



## Solvent-free cyclopalladation on silica gel

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### ARTICLE INFO

#### Article history:

Received 4 August 2009

Received in revised form 24 October 2009

Accepted 26 October 2009

Available online 3 November 2009

#### Keywords:

Cyclopalladated complexes

Cyclopalladation

Reactions on silica gel

Solvent-free reactions

### ABSTRACT

Tertiary, secondary and primary benzylamines, as well as structurally different oxazolines readily reacted with Pd(OAc)<sub>2</sub> on silica gel to form cyclopalladated complexes containing a five or six-membered palladacycle with a (sp<sup>2</sup>)C–Pd or (sp<sup>3</sup>)C–Pd bond. The complexes were obtained in 45–98% yield, which is comparable with or exceeds the yields reported for preparation of the same compounds in solution. Aliphatic (sp<sup>3</sup>)C–H bond activation took place in the cyclopalladation of (*S*)-2-*tert*-butyl-4-phenyl-2-oxazoline on SiO<sub>2</sub> leading to the exclusive formation of the corresponding endo palladacycle, whereas two products were reported for the same reaction performed in AcOH.

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### 1. Introduction

Silica gel's relatively inert composition and amphoteric nature make it ideal for use as a solid support in solvent-free chemical transformations [1]. There are a number of benefits to reactions performed on silica gel, including reducing the amount of solvent used, minimizing hazardous waste and, in many cases, simplified procedures. In addition, reactions carried out on SiO<sub>2</sub> often proceed with high regio- and stereoselectivity and generally under milder conditions than those in solution [2–6]. Although organic transformations on silica gel are well documented, there have been only several reports regarding metalation reactions on SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> [7–11]. Transformations of Pt(II) coordination complexes with benzophenone-derived ligands to the corresponding cycloplatinated derivatives on SiO<sub>2</sub> at 150–200 °C were studied by the Eisenberg and Kukushkin groups [7]. Formation of the (sp<sup>2</sup>)C–Ru and (sp<sup>2</sup>)C–Pd bonds on SiO<sub>2</sub> at 50 and 75 °C, respectively, was reported by Chakravorty and co-workers [8,9]. Ortho-palladation of a triarylphosphite during chromatographic purification on aluminum oxide was reported by Tune and Werner [10]. Most recently, the Dunina group reported preparation of a *C,N*-palladacycle on SiO<sub>2</sub> [11] using our general procedure reported at the ACS conference [12].

Our group's research has been focused on preparation and applications of cyclopalladated complexes. These air-stable compounds have been used as catalysts or precatalysts, chiral auxiliaries and reagents in organic synthesis [13,14]. Preparation of cyclopalladated complexes is usually accomplished by reacting

an organic preligand with a Pd(II) derivative, such as Na<sub>2</sub>PdCl<sub>4</sub> or Pd(OAc)<sub>2</sub>, in an appropriate solvent. The goal of this study was to develop a general method for the cyclopalladation of various preligands on SiO<sub>2</sub> [12]. Effect of SiO<sub>2</sub> on regioselectivity of cyclopalladation was also tested.

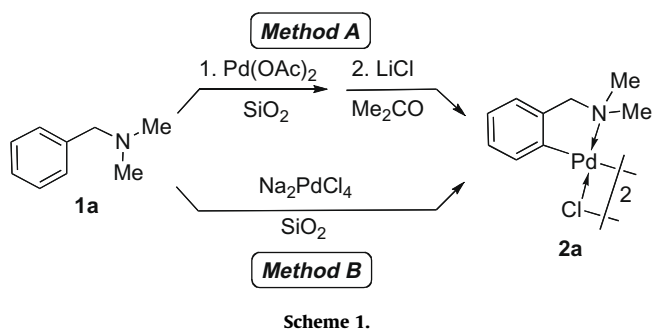
### 2. Results and discussion

The tertiary amine *N,N*-dimethylbenzylamine (**1a**) was chosen as a representative preligand to examine the conditions of cyclopalladation on SiO<sub>2</sub> (Scheme 1). This amine has been shown to undergo cyclopalladation readily in solvents, particularly using Li<sub>2</sub>PdCl<sub>4</sub> or PdCl<sub>2</sub> in MeOH at rt, to provide the cyclopalladated dinuclear complex **2a** in 96% and 68% yield, respectively [15]. In the cyclopalladation of **1a** on SiO<sub>2</sub>, palladium source, time, temperature and silica gel size were varied to determine the best parameters for cyclopalladation (Table 1). Two palladium salts, Pd(OAc)<sub>2</sub> (Method A) and Na<sub>2</sub>PdCl<sub>4</sub> (Method B), were tested. At rt, the use of the stronger palladating agent Pd(OAc)<sub>2</sub> afforded a higher yield of **2a** compared to that of Na<sub>2</sub>PdCl<sub>4</sub> (entries 3 and 6); however, at 85 °C, both methods provided comparable yields of the cyclopalladated complex (entries 1 and 4). In the case of Method A, temperature did not have an impact on the yield of product **2a** (entries 1–3, 87–92%), while in the reactions with Na<sub>2</sub>PdCl<sub>4</sub> a better yield was obtained at a higher temperature (entries 4 and 6). The time reduction from 8 h to 4 h in the reactions with Na<sub>2</sub>PdCl<sub>4</sub> at 85 °C resulted in a decreased yield of **2a** from 84% to 70% (entries 4 and 5). Increasing the reaction time in Method B at rt from 8 h to 49 h gave only a slight improvement in the yield from 59% (entry 6) to 64% (entry 7).

It is known that addition of a weak base often increases the yield of cyclopalladated complexes [16]. To check the effect of a

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**Table 1**  
Cyclopalladation of *N,N*-dimethylbenzylamine (**1a**) on silica gel<sup>a</sup>.

Entry	Method <sup>b</sup>	NaOAc addition	Time (h)	Temp. (°C)	Yield (%) <sup>c</sup>
1	A	N	8	85	87
2	A	N	8	50	88
3	A	N	8	21	92
4	B	N	8	85	84
5	B	N	4	85	70
6	B	N	8	21	59
7	B	N	49	21	64
8	B	N	8	85	88
9	B <sup>d</sup>	Y	8	85	86
10	B <sup>e</sup>	Y	8	85	90

<sup>a</sup> In all experiments, except for entries 9 and 10, the 230–400 mesh SiO<sub>2</sub> was used.

<sup>b</sup> Pd(OAc)<sub>2</sub> was used in Method A and Na<sub>2</sub>PdCl<sub>4</sub> in Method B.

<sup>c</sup> Yields are given for the products purified by column chromatography.

<sup>d</sup> The 100–200 mesh Florisil was used in this experiment.

<sup>e</sup> The 100–230 mesh SiO<sub>2</sub> was used.

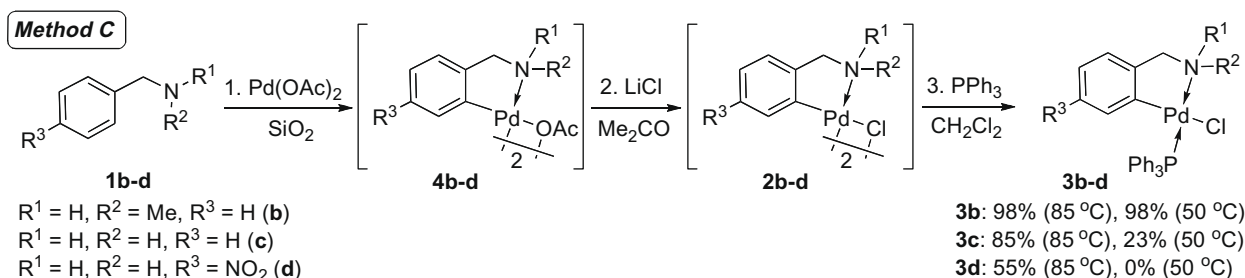
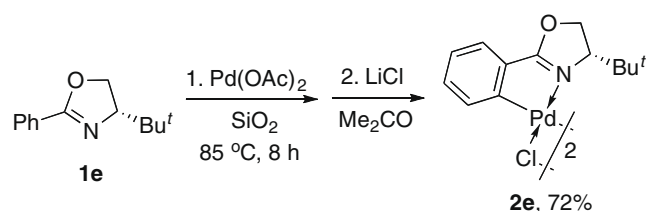
base on the reactions on SiO<sub>2</sub>, NaOAc was added to one of the reaction mixtures with Na<sub>2</sub>PdCl<sub>4</sub>. The yields of the reactions with and without the base were comparable (entries 4 and 8). There was no significant impact on the reaction yield when the 230–400 mesh silica gel used in all experiments was replaced by the 100–230 mesh SiO<sub>2</sub> or Florisil (magnesium silicate, 100–200 mesh) under the same reaction conditions (entries 8–10).

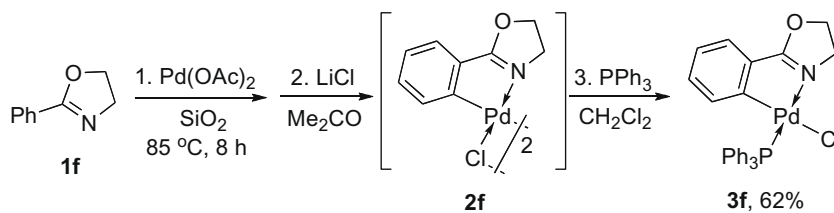
It has been shown that the cyclopalladation of secondary and especially primary amines in solution is more challenging than that of tertiary amines [16–21]. Nevertheless, the cyclopalladation of the secondary *N*-methylbenzylamine (**1b**) and two primary amines, benzylamine (**1c**) and *para*-nitrobenzylamine (**1d**), proved possible on SiO<sub>2</sub> as well. Because the dimeric Cl-bridged cyclopalladated complexes **2b–d** obtained from these amines have low solubility in common organic solvents, it was difficult to remove the products from SiO<sub>2</sub>. Instead of isolating compounds **2b–d**, they were treated with PPh<sub>3</sub> to furnish the corresponding mononuclear phosphine adducts **3b–d**, which are more soluble in solvents. All three steps of Method C – formation of the μ-OAc dimeric cyclopalladated complex on SiO<sub>2</sub>, its conversion to the μ-Cl analogs followed by the treatment with PPh<sub>3</sub> – were carried out as a one-pot reaction sequence (Scheme 2). The cyclopalladation step was accomplished on SiO<sub>2</sub> using Pd(OAc)<sub>2</sub> at 50 and 85 °C. For the PPh<sub>3</sub> adduct **3b** obtained from the secondary amine **1b**, the overall yield of the three step sequence was 98% regardless of the reaction temperature. It is noteworthy that the cyclopalladation of amine **1b** with Pd(OAc)<sub>2</sub> in benzene at 50 °C for 24 h afforded the μ-OAc dimeric complex **4b** in 89% yield, conversion of **4b** to the μ-Cl analog **2b** proceeded in 74% yield, and **3b** was obtained from **2b** in 90% yield [19]. In the reaction of the primary benzylamines **1c** and **1d** on SiO<sub>2</sub> at 85 °C, the yields of the final products **3c** and **3d** were 85% and 55%, respectively, while at 50 °C only 23% of **3c** was obtained and no **3d** was isolated. It is noteworthy that the cyclopalladation of amine **1c** in benzene at 60 °C furnished the μ-OAc dimer **4c** in 53% yield and the conversion of the latter to **2c** took place in 63% yield [19].

The lower yield of 55% for the preparation of **3d** on SiO<sub>2</sub> at 85 °C compared to that for **3c** was not surprising because addition of an electron-withdrawing group in the *para* position of benzylamines greatly reduces the ease of cyclopalladation [16]. It is noteworthy that the 55% yield of **3d** is nearly identical to the reported 54% yield over three steps using a conventional solvent procedure [22]. The reported cyclopalladation of **1d** was carried out in acetone at reflux for 7 h [22].

Cyclopalladation on SiO<sub>2</sub> was also tested for oxazolines. The reaction of (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline (**1e**) with Pd(OAc)<sub>2</sub> on SiO<sub>2</sub> was carried out under the conditions of Method A at 85 °C for 8 h (Scheme 3). The final product of the two-step reaction, the cyclopalladated complex **2e**, was isolated in 72% yield. When the reaction temperature was reduced to 50 °C, the yield dropped to 57%. The literature yield for this complex was 71% over two steps using cyclopalladation in acetic acid [23].

The cyclopalladation of 2-oxazolines without a substituent at position 4 is more difficult than that of **1e** because of the absence of steric promotion [18,23–25]; however, metalation of 2-phenyl-2-oxazoline (**1f**) with Pd(OAc)<sub>2</sub> on SiO<sub>2</sub> was successful. Following Method A (85 °C, 8 h), the dimeric complex **2f** was isolated in 40% yield. However, the removal of this dimer from SiO<sub>2</sub> was difficult due to its low solubility in CH<sub>2</sub>Cl<sub>2</sub> and other common solvents. To form the more soluble PPh<sub>3</sub> adduct **3f**, Method C (85 °C, 8 h for



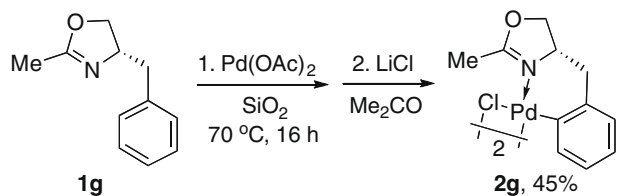


Scheme 4.

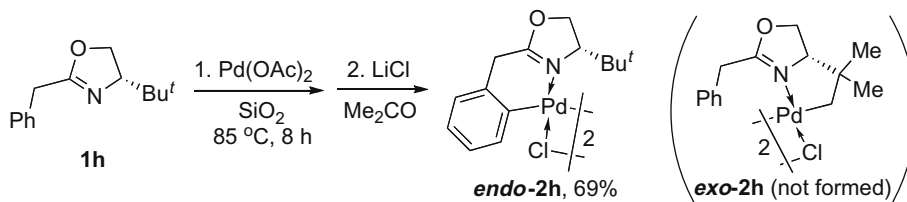
the cyclopalladation step) was also used (Scheme 4). The yield of complex **3f** was 62%, identical to the yield reported for this compound using AcOH as the solvent on the cyclopalladation step [24]. When Method C was employed at a lower temperature (50 °C, 8 h), the yield of **3f** dropped to 16% as it was observed for the primary amines **1c** and **1d**.

It is known that metalation of imines to form complexes of the exo structure, i.e. with the C=N bond in the exo position in respect to the palladacycle, is challenging [26–28]. To check whether exo palladacycles could be formed in the reactions on SiO<sub>2</sub>, oxazoline **1g** was used. The dimeric complex **2g** with a six-membered exo palladacycle was synthesized by Method A in 45% yield (Scheme 5). The lower yield compared to the reported 79% in solution (for the two-step synthesis of **2g** using reflux in MeCN for 3.5 h in the cyclopalladation step) can be partially attributed to the instability of the exo complex **2g**, which decomposes quite readily upon standing at rt [26].

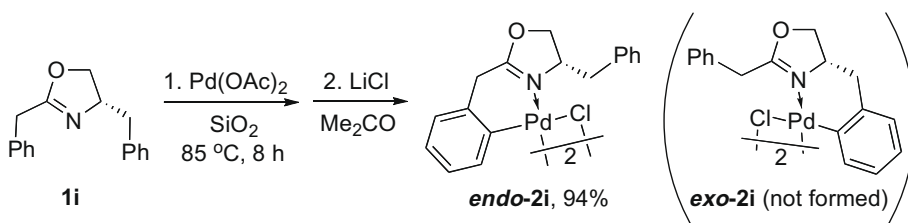
Cyclopalladation of (*S*)-2-benzyl-4-*tert*-butyl-2-oxazoline (**1h**) on SiO<sub>2</sub> provided a six-membered complex of the endo structure (**endo-2h**), i.e. with the C=N bond inside of the palladacycle (Scheme 6). The yield of the complex was 69%, this is higher than



Scheme 5.



Scheme 6.

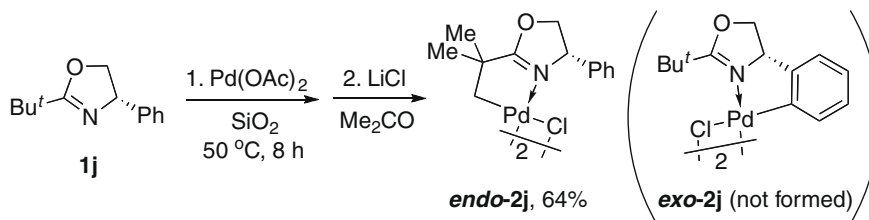


Scheme 7.

60% reported for the cyclopalladation of oxazoline **1h** in MeCN at 76 °C for 20 h [26]. In this reaction, the formation of another compound with the C=N bond in the exo position in respect to the palladacycle containing the (sp<sup>3</sup>)C–Pd bond (**exo-2h**) was possible, but was not observed either on SiO<sub>2</sub> or in solution [26]. This experiment demonstrated that on SiO<sub>2</sub>, as in solution, the (sp<sup>2</sup>)C–H bond activation with the formation of a six-membered endo palladacycle is favored over the alternative (sp<sup>3</sup>)C–H bond activation leading to a five-membered exo palladacycle.

Regioselectivity of cyclopalladation on SiO<sub>2</sub> was also studied using oxazolines **1i** and **1j**. The preligand (*S*)-2,4-dibenzyl-2-oxazoline **1i** can react to form two different six-membered palladacycles, **endo-2i** and **exo-2i**. The cyclopalladation of **1i** in solution resulted in the exclusive formation of the endo isomer (70% in AcOH, 80 °C, 3.5 h; 49% in MeCN, 78 °C, 3 h; 39% in CH<sub>2</sub>Cl<sub>2</sub>, rt, 24 h) [26]. The complete regioselectivity was also observed in the reaction of this preligand with Pd(OAc)<sub>2</sub> on SiO<sub>2</sub> (Method A, Scheme 7). The yield of **endo-2i** in the reaction performed at 85 °C was 94%. When the reaction temperature was reduced to 50 °C, the yield of the product dropped to 58%. The data obtained for this oxazoline demonstrated the preference of endo metalation over exo in reactions carried out on SiO<sub>2</sub>.

A remarkable result was obtained in the reaction of (*S*)-2-*tert*-butyl-4-phenyl-2-oxazoline **1j**. This ligand can undergo metalation to form an endo palladacycle with the (sp<sup>3</sup>)C–Pd bond (**endo-2j**) and an exo palladacycle with the (sp<sup>2</sup>)C–Pd bond (**exo-2j**). It is well known that, in general, activation of aromatic (sp<sup>2</sup>)C–H bonds proceeds more easily than that of aliphatic (sp<sup>3</sup>)C–H bonds [29]. On the other hand, exclusive or predominant formation of endo palladacycles over exo isomers in solutions has been well documented for imines and oxazolines [30–34]. It was found that oxazoline **1j** reacted with Pd(OAc)<sub>2</sub> on SiO<sub>2</sub> followed by treatment with LiCl to



Scheme 8.

form exclusively **endo-2j** in 64% yield with no traces of the *exo* isomer (Scheme 8). The cyclopalladation step was carried out at 50 °C; formation of Pd black was observed at higher temperatures. For comparison, in the cyclopalladation of this preligand in AcOH at 60 °C for 12 h followed by ligand metathesis with LiCl, both complexes **endo-2j** and **exo-2j** were isolated in a 5:1 ratio in a total yield of 59% [29]. To the best of our knowledge, the formation of **endo-2j** is the first example of (sp<sup>3</sup>)C–H bond activation on SiO<sub>2</sub>. The experiment also showed that regioselectivity of cyclopalladation in solution and on SiO<sub>2</sub> can be different.

### 3. Conclusions

Solvent-free cyclopalladation of tertiary, secondary and primary benzylamines, as well as several 2,4-disubstituted 2-oxazolines with Pd(OAc)<sub>2</sub> readily occurs on SiO<sub>2</sub>. The study showed that not only aromatic (sp<sup>2</sup>)C–H but also aliphatic (sp<sup>3</sup>)C–H bond activation can take place on SiO<sub>2</sub>. The developed general methods for cyclopalladation on SiO<sub>2</sub> are complementary to conventional procedures in solution and can be used for isolating cyclopalladated complexes either in a dimeric or a mononuclear form. It was also demonstrated that reactions on SiO<sub>2</sub> could be used to vary regioselectivity of metalation.

### 4. Experimental

#### 4.1. General

<sup>1</sup>H and <sup>13</sup>C NMR spectra (500 and 125 MHz, respectively) were recorded in CDCl<sub>3</sub> using TMS as the internal standard. Measurements were taken on an AVANCE 500 Bruker NMR spectrometer. Analytical TLC was performed using Merck precoated 0.2 mm plates of silica gel 60 F254. Melting points were measured using a Mel-Temp apparatus. The 230–400 and 100–230 mesh SiO<sub>2</sub> was purchased from Natland International Corporation unless otherwise specified. Florisil, 100–200 mesh, benzylamines, Pd(OAc)<sub>2</sub> and 2-phenyl-2-oxazoline were purchased from Sigma-Aldrich Co. Prior to use, Pd(OAc)<sub>2</sub> was dissolved in hot benzene, filtered, then the solvent was removed under reduced pressure. Benzylamines were distilled over KOH. HPLC-grade acetone was used as purchased. CH<sub>2</sub>Cl<sub>2</sub> and other solvents were distilled over CaH<sub>2</sub> prior to use.

#### 4.2. Synthesis of preligands

(*S*)-*tert*-Butyl-2-phenyl-2-oxazoline (**1e**) was synthesized from benzonitrile and (*S*)-leucinol using a published procedure for other oxazolines [35]. (*S*)-4-Benzyl-2-methyl-2-oxazoline (**1f**) was prepared from *L*-alaninol and ethylacetimidate hydrochloride according to a published method [26]. (*S*)-2-Benzyl-4-*tert*-butyl-2-oxazoline (**1h**) was obtained from phenylacetone nitrile and (*S*)-*tert*-leucinol as described in the literature [27]. (*S*)-2,4-Dibenzyl-2-oxazoline (**1i**) was synthesized from phenylacetone nitrile and *L*-phenylalaninol according to a reported procedure [28]. (*S*)-2-*tert*-Butyl-4-phenyl-2-oxazoline (**1j**) was obtained in two steps

from pivaloyl chloride and (*S*)-2-phenylglycinol as described in the literature [30].

#### 4.3. Synthesis of Cl-bridged dimeric cyclopalladated complexes using Pd(OAc)<sub>2</sub> on SiO<sub>2</sub> (Method A)

##### 4.3.1. General procedure

Pd(OAc)<sub>2</sub> (72.5 mg, 0.323 mmol), preligand (0.325 mmol), SiO<sub>2</sub> (0.121 g; 3:8 ratio of the 230–400 mesh SiO<sub>2</sub> in g per preligand in mmol) and 1 mL of CH<sub>2</sub>Cl<sub>2</sub> were mixed together in a vial. The slurry was stirred for 1 min, and then the solvent was completely removed under reduced pressure at rt. The vial was fitted with a rubber septum cap and a 1 mL syringe packed with CaCl<sub>2</sub>. The reaction vial was placed on a hot oil bath to stir for 8 h at 85 °C unless otherwise noted. The crude μ-OAc dimer was washed from SiO<sub>2</sub> by adding CH<sub>2</sub>Cl<sub>2</sub> followed by filtration. CH<sub>2</sub>Cl<sub>2</sub> was then removed under reduced pressure, after which a saturated solution of LiCl in acetone (11 mg/mL) (3.0 mL, 0.78 mmol) was added to the dark brown residue. After stirring the reaction mixture for 15 min, the solvent was removed. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the solution was filtered through Celite to remove excess LiCl. The crude product was isolated as a yellow solid after solvent removal. Recrystallization or column chromatography was required in most cases.

The following compounds were obtained using Method A: di-μ-chlorobis-[2-[(*N,N*-dimethylamino)methyl]phenyl-C<sup>1</sup>,*N*]dipalladium(II) (**2a**, yield 88%, mp 185–187 °C (dec.), lit. data: mp 185–188 and 183–185 °C (dec.) [15]), (*S,S*)-di-μ-chlorobis-[2-(4-*tert*-butyl-2-oxazolin-2-yl)phenyl-C<sup>1</sup>,*N*]dipalladium(II) (**2e**, yield 72%, mp 212–213 °C, lit. data: mp 212–212.5 °C [23]), (*S,S*)-di-μ-chlorobis-[2-[(2-methyl-2-oxazolin-4-yl)methyl]phenyl-C<sup>1</sup>,*N*]dipalladium(II) (**2g**, the cyclopalladation step: 70 °C, 16 h; yield 45%, mp 198–200 °C (dec.), lit. data: mp 198–220 °C (dec.) [26]), (*S,S*)-di-μ-chlorobis-[2-[(4-*tert*-butyl-2-oxazolin-4-yl)methyl]phenyl-C<sup>1</sup>,*N*]dipalladium(II) (**endo-2h**, yield 69%, mp 143–145 °C (dec.), lit. data: mp 143 °C (dec.) [26]), (*S,S*)-di-μ-chlorobis-[2-[(4-benzyl-2-oxazolin-2-yl)methyl]phenyl-C<sup>1</sup>,*N*]dipalladium(II) (**endo-2i**, yield 94%, mp 135–136 °C (dec.), lit. data: mp 134–137 °C [26]), (*S,S*)-di-μ-chlorobis-[2-methyl-2-(4-phenyl-2-oxazolin-2-yl)propyl-C<sup>1</sup>,*N*]dipalladium(II) (**endo-2j**, the cyclopalladation step: 50 °C, 8 h; yield 64%, mp 179–180 °C (dec.), lit. data: mp 180 °C (dec.) [30]). The <sup>1</sup>H NMR data obtained for complexes **2a**, **2e**, **2g**, **endo-2h**, **endo-2i** and **endo-2j** were identical to those reported for these compounds [15,23,26,30].

#### 4.4. Synthesis of Cl-bridged cyclopalladated complexes using Na<sub>2</sub>PdCl<sub>4</sub> on SiO<sub>2</sub> (Method B)

##### 4.4.1. General procedure

Na<sub>2</sub>PdCl<sub>4</sub> (93.0 mg, 0.316 mmol), preligand (0.316 mmol), SiO<sub>2</sub> (0.118 g; 3:8 ratio of the 230–400 mesh SiO<sub>2</sub> in g per preligand in mmol) and 1 mL of CH<sub>2</sub>Cl<sub>2</sub> were mixed together in a vial. The slurry was stirred for 1 min, and then the solvent was completely



removed under reduced pressure. The vial was fitted with a rubber septum cap and a 1 mL syringe packed with CaCl<sub>2</sub>. The reaction vial was placed on a hot oil bath to stir for 8 h at 85 °C unless otherwise noted. The crude  $\mu$ -Cl dimer was washed from SiO<sub>2</sub> by adding CH<sub>2</sub>Cl<sub>2</sub> followed by filtration. CH<sub>2</sub>Cl<sub>2</sub> was then removed under reduced pressure. The crude product was isolated as a yellow solid after solvent removal.

Using Method B, complex **2a** was obtained in 84% yield.

#### 4.5. Synthesis of PPh<sub>3</sub> adducts (Method C)

##### 4.5.1. General procedure

Pd(OAc)<sub>2</sub> (94.4 mg, 0.420 mmol), preligand (0.422 mmol), SiO<sub>2</sub> (0.158 g; 0.375 g of SiO<sub>2</sub> per 1.00 mmol of preligand) and 1 mL of CH<sub>2</sub>Cl<sub>2</sub> were mixed together in a vial. The slurry was stirred for 1 min, and then the solvent was completely removed under reduced pressure. The vial was fitted with a rubber septum cap and a 1 mL syringe packed with CaCl<sub>2</sub>. The reaction vial was placed on a hot oil bath to stir for 8 h at 85 °C unless otherwise noted. A saturated solution of LiCl in acetone (11 mg/mL) (1.8 mL, 0.47 mmol) was added directly to the reaction vial and stirred for 30 min, after which the solvent was removed. CH<sub>2</sub>Cl<sub>2</sub> was added, along with 1 M equiv. of PPh<sub>3</sub> relative to Pd(OAc)<sub>2</sub> (110 mg, 0.420 mmol). The reaction mixture was stirred at rt for 24 h and then CH<sub>2</sub>Cl<sub>2</sub> was removed. The dry residue was washed with hexane to remove excess PPh<sub>3</sub> and then dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The solution was passed through a frit packed with Celite (1.5 cm × 2.5 cm). After solvent removal, the crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane.

The following complexes were synthesized using Method C: chloro-[2-[(*N*-methylamino)methyl]phenyl-*C*<sup>1</sup>,*N*](triphenylphosphine-*P*)palladium(II) (**3b**, yield 98%, mp 124–125 °C (dec.), lit. data: mp 124 °C (dec.) [19]), chloro-[2-(aminomethyl)phenyl-*C*<sup>1</sup>,*N*](triphenylphosphine-*P*)palladium(II) (**3c**, yield 85%, mp 176–180 °C (dec.), lit. data: mp 183 °C (dec.) [19]), chloro-[1-(aminomethyl)-4-nitrophenyl-*C*<sup>2</sup>,*N*](triphenylphosphine-*P*)palladium(II) (**3d**, yield 55%, mp 205–206 °C (dec.), lit. data: mp 210 °C (dec.) [22]), chloro-[2-(2-oxazolin-2-yl)phenyl-*C*<sup>1</sup>,*N*](triphenylphosphine-*P*)palladium(II) (**3f**, yield 62%, mp 150–152 °C (dec.), lit. data: mp 150–152 °C (dec.) [24]). The <sup>1</sup>H NMR data obtained for complexes **3b–d** and **3f** were identical to those reported for these compounds [19,22,24].

#### Acknowledgements

The authors greatly appreciate financial support from ND EPSCoR through NSF Grant No. EPS-0447679.

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