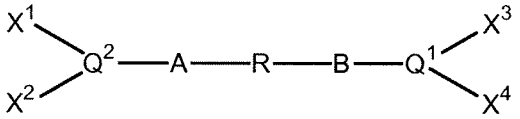
Claims

1 A novel bidentate ligand of general formula (I)

(I)



wherein:

A and B each independently represent a 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 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 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;

the groups X^1 and X^2 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 Q^2 atom is an aromatic carbon which forms part of an aromatic ring substituted at a suitable position in the ring or X^1 and X^2 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 Q^2 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 Q^2; and

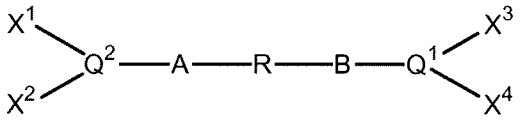
Q^1 and Q^2 each independently represent phosphorus, arsenic or antimony.

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

(b) a bidentate ligand of general formula (I)

(I)



wherein:

A and B each independently represent a 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 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 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;

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 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.

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

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.

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 any of claims 5-8, wherein the further substituent is a C_1-C_7 alkyl group or an -O-C_1-C_7 alkyl group, such as a methyl, ethyl, n-propyl, iso-butyl t-butyl , methoxy or ethoxy group or a relatively inert group such as -CN, -F, -Si(alkyl)$_3$, -COOR^{63}, -C(O)-, or -CF_3.

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-phospha-cyclohexan-4-one)-2-(di-o-tolylphosphino)-o-xylene, 1-(2-(phospha-adamantyl))-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-butyl-phosphinomethyl)-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-butyl benzene; 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 novel complex comprising a novel bidentate ligand of formula I as defined herein coordinated to a metal of Group 8, 9 or 10 or a compound thereof.

17 A novel bidentate ligand as hereinbefore described and with reference to the examples.

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

19 A process for the carbonylation of ethylenically unsaturated compounds according to claim 2, wherein the ethylenically unsaturated compound is ethylene.

20 A bidentate ligand or a process according to any preceding claim wherein A and B are methylene.

21 A process for the carbonylation of ethylenically unsaturated compounds as claimed in claim 2, 19 or 20, wherein 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.

22 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 phosphine, arsine, or stibine ligand of formula I according to any of claims 1 or 3-16 or 20, and
c) optionally, an acid.

23 A catalyst system according to claim 22, 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.

24 A process for the carbonylation of ethylenically unsaturated compounds as claimed in any of claims 2 or 19-21, 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.

25 A process according to any of claims 2, 19-21 or 25, 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.

26 A process according to any of claims 2, 19-21, 25 or 26, 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.

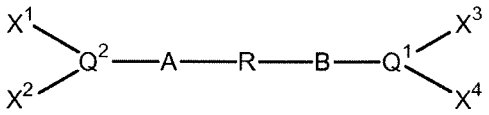
27 A process according to any of claims 2, 19-21 or 25-27, wherein the bidentate ligand is selected from the group defined in claim 13 or the group consisting of the phenyl, isopropyl, o-ethylphenyl and o-methoxyphenyl analogs of the aforementioned o-tolyl ligands.

28 A process according to any of claims 2, 19-21 or 25-28, 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.

Claims

1 A bidentate ligand of general formula (I)

(I)



wherein:

A and B each independently represent a C_1 to C_{10} 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 linking group 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 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;

the groups X^1 and X^2 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 Q^2 atom is an aromatic carbon which forms part of an aromatic ring substituted at a suitable position in the ring or X^1 and X^2 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 Q^2 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 Q^2; and

Q^1 and Q^2 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-phospha-cyclohexan-4-one)-2-(di-o-tolylphosphino)-o-xylene, 1-(2-(phospha-adamantyl))-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-butyl-phosphinomethyl)-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-butyl benzene; 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.