Colloidal Palladium Nanoparticles for Selective Hydrogenation of Styrene Derivatives with Reactive Functional Groups

Mohammed A. Mahdaly,† Jie S. Zhu,‡ Vincent Nguyen, † and Young-Seok Shon*†‡

†Department of Chemistry and Biochemistry and ‡Keck Energy Materials Program, California State University Long Beach, 1250 Bellflower Blvd., Long Beach, California 90840, United States

ABSTRACT: This article presents the catalysis investigation of octanethiolate-capped palladium nanoparticles (C8 PdNP) and phenylethenolate-capped palladium nanoparticles (PhC2 PdNP) for chemoselective catalytic hydrogenation reactions of styrene derivatives in the presence of other reducible functionalities. The results show that the C8 PdNP is highly active under mild reaction conditions (room temperature and atmospheric pressure) and selective for hydrogenating monosubstituted alkene groups without reducing other reactive functional groups such as nitro, halo, carbonyls, and so forth. In comparison, the noncovalent interactions between surface phenyl ligands and aromatic substrates are found to hinder the hydrogenation activity of PhC2 PdNP.

INTRODUCTION

Colloidal metal nanoparticle catalysts are considered semi-heterogeneous because of their homogeneous kinetic traits and heterotopic surface properties. Furthermore, their high surface energy makes colloidal metal nanoparticles very useful catalytic systems that operate with high activity under mild conditions. Due to these advantages over the traditional homogeneous and heterogeneous catalysts, colloidal metal nanoparticles with controlled activity have recently attracted increased research interests for selective organic reactions.1−5

Palladium catalysts have been popularly used for hydrogenation, exceeding the reputation of other metal catalysts such as platinum and rhodium.6−20 One of the reasons for that is their lower metal hydrogen bonding energy compared to those of both Pt and Rh.6 The classical palladium on carbon (Pd/C) is well known for efficient hydrogenation of organic compounds possessing various reducible functionalities.21 However, in general, selective hydrogenation of Pd/C for several highly reactive functionalities has been difficult because of its uncontrollably strong catalytic activity.

Chemoselective hydrogenation of alkene has been studied for many decades using various homogeneous and heterogeneous catalysts especially for the fine chemical and pharmaceutical industries.22−24 For example, common substrates such as unsaturated alkenes often possess other reducible functionalities such as nitro, halo, carbonyl, and so forth. Because the property of organic compounds changes dramatically depending on the functional groups in the molecule, it is crucial to have catalysts with high chemoselectivity for different functional groups. The activity of palladium catalysts could be modulated by using various support systems,21,25 but the present systems still pose problems especially for highly reactive functional groups. In addition, the development of catalysts for chemoselective hydrogenation that operates in mild reaction conditions is extremely desirable.

There have been several studies on chemoselective hydrogenation utilizing supported palladium catalysts including those supported by macromolecules. The chemoselectivity and activity of the supported Pd catalysts depend on the structure and functional groups of the supports, the type of ligands (or adsorbents), and the reaction environments such as solvents, temperature, and pressure.25 These Pd-based catalysts supported on solid materials, such as fibroin (Fib), polyethyleneimine (PEI), boron nitride (BN), molecular sieves (MS), chelate resin (Pd/CR11), ceramic, and spherically shaped activated carbon (Pd/SC), have been intensely reviewed by others.25,26 For example, Pd/Fib could selectivity hydrogenate alkene, alkyne, azide, and nitro functionalities in the presence of other readily reducible functionalities, such as benzyl esters and aryl halides. Furthermore, both Pd/MS and Pd/BN possessed similar catalytic activity, selectively hydrogenating alkenes, alkenes, and azides to the corresponding alkanes and amines without reducing other functionalities within the substrates. The Pd/CR11 catalyst exhibited a high activity for selective hydrogenation of a variety of reducible functionalities, such as alkyne, alkene, azide, nitro, benzyl ester, and aryl benzyl ether, in the presence of benzylic or allylic
alcohol, indicating the moderated deactivation of the catalytic activity that is based on the chelation effect of the iminodiacetate moiety on CR11 to palladium metal. The Pd/SC catalyst exhibited chemoselectivity not only for alkene, alkene, azide, and nitro functionalities but also for the alkyl TBS ether functionality in the presence of other functional groups.

Our research group has shown that PdNPs synthesized using S-alkylsulfonate ligands demonstrate superior catalytic activity for the isomerization of terminal alkenes and the selective hydrogenation of dienes to alkenes.18,26 The results indicated that the partial poisoning of PdNPs by the thiolate ligands allows a superior control over the activity of colloidal PdNP catalysts. In this paper, the partial poisoning of PdNP catalysts by alkanethiolate ligands is investigated for chemoselective hydrogenation of alkene in the presence of various reactive functional groups under mild reaction conditions. Several other methods including Wilkinson’s catalyst have shown to be effective for chemoselective hydrogenation in the presence of reactive functional groups.21,25,27−30 However, the semi-heterogeneous characteristics of PdNPs provide additional benefits including facile separation of PdNPs in their powder form that leads to simple isolation of pure products and high recyclability. These results are compared to other catalysts based on kinetic studies and selectivity outcomes.

## RESULTS AND DISCUSSION

**Chemoselective Hydrogenation by Octanethiolate-Capped Pd Nanoparticles.** The previous work from our group showed that the catalytic hydrogenation of styrene to ethylbenzene is completed in less than 24 h at room temperature and under atmospheric H2 pressure by utilizing 5 mol % C8 PdNP.26 No other product involving hydrogenation of benzene group is detected, indicating a good hydrogenation selectivity for alkene group over aromatic functionality. Since styrene hydrogenation to ethylbenzene is an important process as ethylbenzene is a key compound in the aromatics industry,31,32 the high selectivity of C8 PdNP catalysts that operate under mild reaction conditions is already potentially valuable. The previous studies confirmed the contribution of the p orbitals and planar geometry of the benzene ring in aiding the formation of the di-σ-bonded Pd-alkyl intermediate that is necessary for the hydrogenation process.26,33,34 To further investigate alkanethiolate-capped PdNP as chemoselective hydrogenation catalysts, m-nitrostyrene was first selected as a control system (Scheme 1).

**Scheme 1. Reaction Scheme for Catalytic Hydrogenation of m-Nitrostyrene Using C8 PdNP**

Because the nitro moiety is strongly electron-withdrawing and in general very reactive to Pd catalysts under a hydrogen environment, it was necessary to determine the optimized conditions that provide an efficient hydrogenation activity for less activated alkenes while maintaining high chemoselectivity for hydrogenation of alkene over the nitro group.

The results in Table 1 show that the C8 PdNP catalyst was most effective in the original reaction condition (entry 1: room temperature, 1 atm H2, 5 mol % PdNP, and CDCl3 solvent) with the complete reduction of alkene to alkane without hydrogenating the nitro functional group. The complete hydrogenation of alkene group required 24 h of reaction under this standard condition. However, decreasing the loading of PdNP to 2.5 and 1 mol % resulted in incomplete hydrogenations of alkene with 97 and 76% conversions, respectively, after 24 h (entries 2 and 3). When the concentration of reactants was decreased by ~67%, the hydrogenation of m-nitrostyrene to 1-ethyl-3-nitrobenzene dropped noticeably from 97 to 8% indicating the importance of kinetic collisions (entry 4). The use of polar solvents such as methanol, acetone, and DMSO had negative influence on the catalytic activity of C8 PdNP due to the heterogeneous nature of catalyst conditions (entries 5−7). In comparison, Pd/C was able to hydrogenate both alkene and nitro functional groups under the same mild reaction condition exhibiting its highly active but less selective catalysis nature.

Encouraged by the high selectivity of C8 PdNP for hydrogenation of alkene in the presence of nitro group, we further explored the substrate scope of this catalytic system (Table 2). The possible synergistic effect between the heteroatoms of the nitro group and PdNP was investigated using trans-β-nitrostyrene, ethyl trans-4-nitrocinamate, and 1-nitrocyclohex-1-ene (entries 1−3, respectively). None of these alkenes were reactive toward hydrogenation, and quantitative amounts of starting materials were recovered in all three cases. The results indicated that disubstituted and trisubstituted alkene hydrogenation are challenging for these thiolate-capped PdNP catalysts. We propose that the presence of alkanethiolate ligands sterically hinders the formation of the di-σ bonded intermediate needed for the direct hydrogenation of multi-substituted alkenes.

With the activity and selectivity of C8 PdNP that can be applied to the hydrogenation of monosubstituted alkene, the hydrogenation of various styrene derivatives with other functional groups such as trifluoromethyl, aldehyde, bromo, fluoro, methyl, acetyloxy, and amino groups was investigated (Table 3). The catalytic reactions of alkenes with various reducible functionalities using C8 PdNP resulted in the desirable reduction of C=CC bond in high yields with remarkable selectivity. As shown in the result of control experiment using m-nitrostyrene (entry 2), the catalytic hydrogenation of p-nitrostyrene (entry 3) exhibited the same result, with the complete reduction of alkene to alkane but without the reduction of nitro group. Thus, the position of the

### Table 1. Hydrogenation of m-Nitrostyrene by C8 PdNP in Various Reaction Conditions

| Entry | C8 PdNP (or other catalysts) (mol %) | Solvent | 1-ethyl-3-nitrobenzene (%) |
|-------|------------------------------------|---------|--------------------------|
| 1     | 5                                  | CDCl3   | >99                      |
| 2     | 2.5                                | CDCl3   | 97                       |
| 3     | 1                                  | CDCl3   | 76                       |
| 4     | 2.5                                | CDCl3 (5 mL) | 8               |
| 5     | 2.5                                | CD3OD   | 22                       |
| 6     | 2.5                                | acetone-d6 | 27                     |
| 7     | 2.5                                | DMSO-d6 | 9                        |
| 8     | Pd/C (2.5)                         | CDCl3   | 0’                       |

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Reaction conditions: 50 mL round-bottom flask, m-nitrostyrene (0.5 mmol), C8 PdNP, solvent (3 mL), and 24 h. The reaction condition was heterogeneous. The major product of hydrogenation reaction by Pd/C was 3-amino-1-ethylbenzene.
functionalities on the benzene ring does not affect the activity and selectivity of the C8 PdNP catalyst for styrene hydrogenation. Moreover, the hydrogenation of another substituent using C8 PdNP was not affected by the presence of a strongly electron-withdrawing group, −CF3 (entry 4). The catalytic reactions of challenging substrates that have reducible carbonyl functional groups such as aldehyde and acetoxy substituents also resulted in highly chemoselective hydrogenation of alkene group (entries 5 and 6). Three halogenated styrene substrates, p-fluorostyrene, m-chlorostyrene, and p-bromostyrene, were selectively hydrogenated to the corresponding 1-ethyl-4-fluorobenzene, 1-chloro-3-ethylbenzene, and 1-bromo-4-ethylbenzene, respectively, in high yields without any reductive dehalogenation (entries 7−9). Figure S1 demonstrates the kinetic studies of p-fluorostyrene to 1-ethyl-4-fluorobenzene that is monitored by 1H NMR spectroscopy to obtain a clearer image of chemoselective hydrogenation reaction over time. Moreover, other substituents with strong electron-donating property such as −OCH3 and −NH2 or weakly electron-donating alkyl substituents such as CH3 (entries 10−12) are also fully hydrogenated without any notable change in the activity of the C8 PdNP catalyst. Hence, the presence of electron-withdrawing and electron-donating groups in the styrene substrates does not have any impact on the hydrogenation activity of C8 PdNP. The hydrogenation of phenylacetylene (entry 13) produced a full hydrogenation product in high yield, indicating the overall high activity of C8 PdNP for terminal alkynes. In summary, the C8 PdNP catalyst exhibited high activity toward unsaturated C=C bonds but no reduction of NO2 group and other less reactive functional groups including carbonyl and halogens was observed. The presence of strongly electron-withdrawing (−NO2, −CF3) or electron-donating group (−OCH3, −NH2) had no impact on the catalytic hydrogenation of styrene derivatives by C8 PdNP. The chart in Figure 1 summarizes the chemoselectivity of C8 PdNP and other Pd-based catalysts for hydrogenation of various functional groups.

The selectivity of alkene hydrogenation in the presence of NO2 group is relatively challenging for other supported metal or metal nanoparticle catalysts as they reduce it to the corresponding NH2. In comparison, our C8 PdNP catalyst exhibits an excellent chemoselectivity for alkene hydrogenation that functions under a mild reaction condition. Only a handful of Pd-based catalysts have shown comparable catalytic activity and selectivity without reducing the nitro group. The conversion yields and selectivities in addition to the reaction conditions for the hydrogenation of m-nitrostyrene with other Pd-based catalysts are compared with those of C8 PdNP in Table 4. The layered double hydroxide-supported nanopalladium (LDH-Pd0) catalyst was reported for producing a mixture of products with a low selectivity for 3-ethyl-1-nitrobenzene.35 Pd nanoparticles supported on fibrous silica nanospheres KCC-1-NH2 could be used for the transfer hydrogenation of alkene with the use of HCOOH as a source of hydrogen.36 However, this catalyst reduced both function-

### Table 2. Hydrogenation Scope for Di and Trisubstituted Alkenes with Nitro Group by C8 PdNP
d<sup>a</sup> b

| Entry | Substrate | Product | Result |
|-------|-----------|---------|--------|
| 1     | ![Substrate 1](image1) | ![Product 1](image2) | No reaction |
| 2     | ![Substrate 2](image3) | ![Product 2](image4) | No reaction b |
| 3     | ![Substrate 3](image5) | ![Product 3](image6) | No reaction |

<sup>a</sup>Reaction conditions: 50 mL round-bottom flask, substrate (0.5 mmol), C8 PdNP (2.5 mol %), CDCl3 (2.5 mL), and 24 h. <sup>b</sup>Hydrogenation of ethyl trans-4-nitrocinnamate using Pd/C at the same condition resulted in the reduction of both C=C and NO2 groups.

### Table 3. Catalytic Reactions of Styrene Derivatives Using C8 PdNP

| Entry | Substrate | Product | Yield [%] |
|-------|-----------|---------|-----------|
| 1     | ![Substrate 1](image7) | ![Product 1](image8) | >99 |
| 2     | ![Substrate 2](image9) | ![Product 2](image10) | >99 |
| 3     | ![Substrate 3](image11) | ![Product 3](image12) | >99 |
| 4     | ![Substrate 4](image13) | ![Product 4](image14) | >99 |
| 5     | ![Substrate 5](image15) | ![Product 5](image16) | >99 |
| 6     | ![Substrate 6](image17) | ![Product 6](image18) | >99 |
| 7     | ![Substrate 7](image19) | ![Product 7](image20) | >99 |
| 8     | ![Substrate 8](image21) | ![Product 8](image22) | >99 |
| 9     | ![Substrate 9](image23) | ![Product 9](image24) | >99 |
| 10    | ![Substrate 10](image25) | ![Product 10](image26) | >99 |
| 11    | ![Substrate 11](image27) | ![Product 11](image28) | >99 |
| 12    | ![Substrate 12](image29) | ![Product 12](image30) | >99 |
| 13    | ![Substrate 13](image31) | ![Product 13](image32) | >99 |

<sup>a</sup>Reaction condition: 5 mol % C8 PdNP, 0.5 mmol substrates, room temperature, 3 mL of CDCl3 solvent, and 1 atm H2 for 24 h.
alities of 3-nitrostyrene with 45% conversion yield to 3-ethylaniline. When 3 equiv of formic acid was employed under the same reaction condition, the formation of 3-ethylaniline was observed in higher yield. Thus, both supported Pd catalysts were considered more active but less selective than C8 PdNP for the hydrogenation of 3-nitrostyrene. Other supported Pd catalysts were reported for the hydrogenation of 4-nitrostyrene. Pd/MS5A exhibited a fine selectivity for the hydrogenation of alkene in the presence of nitro group in a mild reaction condition comparable to ours. Yet, the catalyst was not able to selectively hydrogenate the terminal alkene when used for the hydrogenation of styrene derivatives with more electron-donating substituents on the aromatic ring, which limits the utility of the catalyst (vide infra). Palladium nanoparticles immobilized on nitrogen-enriched porous carbon (Pd/NPC) demonstrated a high catalytic activity for the hydrogenation of alkene with HCOOH as the hydrogen donor, but the catalyst achieved the reduction of both C=O and NO2.

Transition-metal complexes were also reported for hydrogenation of styrene derivatives. Potassium bis(η4-anthracene) cobaltate showed a good activity in catalytic hydrogenation reaction with unbiased styrene, but the reaction proceeded much poorer with styrene derivatives with an electron-donating group such as acetoxy. Furthermore, an immobilized rhodium complexe on silica was used for catalytic hydrogenation of alkene with HCOOH as the hydrogen donor, but the catalyst achieved the reduction of both C=O and NO2.

Iron-catalyzed hydrogenation of styrene derivatives was reported with an FeCl3−LiAlH4 catalyst. Although the reaction was operated under a high-pressure condition (10 atm H2), the hydrogenation of 4-fluorostyrene to 1-ethyl-4-fluorobenzene was limited to 77% conversion. The biowaste-derived cobalt chitosan catalysts used for the hydrogenation of C≡C in 4-fluorostyrene yielded 81% of 1-ethyl-4-fluorobenzene in water but required elevated temperature and high H2 pressure. Copper nanoparticles supported on diamond nanoparticle annealed with hydrogen (Cu/DH) were investigated for the hydrogenation of 4-methoxystyrene. The catalyst selectively hydrogenated the alkene group, but the presence of a strong electron-donating substituent caused the reaction to require 30 h to reach 60% conversion. Iron-based homogeneous catalysts bearing a bis(phosphino)amine ligand used for the hydrogenation of 4-methoxystyrene required a much longer reaction time of 168 h to reach full conversion even at a higher operating temperature. All these comparisons clearly demonstrate the high activity and selectivity of C8 PdNP for the chemoselective hydrogenation of styrene derivatives with various reactive functional groups including highly electron-withdrawing and electron-donating groups.

The stability and recyclability of C8 PdNP were examined in the previous work from our group using the same reaction condition that catalyzed the hydrogenation of 2,3-dimethylbuta-1,4-diene. The C8 PdNP catalyst was precipitated and separated from the reaction mixture and then dried without any solvent before being recycled for more catalysis reactions. The results showed that even after seven cycles, the activity and selectivity were maintained at almost same levels. Thus, it is noteworthy to mention that the C8 PdNP catalyst can be reused several times without the significant loss of both its activity and selectivity.

PhC2 PdNP versus C8 PdNP. We have also recently developed and worked on another catalyst, which is phenyl-ethanethiolate-capped Pd nanoparticles (PhC2 PdNP). The PhC2 PdNP has been synthesized with the same thiosulfate protocol that was described earlier and found to have similar average particles size with C8 PdNP. The average size and the surface ligand density of PhC2 PdNP are 1.7 ± 0.8 nm and 0.32 ligand/surface atom, respectively. In comparison, C8 PdNP has an average core size of 2.3 ± 0.9 nm and 0.35 ligand/surface atom, respectively. In comparison, C8 PdNP has an average core size of 2.3 ± 0.9 nm and a ligand density of 0.35 (see the Supporting Information).

Figure 1. Summary of functional group selectivity for C8 PdNP for chemoselective hydrogenation.
used for C8 PdNP (Table 5). The results indicated that the PhC2 PdNP exhibits the same chemoselectivity for the C≡C group in styrene derivatives as that of C8 PdNP but with much lower catalytic activity for all substrates examined here.

| Substrates | Catalysts | Products | Yield % | Time | Reaction conditions |
|------------|-----------|----------|---------|------|--------------------|
| O=N         | C8 PdNP   | O=N      | >99     | 24 h | rt, CDCl₃, 1 atm H₂, 5 mol% Pd |
|            | LDH-Pd0²⁶ | A=75 B=25| 3 h     |      | rt, EtOH, 1 atm H₂, 15 mg catalyst w/ 2 mmol substrate |
|            | PA/KCC-1-NH₂²⁶ | A=75 B=25 | 3 h |      | 100 °C, MeOH, HCOOH, 50 mg catalyst w/ 1 mmol substrate – 6.5 mol% Pd |
| O=N         | C8 PdNP   | O=N      | >99     | 24 h | rt, CDCl₃, 1 atm H₂, 5 mol% Pd |
|            | Pd/M55A²⁷ | 92       | 4 h     |      | rt, MeOH, H₂ balloon, 10 wt% catalyst w/ 0.25 mmol substrate |
|            | Pd/NPC²⁸ | >90      | 5 h     |      | 50 °C, EtOH, HCOOH, 10 mg catalyst w/ 0.25 mmol substrate |
|            | C8 PdNP   | C       | >99     | 24 h | rt, CDCl₃, 1 atm H₂, 5 mol% Pd |
|            | K bis(π⁴-anthracene) CO²⁹ | 69 | 3 h |      | 20 °C, toluene, 2 atm H₂, 1 mol% catalyst |
|            | Br        | C       | >99     | 50 h | rt, toluene, 1.1 atm H₂, 1 mol% catalyst |
|            | Pd/M55A²⁷ | A=71 B=29| 24 h |      | rt, MeOH, H₂ balloon, 10 wt% catalyst w/ 0.25 mmol substrate |
|            | C8 PdNP   | F       | >99     | 24 h | rt, CDCl₃, 1 atm H₂, 5 mol% Pd |
|            | FeCl₂-LiAlH₄³⁰ | 77 | 20 h |      | 18 °C, THF, 10 atm H₂, 5 mol% catalyst |
|            | Co(n)Chitosan-700³² | 85 | 18 h |      | 60 °C, H₂, 10 atm H₂, 2.9 mol% catalyst |
|            | H₂CO⁻      | C8 PdNP | >99     | 24 h | rt, CDCl₃, 1 atm H₂, 5 mol% Pd |
|            | Cu/DH NP³³ | H₂CO⁻   | 60      | 30 h | 60 °C, Ethanol, hydrazine, 20 mg catalyst w/ 1 mmol substrate |
|            | (PNP³⁴)Fe(H)(CO)³⁵ | H₂CO⁻ | >99 | 168 h | 60 °C, CD₃, 1 atm H₂, ~4.9 mol% catalyst |

“The data are chosen from the selectivity results of the substrate example for each type of catalysts. *Reaction conditions are based on temperature, solvent, and H₂ pressure/source.  Room temperature (rt).
Kinetic studies have been conducted for two styrene substrates with different functional groups for both C8 and PhC2 PdNPs. One of the substrates that was chosen for this study is 4-methoxystyrene. As shown in Figure 2a, the two catalysts show clear differences in the initial kinetic activity. After the first hour of the reaction, C8 PdNP produced 56% of the product while PhC2 PdNP produced only 13%. After 24 h, both catalysts achieved the reduction of C==C without reducing the methoxy group. However, the hydrogenation of alkene by PhC2 PdNP resulted in less than 50% conversion and reached a plateau after 6 to 24 h reactions. Another example of the kinetic study was with 4-bromostyrene (Figure 2b). After 1 h, C8 PdNP showed significantly higher yield at nearly 30% whereas PhC2 PdNP displayed much lower yield. The final results after 24 h reaction were quite similar for both PdNP to those of 4-methoxystyrene. These kinetic studies clearly demonstrated that the catalytic reactions of PhC2 PdNP are kinetically much slower than those of C8 PdNP and reach an equilibrium at ~50% conversion.

**Mechanistic Interpretations of the C8 PdNP and PhC2 PdNP Activities.** The mechanistic interpretations for different activities of C8 PdNP and PhC2 PdNP are outlined in Figure 3. The presence of aromatic group in the styrene substrates providing the overlapping p orbitals on the surface of C8 PdNP is previously found to be a reason for the increases in the formation of the di-σ-bonded Pd alkyl intermediate that results in facile hydrogenation (Figure 3a). On the other hand, the catalytic reaction of styrene derivatives with PhC2 PdNP resulted in lower yields for the

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**Table 5. Catalytic Hydrogenation of Styrene Derivatives Using PhC2 PdNP**

| Entry | Substrate | Product | Yield % |
|-------|-----------|---------|---------|
| 1     | ![Substrate](image1.png) | ![Product](image2.png) | 25      |
| 2     | ![Substrate](image3.png) | ![Product](image4.png) | 32      |
| 3     | ![Substrate](image5.png) | ![Product](image6.png) | 43      |
| 4     | ![Substrate](image7.png) | ![Product](image8.png) | 58      |
| 5     | ![Substrate](image9.png) | ![Product](image10.png) | 42      |
| 6     | ![Substrate](image11.png) | ![Product](image12.png) | 44      |
| 7     | ![Substrate](image13.png) | ![Product](image14.png) | 49      |

*a Reaction conditions: 5 mol % PhC2 PdNP, 0.5 mmol substrates, room temperature, 3 mL of CDCl₃ solvent, and 1 atm H₂ for 24 h. b No hydrogenation of other reducible functional groups besides the C==C group was observed.*

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**Figure 2.** Comparison Kinetic Studies between C8 PdNP and PhC2 PdNP: (a) 4-methoxystyrene and (b) 4-bromostyrene.

**Figure 3.** Proposed mechanisms of palladium nanoparticle-catalyzed hydrogenation of styrene with (a) C8 PdNP and (b) PhC2 PdNP.
hydrogenation product. It is proposed that the phenyl group that is present in the surface ligand interferes with the contribution of phenyl group in the substrate (Figure 3b). The noncovalent interaction between surface ligands and substrates has been shown to similarly affect the catalytic selectivity of PdNP.\textsuperscript{33} In specific, for our catalytic system using PhC2 PdNP, the π−π interaction of the aromatic groups between ligand and substrate would reduce the strong interaction of the substrate with the Pd surface. This prevents the essential contribution of phenyl group in the substrate to form a di-π-bonded Pd-alkyl intermediate on the catalyst surface. Therefore, the weaker adsorption of styrene on the Pd nanoparticle surface was directly translated to the slower catalytic hydrogenation by PhC2 PdNP and the equilibrium between the substrate and Pd-alkyl intermediate. Based on the previously reported catalytic activity of PdNP generated from 2-cyclohexyl-1-ethylthiosulfate (CyC2 PdNP) that was similar to that of C8 PdNP,\textsuperscript{18,45} the presence of a large phenyl group, which is smaller than the cyclohexyl group, does not seem to cause any significant steric problem on the nanoparticle surface. Hence, different catalytic activities of PhC2 PdNP should mostly arise from the influence of aromatic π−π interactions between surface ligands and substrates.

\section*{CONCLUSIONS}
Octanethiolate-capped palladium nanoparticles with an average core size of 2.3 nm were used for chemoselective catalytic hydrogenation of various styrene derivatives at room temperature and under atmospheric pressure. This colloidal nano-catalyst exhibited outstanding activity and selectivity for hydrogenating the monosubstituted alkene group to the corresponding alkane in the presence of other reducible functional groups under mild reaction conditions. Various reactive functionalities such as aldehyde, nitro, chloro, bromo, acetoxy, and multisubstituted alkene groups were not reduced by palladium nanoparticles. Furthermore, phenyl-terminated ligand-capped palladium nanoparticles exhibited a decreased catalytic activity for styrene hydrogenation. The influence of ligand—substrate noncovalent interactions on the catalytic activity of Pd nanoparticles was observed from this study. Not only the alkene group but also the alkyne group was fully hydrogenated to alkane using octanethiolate-capped Pd nanoparticles. Considering the importance of chemoselective alkene and alkyn hydrogenation, octanethiolate-capped palladium nanoparticles proved to be a potentially recyclable catalyst that operates under mild conditions and promising for the petrochemical, fine chemical, and pharmaceutical industries.

\section*{EXPERIMENTAL SECTION}

\textbf{Materials.} 1-Bromooctane (C\textsubscript{8}H\textsubscript{17}Br), 2-bromoethylbenzene (C\textsubscript{8}H\textsubscript{12}CH\textsubscript{2}Br), sodium thiosulfate pentahydrate (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}·5H\textsubscript{2}O) for synthesizing the C8 and PhC2 ligands were obtained from Sigma-Aldrich. Tetraoctylammonium bromide (TOAB), sodium borohydride (NaBH\textsubscript{4}), and potassium tetrachloropalladate (II) (K\textsubscript{2}PdCl\textsubscript{4}) (193.128 g/mol), and 20 mmol sodium thiosulfate pentahydrate (248.172 g/mol) was mixed with 40 mL of ethanol and 40 mL of nanopure water. The flask was connected to the reflux condenser. The mixture was refluxed for 3 h, and then the sample was evaporated under reduced pressure by utilizing a rotary evaporator. The white solid product was recrystallized using hot ethanol and a cooling bath to form the ligand as a crystalline solid. The ligand was then stored in a vacuum oven for an extended time.\textsuperscript{18,45} A 500 mL round-bottom flask was charged with 0.4 mmol potassium tetrachloropalladate(II) (K\textsubscript{2}PdCl\textsubscript{4}, 326.428 g/mol) dissolved in 12 mL of nanopure water and 2.0 mmol TOAB (546.81 g/mol) dissolved in 25 mL of toluene and stirred for 15 min. The reaction starts with the phase transfer of the metal precursor PdCl\textsubscript{4}\textsuperscript{2−} from aqueous phase to organic phase using TOAB as the phase transfer agent (Scheme 2). The aqueous layer was separated and discarded using the separatory funnel after the phase transfer. Sodium S-octylthiosulfate ligand (0.8 mmol) was dissolved completely in 10 mL of 25% methanol. The ligand and 2.0 mmol TOAB were added at the same time to the organic layer that was placed in a round-bottom flask, and the mixture was stirred for 15 min. The purpose of the second addition of TOAB is to ensure the transfer of thiosulfate ligands from the aqueous phase to the organic phase and to provide temporary capping for the growing nanoparticle before the thiosulfate ligand is capped onto the nanoparticle. In a falcon tube, 8 mmol NaBH\textsubscript{4} (37.83 g/mol) was dissolved in 7 mL of nanopure water and then added slowly to the stirring reaction flask within 10 s. NaBH\textsubscript{4} is used as the reducing agent that initiates the nucleation growth of Pd nanoparticle. The solution’s color turned black instantly with the addition of NaBH\textsubscript{4}, which indicates the formation of octanethiolate-capped Pd nanoparticles. The reaction was stirred for 3 h. After the stirring, the solution was placed in a separatory funnel to remove the aqueous layer. The organic layer was concentrated by utilizing a rotary evaporator for a few minutes until the solute became a black solid. The Pd nanoparticles were washed with ethanol and methanol several times, alternating between sonication and centrifuging for 15 min before they were dried under vacuum. The black powder of C8

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Scheme_2_Synthesis_of_C8_PdNP.png}
\caption{Scheme 2. Synthesis of C8 PdNP}
\end{figure}
PdNP is easily soluble in organic solvents such as chloroform and toluene and is bench-stable. The synthesis of PhC2 PdNP followed the same procedure that is also available in the previous publication.3

Characterization of Palladium Nanoparticles. 1H NMR spectra were obtained by using Bruker Fourier 400-MHz. The NMR sample of the Pd nanoparticles was prepared in CDCl3. The 1H NMR spectra of C8 PdNP displayed three small peaks at 0.8 ppm for methyl and 1.3 and 1.6 ppm for methylenes (Figure S2). The 1H NMR spectra of PhC2 PdNP displayed one broad peak at 6.8–7.4 ppm for the phenyl group (Figure S3). The broadening of signals corresponding to α- and β-CH2CH2–S proposes that the hydrocarbon species derived from sodium S-octylthiosulfate and sodium 2-phenyl-1-ethylthiosulfate are attached to the nanoparticle.18,45 More spectroscopic characterization results for C8 PdNP and PhC2 PdNP are available in the Supporting Information (Figures S2–S7). Transmission electron microscopy (TEM) images were obtained using a JEOL 1200 EX II electron microscope. The particle size was proved to be around 2.3 ± 0.9 nm for C8 PdNP and 1.7 ± 0.8 nm for PhC2 PdNP by the TEM images and histograms (Figures 4 and 5). The TEM image showed of the solution was transferred to an NMR tube to obtain 1H NMR spectra.

Figure 4. TEM Image and histogram of C8 PdNP. Size analysis indicates that the average core size of C8 PdNP is 2.3 ± 0.9 nm (data obtained from multiple images).

Figure 5. TEM image and histogram of PhC2 PdNP. Size analysis indicates that the average core size of PhC2 PdNP is 1.7 ± 0.8 nm (data obtained from multiple images).

ASSOCIATED CONTENT
5 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03335.

Figure S1: 1H NMR spectra of catalytic reactions of 4-fluorostyrene to 1-ethyl-4-fluorobenzene using C8 PdNP at different reaction times; Figure S2: 1H NMR spectrum of C8 PdNP with the inset spectrum for the area of 0.5–2.0 ppm; Figure S3: 1H NMR spectrum of PhC2 PdNP; Figure S4: UV–vis spectrum of C8 PdNP in CH2Cl2; Figure S5: UV–vis spectrum of PhC2 PdNP in CH2Cl2; Figure S6: FT-IR spectrum of C8 PdNP; Figure S7: FT-IR spectrum of PhC2 PdNP; and Figure S8: TGA result of C8 PdNP (PDF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: ys.shon@csulb.edu. Phone: 562-985-4466. Fax: 562-985-8547.

ORCID
Jie S. Zhu: 0000-0003-3009-4135
Young-Seok Shon: 0000-0003-4765-6130

Author Contributions
M.A.M., J.S.Z., and V.N. conducted the experimental work. M.A.M. wrote the original draft. J.S.Z. developed the experimental methodology. Y.-S.S. supervised the project, provided resources, and edited the draft. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

Fib, fibroin; PEI, polyethyleneimine; BN, boron nitride; MS, molecular sieves; CR11, chelate resin; SC, spherically shaped activated carbon; TBS, tetramethylysilane; DMSO, dimethylsulfoxide; LDH, layered double hydroxides; NPC, nitrogen-enriched porous carbon; DH, diamond nanoparticle annealed with hydrogen; TOAB, tetraoctylammonium bromide; TEM, transmission electron microscopy; TGA, thermogravimetric analysis; NMR, nuclear magnetic resonance

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