

Chiral Bisphosphine BINAP-Stabilized Gold and Palladium Nanoparticles with Small Size and Their Palladium Nanoparticle-Catalyzed Asymmetric Reaction

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The synthesis and characterization of metal nanoparticles have attracted great attention due to their potential applications in optoelectronics, electronics, and catalysis.^{1,2} The property of the protective ligands greatly influences the particle size and the dispersity of metal nanoparticles. For the preparation of metal nanoparticles with small sizes, narrow size distributions, and high stability, the use of various stabilizers such as amine,^{3a} phosphine,^{1,3b} and thiols,^{3c-e} has been extensively studied. As such an example, Schmid and co-workers reported that Ph₃P-stabilized gold nanoparticles were obtained by a reduction of Ph₃PAuCl with diborane.^{3b} Recently, Hutchison and co-workers described a convenient synthesis of Ph₃P-stabilized gold nanoparticles obtained from a reduction of HAuCl₄ with sodium borohydride in the presence of Ph₃P.⁴ However, much less attention has been paid to the preparation of gold and palladium nanoparticles stabilized by bisphosphine, and to related optically active metal nanoparticles. Moreover, their chiral metal nanoparticle-catalyzed asymmetric reactions have not been developed thus far.

Here we report the first synthesis of optically active 2,2'-(diphenylphosphino)-1,1'-binaphthyl [BINAP]-protected gold nanoparticles (BINAP–Au) and palladium nanoparticles (BINAP–Pd) with smaller cores (diameter < 2 nm) and narrower size distribution, and the difference in the particle size between monophosphine Ph₃P-stabilized Pd and bisphosphine BINAP-stabilized Pd nanoparticles. Optically active BINAP represents the most important class of chiral biaryl ligands and has found very extensive applications in asymmetric catalysis.⁵ Most remarkably, we have found that novel chiral BINAP–Pd catalyzed the asymmetric hydrosilylation of styrene with trichlorosilane under mild conditions. This is the first example for the asymmetric hydrosilylation of styrene catalyzed by chiral palladium nanoparticles such as chiral BINAP–Pd. In contrast, a palladium complex coordinated with a chelating bisphosphine ligand such as BINAP did not catalyze the hydrosilylation of olefins with trichlorosilane even upon elevation of the reaction temperature.^{6b,c} Catalytic asymmetric hydrosilylation of alkenes is an important method for the preparation of optically active alcohols.⁶

Synthesis and purification of mono- or bisphosphine-stabilized metal nanoparticles were carried out using a slight modification of the procedure reported by Hutchison et al.⁴ To a vigorously stirred solution of tetraoctylammonium bromide (372 mg, 0.68 mmol) in 10 mL of CH₂Cl₂ was added HAuCl₄·4H₂O (323 mg, 0.78 mmol) in 15 mL of deionized water. A solution of BINAP (1.09 g, 1.75 mmol) in 200 mL of CH₂Cl₂ was added, and the resulting solution was stirred at room temperature. NaBH₄ (388 mg, 10.3 mmol) in 5 mL of deionized water was then added. The mixture was stirred for 3 h at room temperature under an argon atmosphere. After reaction the mixture was washed with water, and the filtrate was evaporated in vacuo to yield BINAP–Au. Purification of BINAP–Au was repeated until no free phosphine or phase-transfer catalyst

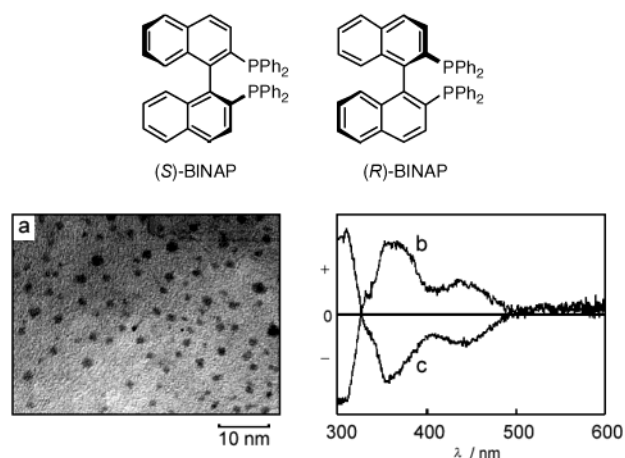


Figure 1. (a) TEM micrograph of BINAP–Au. Circular dichroism spectra of (b) (R)-BINAP–Au and (c) (S)-BINAP–Au in CHCl₃.

remained, as detected by TLC and ¹H NMR spectroscopy. Similarly, BINAP–Pd was prepared by the same procedures as for BINAP–Au using K₂PdCl₄ instead of HAuCl₄. They are remarkably stable both in solution and in the solid state.⁷ At high concentration of phosphine-stabilized gold nanoparticles in CHCl₃, BINAP–Au was more stable than Ph₃P–Au.

The core size and size distribution of BINAP–Au were examined by transmission electron microscopy (TEM) (Figure 1a).⁸ The TEM picture of BINAP–Au showed narrowly dispersed nanoparticles 1.7 ± 0.4 nm in diameter. The UV–vis spectrum of BINAP–Au solution in toluene exhibited no significant plasmon resonance at ~520 nm, which is consistent with its smaller particle size and narrower distribution.⁹ The X-ray photoelectron spectroscopy (XPS) spectrum of BINAP–Au showed the Au 4f binding energies at 84.1 and 87.8 eV, corresponding to the Au⁰ state. There was a feature at 285 eV due to C 1s and 132 eV due to P 2p.

The optically active BINAP-stabilized gold nanoparticles were prepared by a reduction of HAuCl₄ with NaBH₄ in the presence of (R)-(+)- or (S)-(–)-BINAP. The circular dichroism spectra (CD) of optically active (R)-BINAP–Au in CHCl₃ showed positive Cotton effects, while (S)-BINAP–Au showed negative Cotton effects, as shown in Figure 1, b and c. These (R)- and (S)-BINAP–Au nanoparticles were stable against racemization. Thus, new optically active gold nanoparticles in which the chiral center is very close to the surface of the gold nanoparticles have been prepared.

Although a number of studies on palladium nanoparticle-catalyzed reactions have been reported,^{1,2} no clear-cut example of asymmetric reactions catalyzed by chiral phosphine-stabilized palladium nanoparticles has been hitherto known. New phosphine ligand-stabilized palladium nanoparticles (BINAP–Pd, Ph₃P–Pd) were synthesized. The XPS spectrum of BINAP–Pd displayed that the binding energies for the Pd 3d doublet are 336.0 and 341.3 eV.

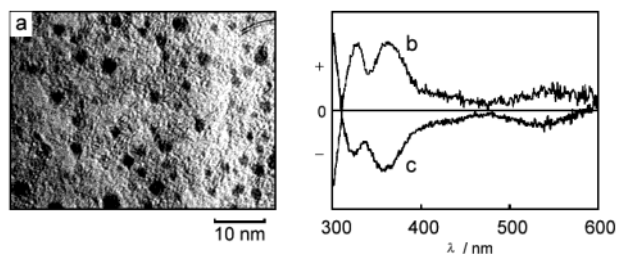


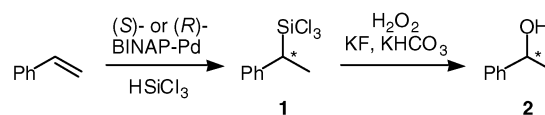
Figure 2. (a) TEM micrograph of BINAP–Pd. Circular dichroism spectra of (b) (*R*)-BINAP–Pd and (c) (*S*)-BINAP–Pd in CHCl₃.

Interestingly, BINAP–Pd has a small core size with a narrow dispersity of 2.0 ± 0.5 nm (Figure 2a), while, Ph₃P–Pd has a larger and less narrow dispersed core (2.6 ± 0.7 nm) compared with BINAP–Pd. These findings indicate that the core size and dispersity are significantly affected by use of mono- and bisphosphines as protective ligands. There is no obvious surface plasmon band in the UV–vis spectrum of BINAP–Pd or Ph₃P–Pd in CHCl₃. The absence of a plasmon band for BINAP–Pd and Ph₃P–Pd is in accord with theoretical predictions¹⁰ and experimental observations for 2.2-nm alkanethiolate-stabilized Pd nanoparticles,¹¹ but not with the report of a 302-nm surface plasmon band for 2.2-nm octadecanethiolate-protected Pd nanoparticles.¹²

Reduction of K₂PdCl₄ with NaBH₄ in the presence of chiral (*R*)- or (*S*)-BINAP afforded the chiral BINAP–Pd. The CD spectra of the chiral palladium nanoparticles in chloroform are presented in Figure 2, b and c, showing positive Cotton effects for (*R*)-BINAP–Pd and negative Cotton effects for (*S*)-BINAP–Pd. Most significantly, these chiral BINAP–Pd showed the capability of promoting hydrosilylation of styrene and its asymmetric induction (vide infra).

To confirm asymmetric catalytic activity of the chiral BINAP–Pd, we have investigated the hydrosilylation of styrene with trichlorosilane in which the hydrosilylation did not proceed in the absence of a catalyst such as palladium–monophosphine complexes. Catalytic asymmetric hydrosilylation is a very useful method for the asymmetric synthesis of optically active alcohols because the carbon–silicon bond in some organosilicon compounds is readily oxidized into a carbon–oxygen bond with retention of configuration at the carbon center.¹³ It has been known that the palladium complexes coordinated with a chelating bisphosphine ligand, 1,2-bis(diphenylphosphino)ethane or BINAP, did not catalyze the hydrosilylation of olefins with trichlorosilane.^{6b,c} Surprisingly, however, new chiral BINAP–Pd nanoparticles catalyzed the hydrosilylation of styrene (Scheme 1).¹⁴ Typically, the hydrosilylation of styrene (6.19 mL, 53.3 mmol) with trichlorosilane (5.33 mL, 53.3 mmol) in the presence of chiral (*S*)-BINAP–Pd (53 mg) at room temperature for 5 h gave 1-phenyl-1-trichlorosilyl ethane (**1**) as a single isomer in 81% yield.¹⁶ The oxidation of **1** with hydrogen peroxide in the presence of potassium fluoride¹³ gave (*S*)-1-phenylethanol (**2**) {[α]_D²⁵ –36.3 (*c* 3.0, CH₂Cl₂)} of 75% ee (enantiomeric excess)¹⁷ in 89% yield. The enantiomeric excess was increased to 95% ee when the hydrosilylation was carried out at 0 °C, while an optically active (*R*)-1-phenylethanol (**2**) was obtained when (*R*)-BINAP–Pd was used for the asymmetric hydrosilylation

Scheme 1



of styrene. Thus, a new chiral BINAP–Pd acts as both promoter and asymmetric induction reagent for the hydrosilylation of styrene.

In summary, we have demonstrated the synthesis of the chiral BINAP–Au and BINAP–Pd, and a new type of catalytic asymmetric induction by the chiral BINAP–Pd. The chiral BINAP–Au and BINAP–Pd showed the small core with narrow size distribution and remarkably high stability. A new chiral BINAP–Pd is an efficient catalyst for the asymmetric hydrosilylation of olefin under mild conditions. We have found a significant difference in the catalytic activity between BINAP–Pd nanoparticles and Pd–BINAP complex. This finding indicates a new aspect in the field of asymmetric reactions catalyzed by chiral phosphine-stabilized metal nanoparticles and transition metal–phosphine complexes. The work reported here points toward a new direction in the design of chiral metal nanoparticle catalysts for asymmetric synthesis. Further work is currently in progress in this and related areas.

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