# N-Heterocyclic NCN-Pincer Palladium Complexes: A Source for General, Highly Efficient Catalysts in Heck, Suzuki, and Sonogashira Coupling Reactions

Fátima Churruca, Raul SanMartin,\* Imanol Tellitu, Esther Domínguez\*

Kimika Organikoa II Saila, Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea, P.O. Box 644, 48080 Bilbao, Spain Fax +34(94)6012748; E-mail: qopsafar@lg.ehu.es

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Abstract: Readily available NCN-pincer palladium complexes comprising two pyrazole units as the source of both N-donor atoms are successfully employed as catalysts in a range of C–C bondforming reactions. Good to excellent results are obtained in all cases regardless of the electronic nature of the substrates, along with more convenient procedures and comparatively much lower catalysts loadings in Suzuki and Sonogashira couplings. This paper presents the first report of a Sonogashira coupling reaction by means of a NCN catalyst.

Key words: palladacycles, catalysis, pincer complexes, cross-coupling

Palladium catalysts have become the unquestionable tool of choice for the achievement of many organic transformations, and among them quite a few C–C bond-forming reactions.<sup>1</sup> Remarkable advances in terms of their catalytic activity by suitable tuning of the ligand properties have provided very effective systems for specific tasks.<sup>2</sup>

In our ongoing investigations towards the palladium-mediated construction of polyheterocyclic systems<sup>3</sup> we envisaged the assembly of new heterogeneous catalysts **1** by anchoring homogeneous palladium catalysts/ligands to solid supports (Scheme 1). As such an approach required a particularly robust metal–ligand connection we opted for NCN-pincer complexes, in which the metal–carbon  $\sigma$ bond, aided by two coordinating N-donor atoms would afford the necessary thermal stability to avoid significant disassociation (leaching).<sup>4</sup> However, this approach was not devoid of risks, since unlike other palladacycles<sup>5</sup> including CNC-, PCP-, and SCS-pincer complexes,<sup>6</sup> the use Table 1 Heck Coupling of Aryl Bromides

R <sup>1</sup>	Br +	$R^{2} = \frac{2 (10^{-1} \text{ mol}\% \text{ Pd})}{K_{2} \text{CO}_{3}, \text{ DMF}}$ 140 °C, 18 h	R <sup>1</sup>	R <sup>2</sup>
Entry	$\mathbb{R}^1$	R <sup>2</sup>	<b>2</b> <sup>a</sup>	Yield (%) <sup>b</sup>
1	Н	СООМе	2a	>99 (100)
2	Н	COOMe	2b	>99 (100)
3	Н	Ph	2a	98 (99)
4	Н	Ph	2b	>99 (100)
5	Ac	COOMe	2a	81 (82)
6	Ac	COOMe	2b	86 (86)
7	F	COOMe	2a	86 (88)
8	F	СООМе	2b	96 (98)

<sup>a</sup> Reaction conditions: ArBr (1 mmol), alkene (1.5 mmol), Na<sub>2</sub>CO<sub>3</sub> (2 mmol), DMF (1 mL), 140 °C.

<sup>b</sup> Determined by NMR spectroscopy on the basis of the amount of starting ArBr. Bis(ethylene glycol) dimethyl ether was used as internal standard. The conversion is displayed in parenthesis. Only *E*-diastereoisomers were detected in all cases.

of NCN-pincers and, to be precise, those comprising two heterocyclic units as the source of both N-donor atoms as catalysts in Suzuki, Heck, or Sonogashira coupling reactions, has been scarce or non-existent.<sup>7</sup> The pioneering work on the synthesis of structurally related complexes



Scheme 1

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#### Scheme 2

bearing no *para*-functionalization made by Steel et al.<sup>8</sup> and a recent report about unconventional routes for ligand introduction for the preparation of other NCN catalysts<sup>4f</sup> finally encouraged us to execute the synthesis outlined in Scheme 1.

Although still far from our overall aim, the synthesis of 1, we wish to report excellent preliminary results obtained with intermediate palladacyclic systems **2a** and **2b** which were employed as homogeneous catalysts of general application to fundamental C–C bond forming reactions.

The synthesis of catalysts 2a and 2b was performed as described in Scheme 2. Nucleophilic substitution<sup>9</sup> by pyrazoles 4a and 4b with readily available dibromide  $3^{10}$  provided ligands 5a and 5b, which were palladated by means of the procedure reported by Steel et al.<sup>8</sup>

Before continuing with our programmed heterogenization sequence, the catalytic activity of the so-formed palladacycles **2a** and **2b**<sup>11</sup> was tested by a series of Heck reaction assays performed under standard conditions<sup>12</sup> (Na<sub>2</sub>CO<sub>3</sub>, DMF, 140 °C, 18 h) with several alkenes and aryl bromides. Good to excellent yields were obtained in all cases (Table 1), with moderate turnover numbers (TONs) up to 71000 (e.g. 71% yield of *E*-methyl cinnamate when 0.01 mol% Pd was employed) in some preliminary experiments.

Encouraged by such promising results, our attention was then focused on the Suzuki cross-coupling reaction. After a more comprehensive study of different conditions,<sup>13</sup> it turned out that the best results were obtained when the reaction was carried out in neat water<sup>14</sup> (0.1 mol% **2a** or

### Table 2 Suzuki Coupling of Aryl Bromides

$R^{1} \xrightarrow{\text{Br}} R^{2} \xrightarrow{\text{B(OH)}_{2}} \frac{2 (10^{-1} \text{ mol}\% \text{ Pd})}{K_{2}\text{CO}_{3}, H_{2}\text{O}} R^{1} \xrightarrow{\text{R}^{2}} R^{2}$ 100 °C, 2 h								
Entry	R <sup>1</sup>	R <sup>2</sup>	<b>2</b> <sup>a</sup>	Yield (%) <sup>b</sup>				
1	Ac	Н	2a	>99 (100)				
2	Ac	Н	<b>2a</b> <sup>c</sup>	>99 (100)				
3	Ac	Н	2b	>99 (100)				
4	F	Н	2a	>99 (100)				
5	F	Н	2b	>99 (100)				
6	Н	Н	2a	>99 (100)				
7	Н	Н	2b	>99 (100)				
8	Me	Н	2a	>99 (100)				
9	Me	Н	2b	92 (92)				
10	OMe	Н	2a	94 (94)				
11	OMe	Н	2b	93 (93)				
12	Ac	OMe	2a	>99 (100)				
13	Ac	OMe	2b	>99 (100)				

<sup>a</sup> Reaction conditions: ArBr (1 mmol), ArB(OH)<sub>2</sub> (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol), H<sub>2</sub>O (1 mL), 100 °C.

<sup>b</sup> Determined by NMR spectroscopy on the basis of the amount of starting ArBr. Bis(ethylene glycol) dimethyl ether was used as internal standard. The conversion is displayed in parenthesis.

 $^{\circ}$  Reaction conditions: ArBr (1 mmol), PhB(OH)<sub>2</sub> (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol), toluene (2 mL), 130  $^{\circ}$ C, 6 h.

**2b**,  $K_2CO_3$ ,  $H_2O$ , 100 °C, 2 h)<sup>15</sup> which could be tentatively attributed to the relatively high solubility of catalysts **2** in water at such temperature (slightly higher than in other organic solvents or solvent mixtures).

As shown in Table 2, the excellent, and in most cases quantitative, yields achieved from several electronically divergent aryl bromides (bearing electron-withdrawing, neutral, and electron-donating substituents) and arylboronic acids reveal the general applicability of pincer complexes **2a** and **2b** to Suzuki–Miyaura biaryl coupling. Although further assays must be performed to establish the minimum amount of catalyst required, TONs up to 8,600,000 have been achieved for catalyst **2a** in the reaction between bromobenzene and phenylboronic acid (86% yield and 100% conversion were obtained with  $10^{-5}$ % Pd, TOF = 1433333).

In addition, the use of water as a solvent, apart from the advantage in terms of sustainability, provides an extremely easy work-up/purification protocol.

Only two examples of possible NCN tridentate ligands applied to Suzuki coupling have been reported so far, and in both cases lower TONs (20–100 and 177500) featured along with *t*-BuOK and DMF or toluene as base and solvents, respectively.<sup>7a,d</sup> In reality, a search in the literature revealed that the catalyst loading presented in this paper is the lowest achieved for a Suzuki–Miyaura coupling catalyzed by any pincer complex.<sup>16</sup>

The fact that the coupling reaction between alkynes and aryl halides (Sonogashira) had never been tried with a NCN-pincer complex prompted us to attempt it with catalysts **2**. After several assays, the optimized conditions (0.1 mol% **2a** or **2b**, pyrrolidine, 100 °C, 6 h),<sup>17</sup> which avoided the use of any copper co-catalyst or co-solvent, provided target aryl acetylenes in good to excellent yields (Table 3).

Although inferior to the above shown TONs in Heck and Suzuki coupling reactions, the excellent value of 80000 obtained in such copper-free Sonogashira reactions<sup>18</sup> constitutes a substantial improvement in comparison with the results provided by previously employed pincer-based catalysts.<sup>19</sup>

To sum up, two readily prepared NCN-pincer palladium complexes feature excellent homogeneous catalytic properties as their application in three of the most common palladium-catalyzed C–C bond forming reactions demonstrates (Heck, Suzuki, and Sonogashira). Good to excellent yields were observed in all cases regardless of the electronic nature of the substrates involved.

Especially remarkable are the convenient procedure and exceedingly high TON achieved in the Suzuki cross-coupling. Also this is the first Sonogashira reaction catalyzed by a NCN-pincer-type catalyst, with the additional bonus of its very low catalyst loading.

Heterogeneization of such advantageous catalysts is currently under investigation in our laboratories.

#### Table 3 Sonogashira Coupling of Aryl and Naphthyl Iodides

R <sup>1</sup> —I +	H 2 (10 <sup>-1</sup> mo pyrrolidine, 1 R <sup>2</sup>	01% Pd) 00 ℃, 6 h	$\mathbb{R}^{1}$	
Entry	<b>R</b> <sup>1</sup>	R <sup>2</sup>	<b>2</b> <sup>a</sup>	Yield $(\%)^b$
1	4-ClPh	Ph	2a	>99 (100)
2	4-ClPh	Ph	2b	>99 (100)
3	4-NO <sub>2</sub> Ph	Ph	2a	88 (98)
4	4-NO <sub>2</sub> Ph	Ph	2b	90 (100)
5	Ph	Ph	2a	92 (100)
6	Ph	Ph	2b	96 (98)
7	Naphthyl	Ph	2a	80 (82)
8	Naphthyl	Ph	2b	79 (80)
9	3-MePh	Ph	2a	91 (92)
10	3-MePh	Ph	2b	94 (94)
11	4-OMePh	Ph	2a	77 (79)
12	4-OMePh	Ph	2a	79 (80)
13	4-ClPh	<i>n</i> -Hex	2b	>99 (100)
14	4-ClPh	<i>n</i> -Hex	2b	>99 (100)

 $^{\rm a}$  Reaction conditions: ArI (1 mmol), alkyne (1.5 mmol), pyrrolidine (2 mL), 100 °C.

<sup>b</sup> Determined by NMR spectroscopy on the basis of the amount of starting ArI. Bis(ethylene glycol) dimethyl ether was used as internal standard. The conversion is displayed in parenthesis.

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152.5 (C-3'), 154.6 (C-4), 166.8 (CO). Anal. calcd for C<sub>20</sub>H<sub>23</sub>ClN<sub>4</sub>O<sub>2</sub>Pd: C, 48.70; H, 4.70; N, 11.36. Found: C, 48.74; H, 4.67; N, 11.35.

- (12) General procedure: A dry 5-mL round-bottom flask was charged with aryl bromide (1 mmol), alkene (1.5 mmol), catalyst **2** (0.001 mmol Pd), and anhyd DMF (1 mL). The mixture was stirred at 140 °C under argon for 18 h. After cooling,  $H_2O$  (10 mL) was added, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhyd Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The residue was dissolved in CDCl<sub>3</sub> and analyzed by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy [bis(ethylene glycol) dimethyl ether as an internal standard]; the identity of every product was confirmed by comparison with spectroscopic data in the literature.
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