

[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 of Invention

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

[0007a] In an aspect, there is provided a compound of structure I:



wherein:

- Ar¹, Ar² and Ar³ are aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²,
 - each of Ar¹, Ar² 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 , Ar^2 and Ar^3 are each independently carbocyclic or heterocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 , Ar^2 and Ar^3 independently has 5, 6 or 7 ring atoms;

• E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 , AsR''_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 or is =S or =O or –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;

• 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– as defined above; and

• m is 0 or 1 or 2; wherein:

– if m is 0, n is 1, n' and n'' are 0 and -- is absent; and

– if 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 D is absent.

[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 as defined above in which $m=1$ or 2 and $\text{M}=\text{Pd}$, or
- a compound of structure I as defined above 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 $\text{M}=\text{Pd}$.

[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 as defined above in which $m=1$ or 2 and $\text{M}=\text{Pd}$, or

• a compound of structure I as defined above 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 $M=\text{Pd}$.

[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 as defined above in which $m=1$ or 2 and $M=\text{Pd}$, or
- a compound of structure I as defined above 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 $M=\text{Pd}$.

[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 as defined above in which $m=$ or 2 and $M=\text{Pd}$, or
- a compound of structure I as defined above 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 $M=\text{Pd}$.

[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 $\text{M}'\text{-Nu}$, 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 , TlR^b , CR_2^b , SiR_2^b , SnR_2^b , PbR_2^b , 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 above in which $m=1$ or 2 and $M=\text{Pd}$, or
- a compound of structure I as defined above 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 $M=\text{Pd}$.

[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 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 above in which $m=1$ or 2 and $M=Pd$, or
- a compound of structure I as defined above 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 $M=Pd$.

[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 as defined above in which $m=1$ or 2 and $M=Pd$, or
- a compound of structure I as defined above 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 $M=Pd$.

[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 as defined above in which $m=1$ or 2 and $M=Pd$, or
- a compound of structure I as defined above 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 $M=Pd$.

[0007l] 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.

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

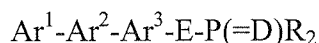


wherein:

- 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'_r 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

[00046] 39. The compound of statement 24 wherein if E is absent, n is 1 and m, n' and n'' are all 0.

[00047] In one ~~aspect~~embodiment of the ~~invention~~disclosure, there is provided a compound of structure I:



wherein:

- Ar¹, Ar² and Ar³ are aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²,
 - each of Ar¹, Ar² 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, Ar² and Ar³ are each independently carbocyclic or heterocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹, Ar² and Ar³ independently has 5, 6 or 7 ring atoms;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂, AsR''₂ and CR''₂;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent or is =S or =O or -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
- 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-as defined above.

[00048] In one option of this ~~aspect~~embodiment, and Ar² is a phenyl ring substituted in the 1 position by Ar¹ and in the 3 position by Ar³ and also substituted in the 2, 4 and 6 positions by alkyl groups such as methyl groups.

[00049] In a particular example of this ~~aspect~~embodiment, M is Pd and Ar² is a phenyl ring substituted in the 1 position by Ar¹ and in the 3 position by Ar³ and also substituted in the 2, 4 and 6 positions by alkyl groups such as methyl groups.

[00050] In another particular example of this ~~aspectembodiment~~, M is Pd, Ar² is a phenyl ring substituted in the 1 position by Ar¹ and in the 3 position by Ar³ and also substituted in the 2, 4 and 6 positions by alkyl groups such as methyl groups and Ar¹ and Ar³ each comprise phenyl rings bonded to Ar², and each, independently, is optionally fused with another aromatic ring, optionally a heteroaromatic ring.

[00051] In this ~~aspectembodiment~~, Ar¹ and Ar³ may each comprise phenyl rings bonded to Ar², and each, independently, optionally fused with another aromatic ring, optionally a heteroaromatic ring. In this ~~aspectembodiment~~, and in the particular examples thereof, D and E may each, independently, be absent or may be O. D may be absent. In some options, D and E are both absent. In other options both are O. In this ~~aspectembodiment~~, and in the particular examples thereof, E-P(=D)R₂ may be in a 1,2- or a 1,3- relationship with Ar² on Ar³.

[00052] In another ~~aspectembodiment~~ of the ~~inventiondisclosure~~ there is provided a compound of structure I:



wherein:

- Ar¹, Ar² and Ar³ are aromatic groups wherein:
 - Ar¹ and Ar³ are in a 1,3 relationship on Ar²,
 - each of Ar¹, Ar² 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, Ar² and Ar³ are each independently carbocyclic or heterocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar¹, Ar² and Ar³ independently has 5, 6 or 7 ring atoms;
- E is absent or is selected from the group consisting of O, S, NR'', SiR''₂, AsR''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 or is =S or =O or –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;
- 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- as defined above; and
- n' and n'' are integers such that the coordination sphere of M is filled (e.g. n'=n''=1).

[00053] In one option of this aspectembodiment, and Ar² is a phenyl ring substituted in the 1 position by Ar¹ and in the 3 position by Ar³ and also substituted in the 2, 4 and 6 positions by alkyl groups such as methyl groups.

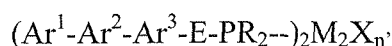
[00054] In a particular example of this aspectembodiment, M is Pd and Ar² is a phenyl ring substituted in the 1 position by Ar¹ and in the 3 position by Ar³ and also substituted in the 2, 4 and 6 positions by alkyl groups such as methyl groups.

[00055] In another particular example of this aspectembodiment, M is Pd, Ar² is a phenyl ring substituted in the 1 position by Ar¹ and in the 3 position by Ar³ and also substituted in the 2, 4 and 6 positions by alkyl groups such as methyl groups and Ar¹ and Ar³ each comprise phenyl rings bonded to Ar², and each, independently, is optionally fused with another aromatic ring, optionally a heteroaromatic ring.

[00056] In this aspectembodiment, Ar¹ and Ar³ may each comprise phenyl rings bonded to Ar², and each, independently, optionally fused with another aromatic ring, optionally a heteroaromatic ring.

In this aspectembodiment, and in the particular examples thereof, D and E may each, independently, be absent or may be O. In some options, D and E are both absent. In other options both are O. In this aspectembodiment, and in the particular examples thereof, E-P(=D)R₂ may be in a 1,2- or a 1,3-relationship with Ar² on Ar³. In this aspectembodiment, and in the particular examples thereof, n' and n'' may be 1.

[00057] In yet another aspectembodiment of the ~~invention-disclosure~~ there is provided 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'_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 , Ar^2 and Ar^3 are each independently carbocyclic or heterocyclic and each is independently monocyclic, bicyclic or polycyclic and each ring of each of Ar^1 , Ar^2 and Ar^3 independently has 5, 6 or 7 ring atoms;
- E is absent or is selected from the group consisting of O, S, NR'' , SiR''_2 , AsR''_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;
- each R is independently alkyl, cycloalkyl, heterocyclyl, heterocycloalkyl, aryl, heteroaryl, alkyloxy, cycloalkyloxy, heterocyclyloxy, heterocycloalkyloxy, aryloxy or heteroaryloxy;
- D is absent or is =S or =O or –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;
- 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– as defined above; and
- and n' is an integer such that the coordination sphere of M is filled (e.g. n' is 2).

[00058] In one option of this ~~aspectembodiment~~, and Ar^2 is a phenyl ring substituted in the 1 position by Ar^1 and in the 3 position by Ar^3 and also substituted in the 2, 4 and 6 positions by alkyl groups such as methyl groups.

[00059] In a particular example of this ~~aspectembodiment~~, M is Pd and Ar^2 is a phenyl ring substituted in the 1 position by Ar^1 and in the 3 position by Ar^3 and also substituted in the 2, 4 and 6 positions by alkyl groups such as methyl groups.

[00060] In another particular example of this aspectembodiment, M is Pd, Ar² is a phenyl ring substituted in the 1 position by Ar¹ and in the 3 position by Ar³ and also substituted in the 2, 4 and 6 positions by alkyl groups such as methyl groups and Ar¹ and Ar³ each comprise phenyl rings bonded to Ar², and each, independently, is optionally fused with another aromatic ring, optionally a heteroaromatic ring.

[00061] In this aspectembodiment, Ar¹ and Ar³ may each comprise phenyl rings bonded to Ar², and each, independently, optionally fused with another aromatic ring, optionally a heteroaromatic ring. In this aspectembodiment, and in the particular examples thereof, D and E may each, independently, be absent or may be O. In some options, D and E are both absent. In other options both are O. In this aspectembodiment, and in the particular examples thereof, E-P(=D)R₂ may be in a 1,2- or a 1,3- relationship with Ar² on Ar³. In this aspectembodiment, and in the particular examples thereof, n' may be 2.

[00062] 40. 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 statement 24 in which m=1 or 2 and M=Pd, or
- a compound of structure I as defined in statement 24 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.

[00063] 41. The process of statement 40 wherein either R^a or compound V or both is substituted with one or more substituents.

[00064] 42. The process of statement 41 wherein each of the one or more substituents is, independently, alkyl, aryl, heteroaryl, halogen, OR^b, NR^bR^c, BR^bR^c, SiR^b₃ or SiR^bR^c₂ 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.

[00065] 43. The process of statement 42 wherein compound V is a boronic acid.