

Long-chain silanes as reducing agents part 1: a facile, efficient and selective route to amine and phosphine-stabilized active Pd-nanoparticles

Bhanu P. S. Chauhan^{a*}, Ramani Thekkathu^a, Leon Prasanth K^a, Manik Mandal^b and Kenrick Lewis^c

Recently, metal nanoparticles have found applications in various fields, which have necessitated exploration of new avenues to obtain such materials. In this publication, a hydrosilane-based reduction and characterization of resulting palladium nanoparticles is achieved using palladium acetate as nanoparticle precursor and octadecylsilane as a reducing agent. The influence of phosphine and amine ligands in the stabilization of nanoparticles is also investigated. In addition, a brief mechanistic proposal of the reduction process is also discussed. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: metal nanoparticles; octadecylsilane; stabilizing agents; TEM; trioctylamine

Introduction

In recent years, noble metal nanoparticles have gained tremendous importance in catalysis due to their implication in various transformations as well as their utility as recyclable catalysts.^[1–8] In high-temperature and high-pressure reactions, metal complexes can be assumed to be stripped of the stabilizing ligands to form metallic nanoparticles. In studies such as Heck coupling,^[9,10] silaesterification, hydrosilylation, hydrosilyoxidation and hydrogenation reactions,^[11,12] noble metal particles have been successfully demonstrated to be the active catalysts.

Much of the work in nanoparticle synthesis domain has indicated a strong preference for bottom-up synthetic routes because of their reproducibility and predictability. Synthesis of active (living) nanoparticles, particularly those of noble metals, has been investigated by various chemical routes^[13–16] in which hydrosilane-mediated reduction of metal complexes were known^[17,18] and has been shown to produce colloids and nanoparticles in the context of hydrosilylation catalysis. We have shown that the polymeric hydrosiloxanes such as poly-(methylhydro)siloxane (PMHS) can efficiently produce noble metal particles as well as stabilizing them in a nanoscale regime.^[11,19] We have also demonstrated that such particles could be redispersed in solvents, which provides a convenient route to production of hybrid-phase catalysts. During these studies, we were intrigued by the possibility of using hydrosilanes with long-chain alkyl groups as stabilizing and solubilizing agents, because of their solubility in organic solvents. This scheme can lead to a new class of silane stabilized nanometal particles. In addition, due to the solubility of the stabilizing agents, this strategy may provide an opportunity to study higher concentrations of nanoparticles in solution by various analytical techniques.

In this manuscript, we describe our preliminary results on the investigation of reduction of palladium (II) acetate {Pd(OAc)₂} with octadecylsilane (ODS) to produce isolable palladium nanoparticles.

In addition, we present our preliminary investigation of the synthesis and characterization of catalytically relevant phosphine and amine-containing palladium nanoparticles.

Results and Discussion

Octadecylsilane is a trihydrosilane and is commercially available in gram quantities. This silane was chosen as a possible reducing agent and its reducing ability was investigated by the reduction of Pd(OAc)₂ with different molar equivalents of ODS (Scheme 1).

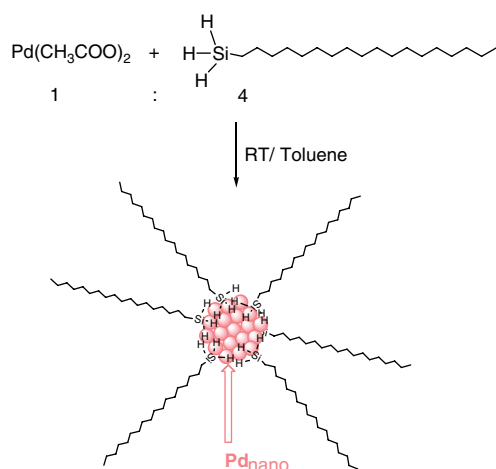
In the preliminary experiment, the reduction of Pd(OAc)₂ was examined in the presence of 1 molar equivalent of ODS. In a round-bottom flask, Pd(OAc)₂ (0.011 g, 0.05 mmol) was dissolved in toluene (45 ml) and kept under positive pressure of nitrogen. To this solution, 5 ml toluene solution of ODS (0.014 g, 0.05 mmol) was added and the resulting mixture was stirred at room temperature. The progress of the reaction was monitored by ultraviolet–visible (UV–vis) spectroscopy because the formation of Pd-nanoparticles leads to a featureless spectrum in UV–vis spectroscopy. In this case the color changes can also be used as a sign of the formation of Pd-nanoparticles, which are known to exhibit a black color. After 2 h of reaction, the mixture was yellowish brown in color, indicating

* Correspondence to: Bhanu P. S. Chauhan, William Paterson University, Department of Chemistry, Science Hall, 300 Pompton Road, Wayne, NJ 07470-2103, USA. E-mail: chauhanbps@wpunj.edu

a Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University, 300 Pompton Road, Wayne, NJ 07470, USA

b The City University of New York at College of Staten Island, NY 10314, USA

c Momentive Performance Materials, 769 Old Saw Mill River Rd, Tarrytown, NY 10591, USA



Scheme 1. Reduction of $\text{Pd}(\text{OAc})_2$ with ODS.

incomplete reduction of palladium acetate. This observation was also confirmed by UV–vis analysis of the mixture, which showed a peak at 399 nm corresponding to palladium acetate. The reaction was further continued even up to 1 week, but still $\text{Pd}(\text{OAc})_2$ was detected in the reaction mixture. The reaction mixture was yellowish brown in color during the total course of the reaction.

This unsuccessful result led us to investigate higher ratios of ODS to complete the reduction process. Thus, 2 molar equivalents of ODS (0.028 g, 0.1 mmol) were added to 1 molar equivalent of $\text{Pd}(\text{OAc})_2$ (0.011 g, 0.05 mmol) under nitrogen in toluene. After 5 h of reaction, the UV–vis spectrum indicated that $\text{Pd}(\text{OAc})_2$ was still present in the reaction mixture, although the color was much darker and black particles were observed on the walls of round-bottom flask. The ratio between $\text{Pd}(\text{OAc})_2$ and ODS was increased to 1 : 4 and the reaction was conducted under similar conditions. Addition of 4 molar equivalents of ODS led to instantaneous color change to black and the peak at 399 nm associated with $\text{Pd}(\text{OAc})_2$ disappeared completely after 1 h of reaction. A featureless spectrum was observed in UV–vis spectroscopy, which was attributed to formation of Pd-nanoparticles.

The UV–vis spectroscopy results were further confirmed by transmission electron microscopy (TEM) analysis of the reaction mixture. One drop of reaction mixture was deposited onto a formvar-coated copper grid. Indeed, Pd-nanoparticles were observed and a representative TEM image along with high resolution image is shown in Fig. 1.

In the TEM micrograph, nanoparticles seem to be connected to each other and display worm-like morphology. This method provides a simple quantitative conversion of Pd complex to Pd-nanoparticles. These particles were found to be stable in solution for up to 6 h but a significant amount of precipitate was observed after 24 h of the storage of the reaction mixture. This observation indicated that these particles were highly active but susceptible to coagulation if stored for longer periods. The long-term solubility and solvent compatibility studies are underway.

Catalytically Relevant Ligand Stabilized Pd-nanoparticles

Because of the short-term stability of the Pd-nanoparticles generated via this method, we decided to add external stabilizing agents to produce nanoparticles, which may lend long-term stability to these particles. The phosphine and amine ligands were chosen because a very large body of palladium-catalyzed

reactions has been carried out with, and/or in presence of, these ligands. The first reaction we investigated was stabilization of ODS-reduced Pd-nanoparticles with triphenylphosphine (TPP). The reaction was carried out with 1 molar equivalent of $\text{Pd}(\text{OAc})_2$, 4 molar equivalents of ODS and 4 molar equivalents of TPP at room temperature. After 1 h of the reaction, the peak at 399 nm associated with $\text{Pd}(\text{OAc})_2$ disappeared completely and a featureless spectrum was observed in UV–vis spectroscopy. After the reduction was complete (~1 h), 4 molar equivalents of TPP were added to this reaction mixture. After overnight stirring at room temperature, ^{31}P -NMR analysis showed the presence of only one peak at $\delta +26$ ppm and complete disappearance of TPP peak at $\delta -5.2$ ppm was observed. This new peak has been attributed to TPP-stabilized Pd-nanoparticles. This analysis indicated that indeed TPP was coordinated to Pd-nanoparticles (Scheme 2). To gain more insight of this process, we investigated the possibility of a one-pot reduction and phosphine stabilization of Pd-nanoparticles. In order to be able to monitor the reduction and stabilization process, the reaction was conducted in a Schlenk tube and benzene d_6 (C_6D_6) was used as solvent. In this reaction, $\text{Pd}(\text{OAc})_2$ (0.011 g, 0.05 mmol) was dissolved in 0.5 ml of C_6D_6 and PPh_3 (0.052 g, 0.2 mmol) was added to this solution and analyzed by ^{31}P -NMR.^[13–17] After 15 min of addition of PPh_3 the characteristic peak of PPh_3 at $\delta -5.2$ ppm completely disappeared and four new peaks at $\delta -1.2$, 15.1, 25.8 and 29.7 ppm were observed. These peaks were attributed to $\text{Pd}(\text{PPh}_3)_n$ -type complexes because it is known that reaction of TPP with $\text{Pd}(\text{OAc})_2$ leads to the formation of the $\text{Pd}(\text{PPh}_3)_n$ -type complexes (see Table 1).^[20–28]

At this juncture, 4 molar equivalents of ODS (0.056 g, 0.2 mmol) were added to this reaction mixture. As soon as the ODS was added, the color of the reaction mixture turned from orange-yellow to black, indicating formation of Pd-nanoparticles. Interestingly, the peaks at $\delta -1.2$, 15.1, 25.8 and 29.7 ppm disappeared and a new peak at $\delta 28.5$ ppm was observed in ^{31}P -NMR spectroscopy (Fig. 2). The formation of Pd-nanoparticles was also corroborated by disappearance of the peak at 399 nm associated with $\text{Pd}(\text{OAc})_2$, leading to a featureless UV–vis spectrum (Fig. 3).

Influence of Mode of Addition

The influence of mode of addition was investigated using ^1H and ^{31}P -NMR spectroscopy. In a Schlenk tube, $\text{Pd}(\text{OAc})_2$ was dissolved in 0.5 ml of C_6D_6 and 4 molar equivalents of TPP (0.052 g, 0.2 mmol) in C_6D_6 (0.5 ml) were added to this solution. The characteristic peak of PPh_3 at $\delta -5.2$ ppm was not present in ^{31}P -NMR but a set of new peaks at $\delta -1.2$, 15.1, 25.8 and 29.7 ppm were observed. In literature, these have been assigned to the $\text{Pd}(\text{PPh}_3)_n$ complexes.^[20–23] In ^1H -NMR a peak at $\delta 2.05$ ppm, which corresponds to $-\text{CH}_3\text{CO}-$ hydrogens of $\text{Pd}(\text{OAc})_2$ was not present anymore but a new peak at $\delta 1.34$ ppm was observed. After stirring the reaction mixture for further 15 min, 4 molar equivalents of ODS (0.056 g, 0.2 mmol) solution in 1 ml C_6D_6 were added. As soon as ODS was added, the color of the reaction mixture turned from orange-yellow to black and the peak attributed to nanoparticle complexed TPP at $\delta 28.5$ ppm was observed in ^{31}P -NMR spectroscopy. Also noteworthy was the disappearance of triplet ($\delta 3.79$ ppm) corresponding to Si–H bonds of ODS in the ^1H -NMR.

To test the influence of mode of addition, we also carried out another reaction in which ODS was added prior to the addition of TPP. In a Schlenk tube $\text{Pd}(\text{OAc})_2$ was dissolved in 0.5 ml of

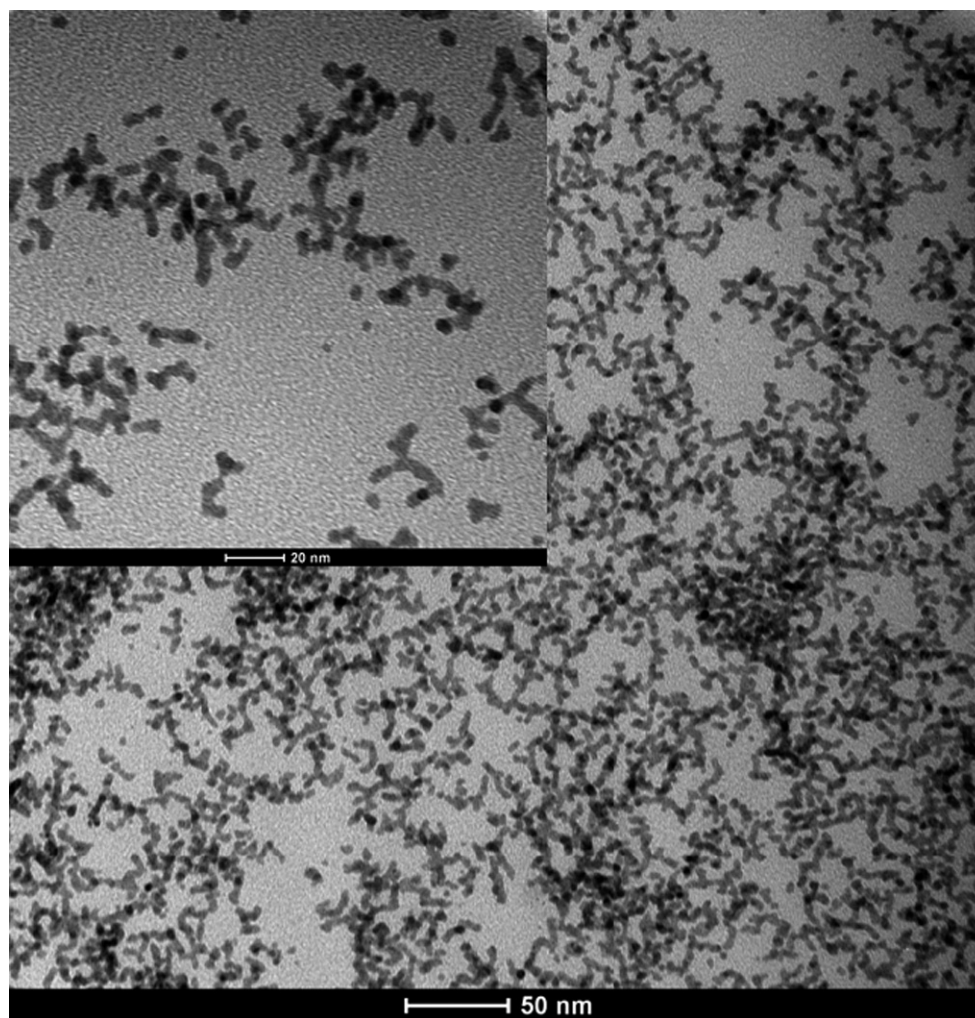


Figure 1. TEM of the reaction mixture of 1 : 4 ratio of Pd(OAc)₂: ODS after 4 h.

C₆D₆ and 4 molar equivalents of ODS (0.056 g, 0.2 mmol) in C₆D₆ (0.5 ml) were added to this solution. As soon as ODS was added, the color of the reaction mixture turned from light yellow to black and also the disappearance of peaks at δ 3.75 ppm (Si–H) and δ 2.05 ppm (CH₃CO) was observed in ¹H-NMR. After stirring the reaction mixture for 1 h, 4 molar equivalents of TPP (0.052 g, 0.2 mmol) solubilized in 1 ml C₆D₆ were added and the reaction was monitored by ³¹P-NMR. A peak at δ –4.62 ppm was observed after 5 min of addition of TPP and peaks at δ –5.36, 15.33, 28.75 and 29.0 ppm were observed after 1 h of the reaction. An increase in the intensity of peak at δ 28.5 ppm and simultaneously the decrease in intensities of the other peaks were observed as the reaction progressed. Finally, after overnight stirring of reaction a single peak at δ 28.5 ppm was observed in ³¹P-NMR spectroscopy. These two experiments indicated that changing the mode of addition for the *in-situ* preparation of nanoparticles does not change the final outcome. However, there is a strong possibility that the reaction process proceeds via different intermediates.

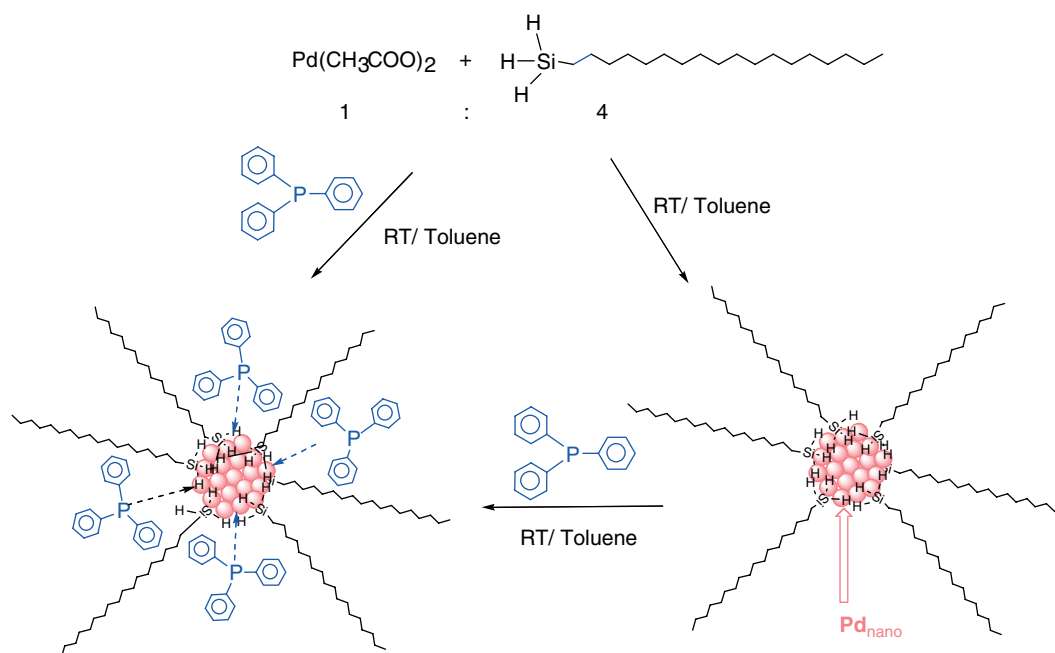
Dilution Studies of Phosphine-stabilized Pd-nanoparticles

When TPP-stabilized Pd-nanoparticles were synthesized under high dilution conditions (in 50 ml toluene), we observed a peak at δ 26.6 ppm instead of a δ 28.5 ppm peak associated with

TPP-stabilized nanoparticles in ³¹P-NMR. To confirm that the both peaks correspond to PPh₃-stabilized Pd-nanoparticles, we devised a new experiment. In this experiment, the product obtained in a Schlenk tube reaction, which showed a peak at δ 28.5 ppm was diluted gradually and analyzed by ³¹P-NMR. We observed a shift towards high field with 10% (δ 27.77 ppm) and 25% dilutions (δ 26.9 ppm), but no further shift was observed on higher dilutions (Fig. 4). This was also confirmed by ¹H-NMR in which there was no significant shift of peaks on dilution. Because of higher concentration of Pd-nanoparticles, we were unable to carry out UV–vis analysis but at 50% and 100% dilutions, as expected, featureless spectra were observed.

Trioctylamine Stabilized Pd-nanoparticles

Amines are well-established metal-coordinating agents and have been shown to provide a very good activity and selectivity variations in the metal complex catalysis. Keeping in mind the future applications of synthesized nanoparticles, we also investigated the preparation and stabilization of amine-containing Pd-nanoparticles. In this case, due to solubility concerns we chose a long alkyl chain amine namely trioctylamine (TOA) as stabilizing agent. The reactions were carried out under identical reaction conditions and molar ratios as in the case of TPP-stabilized



Scheme 2. Formation and stabilization of TPP-Pd-nanoparticles.

Table 1. Phosphorous NMR studies of Pd-nanoparticles stabilized with TPP, and assignment of reactive intermediates with known species

Entry	Observed signals (δ , ppm)	Known signals (δ , ppm)	Literature assignments
1	-1.213(broad)	-4.7, -3.97, -3.84, 2.5, etc.	PPh_3 in equilibrium with Pd(II) or Pd(0). ^[20] (Higher the value of Pd(0) concentration more positive the value will be)
2	15.13	15.08	$\text{Pd}(\text{PPh}_3)_2(\text{OAc})_2$ ^[21]
3	25.87	25.43	$\text{O}=\text{PPh}_3$ ^[22]
4	29.79	29.69	$\text{Pd}(\text{PPh}_3)_4$ or $\text{Pd}(\text{PPh}_3)_3$ ^[23]
5	20.44	22.5	$\text{Pd}(0)(\text{PPh}_3)_n$ ($n < 4$) ^[20]
6	28.5–29	29.47	Nano Pd stabilized by PPh_3 ^[23]

nanoparticles. Thus, a typical reduction reaction was carried out with 1 molar equivalent of $\text{Pd}(\text{OAc})_2$ (0.011 g, 0.05 mmol), in the presence of 4 molar equivalents of ODS (0.056 g, 0.2 mmol) and 4 molar equivalents of TOA (0.08 ml) in 50 ml of toluene. After 1 h of reaction, the peak at 399 nm associated with $\text{Pd}(\text{OAc})_2$ disappeared completely and a featureless spectrum was observed in UV-vis spectroscopy which was attributed to trioctylamine stabilized Pd-nanoparticles. Although some precipitation of nanoparticles was observed at the bottom of reaction flask after a longer time period, we were able to redissolve them by simply shaking the flask (Scheme 3).

Proposed Mechanism

Detailed mechanistic studies are underway but here our preliminary proposal is presented, which is based on the known reactivity of Si-H bonds in the presence of metal complexes. In this process, first insertion of Pd into Si-H bonds takes place followed by reductive elimination to produce Pd-nanoparticle nuclei and acetic acid or silyl ester. The formation of silyl ester is proposed to take place by the reaction of acetic acid with hydrosilane. This is reasonable to assume, because we have demonstrated in our previous work that Pd can catalyze the silylation reaction of hydrosilane in the presence of an acid.^[11] The preliminary evidence for such

a mechanism was gathered by ^1H -NMR spectroscopy. We found that during the reduction process an acetic acid -COOH peak at δ 11.7 ppm was observed in the solution just after the addition of ODS to the reaction mixture. At the same time, ^{29}Si NMR studies indicated that, along with ODS peak (δ -60.0 ppm), new peaks at δ -30.7, -19.6 and -17.0 ppm were also present. These peaks can be associated with the products obtained by oxidation of silane. Although we have not identified the real mechanism, the key intermediates in this reaction seem to be the formation of Si-Pd complex followed by reductive elimination to produce Pd-nanoparticles.

Conclusion

In conclusion, we have demonstrated a very simple, efficient and quantitative method to generate Pd-nanoparticles. We have also shown that these nanoparticles can be attached to phosphine and amine ligands which help us in modulation of various catalytic transformations. We are studying the mechanistic aspects of phosphine and amine coordinated nanoparticles to find effective catalytic conditions for Si-C and Si-O bond formation reactions. Since concentration, solvent coordination ability and reagent play a critical role in nanoparticles stabilization, we are investigating

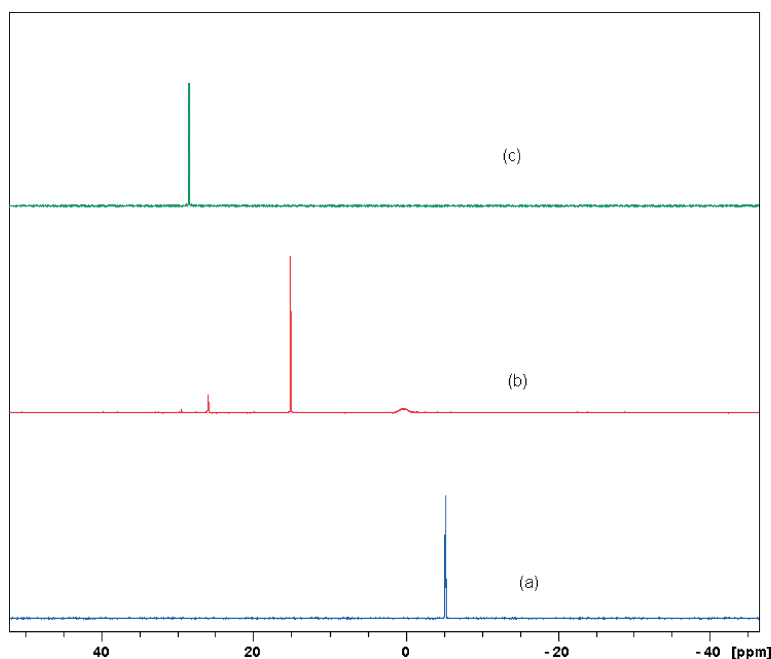


Figure 2. A Schlenk tube reduction reaction of $\text{Pd}(\text{OAc})_2$ in the presence of TPP: (a) TPP; (b) $\text{Pd}(\text{OAc})_2$ + TPP (1 : 4); (c) $\text{Pd}(\text{OAc})_2$ + TPP + ODS (1 : 4 : 4).

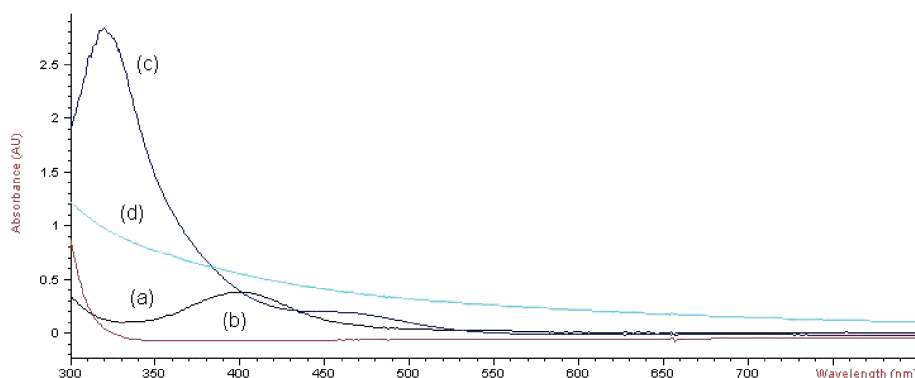


Figure 3. UV-vis spectra of (a) $\text{Pd}(\text{OAc})_2$; (b) TPP; (c) $\text{Pd}(\text{OAc})_2$ + TPP (1 : 4); (d) $\text{Pd}(\text{OAc})_2$ + TPP + ODS (1 : 4 : 4).

these factors in detail and will present result of these studies in near future. Our future work will also involve the precipitation and re-dissolution of these nanoparticles to study their utility as recyclable catalysts.

Experimental

All of the experiments were performed at room temperature (27–30 °C) under a positive pressure of nitrogen. Solvents were purchased from EM science (Merck) and distilled prior to the use. Palladium acetate, octadecylsilane, triphenylphosphine and trioctylamine were purchased from Aldrich Chemical Co. and/or Gelest Chemical Co. and used as received. ^{31}P and ^1H -NMR spectra were recorded on 400 MHz Bruker NMR instrument and were referenced internally to the corresponding solvent shifts.

Preparation of Pd-nanoparticles using Octadecylsilane

Procedure for reaction with one molar equivalent of ODS

In a round-bottom flask, $\text{Pd}(\text{OAc})_2$ (0.011 g, 0.05 mmol) was dissolved in toluene (45 ml) and kept under positive pressure

of nitrogen. To this solution, 5 ml toluene solution of ODS (0.014 g, 0.05 mmol) was added and the resulting mixture was stirred at room temperature. The progress of the reaction was monitored by UV-vis spectroscopy. After 2 h of reaction, the mixture was yellowish brown in color, indicating incomplete reduction of palladium acetate. This observation was also confirmed by UV-vis analysis of the mixture, which showed a peak at 399 nm corresponding to palladium acetate. The stirring was further continued even up to 1 week, but still $\text{Pd}(\text{OAc})_2$ was detected in the reaction mixture. An identical protocol was used for investigation of the reaction in presence of two molar equivalents of ODS.

Procedure for reaction with four molar equivalents of ODS

In a 100 ml round-bottom flask, $\text{Pd}(\text{OAc})_2$ (0.011 g, 0.05 mmol) was dissolved in 45 ml of freshly distilled dry toluene and kept under positive pressure of nitrogen. A 5 ml toluene solution of ODS (0.056 g, 0.2 mmol) was prepared and added to the palladium acetate solution at room temperature using a 10 ml syringe. The resulting reaction mixture was allowed to stir at room temperature. The reaction mixture turned black immediately after the addition

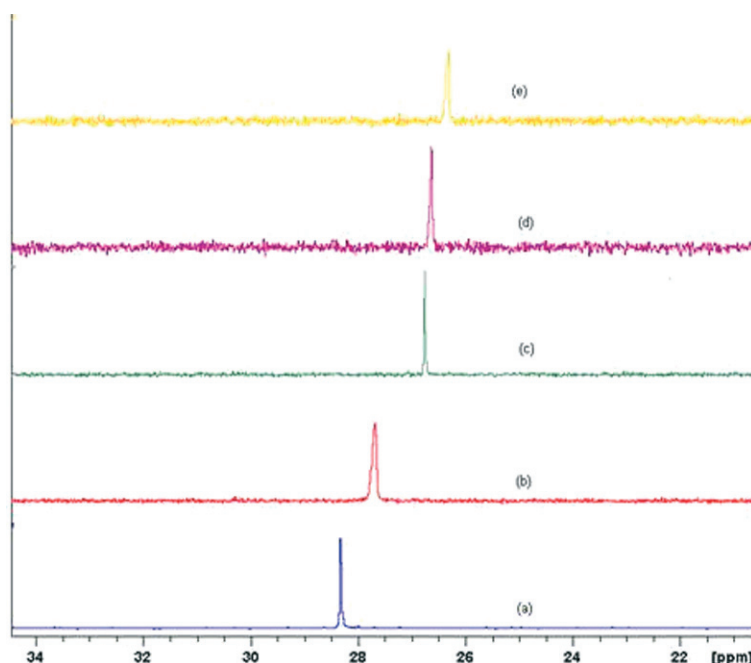
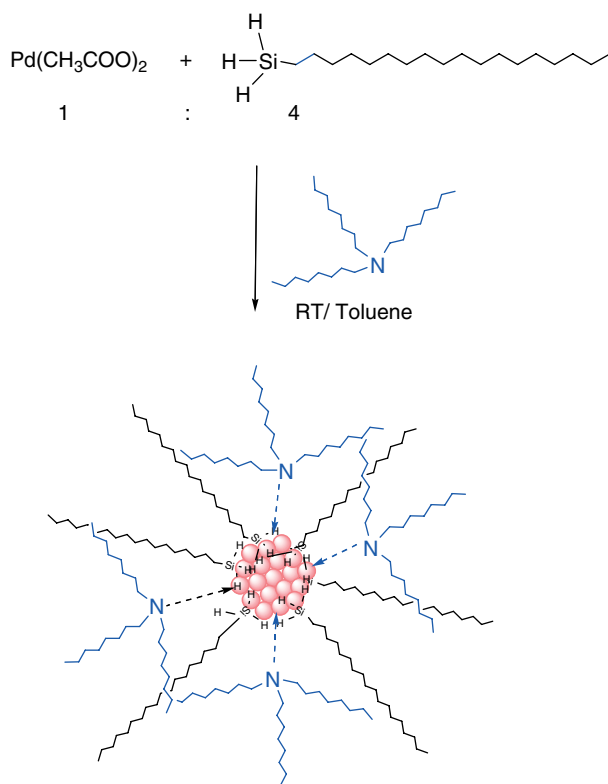


Figure 4. ^{31}P spectra of the reaction mixture (a) without dilution and with (b) 10%, (c) 25%, (d) 50% and (e) 100% dilutions.



Scheme 3. Synthetic scheme for the stabilization of silane reduced TOA-Pd-nanoparticles.

of silane. The mixture was monitored by UV-vis spectroscopy. After 1 h of the stirring, a featureless spectrum corresponding to Pd-nanoparticles was observed. When the particles were stored for more than 6 h, formation of precipitate was observed.

Preparation of Pd-nanoparticles Stabilized by TPP

General procedure for TPP stabilized Pd-nanoparticles

Palladium acetate (0.011 g; 0.05 mmol) was dissolved in 40 ml of toluene in a 100 ml two-necked round-bottom flask under positive pressure of nitrogen. After 15 min, a solution of ODS (0.056 g, 0.2 mmol) in toluene (5 ml) was added to the reaction mixture and the progress of reaction was monitored by UV-vis. A featureless UV-vis spectra was obtained after 1 h of reaction at room temperature. After confirming the conversion of $\text{Pd}(\text{OAc})_2$ to Pd-nanoparticles, a 5 ml toluene solution of TPP (0.052 g, 0.2 mmol) was added to the reaction mixture under positive pressure of nitrogen. This mixture was allowed to stir at room temperature and analyzed by ^{31}P -NMR spectroscopy. For NMR analysis, 0.5 ml reaction mixture was taken in an NMR tube and trace amount of C_6D_6 was added to obtain the lock. $\text{Pd}(\text{OAc})_2 + \text{ODS} + \text{TPP}$, after 1 h of the reaction with TPP: ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) -5.2 (no change in TPP signal); $\text{Pd}(\text{OAc})_2 + \text{TPP} + \text{ODS}$: after overnight, δ (ppm) $+26$.

General procedure for the NMR monitoring of the reduction process/influence of mode of addition

First addition of TPP: in a Schlenk tube, $\text{Pd}(\text{OAc})_2$ (0.011 g, 0.05 mmol) was dissolved in 0.5 ml of C_6D_6 under nitrogen atmosphere and 0.5 ml C_6D_6 solution of TPP (0.052 g, 0.2 mmol) was added to this solution. After 15 min of stirring at room temperature, a 1 ml, C_6D_6 solution of ODS (0.056 g, 0.2 mmol) was introduced to the reaction mixture and the progress of reaction was analyzed by ^{31}P - and ^1H -NMR spectroscopy. $\text{Pd}(\text{OAc})_2$: ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 2.05 (s); TPP: ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 7.1–7.5 (m), ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) -5.2 ; $\text{Pd}(\text{OAc})_2 + \text{TPP}$ 15 min: ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 1.34, 7.5–7.9 (m); ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) -1.2 , 15.1, 25.8, 29.7; $\text{Pd}(\text{OAc})_2 + \text{TPP} + \text{ODS}$ 1 h: ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 0.47 (s), 1.05–1.92 (br, m), 7.18 (br, s), 7.85 (br, s); ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) 28.5.

First addition of ODS: in a Schlenk tube, $\text{Pd}(\text{OAc})_2$ (0.011 g, 0.05 mmol) was dissolved in 0.5 ml of C_6D_6 under nitrogen atmosphere and 0.5 ml C_6D_6 solution of ODS (0.056 g, 0.2 mmol) was added to this solution. After 1 h of stirring at room temperature, 1 ml of a C_6D_6 solution of TPP (0.052 g, 0.2 mmol) was introduced to the reaction mixture and the progress of reaction was analyzed by ^{31}P and ^1H -NMR spectroscopy. ODS: ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 0.67 (m, 2H), 1.03 (t, 3H), 1.35–1.45 (br, m, 32H), 3.79 (t, 3H); $\text{Pd}(\text{OAc})_2$ + ODS: ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 0.39 (s), 1.02 (br, m), 1.45 (br, m), 1.86 (s); $\text{Pd}(\text{OAc})_2$ + ODS + TPP 5 min: ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 0.42 (s), 1.05–1.82 (br), 7.17–7.5 (m), 7.81 (br, s), 8.08 (br, s); ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) –4.62; $\text{Pd}(\text{OAc})_2$ + ODS + TPP 1 h: ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 0.40 (s), 1.05 (s), 1.2–1.82 (br), 7.15–7.27 (m), 7.81 (br, s), 8.08 (br, s); ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) –5.36, 15.33, 28.75; $\text{Pd}(\text{OAc})_2$ + ODS+TPP 24 h: ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 0.47 (s), 1.05–1.92 (br, m), 7.18 (br, s), 7.85 (br, s); ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) 28.5.

Dilution Studies

The above reaction mixture obtained from either methods showed a peak at δ 28.5 ppm was diluted gradually and analyzed by ^{31}P -NMR. A 0.2 ml aliquot of the above reaction mixture was transferred to a NMR tube and 0.3 ml of C_6D_6 was added (10% dilution) to this solution and analyzed by ^1H and ^{31}P -NMR spectroscopy. In similar manner, the reaction mixture was diluted to 25% (0.1 ml in 0.6 ml C_6D_6), 50% (0.1 ml in 1.15 ml C_6D_6) and 100% (0.1 ml in 2.4 ml C_6D_6), as compared with round-bottom flask high-dilution reaction in the presence of 50 ml solvent.

Reaction mixture without dilution: ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm): 0.68 (br), 1.01–1.04 (br), 1.36–1.46 (br m), 1.86 (s), 3.76 (s), 6.98–7.17 (m), 7.56 (t), 7.78 (m), 8.04 (s) ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) 28.5. **Reaction mixture with 10% dilution:** ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 0.43 (s), 1.05 (s), 1.47 (s), 1.69 (s), 1.89 (s), 7.13 (m), 7.83 (m); ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) 27.77. **Reaction mixture with 25% dilution:** ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 0.41 (s), 1.05 (s), 1.47 (br s), 1.65 (s), 1.85 (s), 7.12 (m), 7.82 (m); ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) 26.94. **Reaction mixture with 50% dilution:** ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 0.40 (s), 1.05 (s), 1.47 (br, s), 1.66 (s), 1.82 (s), 7.14 (m), 7.85 (m); ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) 26.9. **Reaction mixture with 100% dilution:** ^1H -NMR (C_6D_6 , 400 MHz); δ (ppm) 0.40 (s), 1.05 (s), 1.45 (br, s), 1.69 (s), 2.24 (s), 7.13 (m), 7.83 (m); ^{31}P -NMR (C_6D_6 , 400 MHz); δ (ppm) 26.65.

Preparation of Pd-nanoparticles Stabilized by TOA

In a two-necked round-bottom flask, $\text{Pd}(\text{OAc})_2$ (0.011 g, 0.05 mmol) was dissolved in 45 ml of dry toluene under positive pressure of nitrogen. To this solution, 4 equivalents of TOA (0.08 ml, 0.2 mmol) were added through syringe and the mixture was stirred at room temperature. After 15 min of stirring, a 5 ml toluene solution of ODS (0.056 g, 0.2 mmol) was added to the reaction mixture and the progress of reaction was analyzed by UV–vis spectroscopy. After 1 h of the reaction at room temperature, a featureless UV–vis spectrum was obtained, indicating the formation of amine

stabilized Pd-nanoparticles. These particles were found to be stable for weeks.

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