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# Cross-coupling reactions catalyzed by an *N*-heterocyclic carbene-Pd(II) complex under aerobic and CuI-free conditions

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**Abstract:** A Pd-complex, (Cat. 3), has been successfully employed as a highly efficient and recyclable catalyst for the Sonogashira and Heck reactions of aryl bromides with various terminal acetylenes and olefins. The catalytic reactions proceed with excellent yields with a low catalyst loading (1.0 mol%) under aerobic and CuI-free conditions. A plausible mechanism has also been proposed for the reaction.

**Keywords:** Suzuki reaction, Sonogashira reaction, Heck reaction, copper-free, NHC-complex

The Palladium catalyzed cross-coupling reaction is one of the most powerful tools for the construction of C-C bonds<sup>1</sup>. The exemplary cross-coupling methodologies encompass Suzuki reactions<sup>1e, 2</sup>, Heck reactions and Sonogashira reactions<sup>3</sup>. In the Heck and Sonogashira reactions, despite numerous other metals proved to be effective for such reactions<sup>5</sup>, conventional palladium complexes such as PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub><sup>3, 4</sup>, often in combination with copper(I) salts, are still the most preferred ones. Although the ligands of those palladium complexes are air-sensitive phosphine-based structures of limited practicality, the catalysts are still being widely employed because the cross-coupling conditions are generally compatible with a broad library of functionalities. Most noticeably, a large number of modified protocols have also been developed to expand the scope of the applications<sup>5a, 6</sup>.

Ever since the initial discovery of the cross-coupling reactions, tremendous endeavor has recently been focused on searching for alternatives, among which electrophiles and aryltosylates have been proven to be a new class of practical surrogates to aryl halides<sup>1c, 7</sup>. Compared to arylhalides, aryltosylates are usually less expensive and more readily available from phenols<sup>8</sup>. Nonetheless, more efficient, moisture- and air- insensitive palladium catalysts<sup>9c, e, 6a, 10</sup> are still being called for to affect the Sonogashira and Heck reaction with low catalyst loadings under copper-free<sup>6f, 9, 10c</sup> and less rigorously anhydrous and anaerobic conditions<sup>9f, 11</sup>.

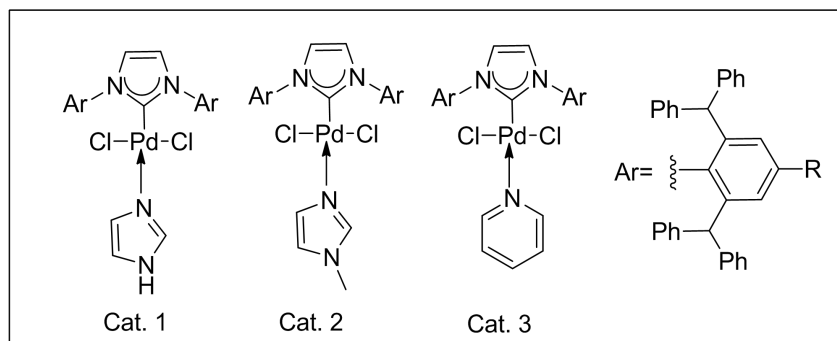
During the past twenty years, significant advances have been made to develop *N*-heterocyclic carbenes (NHCs) and their metal complexes to facilitate various organic transformations. Organ highlighted that bulky yet flexible NHC ligands were able to circumvent various limitations of cross-coupling reactions<sup>9c, 12</sup>. Encouraged by the excellent yields of [Pd-NHC] complex (IPr\*-Pd(II)-Py, Catalyst 3) mediated Suzuki couplings of arylbromides and arylsulfonates with arylboronic acids under aerobic conditions, we further proceeded to investigate its application in

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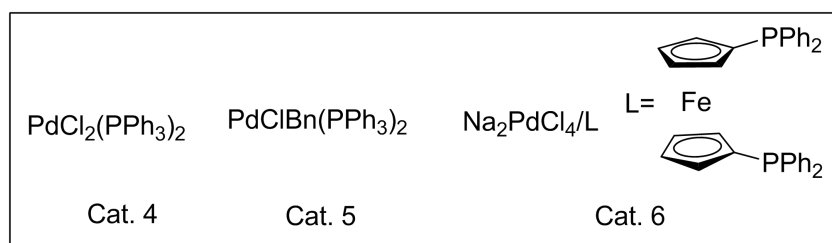
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other cross-couplings.

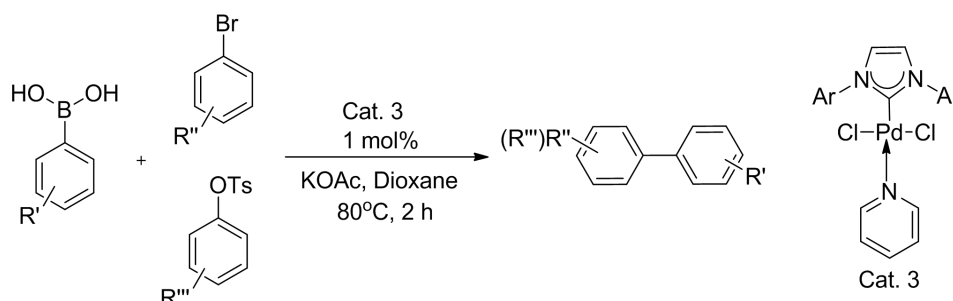
We report herein that Cat. 3 efficiently catalyzes Heck and Sonogashira reactions under CuI-free condition with low catalyst loading (1.0 mol%) in the absence of the protection of inert atmosphere.



**Scheme 1** Catalysts



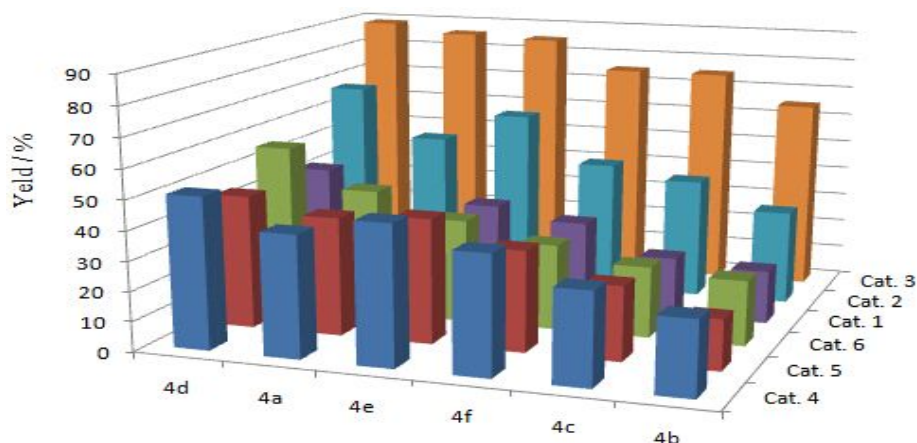
**Scheme 2** Pd(II) catalysts



**Scheme 3** Suzuki cross-coupling reactions

In our previous study of cross-coupling reactions (Scheme 3), it was found that the catalyst Cat. 3 is highly efficient for the Suzuki cross-coupling reaction, and the yield of the idea products are measured up to 93%<sup>13</sup>. Considering the good catalytic performance of Cat. 3, we were encouraged to investigate the catalytic activity of the present catalyst for the Sonogashira and Heck reactions.

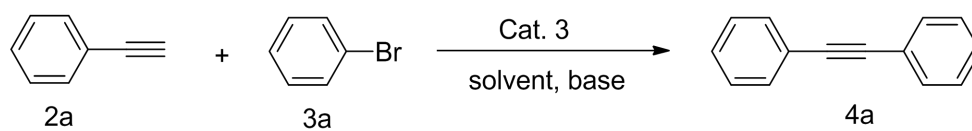
In the presence of Substrate, Pd(II) complex catalytic system is efficient in the reactions (Fig. 1). Great attention should be paid to Cat. 3, which performed much better than that of the others, and the Pd(II) catalysts (Cat. 4, Cat. 5 and Cat. 6) without co-catalyst Cu(I) performed not well than Cat. 3. We proposed that this phenomenon may attribute to the electron-withdrawing group, which could improve the catalyze activity of the complex system (Fig. 1, 4d). Therefore, in this article, we chose Cat. 3 as the catalyst model to the following research.



**Fig. 1** Parallel multisubstrate for the reactions of phenylacetylene with six aryl bromides catalyzed by Pd(II) catalysts

To verify the solvent and base effects on Sonogashira coupling reactions, we investigated the Sonogashira coupling reaction with the present catalyst using the coupling of bromobenzene with phenylacetylene as a model reaction to evaluate the reaction conditions (Table 1).

**Table 1** Optimal conditions for Cat. 3 catalyzed Sonogashira reaction of bromobenzene and phenylacetylene



Entry <sup>a</sup>	Solvent	Base	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>
1	DMSO	Et <sub>3</sub> N	25	1	Trace
2	DMSO	Et <sub>3</sub> N	40	1	21
3	DMSO	Et <sub>3</sub> N	60	1	63
4	DMSO	Et <sub>3</sub> N	80	1	86
5	DMSO	Et <sub>3</sub> N	90	1	89
6	Dioxane	Et <sub>3</sub> N	80	3	78
7	DMF	Et <sub>3</sub> N	80	2.5	76
8	Toluene	Et <sub>3</sub> N	80	4	20
9	DMSO	K <sub>2</sub> CO <sub>3</sub>	80	1	42
10	DMSO	Piperidine	80	1	81
11	DMSO	Pyridine	80	1	82
12	DMSO	No base	80	1	No reaction

<sup>a</sup> Reaction conditions : **2a** (1.2 mmol), **3a** (0.8 mmol), base (2 equiv.), solvent (2 mL), Cat. 3 (1.0 mol%), aerobic condition.

<sup>b</sup> Isolated yields.

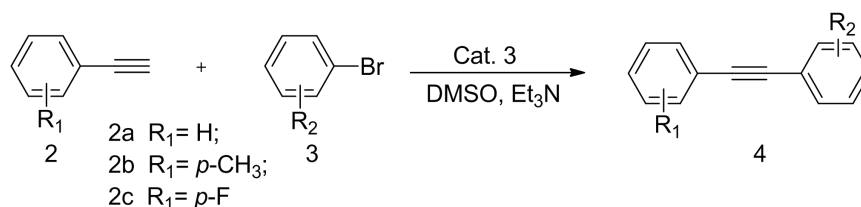
We initiated our investigation by screening for reaction conditions under which the Sonogashira reaction would proceed in the presence of oxygen, and in the absence of copper and phosphine. We observed that the yields of the desired coupling products could be isolated after 1.5 h at 25°C to 80°C in DMSO using Cat. 3 (catalyst loading 1.0 mol%), and TEA as base under aerobic

conditions (Table 1, entries 1-4). Nevertheless, when the temperature was set up to 90°C (Table 1, entry 5), the increasing trend of the isolated yield was dramatically decreased (only 3%). Mensurable yields were also observed with the different solvents including Dioxane, DMF and Toluene (Table 1, entries 6, 7 and 8), however, Toluene as the solvent, gave a much lower amount of conversions than that of other solvents (Table 1, entry 8).

The base often plays an important role in the Sonogashira cross-coupling reactions, different kinds of bases were then screened (Entries 10-12). As shown in the Table 1, organic bases are effective in the present catalytic system, especially TEA. However, inorganic bases are less effective and gave moderate yield of the target product. No conversion was observed in the absence of base.

With the optimized reaction conditions in hand, a variety of aryl bromides, aryltosylates and terminal alkynes have been examined for their generality. The results are summarized in Table 2 and Table 3.

**Table 2** Cat. 3 Catalyzed Sonogashira Coupling of terminal aryl alkyne **2** with aryl bromides **3** under the Optimal Conditions



Entry <sup>a</sup>	Terminal Acetylene	Substrate	Products	Time (h)	Temperature (°C)	Yield (%) <sup>b</sup>
1	2a	<b>3a</b> (Ph-Br)	<b>4a</b>	1	80	86
2 <sup>c</sup>	2a	<b>3b</b> ( <i>p</i> -OHPh-Br)	<b>4b</b>	6	85	65
3	2a	<b>3c</b> ( <i>o</i> -Me- <i>m</i> -MePh-Br)	<b>4c</b>	3	85	75
4	2a	<b>3d</b> ( <i>p</i> -CNPh-Br)	<b>4d</b>	0.7	80	89
5	2a	<b>3e</b> (2-Br-thiophene)	<b>4e</b>	1.5	80	85
6	2a	<b>3f</b> (1-Br-naphthalene)	<b>4f</b>	3	80	75
7 <sup>c</sup>	2b	<b>3b</b>	<b>4g</b>	6	85	60
8	2b	<b>3c</b>	<b>4h</b>	5	85	63
9	2b	<b>3d</b>	<b>4i</b>	1.5	80	83
10	2b	<b>3e</b>	<b>4j</b>	2	80	76
11	2b	<b>3f</b>	<b>4k</b>	4	85	65
12	2c	<b>3a</b>	<b>4l</b>	1.5	80	88
13	2c	<b>3g</b> ( <i>p</i> -CH <sub>3</sub> Ph-Br)	<b>4m</b>	2	80	74
14	2a	<b>3h</b> (2-NH <sub>2</sub> -5-Br-pyrazin)	<b>4s</b>	4.5	80	72
15	2b	<b>3h</b>	<b>4t</b>	5	80	67

<sup>a</sup> Conditions: **2** (1.2 mmol), **3** (0.8 mmol), TEA (2 equiv.), DMSO (2 mL), Cat. 3 (1.0 mol%), aerobic condition.

<sup>b</sup> Isolated yield after flash chromatography.

<sup>c</sup> Inert atmosphere.

As demonstrated in Table 2, all the reactions proceeded smoothly under the optimum reaction

conditions, and the desired products were formed in good yields (63%-89%), showing its wide substrate tolerance. Reaction of aryl bromides with electron-withdrawing substituents such as cyano (Table 2, entries 4 and 9) with phenylacetylene and 4-ethynyltoluene gave excellent yields of expected products (83%-89%), while aryl bromides with electron-donating groups such as hydroxy and methyl (Table 2, entries 2, 7 and 13) gave the corresponding coupling products in a slightly lower yield. Even sterically hindered substrates, such as 1-bromo-2,3-dimethylbenzene, were also successfully coupled in good yields (Table 2, entries 3 and 8), although a slight higher temperature and a longer reaction time were required. To our satisfaction, heterocycle, such as 2-bromothiophene and 5-bromopyrazin-2-amine (Table 2, entries 5, 10, 14 and 15) also gave good yields (67%-85%).

Since only few examples of Sonogashira cross-coupling reactions utilizing aryltosylates have been reported<sup>[8]</sup>, we next wanted to investigate the coupling of various aryltosylates with terminal alkynes. As shown in Table 3, high catalytic activity was observed in the coupling of aryltosylates possessing electron-donating groups such as fused ring (Table 3, entries 2 and 7), and 1-bromo-4-nitrobenzene (Table 3, entries 4 and 9) has electron-deficient aromatic rings also gave the corresponding coupling product under the reaction conditions identified above.

**Table 3** Cat. 3 Catalyzed Sonogashira Coupling of terminal terminal acetylenes **2** with aryltosylates **5** under the Optimal Conditions

$$\text{R}_1\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-H} + \text{R}_2\text{-C}_6\text{H}_4\text{-OTs} \xrightarrow[\text{DMSO, Et}_3\text{N, 85}^\circ\text{C}]{\text{Cat. 3}} \text{R}_1\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-C}_6\text{H}_4\text{-R}_2$$

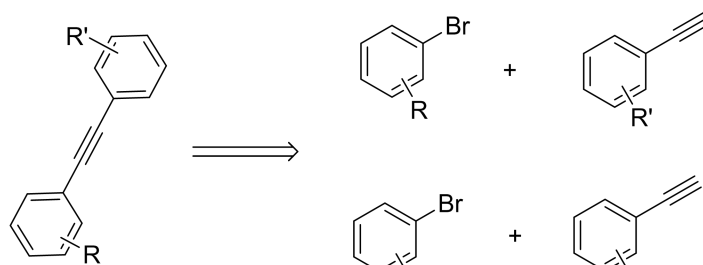
**2**     $\begin{matrix} \text{2a R}_1 = \text{H;} \\ \text{2b R}_1 = p\text{-CH}_3 \end{matrix}$     **5**    **4**

Entry <sup>a</sup>	Terminal Acetylene	Substrate	Product	Time (h)	Yield (%) <sup>b</sup>
1	2a	<b>5a</b> (Ph-OTs)	<b>4a</b>	5	82
2	2a	<b>5b</b> (1-OTs-naphthalene)	<b>4f</b>	7	73
3	2a	<b>5c</b> ( <i>p</i> -ClPh-OTs)	<b>4n</b>	5	83
4	2a	<b>5d</b> ( <i>p</i> -NO <sub>2</sub> Ph-OTs)	<b>4o</b>	4	86
5	2b	<b>5a</b>	<b>4p</b>	6	72
6	2b	<b>5e</b> ( <i>p</i> -CH <sub>3</sub> Ph-OTs)	<b>4q</b>	7	61
7	2b	<b>5b</b>	<b>4k</b>	9	60
8	2b	<b>5c</b>	<b>4r</b>	5	76
9	2b	<b>5d</b>	<b>4u</b>	5	77

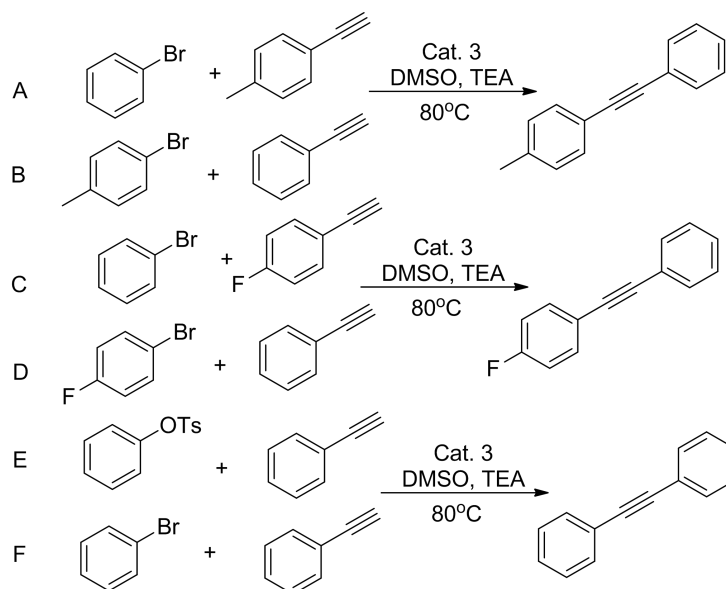
<sup>a</sup> Conditions: **2** (1.2 mmol), **5** (0.8 mmol), TEA (2 equiv.), DMSO (2 mL), Cat. 3 (1.0 mol%), aerobic condition.

<sup>b</sup> Isolated yield after flash chromatography.

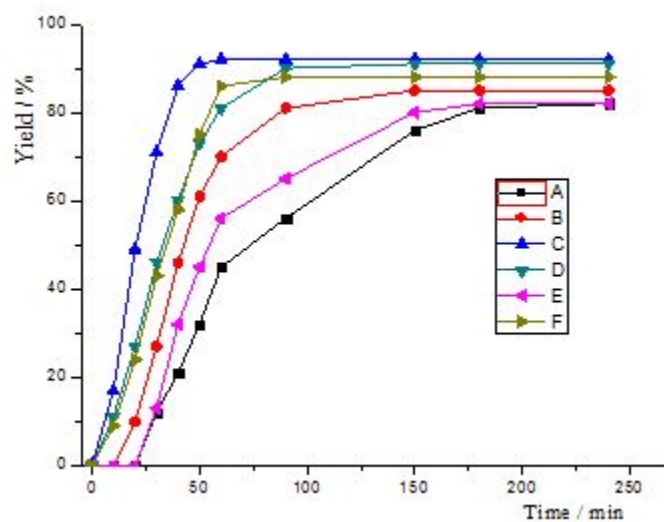
Generally speaking, the synthesis of skew symmetric tolanes can be realized by employing two different measures (Scheme 4). From a synthetic point of view it is important to ask which of the two leads to better yields when R or R' are sterically demanding or undemanding or when R or R' possess electron-releasing or -donating character.



**Scheme 4** Potential Sonogashira Routes to Tolanes



**Scheme 5** Electronic Modifications of Substrates and aryltosylates or aryl bromides for Sonogashira Coupling

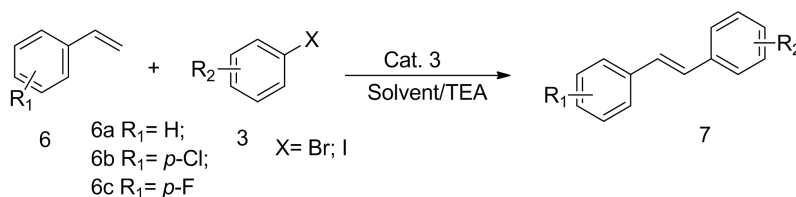


**Fig. 2** Time yield curves for the reactions of Scheme 5

In the first place, we decided to investigate which reaction (Scheme 5) would be more strongly influenced by electronic effects. As the above statement, electron withdrawing groups have an effect on increasing the reactivity of both substrates. The reaction C (Scheme 5, Fig 2) attains 71%

yield via 30 min, at the same time, while the reaction D reaches 46%. However, when the reaction time was prolonged to 90 min, both reactions acquired almost 90% yields. When the reaction B achieved 81% yield after 90 min's reaction, reaction A only exhibited 56% yield. Nonetheless, they all reached to 80% yields after 180 min reaction. For this catalyst system, the reactivity of aryl bromide is higher than that of aryltosylates. After 10 min's reaction, F only gave 9% yield, and, the reaction E has no conversion at all. For all this, they all could reach 80% yields after 150 min's reaction. Finally, the yield of reaction E is lightly lower than that of F.

**Table 4** Cat. 3 Catalyzed Heck Coupling of terminal olefins **6** and aryl bromides **3** under the Optimal Conditions



Entry <sup>a</sup>	Terminal Olefin	Substrate	Products	Time (h)	Yield (%) <sup>b</sup>
1	<b>6a</b>	<b>3a</b>	<b>7a</b>	8	75
2 <sup>c</sup>	<b>6a</b>	<b>3b</b>	<b>7b</b>	16	28
		<b>3k</b> ( <i>p</i> -OHPh-I)		12	62
3	<b>6a</b>	<b>3h</b> ( <i>p</i> -OCH <sub>3</sub> Ph-Br)	<b>7c</b>	24	32
		<b>3l</b> ( <i>p</i> -OCH <sub>3</sub> Ph-I)		15	60
4	<b>6a</b>	<b>3g</b>	<b>7d</b>	10	67
5	<b>6a</b>	<b>3i</b> ( <i>p</i> -ClPh-Br)	<b>7e</b>	8	79
6	<b>6a</b>	<b>3j</b> ( <i>m</i> -FPh-Br)	<b>7f</b>	10	77
7	<b>6b</b>	<b>3h</b>	<b>7g</b>	13	57
8	<b>6b</b>	<b>3i</b>	<b>7h</b>	7	80
9	<b>6b</b>	<b>3j</b>	<b>7i</b>	9	80
10	<b>6c</b>	<b>3h</b>	<b>7j</b>	20	34
		<b>3l</b>		14	62
11	<b>6c</b>	<b>3g</b>	<b>7k</b>	12	73
12	<b>6c</b>	<b>3a</b>	<b>7l</b>	8	78
13	<b>6c</b>	<b>3j</b>	<b>7m</b>	9	81
14	<b>6c</b>	<b>3i</b>	<b>7n</b>	7	85

<sup>a</sup> Conditions: **6** (1.2 mmol), **3** (0.8 mmol), TEA (2 equiv.), Dioxane (2 mL), Cat. 3 (1.0 mol%), aerobic condition.

<sup>b</sup> Isolated yield after flash chromatography.

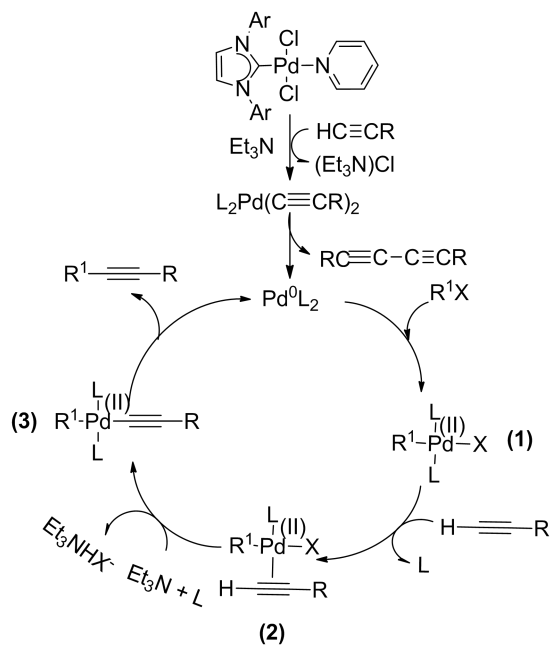
<sup>c</sup> DMF (2mL), Inert atmosphere.

Encouraged by the achievements in the Suzuki and Sonogashira reactions, we further tested the catalytic activity of Cat. 3 in the Heck reactions using various aryl bromides and terminal olefins as substrates. The results of the Heck reactions were summarized in the Table 4. Taking bromobenzene and styrene as substrates, Cat. 3 at a loading of 1.0 mol% afforded 75% yield (Table 4, entry 1). For bromobenzene with electron-withdrawing groups, including -F, -Cl, the reaction proceeded smoothly and 77-85% yields of the corresponding coupling product were



acquired. However, for bromobenzene with an electron-rich group, such as -OCH<sub>3</sub>, -OH, -CH<sub>3</sub>, the reaction proceeded much slower, and only 57-73% yields were obtained.

We proposed a plausible mechanism for this Cat. 3 mediated Sonogashira and Heck coupling reactions (Scheme 6). The Pd(0) species could be generated readily from the reaction of Cat. 3 with substrates, ligands, and TEA<sup>2a, 4, 9e, 14</sup>, and, followed by the oxidative addition of Pd(0) with R<sup>1</sup>X to form intermediate (1). On account of alkalinity of TEA is feeble, the acetylene is not able to deprotonation, therefore, acetylene and Pd complex form intermediate (2), which was further involved in the typical catalytic cycle of Sonogashira coupling reaction. The mechanism is also suitable for Heck cross-coupling reactions.



**Scheme 6** Proposed mechanism for Sonogashira reactions catalyzed by Cat. 3

In summary, the NHC-Pd complex featured with air-insensitivity, was proved to be a highly efficient catalyst for the Suzuki, Sonogashira and Heck coupling reactions. In a simple one-pot procedure free of co-catalyst, this complex is available for a wide range of substrates under mild conditions with good to excellent product yields and a low catalyst loading.

## Acknowledgements

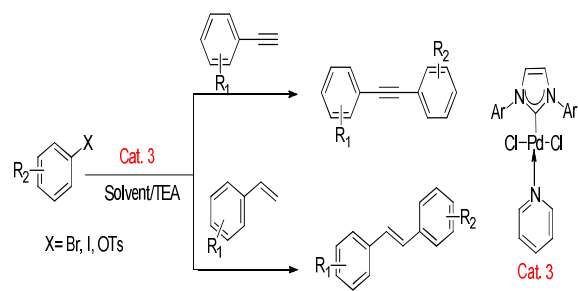
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## GRAPHICAL ABSTRACT



The catalytic reactions proceed with good yields with a low catalyst loading (1 mol%) under aerobic and CuI-free conditions for Sonogashira and Heck reactions.