Facet-Dependent Catalytic Activity of Palladium Nanocrystals in Tsuji–Trost Allylic Amination Reactions with Product Selectivity

Kaushik Chanda, Sourav Rej, Shu-Ya Liu, and Michael H. Huang*^[a]

Pd nanocubes, cuboctahedra, and octahedra with good size control were used to catalyze C–N bond formation in the Tsuji–Trost allylic amination reaction of aniline. Nanocubes gave either monoallylaniline or diallylaniline depending on the amount of allyl bromide used, but the octahedra and cuboctahedra only gave mixtures of monoallylaniline and diallylaniline under the same reaction conditions. The Pd nanocubes were stable over multiple cycles of the reaction. The cubes and octahedra were demonstrated to catalyze the amination reaction by using a wide variety of substituted anilines, but the cubes were the best catalyst with consistently the highest efficiency, product yield, and product selectivity. This work demonstrates that the use of metal nanocrystals with proper facet control is important for catalyzing coupling reactions with product selectivity.

Palladium nanostructures have been shown to efficiently catalyze organic coupling reactions such as the Suzuki and Sonogashira reactions.^[1-3] They are also active in catalyzing hydrogenation and formic acid oxidation reactions.^[4-14] Facet-dependent catalytic activity is a highly interesting but rarely explored direction of Pd nanocrystal research. To investigate facet-dependent catalytic activity, Pd nanoparticles with specific surface facets exposed, such as cubes and octahedra, are needed.^[15–19] Pd nanocrystals synthesized by using similar reaction conditions are most suitable for facet-dependent property studies.^[20,21] Beyond reactions involving C–C bond formation, it would be interesting to examine the facet-dependent catalytic activities of Pd nanocrystals toward new coupling reactions such as the formation of C–N bonds.^[15]

The Tsuji–Trost reaction is a Pd-catalyzed substitution reaction of a nucleophile with a substrate containing a leaving group in an allylic position under basic conditions. It has been proven to be a powerful method for the generation of substi-

[a]	Prof. K. Chanda, ⁺ S. Rej, SY. Liu, Prof. M. H. Huang Department of Chemistry and Frontier Research Center on Fundamental and Applied Science of Matter National Tsing Hua University Hsinchu 30013 (Taiwan) E-mail: hyhuang@mx.nthu.edu.tw
[+]	Present address: Organic Chemistry Division School of Advanced Science VIT University Vellore-632014 (India)
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tuted amines or alcohols with allyl groups and has broad applications in the synthesis of natural products and biologically active molecules.^[22-24] Essentially, only Pd complexes have been used to catalyze these reactions. In two reports, Pd nanoparticles were found to catalyze the allylic amination and allylation of active methylene compounds, but the nanoparticles were not well characterized.^[25,26] It would be interesting to examine facet-dependent catalytic activity of polyhedral Pd nanocrystals for Tsuji-Trost allylic amination reactions.^[27] Previously, strongly facet-dependent catalytic activities were observed in polyhedral Au and Cu₂O nanocrystals.^[28-31] In this study, uniform Pd nanocubes, cuboctahedra, and octahedra synthesized in aqueous solution were employed to catalyze the Tsuji-Trost allylic amination reaction between allyl bromide and aniline. Strongly facet-dependent catalytic activity was observed. Remarkably, the particle facet can affect product selectivity. A possible explanation for this product selectivity is given. Diverse products were synthesized from various aromatic amines by using these Pd nanocrystal catalysts.

We developed a method to directly grow Pd nanocrystals with cubic, cuboctahedral, and octahedral shapes by mixing an aqueous solution of H_2PdCl_4 , cetyltrimethylammonium chloride (CTAC), KBr, KI, and ascorbic acid at 35 °C for 30 min. Table S1 (Supporting Information) provides the exact reagent amounts used to make the Pd nanocrystals. The particles were thoroughly washed to remove the CTAC surfactant. Figure 1 shows representative SEM images of the synthesized Pd cubes, cuboctahedra, and octahedra with average edge lengths of 49, 62, and 50 nm, respectively. Good particle shape control was achieved. The size-distribution histograms of the particles are provided in Figure S1.

We considered the use of these Pd nanocrystals to catalyze Tsuji-Trost allylic amination reactions, because such C-N bondforming reactions are quite useful but are rarely explored with the use of Pd particles. Initially, an aqueous Pd nanocube solution (527 µL) was added to a mixture of allyl bromide (1.25 mmol, 3 equiv.) and aniline (0.42 mmol, 1 equiv.) in the presence of K₂CO₃ (0.83 mmol) as the base to synthesize N-allylbenzenamine (3 a) in water at 65 °C (Table 1, entry 1). After 1.5 h, the crude mixture was purified, and it indicated the formation of only N,N-diallylbenzenamine (4a) with a product yield of 100% and the absence of any other byproducts, as shown by TLC. The diagnostic resonance for the N-CH₂-CH proton in the ¹H NMR spectrum of product **4a** appears as a multiplet at $\delta = 5.84$ ppm. Similarly, the resonance for the N- CH_2 -CH carbon atom in the ¹³C NMR spectrum of **4a** appears at $\delta = 52.7$ ppm. Upon repeating the same reaction with



Figure 1. Representative SEM images of the synthesized Pd a) nanocubes, b) cuboctahedra, and c) octahedra. The scale bars are equal to 100 nm.

Table 1. Comparison of the Tsuji-Trost allylic amination reaction cata- lyzed by Pd nanocubes, cuboctahedra, and octahedra. ^[a]							
I Ia	² + Br	Pd nanopartic 65 ℃, H	les, K ₂ CO ₃	×+ () □			
Entry	1 a [equiv.]	2 [equiv.]	Catalyst	<i>T</i> [h]	3 a/4 a [%] ^[b]		
1	1	3	Pd (cubes)	1.5	0:100		
2	1	1	Pd (cubes)	1.5	80:20		
3	1	0.7	Pd (cubes)	1.0	95:0		
4	1	0.7	Pd (octahedra)	5	30:60		
5	1	0.7	Pd (cuboctahedra)	7	25:50		
[a] Reagents and conditions: 1 a (0.42 mmol), 2 (0.29 mmol), K_2CO_3 (0.83 mmol), and H_2O (2 mL). [b] Yield of isolated product.							

a time of 1.5 h and allyl bromide (1 equiv.), both **3a** and **4a** in a molar ratio of approximately 80:20 were formed (Table 1, entry 2). No other byproducts were formed. The diagnostic resonance for the NH-CH₂-CH proton in the ¹H NMR spectrum of **3a** appears as a multiplet at δ =5.90 ppm, in comparison to the chemical shift of the same proton of congener **4a** at δ = 5.84 ppm. Similarly, the resonance for the NH-CH₂-CH carbon atom in the ¹³C NMR spectrum of **3a** appears at δ =46.4 ppm, whereas the resonance for the same carbon atom appears at δ =52.7 ppm in **4a**.

To obtain 100% formation of **3***a*, a sequential reaction pathway was adopted. The same volume of Pd nanocube solution was first added to a mixture of allyl bromide (0.29 mmol, 0.7 equiv.) and K_2CO_3 (0.83 mmol) with stirring for 15 min at

room temperature, and this was followed by the introduction of aniline (0.42 mmol, 1 equiv.). The mixture was heated in an oil bath at 60°C with vigorous stirring. After 1 h, the crude product was analyzed by ¹H NMR spectroscopy and was confirmed to be 100% 3a with a product yield of 95% (Table 1, entry 3). Upon repeating the same reaction with calculated quantities of Pd octahedra and cuboctahedra (500 and 1021 µL) having the same total particle surface area, products 3a/4a were obtained in ratios of 30:60 and 25:50 after 5 and 7 h, respectively (Table 1, entries 4 and 5). TLC indicated that a mixture of 3a and 4a was still formed after a reaction time of 1.5 h by using Pd octahedra and cuboctahedra as the catalysts. Remarkably, upon using Pd nanocubes as the catalyst, exclusive formation of either 3a or 4a could be achieved simply by tuning the amount of allyl bromide introduced. This is a high level of product selectivity with practical significance. Interestingly, facet-dependent product selectivity in the formation of triazoles by using a click reaction was also observed with Au nanocrystals.[28]

The Pd nanocubes were found to have the highest turnover frequency (TOF) value of 8024 h^{-1} , compared to 1317 and 831 h^{-1} for Pd octahedra and cuboctahedra, respectively (for calculations, see the Supporting Information). The TOF is defined in Equation (1):

$$\frac{moles \ of \ products \ formed}{(moles \ of \ total \ surface \ palladium \ atoms \times reaction \ time)} \quad (1)$$

The unsaturated coordination numbers of the Pd atoms on the (100) and (111) planes are 4 and 3 respectively, so the Pd atoms on the (100) plane are more coordinately unsaturated than those on the (111) plane. This may result in quicker adsorption of allyl bromide on the (100) plane, followed by breaking of the C–Br bond to give fast formation of the π -allyl Pd complex, and then nucleophilic attack to yield 3a (see the mechanism in Figure S2). It is also important to understand why the Pd nanocubes can produce exclusively 3a, but the octahedra generate a mixture of 3a and 4a with the same reagent concentrations. The results can be understood by considering the reaction time. Pd nanocubes take 1 h to complete the reaction, whereas octahedra and cuboctahedra take 5 and 7 h, respectively. Product 3a quickly leaves the nanocube surface, such that 4a is not produced at a sufficiently low allyl bromide concentration. For octahedra and cuboctahedra, if the concentration of 3a increases with the progress of the reaction, it starts to act as a nucleophile in competition with aniline to form 4a. Owing to the fact that the reaction times for octahedra and cuboctahedra are longer than the reaction time for the nanocubes, 3a and 4a are both produced in different ratios. Cubic and cuboctahedral platinum nanoparticles have been shown to result in product selectivity toward benzene hydrogenation, and apparent activation energies have been obtained.^[32,33] It is of course useful to determine activation energies to further explain the observed catalytic activity and product selectivity of the Pd nanocrystals. However, kinetic data need to be obtained. Our simple experimental design is not equipped to obtain such data.



To confirm the heterogeneous nature of the Pd catalysts, additional control experiments were performed by using Pd nanocubes as the catalyst. The reaction was stopped after 30 min to give a product yield of 50%. The solution was centrifuged at 4000 rpm for 10 min, and the supernatant liquid was carefully collected. By using the supernatant liquid, the same coupling reaction was performed under the same reaction conditions. After 3 h, we did not obtain any increase in the reaction product, which indicated that leaching of Pd nanocubes did not occur and that the observed catalytic activity was due to heterogeneous catalysis on the Pd particles. Leaching did not occur possibly because of relatively mild heating to remove dissolved oxygen and the short reaction time. Pd-ion leaching from the Pd nanocrystals by an oxidation reaction has been reported.^[34, 35] The recyclability of the Pd nanocube catalyst was tested by repeating the reaction two more times by using the same Pd nanocubes. Figure S3 shows that the product yield was approximately 84% after three cycles of the reaction. The product yield decreases slightly possibly due to loss of some nanocubes during product extraction. Figure S4 indicates that the particles still retain their cubic shape after three cycles of the Tsuji-Trost allylic amination reaction, which demonstrates that the Pd nanocrystals are effective and reusable catalysts.

The Pd nanocubes were subsequently employed as an effective catalyst to form various monosubstituted anilines from a wide variety of anilines and allyl bromide under the optimized reaction conditions for 1-1.5 h, and the results are summarized in Table 2. The corresponding monosubstituted anilines were obtained as highly regioselective products in high yields after a simple workup procedure involving extraction with organic solvent followed by evaporation. The crude products were confirmed by analysis by ¹H NMR and ¹³C NMR spectroscopy. Substituent effects of the aniline precursors were next examined. The use of substituted anilines containing electron-donating groups or electron-withdrawing groups reacted with allyl bromide under the optimized reaction conditions to afford monosubstituted anilines in high yields. Similarly, Pd octahedra were employed as the catalyst for the Tsuji-Trost allylic amination reaction, and the results are summarized in Table 3. The formation of both monosubstituted and disubstituted anilines in different ratios in good yields was observed in most cases. In two instances, only the monosubstituted products were obtained (Table 3, entries 3 and 8). However, the product yields are less than half of those achieved by using the cubic Pd catalyst (Table 2, entries 3 and 8), and the reaction time is much longer at 5 h. In both cases, the substituted groups are located in the ortho position. Thus, whereas product selectivity can be achieved in some cases for the Pd octahedra, these octahedra remain less reactive than the Pd nanocubes. This work shows the importance of facet control of Pd nanocrystals to achieve product selectivity and improve reaction efficiency.

In summary, uniform Pd nanocubes, cuboctahedra, and octahedra were employed as catalysts in a Tsuji–Trost allylic amination reaction. Pd nanocubes gave a single monosubstituted or disubstituted product in high yields simply by tuning the amount of allyl bromide used, whereas Pd octahedra and cu-



boctahedra yielded mixtures of monosubstituted and disubstituted products in different ratios. The nanocubes were found to be stable to multiple cycles of the reaction. Both the Pd cubes and the octahedra catalyzed the reaction by using a wide variety of substituted anilines in good to high yields, but the cubes were the best catalyst with the highest efficiency and exclusive product selectivity. This study demonstrates the potential of using Pd nanocrystals with facet control to achieve product selectivity and regioselectivity for other organic coupling reactions. This is an important research direction for heterogeneous catalysis.

Experimental Section

Pd nanocrystal catalyzed Tsuji–Trost allylic amination reactions

A 25 mL round-bottomed flask containing a stirrer bar was charged with allyl bromide (0.035 g, 0.29 mmol, 0.7 equiv.), K_2CO_3 (0.115 g, 0.83 mmol, 2.0 equiv.), and water (2 mL). After the mixture was stirred for 1 min at room temperature, a fixed volume of concentrated Pd nanocrystal solution was immediately added to the mixture (527 µL of nanocubes, 500 µL of octahedra, or 1021 µL of cuboctahedra with a calculated total particle surface area of 22 cm²).





Finally, aniline (0.038 g, 0.42 mmol, 1.0 equiv.) was added to the solution. Subsequently, the mixture was heated to 65 °C with stirring. The progress of the reaction was monitored by TLC. Upon completion, the mixture was centrifuged at 6000 rpm for 3 min to remove the nanocrystals and was then partitioned between ethyl acetate and water. The combined organic layer was dried with anhydrous MgSO₄. Concentration of the organic layer yielded the crude product, which was purified by column chromatography (60-120 mesh silica gel, hexane) to provide the coupling product. The same process was repeated two more times to evaluate the recyclability of the cubic catalyst. Upon completion of the reaction, the whole solution was centrifuged at 4000 rpm for 10 min, and the supernatant liquid was carefully removed from the centrifuge tube. Then, deionized water (10 mL) was added with sonication for 1 min, and the solution was centrifuged again at 4000 rpm for 10 min. After removal of water, the same amounts of reagents were added to the nanocrystals for the second cycle of the reaction. To evaluate the extent of versatility of these nanocrystal catalysts, the same C-N coupling reaction was repeated by using aromatic amines with different substituents. Pd nanocubes and octahedra were chosen as the catalysts in these reactions.

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