

Palladium Nanoparticles Supported on an Organic–Inorganic Fluorinated Hybrid Material. Application to Microwave-Based Heck Reaction

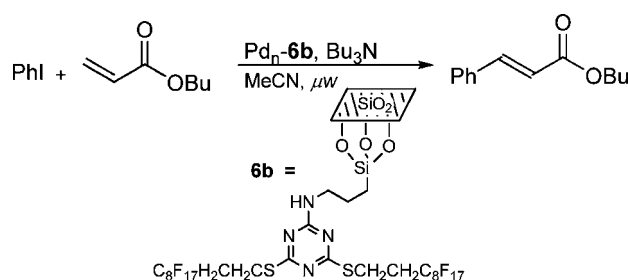
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Received May 12, 2008

ABSTRACT



Phosphine-free palladium nanoparticles were embedded in a fluorinated organic–inorganic hybrid material **6b** prepared by the sol-gel process. The use of $\text{Pd}_n\text{-6b}$ in the Heck coupling reaction under microwave irradiation has been investigated. Recycling studies have shown that the catalyst can be readily recovered and reused several times without significant loss of activity. Reactions and recovery of the solid-supported palladium catalyst system can be carried out in the presence of air, without any particular precaution.

In the area of catalyst recovery, a major effort has been directed toward the preparation and application of nanoparticles.¹ In particular, a large body of work has been dedicated in recent years to the use of palladium nanoparticles (Pd NPs) for the catalytic formation of carbon–carbon bonds.² Dif-

ferent materials have been used to support and stabilize Pd NPs as active catalysts in Heck reactions including polymers,³ micelles of polymers,⁴ layered double hydroxides,⁵ dendrimers,⁶ polyoxometalates,⁷ silica,⁸ titania,⁹ aerogels,¹⁰ zeolites,¹¹ and carbon nanotubes.¹²

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We have previously reported that heavily fluorinated compounds can favor the formation of Pd NPs and that a number of these nanoparticles are catalytically active in C–C bond-forming processes.¹³ Most recently, we reported the synthesis of a 3-fold symmetric fluorinated compound **A** (Figure 1) and showed that the palladium nanoparticles

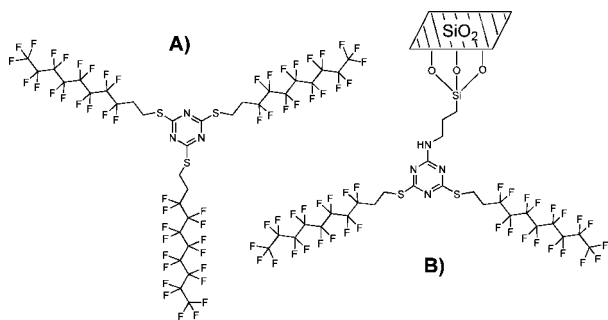


Figure 1. Reported (**A**) and proposed (**B**) fluorinated nanoparticle stabilizers.

stabilized by this agent were active as catalysts in a number of cross-coupling reactions.¹⁴ Furthermore, following the work by Bannwarth and co-workers,¹⁵ we have demonstrated that palladium nanoparticles stabilized by **A** could be embedded within a fluorinated silica gel matrix. The latter material showed promise as a catalyst for the Heck coupling reaction and could be reused 10 times with little loss of activity.¹⁶ During the reaction, however, the material did

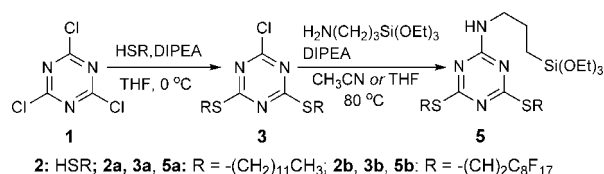
degrade somewhat, and analysis of the supernatant liquid obtained after a catalytic run confirmed the leaching of both palladium and small amounts of the fluorinated stabilizer. When nanoparticles stabilized by **A** were tested under microwave irradiation, the loss of catalytic activity became evident, with the material decomposing rapidly through complete loss of stabilizer and the formation of bulk palladium.

In an effort to create a catalyst compatible with the use of microwave heating, we envisioned the synthesis of a more robust hybrid material with the stabilizer linked covalently to the silica gel matrix. Specifically, we proposed the synthesis of fluorinated stabilizer **B** based on a substituted triazine (Figure 1).

The synthesis of **B** was based on our observation that during the preparation of stabilizer **A** via 3-fold nucleophilic aromatic substitution of 2,4,6-trichloro-1,3,5-triazine, **1**, the degree of substitution could be controlled by adjusting the reaction conditions. In particular, we found that selective introduction of two side-chains could be carried out using aliphatic and polyfluorinated thiols, opening the door for the modular construction of polyfluorinated compounds through the substitution of the remaining chloride. We chose to introduce the bifunctional 3-(triethoxysilyl)propan-1-amine linker, **4**, taking advantage of efficient S_NAr reaction between heteroaromatic chlorides and aliphatic amines.

To rapidly assess the viability of the proposed route, we initially carried out the substitution reaction using a nonfluorinated substrate. As shown in Scheme 1, selective disub-

Scheme 1. Synthesis of Compounds **5a** and **5b**



stitution of trichlorotriazine **1** with a long-chain aliphatic thiol $\text{HSC}_{12}\text{H}_{25}$, **2a**, was accomplished in THF at 0 °C in 2.5 h using diisopropylethylamine (DIPEA) as a base, affording the desired **3a** in quantitative yield.¹⁷ The remaining chloride was substituted with the commercially available silylated amine **4** in CH_3CN at 80 °C giving the trisubstituted **5a** in 96% yield.

Due to the restricted rotation around the Het–N_{aliphatic} bond,¹⁸ NMR spectroscopy of **5a** showed two sets of resonances for the inequivalent –SR fragments in the ¹H NMR spectrum and three aromatic carbon resonances in the ¹³C NMR (see Supporting Information). With the siloxane precursor **5a** in hand, we proceeded to explore the conditions necessary to carry out the sol-gel process on a 15:1 Si(OEt)₄ to **5a** mixture. We quickly found that the usual protocol based

(17) Longer reaction times led to the formation of some of the trisubstituted product.

(18) For similar behavior of other aminotriazines, see: Gulevskaya, A. V.; Maes, B. U. W.; Meyers, C. *Synlett* **2007**, 71.

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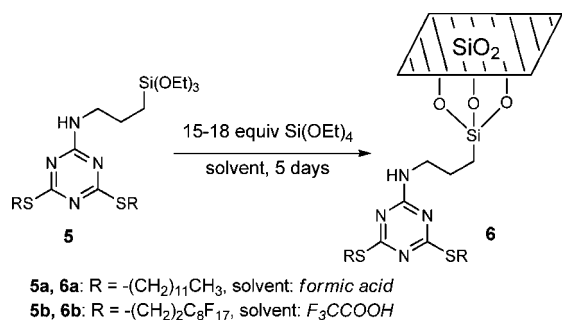
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on a water–methanol mixture using NH_4F catalyst was not suitable for the highly hydrophobic **5a**, leading to a phase separation and the formation of highly inhomogeneous material. After some experimentation, a method described by Sharp and Scherer¹⁹ using formic acid as both solvent and catalyst (Scheme 2) gave excellent results and afforded,

Scheme 2. Sol-Gel Reaction of **5a** and **5b** with $\text{Si}(\text{OEt})_4$



after aging and drying, the hybrid material **6a**, which was characterized by elemental analysis to confirm the incorporation of the organic portion.

Once the conditions had been established for the model process, we turned our attention to the fluorinated material. As shown in Scheme 1, reaction of **1** with the fluorinated thiol $\text{HS}(\text{CH}_2\text{CH}_2)\text{C}_8\text{F}_{17}$, **2b**, in THF at 0 °C afforded the disubstituted derivative **3b** in quantitative yield. Subsequent reaction of **3b** with silylated amine **4** in THF at 80 °C gave, after a Soxhlet extraction, the desired **5b** in 93% yield as a light-orange solid.

Initial attempts to carry out the sol-gel process using precursor **5b** in formic acid were frustrated by the phase separation of the reaction mixture, leading to the formation of a highly heterogeneous material. This was not surprising, given that the incorporation of fluororous materials into a hybrid framework through the sol-gel process is known to be a challenging process, with only a few examples described to date.^{20,21} The difficulty was overcome by conducting the reaction in trifluoroacetic acid, as reported by Sharp and co-workers.²² These conditions led to the formation of a homogeneous mixture and formation, after a 5 day aging period, of the hybrid sol-gel product **6b** (Scheme 2).

(19) Sharp, K. G.; Scherer, G. W. *J. Sol-Gel Sci.* **1997**, *8*, 165.

(20) More commonly, such materials are prepared through the anchorage of the fluororous material onto the preformed activated silica gel. The method, however, failed to achieve sufficient loading when applied to **6b**. For some examples, see: Glatz, H.; Blay, C.; Engelhardt, H.; Bannwarth, W. *Chromatographia* **2004**, *59*, 567, and references therein.

(21) A notable exception is the work by Sharp and coworkers at DuPont. For some examples, see: Sharp, K. G. *Adv. Mater.* **1998**, *10*, 1243, and references cited therein.

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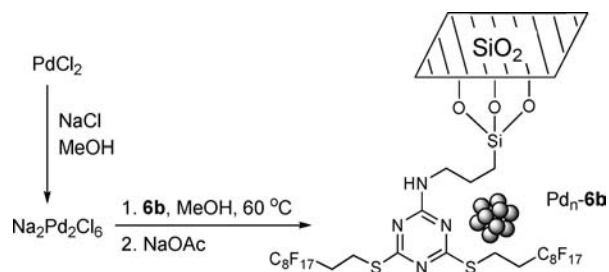
(23) In the reduction of Na_2PdCl_6 with MeOH, the addition of NaOAc has been found to favor the precipitation of Pd⁰ in the form of nanoparticles. See reference 14.

(24) (a) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609. See also: ref 6a and: (b) Thathagar, M. B.; Elshof, J. E.; Rothenberg, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2886.

Incorporation of the fluororous stabilizer into the material was confirmed by elemental analysis, as well as solid state ^{13}C NMR and ^{29}Si spectra (see Supporting Information).

Palladium nanoparticles were prepared by treatment of a methanolic solution of $\text{Na}_2\text{Pd}_2\text{Cl}_6$ with **6b**, affording, after addition of NaOAc,²³ a black solid corresponding to $\text{Pd}_n\cdot\mathbf{6b}$ (Scheme 3).

Scheme 3. Synthesis of the Hybrid Material $\text{Pd}_n\cdot\mathbf{6b}$



This material was found to contain 4% of palladium (see Supporting Information). Transmission electron microscopy (TEM) imaging (Figure 2) revealed that palladium is present

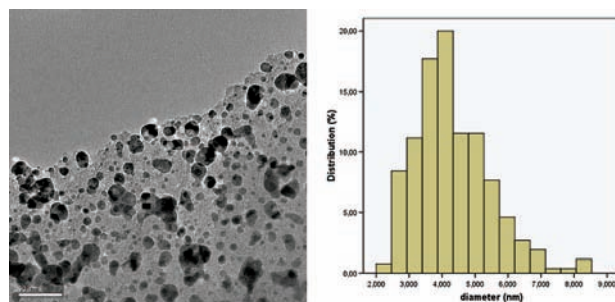


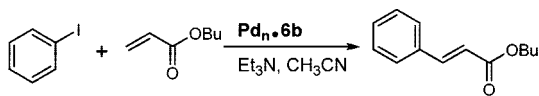
Figure 2. (a) TEM image of $\text{Pd}_n\cdot\mathbf{6b}$. (b) Particle size distribution histogram of $\text{Pd}_n\cdot\mathbf{6b}$.

in the form of nanoparticles with an average particle size of 4 nm.

The catalytic activity and stability of $\text{Pd}_n\cdot\mathbf{6b}$ was initially tested in the model Heck reaction of iodobenzene with butyl acrylate employing 2% Pd. While at 80 °C the reaction was sluggish, raising the temperature to 130 °C allowed the reaction to finish in 24 h. The catalyst could be recovered by filtration, and six consecutive catalytic runs were carried out without the loss of activity (Scheme 4).

We then went on to test the catalytic performance of $\text{Pd}_n\cdot\mathbf{6b}$ employing microwave irradiation (sealed reaction vessel, CEM Discover microwave reactor, IR temperature monitoring). The results are shown in Table 1. Using 2% Pd, the coupling of iodobenzene with butyl acrylate was accomplished in 3 h at 130 °C (at 150 W initial power) (entry 1). The catalyst proved to be robust enough to withstand six rounds of catalysis, without appreciable loss

Scheme 4. Heck Coupling Reaction Using Conventional Heating^a



run	1	2	3	4	5	6
conv ^b , %	99	99	99	99	99	99

^aUsing 2 mol % of Pd and 2.0 equiv of Et₃N at 130 °C. ^bCalibrated GC conversion.

of activity. The reaction time could be reduced to 1.5 h by raising the temperature to 150 °C and setting the initial power to 250 W (entry 2). On the other hand, while the

Table 1. Heck Coupling Using Microwave Irradiation^a

entry	T (°C)	X	time	power (W) ^b	conversion, % ^c
1	130	I	3	150	97, 96, 96, 97, 97, 97
2	150	I	1.5 h	250	97, 96, 95, 97, 92, 95
3	180	I	45 min	275	>99, 93, 93, 83
4	150	Br	3 h	250	—

^a Using 2 mol % of Pd and 2.0 equiv of Et₃N. ^b With the *PowerMax* option enabled (simultaneous cooling while heating); the values indicate the initial power level used. ^c Calibrated GC conversion.

reaction at 180 °C only took 45 min, the catalyst showed reduced activity by the fourth run (entry 3). The catalyst was ineffective for the coupling of bromobenzene, showing, after 3 h at 150 °C, complete unproductive consumption of the aryl halide.

The resistance of Pd_n-6b to leaching was assessed for the same reaction cycles (runs 1 and 5) using conventional heating or microwave irradiation. In all cases, analysis indicated the level of palladium in the crude mixtures to be less than 6 ppm. We have not investigated whether the NPs on the solid surface are the actual catalyst or just a source that leaches active catalyst species.²⁴

In conclusion, we have embedded a fluorine agent within silica gel and have used the resulting framework to stabilize Pd NPs of 4 nm. The material has been shown to be active as a catalyst in Heck coupling reactions, and its stability was improved over that of the fluorine-stabilized nanoparticles noncovalently immobilized on fluorine silica gel. The increased stability allowed for the coupling under microwave irradiation, with up to six consecutive catalytic runs without significant loss of activity.

Acknowledgment. Financial support from Ministerio de Educación y Ciencia (MEC) of Spain (Projects CTQ2005-04968-C02-01, CTQ2006-04204, and CTQ2007-60613/BQU and Consolider Ingenio 2010 (CSD2007-00006)) and DURSI-Generalitat de Catalunya (SGR 2005-00305) is gratefully acknowledged. A.S. has been supported through a Ramon y Cajal contract from the Ministerio de Educación y Ciencia of Spain. S.N. acknowledges MEC for a predoctoral fellowship.

Supporting Information Available: Complete description of experimental details, product characterization, as well as ¹H and ¹³C spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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