[Electronic Supplementary Information]

Facet-Dependent Enhanced Catalytic Activity of Pd Nanocrystals

Minjune Kim,^{†,‡,¶} Yeonjoon Kim,^{†,¶} Jong Wook Hong,^{†,¶} Seihwan Ahn,[†] Woo Youn Kim,^{*,†} and Sang Woo Han^{*,†,‡}

[†]Department of Chemistry and KI for the NanoCentury, KAIST, Daejeon 305-701, Korea [‡]Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon 305-701, Korea

*E-mail: sangwoohan@kaist.ac.kr (SWH); wooyoun@kaist.ac.kr (WYK) These authors contributed equally to this work.

1. Experimental details

1.1. Chemicals and materials

 K_2PdCl_4 (Aldrich, 98%), Na₂PdCl₄ (Aldrich, 98%), K_2PdBr_4 (Aldrich, 98%), PdCl₂ (Aldrich, 99%), Pd(PPh₃)₄ (Aldrich, 99%), L-ascorbic acid (DaeJung Chemicals & Metals Co., 99.5%), cetyltrimethylammonium chloride (CTAC, Aldrich, solution in water, 25 wt%), Pd black (Aldrich, 99.95%), and Pd/C (Aldrich, 10 wt%) were used as received without further treatments. Other chemicals, unless specified, were reagent grade. Highly purified water with a resistivity of greater than 18.0 MΩ·cm was used in the preparation of aqueous solutions.

1.2. Preparation of octahedral and cubic Pd NCs

The synthesis of octahedral and cubic Pd NCs has been done according to our previous report (J. W. Hong, S. W. Kang, B.-S. Choi, D. Kim, S. B. Lee, S. W. Han, ACS Nano 2012, 6, 2410). To synthesize octahedral NCs, 60 mg of citric acid and 60 mg of L-ascorbic acid were put into a 25 mL round-bottom flask and then the aqueous solution of CTAC (100 mM, 8 mL) was injected into the flask. The mixture was heated up to 100 °C. After 10 min, 60 mg of Na₂PdCl₄ dispersed in 3 mL of deionized water was added to the reaction mixture and then the resultant solution was stirred vigorously for 3 h at 100 °C. Then, octahedral Pd NCs were collected and washed with deionized water and acetone, and finally dispersed in toluene. To prepare cubic Pd NCs, an aqueous solution of CTAC (50 mM, 24 mL) was put into a 100 mL round-bottom flask and heated up to 100 °C. The aqueous solutions of L-ascorbic acid (100 mM, 1 mL) and K₂PdCl₄ (5 mM, 10 mL) were then added sequentially to this solution, and the resultant reaction solution was heated at 100 °C for 5 h with vigorous stirring. The synthesized cubic Pd NCs were collected and washed with deionized water and acetone twice, and finally dispersed in toluene. For the catalytic studies, the total amount of Pd in the final solution was measured accurately by using an inductively-coupled plasma-atomic emission spectrometer (ICP-AES, OPTIMA 3300DV).

1.3. Preparation of RD Pd NCs

In a typical synthesis of RD Pd NCs, an aqueous solution of KI (50 mM, 1 mL) was added to an aqueous solution of CTAC (5 mM, 5 mL). The aqueous solutions of K_2PdCl_4 (5 mM, 1 mL) and L-ascorbic acid (50 mM, 1 mL) were then added sequentially to this solution with gentle shaking. The resultant mixture was heated up to 100 °C in a conventional forcedconvection drying oven for 5 h. Then, RD Pd NCs were collected and washed with deionized water, acetone, and toluene. To properly remove the excess amount of stabilizing/capping agents, the prepared RD Pd NCs were collected by centrifugation (14,000 rpm, 5 min) right after the reaction solution was taken out from the oven. Since the temperature of reaction solution was still high, efficient removal of excess amount of stabilizing/capping agents was possible. For the catalytic studies, the total amount of Pd in the final solution was measured accurately by using the ICP-AES.

1.4. Instruments

SEM images were obtained with field-emission scanning electron microscopes (FESEM, Philips Model XL30 S FEG and Magellan 400). TEM images were collected using a JEOL JEM-2010 transmission electron microscope operated at 200 kV or a FEI Tecnai G2 F30 Super-Twin transmission electron microscope operated at 300 kV after placing a drop of the hydrosol on a carbon-coated Cu grid (300 mesh). The effective electron probe size and dwell time used in HAADF-STEM-EDS mapping experiments were 1.5 nm and 200 ms per pixel, respectively. The accurate amounts of Pd were determined by ICP-AES and inductively-coupled plasma-mass spectrometer (ICP-MS, ELAN DRC II). NMR spectra were recorded on a Bruker AVANCE 300 spectrometer in CDCl₃ (300 MHz for ¹H NMR, 75 MHz for ¹³C NMR).

1.5. Buchwald-Hartwig amination

In a standard procedure of Buchwald-Hartwig amination, potassium *tert*-butoxide (672 mg, 6 mmol) was put into an oven-dried 25 mL round-bottom flask and dried under vacuum. After N₂ charging, 7 mL of 1,4-dioxane was injected into the flask and stirred with a stirring rate of 650 rpm at 100 °C. Morpholine (525 μ L, 5 mmol) was injected into the mixture and then 1 mol% of Pd catalyst dispersed in 1 mL of 1,4-dioxane was subsequently added. Then, bromobenzene (420 μ L, 4 mmol) was injected into the reaction solution with an injection rate of 0.1 mL/10 min. The mixture was then heated at 100 °C for 24 h. All the catalytic reactions were conducted at the same temperature (100 °C) with the identical stirring rate (650 rpm). To obtain the chemical yield of product, it was extracted with ethyl acetate (5 mL × 5) after quenching the solution with 1 M HCl (2 mL) and saturated aqueous NaCl (1 mL). After evaporating the collected solution, it was purified by column chromatography using methanol and methylene chloride (1% MeOH/MC).

2. Calculations of turnover frequencies (TOFs)

2.1. Octahedral Pd NCs

To calculate TOF for the octahedral Pd NCs, the number of surface Pd atoms was calculated based on the size distribution of the octahedral Pd NCs (Fig. S1a). The details for the calculation of the number of surface atoms and TOF are given below.

The volume of an octahedral Pd NC, which has an edge length of 25.3 nm (the average edge length of the prepared octahedral Pd NCs), is $\sqrt{2}/3 \times (25.3 \text{ nm})^3 = 7.63 \times 10^3 \text{ nm}^3$. Since the known lattice constant of Pd is 0.389 nm, the volume of a unit cell is $(0.389 \text{ nm})^3 = 5.89 \times 10^2 \text{ nm}^3$. So, the total number of Pd atoms in an octahedral NC with an edge length of 25.3 nm is $(7.63 \times 10^3 \text{ nm}^3 / 5.89 \times 10^{-2} \text{ nm}^3) \times 4 = 5.18 \times 10^5$. In the same way, the total number of Pd atoms in an octahedral NC for each size range in Fig. S1a was calculated. By weighting the relative amount of Pd NCs for each size range, the average value of the total number of Pd atoms in an octahedral NC was then calculated to be 5.34×10^5 .

The edge length of triangular unit on the {111} surface of octahedral Pd NCs is 0.550 nm. The area of triangular unit is $\sqrt{3}/4 \times (0.550 \text{ nm})^2 = 1.31 \times 10^{-1} \text{ nm}^2$. Since the surface area of a triangular plane of an octahedral NC, which has an edge length of 25.3 nm, is $\sqrt{3}/4 \times (25.3 \text{ nm})^2 = 2.77 \times 10^2 \text{ nm}^2$, the surface area of an octahedral Pd NC is $(2.77 \times 10^2 \text{ nm}^2) \times 8 = 2.22 \times 10^3 \text{ nm}^2$. So the total number of surface Pd atoms on an octahedral Pd NC with an edge length of 25.3 nm is $[(2.22 \times 10^3 \text{ nm}^2) / (1.31 \times 10^{-1} \text{ nm}^2)] \times 2 = 3.39 \times 10^4$. In the same way, the total number of surface Pd atoms on an octahedral NC for each size range in Fig. S1a was calculated. By weighting the relative amount of Pd NCs for each size range, the average value of the total number of surface Pd atoms on an octahedral NC was then calculated to be 3.42×10^4 .

The total number of Pd atoms used in the coupling reactions was $(0.04 \times 10^{-3} \text{ mol}) \times (6.02 \times 10^{23} / \text{mol}) = 2.41 \times 10^{19}$. By considering the average value of the total number of Pd atoms in an octahedral NC, the number of the Pd NCs used in the coupling reactions is $(2.41 \times 10^{19}) / (5.34 \times 10^5) = 4.51 \times 10^{13}$. Therefore, the total number of surface Pd atoms is $(4.51 \times 10^{13}) \times (3.42 \times 10^4) = 1.54 \times 10^{18}$. So, TOF is $(0.701 \times 0.004 \text{ mol} \times 6.02 \times 10^{23} / \text{mol}) / (1.54 \times 10^{18} \times 24 \text{ h}) = 45.7 \text{ h}^{-1}$.

2.2. Cubic Pd NCs

To calculate TOF for the cubic Pd NCs, the number of surface Pd atoms was calculated based on the size distribution of the cubic Pd NCs (Fig. S1b). The details for the calculation of the number of surface atoms and TOF are given below.

The volume of a cubic Pd NC, which has an edge length of 27.3 nm (the average edge length of the prepared cubic Pd NCs), is $(27.3 \text{ nm})^3 = 2.03 \times 10^4 \text{ nm}^3$. Since the known lattice constant of Pd is 0.389 nm, the volume of a unit cell is $(0.389 \text{ nm})^3 = 5.89 \times 10^{-2} \text{ nm}^3$. So, the total number of Pd atoms in a cubic NC with an edge length of 27.3 nm is $(2.03 \times 10^4 \text{ nm}^3 / 5.89 \times 10^{-2} \text{ nm}^3) \times 4 = 1.38 \times 10^6$. In the same way, the total number of Pd atoms in a cubic NC for each size range in Fig. S1b was calculated. By weighting the relative amount of Pd

NCs for each size range, the average value of the total number of Pd atoms in a cubic NC was then calculated to be 1.49×10^{6} .

The edge length of square unit on the {100} surface of the cubic Pd NCs is 0.389 nm. The area of square unit is then $(0.389 \text{ nm})^2 = 1.51 \times 10^{-1} \text{ nm}^2$. Since the surface area of a cubic Pd NC with an edge length of 27.3 nm is $(27.3 \text{ nm})^2 \times 6 = 4.47 \times 10^3 \text{ nm}^2$. So, the total number of surface Pd atoms on a cubic NC is $[(4.47 \times 10^3 \text{ nm}^2) / (1.51 \times 10^{-1} \text{ nm}^2)] \times 2 = 5.92 \times 10^4$. In the same way, the total number of surface Pd atoms on a cubic NC for each size range in Fig. S1b was calculated. By weighting the relative amount of Pd NCs for each size range, the average value of the total number of surface Pd atoms on a cubic NC was then calculated to be 6.05×10^4 .

The total number of Pd atoms used in the coupling reactions is $(0.04 \times 10^{-3} \text{ mol}) \times (6.02 \times 10^{23} / \text{mol}) = 2.41 \times 10^{19}$. By considering the average value of the total number of Pd atoms in a cubic NC, the number of the Pd NCs used in the coupling reactions is $(2.41 \times 10^{19}) / (1.49 \times 10^6) = 1.62 \times 10^{13}$. Therefore, the total number of surface Pd atoms is $(1.62 \times 10^{13}) \times (6.05 \times 10^4) = 9.80 \times 10^{17}$. So, TOF is $(0.784 \times 0.004 \text{ mol} \times 6.02 \times 10^{23} / \text{mol}) / (9.80 \times 10^{17} \times 24 \text{ h}) = 80.3 \text{ h}^{-1}$.

2.3. RD Pd NCs

To calculate TOF for the RD Pd NCs, the number of surface Pd atoms was calculated based on the size distribution of the RD Pd NCs (Fig. S1c). The details for the calculation of the number of surface atoms and TOF are given below.

The volume of a RD Pd NC, which has an edge length of 52.3 nm (the average edge length of the prepared RD Pd NCs), is $16\sqrt{3}/9 \times (52.3 \text{ nm})^3 = 4.41 \times 10^5 \text{ nm}^3$. Since the known lattice constant of Pd is 0.389 nm, the volume of a unit cell is $(0.389 \text{ nm})^3 = 5.89 \times 10^{-2} \text{ nm}^3$. So, the total number of Pd atoms in a RD NC with an edge length of 52.3 nm is $(4.41 \times 10^5 \text{ nm}^3 / 5.89 \times 10^{-2} \text{ nm}^3) \times 4 = 2.99 \times 10^7$. In the same way, the total number of Pd atoms in a RD NC for each size range in Fig. S1c was calculated. By weighting the relative amount of Pd NCs for each size range, the average value of the total number of Pd atoms in a RD NC was then calculated to be 3.13×10^7 .

The area of rectangular unit on the {100} surface of the RD Pd NCs is $\sqrt{2} \times (0.389 \text{ nm})^2 = 2.14 \times 10^{-1} \text{ nm}^2$. The surface area of a RD Pd NC with an edge length of 52.3 nm is $8\sqrt{2} \times (52.3 \text{ nm})^2 = 3.09 \times 10^4 \text{ nm}^2$. So, the total number of surface Pd atoms on a RD NC is [(3.09 $\times 10^4 \text{ nm}^2$) / (2.14 $\times 10^{-1} \text{ nm}^2$)] $\times 2 = 2.89 \times 10^5$. In the same way, the total number of surface Pd atoms on a RD NC for each size range in Fig. S1c was calculated. By weighting the relative amount of Pd NCs for each size range, the average value of the total number of surface Pd atoms on a RD NC was then calculated to be 2.92×10^5 .

The total number of Pd atoms used in the coupling reactions is $(0.04 \times 10^{-3} \text{ mol}) \times (6.02 \times 10^{23} / \text{mol}) = 2.41 \times 10^{19}$. By considering the average value of the total number of Pd atoms in a RD NC, the number of the RD Pd NCs used in the coupling reactions is $(2.41 \times 10^{19}) / (3.13 \times 10^7) = 7.70 \times 10^{11}$. Therefore, the total number of surface Pd atoms is $(7.70 \times 10^{11}) \times (2.92 \times 10^5) = 2.25 \times 10^{17}$. So, TOF is $(0.919 \times 0.004 \text{ mol} \times 6.02 \times 10^{23} / \text{mol}) / (2.25 \times 10^{17})$

 \times 24 h) = <u>410 h^{-1}</u>.

2.4. Pd black

The surface area of Pd black is 40-60 m²/g. For the catalytic reaction, 4.25 mg of Pd black was utilized. Therefore, the exposed surface area of Pd black used in the coupling reaction is 0.17-0.255 m². To calculate the TOF of Pd black, we used the average value of surface area, 0.2125 m². Pd atom density on Pd(111) is 1.53×10^{19} atom / m². So, the total number of Pd atoms on the surface is $(0.2125 \text{ m}^2) \times (1.53 \times 10^{19} \text{ atom } / \text{m}^2) = 3.25 \times 10^{18}$. Then, TOF is $(0.15 \times 0.004 \text{ mol} \times 6.02 \times 10^{23} / \text{mol}) / (3.25 \times 10^{18} \times 24 \text{ h}) = 4.63 \text{ h}^{-1}$.

2.5. Pd/C (10 wt%)

The Pd surface area of Pd/C is 48-65 m²/g_{Pd}. For the catalytic reaction, 42.5 mg of Pd/C was utilized. Therefore, the exposed surface area of Pd used in the cross coupling reaction is 0.204-0.276 m². To calculate TOF, we used the average value of surface area, 0.24 m². Pd atom density on Pd(111) is 1.53×10^{19} atom / m². So the total number of surface Pd atoms is $(0.24 \text{ m}^2) \times (1.53 \times 10^{19} \text{ atom / m}^2) = 3.67 \times 10^{18}$. Then, TOF is $(0.21 \times 0.004 \text{ mol} \times 6.02 \times 10^{23} \text{ / mol}) / (3.67 \times 10^{18} \times 24 \text{ h}) = 5.74 \text{ h}^{-1}$.

2.6. Homogeneous Pd catalysts: Pd(PPh₃)₄, PdCl₂, and K₂PdCl₄

The total number of Pd atoms used in the coupling reactions is $(0.04 \times 10^{-3} \text{ mol}) \times (6.02 \times 10^{23} / \text{mol}) = 2.41 \times 10^{19}$. TOF of each catalyst: (1) For Pd(PPh₃)₄, $(0.12 \times 0.004 \text{ mol} \times 6.02 \times 10^{23} / \text{mol}) / (2.41 \times 10^{19} \times 24 \text{ h}) = 0.500 \text{ h}^{-1}$. (2) For PdCl₂, $(0.15 \times 0.004 \text{ mol} \times 6.02 \times 10^{23} / \text{mol}) / (2.41 \times 10^{19} \times 24 \text{ h}) = 0.624 \text{ h}^{-1}$. (3) For K₂PdCl₄, $(0.20 \times 0.004 \text{ mol} \times 6.02 \times 10^{23} / \text{mol}) / (2.41 \times 10^{19} \times 24 \text{ h}) = 0.833 \text{ h}^{-1}$.

3. Supplemental experiment results



Fig. S1 Size distribution of the (a) octahedral, (b) cubic, and (c) RD Pd NCs. The average edge lengths of the octahedral, cubic, and RD Pd NCs are 25.3 ± 3.7 , 27.3 ± 4.2 , and 52.3 ± 10.5 nm, respectively.



Fig. S2 Representative TEM images of commercial heterogeneous Pd catalysts: (a,b) Pd black and (c,d) Pd/C (10 wt%).



Fig. S3 Kinetic data for the reactions with the Pd/C catalyst at different stirring rates.

Stirring rate may have an influence on the catalytic activity of supported catalysts. To check this possibility, bromobenzene and morpholine were subjected to reaction with the commercial Pd/C catalyst at different stirring rates, i.e., 350 and 1150 rpm. Notably, we found that there is no noticeable change in the yield of *N*-phenylmorpholine product at different stirring rates in comparison to that obtained under the typical condition (stirring rate = 650 rpm); the yields at 350, 650, and 1150 rpm were 20, 21, and 19%, respectively. In addition, we also obtained kinetic data for the Pd/C-catalyzed reactions conducted at different stirring rates. Since the product selectivity of the heterogeneous catalysts tested in the present work was almost 100%, the kinetic data can be obtained simply by monitoring the concentration of product over the course of reaction. Fig. S3 is the kinetic data for the reactions with the Pd/C catalyst at different stirring rates. The concentration of the product, *N*-phenylmorpholine, was measured as a function of reaction time by NMR spectroscopy in the presence of 1,1,2,2-tetrachloroethane as an internal standard. As shown in Fig. S3, the reaction rate was not significantly affected by the stirring rate overall, though the initial reaction rate slightly increased as the stirring rate increased.



Fig. S4 Arrhenius plots for the catalytic reactions with the Pd NCs and the Pd/C catalyst.

Since the product selectivity of the heterogeneous catalysts tested in the present work was al most 100%, the kinetic data can be obtained simply by monitoring the concentration of produ ct over the course of reaction. To determine the reaction rates at various temperatures (75, 10 0, and 120 °C), bromobenzene and morpholine were subjected to reaction with the Pd NCs an d the Pd/C catalyst, and the concentration of the product, *N*-phenylmorpholine, was measured by NMR spectroscopy after stirring at 650 rpm for 2 h in the presence of 1,1,2,2-tetrachloroet hane as an internal standard. As shown in Fig. S4, the shape-controlled Pd NCs showed signif icantly higher reaction rate than the commercial Pd/C catalyst, and their reaction rates depend on their shapes (facets). The activation energies of the catalytic reaction for the octahedral, cu bic, and RD Pd NCs, and Pd/C, which were obtained from the Arrhenius plot for each catalyst, were 44.8 ± 4.38 , 37.3 ± 1.57 , 31.3 ± 3.09 , and 47.0 ± 2.12 kJ mol⁻¹, respectively. These kin etic data are in good agreement with the activity trend across different catalysts determined in terms of the reaction yield.



Fig. S5 The catalytic activities of the shape-controlled Pd NCs before and after the treatment with (a) citric acid and (b) KI.

Residual capping agent adsorbed on the surface of nano-sized metal catalysts can affect the r eactivity of catalysts. Therefore, we tried to prepare all the shape-controlled Pd NCs with sam e capping agent (CTAC) and reducing agents (AA) to exclude any undesirable influence of a dsorbates in the comparative study of catalytic reaction. However, it has been inevitable to ad d some amount of citric acid and KI to the reaction mixture for preparing the octahedral and RD Pd NCs, respectively, to manipulate the growth kinetic of Pd NCs. Therefore, residual am ount of citric acid and I- might be present on the catalyst surfaces. To check the influence of c itric acid on the catalytic activity of Pd NCs, the cubic and RD Pd NCs were treated with the i dentical relative amount of citric acid to that used in the preparation of the octahedral Pd NCs for more than 6 h before the catalytic reaction. As shown in Fig. S5a, the catalytic activities o f Pd NCs were barely changed after the treatment of citric acid, unambiguously revealing that the influence of citric acid on the catalysis is negligible. On the other hand, to check the influ ence of I⁻ on the catalysis, the octahedral and cubic Pd NCs were treated with the identical rel ative amount of KI to that used in the preparation of the RD Pd NCs for more than 6 h before the catalytic reaction. As shown in Fig. S5b, there is no significant change in the catalytic acti vities of Pd NCs after the treatment of KI, indicating that the influence of I⁻ on the catalysis is also negligible. This result clearly verifies that the higher catalytic activity of the RD PD NCs compared to other catalysts and the activity trend across different catalysts have no relation to the presence of I⁻ on catalyst surfaces.



Fig. S6 The NMR yields of product as a function of reaction time. The reaction proceeded un der normal condition in condition A. On the other hand, the RD Pd NC catalysts were remove d from the reaction solution after 6 h in condition B, and Hg was added to the reaction solution n after 6 h in condition C.



Fig. S7 HAADF-STEM-EDS mapping images of RD Pd NCs after the reaction with bromobe nzene. Scale bar indicates 20 nm. The EDS-determined atomic percentage of Pd and Br are 9 9.89 and 0.11%, respectively.



Fig. S8 HAADF-STEM-EDS mapping images of RD Pd NCs after the mixing with KBr (4 m mol) in the presence of morpholine (5 mmol) for 24 h. Scale bar indicates 20 nm. The amount of Br atoms adsorbed on the NC surface was less than a detection limit. In fact, the EDS-dete rmined atomic percentage of Pd and Br are 100 and 0%, respectively.



Fig. S9 HAADF-STEM-EDS mapping images of RD Pd NCs after the mixing with KBr (4 m mol) in the absence of morpholine for 24 h. Scale bar indicates 20 nm. The amount of Br ato ms adsorbed on the NC surface was less than a detection limit. In fact, the EDS-determined at omic percentage of Pd and Br are 100 and 0%, respectively.

4. Computational Methods

4.1. Details of DFT calculations

To mimic the Pd surfaces with different low-index facets, a 4-layered slab model with periodic boundary condition (PBC) was employed. The adsorption energy (E_{ads}) on the surface was calculated by using the VASP package with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. The unit cell sizes were $16.507 \times 16.507 \times 27.057$ Å for the Pd(111) with $\alpha = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$, and $16.507 \times 16.507 \times 25.774$ Å and $19.453 \times 16.507 \times 24.141$ Å for the Pd(100) and Pd(110), respectively, with $\alpha = \beta = \gamma = 90^{\circ}$. The $3 \times 3 \times 1$ k-points with Gamma-centered grid were used for all calculations. The cutoff energy was 400 eV. The ionic relaxation was terminated if all forces acting on atoms are smaller than 0.025 eV / Å.

For the calculation of a dimer intermediate formed in homogeneous catalysis, its geometry was optimized using the Gaussian 09 suite of programs^{*} with the B3LYP hybrid functional. The 6-31G(d) basis set was used for C, H, P atoms, and LANL2DZ basis set with effective core potential was used for Pd and Br atoms.

*Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

4.2. *E_{ads}* of aryl bromide to a Pd surface (oxidative addition)

The E_{ads} of aryl bromide to a Pd surface was calculated by the following equation:

$$E_{ads} = E_{NR2} + E_{ArBr-S} - E_{NR2-S} - E_{Ar-Br}$$
(1)

where E_{NR2-S} is the energy of the morpholine adsorbed on the Pd surface, E_{Ar-Br} is the energy of the *o*- or *p*-bromotoluene, E_{NR2} is the energy of the single morpholine molecule, and E_{ArBr-S} is the energy of the *o*- or *p*-bromotoluene adsorbed on the Pd surface. Following Fig. shows the optimized geometries of bromotoluene adsorbed on the Pd surfaces.



[DFT-calculated optimized geometries of *o*- (left column) and *p*-bromotoluene (right column) adsorbed on the (a,b) Pd(111), (c,d) Pd(100), and (e,f) Pd(110).]

4.3. Cleavage energies of Br atom

The cleavage energy of Br was calculated by using the following equation:

$$E_{cl} = E_{Ar-S} + E_{Br-S} - E_{ArBr-S} - E_S \qquad (2)$$

where E_{Ar-S} and E_{Br-S} are the energies of the aryl group and a Br atom on the Pd surface, respectively. In this calculation, it is assumed that the aryl group and Br are infinitely separated through diffusion after dissociation, so there is no interaction between the aryl group and Br. Therefore the energy after diffusion can be calculated simply by the sum of the energies of the aryl group and the Br atom on the surface. E_S , the Pd surface energy, was added to the eqn. (2) to avoid double counting.

4.4. Reductive elimination energy

The reductive elimination energy of the aryl and amine groups was calculated by using the following equation:

$$E_{RE} = E_{ArNR2} + E_{NR2-S} - E_{ArNR2-S} - E_{NR2}$$
(3)

where E_{ArNR2} is the energy of the tolylamine product, and $E_{ArNR2-S}$ is the energy of aryl and amine adsorbed on the surface before the reductive elimination. It was assumed that new amine molecules are adsorbed on the surface again after the reductive elimination of the product because the surface was initially covered by amines. That makes an additional stabilization effect during the reductive elimination.

	E_{ads} of p -	E_{ads} of o -	E_{cl} of p -	E_{cl} of o -	E_{RE} of p -
	bromotoluene	bromotoluene	bromotoluene	bromotoluene	bromotoluene
	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)
Pd(111)	8.817	16.422	-1.387	-1.804	-46.789
Pd(100)	-12.458	-9.154	-3.723	-4.600	-37.398
Pd(110)	-16.753	-14.234	-2.108	-2.469	-19.603

Table S1. E_{ads} , E_{cl} , and E_{RE} of *o*- and *p*-bromotoluene on the surface of Pd(111), Pd(100) and Pd(110).

4.5. Comparison between the intermediate states of heterogeneous and homogeneous catalysis

The geometries of the adsorbed bromotoluene as an important intermediate for the heterogeneous Buchwald-Hartwig amination were compared with that of the dimer intermediate formed in the homogeneous reaction with Pd(PPh₃)₄ complex. Fig. S10 shows the oxidatively-added dimers of o- and p-bromotoluene. Pd-Pd, Pd-Br, and Pd-C distances are also shown in Fig. S10. Fig. S11 presents the Pd-Pd, Pd-Br, and Pd-C distances in the adsorbed o- and p-bromotoluene. By comparing those distances between the homogeneous and heterogeneous cases, relative stability of the adsorbed bromotoluene depending on facets can be understood. The Pd-C bond lengths show no large deviation between both cases. However, Pd-Pd and Pd-Br distances vary depending on the facets. The Pd-Pd distances of Pd(100) and Pd(110) are similar with those of the homogeneous dimers, whereas the Pd-Pd distance of Pd(111) is 0.9-1.0 Å farther away. In addition, the Pd-Br distance of Pd(111) deviates longer than 1.0 Å compared with the homogeneous counterpart. These significant deviations on Pd(111) originate from the relatively dense Pd atoms on its surface. When the aryl bromide is adsorbed on a surface atom, Br feels repulsive potential from its neighboring Pd atoms so that it tends to be apart from the surface atom, resulting in such an elongated Pd-Br distance. On the contrary, surface atoms on Pd(100) and Pd(110) have less coordination number and hence they can afford to accommodate both C and Br tightly. Therefore, the

Pd(111) surface is less suitable to stabilize the adsorption of bromotoluene than on the Pd(100) or Pd(110).



Fig. S10 Optimized geometries of the oxidatively-added dimer of (a) *o*- and (b) *p*-bromotoluene. Pd-Br and Pd-C bond lengths (Å) are shown in black. Pd-Pd distances are shown in red.



Fig. S11 Optimized geometries of *o*- (left column) and *p*-bromotoluene (right column) adsorbed on the (a,b) Pd(111), (c,d) Pd(100), and (e,f) Pd(110). Pd-Pd, Pd-Br, and Pd-C distances (Å) are also denoted.