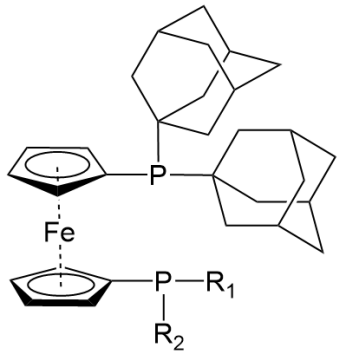
CLAIMS

1. A compound of formula I



I

wherein

R_1 and R_2 are independently selected from the group consisting of C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_1-C_{12} alkoxy, -NR_4R_5, and optionally substituted phenyl;

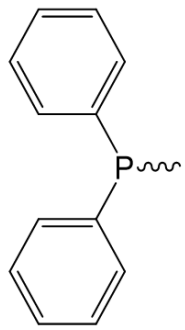
R_4 and R_5 are individually selected from the group consisting of H and C_1-C_{12} alkyl, or R_4 and R_5 together can form a saturated or unsaturated 5- or 6-membered ring, the ring optionally including one or more additional heteroatoms selected from O, S and N, and one or more optional substituents; and

each optional substituent, when present, is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 haloalkyl and C_1-C_4 alkoxy.

2. The compound according to claim 1 wherein R_1 and R_2 are independently selected from the group consisting of phenyl, optionally substituted phenyl, cyclohexyl, isopropyl and *tert*-butyl.

3. The compound according to either of claims 1 or 2 wherein R_1 and R_2 are each substituted phenyl.

4. The compound according to either of claims 1 or 2 wherein -PR_1R_2 is selected from the group consisting of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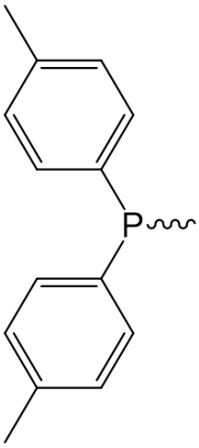
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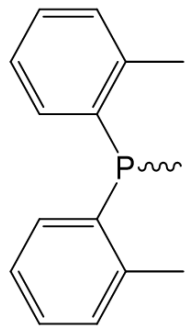
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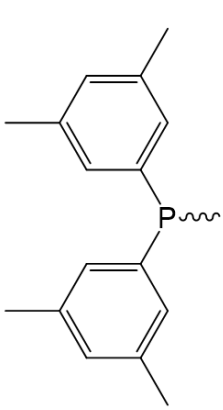
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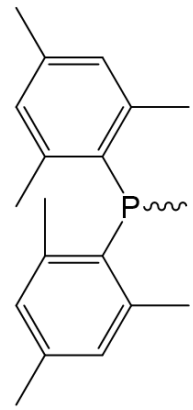
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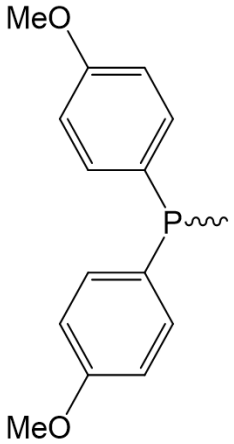
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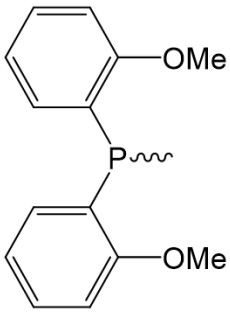
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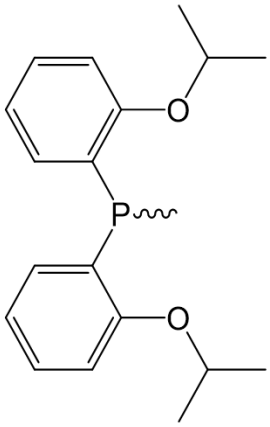
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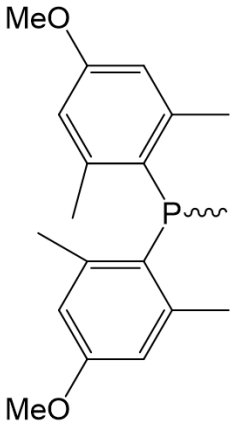
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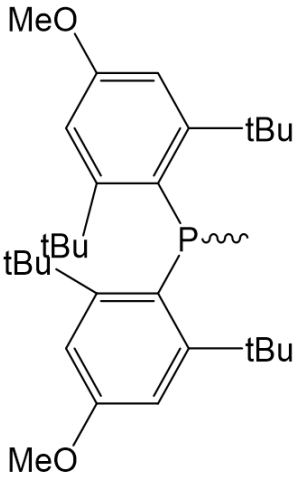
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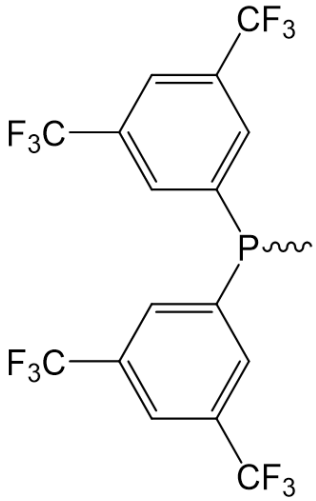
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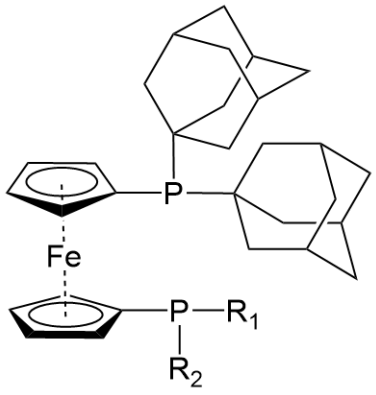
5. A ligand of formula I:



I

wherein

R_1 and R_2 are independently selected from the group consisting of C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_1-C_{12} alkoxy, -NR_4R_5, and optionally substituted phenyl;

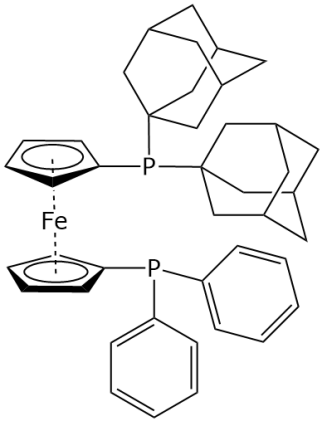
R_4 and R_5 are individually selected from the group consisting of H and C_1-C_{12} alkyl, or R_4 and R_5 together can form a saturated or unsaturated 5- or 6-membered ring, the ring optionally including one or more additional heteroatoms selected from O, S and N, and one or more optional substituents; and

each optional substituent, when present, is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 haloalkyl and C_1-C_4 alkoxy.

6. The ligand according to claim 5 wherein R_1 and R_2 are independently selected from the group consisting of phenyl, optionally substituted phenyl, cyclohexyl, isopropyl and *tert*-butyl.

7. The ligand according to either of claims 5 or 6 wherein R_1 and R_2 are each substituted phenyl.

8. A ligand according to either of claims 5 or 6, wherein the ligand is selected from the group consisting of



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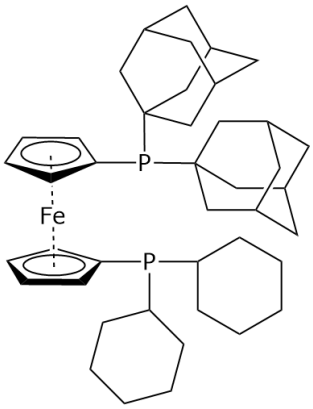

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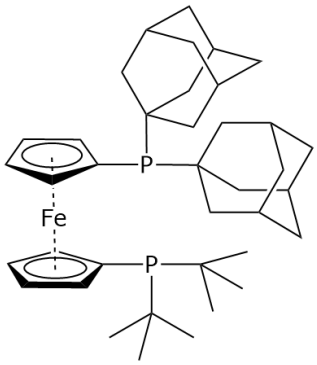

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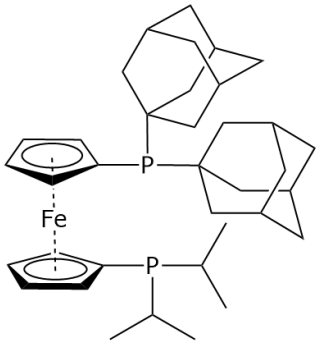

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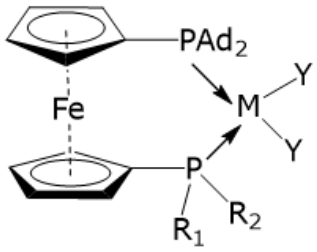
9. A precatalyst of formula II:



II

wherein

Ad is adamantyl;

R_1 and R_2 are independently selected from the group consisting of C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_1-C_{12} alkoxy, -NR_4R_5, and optionally substituted phenyl;

R_4 and R_5 are individually selected from the group consisting of H and C_1-C_{12} alkyl, or R_4 and R_5 together can form a saturated or unsaturated 5- or 6-membered ring, the ring optionally including one or more additional heteroatoms selected from O, S and N, and one or more optional substituents;

each optional substituent, when present, is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 haloalkyl and C_1-C_4 alkoxy;

M is a transition metal selected from Group 9 or Group 10; and

Y is halo.

10. The precatalyst according to claim 9 wherein R_1 and R_2 are independently selected from the group consisting of phenyl, optionally substituted phenyl, cyclohexyl, isopropyl and *tert*-butyl.

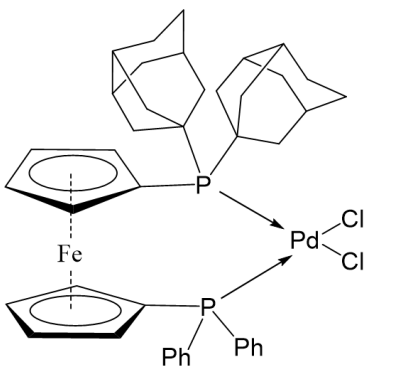
11. The precatalyst according to either of claims 9 or 10 wherein R_1 and R_2 are each substituted phenyl.

12. The precatalyst according to any of claims 9-11 wherein M is selected from the group consisting of Pd, Ni, Rh, Co, Ir and Pt.

13. The precatalyst according to any of claims 9-12 wherein M is Pd.

14. The precatalyst according to any of claims 9-13 wherein Y is selected from chloro, bromo and iodo.

15. The precatalyst according to any of claims 9, 10 or 12-14 selected from the group consisting of



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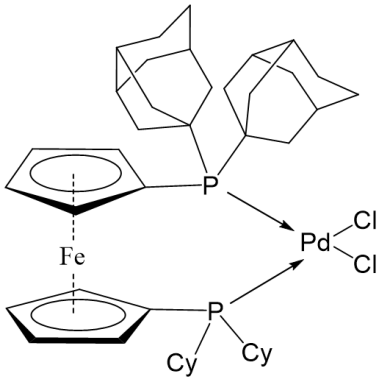

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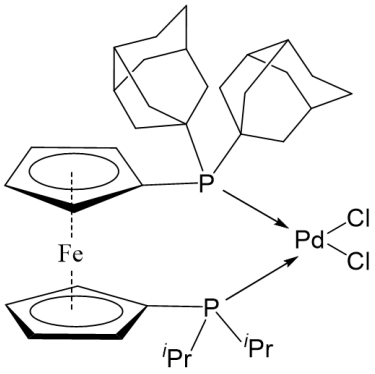

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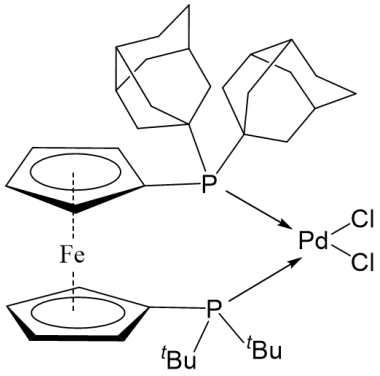

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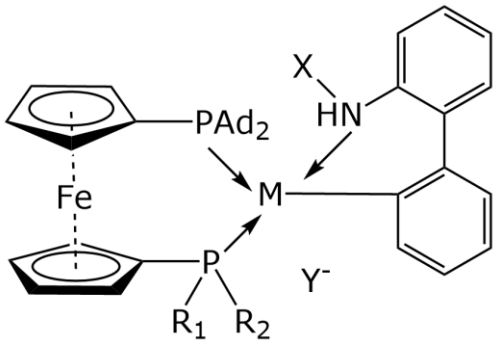
16. A precatalyst of Formula III:



III

wherein

Ad is adamantyl;

R_1 and R_2 are independently selected from the group consisting of C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_1-C_{12} alkoxy, -NR_4R_5, and optionally substituted phenyl;

R_4 and R_5 are individually selected from the group consisting of H and C_1-C_{12} alkyl, or R_4 and R_5 together can form a saturated or unsaturated 5- or 6-membered ring, the ring optionally including one or more additional heteroatoms selected from O, S and N, and one or more optional substituents;

each optional substituent, when present, is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 haloalkyl and C_1-C_4 alkoxy;

M is a transition metal selected from Group 9 or Group 10;

X is selected from the group consisting of H, C_1-C_4 alkyl and phenyl; and

Y^- is an anion selected from the group consisting of halide, triflate ($^-$OTf), tetrafluoroborate ($^-$ BF_4), hexafluorophosphate ($^-$ PF_6), mesylate ($^-$OMs), tosylate ($^-$OTs), tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($^-$ BArF), hexafluoro antimonate ($^-SbF_6$) and combinations thereof.

17. The precatalyst according to claim 16 wherein R_1 and R_2 are independently selected from the group consisting of phenyl, cyclohexyl, isopropyl and *tert*-butyl.

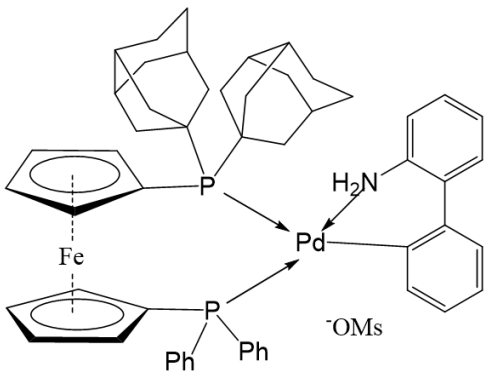
18. The precatalyst according to either of claims 16 or 17 wherein M is selected from the group consisting of Pd, Ni, Rh, Co, Ir and Pt.

19. The precatalyst according to any of claims 16-18 wherein M is Pd.

20. The precatalyst according to any of claims 16-19 wherein X is selected from the group consisting of H, methyl and phenyl.

21. The precatalyst according to any of claims 16-20 wherein Y^- is selected from the group consisting of Cl^-, Br^-, I^-, $^-$OTf, $^-$ BF_4, $^-$OMs, $^-$OTs, $^-$ PF6, $^-$ BArF, and $^-$SbF6.

22. The precatalyst according to any of claims 16-21 selected from the group consisting of



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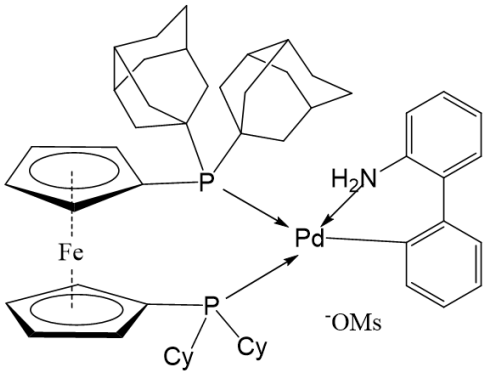

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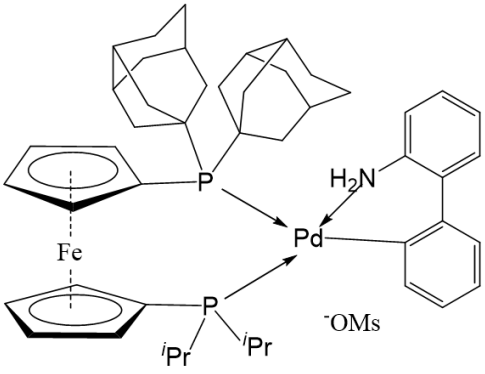

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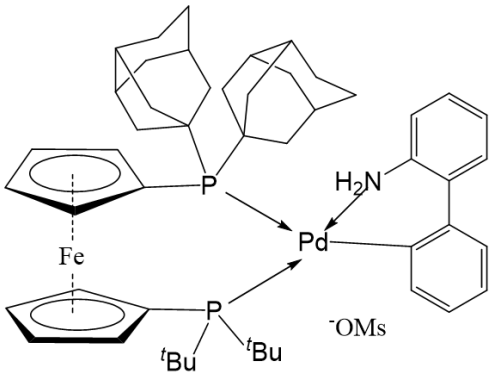

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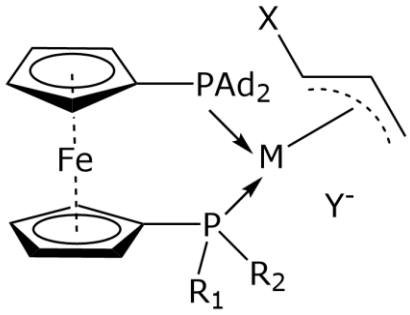
23. A precatalyst of formula IV:



IV

wherein

Ad is adamantyl;

R_1 and R_2 are independently selected from the group consisting of C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_1-C_{12} alkoxy, -NR_4R_5, and optionally substituted phenyl;

R_4 and R_5 are individually selected from the group consisting of H and C_1-C_{12} alkyl, or R_4 and R_5 together can form a saturated or unsaturated 5- or 6-membered ring, the ring optionally including one or more additional heteroatoms selected from O, S and N, and one or more optional substituents;

wherein each optional substituent, when present, is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 haloalkyl and C_1-C_4 alkoxy;

M is a transition metal selected from Group 9 or Group 10;

X is selected from the group consisting of H, C_1-C_4 alkyl and phenyl; and

Y^- is an anion selected from the group consisting of halide, triflate ($^-$OTf), tetrafluoroborate ($^-$ BF_4), hexafluorophosphate ($^-$ PF_6), mesylate ($^-$OMs), tosylate ($^-$OTs), tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($^-$ BArF), hexafluoro antimonate ($^-SbF_6$) and combinations thereof.

24. The precatalyst according to claim 23 wherein R_1 and R_2 are independently selected from the group consisting of phenyl, cyclohexyl, isopropyl and *tert*-butyl.

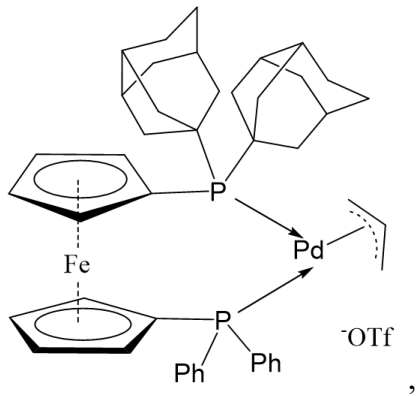
25. The precatalyst according to either of claims 23 or 24 wherein M is selected from the group consisting of Pd, Ni, Rh, Co, Ir and Pt.

26. The precatalyst according to any of claims 23-25 wherein M is Pd.

27. The precatalyst according to any of claims 23-26 wherein X is selected from the group consisting of H, methyl and phenyl.

28. The precatalyst according to any of claims 23-27 wherein Y^- is selected from the group consisting of Cl^-, Br^-, I^-, $^-$OTf, $^-$ BF_4, $^-$OMs, $^-$OTs, $^-$ PF_6, $^-$ BArF, and $^-$SbF6.

29. The precatalyst according to any of claims 23-28 selected from the group consisting of



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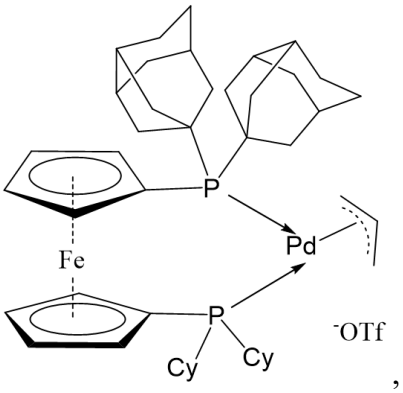

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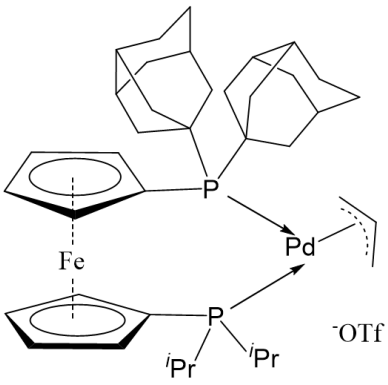

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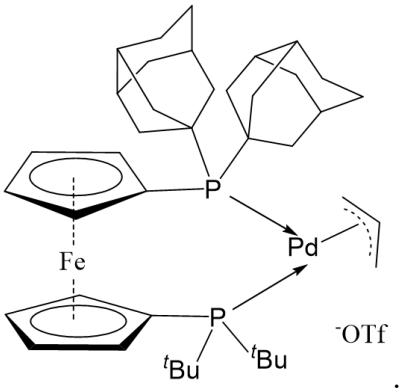

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30. A method for performing a metal-catalyzed P-C cross-coupling reaction comprising the steps of:

contacting a ligand according to any of claims 5-8 with a metal catalyst in the presence of an aromatic solvent and a base in a reaction vessel;

adding a first substrate of formula Ar-X', wherein Ar is aryl and X' is halo and a second substrate of formula R'_2PH, wherein R' is selected from the group consisting of C_1-C_{10} alkyl and C_3-C_{10} cycloalkyl, to the reaction vessel;

heating the reaction vessel to a temperature in the range from 100 °C to 200 °C for a time sufficient to form the carbon-phosphorous bond.

31. The method of claim 30 wherein the ligand is a ligand according to claim 8, the catalyst is a Pd catalyst.

32. A method for performing a metal-catalyzed C_{sp2}-C_{sp3} cross-coupling reaction comprising the steps of:

contacting a precatalyst of Formula II according to any of claims 9-15 with a first substrate and a second substrate in the presence of a solvent in a reaction vessel;

wherein the first substrate is of formula Ar-X', wherein Ar is optionally substituted aryl or optionally substituted heteroaryl and X' is chloro or bromo or iodo;

wherein the second substrate is of formula R'[M], wherein R' is selected from the group consisting of C_1-C_{10} alkyl, C_1-C_{10} fluoroalkyl and C_3-C_{10} cycloalkyl, [M] is selected from the group consisting of Li, MgX', ZnX' and $B(OH)_2$ and related boron reagents, wherein X' is selected from the group consisting of chloro, bromo and iodo;

optionally, heating the reaction vessel and

allowing first substrate and the second substrate to react in the presence of the precatalyst for a time sufficient for the C_{sp2}-C_{sp3} cross-coupling to occur.

33. The method according to claim 32 wherein the first substrate is selected from the group consisting of optionally substituted phenyl, optionally substituted pyridyl, optionally substituted thienyl, and optionally substituted furyl.

34. The method according to either of claims 32 or 33 wherein [M] is Li, the solvent is toluene, and the reaction vessel is not heated.

35. The method according to either of claims 32 or 33 wherein [M] is selected from MgX' and ZnX', the solvent is tetrahydrofuran, and the reaction vessel is heated to 50°C.

36. The method according to either of claims 32 or 33 wherein [M] is $B(OH)_2$, the solvent is toluene and the reaction vessel is heated to 100°C.