

## 氮杂环卡宾羰基氯钌配合物的合成、晶体结构及催化性质

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**摘要:** 合成了 2 个 N-杂环卡宾钌配合物  $[\text{RuCl}_2(\text{L1})(\text{CO})]$  (**1**),  $\text{L1} = (2, 6\text{-二(甲基咪唑-2-鎓盐)吡啶})$  和  $[\text{RuCl}_2(\text{L2})(\text{CO})]$  (**2**),  $\text{L2} = (2, 6\text{-二(正丁基-2-鎓盐)吡啶})$ , 并通过元素分析、红外光谱、核磁共振氢谱和核磁共振碳谱对它们的结构进行了表征, X-射线单晶衍射测定了配合物 **2** 的分子结构, 结果表明配合物 **2** 属单斜晶系,  $C2/c$  空间群,  $a = 1.814\ 8(4)\ \text{nm}$ ,  $b = 1.129\ 2(3)\ \text{nm}$ ,  $c = 1.119\ 6(2)\ \text{nm}$ ,  $\beta = 108.862(3)^\circ$ , 且中心  $\text{Ru(II)}$  离子是六配位, 同时研究了配合物 **1** 和 **2** 在 Suzuki-Miyaura 偶联反应中的催化性质。

**关键词:** N-杂环卡宾; 钌配合物; 晶体结构; 催化性能

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## Synthesis, Crystal Structure and Catalytic Properties of Ruthenium Complexes Bearing N-heterocyclic Carbene Ligand

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**Abstract:** Two new N-heterocyclic carbene ruthenium(II) complexes  $[\text{RuCl}_2(\text{L1})(\text{CO})]$  (**1**)  $\text{L1} = (2, 6\text{-bis(methylimidazol-2-ylidene)pyridine})$  and  $[\text{RuCl}_2(\text{L2})(\text{CO})]$  (**2**)  $\text{L2} = (2, 6\text{-bis(butylimidazol-2-ylidene)pyridine})$ , have been synthesized and fully characterized by elemental analysis, IR spectra,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. The structure of complex **2** has been determined by X-ray crystallography. Complex **2** crystallizes in the Monoclinic system with  $C2/c$  space group,  $a = 1.8148(4)\ \text{nm}$ ,  $b = 1.1292(3)\ \text{nm}$ ,  $c = 1.119\ 6(2)\ \text{nm}$ ,  $\beta = 108.862(3)^\circ$ , and the central  $\text{Ru(II)}$  ion is six-coordinated. The catalytic activities of complexes **1** and **2** in the Suzuki-Miyaura cross-coupling reaction have been investigated. CCDC: 928614.

**Key words:** N-heterocyclic carbene; ruthenium complex; crystal structure; catalysis property

### 0 Introduction

Since the remarkable discovery by Arduengo of isolation of stable N-heterocyclic carbene (NHC)<sup>[1]</sup>, N-heterocyclic carbenes (NHCs) have become a very important class of ligands in organometallic chemistry and homogeneous catalysis<sup>[2-9]</sup> mainly due to their

strong  $\sigma$ -donating ability in metal NHC complexes. While their widespread applications are well documented<sup>[10-13]</sup>, these NHCs are attracting increasing attention and continuing to stimulate various transition-metal catalysis research. Most recently, a great deal of new metal complexes bearing tripodal<sup>[14]</sup>, pincer<sup>[15-17]</sup>, and bridging NHC ligands<sup>[18-19]</sup> have been

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prepared and showed high catalytic properties in hydrogenation, Heck or Suzuki C-C coupling and hydrosilylation reactions. Especially some metal complexes containing CNC-pincer NHC ligands<sup>[20-24]</sup> with large chelating effect are found to be quite robust and actively investigated. Nevertheless, there are only a limited number of ruthenium complexes based on CNC-pincer bis-carbene which are reported and used as effective catalysts<sup>[25-26]</sup>. We herein describe the synthesis and characterization of two new ruthenium complexes with such carbene ligands, along with their catalytic behavior in Suzuki C-C coupling reaction.

## 1 Experimental

### 1.1 Materials and measurement

All manipulations were performed under dry nitrogen using standard Schlenk glassware. The solvents CH<sub>3</sub>CN were dried over CaH<sub>2</sub> and distilled under nitrogen. The carbene precursors 2,6-bis(methylimidazol-2-ylidene)pyridine chloride, 2,6-bis(butylimidazol-2-ylidene)pyridine chloride<sup>[27]</sup> and metal precursor [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub><sup>[28]</sup> were prepared according to the literature methods. Other chemicals were commercially available and used as received without further purification. NMR data were measured on a Bruker AM-500 spectrometer with TMS as internal standard. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analytic instrument. IR spectra were carried out on a Nicolet NEXUS870 FTIR spectrometer with KBr pellets in the range of 400~4 000 cm<sup>-1</sup>. The single-crystal X-ray diffraction data were collected on a Bruker SMART CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm) at 298 K. The conversion and yield of catalytic reaction were monitored by GC 9560.

### 1.2 Synthesis of complex 1 and 2

A mixture of 2, 6-bis(methylimidazol-2-ylidene)pyridine dichloride (187 mg, 0.6 mmol), [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> (136 mg, 0.6 mmol), and NEt<sub>3</sub> (0.84 mL, 6 mmol) in 40 mL of CH<sub>3</sub>CN was refluxed under a dry nitrogen atmosphere for 10 h. All the volatiles were removed under vacuum and the crude residue was purified by

column chromatography with DCM/MeOH (30:1, V/V), affording the yellow product **1**. Yield: 35%. Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>Cl<sub>2</sub>N<sub>5</sub>ORu (%): C, 38.27; H, 2.96, N, 15.95. Found (%): C, 38.38; H, 3.05; N, 15.99. FTIR (KBr, cm<sup>-1</sup>):  $\nu_{\text{CO}}$ , 1926. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz):  $\delta$  8.43 (s, 2H, imidazole H), 8.33 (t,  $J_{\text{H-H}}$ =7.5 Hz, 1H, Pyridine H), 7.93 (d,  $J_{\text{H-H}}$ =8 Hz, 2H, Pyridine H), 7.61 (s, 2H, imidazole H), 4.04 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz):  $\delta$  206.9 (CO), 197.8 (Ru-C), 152.5, 144.1, 124.8.0, 118.1, 106.7 (Pyridine C and imidazole C), 31.1 (CH<sub>3</sub>).

The complex **2** was prepared by the similar procedure. Yield: 32%. Anal. Calcd. for C<sub>20</sub>H<sub>25</sub>Cl<sub>2</sub>N<sub>5</sub>ORu (%): C, 45.89; H, 4.78, N, 13.38. Found (%): C, 45.98; H, 4.90; N, 13.49. FTIR (KBr, cm<sup>-1</sup>):  $\nu_{\text{CO}}$ , 1928. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz):  $\delta$  8.41 (s, 2H, imidazole H), 8.33 (t,  $J_{\text{H-H}}$ =6.5 Hz, 1H, Pyridine H), 7.92 (d, 2H,  $J_{\text{H-H}}$ =8 Hz, Pyridine H), 7.63 (s, 2H, imidazole H), 4.37 (t,  $J_{\text{H-H}}$ =7 Hz, 4H, <sup>n</sup>Bu), 1.95 (quintet,  $J_{\text{H-H}}$ =7.5 Hz, 4H, <sup>n</sup>Bu), 1.43 (sextet,  $J_{\text{H-H}}$ =7.5 Hz, 4H, <sup>n</sup>Bu), 0.95 (t,  $J_{\text{H-H}}$ =7.5 Hz, 6H, <sup>n</sup>Bu). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz):  $\delta$  206.9 (CO), 197.5 (Ru-C), 152.4, 144.2, 123.9, 117.9, 106.6 (Pyridine C and imidazole C), 51.2, 31.1, 19.8, 14.1 (<sup>n</sup>Bu).

### 1.3 Crystal structure determination

A yellow single crystal with dimension of 0.26 mm×0.24 mm×0.22 mm of complex **2** was mounted on the top of a glass fibre for data collection on a Bruker SMART CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm) at 298 K. A total of 5 691 reflections were collected in the range of 2.16°< $\theta$ <25.99°, and 2 125 were unique with  $R_{\text{int}}$ =0.063 3. The structures were solved by direct methods and refined by full-matrix least-squares refinement based on  $F^2$  using the SHELXL-97 program<sup>[29]</sup>. The hydrogen atoms were positioned in idealized positions and refined in the riding-model approximation. Other non-hydrogen atoms were refined with anisotropic thermal parameters. Details of the data collection and refinement results for complex **2** were listed Table 1. Selected bond lengths and angles were given in Table 2.

CCDC: 928614.

**Table 1** Crystal data and structural refinements for complex **2**

Empirical formula	C <sub>20</sub> H <sub>25</sub> Cl <sub>2</sub> N <sub>5</sub> ORu	Absorption coefficient / mm <sup>-1</sup>	0.99
Formula weight	523.42	<i>F</i> (000)	1 064
Temperature / K	298(2)	Crystal size / mm	0.26×0.24×0.22
Wavelength / nm	0.071 073	$\theta$ range for data collection / (°)	2.16 to 25.99
Crystal system	Monoclinic	Limiting indices <i>h</i> , <i>k</i> , <i>l</i>	−22~14, −12~13, −13~13
Space group	<i>C</i> 2/ <i>c</i>	Reflections collected / unique	5 691 / 2 125, <i>R</i> <sub>int</sub> =0.063 3
<i>a</i> / nm	1.814 8(4)	Completeness / %	99.6( $\theta$ =25.99°)
<i>b</i> / nm	1.129 2(3)	Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
<i>c</i> / nm	1.119 6(2)	Data/restraints/parameters	2 125/0/134
$\beta$ / (°)	108.862(3)	Goodness-of-fit on <i>F</i> <sup>2</sup>	1.001
Volume / nm <sup>3</sup>	2.171 2(8)	Final <i>R</i> indices ( <i>I</i> >2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> =0.038 1, <i>wR</i> <sub>2</sub> =0.084 6
<i>Z</i>	4	<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.050 5, <i>wR</i> <sub>2</sub> =0.088 2
<i>D</i> <sub>c</sub> / (g·cm <sup>-3</sup> )	1.601	Largest diff. peak and hole / (e·nm <sup>-3</sup> )	1 133 and −674

**Table 2** Selected bond lengths (nm) and angles (°) for complex **2**

Ru1-C3	0.205 2(3)	Ru1-C11	0.183 6(5)	Ru1-N3	0.206 7(3)
Ru1-Cl1	0.241 7(10)	Ru1-C3 <sup>i</sup>	0.205 2(3)	Ru1-Cl1 <sup>i</sup>	0.241 7(10)
C3-Ru1-Cl1	88.04(9)	C3-Ru1-N3	76.63(9)	C11-Ru1-Cl1	90.98(2)
C11-Ru1-C3	103.37(9)	C11-Ru1-N3	180.0	N3-Ru1-Cl1	89.02(2)
C3-Ru1-C3 <sup>i</sup>	153.25(18)	C11-Ru1-C3 <sup>i</sup>	103.37(9)	Cl1-Ru1-C3 <sup>i</sup>	91.50(9)
C3-Ru1-Cl1 <sup>i</sup>	91.50(9)	C11-Ru1-Cl <sup>i</sup>	90.98(2)	N3-Ru1-Cl1 <sup>i</sup>	89.02(2)
N3-Ru1-C3 <sup>i</sup>	76.63(9)	Cl1-Ru1-Cl1 <sup>i</sup>	178.03(4)		

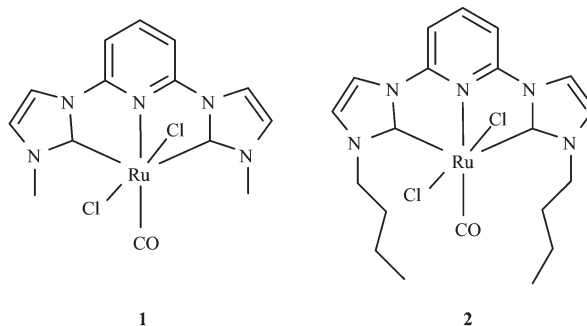
Symmetry codes: <sup>i</sup> −*x*, *y*, 0.5−*z*

## 2 Results and discussion

### 2.1 Synthesis

The reaction of 2,6-bis(methylimidazol-2-ylidene)pyridine dichloride and 2,6-bis(butylimidazol-2-ylidene)pyridine dichloride with excess NEt<sub>3</sub> and metal precursor [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> in refluxing CH<sub>3</sub>CN resulted in the formation of chelating Ru-NHC complexes **1** and **2**

as yellow solids (Scheme 1), respectively. Both complexes are air-stable in solution and in the solid state, and have been characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR spectra and elemental analysis. The <sup>1</sup>H NMR spectra of complexes **1** and **2** show the disappearance of imidazolium C<sub>2</sub>-H proton signals of 2, 6-bis(methylimidazol-2-ylidene)pyridine dichloride, 2, 6-bis(butylimidazol-2-ylidene)pyridine dichloride in



Scheme 1

the range 10 ~12, indicating the deprotonation of imidazoliums and coordination of carbene carbon to the Ru atom. The signal of carbene carbon atoms of complexes **1** and **2** appear at 197.8 and 197.5 in the  $^{13}\text{C}$  NMR spectra, respectively, which are found in the expected range. From the NMR spectra, we conclude that the imidazole rings are symmetry-related in complexes **1** and **2**, and the bis-carbene ligand coordinate to Ru in a chelating CNC-pincer form. The IR spectra show intense absorption bands at 1 926 and 1 928  $\text{cm}^{-1}$  observed in **1** and **2**, respectively, which are assigned to the stretching vibrations of carbonyl groups.

## 2.2 Crystal structure of complex **2**

Yellow single crystal is obtained by slow evaporation  $\text{CH}_3\text{CN}$  solution of **2** in the air. X-ray crystal structure analysis reveals that complex **2** crystallized in Monoclinic system with  $C2/c$  space group. The molecular structure of complex **2** with ellipsoids drawn at 30% probability is shown in Fig.1. The symmetrical unit of complex contains one Ru(II) ion, one pyridine ring, two imidazole rings, two chlorides and one carbonyl group. The central Ru(II) ion is in a distorted octahedral coordination geometry and coordinated with the nitrogen atom from the pyridine ring and two carbene carbons, together with two chlorides and one CO ligand. The CO is *trans* to the nitrogen atom of pyridine ring, and the two chlorides are mutually *trans*. The bond lengths Ru-C<sub>carbene</sub> (0.205 2(3) nm) is shorter than those of the

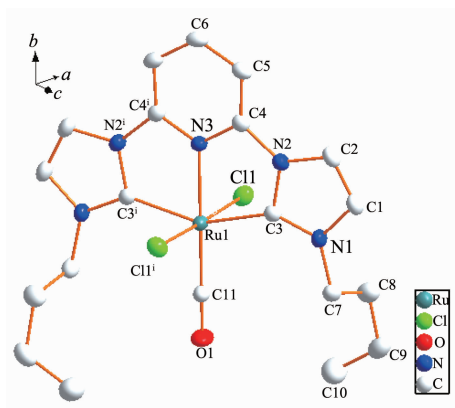
reported pincer-type ruthenium NHC complexes<sup>[25]</sup>. The Ru-N<sub>pyridine</sub> bond distance is 0.206 7 (3) nm, which is in close agreement with those of analogous ruthenium complexes. The Ru-C<sub>CO</sub> bond of 0.183 6(5) nm is fall in the region of known Ru-NHC carbonyl complexes<sup>[25-26]</sup>. The Ru-Cl bond lengths are 0.241 7(10) nm and 0.241 73(10) nm, respectively, which is comparable with those reported for ruthenium carbonyl chlorides complexes<sup>[30]</sup>.

The imidazole is approximately coplanar with pyridine ring. The *trans* Cl-Ru-Cl bond angle in complex **2** is 178.03 (4) $^\circ$ , which is close to 180 $^\circ$ . The C<sub>CO</sub>-Ru-N<sub>pyridine</sub> bond angle is 180.0 $^\circ$ , suggesting that carbonyl group is linear with nitrogen atom of pyridine ring. Two five-membered rings formed by Ru1/N3/C4/ $i$ /N2/ $i$ /C3 $i$  and Ru1/N3/C4/N2/C3 are nearly coplanar.

The hydrogen bonding interactions of complex **2** are shown in Fig.2, where intermolecular hydrogen bonds C2-H2A $\cdots$ Cl1 $i$  and C6-H6A $\cdots$ O1 were formed and listed in Table 3. No  $\pi$ - $\pi$  interaction was observed in the crystal packing diagram of the complex **2**.

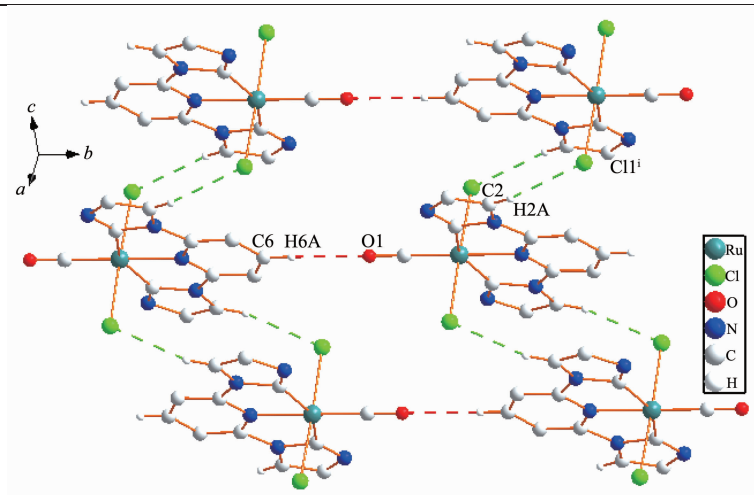
## 2.3 Catalytic properties

Although plenty of ruthenium complexes of NHCs have been found to be active catalysts for a number of important reactions, the CNC-pincer bis-carbene ruthenium complexes as catalyst for Suzuki-Miyaura coupling reaction were rarely studied. Here we explored the catalytic activity of complexes **1** and **2** in the coupling reaction of aryl halide and phenylboronic



The hydrogen atoms were omitted for clarity; Symmetry codes:  $i$   $-x, y, 0.5-z$

Fig.1 Molecular structure of complex **2** with ellipsoids drawn at 30% probability



Part of hydrogen atoms were omitted; Symmetry codes:  $^i x, 1-y, 0.5+z$

Fig.2 Hydrogen bonding interactions (dash lines) in complex **2**

Table 3 Hydrogen bond lengths and bond angles for complex **2**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
C2-H2A...Cl1 <sup>i</sup>	0.093	0.273	0.359 (4)	155.9
C6-H6A...O1	0.093	0.259	0.352 (6)	180.0

Symmetry codes:  $^i x, 1-y, 0.5+z$

Table 4 Suzuki coupling reaction catalyzed by ruthenium complexes **1** and **2**

Entry	Cat.	X	R	$t / \text{h}$	Temperature / $^\circ\text{C}$	Conversion <sup>a</sup> / %	Yield <sup>a</sup> / %
1	complex <b>1</b>	Br	H	24	60	60	57
2	complex <b>1</b>	Br	H	24	80	69	65
3	complex <b>1</b>	Br	H	24	90	78	70
4	complex <b>2</b>	Br	H	24	60	52	49
5	complex <b>2</b>	Br	H	24	80	59	54
6	complex <b>2</b>	Br	H	24	90	70	64
7	complex <b>1</b>	Cl	H	24	90	28	20
8	complex <b>2</b>	Cl	H	24	90	21	13
9	complex <b>1</b>	Br	Me	24	90	72	68
10	complex <b>2</b>	Br	Me	24	90	66	60
11	complex <b>1</b>	Br	OMe	24	90	69	62
12	complex <b>2</b>	Br	OMe	24	90	61	58
13	complex <b>1</b>	Br	COMe	24	90	85	79
14	complex <b>2</b>	Br	COMe	24	90	77	70

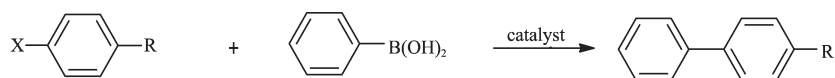
Reaction conditions: aryl halide (0.5 mmol), phenylboronic acid (0.75 mmol), KO<sup>t</sup>Bu (0.8 mmol), solvent (3 mL), catalyst **1** and **2** (1 mol%).

The reaction was carried out under an atmosphere of nitrogen. <sup>a</sup>Conversion and yield were determined by GC chromatography.

acid. We chosen a model reaction involving the Ru-catalyzed Suzuki C-C coupling reaction of bromobenzene and phenylboronic acid to search for

suitable reaction conditions. The highest conversion was obtained when the reaction was carried out at 90  $^\circ\text{C}$  in dioxane. A variety of bases such as KO<sup>t</sup>Bu,

$\text{Cs}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{NaOH}$  were effective for coupling reaction of aryl halide and phenylboronic acid, whereas the results indicated that  $\text{KO}^t\text{Bu}$  is most suitable base leading to higher conversion compared to other bases. The catalytic results were summarized in Table 4. As seen from the Table 4, complexes **1** and **2** exhibit more active catalytic activity to the coupling reaction of aryl bromide and phenylboronic acid (entries 1~6 and 9~14) than that of aryl chloride and phenylboronic acid (entries 7 and 8), which is agreeable with those reported in the literature<sup>[31]</sup>. It is



### 3 Conclusions

In summary, we have successfully synthesized and characterized two new N-heterocyclic carbene ruthenium(II) complexes  $[\text{RuCl}_2(\text{L1})(\text{CO})]$  (**1**) and  $[\text{RuCl}_2(\text{L2})(\text{CO})]$  (**2**). X-ray crystallography confirmed that complex **2** was six-coordinated. Complexes **1** and **2** are efficient catalysts for the Suzuki C-C coupling reaction of aryl halide and phenylboronic acid.

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