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Convenient Synthesis of Palladium Nanoparticles and Catalysis of Hiyama Coupling Reaction in Water

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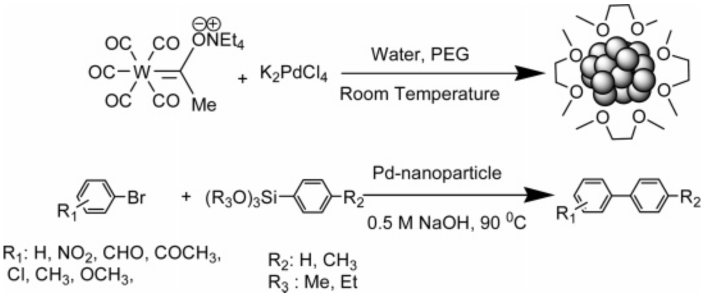
ABSTRACT



An efficient synthesis of Pd nanoparticles in water has been developed using a Fischer carbene complex of tungsten as the reductant and PEG as the capping agent. The colloidal palladium (1 mol %) efficiently catalyzes Hiyama cross-coupling reactions performed in air. Excellent yields of products were obtained with a wide range of substrates. Catalytic activity and stability of the nanoparticles were found to be inversely correlated.

In homogeneous metal-catalyzed reactions, each metal complex molecule in solution functions as the catalyst or as a precatalyst. The ligand environment around the metal atom controls its reactivity and protects it from competitive decomposition pathways. In heterogeneous catalysis, the catalytic surface offers a limited number of "active" sites for catalysis, often necessitating harsher reaction conditions for optimum catalytic efficiency. Of late, nanoparticles emerged as useful and unique catalysts[1] whose efficacy is attributed to their characteristic high surface-to-volume ratio that translates into a larger number of active sites per unit area compared to standard heterogeneous catalysts.[2] The active metal center is devoid of a ligand environment, yet the efficiency and turnover numbers are impressive.

A prominent area of application of palladium nanoparticles in organic chemistry concerns coupling reactions. Catalysis of several reactions such as Stille,[3] Suzuki,[4] and Hiyama[5] coupling by palladium nanoparticles or nanosized mixed metal clusters has been reported.[6−8] In this paper, we focus

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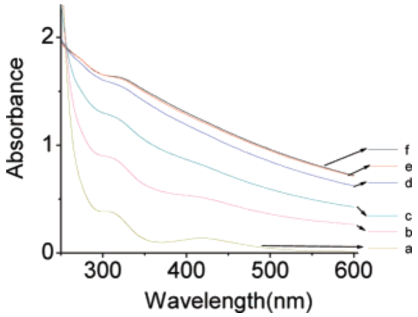

Figure 1. UV−vis spectral change during the addition of aq Fischer carbene solution to aq K_2PdCl_4 solution. Pd/Fischer carbene molar ratio: (a) 1:0, (b) 1:0.087, (c) 1:0.174, (d) 1:0.261, (e) 1:0.348, (f) 1:0.435, respectively.

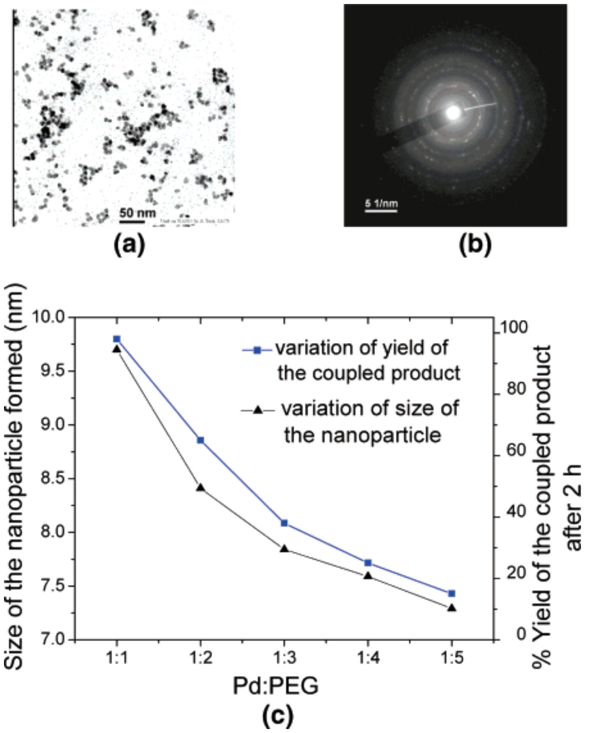

Figure 2. (a) TEM image of the palladium nanoparticles (Pd/PEG 1:2). (b) Electron diffraction pattern of palladium nanoparticles. (c) Plot of the size of a nanoparticle as a function of Pd/PEG molar ratio and % yield of the coupled product.

on catalysis of the Hiyama reaction using arylalkoxysilane.[9] Such a coupling reaction uses organosilicon compounds[10] that have greater stability than organozinc or organomagnesium compounds, and they are less toxic than tin reagents. They are often preferred to organoboron compounds which are either unstable or difficult to purify and frequently lose boron to give undesirable homocoupling products. Although detection of nanoparticles of palladium in Hiyama reaction catalyzed by ligand-supported palladium complexes[8b] has raised a question about their possible involvement as a catalyst, no conclusive evidence is yet available to substantiate such a claim.[11] A recent report on Hiyama coupling reaction catalyzed by the Pd−Ni nanocluster[8a] prompted us to disclose the first example of palladium nanoparticle catalysis for Hiyama reaction *in water* where palladium nanoparticles were prepared by employing a Fischer carbene complex as the reducing agent for K_2PdCl_4. The major advantage of the protocol is 3-fold: all operations are performed in water; no additive other than a small amount of PEG is required; and the temperture of the reaction is usually lower than 100 °C. The products are obtained in excellent yields (>90% for most of the examples, see Table 2).

Commonly encountered methods for the preparation of Pd nanoparticles involve either thermal[12] or sonochemical[13]

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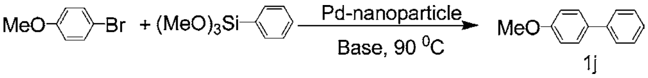
Table 1. Screening of Conditions for Cross-Coupling Reaction in Water[a]



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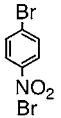
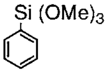
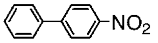
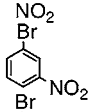
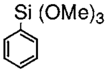
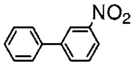
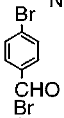
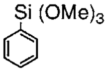
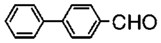
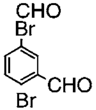
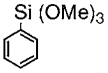
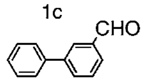
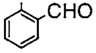
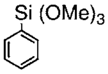
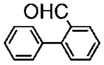
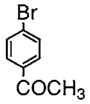
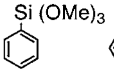
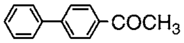
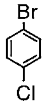
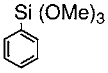
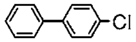
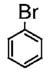
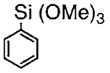
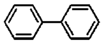
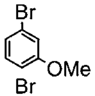
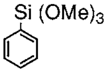
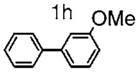
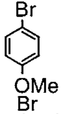
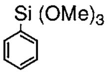
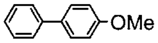
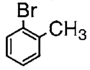
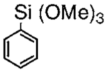
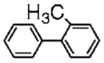
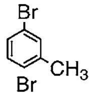
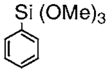
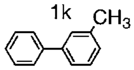
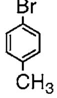
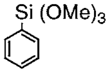
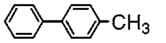
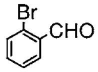
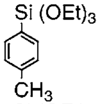
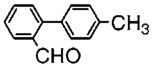
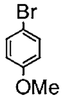
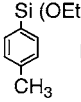
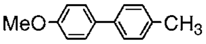
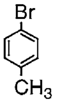
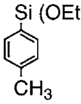
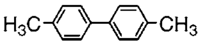
entry	Pd/PEG	base[b]	time (h)	% yield[c]
1	1:1	NaOH	2	98
2	1:2	NaOH	2	65[d]
3	1:2	NaOH	3.5	98
4	1:3	NaOH	2	38[d]
5	1:3	NaOH	6	98
6	1:4	NaOH	2	25[d]
7	1:4	NaOH	8	98
8	1:5	NaOH	2	15[d]
9	1:5	NaOH	10	70[d]
10	1:1	KF	10	–
11	1:1	K_2CO_3	10	20[d]
12	1:1	K_3PO_4	10	–
13	1:1	KOH	2	95
14	1:1	CsF	10	–
15	1:1	CsOAc	10	–
16	1:1	NaOAc	10	–

[a] A weighed amount of K_2PdCl_4 (0.003 g, 0.0092 mmol) and PEG 6000 (60 mg, 0.01 mmol) was dissolved in 4 mL of water. In another portion, 2 mg of the Fischer carbene complex was dissolved in 5 mL of water. The water suspension of the Fischer carbene complex was added to the Pd(II) solution with vigorous stirring resulting in the formation of colloidal Pd (5 min). To this suspension of colloidal Pd were added aryltrialkoxysilane (2 mmol) and aryl bromide (1 mmol), and the mixture was heated at 90 °C for 1 min. Thereafter, 1 mL of 5 M NaOH solution was added dropwise, and stirring was continued until completion of the reaction (2 h). The reaction mixture was then allowed to cool to room temperature and extracted with Et_2O (3 × 20 mL). The combined ethereal layers were dried over anhydrous Na_2SO_4 and concentrated in a vacuum. The residue thus obtained was purified by flash column chromatography on silica gel (230~400 mesh) with either a mixture of petroleum ether and acetone (2−5%) or petroleum ether alone as eluent. [b] 1 mL of 5 M stock solution. [c] Yield of isolated product. [d] Incomplete conversion.

decomposition of organometallic precursors or reduction of metal salts with borohydride or other reducing agents.[14] We developed[15] a mild synthetic method for the generation of colloidal palladium in water utilizing the reducing property of a Fisher carbene complex of tungsten, formally a W(0) compound. An aqueous solution of the metal acylate salt, $(CO)_5W{=}C(CH_3)O(-)\ NEt_4(+)$, was added dropwise to a solution of K_2PdCl_4 containing PEG-6000 in water. (Water-soluble Fischer carbene complexes[16] can be used instead of the metal acylate for this purpose with similar efficiency.) The yellow solution turned dark brown quite rapidly indicating the formation of Pd nanoparticles which were characterized by TEM (Figure 2a), UV (Figure 1), and selected area electron diffraction (SAED) (Figure 2b) (for additional data, see Supporting Information). The mildness of the conditions and the neutral aqueous medium make it an attractive method for the preparation of palladium nanoparticles for synthesis. The Pd nanoparticle thus formed is stable in air for a month.

Table 2. Cross-Coupling Reactions of Arylsiloxanes with Aryl Bromides Catalyzed by a Palladium Nanoparticle in Water[a]

entry	aryl halide	siloxane	product	time (h)	%yield[b]
1			 1a	2.0	95
2			 1b	2.0	96
3			 1c	2.5	95
4			 1d	2.5	94
5			 1e	2.5	95
6			 1f	2.0	98
7			 1g	2.0	92
8			 1h	2.0	98
9			 1i	3.0	95
10			 1j	3.0	98
11			 1k	3.0	95
12			 1l	3.0	95
13			 1m	2.5	95
14			 1n	3.5	90
15			 1o	3.5	88
16			 1p	3.5	89

[a] Aryl bromide (1 mmol), aryltrialkoxysilane (2 mmol), catalyst (1 mol %) under air at 90 °C. [b] Yields of the isolated products.

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Initial studies were performed with 4-bromoanisole (1 mmol), a relatively deactivated aryl bromide, phenyltrimethoxysilane (2 mmol) using an aqueous suspension of colloidal Pd (10 mL, 1 mol %), and a base (0.5 M) under 90 °C in air. Among the inorganic bases tested, *NaOH and KOH gave the desired coupling product in excellent yield* (90−98%, see Table 1). The other bases like K_2CO_3, K_3PO_4, Cs_2CO_3, KF, CsF, NaOAc, or CsOAc afforded only a trace amount of the desired product.

It was observed that the size of the nanoparticles decreases with increasing amount of the stabilizer PEG-6000 (Figure 2c). When Pd/PEG 1:1 (particle size 9.70 nm) was used, the reaction was complete within 2 h. By increasing the amount of PEG, both the particle size and the yield of product diminished in 2 h (Figure 2c). However, the yield of the coupled product for such reactions can be improved to 98% by using a longer reaction time. Lower catalytic activity of the smaller nanoparticles is often attributed to stronger adsorption of reaction intermediates on the particle surface.[17]

Alternatively, the PEG might cover the surface of smaller particles more effectively and block the approach of reactants. El Sayed and co-workers found[18] that catalytic activity and nanoparticle stability were anticorrelated, with capping agents that gave good nanoparticle stability yielding slow reaction rates. For instance, G4 dendrimers imparted good stability but poor reaction rates, whereas G2 dendrimers afforded better coupling rates but relatively poor nanoparticle stability. In our experiments, an increased amount of PEG not only decreased the size of the nanoparticle but also increased its stability, which might explain its diminished catalytic activity.

The present procedure is superior to several earlier methods in that it does not use any organic solvent except for workup. Also, nanoparticles can be used straight after preparation without any purification step,[19] and the entire operation is fluoride-free. The reaction involved hydrophobic reaction partners, yet proceeded with remarkably higher efficiency in water[10f,h] than when cosolvents (THF or DME) were used.

A range of substituted aryl bromides were used as substrates. The entries in Table 2 reveal that both electron-withdrawing (entries 1−7 and 14) and electron-donating (entries 9−13, 15, and 16) substituents yielded excellent results. Even 2-substituted aryl bromides led to excellent yield of the desired biaryl. With 4-chlorobromobenzene as substrate, bromide was selectively replaced by the phenyl group in preference to chloride, as would be expected (entry 7, Table 2).

It is noteworthy that aldehyde did not undergo transition-metal-catalyzed nucleophilic addition by aryltrimethoxysilane as reported recently[21] as a competitive parallel reaction. Chemoselectivity was total and in favor of the Hiyama coupling reaction (entries 3−5 and 14, Table 2). Although the reactions were carried out in air, no noticeable amount of radical-induced dimeric product was formed. Yield of products from reactions involving deactivated aryl bromides remained very high.

In summary, we have reported the use of Fischer carbene complexes of tungsten as a reducing agent to synthesize colloidal palladium capped by PEG in aqueous medium at room temperature. This palladium nanoparticle is stable in air for a month and extremely active in Hiyama cross-coupling reactions. The catalytic reaction is fluoride-free, is free of conventional ligands for palladium, and uses the most benign solvent, i.e., water, for maximum efficiency. Use of palladium nanoparticles in other coupling reactions are being explored and will be reported elsewhere.

Acknowledgment. We thank CSIR and the Department of Science and Technology, India, for financial support. D.S and S.S are thankful to CSIR, India, for their fellowship.

Supporting Information Available: Detailed experimental procedures and characterization data (^1H, ^{13}C) of the coupling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] When the aqueous extract containing residual catalyst was reused for a fresh batch of reaction, product yield was only moderate (<45%). Conditions are being developed to optimize recovery and recyclability of catalyst.[20]

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