A process for the carbonylation of an ethylenically unsaturated compound and a catalyst system.

This invention relates to the carbonylation of ethylenically unsaturated compounds. Specifically, the invention relates to the carbonylation of ethylenically unsaturated compounds in the presence of an enhancer compound.

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 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-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 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 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 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 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 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 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 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.

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.

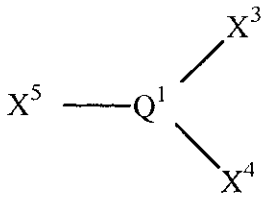
WO 97/38964 discloses the use of halide rate promoters for the carbonylation of ethylenically unsaturated compounds using phobane ligands. Phenol promoters are also mentioned for such phobane ligand carbonylation reactions.

Surprisingly, it has now been discovered that remarkably enhanced stability (TON) and/or reaction rate can be achieved in carbonylation reactions by using a special group of phenolic enhancer compounds.

According to a first aspect of the present invention there is provided a process for the carbonylation of an ethylenically unsaturated compound comprising the step of reacting said compound with carbon monoxide in the presence of a co-reactant having a mobile hydrogen atom and a catalyst system, the catalyst system obtainable by combining:

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

(b) a ligand of general formula (I)



(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;

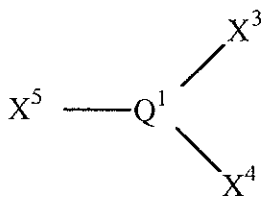
Q^1 represents phosphorus, arsenic or antimony; and

optionally, a source of anions.

characterised in that the catalyst system includes an enhancer compound comprising an aromatic ring or ring system substituted by at least one hydroxyl group wherein the hydroxyl group pKa at 25°C is greater than 3.0 and less than 9.1, the said enhancer compound excluding 3-quinolinol.

According to a second aspect of the present invention there is provided a catalyst system for carbonylation of an ethylenically unsaturated compound, the catalyst system obtainable by combining:

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



(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

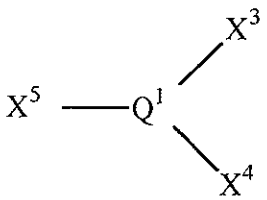
optionally, a source of anions;

characterised in that the catalyst system includes an enhancer compound comprising an aromatic ring or ring system substituted by at least one hydroxyl group wherein the hydroxyl group pKa at 25°C is greater than 3.0 and less than 9.1, the said enhancer compound excluding 3-quinolinol.

Preferably the enhancer compound also excludes compounds having a nitrogen containing ring or ring system.

According to a third aspect of the present invention there is provided a method of increasing the efficacy of a catalyst system for the carbonylation of ethylenically unsaturated compounds using carbon monoxide in the presence of a co-reactant, the catalyst system obtainable by combining

(a) a metal of Group 8, 9 or 10 or a 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

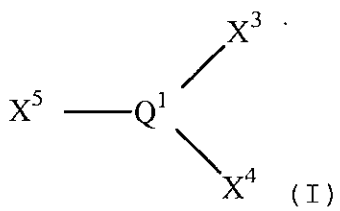
optionally, a source of anions;

characterised in that the method includes the step of adding an enhancer compound comprising an aromatic ring or ring system substituted by at least one hydroxyl group wherein the hydroxyl group pKa at 25°C is greater than 3.0 and less than 9.1.

By efficacy is meant a measurable increase in turnover number for the catalyst system.

According to a fourth aspect of the present invention there is provided a method of increasing the rate of carbonylation of an ethylenically unsaturated compound in a reaction with carbon monoxide in the presence of a co-reactant using a catalyst system obtainable by combining

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



(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

optionally, a source of anions; the said method comprising the step of adding a rate enhancer compound comprising an aromatic ring or ring system substituted by at least one hydroxyl group wherein the hydroxyl group pKa at 25°C is greater than 3.0 and less than 9.1.

In further aspects, the invention extends to the use of the enhancer compound of the third or fourth aspects as an efficacy or rate enhancer.

Preferably, the enhancer compound of the third and/or fourth aspect excludes 3-quinolinol, more preferably, the enhancer compound of the third or fourth aspect excludes compounds having a nitrogen containing ring or ring system.

Advantageously, the enhancer compound of the present invention surprisingly enhances rate for the carbonylation reaction and/or the turnover number for the catalytic metal.

The catalyst system may incorporate one or more solvents as will be described hereinafter. The enhancer compound may, in such cases, be added to the solvent(s) and this may be before or after addition of metal or metal compound

or ligand. Preferably, however, the metal/metal compound and ligand are added to the solvent(s) and preferably, dissolved therein before addition of the enhancer compound.

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 than 3, most preferably, less than 2.

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

The enhancer compound pKa is preferably greater than 4.0, more preferably, greater than 5, most preferably, greater than 6, especially greater than 7 and less than 9.1 so that the effect of the mildly acidic hydroxyl group proton is not expected to have any catalytic effect in the presence of strong acids such as those providing the source of anions.

Accordingly, the catalytic enhancement in the presence of strong acids having a pKa of less than 4 is particularly surprising.

Preferably, the amount of enhancer in the reaction composition is 0.1-15% w/w, more preferably 1-9% w/w, most preferably 2-8% w/w. By reaction composition is meant the catalyst composition including any solvents or other additives and all reactants. The relatively low level of enhancer compound reduces the overall cost of the process

by reducing both cost of enhancer and cost of purification thereafter.

For the purposes of the invention herein, the pKa may be determined by suitable techniques known to those skilled in the art.

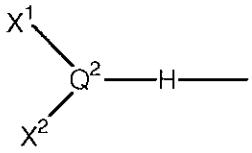
Preferably, the mole ratio of ligand to group 8, 9 or 10 metal for a bidentate ligand is between 1:1 and 100:1, more preferably, 2:1 to 50:1, most preferably, 2:1 to 20:1. For a monodentate, tridentate, etc ligand the mole ratio is varied accordingly.

Preferably, the mole ratio of ligand to acid for a bidentate ligand and a monoprotic acid is between 1:1 and 1:1000, more preferably 1:2 to 1:500, most preferably, 1:3 to 1:100. For a monodentate, tridentate, etc ligand and/or diprotic, or triprotic etc acid, the mole ratio is varied accordingly.

Preferably, the mole ratio of group 8, 9 or 10 metal to acid for a monoprotic acid is from 1:2 to 1:10,000, more preferably, 1:10 to 1:5000, most preferably, 1:50 to 1:1000. For a diprotic, triprotic, etc acid, the mole ratio is varied accordingly.

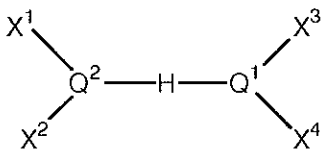
For the avoidance of doubt, the above ratio conditions apply at the start of a batch reaction or during a continuous reaction.

Preferably, the phosphine, arsine or stibine ligand is a bidentate ligand. In such ligands, X^5 may represent



II

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



III

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 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

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

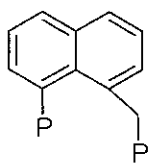
Preferably, the group H has 3-5 atoms in the bridge.

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

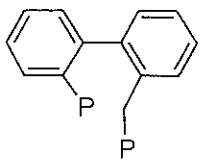
1-6, more preferably, 2-5, most preferably 3 or 4 atoms in the bridge.

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

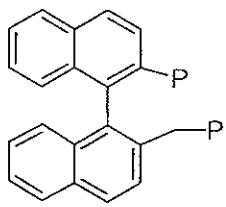
Suitable aliphatic bridging groups include alkylene groups such as 1,2-ethylene, 1-3 propylene, 1,2-propylene, 1,4-butylene, 2,2-dimethyl-1,3-propylene, 2-methyl-1,3-propylene, 1,5-pentylene, $-O-CH_2CH_2-O-$ and $-CH_2-NR-CH_2-$ or partial cycloaliphatic bridges including 1-methylene-cyclohex-2-yl, 1,2-dimethylene-cyclohexane and 1,2-dimethylene-cyclopentane. Suitable aromatic or 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.



1, 8, Napthyl



2, 2', Biphenyl



2, 2' Binapthyl

Suitable enhancer compounds for use with the present invention are compounds having an aromatic ring or ring system which is further substituted with, in addition to the hydroxyl group, an electron withdrawing group. Suitable electron withdrawing groups include cyano,

halide, nitrile, nitro, carbonyl, -COOH, -C(O)H , -C(O)R, -COOR, -C(O)Cl, $-CF_3$, $-SO_3H$, $-NH^+_3$, $-NR^+_3$.

Preferably, substitution is on the same ring as that to which the at least one -OH group is attached, preferably, at the ortho or para positions of the ring with respect to at least one -OH group.

Accordingly, suitable enhancer compounds may be selected from p-cyano-phenol, o-cyano-phenol, p-nitro-phenol, o-nitro-phenol, m-nitro-phenol, p-chloro-phenol, o-chloro-phenol, p-bromo-phenol, o-bromo-phenol, p-hydroxy-benzylic acid, o-hydroxy-benzylic acid, o-hydroxy-benzaldehyde, p-hydroxy-benzaldehyde, p-hydroxy-benzenesulphonic acid , and N-phenol quarternary ammonium derivatives.

The pKa of the enhancer compound is determined in dilute aqueous solution at 25°C unless indicated otherwise.

The ratio (v/v) of ethylenically unsaturated compound 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 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. A possible co-reactant is water so that hydroxcarbonylation takes place. Other co-reactants are also possible such as a carboxylic acid, alcohol, ammonia or an amine, a thiol, or a combination thereof.

If the co-reactant is water, the product obtained will be a carboxylic acid. In the case of carboxylic acids the product is an anhydride. For an alcohol co reactant, the product of the carbonylation is an ester. Similarly, the use of ammonia (NH3) or a primary or secondary amine $R^{81}NH_2$ or $R^{82}R^{83}NH$ will produce an amide, and the use of a thiol $R^{81}SH$ will produce a thioester.

In the above-defined coreactants, 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}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29}, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl or Het, wherein R^{19} to R^{30} are defined herein, and/or be interrupted by one or more oxygen or sulphur atoms, or by silano or dialkylsilcon 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, water is present.

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}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, 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

The thiol co-reactants can be cyclic, part-cyclic, acylic, saturated or unsaturated(including aromatic), 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. 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.

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. Generally, a large surplus of acid over the co-reactant is preferred 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 either a source of hydroxyl groups such as water, as mentioned

above, or 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 comprises an alkanol, particularly a C_1-C_{30} alkanol, which may be optionally substituted with one or more substituents selected from alkyl, aryl, Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29} or $C(O)SR^{30}$ as defined herein. Highly preferred alkanols are C_1-C_8 alkanols such as methanol, ethanol, propanol, iso-propanol, iso-butanol, t-butyl alcohol, n-butanol and chlorocapryl alcohol. Although the monoalkanols are most preferred, poly-alkanols, preferably, selected from di-octa ols 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, sorbase, 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

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 alkanol used. For instance, use of methanol produces the corresponding methyl ester. Conversely, use of water produces the corresponding acids. Accordingly, the invention provides a convenient way of adding the group -C(O)O C_1-C_{30} alkyl or aryl or -C(O)OH across the ethylenically unsaturated bond.

Preferably, the reaction of the present invention is carried out in the presence of a suitable solvent. Suitable solvents will be described hereafter.

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

$$X^1(X^2)- Q^2 - A - R- B - Q^1 - X^3(X^4) \qquad (IV)$$

wherein:

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

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

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

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.

For the avoidance of doubt, references to Group 8, 9 or 10 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 Pd.

When the ethylenically unsaturated compound is a conjugated diene it contains at least two conjugated double bonds in the molecule. By conjugation is meant that the location of the 7c-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 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 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, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$ or $-CF_3$ wherein R^{19} - R^{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.

The person with average skill in the art will further realise that the process of the present invention can also be used to prepare carboxylic mono-acids and/or carboxylic diacids. Carboxylic mono-acids and/or carboxylic diacids are prepared by reacting conjugated dienes with carbon monoxide and using water as a hydroxyl group containing compound. In this case, the carbonylation product, i.e. the carboxylic acid or di- acid can be used as an additional source of anions.

In the case of dienes in particular, the solvent system can advantageously benefit from the presence of an aromatic carboxylic acid. Suitable acids include any optionally substituted C_1-C_{30} aromatic compound such as those based on phenyl, napthyl, cyclopentadienyl anion(s), indenyl, pyridinyl, and pyrollyl groups and having at least one carboxylic acid group associated with the aromatic ring. The pKa of this acid is preferably greater than about 2 measured in dilute aqueous solution at 18°C. The pKa is preferably less than about 6 measured in dilute aqueous solution at 18°C, more preferably, less than 5.

Examples of suitable aromatic carboxylic acids which form part of the solvent include benzoic acids; naphthoic acids; and cyclopentadenyl acids, particularly preferred are substituted aromatic acids, including for example, C_1-C_4 alkyl substituted benzoic acids, such as 2,4,6-trimethyl benzoic acid, or 2,6-dimethyl benzoic acid and O-toluic acid (2-methyl benzoic acid), 2-nitrobenzoic acid, 6-chloro-2-methylolbenzoic acid, 4-aminobenzoic acid, 2-chloro-6-hydroxybenzoic acid, 2-cyanobenzoic acid, 3-cyanobenzoic acid, 4-cyanobenzoic acid 2,4dihydroxybenzoic, 3-nitrobenzoic acid, 2-phenylbenzoic acid, 2-tert-butylbenzoic acid, 2-napthoic acid, 1-napthoic acid, 2,4-dimethylbenzoic acid, 3-methylbenzoic acid, 3,5-dimethylbenzoic acid, 4-hydroxybenzoic acid, 2-fluorobenzoic acid, 3-propoxybenzoic acid, 3-ethoxybenzoic acid, 2-propoxybenzoic acid, 2,2-diphenylpropionic acid, 2-meyhoxyphenylacetic acid, ortho-anisic acid, meta-anisic acid, 4-tert-butylbenzoic acid and 2-ethoxybenzoic acid, .

Preferably, the aromatic carboxylic acid is substituted by only one group in addition to the group bearing the carboxylic acid. Preferably, an alkyl group substitutes the aromatic ring of the carboxylic acid. An especially preferred compound is O-toluic acid.

Additionally or alternatively, a non-aromatic carboxylic acid may be used in the solvent system. Examples of suitable carboxylic acids include: optionally substituted C_1-C_{12}alkanoic acids such as acetic acid , propionic acids, butyric acids, pentanoic acids , hexanoic acids, nonanoic acids; C_1-C_{12} alkenoic acids such as propenoic acids such as acrylic acid, butenoic acids such as methacrylic acid,

pentenoic acids, hexenoic acids and heptenoic acids; lactic acid; which may all where possible be linear or branched, cyclic, part cyclic,or acyclic and apart from that they 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.

A particularly preferred carboxylic acid in the solvent is the acid product of the carbonylation reaction when hydroxycarbonylation is being effected. .

As mentioned above, 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. Preferably, the ligand is in excess of metal mol/mol. Preferably, the ratio of mole equivalents of bidentate ligand : group 8, 9 or 10 metal is greater than 1:1, preferably, greater than 4:1, more preferably, greater than 10:1.

Preferably, the solvent system optionally comprises a carboxylic acid as defined above (preferably an aromatic carboxylic acid) with at least one base solvent.

Suitable solvents with or without the carboxylic acids defined above 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-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 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 x $10^5 Nm^{-2}$. 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, 76^{th} 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 x $10^5 Nm^{-2}$,

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 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 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 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 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 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.

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.

Alternatively, a protic solvent 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 in the art, such as water, 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.

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 donates nor accepts protons.

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 20% vol/vol of the carbon monoxide, more preferably, 1-20% vol/vol of the carbon monoxide, more preferably, 2-15% vol/vol of the carbon monoxide, most preferably 3-10% vol/vol of carbon monoxide.

Hydrogen, if present, is preferably present at a partial pressure of between 1×10^5 and 20×10^5 Pa, preferably between 2×10^5 and 10×10^5 Pa, and most preferably, at a partial pressure of about 5×10^5 Pa.

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 0.001:1 to 100:1 mol/mol. Preferably, the molar ratio of the amount of ethylenically unsaturated compound used in the reaction to the amount of solvent is between 1:1 and 70:1, more preferably, 1:1 to 50:1.

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 10^{-7} to 10^{-1} moles per mole of ethylenically unsaturated compound, more preferably, 10^{-6} to 10^{-2} moles, most preferably 10^{-5} to 10^{-2} moles per mole of ethylenically unsaturated compound. Preferably, the amount of ligand of formulas I-IV to ethylenically unsaturated compound is in the range 10^{-7} to 10^{-1}, more preferably, 10^{-6} to 10^{-2}, most preferably, 10^{-5} to 10^{-2} moles per mole of ethylenically unsaturated compound. Preferably, the 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 -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 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 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 of between 1 x 10^5 $N.m^{-2}$–120 x $10^5 N.m^{-2}$, more preferably 10 x 10^5 $N.m^{-2}$–100 x $10^5 N.m^{-2}$, most preferably 20-90 x 10^5 $N.m^{-2}$. Especially preferred is a CO partial pressure of 40 to 80 x $10^5 N.m^{-2}$.

The cyclic hydrocarbyl structure which R in formulas I-IV 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 (ie more than half) in the structure are carbon. The available adjacent cyclic atoms to which the Q^1 and Q^2 atoms are linked to form part of at least one ring. This ring to which the Q^1 and Q^2 atoms are immediately linked via the linking group 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 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 immmediately attached via the

linking group 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 polycylic 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, pyrollidine, 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 Q^1 and Q^2 atoms are linked 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.

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

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.

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.

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 hydrocarbyl 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, het, hetero, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$ 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 hydrocarbyl 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.

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 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, 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.

Preferably, further substitution of said non-aromatic cyclic hydrocarbyl structure is not on said available adjacent carbon atoms to which said Q^1 and Q^2 atoms are linked. The non-aromatic cyclic hydrocarbyl structure may be substituted at one or more said further cyclic atoms of 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 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.

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 lower alkylcyclooctane- 1,2-diyl, 4, 5, 6, 7 and/or 8 lower alkylcyclononane- 1,2-diyl, 5 and/or 6 lower alkyl piperidinane- 2,3-diyl, 5 and/or 6 lower alkyl morpholinane-2,3-diyl, O-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 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 diyl, 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-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-diyl, 1-lower alkyl pyrollidine -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 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-diyl, 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, 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 5,6-diyls, 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 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.

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.

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 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 above), phosphorus, aryl, arylene, alkaryl, 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 alkylphosphorus.

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, 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 alkylphosphorus wherein 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.

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 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 substituted with groups selected from Y, alkyl, 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 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.

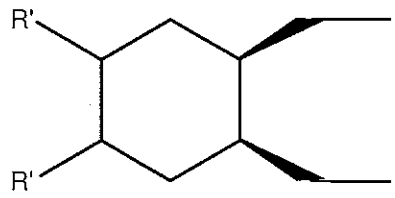
In addition, when S is aryl, the aryl may be substituted with in addition to R^{40}, R^{41}, R^{42} any of the further substituents defined for the non-aromatic bridged structure above.

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

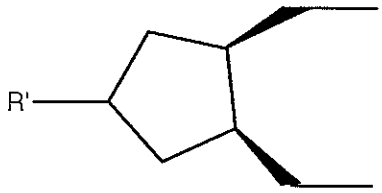
Preferably, when S is Si or C and one or more of R^{40}-R^{42} are hydrogen, at least one of R^{40} -R^{42} should be sufficiently bulky to give the required steric hindrance and such groups are preferably phosphorus, phosphinoalkyl-, a tertiary carbon bearing group such as -t-butyl, -aryl, -alkaryl,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

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

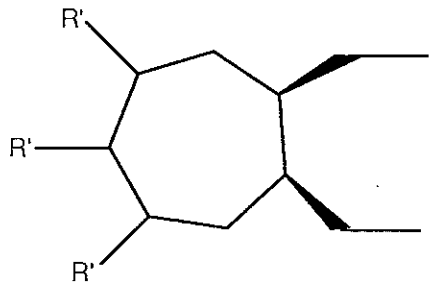
Some typical hydrocarbyl structures are shown below wherein R', R'', R''', R'''' etc are defined in the same way as the substituents on the cyclic atoms above but may also be hydrogen, or represent the hetero atom being non substituted if linked directly to a hetero atom and may be the same or different.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



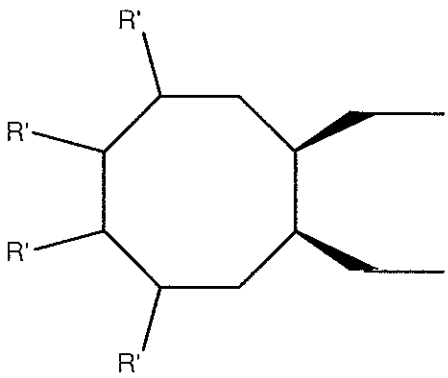
4 and/or 5 substituted cyclohexyl



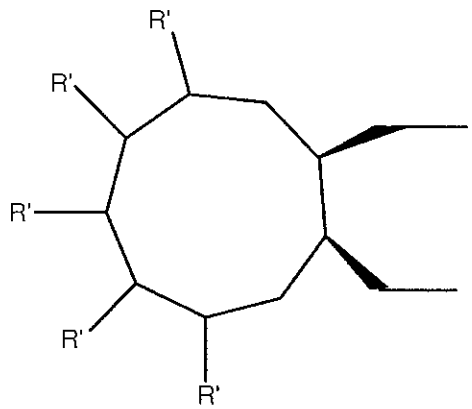
4 substituted cyclopentyl



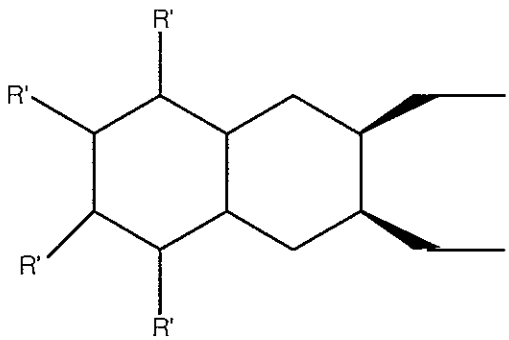
4, 5 and/or 6 substituted cycloheptyl



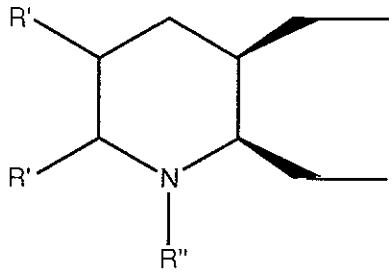
4, 5, 6 and/or 7 substituted cyclooctyl



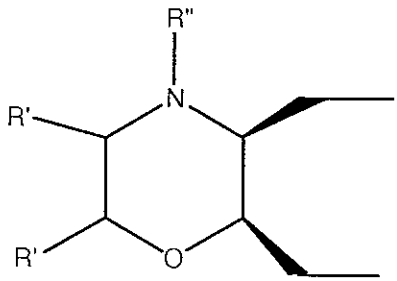
4,5,6,7 and/or 8 substituted cyclononyl



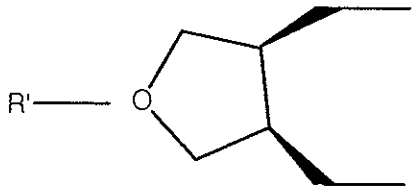
2,3,4 and/or 5 substituted decahydronaphthalene



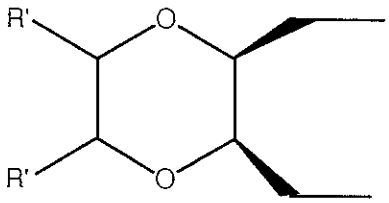
5 and/or 6 substituted piperidines



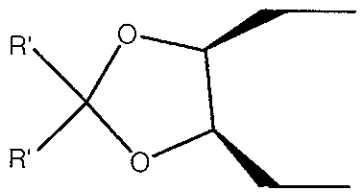
5 and/or 6 substituted morpholines



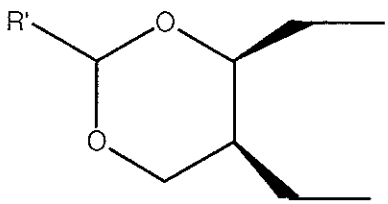
1- substituted furans



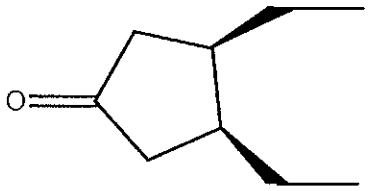
5 and/or 6 substituted 1,4 dioxane

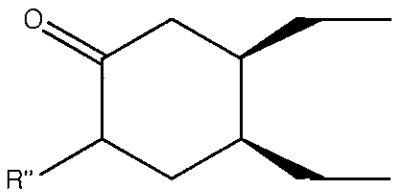


substituted DIOP



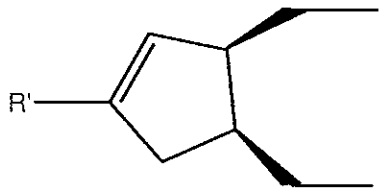
2 - substituted 1,3 dioxane

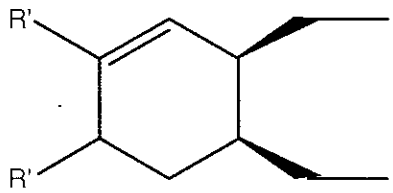




cyclopentanone

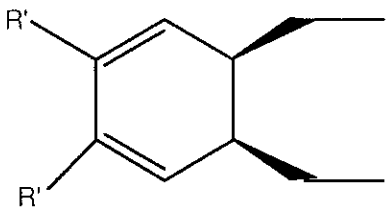
6- substituted cyclohexanone

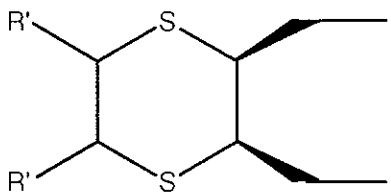




1 - substituted cyclopentenyl

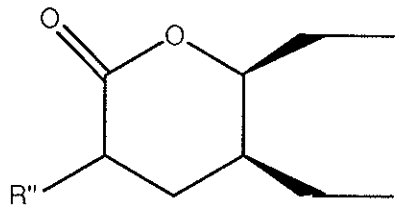
1 and/or 6 - substituted cyclohexenyl

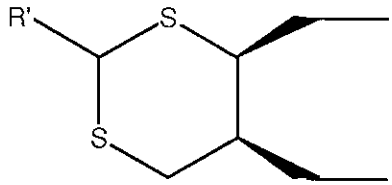




2 and/or 3 substituted cyclohexadienyl

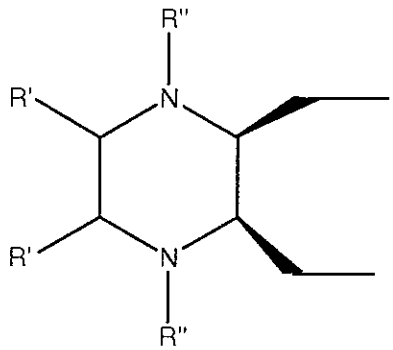
2 and/or 3 substituted 1,4 dithiane

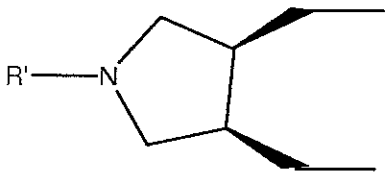




3 - substituted pyrones

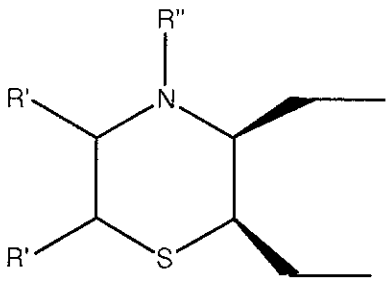
2 - substituted 1,3 dithiane

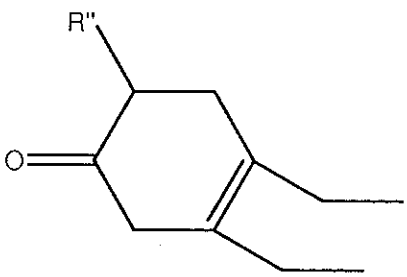




1, 2, 3 , 4 substituted piperizine

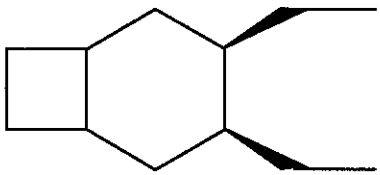
1 substituted pyrollidine



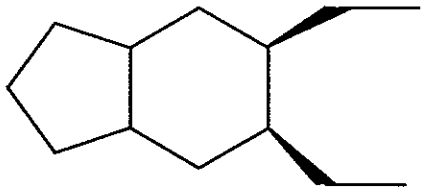


1, 2, 3 substituted thiomorphiline

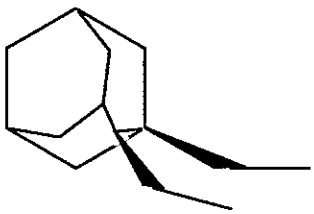
5 substituted cyclohexen-4-one



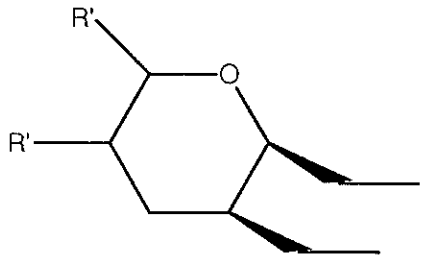
bicyclo[4.2.0] octane



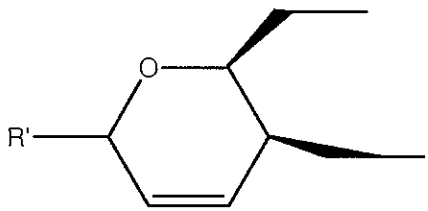
bicyclo[4.3.0]nonane



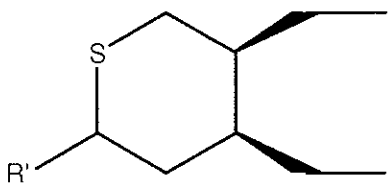
Adamantyl -1,2-diyl



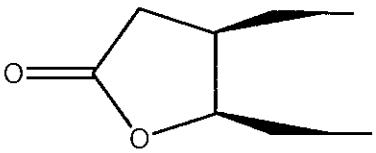
substituted tetrahydropyran

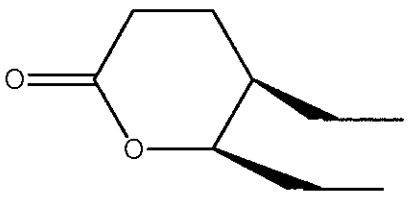


Substituted dihydropyran

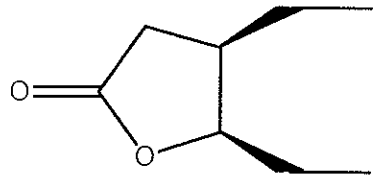


substituted pentamethylene sulphide (substituted tetrahydro-thiopyran



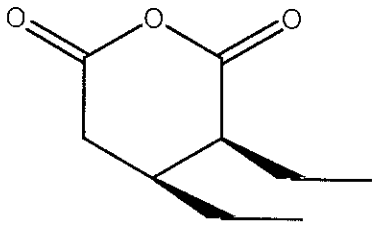


tetrahydro-furan-2-one

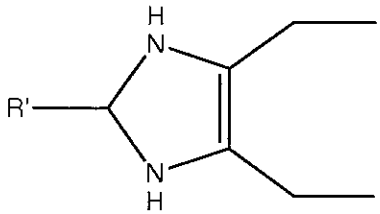


gamma-butyrolactone

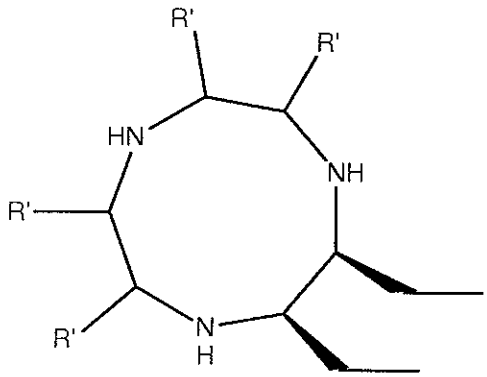
delta-valero lactone 4,5-diyl



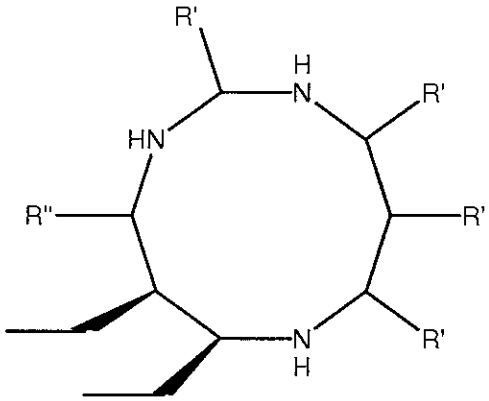
glutaric anhydride



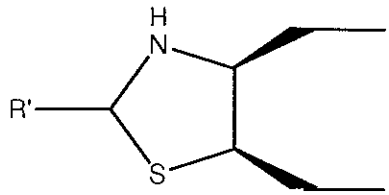
substituted dihydro imidazole



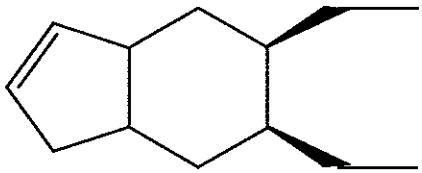
Substituted 1,4,7 triazacyclononane



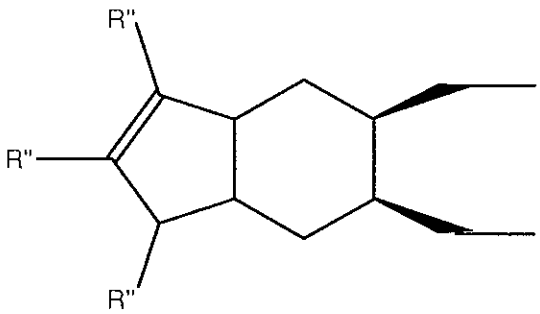
substituted 1,5,9 triazacyclodecane



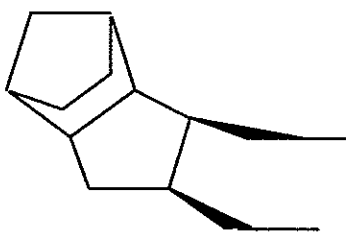
substituted thiazolidine



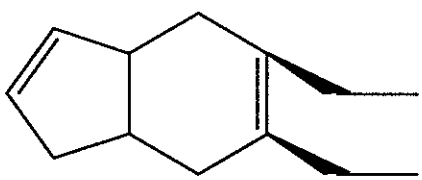
3a,4,5,6,7,7a-hexahydro-1H-indene



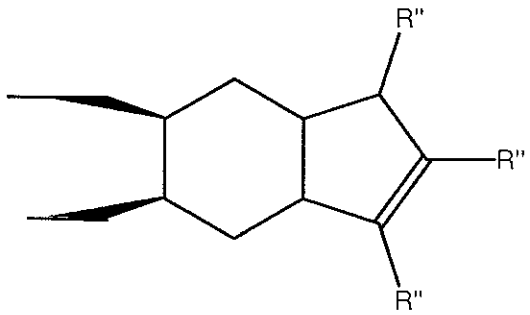
substituted 3a, 4,5,6,7,7a hexahydro-1H-indene



Octahydro -4,7 methano - indene



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



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

In the structures herein, where there is more than one stereisomeric 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 hydrocarbyl structure extends in a trans direction with respect to the A and or B atom ie extends outwardly on the opposite side of the ring.

Preferably, each adjacent cyclic atom to the said 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 ring in the non-aromatic bridged structure;

An additional preferred set of embodiments is found when R represents an aromatic bridged hydrocarbyl structure ie. having at least one aromatic ring to which Q^1 and Q^2 are 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, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27}, $C(O)SR^{27}$, or $-J-Q^3(CR^{13}(R^{14})(R^{15})CR^{16}(R^{17})(R^{18})$ 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 substituted by one or more substituents selected from alkyl, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27} or $C(O)SR^{27}$; wherein R^{19} to R^{27} are defined herein.

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.

Preferably, when present, the substituent(s) Y^x on the aromatic structure has a total $^{x=1-n}\Sigma tY^x$ of atoms other than hydrogen such that $^{x=1-n}\Sigma tY^x$ is ≥ 4, where n is the total number of substituent(s) Y^x and tY^x represents the total 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 located on the same or different cyclic atoms of the aromatic bridged cyclic hydrocarbyl structure. Preferably, there are $\leq$ 10 Y groups ie 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.

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

Preferably, when there is one substituent Y, Y represents 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.

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 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 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 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.

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.

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.

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.

Toluene solutions of $Ni(CO)_4$ 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 equilibriated 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 equilibriated solutions are then 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 Tolmán {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 leaving, directing its incoming pathway, generally providing a more stable catalytic confirmation, or acting otherwise.

A particularly preferred ligand is found when 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 hereinafter. Preferably each Y and/or combination of two or more Y groups is at least as sterically hindering as t-butyl.

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 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 above), phosphorus, aryl, arylene, alkaryl, 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 alkylphosphorus.

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, 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 alkylphosphorus wherein 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.

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 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 cyclic hydrocarbyl structure may be unsubstituted or, when possible be further substituted with groups selected from alkyl, 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 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 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 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 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 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 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 or 2-phenylprop-2-yl, , $-SiMe_3$, -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-, a tertiary carbon bearing group such as -t-butyl, -aryl, -alkaryl, -aralkyl or tertiary silyl.

Preferably, the aromatic bridged cyclic hydrocarbyl 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 polycylic 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, pyrollyl, 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-phenyl-benzene-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-alkyl- naphthalene- 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 benzene -1,2 diyl, 4-(2'-phenylprop-2'-yl) benzene - 1,2 diyl, 4-dimethylsilylbenzene-1,2diyl, 4-di-t-butyl,methylsilyl benzene-1,2diyl, 4-(t-butyldimethylsilyl)-benzene-1,2diyl, 4-t-butylsilyl-benzene-1,2diyl, 4-(tri-t-butylsilyl)-benzene-1,2diyl, 4-(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-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 1')di-t-butyl,methylsilyl ferrocene-1,2diyl, 4-(or 1')(t-butyldimethylsilyl)-ferrocene-1,2diyl, 4-(or 1')t-butylsilyl-ferrocene-1,2diyl, 4-(or 1')(tri-t-butylsilyl)-ferrocene-1,2diyl, 4-(or 1')(2'-tert-butylprop-2'-yl)ferrocene-1,2 diyl, 4-(or 1')(2',2',3',4',4' 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 stereisomeric 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 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, 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, 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 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-alkyl substituted 1,3 dioxane, cyclopentanone, cyclohexanone, cyclopentene, cyclohexene, cyclohexadiene, 1,4 dithiane, piperizine, pyrollidine, thiomorpholine, cyclohexenone, bicyclo[4.2.0]octane, bicyclo[4.3.0]nonane, adamantane, tetrahydropyran, dihydropyran, tetrahydrothiopyran, tetrahydrofuran-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.

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-

(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-phospha-cyclohexan-4-one) benzene, 1-(tert-butyl,adamantylphosphinomethyl)-2-(di-adamantylphosphinomethyl)benzene, 1-[(P-(2,2,6,6,-tetramethyl-phospha-cyclohexan-4-one)methyl)]-2-(phospha-adamantyl)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-phospha-adamantylmethyl)ferrocene, 1,2-bis-α,α-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))dimethylferrocene, and 1-(di-tert-butylphosphinomethyl)-2-(P-(2,2,6,6-

tetramethyl-phospha-cyclohexan-4-one))ferrocene and 1,2-bis(1,3,5,7-tetramethyl-6,9,10-trioxa-2-phospha-adamantylmethyl)benzene; 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.

Examples of suitable substituted non-aromatic bridged bidentate ligands are cis-1,2-bis(di-t-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-trioxa-adamantyl)-4,5-dimethylcyclohexane; cis-1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) 5-methylcyclopentane; cis-1,2-bis(di-adamantylphosphinomethyl)-4,5 dimethylcyclohexane; cis-1,2-bis(di-adamantylphosphinomethyl)-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-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-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-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-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-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)-[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-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-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-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-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-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- 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-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-(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-{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-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)-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-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-t-butylphosphinomethyl)-4,5-diphenyl benzene; 1,2-bis(di-t-butylphosphinomethyl)-4-phenylbenzene; 1,2-bis(di-t-butylphosphinomethyl)-4,5- bis-(trimethylsilyl) benzene; 1,2-bis(di-t-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-t-butylphosphinomethyl)-4,5-diphenylbenzene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4-phenylbenzene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4,5- bis-(trimethylsilyl)benzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4-(trimethylsilyl)benzene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-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; 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-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-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)-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-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-(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-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-(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-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-(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-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) 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-(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-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'-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-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) 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'-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-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-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-(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-(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-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'-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-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-(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-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'-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-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) 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-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) 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-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-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)-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-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-(ditertbutylphosphinomethyl)-2-(P-(2,2,6,6- tetramethyl-phospha-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)-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-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-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) 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-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-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-(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-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-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-(or 1')(trimethylsilyl) ferrocene; 1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl)-4,5-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-(or 1')phenyl ferrocene; 1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-

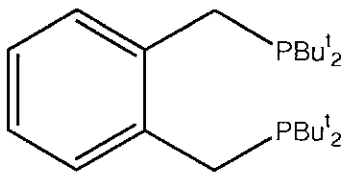
trioxatricyclo{3.3.1.1[3.7]}-decyl)-4,5-bis-(trimethylsilyl) ferrocene; 1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(or 1')(trimethylsilyl) ferrocene; 1,2-bis- (2-phosphinomethyl-1,3,5,7-tetra(trifluoro-methyl)-6,9,10-trioxatricyclo{3.3.1.1[3.7]}decyl)-4,5-diphenyl ferrocene; 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-(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'-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-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-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-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-(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- (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-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- (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-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-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-

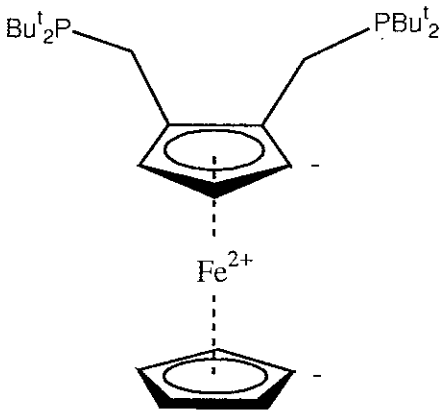
{3.3.1.1[3.7]}decyl)-2-(di-t-butylphosphinomethyl)-4,5- di-(2'-phenylprop-2'-yl) ferrocene; 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-(di-t-butylphosphinomethyl)-4-(or 1')(2'-phenylprop-2'-yl) ferrocene; 1-(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-2-(di-t-butylphosphinomethyl)-4,5-(di-t-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-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'-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'-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-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-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-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 ferrocene.

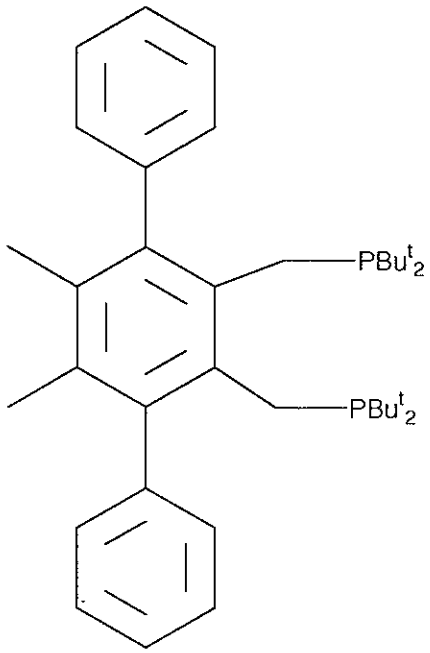
Selected structures of ligands of the invention include:-



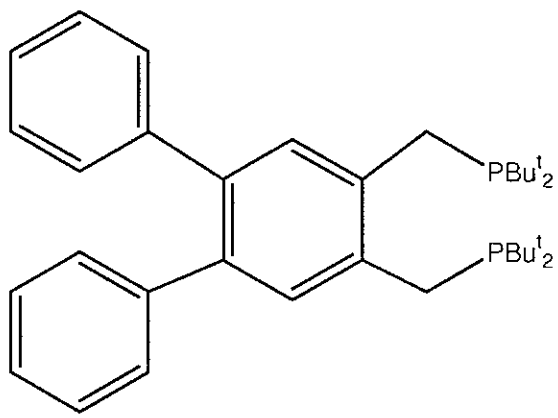
1,2-bis(di-tert-butylphosphinomethyl)benzene



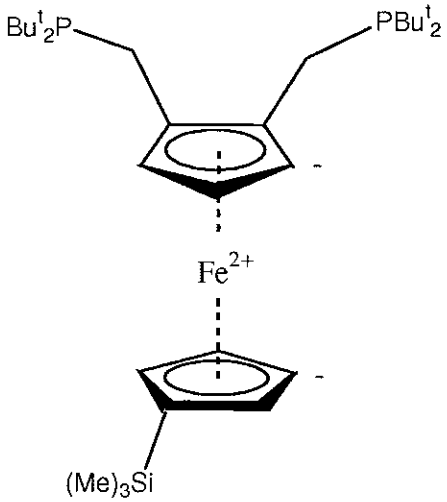
1,2-bis(di-tert-butylphospinomethyl ferrocene



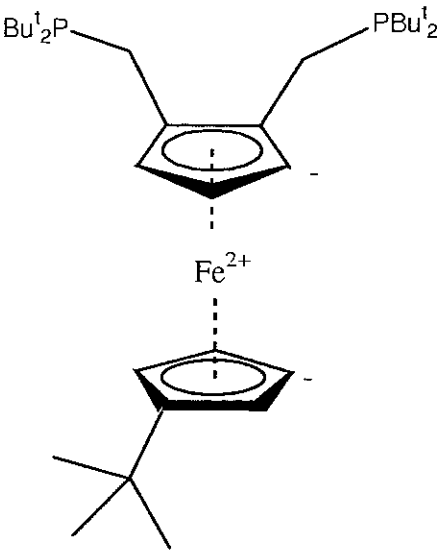
1,2-bis(di-tert-butylphosphinomethyl)-3,6-diphenyl-4,5-dimethyl benzene



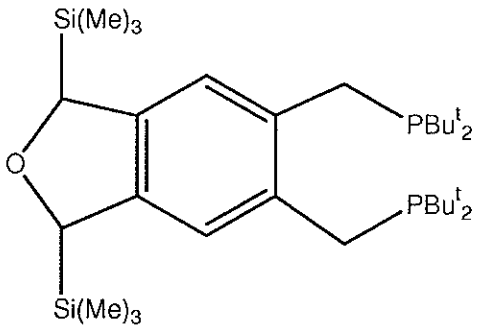
1,2-bis(di-tert-butyl(phosphinomethyl)-4,5-diphenyl benzene



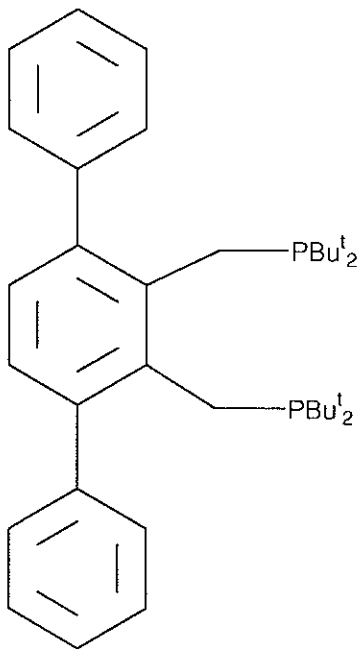
1,2-bis(di-tert-butylphospinomethyl)-1'-trimethylsilyl ferrocene



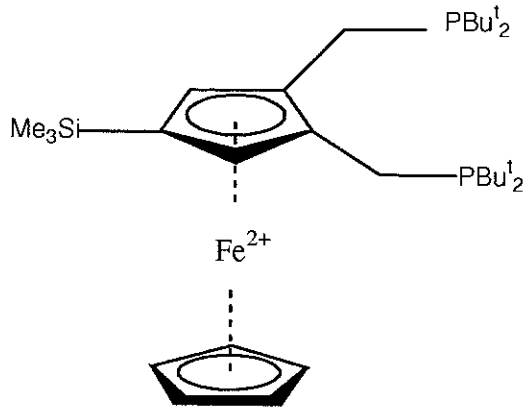
1,2-bis(di-tert-butylphospinomethyl)-1'-tert-butyl ferrocene



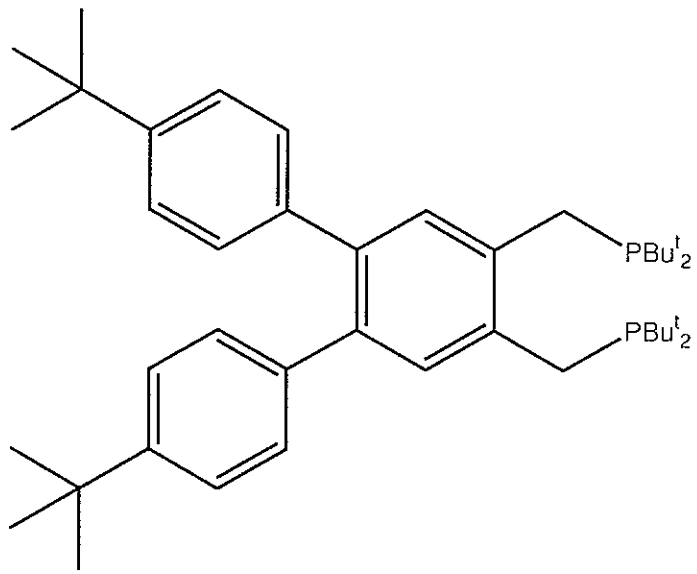
5,6-bis(di-tert-butylphosphinomethyl)-1,3-bis-trimethylsilyl-1,3-dihydroisobenzofuran.



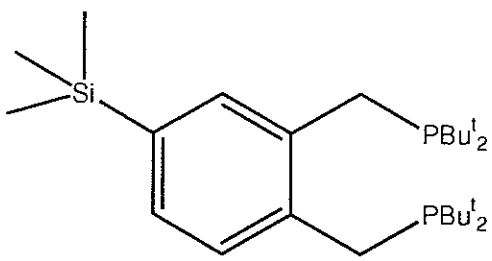
1, 2-bis (di-tert-butylphosphinomethyl)-3,6-diphenyl benzene



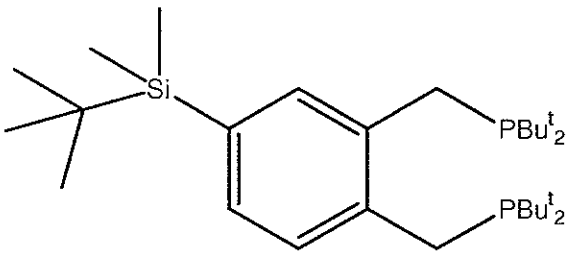
1,2-bis(di-tert-butylphospinomethyl)-4-trimethylsilyl ferrocene



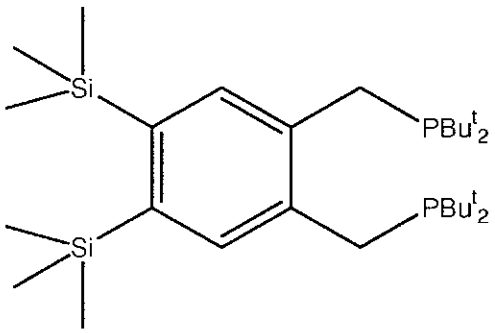
1,2 bis(di-tert-butyl(phosphinomethyl))-4,5- di(4'-tert butyl phenyl) benzene



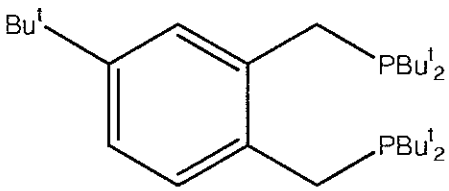
1,2-bis(di-tert-butyl(phosphinomethyl))-4-trimethylsilyl benzene



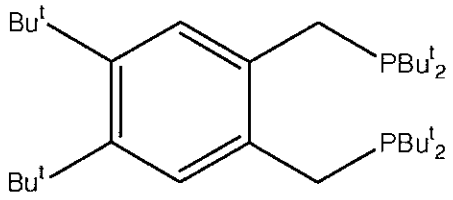
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(tert-butyldimethylsilyl)benzene



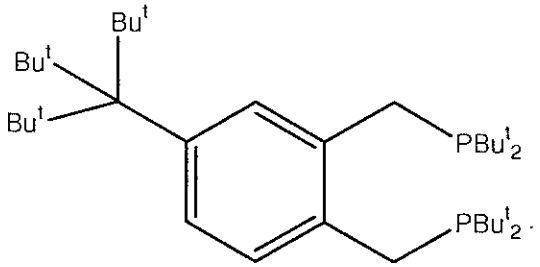
1,2-bis(di-tert-butyl(phosphinomethyl))-4,5-bis(trimethylsilyl)benzene



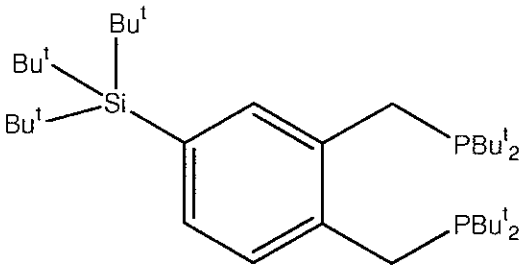
1,2-bis(di-tert-butyl(phosphinomethyl))-4-tert-butyl benzene



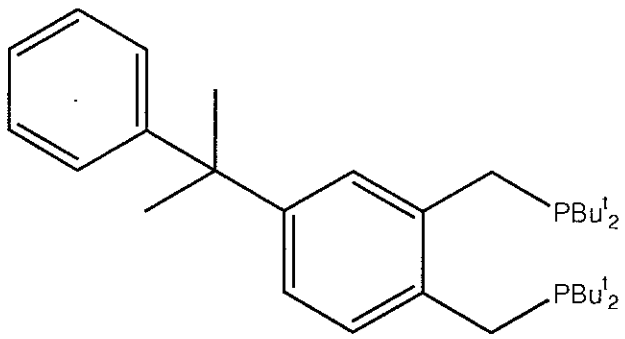
1,2-bis(di-tert-butyl(phosphinomethyl))-4,5-di-tert-butyl benzene



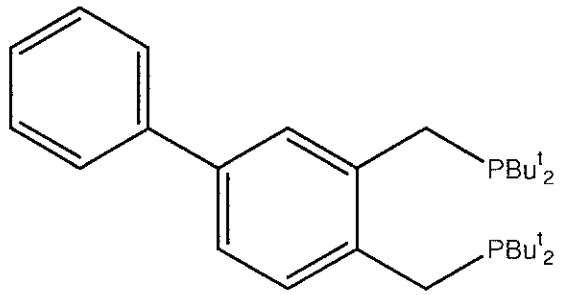
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(tri-tert-butylmethyl)benzene



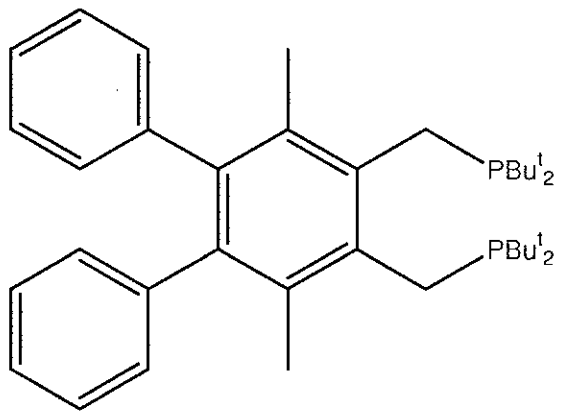
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(tri-tert-butylsilyl)benzene



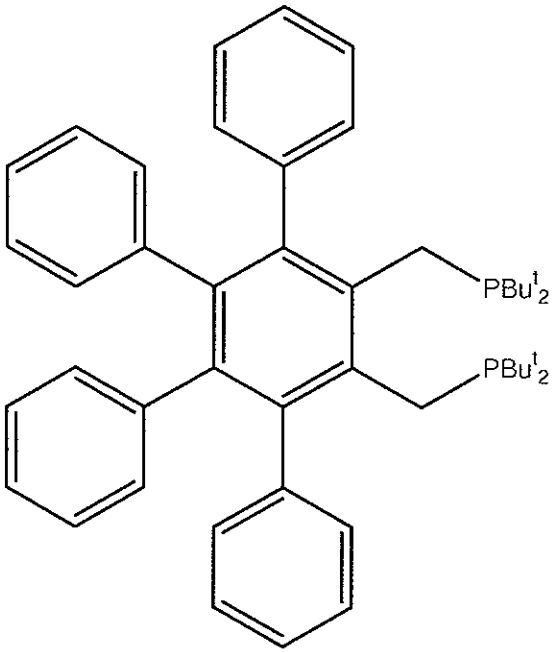
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(2'-phenylprop-2'-yl)benzene



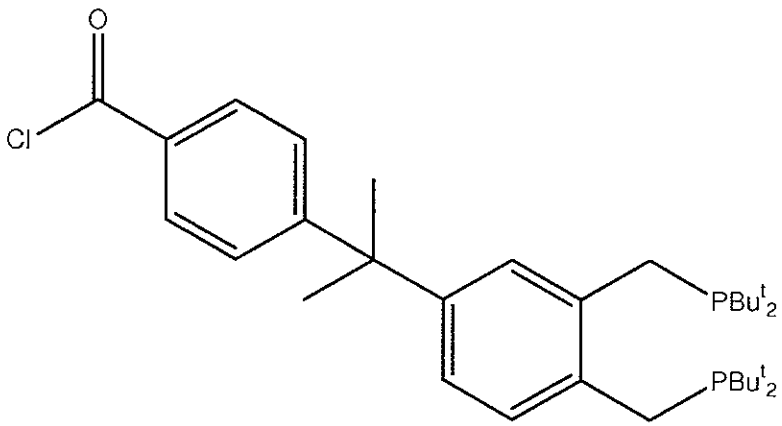
1,2-bis(di-tert-butyl(phosphinomethyl))-4-phenyl benzene



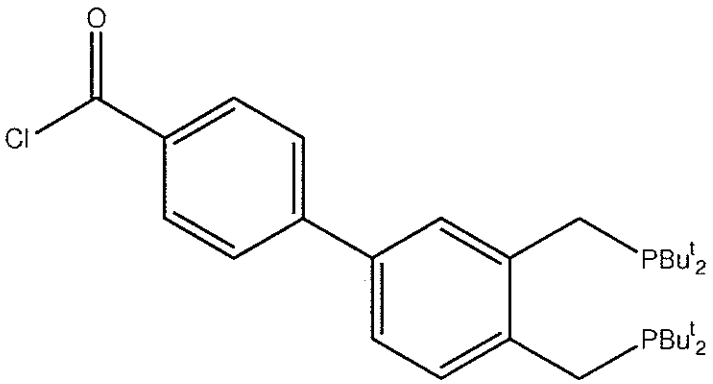
1,2-bis(di-tert-butyl(phosphinomethyl))-3,6-dimethyl-4,5-diphenyl benzene



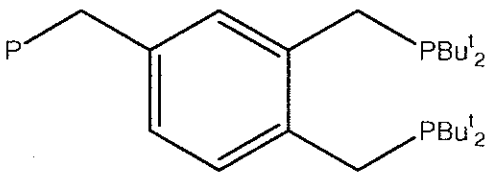
1,2-bis(di-tert-butyl(phosphinomethyl))-3,4,5,6-tetraphenyl benzene



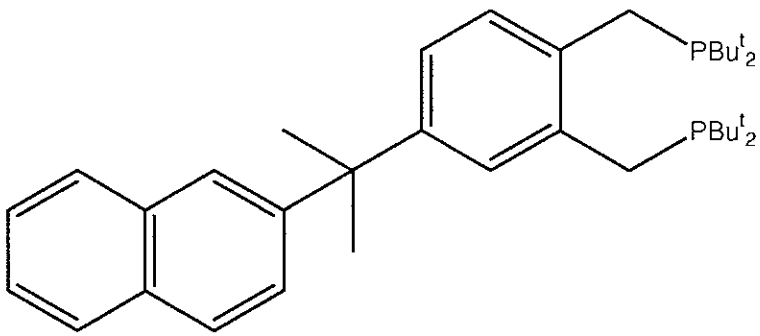
4-(1-{3,4-Bis-[(di-*tert*-butyl-phosphanyl)-methyl]-phenyl}-1-methyl-ethyl)-benzoyl chloride



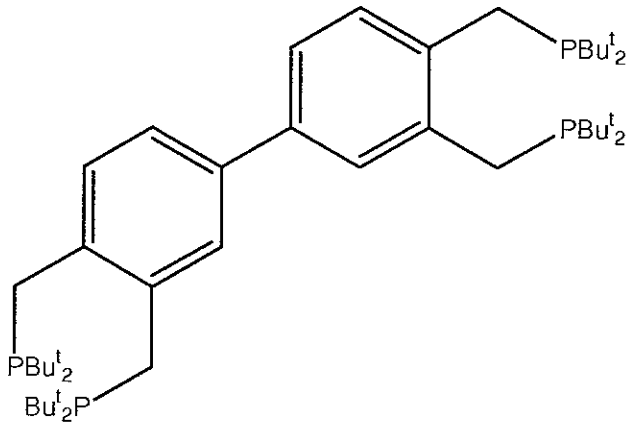
1,2-bis(di-tert-butyl(phosphinomethyl)-4-(4'-chlorocarbonyl-phenyl)benzene



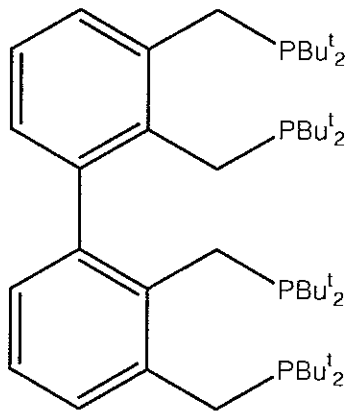
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(phosphinomethyl)benzene



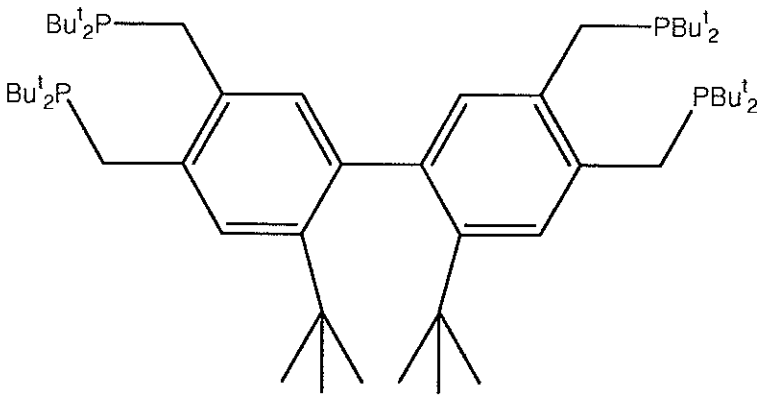
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(2'-naphthylprop-2'-yl) benzene



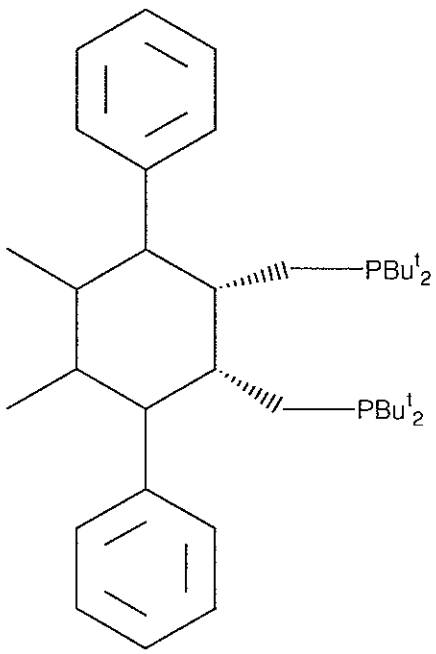
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(3',4'-bis(di-tert-butyl(phosphinomethyl))phenyl)benzene



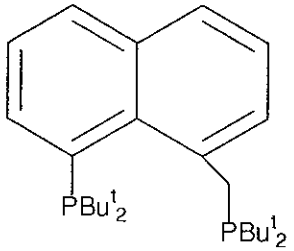
1,2-bis(di-tert-butyl(phosphinomethyl))-3-(2',3'-bis(di-tert-butyl(phosphinomethyl))phenyl)benzene



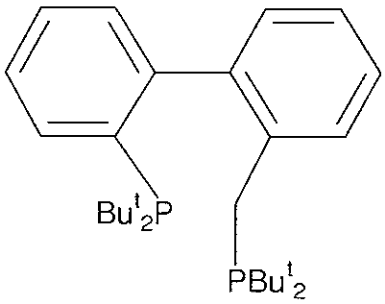
1,2-bis(di-tert-butyl(phosphinomethyl))-4-tertbutyl-5-(2'-tertbutyl-4',5'-bis(di-tert-butyl(phosphinomethyl))phenyl)benzene ,and



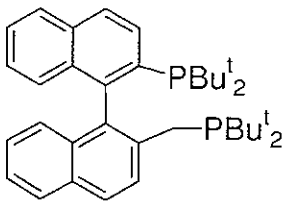
cis-1, 2-bis (di-tert-butylphosphinomethyl), 3, 6, diphenyl-4,5 dimethyl-cyclohexane,



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

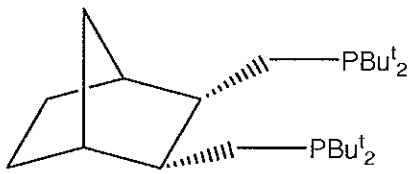


2-(di-tert-butylphosphinomethyl)-2'-(di-tert-butylphosphino)-biphenylene

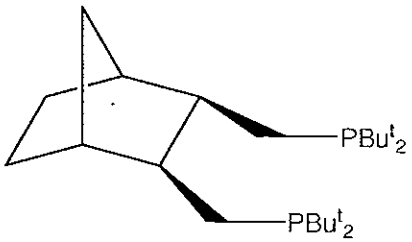


2-(di-tert-butylphosphinomethyl)-2'-(di-tert-butylphosphino)-binaphthylene

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

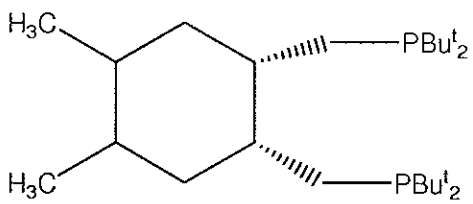


(2-exo, 3-exo)-bicyclo[2.2.1]heptane-2,3-bis(di-tert-butylphosphinomethyl)

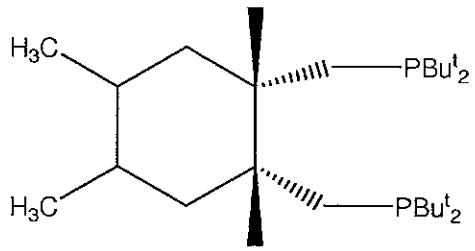


(2-endo, 3-endo)-bicyclo[2.2.1]heptane-2,3-bis(di-tert-butylphosphinomethyl)

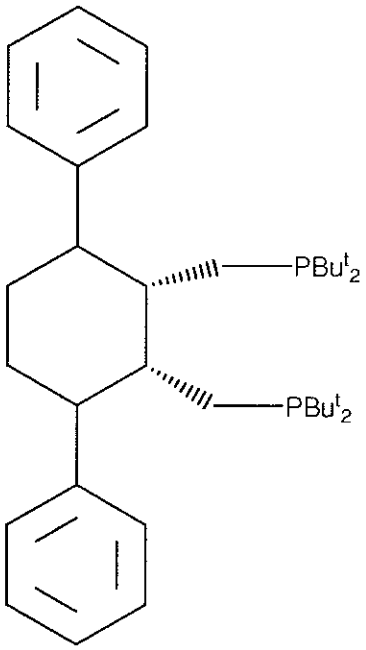
Examples of substituted non-aromatic bridged ligand structures include:-



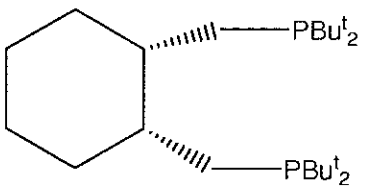
cis-1, 2-bis (di-*tert*-butylphosphinomethyl), 4, 5 dimethylcyclohexane



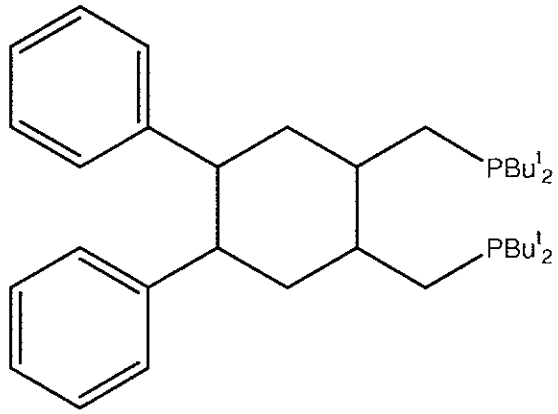
cis-1, 2-bis (di-tert-butylphosphinomethyl), 1, 2, 4, 5 tetramethylcyclohexane



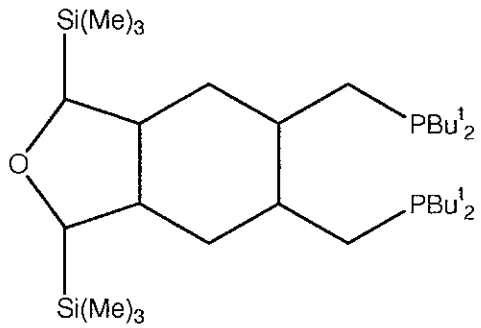
cis-1, 2-bis (di-tert-butylphosphinomethyl), 3, 6, diphenylcyclohexane



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



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



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 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-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

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.

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.

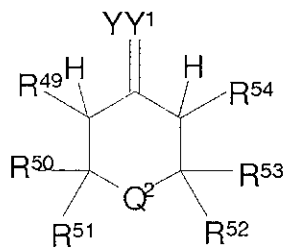
Typically, the group X^1 represents $CR^1(R^2)(R^3)$, X^2 represents $CR^4(R^5)(R^6)$, X^3 represents $CR^7(R^8)(R^9)$ and X^4 represents $CR^{10}(R^{11})(R^{12})$, wherein R^1 to R^{12} represent alkyl, aryl or het.

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,

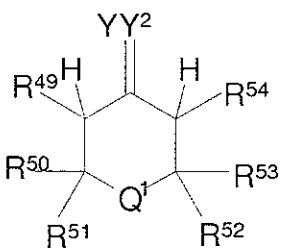
wherein R^{19} to R^{30} are as defined herein, and/or be interrupted by one or more oxygen or sulphur atoms, or by silano or dialkylsilcon groups.

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



(1a)

Similarly, X^3 and X^4 together with Q^1 to which they are attached may form an optionally substituted 2-Q1-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or X^3 and X^4 together with Q^1 to which they are attached may form a ring system of formula 1b



(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.

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 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, aryl or Het;

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;

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

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 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, 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 C_1-C_8 alkyl, especially methyl, trifluoromethyl, $-OR^{19}$ wherein R^{19} is as defined herein particularly unsubstituted C_1-C_8 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 C_1-C_8 alkyl and haloakyls, particularly unsubstituted C_1-C_8 alkyl such as methyl and fluorinated C_1-C_8 alkyl such as trifluoromethyl.

Preferably, 2-meta-adamantyl represents unsubstituted 2-meta-adamantyl or 2-meta-adamantyl substituted with one or more unsubstituted C_1-C_8 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. 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-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-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.

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-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.

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.

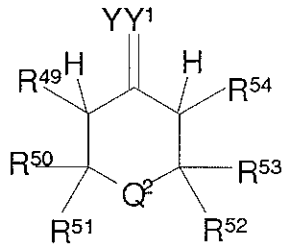
The 2-meta-adamantyl group may be prepared by methods well known to those skilled in the art. Suitably, certain 2-phospha-adamantyl compounds are obtainable from Cytec Canada Inc, Canada. Likewise corresponding 2-meta-adamantyl compounds of formulas I - IV etc may be obtained from the same supplier or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

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 $CR^4(R^5)(R^6)$;

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 2-phospha-adamantyl group;

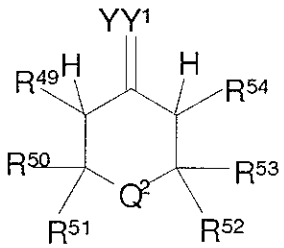
X^3 represents $CR^7(R^8)(R^9)$, X^4 represents $CR^{10}(R^{11})(R^{12})$; and X^1 and X^2 together with Q^2 to which they are attached form a ring system of formula 1a;



(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;

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;



(1a)

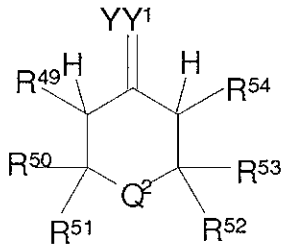
X^3 represents $CR^7(R^8)(R^9)$, X^4 represents adamantyl, X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$;

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 $CR^4(R^5)(R^6)$;

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;

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;

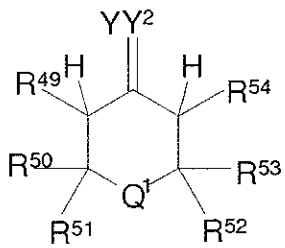


(1a)

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

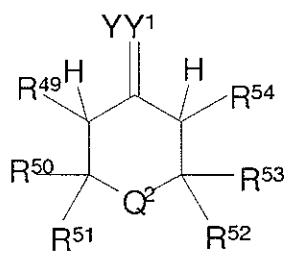
X^1, X^2, X^3 and X^4 represent adamantyl;

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



(1b)

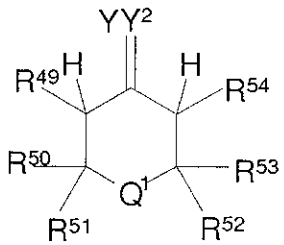
and X^1 and X^2 together with Q^2 to which they are attached form a ring system of formula 1a;



(1a)

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

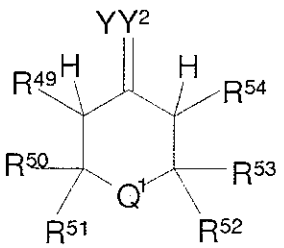


(1b)

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 $CR^4(R^5)(R^6)$;

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



(1b)

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

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

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.

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:-

(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 $CR^4(R^5)(R^6)$;
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

(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 $CR^4(R^5)(R^6)$;
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-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.

(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:

each R^1 to R^{12} is the same and represents methyl;
A and B are the same and represent $-CH_2-$;
R represents benzene-1,2-diyl, ferrocene-1.2-diyl, 4-t-butyl-benzene-1,2-diyl, 4(trimethylsilyl)-

benzene-1,2-diyl.

The term "lower alkylene" which A and B represent in a compound of formula I, when used herein, includes C_0-C_{10} or C_1 to C_{10} groups which, in the latter case, can be bonded at two places on the group to thereby connect the group Q^1 or Q^2 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 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.

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 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 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 one or more (preferably less than 4) oxygen, sulphur, silicon atoms, or by silano or dialkylsilcon groups, or mixtures thereof.

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.

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 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 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} 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}, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, 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 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, 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}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$,

$C(O)NR^{25}R^{26}$, 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, 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 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.

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

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 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 (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 as optionally substituted azetidinyl, pyrrolidinyl, 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.

"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.

The adamantyl, congressyl, norbornyl or 1-norborndienyl group may optionally comprise, besides hydrogen atoms, one or more substituents selected from alkyl, $-OR^{19}$, $-OC(O)R^{20}$, halo, nitro, $-C(O)R^{21}$, $-C(O)OR^{22}$, cyano, aryl, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$,$-CF_3$, $-P(R^{56})R^{57}$, $-PO(R^{58})(R^{59})$, $-PO_3H_2$, $-PO(OR^{60})(OR^{61})$, or $-SO_3R^{62}$, 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.

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, $-OR^{19}$, $-OC(O)R^{20}$, phenyl, $-C(O)OR^{22}$, fluoro, $-SO_3H$, $-N(R^{23})R^{24}$, $-P(R^{56})R^{57}$, $-C(O)N(R^{25})R^{26}$ and $-PO(R^{58})(R^{59})$, $-CF_3$, wherein 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, 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.

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 C_1-C_8 alkyl and trifluoromethyl, particularly unsubstituted C_1-C_8 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.

For the avoidance of doubt, references to Group 8, 9 or 10 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 Pd.

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 C_{12}) acids such as 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; 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 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 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.

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 pKa less than 6 measured in dilute aqueous solution at 25°C. The pKa is preferably less than about 4 measured in dilute aqueous solution at 18°C. Particularly preferred acids have a pKa 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.

For the avoidance of doubt, references to pKa herein are references to pKa measured in dilute aqueous solution at 25°C unless indicated otherwise.

Particularly preferred anions for the carbonylation reaction of a diene are therefore derived from the carboxylic acids and aromatic carboxylic acids listed supra. There may be a mixture of anions but preferably only one source of anions is added to the process. However, it should be appreciated that a further source of anions may be generated by the process ie the acid product of the carbonylation, for instance pentenoic acid in the carbonylation of 1,3-butadiene. Generally, for subtrates which are not pH sensitive a stronger acid is preferred. Particularly preferred acids are the sulphonic acids listed supra.

In the carbonylation reaction the quantity of anion present is not critical to the catalytic behaviour of the catalyst system. The molar ratio of anion to Group 8, 9 or 10 metal/compound may be from 1:1 to 10^7:1, preferably from 2:1 to 10^7:1 most preferably, from 100:1 to 10^5:1 and especially 100:1 and 1000:1. 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.

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

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 hydroxyl group containing compound and, optionally, a source of anions. The ligands of the invention yield a surprisingly high TON in carbonylation

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

Advantageously, use of the catalyst system of the present invention in the carbonylation of ethylenically unsaturated compounds etc also gives good rates especially for alkoxy- and hydroxycarbonylation.

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.

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 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 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.

The process of the present invention provides a surprisingly increased TON for the reaction with ethylenically unsaturated compounds.

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 .

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

$R^{62} - C(O)\ O\ CR^{63} = CR^{64}\ R^{65}$

wherein R^{62} may be selected from hydrogen, alkyl, aryl, Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)\ R^{27}R^{28}$, SR^{29}, $C(O)\ SR^{30}$ wherein R^{19}-R^{30} are as defined herein.

Preferably, R^{62} is selected from hydrogen, alkyl, phenyl 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.

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.

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 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 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 with a suitable optically active acid or base, as appropriate.

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.

Consequently, the commercial viability of the carbonylation reaction may be increased by employing the process of the invention. Especially advantageously, the process of the invention allows for a carbonylation reaction with a high TON number and a high rate of reaction.

It will be appreciated by those skilled in the art that the compounds of formulas (I) to (IV) may function as ligands that coordinate with the Group 8, 9 or 10 metal or compound thereof to form the 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 of formulas (I) to (IV).

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

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.

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

Thus according to a further aspect, the present invention 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.

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 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 a surface area in the range of from 10 to 700 m^2/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 m^2/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 m^2/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.

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 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 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.

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.

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 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.

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

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 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 continuous reaction can continue as long as the TON is commercially acceptable before catalyst requires replenishment.

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.

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 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.

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.

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.

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 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-hydroxybutyricacid), 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 polyvinylpyrollidone (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.

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.

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.

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

Catalysis Examples Using Pd(dba).

Examples 1-3

The solutions for catalyst testing were prepared using standard Schlenk line techniques. In a nitrogen purge glove box, 3.9mg (5.6×10^{-6} moles Pd) of Pd_2dba_3 and 7.5 equivalents of phosphine ligand 1 (L-L) = 1,2-bis(di-tert-butylphosphinomethyl)benzene 16.6mg (4.21×10^{-5} moles), were weighed into a 500ml round bottom flask. The flask was then transferred to a Schlenk line. The ligand and palladium were then dissolved in 125 ml of degassed methyl propionate. In order to aid complexation, the palladium and ligand were dissolved initially in methyl propionate and stirred for a period of 45 minutes, before addition of further solvents to the solution. This allows for the in situ formation of a neutral, trigonal planar Pd (0) complex [Pd(ligand)(dba)].

After complexation, 175 ml of methyl propionate/methanol mixture (50% by weight methanol, 50% by weight methyl propionate) was degassed and added to the flask. Addition of methane sulfonic acid (MSA), 210µl, completed the preparation of the catalyst solution. The final composition of the solution is approximately 70 wt% methylpropionate, 30wt% methanol. At this stage, in examples 1-3, 10g of phenol or the particular enhancer compound is added, and the mixture left to stir for a few minutes to dissolve any residual solid.

The catalytic solution was added to the pre-evacuated autoclave and heated to 100°C. The autoclave was then pressured with 8 bars of ethene above vapour pressure giving a total pressure of 10.2 bars at 100°C. Next the autoclave was pressured to 12.2 bars with addition of CO:

ethene (1:1 gas) charged from a 10 litre reservoir. A regulatory valve ensures that the pressure of the autoclave is maintained throughout the reaction at 12.2bars through constant injection of gas from the 10 litre reservoir. The pressure of the reservoir as well as the reactor temperature were logged throughout the reaction period of 3 hrs. At the end of the 3 hour run the autoclave was cooled and depressurised. The solution was removed into a pre-weighed bottle and the weight of solution removed was calculated. The weight gain across the course of the 3 hour run was then calculated by subtracting the weight of solution removed from the weight of solution added to the autoclave.

The moles produced at any point in either reaction are calculated from the drop in reservoir pressure by assuming ideal gas behaviour and 100% selectivity for methyl propionate, which allowed reaction TON and rate to be obtained. The results are shown in Table 1.

Table 1

Example	Compound Additive	Gas Uptake (10 L res.) (bar)	Max. TON	Weight Gain (g)
1	Phenol (comp)	2.53	81852	19.6
2	4-Cyanophenol	4.43	159580	41.8
3	2-Fluorophenol	3.3	118783	26.9

Accordingly, low pKa enhancer compounds having a pKa less than that of phenol give a greater improvement in catalyst TON.

Examples 4-9

The solutions for catalyst testing were prepared using standard Schlenk line techniques. In a nitrogen purge glove box, 7.8mg (1.12×10^{-5} moles) of Pd_2dba_3 and 7.5 equivalents of phosphine ligand 1 (L-L) = 1,2-bis(di-tert-butylphosphinomethyl)benzene 33.3mg (8.44×10^{-5} moles) were weighed into a 500ml round bottom flask. The flask was then transferred to a Schlenk line. The ligand and palladium were then dissolved in 125 ml of degassed methyl propionate. In order to aid complexation, the palladium and ligand were dissolved initially in methyl propionate and stirred for a period of 45 minutes, before addition of further solvents to the solution. This allows for the in situ formation of a neutral, trigonal planar Pd (0) complex [Pd(ligand)(dba)].

After complexation, 175 ml of methyl propionate/methanol mixture (50% by weight methanol, 50% by weight methyl propionate) was degassed and added to the flask. Addition of methane sulfonic acid (MSA), 420µl, completed the preparation of the catalyst solution. The final composition of the solution is approximately 70 wt% methylpropionate, 30wt% methanol. At this stage, an amount ranging from 0 to 53g of cyano-phenol is added, and the mixture left to stir for a few minutes to dissolve any residual solid. In this set of experiments, the cyanophenol was further purified by recrystallisation before use.

The catalytic solution was added to the pre-evacuated autoclave and heated to 100°C. The autoclave was then pressured with 8 bars of ethene above vapour pressure giving a total pressure of 10.2 bars at 100°C. Next the autoclave was pressured to 12.2 bars with addition of CO: ethene (1:1 gas) charged from the 10 litre reservoir. A

regulatory valve ensures that the pressure of the autoclave is maintained throughout the reaction at 12.2bars through constant injection of gas from the 10 litre reservoir. The pressure of the reservoir as well as the reactor temperature were logged throughout the reaction period of 3 hrs. At the end of the 3 hour run the autoclave was cooled and depressurised. The solution was removed into a pre-weighed bottle and the weight of solution removed was calculated. The weight gain across the course of the 3 hour run was then calculated by subtracting the weight of solution removed from the weight of solution added to the reaction.

The moles produced at any point in either reaction are calculated from the drop in reservoir pressure by assuming ideal gas behaviour and 100% selectivity for methyl propionate, which allowed reaction TON and rate to be obtained. The results are shown in Table 2.

Table 2

Example	**Amount (g) Cyanophenol**	**Weight %**	**Gas Uptake (bar)**	**Max TON**	**Weight gain (g)**
4 (comp)	0 (Standard)	0 (Standard)	4.68	78862	55.2
5	3	1.1	4.47	75277	50.2
6	10	3.7	6.72	113127	84.0
7	25	8.7	6.32	106379	79.3
8	40	13.2	4.97	83606	54.7
9	53	16.8	4.13	69479	44.9

The optimum amount of enhancer compound is less than 10 wt%

Examples 10-14

This set of comparative experiments was done with different amounts of phenol to see what the optimum amount is to produce the highest gains (with 7.8mg Pd_2dba_3, 33.3mg 1,2-bis(di-tert-butylphosphinomethyl)benzene ligand and 420µl methanesulphonic acid). The following table shows the gas uptakes, turn over numbers and weight gains of the runs. To calculate the weight percentage column in the table, the densities of methyl propionate and methanol are multiplied by their respective solvent amounts to give a final mass of solvent. The mass of phenol used can then be taken as a percentage of the total mass of solvent and phenol combined.

E.g. for 25g Phenol:

MeP density = 0.915
MeOH = 0.791

Mass = Density x Volume

Therefore, Mass of solvents = (0.915 x 200) + (0.791 x 100)

= 262.1 g

Total mass including phenol = 287.1

Therefore, Weight % of phenol = (25 / 287.1) x 100

= 8.7%

The solutions for catalyst testing were prepared using standard Schlenk line techniques. In a nitrogen purge glove box, 7.8mg (1.12×10^{-5} moles) of Pd_2dba_3 and 7.5 equivalents of phosphine ligand 1 (L-L) = 1,2-bis(di-tert-butylphosphinomethyl)benzene 33.3mg (8.44×10^{-5} moles)

were weighed into a 500ml round bottom flask. The flask was then transferred to a Schlenk line. The ligand and palladium were then dissolved in 125 ml of degassed methyl propionate. In order to aid complexation, the palladium and ligand were dissolved initially in methyl propionate and stirred for a period of 45 minutes, before addition of further solvents to the solution. This allows for the in situ formation of a neutral, trigonal planar Pd (0) complex [Pd(ligand)(dba)].

After complexation, 175 ml of methyl propionate/methanol mixture (50% by weight methanol, 50% by weight methyl propionate) was degassed and added to the flask. Addition of methane sulfonic acid (MSA), 420µl, completes the preparation of the catalyst solution. The final composition of the solution is approximately 70 wt% methylpropionate, 30 wt% methanol. At this stage an amount ranging from 0 to 53g of phenol is added, and the mixture left to stir for a few minutes to dissolve any residual solid.

The catalytic solution was added to the pre-evacuated autoclave and heated to 100°C. The autoclave was then pressured with 8 bars of ethene above vapour pressure giving a total pressure of 10.2 bars at 100°C. Next the autoclave was pressured to 12.2 bars with addition of CO: ethene (1:1 gas) charged from the 10 litre reservoir. A regulatory valve ensures that the pressure of the autoclave is maintained throughout the reaction at 12.2 bars through constant injection of gas from the 10 litre reservoir. The pressure of the reservoir as well as the reactor temperature were logged throughout the reaction period of 3 hrs At the end of the 3 hour run the autoclave was cooled and depressurised. The solution was removed into a pre-weighed bottle and the weight of

solution removed was calculated. The weight gain across the course of the 3 hour run was then calculated by subtracting the weight of solution removed from the weight of solution added to the reaction.

The moles produced at any point in either reaction are calculated from the drop in reservoir pressure by assuming ideal gas behaviour and 100% selectivity for methyl propionate, which allowed reaction TON and rate to be obtained. The results are shown in Table 3.

Table 3 Examples 4,10-14

Example	Amount (g)	Weight % phenol	Gas Uptake (bar) - 10L Res	Max TON	Weight gain (g)
4	0 (comp)	0	4.68	78862	55.2
10	3 (comp)	1.1	4.43	74645	59.1
11	10 (comp)	3.7	4.07	68530	54.0
12	25 (comp)	8.7	4.20	70638	61.3
13	40 (comp)	13.2	5.17	87191	68.3
14	53 (comp)	16.8	4.75	79916	58.0

From a comparison of table 2 and table 3 results, the quantity of cyanophenol required to achieve the maximum TON is very much less than the amount of phenol required i.e 3-10 wt% for cyanophenol versus 15-20 wt% for phenol. Furthermore the magnitude of the TON improvement is very much greater for cyanophenol at these lower levels.

Examples 15-18

In this series of experiments we have increased the level of methanesulphonic acid and observed an increase in catalyst performance. However addition of enhancer compound still provides a further increase over and above

any benefit derived from acid. The first set of experiments 15-18 is as per example 4 above but using the specific amount of methane sulphonic acid. In example 4 the ratio of acid:Pd is 578:1 and this corresponds to 420µl. In example 15 the Acid:Pd ratio is 770:1 corresponding to 560µl. In example 16 the Acid:Pd ratio is 1032:1 corresponding to 750µl. In example 17 the Acid:Pd ratio is 1156:1 corresponding to 840µl. In example 18 the Acid:Pd ratio is 1280:1 corresponding to 930µl.

Table 4

Example	Acid Eqivalents	Gas Uptake (bar)	TON (mol Pd / mol MeP)	Weight gain (g)
5	578 eq. Acid	4.68	78862	55.2
15	770 eq. Acid	5.52	92783.8	61.0
16	1032 eq. Acid	5.92	99524.1	60.6
17	1156 eq. Acid	4.87	81936.2	52.6
18	1280 eq. Acid	5.30	89097.7	55.5

The optimum acid level was taken to be 1032 equivalents.

Examples 19

Example 19 was carried out in the same manner as example 6 but with 1032 equivalents of acid (750µl) instead of 578 equivalents (420µl).

Table 5

Examples		Gas Uptake (bar)	TON (mol / mol MeP)	Pd Weight gain (g)
16	1032 Acid	eq.5.92	99524.1	60.6
19	1032 acid w/ 4-Cyanophenol.	eq.8.20 10g	137859.3	85.7

It can clearly be seen that the benefit from adding the cyanophenol is observed over and above any benefit gained from increasing acid levels.

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 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 process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

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.

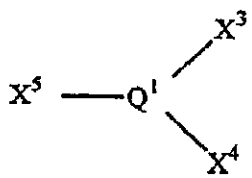
The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of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

CLAIMS

1. A process for the carbonylation of an ethylenically unsaturated compound comprising the step of reacting said compound with carbon monoxide in the presence of a co-reactant having a mobile hydrogen atom and a catalyst system, the catalyst system obtainable by combining:

(a) a metal of Group 8, 9 or 10 or a suitable compound thereof selected from Ru, Pt or Pd;

(b) a ligand of general formula (I)



(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; and

c) optionally, a source of anions;

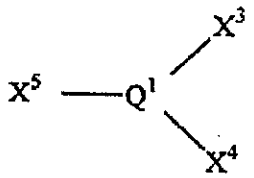
characterised in that the catalyst system includes an enhancer compound comprising an aromatic ring or ring system substituted by at least one hydroxyl group wherein the hydroxyl group pKa at 25°C is greater than 3.0 and

less than 9.1, the said enhancer compound excluding 3-quinolinol.

2. A catalyst system for carbonylation of an ethylenically unsaturated compound, the catalyst system obtainable by combining:

(a) a metal of Group 8, 9 or 10 or a suitable compound thereof selected from Ru, Pt or Pd;

(b) a ligand of general formula (I)



(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; and

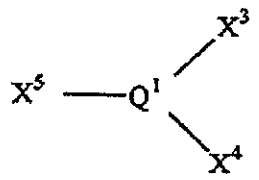
c) optionally, a source of anions;

characterised in that the catalyst system includes an enhancer compound comprising an aromatic ring or ring system substituted by at least one hydroxyl group wherein the hydroxyl group pKa at 25°C is greater than 3.0 and less than 9.1, the said enhancer compound excluding 3-quinolinol.

3. A method of increasing the efficacy of a catalyst system for the carbonylation of ethylenically unsaturated compounds using carbon monoxide in the presence of a co-reactant, the catalyst system obtainable by combining

(a) a metal of Group 8, 9 or 10 or a suitable compound thereof selected from Ru, Pt or Pd;

(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; and

c) optionally, a source of anions;

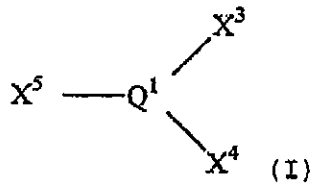
characterised in that the method includes the step of adding an enhancer compound comprising an aromatic ring or ring system substituted by at least one hydroxyl group wherein the hydroxyl group pKa at 25°C is greater than 3.0 and less than 9.1.

4. A method of increasing the rate of carbonylation of an ethylenically unsaturated compound in a reaction with

carbon monoxide in the presence of a co-reactant using a catalyst system obtainable by combining

(a) a metal of Group 8, 9 or 10 or a suitable compound thereof selected from Ru, Pt or Pd;

(b) a ligand of general formula (I)



(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;

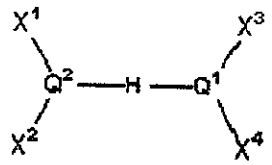
Q^1 represents phosphorus; and

c) optionally, a source of anions;

the said method comprising the step of adding a rate enhancer compound comprising an aromatic ring or ring system substituted by at least one hydroxyl group wherein the hydroxyl group pKa at 25°C is greater than 3.0 and less than 9.1.

5. A process, catalyst system or method according to any of claims 1-4, wherein the amount of enhancer compound in the reaction composition is 0.1-15% w/w.

6. A process, catalyst system or method according to any of claims 1-4, wherein the phosphine ligand is a bidentate ligand of formula II



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 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

Q^1 and Q^2 each independently represent phosphorus.

7. A process, catalyst system or method according to any of claims 1-6, wherein suitable enhancer compounds are selected from compounds having an aromatic ring or ring system which is further substituted with, in addition to the hydroxyl group, an electron withdrawing group.

8. A process, catalyst system or method according to claim 7, wherein the electron withdrawing groups are

selected from cyano, halide, nitrile, nitro, carbonyl, -COOH, -C(O)H , -C(O)R, -COOR, -C(O)Cl, $-CF_3$, $-SO_3H$, $-NH^+_3$, and $-NR^+_3$ groups.

9. A process, catalyst system or method according to any of claims 7 or 8, wherein further substitution is on the same ring as that to which the at least one -OH group is attached and at the ortho or para positions of the ring with respect to at least one -OH group.

10. A process, catalyst system or method according to any of claims 1-9, wherein suitable enhancer compounds are selected from p-cyano-phenol, o-cyano-phenol, p-nitro-phenol, o-nitro-phenol, m-nitro-phenol, p-chloro-phenol, o-chloro-phenol, p-bromo-phenol, o-bromo-phenol, p-hydroxy-benzylic acid, o-hydroxy-benzylic acid, o-hydroxy-benzaldehyde, p-hydroxy-benzaldehyde, p-hydroxy-benzenesulphonic acid , and N-phenol quarternary ammonium derivatives.

11. A process, catalyst system or method according to any of claims 1-10, wherein formula I is a bidentate ligand of general formula (IV)

$$X^1(X^2)- Q^2 - A - R- B - Q^1 - X^3(X^4) \qquad \text{(IV)}$$

wherein:

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

R represents a cyclic hydrocarbyl structure to which Q^1 and Q^2 are linked, via the said linking group, on

available adjacent cyclic atoms of the cyclic hydrocarbyl structure; and

Q^1 and Q^2 each independently represent phosphorus.

12. A process, catalyst system or method according to claim 11, wherein 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.

13. A process, catalyst system or method according to any of claims 1-12, wherein examples of unsubstituted aromatic bridged bidentate ligands of formula I 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-(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-phospha-cyclohexan-4-one) benzene, 1-(tert-butyl,adamantylphosphinomethyl)-2-(di-adamantylphosphinomethyl)benzene, 1-[(P-(2,2,6,6,-tetramethyl-phospha-cyclohexan-4-one)methyl)]-2-(phospha-adamantyl)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-phospha-adamantylmethyl)ferrocene, 1,2-bis-α,α-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))dimethylferrocene, and 1-(di-tert-butylphosphinomethyl)-2-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))ferrocene and 1,2-bis(1,3,5,7-tetramethyl-6,9,10-trioxa-2-phospha-adamantylmethyl)benzene; 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;

wherein examples of suitable substituted non-aromatic bridged bidentate ligands includecis-1,2-bis(di-t-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-trioxa-adamantyl)-4,5-dimethylcyclohexane; cis-1,2-bis(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) 5-methylcyclopentane; cis-1,2-bis(di-adamantylphosphinomethyl)-4,5 dimethylcyclohexane; cis-1,2-bis(di-adamantylphosphinomethyl)-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-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-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-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-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-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)-[1S,2R]cyclohexylmethyl]-P-2,2,6,6- tetramethyl-phospha-cyclohexan-4-one;

wherein examples of suitable non-substituted non-aromatic bridged bidentate ligands include cis-1,2-bis(di-t-butylphosphinomethyl)cyclohexane; cis-1,2-bis(di-t-butylphosphinomethyl)cyclopentane; cis-1,2-bis(di-t-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-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-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-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-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- 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-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-(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-{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-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)-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-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);

and wherein examples of substituted aromatic bridged ligands in accordance with the invention include- 1,2-bis(di-t-butylphosphinomethyl)-4,5-diphenyl benzene; 1,2-bis(di-t-butylphosphinomethyl)-4-phenylbenzene; 1,2-bis(di-t-butylphosphinomethyl)-4,5- bis-(trimethylsilyl) benzene; 1,2-bis(di-t-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-t-butylphosphinomethyl)-4,5-diphenylbenzene; 1- (P,P adamantyl,

t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4-phenylbenzene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4,5- bis-(trimethylsilyl)benzene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4-(trimethylsilyl)benzene; 1- (2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxa-adamantyl) - 2 - (di-t-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; 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-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-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)-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-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-(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-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-(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-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-(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-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) 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-(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-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'-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-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) 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'-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-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-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-(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-(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-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'-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-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-(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-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'-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-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) 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-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) 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-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-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)-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-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-(ditertbutylphosphinomethyl)-2-(P-(2,2,6,6- tetramethyl-phospha-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)-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-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-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) 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-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-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-(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-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-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-(or 1')(trimethylsilyl) ferrocene; 1,2-bis-perfluoro(2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl)-4,5-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-(or 1')phenyl 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; 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-(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'-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-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-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-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-(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- (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-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- (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-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-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-(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-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-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'-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'-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-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-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-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 ferrocene.

14. A catalyst system, process or method according to any preceding claim, wherein the ethylenically unsaturated compound includes 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.

15. A process for the carbonylation of ethylenically unsaturated compounds as hereinbefore described and with reference to the examples.

16. A catalyst system as hereinbefore described and with reference to the examples.

17. A method of increasing the efficacy of a catalyst system as hereinbefore described and with reference to the examples.

18. A method of increasing the rate of carbonylation of an ethylenically unsaturated compound as hereinbefore described and with reference to the examples.