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Palladium nanomaterials in catalytic intramolecular C–H amination reactions†

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Cite this: Chem. Commun., 2014, 50, 9049

Received 11th May 2014, Accepted 9th June 2014

DOI: 10.1039/c4cc03551h

www.rsc.org/chemcomm

Supported palladium nanomaterials catalyzed an intramolecular C-H amination reaction to produce carbazoles in moderate to excellent isolated yields, up to 92%.

The predominance of C-N bonds in various nitrogen-containing natural products and therapeutically important drug molecules has driven the development of new C-N bond forming methodologies.¹ Methods for C-N bond formation range from classical transformations such as reductive carbonyl amination² to newer amination methods, including hydroamination of olefins³ and alkynes,^{3a,4} allylic amination,5 alcohol amination6 and Buchwald-Hartwig C-N bond coupling processes.7 In recent years, Pd-catalyzed C-H amination has emerged as an efficient synthetic method for the construction of C-N bonds.8-12 These homogeneous systems have accomplished both inter-^{10c,d,12} as well as intramolecular^{8,9,10a,b,11} amination via activation of the C-H bond. The use of heterogeneous catalysts such as Pd nanomaterials in these C-H amination reactions have yet to be reported in the literature. The large surface-tovolume ratio of the Pd nanoparticles would make them attractive as catalysts.¹³ Herein, we report our results on the efficient intramolecular C-N bond formation via C-H activation to carbazoles catalyzed by supported Pd nanomaterials.

Eight different types of supported palladium nanomaterials were prepared *via* solution methods¹⁴ (see ESI[†]). The size and morphology of the Pd nanoparticles depended on the preparative method as well as the support used in the synthesis, as shown in the transmission electron microscopy (TEM) images of the Pd nanomaterials (ESI,[†] Fig. S1). For the Ag–Pd, Ag@Pd and Ag₂S@Pd nanomaterials (ESI,[†] Fig. S1a–c), the Pd nanomaterials were first synthesized in solution prior to their deposition onto the carbon support. Thus, the morphology and size of these spherical nanomaterials were well controlled. The particle diameters were in the range of 6–10 nm for

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Ag–Pd and Ag@Pd nanomaterials, and 10–12 nm for Ag₂S@Pd nanomaterials. For the Pd nanomaterials, Pd/C, Pd/CeO₂, Pd/TiO₂, Pd/Al₂O₃ and Pd/SiO₂ (ESI,† Fig. S1d–h), the Pd nanoparticles were synthesized in solution in the presence of the support. In these cases, the Pd nanoparticles have irregular morphology and a broader size distribution of 2–5 nm for Pd/C and Pd/CeO₂, 10–15 nm for Pd/TiO₂ and Pd/Al₂O₃, and 10–35 nm for Pd/SiO₂.

The eight supported palladium nanomaterials were investigated for their catalytic activities in the intramolecular C–H amination reaction with the model substrate 2-acetaminobiphenyl in the presence of 4 Å molecular sieves in dimethyl sulfoxide (DMSO) (Table 1, entries 1–8). With a catalyst loading of 5 mol% Pd and a reaction time of 37 h at 120 °C using O₂ gas as the oxidant, the Pd/C nanomaterial displayed the highest activity, giving the desired carbazole product in 92% isolated yield (Table 1, entry 4). The Pd nanoparticles supported on metal oxides, *i.e.* Pd/CeO₂, Pd/TiO₂ and Pd/Al₂O₃, were also quite active and good yields of 78–86% were

Table 1 $\,$ C–N bond formation via C–H functionalization catalyzed by Pd nanomaterials $^{\rm a}$

| | | 5 mol% Pd catalyst lolecular sieves, DMSO O ₂₁ 120°C, 37 h | S ~ ~ | |
|-------|------------------------|---|-------|--------------------------------|
| | 1a | | 2a | |
| Entry | Catalyst | Pd loading (v | vt%) | $\operatorname{Yield}^{b}(\%)$ |
| 1 | Ag-Pd/C | 4.0 | | 0 |
| 2 | Ag@Pd/C | 4.0 | | 0 |
| 3 | Ag ₂ S@Pd/C | 4.0 | | 0 |
| 4 | Pd/C | 5.6 | | 92 |
| 5 | Pd/CeO_2 | 5.6 | | 86 |
| 6 | Pd/TiO ₂ | 5.6 | | 78 |
| 7 | Pd/Al_2O_3 | 5.6 | | 82 |
| 8 | Pd/SiO ₂ | 5.6 | | 53 |
| 9 | PdCl ₂ | _ | | 8 |
| 10 | $Pd(OAc)_2$ | — | | 86 |

 a Reaction conditions: Pd catalyst (5 mol%), 2-acetaminobiphenyl (0.2 mmol), 4 Å molecular sieves (0.080 g), DMSO (1.0 mL), 120 °C, under O₂, 37 h. b Isolated and unoptimized yield.

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 $[\]dagger$ Electronic supplementary information (ESI) available: Detailed experimental procedures; synthesis of Pd nanomaterials and catalytic experiments; TEM images of Pd nanomaterials; characterization of products; and ¹H and ¹³C NMR spectra of products. See DOI: 10.1039/c4cc03551h

Table 2 C-N bond formation via C-H functionalization catalyzed by Pd/Ca



^{*a*} Reaction conditions: Pd/C catalyst (5 mol%, 5.6 wt% loading of Pd), 2-acetaminobiphenyl (0.2 mmol), 4 Å molecular sieves (0.080 g), solvent (1.0 mL), 120 °C, under O₂, 37 h. ^{*b*} Isolated and unoptimized yield.

attained (Table 1, entries 5–7). A moderate yield of 53% was achieved for Pd/SiO₂ (Table 1, entry 8). On the other hand, Ag–Pd/C, Ag@Pd/C and Ag₂S@Pd/C nanomaterials were inactive for this reaction (Table 1, entries 1–3). While homogeneous PdCl₂ gave a low yield of the product (8%, Table 1, entry 9), homogeneous Pd(OAc)₂ furnished a good yield of the desired product (86%, Table 1, entry 10).

To further optimize this amination reaction, we investigated different conditions using the most active supported Pd/C nanomaterial (Tables 2 and 3). The nature of the reaction media had a profound effect on the C–H amination reaction. DMSO was found to be the best solvent (Table 2, entry 1). No product was obtained when other polar solvents (*N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA) and 1,4-dioxane) and non-polar solvent (toluene) were used (Table 2, entries 2–5).

Oxygen gas was crucial for this amination reaction (Table 3, entry 1) as it was required for the re-oxidation of the reduced Pd(0) species back to the active Pd(π) species (*vide supra*, ESI,† Scheme S1). No product was formed when the reaction mixture was heated under

argon (Table 3, entry 2) and a low yield of 10% was attained in the presence of air (Table 3, entry 3). Molecular sieves were also required as they served to remove the by-product water formed during the reaction. When the reaction was performed in the absence of molecular sieves, there was a significant reduction in the catalytic activity (15% isolated yield, Table 3, entry 4). A lower isolated yield of the product (68%) was obtained when a lower catalyst loading of 2.5 mol% Pd was used (Table 3, entry 5). Comparable yields of 85-88% were achieved when either a higher (135 °C) or a lower (110 °C) reaction temperature was applied (Table 3, entries 6 and 7). This C-H amination reaction was also insensitive to concentration effects as comparable yields of 88-90% were attained when either a higher (0.4 M) or lower (0.1 M) concentration of the reaction mixture was employed (Table 3, entries 8 and 9). The time for the C-H amination reaction catalyzed by the Pd/C nanomaterial could be shortened to 24 h by purging the DMSO solvent with O₂ prior to the reaction (Table 3, entries 10 and 11). The activity of the Pd/C catalyst was also not affected by the use of less molecular sieves (0.040 g instead of 0.080 g) in the reaction. The reaction time could even be shortened to 18 h if the reaction mixture was sonicated and the headspace was re-purged with O_2 at regular intervals (Table 3, entry 12).

With the optimized set of reaction conditions in hand, we explored the scope of this C-H amination reaction catalyzed by the Pd/C nanomaterial (Table 4). The substrates chosen for this study included electron-donating and electron-withdrawing groups on aromatic rings as well as heteroaromatic groups. This C-H amination reaction catalyzed by the Pd/C nanomaterial was amenable to a wide range of substituents with different steric and electronic properties on the ring containing the acetamide group (Table 4, substrates **1l-1q**). Good to excellent yields of 84–92% were attained when either electron-donating (-CH₃, Table 4, substrates **1l-1n**) or electron-withdrawing groups (-F or -CF₃, Table 4, substrates **10-1q**) were present at the *ortho* and/or *para* positions to the acetamide moiety.

| Table 3 | Fable 3 C-N bond formation via C-H functionalization catalyzed by Pd/C ^a | | | | | | | |
|---|---|-------------------|------------------|----------|------------------|----------------------|------------------------|--|
| $\begin{array}{c} & & \\ & & \\ & & \\ & \\ & \\ & \\ & \\ & \\ $ | | | | | | | | |
| | | | 1a | | 2a | | | |
| Entry | Pd (mol%) | Concentration (M) | Temperature (°C) | Time (h) | Atmosphere | Molecular sieves (g) | Yield ^b (%) | |
| 1 | 5.0 | 0.2 | 120 | 37 | O_2 | 0.080 | 92 | |
| 2 | 5.0 | 0.2 | 120 | 37 | Argon | 0.080 | 0 | |
| 3 | 5.0 | 0.2 | 120 | 37 | Air | 0.080 | 10 | |
| 4 | 5.0 | 0.2 | 120 | 37 | O_2 | 0 | 15 | |
| 5 | 2.5 | 0.2 | 120 | 37 | O_2 | 0.080 | 68 | |
| 6 | 5.0 | 0.2 | 110 | 37 | O_2 | 0.080 | 85 | |
| 7 | 5.0 | 0.2 | 135 | 37 | O_2 | 0.080 | 88 | |
| 8 | 5.0 | 0.4 | 120 | 37 | $\overline{O_2}$ | 0.080 | 88 | |
| 9 | 5.0 | 0.1 | 120 | 37 | $\overline{O_2}$ | 0.080 | 90 | |
| 10^{c} | 5.0 | 0.2 | 120 | 24 | $\overline{O_2}$ | 0.080 | 90 | |
| 11^c | 5.0 | 0.2 | 120 | 24 | O_2 | 0.040 | 90 | |
| 12^d | 5.0 | 0.2 | 120 | 18 | O_2 | 0.080 | 90 | |

^{*a*} Reaction conditions: Pd/C catalyst (5 mol%, 5.6 wt% loading of Pd), 2-acetaminobiphenyl (0.2 mmol), 4 Å molecular sieves, DMSO. ^{*b*} Isolated yield. ^{*c*} DMSO was purged with O_2 vigorously for 5 min prior to the reaction. ^{*d*} DMSO was purged with O_2 vigorously for 5 min prior to the reaction. The reaction mixture was sonicated for 30 s, and the headspace was re-purged with O_2 at regular intervals of 6 h during the reaction.

Table 4 Scope of C-N bond formation via C-H functionalization catalyzed by Pd/C^a

| | $5' \xrightarrow{4'}{0} 3'$ $6' \xrightarrow{1'}{1} 1$ $6 \xrightarrow{1}{0} 3$ $4'$ 3 $4'$ 3 $4'$ 3 $4'$ 3 $4'$ 3 $4'$ 3 $4'$ 3 $4'$ 3 $4'$ 3 $4'$ 3 $4'$ 3 $4'$ 3 $4'$ 3 $4'$ $4'$ 3 $4'$ $4'$ $4'$ $4'$ $4'$ $4'$ $4'$ $4'$ | NH5 mol% Pd/ Molecular sie O ₂ , 120 | C catalyst ves, DMSO C, 24 h | 2 | | |
|-------|--|---|---|------------------------|--|--|
| Entry | Product | Ar (in 1) | Ar' (in 1) | Yield ^b (%) | | |
| 1 | 2b | $4-CH_{3}-(C_{6}H_{4})$ | _ | 90 | | |
| 2 | 2c | $4 - OCH_3 - (C_6H_4)$ | _ | 78 | | |
| 3 | 2d | $4 - CF_3 - (C_6H_4)$ | _ | 34 | | |
| 4 | 2e | $4 - F - (C_6 H_4)$ | _ | 83 | | |
| 5 | 2 f | $4-t-Bu-(C_6H_4)$ | — | 87 | | |
| 6 | 2g | $6-CH_{3}-(C_{6}H_{4})$ | — | 68 | | |
| 7 | 2h | $6\text{-OCH}_3\text{-}(C_6H_4)$ | — | 58 | | |
| 8 | 2i | $6-CF_{3}-(C_{6}H_{4})$ | _ | 46 | | |
| 9 | 2j | $6 - F - (C_6 H_4)$ | _ | 64 | | |
| 10 | 2k | $5-CH_{3}-(C_{6}H_{4})$ | _ | 79 | | |
| 11 | 21 | _ | 3',5'-(CH ₃) ₂ -(C ₆ H ₂) | 84 | | |
| 12 | 2m | — | $3'-CH_3-(C_6H_3)$ | 85 | | |
| 13 | 2n | — | $5' - CH_3 - (C_6H_3)$ | 90 | | |
| 14 | 20 | _ | $5' - F - (C_6 H_3)$ | 90 | | |
| 15 | 2p | — | $5' - CF_3 - (C_6H_3)$ | 92 | | |
| 16 | 2 q | — | $3', 5'-F_2-(C_6H_2)$ | 90 | | |

^a Reaction conditions: Pd catalyst (5 mol%), substrate (0.2 mmol), 4 Å molecular sieves (0.040 g), DMSO (1.0 mL, purged with O_2 for 5 min), 120 °C, under O_2 , 24 h. ^b Isolated yield.

On the other hand, the C-H amination was more sensitive to the functional groups on the aromatic ring undergoing the substitution. The presence of a substituent, either electron-rich $(-CH_3 \text{ or } -OCH_3,$ Table 4, substrates 1g and 1h) or electron-poor (-CF₃ or -F, Table 4, substrates 1i and 1j), at the ortho position to the biaryl axis would result in some steric hindrance during the coupling reaction. Hence, lower yields of 46-68% were attained for these substrates. Good to excellent yields of 78-90% were achieved when electron-donating (-CH₃, -OCH₃ or -t-Bu, Table 4, substrates 1b, 1c and 1f) or electronwithdrawing substituents (-F, Table 4, substrate 1e) were present at the para position to the biaryl axis. However, with stronger electronwithdrawing groups such as -CF₃ (Table 4, substrate 1d), a low yield of 34% was attained. With a -CH₃ substituent at the meta position to the biaryl axis (Table 4, substrate 1k), two regioisomeric products could be obtained. In this case, the coupling reaction was controlled by steric factors, and the major carbazole product was achieved with excellent regioselectivity of 20:1 (GCMS analysis).

Heteroaromatic groups were also investigated for this C-H amination reaction (ESI,† Table S1, substrates 1r-1u). However, these substrates could not be coupled to give the desired cyclized product.

The recyclability of the Pd/C catalyst was investigated using 2-acetaminobiphenyl, 1a, as the substrate. After one successive cycle, the catalytic activity decreased by 12% (80% isolated yield of product, 2a) and after two successive cycles, the catalytic activity decreased by 50% (42% isolated yield of product, 2a). TEM analysis of the Pd/C catalyst after the amination showed that the average particle size of the Pd nanoparticles has increased to \sim 20-30 nm (ESI,† Fig. S2). This increase in size of the Pd nanoparticles could be explained by the Ostwald ripening process. During this process, the

atoms from the smaller clusters would detach and then reattach to the more stable surface of the larger clusters.¹⁵ Hence, the larger clusters would grow in size at the expense of the smaller ones. The surface chemistry of the Pd/C catalyst before and after the amination reaction was analyzed using X-ray photoelectron spectroscopy (XPS) (ESI,† Fig. S3). There was no significant change in the Pd 3d XPS peaks before and after the reaction.

To determine the active catalytic species in the C-H amination, a hot filtration test was performed. The reaction mixture was heated at 120 °C under O₂ for 4 h whereby a 37% yield of the product (as determined by GCMS analysis) was achieved. The hot reaction mixture was quickly filtered to remove the solids, and more molecular sieves were added to the filtrate. The resulting mixture was heated at 120 $^{\circ}$ C under O₂ for 14 h. The reaction proceeded further to give a final yield of 74%, indicating that the active catalyst was probably homogeneous in nature. This was further corroborated by the high catalytic activity exhibited by homogeneous Pd(OAc)₂ (Table 1, entry 10). Similar findings were also observed when the hot filtration tests were applied to the Pd/CeO₂, Pd/TiO₂ and Pd/Al₂O₃ nanocatalysts.

To determine the role of O_2 in the amination reaction, several hot filtration experiments were performed (ESI,† Fig. S4 and S5). The Pd/C catalyst, the 2-acetaminobiphenyl substrate and molecular sieves were heated at 120 °C in DMSO under O₂ for 4 h, yielding 37% of the desired product by GCMS analysis (ESI,† Fig. S4). The reaction mixture was filtered hot, followed by addition of more molecular sieves, and further heating at 120 °C for 14 h under either an O₂ or argon atmosphere. In the presence of O₂, the reaction proceeded further to give a final product yield of 74%. On the other hand, under an argon atmosphere, the reaction did not continue and the product yield remained at 37%. This set of hot filtration experiments confirmed that O2 was essential for the regeneration of the active catalyst required for the turnover of the catalytic reaction.

In another set of hot filtration experiments, the reaction mixture was first heated at 120 °C under argon for 4 h, yielding 0% of the product (ESI,† Fig. S5). The reaction mixture was then filtered hot, and allowed to continue at 120 °C for 14 h in the presence of either O2 or argon. Under an argon atmosphere, no product was obtained. However, in the presence of O2, 10% of the product was produced. Small amounts of Pd (8%) (ESI,† Table S2, entry 6) were leached into the DMSO solution when Pd/C was heated at 120 °C under argon for 4 h. The small amount of leached Pd was probably Pd nanoparticles as evidenced from their TEM image (ESI,† Fig. S6). Under an O2 atmosphere, the leached Pd nanoparticles would react with O2 and DMSO to produce soluble active Pd(II) species that would then react with the substrate to yield 10% of the product. These hot filtration experiments proved that O2 was necessary for the leaching of Pd nanoparticles to produce the catalytically active homogeneous Pd(II) species.

Inductively coupled plasma mass spectrometry (ICP-MS) analysis showed that 42% of the Pd was leached into the DMSO solution (probably as Pd-DMSO complexes) after heating the Pd/C catalyst at 120 °C under O₂ for 4 h (ESI,† Table S2, entry 1). DMSO is known to act as a ligand to expedite the redox cycling between Pd(II) and Pd(0)in oxidation reactions.¹⁶ Likewise, for the Pd/CeO₂, Pd/TiO₂, Pd/Al2O3 and Pd/SiO2 catalysts, Pd species were also leached into the DMSO solution (12-25%) (ESI,† Table S2, entries 10-13).

When DMF and DMA were used as the solvent (ESI,† Table S2, entries 2 and 3), ICP-MS analysis indicated that 5% of Pd was leached into the solution. Insignificant Pd leaching occurred when 1,4-dioxane and toluene were used as the solvent (ESI,† Table S2, entries 4 and 5). Very minor Pd leaching was detected when Ag–Pd/C, Ag@Pd/C and Ag₂S@Pd/C catalysts were used (ESI,† Table S2, entries 7–9). These results showed a correlation between the amount of Pd leached into the solution and the catalytic activity of the Pd-based nanocatalyst, further confirming the homogeneous nature of the active catalyst.

Selected Pd nanocatalysts were also subjected to XPS analysis to determine the surface oxidation state of Pd (ESI,† Fig. S7). The Pd 3d XPS spectra of Pd/C, Pd/CeO2, Ag-Pd/C and Ag2S@Pd/C could be deconvoluted into two pairs of doublets. The doublet with a higher binding energy (BE) was attributed to Pd(II), while that with a lower BE was assigned to Pd(0). The inactive Ag-Pd/C nanocomposite material contained mainly Pd(0) surface species (~91%), while the active Pd/C and Pd/CeO2 catalysts and the inactive Ag2S@Pd/C nanomaterial contained more oxidized Pd(II) surface species (~60–88%). The BEs of the Pd(II) $3d_{3/2}$ and $3d_{5/2}$ peaks for the inactive Ag₂S@Pd/C nanomaterial were shifted to lower values (336.9 and 342.1 eV), as compared to the active Pd/C and Pd/CeO₂ catalysts (337.1-337.4 eV and 342.3-342.7 eV). The presence of mainly Pd(0) surface species on Ag-Pd/C and the different types of Pd(II) surface species on Ag2S@Pd/C suggested different Pd surface species and interactions with the support might account for the dissimilar leaching behavior of these inactive nanocomposite materials, as compared to the active Pd/C and Pd/CeO₂ catalysts.

Based on these results, we propose a mechanism for the C–H amination catalyzed by the Pd/C nanomaterial (ESI,[†] Scheme S1). Soluble Pd(π) species could be leached into the solution from the surface defect sites of the Pd nanoparticles. This leaching process could be facilitated by the coordinating DMSO solvent and oxidation to Pd(π) by O₂ gas. The homogeneous Pd(π) species would then form a complex with the amide moiety of the substrate, and activate the aromatic C–H bond. Elimination of the product would generate a Pd(0) species which would re-oxidize to Pd(π) in the presence of DMSO and O₂. Ultimately, the dissolved Pd species would reattach to the existing Pd nanoparticles to form larger clusters. The different catalytic activities of the palladium nanomaterials on different supports could be attributed to the different interactions between

the support and the palladium species, impacting the leaching of the palladium species.

In conclusion, we have achieved an efficient intramolecular C–N bond formation *via* C–H activation to carbazoles catalyzed by supported Pd nanoparticles. The C–H amination catalyzed by the Pd nanoparticles most likely proceeded *via* a soluble Pd species.

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