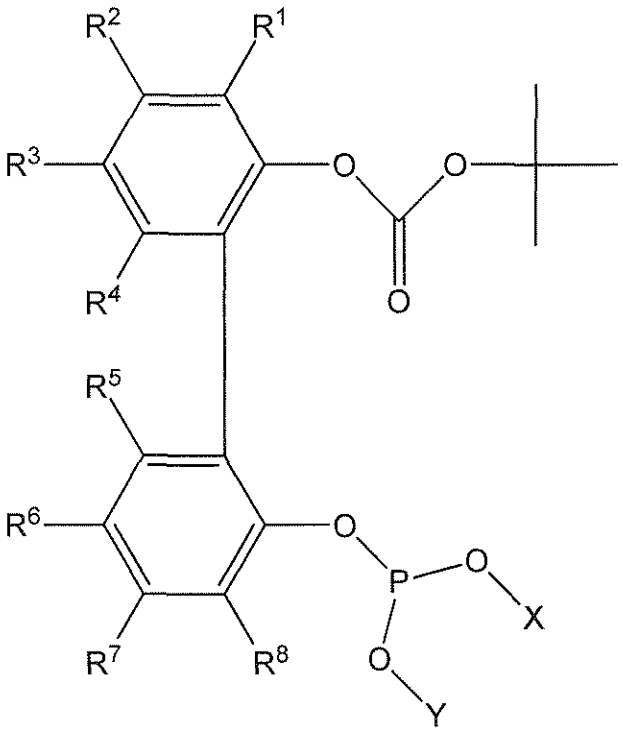
industrial olefin mixtures containing mainly branched olefins having internal double bonds. In the hydroformylation, at the same time, a high proportion of desired terminally hydroformylated products should be obtained.

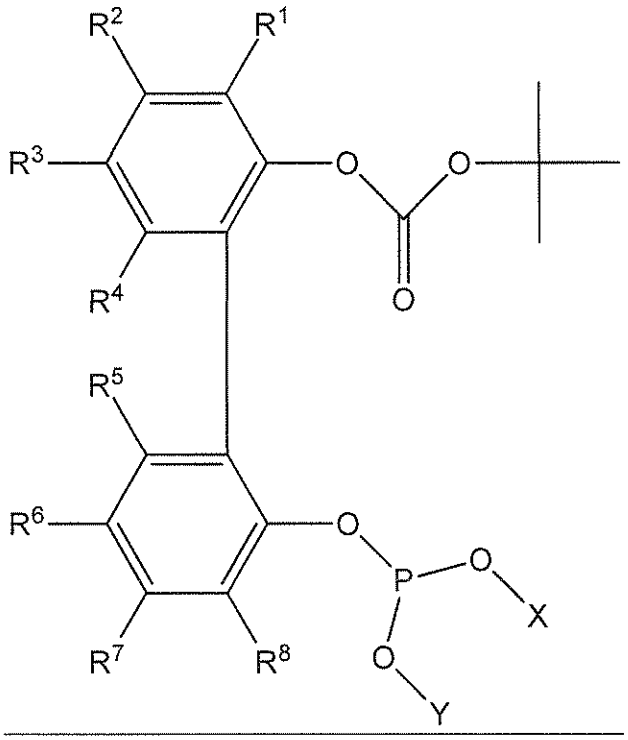
The object is achieved by a ligand according to ~~Claim 1~~the present disclosure.

Ligand having one of the two general structures **I** and **II**:

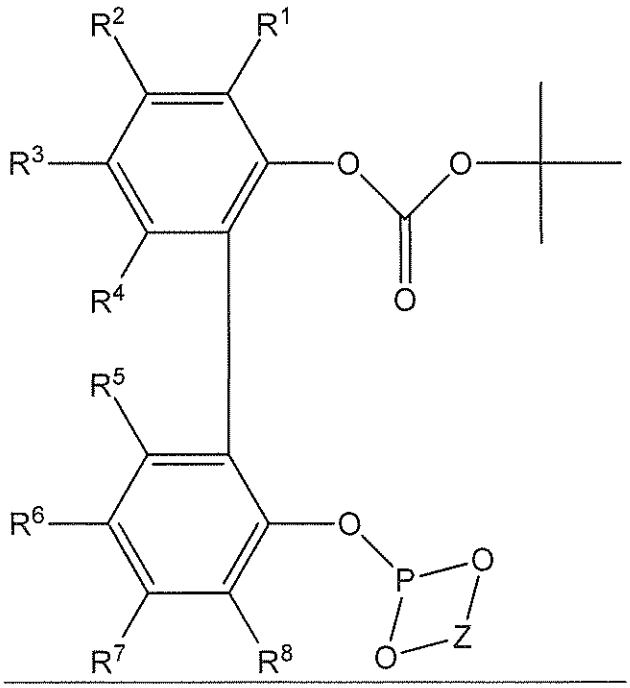


I

In one aspect of the present disclosure, there is provided a ligand having one of the two general structures I and II:



I



II

where

R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8 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, 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]$_2$;

X and Y are each independently selected from:

-$(C_1$-$C_{12})$-alkyl, -$(C_6$-$C_{20})$-aryl, -$(C_6$-$C_{20})$-aryl-$(C_1$-$C_{12})$-alkyl, -$(C_6$-$C_{20})$-aryl-O-$(C_1$-$C_{12})$-alkyl, -$(C_1$-$C_{12})$-alkyl-$(C_6$-$C_{20})$-aryl, -$(C_6$-$C_{20})$-aryl-COO-$(C_1$-$C_{12})$-alkyl, -$(C_6$-$C_{20})$-aryl-CONH-$(C_1$-$C_{12})$-alkyl, -$(C_6$-$C_{20})$-aryl-CON[$(C_1$-$C_{12})$-alkyl]$_2$, -$(C_4$-$C_{20})$-heteroaryl, -$(C_4$-$C_{20})$-heteroaryl-$(C_1$-$C_{12})$-alkyl, -$(C_5$-$C_8)$-cycloalkyl-$(C_4$-$C_{20})$-aryl-CO-$(C_6$-$C_{20})$-aryl,

Z is selected from:

-$(C_1$-$C_{12})$-alkyl-, -$(C_6$-$C_{20})$-aryl-, -$(C_6$-$C_{20})$-aryl-$(C_1$-$C_{12})$-alkyl-, -$(C_1$-$C_{12})$-alkyl-$(C_6$-$C_{20})$-aryl-, -$(C_4$-$C_{20})$-heteroaryl-, -$(C_6$-$C_{20})$-aryl-CO-$(C_6$-$C_{20})$-aryl-, -$(C_6$-$C_{20})$-aryl-$(C_6$-$C_{20})$-aryl-;

where the alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl and heteroaryl groups mentioned may be substituted.

$(C_1$-$C_{12})$-Alkyl and O-$(C_1$-$C_{12})$-alkyl may each 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.

$(C_3$-$C_{12})$-Cycloalkyl and $(C_3$-$C_{12})$-heterocycloalkyl may each 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.

$(C_6$-$C_{20})$-Aryl and -$(C_6$-$C_{20})$-aryl-$(C_6$-$C_{20})$-aryl- may each 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]$_2$.

In the context of the ~~invention~~present 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.

The elucidations relating to the expression -$(C_1$-$C_{12})$-alkyl also apply to the alkyl groups in -O-$(C_1$-$C_{12})$-alkyl, i.e. in -$(C_1$-$C_{12})$-alkoxy. Preferably, these groups are unsubstituted straight-chain or branched -$(C_1$-$C_6)$-alkoxy groups.

Substituted -$(C_1$-$C_{12})$-alkyl groups and substituted -$(C_1$-$C_{12})$-alkoxy 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.

The expression "-(C_3-C_{12})-heterocycloalkyl groups", in the context of the present ~~invention~~disclosure, encompasses nonaromatic saturated or partly unsaturated cycloaliphatic groups having 3 to 12, especially 5 to 12, carbon atoms. The -(C_3-C_{12})-heterocycloalkyl groups have preferably 3 to 8, more preferably 5 or 6, ring atoms. In the heterocycloalkyl groups, as opposed to the cycloalkyl groups, 1, 2, 3 or 4 of the ring carbon atoms are replaced by heteroatoms or heteroatom-containing groups. The heteroatoms or the heteroatom-containing groups are preferably selected from -O-, -S-, -N-, -N(=O)-, -C(=O)- and -S(=O)-. Examples of -(C_3-C_{12})-heterocycloalkyl groups are tetrahydrothiophenyl, tetrahydrofuryl, tetrahydropyranyl and dioxanyl.

Substituted -(C_3-C_{12})-cycloalkyl groups and substituted -(C_3-C_{12})-heterocycloalkyl 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 ~~invention~~disclosure, the expression -(C_6-C_{20})-aryl and -(C_6-C_{20})-aryl-(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 and -(C_6-C_{20})-aryl-(C_6-C_{20})-aryl groups may have one or more (e.g. 1, 2, 3, 4 or 5) substituents, depending on their 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-

-H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -O-(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl, -COO-(C_1-C_{12})-alkyl, -N[(C_1-C_{12})-alkyl]$_2$.

In one embodiment, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16} are each independently selected from:
-H, -(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl;
where alkyl comprises 1-18 carbon atoms, preferably 1-10 carbon atoms, for example primary, secondary or tertiary alkyl groups such as methyl, ethyl, n-propyl, isopropyl, butyl, sec-butyl, t-butyl, t-butylethyl, t-butylpropyl, n-hexyl, amyl, sec-amyl, t-amyl, isooctyl, 2-ethylhexyl, decyl, dodecyl and octadecyl groups.

In one embodiment, R^{11} and R^{14} are each -O-(C_1-C_{12})-alkyl.

In one embodiment, R^{11} and R^{14} are each -OMe.

In one embodiment, R^9 and R^{16} are each -(C_1-C_{12})-alkyl.

In one embodiment, R^9 and R^{16} are each *tert*-butyl.

In one embodiment, R^9, R^{11}, R^{14} and R^{16} are each -(C_1-C_{12})-alkyl.

In one embodiment, R^9, R^{11}, R^{14} and R^{16} are each methyl.

In one embodiment, R^9, R^{11}, R^{14} and R^{16} are each *tert*-butyl.

In one embodiment, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15} and R^{16} are each -H.

As well as the ligands, also ~~claimed~~ disclosed is a complex comprising these ligands.

In another aspect of the present disclosure, there is provided a ~~Complex~~ complex comprising:
- an above-described ligand,
- a metal atom selected from: Rh, Ru, Co, Ir.

In a preferred embodiment, the metal is Rh.

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.

Additionally ~~claimed~~ disclosed is the use of the ligand as ligand in a ligand-metal complex for catalysis of a hydroformylation reaction.

In a further aspect of the present disclosure, there is provided a ~~Use~~ use of an above-described ligand in a ligand-metal complex for catalysis of a hydroformylation reaction.

The process in which the ligand is used as ligand in a ligand-metal complex for conversion of an olefin to an aldehyde is likewise ~~claimed~~disclosed.

In yet another aspect of the present disclosure, there is provided a ~~Process~~ process comprising the process steps of:

a) initially charging an olefin,

b) adding an above-described complex,

or an above-described ligand and a compound including a metal atom selected from: Rh, Ru, Co, Ir,

c) feeding in H_2 and CO,

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

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

The reaction is conducted under customary conditions.

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 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 ligands 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 hydroformylated olefin, even when only a small proportion of olefins having a terminal double bond was present in the reactant.

The invention is to be illustrated in detail hereinafter by working examples.

The following seventy structures (**1** to **70**) show possible working examples of the ligand: