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Facile Synthesis of Various Phosphine-Stabilized Monodisperse Palladium Nanoparticles through the Understanding of Coordination Chemistry of the Nanoparticles

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ABSTRACT

We developed facile synthetic procedures to produce monodisperse palladium nanoparticles stabilized with various phosphine ligands by a better understanding of their coordination chemistry. Compared to small sized phosphines such as triphenylphosphine (TPP), trioctylphosphine (TOP) showed weaker coordination ability to palladium nanoparticles. This result was ascertained based on the ^{31}P NMR spectroscopic results of in situ generated molecular palladium complexes. Since TOP acts as a more efficient surfactant in the preparation of high quality monodisperse palladium nanoparticles than smaller sized phosphines, we conducted surfactant exchange reactions of TOP-stabilized palladium nanoparticles in order to produce monodisperse palladium nanoparticles stabilized with various other phosphines. These monodisperse nanoparticles include monodisperse Pd nanoparticles stabilized with chiral ligands and water-dispersable Pd nanoparticles.

The development of nanometer-sized colloidal particles has been intensively studied, because of their considerable technological and fundamental scientific interest.[1] The surface modification of these colloidal nanoparticles and the related surfactant (or ligand) exchange reactions are very important to facilitate their application to biotechnology, catalysis, and nanocomposites.[2] In particular, various metal nanoparticles have been extensively utilized as catalysts for many organic transformations, and the stabilizing ligands (or surfactants) are known to influence the catalytic activity and selectivity of the nanoparticles.[3] To develop efficient surfactant exchange reactions, it is critical to understand the surface chemistry of colloidal nanoparticles. For example, Dravid and co-workers investigated the chemical interaction of oleic acid surfactant with Co nanoparticles using infrared spectroscopy and X-ray photoelectron spectroscopy.[4]

Palladium nanoparticles have been extensively used as catalysts for many organic reactions that are also catalyzed by organometallic palladium complexes such as olefin hydrogenation and carbon−carbon coupling reactions.[5] Although numerous phosphine-based ligands have been developed for organo-palladium compounds for their applications as catalysts for many organic reactions, these ligands have not been extensively utilized as stabilizing surfactants for palladium nanoparticles. There are very few reports on the coordination chemistry of palladium nanoparticles.[6] For example, El-Sayed and co-workers investigated the effect of reagents and surfactants on the stability of palladium nanoparticles during Suzuki coupling reactions.[6a] Very recently, the Chaudret[7] and Fujihara[8] groups reported on the asymmetric catalytic applications of chiral phosphine stabilized palladium nanoparticles. For their extensive applications, synthesis of palladium nanoparticles stabilized by various ligands has become very important. In addition, comparative studies on the ligand coordination chemistry between metal nanoparticles and organometallic compounds would provide useful information for the catalytic applications of palladium nanoparticles, because it is often very difficult to distinguish between homogeneous catalysis on molecular species and heterogeneous catalysis on metal nanoparticles.[9] Herein we report on the synthesis of monodisperse palladium nanoparticles stabilized with various phosphine ligands, which was made possible through the understanding of the coordination chemistry of phosphine ligands on palladium nanoparticles that was gained using ^{31}P NMR spectroscopy.

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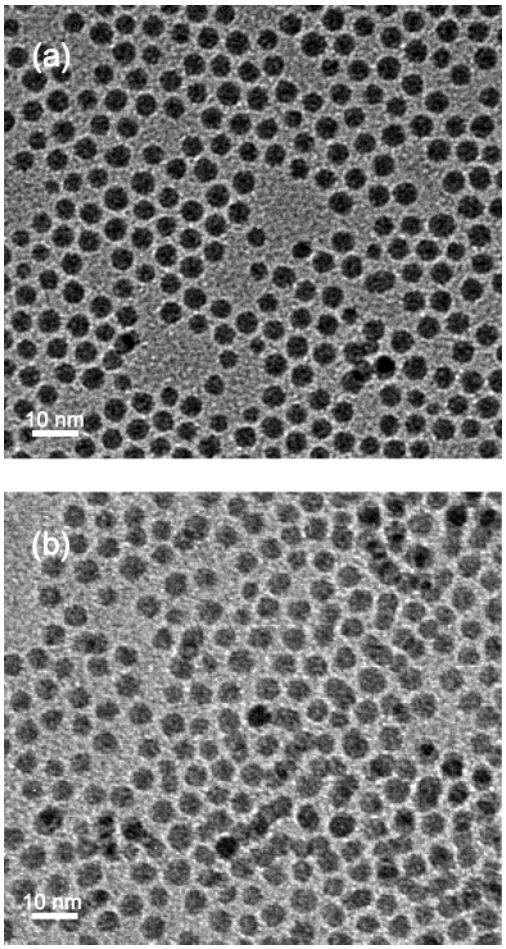
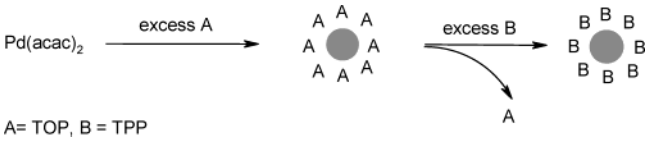


Figure 1. TEM images of the 5 nm sized monodisperse palladium nanoparticles stabilized with TOP (a) and with TPP (b).

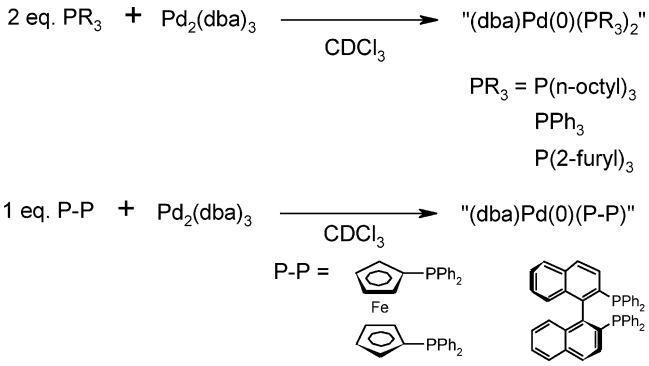
In the current study, we first investigated the coordination chemistry of phosphine ligands on palladium nanoparticles using ^{31}P NMR spectroscopy. Next, we conducted ligand exchange reactions of monodisperse trioctylphosphine (TOP) stabilized Pd nanoparticles with various other ligands. Monodisperse 5 nm sized Pd nanoparticles were synthesized using the procedure reported by our group after a slight modification.[10] Briefly, a reaction mixture containing 0.1 g of $Pd(acac)_2$ (0.33 mmol) and 7 mL of TOP (16 mmol) was slowly heated to 300 °C, and was aged at this temperature for 0.5 h. The resulting solution was cooled to room temperature, the nanoparticles were retrieved by centrifugation, and the excess TOP ligand was washed with methanol. The TEM image showed that the nanoparticles are monodisperse with a particle size of 5 nm (Figure 1a).

We investigated the coordination ability of the phosphine ligands on Pd nanoparticles using ^{31}P NMR spectroscopy. For the comparison study, we prepared "$(dba)Pd(0)(TOP)_2$" and "$(dba)Pd(0)(TPP)_2$" (dba = dibenzylideneacetone) using the reported synthetic procedures (Scheme 2).[11] The coordination of phosphine ligands on palladium nanoparticles is known to induce a downfield shift in the ^{31}P NMR peaks. The ^{31}P NMR peak of TOP stabilized 5 nm sized palladium nanoparticles appeared at 2.89 ppm. In contrast, free TOP exhibited a peak at −30.43 ppm (Figure 2 and Table 1), and the in situ generated "$(dba)Pd(0)(TOP)_2$" showed a peak at

Scheme 1. Synthesis of Monodisperse Pd Nanoparticles via Surfactant Exchange Reaction



Scheme 2. Preparation of "$(dba)Pd(0)(PR_3)_2$" and "(dba)Pd(0)(P−P)"species



10.54 ppm. The peak at 2.89 ppm for the Pd nanoparticles might have resulted from TOPO, which is easily produced by the oxidation of TOP. However, the ^{31}P NMR peak of free TOPO appeared at 48.91 ppm and TOPO did not coordinate on the Pd nanoparticles. Consequently, we were able to unambiguously assign the peak at 2.89 ppm to TOP coordinated on the Pd nanoparticles. The upfield shift in the peak of TOP on Pd nanoparticles compared to the peak of "$(dba)Pd(0)(TOP)_2$" demonstrates that the TOP ligand is less strongly bound to the Pd nanoparticles.

After finding that the TOP ligand (or surfactant) was weakly bound to the Pd nanoparticles, we conducted ligand exchange reactions of TOP stabilized Pd nanoparticles to produce Pd nanoparticles stabilized with various other ligands (Scheme 1). We first tried the ligand exchange reaction of TOP stabilized Pd nanoparticles with triphenylphosphine (TPP), which is the most widely used phosphine ligand for producing coordination compounds. In a typical procedure, 0.2 g of TPP (0.76 mmol) was added to a solution containing 50 mg of the monodisperse 5 nm sized TOP stabilized Pd nanoparticles dispersed in 3 mL of chloroform at room temperature. The resulting mixture was stirred for 12 h at room temperature. The ligand exchanged nanoparticles were retrieved by adding 10 mL of methanol to the solution followed by centrifugation. The TEM image revealed that the TPP stabilized Pd nanoparticles were still very monodisperse with a particle size of 5 nm (Figure 1b). This result is very interesting, in that it demonstrates that monodisperse Pd nanoparticles can be generated by a simple ligand exchange reaction. In some cases, the surfactant exchange reaction resulted in the deterioration of the quality of the nanoparticles, producing nanoparticles with deformed shapes and/or a broadened size distribution.[2b] Unlike the TOP stabilized Pd nanoparticles and TOP−Pd molecular species, the ^{31}P NMR peaks of both the TPP stabilized Pd nanoparticles and the in situ generated "$(dba)Pd(0)TPP_2$" appeared

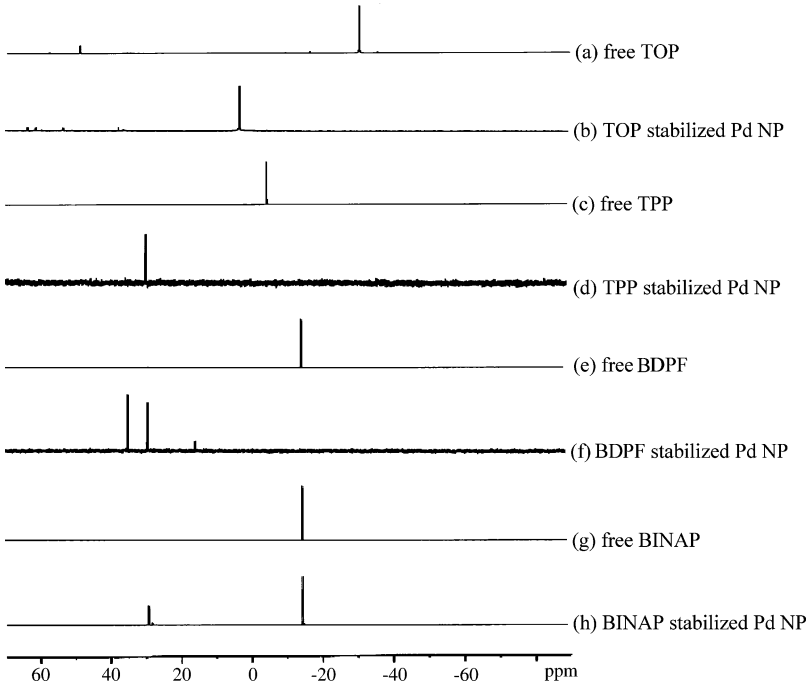


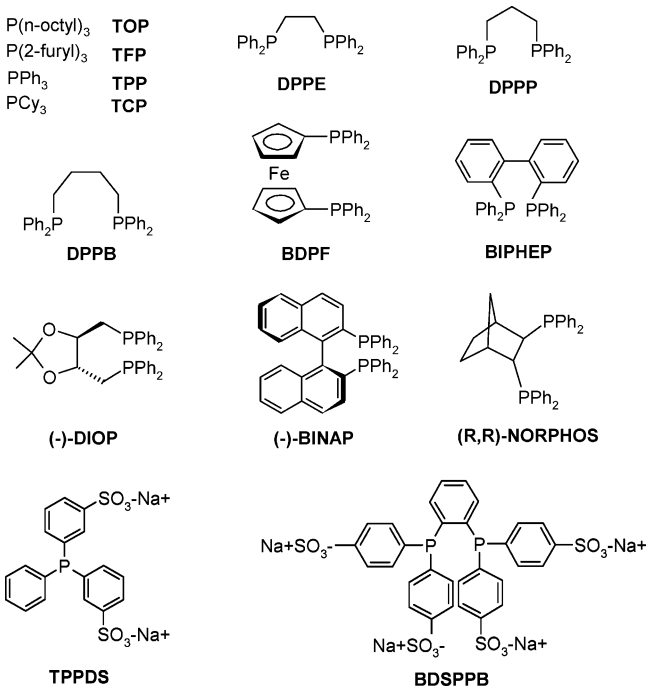
Figure 2. Representative ^{31}P NMR spectra of phosphines and the corresponding phosphine-stabilized Pd nanoparticles.

Table 1. ^{31}P NMR Data of Phosphines, Pd Complexes, and Pd Nanoparticles

used phosphines	^{31}P NMR peaks of free ligands (ppm)	^{31}P NMR peaks of Pd complexes (ppm)	^{31}P NMR peaks of Pd NPs (ppm)
TOP	−30.43	10.54	2.89
TOPO	48.91		
TPP	−5.08	29.47	29.47
TFP	−77.38	−11.35	−11.34
TCP	51.49		58.69
BDPF	−16.85	34.28, 28.76	34.21, 28.49
DPPE	−11.4		32.95
DPPP	−16.39		11.54
DPPB	−13.99		25.37
BIPHEP	−13.99		28.53
(−)-BINAP	−15.04	28.92	28.92
(−)-DIOP	−23.02	16.42	16.51
(R,R)-NORPHOS	0.05, −1.58		32.37, 29.55
TPPDS	−3.33		0.32
BDSPPB	−14.09		0.38

at exactly the same value of 29.47 ppm. It is noteworthy that $(PPh_3)_4Pd(0)$ and $(PPh_3)_2Pd(II)Cl_2$ showed ^{31}P NMR peaks at 29.69 and 23.58 ppm, respectively, because this result demonstrates that the electronic environment of the surface palladium atoms of the TPP coated palladium nanoparticles is similar to that of Pd(0) complexes rather than that of Pd(II) complexes, and that the Pd atoms in the core part of the nanoparticles do not seem to influence the electronic environment of the palladium atoms situated on the shell of the nanoparticles. As a control experiment, we synthesized TPP stabilized Pd nanoparticles via the direct thermal decomposition of Pd precursors in the presence of the TPP ligand. The TEM image of the resulting nanoparticles revealed that the quality of the nanoparticles is poor

Chart 1. Various Phosphine Ligands Employed in This Study



in terms of their size distribution and shape (see Supporting Information). This result can be explained by the strong binding capability of triphenylphophine, which hinders the growth of the nanoparticles.

We conducted further ligand exchange reactions of TOP-stabilized Pd nanoparticles with many other phosphine ligands (Chart 1 and Table 1). The ligand exchange reaction turned out to be broadly applicable, and various phosphine ligands were substituted with TOP ligands in the Pd nanoparticles. The results of the ^{31}P NMR spectroscopic studies of these Pd nanoparticles are summarized in Table

1. The completion of the ligand exchange reactions is characterized by the complete disappearance of the TOP peak in the ^{31}P NMR spectra of the resulting Pd nanoparticles. TOP ligands can easily be substituted not only with monodentate phosphines but also with bidentate phosphines. In the cases of tris-2-furyl phosphine, 1,1′-bisdiphenylphosphinoferrocene, (−)-BINAP and (−)-DIOP, the ^{31}P NMR peaks of the phosphine stabilized palladium nanoparticles and those of the corresponding in situ generated "(dba)Pd(0)$(PR_3)_2$" (or "(dba)Pd(0)(P−P)") molecular species appeared at very similar positions, demonstrating that these ligands bind to the Pd nanoparticles with a similar strength to that observed in the coordination compounds (Table 1).

The strikingly different coordination characteristics of TOP and the small sized phosphines resulted from the difference in the intermolecular interactions of the phosphine ligands. The strong van der Waals interactions between the alkyl chains in the different TOP ligands seem to hinder the effective adsorption of TOP ligands on the surface of the palladium nanoparticles. In contrast, the small sized phosphine ligands, which possess weaker intermolecular interaction, can bind tightly to the palladium nanoparticles.

We conducted ligand exchange reactions of the TOP stabilized Pd nanoparticles with chiral phosphine ligands. Recently, several interesting reports on the asymmetric catalytic applications of chiral ligand stabilized nanoparticles have been published.[7,8] In particular, the Chaudret and Fujihara groups reported interesting reports on the catalytic applications of chiral phosphine stabilized palladium nanoparticles. Chaudret and co-workers synthesized palladium nanoparticles stabilized with the chiral and bulky ligand xylofuranoside diphosphite, and they successfully used these nanoparticles as catalysts for the asymmetric allylic alkylation with an enantiomeric excess of >95%. The corresponding palladium coordination compound with xylofuranoside diphosphite showed better catalytic activity, but much worse enantioselectivity compared to the nanoparticles. These results can be explained by the poor coordination capability of the bulky phosphine ligand on the Pd nanoparticles. Tamura and Fujihara reported that palladium nanoparticles stabilized with the chiral BINAP ligand act as an efficient catalyst for the asymmetric hydrosilylation of styrene under mild conditions, and that the molecular palladium−BINAP complex is inactive under similar reaction conditions. We synthesized monodisperse (S)-BINAP covered palladium nanoparticles by the ligand exchange reaction of the TOP-stabilized Pd nanoparticles (Figure 3). The (S)-BINAP stabilized palladium nanoparticles and the corresponding molecular species showed similar ^{31}P NMR peaks (Table 1).

Recently, various water-dispersable nanoparticles have been synthesized, which have applications in biotechnology and catalysis in aqueous media.[12] We attempted the ligand exchange reactions of the TOP-stabilized Pd nanoparticles with two hydrophilic phosphine ligands, namely 3,3′-phenylphosphinediylbenzenesulfonic acid disodium salt (TPPDS) and 1,2-bis(di-4-sulfonatophenylphosphino)benzene tetrasodium salt (BDSPPB). A 0.32 mmol portion of the

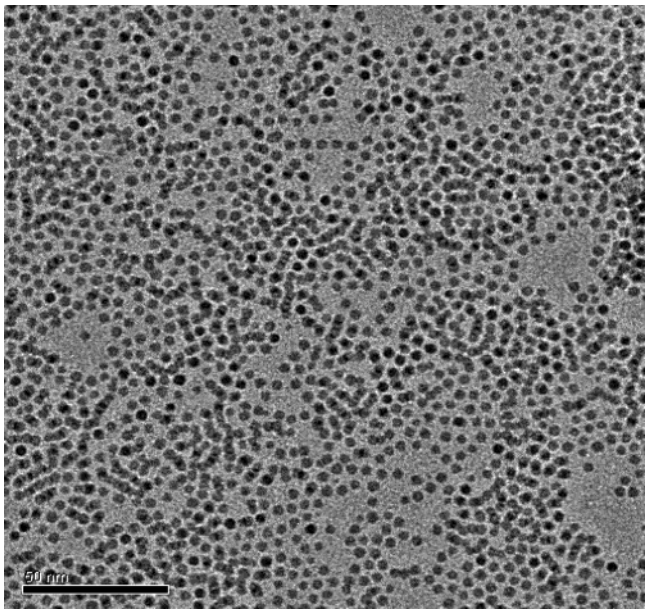


Figure 3. TEM image of the 5 nm sized palladium nanoparticles stabilized with (S)-BINAP.

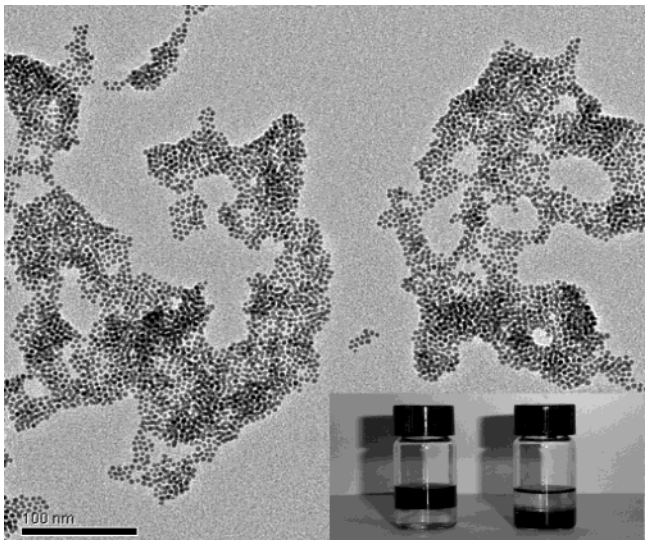


Figure 4. TEM image of palladium nanoparticles stabilized with TPPDS. Inset: The right picture shows that TPPDS stabilized Pd nanoparticles reside in the bottom aqueous layer, and the left picture shows that TOP stabilized Pd nanoparticles reside in the upper hexane layer.

ligand was added to a solution containing 50 mg of the monodisperse 5 nm sized TOP−Pd nanoparticles dispersed in 3 mL of a 1:1 (v/v) mixture of THF and H_2O. The resulting mixture was stirred for 12 h at room temperature. Then, 3 mL of THF was added, and the resulting reaction mixture was centrifuged. The upper portion of the solution was decanted and the resulting slurry containing the nanoparticles was washed several times with 10 mL of methanol. The TEM image of the TPPDS stabilized Pd nanoparticles, which is shown in Figure 4, revealed that the nanoparticles are monodisperse with a particle size of 5 nm. These hydrophilic ligand stabilized nanoparticles can easily be dispersed in water (inset of Figure 4). The effective ligand exchange that took place was confirmed by means of the ^{31}P NMR spectra.

In the case of the TPPDS stabilized nanoparticles, a ^{31}P NMR peak appeared at 3 ppm downshift from that of the free ligand. On the other hand, a 13.7 ppm downshift occurred for the BDSPPB stabilized nanoparticles. The TPPDS stabilized Pd nanoparticles remained stable after they were heated in water at 80 °C for 4 h, demonstrating the stability of the ligand exchanged water dispersable Pd nanoparticles (see Supporting Information).

In conclusion, we studied the coordination chemistry of palladium nanoparticles stabilized with various phosphine ligands using ^{31}P NMR spectroscopy. Compared to the smaller sized phosphine ligands, TOP ligands interact weakly with palladium nanoparticles. This weak coordination of the TOP ligand on the Pd nanoparticles facilitated the ligand exchange reactions required to produce monodisperse Pd nanoparticles stabilized with various other ligands. These nanoparticles include chiral phosphine stabilized Pd nanoparticles and water-dispersable Pd nanoparticles, which are likely to have a wide range of applications in biotechnology and catalysis.

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Supporting Information Available: TEM image of Pd nanoparticles synthesized by directly reacting $Pd(acac)_2$ and TPP and TEM image of water dispersable Pd nanoparticles stabilized with TPPDS after heated at 80 °C for 4 h. This material is available free of charge via the Internet at http://pubs.acs.org.

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