

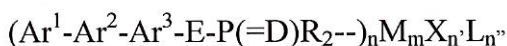
[0005] More recently, particular attention has been aimed at catalyst activity in industry as the inflationary trend of precious metal commodities is a growing concern. In the past, precious metal catalysts were only deemed viable for industrial applications if turnover numbers (TONs) in excess of 10,000 could be achieved. With increasing commodity prices, the performance benchmarks for precious metal catalysts are also rising as companies manage their expenses and margins. Furthermore, as organizations move to greener practices, process improvement efforts to lower the metal content, reduce wastage and improve atom economy in reactions have become key areas of focus to comply with global sustainability initiatives.

[0006] Despite the catalysis research community trending towards developing greener and more productive systems, the need to invent highly active catalysts for challenging reactions and new transformations will always remain high. With a perpetually growing list of new catalysts that are capable of performing well known reactions, it is becoming increasingly difficult for scientists, both at the industrial and academic level, to identify which systems are the most suitable for their application. It is widely acknowledged that examples of catalysts that are highly effective for a multitude of applications are very limited. Thus, improvements to these versatile catalyst systems would be of tremendous value to the research community as they would alleviate the challenging of catalyst selection and improve the synthetic efficiency of functional molecules by being able to perform a sequence of different catalytic reactions in a single pot, or under continuous flow conditions.

Summary

[0007] Embodiments of the disclosure may be described by the following statements.

[0007a] In an aspect, there is provided 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' , 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,

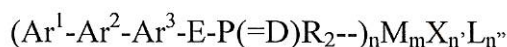
– Ar¹ and Ar³ are each independently carbocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹ and Ar³ independently has 5, 6 or 7 ring atoms; and

– 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 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;

- 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.

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 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;
- 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.

- 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 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.
 4. The compound of claim 3 wherein M is Pd, Ni or Cu.
 5. The compound of claim 4 wherein M is Pd.
 6. The compound of any one of claims 1 to 5 wherein m is 1 or 2 and X is Cl or OAc.
 7. The compound of claim 1 wherein m=1.
 8. The compound of claim 1 wherein m=2 and n'' is 0.
 9. The compound of any one of claims 1 to 8 wherein n=m.
 10. The compound of any one of claims 1 to 9 wherein each R is independently selected from the group consisting of alkyl, cycloalkyl, aryl and heteroaryl.
 11. The compound of claim 10 wherein each R is alkyl or each is aryl, or one is alkyl and the other is aryl.
 12. The compound of any one of claims 1 to 11 wherein n'' is 0, M is Pd and n is 2.
 13. 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.

14. 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.

15. The process of claim 14 wherein no liganding species is present, whereby $m=2$, said process comprising the subsequent step of exposing the compound of structure I in which $m=2$ to a liganding species so as to produce a compound of structure I in which $m=1$ and L is said liganding species or is derived therefrom.

16. The process of claim 14 or claim 15 wherein the liganding species is a phosphine, an amine, an alcohol, a thiol, a silane, an arsine, an olefin, an aromatic compound or a heteroaromatic compound.

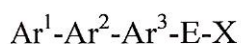
17. The process of any one of claims 14 to 16 wherein M is selected from the group consisting of Pd, Ni, Pt, Cu, Fe, Co, Au, Ag, Rh, Ir, Ru, Os and Mn.

18. The process of any one of claims 14 to 17 wherein the salt or complex of M is a dba, diene, olefin, allyl, silane, nitrile or organonitrile complex (such as $\text{Pd}(\text{PhCN})_2\text{Cl}_2$, $\text{Pd}(\text{CN})_2$ or $\text{Pd}(\text{MeCN})_4(\text{BF}_4)_2$ or $\text{Pd}(\text{COD})(\text{CH}_2\text{TMS})_2$ or $\text{Pd}(\text{NBD})(\text{CH}_2\text{TMS})_2$), or a halide or acetate or cyanide salt or a salt of a pseudohalide, e.g. triflate, of M.

19. The process of claim 17 wherein M is Pd, Ni or Cu.

20. The process of claim 19 wherein M is Pd.

21. The process of any one of claims 14 to 20 comprising reacting a compound of structure III:



wherein Ar^1 , Ar^2 and Ar^3 and E are as defined in claim 1 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 in claim 1 or

a compound of structure $X-P(D)R_2$ wherein R is as defined in claim 1, and subsequently removing the group D, wherein D is =S or =O or $-Z\text{-linker-Z-}$, where each Z independently is O or NH or N-alkyl and linker is an alkyl chain of 2-5 carbon atoms in length

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

so as to produce the compound of structure II.

22. The process of any one of claims 14 to 21 wherein each ring in Ar^1 and Ar^3 has independently, 5 or 6 ring carbon atoms.

23. The process of any one of claims 14 to 22 wherein at least one of Ar^1 and Ar^3 is a fused aromatic ring.

24. The process of any one of claims 14 to 22 wherein each of Ar^1 and Ar^3 is monocyclic, e.g. is a phenyl ring.

25. The process of any one of claims 14 to 24 wherein E is O, S, NR² or absent.
26. The process of any one of claims 14 to 24 wherein the R groups on P are both alkyl or both are aryl or one R is alkyl and one is aryl.
27. The process of claim 21 comprising the step of conducting a metal mediated cross-coupling reaction of a biaryl compound with an aryl compound so as to produce the compound of structure III.
28. The process of claim 27 comprising reacting a compound of structure IV: Ar¹-Ar²A in which A is a leaving group or activating group, e.g. a halogen or a triflate group or a boronic acid or boronic ester, and in which A is meta to Ar¹ on Ar², with a compound of structure XEAr³A or Ar³A in the presence of an electrophile, so as to produce the compound of structure III.
29. The process of claim 28 wherein A is either an electron donating group or an electron withdrawing group.
30. The process of claim 14 comprising:
- providing a 2,4,6-trialkylbiphenyl
 - halogenating said 2,4,6-trialkylbiphenyl in the 3 position
 - metallating the resulting halogenated biphenyl and reacting the resulting intermediate with an o-halophenol to form a 2-hydroxy-2',4',6'-trialkyl-m-terphenyl, or with an o-dihalobenzene to form a 2-halo-2',4',6'-trialkyl-m-terphenyl, and
 - reacting the m-terphenyl with a base and a halodialkylphosphine or halodiarylphosphine or haloalkylarylphosphine to produce a dialkylphosphinite or diarylphosphinite or alkylarylphosphinite of 2-hydroxy-2',4',6'-trialkyl-m-terphenyl respectively or else metallating the m-terphenyl and reacting the resulting intermediate, optionally in the presence of a copper salt and/or lithium salt, and a halodialkylphosphine or halodiarylphosphine or haloalkylarylphosphine to produce a dialkylphosphine or diarylphosphine or alkylarylphosphine respectively, each of said dialkylphosphinite or diarylphosphinite or alkylarylphosphinite or dialkylphosphine or diarylphosphine or alkylarylphosphine being a compound of structure II.
31. The process of claim 30 wherein, in the step of metallating, the intermediate is reacted with an o-halophenol and the subsequent step comprises reacting the resulting m-terphenyl with a base and a halodialkylphosphine or halodiarylphosphine or haloalkylarylphosphine to produce

a dialkylphosphinite or diarylphosphinite or alkylarylphosphinite of 2-hydroxy-2',4',6'-trialkyl-m-terphenyl respectively, each being of structure II in which E is O.

32. The process of claim 31 comprising the subsequent step of reacting the compound of structure II with a palladium halide so as to form a compound of structure I as defined in claim 1 in which E is O, m, n and n' are all 2, n'' is 0 and both R groups are alkyl or both are aryl or one R is alkyl and the other is aryl.

33. The process of claim 31 comprising reacting the compound of structure II with a palladium halide in the presence of a phosphine ligand whereby the process forms a compound of structure I as defined in claim 1 in which E is O, m, n and n' are all 1, n'' is 1 and both R groups are alkyl or both are aryl or one R is alkyl and the other is aryl and L is the phosphine ligand.

34. The process of claim 32 comprising the subsequent step of reacting the compound of structure I with a phosphine ligand, e.g. PCy₃, so as to produce a compound of structure I as defined in claim 1 in which E is O, m, n and n' are all 1, n'' is 1 and both R groups are alkyl or both are aryl or one R is alkyl and the other is aryl and L is the phosphine ligand, e.g. PCy₃.

35. The process of any one of claims 14 to 34 which is conducted as a one pot process without isolation of intermediates or in which any two or more contiguous steps are conducted as a one pot process.

36. The process of any one of claims 14 to 35 which is conducted as a continuous reaction or in which any one or more individual steps thereof is (are) conducted as a continuous reaction.

37. 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 as defined in claim 1 in which m=1 or 2 and M=Pd, or
- a compound of structure I as defined in claim 1 in which m=0 and a palladium salt or complex capable of reacting with the compound of structure I to form a compound of structure I in which m=1 or 2 and M=Pd.

38. The process of claim 37 wherein either R^a or compound V or both is substituted with one or more substituents.
39. The process of claim 38 wherein each of the one or more substituents is, independently, alkyl, aryl, heteroaryl, halogen, OR^b , NR^bR^c , BR^bR^c , SiR^b_3 , $SiR^bR^c_2$, or $SiR^bR^cR^d$, in which R^b , R^c and R^d are each independently H, alkyl, alkenyl, alkynyl, OH, amine, halogen, alkoxyl or aryl.
40. The process of claim 39 wherein compound V is a boronic acid.
41. 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 as defined in claim 1 in which $m=1$ or 2 and $M=Pd$, or
 - a compound of structure I as defined in claim 1 in which $m=0$ and a palladium salt or complex capable of reacting with the compound of structure I to form a compound of structure I in which $m=1$ or 2 and $M=Pd$.
42. The process of claim 41 wherein either R^a or the olefin or both is substituted with one or more substituents.
43. The process of claim 42 wherein each of the one or more substituents is, independently, alkyl, aryl, heteroaryl, halogen, OR^b , NR^bR^c , BR^bR^c , SiR^b_3 or $SiR^bR^c_2$ or $SiR^bR^cR^d$, in which R^b , R^c and R^d are each independently H, alkyl, alkenyl, alkynyl, OH, amine, halogen, alkoxyl or aryl group.
44. 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 as defined in claim 1 in which $m=1$ or 2 and $M=Pd$, or
 - a compound of structure I as defined in claim 1 in which $m=0$ and a palladium salt capable of reacting with the compound of structure I to form a compound of structure I in which $m=1$ or 2 and $M=Pd$.
45. The process of claim 44 wherein R^a is substituted with one or more substituents.

46. The process of claim 45 wherein each of the one or more substituents is, independently, alkyl, aryl, heteroaryl, halogen, OR^b , NR^bR^c , BR^bR^c , SiR^b_3 or SiR^bR^c_2 or $\text{SiR}^b\text{R}^c\text{R}^d$, in which R^b , R^c and R^d are each independently H, alkyl, alkenyl, alkynyl, OH, amine, halogen, alkoxy or aryl.

47. 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 as defined in claim 1 in which $m=$ or 2 and $\text{M}=\text{Pd}$, or
- a compound of structure I as defined in claim 1 in which $m=0$ and a palladium salt capable of reacting with the compound of structure I to form a compound of structure I in which $m=1$ or 2 and $\text{M}=\text{Pd}$.

48. The process of claim 47 wherein R^a is substituted with one or more substituents.

49. The process of claim 48 wherein each of the one or more substituents is, independently, alkyl, aryl, heteroaryl, halogen, OR^b , NR^bR^c , BR^bR^c , SiR^b_3 or SiR^bR^c_2 or $\text{SiR}^b\text{R}^c\text{R}^d$, in which R^b , R^c and R^d are each independently H, alkyl, alkenyl, alkynyl, OH, amine, halogen, alkoxy or aryl.

50. The process of any one of claims 47 to 49 wherein the amine is of the form R^eNH_2 or $\text{R}^e\text{R}^f\text{NH}$ in which R^e and R^f are, independently, alkyl, alkenyl, heteroaryl or aryl groups.

51. 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 $\text{M}'\text{-Nu}$, where $\text{Nu} = \text{OH}$, NR_2 , 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 $\text{M}''\text{R}^b$, where M is Cu, Ag, Zn, AlR, GaR^b , TiR^b , CR^b_2 , SiR^b_2 , SnR^b_2 , PbR^b_2 , 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 as defined in claim 1 in which $m=1$ or 2 and $\text{M}=\text{Pd}$, or
- a compound of structure I as defined in claim 1 in which $m=0$ and a palladium salt capable of reacting with the compound of structure I to form a compound of structure I in which $m=1$ or 2 and $\text{M}=\text{Pd}$.

52. The process of claim 51 wherein R^a is substituted with one or more substituents.

53. The process of claim 52 wherein each of the one or more substituents is, independently, alkyl, aryl, heteroaryl, halogen, OR^c , NR^cR^d , BR^cR^d , SiR^c_3 , SiR^cR^d_2 or $\text{SiR}^c\text{R}^d\text{R}^e$, in which R^c ,

R^d and R^e are each independently H, alkyl, alkenyl, alkynyl, OH, amine, halogen, alkoxy or aryl.

54. A process for making a nitrile compound comprising reacting a compound of structure R^aX in which R 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 as defined in claim 1 in which $m=1$ or 2 and $M=Pd$, or
- a compound of structure I as defined in claim 1 in which $m=0$ and a palladium salt capable of reacting with the compound of structure I to form a compound of structure I in which $m=1$ or 2 and $M=Pd$.

55. The process of claim 54 wherein R is substituted with one or more substituents.

56. The process of claim 55 wherein each of the one or more substituents is, independently, alkyl, aryl, heteroaryl, halogen, OR^c , NR^cR^d , BR^cR^d , SiR^c_3 , or $SiR^cR^d_2$, or $SiR^cR^dR^e$, in which R^c , R^d and R^e are each independently H, alkyl, alkenyl, alkynyl, OH, amine, halogen, alkoxy or aryl.

57. The process of any one of claims 54 to 56 wherein the cyanide is a Group I metal cyanide or HCN.

58. 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 as defined in claim 1 in which $m=1$ or 2 and $M=Pd$, or
- a compound of structure I as defined in claim 1 in which $m=0$ and a palladium salt capable of reacting with the compound of structure I to form a compound of structure I in which $m=1$ or 2 and $M=Pd$.

59. The process of claim 58 wherein R^a is substituted with one or more substituents.

60. The process of claim 59 wherein each of the one or more substituents is, independently, alkyl, aryl, heteroaryl, halogen, OR^c , NR^cR^d , BR^cR^d , SiR^c_3 , $SiR^cR^d_2$, or $SiR^cR^dR^e$, in which R^c , R^d and R^e are each independently H, alkyl, alkenyl, alkynyl, OH, alkoxy or aryl.

61. The process of any one of claim 58 to 60 wherein the phosphorus reagent is $X\text{-PR}^b_2$ or $X_2\text{-PR}^b$ where $X = \text{H}$ or halide, or X_2 is $=\text{O}$ or $=\text{S}$ or the phosphorus reagent is a protected phosphine such as a borane adduct.

62. 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 as defined in claim 1 in which $m=1$ or 2 and $\text{M}=\text{Pd}$, or
- a compound of structure I as defined in claim 1 in which $m=0$ and a palladium salt capable of reacting with the compound of structure I to form a compound of structure I in which $m=1$ or 2 and $\text{M}=\text{Pd}$.

63. The process of claim 62 wherein R^a is substituted with one or more substituents.

64. The process of claim 63 wherein each of the one or more substituents is, independently, alkyl, aryl, heteroaryl, halogen, OR^c , NR^cR^d , BR^cR^d , SiR^c_3 , or SiR^cR^d_2 , or $\text{SiR}^c\text{R}^d\text{R}^e$, in which R^c , R^d and R^e are each independently H, alkyl, alkenyl, alkynyl, OH, amine, halogen, alkoxyl or aryl.

65. Use of a compound of structure I as defined in claim 1 in which $m=1$ or 2 and $\text{M}=\text{Pd}$ as a catalyst.

66. Use according to claim 65, being for catalysis of 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.