

Improved Carbonylation Process

This invention relates to an improved process for the
5 carbonylation of ethylenically unsaturated compounds and,
in particular, a method providing an improved turnover
number (TON) for the catalyst system employed in the
carbonylation.

10 The carbonylation of ethylenically unsaturated compounds
using carbon monoxide in the presence of an alcohol or
water and a catalyst system comprising a group 6, 8, 9 or
10 metal, for example, palladium, and a phosphine ligand,
for example an alkyl phosphine, cycloalkyl phosphine, aryl
15 phosphine, pyridyl phosphine or bidentate phosphine, has
been described in numerous European patents and patent
applications, for example EP-A-0055875, EP-A-04489472, EP-
A-0106379, EP-A-0235864, EP-A-0274795, EP-A-0499329, EP-A-
0386833, EP-A-0441447, EP-A-0489472, EP-A-0282142, EP-A-
20 0227160, EP-A-0495547 and EP-A-0495548. In particular,
EP-A-0227160, EP-A-0495547 and EP-A-0495548 disclose that
bidentate phosphine ligands provide catalyst systems which
enable high reaction rates to be achieved. C3 alkyl
bridges between the phosphorus atoms are exemplified in
25 EP0495548 together with tertiary butyl substituents on the
phosphorus.

WO96/19434 subsequently disclosed that a particular group
of bidentate phosphine compounds having an aryl bridge
30 could provide remarkably stable catalysts which require
little or no replenishment; that use of such bidentate
catalysts leads to reaction rates which are significantly

higher than those previously disclosed; and that little or no impurities are produced at high conversions.

WO 01/68583 discloses rates for the same process as WO
5 96/19434 when used for higher alkenes and when in the presence of an externally added aprotic solvent.

WO 98/42717 discloses a modification to the bidentate phosphines used in EP0495548 wherein one or both
10 phosphorus atoms are incorporated into an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by heteroatoms ("2-PA" group). The examples include a number of alkoxycarbonylations of
15 ethene, propene and some higher terminal and internal olefins.

WO 03/070370 extends the teaching of WO 98/42717 to bidentate phosphines having 1, 2 substituted aryl bridges
20 of the type disclosed in WO96/19434. The suitable olefin substrates disclosed include several types having various substituents.

WO 04/103948 describes both the above types of ligand
25 bridges as useful for 1,3-butadiene carbonylation and WO 05/082830 describes a selection of WO 04/103948 where the tertiary carbon substituents are different from each other on the respective phosphorus atoms.

30 WO 00/56695 relates to the use of phobane ligands for diene alkoxycarbonylation, optionally in the presence of benzoic acids as a source of anions. Hydroxycarbonylation is mentioned as a further possibility but is not

exemplified; it is stated in this case that that the carbonylation product is used as the source of anions.

In industrial processes used to produce chemical products,
5 the avoidance of contamination in the final product is often paramount. In catalytic processes, the introduced chemicals will often include, in addition to the reactants and catalysts, solvents and various other additives necessary to assist the production process.
10 Nevertheless, unnecessary components will be avoided to avoid contamination and/or purification problems later in the process.

In the carbonylation of ethylenically unsaturated
15 compounds using carbon monoxide a co-reactant is generally used. The co-reactant influences the final product. For instance, an alcohol will generate an ester as the final product, ammonia will produce an amide and a carboxylic acid will produce an anhydride. The use of water as co-
20 reactant generally produces the carboxylic acid product. Therefore, depending on the final product desired, a particular co-reactant will need to be present in the reactor. The presence of other possible co-reactants will generally be undesirable, particularly, if the co-reactant
25 is a problematic contaminant. Accordingly, in a process where the co-reactant is other than water, the presence of water would generally be undesirable, particularly if water was a problematic contaminant. In the production of methyl propionate from ethylene and carbon monoxide, the
30 presence of water in the distillation column has been found to be undesirable because it forms an azeotrope with methyl propionate and remains as an impurity.

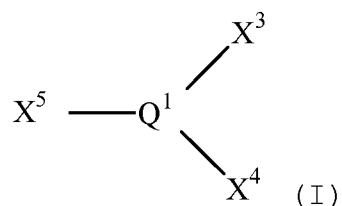
In a process for the carbonylation of an ethylenically unsaturated compound in the presence of a catalyst system obtainable by combining a group 8, 9 or 10 metal or metal compound and a phosphine, arsine or stibine ligand it has
5 been found that the reaction proceeds more favourably in the presence of an acid as a source of anions. However, in a continuous industrial process using metal vessels and parts the presence of acid can cause detrimental corrosion of the metal. Nevertheless, the corrosion power of any
10 acid present generally is far less effective in the absence of water or other polar solvent. In view of the above, in such processes where acid was present, unless the co-reactant was water, it would be advantageous to avoid the presence of water.

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Surprisingly, it has now been found however that small amounts of water dramatically improve the TON of such a catalyst system whilst not significantly affecting corrosion of the metal vessels or producing a significant
20 amount of contamination.

According to a first aspect of the present invention there is provided a method of increasing the TON of a catalyst system for the monocarbonylation of an ethylenically
25 unsaturated compound using carbon monoxide in the presence of a co-reactant, other than water or a source thereof, having a mobile hydrogen atom, the catalyst system obtainable by combining

- 30 (a) a metal of Group 8, 9 or 10 or a suitable compound thereof;
- (b) a ligand of general formula (I)



wherein

5 the groups X^3 and X^4 independently represent univalent radicals of up to 30 atoms or X^3 and X^4 together form a bivalent radical of up to 40 atoms and X^5 has up to 400 atoms;

10 Q^1 represents phosphorus, arsenic or antimony; and

c) optionally, a source of anions;

characterised in that the method includes the step of
15 adding water or a source thereof to the catalyst system.

Preferably, the method is carried out in the presence of an electropositive metal selected from the list consisting of:-titanium, niobium, tantalum, zirconium or alloys
20 thereof; hastelloy, Monel, Inconel and stainless steel. Typically, the hastelloy may be selected from B3, C-4, C-22, C-276, C-2000, G-30, G-35, N AND ULTIMET. Typical Monel grades are alloy 400, R-405, K500, and alloy 600. Typical stainless steel grades are 301, 302, 304, 304L,
25 316, 316L, 317, 317L, 321, 332, 334, 347, 405, 409, 410, 416, 420 and 442. Preferably, the metal is selected from titanium or an alloy thereof or hastelloy.

Suitable titanium alloys include alpha alloys, alpha-beta
30 alloys and beta alloys. Suitable further metals in the

alloy include aluminium (3-10% w/w), copper(1-3% w/w), molybdenum(0.1-20% w/w), vanadium (0.1 - 20%w/w), tin(1-5 % w / w) , zirconium(1-5 % w / w) , silicon(0.05-2%w/w), niobium(0.1-2%w/w), chromium(1-10%w/w) and iron (1-5%w/w) preferably at, if present, the preferred ranges bracketed. Alpha alloys include commercially pure ASTM grades 1,2, 3 and 4 ; Ti/Pd ASTM grade 7 and 11 and alpha compounds such as that with 2.5%w/w Cu known as IMI 230. Other alpha type alloys include IMI 685, IMI829, IMI834 and Ti 1100 or similar grades such as Ti with 8%w/w Al, 1%w/w Mo and 1%w/w V; Ti with 6%w/w Al, 2%w/w Sn, 4%w/w Zr, 2%w/w Mo and 0.08%w/w Si. Suitable Alpha-Beta grades include Ti with 6%w/w Al and 4%w/w V; Ti with 4%w/w Al, 4%w/w Mo, 2%w/w S n a n d 0.5%w/w Si; Ti with 4%w/w Al, 4%w/w Mo, 4%w/w Sn and 0.5%w/w Si (IMI 551); Ti with 6%w/w Al, 6%w/w V and 2%w/w Sn; and Ti with 6%w/w Al, 2%w/w Sn, 4%w/w Zr and 6%w/w Mo. Suitable beta grades include Ti with 3%w/w Al, 8%w/w V, 6%w/w C r , 4%w/w Zr and 4%w/w Mo (Beta C); Ti with 15%w/w Mo, 3%w/w Nb, 3%w/w Al and 0.2%w/w Si (T i m e t a l 21 S) ; and Ti with 15%w/w V, 3%w/w Cr, 3%w/w Sn and 3%w/w Al.

Suitable niobium alloys include:-niobium/ titanium alloys and niobium/zirconium alloys such as niobium one zirc.

Suitable tantalum alloys include: - tantalum-tungsten alloys, and tantalum-niobium alloys such as tantalum with 0.05-5%w/w tungsten and 0-50%w/w niobium. .

Suitable zirconium alloys include: - alloys with hafnium at 1-10%w/w and niobium at 0-5%w/w. Suitable examples include:- Alloys 702, 704, 705 and 706.

Preferably, one or more of the reaction vessel and/or conduits to and from the reaction vessel that come into contact with the catalyst system in the liquid phase are formed of the said electropositive metal and in this manner the process is carried out in the presence of said electropositive metal.

By monocarbonylation is meant the combination of an ethylenically unsaturated moiety and a single carbon monoxide molecule to produce a new insertion carbonylation end product without further insertion of a second or further ethylenically unsaturated compound. Accordingly, the end product of a monocarbonylation reaction cannot be a polymer or oligomer which are both derived from multiple carbon monoxide and ethylenically unsaturated compound insertions into a growing molecule. However, if there is more than one double bond in the ethylenically unsaturated compound then each double bond may combine with a single carbon monoxide molecule to form a new species but further insertion of a second or further ethylenically unsaturated compound will not take place and monocarbonylation should be understood accordingly.

Preferably, the amount of water added to the catalyst system is 0.001-10% w/w liquid phase, more preferably, 0.01-5% w/w, most preferably, 0.02 - 3% w/w, especially 0.05-1.0%w/w liquid phase. Therefore, the amount of water added is preferably, > 0.005%, more preferably, > 0.03%, most preferably, > 0.1% w/w, especially, 0.25% or 0.4%w/w and in any case generally < 7.5% w/w liquid phase. Surprisingly, the addition of water may have the effect of enhancing TON for the monocarbonylation reaction in a newly generated catalytic system and also have a

regenerative TON effect on an existing catalytic system in which the TON has fallen.

The monocarbonylation reaction may be a batch or
5 continuous reaction. Preferably, the method increases the TON in a semi-continuous or continuous process.

Advantageously, the use of a continuous process may maintain the water level continuously and reveals the
10 increased TON. However, even in a continuous process the water may be added periodically rather than continuously to thereby supplement the water in the reactor as necessary to maintain the required TON improvement level.

15 The reaction may therefore be carried out in a suitable reactor. Suitable reactors may be made of the metals and alloys mentioned supra. It will be appreciated by those skilled in the art that the compounds of formulas (I) to (IV) mentioned herein may function as ligands that
20 coordinate with the Group 8, 9 or 10 metal or compound thereof to form the catalytic compounds for use in the invention. Typically, the Group 8, 9 or 10 metal or compound thereof coordinates to the one or more phosphorus, arsenic and/or antimony atoms of the compound
25 of formulas (I) to (IV).

CO-REACTANT

The ratio (mol/mol) of ethylenically unsaturated compound
30 and co-reactant in the reaction can vary between wide limits and suitably lies in the range of 10:1 to 1:500. The co-reactant of the present invention may be any compound other than water having a mobile hydrogen atom,

and capable of reacting as a nucleophile with the ethylenically unsaturated compound under catalytic conditions. The chemical nature of the co-reactant determines the type of product formed. Possible co-reactants are carboxylic acids, alcohols, ammonia or amines, thiols, or a combination thereof.

If the co-reactant is a carboxylic acid the product is an anhydride. For an alcohol co reactant, the product of the carbonylation is an ester. Similarly, the use of ammonia (NH_3) or a primary or secondary amine R^{81}NH_2 or $\text{R}^{82}\text{R}^{83}\text{NH}$ will produce an amide, and the use of a thiol R^{81}SH will produce a thioester.

In the above-defined co-reactants, R^{81} R^{82} and/or R^{83} represent alkyl, alkenyl or aryl groups which may be unsubstituted or may be substituted by one or more substituents selected from halo, cyano, nitro, OR^{19} , OC(O)R^{20} , C(O)R^{21} , C(O)OR^{22} , $\text{NR}^{23}\text{R}^{24}$, $\text{C(O)NR}^{25}\text{R}^{26}$, SR^{29} , C(O)SR^{30} , $\text{C(S)NR}^{27}\text{R}^{28}$, aryl or Het, wherein R^{19} to R^{30} are defined herein, and/or be interrupted by one or more oxygen or sulphur atoms, or by silano or dialkylsilicon groups.

If ammonia or amines are employed, a small portion of co-reactants will react with acid present in the reaction to form an amide and water. Therefore, in the case of ammonia or amine-co-reactants, the water component of the present invention may be generated in situ.

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Preferred amine co-reactants have from 1 to 22, more preferably, 1 to 8 carbon atoms per molecule, and diamine co-reactants preferably have 2 to 22, more preferably 2 to

10 carbon atoms per molecule. The amines can be cyclic, part-cyclic, acyclic, saturated or unsaturated(including aromatic), unsubstituted or substituted by one or more substituents selected from halo, cyano, nitro, OR^{19} ,
5 $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29} , $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl, alkyl, Het, wherein R^{19} to R^{30} are as defined herein and/or be interrupted by one or more (preferably less than a total of 4) oxygen, nitrogen, sulphur, silicon atoms or by silano or dialkyl silicon
10 groups or mixtures thereof

The thiol co-reactants can be cyclic, part-cyclic, acyclic, saturated or unsaturated(including aromatic), unsubstituted or substituted by one or more substituents
15 selected from halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29} , $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl, alkyl, Het, wherein R^{19} to R^{30} are as defined herein and/or be interrupted by one or more (preferably less than a total of 4) oxygen, nitrogen, sulphur, silicon atoms or
20 by silano or dialkyl silicon groups or mixtures thereof. Preferred thiol co-reactants are aliphatic thiols with 1 to 22, more preferably with 1 to 8 carbon atoms per molecule, and aliphatic di-thiols with 2 to 22, more preferably 2 to 8 carbon atoms per molecule.

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If a co-reactant should react with the acid serving as a source of anions, then the amount of the acid to co-reactant should be chosen such that a suitable amount of free acid is still present in the reaction. A large
30 surplus of acid over the co-reactant may be advantageous due to the enhanced reaction rates facilitated by the excess acid.

As mentioned above, the present invention provides a process for the carbonylation of ethylenically unsaturated compounds comprising contacting an ethylenically unsaturated compound with carbon monoxide and a co-reactant. The co-reactant is more preferably an organic molecule having an hydroxyl functional group such as an alkanol.

Suitably, as mentioned above, the co-reactant includes an organic molecule having an hydroxyl functional group. Preferably, the organic molecule having a hydroxyl functional group may be branched or linear, cyclic, acyclic, part cyclic or aliphatic and is, typically an alkanol, particularly a C₁-C₃₀ alkanol, including aryl alcohols, which may be optionally substituted with one or more substituents selected from alkyl, aryl, Het, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)NR²⁷R²⁸, SR²⁹ or C(O)SR³⁰ as defined herein. Highly preferred alkanols are C₁-C₈ alkanols such as methanol, ethanol, propanol, iso-propanol, iso-butanol, t-butyl alcohol, phenol, n-butanol and chlorocapryl alcohol. Although the monoalkanols are most preferred, polyalkanols, preferably, selected from di-octols such as diols, triols, tetra-ols and sugars may also be utilised. Typically, such polyalkanols are selected from 1, 2-ethanediol, 1,3-propanediol, glycerol, 1,2,4 butanetriol, 2-(hydroxymethyl)-1,3-propanediol, 1,2,6 trihydroxyhexane, pentaerythritol, 1,1,1 tri(hydroxymethyl)ethane, nannose, sorbose, galactose and other sugars. Preferred sugars include sucrose, fructose and glucose. Especially preferred alkanols are methanol and ethanol. The most preferred alkanol is methanol. The co-reactant preferably does not include an enhancer compound as defined herein.

The amount of alcohol is not critical. Generally, amounts are used in excess of the amount of substrate to be carbonylated. Thus the alcohol may serve as the reaction
5 solvent as well, although, if desired, separate solvents may also be used.

It will be appreciated that the end product of the reaction is determined at least in part by the source of
10 alkanol used. For instance, use of methanol produces the corresponding methyl ester. Accordingly, the invention provides a convenient way of adding the group $-C(O)O$ C_1-C_{30} alkyl or aryl across the ethylenically unsaturated bond.

15 **SOLVENTS**

Preferably, the reaction of the present invention is carried out in the presence of a suitable solvent. Suitable solvents will be described hereafter. Preferably, the group 8, 9 or 10 metal/metal compound and ligand are
20 added to the solvent(s) and preferably, dissolved therein.

Suitable solvents for use in the present invention include ketones, such as for example methylbutylketone; ethers, such as for example anisole (methyl phenyl ether), 2,5,8-
25 trioxanonane (diglyme), diethyl ether, dimethyl ether, methyl-tert-butylether (MTBE), tetrahydrofuran, diphenylether, diisopropylether and the dimethylether of di-ethylene-glycol; oxanes, such as for example dioxane; esters, such as for example methylacetate, dimethyladipate
30 methyl benzoate, dimethyl phthalate and butyrolactone; amides, such as for example dimethylacetamide, N-methylpyrrolidone and dimethyl formamide; sulfoxides and sulphones, such as for example dimethylsulphoxide, di-

isopropylsulphone, sulfolane (tetrahydrothiophene-2,2-dioxide), 2-methylsulfolane, diethyl sulphone, tetrahydrothiophene 1,1-dioxide and 2-methyl-4-ethylsulfolane; aromatic compounds, including halo variants of such compounds e.g. benzene, toluene, ethyl benzene o-xylene, m-xylene, p-xylene, chlorobenzene, o-dichlorobenzene, m-dichlorobenzene: alkanes, including halo variants of such compounds e.g. hexane, heptane, 2,2,3-trimethylpentane, methylene chloride and carbon tetrachloride; nitriles e.g. benzonitrile and acetonitrile.

Very suitable are aprotic solvents having a dielectric constant that is below a value of 50, more preferably 1-30, most preferably, 1-10, especially in the range of 2 to 8, at 298 or 293K and $1 \times 10^5 \text{Nm}^{-2}$. In the context herein, the dielectric constant for a given co-solvent is used in its normal meaning of representing the ratio of the capacity of a condenser with that substance as dielectric to the capacity of the same condenser with a vacuum for dielectric. Values for the dielectric constants of common organic liquids can be found in general reference books, such as the Handbook of Chemistry and Physics, 76th edition, edited by David R. Lide et al, and published by CRC press in 1995, and are usually quoted for a temperature of about 20°C or 25°C, i.e. about 293.15K or 298.15 K, and atmospheric pressure, i.e. about $1 \times 10^5 \text{Nm}^{-2}$, and can readily be converted to 298.15 K and atmospheric pressure using the conversion factors quoted. If no literature data for a particular compound is available, the dielectric constant may be readily measured using established physico-chemical methods.

Measurement of a dielectric constant of a liquid can easily be performed by various sensors, such as immersion probes, flow-through probes, and cup-type probes, attached to various meters, such as those available from the
5 Brookhaven Instruments Corporation of Holtsville, N.Y. (e.g., model BI-870) and the Scientifica Company of Princeton, N.J. (e.g. models 850 and 870). For consistency of comparison, preferably all measurements for a particular filter system are performed at substantially
10 the same sample temperature, e.g., by use of a water bath. Generally, the measured dielectric constant of a substance will increase at lower temperatures and decrease at higher temperatures. The dielectric constants falling within any ranges herein, may be determined in accordance with ASTM
15 D924.

However, if there is doubt as to which technique to use to determine the dielectric constant a Scientifica Model 870 Dielectric Constant Meter with a 1-200 ϵ range setting
20 should be used.

For example, the dielectric constant of methyl-tert-butyl ether is 4.34 (at 293 K), of dioxane is 2.21 (at 298 K), of toluene is 2.38 (at 298 K), tetrahydrofuran is 7.5 (at
25 295.2 K) and of acetonitrile is 37.5 (at 298 K). The dielectric values are taken from the handbook of chemistry and physics and the temperature of the measurement is given.

30 Alternatively, the reaction may proceed in the absence of an aprotic solvent not generated by the reaction itself. In other words, the only aprotic solvent is the reaction product. This aprotic solvent may be solely generated by

the reaction itself or , more preferably, is added as a solvent initially and then also produced by the reaction itself.

5 Alternatively, a protic solvent other than water or a source thereof may be used. The protic solvent may include a carboxylic acid (as defined above) or an alcohol. Suitable protic solvents include the conventional protic solvents known to the person skilled
10 in the art, such as lower alcohols, such as, for example, methanol, ethanol and isopropanol, and primary and secondary amines. Mixtures of the aprotic and protic co-solvents may also be employed both initially and when generated by the reaction itself.

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By protic solvent is meant any solvent that carries a donatable hydrogen ion such as those attached to oxygen as in a hydroxyl group or nitrogen as in an amine group. By aprotic solvent is meant a type of solvent which neither
20 donates nor accepts protons.

Metal

For the avoidance of doubt, references to Group 8, 9 or 10
25 metals herein should be taken to include Groups 8, 9 and 10 in the modern periodic table nomenclature. By the term "Group 8, 9 or 10" we preferably select metals such as Ru, Rh, Os, Ir, Pt and Pd. Preferably, the metals are selected from Ru, Pt and Pd, more preferably, the metal is
30 Pd.

Anion

Suitable compounds of such Group 8, 9 or 10 metals include salts of such metals with, or compounds comprising weakly coordinated anions derived from, nitric acid; sulphuric acid; lower alkanoic (up to C₁₂) acids such as
5 acetic acid and propionic acid; sulphonic acids such as methane sulphonic acid, chlorosulphonic acid, fluorosulphonic acid, trifluoromethane sulphonic acid, benzene sulphonic acid, naphthalene sulphonic acid, toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid, and 2-hydroxypropane sulphonic acid;
10 sulphonated ion exchange resins (including low acid level sulphonic resins) perhalic acid such as perchloric acid; halogenated carboxylic acids such as trichloroacetic acid and trifluoroacetic acid; orthophosphoric acid; phosphonic
15 acids such as benzenephosphonic acid; and acids derived from interactions between Lewis acids and Broensted acids. Other sources which may provide suitable anions include the optionally halogenated tetraphenyl borate derivatives, e.g. perfluorotetraphenyl borate. Additionally, zero
20 valent palladium complexes particularly those with labile ligands, e.g. triphenylphosphine or alkenes such as dibenzylideneacetone or styrene or tri(dibenzylideneacetone)dipalladium may be used.

25 The above anions may be introduced directly as a compound of the metal but may also be introduced to the catalyst system independently of the metal or metal compound. Preferably, they are introduced as the acid. Preferably, an acid is selected to have a pK_a less than 6 measured in
30 dilute aqueous solution at 25°C. The pK_a is preferably less than about 4 measured in dilute aqueous solution at 18°C. Particularly preferred acids have a pK_a of less than 2 measured in dilute aqueous solution at 25°C but, in the

case of some substrates such as dienes, a pKa of between 2-6 measured in dilute aqueous solution at 18°C is preferred. Suitable acids and salts may be selected from the acids and salts listed supra.

5

Accordingly, preferably, the catalyst system of the present invention includes a source of anions preferably derived from one or more acids having a pKa in aqueous solution at 25°C of less than 6, more preferably, less
10 than 3, most preferably, less than 2.

Addition of such acids to the catalyst system is preferred and provides acidic reaction conditions.

15 For the avoidance of doubt, references to pKa herein are references to pKa measured in dilute aqueous solution at 25°C unless indicated otherwise. For the purposes of the invention herein, the pKa may be determined by suitable techniques known to those skilled in the art.

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Generally, for ethylenically unsaturated substrates which are not pH sensitive a stronger acid is preferred. Particularly preferred acids are the sulphonic acids listed supra.

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In the carbonylation reaction the quantity of anion present is not critical to the catalytic behaviour of the catalyst system. The molar ratio of Group 8, 9 or 10 metal/compound to anion may be from 1:2 to 1:4000, more
30 preferably, 1:2 to 1:1000, most preferably, 1:5 to 1:200, especially, 1:10 to 1:200. Where the anion is provided by an acid and salt, the relative proportion of the acid and salt is not critical. Accordingly, if a co-reactant should

react with an acid serving as source of anions, then the amount of the acid to co-reactant should be chosen such that a suitable amount of free acid is present.

5 **Carbonylating Agent and Process Conditions**

In the process according to the present invention, the carbon monoxide may be used in pure form or diluted with an inert gas such as nitrogen, carbon dioxide or a noble gas such as argon.

Hydrogen may optionally be added to the carbonylation reaction to improve reaction rate. Suitable levels of hydrogen when utilised may be in the ratio of between 0.1 and 10% vol/vol of the carbon monoxide, more preferably, 1-10% vol/vol of the carbon monoxide, more preferably, 2-5% vol/vol of the carbon monoxide, most preferably 3-5% vol/vol of carbon monoxide.

The molar ratio of the amount of ethylenically unsaturated compound used in the reaction to the amount of solvent is not critical and may vary between wide limits, e.g. from 1:1 to 1000:1 mol/mol. Preferably, the molar ratio of the amount of ethylenically unsaturated compound used in the reaction to the amount of solvent is between 1:2 and 1:500, more preferably, 1:2 to 1:100. For the avoidance of doubt, such solvent includes the reaction product and co-reactant.

The amount of the catalyst of the invention used in the carbonylation reaction is not critical. Good results may be obtained, preferably when the amount of Group 8, 9 or 10 metal is in the range 1×10^{-7} to 10^{-1} moles per mole of

ethylenically unsaturated compound, more preferably, 1×10^{-6} to 10^{-1} moles, most preferably 1×10^{-6} to 10^{-2} moles per mole of ethylenically unsaturated compound.

5 Preferably, the amount of ligand of formulas [I-IV] to ethylenically unsaturated compound is in the range 1×10^{-6} to 10^{-1} , more preferably, 1×10^{-6} to 10^{-1} , most preferably, 1×10^{-5} to 10^{-2} moles per mole of ethylenically unsaturated compound. Preferably, the
 10 amount of catalyst is sufficient to produce product at an acceptable rate commercially.

Preferably, the carbonylation is carried out at temperatures of between -30 to 170°C , more preferably -
 15 10°C to 160°C , most preferably 20°C to 150°C . An especially preferred temperature is one chosen between 40°C to 150°C . Alternatively, the carbonylation can be carried out at moderate temperatures, it is particularly advantageous in some circumstances to be able to carry out
 20 the reaction at or around room temperature (20°C).

Preferably, when operating a low temperature carbonylation, the carbonylation is carried out between -30°C to 49°C , more preferably, -10°C to 45°C , still more
 25 preferably 0°C to 45°C , most preferably 10°C to 45°C . Especially preferred is a range of 10 to 35°C .

Preferably, the carbonylation is carried out at a CO partial pressure in the reactor of between $0.01 \times 10^5 \text{ N.m}^{-2}$ to $2 \times 10^5 \text{ N.m}^{-2}$, more preferably $0.02 \times 10^5 \text{ N.m}^{-2}$ to $1 \times 10^5 \text{ N.m}^{-2}$, most preferably 0.05 - $0.5 \times 10^5 \text{ N.m}^{-2}$. Especially preferred is a CO partial pressure of 0.1 to $0.3 \times 10^5 \text{ N.m}^{-2}$.

In the carbonylation reaction of the invention, preferably, the ratio of equivalents of bidentate ligand to group 8, 9 or 10 metal is at least 1:1 mol/mol. The ligand may be in excess of metal mol/mol but is especially between 1:1 and 2:1 mol/mol.

10 Preferably, the mole ratio of ligand to group 8, 9 or 10 metal for a bidentate ligand is between 1:1 and 100:1, more preferably, 1:1 to 50:1, most preferably, 1:1 to 20:1. For a monodentate, tridentate, etc ligand the mole ratio is varied accordingly.

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Preferably, the mole ratio of ligand to acid in the reactor for a bidentate ligand and a monoprotic acid is at least 1:2 and may be up to 1:2000. However, typically, for most applications, a range of 1:2 to 1:500, more typically, 1:5 to 1:100 is sufficient. For a monodentate, tridentate, etc ligand and/or diprotic, or triprotic etc acid, the mole ratio is varied accordingly.

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Preferably, the mole ratio of group 8, 9 or 10 metal to acid for a monoprotic acid is from 1:2 to 1:4000, more preferably, 1:2 to 1:1000, most preferably, 1:5 to 1:200, especially, 1:10 to 1:200.

30

For a diprotic, triprotic, etc acid, the mole ratio is varied accordingly.

For the avoidance of doubt, the above ratio conditions apply at the start of a batch reaction or during a continuous reaction.

As mentioned, the catalyst system of the present invention
5 may be used homogeneously or heterogeneously. Preferably, the catalyst system is used homogeneously.

Suitably, the catalysts of the invention are prepared in a separate step preceding their use in-situ in the
10 carbonylation reaction.

Conveniently, the process of the invention may be carried out by dissolving the Group 8, 9 or 10 metal or compound thereof as defined herein in a suitable solvent such as
15 one of the alkanols or aprotic solvents previously described or a mixture thereof. A particularly preferred solvent would be the product of the specific carbonylation reaction which may be mixed with other solvents or co-reactants. Subsequently, the admixed metal and solvent may
20 be mixed with a compound of formulas I -IV as defined herein.

The carbon monoxide may be used in the presence of other gases which are inert in the reaction. Examples of such
25 gases include hydrogen, nitrogen, carbon dioxide and the noble gases such as argon.

The product of the reaction may be separated from the other components by any suitable means. However, it is an
30 advantage of the present process that significantly fewer by-products are formed thereby reducing the need for further purification after the initial separation of the product as may be evidenced by the generally significantly

higher selectivity. A further advantage is that the other components which contain the catalyst system which may be recycled and/or reused in further reactions with minimal supplementation of fresh catalyst.

5

There is no particular restriction on the duration of the carbonylation except that carbonylation in a timescale which is commercially acceptable is obviously preferred. Carbonylation in a batch reaction may take place in up to
10 48 hours, more typically, in up to 24 hours and most typically in up to 12 hours. Typically, carbonylation is for at least 5 minutes, more typically, at least 30 minutes, most typically, at least 1 hour. In a continuous reaction such time scales are obviously irrelevant and a
15 continuous reaction can continue as long as the TON is commercially acceptable before catalyst requires replenishment. Significantly, in the present invention, this time scale to replenishment can be increased.

20 The catalyst system of the present invention is preferably constituted in the liquid phase which may be formed by one or more of the reactants or by the use of one or more solvents as defined herein.

25 **Ethylenically Unsaturated Compounds**

Suitably, the process of the invention may be used to catalyse the carbonylation of ethylenically unsaturated compounds in the presence of carbon monoxide and a co-
30 reactant, other than water, having a mobile hydrogen atom, and, optionally, a source of anions. The ligands of the invention yield a surprisingly high TON in monocarbonylation reactions, preferably, ethylene,

propylene, 1,3-butadiene, pentenenitrile, and octene monocarbonylation, especially ethylene. Consequently, the commercial viability of a monocarbonylation process will be increased by employing the process of the invention.

5

Advantageously, use of the catalyst system of the present invention in the monocarbonylation of ethylenically unsaturated compounds etc also gives good rates especially for alkoxycarbonylation.

10

References to ethylenically unsaturated compounds herein should be taken to include any one or more unsaturated C-C bond(s) in a compound such as those found in alkenes, alkynes, conjugated and unconjugated dienes, functional alkenes etc.

15

Suitable ethylenically unsaturated compounds for the invention are ethylenically unsaturated compounds having from 2 to 50 carbon atoms per molecule, or mixtures thereof. Suitable ethylenically unsaturated compounds may have one or more isolated or conjugated unsaturated bonds per molecule. Preferred are compounds having from 2 to 20 carbon atoms, or mixtures thereof, yet more preferred are compounds having at most 18 carbon atoms, yet more at most 25 16 carbon atoms, again more preferred compounds have at most 10 carbon atoms. The ethylenically unsaturated compound may further comprise functional groups or heteroatoms, such as nitrogen, sulphur or oxide. Examples include carboxylic acids, esters or nitriles as functional groups. In a preferred group of processes, the 30 ethylenically unsaturated compound is an olefin or a mixture of olefins. Suitable ethylenically unsaturated compounds include acetylene, methyl acetylene, propyl

acetylene, 1,3-butadiene, ethylene, propylene, butylene, isobutylene, pentenes, pentene nitriles, alkyl pentenoates such as methyl 3-pentenoates, pentene acids (such as 2-and 3-pentenoic acid), heptenes, vinyl esters such as vinyl acetate, octenes, dodecenes.

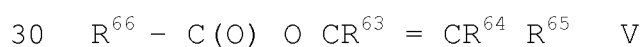
Particularly preferred ethylenically unsaturated compounds are ethylene, vinyl acetate, 1,3-butadiene, alkyl pentenoates, pentenenitriles, pentene acids (such as 3 pentenoic acid), acetylene, heptenes, butylene, octenes, dodecenes and propylene.

Especially preferred ethylenically unsaturated compounds are ethylene, propylene, heptenes, octenes, dodecenes, vinyl acetate, 1,3-butadiene and pentene nitriles, most especially preferred is ethylene.

Still further, it is possible to carbonylate mixtures of alkenes containing internal double bonds and/or branched alkenes with saturated hydrocarbons. Examples are raffinate 1, raffinate 2 and other mixed streams derived from a cracker, or mixed streams derived from alkene dimerisation (butene dimerisation is one specific example) and Fischer Tropsch reactions.

25

References to vinyl esters herein include references to substituted or unsubstituted vinyl ester of formula V:



wherein R^{66} may be selected from hydrogen, alkyl, aryl, Het, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$,

$\text{NR}^{23}\text{R}^{24}$, $\text{C(O)NR}^{25}\text{R}^{26}$, $\text{C(S)R}^{27}\text{R}^{28}$, SR^{29} , C(O)SR^{30} wherein R^{19} - R^{30} are as defined herein.

Preferably, R^{66} is selected from hydrogen, alkyl, phenyl
5 or alkylphenyl, more preferably, hydrogen, phenyl, C_1 - C_6 alkylphenyl or C_1 - C_6 alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl, even more preferably, C_1 - C_6 alkyl, especially methyl.

10 Preferably, R^{63} - R^{65} each independently represents hydrogen, alkyl, aryl or Het as defined herein. Most preferably, R^{63} - R^{65} independently represents hydrogen.

When the ethylenically unsaturated compound is a
15 conjugated diene it contains at least two conjugated double bonds in the molecule. By conjugation is meant that the location of the π -orbital is such that it can overlap other orbitals in the molecule. Thus, the effects of compounds with at least two conjugated double bonds are
20 often different in several ways from those of compounds with no conjugated bonds.

The conjugated diene preferably is a conjugated diene having from 4 to 22, more preferably from 4 to 10 carbon
25 atoms per molecule. The conjugated diene can be substituted with one or more further substituents selected from aryl, alkyl, hetero (preferably oxygen), Het, halo, cyano, nitro, $-\text{OR}^{19}$, $-\text{OC(O)R}^{20}$, $-\text{C(O)R}^{21}$, $-\text{C(O)OR}^{22}$, $-\text{N(R}^{23})\text{R}^{24}$, $-\text{C(O)N(R}^{25})\text{R}^{26}$, $-\text{SR}^{29}$, $-\text{C(O)SR}^{30}$, $-\text{C(S)N(R}^{27})\text{R}^{28}$ or
30 $-\text{CF}_3$ wherein R^{19} - R^{28} are as defined herein or non-substituted. Most preferably, the conjugated diene is selected from conjugated pentadienes, conjugated hexadienes, cyclopentadiene and cyclohexadiene all of

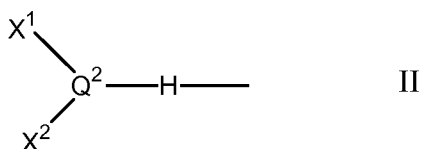
which may be substituted as set out above or unsubstituted. Especially preferred are 1,3-butadiene and 2-methyl-1,3-butadiene and most especially preferred is non-substituted 1,3-butadiene.

5

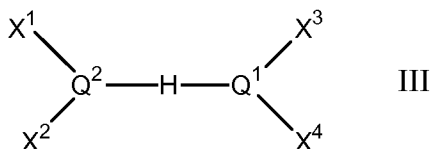
Ligand of General Formula I

Preferably, the phosphine, arsine or stibine ligand is a bidentate ligand. In such ligands, X⁵ may represent

10



Preferably, therefore, the bidentate phosphine, arsine or stibine ligand has a formula III



15

wherein H is a bivalent organic bridging group with 1-6 atoms in the bridge;

20

the groups X¹, X², X³ and X⁴ independently represent univalent radicals of up to 30 atoms, optionally having at least one tertiary carbon atom via which the group is joined to the Q¹ or Q² atom, or X¹ and X² and/or X³ and X⁴ together form a bivalent radical of up to 40 atoms, optionally having at least two tertiary carbon atoms via which the radical is joined to the Q¹ and/or Q² atom; and

25

Q^1 and Q^2 each independently represent phosphorus, arsenic or antimony.

Preferably, the group H has 3-5 atoms in the bridge.

5

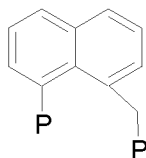
In any case, the bivalent organic bridging group may be an unsubstituted or substituted, branched or linear, cyclic, acyclic or part cyclic aliphatic, aromatic or araliphatic bivalent group having 1-50 atoms in the bridging group and
10 1-6, more preferably, 2-5, most preferably 3 or 4 atoms in the bridge.

The bivalent organic bridging group may be substituted or interrupted by one or more heteroatoms such as O, N, S, P
15 or Si. Such heteroatoms may be found in the bridge but it is preferred that the bridge consists of carbon atoms.

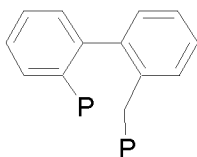
Suitable aliphatic bridging groups include alkylene groups such as 1,2-ethylene, 1-3 propylene, 1,2-propylene, 1,4-butylene, 2,2-dimethyl-1,3-propylene, 2-methyl-1,3-propylene, 1,5-pentylene, -O-CH₂CH₂-O- and -CH₂-NR-CH₂- or partial cycloaliphatic bridges including 1-methylene-cyclohex-2-yl, 1,2-dimethylene-cyclohexane and 1,2-dimethylene-cyclopentane. Suitable aromatic or
25 araliphatic bridges include 1,2-dimethylenebenzene, 1,2-dimethyleneferrocene, 1-methylene-phen-2-yl, 1-methylene-naphth-8-yl, 2-methylene-biphen-2'-yl and 2-methylene-binaphth-2'-yl. Bidentate phosphine aromatic bridged radicals of the latter three are illustrated below.

30

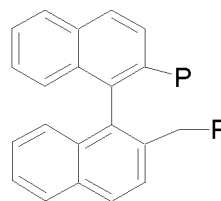
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1, 8, Naphthyl

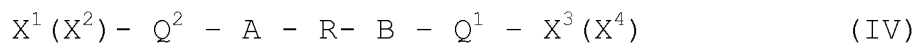


2, 2', Biphenyl



2, 2' Binaphthyl

In one preferred set of embodiments, H in formula II or
 III is the group -A-R-B- so that formula I is a bidentate
 5 ligand of general formula IV



wherein:

10

A and/or B each independently represent optional lower
 alkylene linking groups;

R represents a cyclic hydrocarbyl structure to which Q^1
 15 and Q^2 are linked, via the said linking group if present,
 on available adjacent cyclic atoms of the cyclic
 hydrocarbyl structure; and

Q^1 and Q^2 each independently represent phosphorus, arsenic
 20 or antimony.

Preferably, the groups X^3 and X^4 independently represent
 univalent radicals of up to 30 atoms having at least one
 tertiary carbon atom or X^3 and X^4 together form a bivalent
 25 radical of up to 40 atoms having at least two tertiary
 carbon atoms wherein each said univalent or bivalent
 radical is joined via said at least one or two tertiary
 carbon atoms respectively to the respective atom Q^1 .

Preferably, the groups X^1 and X^2 independently represent univalent radicals of up to 30 atoms having at least one primary, secondary, aromatic ring or tertiary carbon atom or X^1 and X^2 together form a bivalent radical of up to 40 atoms having at least two primary, secondary, aromatic ring or tertiary carbon atoms wherein each said univalent or bivalent radical is joined via said at least one or two primary, secondary, aromatic ring or tertiary carbon atom(s) respectively to the respective atom Q^2 .

Preferably, the groups X^1 , X^2 , X^3 and X^4 independently represent univalent radicals of up to 30 atoms having at least one tertiary carbon atom or X^1 and X^2 and/or X^3 and X^4 together form a bivalent radical of up to 40 atoms having at least two tertiary carbon atoms wherein each said univalent or bivalent radical is joined via said at least one or two tertiary carbon atoms respectively to the appropriate atom Q^1 or Q^2 .

Preferably, when X^1 and X^2 or X^1 and X^2 together are not joined via at least one or two tertiary carbon atom(s) respectively to the respective atom Q^2 , it is particularly preferred that at least one of the groups X^1 or X^2 which is thereby joined to the Q^2 atom via a primary, secondary or aromatic ring carbon includes a substituent. Preferably, the substituent is either on the carbon directly joined to the Q^2 atom or on the carbon adjacent thereto. However, the substituent can be more remote from the Q^2 atom. For instance, it may be up to 5 carbons removed from the Q^2 atom. Accordingly, it is preferred that the carbon joined to the Q^2 atom is an aliphatic secondary carbon atom or the alpha carbon thereto is an aliphatic secondary or

tertiary carbon atom or the carbon joined to the Q² atom is an aromatic carbon which forms part of an aromatic ring substituted at a suitable position in the ring. Preferably, in this case, the substituent is on the atom
5 adjacent the atom in the ring joined to the Q² atom.

Preferably, the further substituent in the preceding paragraph is a C₁-C₇ alkyl group or O- C₁-C₇ alkyl group, such as a methyl, ethyl, n-propyl, iso-butyl t-butyl ,
10 methoxy or ethoxy group or a relatively inert group such as -CN, -F, -Si(alkyl)₃, -COOR⁶⁷, -C(O)-, or -CF₃ wherein R⁶⁷ is alkyl, aryl or Het. Particularly preferred substituents are methyl, ethyl and propyl groups, especially methyl, methoxy or ethyl, more especially,
15 methyl. A preferred range of groups are the C₁-C₇ alkyl, O- C₁-C₇ alkyl substituted phenyl groups, especially, methyl, methoxy or ethyl phenyl groups. In such phenyl embodiments, substitution may be at the ortho, meta or para position, preferably, the ortho or meta position,
20 most preferably, the ortho position of the ring.

Suitable non tertiary carbon joined X¹ or X² groups are prop-2-yl, phen-1-yl, 2-methyl-phen-1-yl, 2-methoxy-phen-1-yl, 2-fluoro-phen-1-yl, 2-trifluoromethyl-phen-1-yl, 2-
25 trimethylsilyl-phen-1-yl, 4-methyl-phen-1-yl, 3-methyl-phen-1-yl, but-2-yl, pent-2-yl, pent-3-yl, 2-ethyl-phen-1-yl, 2-propyl-phen-1-yl and 2-prop-2'-yl-phen-1-yl.

The cyclic hydrocarbonyl structure which R in formula IV
30 represents may be aromatic, non-aromatic, mixed aromatic and non-aromatic, mono-, bi-, tri- or polycyclic, bridged or unbridged, substituted or unsubstituted or interrupted by one or more hetero atoms, with the proviso that the

majority of the cyclic atoms (i.e. more than half) in the structure are carbon. The available adjacent cyclic atoms to which the Q^1 and Q^2 atoms are linked form part of a or the ring of the cyclic hydrocarbyl structure. This ring to which the Q^1 and Q^2 atoms are immediately linked via the linking group, if present, may itself be an aromatic or non-aromatic ring. When the ring to which the Q^1 and Q^2 atoms are directly attached via the linking group, if present, is non-aromatic, any further rings in a bicyclic, tricyclic or polycyclic structure can be aromatic or non-aromatic or a combination thereof. Similarly, when the ring to which the Q^1 and Q^2 atoms are immediately attached via the linking group if present is aromatic, any further rings in the hydrocarbyl structure may be non-aromatic or aromatic or a combination thereof.

For simplicity, these two types of bridging group R will be referred to as an aromatic bridged cyclic hydrocarbyl structure or a non-aromatic bridged cyclic hydrocarbyl structure irrespective of the nature of any further rings joined to the at least one ring to which the Q^1 and Q^2 atoms are linked via the linking groups directly.

The non-aromatic bridged cyclic hydrocarbyl structure which is substituted by A and B at adjacent positions on the at least one non-aromatic ring preferably, has a cis-conformation with respect to the A and B substituents i.e. A and B extend away from the structure on the same side thereof.

Preferably, the non-aromatic bridged cyclic hydrocarbyl structure has from 3 up to 30 cyclic atoms, more preferably from 4 up to 18 cyclic atoms, most preferably

from 4 up to 12 cyclic atoms and especially 5 to 8 cyclic atoms and may be monocyclic or polycyclic. The cyclic atoms may be carbon or hetero, wherein references to hetero herein are references to sulphur, oxygen and/or nitrogen. Typically, the non-aromatic bridged cyclic hydrocarbyl structure has from 2 up to 30 cyclic carbon atoms, more preferably from 3 up to 18 cyclic carbon atoms, most preferably from 3 up to 12 cyclic carbon atoms and especially 3 to 8 cyclic carbon atoms, may be monocyclic or polycyclic and may or may not be interrupted by one or more hetero atoms. Typically, when the non-aromatic bridged cyclic hydrocarbyl structure is polycyclic it is preferably bicyclic or tricyclic. The non-aromatic bridged cyclic hydrocarbyl structure as defined herein may include unsaturated bonds. By cyclic atom is meant an atom which forms part of a cyclic skeleton.

The non-aromatic bridged cyclic hydrocarbyl structure, apart from that it may be interrupted with hetero atoms may be unsubstituted or substituted with one or more further substituents selected from aryl, alkyl, hetero (preferably oxygen), Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$ or $-CF_3$ wherein $R^{19} - R^{30}$ are as defined herein.

The non-aromatic bridged cyclic hydrocarbyl structure may be selected from cyclohexyl, cyclopentyl, cyclobutyl, cyclopropyl, cycloheptyl, cyclooctyl, cyclononyl, tricyclodecyl, piperidinyl, morpholinyl, norbornyl, isonorbornyl, norbornenyl, isonorbornenyl, bicyclo[2,2,2]octyl, tetrahydrofuryl, dioxanyl, O-2,3-

isopropylidene-2,3-dihydroxy-ethyl, cyclopentanonyl, cyclohexanonyl, cyclopentenyl, cyclohexenyl, cyclohexadienyl, cyclobutenyl, cyclopentenonyl, cyclohexenonyl, adamantyl, furans, pyrans, 1,3 dioxane, 1,4 dioxane, oxocene, 7-oxabicyclo[2.2.1]heptane, pentamethylene sulphide, 1,3 dithiane, 1,4 dithiane, furanone, lactone, butyrolactone, pyrone, succinic anhydride, cis and trans 1,2-cyclohexanedicarboxylic anhydride, glutaric anhydride, pyrrolidine, piperazine, imidazole, 1,4,7 triazacyclononane, 1,5,9 triazacyclodecane, thiomorpholine, thiazolidine, 4,5-diphenyl-cyclohexyl, 4 or 5-phenyl-cyclohexyl, 4,5-dimethyl-cyclohexyl, 4 or 5-methylcyclohexyl, 1,2-decalinyl, 2,3,3a,4,5,6,7,7a-octahydro-1H-inden-5,6-yl, 3a,4,5,6,7,7a-hexahydro-1H-inden-5,6-yl, 1,2 or 3 methyl-3a,4,5,6,7,7a hexahydro-1H-inden-5,6-yl, trimethylene norbornanyl, 3a,4,7,7a-tetrahydro-1H-inden-5,6-yl, 1,2 or 3-dimethyl-3a,4,5,6,7,7a-hexahydro-1H-inden-5,6-yls, 1,3-bis(trimethylsilyl)-3a,4,5,6,7,7a-hexahydro-3H-isobenzofuran and wherein the linking group A or B is joined to available non-substituted adjacent cyclic atoms.

R may represent a non-aromatic bridged cyclic hydrocarbyl structure having at least one non-aromatic ring to which the Q¹ and Q² atoms are linked, via the said linking group, if present, on available adjacent cyclic atoms of the at least one ring. Apart from that it may be in the form of a polycyclic structure, the non-aromatic bridged cyclic hydrocarbyl structure may be unsubstituted or substituted with at least one substituent, preferably on at least one further non-adjacent cyclic atom of the at least one ring.

By the term one further non-adjacent cyclic atom is meant any further cyclic atom in the ring which is not adjacent to any one of said available adjacent cyclic atoms to which the Q^1 and Q^2 atoms are linked.

5

However, the cyclic atoms adjacent to the said available adjacent cyclic atoms and cyclic atoms elsewhere in the hydrocarbyl structure may also be substituted and suitable substituents for the cyclic atom(s) are defined herein.

10

For the avoidance of doubt, references to the cyclic atoms adjacent to the said available adjacent cyclic atoms or the like is not intended to refer to one of the said two available adjacent cyclic atoms themselves. As an example, a cyclohexyl ring joined to a Q^1 atom via position 1 on the ring and joined to a Q^2 atom via position 2 on the ring has two said further non adjacent cyclic atoms as defined at ring position 4 and 5 and two adjacent cyclic atoms to the said available adjacent cyclic atoms at positions 3 and 6.

20

The term a non-aromatic bridged cyclic hydrocarbyl structure means that the at least one ring to which the Q^1 and Q^2 atom are linked via B & A respectively is non-aromatic, and aromatic should be interpreted broadly to include not only a phenyl type structure but other rings with aromaticity such as that found in the cyclopentadienyl anion ring of ferrocenyl, but, in any case, does not exclude aromatic substituents on this non-aromatic at least one ring.

30

The substituents on the said cyclic atoms of the non-aromatic bridged hydrocarbyl structure may be selected to

encourage greater stability but not rigidity of conformation in the cyclic hydrocarbonyl structure. The substituents may, therefore, be selected to be of the appropriate size to discourage or lower the rate of non-aromatic ring conformation changes. Such groups may be independently selected from lower alkyl, aryl, hetero, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$ or $-CF_3$, more preferably, lower alkyl, or hetero most preferably, C_1 - C_6 alkyl. Where there are two or more further cyclic atoms in the hydrocarbonyl structure they may each be independently substituted as detailed herein. Accordingly, where two such cyclic atoms are substituted, the substituents may combine to form a further ring structure such as a 3-20 atom ring structure. Such a further ring structure may be saturated or unsaturated, unsubstituted or substituted by one or more substituents selected from halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29} , $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl, alkyl, Het, wherein R^{19} to R^{30} are as defined herein and/or be interrupted by one or more (preferably less than a total of 4) oxygen, nitrogen, sulphur, silicon atoms or by silano or dialkyl silicon groups or mixtures thereof.

25

Particularly preferred substituents are methyl, ethyl, propyl, isopropyl, phenyl, oxo, hydroxy, mercapto, amino, cyano and carboxy. Particularly preferred substituents when two or more further non adjacent cyclic atoms are substituted are x,y-dimethyl, x,y-diethyl, x,y-dipropyl, x,y-di-isopropyl, x,y-diphenyl, x,y-methyl/ethyl, x,y-methyl/phenyl, saturated or unsaturated cyclopentyl, saturated or unsaturated cyclohexyl, 1,3 substituted or

30

unsubstituted 1,3H-furyl, un-substituted cyclohexyl, x,y-oxo/ethyl, x,y-oxo/methyl, disubstitution at a single ring atom is also envisaged, typically, x,x-lower dialkyl. More typical substituents are methyl, ethyl, n-propyl,
 5 iso-propyl, n-butyl, isobutyl, t-butyl, or oxo, most typically methyl or ethyl, or oxo most typically, methyl; wherein x and y stand for available atom positions in the at least one ring.

10 Preferably, further substitution of said non-aromatic cyclic hydrocarbyl structure is not on said available adjacent carbon atoms to which said Q¹ and Q² atoms are linked. The non-aromatic cyclic hydrocarbyl structure may be substituted at one or more said further cyclic atoms of
 15 the hydrocarbyl structure but is preferably substituted at 1, 2, 3 or 4 such cyclic atoms, more preferably 1, 2 or 3, most preferably at 1 or 2 such cyclic atoms, preferably on the at least one non-aromatic ring. The substituted cyclic atoms may be carbon or hetero but are preferably
 20 carbon.

When there are two or more substituents on the said cyclic hydrocarbyl structure they may meet to form a further ring structure unless excluded herein.

25

The non-aromatic bridged cyclic hydrocarbyl structure may be selected from 4 and/or 5 lower alkylcyclohexane- 1,2-diyl, 4 lower alkylcyclopentane- 1,2-diyl, 4, 5 and/or 6 lower alkylcycloheptane- 1,2-diyl, 4, 5, 6 and/or 7
 30 lower alkylcyclooctane- 1,2-diyl, 4, 5, 6, 7 and/or 8 lower alkylcyclononane- 1,2-diyl, 5 and/or 6 lower alkyl piperidine- 2,3-diyl, 5 and/or 6 lower alkyl morpholine- 2,3-diyl, 0-2,3-isopropylidene-2,3-

dihydroxy-ethane- 2,3-diyl, cyclopentan-one -3,4-diyl ,
 cyclohexanone-3,4-diyl, 6-lower alkyl cyclohexanone-3,4-
 diyl, 1-lower alkyl cyclopentene-3,4-diyl, 1 and/or 6
 lower alkyl cyclohexene- 3,4-diyl, 2 and/or 3 lower alkyl
 5 cyclohexadiene- 5,6-diyl, 5 lower alkyl cyclohexen-4-
 one- 1,2-diyl, adamantyl-1-2-diyl, 5 and/or 6 lower
 alkyl tetrahydropyran-2 , 3 di y l , 6-lower alkyl
 dihydropyran-2,3 diyl, 2-lower alkyl 1,3 dioxane - 5,6-
 diyl, 5 and/or 6 lower alkyl-1,4 dioxane -2,3-diyl, 2-
 10 lower alkyl pentamethylene sulphide 4,5-diyl, 2-lower
 alkyl-1,3 dithiane- 5,6- diyl, 2 and/or 3-lower alkyl 1,4
 dithiane -5,6-diyl, tetrahydro-furan-2-one -4,5-diyl,
 delta-valero lactone 4,5-diyl, gamma-butyrolactone 3,4-
 diyl, 2H-dihydropyrone 5,6-diyl, glutaric anhydride 3,4-
 15 diyl, 1-lower alkyl pyrrolidine -3,4-diyl , 2,3 di-lower
 alkyl piperazine -5,6-diyl, 2-lower alkyl dihydro
 imidazole -4,5-diyl, 2,3,5 and/or 6 lower alkyl-1,4,7
 triazacyclononane -8,9-diyl, 2,3,4 and/or 10 lower alkyl-
 1,5,9 triazacyclodecane 6,7-diyl, 2,3- di-lower alkyl
 20 thiomorpholine -5,6 -diyl, 2-lower alkyl- thiazolidine -
 4,5-diyl, 4,5-diphenyl-cyclohexane -1,2-diyl, 4 and/or 5-
 phenyl-cyclohexane-1,2-d i y l , 4,5-dimethyl-cyclohexane-
 1,2-diyl, 4 or 5-methylcyclohexane- 1,2-diyl, 2, 3, 4
 and/or 5 lower alkyl-decahydronaphthalene 8,9-diyl,
 25 bicyclo[4.3.0] nonane-3,4 diyl, 3a,4,5,6,7,7a-hexahydro-
 1H-inden-5,6-diyl, 1, 2 and/or 3 methyl-3a, 4,5,6,7,7a
 hexahydro-1H-inden-5,6-diyl, Octahydro -4,7 methano -
 indene -1,2-diyl, 3a, 4,7,7a-tetrahydro-1H-inden-5,6-diyl,
 1, 2 and/or 3-dimethyl -3a, 4,5,6,7,7a-hexahydro-1H-inden
 30 5,6-d i y l s , 1,3-bis(trimethylsilyl)-3a,4,5,6,7,7a-
 hexahydro-3H-isobenzofuran - 5,6-diyl.

Alternatively, the substituents on the said at least one further non adjacent cyclic atom of the non-aromatic bridged hydrocarbyl structure may be a group Y where Y represents a group which is at least as sterically
 5 hindering as phenyl and when there are two or more substituents Y they are each as sterically hindering as phenyl and/or combine to form a group which is more sterically hindering than phenyl.

10 Preferably, Y represents $-SR^{40}R^{41}R^{42}$ wherein S represents Si, C, N, S, O or aryl and $R^{40}R^{41}R^{42}$ are as defined herein. Preferably each Y and/or combination of two or more Y groups is at least as sterically hindering as t-butyl.

15 More preferably, when there is only one substituent Y, it is at least as sterically hindering as t-butyl whereas where there are two or more substituents Y, they are each at least as sterically hindering as phenyl and at least as sterically hindering as t-butyl if combined into a single
 20 group.

Preferably, when S is aryl, R^{40} , R^{41} and R^{42} are independently hydrogen, alkyl, $-BQ^3-X^3(X^4)$ (wherein B, X^3 and X^4 are as defined herein and Q^3 is defined as Q^1 or Q^2
 25 above), phosphorus, aryl, arylene, alkaryl, arylenealkyl, alkenyl, alkynyl, het, hetero, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$, $-CF_3$, $-SiR^{71}R^{72}R^{73}$ or alkylphosphorus.

30

Preferably, when S is Si, C, N, S or O, R^{40} , R^{41} and R^{42} are independently hydrogen, alkyl, phosphorus, aryl, arylene, alkaryl, aralkyl, arylenealkyl, alkenyl, alkynyl, het,

hetero, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$, $-CF_3$, $-SiR^{71}R^{72}R^{73}$, or alkylphosphorus wherein at least one of $R^{40}-R^{42}$ is not hydrogen and wherein
 5 $R^{19}-R^{30}$ are as defined herein; and $R^{71}-R^{73}$ are defined as $R^{40}-R^{42}$ but are preferably C_1-C_4 alkyl or phenyl.

Preferably, S is Si, C or aryl. However, N, S or O may also be preferred as one or more of the Y groups in
 10 combined groups. For the avoidance of doubt, as oxygen or sulphur can be bivalent, $R^{40} - R^{42}$ can also be lone pairs.

Preferably, in addition to group Y, the non-aromatic bridged structure may be unsubstituted or further
 15 substituted with groups selected from Y, alkyl, aryl, arylene, alkaryl, aralkyl, arylenealkyl, alkenyl, alkynyl, het, hetero, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$, $-CF_3$, $-SiR^{71}R^{72}R^{73}$, or alkylphosphorus
 20 wherein $R^{19}-R^{30}$ are as defined herein; and $R^{71}-R^{73}$ are defined as $R^{40}-R^{42}$ but are preferably C_1-C_4 alkyl or phenyl.

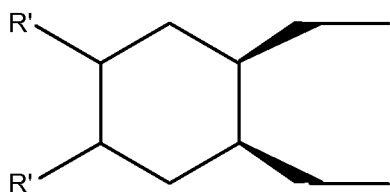
In addition, when S is aryl, the aryl may be substituted with in addition to R^{40} , R^{41} , R^{42} any of the further
 25 substituents defined for the non-aromatic bridged structure above.

More preferred Y substituents may be selected from t-alkyl or t-alkyl, aryl such as -t-butyl, $-SiMe_3$, or 2-
 30 phenylprop-2-yl, -phenyl, alkylphenyl-, phenylalkyl- or phosphinoalkyl- such as phosphinomethyl.

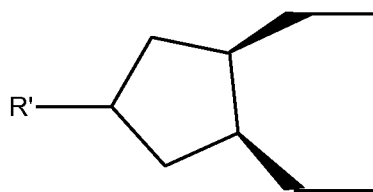
Preferably, when S is Si or C and one or more of R^{40} - R^{42} are hydrogen, at least one of R^{40} - R^{42} should be sufficiently bulky to give the required steric hindrance and such groups are preferably phosphorus, phosphinoalkyl-
 5 , a tertiary carbon bearing group such as -t-butyl, -aryl, -alkaryl, -aralkyl or tertiary silyl.

In some embodiments, there may be two or more said Y substituents on further cyclic atoms of the non-aromatic
 10 bridged structure. Optionally, the said two or more substituents may combine to form a further ring structure such as a cycloaliphatic ring structure.

Some typical hydrocarbyl structures are shown below
 15 wherein R' , R'' , R''' , R'''' etc are defined in the same way as the substituents on the cyclic atoms above but may also be hydrogen, or represent the hetero atom being non substituted if linked directly to a hetero atom and may be the same or different. The diyl methylene linkages to
 20 the phosphorus (not shown) are shown in each case.

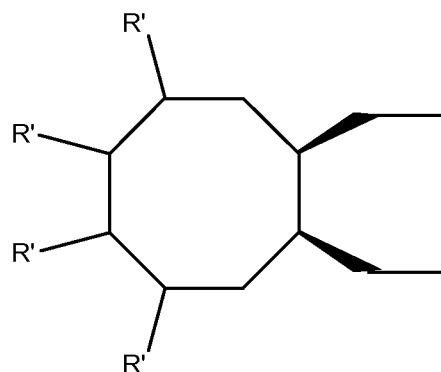
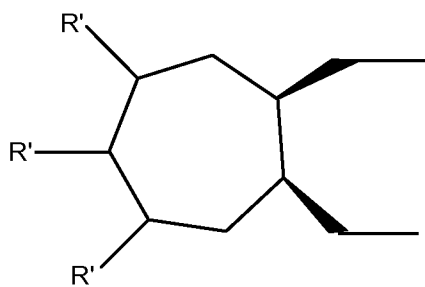


4 and/or 5 substituted cyclohexyl

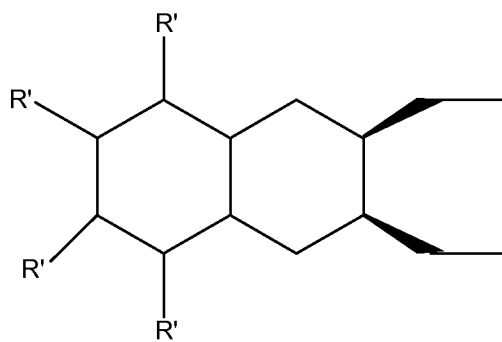
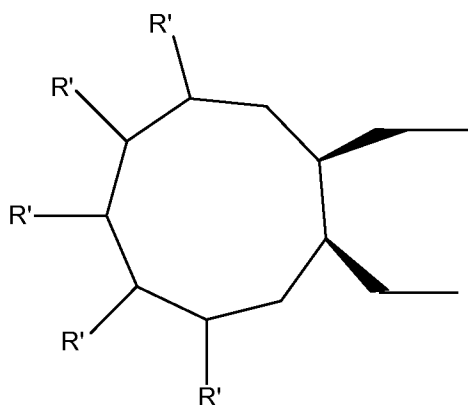


4 substituted
cyclopentyl

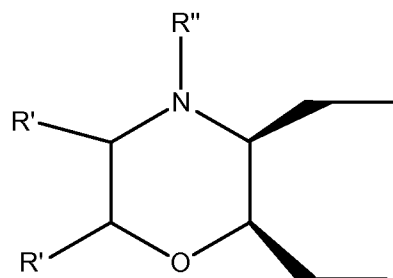
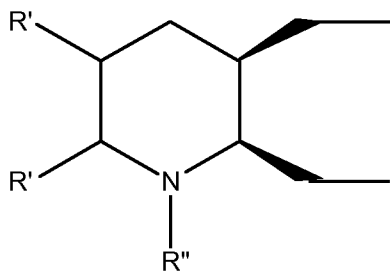
41



5 4, 5 and/or 6 substituted cycloheptyl 4, 5, 6 and/or 7 substituted cyclooctyl

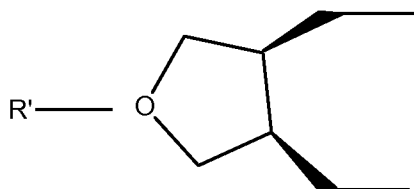


10 4,5,6,7 and/or 8 substituted cyclononyl 2,3,4 and/or 5 substituted decahydronaphthalene

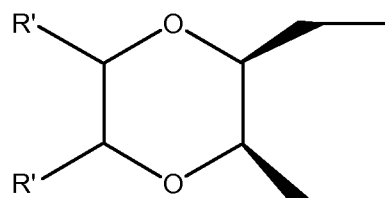


15

5 and/or 6 substituted piperidines 5 and/or 6 substituted morpholines

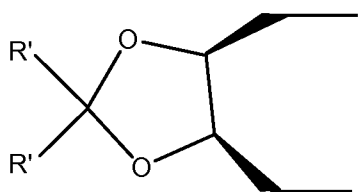


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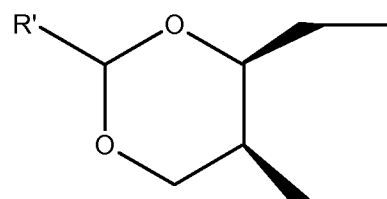


1- Substituted furans

5 and/or 6 substituted 1,4 dioxane

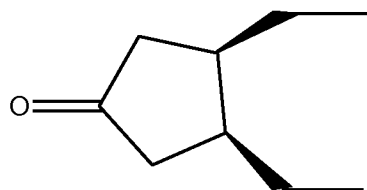


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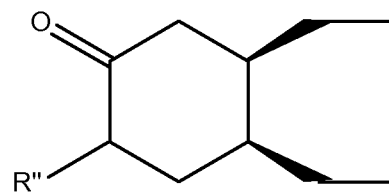


Substituted DIOP

2 - substituted 1,3 dioxane

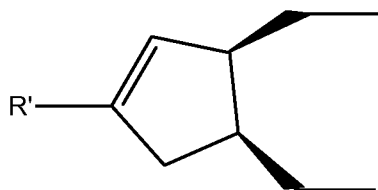


15

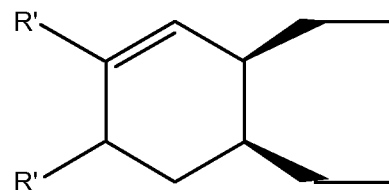


cyclopentanone

6- substituted cyclohexanone

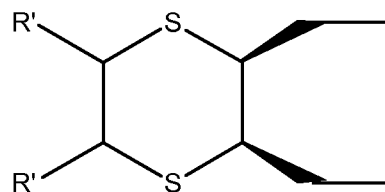
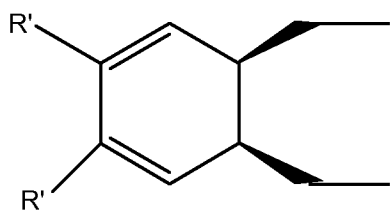


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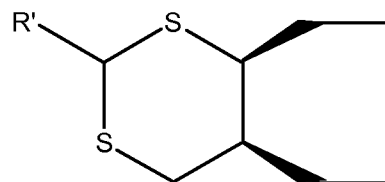
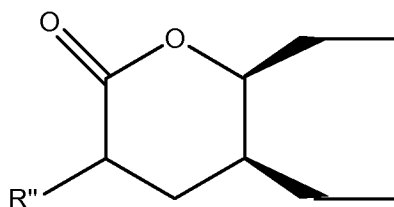


1 - substituted cyclopentenyl 1 and/or 6 - substituted cyclohexenyl

5

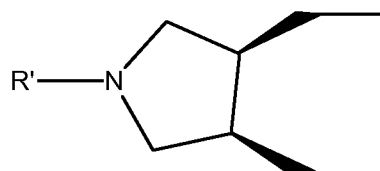
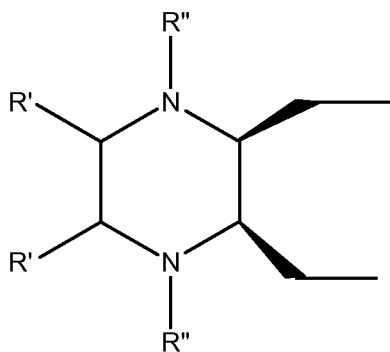


10 2 and/or 3 substituted cyclohexadienyl 2 and / or 3 substituted 1,4 dithiane



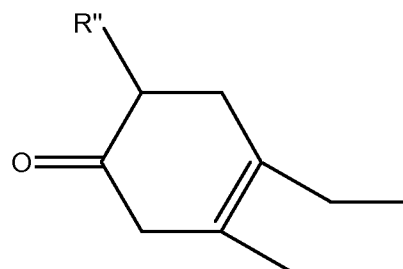
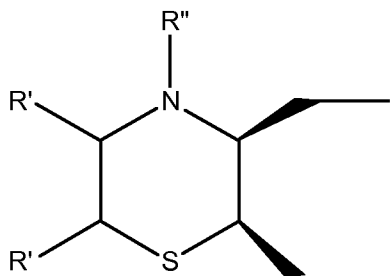
15

3 - Substituted pyrones 2 - substituted 1,3 dithiane



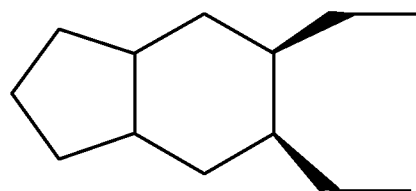
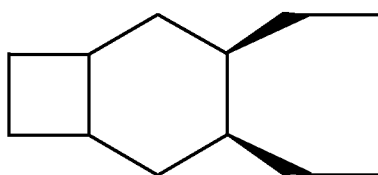
20

1, 2, 3, 4 substituted piperazine 1 substituted
pyrrolidine



5

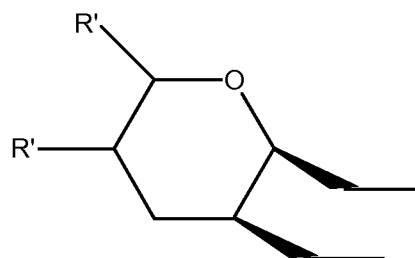
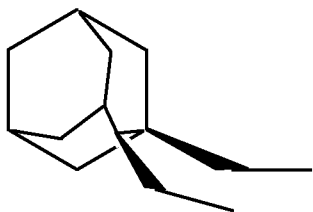
1, 2, 3 substituted thiomorpholine 5 substituted
cyclohexen-4-one



10

Bicyclo [4.2.0] octane

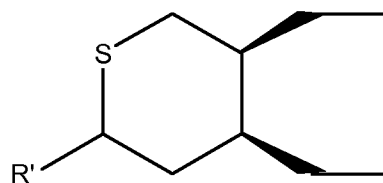
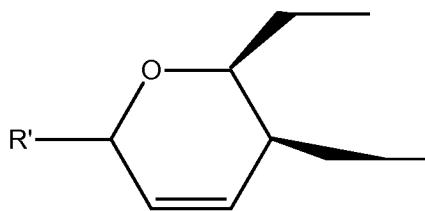
bicyclo [4.3.0] nonane



15

Adamantyl -1,2-diyl

substituted tetrahydropyran

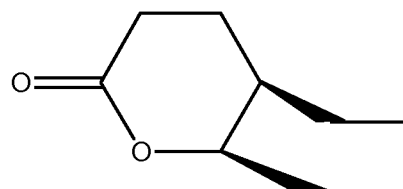
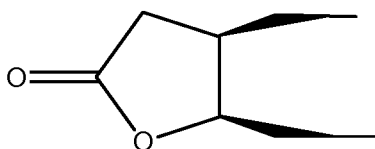


45

Substituted dihydropyran

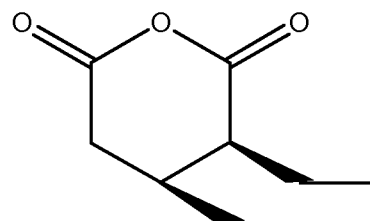
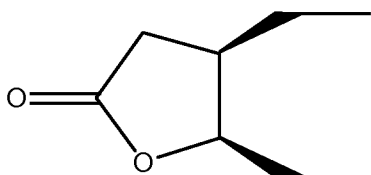
substituted pentamethylene
sulphide (substituted
tetrahydro-thiopyran

5

Tetrahydro-furan-2-one
4,5-diyl

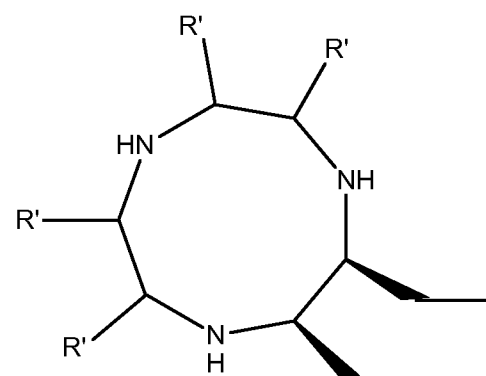
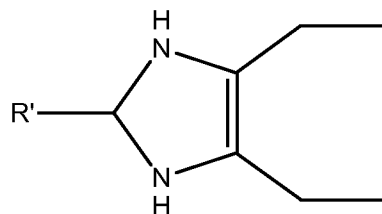
delta-valero lactone

10



gamma-butyrolactone

glutaric anhydride

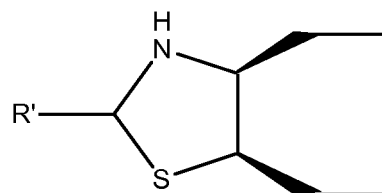
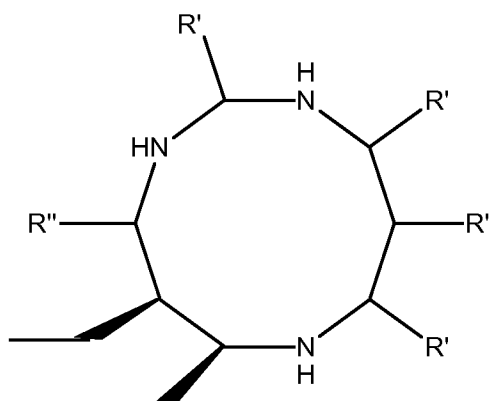


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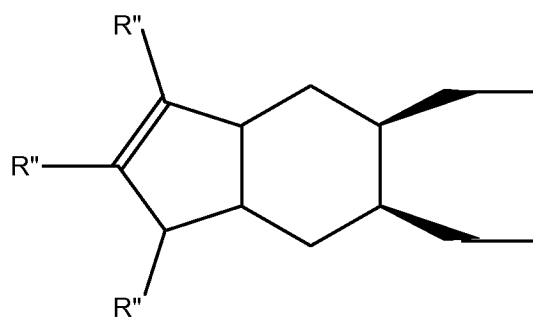
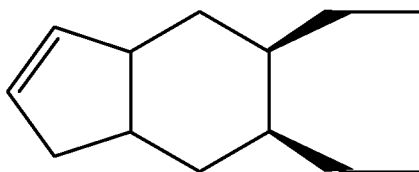
Substituted dihydro imidazole

Substituted 1, 4, 7
triazacyclononane

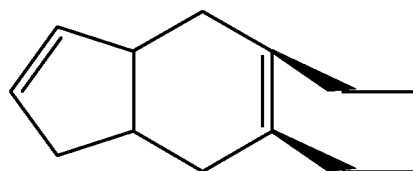
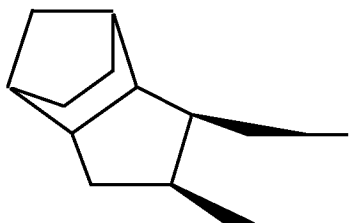
20



5 Substituted 1, 5, 9 triazacyclodecane substituted
thiazolidine

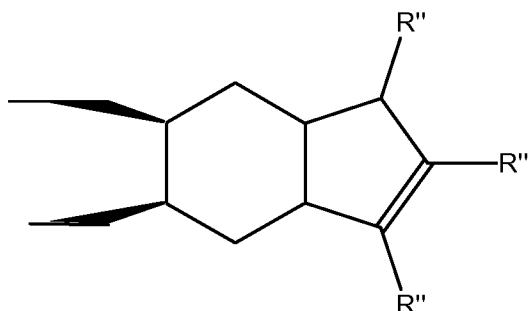


10 3a,4,5,6,7,7a-hexahydro-1H-indene substituted 3a,
4,5,6,7,7a hexahydro-
1H-indene



15

Octahydro -4,7 methano - indene 3a, 4,7,7a-tetrahydro-
1H-indene



Substituted 3a, 4,5,6,7,7a-hexahydro-1H-indene

5 In the structures herein, where there is more than one stereoisomeric form possible, all such stereoisomers are intended. However, where there are substituents it is preferable that the at least one substituent on at least one further cyclic atom of the non-aromatic bridged
 10 hydrocarbyl structure extends in a trans direction with respect to the A and or B atom i.e. extends outwardly on the opposite side of the ring.

Preferably, each adjacent cyclic atom to the said
 15 available adjacent cyclic atom is not substituted so as to form a further 3-8 atom ring structure via the other adjacent cyclic atom to the said available adjacent cyclic atoms in the at least one ring or via an atom adjacent to the said other adjacent atom but outside the at least one
 20 ring in the non-aromatic bridged structure;

An additional preferred set of embodiments is found when R represents an aromatic bridged hydrocarbyl structure i.e. having at least one aromatic ring to which Q^1 and Q^2 are
 25 each linked, via the respective linking group, on available adjacent cyclic atoms of the at least one aromatic ring. The aromatic structure may be substituted with one or more substituent(s).

The aromatic bridged hydrocarbyl structure may, where possible, be substituted with one or more substituents selected from alkyl, aryl, Het, halo, cyano, nitro, OR¹⁹,
 5 OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)NR²⁵R²⁶, SR²⁷, C(O)SR²⁷, or -J-Q³(CR¹³(R¹⁴)(R¹⁵)CR¹⁶(R¹⁷)(R¹⁸) where J represents lower alkylene; or two adjacent substituents together with the cyclic atoms of the ring to which they are attached form a further ring, which is optionally
 10 substituted by one or more substituents selected from alkyl, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)NR²⁵R²⁶, SR²⁷ or C(O)SR²⁷; wherein R¹⁹ to R²⁷ are defined herein.

15 One type of substituent for the aromatic bridged hydrocarbyl structure is the substituent Y^x which may be present on one or more further cyclic atom(s), preferably aromatic cyclic atom of the aromatic bridged cyclic hydrocarbyl structure.

20

Preferably, when present, the substituent(s) Y^x on the aromatic structure has a total $\sum_{x=1-n}^{\infty} \text{tY}^x$ of atoms other than hydrogen such that $\sum_{x=1-n}^{\infty} \text{tY}^x$ is ≥ 4 , where n is the total number of substituent(s) Y^x and tY^x represents the total
 25 number of atoms other than hydrogen on a particular substituent Y^x.

Typically, when there is more than one substituent Y^x hereinafter also referred to as simply Y, any two may be
 30 located on the same or different cyclic atoms of the aromatic bridged cyclic hydrocarbyl structure. Preferably, there are ≤ 10 Y groups i.e. n is 1 to 10, more preferably there are 1-6 Y groups, most preferably 1-4 Y groups on

the aromatic structure and, especially, 1, 2 or 3 substituent Y groups on the aromatic structure. The substituted cyclic aromatic atoms may be carbon or hetero but are preferably carbon.

5

Preferably, when present, $\sum_{x=1}^n Y^x$ is between 4-100, more preferably, 4-60, most preferably, 4-20, especially 4-12.

Preferably, when there is one substituent Y, Y represents
10 a group which is at least as sterically hindering as phenyl and when there are two or more substituents Y they are each as sterically hindering as phenyl and/or combine to form a group which is more sterically hindering than phenyl.

15

By sterically hindering herein, whether in the context of the groups R^1 - R^{12} described hereinafter or the substituent Y, or otherwise, we mean the term as readily understood by those skilled in the art but for the avoidance of any
20 doubt, the term more sterically hindering than phenyl can be taken to mean having a lower degree of substitution (DS) than PH_2Ph when PH_2Y (representing the group Y) is reacted with $Ni(0)(CO)_4$ in eightfold excess according to the conditions below. Similarly, references to more
25 sterically hindering than t-butyl can be taken as references to DS values compared with PH_2t-Bu etc. If, for instance, two Y groups are being compared and PHY^1 is not more sterically hindered than the reference then PHY^1Y^2 should be compared with the reference. Similarly, if three
30 Y groups are being compared and PHY^1 or PHY^1Y^2 are not already determined to be more sterically hindered than the standard then $PY^1Y^2Y^3$ should be compared. If there are more

than three Y groups they should be taken to be more sterically hindered than t-butyl.

5 Steric hindrance in the context of the invention herein is discussed on page 14 et seq of "Homogenous Transition Metal Catalysis - A Gentle Art", by C. Masters, published by Chapman and Hall 1981.

10 Tolman ("Phosphorus Ligand Exchange Equilibria on Zerovalent Nickel. A Dominant Role for Steric Effects", Journal of American Chemical Society, 92, 1970, 2956-2965) has concluded that the property of the ligands which primarily determines the stability of the Ni (0) complexes is their size rather than their electronic character.

15

To determine the relative steric hindrance of a group Y or other substituent the method of Tolman to determine DS may be used on the phosphorus analogue of the group to be determined as set out above.

20

Toluene solutions of $\text{Ni}(\text{CO})_4$ were treated with an eightfold excess of phosphorus ligand; substitution of CO by ligand was followed by means of the carbonyl stretching vibrations in the infrared spectrum. The solutions were
25 equilibrated by heating in sealed tubes for 64 hr at 100° . Further heating at 100° for an additional 74hrs did not significantly change the spectra. The frequencies and intensities of the carbonyl stretching bands in the spectra of the equilibrated solutions are then
30 determined. The degree of substitution can be estimated semiquantitatively from the relative intensities and the assumption that the extinction coefficients of the bands are all of the same order of magnitude. For example, in

the case of $P(C_6H_{11})_3$ the A_1 band of $Ni(CO)_3L$ and the B_1 band of $Ni(CO)_2L_2$ are of about the same intensity, so that the degree of substitution is estimated at 1.5. If this experiment fails to distinguish the respective ligands then the diphenyl phosphorus PPh_2H or di-*t*-butyl phosphorus should be compared to the PY_2H equivalent as the case may be. Still further, if this also fails to distinguish the ligands then the PPh_3 or $P(^tBu)_3$ ligand should be compared to PY_3 , as the case may be. Such further experimentation may be required with small ligands which fully substitute the $Ni(CO)_4$ complex.

The group Y may also be defined by reference to its cone angle which can be defined in the context of the invention as the apex angle of a cylindrical cone centred at the midpoint of the aromatic ring. By midpoint is meant a point in the plane of the ring which is equidistant from the cyclic ring atoms.

Preferably, the cone angle of the at least one group Y or the sum of the cone angles of two or more Y groups is at least 10° , more preferably, at least 20° , most preferably, at least 30° . Cone angle should be measured according to the method of Tolman {C. A. Tolman Chem. Rev. 77, (1977), 313-348} except that the apex angle of the cone is now centred at the midpoint of the aromatic ring. This modified use of Tolman cone angles has been used in other systems to measure steric effects such as those in cyclopentadienyl zirconium ethene polymerisation catalysts (Journal of Molecular Catalysis: Chemical 188, (2002), 105-113).

The substituents Y are selected to be of the appropriate size to provide steric hindrance with respect to the active site between the Q^1 and Q^2 atoms. However, it is not known whether the substituent is preventing the metal
5 leaving, directing its incoming pathway, generally providing a more stable catalytic confirmation, or acting otherwise.

A particularly preferred ligand is found when Y represents
10 $-SR^{40}R^{41}R^{42}$ wherein S represents Si, C, N, S, O or aryl and $R^{40}R^{41}R^{42}$ are as defined hereinafter. Preferably each Y and/or combination of two or more Y groups is at least as sterically hindering as t-butyl.

15 More preferably, when there is only one substituent Y, it is at least as sterically hindering as t-butyl whereas where there are two or more substituents Y, they are each at least as sterically hindering as phenyl and at least as sterically hindering as t-butyl if considered as a single
20 group.

Preferably, when S is aryl, R^{40} , R^{41} and R^{42} are independently hydrogen, alkyl, $-BQ^3-X^3(X^4)$ (wherein B, X^3 and X^4 are as defined herein and Q^3 is defined as Q^1 or Q^2
25 above), phosphorus, aryl, arylene, alkaryl, arylenealkyl, alkenyl, alkynyl, het, hetero, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$, $-CF_3$, $-SiR^{71}R^{72}R^{73}$ or alkylphosphorus.

30 Preferably, when S is Si, C, N, S or O, R^{40} , R^{41} and R^{42} are independently hydrogen, alkyl, phosphorus, aryl, arylene, alkaryl, aralkyl, arylenealkyl, alkenyl, alkynyl, het,

hetero, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$, $-CF_3$, $-SiR^{71}R^{72}R^{73}$, or alkylphosphorus wherein at least one of $R^{40}-R^{42}$ is not hydrogen and wherein
 5 $R^{19}-R^{30}$ are as defined herein,; and $R^{71}-R^{73}$ are defined as $R^{40}-R^{42}$ but are preferably C_1-C_4 alkyl or phenyl.

Preferably, S is Si, C or aryl. However, N, S or O may also be preferred as one or more of the Y groups in
 10 combined or in the case of multiple Y groups. For the avoidance of doubt, as oxygen or sulphur can be bivalent, $R^{40} - R^{42}$ can also be lone pairs.

Preferably, in addition to group Y, the aromatic bridged
 15 cyclic hydrocarbyl structure may be unsubstituted or, when possible be further substituted with groups selected from alkyl, aryl, arylene, alkaryl, aralkyl, arylenealkyl, alkenyl, alkynyl, het, hetero, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$, $-CF_3$, $-SiR^{71}R^{72}R^{73}$, or
 20 alkylphosphorus wherein $R^{19}-R^{30}$ are as defined herein; and $R^{71}-R^{73}$ are defined as $R^{40}-R^{42}$ but are preferably C_1-C_4 alkyl or phenyl. In addition, the at least one aromatic ring can be part of a metallocene complex, for instance when R
 25 is a cyclopentadienyl or indenyl anion it may form part of a metal complex such as ferrocenyl, ruthenocyl, molybdenocenyl or indenyl equivalents.

Such complexes should be considered as aromatic bridged
 30 cyclic hydrocarbyl structures within the context of the present invention and when they include more than one aromatic ring, the substituent(s) Y^x or otherwise may be on the same aromatic ring as that to which the Q^1 and Q^2

atoms are linked or a further aromatic ring of the structure. For instance, in the case of a metallocene, the substituents may be on any one or more rings of the metallocene structure and this may be the same or a
5 different ring than that to which Q^1 and Q^2 are linked.

Suitable metallocene type ligands which may be substituted as defined herein will be known to the skilled person and are extensively defined in WO 04/024322. A particularly
10 preferred Y substituent for such aromatic anions is when S is Si.

In general, however, when S is aryl, the aryl may be unsubstituted or further substituted with, in addition to
15 R^{40} , R^{41} , R^{42} , any of the further substituents defined for the aromatic structure above.

More preferred Y substituents in the present invention may be selected from t-alkyl or t-alkyl,aryl such as -t-butyl
20 or 2-phenylprop-2-yl, , -SiMe₃, -phenyl, alkylphenyl-, phenylalkyl- or phosphinoalkyl- such as phosphinomethyl.

Preferably, when S is Si or C and one or more of R^{40} - R^{42} are hydrogen, at least one of R^{40} - R^{42} should be
25 sufficiently bulky to give the required steric hindrance and such groups are preferably phosphorus, phosphinoalkyl-, a tertiary carbon bearing group such as -t-butyl, -aryl, -alkaryl, -aralkyl or tertiary silyl.

30 Preferably, the aromatic bridged cyclic hydrocarbonyl structure has, including substituents, from 5 up to 70 cyclic atoms, more preferably, 5 to 40 cyclic atoms, most

preferably, 5-22 cyclic atoms; especially 5 or 6 cyclic atoms, if not a metallocene complex.

Preferably, the aromatic bridged cyclic hydrocarbyl structure may be monocyclic or polycyclic. The cyclic aromatic atoms may be carbon or hetero, wherein references to hetero herein are references to sulphur, oxygen and/or nitrogen. However, it is preferred that the Q^1 and Q^2 atoms are linked to available adjacent cyclic carbon atoms of the at least one aromatic ring. Typically, when the cyclic hydrocarbyl structure is polycyclic it is preferably bicyclic or tricyclic. The further cycles in the aromatic bridged cyclic hydrocarbyl structure may or may not themselves be aromatic and the term aromatic bridged cyclic hydrocarbyl structure should be understood accordingly. A non-aromatic cyclic ring(s) as defined herein may include unsaturated bonds. By cyclic atom is meant an atom which forms part of a cyclic skeleton.

Preferably, the aromatic bridged cyclic hydrocarbyl structure whether substituted or otherwise preferably comprises less than 200 atoms, more preferably, less than 150 atoms, more preferably, less than 100 atoms.

By the term one further cyclic atom of the aromatic bridged hydrocarbyl structure is meant any further cyclic atom in the aromatic structure which is not an available adjacent cyclic atom of the at least one aromatic ring to which the Q^1 or Q^2 atoms are linked, via the linking group.

As mentioned above, the immediate adjacent cyclic atoms on either side of the said available adjacent cyclic atoms

are preferably not substituted. As an example, an aromatic phenyl ring joined to a Q^1 atom via position 1 on the ring and joined to a Q^2 atom via position 2 on the ring has preferably one or more said further aromatic cyclic atoms substituted at ring position 4 and/or 5 and two immediate adjacent cyclic atoms to the said available adjacent cyclic atoms not substituted at positions 3 and 6. However, this is only a preferred substituent arrangement and substitution at ring positions 3 and 6, for example, is possible.

The term aromatic ring or aromatic bridged means that the at least one ring or bridge to which the Q^1 and Q^2 atom are immediately linked via B & A respectively is aromatic, and aromatic should preferably be interpreted broadly to include not only a phenyl, cyclopentadienyl anion, pyrrolyl, pyridinyl, type structures but other rings with aromaticity such as that found in any ring with delocalised Pi electrons able to move freely in the said ring.

Preferred aromatic rings have 5 or 6 atoms in the ring but rings with $4n + 2$ pi electrons are also possible such as [14] annulene, [18] annulene, etc

The aromatic bridged cyclic hydrocarbyl structure may be selected from benzene-1,2-diyl, ferrocene-1,2-diyl, naphthalene-1,2-diyl, 4 or 5 methyl benzene-1,2-diyl, 1'-methyl ferrocene-1,2-diyl, 4 and/or 5 t-alkylbenzene-1,2-diyl, 4,5-diphenyl-benzene -1,2-diyl, 4 and/or 5-phenylbenzene-1,2-diyl, 4,5-di-t-butyl-benzene-1,2-diyl, 4 or 5-t-butylbenzene-1,2-diyl, 2, 3, 4 and/or 5 t-alkylnaphthalene-8,9-diyl, 1H-inden-5,6-diyl, 1, 2 and/or 3

methyl-1H-inden-5,6-diyl, 4,7 methano -1H- indene -1,2-
 diyl, 1, 2 and/or 3-dimethyl -1H-inden 5,6-diyls, 1,3-
 bis(trimethylsilyl)- isobenzofuran - 5,6-diyl, 4-
 (trimethylsilyl) benzene-1,2 diyl, 4-phosphinomethyl
 5 benzene -1,2 diyl, 4-(2'-phenylprop-2'-yl) benzene - 1,2
 diyl, 4-dimethylsilylbenzene-1,2 diyl, 4-di-t-
 butyl, methylsilyl benzene-1,2 diyl, 4-(t-
 butyldimethylsilyl)-benzene-1,2 diyl, 4-t-butylsilyl-
 benzene-1,2diyl, 4-(tri-t-butylsilyl)-benzene-1,2diyl, 4-
 10 (2'-tert-butylprop-2'-yl)benzene-1,2 diyl, 4-
 (2',2',3',4',4' pentamethyl-pent-3'-yl)-benzene-1,2diyl,
 4-(2',2',4',4'-tetramethyl,3'-t-butyl-pent-3'-yl)-benzene-
 1,2 diyl, 4-(or 1')t-alkylferrocene- 1,2-diyl, 4,5-
 diphenyl-ferrocene -1,2-diyl, 4-(or 1')phenyl-ferrocene-
 15 1,2-diyl, 4,5-di-t-butyl-ferrocene- 1,2-diyl, 4-(or 1')t-
 butylferrocene- 1,2-diyl, 4-(or 1')(trimethylsilyl)
 ferrocene-1,2 diyl, 4-(or 1')phosphinomethyl ferrocene -
 1,2 diyl, 4-(or 1')(2'-phenylprop-2'-yl) ferrocene - 1,2
 diyl, 4-(or 1')dimethylsilylferrocene-1,2diyl, 4-(or
 20 1')di-t-butyl,methylsilyl ferrocene-1,2diyl, 4-(or 1')(t-
 butyldimethylsilyl)-ferrocene-1,2 diyl, 4-(or 1')t-
 butylsilyl-ferrocene-1,2diyl, 4-(or 1')(tri-t-butylsilyl)-
 ferrocene-1,2 diyl, 4-(or 1')(2'-tert-butylprop-2'-
 yl)ferrocene-1,2 diyl, 4-(or 1')(2',2',3',4',4'
 25 pentamethyl-pent-3'-yl)-ferrocene-1,2diyl, 4-(or
 1')(2',2',4',4'-tetramethyl,3'-t-butyl-pent-3'-yl)-
 ferrocene-1,2 diyl.

In the structures herein, where there is more than one
 30 stereoisomeric form possible, all such stereoisomers are
 intended.

As mentioned above, in some embodiments, there may be two substituents on further cyclic atoms of the aromatic structure. Optionally, the said two or more substituents may, especially when on neighbouring cyclic atoms, combine
 5 to form a further ring structure such as a cycloaliphatic ring structure.

Such cycloaliphatic ring structures may be saturated or unsaturated, bridged or unbridged, substituted with alkyl,
 10 Y groups as defined herein, aryl, arylene, alkaryl, aralkyl, arylenalkyl, alkenyl, alkynyl, het, hetero, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$, $-CF_3$, $-SiR^{71}R^{72}R^{73}$, or phosphinoalkyl wherein, when present,
 15 at least one of $R^{40}-R^{42}$ is not hydrogen and wherein $R^{19}-R^{30}$ are as defined herein; and $R^{71}-R^{73}$ are defined as $R^{40}-R^{42}$ but are preferably C_1-C_4 alkyl or phenyl and/or be interrupted by one or more (preferably less than a total of 4) oxygen, nitrogen, sulphur, silicon atoms or by
 20 silano or dialkyl silicon groups or mixtures thereof.

Examples of such structures include piperidine, pyridine, morpholine, cyclohexane, cycloheptane, cyclooctane, cyclononane, furan, dioxane, alkyl substituted DIOP, 2-
 25 alkyl substituted 1,3 dioxane, cyclopentanone, cyclohexanone, cyclopentene, cyclohexene, cyclohexadiene, 1,4 dithiane, piperazine, pyrrolidine, thiomorpholine, cyclohexenone, bicyclo[4.2.0]octane, bicyclo[4.3.0]nonane, adamantane, tetrahydropyran, dihydropyran,
 30 tetrahydrothiopyran, tetrahydro-furan-2-one, delta valerolactone, gamma-butyrolactone, glutaric anhydride, dihydroimidazole, triazacyclononane, triazacyclodecane, thiazolidine, hexahydro-1H-indene (5,6 diyl), octahydro-

4,7 methano-indene (1,2 diyl) and tetrahydro-1H-indene (5,6 diyl) all of which may be unsubstituted or substituted as defined for aryl herein.

5 Specific but non-limiting examples of unsubstituted aromatic bridged bidentate ligands within this invention include the following: 1,2-bis-(di-tert-butylphosphinomethyl)benzene, 1,2-bis-(di-tert-pentylphosphinomethyl)benzene, 1,2-bis-(di-tert-butylphosphinomethyl)naphthalene, 1,2-bis(diadamantylphosphinomethyl)benzene, 1,2-bis(di-3,5-dimethyladamantylphosphinomethyl)benzene, 1,2-bis(di-5-tert-butyladamantylphosphinomethyl)benzene, 1,2-bis(1-adamantyl tert-butyl-phosphinomethyl)benzene, 1,2-bis-
 10 (2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-o-xylene, 1,2-bis-(2-(phospha-adamantyl))-o-xylene, 1-(diadamantylphosphinomethyl)-2-(di-tert-butylphosphinomethyl)benzene, 1-(di-tert-butylphosphinomethyl)-2-(dicongressylphosphinomethyl)benzene, 1-(di-tert-butylphosphino)-2-(phospha-adamantyl)o-xylene, 1-(diadamantylphosphino)-2-(phospha-adamantyl)o-xylene, 1-(di-tert-butylphosphino)-2-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))o-xylene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(phospha-adamantyl)o-xylene, 1-(di-tert-butylphosphinomethyl)-2-(di-tert-butylphosphino)benzene, 1-(phospha-adamantyl)-2-(phospha-adamantyl)methylbenzene, 1-(diadamantylphosphinomethyl)-2-(diadamantylphosphino)benzene, 1-(2-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-benzyl)-2,2,6,6-tetramethyl-phospha-cyclohexan-4-one, 1-(di-tert-butylphosphinomethyl)-2-(phospha-adamantyl)benzene, 1-(di-

tert-butylphosphinomethyl)-2-(diadamantylphosphino)benzene, 1-(di-tert-butylphosphinomethyl)-2-(P-(2,2,6,6-tetramethyl-phosphacyclohexan-4-one) benzene, 1-(tert-butyl,adamantylphosphinomethyl)-2-(diadamantylphosphinomethyl)benzene, 1-[(P-(2,2,6,6-tetramethyl-phosphacyclohexan-4-one)methyl)]-2-(phosphaadamantyl)benzene, 1,2-bis-(ditertbutylphosphinomethyl)ferrocene, 1,2,3-tris-(ditertbutylphosphinomethyl)ferrocene, 1,2-bis(1,3,5,7-tetramethyl-6,9,10-trioxa-2-phosphaadamantylmethyl)ferrocene, 1,2-bis- α,α -(P-(2,2,6,6-tetramethyl-phosphacyclohexan-4-one))dimethylferrocene, and 1-(di-tert-butylphosphinomethyl)-2-(P-(2,2,6,6-tetramethyl-phosphacyclohexan-4-one))ferrocene and 1,2-bis(1,3,5,7-tetramethyl-6,9,10-trioxa-2-phosphaadamantylmethyl)benzene; wherein "phosphaadamantyl" is selected from 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl, 2-phospha-1,3,5-trimethyl-6,9,10-trioxadamantyl, 2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxadamantyl or 2-phospha-1,3,5-tri(trifluoromethyl)-6,9,10-trioxadamantyl.

Examples of suitable substituted non-aromatic bridged bidentate ligands are cis-1,2-bis(di-tert-butylphosphinomethyl)-4,5-dimethyl cyclohexane; cis-1,2-bis(di-t-butylphosphinomethyl)-5-methylcyclopentane; cis-1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxaadamantyl)-4,5-dimethylcyclohexane; cis-1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxaadamantyl) 5-methylcyclopentane; cis-1,2-bis(diadamantylphosphinomethyl)-4,5 dimethylcyclohexane; cis-1,2-bis(diadamantylphosphinomethyl)-5-methyl

cyclopentane; cis-1- (P, P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4,5-dimethylcyclohexane; cis-1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-5-methylcyclopentane; cis-1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl)4,5- dimethylcyclohexane; cis-1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl)-5-methyl cyclopentane; cis-1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) -2- (diadamantylphosphinomethyl)-5-methyl cyclohexane; cis-1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-2-(diadamantylphosphinomethyl)-5-methyl cyclopentane; cis-1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) -2- (diadamantylphosphinomethyl)cyclobutane; cis-1-(di-t-butylphosphinomethyl)-2- (diadamantylphosphinomethyl)-4,5-dimethyl cyclohexane; cis-1-(di-t-butylphosphinomethyl)-2- (diadamantylphosphinomethyl)-5-methyl cyclopentane; cis-1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-4,5-dimethyl cyclohexane; cis-1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-5-methyl cyclopentane; cis-1- (2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2- (di-t-butylphosphinomethyl)-4,5-dimethyl cyclohexane; cis-1- (2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2- (di-t-butylphosphinomethyl)-5-methyl cyclopentane; cis-1- (2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2- (diadamantylphosphinomethyl)-4,5-dimethyl cyclohexane;

cis-1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)-5-methyl cyclopentane;
 cis-1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-
 5 tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl)-
 4,5-dimethyl cyclohexane; cis-1,2-bis-perfluoro(2-
 phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-5-methyl cyclopentane;
 cis-1,2-bis- (2-phosphinomethyl-1,3,5,7-tetra(trifluoro-
 10 methyl)-6,9,10-trioxatricyclo{3.3.1.1[3.7]}decyl)-4,5-
 dimethyl cyclohexane; cis-1,2-bis- (2-
 phosphinomethyl-1,3,5,7-tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-5-methyl cyclopentane.
 ; cis-1- (2-phosphino-1,3,5,7-tetramethyl-6,9,10-trioxa-
 15 adamantyl)-2-(di-t-butylphosphinomethyl)-4,5-
 dimethylcyclohexane; cis-1- (2-phosphinomethyl-1,3,5,7-
 tetramethyl-6,9,10-trioxa-adamantyl)-2-(2-phosphino-
 1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) -4,5-dimethyl
 cyclohexane; cis-1- (di-t-butylphosphino)-2-(di-t-
 20 butylphosphinomethyl) -4,5-dimethyl cyclohexane; cis-1-
 (di-adamantylphosphino)-2-(di-t-butylphosphinomethyl) -
 4,5-dimethyl cyclohexane; cis-1- (di-adamantylphosphino)-
 2-(di-adamantylphosphinomethyl) -4,5-dimethyl cyclohexane;
 cis-1- (2-phosphino-1,3,5,7-tetramethyl-6,9,10-trioxa-
 25 adamantyl)-2-(di-adamantylphosphinomethyl) -4,5-dimethyl
 cyclohexane; cis-1- (P-(2,2,6,6- tetramethyl-phospha-
 cyclohexan-4-one))-2-(di-t-butylphosphinomethyl) -4,5-
 dimethyl cyclohexane; 1-[4,5-dimethyl-2-P-(2,2,6,6-
 tetramethyl-phospha-cyclohexan-4-one)-
 30 [1S,2R]cyclohexylmethyl]-P-2,2,6,6- tetramethyl-phospha-
 cyclohexan-4-one.

Examples of suitable non-substituted non-aromatic bridged
 bidentate ligands are cis-1,2-bis(di-t-
 butylphosphinomethyl)cyclohexane; cis-1,2-bis(di-t-
 butylphosphinomethyl)cyclopentane; cis-1,2-bis(di-t-
 5 butylphosphinomethyl)cyclobutane; cis-1,2-bis(2-
 phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-
 adamantyl)cyclohexane; cis-1,2-bis(2-phosphinomethyl-
 1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)cyclopentane;
 cis-1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 10 trioxa-adamantyl)cyclobutane; cis-1,2-bis(di-
 adamantylphosphinomethyl)cyclohexane; cis-1,2-bis(di-
 adamantylphosphinomethyl)cyclopentane; cis-1,2-bis(di-
 adamantylphosphinomethyl)cyclobutane; cis-1,2-bis (P-
 (2,2,6,6- tetramethyl-phospha-cyclohexan-4-
 15 one))dimethylcyclohexane, cis-1- (P,P-adamantyl, t-butyl-
 phosphinomethyl)-2-(di-t-butylphosphinomethyl)cyclohexane;
 cis-1- (2-phosphino-1,3,5,7-tetramethyl-6,9,10-trioxa-
 adamantyl)-2-(di-t-
 butylphosphinomethyl)cyclohexane; cis-1- (2-
 20 phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-
 adamantyl)-2-(2-phosphino-1,3,5,7-tetramethyl-6,9,10-
 trioxa-adamantyl)cyclohexane; cis-1- (di-t-
 butylphosphino)-2-(di-t-butylphosphinomethyl)cyclohexane;
 cis-1- (di-adamantylphosphino)-2-(di-t-
 25 butylphosphinomethyl)cyclohexane; cis-1- (di-
 adamantylphosphino)-2-(di-
 adamantylphosphinomethyl)cyclohexane; cis-1- (2-phosphino-
 1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-2-(di-
 adamantylphosphinomethyl)cyclohexane; cis-1- (P-(2,2,6,6-
 30 tetramethyl-phospha-cyclohexan-4-one))-2-(di-t-
 butylphosphinomethyl)cyclohexane; cis-1- (P-(2,2,6,6-
 tetramethyl-phospha-cyclohexan-4-one))-2-(P-(2,2,6,6-
 tetramethyl-phospha-cyclohexan-4-one))methylcyclohexane;

cis-1- (P,P-adamantyl, t-butyl-phosphinomethyl)-2-(di-t-butylphosphinomethyl)cyclopentane; cis-1- (P,P-adamantyl, t-butyl-phosphinomethyl)-2-(di-t-butylphosphinomethyl)cyclobutane; cis-1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl) cyclohexane; cis-1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl)cyclopentane; cis-1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl) cyclobutane; cis-1-(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) -2-(diadamantylphosphinomethyl)cyclohexane; cis-1-(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-2-(diadamantylphosphinomethyl)cyclopentane; cis-1-(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) -2-(diadamantylphosphinomethyl)cyclobutane; cis-1-(di-t-butylphosphinomethyl)-2-(diadamantylphosphinomethyl)cyclohexane; cis-1-(di-t-butylphosphinomethyl)-2-(diadamantylphosphinomethyl)cyclopentane; cis-1-(di-t-butylphosphinomethyl)-2-(diadamantylphosphinomethyl)cyclobutane; cis-1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)cyclohexane; cis-1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)cyclopentane; cis-1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)cyclobutane; cis-1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-(di-t-

butylphosphinomethyl)cyclohexane; cis-1-(2-
 phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(di-t-
 butylphosphinomethyl)cyclopentane; cis-1-(2-
 5 phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(di-t-
 butylphosphinomethyl)cyclobutane; cis-1-(2-
 phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-
 10 (diadamantylphosphinomethyl)cyclohexane; cis-1-(2-
 phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)cyclopentane; cis-1-(2-
 phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 15 {3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)cyclobutane; cis-1,2-bis-
 perfluoro(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}-decyl)cyclohexane; cis-1,2-
 bis-perfluoro(2-phosphinomethyl-1,3,5,7-tetramethyl-
 20 6,9,10-trioxatricyclo{3.3.1.1[3.7]}decyl)cyclopentane;
 cis-1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-
 tetramethyl-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)cyclobutane; cis-1,2-
 bis- (2-phosphinomethyl-1,3,5,7-tetra(trifluoro-methyl)-
 25 6,9,10-trioxatricyclo{3.3.1.1[3.7]}decyl)cyclohexane;
 cis-1,2-bis- (2-phosphinomethyl-1,3,5,7-tetra(trifluoro-
 methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)cyclopentane; and
 cis-1,2-bis- (2-phosphinomethyl-1,3,5,7-tetra(trifluoro-
 30 methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)cyclobutane, (2-exo, 3-
 exo)-bicyclo[2.2.1]heptane-2,3-bis(di-tert-
 butylphosphinomethyl) and (2-endo, 3-endo)-

bicyclo[2.2.1]heptane-2,3-bis(di-tert-butylphosphinomethyl)...

Examples of substituted aromatic bridged ligands in accordance with the invention include 1,2-bis(di-tert-butylphosphinomethyl)-4,5-diphenyl benzene; 1,2-bis(di-tert-butylphosphinomethyl)-4-phenylbenzene; 1,2-bis(di-tert-butylphosphinomethyl)-4,5-bis-(trimethylsilyl) benzene; 1,2-bis(di-tert-butylphosphinomethyl)-4-(trimethylsilyl)benzene; 1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-4,5-diphenylbenzene; 1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-4-phenylbenzene; 1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-4,5-bis-(trimethylsilyl)benzene; 1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-4-(trimethylsilyl)benzene; 1,2-bis(di-adamantylphosphinomethyl)-4,5 diphenylbenzene; 1,2-bis(di-adamantylphosphinomethyl)-4-phenyl benzene; 1,2-bis(di-adamantylphosphinomethyl)-4,5 bis-(trimethylsilyl)benzene; 1,2-bis(di-adamantylphosphinomethyl)-4-(trimethylsilyl) benzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-tert-butylphosphinomethyl)-4,5-diphenylbenzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-tert-butylphosphinomethyl)-4-phenylbenzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-tert-butylphosphinomethyl)-4,5-bis-(trimethylsilyl)benzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-tert-butylphosphinomethyl)-4-(trimethylsilyl)benzene; 1-(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-2-(di-tert-butylphosphinomethyl)-4,5-diphenylbenzene; 1-(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-

adamantyl) - 2 - (di-t-butylphosphinomethyl)-4-phenyl
benzene; ; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-
6,9,10-trioxa-adamantyl) - 2 - (di-t-
butylphosphinomethyl)4,5- bis-(trimethylsilyl)benzene;
5 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-
adamantyl) - 2 - (di-t-butylphosphinomethyl)-4-
(trimethylsilyl) benzene; 1-(2-phosphinomethyl-1,3,5,7-
tetramethyl-6,9,10-trioxa-adamantyl) -2-
(diadamantylphosphinomethyl)-4,5-diphenyl benzene; 1-(2-
10 phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-
adamantyl)-2-(diadamantylphosphinomethyl)-4-phenyl
benzene; 1-(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
trioxa-adamantyl) -2- (diadamantylphosphinomethyl)-4,5-
bis-(trimethylsilyl) benzene; 1-(2-phosphinomethyl-
15 1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-2-
(diadamantylphosphinomethyl)-4-(trimethylsilyl) benzene;
1-(di-t-butylphosphinomethyl)-2-
(diadamantylphosphinomethyl)-4,5-diphenyl benzene; 1-(di-
t-butylphosphinomethyl)-2- (diadamantylphosphinomethyl)-
20 4-phenyl benzene; 1-(di-t-butylphosphinomethyl)-2-
(diadamantylphosphinomethyl)-4,5-bis-(trimethylsilyl)
benzene; 1-(di-t-butylphosphinomethyl)-2-
(diadamantylphosphinomethyl)-4-(trimethylsilyl) benzene;
1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
25 trioxatricyclo-{3.3.1.1[3.7]}decyl)-4,5-diphenyl benzene;
1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
trioxatricyclo-{3.3.1.1[3.7]}decyl)-4-phenyl benzene;
1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
trioxatricyclo-{3.3.1.1[3.7]}decyl)-4,5-bis-(
30 trimethylsilyl) benzene; 1,2-bis(2-phosphinomethyl-
1,3,5-trimethyl-6,9,10-trioxatricyclo-
{3.3.1.1[3.7]}decyl)-4-(trimethylsilyl) benzene; 1-(2-
phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-

{3.3.1.1[3.7]}decyl)-2-(di-t-butylphosphinomethyl)-4,5-
 diphenyl benzene; 1-(2-phosphinomethyl-1,3,5-trimethyl-
 6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-(di-t-
 butylphosphinomethyl)-4-phenyl benzene; 1-(2-
 5 phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(di-t-butylphosphinomethyl)-4,5-
 bis-(trimethylsilyl) benzene; 1-(2-phosphinomethyl-
 1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(di-t-butylphosphinomethyl)-4-
 10 (trimethylsilyl) benzene; 1-(2-phosphinomethyl-1,3,5-
 trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)-4,5-diphenyl benzene; 1-(2-
 phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(diadamantylphosphinomethyl)-4-
 15 phenyl benzene; ; 1-(2-phosphinomethyl-1,3,5-trimethyl-
 6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)-4,5-bis-(trimethylsilyl)
 benzene; 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 20 (diadamantylphosphinomethyl)-4-(trimethylsilyl) benzene;
 1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-tetramethyl-
 6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl)-4,5-diphenyl
 benzene; 1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-
 tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl)-4-
 25 phenyl benzene; 1,2-bis-perfluoro(2-phosphinomethyl-
 1,3,5,7-tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-
 decyl)-4,5-bis-(trimethylsilyl) benzene; 1,2-bis-
 perfluoro(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(trimethylsilyl)
 30 benzene; 1,2-bis-(2-phosphinomethyl-1,3,5,7-
 tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4,5-diphenyl benzene;
 1,2-bis-(2-phosphinomethyl-1,3,5,7-tetra(trifluoro-

methyl)-6,9,10-trioxatricyclo{3.3.1.1[3.7]}decyl)-4-phenyl
 benzene; 1,2-bis-(2-phosphinomethyl-1,3,5,7-
 tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4,5-bis-(
 5 trimethylsilyl) benzene; 1,2-bis-(2-phosphinomethyl-
 1,3,5,7-tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(trimethylsilyl)
 benzene; 1,2-bis(di-t-butylphosphinomethyl)-4,5-di-(2'-
 phenylprop-2'-yl) benzene; 1,2-bis(di-t-
 10 butylphosphinomethyl)-4-(2'-phenylprop-2'-yl)benzene;
 1,2-bis(di-t-butylphosphinomethyl)-4,5- di-t-butyl
 benzene; 1,2-bis(di-t-butylphosphinomethyl)-4-t-
 butylbenzene; 1,2-bis(2-phosphinomethyl-1,3,5,7-
 tetramethyl-6,9,10-trioxa-adamantyl)-4,5- di-(2'-
 15 phenylprop-2'-yl)benzene; 1,2-bis(2-phosphinomethyl-
 1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-4-(2'-
 phenylprop-2'-yl) benzene; 1,2-bis(2-phosphinomethyl-
 1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-4,5-(di-t-
 butyl)benzene; 1,2-bis(2-phosphinomethyl-1,3,5,7-
 20 tetramethyl-6,9,10-trioxa-adamantyl)-4-t-butylbenzene;
 1,2-bis(di-adamantylphosphinomethyl)-4,5-di-(2'-
 phenylprop-2'-yl) benzene; 1,2-bis(di-
 adamantylphosphinomethyl)-4-(2'-phenylprop-2'-yl) benzene;
 1,2-bis(di-adamantylphosphinomethyl)-4,5-(di-t-butyl)
 25 benzene; 1,2-bis(di-adamantylphosphinomethyl)-4-t-butyl
 benzene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-
 (di-t-butylphosphinomethyl)-4,5- di-(2'-phenylprop-2'-
 yl)benzene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-
 2-(di-t-butylphosphinomethyl)-4-(2'-phenylprop-2'-
 30 yl)benzene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-
 2-(di-t-butylphosphinomethyl)-4,5-(di-t-butyl)benzene; 1-
 (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-
 butylphosphinomethyl)-4-t-butylbenzene; 1- (2-

phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-
 adamantyl) - 2 - (di-t-butylphosphinomethyl)4,5- di-(2'-
 phenylprop-2'-yl)benzene; 1- (2-phosphinomethyl-1,3,5,7-
 tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-
 5 butylphosphinomethyl)-4-(2'-phenylprop-2'-yl) benzene; 1-
 (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-
 adamantyl) - 2 - (di-t-butylphosphinomethyl)4,5-(di-t-
 butyl)benzene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-
 6,9,10-trioxa-adamantyl) - 2 - (di-t-
 10 butylphosphinomethyl)-4-t-butyl benzene; 1-(2-
 phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-
 adamantyl) -2- (diadamantylphosphinomethyl)-4,5- di-(2'-
 phenylprop-2'-yl) benzene; 1-(2-phosphinomethyl-1,3,5,7-
 tetramethyl-6,9,10-trioxa-adamantyl)-2-
 15 (diadamantylphosphinomethyl)-4-(2'-phenylprop-2'-yl)
 benzene; 1-(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 trioxa-adamantyl) -2- (diadamantylphosphinomethyl)-4,5-
 (di-t-butyl) benzene; 1-(2-phosphinomethyl-1,3,5,7-
 tetramethyl-6,9,10-trioxa-adamantyl)-2-
 20 (diadamantylphosphinomethyl)-4-t-butyl benzene; 1-(di-t-
 butylphosphinomethyl)-2- (diadamantylphosphinomethyl)-
 4,5- di-(2'-phenylprop-2'-yl) benzene; 1-(di-t-
 butylphosphinomethyl)-2- (diadamantylphosphinomethyl)-4-
 (2'-phenylprop-2'-yl) benzene; 1-(di-t-
 25 butylphosphinomethyl)-2- (diadamantylphosphinomethyl)-
 4,5-(di-t-butyl) benzene; 1-(di-t-butylphosphinomethyl)-
 2- (diadamantylphosphinomethyl)-4-t-butyl benzene; 1,2-
 bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 trioxatricyclo-{3.3.1.1[3.7]}decyl)-4,5- di-(2'-
 30 phenylprop-2'-yl) benzene; 1,2-bis(2-phosphinomethyl-
 1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-4-(2'-phenylprop-2'-yl) benzene; 1,2-
 bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-

trioxatricyclo-{3.3.1.1[3.7]}decyl)-4,5-(di-t-butyl)
 benzene; 1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-
 6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-4-t-butyl
 benzene; 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 5 trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-(di-t-
 butylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)
 benzene; 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-(di-t-
 butylphosphinomethyl)-4-(2'-phenylprop-2'-yl) benzene; 1-
 10 (2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(di-t-butylphosphinomethyl)-4,5-
 (di-t-butyl) benzene; 1-(2-phosphinomethyl-1,3,5-
 trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 (di-t-butylphosphinomethyl)-4-t-butyl benzene; 1-(2-
 15 phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(diadamantylphosphinomethyl)-4,5-
 di-(2'-phenylprop-2'-yl) benzene; 1-(2-phosphinomethyl-
 1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(diadamantylphosphinomethyl)-4-(2'-
 20 phenylprop-2'-yl) benzene; 1-(2-phosphinomethyl-1,3,5-
 trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)-4,5-(di-t-butyl) benzene; 1-
 (2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(diadamantylphosphinomethyl)-4-t-
 25 butyl benzene; 1,2-bis-perfluoro(2-phosphinomethyl-
 1,3,5,7-tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-
 decyl)-4,5-di-(2'-phenylprop-2'-yl) benzene; 1,2-bis-
 perfluoro(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(2'-phenylprop-2'-yl)
 30 benzene; 1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-
 tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl)-
 4,5-(di-t-butyl) benzene; 1,2-bis-perfluoro(2-
 phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-

trioxatricyclo{3.3.1.1[3.7]}decyl)-4-t-butyl benzene;
 1,2-bis-(2-phosphinomethyl-1,3,5,7-tetra(trifluoro-
 methyl)-6,9,10-trioxatricyclo{3.3.1.1[3.7]}decyl)-4,5-di-
 (2'-phenylprop-2'-yl) benzene; 1,2-bis-(2-
 5 phosphinomethyl-1,3,5,7-tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(2'-phenylprop-2'-yl)
 benzene; 1,2-bis-(2-phosphinomethyl-1,3,5,7-
 tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4,5-(di-t-butyl)
 10 benzene; 1,2-bis-(2-phosphinomethyl-1,3,5,7-
 tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4-t-butyl benzene, 1,2-
 bis-(P-(2,2,6,6-tetramethyl-phosphinomethyl-cyclohexan-4-
 one)-4-(trimethylsilyl)benzene, 1-(di-tert-
 15 butylphosphinomethyl)-2-(phospha-adamantyl)-4-
 (trimethylsilyl)benzene, 1-(diadamantylphosphinomethyl)-2-
 (phospha-adamantyl)-4-(trimethylsilyl)benzene, 1-
 (phospha-adamantyl)-2-(phospha-adamantyl)-4-
 (trimethylsilyl)methylbenzene, 1-(di-tert-
 20 butylphosphinomethyl)-2-(di-tert-butylphosphino)-4-
 (trimethylsilyl)benzene, 1-(diadamantylphosphinomethyl)-2-
 (diadamantylphosphino)-4-(trimethylsilyl)benzene, 1-(di-
 tert-butylphosphinomethyl)-2-(diadamantylphosphino)-4-
 (trimethylsilyl)benzene, 1-(di-tert-butylphosphinomethyl)-
 25 2-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-4-
 (trimethylsilyl)benzene, 1-(di-tert-
 butylphosphinomethyl)-2-(P-(2,2,6,6-tetramethyl-phospha-
 cyclohexan-4-one)-4-(trimethylsilyl)benzene, 1-(2-(P-
 (2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-4-
 30 trimethylsilylbenzyl)-2,2,6,6-tetramethyl-phospha-
 cyclohexan-4-one, 1-(tert-butyl,adamantylphosphino)-2-(di-
 adamantylphosphinomethyl)-4-(trimethylsilyl)benzene - and
 wherein "phospha-adamantyl" is selected from 2-phospha-

1,3,5,7-tetramethyl-6,9,10-trioxadamantyl,2-phospha-1,3,5-trimethyl-6,9,10 trioxadamantyl, 2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxadamantyl or 2-phospha-1,3,5-tri(trifluoromethyl)-6,9,10-trioxadamantyl-, 1-

5 (ditertbutylphosphinomethyl)-2-(P-(2,2,6,6-tetramethylphospha-cyclohexan-4-one)) -4-(trimethylsilyl)ferrocene, 1,2-bis(di-t-butylphosphinomethyl)-4,5-diphenyl ferrocene; 1,2-bis(di-t-butylphosphinomethyl)-4-(or 1')phenylferrocene; 1,2-bis(di-t-butylphosphinomethyl)-

10 4,5-bis-(trimethylsilyl) ferrocene; 1,2-bis(di-t-butylphosphinomethyl)-4-(or 1')(trimethylsilyl)ferrocene; 1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-4,5-diphenylferrocene; 1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-

15 adamantyl) 4-(or 1')phenylferrocene; 1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-4,5-bis-(trimethylsilyl)ferrocene; 1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) 4-(or 1')(trimethylsilyl)ferrocene; 1,2-

20 bis(di-adamantylphosphinomethyl)-4,5 diphenylferrocene; 1,2-bis(di-adamantylphosphinomethyl)-4-(or 1')phenyl ferrocene; 1,2-bis(di-adamantylphosphinomethyl)-4,5 bis-(trimethylsilyl)ferrocene; 1,2-bis(di-adamantylphosphinomethyl)-4-(or 1')(trimethylsilyl)

25 ferrocene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4,5-diphenylferrocene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4-(or 1')phenylferrocene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-

30 butylphosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4-(or 1')(trimethylsilyl)ferrocene; 1-(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-

adamantyl) - 2 - (di-t-butylphosphinomethyl)4,5-diphenylferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl)-4-(or 1')phenyl ferrocene; ; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl)4,5-bis-(trimethylsilyl)ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl)-4-(or 1')(trimethylsilyl) ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) -2- (diadamantylphosphinomethyl)-4,5-diphenyl ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-2- (diadamantylphosphinomethyl)-4-(or 1')phenyl ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) -2- (diadamantylphosphinomethyl)-4,5-bis-(trimethylsilyl) ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-2- (diadamantylphosphinomethyl)-4-(or 1')(trimethylsilyl) ferrocene; 1- (di-t-butylphosphinomethyl)-2- (diadamantylphosphinomethyl)-4,5-diphenyl ferrocene; 1- (di-t-butylphosphinomethyl)-2- (diadamantylphosphinomethyl)-4-(or 1')phenyl ferrocene; 1- (di-t-butylphosphinomethyl)-2- (diadamantylphosphinomethyl)-4,5-bis-(trimethylsilyl) ferrocene; 1- (di-t-butylphosphinomethyl)-2- (diadamantylphosphinomethyl)-4-(or 1')(trimethylsilyl) ferrocene; 1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-4,5-diphenyl ferrocene; 1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-4-(or 1')phenyl ferrocene; 1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-4,5-bis-(trimethylsilyl) ferrocene; 1,2-bis(2-phosphinomethyl-

1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-4-(or 1') (trimethylsilyl) ferrocene;
 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-(di-t-
 5 butylphosphinomethyl)-4,5-diphenyl ferrocene; 1-(2-
 phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(di-t-butylphosphinomethyl)-4-(or
 1') phenyl ferrocene; 1-(2-phosphinomethyl-1,3,5-
 trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 10 (di-t-butylphosphinomethyl)-4,5-bis-(trimethylsilyl)
 ferrocene; 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-(di-t-
 butylphosphinomethyl)-4-(or 1') (trimethylsilyl) ferrocene;
 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 15 trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)-4,5-diphenyl ferrocene; 1-
 (2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(diadamantylphosphinomethyl)-4-(or
 1') phenyl ferrocene; ; 1-(2-phosphinomethyl-1,3,5-
 20 trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)-4,5-bis-(trimethylsilyl)
 ferrocene; 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)-4-(o r 1') (trimethylsilyl)
 25 ferrocene; 1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-
 tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl)-
 4,5-diphenyl ferrocene; 1,2-bis-perfluoro(2-
 phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(o r 1') phenyl
 30 ferrocene; 1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-
 tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl)-
 4,5-bis-(trimethylsilyl) ferrocene; 1,2-bis-
 perfluoro(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-

trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(or
 1') (trimethylsilyl) ferrocene; 1,2-bis- (2-
 phosphinomethyl-1,3,5,7-tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4,5-diphenyl ferrocene;
 5 1,2-bis- (2-phosphinomethyl-1,3,5,7-tetra(trifluoro-
 methyl)-6,9,10-trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(or
 1')phenyl ferrocene; 1,2-bis- (2-phosphinomethyl-1,3,5,7-
 tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4,5-bis-(
 10 trimethylsilyl) ferrocene; 1,2-bis- (2-phosphinomethyl-
 1,3,5,7-tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(or
 1') (trimethylsilyl) ferrocene; 1,2-bis(di-t-
 butylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-
 15 yl) ferrocene; 1,2-bis(di-t-butylphosphinomethyl)-4-(or
 1') (2'-phenylprop-2'-yl) ferrocene; 1,2-bis(di-t-
 butylphosphinomethyl)-4,5- di-t-butyl ferrocene; 1,2-
 bis(di-t-butylphosphinomethyl)-4-(or 1')t-butylferrocene;
 1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 20 trioxa-adamantyl)-4,5- di-(2'-phenylprop-2'-yl) ferrocene;
 1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 trioxa-adamantyl)-4-(or 1') (2'-phenylprop-2'-yl) ferrocene;
 1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 trioxa-adamantyl)-4,5-(di-t-butyl) ferrocene; 1,2-bis(2-
 25 phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-
 adamantyl)-4-(or 1')t-butylferrocene; 1,2-bis(di-
 adamantylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)
 ferrocene; 1,2-bis(di-adamantylphosphinomethyl)-4-(or
 1') (2'-phenylprop-2'-yl) ferrocene; 1,2-bis(di-
 30 adamantylphosphinomethyl)-4,5-(di-t-butyl) ferrocene;
 1,2-bis(di-adamantylphosphinomethyl)-4-(or 1')t-butyl
 ferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-
 (di-t-butylphosphinomethyl)-4,5- di-(2'-phenylprop-2'-

yl)ferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4-(or 1') (2'-phenylprop-2'-yl)ferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4,5-

5 (di-t-butyl)ferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4-(or 1') t-butylferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl)4,5- di-(2'-phenylprop-2'-yl)ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl)-4-(or 1') (2'-phenylprop-2'-yl)ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl)4,5-(di-t-butyl)ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-butylphosphinomethyl)-4-(or 1') t-butyl ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) -2-

20 (diadamantylphosphinomethyl)-4,5- di-(2'-phenylprop-2'-yl)ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-2-(diadamantylphosphinomethyl)-4-(or 1') (2'-phenylprop-2'-yl) ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-

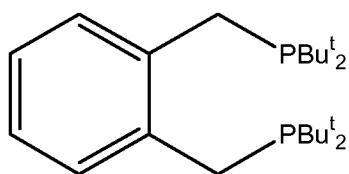
25 adamantyl) -2- (diadamantylphosphinomethyl)-4,5-(di-t-butyl) ferrocene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl)-2-(diadamantylphosphinomethyl)-4-(or 1') t-butyl ferrocene; 1- (di-t-butylphosphinomethyl)-2-

30 (diadamantylphosphinomethyl)-4,5- di-(2'-phenylprop-2'-yl)ferrocene; 1- (di-t-butylphosphinomethyl)-2-(diadamantylphosphinomethyl)-4-(or 1') (2'-phenylprop-2'-yl) ferrocene; 1- (di-t-butylphosphinomethyl)-2-

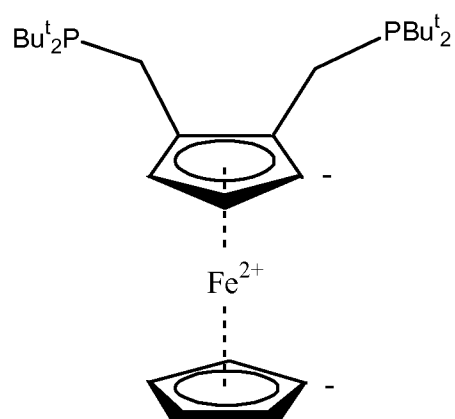
(diadamantylphosphinomethyl)-4,5-(di-t-butyl) ferrocene;
 1-(di-t-butylphosphinomethyl)-2-
 (diadamantylphosphinomethyl)-4-(or 1')t-butyl ferrocene;
 1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 5 trioxatricyclo-{3.3.1.1[3.7]}decyl)-4,5- di-(2'-
 phenylprop-2'-yl) ferrocene; 1,2-bis(2-phosphinomethyl-
 1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-4-(or 1')(2'-phenylprop-2'-yl)
 ferrocene; 1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-
 10 6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-4,5-(di-t-
 butyl) ferrocene; 1,2-bis(2-phosphinomethyl-1,3,5-
 trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-4-(or
 1')t-butyl ferrocene; 1-(2-phosphinomethyl-1,3,5-
 trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 15 (di-t-butylphosphinomethyl)-4,5- di-(2'-phenylprop-2'-yl)
 ferrocene; 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-(di-t-
 butylphosphinomethyl)-4-(or 1')(2'-phenylprop-2'-yl)
 ferrocene; 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 20 trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-(di-t-
 butylphosphinomethyl)-4,5-(di-t-butyl) ferrocene; 1-(2-
 phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-
 {3.3.1.1[3.7]}decyl)-2-(di-t-butylphosphinomethyl)-4-(or
 1')t-butyl ferrocene; 1-(2-phosphinomethyl-1,3,5-
 25 trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)
 ferrocene; 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-
 trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)-4-(or 1')(2'-phenylprop-2'-
 30 yl) ferrocene; 1-(2-phosphinomethyl-1,3,5-trimethyl-
 6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-
 (diadamantylphosphinomethyl)-4,5-(di-t-butyl) ferrocene;
 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-

trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-(
 (diadamantylphosphinomethyl)-4-(or 1')t-butyl ferrocene;
 1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-tetramethyl-
 6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl)-4,5-di-(2'-
 5 phenylprop-2'-yl) ferrocene; 1,2-bis-perfluoro(2-
 phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(or 1')(2'-
 phenylprop-2'-yl) ferrocene; 1,2-bis-perfluoro(2-
 phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-
 10 trioxatricyclo{3.3.1.1[3.7]}-decyl)-4,5-(di-t-butyl)
 ferrocene; 1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-
 tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}decyl)-4-
 (or 1')t-butyl ferrocene; 1,2-bis-(2-phosphinomethyl-
 1,3,5,7-tetra(trifluoro-methyl)-6,9,10-
 15 trioxatricyclo{3.3.1.1[3.7]}decyl)-4,5-di-(2'-phenylprop-
 2'-yl) ferrocene; 1,2-bis-(2-phosphinomethyl-1,3,5,7-
 tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(or 1')(2'-
 phenylprop-2'-yl) ferrocene; 1,2-bis-(2-phosphinomethyl-
 20 1,3,5,7-tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4,5-(di-t-butyl)
 ferrocene; 1,2-bis-(2-phosphinomethyl-1,3,5,7-
 tetra(trifluoro-methyl)-6,9,10-
 trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(or 1')t-butyl
 25 ferrocene.

Selected structures of ligands of the invention include:-

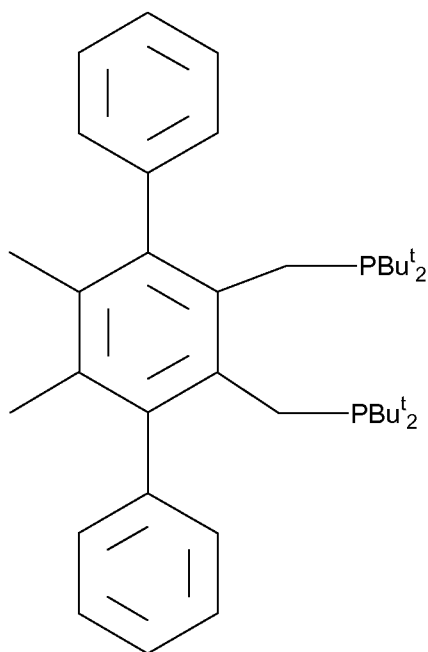


1,2-bis(di-tert-butylphosphinomethyl)benzene



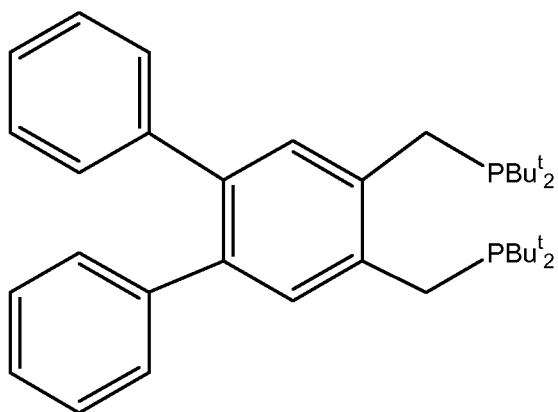
1,2-bis(di-tert-butylphosphinomethyl) ferrocene

5

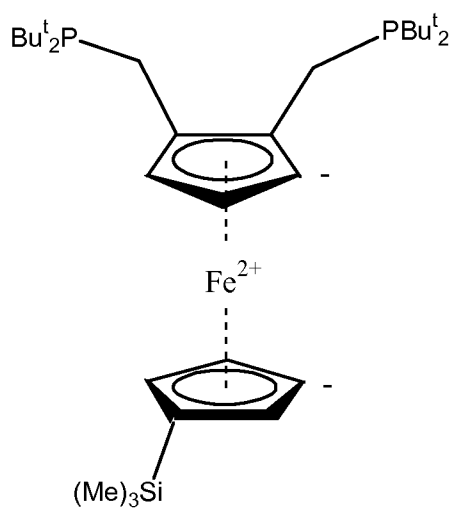


1,2-bis(di-tert-butylphosphinomethyl)-3,6-diphenyl-4,5-
10 dimethyl benzene

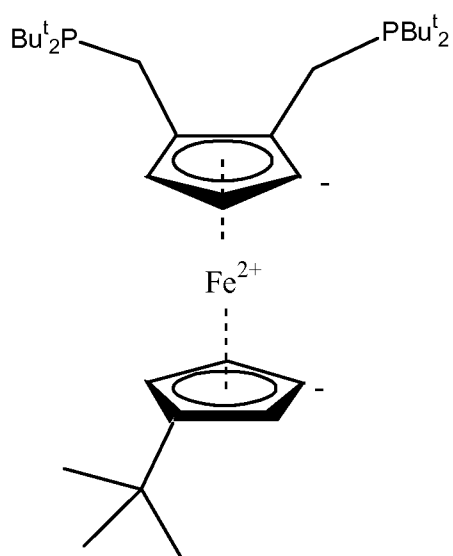
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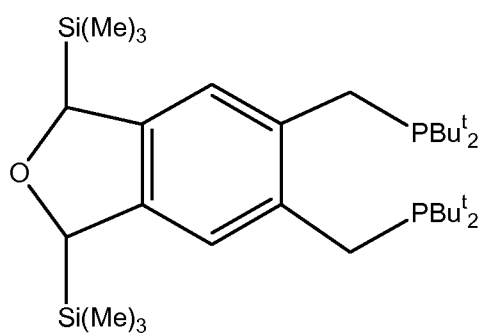
1,2-bis(di-tert-butyl (phosphinomethyl))-4,5-diphenyl
5 benzene



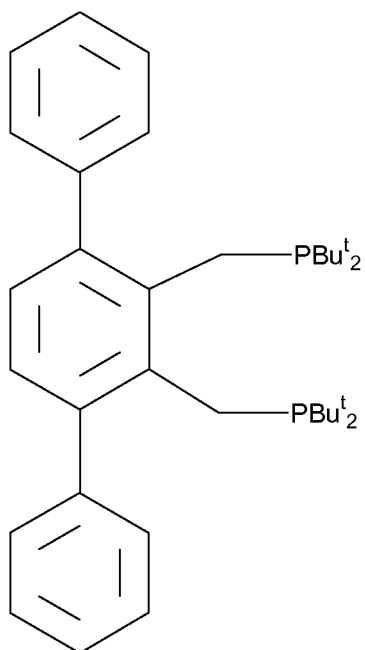
1,2-bis(di-tert-butylphosphinomethyl)-1'-trimethylsilyl
10 ferrocene



1,2-bis(di-tert-butylphosphinomethyl)-1'-tert-butyl
5 ferrocene

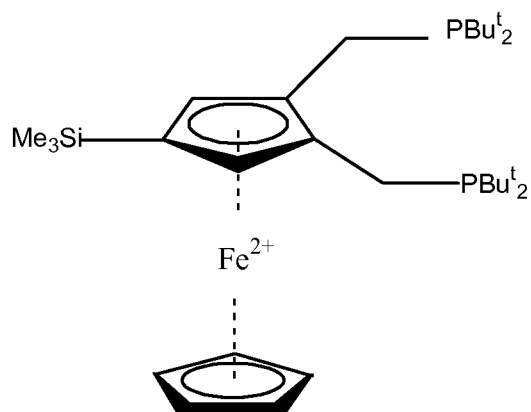


5,6-bis(di-tert-butylphosphinomethyl)-1,3-bis-
10 trimethylsilyl-1,3-dihydroisobenzofuran.

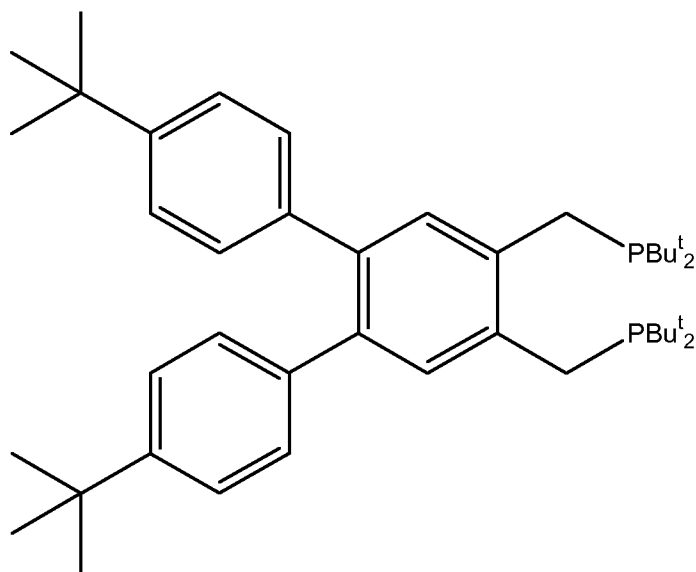


1, 2-bis (di-tert-butylphosphinomethyl)-3,6-diphenyl
benzene

5

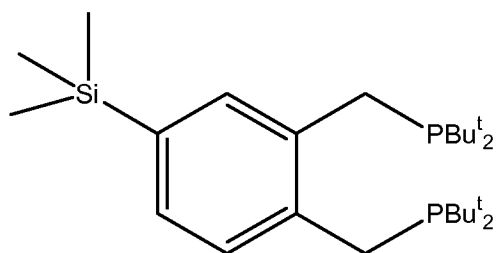


1,2-bis (di-tert-butylphosphinomethyl)-4-trimethylsilyl
ferrocene



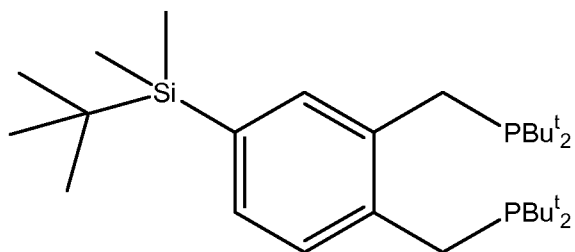
1,2-bis(di-tert-butyl (phosphinomethyl))-4,5-di(4'-tert-butyl phenyl) benzene

5



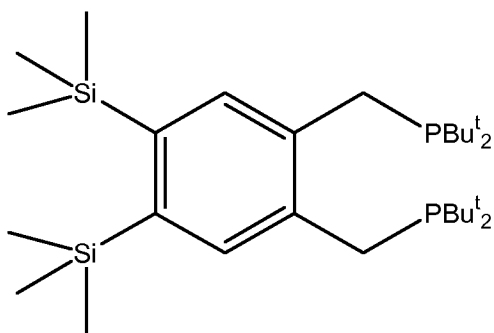
1,2-bis(di-tert-butyl (phosphinomethyl))-4-trimethylsilyl benzene

10

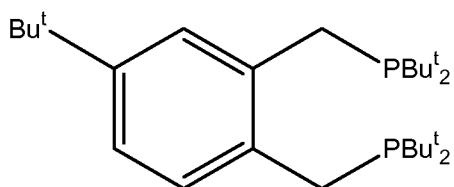


1,2-bis(di-tert-butyl (phosphinomethyl))-4-(tert-butyl dimethylsilyl) benzene

15



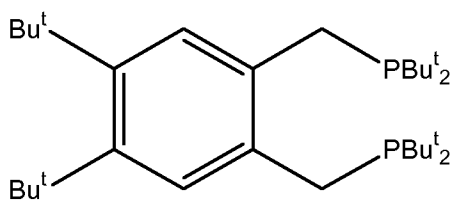
1,2-bis(di-tert-butyl(phosphinomethyl))-4,5-
5 bis(trimethylsilyl)benzene



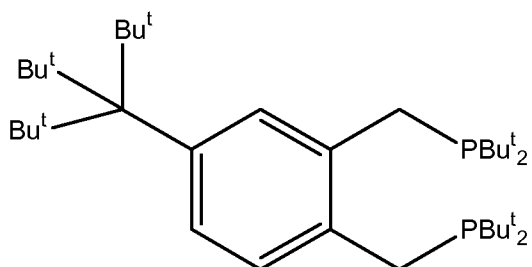
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1,2-bis(di-tert-butyl(phosphinomethyl))-4-tert-butyl
10 benzene

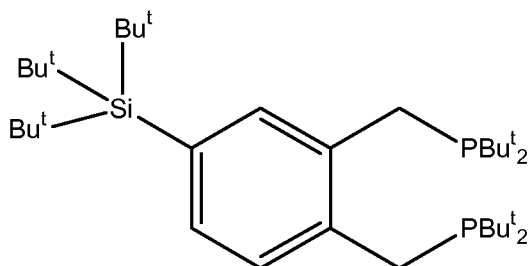
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15  1,2-bis(di-tert-butyl(phosphinomethyl))-4,5-di-tert-butyl
    benzene
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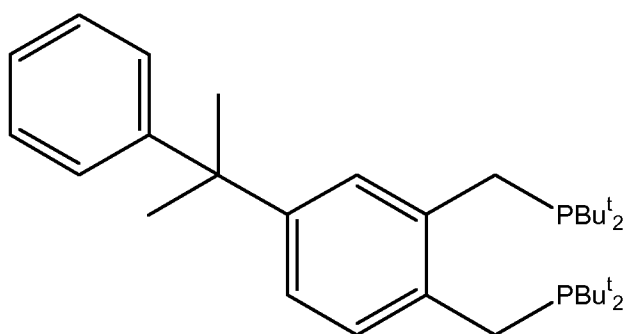


1,2-bis(di-tert-butyl(phosphinomethyl))-4-(tri-tert-butylmethyl)benzene



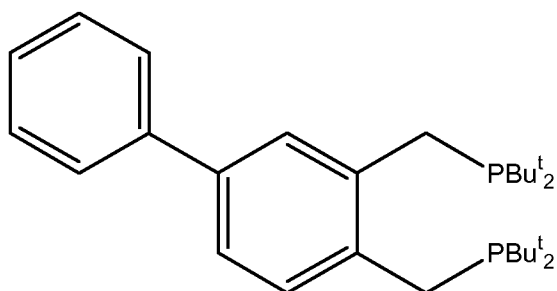
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1,2-bis(di-tert-butyl(phosphinomethyl))-4-(tri-tert-butylsilyl)benzene

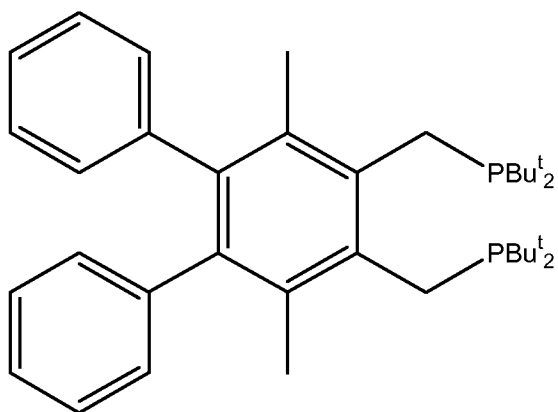


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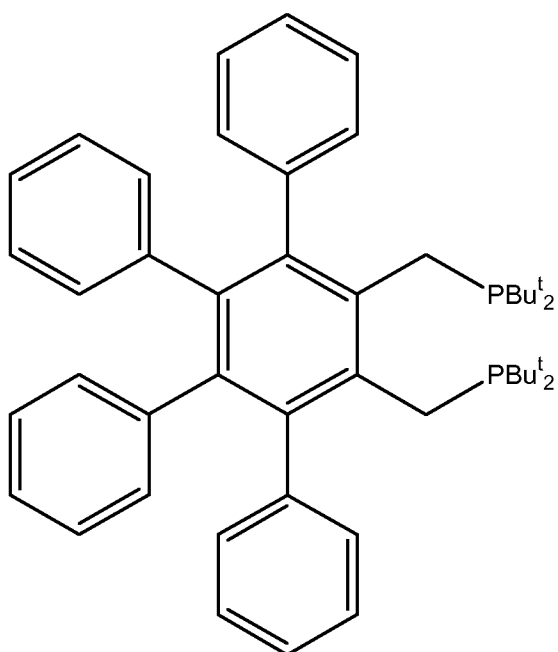
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(2'-phenylprop-2'-yl)benzene



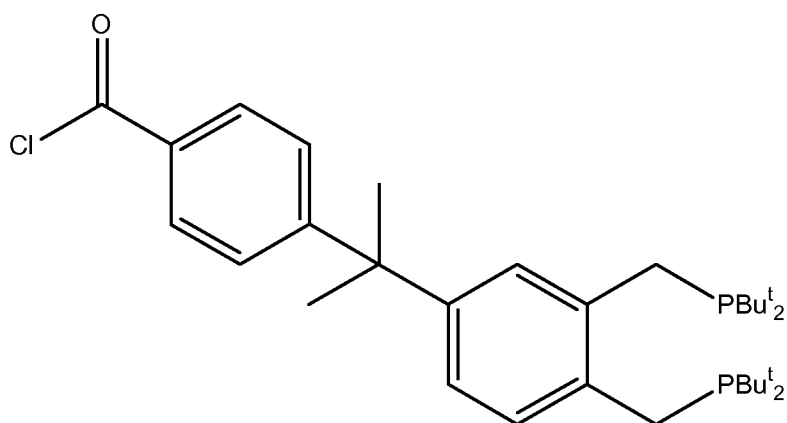
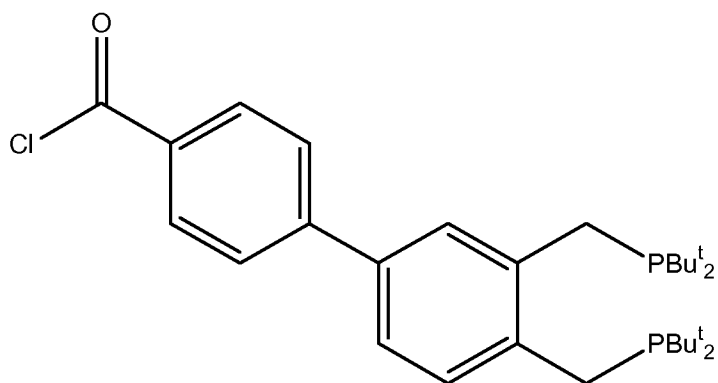
15 1,2-bis(di-tert-butyl(phosphinomethyl))-4-phenyl benzene



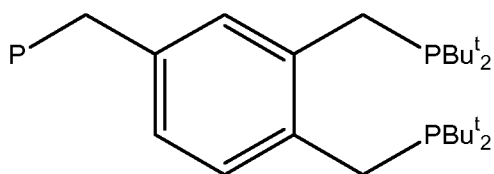
1,2-bis(di-tert-butyl (phosphinomethyl))-3,6-dimethyl-4,5-
5 diphenyl benzene



1,2-bis(di-tert-butyl (phosphinomethyl))-3,4,5,6-
tetraphenyl benzene

4-(1-{3,4-Bis-[(di-*tert*-butyl-phosphanyl)-methyl]-phenyl}-1-methyl-ethyl)-benzoyl chloride

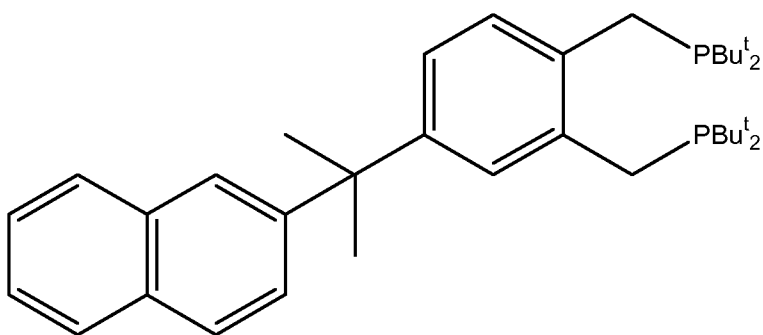
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1,2-bis(di-*tert*-butyl(phosphinomethyl))-4-(4'-chlorocarbonyl-phenyl)benzene

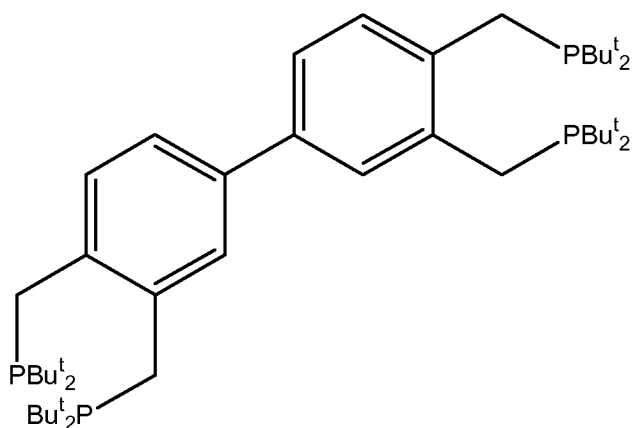
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1,2-bis(di-*tert*-butyl(phosphinomethyl))-4-(phosphinomethyl)benzene

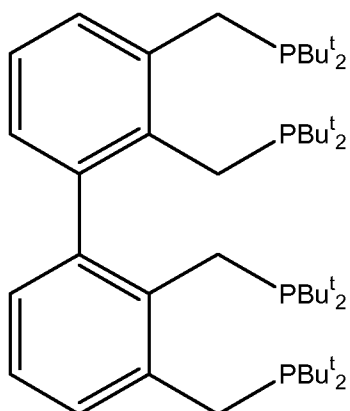
89



1,2-bis(di-tert-butyl (phosphinomethyl))-4-(2'-
5 naphthylprop-2'-yl) benzene



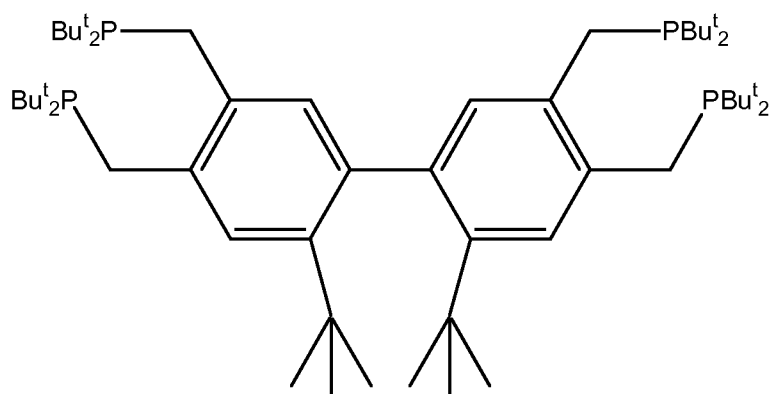
1,2-bis(di-tert-butyl (phosphinomethyl))-4-(3',4'-bis(di-
tert-butyl (phosphinomethyl))phenyl) benzene



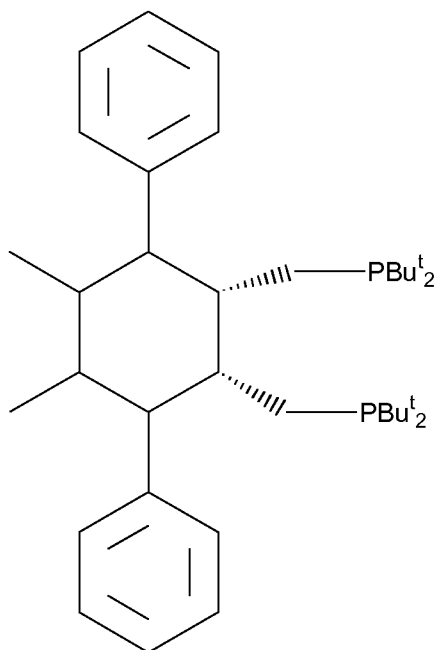
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1,2-bis(di-tert-butyl (phosphinomethyl))-3-(2',3'-bis(di-
tert-butyl (phosphinomethyl))phenyl) benzene

90

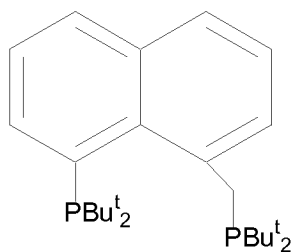


1,2-bis(di-tert-butyl(phosphinomethyl))-4-tertbutyl-5-(2'-tertbutyl-4',5'-bis(di-tert-butyl(phosphinomethyl))phenyl)benzene, and

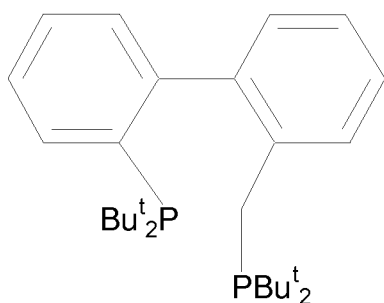


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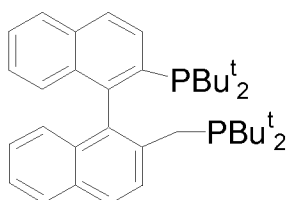
cis-1, 2-bis (di-tert-butylphosphinomethyl), 3, 6, diphenyl-4,5 dimethyl-cyclohexane,



1-(di-tert-butylphosphino)-8-(di-tertbutylphosphinomethyl)-naphthalene

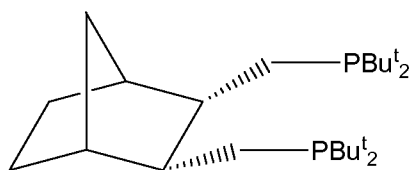


2-(di-tert-butylphosphino)-2'-(di-tert-butylphosphinomethyl)-biphenylene



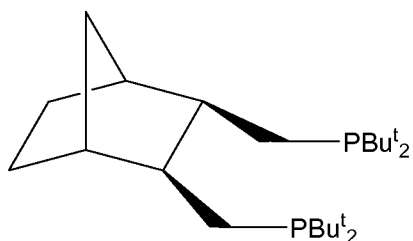
2-(di-tert-butylphosphino)-2'-(di-tert-butylphosphinomethyl)-binaphthylene

Examples of norbornyl bridge non-aromatic bridged ligands
 5 include:-



(2-exo, 3-exo)-bicyclo[2.2.1]heptane-2,3-bis(di-tert-butylphosphinomethyl)

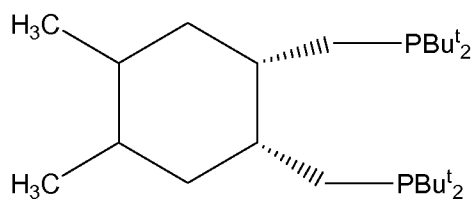
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(2-endo, 3-endo)-bicyclo[2.2.1]heptane-2,3-bis(di-tert-butylphosphinomethyl)

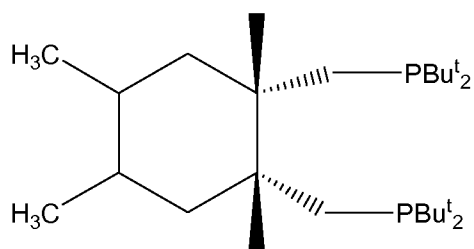
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Examples of substituted non-aromatic bridged ligand structures include:-



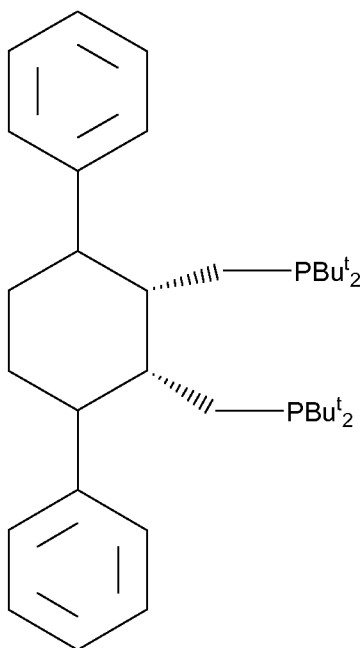
15

cis-1,2-bis(di-tert-butylphosphinomethyl), 4,5-dimethylcyclohexane

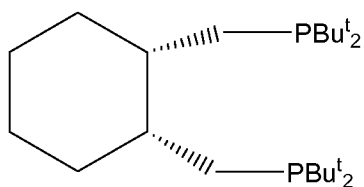


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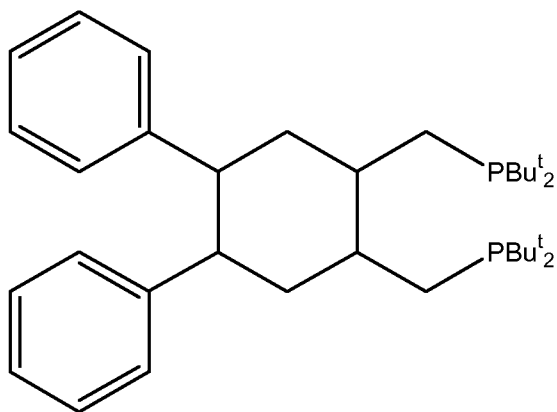
cis-1, 2-bis (di-*tert*-butylphosphinomethyl), 1, 2, 4, 5
tetramethylcyclohexane



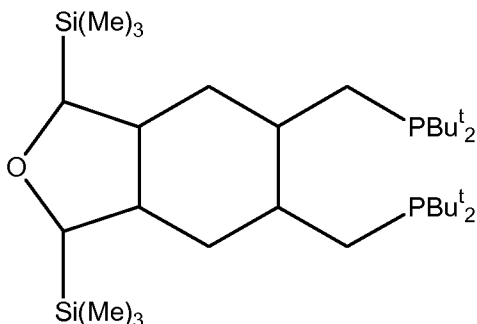
cis-1, 2-bis (di-*tert*-butylphosphinomethyl), 3, 6,
5 diphenylcyclohexane



cis- 1, 2-bis (di-*tert*-butylphosphinomethyl) cyclohexane



cis-1,2-bis(di-tert-butyl(phosphinomethyl))-4,5-diphenyl
cyclohexane



5 cis-5,6-bis(di-tert-butylphosphinomethyl)-1,3-
bis(trimethylsilyl)-3a,4,5,6,7,7a-hexahydro-1,3H-
isobenzofuran.

In the above example structures of ligands of general
10 formulas (I)-(IV), one or more of the X^1 - X^4 tertiary
carbon bearing groups, t-butyl, attached to the Q^1 and/or
 Q^2 group phosphorus may be replaced by a suitable
alternative. Preferred alternatives are adamantyl, 1,3-
dimethyl adamantyl, congressyl, norbornyl or 1-
15 norbondienyl, or X^1 and X^2 together and/or X^3 and X^4
together form together with the phosphorus a 2-phospha-
tricyclo[3.3.1.1{3,7}]decyl group such as 2-phospha-
1,3,5,7-tetramethyl-6,9,10-trioxadamantyl or 2-phospha-
1,3,5-trimethyl-6,9,10-trioxadamantyl. In most
20 embodiments, it is preferred that the X^1 - X^4 groups or the
combined X^1/X^2 and X^3/X^4 groups are the same but it may
also be advantageous to use different groups to produce
asymmetry around the active site in these selected ligands
and generally in this invention.

25

Similarly, one of the linking groups A or B may be absent
so that only A or B is methylene and the phosphorus atom
not connected to the methylene group is connected directly

to the ring carbon giving a 3 carbon bridge between the phosphorus atoms.

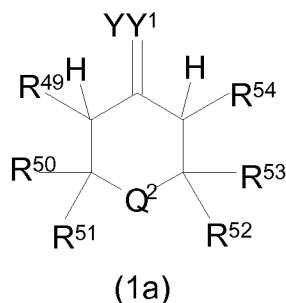
Typically, the group X^1 represents $CR^1(R^2)(R^3)$, X^2 represents $CR^4(R^5)(R^6)$, X^3 represents $CR^7(R^8)(R^9)$ and X^4 represents $CR^{10}(R^{11})(R^{12})$, wherein R^1 to R^{12} represent alkyl, aryl or het.

Particularly preferred is when the organic groups $R^1 - R^3$, $R^4 - R^6$, $R^7 - R^9$ and /or $R^{10} - R^{12}$ or, alternatively, $R^1 - R^6$ and/or $R^7 - R^{12}$ when associated with their respective tertiary carbon atom(s) form composite groups which are at least as sterically hindering as t-butyl(s).

The steric composite groups may be cyclic, part-cyclic or acyclic. When cyclic or part cyclic, the group may be substituted or unsubstituted or saturated or unsaturated. The cyclic or part cyclic groups may preferably contain, including the tertiary carbon atom(s), from $C_4 - C_{34}$, more preferably $C_8 - C_{24}$, most preferably $C_{10} - C_{20}$ carbon atoms in the cyclic structure. The cyclic structure may be substituted by one or more substituents selected from halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29} , $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl or Het, wherein R^{19} to R^{30} are as defined herein, and/or be interrupted by one or more oxygen or sulphur atoms, or by silano or dialkylsilcon groups.

In particular, when cyclic, X^1 , X^2 , X^3 and/or X^4 may represent congressyl, norbornyl, 1-norbornadienyl or adamantyl, or X^1 and X^2 together with Q^2 to which they are attached form an optionally substituted 2- Q^2 -tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof,

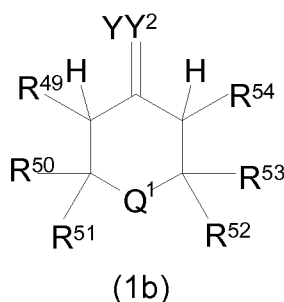
or X^1 and X^2 together with Q^2 to which they are attached form a ring system of formula 1a



5

Similarly, X^3 and X^4 together with Q^1 to which they are attached may form an optionally substituted 2- Q^1 -tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof,

10 may form a ring system of formula 1b



Alternatively, one or more of the groups X^1 , X^2 , X^3 and/or X^4 may represent a solid phase to which the ligand is attached.

15

Particularly preferred is when X^1 , X^2 , X^3 and X^4 or X^1 and X^2 together with its respective Q^2 atom and X^3 and X^4 together with its respective Q^1 atom are the same or when

20 X^1 and X^3 are the same whilst X^2 and X^4 are different but the same as each other.

In preferred embodiments, R^1 to R^{12} and R^{13} - R^{18} each independently represent alkyl, aryl, or Het;

R^{19} to R^{30} each independently represent hydrogen, alkyl,
5 aryl or Het; R^{19} represents hydrogen, unsubstituted C_1 - C_8 alkyl or phenyl, R^{20} , R^{22} , R^{23} , R^{24} , R^{25} , R^{26} each independently represent hydrogen or unsubstituted C_1 - C_8 alkyl,

10 R^{49} and R^{54} , when present, each independently represent hydrogen, alkyl or aryl;

R^{50} to R^{53} , when present, each independently represent alkyl, aryl or Het;

15

YY^1 and YY^2 , when present, each independently represent oxygen, sulfur or $N-R^{55}$, wherein R^{55} represents hydrogen, alkyl or aryl.

20 Preferably, R^1 to R^{12} herein each independently represent alkyl or aryl. More preferably, R^1 to R^{12} each independently represent C_1 to C_6 alkyl, C_1 - C_6 alkyl phenyl (wherein the phenyl group is optionally substituted as aryl as defined herein) or phenyl (wherein the phenyl
25 group is optionally substituted as aryl as defined herein). Even more preferably, R^1 to R^{12} each independently represent C_1 to C_6 alkyl, which is optionally substituted as alkyl as defined herein. Most preferably, R^1 to R^{12} each represent non-substituted C_1 to C_6 alkyl such as methyl,
30 ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl, especially methyl.

In a particularly preferred embodiment of the present invention R^1 , R^4 , R^7 and R^{10} each represent the same alkyl, aryl or Het moiety as defined herein, R^2 , R^5 , R^8 and R^{11} each represent the same alkyl, aryl or Het moiety as defined herein, and R^3 , R^6 , R^9 and R^{12} each represent the same alkyl, aryl or Het moiety as defined herein. More preferably R^1 , R^4 , R^7 and R^{10} each represent the same C_1 - C_6 alkyl, particularly non-substituted C_1 - C_6 alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl or cyclohexyl; R^2 , R^5 , R^8 and R^{11} each independently represent the same C_1 - C_6 alkyl as defined above; and R^3 , R^6 , R^9 and R^{12} each independently represent the same C_1 - C_6 alkyl as defined above. For example: R^1 , R^4 , R^7 and R^{10} each represent methyl; R^2 , R^5 , R^8 and R^{11} each represent ethyl; and, R^3 , R^6 , R^9 and R^{12} each represent n-butyl or n-pentyl.

In an especially preferred embodiment of the present invention each R^1 to R^{12} group represents the same alkyl, aryl, or Het moiety as defined herein. Preferably, when alkyl groups, each R^1 to R^{12} represents the same C_1 to C_6 alkyl group, particularly non-substituted C_1 - C_6 alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl. More preferably, each R^1 to R^{12} represents methyl or tert-butyl, most preferably, methyl.

The 2- Q^2 (or Q^1)-tricyclo[3.3.1.1.{3,7}]decyl group (referred to hereinafter as a 2-meta-adamantyl group for convenience wherein 2-meta-adamantyl is a reference to Q^1 or Q^2 being an arsenic, antimony or phosphorus atom i.e. 2-arsa-adamantyl and/or 2-stiba-adamantyl and/or 2-phospha-adamantyl, preferably, 2-phospha-adamantyl) may

optionally comprise, beside hydrogen atoms, one or more substituents. Suitable substituents include those substituents as defined herein in respect of the adamantyl group. Highly preferred substituents include alkyl, particularly unsubstituted C₁-C₈ alkyl, especially methyl, trifluoromethyl, -OR¹⁹ wherein R¹⁹ is as defined herein particularly unsubstituted C₁-C₈ alkyl or aryl, and 4-dodecylphenyl. When the 2-meta-adamantyl group includes more than one substituent, preferably each substituent is identical.

Preferably, the 2-meta-adamantyl group is substituted on one or more of the 1, 3, 5 or 7 positions with a substituent as defined herein. More preferably, the 2-meta-adamantyl group is substituted on each of the 1, 3 and 5 positions. Suitably, such an arrangement means the Q atom of the 2-meta-adamantyl group is bonded to carbon atoms in the adamantyl skeleton having no hydrogen atoms. Most preferably, the 2-meta-adamantyl group is substituted on each of the 1, 3, 5 and 7 positions. When the 2-meta-adamantyl group includes more than 1 substituent preferably each substituent is identical. Especially preferred substituents are unsubstituted C₁-C₈ alkyl and haloalkyls, particularly unsubstituted C₁-C₈ alkyl such as methyl and fluorinated C₁-C₈ alkyl such as trifluoromethyl.

Preferably, 2-meta-adamantyl represents unsubstituted 2-meta-adamantyl or 2-meta-adamantyl substituted with one or more unsubstituted C₁-C₈ alkyl substituents, or a combination thereof.

Preferably, the 2-meta-adamantyl group includes additional heteroatoms, other than the 2-Q atom, in the 2-meta-adamantyl skeleton. Suitable additional heteroatoms include oxygen and sulphur atoms, especially oxygen atoms.

5 More preferably, the 2-meta-adamantyl group includes one or more additional heteroatoms in the 6, 9 and 10 positions. Even more preferably, the 2-meta-adamantyl group includes an additional heteroatom in each of the 6, 9 and 10 positions. Most preferably, when the 2-meta-

10 adamantyl group includes two or more additional heteroatoms in the 2-meta-adamantyl skeleton, each of the additional heteroatoms are identical. Preferably, the 2-meta-adamantyl includes one or more oxygen atoms in the 2-meta-adamantyl skeleton. An especially preferred 2-meta-

15 adamantyl group, which may optionally be substituted with one or more substituents as defined herein, includes an oxygen atom in each of the 6, 9 and 10 positions of the 2-meta-adamantyl skeleton.

20 Highly preferred 2-meta-adamantyl groups as defined herein include 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl, 2-phospha-1,3,5-trimethyl-6,9,10-trioxadamantyl, 2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxadamantyl group, and 2-phospha-1,3,5-

25 tri(trifluoromethyl)-6,9,10-trioxadamantyl group. Most preferably, the 2-phospha-adamantyl is selected from 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group or 2-phospha-1,3,5,-trimethyl-6,9,10-trioxadamantyl group.

30 Preferably, when more than one 2-meta-adamantyl group is present in a compound of formula I - IV, each 2-meta-adamantyl group is identical. However, it can also be advantageous if asymmetric ligands are prepared and if

such ligands include a 2-meta-adamantyl group incorporating the Q^1 atom then other groups can be found on the Q^2 atom or vice versa.

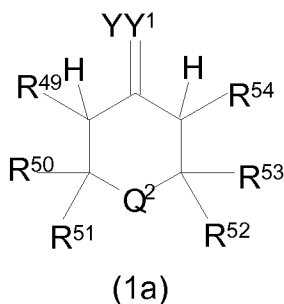
5 The 2-meta-adamantyl group may be prepared by methods well known to those skilled in the art. Suitably, certain 2-phospha-adamantyl compounds are obtainable from Cytec Canada Inc, Canada. Likewise corresponding 2-meta-adamantyl compounds of formulas I - IV etc may be obtained
10 from the same supplier or prepared by analogous methods.

Preferred embodiments of the present invention include those wherein:

15 X^3 represents $CR^7(R^8)(R^9)$, X^4 represents $CR^{10}(R^{11})(R^{12})$, X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$;

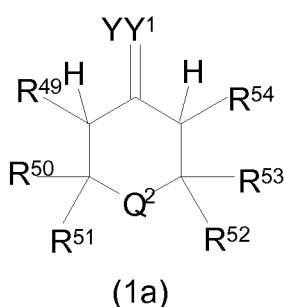
X^3 represents $CR^7(R^8)(R^9)$, X^4 represents $CR^{10}(R^{11})(R^{12})$, and X^1 and X^2 together with Q^2 to which they are attached form
20 a 2-phospha-adamantyl group;

X^3 represents $CR^7(R^8)(R^9)$, X^4 represents $CR^{10}(R^{11})(R^{12})$; and X^1 and X^2 together with Q^2 to which they are attached form a ring system of formula 1a;



X^3 represents $CR^7(R^8)(R^9)$, X^4 represents adamantyl, and X^1 and X^2 together with Q^2 to which they are attached form a 2-phospha-adamantyl group;

- 5 X^3 represents $CR^7(R^8)(R^9)$, X^4 represents adamantyl and X^1 and X^2 together with Q^2 to which they are attached form a ring system of formula 1a;



10

X^3 represents $CR^7(R^8)(R^9)$, X^4 represents adamantyl, X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$;

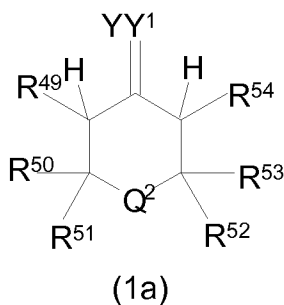
- 15 X^3 represents $CR^7(R^8)(R^9)$, X^4 represents congressyl, and X^1 and X^2 together with Q^2 to which they are attached form a 2-phospha-adamantyl group;

X^3 represents $CR^7(R^8)(R^9)$, X^4 represents congressyl, X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$;

20

X^3 and X^4 independently represent adamantyl, and X^1 and X^2 together with Q^2 to which they are attached form a 2-phospha-adamantyl group;

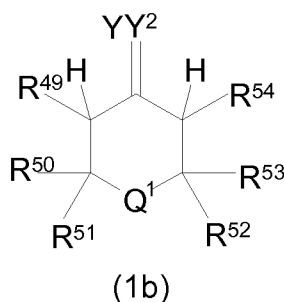
- 25 X^3 and X^4 independently represent adamantyl, and X^1 and X^2 together with Q^2 to which they are attached form a ring system of formula 1a;



X^3 and X^4 independently represent adamantyl, X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$;

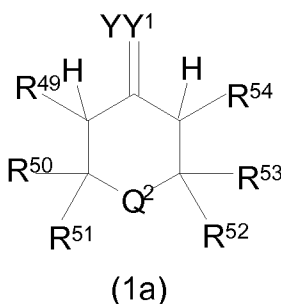
5 X^1 , X^2 , X^3 and X^4 represent adamantyl;

X^3 and X^4 together with Q^1 to which they are attached may form a ring system of formula 1b



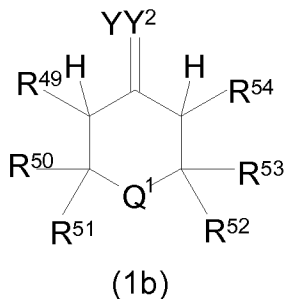
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and X^1 and X^2 together with Q^2 to which they are attached form a ring system of formula 1a;



15 X^3 and X^4 independently represent congressyl, and X^1 and X^2 together with Q^2 to which they are attached form a 2-phospha-adamantyl group;

X^3 and X^4 together with Q^1 to which they are attached may form a ring system of formula 1b

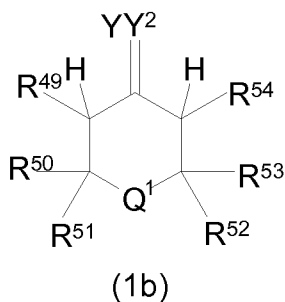


5 and X^1 and X^2 together with Q^2 , to which they are attached form a 2-phospha-adamantyl group;

X^3 and X^4 independently represent congressyl, and X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$;

10

X^3 and X^4 together with Q^1 to which they are attached may form a ring system of formula 1b



X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$;

15

X^3 and X^4 together with Q^1 to which they are attached form a 2-phospha-adamantyl group, and X^1 and X^2 together with Q^2 to which they are attached form a 2-phospha-adamantyl group

20

Highly preferred embodiments of the present invention include those wherein:

X^3 represents $CR^7(R^8)(R^9)$, X^4 represents $CR^{10}(R^{11})(R^{12})$, X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$; especially where R^1 - R^{12} are methyl.

- 5 Preferably in a compound of formula IV, X^3 is identical to X^4 and/or X^1 is identical to X^2 .

Particularly preferred combinations in the present invention include those wherein:-

10

- (1) X^3 represents $CR^7(R^8)(R^9)$, X^4 represents $CR^{10}(R^{11})(R^{12})$, X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$;

15

A and B are the same and represent $-CH_2-$ or A is $-CH_2$ and B is not present so that the phosphorus is joined directly to the group R;

Q^1 and Q^2 both represent phosphorus linked to the R group at ring positions 1 and 2;

R represents 4-(trimethylsilyl)-benzene-1,2-diyl

20

- (2) X^3 represents $CR^7(R^8)(R^9)$, X^4 represents $CR^{10}(R^{11})(R^{12})$, X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$;

25

A and B are the same and represent $-CH_2-$ or A is $-CH_2$ and B is not present so that the phosphorus is joined directly to the group R;

30

Q^1 and Q^2 both represent phosphorus linked to the R group at ring positions 1 and 2;

R represents 4-t-butyl-benzene-1,2-diyl.

- (3) X^3 and X^4 together with Q^1 to which they are attached form a 2-phospha-adamantyl group, and, X^1 and X^2 together with Q^2 to which they are attached form a 2-phospha-adamantyl group;
- A and B are the same and represent $-CH_2-$ or A is $-CH_2$ and B is not present so that the phosphorus is joined directly to the group R;
- Q^1 and Q^2 both represent phosphorus linked to the R group at ring positions 1 and 2;
- R represents 4-(trimethylsilyl)-benzene-1,2-diyl.
- (4) X^1 , X^2 , X^3 and X^4 represent adamantyl;
- A and B are the same and represent $-CH_2-$ or A is $-CH_2$ and B is not present so that the phosphorus is joined directly to the group R;
- Q^1 and Q^2 both represent phosphorus linked to the R group at ring positions 1 and 2;
- R represents 4-(trimethylsilyl)-benzene-1,2-diyl.
- (5) X^3 represents $CR^7(R^8)(R^9)$, X^4 represents $CR^{10}(R^{11})(R^{12})$, X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$;
- A and B are the same and represent $-CH_2-$ or A is $-CH_2$ and B is not present so that the phosphorus is joined directly to the group R;
- Q^1 and Q^2 both represent phosphorus linked to the R group at ring positions 1 and 2;
- R represents ferrocene or benzene-1,2-diyl
- (6) X^3 and X^4 together with Q^1 to which they are attached form a 2-phospha-adamantyl group, and, X^1 and X^2

together with Q^2 to which they are attached form a 2-phospha-adamantyl group;

A and B are the same and represent $-CH_2-$ or A is $-CH_2$ and B is not present so that the phosphorus is joined directly to the group R;

Q^1 and Q^2 both represent phosphorus linked to the R group at ring positions 1 and 2;

R represents ferrocene or benzene-1,2-diyl.

10 (7) X^1 , X^2 , X^3 and X^4 represent adamantyl;

A and B are the same and represent $-CH_2-$ or A is $-CH_2$ and B is not present so that the phosphorus is joined directly to the group R;

Q^1 and Q^2 both represent phosphorus linked to the R group at ring positions 1 and 2;

R represents ferrocene or benzene-1,2-diyl.

Preferably, in the compound of formula IV, A and/or B each independently represents C_1 to C_6 alkylene which is optionally substituted as defined herein, for example with alkyl groups. Preferably, the lower alkylene groups which A and/or B represent are non-substituted. Particularly preferred alkylene which A and B may independently represent are $-CH_2-$ or $-C_2H_4-$. Most preferably, each of A and B represent the same alkylene as defined herein, particularly $-CH_2-$. or A represents $-CH_2-$ and B is not present or vice versa

Still further preferred compounds of formulas I-IV include those wherein:

R^1 to R^{12} are alkyl and are the same and preferably, each represents C_1 to C_6 alkyl, particularly methyl.

Especially preferred specific compounds of formulas I-IV include those wherein:

- 5 each R^1 to R^{12} is the same and represents methyl;
A and B are the same and represent $-\text{CH}_2-$;
R represents benzene-1,2-diyl, ferrocene-1,2-diyl, 4-
butyl-benzene-1,2-diyl, 4(trimethylsilyl)-
benzene-1,2-diyl.

10

The adamantyl, congressyl, norbornyl or 1-norborndienyl group may optionally comprise, besides hydrogen atoms, one or more substituents selected from alkyl, $-\text{OR}^{19}$, $-\text{OC}(\text{O})\text{R}^{20}$, halo, nitro, $-\text{C}(\text{O})\text{R}^{21}$, $-\text{C}(\text{O})\text{OR}^{22}$, cyano, aryl, $-\text{N}(\text{R}^{23})\text{R}^{24}$, $-\text{C}(\text{O})\text{N}(\text{R}^{25})\text{R}^{26}$, $-\text{C}(\text{S})(\text{R}^{27})\text{R}^{28}$, $-\text{SR}^{29}$, $-\text{C}(\text{O})\text{SR}^{30}$, $-\text{CF}_3$, $-\text{P}(\text{R}^{56})\text{R}^{57}$, $-\text{PO}(\text{R}^{58})(\text{R}^{59})$, $-\text{PO}_3\text{H}_2$, $-\text{PO}(\text{OR}^{60})(\text{OR}^{61})$, or $-\text{SO}_3\text{R}^{62}$, wherein R^{19} - R^{30} , alkyl, halo, cyano and aryl are as defined herein and R^{56} to R^{62} each independently represent hydrogen, alkyl, aryl or Het.

20

Suitably, when the adamantyl, congressyl, norbornyl or 1-norborndienyl group is substituted with one or more substituents as defined above, highly preferred substituents include unsubstituted C_1 to C_8 alkyl, $-\text{OR}^{19}$, $-\text{OC}(\text{O})\text{R}^{20}$, phenyl, $-\text{C}(\text{O})\text{OR}^{22}$, fluoro, $-\text{SO}_3\text{H}$, $-\text{N}(\text{R}^{23})\text{R}^{24}$, $-\text{P}(\text{R}^{56})\text{R}^{57}$, $-\text{C}(\text{O})\text{N}(\text{R}^{25})\text{R}^{26}$ and $-\text{PO}(\text{R}^{58})(\text{R}^{59})$, $-\text{CF}_3$, wherein R^{19} - R^{26} are as defined herein, R^{56} to R^{59} each independently represent unsubstituted C_1 - C_8 alkyl or phenyl. In a particularly preferred embodiment the substituents are C_1 to C_8 alkyl, more preferably, methyl such as found in 1,3 dimethyl adamantyl.

30

Suitably, the adamantyl, congressyl, norbornyl or 1-norborndienyl group may comprise, besides hydrogen atoms, up to 10 substituents as defined above, preferably up to 5 substituents as defined above, more preferably up to 3 substituents as defined above. Suitably, when the adamantyl, congressyl, norbornyl or 1-norborndienyl group comprises, besides hydrogen atoms, one or more substituents as defined herein, preferably each substituent is identical. Preferred substituents are unsubstituted C₁-C₈ alkyl and trifluoromethyl, particularly unsubstituted C₁-C₈ alkyl such as methyl. A highly preferred adamantyl, congressyl, norbornyl or 1-norborndienyl group comprises hydrogen atoms only i.e. the adamantyl congressyl, norbornyl or 1-norborndienyl group is not substituted.

Preferably, when more than one adamantyl, congressyl, norbornyl or 1-norborndienyl group is present in a compound of formulas I-IV, each such group is identical.

Preferably, the bidentate ligand is a bidentate phosphine, arsine or stibine ligand, preferably, a bidentate phosphine ligand. Particularly preferred is the bidentate phosphine ligand 1,2-bis(di-*t*-butylphosphino) *o*-xylene.

Definitions

The term "lower alkylene" which A and B represent in a compound of formulas I-IV, when used herein, includes C₀-C₁₀ or C₁ to C₁₀ groups which, in the latter case, can be bonded at two places on the group to thereby connect the group Q¹ or Q² to the R group, and, in the latter case, is otherwise defined in the same way as "alkyl" below.

Nevertheless, in the latter case, methylene is most preferred. In the former case, by C_0 is meant that the group Q^1 or Q^2 is connected directly to the R group and there is no C_1 - C_{10} lower alkylene group and in this case
5 only one of A and B is a C_1 - C_{10} lower alkylene. In any case, when one of the groups A or B is C_0 then the other group cannot be C_0 and must be a C_1 - C_{10} group as defined herein and, therefore, at least one of A and B is a C_1 - C_{10} "lower alkylene" group so that the term "optional" should
10 be understood accordingly.

The term "alkyl" when used herein, means C_1 to C_{10} alkyl and includes methyl, ethyl, ethenyl, propyl, propenyl butyl, butenyl, pentyl, pentenyl, hexyl, hexenyl and
15 heptyl groups. Unless otherwise specified, alkyl groups may, when there is a sufficient number of carbon atoms, be linear or branched (particularly preferred branched groups include t-butyl and isopropyl), be saturated or unsaturated, be cyclic, acyclic or part cyclic/acyclic, be
20 unsubstituted, substituted or terminated by one or more substituents selected from halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29} , $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, unsubstituted or substituted aryl, or unsubstituted or substituted Het and/or be interrupted by
25 one or more (preferably less than 4) oxygen, sulphur, silicon atoms, or by silano or dialkylsilcon groups, or mixtures thereof.

R^1 to R^{12} and R^{13} - R^{18} each independently represent alkyl, aryl, or Het unless X^1 or X^2 is joined to the Q^2 atom via a non tertiary carbon in which case they can each also
30 represent hydrogen.

R^{19} to R^{30} herein each independently represent hydrogen, halo, unsubstituted or substituted aryl or unsubstituted or substituted alkyl, or, in the case of R^{21} , additionally, halo, nitro, cyano, thio and amino.
5 Preferably, R^{19} to R^{30} represents hydrogen, unsubstituted C_1 - C_8 alkyl or phenyl, more preferably, hydrogen or unsubstituted C_1 - C_8 alkyl.

R^{49} and R^{54} each independently represent hydrogen, alkyl or
10 aryl. R^{50} to R^{53} each independently represent alkyl, aryl or Het. YY^1 and YY^2 each independently represent oxygen, sulfur or $N-R^{55}$, wherein R^{55} represents hydrogen, alkyl or aryl.

15 The term "Ar" or "aryl" when used herein, includes five-to-ten-membered, preferably five to eight membered, carbocyclic aromatic or pseudo aromatic groups, such as phenyl, cyclopentadienyl and indenyl anions and naphthyl, which groups may be unsubstituted or as one option
20 substituted with one or more substituents selected from unsubstituted or substituted aryl, alkyl (which group may itself be unsubstituted or substituted or terminated as defined herein), Het (which group may itself be unsubstituted or substituted or terminated as defined
25 herein), halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29} , $C(O)SR^{30}$ or $C(S)NR^{27}R^{28}$ wherein R^{19} to R^{30} are as defined herein.

The term "alkenyl" when used herein, means C_2 to C_{10}
30 alkenyl and includes ethenyl, propenyl, butenyl, pentenyl, and hexenyl groups. Unless otherwise specified, alkenyl groups may, when there is a sufficient number of carbon atoms, be linear or branched, be saturated or unsaturated,

be cyclic, acyclic or part cyclic/acyclic, be unsubstituted, substituted or terminated by one or more substituents selected from halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29} ,
5 $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, unsubstituted or substituted aryl, or unsubstituted or substituted Het, wherein R^{19} to R^{30} are defined herein and/or be interrupted by one or more (preferably less than 4) oxygen, sulphur, silicon atoms, or by silano or dialkylsilcon groups, or mixtures
10 thereof.

The term "alkynyl" when used herein, means C_2 to C_{10} alkynyl and includes ethynyl, propynyl, butynyl, pentynyl, and hexynyl groups. Unless otherwise specified,
15 alkynyl groups may, when there is a sufficient number of carbon atoms, be linear or branched, be saturated or unsaturated, be cyclic, acyclic or part cyclic/acyclic, be unsubstituted, substituted or terminated by one or more substituents selected from halo, cyano, nitro, OR^{19} ,
20 $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29} , $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, unsubstituted or substituted aryl, or unsubstituted or substituted Het, wherein R^{19} to R^{30} are defined herein and/or be interrupted by one or more (preferably less than 4) oxygen, sulphur, silicon atoms,
25 or by silano or dialkylsilcon groups, or mixtures thereof.

The terms "alkyl", "aralkyl", "alkaryl", "arylenealkyl" or the like should, in the absence of information to the
30 contrary, be taken to be in accordance with the above definition of "alkyl" as far as the alkyl or alk portion of the group is concerned.

The above Ar or aryl groups may be attached by one or more covalent bonds but references to "arylene" or "arylenealkyl" or the like herein should be understood as two covalent bond attachment but otherwise be defined as Ar or aryl above as far as the arylene portion of the group is concerned. References to "alkaryl", "aralkyl" or the like should be taken as references to Ar or aryl above as far as the Ar or aryl portion of the group is concerned.

10

Halo groups with which the above-mentioned groups may be substituted or terminated include fluoro, chloro, bromo and iodo.

15 The term "Het", when used herein, includes four- to twelve-membered, preferably four- to ten-membered ring systems, which rings contain one or more heteroatoms selected from nitrogen, oxygen, sulfur and mixtures thereof, and which rings contain no, one or more double
20 bonds or may be non-aromatic, partly aromatic or wholly aromatic in character. The ring systems may be monocyclic, bicyclic or fused. Each "Het" group identified herein may be unsubstituted or substituted by one or more substituents selected from halo, cyano, nitro, oxo, alkyl
25 (which alkyl group may itself be unsubstituted or substituted or terminated as defined herein) $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$ or $-C(S)N(R^{27})R^{28}$ wherein R^{19} to R^{30} are as defined herein. The term "Het" thus includes groups such
30 as optionally substituted azetidiny, pyrrolidiny, imidazolyl, indolyl, furanyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, thiadiazolyl, triazolyl, oxatriazolyl, thiatriazolyl, pyridazinyl, morpholinyl,

pyrimidinyl, pyrazinyl, quinolinyl, isoquinolinyl, piperidinyl, pyrazolyl and piperazinyl. Substitution at Het may be at a carbon atom of the Het ring or, where appropriate, at one or more of the heteroatoms.

5

"Het" groups may also be in the form of an N oxide.

The term hetero as mentioned herein means nitrogen, oxygen, sulfur or mixtures thereof.

10

The catalyst compounds of the present invention may act as a "heterogeneous" catalyst or a "homogeneous" catalyst, preferably, a homogenous catalyst.

15 By the term "homogeneous" catalyst we mean a catalyst, i.e. a compound of the invention, which is not supported but is simply admixed or formed in-situ with the reactants of the carbonylation reaction, preferably in a suitable solvent as described herein.

20

By the term "heterogeneous" catalyst we mean a catalyst, i.e. the compound of the invention, which is carried on a support.

25 Where a compound of a formula herein (e.g. formulas I - V) contains an alkenyl group or a cycloalkyl moiety as defined, cis (E) and trans (Z) isomerism may also occur. The present invention includes the individual stereoisomers of the compounds of any of the formulas
30 defined herein and, where appropriate, the individual tautomeric forms thereof, together with mixtures thereof. Separation of diastereoisomers or cis and trans isomers may be achieved by conventional techniques, e.g. by

fractional crystallisation, chromatography or H.P.L.C. of a stereoisomeric mixture of a compound one of the formulas or a suitable salt or derivative thereof. An individual enantiomer of a compound of one of the formulas may also
5 be prepared from a corresponding optically pure intermediate or by resolution, such as by H.P.L.C. of the corresponding racemate using a suitable chiral support or by fractional crystallisation of the diastereoisomeric salts formed by reaction of the corresponding racemate
10 with a suitable optically active acid or base, as appropriate.

Support and Dispersant

According to a further aspect, the present invention
15 provides a process for the carbonylation of an ethylenically unsaturated compound as defined herein wherein the process is carried out with the catalyst comprising a support, preferably an insoluble support.

20 Preferably, the support comprises a polymer such as a polyolefin, polystyrene or polystyrene copolymer such as a divinylbenzene copolymer or other suitable polymers or copolymers known to those skilled in the art; a silicon derivative such as a functionalised silica, a silicone or
25 a silicone rubber; or other porous particulate material such as for example inorganic oxides and inorganic chlorides.

Preferably the support material is porous silica which has
30 a surface area in the range of from 10 to 700 m²/g, a total pore volume in the range of from 0.1 to 4.0 cc/g and an average particle size in the range of from 10 to 500µm. More preferably, the surface area is in the range of from

50 to 500 m²/g, the pore volume is in the range of from 0.5 to 2.5 cc/g and the average particle size is in the range of from 20 to 200 μm. Most desirably the surface area is in the range of from 100 to 400 m²/g, the pore volume is in the range of from 0.8 to 3.0 cc/g and the average particle size is in the range of from 30 to 100 μm. The average pore size of typical porous support materials is in the range of from 10 to 1000 Å. Preferably, a support material is used that has an average pore diameter of from 50 to 500 Å, and most desirably from 75 to 350 Å. It may be particularly desirable to dehydrate the silica at a temperature of from 100°C to 800°C anywhere from 3 to 24 hours.

Suitably, the support may be flexible or a rigid support, the insoluble support is coated and/or impregnated with the compounds of the process of the invention by techniques well known to those skilled in the art.

Alternatively, the compounds of the process of the invention are fixed to the surface of an insoluble support, optionally via a covalent bond, and the arrangement optionally includes a bifunctional spacer molecule to space the compound from the insoluble support.

25

The compounds of the invention may be fixed to the surface of the insoluble support by promoting reaction of a functional group present in the compound of formula I, II, III or IV with a complimentary reactive group present on or previously inserted into the support. The combination of the reactive group of the support with a complimentary substituent of the compound of the invention provides a heterogeneous catalyst where the compound of the invention

30

and the support are linked via a linkage such as an ether, ester, amide, amine, urea, keto group.

The choice of reaction conditions to link a compound of
5 the process of the present invention to the support depends upon the groups of the support. For example, reagents such as carbodiimides, 1,1'-carbonyldiimidazole, and processes such as the use of mixed anhydrides, reductive amination may be employed.

10

According to a further aspect, the present invention provides the use of the process or catalyst of any aspect of the invention wherein the catalyst is attached to a support.

15

Additionally, the bidentate ligand may be bonded to a suitable polymeric substrate via at least one of the bridge substituents (including the cyclic atoms), the bridging group X, the linking group A or the linking group
20 B e.g. cis-1, 2-bis (di-t-butylphosphinomethyl) benzene may be bonded, preferably, via the 3, 4, 5 or 6 cyclic carbons of the benzene group to polystyrene to give an immobile heterogeneous catalyst.

25 The use of stabilising compounds with the catalyst system may also be beneficial in improving recovery of metal which has been lost from the catalyst system. When the catalyst system is utilized in a liquid reaction medium such stabilizing compounds may assist recovery of the
30 group 8, 9 or 10 metal.

Preferably, therefore, the catalyst system includes in a liquid reaction medium a polymeric dispersant dissolved in

a liquid carrier, said polymeric dispersant being capable of stabilising a colloidal suspension of particles of the group 8, 9 or 10 metal or metal compound of the catalyst system within the liquid carrier.

5

The liquid reaction medium may be a solvent for the reaction or may comprise one or more of the reactants or reaction products themselves. The reactants and reaction products in liquid form may be miscible with or dissolved in a solvent or liquid diluent.

10

The polymeric dispersant is soluble in the liquid reaction medium, but should not significantly increase the viscosity of the reaction medium in a way which would be detrimental to reaction kinetics or heat transfer. The solubility of the dispersant in the liquid medium under the reaction conditions of temperature and pressure should not be so great as to deter significantly the adsorption of the dispersant molecules onto the metal particles.

15

20

The polymeric dispersant is capable of stabilising a colloidal suspension of particles of said group 8, 9 or 10 metal or metal compound within the liquid reaction medium such that the metal particles formed as a result of catalyst degradation are held in suspension in the liquid reaction medium and are discharged from the reactor along with the liquid for reclamation and optionally for re-use in making further quantities of catalyst. The metal particles are normally of colloidal dimensions, e.g. in the range 5 - 100 nm average particle size although larger particles may form in some cases. Portions of the polymeric dispersant are adsorbed onto the surface of the metal particles whilst the remainder of the dispersant

25

30

molecules remain at least partially solvated by the liquid reaction medium and in this way the dispersed group 8, 9 or 10 metal particles are stabilised against settling on the walls of the reactor or in reactor dead spaces and against forming agglomerates of metal particles which may grow by collision of particles and eventually coagulate. Some agglomeration of particles may occur even in the presence of a suitable dispersant but when the dispersant type and concentration is optimised then such agglomeration should be at a relatively low level and the agglomerates may form only loosely so that they may be broken up and the particles redispersed by agitation.

The polymeric dispersant may include homopolymers or copolymers including polymers such as graft copolymers and star polymers.

Preferably, the polymeric dispersant has sufficiently acidic or basic functionality to substantially stabilise the colloidal suspension of said group 8, 9 or 10 metal or metal compound.

By substantially stabilise is meant that the precipitation of the group 8, 9 or 10 metal from the solution phase is substantially avoided.

Particularly preferred dispersants for this purpose include acidic or basic polymers including carboxylic acids, sulphonic acids, amines and amides such as polyacrylates or heterocycle, particularly nitrogen heterocycle, substituted polyvinyl polymers such as polyvinyl pyrrolidone or copolymers of the aforesaid.

Examples of such polymeric dispersants may be selected from polyvinylpyrrolidone, polyacrylamide, polyacrylonitrile, polyethylenimine, polyglycine, polyacrylic acid, polymethacrylic acid, poly(3-hydroxybutyric acid), poly-L-leucine, poly-L-methionine, poly-L-proline, poly-L-serine, poly-L-tyrosine, poly(vinylbenzenesulphonic acid) and poly(vinylsulphonic acid), acylated polyethylenimine. Suitable acylated polyethylenimines are described in BASF patent publication EP1330309 A1 and US 6,723,882.

Preferably, the polymeric dispersant incorporates acidic or basic moieties either pendant or within the polymer backbone. Preferably, the acidic moieties have a dissociation constant (pK_a) of less than 6.0, more preferably, less than 5.0, most preferably less than 4.5. Preferably, the basic moieties have a base dissociation constant (pK_b) being of less than 6.0, more preferably less than 5.0 and most preferably less than 4.5, pK_a and pK_b being measured in dilute aqueous solution at 25°C.

Suitable polymeric dispersants, in addition to being soluble in the reaction medium at reaction conditions, contain at least one acidic or basic moiety, either within the polymer backbone or as a pendant group. We have found that polymers incorporating acid and amide moieties such as polyvinylpyrrolidone (PVP) and polyacrylates such as polyacrylic acid (PAA) are particularly suitable. The molecular weight of the polymer which is suitable for use in the invention depends upon the nature of the reaction medium and the solubility of the polymer therein. We have found that normally the average molecular weight is less than 100,000. Preferably, the average molecular weight is

in the range 1,000 - 200,000, more preferably, 5,000 - 100,000, most preferably, 10,000 - 40,000 e.g. Mw is preferably in the range 10,000 - 80,000, more preferably 20,000 - 60,000 when PVP is used and of the order of 1,000 - 10,000 in the case of PAA.

The effective concentration of the dispersant within the reaction medium should be determined for each reaction/catalyst system which is to be used.

10

The dispersed group 8, 9 or 10 metal may be recovered from the liquid stream removed from the reactor e.g. by filtration and then either disposed of or processed for re-use as a catalyst or other applications. In a continuous process the liquid stream may be circulated through an external heat-exchanger and in such cases it may be convenient to locate filters for the palladium particles in these circulation apparatus.

Preferably, the polymer:metal mass ratio in g/g is between 1:1 and 1000:1, more preferably, between 1:1 and 400:1, most preferably, between 1:1 and 200:1. Preferably, the polymer:metal mass ratio in g/g is up to 1000, more preferably, up to 400, most preferably, up to 200.

25

Preferably, the carbonylation reaction is an anaerobic reaction. In other words, typically the reaction takes place generally in the absence of oxygen.

Conveniently, the process of the invention may utilise highly stable compounds under typical carbonylation reaction conditions such that they require little or no replenishment. Conveniently, the process of the invention

may have a high rate for the carbonylation reaction. Conveniently, the process of the invention may promote high conversion rates, thereby yielding the desired product in high yield with little or no impurities.

5 Consequently, the commercial viability of the carbonylation reaction may be increased by employing the process of the invention. It is especially advantageous that the process of the invention provides a carbonylation reaction with a high TON number.

10

It will be appreciated that any of the features set forth in the first aspect of the invention may be regarded as preferred features of the second, third or other aspect of the present invention and vice versa.

15

The invention will now be described and illustrated by way of the following non-limiting examples and comparative examples wherein:-

20 Figure 1 is a schematic view of the process of the present invention;

Figure 2 is a graph of Pd TON versus days online for a single water addition step;

Figure 3 is a graph for Pd TON versus days online for
25 multiple water addition steps.

Experimental

The continuous process for the catalysed preparation of
30 methyl propanoate from ethylene, carbon monoxide and methanol utilises the reaction of purified streams of carbon monoxide, ethylene and methanol in the liquid phase, in the presence of a catalyst system, to generate

the desired product, methyl propanoate. Figure 1 is a schematic drawing of the equipment used with relevant feed rates when water is being fed on a continuous basis to maintain a level of 3% w/w in the reactor vessel.
5 However, the flow diagram is equally applicable to comparative experiments when water is absent.

The reactions were generally carried out at 100°C and at 12 barg pressure in the reactor vessel (18). The reactor
10 vessel (18) is a 1L reaction autoclave.

The catalyst system was made up of three components, being a palladium salt, a phosphine ligand and an acid. The three catalyst components, when combined together and
15 dissolved in the reaction mixture, constitute the reaction catalyst or catalyst system, a homogeneous catalyst, which, in the case of ethylene, converted dissolved carbon monoxide and ethylene to the product methyl propanoate in the liquid phase.

20

Catalyst Production Procedure

Into a 5 litre round bottom flask under an inert
25 atmosphere is placed 3960ml of methyl propanoate and 40ml of methanol. This material is sparged with nitrogen for 3 hours to ensure that it is thoroughly deoxygenated. To this solution is added 172.5mg of palladium dba (a mixture of tris(dibenzylideneacetone)dipalladium($\text{Pd}_2(\text{dba})_3$) and
30 tris(dibenzylideneacetone)palladium($\text{Pd}(\text{dba})_3$) (Aldrich)-Pd assay 20.04% Pd and 160mg 1,2-bis(di-tert-butylphosphinomethyl)benzene. This equates to 3.25×10^{-4} moles of palladium and 4.06×10^{-4} moles of phosphine

ligand, a ratio of palladium:phosphine of 1:1.25. The palladium salt and phosphine ligand are allowed to complex for 12 hours before the addition of 420ul of methanesulphonic acid. This results in a ratio of
5 palladium:methanesulphonic acid of 1:20. This completes the preparation of the catalyst which is now ready for use. The palladium concentration of the catalyst solution is 9.44 ppm Pd. The MW of palladium used for calculation of palladium feed rate is 106.4 daltons.

10

During continuous operation, the catalyst decomposed at a slow but steady rate, and needs to be replaced by adding fresh catalyst. Otherwise, the rate of generation of the product, methyl propanoate reduced.

15

The reactor vessel was fitted with an agitator. Gas entering into the reactor vessel via an entry pipe at the base (such that the gas passed up through the reaction mixture continuously) was dispersed by the agitator into
20 fine bubbles. In this way the ethylene and carbon monoxide were dissolved in the reaction mix.

25

Ethylene and carbon monoxide gases were not recycled in this series of experiments, but recycling of these gases can also be carried out when the industrial process requires it.

30

The ethylene and carbon monoxide not consumed in the reaction passed into the reactor headspace and were eventually allowed to pass out to an exit vent. Infra-red analysis of the vent gas and outgoing flow rate were measured by a Rosemount NGA 2000 IR analyser. Fresh methanol was added continuously to the reactor vessel, in

order to replace the methanol that had been used up in the reaction allowing the reactor composition to be maintained.

5 The reactor vessel (18) held the bulk liquid reaction mixture along with the three components of the homogeneous catalyst (a palladium salt, a phosphine ligand, and a sulphonic acid).

10 In order to recover the product methyl propanoate, a stream of reaction mixture was passed continuously out of the reactor (18) and into a flash distillation column (20).

15 The distillation column (20), being a single stage "flash" type distillation column, provided a means of separating a fraction of the methyl propanoate and methanol components of the reaction mixture from the non-volatile dissolved catalyst components. This was achieved by vaporising a
20 fraction of the reaction mixture as it passed through the flash column (20). The part of the reaction mixture which remained as liquid after passing through the flash column (20), and which still contained useful catalyst components, was returned to the reactor vessel (18) so
25 that the catalyst components could take part in the on-going reaction. This recirculating flow of catalyst can be used to regulate the catalyst flow into the reactor. The flash column liquid phase catalyst concentration is higher than that of the liquid phase in the reactor.

30

The vapour from the top of the flash distillation column is collected in the product vessel (22), analysed by GC and weighed as a separate measure of productivity. If the

methyl propanoate product is required free of methanol, a second distillation column is needed (not shown). In this case, the vapour stream from the flash column (20), which would be a mixture of methyl propanoate and methanol would be passed into a second distillation column, where the pure methyl propanoate would be generated as the heavier product, and taken off from the base of the column. A low boiling mixture of methanol and methyl propanoate will be generated as the light product, and be removed continuously from the top of the MeP purification column. In order to utilise the methanol as efficiently as possible in the process, the low boiling mixture of methanol and methyl propanoate could then be returned continuously to the reactor vessel.

15

All liquid feed rates of methanol, water, catalyst, liquid leaving the reactor and any recirculating flow of liquid from the distillation column were set by Gilson pumps.

20 After start up of the continuous reactor unit, when the desired rate of generation of methyl propanoate had been achieved, a process of gradual reduction of the feed rate of the reaction catalyst was undertaken.

25 In order to sustain the rate of generation of methyl propanoate it was necessary to continuously replace the reaction catalyst which was lost to decomposition with fresh reaction catalyst at a rate which balanced the rate of loss.

30

This led to the situation where the standing concentrations of catalyst components became constant for a given rate of generation of methyl propanoate, and were

just able to sustain flow sheet reaction rate, as indicated by constant concentrations of carbon monoxide and ethylene in the gas filled headspace area of the reactor vessel. At this point balance point, the rate of
5 palladium decomposition was balanced exactly by the rate of addition of fresh palladium.

From the rate of addition of fresh reaction catalyst under balance point conditions, the palladium rate of addition
10 and thus palladium turnover number (TON) was calculated. This is defined as the number of moles of methyl propanoate generated per hour, for each mole of palladium consumed by the decomposition process per hour.

15 Upon reaching a steady state at a predetermined set of control conditions, the instantaneous values of all of the variables were recorded, and used as representative data to show the performance of the process under the conditions in use at the time.

20

To gather data on the effect of water on palladium turnover number, all variables were held constant except the levels of water in the reaction mixture. These levels were changed to show the effect on catalyst TON. The
25 additions were then followed by careful adjustment to make sure the rate of production of methyl propanoate remained constant. The level of water in the reactor is set by initially adding a fixed quantity and maintained by feeding a constant amount. The constant feed was required
30 as water was constantly lost in the flash distillation column.

In this way, results were drawn up which showed clearly

the changes to catalyst stability that were caused by the variations in the water level.

Table 1 shows the effect of 3% w/w water in the MeP
5 reactor on palladium turnover number (TON). The unit was initially run for several weeks without water addition and balance points recorded. Water addition was then initiated and a balance point recorded some time after initiation of water addition. The Pd TON recorded at this
10 time after initiation of water addition was 6.7 million versus 2.33 million without water addition. The water addition was then terminated and the water level in the reactor then dropped to <300ppm water within 2 days. Balance points were recorded over the next few weeks. The
15 catalyst feed rate was steadily increased as the Pd TON was slowly dropping back to close to its pre-water addition level. Table 1 illustrates the steady decline in Pd TON after the continuous feed of water is stopped. This is also illustrated in Figure 2.

20

Palladium (TON)

The palladium turnover number is calculated based on CO
25 usage as follows :

1. CO usage in Normal Litres(NL)/hr = CO fed to reactor
- CO exiting reactor. The CO exiting the reactor has two components.

30 i) CO in reactor exit gas. CO exiting as gas =
Headspace CO% x Total exit flow/100
Total exit flow for a given headspace CO is determined using a flow meter. The headspace

%CO is determined by Infra-Red analysis using a Rosemount NGA 2000 IR analyser.

5 ii) CO dissolved in the liquid phase. First the total gas dissolved in the liquid phase is calculated as the difference between the inlet flows and the total exit gas flow. The % of this which is CO is calculated using the headspace CO %. This assumes gas and liquid are well mixed in the reactor and therefore
10 the liquid phase gas concentration resembles the gas phase exit composition.

2. The reaction is assumed to be 100% selective to MeP for simplicity (actual value is >99.6% determined by
15 GC). Therefore CO usage in moles/hr converts directly to MeP produced in moles/hr

3. TON in moles MeP/mole Pd is calculated by dividing the MeP produced in moles/hr by the palladium fed in gmoles/hr. The palladium fed is calculated knowing
20 the concentration of palladium in the catalyst feed and the rate of addition to the reactor.

4. An example calculation using the data from from Table 1, column 1 is as follows

25 i) CO fed = 62.7NL/hr, Ethene fed = 217.8 NL/hr

 ii) Total gas exit flow at 5.0% headspace CO =
 152.4 NL/hr

30

 iii) CO in exit flow = 5.0% of 152.4 = 7.62 NL/hr

- iv) Gas lost as dissolved gas = total added gas -
(total reacted gas + gas exit flow)
= 280.5 - (110.16 + 152.4)
= 17.64 NL/hr
- 5
- v) CO dissolved in liquid exit = 5% of 17.64 =
0.88 NL/hr
- vi) Total CO usage = 62.77 - (7.62 + 0.88) =
10 54.27 NL/hr
- vii) CO usage in moles/hr = 54.27/24 = 2.26
moles/hr
- 15 viii) MeP produced = 2.26 moles/hr
- ix) Pd concentration in catalyst feed = 8.1224 x
10⁻⁵ gmoles/litre
- 20 x) Catalyst feed rate = 0.207 ml/min
- xi) Pd feedrate = 1.0088 x 10⁻⁶ gmoles/hr
- xii) TON = (viii)/(xi) = 2.24 million
25 molesMeP/mole Pd

All other TON's are calculated in a similar manner.

Table 2 shows the rapid establishment of high Pd TON on
30 initiation of water feed. Stopping the water feed results
in a drop in Pd TON over a 14 day period back to a
baseline figure of around 2.0 million. Starting water
addition again results in re-establishment of high Pd TON

which is retained even when the rate of water feed is dropped resulting in water levels in the reactor of 0.6% w/w. This is also illustrated in figure 3.

5 Attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and
10 documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or
15 process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Table 1						
Days	1-4	4-32	32-49	49-59	59-64	64-68
Recordal Day	4	29	49	59	64	68
Days online	3	31	48	58	63	67
Feeds						
CO feed rate NL/min	1.045	1.045	1.045	1.045	1.045	1.045
Ethylene feed rate NL/min	3.63	3.63	3.63	3.63	3.63	3.63
MeOH feed rate ml/min	4.50	4.50	4.50	4.35	4.25	4.28
Catalyst feed rate ml/min	0.207	0.207	0.072	0.108	0.135	0.18
Flash recirc rate ml/min	1.87	1.87	1.83	1.78	1.79	1.81
Water feed rate ml/min	0	0	0.15	0	0	0
Reactor						
Level ml	610	610	610	610	610	610
Composition w't% MeP:MeOH	30.75/69.3	30.25/69.75	31.5/68.5	31.1/68.9	30.8/69.2	30.9/69.1
Temperature °C	100	100	100	100	100	100
Reactor exit gas composition %CO	5.0	4.05	4.07	4.47	5.12	4.99
Reactor Exit Flow NL/min (by flow meter)	2.54	2.48	2.48	2.50	2.54	2.53
Water % in Reactor	<300ppm	<300ppm	3.2%	<300ppm	<300ppm	<300ppm
Flash						
Level ml	100	100	100	100	100	100
Gas Lost in liquid flow exiting reactor NL/min	0.294	0.301	0.302	0.304	0.300	0.294
TON						
TON on Pd mol/mol	2.25m	2.35m	6.67m	4.39m	3.43m	2.59m

Table 2						
Days	1-19	19-32	32-55	55-61	61-65	65-68
Days online	18	31	54	60	64	67
Recordal Day	19	30	54	61	65	68
Feeds						
CO feed rate NL/min	1.045	1.045	1.045	1.045	1.045	1.045
Ethylene feed rate NL/min	3.63	3.63	3.63	3.63	3.63	3.63
MeOH feed rate ml/min	4.4	4.5	4.4	4.4	4.5	4.5
Catalyst feed rate ml/min	0.072	0.225	0.072	0.072	0.072	0.072
Flash recirc rate ml/min	1.5	1.5	1.5	1.5	1.5	1.5
Water feed rate ml/min	0.15	0	0.15	0.03	0.03	0.03
Reactor						
Level ml	610	610	610	610	610	610
Composition w't%	28.61/ 71.39	30.25/ 69.75	30.06/ 69.94	28.51/ 71.49	30.01/ 69.99	29.28/ 70.72
Temperature °C	100	100	100	100	100	100
Reactor exit gas composition %CO	3.1	4.05	2.72	3.10	3.31	3.2
Reactor Exit Flow NL/min	2.42	2.48	2.40	2.42	2.43	2.42
Water % in Reactor	3.0	<300ppm	3.2	0.6	0.8	0.6
Flash						
Level ml	100	100	100	100	100	100
Gas Lost in liquid flow exiting reactor NL/min	18.60	18.05	18.63	18.60	18.65	18.89
TON						
TON on Pd mol/mol	6.88m	2.14m	6.96m	6.88m	6.83m	6.86m

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each

feature disclosed is one example only of a generic series of equivalent or similar features.

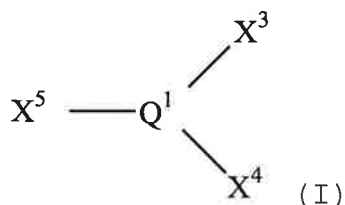
The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A method of increasing the TON of a catalyst system for the monocarbonylation of an ethylenically unsaturated compound using carbon monoxide in the presence of a co-reactant, other than water or a source thereof, having a mobile hydrogen atom, the catalyst system obtainable by combining:

(a) a metal of Group 8, 9 or 10 or a suitable compound thereof;

(b) a ligand of general formula (I)



wherein

the groups X^3 and X^4 independently represent univalent radicals of up to 30 atoms or X^3 and X^4 together form a bivalent radical of up to 40 atoms and X^5 has up to 400 atoms;

Q^1 represents phosphorus, arsenic or antimony; and

c) optionally, a source of anions;

wherein the method includes the step of adding water or a source thereof to the catalyst system and characterised in that the method is carried out in the presence of an electropositive metal.

wherein the electropositive metal is selected from the list consisting of titanium, niobium, tantalum, zirconium or alloys thereof, hastelloy, Monel, Inconel and stainless steel.

2. A method according to claim 1, wherein the catalyst system is in the liquid phase.

3. A method according to claim 2, wherein one or more of the reaction vessel and/or conduits to and from the reaction vessel that come into contact with the catalyst system in the liquid phase are formed of the said electropositive metal.

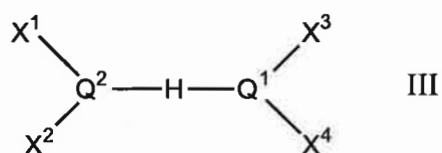
4. A method according to claims 2 or 3, wherein the amount of water added to the catalyst system is greater than 0.03% w/w liquid phase.

5. A method according to claims 2 or 3, wherein the amount of water added to the catalyst system is 0.01-5% w/w liquid phase.

6. A method according to any preceding claim, wherein the monocarbonylation is a continuous process.

7. A method according to any preceding claim, wherein the ethylenically unsaturated compound is selected from acetylene, methyl acetylene, propyl acetylene, 1,3-butadiene, ethylene, propylene, butylene, isobutylene, pentenes, pentene nitriles, alkyl pentenoates such as methyl 3-pentenoates, pentene acids (such as 2-and 3-pentenoic acid), heptenes, vinyl esters such as vinyl acetate, octenes, dodecenenes.

8. A method according to any preceding claim, wherein the ligand has a formula III



5 wherein H is a bivalent organic bridging group with 1-6 atoms
in the bridge;

the groups X^1 , X^2 , X^3 and X^4 independently represent univalent
radicals of up to 30 atoms, optionally having at least one
10 tertiary carbon atom via which the group is joined to the Q^1 or
 Q^2 atom, or X^1 and X^2 and/or X^3 and X^4 together form a bivalent
radical of up to 40 atoms, optionally having at least two
tertiary carbon atoms via which the radical is joined to the Q^1
and/or Q^2 atom; and

15 Q^1 and Q^2 each independently represent phosphorus, arsenic or
antimony.

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