

**Process for the Carbonylation of Ethylenically Unsaturated Compounds,
Novel Carbonylation Ligands and Catalyst Systems incorporating such
Ligands**

5 The present invention relates to a process for the carbonylation of
selected ethylenically unsaturated compounds, particularly alkoxy and
hydroxy-carbonylation thereof, novel bidentate ligands and novel
catalyst systems incorporating such ligands. The carbonylation of
10 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
15 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
20 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
25 bidentate phosphine compounds with tertiary carbon groups but 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 in EP0495548; that little or no impurities
30 are produced at high conversions; and that the product has a high
selectivity for the acid or ester product and gives no polymer.

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

WO 98/42717 discloses a modification to the bidentate phosphines used
in EP0495548 wherein the tertiary carbon groups are utilised by one
or both phosphorus atoms being incorporated into an optionally
40 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). Assymmetric ligands are envisaged but not exemplified. The examples include a number of alkoxy-carbonylations of ethene, propene and some higher terminal and internal olefins using symmetrical PA groups incorporating each phosphorus and substituting each adjacent carbon in the PA groups so that the carbons joined to the phosphorus are tertiary. There are no examples of the use of secondary or primary carbons joined to the phosphorus. Improved rates and improved yields for carbonylation of internally unsaturated olefins are found when compared to 1,3-bis(di-
t-butylphosphino)propane.

WO 03/070370 extends the particular tertiary carbon phosphorus substituent ligands taught in WO 98/42717 to bidentate phosphines having 1, 2 substituted aryl bridges of the type disclosed in WO96/19434.

WO 04/103948 describes both the above types of ligand bridges as useful for butadiene carbonylation and WO 05/082830 describes a selection of WO 04/103948 where the tertiary carbon substituents are different on the respective phosphorus atoms leading to improved reaction rate.

It is known that the use of primary, secondary and aromatic carbon substituents on the bidentate phosphorus ligands lead to no or polymer products in the carbonylation of certain ethylenically unsaturated compounds. The general process for the production of polyketone polymers has been known for many years. EP 121,965, EP 181,014 and EP 213,671 describe processes which involve the use of a bidentate phosphine ligand with a group VIII metal such as palladium and an acid having a pKa of less than 6. US 4,950,703 teaches that a preferred catalyst composition for producing polyketone polymer uses palladium, a suitable acid and 1,3-bis(diphenylphosphine)propane or 1,3-bis[di(2-methoxyphenyl)phosphino]propane.

For instance US5369074 teaches that such aromatic group substituted ligands as 1,2-bis-(diphenylphosphino)propane and alkyl substituted bidentate ligands joined to the phosphorus via a -CH₂ group give a range of molecular weight polyketone polymer products in good yield in the carbonylation of ethylene using carbon monoxide.

It is known from W001/87899 that ligands with the cyclic groups known as phobanes, for example, 9-phosphabicyclononane, joined to the phosphorus via a secondary carbon and with an alkylene bridge can give good selectivity and non-polymer product in such carbonylation reactions. In WO 05/082830 an asymmetric bidentate phosphine ligand is disclosed having tertiary carbons on one phosphorus and the phobane secondary carbons on the other phosphorus. Unsurprisingly, the reaction still gives a good selectivity to the ester product.

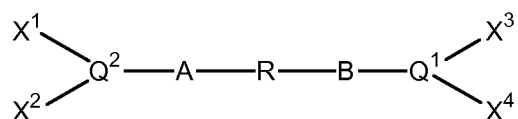
In the production of acid or ester products or other products with other co-reactants, it is not desirable to have polymer or oligomer products as these will reduce yield and interfere with the reaction process. Accordingly, it is important to select ligands which are known to favour non-polymer/oligomer products in such reactions, particularly when carbonylating ethylenically unsaturated compounds with a tendency to polymerise to polyketones in the presence of carbon monoxide. Surprisingly, it has now been found that a certain group of aromatic bridged asymmetric bidentate ligands do not give polymer product using the above types of alkyl and aromatic group substituted bidentate ligands when in combination with tertiary carbon substituents and that these ligands also display improved stability in such reactions.

According to the first aspect of the present invention there is provided a novel bidentate ligand according to claim 1.

According to a further aspect of the present invention there is provided a catalyst system capable of catalysing the carbonylation of an ethylenically unsaturated compound, which system is obtainable by combining:

- a) a metal of Group 8, 9 or 10 or a compound thereof,
- b) a bidentate ligand of formula I, and
- c) an acid,

wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand;



wherein:

- 5 A and B each independently represent an optional lower alkylene linking group;

R represents a hydrocarbyl aromatic structure having at least one aromatic ring to which Q^1 and Q^2 are each linked, via the respective
 10 linking group, if present, on available adjacent atoms of the at least one aromatic ring;

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
 15 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 ;

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

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

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Advantageously, by joining the groups X^1 and X^2 to the Q^2 atom via non-tertiary carbon atoms it has been found that a catalyst system utilising such ligands in carbonylation reactions has surprisingly improved stability over an equivalent system using tertiary carbon
 35 atoms joined to both Q^1 and Q^2 . Typically, the turnover number (TON) (moles of metal/moles of product) for the carbonylation reaction, especially, hydroxy - or alkoxy-carbonylation is improved. In particular, the TON is improved in a reaction using a recycled ligand

compared with ligands where X^1 and X^2 are joined to the Q^2 atom via tertiary carbon atoms. Preferably, the ligands of the invention are utilised in continuous carbonylation reactions but batch reactions, particularly repeat batch reactions will also benefit.

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Therefore, according to a second aspect of the present invention there is provided a process for the carbonylation of ethylenically unsaturated compounds according to claim 2.

10 Preferably, the groups X^1 and X^2 are selected from C_1 - C_{20} alkyl, C_1 - C_{20} alkenyl, C_1 - C_{20} alkynyl or C_1 - C_{20} aryl groups.

It is particularly preferred that at least one of the groups X^1 or X^2 includes a substituent. Preferably, the substituent is either on the
 15 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
 20 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.

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Preferably, the further substituent 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, -COOR⁶³, -C(O)-, or -CF₃ wherein R⁶³ is alkyl, aryl or Het.
 30 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
 35 ortho, meta or para position, preferably, the ortho or meta position, most preferably, the ortho position of the ring.

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Suitable 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.

5 Preferably, in the process of the invention the catalyst system also includes an acid and said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in a greater than 2:1 molar excess compared to said ligand.

10 Accordingly, according to a third aspect of the present invention there is provided a catalyst system capable of catalysing the carbonylation of an ethylenically unsaturated compound, which system is obtainable by combining:

- 15 a) a metal of Group 8, 9 or 10 or a compound thereof,
b) a bidentate phosphine, arsine, or stibine ligand of formula I as claimed herein, and
c) optionally, an acid.

20 Preferably, in the third aspect, said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand.

25 Suitably, all of components a) to c) of the catalyst system of the present invention can be added in situ to the reaction vessel wherein the carbonylation is to take place. Alternatively, the components a) to c) can be added sequentially in any order to form the catalyst system, or in some specified order, either directly into the vessel
30 or outside the vessel and then added to the vessel. For instance, the acid component c) may first be added to the bidentate ligand component b), to form a protonated ligand, and then the protonated ligand can be added to the metal or compound thereof (component a)) to form the catalyst system. Alternatively, the ligand component b)
35 and metal or compound thereof (component a)) can be mixed to form a chelated metal compound, and the acid (component c)) is then added. Alternatively, any two components can be reacted together to form an intermediate moiety which is then either added to the reaction vessel and the third component added, or is first reacted with the third
40 component and then added to the reaction vessel.

As such, the present invention is directed to a process and catalyst system wherein the relative molar concentrations of both the bidentate ligand and the acid are at levels in excess of those previously envisaged, leading to surprising and unexpected advantages when using the catalyst system in the carbonylation of ethylenically unsaturated compounds in combination with the ligands defined herein, and the alleviation or at least reduction of at least some of the disadvantages of the prior art systems. In particular, the use of a catalyst system of the present invention leads at least to a more stable system, increased reaction rates, improved turnover numbers in carbonylation reactions of ethylenically unsaturated compounds, improved selectivity, improved conversion and an avoidance of polymerisation.

As stated above, the ligand is present in the catalyst system, or precursor thereto, in such quantity that the ratio of said ligand to the said metal (i.e. component b) to component a)) is at least a 2:1 molar ratio. Preferably, the ratio of said ligand to the said metal is greater than a 2:1 molar ratio, more preferably in the range 2:1 to 1000:1, even more preferably in the range 2.5:1 to 1000:1, yet more preferably in the range 3:1 to 1000:1, even more preferably in the range 5:1 to 750:1, still more preferably in the range greater than 5:1 to 750:1, yet more preferably in the range greater than 5:1 to 500:1, still more preferably in the range 10:1 to 500:1, yet still more preferably in the range 20:1 to 400:1, even more preferably in the range 50:1 to 250:1, most preferably in the range in excess of 50:1, for example 51:1 and upwards, more specifically 51:1 to 250:1 or even to 1000:1. Alternatively, the said ratio can be in the range 15:1 to 45:1, preferably 20:1 to 40:1, more preferably 25:1 to 35:1.

As stated above, the acid is present in the catalyst system, or precursor thereto, in such quantity that the ratio of said acid to the said ligand (i.e. component c) to component b)) is at least a 2:1 molar ratio. Preferably, the ratio of said acid to the said ligand is greater than a 2:1 molar ratio, more preferably in the range 2:1 to 100:1, even more preferably in the range 4:1 to 100:1, yet more preferably in the range 5:1 to 95:1, still more preferably in the range greater than 5:1 to 95:1, yet more preferably in the range greater than 5:1 to 75:1, more preferably in the range 10:1 to 50:1,

even more preferably in the range 20:1 to 40:1, still more preferably in the range greater than 20:1 to 40:1 (e.g. 25:1 to 40:1, or 25:1 to less than 30:1), most preferably in excess of 30:1, suitably with any of the upper limits provided hereinbefore (e.g. 30:1 to 40:1).

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By "acid", we mean an acid or salt thereof, and references to acid should be construed accordingly.

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The advantages in working within the ligand to metal, and acid to ligand ratios, set out above are manifest in that the stability of the catalyst system is further improved, as evidenced by increases in the turnover number (TON) of the metal. By improving the stability of the catalyst system, the usage of metal in the carbonylation reaction scheme is kept to a minimum.

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Without wishing to be bound by theory, it is believed that by working within the specific ratio ranges noted herein, it is surprisingly found that the ligand component of the catalyst system is protected against inadvertent aerial oxidation (in instances where there is any ingress of air into the reaction system), and the overall stability of the catalyst system is improved, thus keeping the usage of the metal component of the catalyst system to a minimum. Moreover, the forward reaction rate of the reaction is surprisingly improved.

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In effect, the level of acid should be such that for the particular bidentate ligand employed, the level of acid should be such that phosphine, arsine or stibine is fully protonated. Hence, to show the improved effects, the level of ligand should be above some minimum level, as given by the ligand:metal molar ratio, and the level of acid should be above some minimum level with respect to the level of ligand present to encourage protonation, as given by the acid:ligand molar ratio.

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Preferably, the acid is present in the catalyst system, or precursor thereto, in such quantity that the molar ratio of said acid to said metal (i.e. component c) to component a)) is at least 4:1, more preferably from 4:1 to 100000:1, even more preferably 10:1 to 75000:1, yet more preferably 20:1 to 50000:1, yet still more preferably 25:1 to 50000:1, yet still more preferably 30:1 to 50000:1, yet even more preferably 40:1 to 40000:1, still more preferably 100:1 to 25000:1, yet still more preferably 200:1 to 25000:1, most preferably 550:1 to 20000:1, or greater than 2000:1 to

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20000:1. Alternatively, the said ratio can be in the range 125:1 to 485:1, more preferably 150:1 to 450:1, even more preferably 175:1 to 425:1, yet even more preferably 200:1 to 400:1, most preferably 225:1 to 375:1.

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For the avoidance of any doubt, all of the aforementioned ratios and ratio ranges apply to all of the ligand embodiments set out in more detail hereinafter.

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Still further, with the ligands of the present invention, by optimising TON using the system described above, the surprising recyclability and low polymerisation found with the ligands of the present invention becomes more apparent.

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Bridging Group R

Preferably, the group R which is joined to A and B, as defined, on available adjacent atoms of the at least one aromatic ring, is also substituted with one or more substituent(s) Y^x on one or more further aromatic cyclic atom(s) of the aromatic structure. Preferably, 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 .

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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 aromatic cyclic atoms of the aromatic structure. Preferably, there are ≤ 10 Y groups ie n is 1 to 10, more preferably there are 1-6 Y groups, most preferably 1-4 Y groups on the aromatic structure and, especially, 1, 2 or 3 substituent Y groups on the aromatic structure. The substituted cyclic aromatic atoms may be carbon or hetero but are preferably carbon.

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Preferably, $\sum_{x=1-n} tY^x$ 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
5 hindering than phenyl.

By sterically hindering herein, whether in the context of the groups R^1 - R^{12} described hereinafter or the substituent Y, we mean the term as readily understood by those skilled in the art but for the avoidance
10 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
15 references to DS values compared with PH_2t-Bu etc. If two Y groups are being compared and PHY^1 is not more sterically hindered than the reference then PHY^1Y^2 should be compared with the reference. Similarly, if three Y groups are being compared and PHY^1 or PHY^1Y^2 are not already determined to be more sterically hindered than the
20 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
25 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
30 Society, 92, 1970, 2956-2965) has concluded that the property of the ligands which primarily determines the stability of the $Ni(0)$ complexes is their size rather than their electronic character.

To determine the relative steric hindrance of a group Y the method of
35 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
40 of the carbonyl stretching vibrations in the infrared spectrum. The

solutions were equilibrated by heating in sealed tubes for 64 hr at 100°. Further heating at 100° for an additional 74hrs did not significantly change the spectra. The frequencies and intensities of the carbonyl stretching bands in the spectra of the equilibrated solutions are then 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.

$R^{19}-R^{30}$ referred to herein may independently be generally selected from hydrogen, unsubstituted or substituted aryl or unsubstituted or substituted alkyl, in addition R^{21} may be nitro, halo, amino or thio.

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 structure may be unsubstituted or, when possible be further substituted with groups selected from Y (on the non-aromatic cyclic atoms), alkyl, aryl, arylene, alkaryl, aralkyl, arylenealkyl, alkenyl, alkynyl, het, hetero, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$, $-CF_3$, $-SiR^{71}R^{72}R^{73}$, or alkylphosphorus wherein $R^{19}-R^{30}$ are as defined herein and in the case of Y or a group fulfilling the definition of Y of the first aspect the attachment is to a non- cyclic aromatic atom of the aromatic structure; 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 structures within the context of the present invention so that, when they include more than one aromatic ring, the substituent(s) Y^* 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 substituent Y^* may be on any one or more rings of the metallocene structure and this may be the same or a different ring to which Q^1 and Q^2 are linked.

Suitable metallocene type ligands which may be substituted with a group Y 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 further unsubstituted or 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 hydrocarbyl aromatic 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 hydrocarbyl aromatic structure may be monocyclic or polycyclic. The cyclic aromatic atoms may be carbon or hetero, wherein references to hetero herein are references to sulphur, oxygen and/or nitrogen. However, it is preferred that the Q^1 and Q^2 atoms are linked to available adjacent cyclic carbon atoms of the at least one aromatic ring. Typically, when the cyclic hydrocarbyl structure is polycyclic it is preferably bicyclic or tricyclic. The further cycles in the aromatic structure may or may not themselves be aromatic and aromatic 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 bridging group $-R(Y^X)_n$, whether further 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 aromatic cyclic atom of the aromatic structure is meant any further aromatic 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.

Preferably, the immediately 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 the two immediately

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.

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The term aromatic ring means that the at least one ring to which the Q^1 and Q^2 atom are linked via B & A respectively is aromatic, and aromatic should preferably be interpreted broadly to include not only a phenyl, cyclopentadienyl anion, pyrrolyl, pyridinyl, type
10 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
15 $4n + 2$ pi electrons are also possible such as [14] annulene, [18] annulene, etc

The hydrocarbyl aromatic structure R may be selected from benzene-1,2 diyl, ferrocene-1,2-diyl, naphthalene-2,3-diyl, 4 or 5 methyl
20 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
25 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-
30 1,2diyl, 4-(t-butyl dimethylsilyl)-benzene-1,2diyl, 4-t-butylsilylbenzene-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-
35 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-
40 (or 1')di-t-butyl,methylsilyl ferrocene-1,2diyl, 4-(or 1')(t-

butyldimethylsilyl)-ferrocene-1,2diyl, 4-(or 1')t-butylsilyl-ferrocene-1,2diyl, 4-(or 1')(tri-t-butylsilyl)-ferrocene-1,2diyl, 4-(or 1')(2'-tert-butylprop-2'-yl)ferrocene-1,2 diyl, 4-(or 1')(2',2',3',4',4' pentamethyl-pent-3'-yl)-ferrocene-1,2diyl, 4-(or 1')(2',2',4',4'-tetramethyl,3'-t-butyl-pent-3'-yl)-ferrocene-1,2 diyl.

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

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

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Such cycloaliphatic ring structures may be saturated or unsaturated, bridged or unbridged, substituted with alkyl, Y groups as defined herein, aryl, arylene, alkaryl, aralkyl, arylenealkyl, alkenyl, alkynyl, het, hetero, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-SR^{29}$, $-C(O)SR^{30}$, $-C(S)N(R^{27})R^{28}$, $-CF_3$, $-SiR^{71}R^{72}R^{73}$, or 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.

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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, piperazine, pyrrolidine, 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

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

However, whether forming combined groups or otherwise, it is preferred that the immediate adjacent aromatic cyclic atoms, on either side of the said available adjacent cyclic atoms to which Q^1 and Q^2 are linked, via the said linking group, are un-substituted and preferable substitution is elsewhere on the at least one aromatic ring or elsewhere in the aromatic structure when the aromatic structure comprises more than one aromatic ring and the preferred position of combined Y substituents should be understood accordingly.

Specific but non-limiting examples of unsubstituted and substituted aromatic bridged bidentate ligands within this invention are set out in the claims.

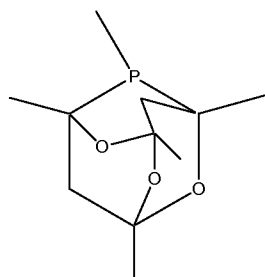
Alternatively, further examples of unsubstituted and substituted aromatic bridged bidentate ligands include the phenyl, isopropyl, o-ethylphenyl and o-methoxyphenyl analogs of the above mentioned o-tolyl ligands i.e. 1-(di-tert-butylphosphinomethyl)-2-(diphenylphosphinomethyl)benzene etc.

In the above lists of ligands the term "phosphinomethyl-adamantyl" means any one of the following groups 2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl, 2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl 2-phosphinomethyl-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl, 2-phosphinomethyl-perfluoro-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl or 2-phosphinomethyl-1,3,5-tri(trifluoromethyl)-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl.

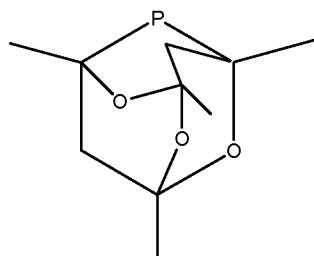
In the above lists of ligands the term "phospha-adamantyl" means any one of the following groups 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl, 2-phospha-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl, 2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl, perfluoro(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl or 2-phospha-1,3,5-tri(trifluoromethyl)-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl.

For avoidance of doubt the structure of 2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl etc is as follows:-

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Similarly, the structure of 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl is as follows:-

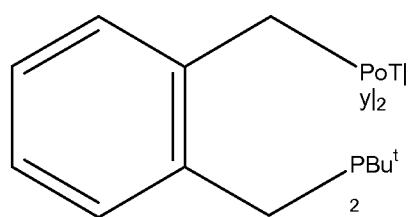


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It will be appreciated that in all cases the phosphorus is attached to two tertiary carbon atoms in the phospha-adamantyl skeleton.

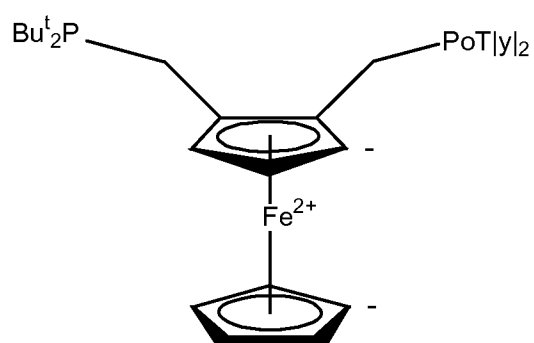
Selected structures of ligands of the invention include:-

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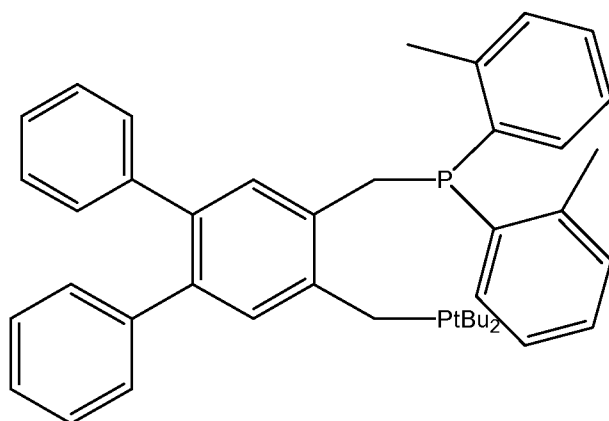


1-(di-tert-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)benzene

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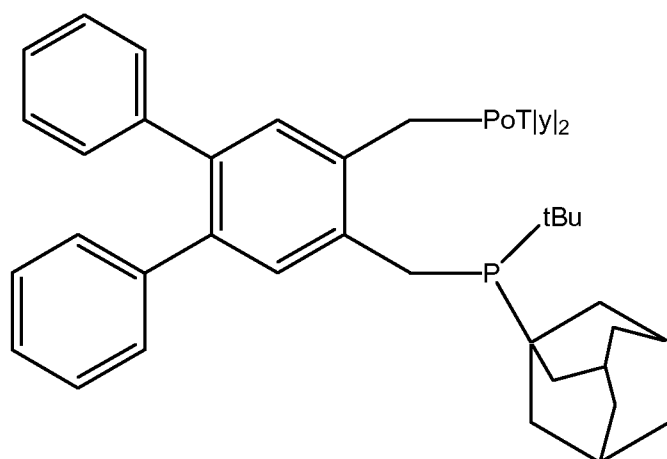


1-(di-tert-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl) ferrocene,



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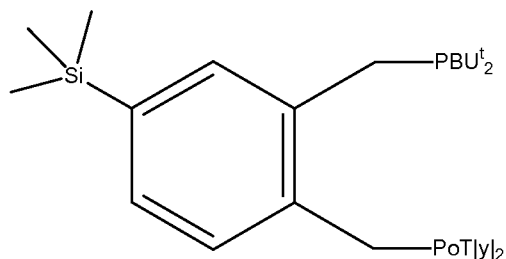
1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-diphenyl benzene;



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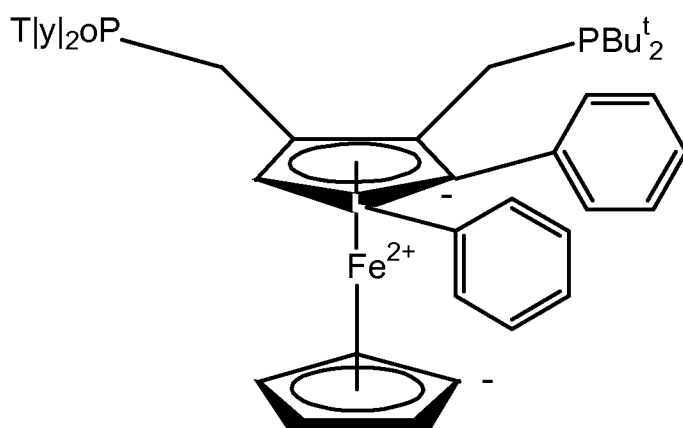
wherein oTlyl represents o-tolyl

1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-diphenylbenzene;



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1-(di-o-tolylphosphinomethyl)-2-(di-tert-butylphosphino)-4-(trimethylsilyl)benzene



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1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-diphenyl ferrocene;

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In the above example structures of ligands 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

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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 as shown in some of the above structures 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.

10 Substituents X^{1-4}

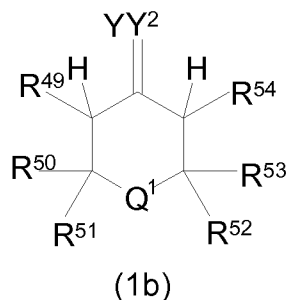
Subject to the restrictions defined in the claims the substituents X^{1-4} may represent various groups. For instance, the group X^1 may represent $CH(R^2)(R^3)$, X^2 may represent $CH(R^4)(R^5)$, X^3 may represent $CR^7(R^8)(R^9)$ and X^4 may represent $CR^{10}(R^{11})(R^{12})$, wherein R^2 to R^5 represent hydrogen, alkyl, aryl or het and R^7 - R^{12} represent alkyl, aryl or het. Alternatively, X^1 represents Ar and/or X^2 represents Ar. Preferably, when X^1 and/or X^2 represents Ar, the group is substituted by a C_1 - C_7 alkyl group, O- C_1 - C_7 alkyl group, -CN, -F, -Si(alkyl)₃, -COOalkyl, -C(O)-, or -CF₃. Preferably, the Ar group is substituted at the carbon adjacent the Q bonded ring carbon i.e. the ortho position in a phenyl ring.

Particularly preferred is when the organic groups R^7 - R^9 and /or R^{10} - R^{12} or, alternatively, 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 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} each independently represent hydrogen, aryl or alkyl, and/or be interrupted by one or more oxygen or sulphur atoms, or by silano or dialkylsilcon groups.

In particular, when cyclic, X^3 and/or X^4 may represent congressyl, norbornyl, 1-norbornadienyl or adamantyl.

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



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

Particularly preferred is when X^3 and X^4 are the same and X^1 and X^2 are the same.

- 15 In preferred embodiments, R^2 to R^5 each independently represent hydrogen, alkyl, aryl, or Het and R^7 to R^{12} each independently represent alkyl, aryl, or Het;

- 20 R^{19} to R^{30} each independently represent hydrogen, alkyl, aryl or Het;

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

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

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

- 30 Preferably, R^2 to R^5 and R^7 to R^{12} when not hydrogen each independently represent alkyl or aryl. More preferably, R^2 to R^5 and R^7 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^2 to R^5 and R^7 to R^{12} each independently represent C_1 to C_6 alkyl, which is optionally substituted as alkyl as defined herein. Most preferably, R^2 to R^5 and R^7 to R^{12} each represent non-substituted C_1 to C_6 alkyl such as methyl,
 5 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^4 , R^7 and R^{10} each represent the same alkyl, aryl or Het moiety as defined
 10 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^9 and R^{12} each represent the same alkyl, aryl or Het moiety as defined herein. More preferably 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,
 15 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^9 and R^{12} each independently represent the same C_1 - C_6 alkyl as defined above. For example: 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^9 and R^{12}
 20 each represent n-butyl or n-pentyl.

In an especially preferred embodiment of the present invention each R^2 to R^5 and R^7 to R^{12} group represents the same alkyl, aryl, or Het moiety as defined herein. Preferably, when alkyl groups, each R^1 to
 25 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.

30 The term "lower alkylene" which A and B represent in a compound of formula I, when used herein, includes C_1 to C_{10} groups which can be bonded at two places on the group to thereby connect the group Q^1 or Q^2 to the R group, and is otherwise defined in the same way as "alkyl"
 35 below. Nevertheless, methylene is most preferred. By the optional case for A and B is meant that the group Q^1 or Q^2 can be connected directly to the R group and there is the option of no intermediate C_1 - C_{10} lower alkylene group. However, in this case, it is preferred that at least one of A and B is not optionally omitted and is a C_1 - C_{10}
 40 lower alkylene. In any case, when one of the groups A or B is

optionally not present then the other group is preferably present and may be a C₁-C₁₀ group as defined herein and, therefore, it is preferred that at least one of A and B is a C₁-C₁₀ "lower alkylene" group.

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The term "alkyl" when used herein, means, unless indicated otherwise, C₁ to C₁₀ alkyl and includes methyl, ethyl, propyl, butyl, pentyl, hexyl, and heptyl groups. Unless otherwise specified, alkyl groups may, when there is a sufficient number of carbon atoms, be linear or
 10 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, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, SR²⁹, C(O)SR³⁰, C(S)NR²⁷R²⁸,
 15 unsubstituted or substituted aryl, or unsubstituted or substituted Het, wherein R¹⁹ to R³⁰ each independently represent hydrogen, halo, unsubstituted or substituted aryl or unsubstituted or substituted alkyl, or, in the case of R²¹, halo, nitro, cyano and amino and/or be interrupted by one or more (preferably less than 4) oxygen, sulphur,
 20 silicon atoms, or by silano or dialkylsilcon groups, or mixtures thereof.

The term "Ar" or "aryl" when used herein, includes five-to-ten-membered, preferably five to eight membered, carbocyclic aromatic or
 25 pseudo aromatic groups, such as phenyl, cyclopentadienyl and indenyl anions and naphthyl, which groups may be unsubstituted or 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
 30 itself be unsubstituted or substituted or terminated as defined herein), halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, SR²⁹, C(O)SR³⁰ or C(S)NR²⁷R²⁸ wherein R¹⁹ to R³⁰ each independently represent hydrogen, unsubstituted or substituted aryl or alkyl (which alkyl group may itself be unsubstituted or
 35 substituted or terminated as defined herein), or, in the case of R²¹, halo, nitro, cyano or amino.

The term "alkenyl" when used herein, means C₂ to C₁₀ alkenyl and includes ethenyl, propenyl, butenyl, pentenyl, and hexenyl groups.
 40 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, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, SR²⁹, C(O)SR³⁰, C(S)NR²⁷R²⁸, unsubstituted or substituted aryl, or unsubstituted or substituted Het, wherein R¹⁹ to R³⁰ are defined as for alkyl above 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 C₂ to C₁₀ 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, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, SR²⁹, C(O)SR³⁰, C(S)NR²⁷R²⁸, unsubstituted or substituted aryl, or unsubstituted or substituted Het, wherein R¹⁹ to R³⁰ are defined as for alkyl above 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} each independently represent hydrogen, unsubstituted or substituted aryl or alkyl (which alkyl group itself may be unsubstituted or substituted or terminated as defined herein) or, in the case of R^{21} , halo, nitro, amino or cyano. The term "Het" thus includes groups such as optionally substituted azetidiny, pyrrolidinyl, imidazolyl, indolyl, furanyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, thiadiazolyl, triazolyl, oxatriazolyl, thiatriazolyl, pyridazinyl, morpholinyl, pyrimidinyl, pyrazinyl, quinolinyl, isoquinolinyl, piperidinyl, pyrazolyl and piperazinyl. Substitution at Het may be at a carbon atom of the Het ring or, where appropriate, at one or more of the heteroatoms.

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

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

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

Suitably, when the adamantyl, congressyl, norbornyl or 1-norborndienyl group is substituted with one or more substituents as defined above, highly preferred substituents include unsubstituted C_1 to C_8 alkyl, $-OR^{19}$, $-OC(O)R^{20}$, phenyl, $-C(O)OR^{22}$, fluoro, $-SO_3H$, -

$N(R^{23})R^{24}$, $-P(R^{56})R^{57}$, $-C(O)N(R^{25})R^{26}$ and $-PO(R^{58})(R^{59})$, $-CF_3$, wherein R^{19} represents hydrogen, unsubstituted C_1 - C_8 alkyl or phenyl, R^{20} , R^{22} , R^{23} , R^{24} , R^{25} , R^{26} each independently represent hydrogen or unsubstituted C_1 - C_8 alkyl, R^{56} to R^{59} each independently represent unsubstituted C_1 - C_8 alkyl or phenyl. In a particularly preferred embodiment the substituents are C_1 to C_8 alkyl, more preferably, methyl such as found in 1,3 dimethyl adamantyl.

Suitably, the adamantyl, congressyl, norbornyl or 1-norborndienyl group may comprise, besides hydrogen atoms, up to 10 substituents as defined above, preferably up to 5 substituents as defined above, more preferably up to 3 substituents as defined above. Suitably, when the adamantyl, congressyl, norbornyl or 1-norborndienyl group comprises, besides hydrogen atoms, one or more substituents as defined herein, preferably each substituent is identical. Preferred substituents are unsubstituted C_1 - C_8 alkyl and trifluoromethyl, particularly unsubstituted C_1 - C_8 alkyl such as methyl. A highly preferred adamantyl, congressyl, norbornyl or 1-norborndienyl group comprises hydrogen atoms only i.e. the adamantyl congressyl, norbornyl or 1-norborndienyl group is not substituted.

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

The 2- 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 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 Q¹ atom of the 2-meta-adamantyl group is bonded to carbon atoms in the adamantyl skeleton having no hydrogen atoms. Most preferably, the 2-meta-adamantyl group is substituted on each of the 1, 3, 5 and 7 positions. When the 2-meta-adamantyl group includes more than 1 substituent preferably each substituent is identical. Especially preferred substituents are unsubstituted C₁-C₈ alkyl and haloalkyls, particularly unsubstituted C₁-C₈ alkyl such as methyl and fluorinated C₁-C₈ alkyl such as trifluoromethyl.

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

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

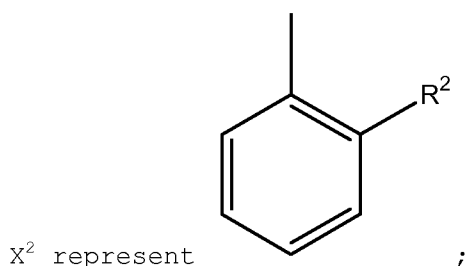
5 The 2-meta-adamantyl group may be prepared by methods well known to those skilled in the art. Suitably, certain 2-phospha-adamantyl compounds are obtainable from Cytec Canada Inc, Canada. Likewise corresponding 2-meta-adamantyl compounds of formula I etc may be obtained from the same supplier or prepared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

10 Subject to the restrictions of the claims, preferred embodiments of the present invention include those wherein:

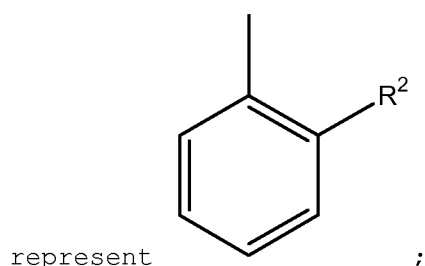
X^3 represents $CR^7(R^8)(R^9)$, X^4 represents $CR^{10}(R^{11})(R^{12})$, X^1 represents $CH(R^2)(R^3)$ and X^2 represents $CR^4(R^5)H$;

15

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



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



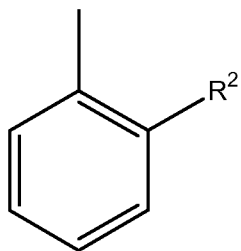
20

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

25

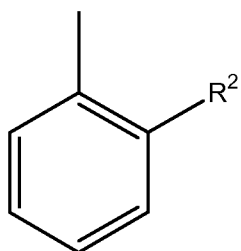
X^3 represents $CR^7(R^8)(R^9)$, X^4 represents congressyl, and X^1 represents $CH(R^2)(R^3)$ and X^2 represents $CR^4(R^5)H$;

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



represent ;

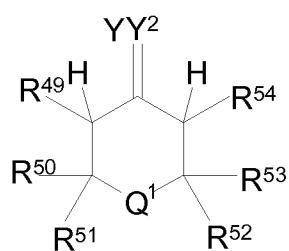
X^3 and X^4 independently represent adamantyl, and X^1 and X^2



5 represent ;

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

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

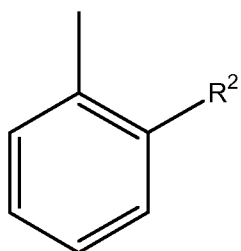


(1b)

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

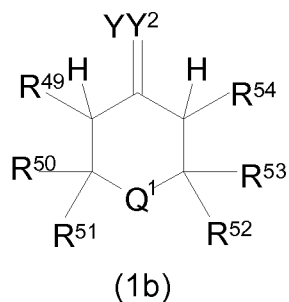
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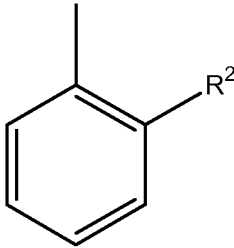
X^3 and X^4 independently represent congressyl, and X^1 and X^2



represent ;

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

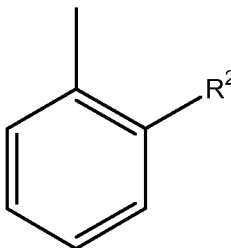


5 and X^1 and X^2 represent  ;

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

10 X^3 and X^4 together with Q^1 to which they are attached form a 2-phospha-adamantyl group, and X^1 represents $CH(R^2)(R^3)$ and X^2 represents $CR^4(R^5)H$;

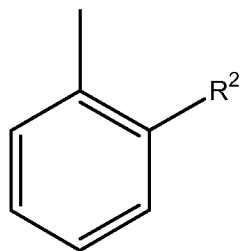
X^3 and X^4 together with Q^1 to which they are attached form a 2-

15 phospha-adamantyl group, and X^1 and X^2 represent  ;

Highly preferred embodiments of the present invention include those wherein:

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

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

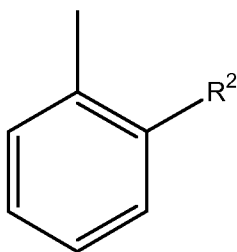


X^2 represent .

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

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

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



and X^2 represent ;

A and B are the same and represent $-CH_2-$;

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

15

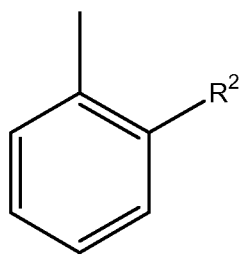
(2) X^3 represents $CR^7(R^8)(R^9)$, X^4 represents $CR^{10}(R^{11})(R^{12})$, X^1
represents $CH(R^2)(R^3)$ and X^2 represents $CH(R^4)(R^5)$;

A and B are the same and represent $-CH_2-$;

20

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

(3) X^3 and X^4 together with Q^1 to which they are attached form a 2-
25 phospho-adamantyl group, and X^1 and X^2 represent



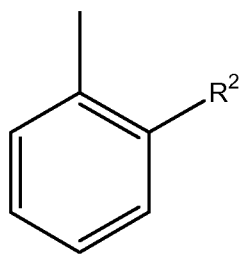
;

A and B are the same and represent -CH₂-;

Q¹ and Q² both represent phosphorus linked to the R group at ring positions 1 and 2.

5

(4) X³ and X⁴ represent adamantyl and X¹ and X² represent



;

A and B are the same and represent -CH₂-;

Q¹ and Q² both represent phosphorus linked to the R group at ring positions 1 and 2.

10

Preferably, in the above embodiments, R² - R⁵ are methyl or ethyl.

Preferably, in the compound of formula I, A and B each independently represents C₁ to C₆ alkylene which is optionally substituted as defined herein, for example with alkyl groups. Preferably, the lower alkylene groups which A and B represent are non-substituted. Particularly preferred alkylenes which A and B may independently represent are -CH₂- or -C₂H₄-. Most preferably, each of A and B represent the same alkylene as defined herein, particularly -CH₂-.

15

Alternatively, one of A or B is omitted ie Q² or Q¹ is connected directly to the group R and the other Q group is not connected directly to the group R and is a C₁ to C₆ alkylene, preferably -CH₂- or -C₂H₄-, most preferably, -CH₂-.

20

Still further preferred compounds of formula I include those wherein:

25

R² to R⁵ and R⁷ to R¹² are alkyl and are the same and preferably, each represents C₁ to C₆ alkyl, particularly methyl.

Especially preferred specific compounds of formula I include those wherein:

each R^7 to R^{12} is the same and represents methyl;

5 A and B are the same and represent $-CH_2-$;

R represents benzene-1,2-diyl.

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
10 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.

15 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 alkanolic (up to C_{12}) acids such as acetic acid and propionic acid; sulphonamic acids such as methane sulphonamic acid, chlorosulphonamic acid, fluorosulphonamic acid,
20 trifluoromethane sulphonamic acid, benzene sulphonamic acid, naphthalene sulphonamic acid, toluene sulphonamic acid, e.g. p-toluene sulphonamic acid, t-butyl sulphonamic acid, and 2-hydroxypropane sulphonamic acid; sulphonated ion exchange resins (including low acid level sulphonamic resins) perhalic acid such as perchloric acid; halogenated carboxylic
25 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 Brønsted acids. Other sources which may provide suitable anions include the optionally halogenated tetraphenyl borate derivatives,
30 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 should
35 preferably be introduced to the catalyst system independently of the metal or metal compound.

The anion may be derived from or introduced as one or more of an acid having a pK_a measured in dilute aqueous solution at 18°C of less than
40 6, more preferably, less than 5, most preferably less than 4, a salt

with a cation that does not interfere with the reaction, e.g. metal salts or largely organic salts such as alkyl ammonium, and a precursor, such as an ester, that can break down under reaction conditions to generate the anion in situ. Suitable acids and salts
 5 include the acids and salts listed supra.

Particularly preferred acid promoters for an alkoxy carbonylation are the sulfonic acids, including the sulfonated ion exchange resins, and the carboxylic acids listed supra. The low level acid ion exchange
 10 resins that may be used preferably provide a level of $\text{SO}_3\text{H}/\text{Pd}$ ratio in the reaction of less than 35 mol/mol, more preferably less than 25 mol/mol, most preferably less than 15 mol/mol. Typical ranges for the SO_3H concentration provided by the resin are in the range 1-40 mol/mol Pd, more typically, 2-30 mol/mol Pd, most typically 3-20
 15 mol/mol Pd.

Generally the anion(s) can be selected which is appropriate to the reaction. Certain ethylenically unsaturated compounds may be more sensitive to the pKa of the acid of the anion than others and
 20 conditions and solvent can be varied as appropriate within the skill of the person in the art. For instance, in butadiene carbonylation the pKa of the acid of the anion should be greater than 2 in dilute aqueous solution at 18°C, more preferably, having a pKa between 2 and 5.

25 In a carbonylation reaction, the quantity of anion present is not critical to the catalytic behaviour of the catalyst system. The molar ratio of anion to Group 8, 9 or 10 metal or compound may be from 1:1 to 10000:1, preferably from 10:1 to 2000:1 and particularly from
 30 100:1 to 1000:1. Where the anion is provided by an acid and salt, the relative proportion of the acid and salt is not critical. However, where an anion is provided by acid or partially provided by acid the ratio of acid to group 8, 9 or 10 metal is preferably, in the same ratios as the anion to metal or compound above. By H^+ is
 35 meant the amount of active acidic sites so that a mole of monobasic acid would have 1 mole of H^+ whereas a mole of dibasic acid would have 2 moles of H^+ and tribasic acids etc should be interpreted accordingly. Similarly, by C^{2+} is meant moles of metal having a 2+ cationic charge so that for M^+ ions the ratio of the metal cation

should be adjusted accordingly. For example, an M^+ cation should be taken as having 0.5 moles of C^{2+} per mole of M^+ .

5 In an alkoxycarbonylation reaction, preferably, the ratio of bidentate ligand to acid is at least 1:2 mol/mol(H^+) and preferably, the ratio of bidentate ligand to group 8, 9 or 10 metal is at least 1:1 mol/mol(C^{2+}). Preferably, the ligand is in excess of metal mol/mol(C^{2+}) and preferably in excess of a ratio of 1:2 mol/mol(H^+) with the acid. Excess ligand is advantageous as the ligand itself may
10 act as a base to buffer the acid levels in the reaction and prevent degradation of substrate. On the other hand the presence of acid activates the reaction mix and improves the overall rate of reaction.

15 In an hydroxycarbonylation reaction, preferably, the ratio of bidentate ligand to acid is at least 1:2 mol/mol(H^+) and preferably, the ratio of bidentate ligand to group 8, 9 or 10 metal is at least 1:1 mol/mol(C^{2+}). Preferably, the ligand is in excess of metal mol/mol(C^{2+}). Excess ligand may be advantageous as the ligand itself may act as a base to buffer the acid levels in the reaction and
20 prevent degradation of substrate. On the other hand the presence of acid activates the reaction mix and improves the overall rate of reaction.

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

Suitably, the process of the invention may be used to catalyse the carbonylation of ethylenically unsaturated compounds in the presence
30 of carbon monoxide and a hydroxyl group containing compound and, optionally, a source of anions. The ligands of the invention yield a surprisingly high TON in carbonylation reactions such as ethylene, propylene, 1,3-butadiene, pentenenitrile, and octene carbonylation. Consequently, the commercial viability of a carbonylation process
35 will be increased by employing the process of the invention.

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

The process of the present invention may be a batch or continuous process. However, in aging tests on the ligands of the present invention, the ligands have been found to be surprisingly resistant to decay and maintain activity after several re-cycles. Accordingly,
5 the process of the present invention is particularly suited to a continuous process.

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

Suitable ethylenically unsaturated compounds for the invention are ethylenically unsaturated compounds having from 2 to 50 carbon atoms
15 per molecule, or mixtures thereof. Suitable ethylenically unsaturated compounds may have one or more isolated or conjugated unsaturated bonds per molecule. Preferred are compounds having from 2 to 20 carbon atoms, or mixtures thereof, yet more preferred are compounds having at most 18 carbon atoms, yet more at most 16 carbon atoms,
20 again more preferred compounds have at most 10 carbon atoms. In a preferred group of processes, the ethylenically unsaturated compound is an olefin or a mixture of olefins. Suitable ethylenically unsaturated compounds include acetylene, methyl acetylene, propyl acetylene, 1,3-butadiene, ethylene, propylene, butylene, isobutylene,
25 pentenes, pentene nitriles, alkyl pentenoates such as methyl 3-pentenoates, pentene acids (such as 2-and 3-pentenoic acid), heptenes, octenes, dodecenes.

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

Especially preferred ethylenically unsaturated compounds are
35 ethylene, propylene, heptenes, octenes, dodecenes, 1,3-butadiene and pentene nitriles.

Still further, it is possible to carbonylate mixtures of alkenes containing internal double bonds and/or branched alkenes with
40 saturated hydrocarbons. Examples are raffinate 1, raffinate 2 and

other mixed streams derived from a cracker , or mixed streams derived from alkene dimerisation (butene dimerisation is one specific example) and fischer tropsch reactions .

- 5 Reference to ethylenically unsaturated compounds herein excludes vinyl esters including vinyl acetate and other functionalised alkenes .

- 10 Where a compound of a formula herein (e.g. formula I) 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
15 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
20 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
25 appropriate.

All stereoisomers are included within the scope of the process of the invention.

- 30 It will be appreciated by those skilled in the art that the compounds of formula (I) 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
35 antimony atoms of the compound of formula (I).

- As mentioned above, the present invention provides a process for the carbonylation of ethylenically unsaturated compound such as those listed supra comprising contacting an ethylenically unsaturated
40 compound with carbon monoxide and a source of hydroxyl groups such as

water or an alkanol in the presence of a catalyst compound as defined in the present invention.

Suitably, the source of hydroxyl groups includes an organic molecule
 5 having an hydroxyl functional group. Preferably, the organic molecule having a hydroxyl functional group may be branched or linear, and comprises an alkanol, particularly a C₁-C₃₀ alkanol, including aryl alkanols, which may be optionally substituted with one or more substituents selected from alkyl, aryl, Het, halo, cyano, nitro, OR¹⁹,
 10 OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)NR²⁷R²⁸, SR²⁹ or C(O)SR³⁰ as defined herein. Highly preferred alkanols are C₁-C₈ alkanols such as methanol, ethanol, propanol, iso-propanol, iso-butanol, t-butyl alcohol, n-butanol, phenol and chlorocapryl alcohol. Although the monoalkanols are most preferred, poly-alkanols,
 15 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,
 20 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 amount of alcohol is not critical. Generally, amounts are used in
 25 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
 30 determined at least in part by the source of alkanol used. For instance, use of methanol produces the corresponding methyl ester. Conversely, use of water produces the corresponding acids. Accordingly, the invention provides a convenient way of adding the group -C(O)O C₁-C₃₀ alkyl or aryl or -C(O)OH across the ethylenically
 35 unsaturated bond.

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

amounts of hydrogen, typically less than 5% by volume, may also be present.

5 The ratio (volume/volume) of ethylenically unsaturated compounds to hydroxyl group source in a liquid phase reaction medium may vary between wide limits and suitably lies in the range of 1:0.1 to 1:10, preferably from between 2:1 to 1:2 and up to a large excess of alkanol or water when the latter is also the reaction solvent such as up to a 100:1 excess of alkanol or water. However, if the
10 ethylenically unsaturated compound is a gas at the reaction temperature it may be present at lower levels in the liquid phase reaction medium such as at a ratio to hydroxyl group source of 1:20,000 to 1:10 more preferably, 1:10,000 to 1:50, most preferably, 1:5000 to 1:500

15

The amount of the catalyst of the invention used in the carbonylation process is not critical. Good results may be obtained when, preferably, the amount of Group 8, 9 or 10 metal is in the range 10^{-7} to 10^{-1} , more preferably, 10^{-6} to 10^{-2} , most preferably, 10^{-5} to 10^{-2}
20 moles per mole of ethylenically unsaturated compound in the liquid phase carbonylation reaction medium.

Suitably, although non-essential to the invention, the carbonylation of ethylenically unsaturated compound as defined herein may be
25 performed in one or more aprotic solvents. Suitable solvents 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, tetrahydrofuran, diphenylether, diisopropylether and the dimethylether of di-ethylene-glycol; esters,
30 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, diisopropylsulphone, sulfolane (tetrahydrothiophene-2,2-dioxide), 2-methylsulfolane, diethyl sulphone, tetrahydrothiophene 1,1-dioxide
35 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

egg, 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
 5 is below a value of 50, more preferably in the range of 3 to 8, at
 298.15 K and $1 \times 10^5 \text{ Nm}^{-2}$. In the present context, the dielectric
 constant for a given solvent is used in its normal meaning of
 representing the ratio of the capacity of a condenser with that
 10 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
 15 quoted for a temperature of about 20°C or 25°C, i.e. about 293.15 K or
 298.15 K, and atmospheric pressure, i.e. about $1 \times 10^5 \text{ Nm}^{-2}$, or can
 readily be converted to that temperature and 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.

20

For example, the dielectric constant of anisole is 4.3 (at 294.2 K),
 of diethyl ether is 4.3 (at 293.2 K), of sulfolane is 43.4 (at 303.2
 K), of methylpentanoate is 5.0 (at 293.2 K), of diphenylether is 3.7
 (at 283.2 K), of dimethyladipate is 6.8 (at 293.2 K), of
 25 tetrahydrofuran is 7.5 (at 295.2 K), of methylnonanoate is 3.9 (at
 293.2 K). A preferred aprotic solvent is anisole.

In the presence of an alkanol, an aprotic solvent will be generated
 by the reaction as the ester carbonylation product of the
 30 ethylenically unsaturated compound, carbon monoxide and the alkanol
 is an aprotic solvent.

The process may be carried out in an excess of aprotic solvent, i.e.
 at a ratio (v/v) of aprotic solvent to alkanol of at least 1:1.
 35 Preferably, this ratio ranges from 1:1 to 10:1 and more preferably
 from 1:1 to 5:1. Most preferably the ratio (v/v) ranges from 1.5:1 to
 3:1.

Despite the foregoing it is preferred that the reaction is carried out in the absence of any external added aprotic solvent i.e. in the absence of an aprotic solvent not generated by the reaction itself.

5 During hydroxycarbonylation, the presence of a protic solvent is also preferred. The protic solvent may include a carboxylic acid or an alcohol. Mixtures of the aprotic and protic solvents may also be employed.

10 Hydrogen may be added to the carbonylation reaction to improve reaction rate. Suitable levels of hydrogen when utilised may be in the ratio of between 0.1 and 20% vol/vol of the carbon monoxide, more preferably, 1-20% vol/vol of the carbon monoxide, more preferably, 2-15% vol/vol of the carbon monoxide, most preferably 3-10% vol/vol of
15 carbon monoxide.

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

20

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 (e.g. the ethylenically unsaturated compound, the hydroxyl
25 containing compound and carbon monoxide), 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.

30

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

35

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
40 silica, a silicone or a silicone rubber; or other porous particulate

material such as for example inorganic oxides and inorganic chlorides.

- 5 Preferably the support material is porous silica which has a surface area in the range of from 10 to 700 m²/g, a total pore volume in the range of from 0.1 to 4.0 cc/g and an average particle size in the range of from 10 to 500 μm. More preferably, the surface area is in the range of from 50 to 500 m²/g, the pore volume is in the range of from 0.5 to 2.5 cc/g and the average particle size is in the range of from 20 to 200 μm. Most desirably the surface area is in the range of from 100 to 400 m²/g, the pore volume is in the range of from 0.8 to 3.0 cc/g and the average particle size is in the range of from 30 to 100 μm. The average pore size of typical porous support materials is in the range of from 10 to 1000 Å. Preferably, a support material is used that has an average pore diameter of from 50 to 500 Å, and most desirably from 75 to 350 Å. It may be particularly desirable to dehydrate the silica at a temperature of from 100°C to 800°C anywhere from 3 to 24 hours.
- 10
- 15
- 20 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.
- 25 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.
- 30 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, for example a substituent of the aromatic structure, 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.
- 35

The choice of reaction conditions to link a compound of the process of the present invention to the support depends upon the ethylenically unsaturated compound and 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 ligand catalyst composition of any aspect of the invention wherein the catalyst is attached to a support.

Additionally, the bidentate phosphine may be bonded to a suitable polymeric substrate via at least one of the bridge substituents, the bridging group R, the linking group A or the linking group B may be bonded, preferably, via the 3, 5 or 6 cyclic carbons of the benzene group to polystyrene to give an immobile heterogeneous catalyst.

The amount of bidentate ligand used can vary within wide limits. Preferably, the bidentate ligand is present in an amount such that the ratio of the number of moles of the bidentate ligand present to the number of moles of the Group 8, 9 or 10 metal present is from 1 to 50 e.g. 1 to 15 and particularly from 1 to 10 mol per mol of metal. More preferably, the mol: mol range of compounds of formula I to Group 8, 9 or 10 metal is in the range of 1:1 to 20:1, most preferably in the range of 1:1 to 10:1 or even 1:1 to 1.5:1. Conveniently, the possibility of applying these low molar ratios is advantageous, as it avoids the use of an excess of the compound of formula I and hence minimises the consumption of these usually expensive compounds. 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 (a particularly preferred solvent would be the ester or acid product of the specific carbonylation reaction e.g. methyl propionate for ethylene carbonylation) and subsequently admixing with a compound of formula I as defined herein.

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

- 5 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
- 10 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.
- 15 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 . Advantageously, the carbonylation can be carried out at moderate temperatures, it is particularly advantageous
- 20 to be able to carry out the reaction at room temperature (20°C).

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

- Preferably, the carbonylation is carried out at a CO partial pressure of between $0.80 \times 10^5 \text{ N.m}^{-2}$ – $90 \times 10^5 \text{ N.m}^{-2}$, more preferably $1 \times 10^5 \text{ N.m}^{-2}$ – $65 \times 10^5 \text{ N.m}^{-2}$, most preferably 1 – $50 \times 10^5 \text{ N.m}^{-2}$. Especially preferred
- 30 is a CO partial pressure of 5 to $45 \times 10^5 \text{ N.m}^{-2}$.

- Preferably, a low pressure carbonylation is also envisaged. Preferably, when operating a low pressure carbonylation the carbonylation is carried out at a CO partial pressure of between 0.1
- 35 to $5 \times 10^5 \text{ N.m}^{-2}$, more preferably 0.2 to $2 \times 10^5 \text{ N.m}^{-2}$, most preferably 0.5 to $1.5 \times 10^5 \text{ N.m}^{-2}$.

- There is no particular restriction on the duration of the carbonylation except that carbonylation in a timescale which is
- 40 commercially acceptable is obviously preferred. Carbonylation in a

batch reaction may take place in up to 48 hours, more typically, in up to 24 hours and most typically in up to 12 hours. Typically, carbonylation is for at least 5 minutes, more typically, at least 30 minutes, most typically, at least 1 hour. In a continuous reaction
5 such time scales are obviously irrelevant and a continuous reaction can continue as long as the TON is commercially acceptable before catalyst requires replenishment.

The catalyst system of the present invention is preferably
10 constituted in the liquid phase which may be formed by one or more of the reactants or by the use of a suitable solvent.

The use of stabilising compounds with the catalyst system may also be beneficial in improving recovery of metal which has been lost from
15 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
20 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.

25 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.

30 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
35 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
40 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

5 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

10 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

15 presence of a suitable dispersant but when the dispersant type and concentration is optimised then such agglomeration should be at a relatively low level and the agglomerates may form only loosely so that they may be broken up and the particles redispersed by agitation.

20 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

25 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

30 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

35 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,

40 polyethylenimine, polyglycine, polyacrylic acid, polymethacrylic

acid, poly(3-hydroxybutyric acid), poly-L-leucine, poly-L-methionine, poly-L-proline, poly-L-serine, poly-L-tyrosine, poly(vinylbenzenesulphonic acid) and poly(vinylsulphonic acid), acylated polyethylenimine. Suitable acylated polyethylenimines are described in BASF patent publication EP1330309 A1 and US 6,723,882.

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

Suitable polymeric dispersants, in addition to being soluble in the reaction medium at reaction conditions, contain at least one acidic or basic moiety, either within the polymer backbone or as a pendant group. We have found that polymers incorporating acid and amide moieties such as polyvinylpyrrolidone (PVP) and polyacrylates such as polyacrylic acid (PAA) are particularly suitable. The molecular weight of the polymer which is suitable for use in the invention depends upon the nature of the reaction medium and the solubility of the polymer therein. We have found that normally the average molecular weight is less than 100,000. Preferably, the average molecular weight is in the range 1,000 - 200,000, more preferably, 5,000 - 100,000, most preferably, 10,000 - 40,000 e.g. Mw is preferably in the range 10,000 - 80,000, more preferably 20,000 - 60,000 when PVP is used and of the order of 1,000 - 10,000 in the case of PAA.

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

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.

5 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.

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

15 The invention not only extends to novel bidentate ligands of formula (I) but also novel complexes of such ligands with the metal of Group 8, 9 or 10 or a compound thereof.

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

Preparative Examples

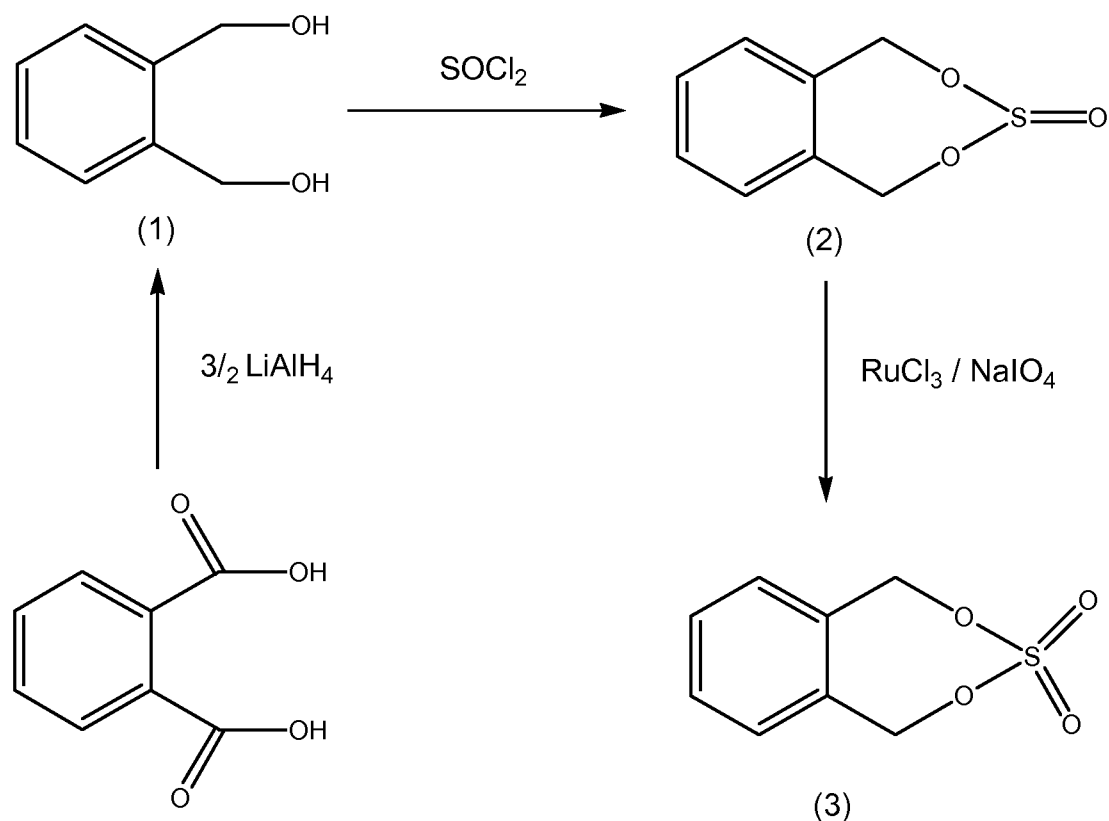
Preparation of cyclic sulphate of 1,2-benzenedimethanol (3)

25

The method employed for the synthesis of phosphine ligands of the derivatives of the examples starts with the synthesis of the cyclic sulphate (3). The cyclic sulphate compound (3) is formed in a two step synthesis. The commercially available di-alcohol 1,2-benzenedimethanol (1) (which can also be prepared by the lithium aluminium hydride reduction of phthalic acid) was reacted with thionyl chloride (SOCl₂) in dichloromethane to give the cyclic sulphite complex (2). The cyclic sulphite complex was then oxidised with sodium periodate and ruthenium trichloride to give the cyclic sulphate complex (3).

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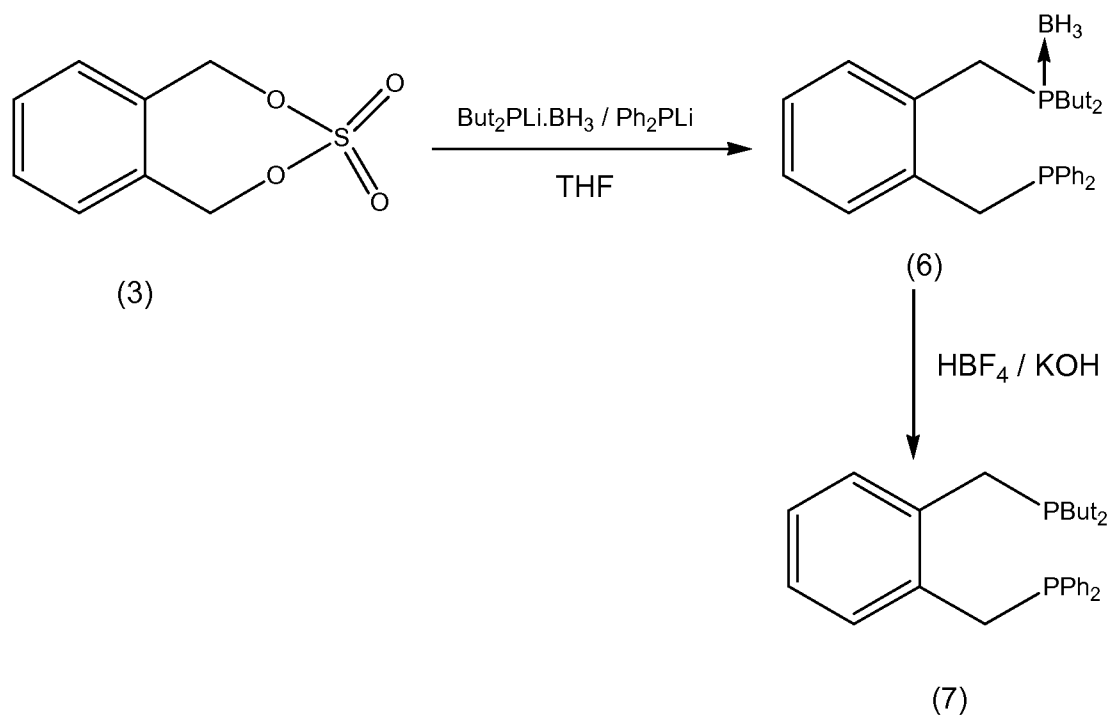
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5 Preparation of 1-(di-tert-butylphosphinomethane)-2-(diphenylphosphinomethane)benzene (7)

10 The mixed phosphine (7) was prepared in a two step process; the cyclic sulphate was sequentially reacted with the lithium salt of $\text{Bu}^t_2\text{PH.BH}_3$ (4) followed by the lithium salt of Ph_2PH (5). The boron protected phosphine (6) was then de-boronated by the addition of tetrafluoroboric acid the in-situ prepared bis-phosphonium salt was then reduced to the free phosphine (7) by addition of potassium hydroxide. The other three mixed phosphines were prepared in a similar manner to (7).

15



5 Experimental

General

Unless stated to the contrary all manipulations were performed under an atmosphere of Nitrogen using standard Schlenk line, cannula and glovebox techniques. All NMR experiments were performed using CDCl_3 as the solvent.

Preparation of cyclic sulphate (3)

The dialcohol (1) (21.2g, 153mmol) was partially dissolved in dichloromethane (250ml). To this was added thionyl chloride (13.8ml, 189mmol) slowly. This gave a large volume of gas evolution. The resultant solution was then heated to reflux (50°C) for 90 minutes. The resultant solution was then cooled to room temperature and stirred overnight. At this point the cyclic sulfite complex (2) had been formed. The solvent was then removed under vacuum to give a pale brown oil. The cyclic sulfite was then diluted with dichloromethane (100ml), acetonitrile (100ml) and water (150ml). To the resultant biphasic solution was added sodium periodate (65.3g, 306mmol) and

Ruthenium trichloride hydrate (300mg). The resultant suspension was then stirred at room temperature for one hour during time a large volume of white precipitate was formed. The final suspension was diluted with water (100ml) and ether (100ml) added. The organic layer was collected by separation and the aqueous residues washed with ether (2*100ml). The combined organic extracts were then washed with water (2*200ml) before being dried over sodium sulphate. The organic extracts were then filtered through filter paper containing celite. This gave an off-colourless solution. The solvent was then removed under vacuum to give an off white solid. The solid was stored in the freezer at -20°C. Yield =24.6g, 80%. ¹H NMR (500MHz, CDCl₃, δ), 7.46 (m, 2H, Ph), 7.38 (m, 2H, Ph), 5.44 (s, 4H, CH₂) ppm.

15 Preparation of di-tert-butylphosphine borane (4)

Di-tert-butylphosphine chloride (34g, 188.41mmol) was added to a Schlenk flask followed by diethyl ether (200ml). The ether solution was cooled in a cold water bath and LiAlH₄ (1M in diethyl ether, 100ml, 100mmol) was added slowly. This gave a yellow suspension which was allowed to stir at room temperature overnight. The suspension was quenched by the addition of water (50ml, degassed with nitrogen for 20 minutes). This gave a biphasic solution. The upper (organic layer) was cannula transferred into a clean Schlenk and the aqueous residues washed with a further 100ml of ether. The ether extracts were combined and dried with sodium sulphate. The ether extracts were then cannula transferred into a clean Schlenk and the ether removed by distillation. This gave a colourless oil. The colourless oil was then diluted with THF (200ml) and cooled to 0°C, to this was added BH₃ in THF (1M solution, 250ml, 250mmol). The resultant solution was then stirred at room temperature overnight. The solvent was then removed under vacuum to give a white crystalline solid which was then isolated in the glovebox. Yield = 22.1g, 73% yield. ³¹P {¹H} NMR (80 MHz, CDCl₃, δ): δ 49.23 ppm (multiplet).

35 Preparation of diphenylphosphine (5)

Diphenylchlorophosphine (34.8ml, 188.41mmol) was added to a Schlenk flask followed by diethyl ether (200ml). The ether solution was cooled in a cold water bath and LiAlH₄ (1M in diethyl ether, 100ml,

100mmol) was added slowly. This gave a yellow suspension which was allowed to stir at room temperature overnight. The suspension was quenched by the addition of HCl (conc. 20ml) in water (40ml, degassed with nitrogen for 20 minutes). This gave a biphasic solution. The upper (organic layer) was cannula transferred into a clean Schlenk and the aqueous residues washed with a further 100ml of ether. The ether extracts were combined and dried with sodium sulphate. The ether extracts were then dried under vacuum. This gave a pale yellow oil, yield = 36g. The phosphine was stored in the freezer. ^{31}P $\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3 , δ): -37.9 ppm

NB. Diphenyl phosphine is light and thermally sensitive and should be stored in the freezer. As a modification of this procedure the ether should be removed under vacuum rather than by distillation due to the high boiling point of the phosphine.

Preparation of di-tert-butylphosphine (5b)

Di-tert-butylphosphine chloride (34g, 188.41mmol) was added to a Schlenk flask followed by diethyl ether (200ml). The ether solution was cooled in a cold water bath and LiAlH_4 (1M in diethyl ether, 100ml, 100mmol) was added slowly. This gave a yellow suspension which was allowed to stir at room temperature overnight. The suspension was quenched by the water (50ml, degassed with nitrogen for 20 minutes). This gave a biphasic solution. The upper (organic layer) was cannula transferred into a clean Schlenk and the aqueous residues washed with a further 100ml of ether. The ether extracts were combined and dried with sodium sulphate. The ether extracts were then cannula transferred into a clean Schlenk and the ether removed by distillation. This gave a colourless oil. Yield = 22.0g, 80%. ^{31}P $\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3): δ 21.0 ppm

Preparation of 1-(di-tert-butylphosphino{borane}methyl)-2-(diphenylphosphinomethyl)benzene (6)

The $\text{Bu}^t_2\text{PH.BH}_3$ (4) (9.68g, 60.50mmol) was dissolved in THF (70ml), to this was added Bu^nLi (2.5M in hexanes, 28.6ml, 71.39mmol). The resultant yellow solution was stirred for one hour. The cyclic sulphate (3) (11.0g, 55.0mmol) was dissolved in THF (100ml) and cooled to -78°C . The lithium phosphide solution was then added dropwise to the cyclic sulphate solution. After addition was complete

the resultant solution was stirred at -78°C for thirty minutes before being allowed to warm to room temperature. The solution was then stirred for three hours at room temperature. The solution was then cooled to -78°C .

- 5 The diphenyl phosphine (**5**) (85% pure, due to decomposition, 11.05ml, 60.0mmolmmol) was diluted with THF (70ml). To this was added $\text{Bu}^{\text{n}}\text{Li}$ (2.5M in hexanes, 26.4ml, 65.95 mmol). The resultant red solution was then added dropwise to the cyclic sulphate solution at -78°C . After the addition was complete the solution was stirred at -78°C for
 10 thirty minutes before being allowed to warm up to room temperature and then stirred overnight. The solvent was then removed under vacuum to give a yellow solid/gel. Ether (250ml) was then added followed by water (100ml, degassed for thirty minutes with nitrogen). This gave a biphasic solution. The organic (upper) phase was cannula transferred
 15 into a clean Schlenk and the aqueous residues washed with ether (2*100ml). The ether extracts were then combined and dried over sodium sulphate. The dried ether extracts were then cannula transferred into a clean Schlenk and dried under vacuum. This gave a pale yellow oil, yield = 27.9g.

20

Preparation of 1-(di-tert-butylphosphinomethyl)-2-(diphenylphosphinomethyl)benzene (7**)**

- The 1-(di-tert-butylphosphino{borane}methyl)-2-(
 25 diphenylphosphinomethyl)benzene (**6**) complex (27.9g, maximum yield =55mmol) was dissolved in MTBE (250ml). To this was added tetrafluroboric acid (45.2ml, 330mmol). This gave gas evolution and the formation of a white precipitate. The resultant suspension was then heated to 63°C for 16 hours. The solvent was removed under
 30 vacuum to give a pale yellow solution. To this was added KOH (30g, 455mmol) in water (75ml, degassed with nitrogen for 30 minutes). This gave the formation of an off-white precipitate. Diethyl ether (300ml) was added and the ether soluble material cannula transferred into a clean Schlenk. The aqueous residues were then washed with diethyl
 35 ether (2*100ml). The ether extracts were then combined and dried over sodium sulphate. The ether extract were then cannula transferred into a clean Schlenk and dried under vacuum. This gave a pale yellow sticky solid. Yield = 8.0g. The solid was suspended in methanol (50ml) and heated to reflux, the resultant solution was then cooled
 40 to room temperature and stood in the freezer overnight. This gave a

large volume of an off-white solid. The solid was isolated by filtration and dried under vacuum. This gave a free flowing off-white solid. Yield = 5.6g, 23%. 95% pure. ^{31}P { ^1H .} NMR (CDCl_3 , 161.9MHz, δ); 28.4 (s), -13.1 (s) ppm

5

Preparation of Di-iso-propylphosphine borane (10)

Di-iso-propylphosphine chloride (40g, 262.1mmol) was added to a Schlenk flask followed by diethyl ether (200ml). The ether solution
 10 was cooled in a cold water bath and LiAlH_4 (1M in diethyl ether, 150ml, 150mmol) was added slowly. This gave a yellow suspension which was allowed to stir at room temperature overnight. The suspension was quenched by the addition of water (50ml, degassed with nitrogen for 20 minutes). This gave a biphasic solution. The upper (organic layer)
 15 was cannula transferred into a clean Schlenk and the aqueous residues washed with a further 100ml of ether. The ether extracts were combined and dried with sodium sulphate. The ether extracts were then cannula transferred into a clean Schlenk and the ether removed by distillation. This gave a colourless oil. The colourless oil was then
 20 diluted with THF (200ml) and cooled to 0°C , to this was added BH_3 in THF (1M solution, 300ml, 300mmol). The resultant solution was then stirred at room temperature overnight. The solvent was then removed under vacuum to give a colourless oil. Yield = 27.1g, 79% yield. ^{31}P { ^1H } NMR (CDCl_3 , 161.9MHz, δ); 28.0 (m), ppm

25

Preparation of 1-(di-tert-butylphosphino{borane}methyl)-2-(di-iso-propylphosphino{borane}methyl)benzene (11)

30 The $\text{Bu}^t_2\text{PH.BH}_3$ (**4**) (12.12g, 75.75mmol) was dissolved in THF (100ml), to this was added Bu^nLi (2.5M in hexanes, 30.5ml, 75.75mmol). The resultant yellow solution was stirred for one hour. The cyclic sulphate (**3**) (15.15g, 75.75mmol) was dissolved in THF (100ml) and cooled to -78°C . The lithium phosphide solution was then added
 35 dropwise to the cyclic sulphate solution. After addition was complete the resultant solution was stirred at -78°C for thirty minutes before being allowed to warm to room temperature. The solution was then stirred for thirty minutes at room temperature. The solution was then cooled to -78°C .
 40 The di-iso-propylphosphine borane (**10**) (10g, 75.75mmol) was diluted with THF (70ml) and cooled to 0°C . To this was added Bu^nLi (2.5M in

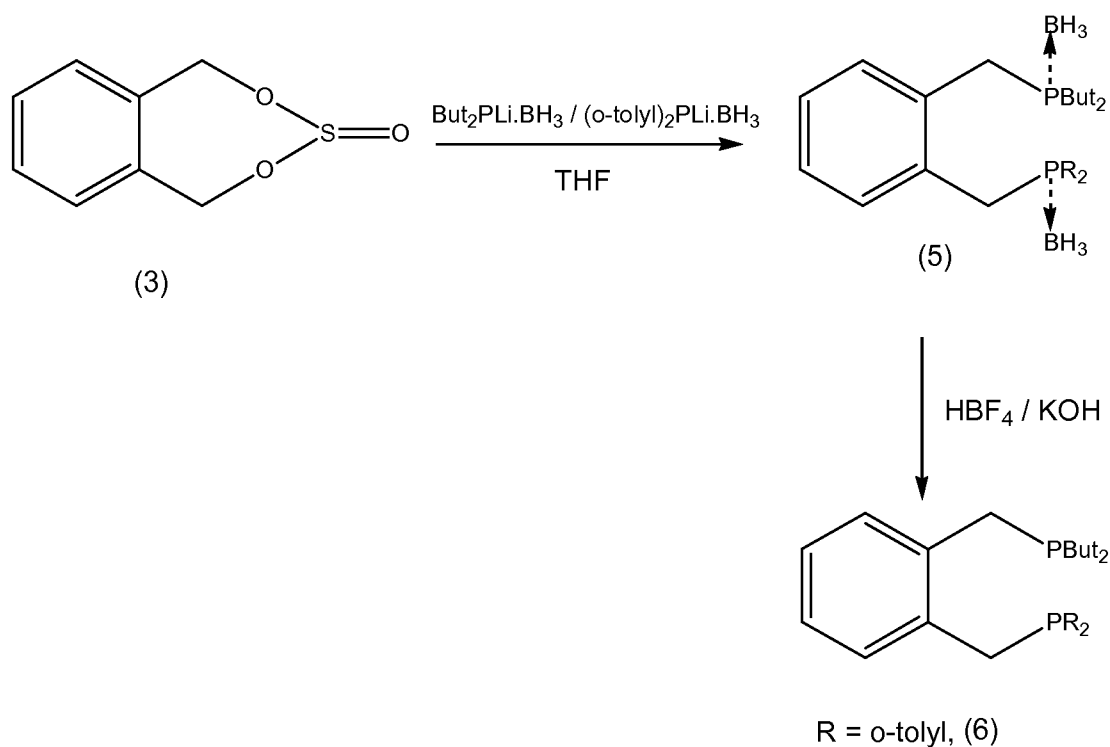
hexanes, 30.5ml, 75.75mmol). The resultant yellow solution was then allowed to warm to room temperature. The solution was then stirred for 30 minutes at room temperature. This solution was then added dropwise to the cyclic sulphate solution at -78°C. After the addition was complete the solution was stirred at -78°C for thirty minutes before being allowed to warm up to room temperature and then stirred overnight. The solvent was then removed under vacuum to give a yellow solid/gel. Ether (250ml) was then added followed by water (100ml, degassed for thirty minutes with nitrogen). This gave a biphasic solution. The organic (upper) phase was cannula transferred into a clean Schlenk and the aqueous residues washed with ether (250ml). The ether extracts were then combined and dried over sodium sulphate. The dried ether extracts were then cannula transferred into a clean Schlenk and dried under vacuum. This gave a pale yellow solid, yield = 30.27g.

Preparation of 1-(di-*tert*-butylphosphinomethyl)-2-(di-*iso*-propylphosphinomethyl)benzene (12)

The 1-(di-*tert*-butylphosphino{borane}methyl)-2-(di-*iso*-propylphosphino{borane}methyl)benzene (11) complex (30.27g, maximum yield = 75.75mmol) was dissolved in MTBE (300ml). To this was added tetrafluoroboric acid (63ml, 454.5mmol). This gave gas evolution and the formation of a white precipitate. The resultant suspension was then heated to 57°C for 16 hours. The solvent was removed under vacuum to give a pale yellow solution. To this was added KOH (40g, 605mmol) in water (50ml, degassed with nitrogen for 30 minutes). This gave the formation of an off-white precipitate. Pentane (2*250) was added and the pentane soluble material cannula transferred into a clean Schlenk. The pentane extracts were then dried over sodium sulphate. The pentane extracts were then cannula transferred into a clean Schlenk and dried under vacuum. This gave a pale yellow oil. Yield = 10.0g. The aqueous residues were then extracted with more pentane (2*250ml), the pentane soluble material were cannula transferred into a clean Schlenk. The pentane extracts were then dried over sodium sulphate. The pentane extracts were then cannula transferred into a clean Schlenk and dried under vacuum, yield = 4.9 g. The combined yield = 14.9g, 54%. 95% pure. ³¹P {¹H.} NMR (CDCl₃, 202.3MHz, δ); 28.3 (s), 5.1 (s) ppm.

Preparation of 1-(di-tert-butylphosphinomethane)-2-(di-o-tolylphosphinomethane)benzene (6)

Phosphine (6) was prepared in a two step process; the cyclic sulphate was sequentially reacted with the lithium salt of $\text{Bu}^t_2\text{PH.BH}_3$ followed by the lithium salt of $(o\text{-tolyl})_2\text{PH.BH}_3$ (4). The intermediate boron protected phosphine (5) was then de-boronated by the addition of tetrafluoroboric acid, the in-situ prepared bis-phosphonium salt was then reduced to the free phosphine (7) by the addition of potassium hydroxide.



15 Preparation of di-o-tolylphosphine borane (4)

Di-o-tolylphosphine chloride (10g, 40.2mmol) was added to a Schlenk flask followed by diethyl ether (200ml). The ether solution was cooled in a cold water bath and LiAlH_4 (1M in diethyl ether, 100ml, 100mmol) was added slowly. This gave a suspension which was then allowed to stir at room temperature overnight. The suspension was quenched by the addition of water (50ml, degassed with nitrogen for 20 minutes). This gave a biphasic solution. The upper (organic layer) was cannula transferred into a clean Schlenk and the aqueous residues washed with a further 100ml of ether. The ether extracts were

combined and dried with sodium sulphate. The ether extracts were then cannula transferred into a clean Schlenk and the ether removed under. This gave a white solid. The white solid was then dissolved in THF (200ml) and cooled to 0°C, to this was added BH₃ in THF (1M solution, 100ml, 100mmol). The resultant solution was then stirred at room temperature overnight. The solvent was then removed under vacuum to give a white waxy solid. Yield = 8.5g, 93%, ³¹P {¹H} NMR (CDCl₃, 161.9MHz, δ); 18.9(s), ppm

10 Preparation of 1-(di-tert-butylphosphino{borane}methyl)-2-(di-o-tolylphosphino{borane}methyl)benzene (5)

The Bu^t₂PH.BH₃ (6.11g, 37.3mmol) was dissolved in THF (70ml), to this was added BuⁿLi (2.5M in hexanes, 15.0ml, 37.3mmol). The resultant yellow solution was stirred for one hour. The cyclic sulphate (3) (7.46g, 37.3mmol) was dissolved in THF (100ml) and cooled to -78°C. The lithium phosphide solution was then added dropwise to the cyclic sulphate solution. After addition was complete the resultant solution was stirred at -78°C for thirty minutes before being allowed to warm to room temperature. The solution was then stirred for three hours at room temperature. The solution was then cooled to -78°C.

The bis(o-tolyl)phosphine borane (4) (8.50g, 37.3mmol) was dissolved with THF (70ml). To this was added BuⁿLi (2.5M in hexanes, 15.0ml, 37.3 mmol). The resultant orange/red solution was then added dropwise to the cyclic sulphate solution at -78°C. After the addition was complete the solution was stirred at -78°C for thirty minutes before being allowed to warm up to room temperature and then stirred overnight. The solvent was then removed under vacuum to give a yellow solid/gel. Ether (250ml) was then added followed by water (100ml, degassed for thirty minutes with nitrogen). This gave a biphasic solution. The organic (upper) phase was cannula transferred into a clean Schlenk and the aqueous residues washed with ether (2*100ml). The ether extracts were then combined and dried over sodium sulphate. The dried ether extracts were then cannula transferred into a clean Schlenk and dried under vacuum. This gave a pale yellow oil, yield = 13.3g.

40 Preparation of 1-(di-tert-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)benzene (6)

The 1-(di-tert-butylphosphino{borane}methyl)-2-(di-*o*-tolylphosphino{borane}methyl)benzene (**5**) complex (13.3g, maximum yield = 37.3mmol) was dissolved in MTBE (250ml). To this was added tetrafluoroboric acid (31.0ml, 273.7mmol). This gave gas evolution and the formation of a white precipitate. The resultant suspension was then heated to 63°C for 16 hours. The solvent was removed under vacuum to give a pale yellow solution. To this was added KOH (30g, 300mmol) in water (75ml, degassed with nitrogen for 30 minutes). This gave the formation of an off-white precipitate. Pentane (300ml) was added and the ether soluble material cannula transferred into a clean Schlenk. The aqueous residues were then washed with pentane (200ml). The pentane extracts were then combined and dried over sodium sulphate. The ether extract were then cannula transferred into a clean Schlenk and dried under vacuum. This gave a pale orange solid. Yield = 9.7g. The solid was suspended in methanol (40ml) and heated to reflux; the resultant white suspension was then cooled to room temperature and the methanol soluble material removed by cannula. The insoluble white material was then dried under vacuum and isolated in the glovebox. Yield = 3.4g, 24%. 95% pure. ³¹P {¹H} NMR (CDCl₃, 161.9MHz, δ); 29.8 (s), -35.0 (s) ppm

Preparation of 1,2-bis(1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantanemethyl)benzene (14**)**

The phosphine (**14**) was prepared by the addition of the lithium salt of 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane borane (**8**) with dichloro-*o*-xylene. The intermediate boron protected phosphine was then de-protected by the addition of diethylamine to give the target molecule.

Preparation 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane borane (8**)**

The phosphine 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane (7.34g, 34mmol) (**7**) was added to a 500ml Schlenk flask. To this was added BH₃ (1M in THF, 100ml, 100mmol). The resultant solution was then stood overnight. The boranated phosphine was kept as a solution until required.

Preparation of 1,2-bis(1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantanemethyl)benzene (14)

The 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane borane
 5 solution (8) (70mmol) was dried under vacuum and then redissolved in THF (100ml). The THF solution was then cooled to -78°C and $\text{Bu}^{\text{n}}\text{Li}$ (2.5M in hexanes, 28.0ml, 70mmol) was added, this solution was then immediately added to a solution of 1,2-bis(chloromethyl)benzene (6.08g, 35mmol) at -78°C . The resultant solution was then stirred at
 10 -78°C for thirty minutes before warming to room temperature and stirring at room temperature overnight. After 90 minutes a white suspension was observed. Diethylamine (40ml, degassed with Nitrogen for 20 minutes) was added to the suspension and the suspension heated to reflux for two hours. The resultant suspension was then cooled to
 15 room temperature and then dried under vacuum. The residue was suspended in toluene (300ml) and then water (100ml, degassed with Nitrogen for 20 minutes) was then added. The upper (organic) phase was cannula transferred into a clean Schlenk flask and solvent removed under vacuum. This gave a white paste which was then
 20 suspended in methanol (40ml). The suspension was then heated to reflux and then allowed to cool to room temperature. The methanol soluble material was removed by cannula and the white solid dried under vacuum. The white solid was then isolated in the glovebox. Yield = 10.5g. 95% pure. ^{31}P { ^1H .} NMR (CDCl_3 , 161.9MHz, δ); 28.4 (s),
 25 -13.1 (s) ppm

Preparation of cyclic sulphate (1)

The 1,2-benzenedimethanol (21.2g, 153mmol) was partially dissolved in
 30 dichloromethane (250ml). To this was added thionyl chloride (13.8ml, 189mmol) slowly. This gave a large volume of gas evolution. The resultant solution was then heated to reflux (50°C) for 90 minutes. The resultant solution was then cooled to room temperature and stirred overnight. The solvent was then removed under vacuum to give
 35 a pale brown oil. The residue was then diluted with dichloromethane (100ml), acetonitrile (100ml) and water (150ml). To the resultant biphasic solution was added sodium periodate (65.3g, 305.3mmol) and Ruthenium trichloride hydrate (300mg). The resultant suspension was then stirred at room temperature for one hour during time a large
 40 volume of white precipitate was formed. The final suspension was

diluted with water (100ml) and ether (100ml) added. The organic layer was collected by separation and the aqueous residues washed with ether (2*100ml). The combined organic extracts were then washed with water (2*200ml) before being dried over sodium sulphate. The organic
 5 extracts were then filtered through filter paper containing celite. This gave an off-colourless solution. The solvent was then removed under vacuum to give an off white solid. The solid was stored in the freezer at -20°C. Yield =24.6g, 80%. 99% pure by ^1H NMR.

10 Preparation of di-tert-butylphosphine borane (2)

Di-tert-butylphosphine chloride (34g, 188.41mmol) was added to a Schlenk flask followed by diethyl ether (200ml). The ether solution was cooled in a cold water bath and LiAlH_4 (1M in diethyl ether,
 15 100ml, 100mmol) was added slowly. This gave a yellow suspension which was allowed to stir at room temperature overnight. The suspension was quenched by the addition of water (50ml, degassed with nitrogen for 20 minutes). This gave a biphasic solution. The upper (organic layer) was cannula transferred into a clean Schlenk and the aqueous residues
 20 washed with a further 100ml of ether. The ether extracts were combined and dried with sodium sulphate. The ether extracts were then cannula transferred into a clean Schlenk and the ether removed by distillation. This gave a colourless oil. The colourless oil was then diluted with THF (200ml) and cooled to 0°C, to this was added BH_3 in
 25 THF (1M solution, 250ml, 250mmol). The resultant solution was then stirred at room temperature overnight. The solvent was then removed under vacuum to give a white crystalline solid which was then isolated in the glovebox. Yield = 22.1g, 73% yield. ^{31}P { ^1H } NMR (80 MHz, CDCl_3 , δ): δ 49.23 ppm (multiplet).

30

Preparation of bis(o-ethylphenyl)phosphine oxide (3a)

Into a 1L Schlenk flask was added small (4cm) pieces of magnesium
 35 ribbon (7.23g, 297.5mmol). To this was added a few crystals of iodine and THF (400ml). The solution was then placed in a hot water bath for 20 minutes until the orange colour of the solution has faded to pale yellow. The hot water bath was then removed and the bromide (50g, 270.4mmol) was added dropwise over 90 minutes. This gave a brown
 40 solution and a small amount of unreacted magnesium. The solution was

then stirred at room temperature for 30 minutes before the diethyl phosphite (11.22ml, 87.2mmol) was added dropwise. The resultant solution was then stirred overnight. The reaction was quenched with hydrochloric acid (50ml) which was added slowly to the reaction solution. This was then followed by the addition of water (200ml) and toluene (300ml). This gave a bi-phasic solution. The upper organic phase was collected by separation and washed with water (200ml), saturated potassium carbonate solution (200ml) and water (200ml). The organic phase was then dried over magnesium sulphate and then filtered. The filtrate was then dried under vacuum to give a pale yellow solid (**3a**). Yield = 17.21g, 76 %.

Preparation of bis(*o*-ethylphenyl)phosphine (**3b**)

Into a 1L Schlenk flask was added the phosphine oxide (**3a**) (17.21g, 66.7mmol). To this was added acetonitrile (400ml) and triethylamine (27.9ml, 200.1 mmol). Then trichlorosilane (20.2ml, 200.1mmol) was added slowly. The addition of the trichlorosilane gave the formation of some white precipitate. The resultant mixture was then refluxed overnight. The resultant suspension was then cooled to 0° in an ice bath and a solution of potassium hydroxide (40g) in water (200ml) which had been degassed with nitrogen gas was added slowly. This gave a bi-phasic mixture. Additional acetonitrile (100ml) was then added. The upper organic phase was then removed by cannula into a clean Schlenk flask and the solvent removed under vacuum. This gave an off-white solid (**3b**). Yield = 13.60g, 84 %.

Preparation of 1-(di-*tert*-butylphosphino{borane}methyl)-2-(di-*o*-ethylphosphinomethyl)benzene (**3c**)

The $\text{Bu}^t_2\text{PH.BH}_3$ (**2**) (9.27g, 56.2mmol) was dissolved in THF (100ml), to this was added Bu^nLi (2.5M in hexanes, 22.5ml, 56.2mmol). The resultant yellow solution was stirred for one hour. The cyclic sulphate (**1**) (11.24g, 56.2mmol) was dissolved in THF (100ml) and cooled to -78°C. The lithium phosphide solution was then added dropwise to the cyclic sulphate solution. After addition was complete the resultant solution was stirred at -78°C for thirty minutes before being allowed to warm to room temperature. The solution was then stirred for thirty minutes at room temperature. The solution was then cooled to -78°C.

The bis(o-ethylphenyl)phosphine (**3b**) (13.60g, 56.2mmol) was dissolved with THF (100ml). To this was added BuⁿLi (2.5M in hexanes, 22.5ml, 56.2 mmol) at -78°C this gave the formation of an orange/red solution. The resultant solution was then stirred for thirty minutes
 5 before being removed from the cold bath and was then added slowly to the cyclic sulphate solution at -78°C. After the addition was complete the solution was stirred at -78°C for thirty minutes before being allowed to warm up to room temperature and then stirred overnight. The solvent was then removed under vacuum to give a yellow
 10 solid/gel. Ether (350ml) was then added followed by water (100ml, degassed for thirty minutes with nitrogen). This gave a biphasic solution. The organic (upper) phase was cannula transferred into a clean Schlenk and the aqueous residues washed with ether (2*100ml). The ether extracts were then combined and dried over sodium sulphate.
 15 The dried ether extracts were then cannula transferred into a clean Schlenk and dried under vacuum. This gave a white solid, yield = 18.2g.

Preparation of 1-(di-tert-butylphosphinomethyl)-2-(di-o-ethylphosphinomethyl)benzene (3d)
 20

The 1-(di-tert-butylphosphinomethyl)-2-(di-o-ethylphosphinomethyl)benzene complex (**3d**) (18.2g, maximum yield =56.2mmol) was dissolved in MTBE (400ml). To this was added
 25 tetrafluoroboric acid (46.3ml, 337.2mmol). This gave gas evolution and the formation of a white precipitate. The resultant suspension was then heated to 63°C overnight. The solvent was then removed under vacuum to give a pale yellow solution. To this was added KOH (40g, 606mmol) in water (200ml, degassed with nitrogen for 30 minutes).
 30 This gave the formation of an off-white precipitate. Pentane (400ml) was added and the pentane soluble material cannula transferred into a clean Schlenk. The aqueous residues were then washed with pentane (100ml). The pentane extracts were then combined and dried under vacuum. This gave a pale yellow solid. The solid was then suspended
 35 in methanol (40ml) and heated to reflux; the resultant white suspension was then cooled to room temperature and the methanol soluble material removed by cannula. The insoluble white material was then dried under vacuum. Yield = 9.2g, sample was not sufficiently pure for use in catalysis so an additional purification step was
 40 added.

Purification of 1-(di-tert-butylphosphinomethyl)-2-(di-o-ethylphosphinomethyl)benzene (3d)

- 5 The crude phosphine (9.2g, assume 18.78mmol if 100% pure) was dissolved in diethyl ether (400ml). To this was added methane sulphonic acid (1.22ml, 18.78mmol), this gave the immediate formation of a white suspension, the ether soluble material was then cannula transferred into a clean Schlenk flask and the residue dried under vacuum. To the ether soluble material was added a further equivalent of methane sulphonic acid (1.22ml, 18.78mmol) again this gave the immediate formation of a white suspension. The ether soluble material was then cannula transferred into a clean Schlenk flask and the residue dried under vacuum. The first ether insoluble residue was
- 10 reacted with a solution of potassium hydroxide (2.48g, 37.56mmol) in water (50ml, which had been degassed with nitrogen gas for thirty minutes). This gave the formation of a white suspension. Pentane (400ml) was then added and the suspension rapidly stirred for twenty minutes. The upper organic phase was then cannula transferred into a clean Schlenk flask and the solvent removed under vacuum. This gave a white solid yield = 3.71g, 13%, which was greater than 95% pure by ^{31}P { ^1H } and ^1H NMR. This was then removed from the flask and stored in the glovebox.
- 20 The second ether insoluble fraction was reacted with a solution of potassium hydroxide (2.48g, 37.56mmol) in water (50ml, which had been degassed with nitrogen gas for thirty minutes). This gave the formation of a white suspension. Pentane (400ml) was then added and the suspension rapidly stirred for twenty minutes. The upper organic phase was then cannula transferred into a clean Schlenk flask and the solvent removed under vacuum. This gave a white solid yield = 1.90g, which was about 80% pure by NMR.
- 30

Carbonylation Examples

35

General

Carbonylation is carried out as follows and the results with the ligands of examples 1-6 and comparative examples 1 and 2 are shown in tables 1-7.

40

Recycling Examples

Experimental

- 5 Using standard Schlenk line techniques, reaction solutions were prepared by dissolving 22mg Pd(OAc)₂ (0.1 mmole) and 0.5 mmole of ligand (5 molar equivalents) in 300ml of methanol solvent. The palladium and ligand were allowed to complex before the addition of 2.92ml (45 mmole) of methane sulfonic acid (450 molar equivalents)
- 10 completed the preparation of the catalyst solution. The catalytic solution was added to the pre-evacuated autoclave and heated to 100°C at which point the pressure generated by the solvent was 2.3 bar. The autoclave was then pressured to 12.3 bars with addition of CO: ethene (1:1 gas) charged from a 10 litre reservoir at
- 15 higher pressure. A regulatory valve ensures that the pressure of the autoclave is maintained throughout the reaction at 12.3 bars through constant injection of gas from the 10 litre reservoir. The pressure of the reservoir as well as the reactor temperature was logged throughout the reaction period of 3 hrs. The moles of product
- 20 produced at any point in the reaction can be calculated from the drop in reservoir pressure by assuming ideal gas behaviour and 100% selectivity for methyl propionate, allowing reaction TON with the particular ligand to be obtained.
- After the reaction period, the autoclave was cooled and vented. The
- 25 reaction solution was collected from the base of the vessel and immediately placed under an inert atmosphere. In examples where recycling was undertaken the solution was then reduced under pressure, to approximately 20mls. This concentrated solution, was left to stand overnight under an inert atmosphere and was then used
- 30 to form the basis of the next reaction solution with addition of 300ml of methanol. This recycled material was then added to the autoclave and reacted under the same set of conditions as before. The catalyst was recycled in this way, until a significant drop in reaction TON was observed.
- 35 Selectivity to product was determined using GC calibrated with appropriate standards.

Example 1

- Examples 1 and 2 show surprisingly high turnover numbers and no polymerisation in the carbonylation of ethylene using asymmetric ligands having no tertiary carbon atoms on one of the phosphorus atoms. Comparative example 1 illustrates results for a ligand with
- 5 tertiary carbon atoms on both phosphorus atoms (1,2-bis-(2-phosphadamantyl)o-xylene). It can be seen that the system with the asymmetric aromatic bridged ligands having non tertiary carbon atoms outperforms the exclusively tertiary carbon substituted ligand.

10 Table 1 Example 1

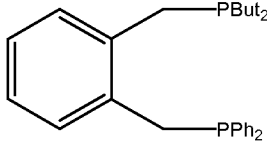
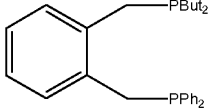
 ortho-tolyl Ph =	
22mg Pd(OAc) ₂ CO:Ethene 50:50 , 300ml MeOH 100°C, 3 hrs. Selectivity for MEP >99%	
Run	Gas Uptake (bar) (10 Litre)
Run 1	20.0
Run 2	18.7

Table 2 Example 2

 phen-1-yl Ph = 2-ethyl-	
22mg Pd(OAc) ₂ CO:Ethene 50:50 , 300ml MeOH 100°C, 3 hrs >99%	
Run	Gas Uptake (bar) (10 Litre)
Run 1	20.7

Comparative Example 1

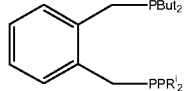
Table 3 Comparative Example 1

1,2-bis-(2-phospha- adamantyl) o-xylene		
22mg Pd(OAc) ₂ CO:Ethene 50:50 , 300ml MeOH 100 ⁰ C, 3 hrs		
	Gas Uptake (bar) (10 Litre)	Ave Rate (moles MEP/moles Pd/hr
Example 1 (comp)	15.7	14036

5 Example 3

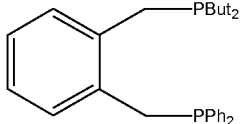
Examples 3 and 4 illustrate that the ligands are remarkably stable and can continue to give good results after several re-cycles.

10 Table 4 Example 3

		
22mg Pd(OAc) ₂ CO:Ethene 50:50 , 300ml MeOH 100 ⁰ C, 3 hrs		
Run	Gas Uptake (bar) (10 Litre)	% of initial activity
Initial Run	12.9	100
recycle 1	8.7	67.4
recycle 2	10.7	82.9
recycle 3	8.4	65.1
recycle 4	9.5	73.6
recycle 5	5.9	45.7
recycle 6	3.8	29.4
recycle 7	4.8	37.2
recycle 8	3.8	29.4

recycle 9	2.1	16.3
Selectivity for MEP >99%		

Table 5 Example 4

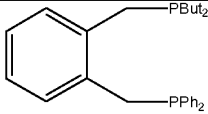
		
22mg Pd(OAc) ₂ CO:Ethene 50:50 , 300ml MeOH 100 ⁰ C, 3 hrs		
Run	Gas Uptake (bar) (10 Litre)	% of initial activity
Run 1	10.9	100
recycle 1	13.7	125.7
recycle 2	11.4	104.5
recycle 3	9.8	89.9
recycle 4	7.8	71.6
recycle 5	6.5	59.6
recycle 6	4.4	40.4
recycle 7	3.5	32.1
recycle 8	2.5	22.9
recycle 9	1.7	15.6

Examples 5 and 6

5

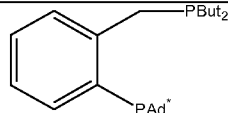
The following example illustrates that even at high temperatures no decomposition or polymerisation takes place and also higher turnover numbers can be obtained.

10 Table 6 Examples 5 and 6

	Gas Uptake (bar) (10 Litre)
22mg Pd(OAc) ₂ CO:Ethene 50:50 , 300ml MeOH	

110 ⁰ C + 120 ⁰ C, 3 hrs	
Ex. 5 Run @ 110 ⁰ C	17.3
Ex. 6 Run @ 120 ⁰ C	25.0

Table 7 Comparative Example 2

		
22mg Pd(OAc) ₂ CO:Ethene 50:50 , 300ml MeOH 100 ⁰ C, 3 hrs		
Run	Gas Uptake (bar) (10 Litre)	% of initial activity
Initial Run	27.3	100
recycle 1	20.3	74.4
recycle 2	4.0	14.6
recycle 3	3.3	12.1

5 The reader's 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.

10

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.

15

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

20

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

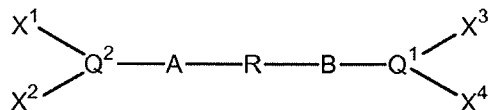
5 The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination,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

10

Claims

1 A bidentate ligand of general formula (I)

(I)



wherein:

A and B each independently represent a C₁ to C₁₀ alkylene linking group;

R represents a hydrocarbyl aromatic structure having at least one aromatic ring to which Q¹ and Q² are each linked, via the respective linking group on available adjacent atoms of the at least one aromatic ring;

the groups X³ and X⁴ independently represent univalent radicals of up to 30 atoms having at least one tertiary carbon atom or X³ and X⁴ 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 Q¹;

the groups X¹ and X² independently represent univalent radicals of up to 30 atoms having at least one primary or aromatic ring carbon atom wherein, in the latter case, the carbon joined to the Q² atom is an aromatic carbon which forms part of an aromatic ring substituted at a suitable position in the ring or X¹ and X² together form a bivalent radical of up to 40 atoms having at least two primary or aromatic ring carbon atoms wherein, in the latter case, the carbons joined to the Q² atom are aromatic carbons which each form part of an aromatic ring substituted at a suitable position in the ring and wherein each said univalent or bivalent radical is joined via said at least one or two primary or aromatic ring carbon atom(s) respectively to the respective atom Q²; and

Q¹ and Q² represent phosphorus.

2 A process for the carbonylation of ethylenically unsaturated compounds selected from acetylene, methyl acetylene, propyl acetylene, 1,3-butadiene, ethylene, propylene, butylene, isobutylene, pentenes, pentene nitriles, alkyl pentenoates, pentene acids, heptenes, octenes, dodecenes and mixtures thereof comprising reacting said compound with carbon monoxide in the presence of a source of hydroxyl groups, optionally, a source of anions and of a catalyst system, the catalyst system obtainable by combining:

- (a) palladium or a compound thereof; and
- (b) a bidentate ligand according to claim 1.

3 A bidentate ligand according to claim 1, wherein the groups X^1 and X^2 are selected from C_1 - C_{20} alkyl, C_1 - C_{20} alkenyl, C_1 - C_{20} alkynyl or C_1 - C_{20} aryl groups.

4 A bidentate ligand according to claim 1 or 3, wherein the group X^1 represents aryl and/or the group X^2 represents aryl.

5 A bidentate ligand according to any of claims 1, 3 or 4, wherein at least one of the groups X^1 or X^2 includes one or more substituents selected from a C_1 - C_7 alkyl group or an $-O$ - C_1 - C_7 alkyl group, $-CN$, $-F$, $-Si(alkyl)_3$, $-COOR^{63}$, $-C(O)-$, or $-CF_3$.

6 A bidentate ligand according to claim 5, wherein the X^1 or X^2 substituent is on a carbon immediately adjacent to the carbon directly joined to the Q^2 atom.

7 A bidentate ligand according to any of claims 1 or 3-6, wherein the X^1 and/or X^2 group has an alpha carbon atom and the alpha carbon atom of the X^1 and/or X^2 group is an aliphatic secondary or tertiary carbon atom.

8 A bidentate ligand according to any preceding claim, wherein the carbon joined to the Q^2 atom is an aromatic carbon which forms part of an aromatic ring substituted on the atom adjacent the atom in the ring joined to the Q^2 atom.

9. A bidentate ligand according to claim 5, wherein the further substituent is methyl, ethyl, n-propyl, iso-butyl, t-butyl, methoxy or ethoxy.

10 A bidentate ligand according to any of claims 1 -7, wherein the X^1 and X^2 groups are C_1-C_7 alkyl or $O-C_1-C_7$ alkyl substituted phenyl groups.

11 A bidentate ligand according to claim 1, wherein the carbon joined to the Q^2 atom is an aromatic carbon which forms part of an aromatic ring substituted at the ortho or meta position of the ring with respect to the Q^2 atom.

12 A bidentate ligand according to any of claims 1 or 3-10, wherein the X^1 or X^2 groups are selected from the group consisting of methyl, ethyl, propyl, 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, butyl, pentyl, neopentyl, 2-ethyl-phen-1-yl, 2-propyl-phen-1-yl and 2-prop-2'-yl-phen-1-yl.

13 A bidentate ligand according to claim 1 selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)benzene, 1-(di-tert-pentylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)benzene, 1-(di-tert-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)naphthalene, 1-(diadamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)benzene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)benzene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)benzene, 1-(1-adamantyl tert-butyl-phosphinomethyl)-2-(di-o-tolylphosphinomethyl)benzene, 1-(2,2,6,6-tetramethyl-phosphacyclohexan-4-one)-2-(di-o-tolylphosphino)-o-xylene, 1-(2-(phosphadamantyl))-2-(di-o-tolylphosphino)-o-xylene, 1-(dicongressylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)benzene, 1-(di-tert-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)ferrocene, 1-(di-5-tert-

butyladamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl) ferrocene, 1-(1-adamantyl tert-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-o-tolylphosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-o-tolylphosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-o-tolylphosphinomethyl) ferrocene, 1-(di-o-tolylphosphinomethyl)-2,3-bis-(ditertbutylphosphinomethyl) ferrocene;.

1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-diphenyl benzene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-phenylbenzene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-bis-(trimethylsilyl) benzene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(trimethylsilyl)benzene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)benzene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(2'-phenylprop-2'-yl)benzene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-di-t-butylbenzene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-t-butylbenzene;

1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl)-4,5-diphenylbenzene; 1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl)-4-phenylbenzene; 1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl)-4,5-bis-(trimethylsilyl)benzene; 1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl)-4-(trimethylsilyl)benzene; 1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)benzene; 1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl)-4-(2'-phenylprop-2'-yl)benzene; 1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl)-4,5-(di-t-butyl)benzene; 1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl)-4-t-butylbenzene;

1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-diphenylbenzene; 1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-phenyl benzene; 1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-bis-(trimethylsilyl)benzene; 1-(di-adamantylphosphinomethyl)-2-(di-o-

tolylphosphinomethyl)-4-(trimethylsilyl)benzene; 1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)benzene; 1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(2'-phenylprop-2'-yl)benzene; 1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-(di-t-butyl)benzene; 1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-t-butylbenzene;

1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4,5 diphenylmethylbenzene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4-phenyl methylbenzene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4,5 bis-(trimethylsilyl)methylbenzene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4-(trimethylsilyl)methylbenzene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)methylbenzene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4-(2'-phenylprop-2'-yl)methylbenzene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4,5-(di-t-butyl)methylbenzene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4-t-butylmethylbenzene;

1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-diphenylbenzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-phenylbenzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5- bis-(trimethylsilyl)benzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(trimethylsilyl)benzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5- di-(2'-phenylprop-2'-yl)benzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(2'-phenylprop-2'-yl)benzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-(di-t-butyl)benzene; 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-t-butylbenzene;

1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-diphenyl ferrocene; 1-(di-t-butylphosphinomethyl)-2-(di-o-

tolylphosphinomethyl)-4-(or 1')phenylferrocene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-bis-(trimethylsilyl) ferrocene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(or 1')(trimethylsilyl) ferrocene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl) ferrocene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(or 1')(2'-phenylprop-2'-yl) ferrocene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-di-t-butyl ferrocene; 1-(di-t-butylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(or 1')t-butylferrocene;

1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl)-4,5-diphenylferrocene; 1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl) 4-(or 1')phenylferrocene; 1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl)-4,5-bis-(trimethylsilyl) ferrocene; 1-(2-phosphinomethyl-adamantyl)-2-(di-o-tolylphosphinomethyl) 4-(or 1')(trimethylsilyl) ferrocene; 1-(2-phosphinomethyl-adamantyl) -2-(di-o-tolylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl) ferrocene; 1-(2-phosphinomethyl-adamantyl) -2-(di-o-tolylphosphinomethyl)-4-(or 1')(2'-phenylprop-2'-yl) ferrocene; 1-(2-phosphinomethyl-adamantyl) -2-(di-o-tolylphosphinomethyl)-4,5-(di-t-butyl) ferrocene; 1-(2-phosphinomethyl-adamantyl) -2-(di-o-tolylphosphinomethyl)-4-(or 1')t-butylferrocene;

1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5 diphenylferrocene; 1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(or 1')phenyl ferrocene; 1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5 bis-(trimethylsilyl) ferrocene; 1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(or 1')(trimethylsilyl) ferrocene; 1-(di-adamantylphosphinomethyl) -2-(di-o-tolylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl) ferrocene; 1-(di-adamantylphosphinomethyl) -2-(di-o-tolylphosphinomethyl)-4-(or 1')(2'-phenylprop-2'-yl) ferrocene; 1-(di-adamantylphosphinomethyl) -2-(di-o-tolylphosphinomethyl)-4,5-(di-t-butyl) ferrocene; 1-(di-adamantylphosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(or 1')t-butyl ferrocene;

1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-diphenylferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(or

1')phenylferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5- bis-(trimethylsilyl)ferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(or 1')(trimethylsilyl)ferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5- di-(2'-phenylprop-2'-yl)ferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(or 1')(2'-phenylprop-2'-yl)ferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4,5-(di-t-butyl)ferrocene; 1- (P,P adamantyl, t-butyl phosphinomethyl)-2-(di-o-tolylphosphinomethyl)-4-(or 1')t-butylferrocene;

1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4,5 diphenyl-methylferrocene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4-(or 1')phenyl-methylferrocene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4,5 bis-(trimethylsilyl)-methylferrocene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4-(or 1')(trimethylsilyl)-methylferrocene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)-methylferrocene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4-(or 1')(2'-phenylprop-2'-yl)-methylferrocene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4,5-(di-t-butyl)-methylferrocene; 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-o-tolylphosphinomethyl)-4-(or 1')t-butyl-methylferrocene;

or the group consisting of the o-ethylphenyl and o-methoxyphenyl analogs of the above mentioned o-tolyl ligands.

14 A bidentate ligand according to any of claims 1, 3, 5-7 or 9, wherein the group X^1 represents $CH(R^2)(R^3)$, X^2 represents $CH(R^4)(R^5)$, X^3 represents $CR^7(R^8)(R^9)$ and X^4 represents $CR^{10}(R^{11})(R^{12})$, wherein R^2 and R^4 represent hydrogen and R^3 , R^5 and R^7 - R^{12} represent alkyl, aryl or het.

15 A bidentate ligand according to any of claims 1- 14 wherein X^3 represents $CR^7(R^8)(R^9)$ and X^4 represents $CR^{10}(R^{11})(R^{12})$ and wherein the

organic groups R^7 - R^9 and /or R^{10} - R^{12} or, alternatively, 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).

16 A complex comprising a novel bidentate ligand of formula I as claimed in any of claims 1 or 3 - 15 coordinated to palladium or a compound thereof.

17 A catalyst system capable of catalysing the carbonylation of an ethylenically unsaturated compound, which system is obtainable by combining:

- a) palladium or a compound thereof,
- b) a bidentate phosphine ligand of formula I according to any of claims 1 or 3-16, and
- c) optionally, an acid.

18 A process for the carbonylation of ethylenically unsaturated compounds as claimed in claim 2, wherein the X^1 or X^2 substituent on the bidentate ligand is either on the carbon directly joined to the Q^2 atom or on a carbon adjacent thereto.

19 A process according to any of claims 2 or 18, wherein the X^1 and/or X^2 group carbon joined to the Q^2 atom is an aliphatic secondary carbon atom, or the alpha carbon of the X^1 and/or X^2 group 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.

20 A process according to any of claims 2, 18 or 19, wherein the X^1 or X^2 groups are selected from the group consisting of 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.

21 A process according to any of claims 2, or 18 - 20, wherein the bidentate ligand is selected from the group defined in claim 13

or the group consisting of the phenyl, isopropyl, o-ethylphenyl and o-methoxyphenyl analogs of the aforementioned o-tolyl ligands.

22 A process according to any of claims 2, or 18 - 21, wherein the group X^1 represents $CH(R^2)(R^3)$, X^2 represents $CH(R^4)(R^5)$, X^3 represents $CR^7(R^8)(R^9)$ and X^4 represents $CR^{10}(R^{11})(R^{12})$, wherein R^2 to R^5 represent hydrogen, alkyl, aryl or het and R^7 - R^{12} represent alkyl, aryl or het,

wherein Het includes four- to twelve-membered ring systems, which rings contain one or more heteroatoms selected from nitrogen, oxygen, sulfur and mixtures thereof or may also be in the form of an N oxide.