

Synthesis of small palladium nanoparticles stabilized by bisphosphine BINAP bearing an alkyl chain and their palladium nanoparticle-catalyzed carbon–carbon coupling reactions under room-temperature

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A new bisphosphine ligand, C₈-BINAP, and C₈-BINAP-stabilized palladium nanoparticles have been prepared; C₈-BINAP was found to be an effective protecting ligand for preparing and stabilizing palladium nanoparticles with very small core size and narrow size distribution and the C₈-BINAP–Pd nanoparticles behave as an efficient catalyst for carbon–carbon coupling reactions at room temperature.

Metal nanoparticles have attracted a remarkable academic and industrial research effort due to their potential applications, ranging from fundamental studies in quantum physics to catalysts.¹ In recent years, great interest has been placed on the use of metal nanoparticles for nanocatalysis.^{1,2} Control of the surface properties and reactivities of metal nanoparticles is an important aspect of developing nanomaterial applications. The size, shape, and surface properties of metal nanoparticles are crucially controlled by the nature of protective ligands. The physical and chemical properties of metal nanoparticles can be tuned by variations in both the nature of the ligand shell, and the size of the metal core. Generally, transition metal nanoparticles with small particle size (1–3 nm) have high catalytic activity and obvious size-dependent properties. For the preparation of metal nanoparticles with small sizes, narrow size distributions, and stability, the use of various stabilizers such as amines, phosphines, and thiols, has been extensively studied.^{1,3} Although a number of thiol-stabilized metal nanoparticles have been reported,^{1,3,de} metal nanoparticles stabilized by bisphosphines have received much less attention.⁴ Previously we reported that optically active bisphosphine, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl [BINAP]-stabilized palladium nanoparticles catalyzed asymmetric hydrosilylation of styrene with trichlorosilane under mild conditions.⁵

In our recent research efforts, special emphasis has been placed on the elucidation of structural driving forces in the control of particle size and shape, and the reactivity of metal nanoparticles stabilized by bisphosphines such as BINAP-derivatives. The key structural elements of a new bisphosphine, 6-octyl-substituted BINAP (C₈-BINAP), as a protective ligand in this study consist of the BINAP phosphine for the coordination site and an alkyl chain for the stabilization of nanoparticles *via* van der Waals interactions (Fig. 1). We have synthesized a new BINAP derivative

(C₈-BINAP) which is a potential candidate as a protective agent to control, not only the particle size, but also the interfacial reactivity of metal nanoparticles. We have found that the C₈-BINAP-stabilized palladium nanoparticles (C₈-BINAP–Pd) have a small core size and narrow size distribution (1.2 ± 0.2 nm) and are remarkably stable. Moreover, we have found that C₈-BINAP–Pd nanoparticles can efficiently catalyze Stille and Suzuki coupling reactions at room temperature, in which the C₈-BINAP–Pd nanoparticles can be recovered after the reaction and reused. Palladium nanoparticles have been of increasing scientific interest as a catalyst for organic carbon–carbon bond formation reactions such as Stille and Suzuki cross-coupling reactions.^{2,6–9} In general, palladium complexes and palladium nanoparticles have been used as catalysts for the carbon–carbon couplings which are among the most powerful methods in organic synthesis; the reactions have been performed by heating or refluxing.^{2,6–9} Much less is known about the room-temperature carbon–carbon coupling reactions catalyzed by phosphine-stabilized palladium nanoparticles. This communication reports the synthesis of a new type of bisphosphine protective ligand, C₈-BINAP, and its ligand-stabilized palladium nanoparticles (C₈-BINAP–Pd), and room-temperature Stille and Suzuki coupling reactions catalyzed by the C₈-BINAP–Pd nanoparticles.

A new bisphosphine (C₈-BINAP) was synthesized according to Scheme 1 using 6-hydroxymethyl-2,2'-bis(methoxymethyl)-1,1'-binaphthol (**7**)¹⁰ obtained by the reported method.¹¹ A typical procedure for the preparation of C₈-BINAP–Pd nanoparticles is as follows. To a vigorously stirred solution of K₂PdCl₄ (65 mg, 0.2 mmol) in 5 mL of MeOH, 10 mL of deionized water, and 30 mL of THF was added bisphosphine C₈-BINAP (156 mg, 0.2 mmol) in 20 mL of THF. NaBH₄ (76 mg, 2 mmol) in 5 mL of deionized water was then added. The mixture was stirred for 1 h at room temperature. After the reaction, the filtrate was evaporated *in vacuo* to yield C₈-BINAP–Pd nanoparticles. Purification (dichloromethane–*n*-hexane) of C₈-BINAP–Pd was repeated until no free phosphine remained, as detected by TLC, ¹H and ¹³C

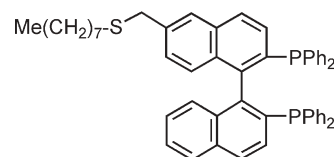
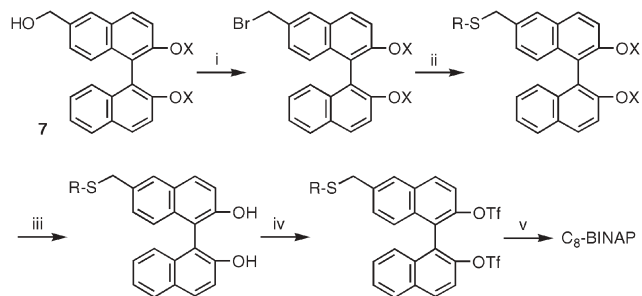


Fig. 1 Structure of C₈-BINAP. Bisphosphine (C₈-BINAP) used to derive the bisphosphine-stabilized palladium nanoparticles (C₈-BINAP–Pd).

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Scheme 1 Reagents and conditions. X = $-\text{CH}_2\text{OMe}$, R = $-(\text{CH}_2)_7\text{Me}$, Tf = CF_3SO_2 ; (i) CBr_4 , PPh_3 , THF, rt, 30 min; (ii) $\text{Me}(\text{CH}_2)_7\text{SH}$, NaH, THF, rt, 3 h; (iii) *i*-PrOH, HCl, 40 °C, 6 h; (iv) $(\text{CF}_3\text{SO}_2)_2\text{O}$, pyridine, CH_2Cl_2 , 0 °C, 3 h; (v) [1,2-bis(diphenylphosphino)ethane]dichloronickel(II), 1,4-diazabicyclo[2.2.2]octane, Ph_2PH , anhydrous DMF, 100 °C, 3 days.

NMR spectroscopy. $\text{C}_8\text{-BINAP-Pd}$ nanoparticles are remarkably stable both in solution, as well as in the solid state.

The particle size and size distribution of $\text{C}_8\text{-BINAP-Pd}$ were analyzed by transmission electron microscopy (TEM) and annular dark-field scanning transmission electron microscopy (ADF-STEM). As shown in Fig. 2(a–c), narrowly dispersed palladium nanoparticles were produced in the one-pot synthesis. The core size of $\text{C}_8\text{-BINAP-Pd}$ is very small 1.2 ± 0.2 nm. The particle size of $\text{C}_8\text{-BINAP-Pd}$ was also obtained using small angle X-ray scattering (SAXS). From SAXS analysis of $\text{C}_8\text{-BINAP-Pd}$ an average particle size of 1.2 nm was determined.¹² The particle size of $\text{C}_8\text{-BINAP-Pd}$ is much smaller than that of BINAP-stabilized palladium nanoparticles (2.0 ± 0.5 nm).⁵

The X-ray photoelectron spectroscopy (XPS) spectrum of $\text{C}_8\text{-BINAP-Pd}$ displayed that the binding energies for the Pd 3d doublet are 336.0 and 341.3 eV. There was a feature at 285 eV due to C 1s and 132 eV due to P 2p. There is no obvious surface

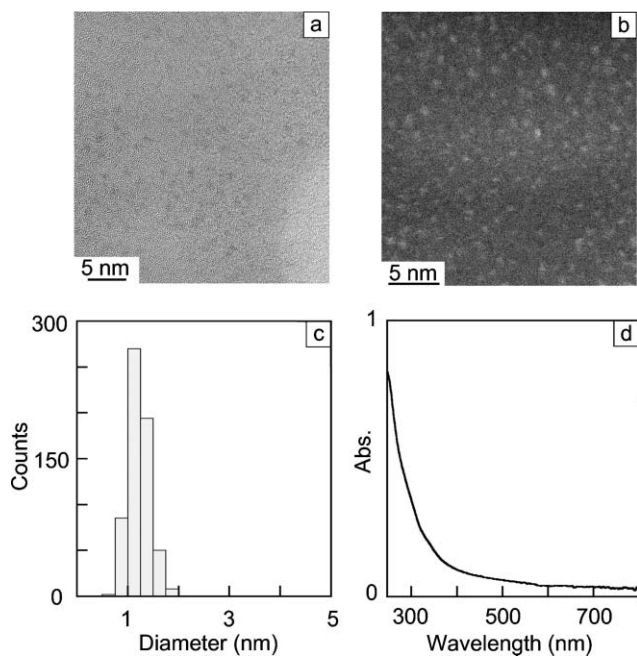
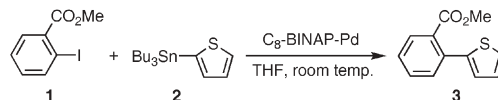


Fig. 2 (a) TEM and (b) ADF-STEM micrographs, (c) histogram of size distribution for $\text{C}_8\text{-BINAP-Pd}$. (d) UV-vis spectrum of $\text{C}_8\text{-BINAP-Pd}$ in CH_2Cl_2 .



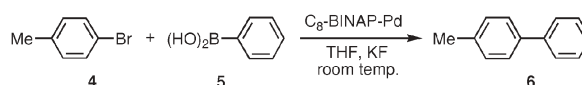
Scheme 2

plasmon band in the UV-vis spectrum of $\text{C}_8\text{-BINAP-Pd}$ in CH_2Cl_2 [Fig. 2(d)]. The absence of a plasmon band for $\text{C}_8\text{-BINAP-Pd}$ is in accord with theoretical predictions¹³ and experimental observations for 2.2 nm alkanethiolate-stabilized Pd nanoparticles,¹⁴ but not with the report of a 302 nm surface plasmon band for 2.2 nm octadecanethiolate-protected Pd nanoparticles.¹⁵

Thermal gravimetric analysis was carried out to estimate the total organic content of $\text{C}_8\text{-BINAP-Pd}$. On heating to 720 °C, $\text{C}_8\text{-BINAP-Pd}$ displays a 77% mass loss, corresponding to 25 $\text{C}_8\text{-BINAP}$ ligands on an assumed 55-atom palladium cluster.

The catalytic properties of $\text{C}_8\text{-BINAP-Pd}$ nanoparticles dispersed in organic solvent were tested in two very important carbon-carbon bond-forming reactions, the Stille and Suzuki coupling reactions. It has been known that Stille and Suzuki coupling reactions were carried out under heating.^{8,9} Significantly, however, $\text{C}_8\text{-BINAP-Pd}$ nanoparticle-catalyzed cross-coupling reactions, Stille reaction of methyl 2-iodobenzoate (**1**) with 2-(tributylstannyl)thiophene (**2**) and Suzuki reaction of 4-bromotoluene (**4**) with phenylboronic acid (**5**), were found to proceed smoothly at room temperature to give the corresponding coupling products in good yields (Scheme 2 for Stille reaction and Scheme 3 for Suzuki reaction). Typically, a mixture of **1** (0.15 mL, 1 mmol) and **2** (0.32 mL, 1 mmol) in the presence of $\text{C}_8\text{-BINAP-Pd}$ (20 mg, 0.06 mol%) in anhydrous THF was stirred at room temperature under argon for 4 h. After work-up, the crude products were purified by silica-gel column chromatography (*n*-hexane:benzene = 1:1) to give the coupling product (**3**) in 91% yield.¹⁶ The catalytic activity of $\text{C}_8\text{-BINAP-Pd}$ was preserved in the presence of a thio-containing substrate which is known to poison colloidal palladium nanoparticle catalysts.¹⁷ Separation of the products from the catalyst is easy, and the $\text{C}_8\text{-BINAP-Pd}$ recovered from the reaction was freely soluble in organic solvents, indicating that the palladium core had not agglomerated under the reaction conditions. More interestingly, in the second recycle reaction using the recovered $\text{C}_8\text{-BINAP-Pd}$, the coupling product **3** was obtained in 90% yield under the same conditions. This finding indicates that the nanocatalyst, $\text{C}_8\text{-BINAP-Pd}$, can be reused under the same conditions with essentially no loss in activity. Thus, the bisphosphine ($\text{C}_8\text{-BINAP}$), unlike polymer, serves as the supporting material for keeping the nanoparticles from aggregation and facilitates the synthesis and reuse of the catalysis. Generally, polymeric materials and dendrimers have been used as stabilizers (protective ligands) of recyclable metal nanoparticles in catalysis.⁷

A small amount of $\text{C}_8\text{-BINAP-Pd}$ (0.02 mol%) was also effective for a Suzuki coupling reaction under room temperature (Scheme 3), *i.e.*, the reaction of **4** (171 mg, 1 mmol) with **5** (186 mg,



Scheme 3

1.5 mmol) in the presence of C₈-BINAP-Pd (5 mg, 0.02 mol%) and KF (174 mg, 3 mmol) in THF (1.5 mL) at room temperature for 24 h afforded the coupling product (**6**) in 83% isolated yield. These results demonstrate that C₈-BINAP-Pd nanoparticles were shown to be an effective nanocatalyst for the Stille and Suzuki coupling reactions. The nanocatalyst was found to be very stable, as evidenced by TEM and XPS analysis, and did not show any decrease in activity with time.

In summary, a new protective ligand, C₈-BINAP, bearing an octyl group as a tuning site, induced the formation of remarkably stable palladium nanoparticles (C₈-BINAP-Pd) with very small core size and narrow size distribution. The C₈-BINAP-Pd nanoparticles were found to be a versatile catalyst for carbon-carbon coupling reactions of haloarenes at room temperature. The recycling of C₈-BINAP-Pd is possible without loss of activity. The work reported here points to a new direction to design protective ligands and nanocatalysts for carbon-carbon coupling reactions at room-temperature. Further work is currently in progress in this and related areas.

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