of the bisphosphite ligand noticeably affects the yield of the reaction, since these ligands are less active when dibutene, for example, is used as substrate.

WO 2007/149143 discloses mixtures of two to five triaryl phosphites which are liquid under ambient conditions. These triaryl phosphites have at least one alkyl substituent, more specifically a tert-butyl or tert-pentyl substituent. The mixtures are used as stabilizers/antioxidants for polymer resins, especially thermoplastic resins or elastomers.

US 8, 258, 215 B2 describes phosphites which are used for stabilizing polymers. These phosphites have either one aromatic radical and two aliphatic radicals or two aromatic radical and one aliphatic radicals.

It is therefore desirable to develop a catalyst system which does not have the disadvantages exhibited in the prior art.

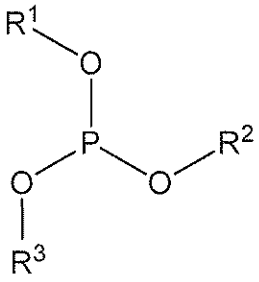
It was therefore an object of the ~~present invention~~embodiments disclosed herein to provide a catalyst system for

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.

In a first aspect, there is provided a Mmixture 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:

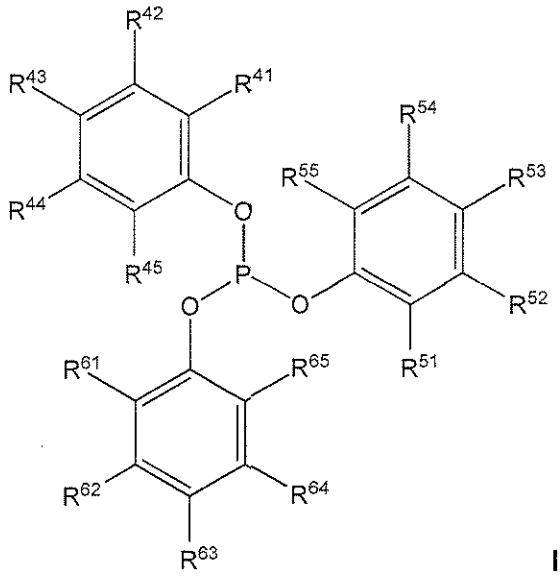
-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl, -(C_3-C_{12})-cycloalkyl,

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.

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

chain or branched -(C_1-C_8)-alkyl groups and most preferably -(C_1-C_6)-alkyl groups. Examples of (C_1-C_{12})-alkyl groups are especially methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, 2-pentyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, 2,2-dimethylpropyl, 1-ethylpropyl, n-hexyl, 2-hexyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 2,2-dimethylbutyl, 1,3-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethylbutyl, 1-ethyl-2-methylpropyl, n-heptyl, 2-heptyl, 3-heptyl, 2-ethylpentyl, 1-propylbutyl, n-octyl, 2-ethylhexyl, 2-propylheptyl, nonyl, decyl.

Substituted -(C_1-C_{12})-alkyl groups may have one or more substituents, depending on their chain length. The substituents are preferably each independently selected from -(C_3-C_{12})-cycloalkyl, -(C_3-C_{12})-heterocycloalkyl, -(C_6-C_{20})-aryl, fluorine, chlorine, cyano, formyl, acyl or alkoxycarbonyl.

The expression "-(C_3-C_{12})-cycloalkyl", in the context of the present ~~invention~~disclosure, encompasses mono-, bi- or tricyclic hydrocarbyl radicals having 3 to 12, especially 5 to 12, carbon atoms. These include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclododecyl, cyclopentadecyl, norbonyl and adamantyl.

Substituted -(C_3-C_{12})-cycloalkyl groups may have one or more (e.g. 1, 2, 3, 4 or 5) further substituents, depending on their ring size. These substituents are preferably each independently 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 or alkoxycarbonyl. Substituted -(C_3-C_{12})-cycloalkyl groups preferably bear one or more -(C_1-C_6)-alkyl groups. Substituted -(C_3-C_{12})-heterocycloalkyl groups preferably bear one or more -(C_1-C_6)-alkyl groups.

In the context of the present disclosure~~invention~~, the expression "-(C_6-C_{20})-aryl" encompasses mono- or polycyclic aromatic hydrocarbyl radicals. These have 6 to 20 ring atoms, more preferably 6 to 14 ring atoms, especially 6 to 10 ring atoms. Aryl is preferably -(C_6-C_{10})-aryl and -(C_6-C_{10})-aryl-(C_6-C_{10})-aryl-. Aryl is especially phenyl, naphthyl, indenyl, fluorenyl, anthracenyl, phenanthrenyl, naphthacenyl, chrysenyl, pyrenyl, coronenyl. More particularly, aryl is phenyl, naphthyl and anthracenyl.

Substituted -(C_6-C_{20})-aryl groups may have one or more (e.g. 1, 2, 3, 4 or 5) substituents, depending on the ring size. These substituents are preferably 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 (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]$_2$.

Substituted -(C_6-C_{20})-aryl groups are preferably substituted -(C_6-C_{10})-aryl groups and -(C_6-C_{10})-aryl-(C_6-C_{10})-aryl groups, especially substituted phenyl or substituted naphthyl or substituted anthracenyl. Substituted -(C_6-C_{20})-aryl groups preferably bear one or more, for example 1, 2, 3, 4 or 5, substituents selected from -(C_1-C_{12})-alkyl groups, -(C_1-C_{12})-alkoxy groups.

In one embodiment, R^1 is -(C_1-C_{12})-alkyl.

In one embodiment, R^1 is -CH_2CH_3.

In one embodiment, at least one of the R^1, R^2, R^3 radicals is not the same as the two other radicals.

In one embodiment, R^1 is not the same as one of the R^2, R^3 radicals.

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

In one embodiment, R^{45}, R^{55}, R^{65} are each -H.

In one embodiment, the mixture is solid at 25°C.
The term "solid" in this context is understood to mean the state of matter, which delimits the mixture, for example, from a liquid mixture.

As well as the mixture, a complex mixture including such a mixture is also ~~claimed~~disclosed.

In a second aspect, there is provided a ~~C~~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 ~~claimed~~ 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 ~~U~~use of an above-described mixture in a complex mixture for catalysis of a hydroformylation reaction.

In addition, also ~~claimed~~ disclosed is the hydroformylation reaction.

In a fourth aspect, there is provided a ~~P~~process comprising the process steps of: