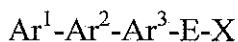


[0007b] In another aspect, there is provided a process for making a compound of structure I as defined above, said process comprising reacting a compound of structure II:



wherein Ar^1 , Ar^2 and Ar^3 , E and R are as defined above and Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 , with a salt or complex of M, optionally in the presence of a liganding species.

[0007c] A process for making a compound of structure II as defined above comprising reacting a compound of structure III:



wherein Ar^1 , Ar^2 and Ar^3 and E are as defined above and Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ,

with either:

a compound of structure X-PR_2 , wherein R is as defined above or

a compound of structure X-P(D)R_2 wherein R is as defined above, and subsequently removing the group D, wherein D is =S or =O or $-\text{Z-linker-Z}-$, where each Z independently is O or NH or N-alkyl and linker is an alkyl chain of 2-5 carbon atoms in length

wherein each X is independently selected from the group consisting of H, F, Br, Cl, I, OTf, dba, OC(=O)CF_3 and OAc.

[0007d] In another aspect, there is provided a process for making a coupled compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate, with a compound V comprising an element M bonded directly to an alkyl, alkenyl, alkynyl, aryl or heteroaryl group, in which M is an element in one of groups 1, 2, 11, 12, 13 or 14, in the presence of either:

- a compound of structure I in which $\text{M}=\text{Pd}$;
(I) $(\text{Ar}^1\text{-Ar}^2\text{-Ar}^3\text{-E-P(=D)R}_2\text{--})_n\text{M}_m\text{X}_n\text{L}_n$

wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
 - each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
 - Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
 - Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), $\text{OC}(=\text{O})\text{CF}_3$ and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is $-\text{Z-linker-Z}-$,

where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:

(II) Ar¹-Ar²-Ar³-E-PR₂

wherein:

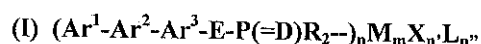
- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and

- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt or complex capable of reacting with the compound of structure II to form a compound of structure I in which M=Pd.

[0007e] In another aspect, there is provided a process for making a olefinic compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with an olefin in the presence of either:

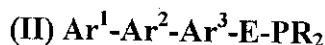
- a compound of structure I in which M=Pd:



wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;

- E is absent or is selected from the group consisting of O, S, NRⁿ, SiRⁿ₂ and CRⁿ₂;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), OC(=O)CF₃ and OAc;
- L is absent or is selected from the group consisting of PRⁿ₂, NRⁿ₂, ORⁿ, SRⁿ, SiRⁿ₃, AsRⁿ₃, alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each Rⁿ is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or Rⁿ₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:



wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR', wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or

heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,

- Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
- Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is $-Z\text{-linker-Z-}$, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt or complex capable of reacting with the compound of structure II to form a compound of structure I in which $M = Pd$.

[0007f] In another aspect, there is provided a process for making an alkynyl compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with a terminal alkyne in the presence of either:

- a compound of structure I in which $M = Pd$:
(I) $(Ar^1-Ar^2-Ar^3-E-P(=D)R_2--)_nM_mX_n.L_n$

wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:

- Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
- each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
- Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
- Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), $\text{OC}(=\text{O})\text{CF}_3$ and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is $-\text{Z}-$ linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:

(II) Ar¹-Ar²-Ar³-E-PR₂

wherein:

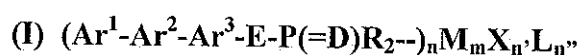
- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-,

where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which $M = \text{Pd}$.

[0007g] In another aspect, there is provided a process for making an amine compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with a primary or secondary amine in the presence of either:

- a compound of structure I in which $M = \text{Pd}$:



wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
 - each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
 - Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
 - Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;

- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), $\text{OC}(=\text{O})\text{CF}_3$ and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is $-\text{Z}-\text{linker}-\text{Z}-$, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar^3 ortho to E; or
- a compound of structure II:

(II) $\text{Ar}^1-\text{Ar}^2-\text{Ar}^3-\text{E}-\text{PR}_2$

wherein:

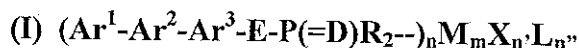
- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
 - each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR' , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,

- Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
- Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is –Z-linker-Z–, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which M=Pd.

[0007h] In another aspect, there is provided a process for making an aryl carbonyl compound, e.g. a ketone or aldehyde or acid or ester, comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with carbon monoxide and a nucleophile M'-Nu, where Nu = OH, NR₂, alkyl, aryl, SR, or OR^a where each R^a is as described above, and M' is H or a Group 1 or Group 2 (alkyl or alkaline earth) metal ion or is M''R^b, where M'' is Cu, Ag, Zn, AlR^b, GaR^b, TiR^b, CR^b₂, SiR^b₂, SnR^b₂, PbR^b₂, NR^b or AsR^b, where R^b is alkyl, alkenyl, alkynyl, aryl or heteroaryl, in the presence of either:

- a compound of structure I in which $M = Pd$:



wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
 - each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
 - Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
 - Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), $OC(=O)CF_3$ and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;

- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:

(II) Ar¹-Ar²-Ar³-E-PR₂

wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently

halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;

- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is $-Z\text{-linker-Z-}$, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which $M = Pd$.

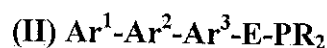
[0007i] In another aspect, there is provided a process for making a nitrile compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with a cyanide in the presence of either:

- a compound of structure I in which $M = Pd$:
(I) $(Ar^1-Ar^2-Ar^3-E-P(=D)R_2--)_nM_mX_nL_n$

wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
 - each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and

- Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), $\text{OC}(=\text{O})\text{CF}_3$ and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is $-\text{Z}-$ linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar^3 ortho to E; or
- a compound of structure II:



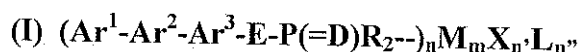
wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is –Z-linker-Z–, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which M=Pd.

[0007j] In another aspect, there is provided a process for making a phosphorus compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with a phosphorus reagent in the presence of either:

- a compound of structure I in which M=Pd:



wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
 - each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
 - Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
 - Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), $OC(=O)CF_3$ and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;

- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:

(II) Ar¹-Ar²-Ar³-E-PR₂

wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;

- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which M=Pd.

[0007k] In another aspect, there is provided a process for making an ether comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with an alcohol in the presence of either:

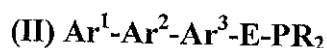
- a compound of structure I in which M=Pd:
(I) (Ar¹-Ar²-Ar³-E-P(=D)R₂--)_nM_mX_nL_n

wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently

halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;

- E is absent or is selected from the group consisting of O, S, NRⁿ, SiRⁿ₂ and CRⁿ₂;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), OC(=O)CF₃ and OAc;
- L is absent or is selected from the group consisting of PRⁿ₂, NRⁿ₂, ORⁿ, SRⁿ, SiRⁿ₃, AsRⁿ₃, alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each Rⁿ is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or Rⁿ₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:



wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;

- each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
- Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
- Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is –Z-linker-Z–, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which M=Pd.

[00071] In another aspect, there is provided the use of a compound of structure I as defined above in which m=1 or 2 and M=Pd as a catalyst; optionally for a reaction selected from the group consisting of Suzuki-Miyaura, Kumada, Stille, Negishi and Hiyama coupling reactions, Heck and Sonogashira reactions, Buchwald-Hartwig amination, Heck carbonylation, alkoxylation, cyanation, phosphination and metal mediated coupling reactions.

[0008] 1. A process for making a compound of structure I:

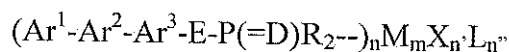


wherein:

- Ar^1 , Ar^2 and Ar^3 are aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ,
 - each of Ar^1 , Ar^2 and Ar^3 optionally comprises one or more ring substituents of formula YR' , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, heterocyclyl, cycloheteroaryl, aryl

CLAIMS

1. A compound of structure I:



wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
 - each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
 - Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), OC(=O)CF_3 and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;

- D is absent;
 - each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
 - m is 1 or 2;
 - n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
 - M is bonded to a ring atom of Ar³ ortho to E.
2. The compound of claim 1 wherein E is O or S or NR''.
 3. The compound of claim 1 or 2 wherein n is 1 or 2 and M is selected from the group consisting of Pd, Ni, Pt, Cu, Fe, Co, Au, Ag, Rh, Ir, Ru, Os or Mn; preferably wherein M is Pd, Ni or Cu; more preferably wherein M is Pd.
 4. The compound of any one of claims 1 to 3 wherein m is 1 or 2 and X is Cl or OAc.
 5. The compound of claim 1 wherein m=1.
 6. The compound of claim 1 wherein m=2 and n'' is 0.
 7. The compound of any one of claims 1 to 6 wherein n=m.
 8. The compound of any one of claims 1 to 7 wherein each R is independently selected from the group consisting of alkyl, cycloalkyl, aryl and heteroaryl; preferably wherein each R is alkyl or each is aryl, or one is alkyl and the other is aryl.
 9. The compound of any one of claims 1 to 8 wherein n'' is 0, M is Pd and n is 2.
 10. The compound of claim 1 wherein Ar¹ is phenyl, Ar² is 2,4,6-trimethylphenyl or 2,4,6-triisopropylphenyl, Ar³ is phenyl, E is O, R attached to P is each alkyl or each is aryl, or one is alkyl and the other is aryl, and n is 1 and m is 1, n' is 1 and n'' is 0 and M is Pd.

11. A process for making a compound of structure I as defined in claim 1, said process comprising reacting a compound of structure II:

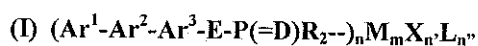


wherein Ar^1 , Ar^2 and Ar^3 , E and R are as defined in claim 1 and Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ,

with a salt or complex of M, optionally in the presence of a liganding species.

12. A process for making a coupled compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate, with a compound V comprising an element M bonded directly to an alkyl, alkenyl, alkynyl, aryl or heteroaryl group, in which M is an element in one of groups 1, 2, 11, 12, 13 or 14, in the presence of either:

- a compound of structure I in which $\text{M}=\text{Pd}$:

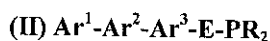


wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
 - each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
 - Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2

or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;

- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), OC(=O)CF₃ and OAc;
- L is absent or is selected from the group consisting of PR''₂, NR''₂, OR'', SR'', SiR''₃, AsR''₃, alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:



wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B,

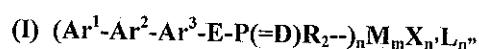
N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,

- Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
- Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt or complex capable of reacting with the compound of structure II to form a compound of structure I in which M=Pd.

13. A process for making a olefinic compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with an olefin in the presence of either:

- a compound of structure I in which M=Pd:



wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:

- Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
- each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
- Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
- Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), OC(=O)CF₃ and OAc;
- L is absent or is selected from the group consisting of PR''₂, NR''₂, OR'', SR'', SiR''₃, AsR''₃, alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-

linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:

(II) Ar¹-Ar²-Ar³-E-PR₂

wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and

- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt or complex capable of reacting with the compound of structure II to form a compound of structure I in which M=Pd.

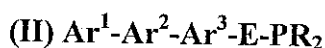
14. A process for making an alkynyl compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with a terminal alkyne in the presence of either:

- a compound of structure I in which M=Pd:
(I) (Ar¹-Ar²-Ar³-E-P(=D)R₂--)_nM_mX_nL_n,

wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;

- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), OC(=O)CF₃ and OAc;
- L is absent or is selected from the group consisting of PR''₂, NR''₂, OR'', SR'', SiR''₃, AsR''₃, alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:



wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR', wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl

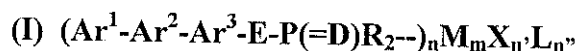
or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,

- Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
- Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is $-Z-$ linker- $Z-$, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which $M=Pd$.

15. A process for making an amine compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with a primary or secondary amine in the presence of either:

- a compound of structure I in which $M=Pd$:



wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:

- Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
- each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
- Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), $\text{OC}(=\text{O})\text{CF}_3$ and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is –Z–

linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:

(II) Ar¹-Ar²-Ar³-E-PR₂

wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and

- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which M=Pd.

16. A process for making an aryl carbonyl compound, e.g. a ketone or aldehyde or acid or ester, comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with carbon monoxide and a nucleophile M'-Nu, where Nu = OH, NR₂, alkyl, aryl, SR, or OR^a where each R^a is as described above, and M' is H or a Group 1 or Group 2 (alkyl or alkaline earth) metal ion or is M''R^b, where M'' is Cu, Ag, Zn, AlR^b, GaR^b, TiR^b, CR^b₂, SiR^b₂, SnR^b₂, PbR^b₂, NR^b or AsR^b, where R^b is alkyl, alkenyl, alkynyl, aryl or heteroaryl, in the presence of either:

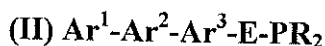
- a compound of structure I in which M=Pd:
(I) (Ar¹-Ar²-Ar³-E-P(=D)R₂--)_nM_mX_nL_n

wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is

independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;

- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), $\text{OC}(=\text{O})\text{CF}_3$ and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is $-\text{Z}-$ linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar^3 ortho to E; or
- a compound of structure II:



wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;

- each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
- Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
- Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is $-\text{Z}-$ linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which $\text{M}=\text{Pd}$.

17. A process for making a nitrile compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with a cyanide in the presence of either:

- a compound of structure I in which $\text{M}=\text{Pd}$:
(I) $(\text{Ar}^1-\text{Ar}^2-\text{Ar}^3-\text{E}-\text{P}(=\text{D})\text{R}_2--)_n\text{M}_m\text{X}_n\cdot\text{L}_n$

wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
 - each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
 - Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), $\text{OC}(=\text{O})\text{CF}_3$ and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;

- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:

(II) Ar¹-Ar²-Ar³-E-PR₂

wherein:

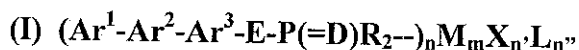
- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;

- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which M=Pd.

18. A process for making a phosphorus compound comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with a phosphorus reagent in the presence of either:

- a compound of structure I in which M=Pd:



wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2

or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;

- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), $\text{OC}(=\text{O})\text{CF}_3$ and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is $-\text{Z}-$ linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;
- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar^3 ortho to E; or
- a compound of structure II:

(II) $\text{Ar}^1\text{-Ar}^2\text{-Ar}^3\text{-E-PR}_2$

wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
 - each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r , wherein each Y independently is absent or is O, S, B,

N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si,

- Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
- Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is —Z-linker-Z—, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which M=Pd.

19. A process for making an ether comprising reacting a compound of structure R^aX in which R^a is alkyl, alkenyl, alkynyl, aryl or heteroaryl and X is a leaving group such as halide or triflate with an alcohol in the presence of either:

- a compound of structure I in which M=Pd:
(I) (Ar¹-Ar²-Ar³-E-P(=D)R₂--)_nM_mX_n·L_n

wherein:

- Ar^1 , Ar^2 and Ar^3 are carbocyclic aromatic groups wherein:
 - Ar^1 and Ar^3 are in a 1,3 relationship on Ar^2 ;
 - each of Ar^1 and Ar^3 optionally comprises one or more ring substituents of formula YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
 - Ar^1 and Ar^3 are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 and Ar^3 independently has 5, 6 or 7 ring atoms; and
 - Ar^2 is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r , wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 and CR''_2 ;
- M is a complexing metal;
- X is selected from the group consisting of H, F, Br, Cl, I, OTf, dba (dibenzylidene acetone), $\text{OC}(=\text{O})\text{CF}_3$ and OAc;
- L is absent or is selected from the group consisting of PR''_2 , NR''_2 , OR'' , SR'' , SiR''_3 , AsR''_3 , alkene, alkyne, aryl and heteroaryl, each of said alkene, alkyne, aryl and heteroaryl being optionally substituted, for example with one or more halogens and/or with one or more R groups as defined herein, wherein if L is absent, n is not 1;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent;
- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''_2 is $-\text{Z}-$

linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

- m is 1 or 2;
- n is 1 or 2 and n' and n'' are integers such that the coordination sphere of M is filled; and
- M is bonded to a ring atom of Ar³ ortho to E; or
- a compound of structure II:

(II) Ar¹-Ar²-Ar³-E-PR₂

wherein:

- Ar¹, Ar² and Ar³ are carbocyclic aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²;
 - each of Ar¹ and Ar³ optionally comprises one or more ring substituents of formula YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently H, halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
 - Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and
 - Ar² is a monocyclic carbocyclic ring having 6 ring atoms, a single hydrogen atom directly attached thereto in the 5' position, and being substituted in the 2', 4' and 6' positions by YR'_r, wherein each Y independently is absent or is O, S, B, N or Si and each R' is independently halogen, alkyl, cycloalkyl, aryl or heteroaryl and r is 1, 2 or 3, where r is 1 if Y is absent or is O or S, 2 if Y is B or N and 3 if Y is Si;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂ and CR''₂;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy; and

- each R'' is independently H, alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl, each other than H being optionally substituted, or R''₂ is -Z-linker-Z-, where each Z independently is O or NH or N-alkyl, and linker is an alkyl chain of 2-5 carbon atoms in length;

and a palladium salt capable of reacting with the compound of structure II to form a compound of structure I in which M=Pd.

20. Use of a compound of structure I as defined in claim 1 in which m=1 or 2 and M=Pd as a catalyst; optionally for a reaction selected from the group consisting of Suzuki-Miyaura, Kumada, Stille, Negishi and Hiyama coupling reactions, Heck and Sonogashira reactions, Buchwald-Hartwig amination, Heck carbonylation, alkoxylation, cyanation, phosphination and metal mediated coupling reactions.