Inorganic Chemistry
Cite This: Inorg. Chem. XXXX, XXX, XXX−XXX
Communication
pubs.acs.org/IC

Nanosized Bispyrazole-Based Cryptand-Stabilized Palladium(0) Nanoparticles: A Reusable Heterogeneous Catalyst for the Suzuki−Miyaura Coupling Reaction in Water

Ashish Verma, Kapil Tomar, and Parimal K. Bharadwaj*

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India

Supporting Information

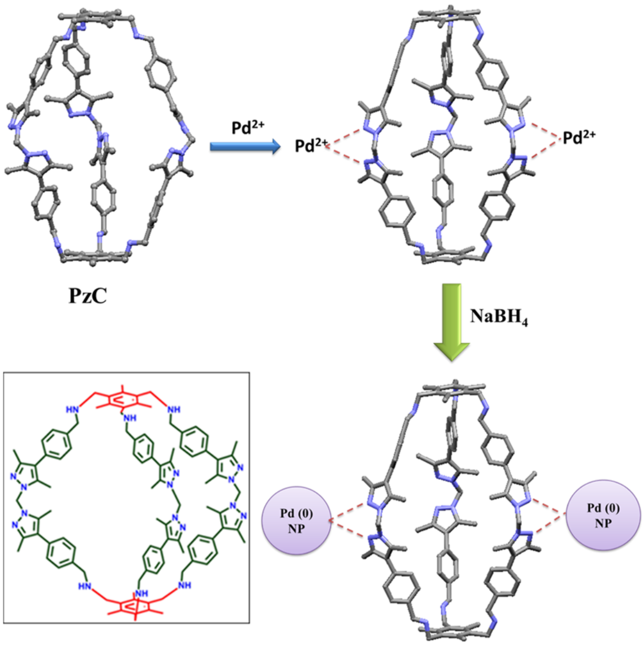
ABSTRACT: A macrobicyclic cryptand with a long rigid cavity incorporating a chelating bispyrazole moiety in each of the three bridges was synthesized. The multiple chelating metal binding sites were utilized for the controlled synthesis and stabilization of ultrafine palladium nanoparticles (Pd NPs) of nearly ∼2 nm size. The as-synthesized Pd NPs were characterized by X-ray photoelectron spectroscopy, transmission electron microscopy, and powder X-ray diffraction. The well-dispersed cryptand-stabilized nanoparticles are found to catalyze the C−C bond-forming Suzuki−Miyaura reaction heterogeneously using water as a green solvent.

Cryptands are the first studied examples of functional cage molecules, which initially were used for the selective recognition of cations.[1] At the beginning of the development of these organic compounds, bond formation was rather irreversible in nature, affording the desired product at yields.[2] The reversible nature of imine bonds was then observed, and after that, organic cage molecules can be synthesized in high overall yields.[3] This kind of synthetic approach, which is also called dynamic covalent synthesis,[4,5] is nowadays most frequently used for the synthesis of various sizes and shapes of organic molecules of high and complex structures from simple building blocks because a one-pot step can be achieved.[6] An attractive feature of these cage molecules is their solubility in common organic solvents, which makes their processing easier compared to insoluble porous solids. These cage molecules have attracted enormous attention in recent years with applications in wide areas like, sensing,[7] gas storage/separation,[8] catalysis,[9] drug delivery,[10] molecular separation,[11] light harvesting,[12] and proton conduction.[13]

Metal nanoparticles (MNPs) exhibit high surface area,[14,15] which results in a very large number of catalytically active sites, making them excellent heterogeneous catalysts for various organic transformation reactions.[16] However, unstabilized MNPs can aggregate, leading to impairment of the catalytic activities.[17] Hence, there have been constant efforts to investigate different solid support materials for the fabrication/stabilization of MNPs over the past few years.[18−24] The use of cryptands and other porous organic cage molecules to stabilize the MNPs is a recent advancement in this area.[25−30] Our interest in the synthesis of novel cryptands prompted us to investigate new porous organic cage molecules for the capping/stabilization of MNPs for heterogeneous catalytic purposes. We envisioned that cryptands bearing chelating moieties in the bridges could serve as exocyclic binding sites for MNPs, leading to the controlled synthesis of MNPs, and such cryptand-capped/stabilized nanoparticles will be ideal candidates for catalysis.

Herein, we report a cryptand incorporating bispyrazole moieties that can serve as anchoring sites for the controlled synthesis of palladium nanoparticles (Pd NPs; Scheme 1). The cryptand-capped/stabilized Pd NPs are further utilized as heterogeneous catalysts for the C−C bond-forming Suzuki−Miyaura coupling reactions in water as a green solvent.

Scheme 1. Schematic Diagram Showing the Process of Pd NP Synthesis at the Bispyrazole Site of PzC



The highly porous cryptand **PzC** was prepared via the [2 + 3] Schiff base condensation reaction of the bispyrazole-based dialdehdye with a tripodal aromatic amine, as described in our recent report.[30] This cryptand was found to stabilize gold nanoparticles.[30] Another cryptand, where the bridgehead was nitrogen in place of the aromatic ring as in the present case, was found through crystallographic investigation to bind metal ions

Received: October 24, 2018

DOI: 10.1021/acs.inorgchem.8b03015

at the bispyrazole moiety that turned[31] outward upon metal complexation (Figure S2b). Therefore, it was presumed that when the cryptand was reacted with $Pd(OAc)_2$, the bispyrazole moiety turned[31] outward and acted as a nucleation site for metal aggregation (Scheme 1). The length of the cryptand from the crystal structure was found to be around 2 nm, while the average size of the Pd(0) NPs was 2.24 nm, which suggested that about five or more cryptand molecules formed an intermolecular cavity via aggregation to stabilize the nanoparticle.

The cryptand **PzC**-stabilized Pd(0) NPs were prepared by stirring the cryptand with $Pd(OAc)_2$ vigorously in methanol and $CHCl_3$ (1:1) for 2 h at room temperature, which afforded a yellow solution. Solid $NaBH_4$ was added portionwise until the solution turned black with the appearance of a precipitate. Upon completion of the reaction, the solvent was removed, and the black precipitate that remained was washed several times with deionized water and methanol via centrifugation, followed by drying under vacuum to obtain **Pd(0)·PzC** as a black solid.

The high-resolution transmission electron microscopy (HRTEM) images of the as-obtained material showed well-dispersed nanoparticles of mean size 2.24 nm and a narrow distribution of the particle size (Figure 1a). With the internal cavity size of **PzC** (1.2 nm) being much smaller compared to that of the as-obtained Pd(0) NPs (2.24 nm), the nanoparticles would reside outside the cryptand. As observed from the $CoCl_2$ complex of **PzC** (see the Supporting Information), where the metal ions were bound in an exocyclic manner to the bispyrazole unit, stabilization of Pd(0) NPs anchoring at the bispyrazole unit from outside the cavity is well justified (Scheme 1). Loading of palladium was measured by inductively coupled plasma mass spectrometry to be ~34 wt %. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging and energy-dispersive X-ray (EDX) mapping analysis showed that carbon and nitrogen were homogeneously distributed around the Pd NPs (Figure 1). Additionally, X-ray photoelectron spectroscopy (XPS) data (Figure 1b) were consistent with the formation of Pd(0) NPs, showing binding energies of 334.4 and 339.2 eV, attributable[32] to Pd(0) $3d_{5/2}$ and $3d_{3/2}$, respectively. Also, peaks at 2θ values of ~40, 47, 68, 82, and 87° in the powder X-ray diffraction (PXRD) pattern could[33] be assigned to the (111), (200), (220), (311), and (222) lattice planes, respectively, consistent with the face-centered-cubic structure of palladium (Figure 2). The observed peak at 39.8° was due to metallic palladium, indicating the formation of a Pd NP cryptand composite for the reduced material. Further, to explore the role of **PzC** in the stabilization of nanoparticles, the syntheses of Pd NPs were performed in the presence of bispyrazole dialdehyde (precursor of the cryptand) and also in the absence of **PzC**. The TEM images (Figures S16 and 17) in both cases revealed the agglomeration of reduced palladium particles. The result showed the role of **PzC** in stabilization of the nanoparticles. We have also performed the thermal-annealing experiment of the as-synthesized **Pd(0)·PzC** material at 100 and 200 °C to test the stability of the nanoparticles. No considerable change in the size/shape of Pd NPs with any agglomeration could be observed in the HRTEM images (Figures S18 and S19).

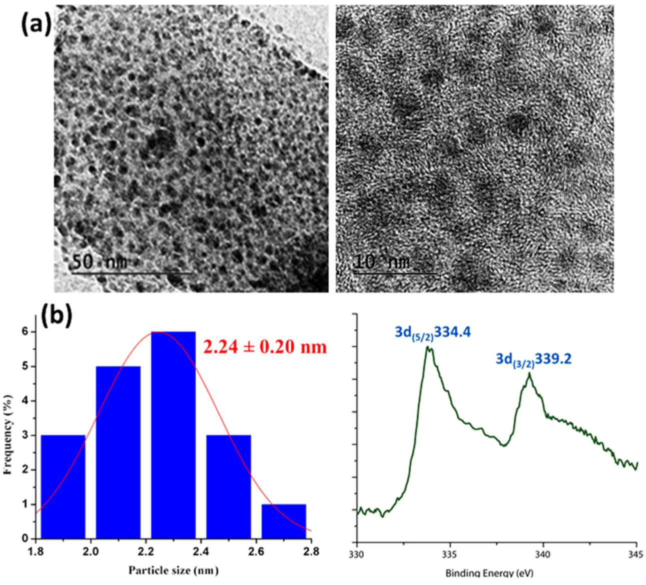


Figure 1. (a) TEM images of **Pd(0)·PzC** at different magnifications. (b) Particle-size distribution and XPS spectrum of **Pd(0)·PzC**.

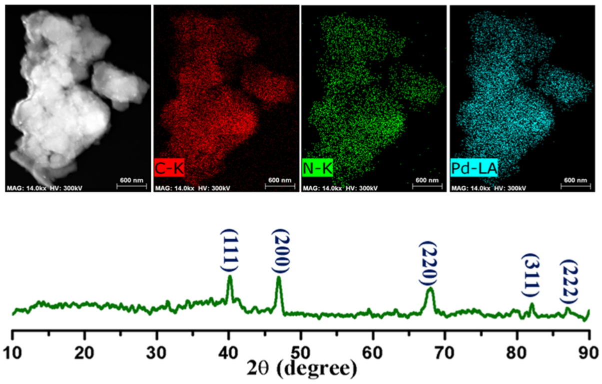
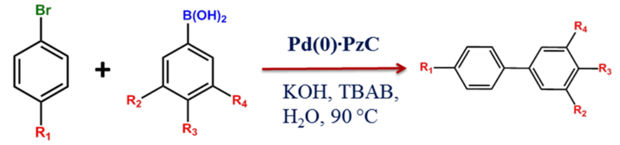


Figure 2. HAADF-STEM image and corresponding EDX mapping of **Pd(0)·PzC** (color code: C, red; N, green; Pd, cyan) and PXRD pattern of **Pd(0)·PzC**.

The C−C bond-forming reactions are important reactions in organic chemistry because they can easily link several functional moieties together. One such reaction is the Suzuki coupling between aryl halides and boronic acids. A number of homogeneous palladium catalysts were explored for this purpose with high selectivity, activity, and low catalyst loading.[34] Also, in some cases, water was used as a green solvent by several workers.[35] However, recovery of the catalyst and its reuse remained a big issue here. To circumvent this shortcoming, palladium complexes or nanoparticles were immobilized on solid supports like silica,[36] activated carbon (charcoal),[37] organic polymers,[38] and metal−organic frameworks.[39] Most of these methods still suffer from drawbacks like the use of expensive phosphines, additives, and severe reaction conditions besides the lack of stability. This scenario prompted us to further develop new active and stable heterogeneous catalysts for these important organic transformations.

In this paper, the catalytic activity of the cryptand-anchored Pd NPs was explored for the Suzuki−Miyura C−C coupling reaction. The reaction between bromobenzene and phenylboronic acid was selected as the model. For this, a catalytic amount of **Pd(0)·PzC** was placed in a 5 mL round-bottom flask followed by the addition of the two reactants along with KOH. The reaction was performed in water as the solvent at 90 °C in air. The progress of the reaction was monitored by thin-layer chromatography, and formation of the desired products could be confirmed by the ^{1}H NMR spectra (Figures S6−S15). It showed that bromobenzene and phenylboronic acid afforded a good yield of the product, which encouraged us to investigate this reaction with substrates having different substituents. A look at the results of the reactions summarized in Table 1 revealed that both electron-donating and -withdrawing substituents gave fairly good yields. The catalyst after one catalytic cycle could be easily separated by filtration and washed with water and acetone, followed by drying at room temerature to regenerate the catalyst. We also performed these reactions by replacing the **Pd(0)·PzC** catalyst with cryptand-free Pd(0) particles, a Pd(OAc)$_2$ salt, and metal-free cryptand **PzC** only. The free Pd(0) particles were prepared by reducing Pd(OAc)$_2$ with NaBH$_4$. The resultant black precipitate of Pd(0) was characterized by TEM (Figure S17). In the case of free Pd(0) particles, very low yields were found, while with Pd(OAc)$_2$, about 34% product formation was observed (Table 1). Metal-free cryptand **PzC** failed to afford any product.

Table 1. Results of the Suzuki−Miyaura Coupling Reactions in Water Catalyzed by Pd(0)·PzC[a]



			% yield[b]		
entry	halobenzene (R_1)	boronic acid (R_2, R_3, R_4)	Pd(0) particles	Pd(OAc)$_2$	**Pd(0)·PzC**
1	H	R_2, R_3, R_4 = H	7	32	94
2	−CH$_3$	R_2, R_3, R_4 = H	5	21	84
3	−OH	R_2, R_3, R_4 = H	8	33	97
4	−NO$_2$	R_2, R_3, R_4 = H	6	26	93
5	−CHO	R_2, R_3, R_4 = H	9	31	95
6	−C(O)CH$_3$	R_2, R_3, R_4 = H	10	33	96
7	−C(O)CH$_3$	R_2, R_4 = −CH$_3$, R_3 = H	6	22	85
8	−C(O)CH$_3$	R_2, R_4 = −C(O)OEt, R_3 = H	9	31	94
9	−C(O)CH$_3$	R_2, R_4 = H, R_3 = −C(O)OEt	8	28	92
10	−C(O)CH$_3$	R_2, R_4 = H, R_3 = −OCH$_3$	11	34	98

[a] Reaction conditions: RBr (1.0 mmol), boronic acid (1.2 mmol), KOH (2.0 mmol), tetrabutylammonium bromide (0.6 mmol), catalyst (3 mol %), and water (3 mL) in air at 90 °C for 2 h. [b] Isolated yields after silica gel chromatography.

The performance of the catalyst was checked for up to three cycles to evaluate its reusability, and no significant loss of activity was found at least up to three cycles (Figure S4). The TEM images of the recovered material after three cycles suggest no considerable change in the nanoparticle size and morphology (Figure 3). PXRD patterns of the material after each cycle were also recorded, which showed negligible change after each catalytic cycle (Figure S3). Besides, the hot filtration test carried out with the system indicated negligible leaching of palladium particles (Figure S5) into the solution phase, proving the heterogeneous nature of the reactions.

In summary, we synthesized a novel bispyrazole-based cryptand having chelating bispyrazole moieties. The cryptand was used for the synthesis and stabilization of Pd NPs. The strong binding affinity of the Pd^{2+} ions toward the bispyrazole moiety of the cryptand is considered to be the governing factor during the nucleation of Pd NPs, whereas aromatic moieties protect the nanoparticles from agglomeration.

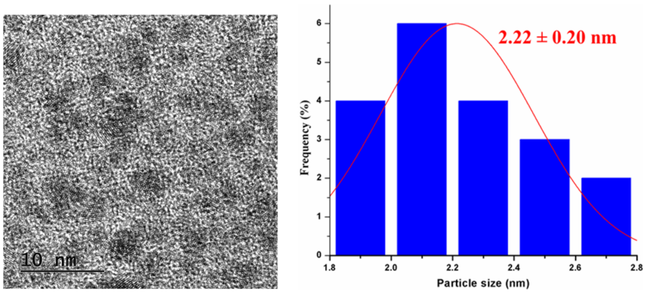


Figure 3. HRTEM image of **Pd(0)·PzC** and the particle-size distribution after three cycles of catalysis.

The cage-capped Pd NPs were found to be excellent catalysts for the Suzuki−Miyuara reaction in water with a variety of functional groups. The promising features of the system include a wide variety of functional group tolerances, reusability, high yield, and water as the solvent.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b03015.

Experimental details, characterization procedures, IR, NMR, TGA, and PXRD patterns (PDF)

Accession Codes

CCDC 1883649 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pkb@iitk.ac.in.

ORCID

Parimal K. Bharadwaj: 0000-0003-3347-8791

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the DST, New Delhi, India (to P.K.B.), and SRF from the IIT Kanpur, India (to A.V.) and financial support in the form of a postdoc fellowship from SERB (DST) (YSS/2015/001088) to K.T.

■ REFERENCES

(1) Lehn, J. M. Supramolecular Chemistry: Receptors, Catalysts, and Carriers. *Science* **1985**, *227*, 849−856.

(2) Newkome, G. R.; Majestic, V.; Fronczek, F.; Atwood, J. L. Synthesis and x-ray structure of N[(CH2)2O(2,6-C6H3N)O(CH2)-2]3N: a D3 macrobicyclic ligand capped by two sp2 nitrogen atoms. *J. Am. Chem. Soc.* **1979**, *101*, 1047−1048.

(3) Quan, M. L. C.; Cram, D. J. Constrictive binding of large guests by a hemicarcerand containing four portals. *J. Am. Chem. Soc.* **1991**, *113*, 2754−2755.

(4) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. Dynamic Covalent Chemistry. *Angew. Chem., Int. Ed.* **2002**, *41*, 898−952.

(5) Jin, Y.; Yu, C.; Denman, R. J.; Zhang, W. Recent advances in dynamic covalent chemistry. *Chem. Soc. Rev.* **2013**, *42*, 6634−6654.

(6) Acharyya, K.; Mukherjee, S.; Mukherjee, P. S. Molecular Marriage through Partner Preferences in Covalent Cage Formation and Cage-to-Cage Transformation. *J. Am. Chem. Soc.* **2013**, *135*, 554−557.

(7) Francesconi, O.; Ienco, A.; Moneti, G.; Nativi, C.; Roelens, S. A self-assembled pyrrolic cage receptor specifically recognizes beta-glucopyranosides. *Angew. Chem., Int. Ed.* **2006**, *45*, 6693−6696.

(8) Tozawa, T.; Jones, J. T. A.; Swamy, S. I.; Jiang, S.; Adams, D. J.; Shakespeare, S.; Clowes, R.; Bradshaw, D.; Hasell, T.; Chong, S. Y.; Tang, C.; Thompson, S.; Parker, J.; Trewin, A.; Bacsa, J.; Slawin, A. M. Z.; Steiner, A.; Cooper, A. I. Porous organic cages. *Nat. Mater.* **2009**, *8*, 973−978.

(9) Yang, X.; Sun, J.-K.; Kitta, M.; Pang, H.; Xu, Q. Encapsulating highly catalytically active metal nanoclusters inside porous organic cages. *Nature Catalysis* **2018**, *1*, 214−220.

(10) Lin, Z.; Sun, J.; Efremovska, B.; Warmuth, R. Assembly of Water-Soluble, Dynamic, Covalent Container Molecules and Their Application in the Room-Temperature Stabilization of Protoadamantene. *Chem. - Eur. J.* **2012**, *18*, 12864−12872.

(11) Zhang, C.; Wang, Q.; Long, H.; Zhang, W. A Highly C_{70} Selective Shape-Persistent Rectangular Prism Constructed through One-Step Alkyne Metathesis. *J. Am. Chem. Soc.* **2011**, *133*, 20995−21001.

(12) Ortiz, M.; Cho, S.; Niklas, J.; Kim, S.; Poluektov, O. G.; Zhang, W.; Rumbles, G.; Park, J. Through-Space Ultrafast Photoinduced Electron Transfer Dynamics of a C_{70}-Encapsulated Bisporphyrin Covalent Organic Polyhedron in a Low-Dielectric Medium. *J. Am. Chem. Soc.* **2017**, *139*, 4286−4289.

(13) Liu, M.; Chen, L.; Lewis, S.; Chong, S. Y.; Little, M. A.; Hasell, T.; Aldous, I. M.; Brown, C. M.; Smith, M. W.; Morrison, C. A.; Hardwick, L. J.; Cooper, A. I. Three-dimensional protonic conductivity in porous organic cage solids. *Nat. Commun.* **2016**, *7*, 12750−12759.

(14) McCaffrey, R.; Long, H.; Jin, Y.; Sanders, A.; Park, W.; Zhang, W. Template Synthesis of Gold Nanoparticles with an Organic Molecular Cage. *J. Am. Chem. Soc.* **2014**, *136*, 1782−1785.

(15) Qiu, L.; McCaffrey, R.; Zhang, W. Synthesis of Metallic Nanoparticles Using Closed-Shell Structures as Templates. *Chem. - Asian J.* **2018**, *13*, 362−372.

(16) Li, Z.; Liu, J.; Xia, C.; Li, F. Nitrogen-Functionalized Ordered Mesoporous Carbons as Multifunctional Supports of Ultrasmall Pd Nanoparticles for Hydrogenation of Phenol. *ACS Catal.* **2013**, *3*, 2440−2448.

(17) White, R. J.; Luque, R.; Budarin, V. L.; Clark, J. H.; Macquarrie, D. J. Supported metal nanoparticles on porous materials. Methods and applications. *Chem. Soc. Rev.* **2009**, *38*, 481−494.

(18) Nasir Baig, N. R.; Varma, R. S. Magnetic Silica-Supported Ruthenium Nanoparticles: An Efficient Catalyst for Transfer Hydrogenation of Carbonyl Compounds. *ACS Sustainable Chem. Eng.* **2013**, *1*, 805−809.

(19) Prieto, G.; Zečević, J.; Friedrich, H.; de Jong, K. P.; de Jongh, P. E. Towards stable catalysts by controlling collective properties of supported metal nanoparticles. *Nat. Mater.* **2013**, *12*, 34−39.

(20) Lu, S.; Hu, Y.; Wan, S.; McCaffrey, R.; Jin, Y.; Gu, H.; Zhang, W. Synthesis of Ultrafine and Highly Dispersed Metal Nanoparticles Confined in a Thioether-Containing Covalent Organic Framework and Their Catalytic Applications. *J. Am. Chem. Soc.* **2017**, *139*, 17082−17088.

(21) Aijaz, A.; Karkamkar, A.; Choi, Y. J.; Tsumori, N.; Ronnebro, E.; Autrey, T.; Shioyama, H.; Xu, Q. Immobilizing Highly Catalytically Active Pt Nanoparticles inside the Pores of Metal−Organic Framework: A Double Solvents Approach. *J. Am. Chem. Soc.* **2012**, *134*, 13926−13929.

(22) Hermes, S.; Schroter, M. K.; Schmid, R.; Khodeir, L.; Muhler, M.; Tissler, A.; Fischer, R. W.; Fischer, R. A. Metal@MOF: loading of highly porous coordination polymers host lattices by metal organic chemical vapor deposition. *Angew. Chem., Int. Ed.* **2005**, *44*, 6237−6241.

(23) Li, L.; Zhao, H.; Wang, J.; Wang, R. Facile Fabrication of Ultrafine Palladium Nanoparticles with Size- and Location-Control in Click-Based Porous Organic Polymers. *ACS Nano* **2014**, *8*, 5352−5364.

(24) Pachfule, P.; Kandambeth, S.; Díaz Díaz, D.; Banerjee, R. Highly stable covalent organic framework−Au nanoparticles hybrids for enhanced activity for nitrophenol reduction. *Chem. Commun.* **2014**, *50*, 3169−3172.

(25) Mondal, B.; Acharyya, K.; Howlader, P.; Mukherjee, P. S. Molecular Cage Impregnated Palladium Nanoparticles: Efficient, Additive-Free Heterogeneous Catalysts for Cyanation of Aryl Halides. *J. Am. Chem. Soc.* **2016**, *138*, 1709−1716.

(26) Zhang, Y.; Xiong, Y.; Ge, J.; Lin, R.; Chen, C.; Peng, Q.; Wang, D.; Li, Y. Porous organic cage stabilised palladium nanoparticles: efficient heterogeneous catalysts for carbonylation reaction of aryl halides. *Chem. Commun.* **2018**, *54*, 2796−2799.

(27) Sun, J.-K.; Zhan, W.-W.; Akita, T.; Xu, Q. Toward Homogenization of Heterogeneous Metal Nanoparticle Catalysts with Enhanced Catalytic Performance: Soluble Porous Organic Cage as a Stabilizer and Homogenizer. *J. Am. Chem. Soc.* **2015**, *137*, 7063−7066.

(28) Mondal, B.; Mukherjee, P. S. Cage Encapsulated Gold Nanoparticles as Heterogeneous Photocatalyst for Facile and Selective Reduction of Nitroarenes to Azo Compounds. *J. Am. Chem. Soc.* **2018**, *140*, 12592−12601.

(29) Qiu, L.; McCaffrey, R.; Jin, Y.; Gong, Y.; Hu, Y.; Sun, H.; Park, W.; Zhang, W. Cage-templated synthesis of highly stable palladium nanoparticles and their catalytic activities in Suzuki−Miyaura coupling. *Chem. Sci.* **2018**, *9*, 676−680.

(30) Saini, M.; Verma, A.; Tomar, K.; Bharadwaj, P. K.; Sadhu, K. K. Regioisomeric cryptands stabilized gold suprasphere and elongated dodecahedron supraparticle for reversible host-guest chemistry. *Chem. Commun.* **2018**, *54*, 12836−12839.

(31) Verma, A.; Tomar, K.; Bharadwaj, P. K. Unpublished results.

(32) Brun, M.; Berthet, A.; Bertolini, J. C. XPS, AES and Auger parameter of Pd and PdO. *J. Electron Spectrosc. Relat. Phenom.* **1999**, *104*, 55−60.

(33) Hull, A. W. X—Ray Crystal Analysis of Thirteen Common Metals. *Phys. Rev.* **1921**, *17*, 571−588.

(34) Johansson-Seechurn, C. C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. Palladium-Catalyzed Cross-Coupling: A Historical Contextual Perspective to the 2010 Nobel Prize. *Angew. Chem., Int. Ed.* **2012**, *51*, 5062.

(35) Han, J.; Liu, Y.; Guo, R. Facile Synthesis of Highly Stable Gold Nanoparticles and Their Unexpected Excellent Catalytic Activity for Suzuki−Miyaura Cross-Coupling Reaction in Water. *J. Am. Chem. Soc.* **2009**, *131*, 2060−2061.

(36) Hagiwara, H.; Sugawara, Y.; Hoshi, T.; Suzuki, T. Sustainable Mizoroki−Heck reaction in water: remarkably high activity of $Pd(OAc)_2$ immobilized on reversed phase silica gel with the aid of an ionic liquid. *Chem. Commun.* **2005**, *0*, 2942−2944.

(37) Kohler, K.; Heidenreich, R. G.; Krauter, J. G. E.; Pietsch, J. Highly active palladium/activated carbon catalysts for heck reactions: Correlation of activity, catalyst properties, and Pd leaching. *Chem. - Eur. J.* **2002**, *8*, 622−631.

(38) Modak, A.; Mondal, J.; Sasidharan, M.; Bhaumik, A. Triazine functionalized ordered mesoporous polymer: a novel solid support for Pd-mediated C−C cross-coupling reactions in water. *Green Chem.* **2011**, *13*, 1317−1331.

(39) Huang, Y.; Gao, S.; Liu, T.; Lü, J.; Lin, X.; Li, H.; Cao, R. Palladium Nanoparticles Supported on Mixed-Linker Metal−Organic Frameworks as Highly Active Catalysts for Heck Reactions. *ChemPlusChem* **2012**, *77*, 106−112.

DOI: 10.1021/acs.inorgchem.8b03015
Inorg. Chem. XXXX, XXX, XXX−XXX