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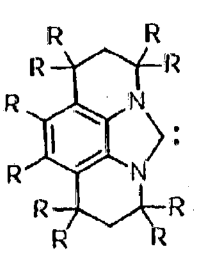
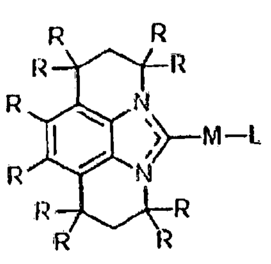
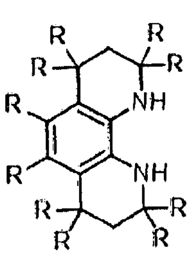


Formula (I)



Formula (II)



Formula (IV)

(57) Abstract: The present invention relates to novel N-heterocyclic carbenes compounds and process of the preparation thereof. The present invention further relates to the use of use of these novel N-heterocyclic carbenes as ligand in the Suzuki-Miyaura cross coupling reactions.

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NOVEL N-HETEROCYCLIC CARBENE COMPOUNDS, THEIR PREPARATION AND USE

FIELD OF THE INVENTION:

The present invention relates to novel N-heterocyclic carbine compounds and process of the preparation thereof. More particularly, the present invention relates to novel N-heterocyclic carbenes compounds, their preparation and use of these novel N-heterocyclic carbenes as ligand in the Suzuki-Miyaura cross coupling reactions.

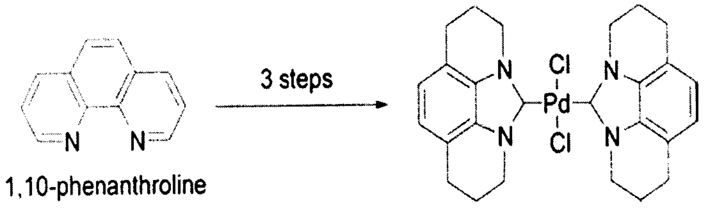
BACKGROUND AND PRIOR ART:

Recently N-heterocyclic carbenes (NHCs) have emerged as an important class of ligands and catalysts because of their several attractive features, and they have thus received significant attention from the scientific community. A transition metal carbene complex is an organometallic compound featuring a divalent carbene organic ligand. Carbene complexes for almost all transition metals have been reported and many reactions utilizing them have been reported. NHC's are generally derived from persistent carbenes which are stable compound of divalent carbon.

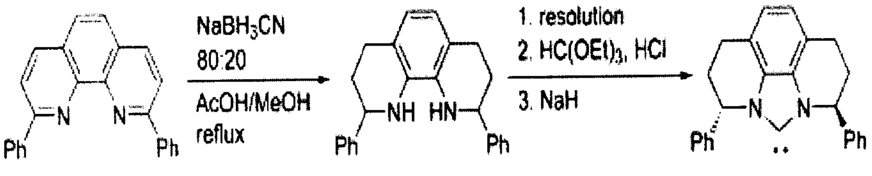
Metal complexes with N-heterocyclic carbene (NHC) ligands are widely used in chemistry due to their catalytic properties and applied for olefin metathesis among other reactions. The enhanced application of this type of organometallics has over the last few years also triggered a steadily increasing number of studies in the fields of medicinal chemistry, which take advantage of the fascinating chemical properties of these complexes.

Article titled "Suzuki–Miyaura cross-Coupling reactions mediated by palladium/imidazoliumsalt systems" by GA Grasa et al. published in *Organometallics*, 2002, 21 (14), pp 2866–2873 reports nucleophilic N-heterocyclic carbenes (NHC) used as ancillary ligands in palladium-mediated Suzuki–Miyaura cross-coupling reactions involving aryl chlorides or aryl triflates with arylboronic acids. The scope of the coupling process using Pd(0) or Pd(II) sources and an imidazolium salt in the presence of a base, Cs_2CO_3, was tested using various substrates.

Article titled "A benzimidazole-based N-heterocyclic carbene derived from 1,10-phenanthroline" by C Metallinos et al. published in *Org. Lett.*, 2004, 6 (20), pp 3641–3644 reports a catalytically active palladium-complexed tetracyclic N-heterocyclic carbene (NHC) was prepared in three steps from commercially available 1,10-phenanthroline by using a reduction cyclization–deprotonation sequence. The new carbene framework is a prototype for the development of a series of chiral N-heterocyclic carbenes.



Article titled "Reduction of substituted 1,10-phenanthrolines as a route to rigid chiral benzimidazolylidenes" by C Metallinos et al. published in *Tetrahedron,* Volume 62, Issue 48, 27 November 2006, Pages 11145–11157 reports substituted 1,10-phenanthrolines which are reduced to octahydrophenanthrolines in moderate to good yields with $NaBH_3CN$ in acetic acid/methanol. The exact solvent composition is described to avoid the formation of tetrahydrophenanthrolines and N-alkylated by products, and to optimize the formation of octahydrophenanthrolines. Resolution of a racemic reduction product gives an enantiomerically pure C_2-symmetric diamine from which the corresponding rigid benzimidazolylidene is prepared, whereas reduction of chiral phenanthrolines derived from bicyclic ketones affords diastereomerically pure diamines, which may also be converted to benzimidazolylidenes.



Article titled "Neutral and cationic iridium(I) complexes bearing chiral phenanthroline-derived benzimidazolylidenes: synthetic, structural, and catalytic studies" by C Metallinos et al. published in *Organometallics*, 2009, 28 (4), pp 1233–1242 reports a synthesis and characterization of series of neutral and cationic iridium(I) complexes bearing chiral and achiral phenanthroline-derived benzimidazolylidene ligands. Spectroscopic and crystallographic data indicate that the principal plane of the NHC ligand in the achiral complexes is positioned orthogonally with respect to the Ir–Cl or Ir–P bonds, while the planes of NHC ligands in the corresponding chiral complexes are twisted by a torsion angle that depends on the size of the 2,9-substituents. All of the new complexes showed varying degrees of catalytic activity and enantioselectivity toward hydrogenation of acetamidoacrylates, with the best results being achieved using 2,9-diphenyl-substituted (S,S)-20a, which afforded (−)-(R)-methyl 2-acetamidopropanoate (12a) in 97% yield and 81% ee.

Article titled "Preparation of NHC borane complexes by lewis base exchange with amine– and phosphine–boranes" by MM Brahmi el al. published in *J. Org. Chem.*, 2010, 75 (20), pp 6983–6985 reports a versatile new method for the preparation of NHC boranes starting from two stable, readily available reactants—an heterocyclic salt and an amine or phosphine–borane. It uses a Lewis base exchange at boron and provides easy access to new NHC boranes, in particular B-substituted borane ones.

Only the group of Metallinos has reported the synthesis of fused tetracyclic NHCs and showed their application. Considering the importance of NHCs in several important reactions. Therefore there is a need to search for new NHCs with varying structural motifs by using simple and scalable chemistry.

OBJECTIVE OF INVENTION:

The main objective of the present invention is to provide novel N-heterocyclic carbene compounds of formula (I) and process for preparation thereof.

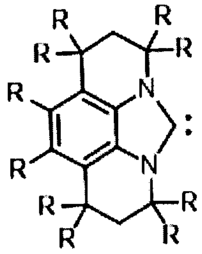
Another objective of the present invention is to provide novel N-heterocyclic carbene metal complexes of formula (II) and process for preparation thereof.

Yet another objective of the present invention is to providea derivatives of novel N-heterocyclic carbene of formula (III) and process for preparation thereof.

Still another objective of the present invention is to provide a method of catalytic Suzuki-Miyaura cross-coupling of aryl halides with arylboronic acids using novel N-heterocyclic carbene palladium complex.

SUMMARY OF THE INVENTION:

Accordingly the present invention provides an N-heterocyclic carbene ligand precursor compound comprising a compound of formula (I), metal complexes and derivatives thereof



Formula (I)

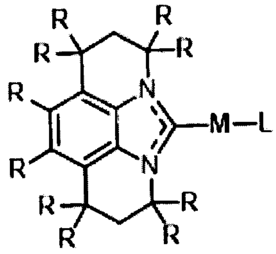
Wherein, R is H, alkyl, aryl, aralkyl; substituted alkyl and substituted aralkyl; Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain hetero atoms like O, N, and S.

In an embodiment of the present invention, the process for the preparation of N-heterocyclic carbene ligand precursor comprising the following steps:

a) Adding a solution of 1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one **1** in anhydrous DMF to a suspension of (NaH) sodium hydride in anhydrous DMF and stir for 30 min at 0°C followed by addition of a solution of 3,3-dimethylallyl bromide with constant stirring at room temperature for 6.5h to obtain **2**;
b) Adding a solution of **2** of step (a)in chlorobenzene to a suspension of ($AlCl_3$) Aluminium chloride in chlorobenzene followed by stirring at room temperature for 2h to obtain**3**;
c) Adding a solution of **3** of step (b) in THF to a suspension of Lithium aluminium hydride in THF followed by refluxing for 1h which was again heating at reflux with 6 N aqueous HCl for 1h to obtain **4**;

d) Heating a solution of **4** of step (c) in triethyl orthofomate and HCl at 80°C for 14 h under argon atmosphere and for 2 h at the same temparature in air to obtain N-heterocyclic carbene ligand precursor;

In still another embodiment of the present invention, the N-heterocyclic carbene metal complex comprising a compound of formula (II)



Formula (II)

Wherein, R is H, alkyl, aryl, aralkyl; substituted Alkyl and substituted aralkyl;

Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain hetero atoms like O, N, S;

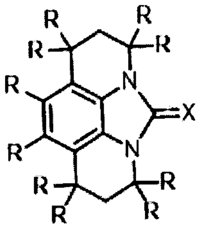
M is Pd,

L is ligands L can be carbene having Formula (I) or any heterocycle containing Nitrogen which can be further substituted.

In yet another embodiment of the present invention, the process for the preparation of N-heterocyclic carbene metal complex further comprising refluxing the reaction mixture of N-heterocyclic carbene ligand precursor (**5**) and $Pd(OAc)_2$ in THF for 1 h to obtainN-heterocyclic carbene metal complex (**8**),

or heating the reaction mixture of N-heterocyclic carbene ligand precursor (**5**), $PdCl_2$ and potassium carbonate in pyridine in microwave at 150°C for 30 min to obtain N-heterocyclic carbene metal complex (**9**).

In still another embodiment of the present invention the derivative of N-heterocyclic carbine compound comprising a compound of formula (III)



Formula (III)

Wherein, R is H, alkyl, aryl, aralkyl; substituted alkyl and substituted aralkyl;
Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain hetero atoms like O, N, S;
X is O, S.

In yet another embodiment of the present invention, the derivative of N-heterocyclic carbene compound is selected from selected from 1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-5*H*-imidazo[1,5,4,3-*lmn*][1,10]phenanthroline-5-thione and 5-(λ^4-boranyl)-1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-4- λ ^{4}-imidazo-[3,4,5,1-*lmn*][1,10]phenanthroline.

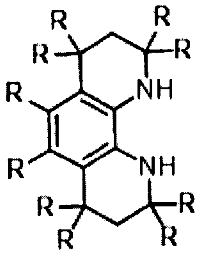
In still another embodiment of the present invention,The process for the preparation of derivative of N-heterocyclic carbene compound of formula (III) comprising the step of stirring sodium bis(trimethylsilyl)amide and a suspension of of N-heterocyclic carbene ligand precursor 5 in tetrahydrofuran at −78 °C followed by addition of Borane tetrahydrofuran complex solution (BH_3.THF) with constant stirring at room temparation for 5h to obtain 5-(λ^4-boranyl)-1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-4 λ^4-imidazo-[3,4,5,1-*lmn*][1,10]phenanthroline (7).

In yet another embodiment of the present invention,the process for the preparation of derivative of N-heterocyclic carbene compound of formula (III) comprising the steps of

a) stirring N-heterocyclic carbene ligand precursor 5 and sodium hydride (NaH) in THF for 1 h at room temparature;

b) adding S_8in THFfolowed by stirring at room temparature for further additional 2h to obtain 1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-5H-imidazo[1,5,4,3-lmn][1,10]phenanthroline-5-thione (6).

In still another embodiment of the present invention, a compound of formula (IV) for preparing N-heterocyclic carbene ligand precursor of formula (I)



Formula (IV)

Wherein, R is H, alkyl, aryl, aralkyl; substituted alkyl and substituted aralkyl;

Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain heteroatoms like O, N, S;

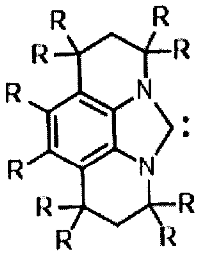
In yet another embodiment of the present invention, a method of catalytic Suzuki-Miyaura cross-coupling of aryl halides with aryl boronic acids using novel N-heterocyclic carbenepalladium complex according to any of the previous claims, comprising stirring a solution of aryl boronic acids selected from the group consisting of phenyl boronic acid, (4-methoxyphenyl)boronic acid, (3-nitrophenyl)boronic acid, naphthalen-1-ylboronic acid, (4-(hydroxymethyl)phenyl)boronic acid, 4-boronobenzoic acid, (4-acetylphenyl)boronic acid, furan-2-ylboronic acid; aryl halides selected from the group consisting of 1-(4-bromophenyl)ethan-1-one, 1-bromo-4-methoxybenzene,chlorobenzene, 4-chlorophenol, 4-bromophenol, 3-bromopyridine, 2-bromothiophene, 2-bromoaniline; tripotassium phosphate $K_3PO_4$and N-heterocyclic carbene palladium complex in DMF at room temperature for 2 h.

In still another aspect, the present invention provides a method of catalytic Suzuki-Miyaura cross-coupling of aryl halides with arylboronic acids using novel N-heterocyclic carbene palladium complexat room temperature with very low catalyst loading.

DETAILED DESCRIPTION OF THE INVENTION:

The invention will now be described in detail in connection with certain preferred and optional embodiments, so that various aspects thereof may be more fully understood and appreciated.

In an embodiment, the present invention provides anN-heterocyclic carbene ligand precursor of formula (I)



Formula (I)

Wherein, R is H, alkyl, aryl, aralkyl; substituted alkyl and substituted aralkyl;
Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain heteroatoms like O, N, and S.

In another embodiment, the present invention providea process for the preparation of N-heterocyclic carbene ligand precursor comprising the steps of:

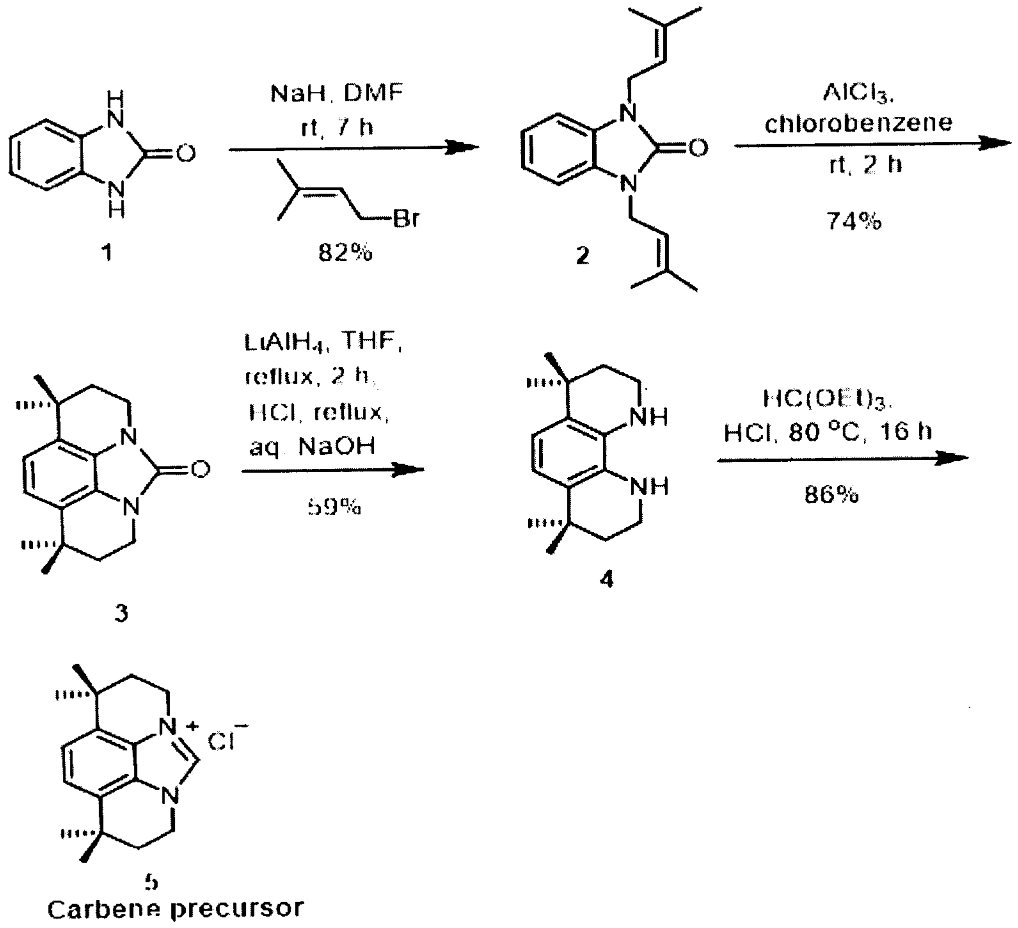
a) Adding a solution of 1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one in anhydrous DMF to a suspension of Sodium hydride NaH in anhydrous DMF and stir for 30 min at 0°C followed by addition of a solution of 3,3-dimethylallyl bromide with constant stirring at room temperature for 6.5h to obtain **2**;

b) Adding a solution of **2** of step (a)in chlorobenzene to a suspension of aluminium chloride $AlCl_3$ in chlorobenzene followed by stirring at room temperature for 2h to obtain**3**;

c) Adding a solution of **3** of step (b) in THF to a suspension of Lithium aluminium hydride in THF followed by refluxing for 1h. which was again heating at reflux with 6 N aqueous HCl for 1h to obtain **4**;

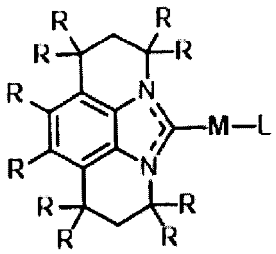
d) Heating a solution of **4** of step (c) in triethyl orthofomate and HCl at 80°C for 14 h under argon atmosphere and for 2 h at the same temparature in air to obtain N-heterocyclic carbene ligand precursor **5**;

The process for the preparation of N-heterocyclic carbene ligand precursor is shown below in Scheme-1:



Scheme: 1

In still another embodiment, the present invention provide an N-heterocyclic carbene metal complex comprising a compound of formula (II)



Formula (II)

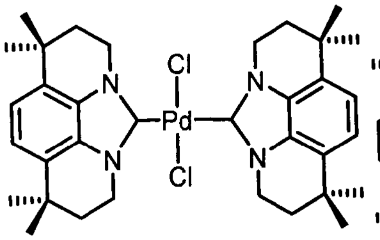
Wherein, R is H, alkyl, aryl, aralkyl; substituted Alkyl and substituted aralkyl;

Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain heteroatoms like O, N, S;

M is Pd,

L is ligands. L can be carbene having Formula (I) or any heterocycle containing Nitrogen which can be further substituted.

The N-heterocyclic carbene metal complexof formula (II) is selected from following compounds of formula **8** and **9** as shown below:



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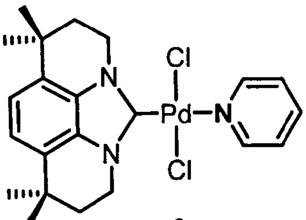

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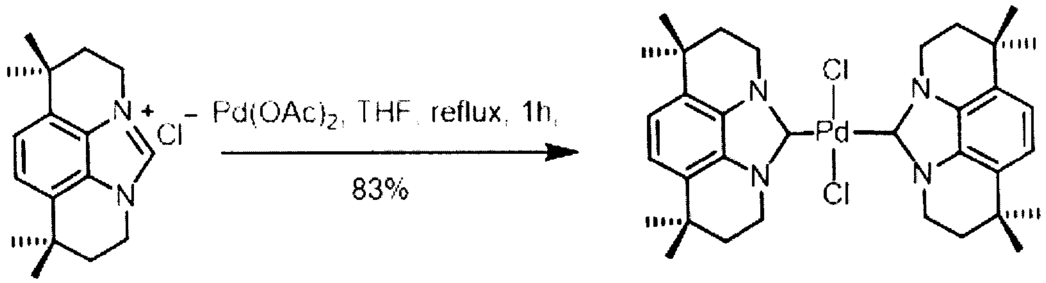
The process for the preparation of N-heterocyclic carbene metal complex of formula (8) comprising refluxing the reaction mixture of N-heterocyclic carbene ligand precursor (5) and Pd(OAc)$_2$in THF for 1 h.

The process for the preparation of N-heterocyclic carbene metal complex of formula (8) is as shown in scheme 2 below:



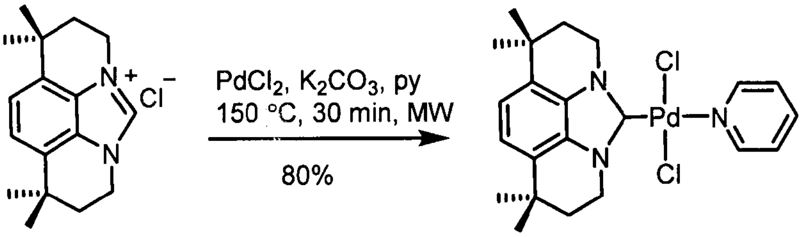
5

NHC-Pd complex I
8

Scheme: 2

The process for the preparation of N-heterocyclic carbene metal complex of formula (9) comprising heating the reaction mixture of N-heterocyclic carbene ligand precursor (**5**), $PdCl_2$ and potassium carbonate in pyridine in microwave at 150°C for 30 min.

The process for the preparation of N-heterocyclic carbene metal complex of formula (9) is as shown in scheme 3 below:



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NHC-Pd complex-II
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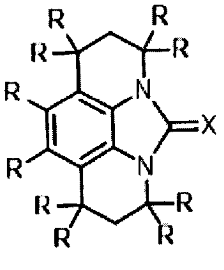
Scheme: 3

In one embodiment, the present invention provide an derivatives of N-heterocyclic carbene of formula (III)



Formula (III)

Wherein, R = H, alkyl, aryl, aralkyl;

Alkyl and aralkyl can be further substituted

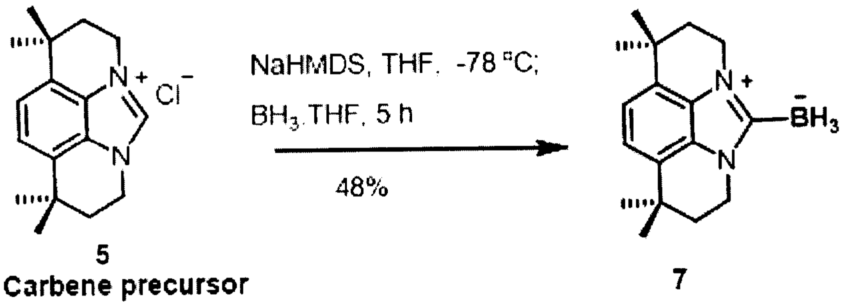
Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain heteroatoms like O, N, S;

X = O, S;

The derivatives of N-heterocyclic carbene of formula (III) are preferably selected form 1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-5*H*-imidazo[1,5,4,3-*lmn*][1,10]phenanthroline-5-thioneand 5-(λ^4-boranyl)-1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-4-λ^4-imidazo-[3,4,5,1-*lmn*][1,10]phenanthroline.

The process for the preparation of 5-(λ^4-boranyl)-1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-4-λ^4-imidazo-[3,4,5,1-*lmn*][1,10]phenanthrolinecomprising the step of stirring sodium bis(trimethylsilyl)amide and a suspension of of N-heterocyclic carbene ligand precursor **5** in tetrahydrofuran at −78 °C followed by addition of borane tetrahydrofuran complex BH_3.THF with constatn stirring at room temparation for 5h to obtain 5-(λ^4-boranyl)-1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-4-λ^4-imidazo-[3,4,5,1-*lmn*][1,10]phenanthroline.

The process for the preparation of 5-(λ^4-boranyl)-1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-4-λ^4-imidazo-[3,4,5,1-*lmn*][1,10]phenanthroline is as shown in scheme 4 below:



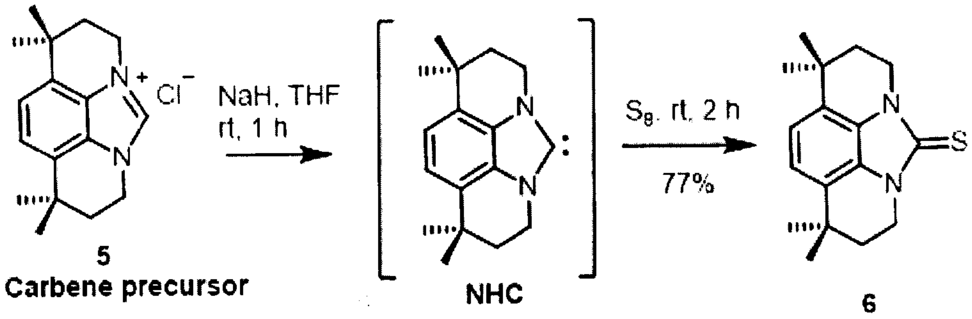
Scheme: 4

The process for the preparation of 1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-5*H*-imidazo[1,5,4,3-*lmn*][1,10]phenanthroline-5-thionecomprising the step of:

a) Stirring N-heterocyclic carbene ligand precursor 5 and sodium hydride NaH in THF for 1 h at room temparature;

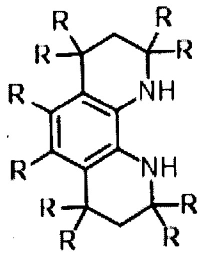
b) Adding S_8in THF followed by stirring at room temparature for further additional 2h to obtain 1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-5H-imidazo[1,5,4,3-lmn][1,10]phenanthroline-5-thione (6).

The process for the preparation of 1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-5*H*-imidazo[1,5,4,3-*lmn*][1,10]phenanthroline-5-thione is as shown in scheme 5 below:



Scheme: 5

In one embodiment, the present invention provide an intermediate of formula (IV) which is used for the preparation of N-heterocyclic carbene of formula (I).



Formula (IV)

Wherein, R = H, alkyl, aryl, aralkyl; substituted Alkyl and substituted aralkyl;

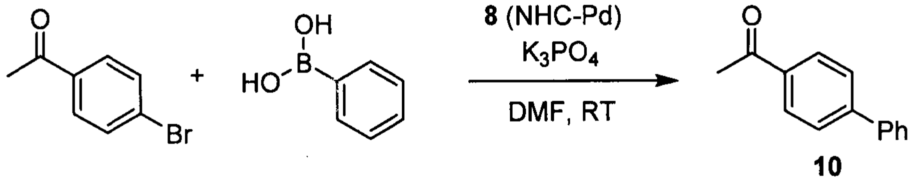
Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain heteroatoms like O, N, S;

In one embodiment, the present invention provide a method of catalytic Suzuki-Miyaura cross-coupling of aryl halides with arylboronic acids using novel N-heterocyclic carbene palladium complex, comprising stirring a solution of arylboronic acids, aryl halides, tripotassium phosphate K_3PO_4 and N-heterocyclic carbene palladium complex in DMF at room temperature for 2 h.

In preferred embodiment, the aryl halides as used herein are preferably selected from1-(4-bromophenyl)ethan-1-one,1-bromo-4-methoxybenzene,chlorobenzene, 4-chlorophenol,4-bromophenol, 3-bromopyridine,2-bromothiophene,2-bromoaniline.

In another preferred embodiment, the arylboronic acids as used herein are selected form Phenyl boronic acid, (4-methoxyphenyl)boronic acid,(3-nitrophenyl)boronic acid,naphthalen-1-ylboronic acid,(4-(hydroxymethyl)phenyl)boronic acid,4-boronobenzoic acid,(4-acetylphenyl)boronic acid,furan-2-ylboronic acid.

The use of NHC-Pd complex (8) in catalysis of Suzuki-Miyaura coupling reaction is shown below in Scheme 6:

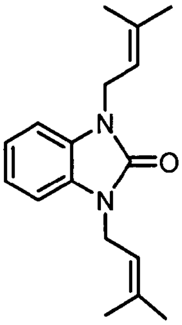


Scheme: 6

The following examples, which include preferred embodiments, will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purpose of illustrative discussion of preferred embodiments of the invention.

Examples:

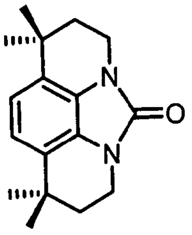
Example 1: Synthesis of 1,3-bis(3-methylbut-2-en-1-yl)-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (2) :



2

In an oven dried 100 mL side armed flask, a suspension of 60% NaH (2.0 g, 50 mmol) in anhydrous DMF (10 mL) was cooled to 0°C. The solution of 1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one **1** (2.68 g, 20 mmol) in anhydrous DMF (15 mL) was added drop wise to it. After vigorous stirring for 30 min at the same temperature; the solution of 90% 3,3-dimethylallyl bromide (5.3 mL, 45 mmol) was added and the reaction mass was allowed to warm to room temperature. Following the completion of reaction (6.5 h) by TLC, it was quenched with ice cold solution of ammonium chloride and extracted with ethyl acetate (3 x 30 mL). The organic layer was washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue obtained was purified by column chromatography using ethyl acetate: petroleum ether (1:5) as the eluent to get **2** (4.42 g, 82%) as white solid. Mp 74–75°C; R_f (15% ethyl acetate/ hexane): 0.2; IR (Nujol) ν/cm^{-1}:2926, 2852, 1670, 1632; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.72 (s, 6H), 1.85 (s, 6H), 4.48 (d, J = 6.71 Hz, 4H), 5.27 (dd, J = 6.72 Hz, 2H), 6.94 (dd, J = 5.80, 3.35 Hz, 2H), 7.05 (dd, J = 5.80, 3.35 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:28.4, 31.7, 36.5, 37.5, 115.4, 123.6, 125.8, 152.7; HRMS (ESI^+) for$C_{17}H_{22}N_2O$;Calculated:271.1810 $[M+H]^+$;Found:271.1805.

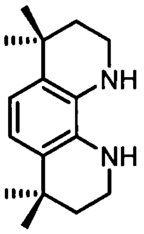
Example 2: Synthesis of 1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-5*H*-Imidazo [1,5,4,3*lmn*] [1,10]phenanthrolin-5-one (3) :



3

To the ice cold suspension of Aluminum chloride $AlCl_3$ (5.6 g, 42 mol) in anhydrous chlorobenzene (15 mL), the solution of **2** (3.78 g, 14 mmol) in the same solvent (15 mL) was added. The wine red solution was stirred at room temperature and monitored by TLC. After completion of the reaction (2 h), it was poured on ice cold water (20 mL) containing 1N HCl (10 mL). White emulsion was extracted with ethyl acetate (3 × 25 mL) and organic layer was washed with saturated $NaHCO_3$ (30 mL) followed by brine (30 mL). It was dried over anhydrous Na_2SO_4 and concentrated to get crude product, which was purified by column chromatography using ethyl acetate: pet ether (1:3) as the eluent to result in **3** (2.8 g, 74%) as white solid. Mp 197−198°C; R_f (20% ethyl acetate/ hexane): 0.2;IR (Nujol) ν/cm^{-1}:2948, 2922, 2856, 1712, 1628, 1134; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.34 (s, 12H), 1.89 (t, J = 5.80 Hz, 4H), 3.89 (t, J = 5.80 Hz, 4H), 6.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.4, 31.8, 36.5, 37.6, 115.1, 123.6, 125.8, 152.7; HRMS (ESI$^+$) for$C_{17}H_{22}N_2O$;Calculated:271.1810 $[M+H]^+$;Found:271.1805.

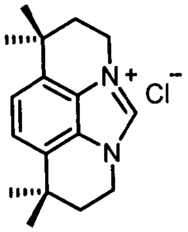
Example 3: Synthsis of 4,4,7,7-tetramethyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (4):



4

The solution of **3** (2.7 g, 10 mmol)in anhydrousTHF(30 mL) was dropwise added to the ice-cold suspension of 80% Lithium aluminium hydride (2.38 g, 50 mmol) in THF. The reaction mass was refluxed and monitored by TLC (1 h). The reaction mass was cooled to 0 °C and quinched by causious addition of cold water followed by NaOH. The white precipitate was filtered off and the filtrate and washings were dried over anhydrous Na_2SO_4. The evaporation of solvent resulted in white solid which was dissolved in 6N HCl (30 mL) and refluxed for 1h. After cooling to room temperature, the reaction mass was washed with diethyl ether (30 mL) and aqueous layer was basicified with NaOH up to pH 11. It was extracted with ethyl acetate (3 × 20 mL) and organic layer was washed with brine (30 mL). It was dried over anhydrous Na_2SO_4 and concentrated to get crude product, which was purified by column chromatography using ethyl acetate: pet ether (1:4) as the eluent to get **4** (1.42 g, 59%) as light red solid. Mp 136–137°C; R_f (15% ethyl acetate/ hexane): 0.3; IR (Nujol) ν/cm^{-1}:3409, 3348, 3298, 2958, 2922, 1608, 1568; ^{1}H NMR 400 MHz, $CDCl_3$) δ: 1.25 (s, 12H), 1.69 (t, J = 5.31 Hz, 4H), 3.26 (t, J = 5.81 Hz, 4H), 6.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.8, 32.4, 38.9, 39.6, 117.1, 129.8, 132.3; HRMS (ESI$^+$) for$C_{16}H_{24}N_2$;Calculated:245.2012 $[M+H]^+$;Found:245.2006.

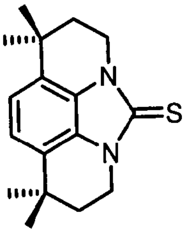
Example 4: Synthsis of1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydroimidazo[1,5,4,3-lmn][1,10]phenanthrolin-4-ium chloride (5):



5

The diamine **4** (1.22 g, 5 mmol) was dissolved in triethyl orthofomate (85 mL) and treated with HCl (0.42 mL,5 mmol). It was heated at 70 °C for 14 h under argon and for 2 h at the same temperature in air. The solution was cooled to room temperature and the salt was precipitated by addition of diethyl ether (50 mL). It was filtered through the Bückner funnel and dried under vacuum to yield **5** (1.25 g, 86%) as a white powder. Mp > 295°C; IR (Nujol) ν/cm^{-1}:3323, 3242, 3115, 2953, 1641, 1623; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.44 (s, 12H), 2.14 (t, J = 5.95 Hz, 4H), 4.76 (t, J = 5.94 Hz, 4H), 7.36 (s, 2H), 11.07 (s, 1H); ^{13}C NMR (55 MHz, $CDCl_3$) δ:28.0, 31.9, 37.3, 42.6, 121.2, 126.3, 131.6, 138.8; HRMS (ESI$^+$) for$C_{17}H_{22}ClN_2$;Calculated:255.1856 $[M-Cl]^+$;Found:255.1853.

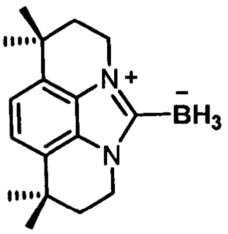
Example 5: Synthsis of 1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-5*H*-imidazo[1,5,4,3-*lmn*][1,10]phenanthroline-5-thione (6):



6

The benzimidazolium chloride **5** (58 mg, 0.2 mmol) and 60% sodium hydride NaH (8 mg, 0.2 mmol) were suspended in anhydrous THF (6 mL) and stirred at room temperature for 1 h. During this time, the suspension becomes yellow-orange. To this the supension of S_8 (51 mg, 0.2 mol) in anhdrous THF (5 mL) was added drowise to get almost a colourless reaction mixture. After stirring at room temperature for additional 2 h, ice-cold water was added and the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was washed with brine (5 mL) and dried over anhydrous Na_2SO_4. Evaporation of solvent, followed by colum chromatographic purification of the crude product using ethyl acetate: petroleum ether (1:4) as the eluent yielded **6**(45 mg, 77%) as white solid. Mp 236–237°C; R_f (15% ethyl acetate/ hexane): 0.2; IR (Nujol) ν/cm^{-1}:3018, 2963, 3298, 2958, 2922, 1608, 1568; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.36 (s, 12H), 1.99 (t, J = 5.78 Hz, 4H), 4.15 (t, J = 5.80 Hz, 4H), 7.01 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 28.3, 32.0, 37.7, 39.3, 117.1, 126.9, 127.2, 165.3; HRMS (ESI$^+$) for$C_{17}H_{22}N_2S$;Calculated:287.1576 [M+H]$^+$;Found:287.1572.

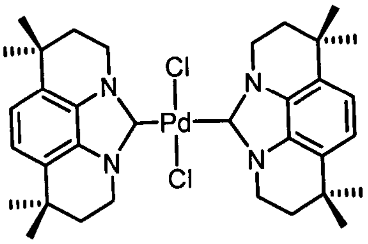
Example 6: Synthesis of 5-(λ^4-boranyl)-1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-4 λ^4-imidazo-[3,4,5,1-*lmn*][1,10]phenanthroline (7) :



7

In an oven dried 25 mL two neck round bottom flask, the suspension of benzimidazolium chloride **5** (290 mg, 1 mmol) in anhydrous THF (10 mL) was cooled to −78°C. To this, 1 M solution of Sodium bis(trimethylsilyl)amide (NaHMDS) (1.0 mL) was added dropise and stirring continued at the same temperature for 1 h. The 1 M solution of Borane tetrahydrofuran complex solution (BH_3.THF) (1.0 mL, 1 mmol) was then added dropwise and the reaction mass was slowly warmed to room temperature and stirred for additional 4h. The volitiles were removed on rotavapor and the crude product was purified by column chromatograpy through a small pad of silicagel using DCM as the eluent to yield **7** (128 mg, 48%) as a reddish solid. Mp 183−185°C; IR (Nujol) ν/cm^{-1}:3024, 2964, 1687, 1656, 1504; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.34 (s, 12H), 1.80 (t, J = 5.77 Hz, 4H), 3.89 (t, J = 6.02 Hz, 4H), 6.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.4, 31.8, 36.5, 37.6, 115.4, 123.6, 125.8,152.7; Elemental analysis: $C_{17}H_{25}BN_2$ requires: C, 76.13; H, 9.40; N, 10.44; found: C, 76.17; H, 9.35; N, 10.26 %

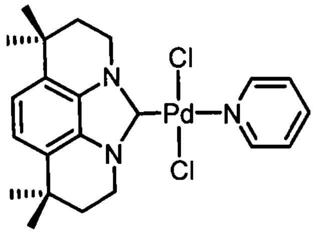
Example 7: Synthesis of NHC-Palladium complex I (8) :



8

The benzimidazolium chloride **5** (290 mg, 1 mmol) and $Pd(OAc)_2$ (112 mg, 0.5 mmol) were charged in an oven dried two neck round bottom flask equipped with reflux condensor. The whole assembly was flushed with argon and anhydros THF (15 mL) was added to get white suspension. It was then heated at reflux for 1 h; during which color changes to pale grey. It was cooled to room temperature and volitiles were removed on rotavapor. The residue was redissolved in THF (10 mL) and the product was precipitated by addition of pet ether (40 mL). It was filtered through the Whatmann filter paper and dried under vacuum to get **8** (285 mg, 83%) as a light grey solid. Compoud data indicates mixture of isomers. Mp 190°C (with decomposion); IR (Nujol) ν/cm^{-1}:3014, 2974, 1596, 1475, 1403; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.30-1.4.(m, 24H), 1.92 (s, 4H), 2.09 (s, 4H), 4.07 (s, 4H), 4.93 (s, 4H), 7.06 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.7, 28.4, 31.8, 43.1, 129.3, 147.5, 167.8, 182.7; Elemental analysis: $C_{34}H_{44}Cl_2N_4Pd$ requires: C, 59.52; H, 6.46; N, 8.17; found: C, 59.22; H, 6.17; N, 8.13 %

Example 8: Synthesis of NHC-Palladium complex II (9):

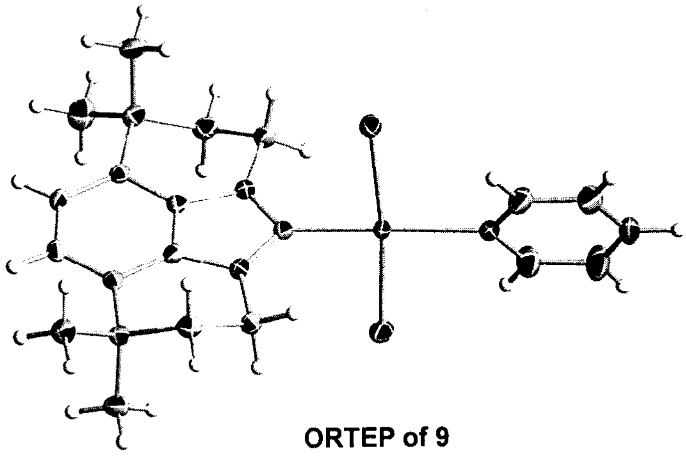


NHC-Pd complex-II
9

The benzimidazolium chloride 5 (100 mg, 0.34 mmol), $PdCl_2$ (60 mg, 0.34 mmol) and potassium carbonate (190 mg, 1.37 mmol) in pyridine (2.0 mL) were charged in an oven dried microwave vial. It was then heated in microwave at 150°C for 30 min. It was cooled to room temperature and the mixture was filtered through silica gel washing it with dichloromethane (3 mL). The volatiles were removed and the crude product was purified by column chromatography through a small pad of silica gel using dichloromethane as the eluent to yield 9 (145 mg, 80%) as a light yellow solid. Mp 175 °C (with decomposition); IR (Nujol) ν/cm-1: 3014, 2915, 1596, 1491, 1350; 1H NMR (400 MHz, CDC13) δ: 9.03 (dd, J = 6.60, 1.71 Hz, 2H), 7.81 (tt, J = 7.58, 1.47 Hz, 1H), 7.40 (ddd, J = 7.58, 6.36, 1.47 Hz, 2H), 7.04 (s, 2H), 4.78 (t, J = 5.87, 4H), 2.10 (t, J = 6.12, 4H), 1.39 (s, 12H); 13C NMR (100 MHz, $CDCl_3$) δ: 155.1, 151.2, 138.0, 129.6, 128.9, 124.5, 117.6, 42.9, 38.1, 31.9, 28.4.Elemental analysis: $C_{22}H_{27}Cl_2N_3Pd$ requires: C, 51.73; H, 5.33; N, 8.23; found: C, 51.36; H, 5.04; N, 8.02 %.

Crystallographic data for 9

($C_{22}H_{27}Ci_{2}N_{3}Pd$): *M* = 510.77, Crystal dimensions 0.68 x 0.32 x 0.11 mm$_3$, triclinic, space group *P-1*, *a* = 5.6847(6), *b* = 14.0640(14), *c* = 14.3961(14) Å, □ = 108.211(4)°, □ = 95.732(4)°, □ = 95.371(4)°, *V* = 1078.32(19)Å$_3$, *Z* = 2, □$_{calcd}$ = 1.573 gcm$_{-3}$, *μ* (Mo-K□) = 1.121 mm$_{-1}$, *F(000)* = 520, 2□$_{max}$ = 50.00□, *T* = 150(2) K, 17520 reflections collected, 3781 unique reflections (*R*$_{int}$=0.0214), 3732 observed (*I* > 2□ (*I*)) reflections, 258 refined parameters, *R* value 0.0198, *wR*2 = 0.504, (all data *R* = 0.0202, *wR*2 = 0.0507), *S* = 1.149, minimum and maximum transmission 0.516 and 0.887; maximum and minimum residual electron densities +0.44 and –0.37 e $Å^{-3}$. All the H-atoms were placed in geometrically idealized position (C-H = 0.95 Å for the phenyl H-atom, C-H = 0.99 Å for the methylene H-atom and C-H = 0.98 Å for the methyl H-atom) and constrained to ride on their parent atoms [$U_{iso}(H) = 1.2U_{eq}(C)$ for the phenyl and methylene groups and $U_{iso}(H) = 1.5\ U_{eq}(C)$ for the methyl group].



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Example 9:Procedure for the conventional Suzuki-Miyaura cross-coupling reaction:

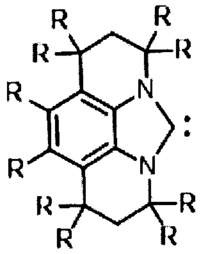
The 10 mL round bottom flask was charged with phenylboronic acid (122 mg, 1 mmol), 4-bromoacetophenone (199 mg, 1 mmol), tripotassium phosphate K_3PO_4 (424 mg, 2 mmol) and palladium complex 8 (3.5 mg, 0.005 mmol) under argon. DMF (2.0 mL) was added to form the white suspension which was stirred vigorously at room temperature and monitored by TLC for the consumption of 4-bromoacetophenone. The reaction mass turned yellow-red suspension after 1 h. After completion of the reaction (2 h), ice cold water was added to the reaction mass and it was extracted with ethyl acetate (3 × 10 mL). The organic layer was washed with saturated NaHCO3 (10 mL) and brine (10 mL) and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography to yield 10 (185 mg, 94%) as white solid. Mp 121–123°C. 1H NMR ($CDCl_3$, 200 MHz) δ: 8.05 (d, J = 8.40 Hz, 2H), 7.57–7.69 (m, 4H), 7.35–7.48 (m, 3H), 2.64 (s, 3H).

Advantages of invention:

1. Novel N-Heterocyclic Carbene (NHC)
2. First and general synthesis of this kind NHC
3. Demonstrated the utility of this ligand in Suzuki-Miyaura coupling reaction through Pd complex under mild conditions.
4. It may be useful as catalysts or reagents in many transformations

We Claim,

1. An N-heterocyclic carbene ligand precursor compound comprising a compound of formula (I), metal complexes and derivatives thereof

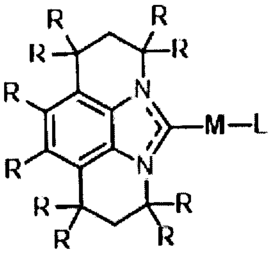


Formula (I)

Wherein, R is H, alkyl, aryl, aralkyl; substituted alkyl and substituted aralkyl;

Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain hetero atoms like O, N, and S.

2. A process for the preparation of N-heterocyclic carbene ligand precursor according to claim 1, comprising the following steps:
    e) adding a solution of 1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one **1** in anhydrous DMF to a suspension of sodium hydride NaH in anhydrous DMF and stir for 30 min at 0°C followed by addition of a solution of 3,3-dimethylallyl bromide with constant stirring at room temperature for 6.5h to obtain **2**;
    f) adding a solution of **2** of step (a)in chlorobenzene to a suspension of aluminium chloride $AlCl_3$ in chlorobenzene followed by stirring at room temperature for 2h to obtain**3**;
    g) adding a solution of **3** of step (b) in THF to a suspension of Lithium aluminium hydride in THF followed by refluxing for 1h. which was again heating at reflux with 6 N aqueous HCl for 1h to obtain **4**;
    h) heating a solution of **4** of step (c) in triethyl orthofomate and HCl at 70°C for 14 h under argon atmosphere and for 2 h at the same temparature in air to obtain N-heterocyclic carbene ligand precursor;
3. The N-heterocyclic carbene ligand precursor compound as claimed in claim 1, wherein the N-heterocyclic carbene metal complex comprising a compound of formula (II)



Formula (II)

Wherein, R is H, alkyl, aryl, aralkyl; substituted Alkyl and substituted aralkyl;

Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain hetero atoms like O, N, S;

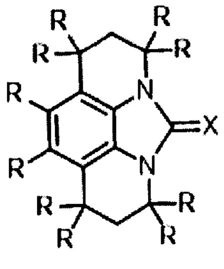
M isPd,

L is ligands. L can be carbene having Formula (I) or any heterocycle containing Nitrogen which can be further substituted.

4. The process for the preparation of N-heterocyclic carbene metal complex as claimed in claim 3 further comprising refluxing the reaction mixture of N-heterocyclic carbene ligand precursor (**5**) and Pd(OAc)$_2$in THF for 1 h to obtain N-heterocyclic carbene metal complex (**8**),

   or heating the reaction mixture of N-heterocyclic carbene ligand precursor (**5**), PdCl$_2$ and potassium carbonate in pyridine in microwave at 150°C for 30 min to obtain N-heterocyclic carbene metal complex (**9**).

5. The N-heterocyclic carbene ligand precursor compound as claimed in claim 1wherein the derivative of N-heterocyclic carbene comprising a compound of formula (III)



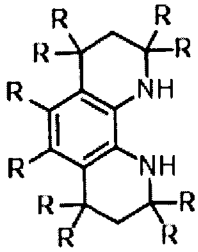
Formula (III)

Wherein, R is H, alkyl, aryl, aralkyl; substituted alkyl and substituted aralkyl;

Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain hetero atoms like O, N, S;

X is O, S;

6. The derivative of N-heterocyclic carbene comprising a compound of formula (III) according to claim 5, wherein the derivative is selected from selected from 1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-5*H*-imidazo[1,5,4,3-*lmn*][1,10]phenanthroline-5-thione and 5-(λ^4-boranyl)-1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-4- λ^4-imidazo-[3,4,5,1-*lmn*][1,10]phenanthroline.
7. The process for the preparation of derivative of N-heterocyclic carbene compound of formula (III) as claimed in claim 6, wherein the process comprising the step of stirring sodium bis(trimethylsilyl)amide and a suspension of of N-heterocyclic carbene ligand precursor 5 in tetrahydrofuran at −78 °C followed by addition of BH_3.THF with constant stirring at room temparation for 4h to obtain 5-(λ^4-boranyl)-1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-4 λ^4-imidazo-[3,4,5,1-*lmn*][1,10]phenanthroline (7).
8. The process for the preparation of derivative of N-heterocyclic carbene compound of formula (III) as claimed in claim 6, wherein the process comprising the step of
   - c) stirring N-heterocyclic carbene ligand precursor 5 and sodium hydride NaH in THF for 1 h at room temparature;
   - d) adding S_8in THFfolowed by stirring at room temparature for further additional 2h to obtain 1,1,9,9-tetramethyl-1,2,3,7,8,9-hexahydro-5H-imidazo[1,5,4,3-lmn][1,10]phenanthroline-5-thione (6).
9. A compound of formula (IV) for preparing N-heterocyclic carbene ligand precursor of formula (I) according to claim 1,



Formula (IV)

Wherein, R is H, alkyl, aryl, aralkyl; substituted alkyl and substituted aralkyl;

Two R groups on same carbon or adjacent carbons can form a cyclic 3-8 membered ring which additionally may contain heteroatoms like O, N, S;

10. A method of catalytic Suzuki-Miyaura cross-coupling of aryl halides with aryl boronic acids using novel N-heterocyclic carbene palladium complex according to any of the previous claims, comprising stirring a solution of aryl boronic acids selected from the group consisting of phenyl boronic acid, (4-methoxyphenyl)boronic acid, (3-nitrophenyl)boronic acid, naphthalen-1-ylboronic acid, (4-(hydroxymethyl)phenyl)boronic acid, 4-boronobenzoic acid, (4-acetylphenyl)boronicacid, furan-2-ylboronic acid; aryl halides selected from the group consisting of 1-(4-bromophenyl)ethan-1-one, 1-bromo-4-methoxybenzene,chlorobenzene, 4-chlorophenol, 4-bromophenol, 3-bromopyridine, 2-bromothiophene, 2-bromoaniline; tripotassium phosphate K_3PO_4 and N-heterocyclic carbene palladium complex in DMF at room temperature for 2 h.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2014/000804

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D487/14 C07B37/04 C07F15/00 C07D471/06 C07F5/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D C07B C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	COSTA METALLINOS ET AL: "A Benzimidazole-Based N -Heterocyclic Carbene Derived from 1,10-Phenanthroline", ORGANIC LETTERS, vol. 6, no. 20, 1 September 2004 (2004-09-01), pages 3641-3644, XP055179968, ISSN: 1523-7060, DOI: 10.1021/ol048393k cited in the application	1,3,5,9, 10
A	abstract compounds 3,4,10,11,17,18 * scheme 3 * ----- -/--	2,4,6-8

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 29 April 2015	Date of mailing of the international search report 15/05/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Eberhard, Michael

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	METALLINOS C ET AL: "Reduction of substituted 1,10-phenanthrolines as a route to rigid chiral benzimidazolylidenes", TETRAHEDRON, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 62, no. 48, 27 November 2006 (2006-11-27), pages 11145-11157, XP025002819, ISSN: 0040-4020, DOI: 10.1016/J.TET.2006.09.023 [retrieved on 2006-11-27] cited in the application	1,3,5,9, 10
A	* schemes 1, 7, 8 * compounds 8,10,23,19f,19a -----	2,4,6-8
X	COSTA METALLINOS ET AL: "Neutral and Cationic Iridium(I) Complexes Bearing Chiral Phenanthroline-Derived Benzimidazolylidenes: Synthetic, Structural, and Catalytic Studies", ORGANOMETALLICS, vol. 28, no. 4, 23 February 2009 (2009-02-23), pages 1233-1242, XP055179967, ISSN: 0276-7333, DOI: 10.1021/om801063w cited in the application compounds 7-10,16a, 16b -----	1,9
X	DMITRY G. GUSEV: "Electronic and Steric Parameters of 76 N-Heterocyclic Carbenes in Ni(CO) 3 (NHC)", ORGANOMETALLICS, vol. 28, no. 22, 23 November 2009 (2009-11-23), pages 6458-6461, XP055180920, ISSN: 0276-7333, DOI: 10.1021/om900654g * Chart 1 "ImPhen", ImPhenPh2" * -----	1
X,P	REVANNATH L. SUTAR ET AL: "A General Approach to N-Heterocyclic Carbenes with a Fused Tetracyclic Core: Ligands for Suzuki-Miyaura Cross-Coupling Reaction", EUROPEAN JOURNAL OF ORGANIC CHEMISTRY, vol. 2014, no. 21, 23 July 2014 (2014-07-23), pages 4482-4486, XP055179965, ISSN: 1434-193X, DOI: 10.1002/ejoc.201402378 the whole document -----	1-10