# Accepted Manuscript

Nickel(II) complexes of amine functionalized N-heterocyclic carbenes (NHCs), synthesis and catalysis in Kumada coupling of aryl chlorides

Shumiao Zhang, Xiaoyan Li, Hongjian Sun, Olaf Fuhr, Dieter Fenske

PII: S0022-328X(16)30317-5

DOI: 10.1016/j.jorganchem.2016.07.024

Reference: JOM 19575

To appear in: Journal of Organometallic Chemistry

Received Date: 6 April 2016

Revised Date: 20 June 2016

Accepted Date: 29 July 2016

Please cite this article as: S. Zhang, X. Li, H. Sun, O. Fuhr, D. Fenske, Nickel(II) complexes of amine functionalized N-heterocyclic carbenes (NHCs), synthesis and catalysis in Kumada coupling of aryl chlorides, *Journal of Organometallic Chemistry* (2016), doi: 10.1016/j.jorganchem.2016.07.024.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



# Pictogram

Nickel(II) Complexes of Amine Functionalized N-Heterocyclic Carbenes (NHCs), Synthesis and Catalysis in Kumada Coupling of Aryl Chlorides

Shumiao Zhang, <sup>a</sup>Xiaoyan Li,<sup>a</sup> Hongjian Sun<sup>\*,a</sup>, Olaf Fuhr,<sup>b</sup> Dieter Fenske<sup>b</sup>

School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250199 Jinan, PR China



# Nickel(II) Complexes of Amine Functionalized N-Heterocyclic Carbenes (NHCs), Synthesis and Catalysis in Kumada Coupling of Aryl Chlorides

Shumiao Zhang,<sup>a</sup> Xiaoyan Li,<sup>a</sup> Hongjian Sun<sup>\*,a</sup>, Olaf Fuhr,<sup>b</sup> Dieter Fenske<sup>b</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250199 Jinan, PR China,\*E-mail: hjsun@sdu.edu.cn
 <sup>b</sup> Institutfür Nanotechnologie (INT) und Karlsruher Nano-Micro-Facility (KNMF), Karlsruher Institutfür Technologie (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

### Abstract

A new amine functionalized double chelate NHC nickel complex 2 was synthesized and characterized. Complexes 4a and 4b were generated through an improved synthetic method. Catalytic ability of the three nickel complexes were tested in Kumada coupling reaction. Complex 2 showed the best catalytic activity among them. With only 0.5 mol% of complex 2, the coupling of aryl chlorides with Grignard reagents received good yields.

Keywords: Amine-fuctionalized; NHCs; Nickel; Kumada coupling

\*Corresponding author. Tel.: + 86 531 88361350; Fax: + 86 531 88564464. E-mail: hjsun@sdu.edu.cn.

# 1. Introduction

Transition metal complexes of N-heterocyclic carbene ligands are of great importance in organometallic studies and catalytic application.<sup>1</sup>A significant component among

the NHCs is the functionalized NHC ligands. Because of the diversity of functional groups in the NHCs, the metal complexes could be pincer complexes<sup>2</sup>, bidentate complexes<sup>3</sup>, sandwich or half-sandwich complexes<sup>4</sup>. Difference of the functional groups brings up diverse character of the metal complexes, so they can catalyze reactions such as Suzuki coupling<sup>2b,2g,5</sup>, Kumada coupling<sup>2j,6</sup>, hydrosilylation<sup>7</sup>, and Heck reaction.<sup>3,8</sup>

The first amino NHC transition metal complex containing a secondary alky amine moiety was reported by Douthwaite's group<sup>9</sup>, and this kind of ligand was used for synthesis of a series of palladium complexes<sup>10</sup>. The diarylamine functionalized NHC ligand was first reported by Luo's group<sup>5a</sup>. The palladium<sup>5a,11</sup>, nickel<sup>5b</sup>, platinum<sup>11</sup>, and rare earth metal<sup>12</sup> complexes were synthesized from this kind of ligand. The NH/NH<sub>2</sub> moieties inreported [C, N] type NHCs were mainly coordinated to the metal center<sup>8a,7d,13</sup> and in a few cases the NH protons could be deprotonated by bases<sup>11,14</sup>. Transition metal complexes of NHCs containing carbazide backbone were first reported by Kunz's group<sup>15</sup>. In the examples of amido NHC complexes<sup>16</sup>, the NH protons were activated and the nitrogen atom was coordinated to the metal center to form bidentate or tetradentate complexes.

Palladium and platinum aryl amine functionalized [C, N] type complexes were reported previously. But nickel complex with this kind of ligand has not been studied. Here we report a diarylamine functionalized [C, N] type NHC ligand. While generating the nickel(II) complex, a double chelate homoleptic complex was obtained. The nickel complex was proved to be efficient in Kumada coupling reactions of aryl chlorides.

#### 2. Results and Discussion



Scheme 1 Preparation of 1

The preparation of ligand **1** is shown in **Scheme 1**. In the proton NMR spectrum of **1**, the amine proton and the NHC proton were appeared at 7.77 and 9.90 ppm respectively. Reaction of ligand **1** with 0.5 equivalent Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in pyridine, using K<sub>2</sub>CO<sub>3</sub> as base, at 90 °C for 2 hours produced complex **2** in a yield of 91% (**Scheme 2**). In the proton NMR spectrum of complex **2**, the aryl methyl group and the *i*Pr methyl groups in the two ligands showed up separately because the ligands were blocked and the methyl groups orientated in different chemical environments. Red crystal of complex **2** was obtained by slow evaporation of a mixture of CH<sub>2</sub>Cl<sub>2</sub> and petroleum ether. The structure was identified through X-ray crystallographic analysis (**Fig. 1**). The configuration of central Ni is square-planar. The Ni-C<sub>carbene</sub> bond length (C14-Ni1) is 1.865(2)Å and the Ni-N<sub>amine</sub> bond length (N1-Ni1) is 1.945(1)Å.



Scheme 2 Preparation of nickel complex 2



**Fig. 1** Crystal structure of complex **2**, 50% probability level, hydrogen atoms omitted. Selected bond lengths (Å) and angles (deg): C14-Ni1 1.865(2), N1-Ni1 1.945(1), C14-Ni1-N1a168.37(6), C14a-Ni1-N1 168.37(6), C14-Ni1-N1 84.70(6), C14-Ni1-C14a95.37(9).

A new synthetic method for known complex **4a** and **4b** was carried out (**Scheme 3**). Reaction of ligands **3a/3b** with Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> using Et<sub>3</sub>N as base in THF for 36h provided **4a/4b** in the yields of 36%/37%. In the published synthetic pathway<sup>5b</sup>, Ag<sub>2</sub>O was used to carry out the transmetalation. This is a traditional approach to obtain NHC metal complexes. Our new method is a one-step reaction without using more precious Ag. To synthesize these complexes (**4a** and **4b**), we have tried a lot of methods. Not only Et<sub>3</sub>N could be used in the process, *n*BuLi worked as well. Comparing these methods with the transmetalation way, Et<sub>3</sub>N is the best reagent for the reaction. The solvent is reusable in this case. This new method made the process more convenient without losing yields. In the crystal structure of **4a** (**Fig. 2**), the Ni-C<sub>carbene</sub> bond length (C8-Ni1 = 1.902(3) Å) is longer than that (C14-Ni1 1.865(2) Å) in complex **2** and the Ni-N<sub>amine</sub> bond length (N1-Ni1 1.891(4) Å) is shorter than that (N1-Ni1 1.945(1) Å)in complex **2** due to the strong *trans*-influence of the C<sub>carbene</sub> atom.



Scheme 3 New synthetic method for complexes 4a and 4b.



Fig. 2 Crystal structure of complex 4a, 50% probability level, hydrogen atoms omitted. Selected bond lengths (Å) and angles (deg): C8-Ni1 1.902(3), N1-Ni1 1.891(4), Ni1-Cl1 2.1847(19), C8-Ni1-N1 87.27(12), C8-Ni1-Cl1 92.73(12), N1-Ni1-Cl1 180.0, C8-Ni1-C8a174.5(2).

With the three nickel complexes, we tested their catalytic property for Kumada coupling reactions. As shown in Table 1, the reaction conditions were optimized by coupling of 4-chloroanisole with phenylmagnesium bromide. At first, we added the substrate in the order of catalyst, solvent, 4-chloroanisole and phenylmagnesium bromide (entries 1-3, **Table 1**). It seems that higher temperature benefits the reaction (entry 2, **Table 1**). In an accidental trial, phenylmagnesium bromide was added before 4-chloroanisole, the reaction completed in a conversion of 99% (entry 4, **Table 1**). This phenomenon implies that the reaction rate of active Ni(0) species with substrates is faster than the generation of Ni(0). If the Grignard reagent is added before aryl chloride, it only reacts with the Ni(II) complex to generate Ni(0). If the Grignard reagent is added after aryl chloride, once Ni(0) comes up, the competition begins and consequently only part of the catalyst works during the tested time due to the

unsatisfactory solubility of complex **2**. Then the catalyst loading was reduced and the temperature was set to be 40 °C (entries 5-9, **Table 1**). The catalyst loading could be lowered to 0.5 mol% to keep the conversion to 99%. Higher temperature was tried but more homocoupling product of phenylmagnesium was found. DMSO and toluene were also used as solvent (entries 10-11, **Table 1**). However, the result was not as good as the reaction in THF. Complexes **4a** and **4b** showed poor catalytic ability (entries 12-13, **Table 1**). Therefore, the best conditions for the Kumada coupling reaction are 0.5 mol% of complex **2** as catalyst, reacting in THF at 40 °C for 24h (entry 7, **Table1**).

Table1 Optimization of reaction conditions for Kumada coupling reaction



Entry	Cat.	Cat./	Solvent	T/°C	Conversion
-		mol%	Y		/% <sup>a</sup>
1	2	1	THF	25	30 <sup>b</sup>
2	2	1	THF	40	92 <sup>b</sup>
3	2	2	THF	25	64 <sup><i>b</i></sup>
4	2	2	THF	25	99
5	2	1	THF	25	9
6	2	1	THF	40	99
7	2	0.5	THF	40	99
8	2	0.3	THF	40	84
9	2	0.1	THF	40	26
10	2	0.5	toluene	40	34
11	2	0.5	DMSO	40	24
12	<b>4</b> a	2	THF	40	trace
13	<b>4</b> b	2	THF	40	15

<sup>*a*</sup>General condition: 1.0 mmol of aryl chloride, 1.5 mmol of Grignard reagent, 2 mL THF, 24h. All the conversionswere determined by GC.

<sup>b</sup>Add PhMgBr after 4-chloroanisole.

With the optimized reaction conditions, substrates were explored and shown in Table 2. Aryl chloride with  $-CF_3$  group in *para*-position gave a lower yield (5c and 5e, Table 2). A sterically hindered group in any chloride has negative influence for the reaction (5b and 5d, Table 2). 2-Naphthylmagnesium bromide went on the coupling reaction almost quantitatively (5f and 5g, Table 2), while 2-pyridylmagnesium bromide had a lower reaction activity (5h and 5i, Table 2). With dichlorides as *p*-dichlorobenzene o-dichlorobenzene generated substrates, and only mono-substituted products (5j and 5l, Table 2). For *m*-dichlorobenzene, a mixture of mono- and di-substituted products was detected under the general conditions. By increasing the amount of Grignard reagent to 2.5 mmol and raising the catalyst loading to 1 mol%, the corresponding *m*-terphenyl was obtained in 98% (5k, Table 2). The results of Kumada coupling reactions using complex 2 as catalyst showed that the catalyst loading is lower while the yields remain high comparing to those of the catalysts with similar structures<sup>2d, 2j, 6b</sup>.

0	Ar-Cl + Ar'-MgBr -	HF → Ar-Ar	
ArCl	Ar'MgBr	Products	yields/%
о- Сі	MgBr	5a	99
CICI	MgBr	5b	88
F <sub>3</sub> C-CI	MgBr	5c	84
CICI	O	5d	87

Table 2 Kumada coupling of aryl chlorides with Grignard reagents<sup>a</sup>

0 5 mall/ 2

7



<sup>*a*</sup>General condition: 1.0 mmol of aryl chloride, 1.5 mmol of Grignard reagent, 0.005 mmol of complex **2**, 2 mL THF, 40 °C, 24h. Isolated yields.

<sup>b</sup>2.5 mmol of Grignard reagent, 0.01 mmol of complex 2, di-substituted product gained.

#### 3. Conclusions

In conclusion, a new amine functionalized NHC nickel(II) complex 2 was generated. Complexes 4a and 4b were synthesized in an improved method. Catalytic ability of the three nickel complexes were tested in Kumada coupling reactions and complex 2 proved to be efficient with a catalyst loading of 0.5 mol%.

## 4. Experimental

General information. All the reactions for Kumada coupling and the reaction for

synthesis of complex **4a** were carried out using standard Schlenk techniques under nitrogen atmosphere. THF and toluene were dried by Na using benzophenone as indicator and distilled under N<sub>2</sub>. DMSO was dried by CaH<sub>2</sub> and distilled under N<sub>2</sub>. Other chemicals obtained commercially were used as received. <sup>1</sup>H NMR, <sup>13</sup>C NMR were recorded on 300 MHz Bruker instrument. X-ray crystallography was carried out on a Bruker Smart 1000 diffractometer. Elemental analyses were carried out on an Elementar Vario ELIII instrument. High Resolution Mass Spectra were carried out using Agilent 6510 (PLgel10um500A 300X25mm).

mmol) **Synthesis** 2-Bromoaniline (1.00)of ligand 1. 5.8 and g. 4-methylphenylboronic acid (0.82 g, 6.0 mmol) were put in a round bottom bottle. Cu(OAc)<sub>2</sub> (1.57 g, 8.7 mmol) was added as catalyst, then NEt<sub>3</sub> (1.75 g, 17.4 mmol) was added as base in 50 mL CH<sub>2</sub>Cl<sub>2</sub>. After stirring for 24h in room temperature, 2-bromo-N-(p-tolyl)aniline was separated through column chromatography with petroleum ether : acetic ether 10:1 as eluent in a yield of 70%(1.06 g). The next step was using 2-bromo-N-(p-tolyl)aniline (1.00 g, 3.8 mmol), imidazole (0.31 g, 4.6 mmol), K<sub>2</sub>CO<sub>3</sub> (1.05 g, 7.6 mmol), CuO (0.03 g, 0.4 mmol), after dissolved in 20 mL DMSO, the mixture was heated to 180°C for 3h. Water was added after cooling to  $CH_2Cl_2$ room temperature and was added to extract the product. 2-imidazole-N-(p-tolyl)aniline was gained through column chromatography with acetic ether as eluent in a yield of 56%(0.53 g). The last step is 2-imidazole-N-(p-tolyl)aniline(1.00 g, 4.0 mmol) and iPrBr(0.49 g, 4.0 mmol) heated to 90 °C in 20 mL MeCN in a sealed tube for 18h. Ligand 1 is obtained as brown powder by removing the solvent in a yield of 95%(1.42 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) : 9.91 (1H, s), 7.77 (1H, s), 7.43 (1H, d, J=9.0 Hz), 7.37-7.34 (3H, m), 7.30 (1H, dd, J=9.0 Hz, 3.0 Hz), 7.14-7.10 (2H, m), 7.04-6.98 (3H, m), 4.90 (1H, m), 2.25 (3H, s), 1.63 (6H, d, J=9.0 Hz).<sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) :140.19, 139.75, 136.36, 131.26, 130.73, 129.65, 126.66, 125.43, 123.11, 121.63, 121.27, 119.74, 118.88, 53.54, 22.77, 20.69.

IR (v, cm<sup>-1</sup>): 3192, 3149, 3057, 1598, 1562, 1517, 1377, 1317, 1205, 1110, 806, 746.

9

Synthesis of complex 2 . Ligand 1 (0.15 g, 0.4 mmol), Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.13 g, 0.2 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.28 g, 2.0 mmol) were put in a round bottom bottle, 5 mL pyridine was added as solvent. The mixture was heated to 90°C for 2h. After cooling to room temperature, pyridine was removed and CH<sub>2</sub>Cl<sub>2</sub> was added to extract the product. Complex 2 was gained as orange powder in a yield of 91%(0.128 g). Red crystal of complex 2 is obtained by slow evaporation of the mixture of CH<sub>2</sub>Cl<sub>2</sub> and petroleum ether. Dec. > 173°C. IR (Nujol mull, cm<sup>-1</sup>): 3162, 3131, 1606, 1589, 1556, 1377, 1340, 724. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.62-7.38 (7H, m), 7.22 (4H, s), 6.87 (5H, m), 6.51 (4H, m), 3.90 (2H, m), 1.46 (3H,s), 1.30 (6H, d, *J*=6.0 Hz), 1.18 (3H, s), 0.91 (6H, d, 6.0 Hz). Anal. Calcd for C<sub>38</sub>H<sub>40</sub>N<sub>6</sub>Ni (639.47 g/mol): C, 71.37; H, 6.30; N, 13.13. Found: C, 71.69; H, 6.27; N, 12.97. HRMS-ESI(m/z) Calcd for C<sub>38</sub>H<sub>40</sub>N<sub>6</sub>Ni[M-H]: 637.2590; Found: 637.2562.

**Synthesis of ligands 3a and 3b.** Ligands **3a** and **3b** were synthesized according to reference<sup>5a</sup>. <sup>1</sup>H NMR of **3a** (300 MHz, CDCl<sub>3</sub>) : 10.42 (2H, s), 8.46 (1H, s), 7.49-7.40 (8H, m), 7.38-7.35 (6H, m), 7.10-7.05 (6H, m), 5.74 (4H, s), 2.27 (6H, s). <sup>1</sup>H NMR of **3b** (300 MHz, CDCl<sub>3</sub>) :9.89 (2H, s), 7.78 (1H, s), 7.65 (2H, s), 7.48 (2H, s), 7.18-7.09 (6H, m), 4.46 (4H, t, *J*=7.5Hz), 2.31 (6H, s), 1.91 (4H, m), 1.40 (4H, m), 0.97 (6H, t, *J*=7.5Hz).

Synthesis of complex 4a. 3a (0.12 g, 0.20 mmol) and Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.13 g, 0.20 mmol) were put in a round bottom bottle. Then 20 mL THF was added to the mixture. NEt<sub>3</sub> (0.08 g, 0.25 mmol) was added. The mixture was stirred for 36h at room temperature and the solution turned purple. The solvent was removed under pressure and the rude product was purified through flash chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent. The final product was obtained as purple powder in a yield of 36%. The purple crystal of 4a was gained from slow evaporation of the mixture of CH<sub>2</sub>Cl<sub>2</sub> and petroleum ether. <sup>1</sup>H NMR of 4a (300 MHz, CDCl<sub>3</sub>) : 7.42-7.39 (4H, m), 7.32 (2H, d, J=2.1 Hz), 7.23-7.15 (8H, m), 6.79-6.74 (6H, m), 5.94 (2H, d, J=14.7 Hz), 5.97 (2H, 10

d, *J*=15.0 Hz), 2.35 (6H, s).

<sup>13</sup>C NMR of **4a** (300 MHz, CDCl<sub>3</sub>) :162.27, 140.64, 137.62, 132.45, 128.51, 128.03, 127.57, 127.27, 126.61, 124.07, 123.21, 119.52, 117.18, 53.64, 20.75. Calcd for C<sub>34</sub>H<sub>30</sub>ClN<sub>5</sub>Ni (602.79 g/mol): C, 67.75; H, 5.02; N, 11.62. Found: C, 67.35; H, 5.27; N, 11.30.

**Synthesis of complex 4b.** The synthetic procedure is the same as complex **4a**. Purple powder gained in a yield of 37%. <sup>1</sup>H NMR of **4b** (300 MHz, CDCl<sub>3</sub>) : 7.33 (2H, d, J=3.0 Hz), 7.20 (2H, s), 6.95 (2H, d, J=3.0 Hz), 6.68 (4H, s), 4.63 (2H,m), 4.27 (2H, m), 2.32 (6H, s), 2.01 (2H, m), 1.78 (2H, m), 1.32 (4H, m), 0.87 (6H, t, J=9.0 Hz). <sup>13</sup>C NMR of **4b** (300 MHz, CDCl<sub>3</sub>) : 161.58, 140.59, 132.04, 126.98, 126.28, 123.91, 122.89, 119.35, 116.69, 49.81, 33.55, 20.71, 19.72, 13.66. Calcd for C<sub>28</sub>H<sub>34</sub>ClN<sub>5</sub>Ni (534.75 g/mol): C, 62.89; H, 6.41; N, 13.10. Found: C, 63.14; H, 6.46; N, 13.29.

# X-ray structure determination and crystal data for complexes 2 and 4a.

Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were resolved by direct or Patterson methods with the SHELXS-97 program and were refined on  $F^2$  with SHELXTL. Hydrogen atoms were included in calculated positions and were refined using a riding model. CCDC-1433108 (2) and CCDC-1032787 (4a) contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Cambridge CB2 1EZ, Road. UK (fax (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for complex **2** :  $C_{38}H_{40}N_6Ni$ , Mr = 639.47 g/mol, monoclinic, space group C2/c, a = 14.158 (2) Å, b = 15.170(2) Å, c = 15.835(2) Å,  $\beta = 108.111(1)^\circ$ , V = 3232.5(6) Å<sup>3</sup>, T = 173 (2) K, Z = 4, Dc = 1.314 g/cm<sup>3</sup>,  $\mu = 0.637$  mm<sup>-1</sup>. A total of 12458 reflections were collected, 3733 unique (Rint = 0.0252), R1 =0.0300 (for 3733 reflections with I > 2 sigma(I)), wR2 = 0.0754 (all data),CCDC No. 1433108. Crystal data for complex **4a** :  $C_{34}H_{30}ClN_5Ni$ , Mr = 602.79, monoclinic, space group C2/c, a = 16.342(1) Å, b = 9.4476(6) Å, c = 18.8740(9) Å,  $\beta = 102.865(4)^{\circ}$ , V = 2840.8(3) Å<sup>3</sup>, T = 296 (2) K, Z = 4, Dc = 1.409 g/cm<sup>3</sup>,  $\mu = 2.104$  mm<sup>-1</sup>. A total of 6282 reflections were collected, 2237 unique (Rint = 0.0490), R1 =0.0492 (for 2237 reflections with I > 2 sigma(I)), wR2 = 0.1329 (all data), CCDC No. 1032787.

General procedure for Kumada coupling reactions. A Schlenk tube was charged with nickel complex and changed the atmosphere into  $N_2$ . Then THF (2 mL), Grignard reagent (1.5 mmol) and aryl chloride (1.0 mmol) were added in order. The tube was heated to 40 °C and stirred for 24h. After cooling to room temperature, 1 mL water was added. The water phase was extracted by ether for 3 times (5 mL each time) and the organic phase was collected. The products were obtained through column chromatography using petroleum ether as eluent.

#### NMR data for coupling products.

<sup>1</sup>H NMR of **5a** (300 MHz, CDCl<sub>3</sub>) : 7.57-7.49 (4H, m), 7.41 (2H, t, *J*=6.0 Hz), 7.30 (1H, m), 6.98 (2H, dt, *J*=9.0 Hz, 3.0Hz), 3.85 (3H, s).

<sup>1</sup>H NMR of **5b** (300 MHz, CDCl<sub>3</sub>) : 7.44-7.39 (3H, m), 7.36-7.31 (3H, m), 7.27 (2H, m), 7.24 (1H, m), 2.27 (3H, s).

<sup>1</sup>H NMR of **5c** (300 MHz, CDCl<sub>3</sub>) : 7.69 (4H, s), 7.60 (2H, m), 7.50-7.37 (3H, m).

<sup>1</sup>H NMR of **5d** (300 MHz, CDCl<sub>3</sub>) : 7.27-7.22 (6H, m), 6.95 (2H, m), 3.85 (3H, s), 2.28 (3H, s).

<sup>1</sup>H NMR of **5e** (300 MHz, CDCl<sub>3</sub>) : 7.66 (4H, s), 7.54 (2H, dt, *J*=9.0 Hz, 3.0Hz), 7.00 (2H, dt, *J*=9.0 Hz, 3.0 Hz), 3.87 (3H, s).

<sup>1</sup>H NMR of **5f** (300 MHz, CDCl<sub>3</sub>) : 7.92-7.82 (3H, m), 7.55-7.39 (9H, m).

<sup>1</sup>H NMR of **5g** (300 MHz, CDCl<sub>3</sub>) : 7.91 (2H, t, *J*=9.0 Hz), 7.83 (1H, d, *J*=9.0 Hz), 7.51-7.41 (6H, m), 7.03 (2H, dt, *J*=9.0 Hz, 3.0 Hz), 3.90 (3H, s).

<sup>1</sup>H NMR of **5h** (300 MHz, CDCl<sub>3</sub>) : 8.65 (1H, dq, *J*=4.8Hz, 0.9 Hz), 7.95 (2H, dt, *J*=9.0Hz, 3.0 Hz), 7.74-7.65 (2H, m), 7.19-7.15 (1H, m), 7.00 (2H, dt, *J*=9.0Hz, 3.0Hz), 3.86 (3H, s).

<sup>1</sup>H NMR of **5i** (300 MHz, CDCl<sub>3</sub>) : 8.70 (1H, dt, *J*=3.8Hz, 1.2Hz), 8.01-7.97 (2H, m), 7.78-7.71 (2H, m), 7.51-7.38 (3H, m), 7.24-7.21 (1H, m).

<sup>1</sup>H NMR of **5j** (300 MHz, CDCl<sub>3</sub>) : 7.55-7.45 (4H, m), 7.37 (2H, dt, *J*=9.0 Hz, 3.0 Hz), 6.97 (2H, dt, *J*=9.0 Hz, 3.0 Hz), 3.85 (3H, s).

<sup>1</sup>H NMR of **5**k (300 MHz, CDCl<sub>3</sub>) : 7.72 (1H, s), 7.61-7.56 (4H, m), 7.50-7.47 (3H, m), 7.00 (4H, dt, *J*=9.0 Hz, 3.0 Hz), 3.87 (6H, s).

<sup>1</sup>H NMR of **5**I (300 MHz, CDCl<sub>3</sub>) : 7.52 (1H, m), 7.44-7.39 (2H, m), 7.35-7.27 (2H, m), 7.24-7.19 (1H, m), 6.98 (2H, dt, *J*=9.0 Hz, 3.0 Hz), 3.85 (3H, s).

**Supplementary material:** Electronic Supplementary Information (ESI) available: NMR spectra, crystallographic data for **2** CCDC 1433108 and **4a** CCDC 1032787.

## Acknowledgements

Support of this work by NSFC (No.s21572119/21272138 ) is gratefully acknowledged.

#### References

- (a) M. Bierenstiel, E. D. Cross, Coord. Chem. Rev. 255 (2011) 574. (b) S.
   D-González, N. Marion, S. P. Nolan, Chem. Rev. 109 (2009) 3612.
- 2 (a) S. W. Reilly, H. K. Box, G. R. Kuchenbeiser, R. J. Rubio, C. S. Letko, K. D. Cousineau, T. K. Hollis, Tetrahedron Lett. 55 (2014) 6738. (b) K. Inamoto, J.-i. Kuroda, E. Kwon, K. Hiroya, T. Doi, J.Organomet. Chem. 694 (2009) 389. (c) N. Merle, K. W. Törnroos, V. R. Jensen, E. L. Roux, J.Organomet. Chem. 696 (2011) 1691. (d) K. D. M. MaGee, G. Travers, B. W. Skelton, M. Massi, A. D. Payne, D. H. Brown, Aust. J. Chem. 65 (2012) 823. (e) A. A. Danopoulos, N. Tsoureas, J. C. Green, M. B. Hursthouse, Chem. Commun. (2003) 756. (f) M. H.-Juárez, M. Vaquero, E. Álvarez, V. Salazar, A. Suárez, Dalton Trans. 42 (2013) 351. (g) F. Godoy, C. Segarra, M. Poyatos, E. Peris, Organometallics 30 (2011) 684. (h) M. H.-Juárez, J. L.-Serrano, P. Lara, J. P. M-Cerón, M. Vaquero, E. Álvarez, V. Salazar, A. Suírez, Chem. Eur. J. 21 (2015) 7540. (i) X. Zhang, A. M. Wright, N. J. DeYonker, T. K. Hollis, N. I. Hammer, C. E. Webster, E. J. Valente, Organometallics, 31 (2012) 1664. (j) Y. Sun, X. Li, H. Sun, Dalton Trans. 43 (2014) 9410.
- 3 N. Tsoureas, A. A. Danopoulos, A. A. D. Tulloch, M. E. Light, Organometallics 22 (2003) 4750.
- 4 (a) J. M. S. Cardoso, B. Royo, Chem. Commun. 48 (2012) 4944. (b) H.-M. Sun,
  D.-M. Hu, Y.-S. Wang, Q. Shen, Y. Zhang, J.Organomet. Chem. 692 (2007)
  903. (c) C. Segarra, E. M.-Marzá, M. Benítez, J. A. Mata, E. Peris, Angew.
  Chem. Int. Ed. 51 (2012) 10841.
- 5 (a) W. Wei, Y. Qin, M. Luo, P. Xia, M. S. Wong, Organometallics 27 (2008)
  2268. (b) S. Wang, F. Ren, Y. Qiu, M. Luo, J.Organomet. Chem. 788 (2015) 27.
- 6 (a) K. Matsubara, K. Ueno, Y. Shibata, Organometallics 25 (2006) 3422. (b) Z.
  Xi, B. Liu, W. Chen, J. Org. Chem. 73 (2008) 3954. (c) W.-J. Guo, Z.-X. Wang,
  J. Org. Chem. 78 (2013) 1054.
- 7 (a) A. Zanardi, E. Peris, J. A. Mata, New. J. Chem. 32 (2008) 120. (b) T. Chen,
  X-G Liu, M. Shi, Tetrahedron 63 (2007) 4874. (c) S. Kawabata, H. Tokura, H.

14

Chiyojima, M. Okamoto, S. Sakaguchi, Adv. Synth. Catal. 354 (2012) 807. (d)M. V. Jiménez, J. J. P.-Torrente, M. I. Bartolomé, V. Gierz, F. J. Lahoz, L. A.Oro, Organometallics 27 (2008) 224.

- 8 (a) C.-C. Tsai, W.-C. Shih, C.-H. Fang, C.-Y. Li, T.-G. Ong, G. P. A. Yap, J. Am. Chem. Soc. 132 (2010) 11887. (b) I. Peñafiel, I. M. Pastor, M. Yus, Eur. J. Org. Chem. (2012) 3151. (c) S. G. Fiddy, J. Evans, T. Neisius, M. A. Newton, N. Tsoureas, A. A. D. Tulloch, A. A. Danopoulos, Chem. Eur. J. 13 (2007) 3652. (d) D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, Organometallics 25 (2006) 4850.
- 9 R. E. Douthwaite, J. Houghton, B. M. Kariuki, Chem. Commun. (2004) 698.
- 10J. Houghton, G. Dyson, R. E. Douthwaite, A. C. Whitwood, B. M. Kariuki, Dalton Trans. (2007) 3065.
- 11 W. B. Cross, C. G. Daly, R. L. Ackerman, I. R. George, K. Singh, Dalton Trans. 40 (2011) 495.
- 12 X. Gu, X. Zhu, Y. Wei, S. Wang, S. Zhou, G. Zhang, X. Mu, Organometallics 33 (2014) 2372.
- 13 (a) L. G. Bonnet, R. E. Douthwaite, R. Hodgson, J. Houghton, B. M. Kariuki,
  S. Simonovic, Dalton Trans. (2004) 3528. (b) B. Ballarin, L. Busetto, M. C.
  Cassani, C. Femoni, A. M. Ferrari, I. Miletto, G. Caputo, Dalton Trans. 41
  (2012) 2445. (c) W. W. N. O., A. J. Lough, R. H. Morris, Organometallics 28
  (2009) 6755. (d) Y.-P. Huang, C.-C. Tsai, W.-C. Shih, Y.-C. Chang, S.-T. Lin, G.
  P. A. Yap, I. Chao, T.-G. Ong, Organometallics 28 (2009) 4316.
- 14 (a) W. B. Cross, C. G. Daly, Y. Boutadla, K. Singh, Dalton Trans. 40 (2011)9722. (b) H. Jong, B. O. Patrick, M. D. Fryzuk, Can. J. Chem. 86 (2008) 803.
- 15 (a) A. Seyboldt, B. Wucher, M. Alles, F. Rominger, C. M.-Mössmer, D. Kunz, J.Organomet. Chem. 775 (2015) 202. (b) E. Jürgens, B. Wucher, F. Rominger, K. W. Törnroos, D. Kunz, Chem. Commun. 51 (2015) 1897. (c) M. Moser, B. Wucher, D. Kunz, F. Rominger, Organometalics 26 (2007) 1024. (d) A. Seyboldt, B. Wucher, S. Hohnstein, K. Eichele, F. Rominger, K. W. Törnroos, D. Kunz, Organometallics 34 (2015) 2717.

16(a) K. V. Tan, J. L. Dutton, B. W. Skelton, D. J. D. Wilson, P. J. Barnard, Organometallics 32 (2013) 1913. (b) Y. Unger, T. Strassner, J.Organomet. Chem. 713 (2012) 203. (c) A. Kumar, L. P. Bheeter, M. K. Gangwar, J.-B. Sortais, C. Darcel, P. Ghosh, J.Organomet. Chem. 786 (2015) 63. (d) S. Kumar, A. Narayanan, M. N. Rao, M. M. Shaikh, P. Ghosh, J. Chem. Sci. 123 (2011) 791.

# Highlights:

Amine Functionalized N-Heterocyclic Carbenes (NHCs) > Nickel complex > Kumada

Coupling of Aryl Chlorides