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## Journal of Organometallic Chemistry



# Trinuclear copper(I) complex of 1,3-bis(2-pyridinylmethyl)imidazolylidene as a carbene-transfer reagent for the preparation of catalytically active nickel(II) and palladium(II) complexes

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#### ARTICLE INFO

Article history: Received 10 July 2011 Received in revised form 11 September 2011 Accepted 13 September 2011

Keywords: N-heterocyclic carbene Copper Nickel Palladium C-C coupling

## ABSTRACT

Reactions of 1,3-bis(pyridin-2-ylmethyl)-1H-imidazol-3-ium hexafluorophosphate, ([HL1](PF<sub>6</sub>), L1 = 1,3-bis(pyridin-2-ylmethyl)imidazolylidene) and 1,3-bis(pyridin-2-ylmethyl)-1H-benzimidazol-3-ium hexafluorophosphate ([HL2](PF<sub>6</sub>), L2 = 1,3-bis(pyridin-2-ylmethyl)benzoimidazolylidene) with cuprous oxide in acetonitrile readily yielded trinuclear complexes  $[Cu_3(L1)_3(PF_6)_3]$  (1) and  $[Cu_3(L2)_3(PF_6)_3]$  (2). Treatment of 1 with Ni(PPh\_3)\_2Cl\_2 and Pd(cod)Cl\_2 gave [Ni(L1)Cl](PF<sub>6</sub>) (3) and [Pd(L1)Cl](PF<sub>6</sub>) (4), respectively, due to transmetalation. [Ni(L1)\_2](PF<sub>6</sub>)\_2 (5) was obtained from the reaction of  $[Cu_3(L1)_3(PF_6)_3]$  and Raney nickel in acetonitrile. All these complexes have been fully characterized. Both 1 and 2 consist of a triangular Cu<sub>3</sub> core with each Cu–Cu bond capped by an imidazolylidene group. Each imidazolylidene acts as a bridging ligand in a  $\mu_2$  mode and is bonded equally to two Cu(1) ions. The pincer nickel and palladium complexes are square-planar and contain a tridentate NCN ligand. Complexes **3** and **4** are efficient catalyst precursors for Kumada–Corriu and Suzuki–Miyaura coupling reactions of aryl halides with organometallic reagents.

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## 1. Introduction

N-Heterocyclic carbenes (NHCs) have become one of the most important class ligands in homogeneous catalysis and organometallic chemistry due to their strong  $\sigma$ -donors properties and ease of preparation in recent decades [1,2]. Transition metal complexes of NHCs are normally stable to air, moisture, and heat that are suitable catalyst precursors. Therefore, a large number of nickel [3-7] and palladium [8-12] complexes of NHC ligands have been prepared and structurally characterized. A pincer ligand with one or more NHC carbene donors combining the advantages of NHC ligands to facilitate oxidative addition of substrates to metals would be a good choice for the development of robust catalysts in organic synthesis. Metal pincer complexes involving tridentate C^N^C [13–18], C^C^C [19-23], N^C^N [24-27], and P^C^P [28-30] ligands containing at least one NHC carbene donor have been recently reported. These complexes show their enhanced catalytic activity in many organic reactions especially in C–C coupling reactions [16,20,25,28]. Pincer complexes of transition metals such as iridium [31], rhodium [32], ruthenium [33,34], and osmium [35] have found applications in

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olefin metathesis, hydrogen transfer, hydrosilylation, hydroformylation and polymerization reactions.

Our interest in this area involves the design and synthesis of transition metal complexes bearing multidentate NHC ligands because such mixed C^N ligand would allow a further fine-tuning of the metal coordination and catalysis [36–40]. We have reported that mono- or dinuclear nickel complexes containing functionalized NHC ligands showed enhancement of catalytic activities in homogeneous catalysis [41,42]. Here in this paper, we report the synthesis and structural characterization of trinuclear copper(I) complexes,  $[Cu_3(L)_3](PF_6)_3$  (L = 1,3-bis(pyridin-2-ylmethyl)imidazolylidene and 1,3-bis(pyridin-2-ylmethyl)benzimidazolylidene) and pincer  $[M(L1)Cl](PF_6)$  (M = Ni and Pd) complexes. The catalytic applications of nickel(II) and palladium(II) complexes in Kumada–Corriu coupling and Suzuki–Miyaura Coupling reactions were also studied.

## 2. Results and discussion

## 2.1. Synthesis and structural characterization of $[Cu_3(L)_3](PF_6)_3$

The imidazolium salts, 1,3-bis(pyridin-2-ylmethyl)imidazolium hexafluorophosphate ([HL1](PF<sub>6</sub>)) and 1,3-bis(pyridin-2-ylmethyl)



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<sup>0022-328</sup>X/\$ – see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2011.09.008

benzimidazolium hexafluorophosphate ([HL2](PF<sub>6</sub>)) were prepared according to the known procedures [43,44]. As shown in Scheme 1, reactions of [HL1](PF<sub>6</sub>) and [HL2](PF<sub>6</sub>) with cuprous oxide in acetonitrile led to the isolation of  $[Cu_3(L1)_3](PF_6)_3$  (1) and  $[Cu_3(L2)_3](PF_6)_3$  (2) as colorless solids in high yields. The formulation of **1** and **2** was determined by elemental analysis and further confirmed by NMR measurements. In their <sup>1</sup>H NMR spectra, the absence of acidic CH proton resonances illustrates the formation of Cu–C bonds. The <sup>13</sup>C NMR spectra of **1** and **2** exhibit resonance signals at 169 and 176 ppm ascribed to the carbenic carbon atoms. The positive ion ESI–MS spectra show m/z peaks at 1230.70 and 1380.76 amu corresponding to  $[Cu_3(L)_3(PF_6)_2]^+$ . The compounds undergo extensive fragmentation through loss of ligand and copper atom. The intense peaks at 770.73, 313.18 amu for 1 and 872.76, 363.43 amu for **2** were ascribed to  $[Cu_2(L)_2(PF_6)]^+$  and  $[Cu(L)_2]^+$ fragments, respectively.

These copper(I)–NHC complexes are stable toward light and air. The single crystals suitable for X-ray diffraction were grown by slow diffusion of Et<sub>2</sub>O into their CH<sub>3</sub>CN and DMSO solutions. The structures of 1 and 2 are shown in Figs. 1 and 2. The two complexes have the same structures consisting of a triangular Cu<sub>3</sub> core. The three copper atoms are bridged by three pyridine functionalized NHC ligands forming a Cu<sub>3</sub> ring with three Cu–Cu–Cu angels being 60.190(15), 60.190(15), 59.62(3)° for 1 and 60.305(14), 59.117(14),  $60.577(14)^{\circ}$  for **2**. Each copper ion is coordinated by two pyridine and two imidazolylidene ligands displaying a distorted tetrahedral geometry. The Cu–Cu distances are around 2.50 Å showing weak metal-metal interaction. Cuprophilic interaction has been found in many Cu(I) complexes and employed as an element for the construction of supramolecular assemblages [45-48]. The Cu-N and Cu-C bond distances fall in the range of 2.117-2.167 Å and 2.022-2.056 Å, respectively, which are slightly longer than other copper(I)-NHC complexes [49-53]. Imidazolylidene acts as a bridging ligand in a  $\mu_2$  mode and bonded equally to two Cu(I) ions, which is only observed in a few silver(I) and copper(I) complexes [54-57].

# 2.2. Synthesis and structural characterization of $[Ni(L1)Cl](PF_6)$ and $[Pd(L1)Cl](PF_6)$

Carbene-transfer reaction using a silver–NHC complex as the carbene source has been widely employed for the preparation of transition metal NHC complexes [1]. The gold(I) and Cu(I)–NHC complexes have been scarcely used. [58,59]. Reaction of **1** with three equivalent of Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in acetonitrile readily afforded [Ni(L1)Cl](PF<sub>6</sub>) (**3**) as a red solid in 75% yield (Scheme 2). The compound is soluble in DMSO but decomposes slowly. The <sup>1</sup>H NMR spectrum of **3** in acetone shows characteristic resonance signals due to the pyridyl and imidazolylidene groups. However, the satisfactory <sup>13</sup>C NMR spectrum was not obtained because of its poor solubility in acetone. ESI–MS spectrum of **3** shows the base peak at



Scheme 1. Synthesis of [Cu<sub>3</sub>(L1)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub> (1) and [Cu<sub>3</sub>(L2)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub> (2).



**Fig. 1.** ORTEP drawing of **1** showing atomic numbering scheme at 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Cu(1)-Cu(1)#1 2.500 (1), Cu(1)-Cu(2) 2.515(1), Cu(1)-C(16) 2.050(6), Cu(1)-C(1) 2.056(5), Cu(1)-N(4) 2.156(4), Cu(1)-N(6) 2.159(4), Cu(2)-C(1) 2.048(4), Cu(2)-N(3) 2.167(4), Cu(1) #1-Cu(1)-Cu(2) 60.190(15), Cu(1)#1-Cu(2)-Cu(1) 59.62(3). Symmetry code: #1 - x + 2, y, -z + 1/2.

343.11 amu assignable to  $[Ni(L1)Cl]^+$ . X-ray crystallographic analysis showed that **3** has a square-planar geometry with nickel center surrounded by the pincer NCN ligand and a chloride ion (Fig. 3). The Ni–C (1.836(8) Å) and Ni–N distances (1.934(6) and 1.942(5) Å) are



Fig. 2. ORTEP drawing of 2 showing atomic numbering scheme at 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Cu(1)-C(37) 2.024(2), Cu(1)-C(7) 2.030(2), Cu(1)-N(1) 2.117(2), Cu(1)-N(9) 2.125(2), Cu(2)-C(50) 2.022(2), Cu(2)-C(7) 2.025(2), Cu(2)-N(5) 2.135(2), Cu(2)-N(4) 2.139(2), Cu(3)-C(37) 2.041(3), Cu(3)-C(50) 2.055(3), Cu(3)-N(8) 2.129(2), Cu(3)-N(12) 2.139(2), Cu(1)-Cu(3) 2.475(1), Cu(1)-Cu(2) 2.512(1), Cu(2)-Cu(3) 2.506(1), Cu(3)-Cu(1)-Cu(2) 60.305(14), Cu(3)-Cu(2)-Cu(1) 59.117(14), Cu(1)-Cu(2) 60.577(14).



Scheme 2. Synthesis of [Ni(L1)Cl](PF<sub>6</sub>) (3) and [Pd(L1)Cl](PF<sub>6</sub>) (4).

normal as compared to those of many known nickel–NHC complexes [3–7].

Similarly, reaction of **1** with three equivalent of Pd(cod)Cl<sub>2</sub> could generate  $[Pd(L1)Cl](PF_6)$  (4) which was isolated as a pale yellow solid (Scheme 2). The formation of **4** was confirmed by the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. The <sup>13</sup>C NMR spectrum of **4** exhibits a resonance peak at 153.2 ppm, which is ascribed to the carbenic carbon atom. ESI–MS spectrum of **4** shows the base peak at 390.13 amu assignable to [Pd(L1)Cl]<sup>+</sup>. Complex **4** was further identified by Xray crystallography. The palladium complex is isostructural with **3**, and its structure together with **3** is shown in Fig. 3. The palladium atom is coordinated by two nitrogen atoms of pyridine, a carbon atom of imidazolylidene and a chloride ion in a slightly distorted square-planar geometry. The Pd-C distance (1.952(8) Å) and Pd-N distance (2.062(3) and 2.073(3) Å) are consistent with the reported values in known Pd-NHC complexes [8-12]. A structurally related pincer palladium complex supported by 1,3-dipicolyl-4,5dihydroimidazol-2-ylidene has been recently reported [58] and the Pd–C distance in **4** is similar to that of the complex with saturated NHC ligand.

#### 2.3. Reaction of 1 with nickel powder

We have previously reported that M-NHC (M = Cu, Fe, Co, Ni) complexes could be produced by reaction of a Ag(I)-NHC complex



**Fig. 3.** ORTEP drawing of **3** (M = Ni) and **4** (M = Pd) showing atomic numbering scheme at 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg) for: **3** (M = Ni) Ni(1)–C(1) 1.837(4), Ni(1)–N(3) 1.936(3), Ni(1)–N(4) 1.943(3), Ni(1)–Cl 2.2359(10), C(1)–Ni(1)–N(3) 86.73(14), C(1)–Ni(1)–N(4) 86.99(14), N(3)–Ni(1)–N(4) 172.81(13), C(1)–Ni(1)–Cl 179.04(12), N(3)–Ni(1)–Cl 94.(9), N(4)–Ni(1)–C 92.29(9). For **4**: Pd(1)–C(1) 1.929(4), Pd(1)–N(4) 2.062(3), Pd(1)–N(3) 2.073(3), Pd(1)–Cl(1) 2.3737(9), C(1)–Pd(1)–N(4) 86.68(13), C(1)–Pd(1)–N(3) 87.45(13), N(4)–Pd(1)–N(3) 174.03(11), C(1)–Pd(1)–Cl(1) 177.56(11), N(4)–Pd(1)–Cl(1) 92.94(8), N(3)–Pd(1)–Cl(1) 2.97(8).

with a metal powder [60]. Interestingly, reaction of **1** with an excess of Raney Ni gave a nickel complex  $[Ni(L1)_2](PF_6)_2$  (**5**), which was isolated as an air stable pale yellow solid in good yield (Scheme 3). This compound gave analytical data consistent with the calculated C, H, and N percentages. In the <sup>1</sup>H NMR spectrum of **5**, the methylenes linking imidazolylidene and pyridine show their peaks as four doublets at 6.51, 5.77, 5.16 and 4.38 ppm illustrating that the rotation of methylene groups is prohibited upon complexation. The imidazolylidene backbone protons appear at 7.57 and 7.28 ppm as singlets. The <sup>13</sup>C NMR spectrum of **5** exhibits a resonance signal at 159 ppm ascribed to the carbenic carbon atom. The ESI–MS spectrum of **5** shows peak at 702.69 and 307.15 amu assignable to  $[Ni(L1)_2(PF_6)]^+$  and  $[Ni(L1)(PF_6)]^+$ , respectively.

Crystals suitable for X-ray crystallography of **5** were obtained by slow diffusion of diethyl ether into its acetonitrile solution. The molecular structure of **5** is depicted in Fig. 4. The central nickel is locked in a square-planar geometry surrounded by two imidazo-lylidene and two pyridyl groups with the same donating atoms *cis*-arranged. The Ni–C distance (1.853 and 1.869 Å) and Ni–N distance (1.955 and 1.958 Å) are quite normal as compared to many known nickel–NHC complexes having square-planar geometry [3–7].

# 2.4. Catalytic Kumada–Corriu and Suzuki–Miyaura coupling reaction

We have recently reported that the well defined mononuclear and dinuclear nickel NHC complexes are efficient catalyst precursors for Kumuda coupling reactions of various aryl halides and Grignard reagents at room temperature [41]. Under the similar reaction conditions, we examined the catalytic activities of 3 for cross coupling of aryl halides with arylmagnesium bromides at room temperature. The results are given in Table 1. Complex 3 was found to be active for the coupling of tolylmagnesium bromide and various aryl chlorides giving the target products in good to excellent yields (Table 1, entries 1–8). The catalyst is also suitable for heteroaryl chlorides, and the target products could be obtained in nearly quantitative yields (Table 1, entries 9-10). Especially, 2-, 3and 4-chlorobenzonitrile could be coupled with tolylmagnesium bromide giving corresponding products in excellent yields. In addition, **3** is also quite efficient for double C–C couplings of a few aryl dichlorides (Table 1, entries 11-15) at a catalyst loading of 1 mol%.

The pincer palladium complex **4** is thermally stable and inert toward air and moisture in the solid state and in solution. Thus we investigated the catalytic activity of **4** for Suzuki coupling reaction in air using water as the solvent [25]. The results are listed in Table 2. We first screened the bases using 4-bromoacetophenone and phenylboronic acid as the substrates (Table 2, entries 1–4).  $Cs_2CO_3$  was found to be the best base for the Pd-catalyzed Suzuki reaction. When 0.01 mol% of **4** was used, the reaction gave 4-



Scheme 3. Synthesis of [Ni(L1)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (5).

acetylbiphenyl in 69% yield. When the catalyst loading was increased to 0.1 mol% the reaction could be completed within 2 h in a quantitative yield (Table 2, entry 5). Both electro-rich and electron-deficient arylboronic acids gave excellent yields within 2 h under the mild condition (Table 2, entries 6-13). Steric hindered substrate 2-bromotoluene gave a relative lower yield (Table 2, entry 14). The catalyst system is also efficient for the coupling reaction of 4-bromoanisole and phenylboronic acid, the target product could be obtained in nearly quantitative yield (Table 2, entry 15). It has been reported that [Pd(Me)(1,3-di(2-picolyl)imidazolin-2-ylidene)] BF<sub>4</sub> catalyzed Suzuki coupling of 4-bromoacetophenone and phenylboronic acid to give 1-(1,1'-biphenyl-4-yl)ethanone in a conversion of 71% after 48 h in refluxing toluene with a catalyst loading of  $4 \times 10^{-4}$  mol% [43]. When the same amount of **4** was applied to the same reaction in water at 100 °C, we did not observe the formation of 1-(1,1'-biphenyl-4-yl)ethanone. When  $4 \times 10^{-3}$  mol% of **4** was used, the reaction gave 1-(1,1'-biphenyl-4-yl)ethanone in 39% yield within 12 h.

## 3. Conclusions

In summary, we have demonstrated that the transmetalation reactions using Cu(I)–NHC complex as the carbene source can be employed for the preparation of nickel and palladium complexes. The copper–NHC complexes can be easily prepared from



**Fig. 4.** Structural view of **5** showing 30% thermal ellipsoids. All H atoms and  $PF_6^-$  were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni–C(26) 1.849(5), Ni–C(2) 1.867(6), Ni–N(4) 1.953(4), Ni–N(1) 1.954(5), C(26)–Ni–C(2) 93.0(2), C(2)–Ni–N(4) 87.7(2), C(26)–Ni–N(1) 86.8(2), C(2)–Ni–N(1) 178.4(2), N(4)–Ni–N(1) 92.53(18).

imidazolium salts and cuprous oxide or copper powder as we previously reported. Thus the transmetalation reaction offers new synthetic methodology for nickel and palladium NHC complexes. Copper complexes **1** and **2** consist of a triangular Cu<sub>3</sub> core representing rare examples of copper clusters supported by NHC ligands. The pincer nickel and palladium complexes mono(NHC) complexes show good catalytic activity in Kumada–Corriu and Suzu-ki–Miyaura coupling reactions under mild conditions.

## 4. Experimental section

#### 4.1. General procedures

All chemicals were of reagent grade quality obtained from commercial sources and used as received, unless stated otherwise. [HL1](PF<sub>6</sub>) and [HL2](PF<sub>6</sub>) were prepared according to the known procedures [43,44]. Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> was synthesized according to the reported methods [61]. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts ( $\delta$ ) are expressed in ppm downfield to TMS at  $\delta$  = 0 ppm and coupling constants (*J*) are expressed in Hz. ESI–mass spectral data were acquired using a Waters Micromass ZQ mass spectrometer (+ mode, ESI source).

## 4.2. Synthesis of complexes 1–5

#### 4.2.1. Synthesis of [Cu<sub>3</sub>(L1)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>, 1

A solution of [HL1](PF<sub>6</sub>) (396.0 mg, 1.0 mmol) in 10 mL of acetonitrile was treated with Cu<sub>2</sub>O (143.2 mg, 1.0 mmol) at 50 °C. After it was stirred for 12 h, the solution was filtered. The filtrate was then concentrated to *ca*. 2 mL. Slow diffusion of diethyl ether into the acetonitrile solution afforded a colorless solid. Yield: 394 mg, 86%. Anal. Calcd for C<sub>45</sub>H<sub>42</sub>Cu<sub>3</sub>F<sub>18</sub>N<sub>12</sub>P<sub>3</sub> ([Cu<sub>3</sub>(L1)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>): C, 39.27; H, 3.08; N, 12.21. Found: C, 39.19; H, 3.02; N, 12.02. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.02 (t, *J* = 7.6 Hz, C<sub>5</sub>H<sub>4</sub>N, 6H), 7.67 (s, C<sub>5</sub>H<sub>4</sub>N + C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 9H), 7.65 (s, C<sub>5</sub>H<sub>4</sub>N, 3H), 7.30 (t, *J* = 6.4 Hz, C<sub>5</sub>H<sub>4</sub>N, 6H), 6.43, (d, C<sub>5</sub>H<sub>4</sub>N, *J* = 5.2 Hz, 6H), 5.01 (d, CH<sub>2</sub>, *J* = 14.8 Hz, 6H), 5.00 (d, CH<sub>2</sub>, *J* = 14.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  168.7 (Cu–C), 154.4, 148.5, 140.0, 125.2, 124.7, 124.6, 53.8 (CH<sub>2</sub>).

#### 4.2.2. Synthesis of [Cu<sub>3</sub>(L2)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>, **2**

According to the same procedure as described for **1**, complex **2** was obtained as a colorless soild. Yield: 457 mg, 90%. Anal. Calcd for  $C_{57}H_{48}Cu_3F_{18}N_{12}P_3$  ([ $Cu_3(L2)_3$ ](PF<sub>6</sub>)<sub>3</sub>): C, 44.85; H, 3.17; N, 11.01. Found: C, 44.69; H, 3.20; N, 11.12. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.05–7.99 (m, C<sub>5</sub>H<sub>4</sub>N + C<sub>6</sub>H<sub>4</sub>, 18H), 7.51 (dd,  $J_1$  = 2.8 Hz,  $J_2$  = 6.0 Hz, C<sub>5</sub>H<sub>4</sub>N, 6H), 7.15 (t, J = 6.0 Hz, C<sub>5</sub>H<sub>4</sub>N, 6H), 6.16 (d, J = 4.2 Hz, C<sub>5</sub>H<sub>4</sub>N, 6H), 5.68, (d, CH<sub>2</sub>, J = 15.2 Hz, 6H), 5.32 (d, CH<sub>2</sub>, J = 15.2 Hz, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  176.2 (Cu–C), 154.1, 148.2, 140.5, 134.7, 125.5, 125.3, 125.0, 111.4, 50.5.

### Table 1

Kumada–Corriu coupling reactions catalyzed by [Ni(L1)Cl](PF<sub>6</sub>).<sup>a</sup>

	<b>3</b> , rt						
	─────────────────────────────────────	THF, 12 h					
Entry	Ar-Cl	Products	Yield (%)				
1	СІ		88				
2	MeO-CI		91				
3	CI		83				
4	F <sub>3</sub> C-CI	F <sub>3</sub> C-	>99				
5			82				
6	CI NC		76				
7	CI CN		85				
8	CI		92				
9	✓_N CI		>99				
10	⟨¯N→CI N	$\langle N \rangle$	>99				
11	сі– 🦢 сі		76 <sup>b</sup>				
12	CICI		83 <sup>b</sup>				
13	CI		60 <sup>b</sup>				
14	CI		80 <sup>b</sup>				
15			>99 <sup>b</sup>				

<sup>a</sup> Reaction conditions: aryl chloride 1.0 mmol, Grignard reagent 1.2 mmol, **3** 0.5 mol%, THF 3 mL, room temperature, 12 h, under N<sub>2</sub>.
<sup>b</sup> Aryl chloride 1.0 mmol, Grignard reagent 2.4 mmol, **3** 1.0 mol%.

#### Table 2

Suzuki–Miyaura coupling reactions catalyzed by [Pd(L1)Cl](PF<sub>6</sub>).<sup>a</sup>



<sup>a</sup> Reaction conditions: aryl bromine 1.0 mmol, arylboronic acid 1.2 mmol, base 1.5 mmol, H<sub>2</sub>O 3 mL, 100 °C, in air, 2 h, GC yields.

## 4.2.3. Synthesis of [Ni(L1)Cl](PF<sub>6</sub>), 3

A solution of **1** (137.6 mg, 0.10 mmol) in 6 mL of acetonitrile was treated with Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (196.2 mg, 0.30 mmol) at room temperature. After it was stirred for 12 h, the solution was filtered. The filtrate was concentrated to *ca*. 3 mL and slow diffusion of diethyl ether into the solution afforded a red precipitate which was collected and washed with Et<sub>2</sub>O. Yield: 110 mg, 75%. Anal. Calcd for C<sub>15</sub>H<sub>14</sub>ClF<sub>6</sub>N<sub>4</sub>PNi ([Ni(L1)Cl](PF<sub>6</sub>)): C, 36.81; H, 2.88; N, 11.45. Found: C, 36.98; H, 2.82; N, 11.32. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>): 9.24 (s, C<sub>5</sub>H<sub>4</sub>N, 2H), 8.09 (t, *J* = 7.6 Hz, C<sub>5</sub>H<sub>4</sub>N, 2H), 7.81 (d, *J* = 6.4 Hz, C<sub>5</sub>H<sub>4</sub>N, 2H), 7.60 (s, 2H, C<sub>5</sub>H<sub>4</sub>N), 7.63 (s, C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 2H), 5.95 (s, CH<sub>2</sub>, 4H).

#### 4.2.4. Synthesis of [Pd(L1)Cl](PF<sub>6</sub>), **4**

The compound was obtained as a pale yellow solid using the same procedure as for **3** by using **1** (137.6 mg, 0.1 mmol) and Pd(cod)Cl<sub>2</sub> (86 mg, 0.3 mmol). Yield: 109 mg, 68%. Anal. Calcd for C<sub>15</sub>H<sub>14</sub>ClF<sub>6</sub>N<sub>4</sub>PPd ([Pd(L1)Cl](PF<sub>6</sub>)): C, 33.54; H, 2.63; N, 10.43. Found: C, 33.61; H, 2.64; N, 10.14. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.54 (d, *J* = 5.2 Hz, C<sub>4</sub>H<sub>4</sub>N, 2H), 8.27 (d, *J* = 7.6 Hz, C<sub>5</sub>H<sub>4</sub>N, 2H), 7.88 (d, *J* = 7.6 Hz, C<sub>5</sub>H<sub>4</sub>N, 2H), 7.68 (t, *J* = 6.8 Hz, C<sub>5</sub>H<sub>4</sub>N, 2H), 7.62 (s, C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 2H), 5.70 (s, CH<sub>2</sub>, 4H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  162.8 (Pd-C), 157.2, 144.7, 124.5, 121.3, 119.2, 66.6.

#### Table 3

Summary of X-ray crystallographic data for ${f 1}$	-5
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## 4.2.5. Synthesis of [Ni(L1)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, 5

A solution of **1** (137.6 mg, 0.1 mmol) in 6 mL of acetonitrile was treated with an excess of Raney nickel powder (*ca*. 100 mg) at 50 °C. After it was stirred for 12 h, the solution was filtered. The filtrate was then concentrated to *ca*. 2 mL. Addition of Et<sub>2</sub>O (20 mL) to the filtrate afforded a yellow solid which was collected and washed with Et<sub>2</sub>O. Yield: 114 mg, 90%. Anal. Calcd for C<sub>30</sub>H<sub>28</sub>F<sub>12</sub>N<sub>8</sub>P<sub>2</sub>Ni ([Ni(L1)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>): C, 42.43; H, 3.32; N, 13.19. Found: C, 42.64; H, 3.30; N, 13.36. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.77 (d, *J* = 4.0 Hz, C<sub>5</sub>H<sub>4</sub>N, 2H), 8.11 (m, C<sub>5</sub>H<sub>4</sub>N, 4H), 7.87 (d, *J* = 8.0 Hz, C<sub>5</sub>H<sub>4</sub>N, 2H), 7.78 (t, *J* = 7.6 Hz, C<sub>5</sub>H<sub>4</sub>N, 2H), 7.57 (s, C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>, 2H), 7.43 (t, *J* = 5.6 Hz, C<sub>5</sub>H<sub>4</sub>N, 2H), 7.26 (s, C<sub>5</sub>H<sub>4</sub>N, 1H), 6.51, 5.77, 5.16, 4.38 (both d, *J* = 15.2 Hz, CH<sub>2</sub>, each 2H), <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  159.1 (Ni–C), 155.4, 154.7, 153.9, 152.7, 150.2, 150.0, 125.6, 124.7, 124.1, 124.0, 123.7, 122.9, 122.7, 141.3, 138.0, 54.4, 54.2, 53.6.

#### 4.3. X-ray structural determination

Single-crystal X-ray diffraction data for complexes were collected at 293(2) K on a Gemini Ultra Atlas/CCD area-detector diffractometer with a CuK $\alpha$  radiation ( $\lambda$  = 1.54718 Å) for **2** or MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å) for **1** and **3–5** by using a  $\omega$ –2 $\theta$  scan

	1·2DMSO	$2 \cdot 3CH_3CN$	3	4	5
Formula	C <sub>49</sub> H <sub>54</sub> Cu <sub>3</sub> F <sub>18</sub> N <sub>12</sub> O <sub>2</sub> P <sub>3</sub> S <sub>2</sub>	C <sub>63</sub> H <sub>57</sub> Cu <sub>3</sub> F <sub>18</sub> N <sub>15</sub> P <sub>3</sub>	C15H14ClF6N4NiP	C <sub>15</sub> H <sub>14</sub> ClF <sub>6</sub> N <sub>4</sub> PPd	C30H28C10F12N8NiP2
Fw.	1532.69	1649.77	489.43	537.12	849.25
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	C2/c	$P2_1/c$	<i>P</i> – 1	P-1	$P2_1/c$
a/Å	11.8098(3)	11.2764(4)	8.1371(3)	8.9632(4)	8.1683(8)
b/Å	29.8634(10)	27.9137(10)	9.2795(5)	9.9849(4)	20.554(3)
c/Å	20.8315(5)	21.8117(8)	12.6571(5)	11.5953(6)	20.832(2)
β/deg	90.478(2)	94.057(3)	104.388(3)	84.321(4)	95.393(9)
V/Å <sup>3</sup>	7346.6	6848.4(4)	892.02(7)	914.42(7)	3482.0
Z	4	4	2	2	4
D/g cm <sup>-3</sup>	1.386	1.600	1.822	1.951	1.620
Reflns collected	16,508	31,687	5949	5700	14,314
Ind reflns, R <sub>int</sub>	6481, 0.0359	11,883, 0.0313	3133, 0.0151	3219, 0.0139	6116, 0.0608
Goodness-of-fit on $F^2$	1.060	1.041	1.056	1.046	0.981
R1, wR2 $[I > 2\sigma(I)]$	0.0679, 0.2024	0.0384, 0.0939	0.0456, 0.1305	0.0321, 0.0886	0.0651, 0.1436
R1, wR2 (all data)	0.0934, 0.2236	0.616, -0.422	0.0528, 0.1349	0.0344, 0.0902	0.1233, 0.1545
Largest diff. peak and hole, e $Å^{-3}$	0.902, -0.728	1.104, -0.489	1.116, -0.658	1.313, -0.753	0.616, -0.422

mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the Oxford Diffraction CrysAlisPro software [62]. All structures were solved by direct methods and refined against  $F^2$  by the fullmatrix least-squares techniques [63]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their calculated positions. Details of the X-ray experiments and crystal data are summarized in Table 3.

## Acknowledgments

We gratefully acknowledge the financial support of the NSF of China (21072170) and the Fundamental Research Fund for the Central Universities (2010QNA3004).

#### Appendix A. Supplementary material

CCDC 831857 and 830969-830972 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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