A Continuous Process for the Carbonylation of Ethylene

This invention relates to an improved continuous process for the carbonylation of ethylene, in particular, a method providing an improved turnover number (TON) for the catalyst system employed in the carbonylation.

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.

EP0970038A1 discloses a liquid phase reaction using carbon monoxide and a catalyst system for the carbonylation of ethylene. The gas phase ratio of ethylene:CO is held above 1:1. The preferred range is 7:1 to 15:1 which is said to improve the TON of the catalyst. At the same time the ethylene:CO incoming gas feed is taught at 1:1 to replenish the ethylene and carbon monoxide consumed in the

reaction. However, it has now been surprisingly found that in a continuous process a higher gas phase ratio and a higher feed rate gives an even further improvement in the TON.

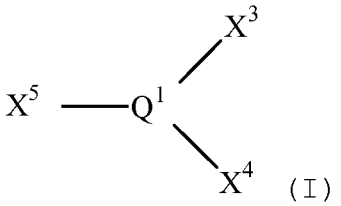
According to a first aspect of the present invention there is provided a continuous process for the carbonylation of ethylene in a liquid phase using carbon monoxide in the presence of a co-reactant having a mobile hydrogen atom and a suitable catalyst system comprising the steps of:-

(i) forming a liquid phase comprising the co-reactant having a mobile hydrogen atom and the suitable catalyst system;

the catalyst system obtainable by combining:

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

(b) a ligand of general formula (I)



(I)

wherein

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

Q^1 represents phosphorus, arsenic or antimony; and

c) optionally, a source of anions;

(ii) forming a gaseous phase in contact with the liquid phase by providing at least an ethylene gas input feed stream and a carbon monoxide gas input feed stream wherein the ethylene:CO molar ratio entering the liquid phase from the input feed streams is greater than 2:1;

(iii) reacting ethylene with carbon monoxide in the presence of the co-reactant, and of the suitable catalyst system in the liquid phase;

wherein the ethylene:CO gas molar ratio in the gaseous phase is between 20:1 and 1000:1.

By continuous is meant that the reaction process continues beyond that of a simple batch reaction where a batch of reactants and catalyst are allowed to react to completion without further reactant or catalyst input either with or without removal of product during the reaction. In a continuous reaction, one or more of the reactants may be fed continuously so that the reaction can continue for at least as long as the catalyst does not need replenishment but may also extend to the situation where degraded catalyst is replenished as the reaction proceeds and, in either case, also includes removal of the product from the reactor as the reaction proceeds.

Preferably, the catalyst is replenished as the reaction proceeds, more preferably, the catalyst concentration is generally maintained throughout the continuous reaction so

that the rate of addition matches the rate of catalyst decay. In addition, it is preferred that the reactants are fed continuously to the reactor. Further, it is preferred that the product is continuously removed from the reactor. Further, it is preferred that the unreacted reactant gases are continuously recycled back into the reactor. Still, further it is preferred that the unreacted liquid reactants are continuously recycled back to the reactor.

Preferably, the ethylene and carbon monoxide input feed streams are combined into a single input feed stream prior to contact with the liquid phase and therefore the ethylene:CO molar ratio in the single combined input feed stream is greater than 2:1. However, if the input feed streams are fed into the liquid phase separately then they preferably do so simultaneously to achieve the required input ratio continuously.

Gas Phase Reactant Ratios

The reactor includes provision for a gaseous phase. Typically, a headspace above the liquid phase is provided to allow the establishment of a headspace gaseous phase in the reactor.

Preferably, the ethylene:CO gas molar ratio in the gaseous phase of the reactor is between 40:1 and 200:1, more preferably between 55:1 and 150:1, optionally, between 25:1 and 49:1. Typically, the ethylene:CO gas molar ratio in the reactor is either between 30:1 and 49:1 or 51:1 and 150:1. In any case, a gas phase molar ratio of ethylene:CO

of 50:1 in the reactor may be excluded from the scope of the invention.

Preferably, in a continuous process according to the present invention, the gas phase ethylene and CO are recycled back into the liquid phase of the reactor via the input feed stream, typically, more than 40% by volume of the ethylene and CO are recycled back into the liquid phase of the reactor, more typically, more than 50% by volume of the ethylene and CO are recycled back into the liquid phase of the reactor, most typically, 60% by volume of the gas phase ethylene and CO is recycled back into the liquid phase of the reactor.

Feed Stream Reactant Ratios

Preferably, the ethylene:CO molar ratio in the gaseous input feed stream(s) of the reactor (including any recycled ethylene and CO) is between 2:1 and 20:1, more preferably, between 2:1 and 10:1, most preferably, between 3:1 and 6:1, especially, 4:1. Typically, the gas feed stream is introduced directly into the liquid phase.

Liquid Phase Reactant Ratios

Advantageously, by feeding the gas ratio of ethylene:CO claimed into the liquid phase and holding the gas phase above the liquid phase in the reactor at the claimed ratio, the amount of CO in the liquid phase is dramatically lowered which leads to a surprisingly increased TON. However, in a continuous process it is not easy to determine the ethylene:CO ratio in the liquid phase because any analysis in real-time is compromised by the reaction proceeding during the course of the analysis.

Nevertheless, by the use of Henry's constant and the partial pressure in the gas phase, it is possible to calculate the liquid phase concentration of CO. On this basis, preferably, the ethylene:CO molar ratio in the liquid phase is between 10:1 and 1000:1.

Preferably, the gaseous feed stream is directed into the liquid phase for reaction and after passing therethrough, any unreacted gases enter the gas phase which eventually stabilises to be in equilibrium with the liquid phase.

Preferably, the molar ratio of ethylene:CO in the liquid phase is greater than 10:1, more preferably, greater than 20:1 and most preferably greater than 30:1 with, in any case, an optional upper limit of 1000:1. A preferred molar ratio of ethylene:CO in the liquid phase is 30:1 to 600:1, more preferably, a molar ratio of 50:1 to 300:1, most preferably, a molar ratio of 75:1 to 300:1.

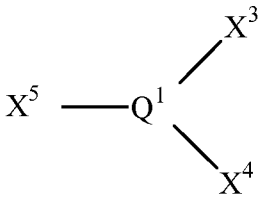
Therefore, according to a further aspect of the present invention there is provided a continuous process for the carbonylation of ethylene in a liquid phase using carbon monoxide in the presence of a co-reactant having a mobile hydrogen atom and a suitable catalyst system comprising the steps of:-

(i) forming a liquid phase comprising the co-reactant having a mobile hydrogen atom and the suitable catalyst system;

the catalyst system obtainable by combining:

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

(b) a ligand of general formula (I)



(I)

wherein

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

Q^1 represents phosphorus, arsenic or antimony; and

c) optionally, a source of anions;

(ii) forming a gaseous phase in contact with the liquid phase by providing at least an ethylene gas input feed stream and a carbon monoxide gas input feed stream to the liquid phase;

(iii) reacting ethylene with carbon monoxide in the presence of the co-reactant, and of the suitable catalyst system in the liquid phase;

wherein the molar ratio of ethylene:CO in the liquid phase is greater than 10:1.

Preferably, the ethylene:CO molar ratio entering the liquid phase from the input feed streams is greater than 2:1. Preferably, the ethylene:CO gas molar ratio in the gaseous phase is between 20:1 and 1000:1.

The liquid phase compositions of CO and Ethylene have been determined using an equilibrium flash calculation. This calculation accounts for non-ideality in the liquid phase by the UNIQUAC activity coefficient model, and non-ideality in the vapour phase by the Redlich Kwong equations of state. Parameters in these models have been experimentally measured (including the Henry constants for CO and Ethylene) for the components of interest.

Other Gases

The carbon monoxide or ethylene may be used in the presence of other gases which are generally inert in the in the reaction. Suitable gases include hydrogen, nitrogen, carbon dioxide, ethane and methane or any of the noble gases such as argon.

The level of any such inert gas in the gaseous phase is between 0-75% by volume, more typically, 5-70% by volume, most typically, 15-35% by volume.

Typically, the ethylene, CO and optional inert or other gases are initially introduced into the liquid phase by the gas feed stream.

Gas Mixing

Preferably, the liquid phase is well mixed during the reaction. A preferred type of mixing is achieved using a

dual impeller mixer which mixes in two opposed directions in the reactor so that forward flow and back flow are achieved simultaneously.

Dual impeller systems for dispersing a gas in a liquid, in a vessel are known. Specifically, in a paper by Kuboi, entitled "The Power Drawn by Dual Impeller Systems Under Gassed and Ungassed Conditions" Fourth European Conference on Mixing, April 27-29 1982, the combination of two axially spaced 45° pitched blade turbines is disclosed whereby a first impeller is mounted below a second impeller on a common shaft. The impeller blades are orientated such that the first impeller projects liquid upwards and outwards and the second impeller projects liquid downwards and outwards. Under gassed conditions, as gas is introduced into the vessel, the first impeller causes the incoming flow of gas bubbles to split so that some of the flow is driven radially outwards towards the walls of the vessel, and some is driven axially upwards towards the second impeller.

The effectiveness of the two impeller system under gassing conditions depends upon the speed of rotation of the impellers. At lower speeds it is possible that the bubbles that have been projected upwards by the first impeller are not affected by the second impeller. The second impeller is unable to overcome buoyancy forces and therefore the second impeller plays no part in the dispersion of gas in the liquid. Only when the rotational speed of the second impeller is increased are the buoyancy forces overcome, disadvantageously, non-uniform dispersion of the gas in the liquid results. This is shown in Figure 1 of the application. In order to achieve uniform dispersion,

further disadvantageously, the rotational speed of the second impeller has to be sharply increased.

It is highly desirable to be able to achieve complete uniform dispersion in an industrial process. In industrial processes where gas/liquid mass transfer is an essential feature, this aids controllability and enhances reactor performance. In such processes, when the gas is well dispersed, a region of reasonably uniform turbulent

kinetic eddy dissipation can exist in the liquid between and around the impellers which controls coalescence and breakup of the bubbles. If the gas dispersion is highly non-uniform, undesirable coalescence can result in a sharp increase in bubble size and therefore, the surface area for interface mass transfer to occur is reduced. Advantageously, a controlled turbulent kinetic energy dissipation field results in a narrow bubble size distribution over a range of impeller specific powers.

Preferably, therefore, the present invention includes a mixing apparatus which enables controllable mixing of fluids or solids whilst simultaneously providing an effective mixing environment.

Preferably, the mixing apparatus for mixing the fluids of the present invention in the reactor comprises a shaft rotatable about its longitudinal axis, a first and a second radially extending impeller mounted on the shaft in the liquid phase and respectively axially spaced apart, the first impeller comprising a plurality of curved blades operable to move said fluids in an axial direction towards the second impeller, and the second impeller comprises a

plurality of curved blades operable to move said fluids in an axial direction towards the first impeller.

Preferably, the blades on each impeller are inward pumping into the space between the impellers. In the case of a typical substantially vertical shaft, the lower impeller is, therefore, upward pumping and the upper impeller is downward pumping. Preferably, the blades of each impeller are hydrofoil blades. A suitable hydrofoil blade is the Chemineer Maxflo™ W. Alternatively, the Lightnin A315™, A320™ or A340™ may be used.

Obviously, the fluids of the present invention to be mixed in the liquid phase comprise a liquid and a gas.

Preferably, the first impeller and the second impeller each comprise two or more curved blades, more preferably, three or more curved blades. Most preferably, are impellers with four curved blades. The provision of an impeller with a large number of curved blades increases the shear forces acting to break up large bubbles. The small bubbles produced have a smaller average bubble diameter than those produced with a first impeller and/or a second impeller with fewer curved blades and therefore, the available surface area for a reaction to occur is increased.

Preferably, the diameter of the first impeller is the same as the diameter of the second impeller. Preferably, the diameter of each impeller is substantially half the diameter of the reaction vessel in which said impeller is mounted.

Preferably, the axial distance between the first impeller and the second impeller is at least one impeller diameter apart. In this configuration, the turbulence created by the opposing impellers is an equilibrium in the central mixing zone which allows for prediction of bubble size and therefore control of the reaction occurring.

It is preferable that the total power drawn by the combination of impellers is low. Preferably, the impellers operate at a low power number, preferably substantially between 1 to 5, more preferably, substantially between 1 to 3, most preferably substantially 1.75. In so doing, the system consumes less energy than conventional systems which operate at power numbers of typically 3.2. The power may be measured using conventional equipment, for example, strain gauges.

Preferably, when operating at a low power number complete uniform dispersed phase distribution is achieved. This is highly desirable and is because of the energy efficiency of the blades, preferably hydrofoil blades.

Preferably, the specific power used when the first impeller and the second impeller rotate is substantially between $50W/m^3$ to $900W/m^3$, more preferably, substantially between $100W/m^3$ to $800W/m^3$.

Preferably, when dual opposed Maxflo type impellers are used in the system, the preferred specific power is substantially between $50W/m^3$ to $900W/m^3$. Preferably, when BT-6 type impellers are used, the preferred specific power

is substantially between 400W/m^3 to 3200W/m^3. At such specific powers, a narrow bubble size distribution is maintained and the reaction is controlled.

Preferably, when dual opposed Maxflo impellers are used, the arithmetic mean size (d_{10}) is substantially between 250µm to 550µm and the surface volume mean diameter (d_{32}) is substantially between 400µm to 750µm. Preferably, when operating at substantially 750rpm, the d_{10} is substantially between 250µm to 350µm, most preferably substantially 296µm, and preferably, the d_{32} is substantially between 400µm to 500µm, most preferably substantially 450µm. Preferably, when operating at substantially 991rpm, the d_{10} is substantially between 300µm to 400µm, most preferably substantially 330µm, and preferably, the d_{32} is substantially between 460µm to 560µm, most preferably substantially 510µm. Preferably, when operating at substantially 1200rpm, the d_{10} is substantially between 350µm to 450µm, most preferably substantially 394µm, and preferably, the d_{32} is substantially between 450µm to 550µm, most preferably substantially 500µm.

Preferably, when BT-6 type impellers are used, the d_{10} is substantially between 250µm to 1500µm. Particularly, when operating at substantially 251rpm, preferably the d_{10} is substantially between 550µm to 650µm, most preferably substantially 633µm, and the d_{32} is preferably substantially between 800µm to 1000µm, most preferably substantially 978µm. Preferably, when operating at substantially 380rpm, the d_{10} is preferably substantially between 800µm to 900µm, most preferably substantially 841µm, and the d_{32} is preferably substantially between

1000µm to 1500µm, most preferably substantially 1345µm. At substantially 500rpm, the d_{10} is preferably substantially between 500µm to 600µm, most preferably substantially 597µm, and the d_{32} is preferably substantially between 700µm to 800µm, most preferably substantially 721µm. Preferably, when operating at substantially 765rpm, the d_{10} is preferably substantially between 300µm to 400µm, most preferably substantially 378µm, and the d_{32} is preferably substantially between 400µm to 500µm, most preferably substantially 445µm.

In the reactor the gas is sparged into an agitated liquid medium, preferably, the sparged gas rate is substantially between 0.05 to 1.0 m^3/s, preferably substantially between 0.1 to 0.5m^3/s, most preferably substantially 0.13m^3/s at an impeller speed of preferably between 50rpm to 1200rpm, most preferably substantially 50rpm to 200rpm.

The critical dispersion speed for achieving dispersion in a dual opposed flow hydrofoil system in a vessel having a diameter of preferably substantially between 1 to 10m, more preferably, substantially between 2 to 5m, is preferably substantially between 1 to 100rpm, preferably substantially between 5 to 50rpm, more preferably substantially between 10 to 20rpm, most preferably substantially 14rpm.

Ligands

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).

CO-REACTANT

The ratio (v/v) of ethylene and co-reactant in the reaction can vary between wide limits and suitably lies in the range of 10:1 to 1:500.

The co- reactant of the present invention may be any compound other than water having a mobile hydrogen atom, and capable of reacting as a nucleophile with ethylene under catalytic conditions. The chemical nature of the co-reactant determines the type of product formed. Possible co-reactants are carboxylic acids, alcohols, ammonia or amines, thiols, or a combination thereof.

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

In the above-defined co-reactants, R^{81} R^{82} and/or R^{83} represent alkyl, alkenyl or aryl groups which may be unsubstituted or may be substituted by one or more substituents selected from halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, 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 dialkylsilicon groups.

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

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, 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. 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 ethylene comprising contacting ethylene with carbon monoxide and a co-reactant. The co-reactant is more preferably an organic molecule having a hydroxyl functional group such as an alkanol.

Suitably, as mentioned above, the co-reactant preferably includes an organic molecule having a 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, including aryl alcohols, 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, phenol, 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. 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 ethylene double bond.

SOLVENTS

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

Suitable solvents for use in the present invention include ketones, such as for example methylbutylketone; ethers,

such as for example anisole (methyl phenyl ether), 2,5,8-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, 76th

edition, edited by David R. Lide et al, and published by CRC press in 1995, and are usually quoted for a temperature of about 20°C or 25°C, i.e. about 293.15k or 298.15 K, and atmospheric pressure, i.e. about 1 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. A particularly preferred aprotic solvent is methyl propionate.

Alternatively, a protic solvent other than water 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 lower alcohols, such as, for example, methanol, ethanol and isopropanol, and primary and secondary amines, particularly methanol. Mixtures of the aprotic and protic co-solvents may also be employed both initially and when generated by the reaction itself, particularly methyl propionate and methanol.

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.

Metal

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.

Anion

Suitable compounds of such Group 8, 9 or 10 metals include salts of such metals with, or compounds comprising weakly coordinated anions derived from, nitric acid; sulphuric acid; lower alkanoic (up to 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.

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

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

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

Generally, for ethylene which is 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 Group 8, 9 or 10 metal/compound to anion may be from 1:2 to 1:4000, more preferably, 1:2 to 1:1000, most preferably, 1:5 to 1:200, especially, 1:10 to 1:200. 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.

Carbonylating Agent and Process Conditions

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

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

The molar ratio of the amount of ethylene used in the reaction to the amount of solvent (when present) may vary between wide limits, e.g. from 1:1 to 1:1000 mol/mol. Preferably, the molar ratio of the amount of ethylene used in the reaction to the amount of solvent is between 1:5 and 1:500 , more preferably, 1:10 and 1:100. For the avoidance of doubt, such solvent includes the reaction product and co-reactant.

The amount of the catalyst of the invention used in the carbonylation reaction is not critical. Good results may be obtained, preferably when the amount of Group 8, 9 or 10 metal is in the range 1 x 10^{-7} to 10^{-1} moles per mole of ethylenically unsaturated compound, more preferably, 1 x 10^{-6} to 10^{-1} moles, most preferably 1 x 10^{-6} 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 1 x 10^{-6} to 10^{-1}, more preferably, 1 x 10^{-6} to 10^{-1}, most preferably, 1 x 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.

Preferably, the carbonylation is carried out at a CO partial pressure in the reactor of between 0.01 x 10^{5} N.m^{-}

^{2}-2 x 10^{5}N.m^{-2}, more preferably 0.02 x 10^{5} N.m^{-2}-1 x 10^{5}N.m^{-2}, most preferably 0.05-0.5 x 10^{5} N.m^{-2}. Especially preferred is a CO partial pressure of 0.1 to 0.3 x 10^{5}N.m^{-2}.

High ligand to group 8, 9 or 10 metal ratios are generally used to improve turnover number on metal. However, the high TON found by use of the gas ratios in the present invention allows much lower ligand ratios to be used. This has important commercial benefits as high ligand ratios can result in increased ligand degradation and increased cost. Accordingly, in the present invention, the ligand to metal molar ratio in the liquid phase is typically between 1:1 and 2:1. Nevertheless, the mole ratio of ligand to group 8, 9 or 10 metal for a bidentate ligand can still be between 1:1 and 100:1, more preferably, 1:1 to 50:1, most preferably, 1:1 to 20:1. For a monodentate, tridentate, etc ligand the mole ratio is varied accordingly. However, for commercial reasons, as mentioned above, the bidentate ligand to metal ratio is preferably between 1:1 and 2:1.

Preferably, the mole ratio of ligand to acid in the reactor for a bidentate ligand and a monoprotic acid is between 1:2 and 1:2000, more preferably 1:2 to 1:500, most preferably, 1:5 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 1:4000, more preferably, 1:2 to 1:1000, most preferably, 1:5 to 1:200, especially, 1:10 to 1:200.

For the avoidance of doubt, the above ratio conditions are given for the continuous reaction.

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

Suitably, the catalysts of the invention are prepared in a separate step preceding their use in-situ in the 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. Alternatively, the metal and compound of formulas I-IV may be added to the solvent simultaneously or the compound may be dissolved and then the metal may be dissolved subsequently.

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, ethane and methane 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.

In particular, the gaseous phase may be recycled into the gas feed stream which may then be adjusted with fresh supplies of carbon monoxide and ethylene as required to provide the desired input gas feed stream.

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

Support and Dispersant

According to a further aspect, the present invention provides a process for the carbonylation of ethylene 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.

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 re-dispersed 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.

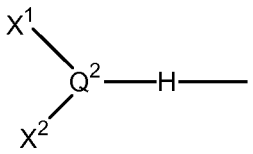
Preferably, the polymer:metal mass ratio in g/g is between 1:1 and 1000:1, more preferably, between 1:1 and 400:1, most preferably, between 1:1 and 200:1. Preferably, the polymer:metal mass ratio in g/g is up to 1000, more preferably, up to 400, most preferably, up to 200.

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. It is especially advantageous that the process of the invention provides a carbonylation reaction with a high TON number.

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.

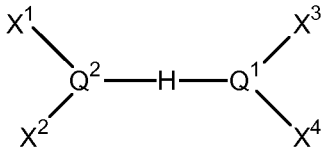
Ligand of General Formula I

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

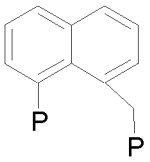
Q^1 and Q^2 each independently represent phosphorus, arsenic or antimony.

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

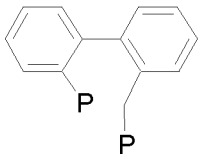
In any case, the bivalent organic bridging group may be an unsubstituted or substituted, branched or linear, cyclic, acyclic or part cyclic aliphatic, aromatic or araliphatic bivalent group having 1-50 atoms in the bridging group and 1-6, more preferably, 2-5, most preferably 3 or 4 atoms in the bridge.

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.

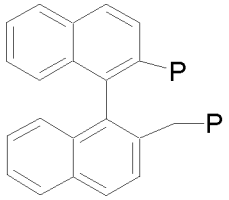
Suitable aliphatic bridging groups include alkylene groups such as 1,2-ethylene, 1-3 propylene, 1,2-propylene, 1,4-butylene, 2,2-dimethyl-1,3-propylene, 2-methyl-1,3-propylene, 1,5-pentylene, $-O-CH_2CH_2-O-$ and $-CH_2-NR-CH_2-$ or partial cycloaliphatic bridges including 1-methylene-cyclohex-2-yl,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

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 optional lower alkylene linking groups;

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

on available adjacent cyclic atoms of the cyclic hydrocarbyl structure; and

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

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

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

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

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

Preferably, the further substituent in the preceding paragraph is a C_1-C_7 alkyl group or O- C_1-C_7 alkyl group, such as a methyl, ethyl, n-propyl, iso-butyl t-butyl , methoxy or ethoxy group or a relatively inert group such as -CN, -F, -Si(alkyl)$_3$, -COOR^{63}, -C(O)-, or -CF_3 wherein R^{63} is alkyl, aryl or Het. Particularly preferred substituents are methyl, ethyl and propyl groups, especially methyl, methoxy or ethyl, more especially, methyl. A preferred range of groups are the C_1-C_7 alkyl, O- C_1-C_7 alkyl substituted phenyl groups, especially, methyl, methoxy or ethyl phenyl groups. In such phenyl embodiments, substitution may be at the ortho, meta or para position, preferably, the ortho or meta position, most preferably, the ortho position of the ring.

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

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

For simplicity, these two types of bridging group R will be referred to as an aromatic bridged cyclic hydrocarbyl structure or a non-aromatic bridged cyclic hydrocarbyl structure irrespective of the nature of any further rings

joined to the at least one ring to which the Q^1 and Q^2 atoms are linked via the linking groups directly.

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

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

The non-aromatic bridged cyclic hydrocarbyl structure, apart from that it may be interrupted with hetero atoms

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

The non-aromatic bridged cyclic hydrocarbyl structure may be selected from cyclohexyl, cyclopentyl, cyclobutyl, cyclopropyl, cycloheptyl, cyclooctyl, cyclononyl, tricyclodecyl, piperidinyl, morpholinyl, norbornyl, isonorbornyl, norbornenyl, isonorbornenyl, bicyclo[2,2,2]octyl, tetrahydrofuryl, dioxanyl, O-2,3-isopropylidene-2,3-dihydroxy-ethyl, cyclopentanonyl, cyclohexanonyl, cyclopentenyl, cyclohexenyl, cyclohexadienyl, cyclobutenyl, cyclopentenonyl, cyclohexenonyl, adamantyl, furans, pyrans, 1,3 dioxane, 1,4 dioxane, oxocene, 7-oxabicyclo[2.2.1]heptane, pentamethylene sulphide, 1,3 dithiane, 1,4 dithiane, furanone, lactone, butyrolactone, pyrone, succinic anhydride, cis and trans 1,2-cyclohexanedicarboxylic anhydride, glutaric anhydride, 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, via the said linking group, if present, on available adjacent cyclic atoms of the at least one ring. Apart from that it may be in the form of a polycyclic structure, the non-aromatic bridged cyclic hydrocarbyl structure may be unsubstituted or substituted with at least one substituent, preferably on at least one further non-adjacent cyclic atom of the at least one ring.

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

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

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.

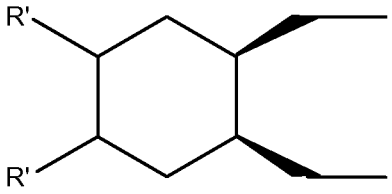
In addition, when S is aryl, the aryl may be substituted with in addition to R^{40}, R^{41}, R^{42} any of the further substituents defined for the non-aromatic bridged structure above.

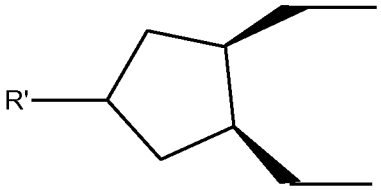
More preferred Y substituents may be selected from t-alkyl or t-alkyl, aryl such as -t-butyl, $-SiMe_3$, or 2-phenylprop-2-yl, -phenyl, alkylphenyl-, phenylalkyl- or phosphinoalkyl- such as phosphinomethyl.

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.

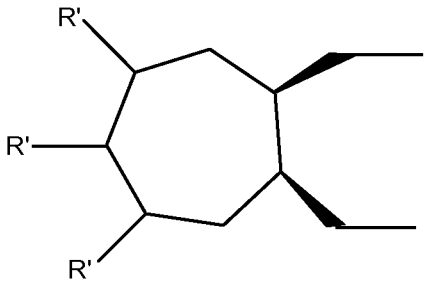
In some embodiments, there may be two or more said Y substituents on further cyclic atoms of the non-aromatic bridged structure. Optionally, the said two or more substituents may combine to form a further ring structure such as a cycloaliphatic ring structure.

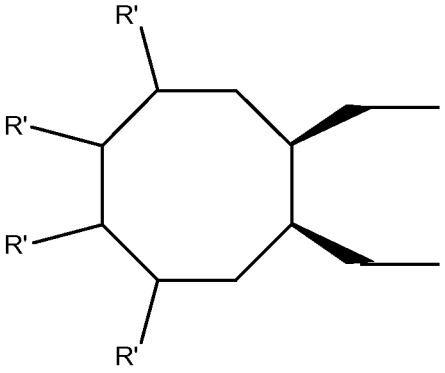
Some typical hydrocarbyl structures are shown below wherein R', R'', R''', R'''' etc are defined in the same way as the substituents on the cyclic atoms above but may also be hydrogen, or represent the hetero atom being non substituted if linked directly to a hetero atom and may be the same or different.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



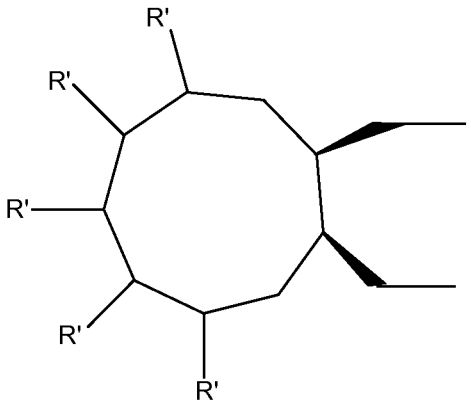


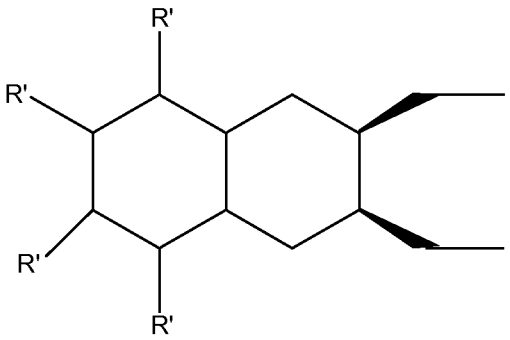
4 and/or 5 substituted cyclohexyl 4 substituted cyclopentyl



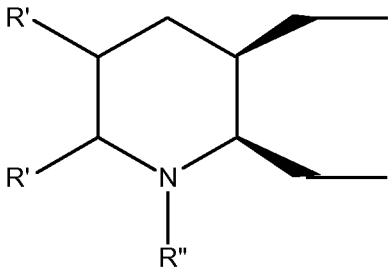


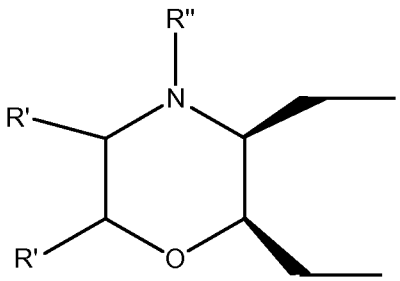
4, 5 and/or 6 substituted cycloheptyl 4, 5, 6 and/or 7 substituted cyclooctyl



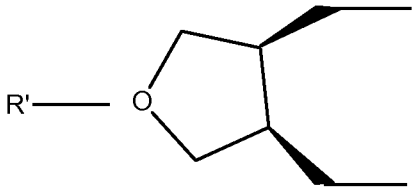


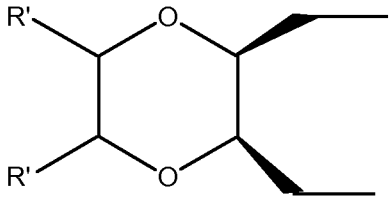
4,5,6,7 and/or 8 substituted cyclononyl 2,3,4 and/or 5 substituted decahydronaphthalene



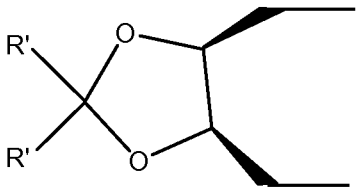


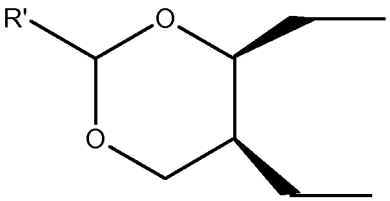
5 and/or 6 substituted piperidines 5 and/or 6 substituted morpholines



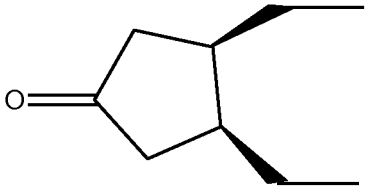


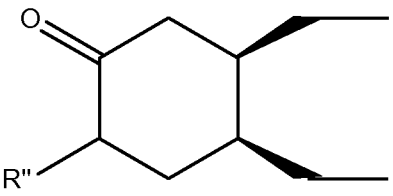
1- Substituted furans 5 and/or 6 substituted 1, 4 dioxane



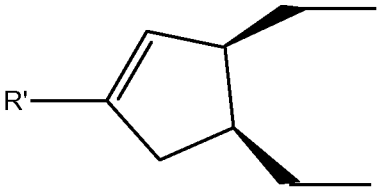


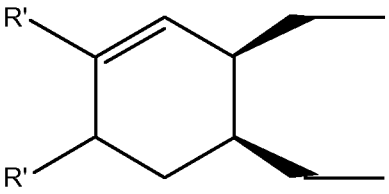
Substituted DIOP 2 - substituted 1, 3 dioxane



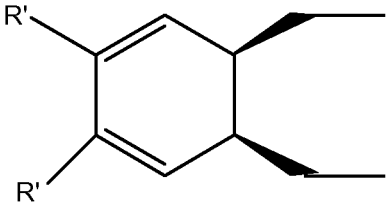


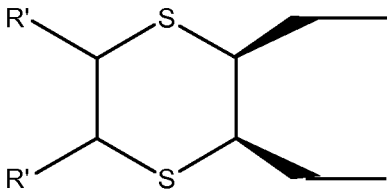
cyclopentanone 6- substituted cyclohexanone



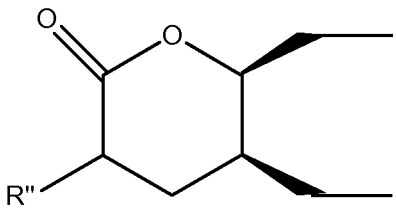


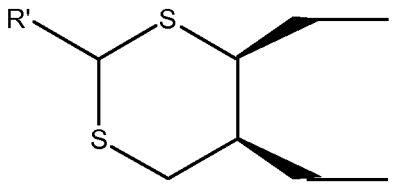
1 - substituted cyclopentenyl 1 and/or 6 - substituted cyclohexenyl



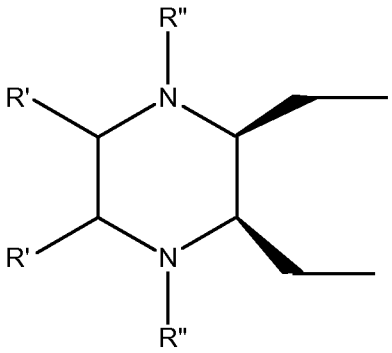


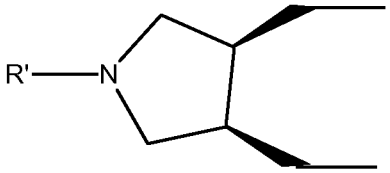
2 and/or 3 substituted cyclohexadienyl 2 and/or 3 substituted 1,4 dithiane



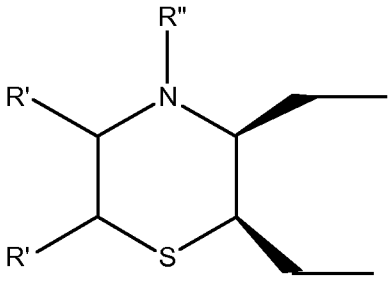


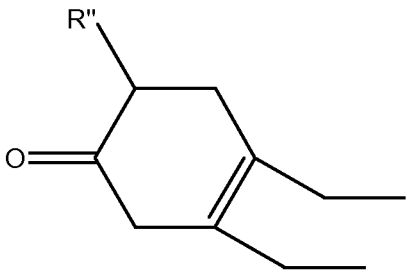
3 - Substituted pyrones 2 - substituted 1, 3 dithiane





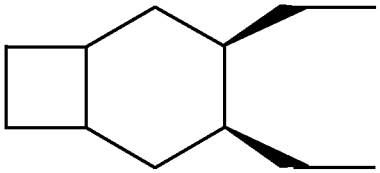
1, 2, 3 , 4 substituted piperizine 1 substituted pyrollidine



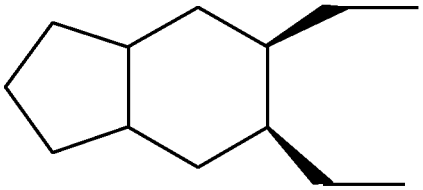


1, 2, 3 substituted thiomorphiline 5 substituted cyclohexen-4-one

55

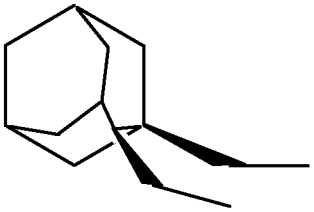


Bicyclo [4.2.0] octane

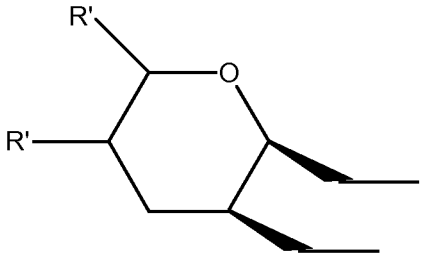


bicyclo [4.3.0] nonane

5

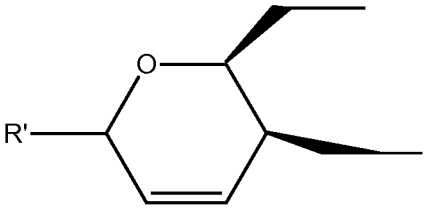


Adamantyl -1,2-diyl

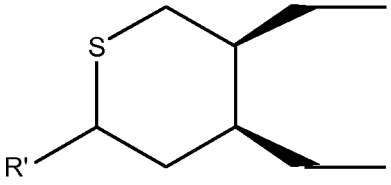


substituted tetrahydropyran

10

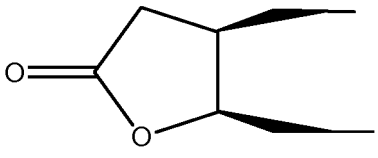


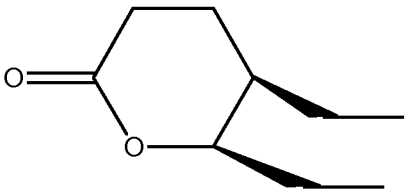
Substituted dihydropyran

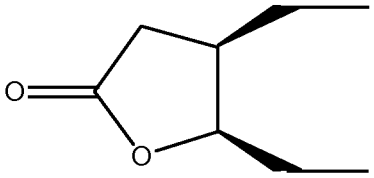
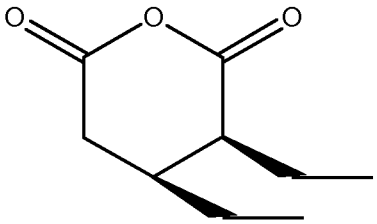
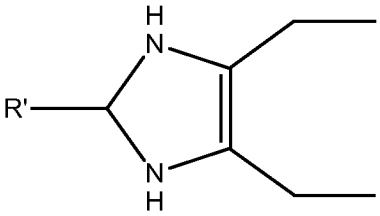
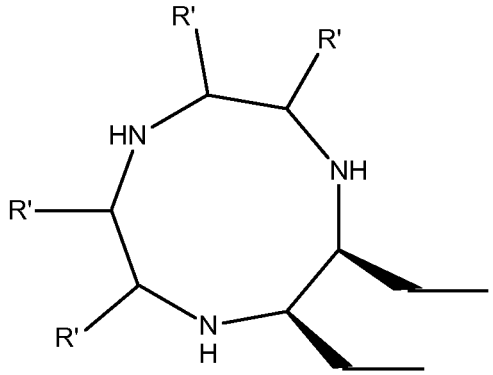


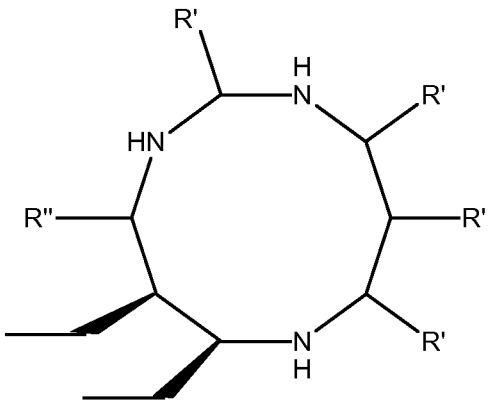
substituted pentamethylene sulphide (substituted tetrahydro-thiopyran

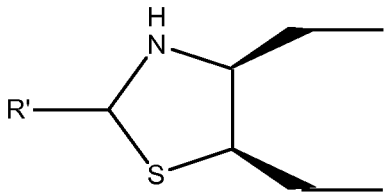
15



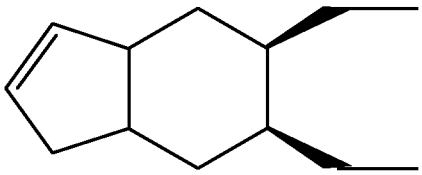


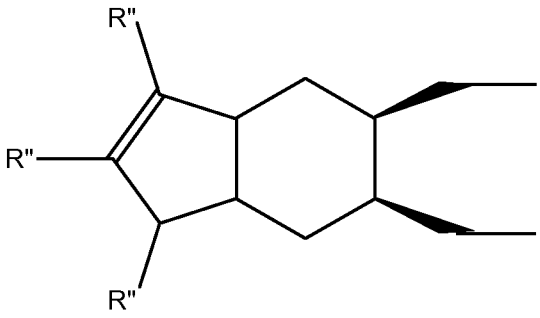
Tetrahydro-furan-2-one	delta-valero lactone
4,5-diyl	
	
gamma-butyrolactone	glutaric anhydride
	
Substituted dihydro imidazole	Substituted 1, 4, 7 triazacyclononane



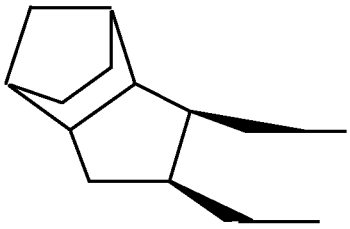


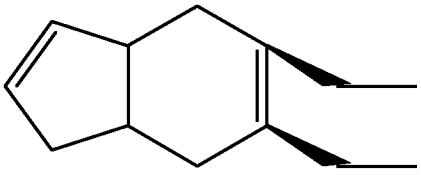
Substituted 1, 5, 9 triazacyclodecane substituted thiazolidine



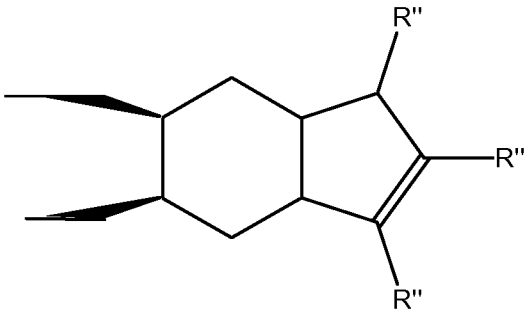


3a,4,5,6,7,7a-hexahydro-1H-indene substituted 3a, 4,5,6,7,7a hexahydro-1H-indene





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

Preferably, each adjacent cyclic atom to the said 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 i.e. 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 $\sum_{X=1-n} tY^x$ of atoms other than hydrogen such that $\sum_{X=1-n} tY^x$ 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 ≤ 10 Y groups i.e. n is 1 to 10, more preferably there are 1-6 Y groups, most preferably 1-4 Y groups on the aromatic structure and, especially, 1, 2 or 3 substituent Y groups on the aromatic structure. The substituted cyclic aromatic atoms may be carbon or hetero but are preferably carbon.

Preferably, when present, $^{X=1-n}\square tY^{x}$ 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 $PHY^{1}Y^{2}$ should be compared with the reference. Similarly, if three Y groups are being compared and PHY^{1} or $PHY^{1}Y^{2}$ 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 (O) 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 Tolman {C. A. Tolman Chem. Rev. 77, (1977), 313-348} except that the apex angle of the cone is now centred at the midpoint of the aromatic ring. This modified use of Tolman cone angles has been used in other systems to measure steric effects such as those in cyclopentadienyl zirconium ethene polymerisation catalysts (Journal of Molecular Catalysis: Chemical 188,(2002), 105-113).

The substituents Y are selected to be of the appropriate size to provide steric hindrance with respect to the active site between the Q^1 and Q^2 atoms. However, it is not known whether the substituent is preventing the metal 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-1,2 diyl, 4-(t-butyldimethylsilyl)-benzene-1,2 diyl, 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-1,2 diyl, 4-(or 1')t-butylsilyl-ferrocene-1,2diyl, 4-(or 1')(tri-t-butylsilyl)-ferrocene-1,2 diyl, 4-(or 1')(2'-tert-butylprop-2'-yl)ferrocene-1, 2 diyl, 4-(or 1')(2',2',3',4',4' pentamethyl-pent-3'-yl)-ferrocene-1, 2 diyl, 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, tetrahydro-furan-2-one, delta valerolactone, gamma-butyrolactone, glutaric anhydride, dihydroimidazole, triazacyclononane, triazacyclodecane, thiazolidine, hexahydro-1H-indene (5,6 diyl), octahydro-

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

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-(t r i m e t h y l s i l y l) b e n z e n e ; 1,2-bis(di-adamantylphosphinomethyl)-4-(trimethylsilyl) benzene; 1-(P , P adamantyl, t-b u t y l phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4,5-diphenylbenzene; 1- (P,P ad a m a n t y l , t-b u t y l phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4-phenylbenzene; 1- (P,P adamantyl, t-b u t y l phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4,5- bis-(trimethylsilyl)benzene; 1- (P,P adamantyl, t-b u t y l 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-b u t y l 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'-y l) be n z e n e ; 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) b e n z e n e ; 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) b e n z e n e ; 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-(t r i m e t h y l s i l y l) m e t h y l b e n z e n e , 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-(t r i m e t h y l s i l y l) b e n z e n e , 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-(o r 1')phenyl ferrocene; 1,2-bis(di-adamantylphosphinomethyl)-4,5 bis-(t r i m e t h y l s i l y l) f e r r o c e n e ; 1,2-bis(di-adamantylphosphinomethyl)-4-(o r 1')(trimethylsilyl) ferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4,5-diphenylferrocene; 1-(P , P adamantyl, t-b u t y l phosphinomethyl)-2-(di-t-butylphosphinomethyl)-4-(or 1')phenylferrocene; 1- (P,P a d a m a n t y l , t-b u t y l 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-

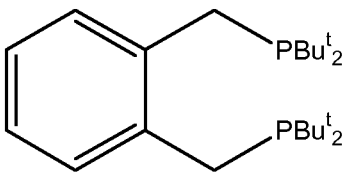
trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(or 1')(trimethylsilyl) ferrocene; 1,2-bis- (2-phosphinomethyl-1,3,5,7-tetra(trifluoro-methyl)-6,9,10-trioxatricyclo{3.3.1.1[3.7]}decyl)-4,5-diphenyl ferrocene; 1,2-bis- (2-phosphinomethyl-1,3,5,7-tetra(trifluoro-methyl)-6,9,10-trioxatricyclo{3.3.1.1[3.7]}decyl)-4-(or 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-(o r 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-(o r 1')(2'-phenylprop-2'-y l) 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-(o r 1')(2'-phenylprop-2'-y l) ferrocene; 1-(di-t-butylphosphinomethyl)-2-

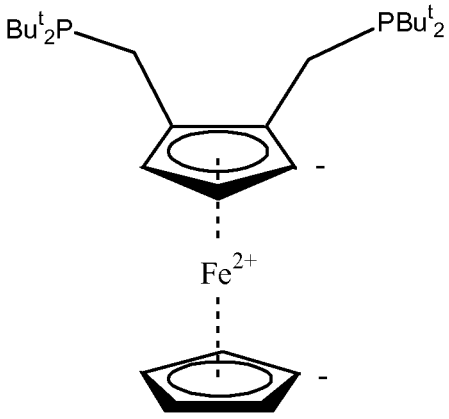
(diadamantylphosphinomethyl)-4,5-(di-t-butyl) ferrocene; 1-(di-t-butylphosphinomethyl)-2-(diadamantylphosphinomethyl)-4-(or 1')t-butyl ferrocene; 1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-4,5- di-(2'-phenylprop-2'-yl) ferrocene; 1,2-bis(2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl)-4-(or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

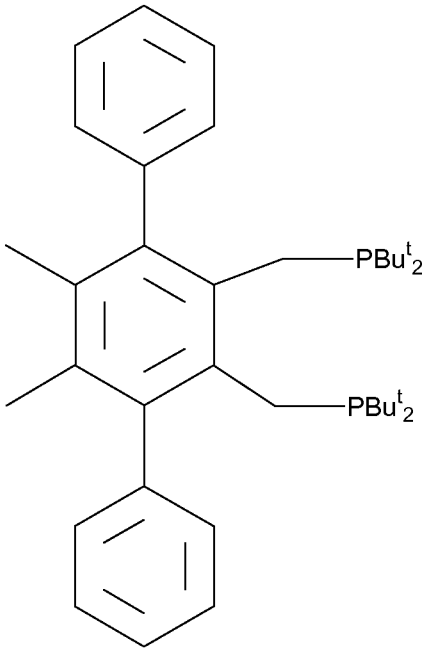
Selected structures of ligands of the invention include:-



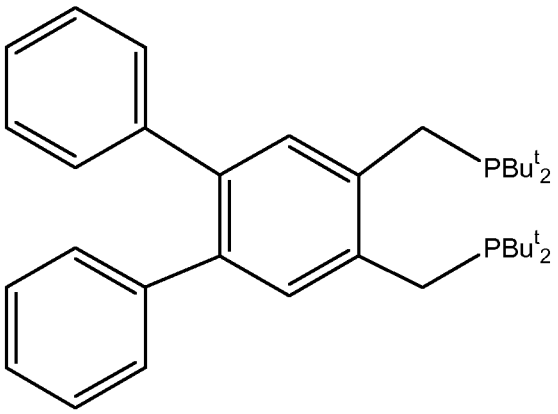
1,2-bis(di-tert-butylphosphinomethyl)benzene



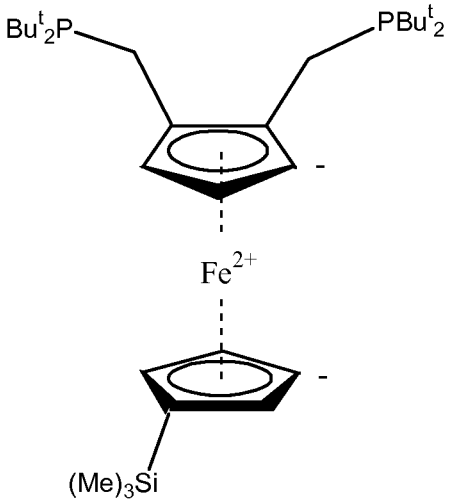
1,2-bis(di-tert-butylphospinomethyl ferrocene



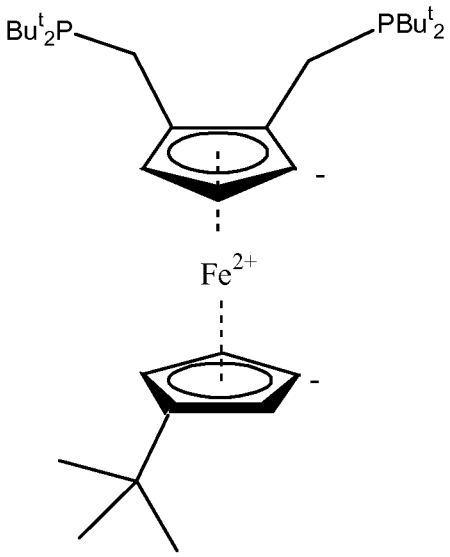
1,2-bis(di-tert-butylphosphinomethyl)-3,6-diphenyl-4,5-dimethyl benzene



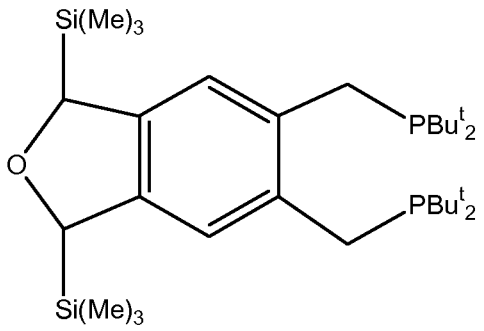
1,2-bis(di-tert-butyl(phosphinomethyl)-4,5-diphenyl benzene



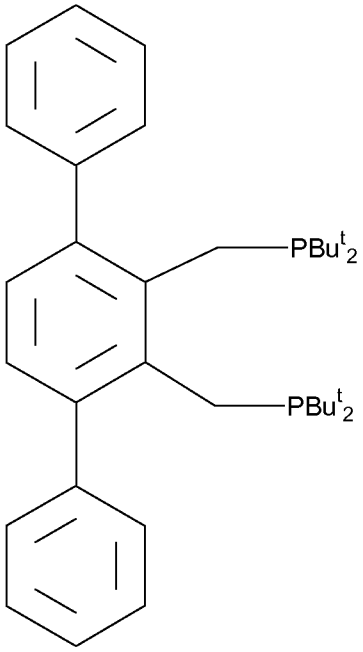
1,2-bis(di-tert-butylphospinomethyl)-1'-trimethylsilyl ferrocene



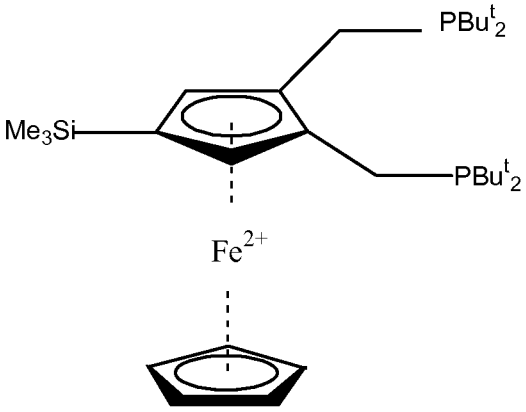
1,2-bis(di-tert-butylphospinomethyl)-1'-tert-butyl ferrocene



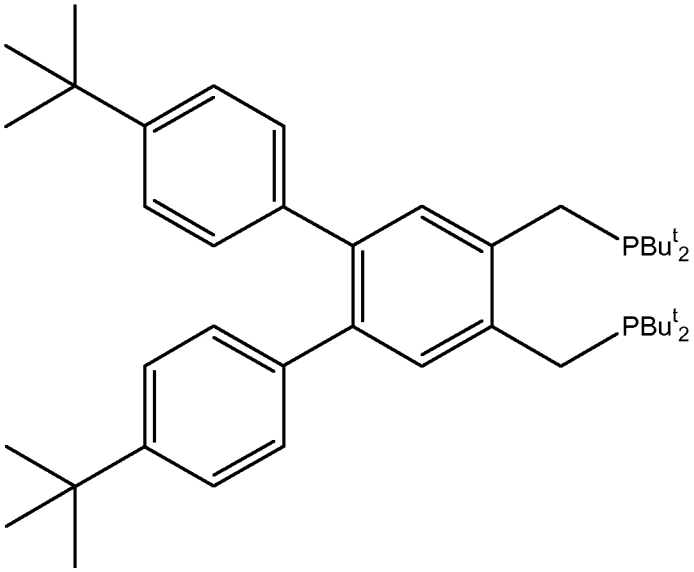
5,6-bis(di-tert-butylphosphinomethyl)-1,3-bis-trimethylsilyl-1,3-dihydroisobenzofuran.



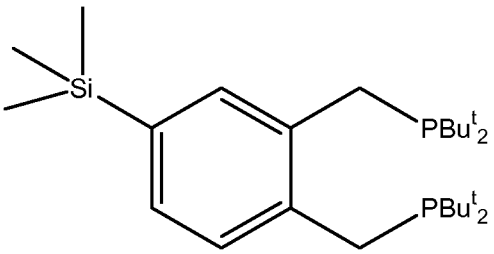
1,2-bis(di-tert-butylphosphinomethyl)-3,6-diphenyl benzene



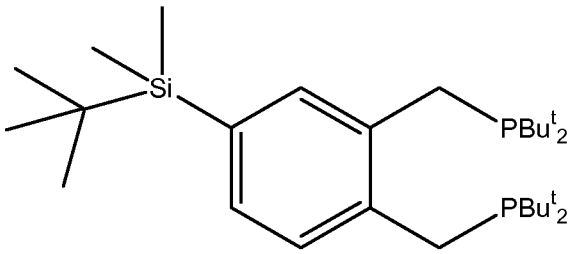
1,2-bis(di-tert-butylphospinomethyl)-4-trimethylsilyl ferrocene



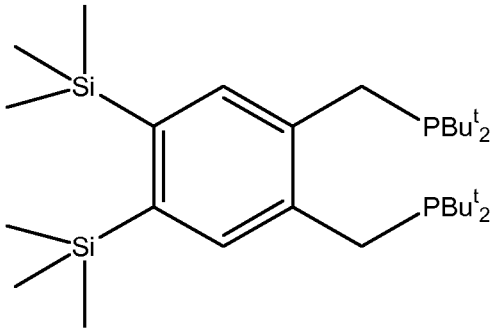
1,2 bis(di-tert-butyl(phosphinomethyl))-4,5- di(4'-tert butyl phenyl) benzene



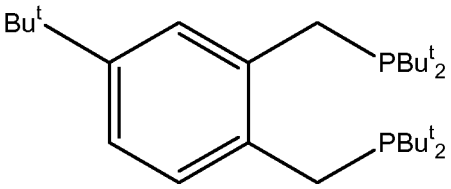
1,2-bis(di-tert-butyl(phosphinomethyl))-4-trimethylsilyl benzene



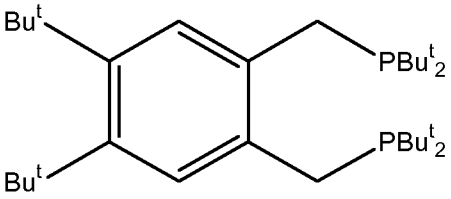
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(tert-butyldimethylsilyl)benzene



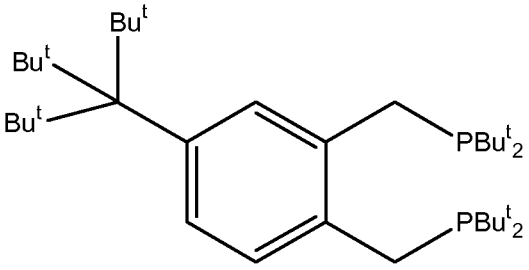
1,2-bis(di-tert-butyl(phosphinomethyl))-4,5-bis(trimethylsilyl)benzene



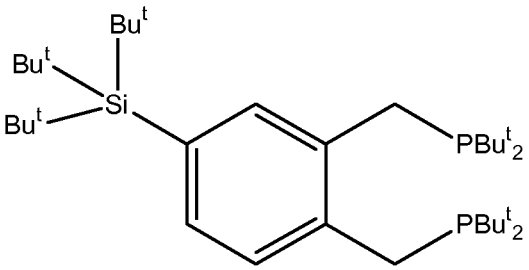
1,2-bis(di-tert-butyl(phosphinomethyl))-4-tert-butyl benzene



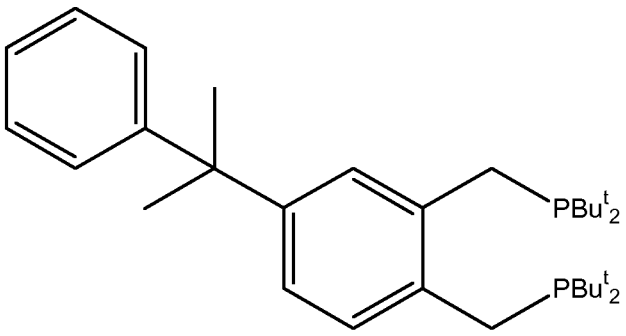
1,2-bis(di-tert-butyl(phosphinomethyl))-4,5-di-tert-butyl benzene



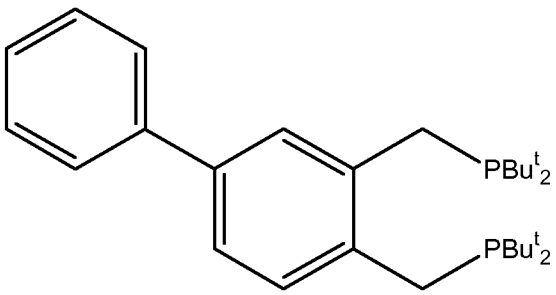
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(tri-tert-butylmethyl)benzene



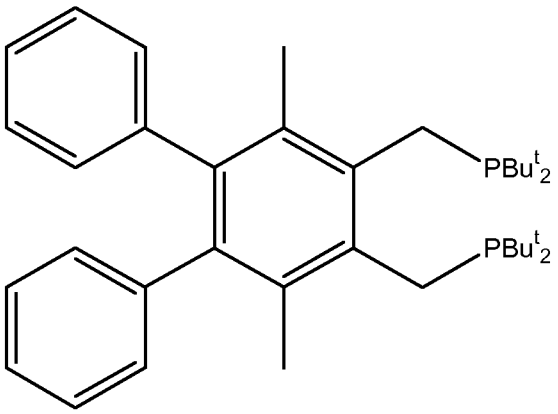
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(tri-tert-butylsilyl)benzene



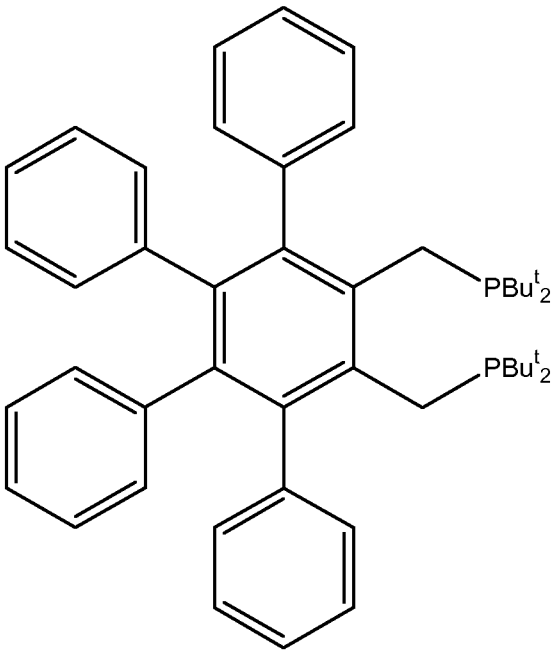
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(2'-phenylprop-2'-yl)benzene



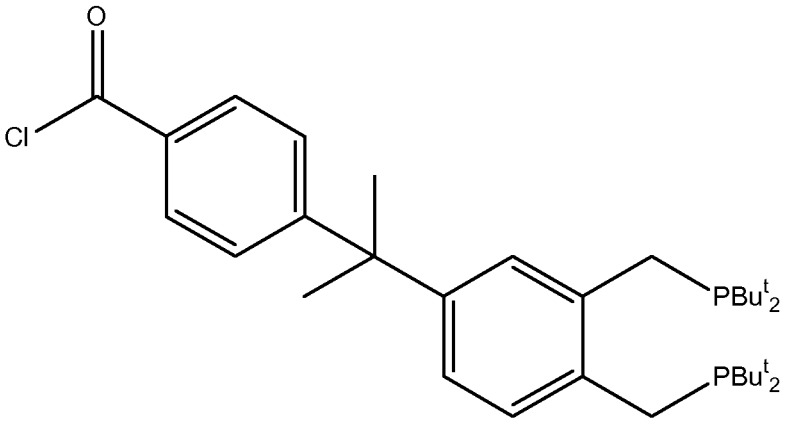
1,2-bis(di-tert-butyl(phosphinomethyl))-4-phenyl benzene



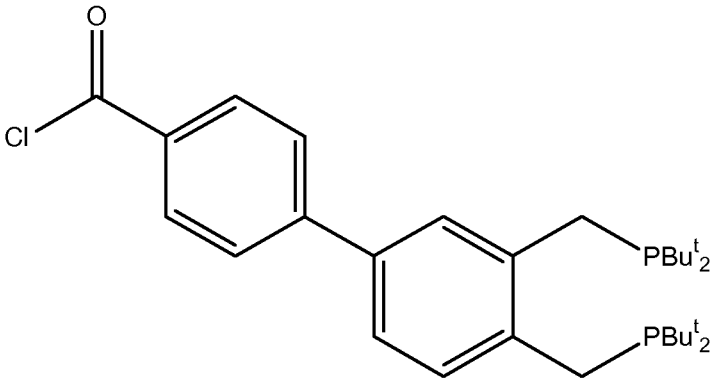
1,2-bis(di-tert-butyl(phosphinomethyl))-3,6-dimethyl-4,5-diphenyl benzene



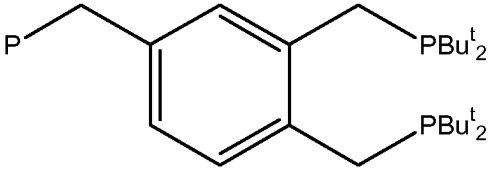
1,2-bis(di-tert-butyl(phosphinomethyl))-3,4,5,6-tetraphenyl benzene



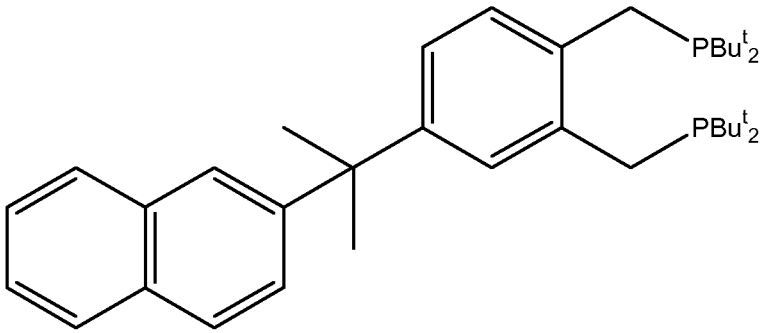
4-(1-{3,4-Bis-[(di-*tert*-butyl-phosphanyl)-methyl]-phenyl}-1-methyl-ethyl)-benzoyl chloride



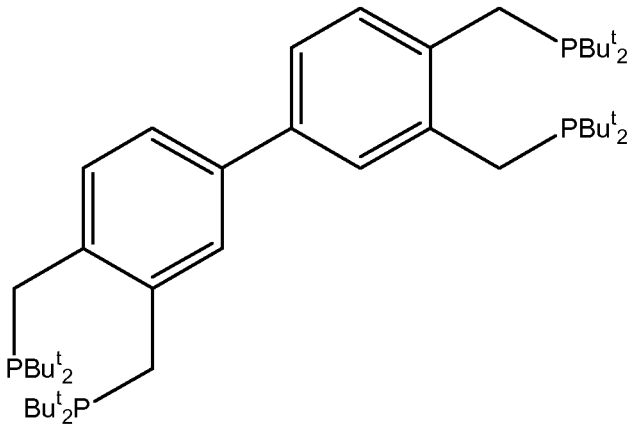
1,2-bis(di-tert-butyl(phosphinomethyl)-4-(4'-chlorocarbonyl-phenyl)benzene



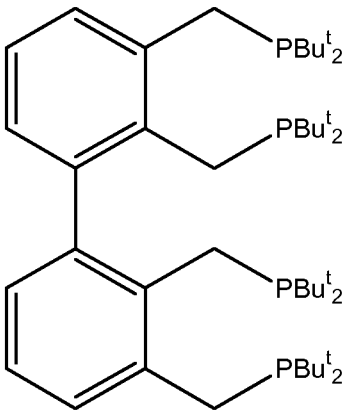
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(phosphinomethyl)benzene



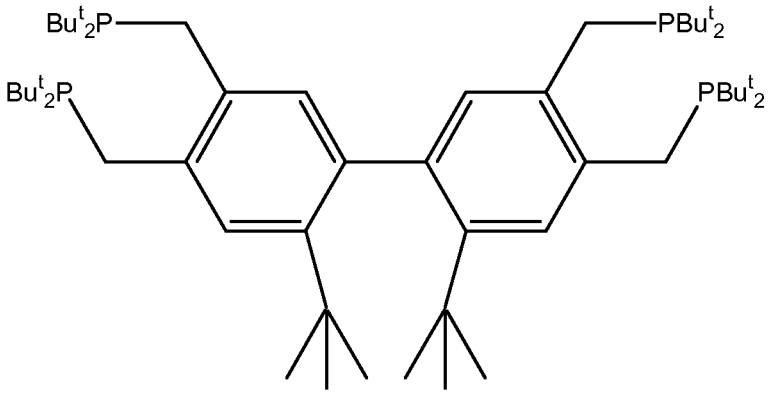
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(2'-naphthylprop-2'-yl) benzene



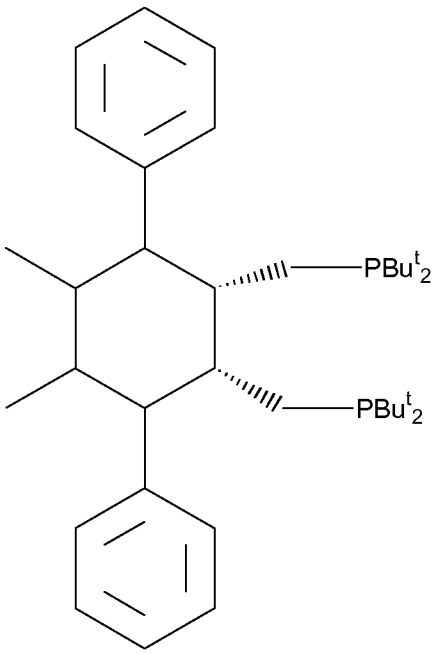
1,2-bis(di-tert-butyl(phosphinomethyl))-4-(3',4'-bis(di-tert-butyl(phosphinomethyl))phenyl)benzene



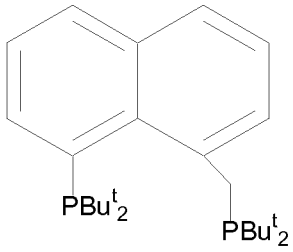
1,2-bis(di-tert-butyl(phosphinomethyl))-3-(2′,3′-bis(di-tert-butyl(phosphinomethyl))phenyl)benzene



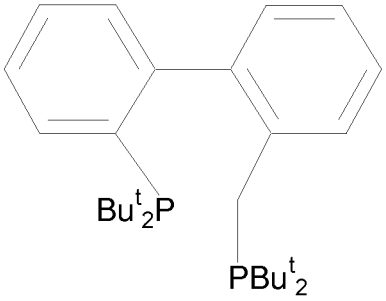
1,2-bis(di-tert-butyl(phosphinomethyl))-4-tertbutyl-5-(2′-tertbutyl-4′,5′-bis(di-tert-butyl(phosphinomethyl))phenyl)benzene ,and



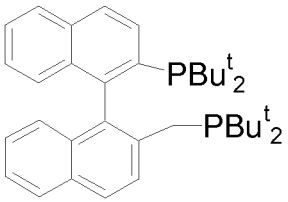
cis-1, 2-bis (di-tert-butylphosphinomethyl), 3, 6, diphenyl-4,5 dimethyl-cyclohexane,



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

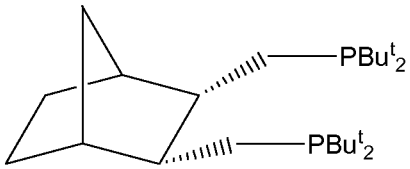


2-(di-tert-butylphosphinomethyl)-2'-(di-tert-butylphosphino)-biphenylene

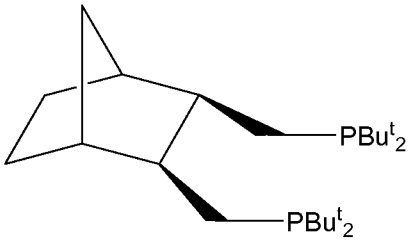


2-(di-tert-butylphosphinomethyl)-2'-(di-tert-butylphosphino)-binaphthylene

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

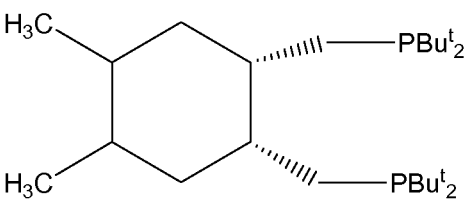


(2-exo, 3-exo)-bicyclo[2.2.1]heptane-2,3-bis(di-tert-butylphosphinomethyl)

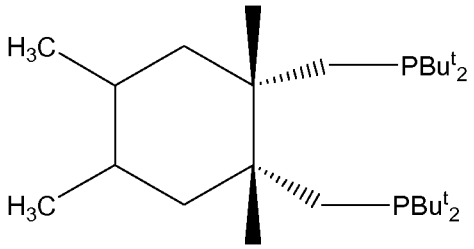


(2-endo, 3-endo)-bicyclo[2.2.1]heptane-2,3-bis(di-tert-butylphosphinomethyl)

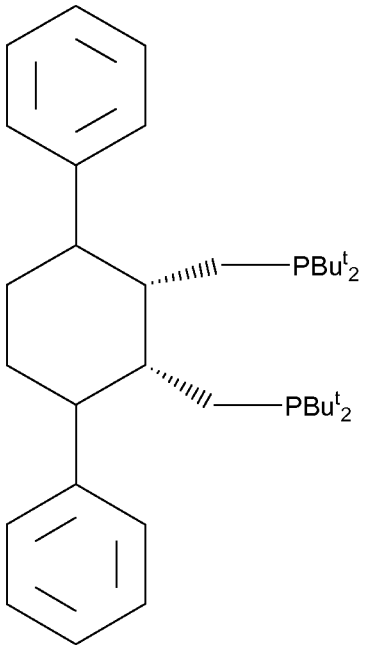
Examples of substituted non-aromatic bridged ligand structures include:-



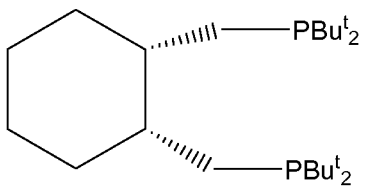
cis-1, 2-bis (di-*tert*-butylphosphinomethyl), 4, 5 dimethylcyclohexane



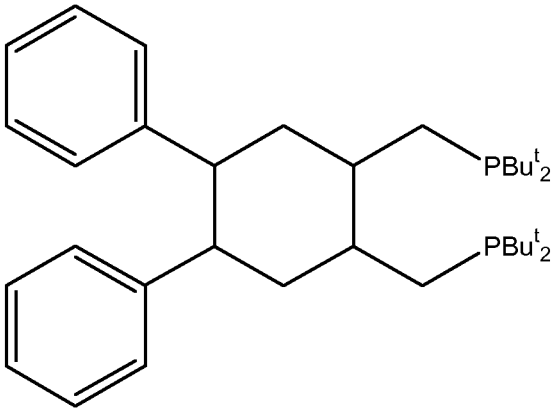
cis-1, 2-bis (di-tert-butylphosphinomethyl), 1, 2, 4, 5 tetramethylcyclohexane



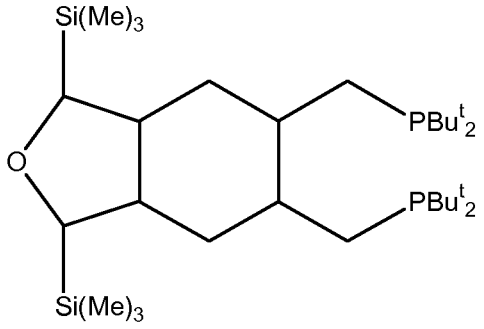
cis-1, 2-bis (di-tert-butylphosphinomethyl), 3, 6, diphenylcyclohexane



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.

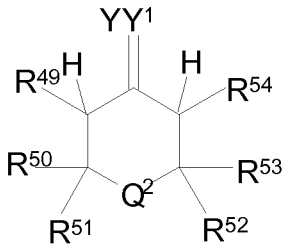
Typically, the group X^1 represents $CR^1(R^2)(R^3)$, X^2 represents $CR^4(R^5)(R^6)$, X^3 represents $CR^7(R^8)(R^9)$ and X^4 represents $CR^{10}(R^{11})(R^{12})$, wherein R^1 to R^{12} represent alkyl, aryl or het.

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

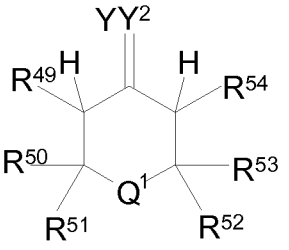
halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29}, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl or Het, wherein R^{19} to R^{30} are as defined herein, and/or be interrupted by one or more oxygen or sulphur atoms, or by silano or dialkylsilcon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

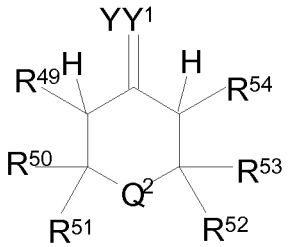
The 2-meta-adamantyl group may be prepared by methods well known to those skilled in the art. Suitably, certain 2-phospha-adamantyl compounds are obtainable from Cytec Canada Inc, Canada. Likewise corresponding 2-meta-adamantyl compounds of formulas I - IV etc may be obtained from the same supplier or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

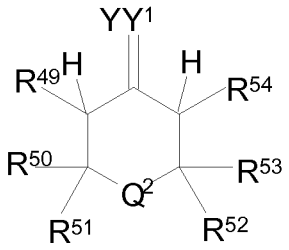
X^3 represents $CR^7(R^8)(R^9)$, X^4 represents $CR^{10}(R^{11})(R^{12})$; and X^1 and X^2 together with Q^2 to which they are attached form a ring system of formula 1a;



(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)

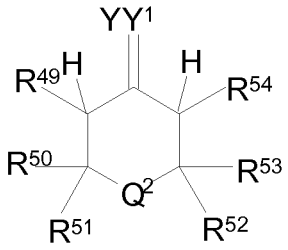
X^3 represents $CR^7(R^8)(R^9)$, X^4 represents adamantyl, X^1 represents $CR^1(R^2)(R^3)$ and X^2 represents $CR^4(R^5)(R^6)$;

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;

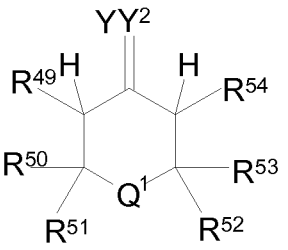


(1a)

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

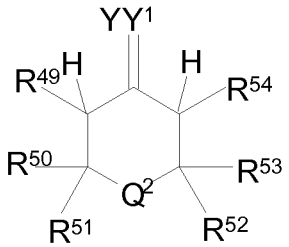
X^1, X^2, X^3 and X^4 represent adamantyl;

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



(1b)

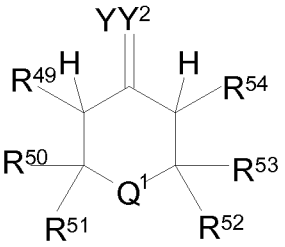
and X^1 and X^2 together with Q^2 to which they are attached form a ring system of formula 1a;



(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

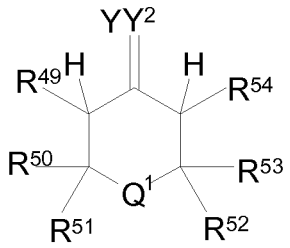


(1b)

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 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}-R^{26} are as defined herein, R^{56} to R^{59} each independently represent unsubstituted C_1-C_8 alkyl or phenyl. In a particularly preferred embodiment the substituents are C_1 to C_8 alkyl, more preferably, methyl such as found in 1,3 dimethyl adamantyl.

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. Particularly preferred is the bidentate phosphine ligand 1,2-bis(di-t-butylphophino)o-xylene.

Definitions

The term "lower alkylene" which A and B represent in a compound of formulas I-IV, 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 so that the term "optional" should be understood accordingly.

The term "alkyl" when used herein, means C_1 to C_{10} alkyl and includes methyl, ethyl, ethenyl, propyl, propenyl butyl, butenyl, pentyl, pentenyl, hexyl, hexenyl and 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^1 to R^{12} and R^{13} - R^{18} each independently represent alkyl, aryl, or Het unless X^1 or X^2 is joined to the Q^2 atom via a non tertiary carbon in which case they can each also represent hydrogen.

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

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 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.

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.

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

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

Referring to figure 1, a continuous process for the reaction of purified streams of carbon monoxide, ethylene and methanol in the liquid phase, in the presence of a catalyst system, to generate the desired product, methyl propanoate is shown. A reactor tank 2 accommodates a liquid phase 4 and a gas phase 6. The liquid phase 6 is stirred by means of a pair of mixing blades 8, 10 located below the liquid phase surface in axially spaced relationship on drive shaft 12 driven by motor 14. A typical input gas stream 16 of 60% ethylene, 20% carbon monoxide and 20% of inert gases enters the reactor tank 2 near the base of the reactor tank side wall 18 and below the level of the liquid phase in the tank 2. The 20% of inert gases are typically made up of ethane 8%, methane 4%, carbon dioxide 0.4%, with nitrogen and argon making up the balance of 7.6%. The level and composition of the inerts will vary depending on the impurities present in the feed gas and guard bed efficiencies. The gas entering into the reactor vessel at the base passes up through the reaction mixture continuously and is dispersed by the agitator mixing blades 8, 10 into fine bubbles. In this way the ethylene and carbon monoxide were dissolved

in the reaction mix. The input gas stream 16 comprises an ethylene feed stream 30 and a carbon monoxide feed stream 32 which each proceed from their source (not shown) to the input gas stream, each via a respective guard bed 34, 36. The reactor tank 2 has a liquid phase exit pipe 20 located in the base wall 22 thereof to facilitate transport of the impure product methyl propionate stream to a flash column 24 and a gas phase exit pipe 26 located in the top wall 28 of the reactor 2 to facilitate transport of the headspace gas back to the input feed stream.

Depending upon process conditions, some of the MeP product stream in the liquid phase exit pipe 20 may be taken off and immediately recycled into the head of the reactor 2 as first impure MEP feedback stream 38. The bulk of the product stream is, however, fed for separation to a single stage 'flash' type distillation column 24 where the bulk of the MEP and methanol is flashed overhead and directed to the purification column 40 via flash column overhead conduit 42. The heavy fraction which remained as liquid after being passed through the flash column contains useful catalyst components and is thus recycled back into the reactor 2 via an exit pipe 44 located in the base of the flash column 24. Some of the heavy fraction may be cycled through a catalyst concentration loop 46 and back into the base of the flash column until it has reached the desired concentration or in order to avoid return of too much catalyst back to the reactor 2.

As the methyl propanoate product is required free of methanol, a second distillation column is needed. The methyl propionate flash column overhead stream is therefore fed into purification column 40 where the pure

methyl propionate is removed from the base thereof as the heavy fraction and fed via purification column base exit pipe 48 to the methyl propionate product tank 50. A low boiling mixture of methanol and methyl propanoate is generated as the light product, and is removed continuously from the top of the MeP purification column. The liquid portion of the lighter fraction removed from the purification column 40 containing MeP and methanol may be recycled to the reactor 2 or refluxed back into the purification column whereas the gas fraction which is predominantly ethylene is returned to the ethylene feed stream via an ethylene compressor 52 and headspace compressor 54.

As mentioned previously, the liquid portion of the purification overhead may be refluxed back into the purification column or may be recycled back into the reactor 2. For the purpose of recycling, the purification column recycle pipe 56 is connected with the flash column exit pipe 44. The combined recycle pipe is also connected to the incoming fresh catalyst feed pipe 57 to form a second liquid input pipe 58 for the reactor 2. The second liquid input pipe 58 is further connected to methanol input pipe 60 which feeds methanol into the combined recycle pipe at the desired rate from the methanol stripper output 62. The methanol stripper 64 is connected to a source of fresh methanol 66 for this purpose.

The reaction in reactor vessel 2 was carried out at 100°C and at between 9 and 15 barg pressure.

The catalyst system was made up as follows. Into a $15m^3$ catalyst make-up tank blanketed under nitrogen is added

11600 litres of methyl propanoate and 117 litres of methanol. This material is sparged with nitrogen for 3 hours to ensure that it is thoroughly deoxygenated. To this solution is added 5.1Kg of palladium dba (a mixture of tris(dibenzylideneacetone)dipalladium($Pd_2(dba)_3$) and tris(dibenzylideneacetone)palladium($Pd(dba)_3$) Heraeus- Pd assay 19.60% Pd (equivalent to 1.0Kg of Pd metal) and 23.35Kg of a 20%w/w solution of 1,2-bis(di-tert-butylphosphinomethyl)benzene in MeP. This equates to 9.40 moles of palladium and 11.85 moles of phosphine ligand, a ratio of palladium:phosphine of 1:1.26. The palladium salt and phosphine ligand are allowed to complex for 12 hours before the addition of 13.9 litres of a 70% w/w solution of methanesulphonic acid in water (133.53 moles of MSA). This results in a mole ratio of palladium:methanesulphonic acid of 1:14.2. This completes the preparation of the catalyst which is now ready for use and is fed at a low but continuous flow-rate directly through the fresh catalyst feed pipe 48 into Reactor 2. The palladium concentration of the catalyst solution is approximately 93ppm Pd as calculated from the values above. The MW of palladium used for calculation of palladium feed rate is 106.4 Daltons. The palladium catalyst feed at this concentration generally results in a Pd concentration in the reactor of between 25-40ppm.
During the above continuous operation, the catalyst decomposes at a slow but steady rate, and is replaced by adding fresh catalyst made up as above.

As set out above, the gas fed to the reactor comprises a mixture of :

1. reactor exit gas recycle consisting of unreacted CO and ethene and any inert gases;

2. ethylene recycle from the top of MeP purification column; and
3. fresh CO and ethene

As set out above, the liquid feeds to the reactor comprise:

1. fresh methanol added continuously to the reactor vessel, in order to replace the methanol that has been used up in the reaction allowing the reactor composition to be maintained;
2. catalyst recycle fed back to the reactor from the MeP flash column;
3. MeP purification column overheads, a source of fresh methanol and MeP to replace methanol consumed in the formation of MeP and to maintain the MeP:Methanol composition ratio in the reactor;
4. fresh catalyst feed to replace that which is lost due to catalyst decomposition reactions.

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

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

This led to the situation where the standing concentrations of catalyst components became constant for

a given rate of generation of methyl propanoate, and just able to sustain flow sheet reaction rate, as indicated by constant concentrations of carbon monoxide and ethylene in the headspace area of the reactor vessel. This was called the balance point, because under these conditions the rate of palladium decomposition was balanced exactly by the rate of addition of fresh palladium.

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

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

Examples 1-3

Preparation of Methyl Propanoate from Ethylene, Carbon Monoxide and Methanol

Relevant flow rates and associated palladium turnover numbers (TON) are shown in Table 1.

To gather data on the effect of headspace gas ratios on palladium turnover number, all variables were held constant except the levels of CO and ethylene in the reactor headspace. These were varied by allowing the

catalyst concentration to vary by temporarily decreasing or increasing the catalyst feed to the reactor, so that the fraction of carbon monoxide consumed as the gas mixture passed through the reactor was slightly lower or higher. If the catalyst concentration is dropped temporarily, this causes the headspace CO level to rise because the incoming feed stream ratio is much higher in CO compared to the headspace. This rise in CO concentration can be allowed to continue until the CO concentration has reached the required level. Equilibrium of catalyst feed can then be re-established at the higher CO headspace concentration. Alternatively, if the catalyst concentration is elevated temporarily, this causes the CO concentration in the reactor headspace to drop relative to the ethylene in the headspace because ethylene in the feed stream is in excess but only one ethylene and CO molecule are used up in each reaction. The equilibrium of catalyst feed with decay can then be re-established at the lower CO concentration. The levels of CO and ethylene in the headspace were thus changed to show the effect of gas ratios on catalyst TON. After the changes to CO and ethylene gas phase levels were made, the process was brought to a new balance point at those levels by careful adjustment of the catalyst feed rate to make sure the rate of production of methyl propanoate remained constant. In this way, results were drawn up which showed clearly the changes to catalyst stability that were caused by the variations in the ethylene:carbon monoxide headspace ratio. The production unit was run for at least 7 days under each set of conditions and the values were averaged over this extended period. The results are shown in table 1.

The exact concentration of Palladium in the fresh catalyst feed to the reactor is critical to calculation of turnover number results. The concentration of palladium in the fresh catalyst being fed to the system may also be cross-checkedby ICP-mass-spec analysis to confirm the calculated values aboveTable 1 shows the effect of changes in the headspace CO concentration on palladium turnover number (TON). All the results are surprisingly higher than those expected for this catalyst system based upon previous work in this area as exemplified for instance by EP0970038A1 and WO2005079981. Palladium turnover number is calculated based on MeP produced as follows :

1. TON in moles MeP/mole Pd is calculated by dividing the MeP produced in moles/hr by the palladium fed in gmoles/hr. The palladium fed is calculated knowing the concentration of palladium in the catalyst feed and the rate of addition to the reactor.
2. An example calculation using the data from Table 1, column 1 is as follows:-

   i) MeP produced = 15.5 tonnes/hr

   ii) MeP produced = 176.14 x 10^3moles/hr (assumes MW MeP = 88)

   iii) Catalyst feed rate = 16.32 Kg/hr

   iv) Pd concentration in catalyst feed = 93.0ppm Pd = 1.518 g/hr

   v) Pd feed rate = 1.43 x 10^{-2} moles Pd/hr (assumes MW Pd = 106.4)

vi) TON = Moles MeP Produced/Moles Pd fed

= 12.48 Million moles MeP/mole Pd

All other TON values are calculated in a similar manner.

Table 1

Example	1	2	3
	0.97% H/S CO	1.83% H/S CO	2.24% H/S CO
H/S Ethene %	65.40	70.64	79.31
H/S Inerts %	32.85	27.52	18.45
H/S Ethene:CO	67.42	38.60	35.40
Liquid phase MeOH %+	25.09	24.60	26.27
Liquid phase MeP %+	74.91	75.40	73.73
Liquid phase CO w't frac	4.55E-05	8.6E-05	1.08E-04
Liquid phase Ethene w't frac	0.013	0.014	0.0158
Liquid phase Ethene:CO	285.71	162.79	146.30
MeP Production rate Tonnes/hr	15.7	15.9	15.9
Catalyst feed rate Kg/hr	16.32	20.26	22.69
CO Flow Kg/hr	5000	5000	5000
Ethene Flow Kg/hr	5000	5000	5000

H / S Recirc. Flow Kg/hr	12935	12992	12819
Methanol feed rate Kg/hr	6200	6200	6200
T O N (moles MeP/mole Pd)	12.48 million	10.21 million	9.27 million

+ Disregarding gas contribution

H/S - Headspace

By contrast, operating above 5% CO in the headspace resulted in rapid deterioration in catalyst performance as measured by TON. On the other hand, operating above an ethylene:CO ratio of 1000:1 led to a very low rate of reaction and hence low productivity.

Infra-red analysis of the headspace gas and outgoing flow rate were measured by an Emerson Rosemount CAT 100 IR analyser.

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

All input flows (ethylene, methyl propionate, carbon monoxide, catalyst and methanol together with the combined MEP/methanol recycle input) were measured using Emerson Rosemount Coriolis flow meters, 2700R1EEFEZZZ for ethylene and catalyst and 270011EEFEZZZ for carbon monoxide, methyl propionate and methanol.

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

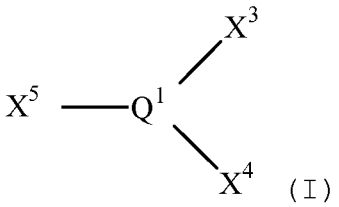
1. A continuous process for the carbonylation of ethylene in a liquid phase using carbon monoxide in the presence of a co-reactant having a mobile hydrogen atom and a suitable catalyst system comprising the steps of:-

(i) forming a liquid phase comprising the co-reactant having a mobile hydrogen atom and the suitable catalyst system;

the catalyst system obtainable by combining:

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

(b) a ligand of general formula (I)



(I)

wherein

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

Q^1 represents phosphorus, arsenic or antimony; and

c) optionally, a source of anions;

(ii) forming a gaseous phase in contact with the liquid phase by providing at least an ethylene gas input feed stream and a carbon monoxide gas input feed stream wherein the ethylene:CO molar ratio entering the liquid phase from the input feed streams is greater than 2:1;

(iii) reacting ethylene with carbon monoxide in the presence of the co-reactant, and of the suitable catalyst system in the liquid phase;

wherein the ethylene:CO gas molar ratio in the gaseous phase is between 20:1 and 1000:1.

2. A process according to claim 1, wherein the catalyst is replenished as the reaction proceeds.

3. A process according to claim 1 or 2, wherein the catalyst concentration is generally maintained throughout the continuous reaction so that the rate of addition matches the rate of catalyst decay.

4. A process according to any preceding claim, wherein the ethylene and carbon monoxide input feed streams are combined into a single input feed stream prior to contact with the liquid phase and therefore the ethylene:CO molar ratio in the single combined input feed stream is greater than 2:1.

5. A process according to any preceding claim, wherein the ethylene:CO gas molar ratio in the gaseous phase of the reactor is between 40:1 and 200:1.

6. A process according to any preceding claim, wherein the ethylene:CO gas molar ratio in the reactor is either between 30:1 and 49:1 or 51:1 and 150:1.

7. A process according to any preceding claim, wherein the ethylene:CO molar ratio in the gaseous input feed stream(s) of the reactor (including any recycled ethylene and CO) is between 2:1 and 20:1.

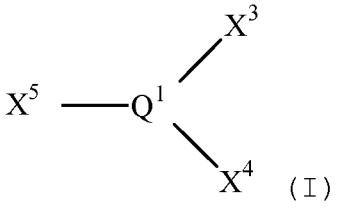
8. A process according to any preceding claim, wherein the molar ratio of ethylene:CO in the liquid phase is greater than 10:1.

9. A continuous process for the carbonylation of ethylene in a liquid phase using carbon monoxide in the presence of a co-reactant having a mobile hydrogen atom and a suitable catalyst system comprising the steps of:-

(i) forming a liquid phase comprising the co-reactant having a mobile hydrogen atom and the suitable catalyst system;

the catalyst system obtainable by combining:

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



(I)

wherein

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

Q^1 represents phosphorus, arsenic or antimony; and

c) optionally, a source of anions;

(ii) forming a gaseous phase in contact with the liquid phase by providing at least an ethylene gas input feed stream and a carbon monoxide gas input feed stream to the liquid phase;

(iii) reacting ethylene with carbon monoxide in the presence of the co-reactant, and of the suitable catalyst system in the liquid phase;

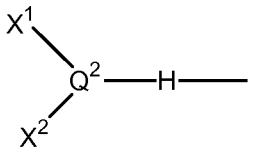
wherein the molar ratio of ethylene:CO in the liquid phase is greater than 10:1.

10. A process according to any preceding claim, wherein preferably, the ethylene:CO molar ratio entering the liquid phase from the input feed streams is greater than 2:1.

11. A process according to any preceding claim, wherein preferably, the liquid phase is well mixed during the reaction.

12. A process according to any preceding claim, wherein the liquid phase is mixed using a dual impeller mixer which mixes in two opposed directions in the reactor so that forward flow and back flow are achieved simultaneously.

13. A process according to any preceding claim, wherein the phosphine, arsine or stibine ligand is a bidentate ligand, wherein X^5 represents



II

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

and 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.

14. A process as hereinbefore described with reference to the examples and/or drawings.