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Synthesis, Structure and Catalysis of NHC-Pd(II) Complex Based on Tetradentate Mixed Ligand

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Bis-benzimidazolium   salt
(S)-2,2'-bis[2''-(N-picolyl-benzimidazoliumyl)ethoxy]-1,1'-binaphthyl
hexafluorophosphate **[(S)-LH₂]·(PF₆)₂** and its NHC palladium(II) complex
[(S)-LPd](PF$_6$)$_2$ (**1**) have been prepared and characterized. Complex **1** is formed by
one tetradentate mixed ligand **(S)-L** and one Pd(II) ion, in which one 15-membered
ring and two 6-membered rings are contained. In this complex, the intramolecular π-π
interactions between naphthalene rings and benzimidazole rings are observed.
Additionally, the catalytic activity of complex **1** in three types of C-C coupling
reactions (Suzuki-Miyaura, Heck-Mizoroki and Sonogashira reactions) was
investigated. The results show that complex **1** is an effective catalyst in these coupling
reactions.

Keywords: N-heterocyclic carbene, palladium(II) complex, structure, catalysis

Introduction

N-Heterocyclic carbenes (NHCs) have become a type of important ligands of
organometallic chemistry and catalysis.[1] NHC ligands can form strong carbon-metal
bonds with transition metals due to the strong σ-donating ability of carbene carbon.[2]
So far, numerous successful methods have been developed to synthesize NHC
complexes with different metal centers. Among these NHC-metal complexes, NHC
palladium(II) complexes play a very important role in the N-heterocyclic carbene

chemistry, [3, 4] and they have turned out to be efficient catalysts for some C-C coupling reactions, such as Suzuki-Miyaura, Heck-Mizoroki and Sonogashira reactions.[5] Compared with palladium(II) complexes based on phosphine ligands, NHC palladium(II) complexes have better stability to air and moisture and catalytic activity.[6] Some NHC palladium(II) complexes bearing monodentate or polydentate ligands have been prepared and studied, and they show good catalytic activity in the construction of C-C, C-N and other C-heteroatom bonds.[4, 7-9] In order to improve further catalytic activity of NHC palladium(II) complexes, some heteroatoms (P,[10] N,[10a, 11] or O[12]) were introduced into NHC ligands. The research results show that the catalytic activity of palladium(II) complexes bearing mixed ligands of NHC and heteroatoms can be improved remarkably, and the reason may be that strong coordinating NHC and weak coordinating heteroatoms easily form catalytically active species with vacant coordination sites. Therefore, these NHC palladium(II) complexes bearing mixed ligands may have potential applications in organic reactions.[13]

We are interested in NHC palladium(II) complexes with mixed ligands. Herein, we report the preparation of bis-benzimidazolium salt (S)-2,2'-bis[2''-(N-picolyl-benzimidazoliumyl)ethoxy]-1,1'-binaphthyl hexafluorophosphate [(S)-LH$_2$]·(PF$_6$)$_2$, as well as the preparation and structure of N-heterocyclic carbene palladium(II) complex [(S)-LPd](PF$_6$)$_2$ (**1**). Additionally, the catalytic activity of complex **1** in three types of C-C coupling reactions (Suzuki-Miyaura, Heck-Mizoroki and Sonogashira reactions) was investigated.

Results and discussion

Synthesis and characterizations of precursor [(S)-LH$_2$]·(PF$_6$)$_2$. As shown in Scheme 1, the (S)-2,2'-dihydroxy-1,1'-binaphthyl as starting material was reacted with 2-chloroethanol to afford (S)-2,2'-di(2''-hydroxyethoxy)-1,1'-binaphthyl, followed by chlorination of hydroxyl groups with thionyl chloride to form (S)-2,2'-di(2''-chloroethoxy)-1,1'-binaphthyl, which was reacted with N-picolyl-benzimidazole in toluene to afford the bis-benzimidazolium salt [(S)-LH$_2$]·Cl$_2$, and subsequent anion exchange with ammonium hexafluorophosphate

in   methanol   was   carried   out   to   give
(S)-2,2'-bis[2''-(N-picolyl-benzimidazoliumyl)ethoxy]-1,1'-binaphthyl

hexafluorophosphate (**[(S)-LH$_2$]·(PF$_6$)$_2$**). This precursor is stable toward air and moisture, and soluble in organic solvents, such as CH$_2$Cl$_2$, CH$_3$CN and DMSO, however, the solubility is poor in water, petroleum ether and diethyl ether. In the ^{1}H NMR spectra of **[(S)-LH$_2$]·(PF$_6$)$_2$**, the proton signals (NC*H*N) of benzimidazolium appear at δ = 9.43 ppm, which is consistent with the chemical shifts of reported benzimidazolium salts.[14]
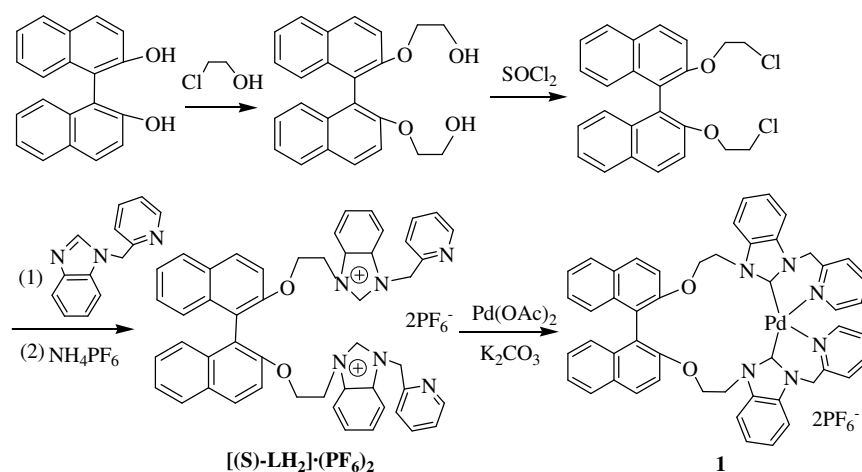
Scheme 1 Preparation of precursor **[(S)-LH$_2$]·(PF$_6$)$_2$** and complex **1**

Synthesis, characterization and structure of complex 1. As shown in Scheme 1, complex [(S)-LPd](PF$_6$)$_2$ (**1**) was prepared via the reaction of **[(S)-LH$_2$]·(PF$_6$)$_2$** with Pd(OAc)$_2$ in the presence of K$_2$CO$_3$ in acetonitrile/ethylene glycol solution. The single crystals of complex **1** suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into its solution. Complex **1** is stable to heat, air and moisture, soluble in CH$_3$CN and DMSO, but scarcely soluble in diethyl ether and hydrocarbon solvents. In the ^{1}H NMR spectra of **1**, the disappearance of the resonances for the benzimidazolium protons (NC*H*N) shows the formation of the expected metal carbene complexes, and the chemical shifts of other hydrogen atoms are similar to those of corresponding precursor. In ^{13}C NMR spectra, the signals for the carbene carbon of **1** appear at δ = 179.2 ppm, which are similar to known metal carbene complexes.[15]

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Complex **1** is formed by one tetradentate mixed ligand **(S)-L** and one Pd(II) ion, in which one 15-membered ring and two 6-membered rings are contained (Fig. 1). The Pd(II) ion is tetra-coordinated with two carbene carbon atoms and two nitrogen atoms from two pyridine rings to adopt a square-planar geometry. The bond distances of Pd-C and Pd-N are 1.966(3)-1.976(3) Å and 2.095(3)-2.098(3) Å, respectively. The bond angles of C(7)-Pd(1)-C(38) and N(1)-Pd(1)-N(6) are 96.0(1)° and 94.4(1)°, respectively. The bond angles of C-Pd-N are from 84.9(1)° to 175.0(1)°. These values are similar to those of reported NHC-Pd(II) complexes.[16] The axial chirality of complex **1** is consistent with corresponding precursor because its chiral binaphthyl unit (S configuration) was not changed during the preparation of metal complex. In this complex, two naphthalene rings form the dihedral angle of 69.2(3)°, and the dihedral angle between two benzimidazole rings is 87.2(2)°. The dihedral angle between benzimidazole ring and adjacent pyridine ring is 71.5(3)°, and the dihedral angle between two pyridine rings is 50.7(4)°. The internal ring angles (N-C-N) at the carbene centers are 107.1(3)° and 107.6(3)°, and these values are similar to those of known NHC-metal complexes.[15] Besides, the intramolecular π-π interactions between the naphthalene rings and the benzimidazole rings are observed[17] with the face-to-face distance of 3.405(4) Å and the center-to-center distance of 3.858(3) Å.

In the crystal packing of **1**, 2D supramolecular layer is formed through three types of $\pi\cdots\pi$ stacking interactions as shown in Fig. S1. In three types of $\pi\cdots\pi$ stacking interactions, one is from intermolecular pyridine rings with the face-to-face distance of 3.761(7) Å and the center-to-center distance of 3.773(2) Å, and another is from intermolecular benzimidazole rings with the face-to-face distance of 3.654(5) Å and the center-to-center distance of 3.659(3) Å, and third is from naphthalene rings and pyridine rings with the face-to-face distance of 3.534(5) Å and the center-to-center distance of 3.901(3) Å.
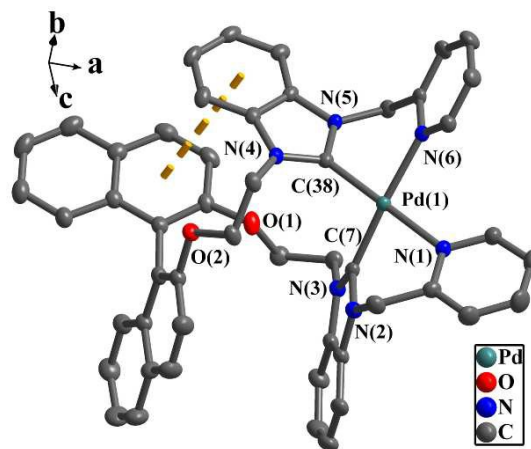
4

Fig. 1. Perspective view of **1**. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): C(38)-Pd(1) 1.966(3), C(7)-Pd(1) 1.976(3), N(6)-Pd(1) 2.095(3), N(1)-Pd(1) 2.098(3), O(1)-C(15) 1.409(4), O(2)-C(36) 1.432(4); N(4)-C(38)-N(5) 107.6(3), N(2)-C(7)-N(3) 107.1(3), C(38)-Pd(1)-C(7) 96.0(1), C(38)-Pd(1)-N(6) 84.9(1), N(1)-Pd(1)-N(6) 94.4(1), C(7)-Pd(1)-N(1) 85.2(1), C(7)-Pd(1)-N(6) 172.3(1), C(38)-Pd(1)-N(1) 175.0(1).
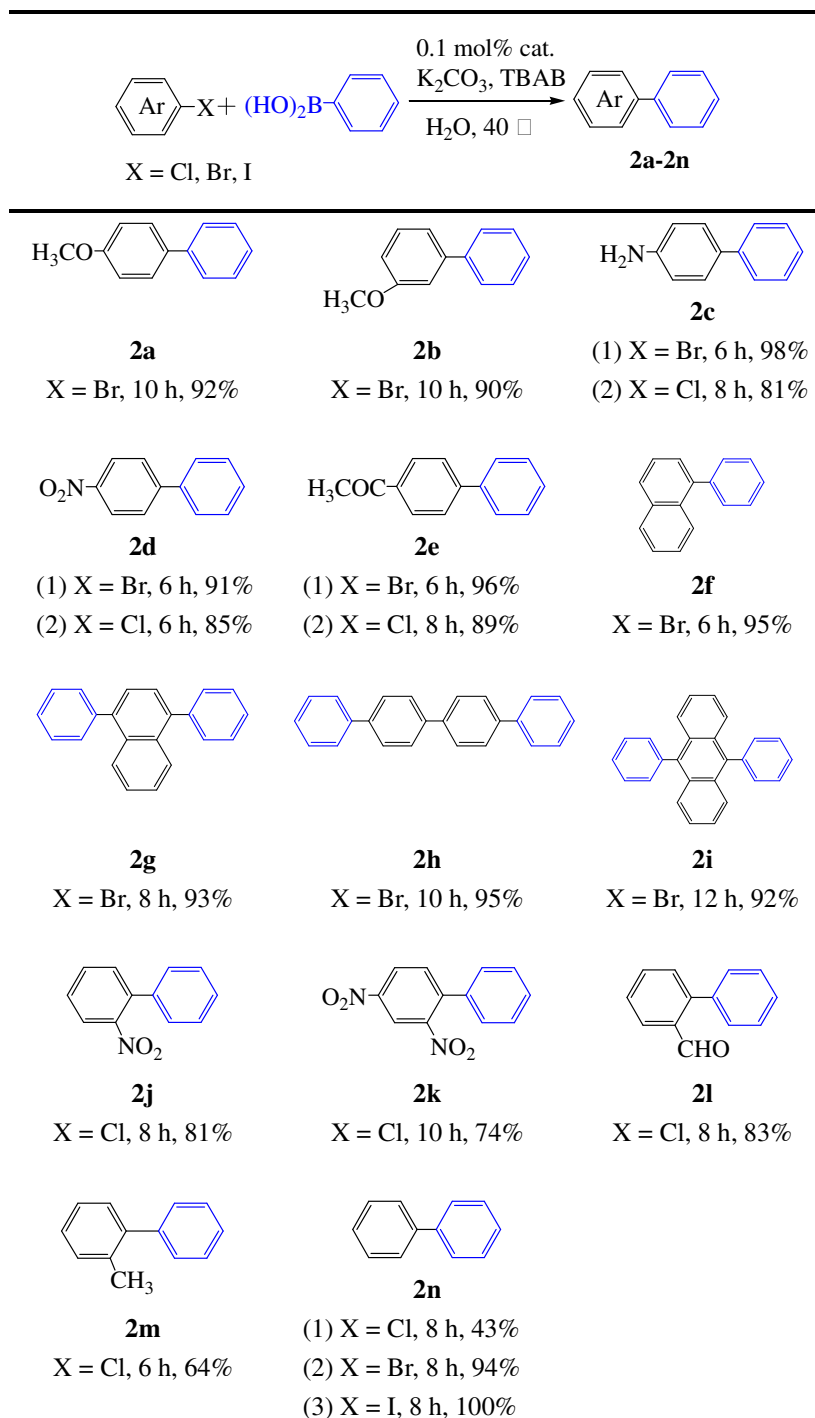
Catalytic activity of NHC-Pd(II) complex 1 in the Suzuki-Miyaura reaction. The Suzuki-Miyaura reaction, a cross-coupling process between an organoboron reagent and an aryl halide, has become a successful and useful tools for forming C-C bonds.[18] In order to examine the catalytic activity of NHC-Pd(II) complex **1** in the Suzuki-Miyaura reaction, we chose the cross-coupling reaction of 4-bromotoluene with phenylboronic acid as a model reaction in the air to test the effects of solvent and base (Table S1 in Supplementary Information). Use of K_2CO_3 as base and water as solvent gave 97% coupling yield at 40 °C over the course of 12 h in the presence of air (Table S1, Entry 1), whereas use of CH_3OH/H_2O (1:1) as solvent gave 98% yield in 6 h (Table S1, Entry 2). Use of K_2CO_3 as base and other solvents (such as MeOH, C_2H_5OH, 1,4-dioxane, THF or C_2H_5OH/H_2O (1:1)) gave yields of 7-80% (Table S1, Entries 3-7). Additionally, use of water as solvent and other common bases (such as ^tBuOK, $K_3PO_4 \cdot 3H_2O$ and NaOAc) gave yields of 52-74% (Table S1, Entries 8-10). Under conditions similar to those of entry 1 (but the time being shorten from 12 h to 6 h), 10 mol% of TBAB were added to afford 99% yield (Table S1, Entry 11). The

result indicates that the reaction could be effectively improved in the presence of TBAB. It has been known that the addition of TBAB as a co-catalyst can enhance the activity of many catalytic systems. Besides, TBAB is able to activate and stabilize palladium(0) species generated in situ, which is believed to be the real catalytically active species.[19] Based on this extensive screening, water and K_2CO_3 were found to be the efficient solvent and base in the presence of 10 mol% TBAB with a catalyst loading of 0.1 mol% of complex **1** at 40 ˚C in the air, and these conditions proved ideal. Reactions were monitored by GC at appropriate time intervals. Althouth the good yield can be also obtained using CH_3OH/H_2O (1:1) as solvent, we chose water as solvent for the purpose of environmental benignancy.

We attempted cross-coupling reactions of various aryl halides with phenylboronic acids under the optimal reaction conditions. The catalyst is highly efficient toward the coupling of aryl bromides (or aryl dibromides) with phenylboronic acid to afford excellent yields of 90-98% (Table 1, **2a**, **2b**, **2c**(1)-**2e**(1) and **2f**-**2i, 2n**(2)). The catalyst is also effective toward the coupling of aryl chlorides bearing electronic-donating or -withdrawing substituents with phenylboronic acid to give moderate to high yields of 64-89% (Table 1, **2c**(2)-**2e**(2) and **2j**-**2m**). Coupling reaction of chlorobenzene with phenylboronic acid gave relatively poor yields of 43% (Table 1, **2n**(1)). The coupling of iodobenzene with phenylboronic acid gave quantitative yield (Table 1, **2n**(3)).

In order to further study the influence of the ligand on catalysis, the control experiment was performed using 4-bromotoluene and phenylboronic acid as substrates, in which $Pd(OAc)_2$ (or $PdCl_2$) and TBAB were added in the absence of the ligand with the optimized conditions. Only 39% for $Pd(OAc)_2$ and 32% for $PdCl_2$ desired coupling product were obtained, and these values are smaller than 99% yield in the case of complex **1** as catalyst. This result highlights the preponderant catalytic role of the ligand in these aqueous and aerobic coupling reactions.

Table 1 Suzuki-Miyaura Reaction of aryl halides with phenylboronic acid catalyzed by complex **1**[a]

Reaction scheme:

Ar—X + (HO)$_2$B—〇 → Ar—〇—〇

0.1 mol% cat.
K$_2$CO$_3$, TBAB
H$_2$O, 40 □

X = Cl, Br, I   **2a-2n**

2a
X = Br, 10 h, 92%

2b
X = Br, 10 h, 90%

2c
(1) X = Br, 6 h, 98%
(2) X = Cl, 8 h, 81%

2d
(1) X = Br, 6 h, 91%
(2) X = Cl, 6 h, 85%

2e
(1) X = Br, 6 h, 96%
(2) X = Cl, 8 h, 89%

2f
X = Br, 6 h, 95%

2g
X = Br, 8 h, 93%

2h
X = Br, 10 h, 95%

2i
X = Br, 12 h, 92%

2j
X = Cl, 8 h, 81%

2k
X = Cl, 10 h, 74%

2l
X = Cl, 8 h, 83%

2m
X = Cl, 6 h, 64%

2n
(1) X = Cl, 8 h, 43%
(2) X = Br, 8 h, 94%
(3) X = I, 8 h, 100%

[a] Reaction conditions: Aryl halide (0.5 mmol), phenylboronic acid (0.6 mmol), K$_2$CO$_3$ (1.2 mmol), complex **1** (0.1 mol %), TBAB (10 mol %), H$_2$O (6 mL) at 40 ˚C in the air.

[b] Reactions were monitored by TLC.

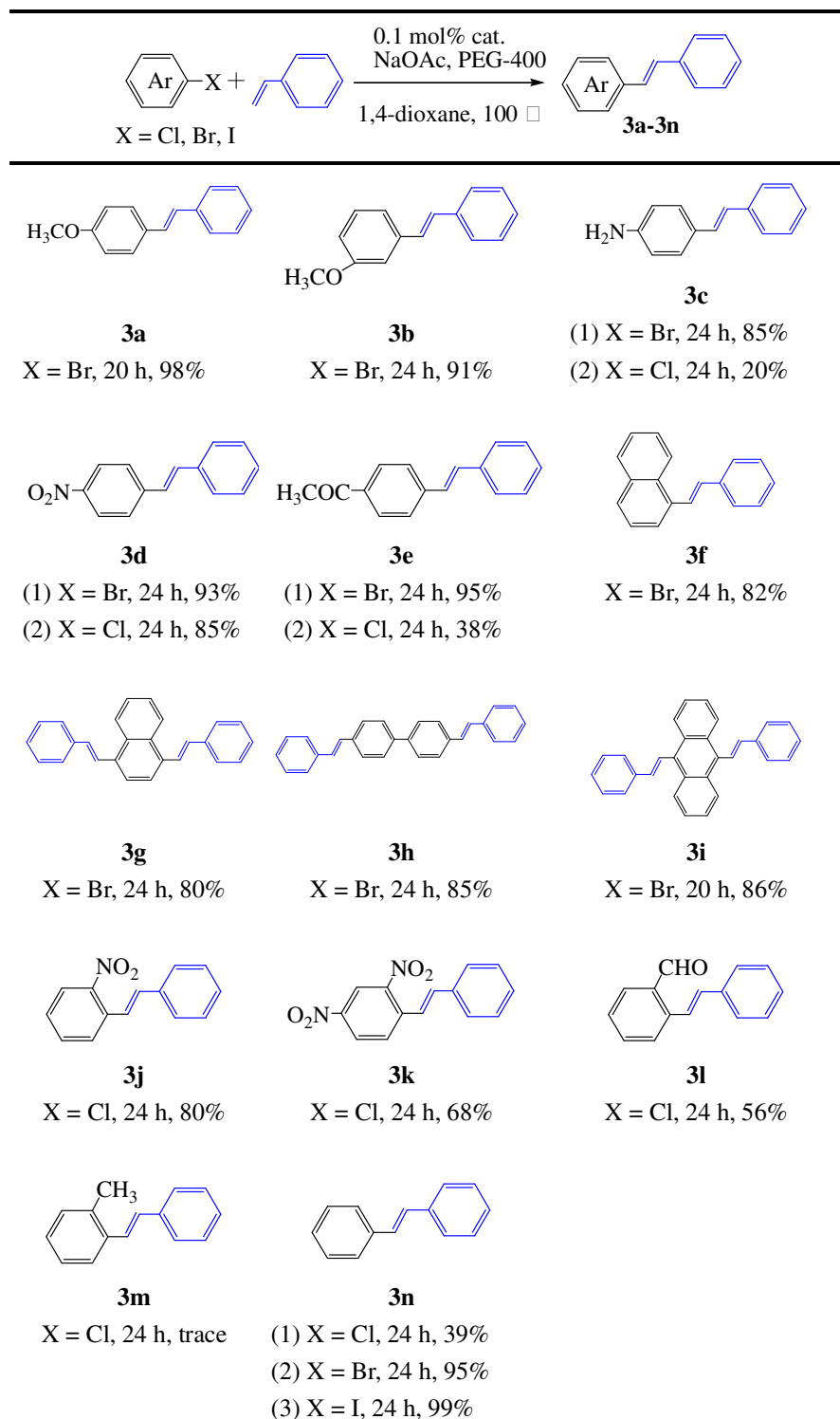[c] Isolated yield using aryl halide as a standard.

The above results show that complex **1** has high stability to both air and water, while also demonstrating excellent tolerance of various functional groups. Additionally, complex **1** can resolve partly in aqueous medium due to the existence of hydrophilic groups (such as oxygen atom and nitrogen atom). These qualities make **1** a valuable precatalyst for thermally sensitive substrates. This provides an effective phosphine-free catalyst system for facile coupling of aryl halides with aryl boronic acids in water under mild and aerobic conditions. These favorable reaction conditions of Suzuki-Miyaura reaction are important toward ensuring environmental responsibility while also reducing costs for fine chemical and pharmaceutical industries.

Catalytic activity of NHC-Pd(II) complex 1 in the Heck-Mizoroki reaction. The Heck reaction has evolved significantly from its original mode as the arylation of olefins with aryl iodides, and it is a powerful tool for the coupling of less reactive bromides, chlorides and pseudo-halides such as triflates, tosylates, mesylates, and aryl diazonium salts.[20] We chose bromobenzene and styrene as the coupling partners to test the solvent and base effects in the air (Table S2). Using 1,4-dioxane as solvent and NaOAc as base gave 92% coupling yields at 120 ˚C over the course of 24 h in the presence of air (Table S2, Entry 1), whereas using other bases (such as K_2CO_3, $K_3PO_4 \cdot 3H_2O$, Et_3N, ^tBuOK, KOH, $NaHCO_3$ and Cs_2CO_3) gave the yields of 15-83% (Table S2, Entries 2-8). Using NaOAc as base and other solvents (such as H_2O, DMF, CH_3CN, THF, DME or DMSO) gave the yields from trace to 61% (Table S2, Entries 9-15). Under conditions similar to those of entry 1 (but temperature being dropped from 120 ˚C to 100 ˚C), 10 mol% of PEG-400 was added to give coupling yields of 95% (Table S2, Entry 16). This result shows that the reaction could be dramatically improved in the presence of PEG-400. It has been known that the addition of PEG-400 as a co-catalyst can enhance the activity of many catalytic systems.[21] Based on this extensive screening, 1,4-dioxane and NaOAc were found to be the efficient solvent and base in the presence of 10 mol% of PEG-400 as co-catalyst with a catalyst

loading of 0.1 mol% of complex **1** at 100 ˚C in the air, thus giving the optimal coupling result.

We attempted cross-coupling reactions of various aryl halides with styrene under the optimal reaction conditions. The cross-coupling of various aryl bromides with styrene gave good to excellent yields of 80-98% (Table 2，**3a**, **3b**, **3c**(1)-**3e**(1) and **3f**-**3i**). The coupling of 4-chloronitrobenzene or 2-chloronitrobenzene with styrene gave good yields of 85% or 80%, respectively (Table 2, **3d**(2) and **3j**). The coupling of 4-chloroaniline, 4-chloroacetophenone, 2,4-dinitrochlorobenzene, 2-chlorobenzaldehyde or chlorobenzene with styrene gave relatively poor yields of 20-56% (Table 2, **3c**(2), **3e**(2), **3k**, **3l** and **3n**(1)). And 2-chlorotoluene even gave trace coupling yield (Table 3: **3m**). The catalyst is highly efficient in the coupling of iodobenzene with styrene to give almost quantitative yield (Table 2, **3n**(3)). Notably, there is high selectivity for the *trans* product in this reaction system. Hardly any *cis* products could be detected after the reaction. The *trans* isomer appears to be the dominant conformation assumed during the course of these reactions.

Considering all these facts, complex **1** is an effective catalyst for Heck-Mizoroki reaction. In order to further study the influence of the ligand on catalysis, the control experiment was performed using bromobenzene and styrene as substrates, in which Pd(OAc)$_2$ (or PdCl$_2$) and PEG-400 were added in the absence of the ligand with the optimized conditions. Only 26% for Pd(OAc)$_2$ and 21% for PdCl$_2$ coupling product were obtained, and these values are smaller than 95% yield in the case of complex **1** as catalyst. This result highlights the preponderant catalytic role of the ligand in the coupling reactions.

Table 2 Heck-Mizoroki reaction of aryl halides with styrene catalyzed by complex **1**[a]

X = Cl, Br, I

0.1 mol% cat.
NaOAc, PEG-400

1,4-dioxane, 100 □

3a-3n

3a
X = Br, 20 h, 98%

3b
X = Br, 24 h, 91%

3c
(1) X = Br, 24 h, 85%
(2) X = Cl, 24 h, 20%

3d
(1) X = Br, 24 h, 93%
(2) X = Cl, 24 h, 85%

3e
(1) X = Br, 24 h, 95%
(2) X = Cl, 24 h, 38%

3f
X = Br, 24 h, 82%

3g
X = Br, 24 h, 80%

3h
X = Br, 24 h, 85%

3i
X = Br, 20 h, 86%

3j
X = Cl, 24 h, 80%

3k
X = Cl, 24 h, 68%

3l
X = Cl, 24 h, 56%

3m
X = Cl, 24 h, trace

3n
(1) X = Cl, 24 h, 39%
(2) X = Br, 24 h, 95%
(3) X = I, 24 h, 99%

[a] Reaction conditions: aryl halide (0.5 mmol), styrene (0.6 mmol), K_2CO_3 (1.2 mmol), complex **1** (0.1 mol%), PEG-400 (10 mol%), 1,4-dioxane (6 mL), 100 °C in air.
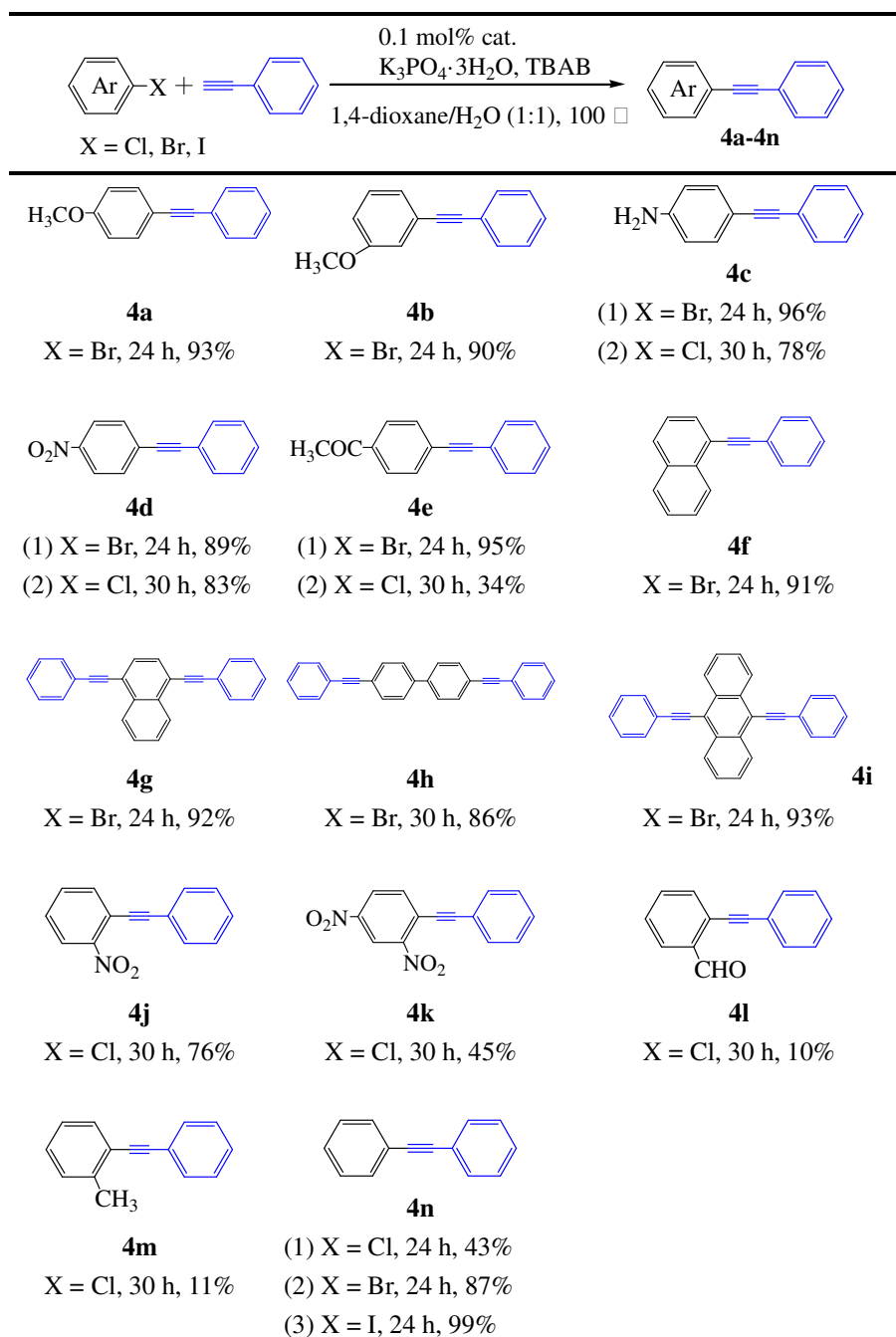
[b] Monitored by TLC.

[c] Isolated yield using aryl halide as a standard.

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Catalytic activity of NHC-Pd(II) complex 1 in the Sonogashira reaction. In order

to prove that complex **1** would be a good precatalyst for the Sonogashira reaction, we

chose the cross-coupling reaction of 4-bromoanisole with phenylacetylene as a model

reaction to test the solvent, base and catalyst activity in the air.[22] As illustrated in

Table S3, using $K_3PO_4 \cdot 3H_2O$ as base and 1,4-dioxane/H_2O (1:1) as solvent gave 79%

yield at 100 ˚C over the course of 24 h in the presence of air (Table S3, entry 1). In the

same conditions, when 10 mol% of TBAB was added, the yield rose to 93% (Table S3,

entry 2). Using Cs_2CO_3 as base and other solvents (such as 1,4-dioxane, DMF, DMSO,

CH_3CN, H_2O, THF, DMF/H_2O (1:1) or 1,4-dioxane/H_2O (1:1)) gave yields from trace

to 69% (Table S3, Entries 3-10). Using 1,4-dioxane/H_2O (1:1) as solvent in the

presence of 10 mol% of PPh_3 or TBAB, the different bases (such as K_2CO_3, KOH,

NaOAc, Et_3N or $NaHCO_3$) were investigated to give the yields of 70-91% (Table S3,

Entries 11-17). Based on this extensive screening, 1,4-dioxane/H_2O (1:1) and

$K_3PO_4 \cdot 3H_2O$ were proved to be the efficient solvent and base in the presence of 10

mol% of TBAB with a catalyst loading of 0.1 mol% of complex **1**, thus giving the

optimal coupling result.

We attempted the cross-coupling reactions of various aryl halides with

phenylacetylene under the optimized conditions. Various aryl bromides could be

easily coupled to phenylacetylene to give the good to excellent yields of 86-96%

(Table 3, **4a**, **4b**, **4c**(1)-**4e**(1), **4f**-**4i** and **4n**(2)). Coupling reactions of 4-chloroaniline,

4-chloronitrobenzene or 2-chloronitrobenzene with phenylacetylene gave good yields

of 76-83% (Table 3, **4c**(2), **4d**(2) and **4j**). While the couplings of

4-chloroacetophenone, 2,4-dinitrochlorobenzene, 2-chlorobenzaldehyde,

2-chlorotoluene or chlorobenzene with phenylboronic acid gave poor yields of

10-45% (Table 3, **4e**(2), **4k**-**4m** and **4n**(1)). The catalyst was highly efficient in the

coupling of iodobenzene with phenylacetylene to give almost quantitative yield (Table

3, **4n**(3)). The above results show complex **1** is an effective precatalyst for

Sonogashira reaction. Additionally, a control experiment was also performed using

4-bromoanisole with phenylacetylene as substrates, in which $Pd(OAc)_2$ (or $PdCl_2$) and

TBAB were added without the ligand with the optimized conditions. Only 31% for

Pd(OAc)$_2$ and 29% for PdCl$_2$ coupling product were obtained, and these values are smaller than 93% yield in the case of complex **1** as catalyst. This result highlights the preponderant catalytic role in the coupling reaction.

Table 3 Sonogashira reaction of aryl halides with phenylacetylene catalyzed by complex **1**[a]

Ar—X + ≡—⟨⟩
0.1 mol% cat.
K$_3$PO$_4$·3H$_2$O, TBAB
1,4-dioxane/H$_2$O (1:1), 100 □
→ Ar—≡—⟨⟩
4a-4n

X = Cl, Br, I

4a
X = Br, 24 h, 93%

4b
X = Br, 24 h, 90%

4c
(1) X = Br, 24 h, 96%
(2) X = Cl, 30 h, 78%

4d
(1) X = Br, 24 h, 89%
(2) X = Cl, 30 h, 83%

4e
(1) X = Br, 24 h, 95%
(2) X = Cl, 30 h, 34%

4f
X = Br, 24 h, 91%

4g
X = Br, 24 h, 92%

4h
X = Br, 30 h, 86%

4i
X = Br, 24 h, 93%

4j
X = Cl, 30 h, 76%

4k
X = Cl, 30 h, 45%

4l
X = Cl, 30 h, 10%

4m
X = Cl, 30 h, 11%

4n
(1) X = Cl, 24 h, 43%
(2) X = Br, 24 h, 87%
(3) X = I, 24 h, 99%

[a] Reaction conditions: aryl halide (0.5 mmol), phenylacetylene (0.6 mmol), base (1.2 mmol),

complex **1** (0.1 mol%), TBAB (10 mol%), 1,4-dioxane/H_2O (6 mL), 100 °C in air.

[b] Monitored by TLC.

[c] Isolated yield using aryl halide as a standard.

It is noteworthy that the good catalytic activity of NHC-Pd(II) complex **1** can be ascribed to the strong donating ability of NHC and the weak coordination of nitrogen. The weak coordinating abilities of nitrogen atoms allow them to readily dissociate from metal centers thus creating catalytically active species with vacant coordination sites. The strong Pd-C bond presumably facilitates oxidative addition of aryl halogens to the metal. The dynamic dissociation and association of nitrogen atoms allows the approach of substrate to the metal center, and the substituents on the benzimidazole rings favor stabilization of the active metal species after reductive elimination of the products.

Additionally, the reaction conditions (catalyst loading, temperature, solvents and bases) between the present paper and literatures are compared as shown in Table S4. The catalyst loading of complex **1** is all 0.1% in three types of C-C coupling reactions, which is same as the most case of reported data in Suzuki-Miyaura[22(b), 23] and Heck-Mizoroki reactions,[22(b), 23(k), 23(l), 24] whereas this value is smaller than reported data (1-4%) in Sonogashira reaction.[22, 23m, 25] The reaction temperature for these reactions in the present paper is in the middle of reported data (in three types of C-C coupling reactions: 40 °C, 100 °C and 100 °C, respectively, in the present paper; 25-140 °C, 80-150 °C and 80-120 °C, respectively, in literatures). In the present paper, pure water, organic solvent and water/organic solvent are used, respectively, in three types of C-C coupling reactions, and the similar cases can be also found in reported results. In the use of bases, we selected inexpensive K_2CO_3, NaOAc and $K_3PO_4 \cdot 3H_2O$, respectively, in three types of C-C coupling reactions, and the similar bases are also used in literatures.

On the whole, the results obtained using tetradentate Pd(II) complex **1** as catalyst in most Suzuki-Miyaura, Heck-Mizoroki and Sonogashira reactions are similar to or slightly better than those of related NHC Pd(II) complexes. By the analysis and comparison of complex **1** with other NHC metallic catalysts published,[26-28] we can

know that the catalytic activity of a catalyst is related to a number of factors such as the steric hindrance and electronic effects of different substituents around Pd, as well as the stability and solubility of complexes. Besides, the reaction conditions are also unneglected factors.

Conclusion

In summary, bis-benzimidazolium salt **[(S)-LH$_2$]·(PF$_6$)$_2$** and its NHC palladium(II) complex **1** have been prepared and characterized. In the crystal structure of complex **1**, one 15-membered ring and two 6-membered rings are contained. Additionally, the catalytic activity of the complex **1** in three types of C-C coupling reactions (Suzuki-Miyaura, Heck-Mizoroki and Sonogashira reactions) was studied. The results show that complex **1** can smoothly catalyze most Suzuki-Miyaura reactions of various aryl halides (iodide, bromide and chloride) with arylboronic acids using water as solvent and K$_2$CO$_3$ as base in the air at 40 ˚C to afford moderate to high yields. Likewise, most Heck-Mizoroki or Sonogashira reactions can also be performed efficiently at 100 ˚C in the air.

Compared with reported NHC Pd(II) complexes, complex **1** shows similar or slightly better catalytic activity in these coupling reactions. Complex **1** may be a valuable precatalyst for the preparation of diaryl derivatives, styrene derivatives or phenylacetylene derivatives. Further studies of new organometallic complexes from precursor **[(S)-LH$_2$]·(PF$_6$)$_2$** as well as analogous ligands are underway.

Experimental section

General procedures. N-Picolyl-benzimidazole was prepared according to the literature method.[29] All the reagents for synthesis and analyses were of analytical grade and used without further purification. Melting points were determined on an Digital Vision MP Instrument. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. Chemical shifts, δ, are reported in ppm relative to the internal standard TMS for both ^{1}H and ^{13}C NMR. *J* values are given in Hz. The elemental analyses of all compounds were obtained from the powder compounds

recrystallised. GC analyses were carried out with a capillary column (CB*P*ī or CBP-5, 0.25 mm i.d × 40 m).

Preparation of (S)-2,2'-di(2''-hydroxyethoxy)-1,1'-binaphthyl. A DMF (100 mL) suspension of (S)-2,2'-dihydroxy-1,1'-binaphthyl (5.000 g, 17.4 mmol) and potassium carbonate (9.646 g, 69.9 mmol) was stirred for 1 h at 50 °C. Then 2-chloroethanol (5.628 g, 69.9 mmol) was added dropwise, and stirred continually for 24 h under refluxing. The solvent was removed under vacuum, and 500 mL water was added. The solution was extracted with CH_2Cl_2 (3 × 30 mL) and the extracting solution was dried over anhydrous $MgSO_4$. After removing CH_2Cl_2, a pale yellow oil was obtained, and the crude product was recrystallized with MeOH to give (S)-2,2'-di(2''-hydroxyethoxy)-1,1'-binaphthyl as a white powder. Yield: 6.008 g (92%). M.p.: 112-114 °C. Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.98; H, 5.92%. Found: C, 76.63; H, 5.88%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.8 Hz, 2H, Ar*H*), 7.93 (d, J = 8.0 Hz, 2H, Ar*H*), 7.48 (d, J = 9.2 Hz, 2H, Ar*H*), 7.41 (t, J = 7.4 Hz, 2H, Ar*H*), 7.30 (t, J = 7.4 Hz, 2H, Ar*H*), 7.17 (d, J = 8.4 Hz, 2H, Ar*H*), 4.28 (m, 2H, C*H*$_2$), 4.08 (m, 2H, C*H*$_2$), 3.66 (m, 4H, C*H*$_2$), 2.31 (s, 2H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5 (Ph*C*), 133.8 (Ph*C*), 129.8 (Ph*C*), 129.6 (Ph*C*), 128.1 (Ph*C*), 126.7 (Ph*C*), 125.2 (Ph*C*), 124.2 (Ph*C*), 120.3 (Ph*C*), 115.9 (Ph*C*), 71.7 (O*C*H$_2$CH$_2$), 61.2 (OCH$_2$*C*H$_2$).

Preparation of (S)-2,2'-di(2''-chloroethoxy)-1,1'-binaphthyl. To a chloroform (100 mL) solution of (S)-2,2'-di(2''-hydroxyethoxy)-1,1'-binaphthyl (5.000 g, 13.4 mmol) and pyridine (5.288 g, 66.8 mmol), thionyl chloride (7.947 g, 66.8 mmol) was added dropwise at room temperature within 1 h. Then the solution was stirred continually for 12 h at 70 °C. The mixture was cooled and washed with water (3 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$. After removing chloroform, (S)-2,2'-di(2''-chloroethoxy)-1,1'-binaphthyl was obtained as a pale yellow powder. Yield: 3.571 g (65%). M.p.: 101-103 °C. Anal. Calcd for $C_{24}H_{20}O_2Cl_2$: C, 70.08; H, 4.90%. Found: C, 70.37; H, 5.14%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.8 Hz, 2H, Ar*H*), 7.88 (d, J = 8.4 Hz, 2H, Ar*H*), 7.43 (d, J = 8.8 Hz, 2H, Ar*H*), 7.37 (t, J =

7.4 Hz, 2H, Ar*H*), 7.25 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.13 (d, *J* = 8.4 Hz, 2H, Ar*H*), 4.22(m, 4H, C*H*$_2$), 3.40 (m, 4H, C*H*$_2$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 153.6 (Ph*C*), 147.9 (Ph*C*), 134.0 (Ph*C*), 129.6 (Ph*C*), 127.9 (Ph*C*), 126.5 (Ph*C*), 125.4 (Ph*C*), 124.1 (Ph*C*), 121.0 (Ph*C*), 116.3 (Ph*C*), 70.1 (O*C*H$_2$CH$_2$), 41.7 (OCH$_2$*C*H$_2$).

Preparation of [(S)-LH$_2$]·(PF$_6$)$_2$. A toluene (35 mL) solution of N-picolyl-benzimidazole (1.274 g, 6.1 mmol) and (S)-2,2'-di(2''-chloroethoxy)-1,1'-binaphthyl (1.000 g, 2.4 mmol) was stirred for 7 days under refluxing, and a brown oil of (S)-2,2'-bis[2''-(N-picolyl-benzimidazoliumyl)ethoxy]-1,1'-binaphthyl chloride was obtained after the solvent was removed via a rotary evaporator. Then NH$_4$PF$_6$ (0.938 g, 5.7 mmol) was added to a methanol solution (100 ml) of (S)-2,2'-bis[2''-(N-picolyl-benzimidazoliumyl)ethoxy]-1,1'-binaphthyl chloride (2.016 g, 2.4 mmol) with stirring for 3 days, and a white precipitate was formed. The precipitate was collected by filtration and washed with a small portion of methanol to give **[(S)-LH$_2$]·(PF$_6$)$_2$**. Yield: 1.734 g (68%). M.p.: 148-150 $^{\circ}$C. Anal. Calcd for C$_{50}$H$_{42}$F$_{12}$N$_6$O$_2$P$_2$: C, 57.25; H, 4.03; N, 8.01%. Found: C, 57.62; H, 4.41; N, 8.35%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.43 (s, 2H, 2-bimi*H*), 8.43 (d, *J* = 4.4 Hz, 2H, Ar*H*), 7.98 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.90 (q, *J* = 2.6 Hz, 4H, Ar*H*), 7.77 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.63 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.50 (t, *J* = 7.8 Hz, 2H, Ar*H*), 7.43 (d, *J* = 9.6 Hz, 2H, Ar*H*), 7.37 (q, *J* = 4.0 Hz, 2H, Ar*H*), 7.28 (t, *J* = 8.4 Hz, 4H, Ar*H*), 7.21 (t, *J* = 7.8 Hz, 2H, Ar*H*), 6.99 (m, *J* = 5.0 Hz, 2H, Ar*H*), 6.58 (d, *J* = 8.4 Hz, 2H, Ar*H*), 5.68 (m, 3H, C*H*$_2$), 4,63 (t, *J* = 4.6 Hz, 3H, C*H*$_2$), 4.38 (t, *J* = 4.4 Hz, 3H, C*H*$_2$), 4.15 (q, *J* = 5.2 Hz, 3H, C*H*$_2$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.1 (Ar*C*), 149.9 (Ar*C*), 142.9 (Ar*C*), 138.0 (Ar*C*), 132.9 (bimi-N*C*N), 131.1 (Ar*C*), 130.9 (Ar*C*), 130.0 (Ar*C*), 129.3 (Ar*C*), 128.4 (Ar*C*), 126.8 (Ar*C*), 126.7 (Ar*C*), 126.6 (Ar*C*), 126.4 (Ar*C*), 125.5 (Ar*C*), 125.0 (Ar*C*), 124.2 (Ar*C*), 123.2 (Ar*C*), 119.6 (Ar*C*), 116.3 (Ar*C*), 114.0 (Ar*C*), 113.0 (Ar*C*), 67.8 (O*C*H$_2$CH$_2$), 51.2 (OCH$_2$*C*H$_2$), 49.0 (*C*H$_2$), 47.2 (*C*H$_2$) (bimi = benzimidazole).

Prepartion of [(S)-LPd](PF$_6$)$_2$ (1). An acetonitrile/ethylene glycol (20 mL, v:v = 1:1) suspension of K$_2$CO$_3$ (0.179 g, 1.3 mmol), **[(S)-LH$_2$]·(PF$_6$)$_2$** (0.209 g, 0.2 mmol) and Pd(OAc)$_2$ (0.042 g, 0.2 mmol) was stirred for 24 h under 60 °C. The resulting solution was filtered and concentrated to 10 mL, and Et$_2$O (5 mL) was added to precipitate **1** as a yellow powder. Yield: 0.057 g (25%). M.p.: 280-282 °C. Anal. Calcd for C$_{50}$H$_{40}$F$_{12}$N$_6$O$_2$P$_2$Pd: C, 52.07; H, 3.49; N, 7.29%. Found: C, 52.34; H, 3.63; N, 7.52%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.24 (m, 7H, PhH), 7.98 (m, 4H, PhH), 7.80 (d, J = 8.4 Hz, 2H, PhH), 7.65 (t, J = 6.6 Hz, 2H, PhH), 7.44 (m, 7H, PhH), 4.90 (m, 2H, CH_2), 4.52 (m, 2H, CH_2), 4.24 (m, 2H, CH_2), 2.89 (s, 3H, CH_2), 2.73 (s, 3H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 179.2 (bimi-NCN), 154.5 (PhC), 153.8 (PhC), 153.2 (PhC), 147.5 (PhC), 135.2 (PhC), 133.6 (PhC), 133.0 (PhC), 129.6 (PhC), 129.5 (PhC), 126.6 (PhC), 126.4 (PhC), 125.8 (PhC), 125.2 (PhC), 124.7 (PhC), 124.6 (CH$_3$), 112.4 (PhC), 111.7 (PhC), 68.9 (CH$_2$), 63.3 (CH$_2$), 62.9 (CH$_2$).

General procedure for the Suzuki-Miyaura reaction. In a typical reaction, aryl halide (0.5 mmol), arylboronic acid (0.6 mmol), base (1.2 mmol), NHC-Pd(II) complex **1** (0.1 mol%) and TBAB (10 mol%) in solvent (6 mL) were stirred at 40 °C in air. After the desired reaction time, the reaction was stopped, and water (20 mL) was added to the reaction mixture. The mixture was extracted by n-hexane (10 mL × 3), and the organic layer was washed with water (10 mL × 3) and dried over anhydrous MgSO$_4$. For the determination of GC-MS yields, the above solution was filtered through a thin pad of silica gel (elution with CH$_2$Cl$_2$ (100 mL)) and concentrated to 5 mL. n-Tridecane (92 mg) was added as internal standard. The isolated products were purified by column chromatography on silica gel using a mixture of n-hexane and dichloromethane (from pure n-hexane to n-hexane/dichloromethane = 10/1) as eluant. The isolated yields were determined using aryl halides as standards.

General procedure for the Heck-Mizoroki reaction. A mixture of aryl halide (0.5 mmol), styrene (0.6 mmol), base (1.2 mmol), complex **1** (0.1 mol%) and PEG-400 (10

mol%) in solvent (6 mL) was stirred at 100 ˚C or 120 ˚C in air. After the desired reaction time, the reaction was stopped, and water (20 mL) was added to the reaction mixture. The mixture was extracted by ethyl ether (10 mL × 3), and the organic layer was washed with water (10 mL × 3) and dried over anhydrous $MgSO_4$. Then the solution was filtered and concentrated to about 2 mL. The isolated products were purified by column chromatography on silica gel using a mixture of n-hexane and dichloromethane (from pure n-hexane to n-hexane/dichloromethane = 10/1) as eluant. The isolated yields were determined using aryl halides as standards.

General procedure for the Sonogashira reaction. A mixture of aryl halide (0.5 mmol), phenylacetylene (0.6 mmol), base (1.2 mmol), complex **1** (0.1 mol%) and TBAB (10 mol%) in solvent (6 mL) was stirred at 100 ˚C in air. After the desired reaction time, the reaction was stopped, and water (20 mL) was added to the reaction mixture. The mixture was extracted by diethyl ether (10 mL × 3), and the organic layer was washed with water (10 mL × 3) and dried over anhydrous $MgSO_4$. Then the solution was filtered and concentrated to about 2 mL. The isolated products were purified by column chromatography on silica gel using a mixture of n-hexane and dichloromethane (from pure n-hexane to n-hexane/dichloromethane = 10/1) as eluant. The isolated yields were determined using aryl halides as standards

X-ray data collection and structure determinations. X-ray single-crystal diffraction data for complexs were collected by using a Bruker Apex II CCD diffractometer at 173(2) K for **1** with Mo-Ka radiation (λ = 0.71073 Å) by ω scan mode. There was no evidence of crystal decay during data collection in all cases. Semiempirical absorption corrections were applied by using SADABS and the program SAINT was used for integration of the diffraction profiles.[30] All structures were solved by direct methods by using the SHELXS program of the SHELXTL package and refined with SHELXL[31] by the full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2. Hydrogen atoms bonded to C atoms were placed geometrically and presumably solvent H atoms were

first located in difference Fourier maps and then fixed in the calculated sites. Further details for crystallographic data and structural analysis are listed in Table 4. Figures were generated by using Crystal-Maker.[32]

Table 4 Summary of crystallographic data complex **1**

$1 \cdot 0.5C_2H_6O_2$			
Chemical formula	$C_{50}H_{40}F_{12}N_6O_2P_2Pd$ $\cdot 0.5C_2H_6O_2$	$F(000)$	1198
Formula weight	1184.25	Cryst size, mm	$0.18 \times 0.17 \times 0.15$
Cryst syst	Triclinic	$\theta_{min}, \theta_{max}$, deg	1.36, 25.01
Space group	$P\bar{1}$	T, K	173(2)
a, Å	12.526(1)	No. of data collected	12770
b, Å	14.488(1)	No. of unique data	8625
c, Å	15.330(1)	No. of refined params	677
α, deg	98.5(1)	Goodness-of-fit on $F^{2\ a}$	1.016
β, deg	95.0(1)	Final R indices[b] $[I > 2\sigma(I)]$	
γ, deg	115.0(1)	R_1	0.0397
V, Å^3	2456.2(3)	wR_2	0.1012
Z	2	R indices (all data)	
D_{calcd}, Mg m^{-3}	1.601	R_1	0.0469
Abs coeff, mm^{-1}	0.540	wR_2	0.1077

$^aGOF = [\Sigma w(F_o^2 - F_c^2)^2/(n\text{-}p)]^{1/2}$, where n is the number of reflection and p is the number of parameters refined. $^bR_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

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Supplementary information

Tables and figures for complex **1**, and ^{1}H NMR and ^{13}C NMR spectra for precursor, complex and all coupling products in Suzuki-Miyaura, Heck-Mizoroki and Sonogashira reactions. CCDC 1023636 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via

http//www.ccdc.cam.ac.uk/conts/retrieving.html,   or   from   the   Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44)

1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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A table of contents entry:

NHC-Pd(II) complex **1** has been prepared. The catalytic activity of **1** in C-C coupling reactions was studied.
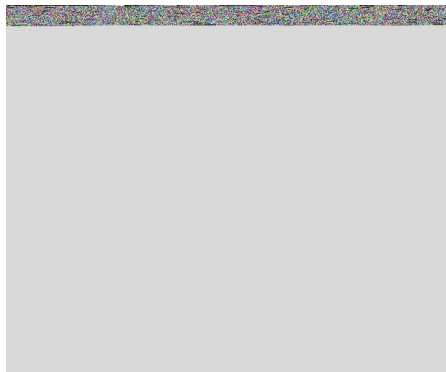
Software of Graphics:

Scheme 1: Chem Draw 8.0

Fig. 1: Diamand 3.0