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“Polysiloxane-Pd” Nanocomposites as Recyclable Chemoselective Hydrogenation Catalysts

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Abstract: Polysiloxane-encapsulated “Pd”-nanoclusters were generated by reduction of $Pd(OAc)_2$ with polymethylhydrosiloxane, which functions as a reducing agent as well as a capping material for production and stabilization of catalytically active “Pd”-nanoparticles. Chemoselective hydrogenation of functional conjugated alkenes was achieved by in-situ- or ex-situ-generated polysiloxane-stabilized “Pd”-nanoclusters under mild reaction conditions in high yields. Electron microscopy, UV−vis, and NMR studies of the reaction mixture during the catalytic transformation were performed and, in conjunction with catalyst poisoning experiments, demonstrated unequivocally the role of polysiloxane-encapsulated “Pd”-nanoclusters as the real catalytic species. The recyclability of the “Pd”-nanoclusters was established by reusing the solid left after the reaction.

Introduction

The search for more efficient catalytic systems that might combine the advantages of both homogeneous (catalyst modulation) and heterogeneous (catalyst recycling) catalysis is one of the most exciting challenges of modern chemistry.[1a] More recently, with the advances of nanochemistry, it has been possible to prepare “soluble” analogues of heterogeneous catalysts in the form of metal nanoclusters.[1] Metal nanoclusters show an unparalleled combination of reactivity, selectivity, and recyclability as catalyst.[2] These catalytic properties arise due to the structural specificities of the nanoclusters. As an example, a high degree of selectivity is exhibited by epitaxially grown nanoclusters because different faces of the crystals manifest different selectivity and activity for the same transformation.[3]

Chemoselective hydrogenation of conjugated alkenes is an important class of reaction used extensively in the petroleum and vegetable oil industries. Both heterogeneous[4] and homogeneous[5] catalysts are employed to achieve selective hydrogenation. In a recent report by our group, we disclosed a new strategy for the generation of polysiloxane-stabilized “Pd” colloids and evidenced their utility as a potent catalyst with better selectivity, activity, and recyclability for selective silaesterification of siloxane polymers.[6] While examining the scope of this strategy to devise catalytic routes for grafting polysiloxanes with functional moieties such as alkenes, we examined polysubstitution reactions of poly(methylhydro)siloxane (PMHS) with styrene.

To our surprise, in place of generating hydrosilylated copolymers, hydrogenation of styrene to ethylbenzene was obtained. During these studies, the following interesting observations led us to investigate this catalysis in detail. (i) When polyhydrosilanes were added to the reaction mixture containing catalytic amounts of $Pd(OAc)_2$, the color of the solution turned black accompanied by gas formation, presumably H_2. (ii) After the transformation was complete, a black precipitate was formed, and the solution became colorless. (iii) The black precipitate can be redispersed in the solution in the presence of polyhydrosiloxanes and was equally active for hydrogenation reactions, thus allowing recyclability.

In this publication, we describe a new approach to “Pd-polysiloxane” nanocomposite-catalyzed one-pot, highly efficient chemoselective hydrogenation of functional conjugated alkenes at room temperature (Scheme 2). This strategy involves poly-

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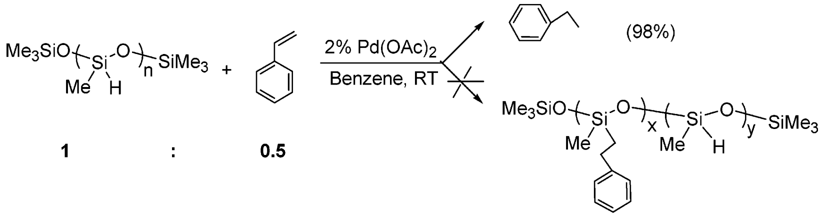
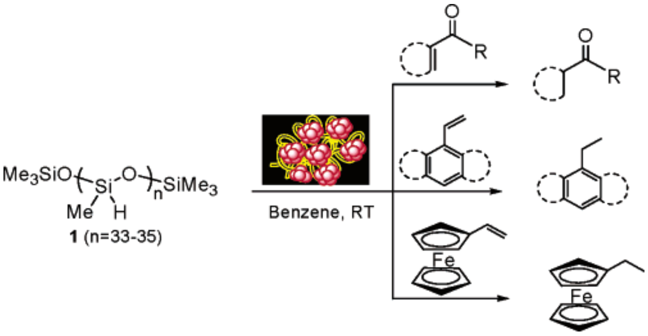
Scheme 1. Selective Reduction of Styrene



Scheme 2. Polysiloxane-Stabilized “Pd”-Nanoclusters-Catalyzed Reduction of Alkenes



hydrosiloxane as the hydrogen source for reduction of alkenes as well as the stabilizing agent for catalytically active “Pd”-nanoclusters. We also critically examine the role of “Pd” clusters as recyclable catalysts, examine the mechanism of their regeneration, and provide evidence that the hybrids of polysiloxane and Pd colloids can be regarded as molecular entities, which inherit the profitable solution behavior of silicon polymers and the catalytic activity of metal nanoparticles.

Results and Discussion

Investigations of the Nature of the True Catalyst. A problem that has caused considerable consternation in the study of nanocluster catalysis is the difficult task of distinguishing homogeneous, single metal-complex catalysts from soluble nanocluster or colloid (vide supra) catalysts. The literature in this area dates back to about 1980 and includes contributions from Maitlis,[7a] Whitesides,[7b,c] Crabtree,[7d−f] Collman,[7g] Lewis,[7h,i] and Finke.[7j−l] Recently, Finke and co-workers[7l] outlined a thorough and more general approach for distinguishing the nanocluster catalysis from single metal-complex catalysis. In the present catalysis, studies as outlined in Figure 1 were performed to critically investigate the catalytic action of “Pd-polysiloxane” nanoconjugates.

We performed the following experiments to delineate the real catalysts in this process: (1) UV−vis studies of the precursors and their transformation to catalytically active nanoclusters; (2) in-situ characterization studies, emphasizing TEM studies during the catalysis; (3) quantitative poisoning studies; and (4) recyclability and reproducibility studies emphasizing the (i) regeneration of the active nanoclusters, (ii) independent generation of the nanoclusters and their catalytic actions, and (iii) size and solubility effects on the catalysis.

(1) UV−Vis Studies of the Precursors and Their Transformation to Catalytically Active Nanoclusters. In a typical experiment, $Pd(OAc)_2$ (0.02 mmol, 0.005 g), poly(methylhydro)-siloxane **1** (PMHS) (2.00 mmol, 0.12 mL), and styrene (1.00 mmol, 0.12 mL) were dissolved in 2.5 mL of benzene (Scheme 1). The color of the reaction mixture turned black after 15−20 min of induction period, indicating the conversion of $Pd(OAc)_2$ to “Pd”-nanoclusters. The color change was corroborated by UV−vis analysis of the reaction mixture. The peak at 397 nm, which was indicative of $Pd(OAc)_2$, disappeared after the color change, and a featureless absorption associated with “Pd”-nanoparticles was observed (see Supporting Information). The color changes and absorption spectra correlate well with the UV−vis spectra of “Pd”-nanoparticles simulated by Creighton and co-workers.[8]

(2) In-Situ Characterization Studies, Emphasizing TEM Studies During the Catalysis. Transmission electron microscopy (TEM) characterization of the crude reaction mixture was also performed. Only samples that were taken after the induction period contained “Pd”-nanoparticles. The samples were directly deposited on a carbon grid without workup; the process can be viewed as “in-situ” TEM analysis. As is evident by the TEM image of the reaction mixture, “Pd”-nanoclusters encapsulated by polysiloxane were present in the reaction mixture during the catalysis (Figure 2). This image is taken from a randomly chosen part of the substrate, and it is a good representation of the overall sizes and shapes of the particles. The particle size analysis of 200 particles showed 60% of the particles in the 3.5 nm size regime. The catalysis was continued for 4 h and led to complete consumption of styrene to produce the corresponding reduced product, ethylbenzene, in quantitative yield.

After the reaction was over, the mixture turned clear, and a black solid precipitated out. Characterization of the solid was carried out with electron microscopy, multinuclear NMR techniques, FT-IR, and UV−vis spectroscopy. Scanning electron microscopy (SEM) analysis of the solid affirmed the presence of “Pd”-nanoclusters in the size regime of 40−60 nm. After the product was removed, the recovered black solid was washed with an excess of toluene and was reused as catalyst for hydrogenation reactions. An almost similar reactivity was observed as compared to in-situ-generated “Pd”-nanoclusters. The UV−vis spectra and TEM analysis of the reaction mixture indicated that polysiloxane-encapsulated “Pd”-nanoclusters (2−3 nm) were regenerated after the addition of reactants. These observations imply that the addition of **1** to bigger nanoclusters

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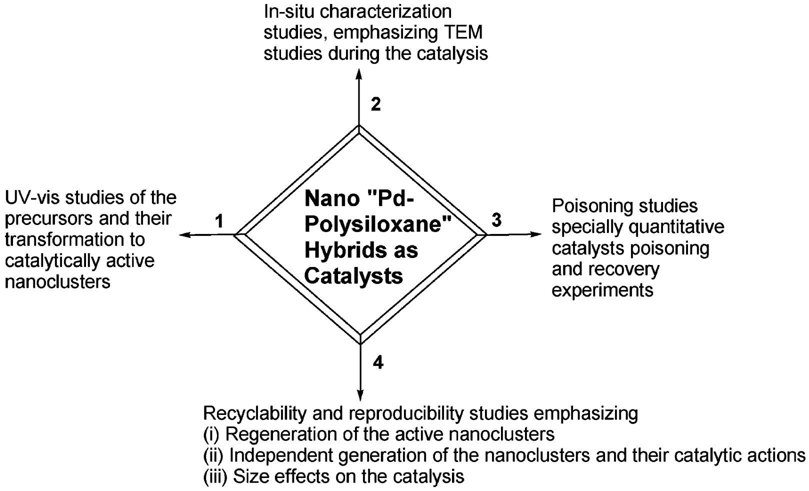

Figure 1. Schematic drawing of investigations performed to establish "Pd-polysiloxane" nanocomposites as real recyclable catalysts.

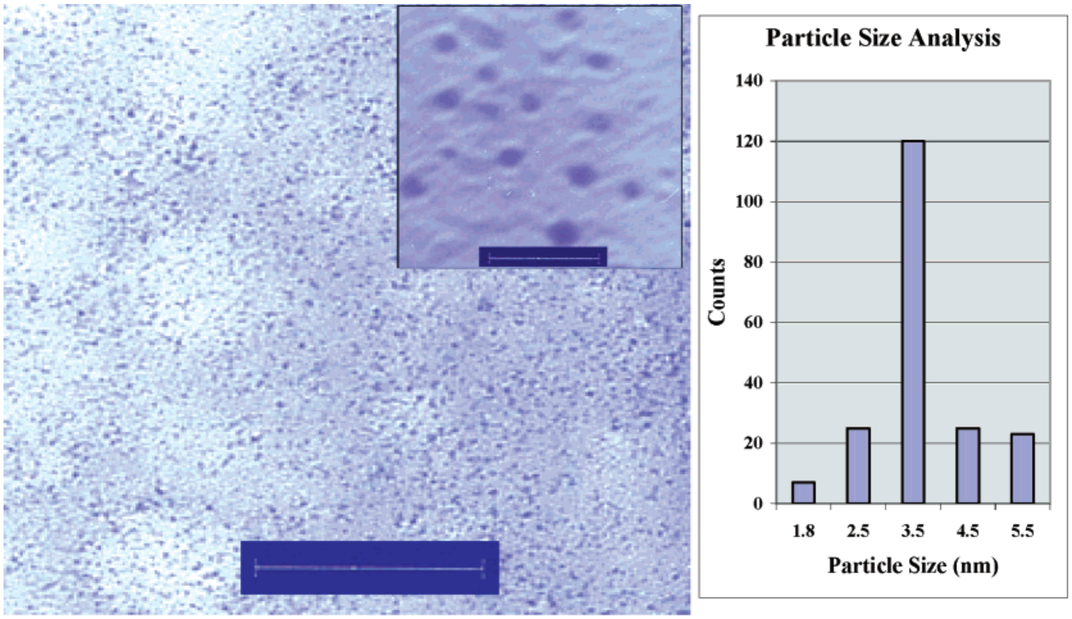

Figure 2. TEM (bar 100 nm) and particle size analysis of the reaction mixture during the catalytic conversion of styrene to ethylbenzene. The inset shows the high-resolution image of the nanoparticles (bar 20 nm).

leads to regeneration of stable small nanoclusters (2−4 nm) from the solid, which contained "Pd"-nanoclusters in the size regime of 40−60 nm. This unique aspect of the catalysis is systematically examined in the section titled recycling and reproducibility studies.

(3) Catalyst Poisoning Studies. To further probe "Pd"-nanocluster catalysis, poisoning tests were carried out. Mercury is known to poison metal colloids due to physioabsorption of the metal colloids on the mercury surface and also because of the facile formation of amalgam with metals such as Pt, Pd, and Ni. Mercury poisoning experiments were carried out after ensuring that "Pd"-nanoclusters were formed and catalytic transformation of alkene to alkanes had ensued. In a standard reaction mixture, styrene (1 mmol), PMHS (2 mmol), and $Pd(OAc)_2$ (0.05 mmol) were stirred at room temperature for 30 min to ensure the formation of "Pd"-nanoclusters. NMR analysis of the reaction mixture indicated 10% transformation of styrene to ethylbenzene. At this juncture, mercury (~2 equiv with respect to Pd) was added to reaction mixture. Just after the mercury addition, the reaction mixture turned colorless. Progress of the reaction was also followed by NMR. Only 13−15% conversion to desired product was observed even after 24 h of reaction. The mixture was examined by TEM before and after the addition of mercury. As is clear from the TEM images of the reaction mixture (Figure 3a), "Pd"-nanoclusters present in the solution before the addition of mercury disappeared after the addition (Figure 3b). This experiment strongly suggests that polysiloxane-stabilized "Pd"-nanoclusters were the real catalyst.

Additional poisoning tests were performed with dodecanethiol (DDT). Thiols are strong coordinating ligands and are known to passivate the active sites present on the surface of the metal nanoclusters, making them inactive catalysts. The catalytic activity of the nanoparticles was periodically examined in the presence of varying amounts of DDT after validating the presence of nanoclusters in the solution. The results are summarized in Table 1. In presence of 0.5 equiv of DDT (with respect to Pd), 40% conversion to reduction product was observed, indicating comparatively less opportunities for reactant to catalyst interactions. On the other hand, when enough DDT (1 to 2 equiv) required to passivate the total surface of

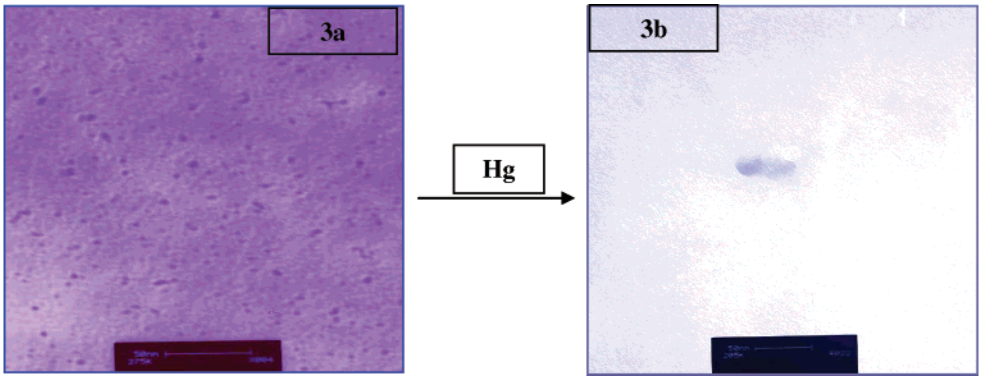

Figure 3. TEM images obtained by depositing the crude reaction solution before (3a) and after (3b) the addition of the Hg.

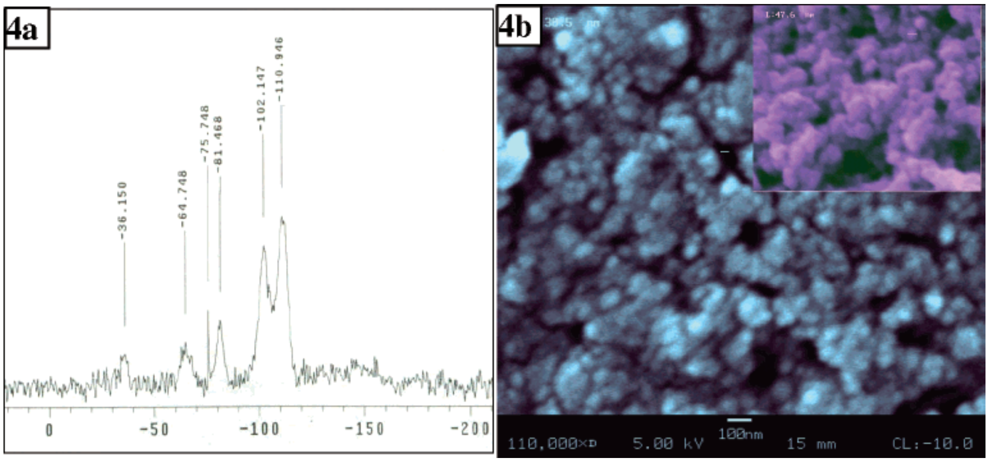

Figure 4. ^{29}Si CPMAS NMR (4a) signatures and SEM (4b, inset shows the high-resolution image) of the polysiloxane-stabilized isolable “Pd”-nanoparticles.

Table 1. Poisoning Studies of “Pd”-Nanocluster-Catalyzed Reduction of Styrene in the Presence of DDA

time (h)	% conv (0.5 equiv of DDT)	% conv (1 equiv of DDT)	% conv (2 equiv of DDT)
4	10	8	0
8	25	10	0
24	40	10	0

nanoparticles was employed, no further reaction took place. During and after the poisoning studies, the reaction mixture was also assayed by TEM, which showed the presence of nanoclusters in the solution after the addition of dodecanethiol (see Supporting Information). The presence of nanoclusters indicated that dodecanethiol coordinates to soluble clusters and renders them inactive as catalyst.

(4) Recyclability and Reproducibility Studies. (i) Independent Synthesis of Siloxane-Stabilized “Pd”-Nanoclusters and Their Characterization. Pd(OAc)$_2$ (0.09 g, 0.4 mmol) was dissolved in 20 mL of benzene, and PMHS (0.72 mL, 12.0 mmol) was added at room temperature. The reaction was carried out in air. The color of the solution changed from yellow to black within 5 min of stirring. Stirring was stopped after 2−3 h. The reaction mixture was filtered under vacuum, and the residue was collected after washing with an excess of toluene. The solid obtained was characterized with various techniques. ^{29}Si CPMAS NMR (Figure 4a) of the obtained solid displayed peaks at δ −36.15, −64.74, and −75.74 ppm corresponding to a polymeric network containing Si−H, SiOCOR, and Si−OH moieties, respectively. The signals at δ 102 and −111 ppm indicate a fully condensed silica network. The presence of these moieties was further documented by FT-IR spectra, which showed characteristic signals associated with Si−H and Si−O−Si bonds. SEM analysis (Figure 4b) of this solid was also undertaken. Particles were found to be in the nanometer size regime (40−50 nm) and were stabilized by the polymeric network.

(ii) Recyclability Studies. The regeneration of “Pd”-nanoclusters is of crucial importance for maintaining catalytic activity after several recyclings. During the recycling experiments, we observed that as soon as **1** was added to the reaction mixture, the color of the solution changed to black after 15−20 min of stirring the reaction mixture at room temperature. This color change also triggers the reduction of alkene (NMR monitoring of the reaction mixture indicated only traces of reduction product before the color change). This observation led us to hypothesize that addition of **1** (i.e., PMHS) leads to regeneration of small soluble nanoclusters (2−3 nm) from the solid, which contained “Pd”-nanoclusters in the size regime of 40−60 nm. To gain more insight and to elucidate the polysiloxane-induced regeneration (decrease in size) and stabilization process, the following experiments were performed: (a) the reduction reaction was carried out using H$_2$ as a reductant in place of polysiloxane **1** under identical reaction conditions and molar ratios;[9] (b) the reduction reaction was carried out using H$_2$ as a reductant in the presence of an analogous polymeric structure such as poly(dimethylsiloxane) PDMS $\{O-(SiMe_2-O-)_n-\}$, which does not contain Si−H bonds; (c) an experiment was performed in

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[9] We are thankful to one of the reviewer’s who suggested an experiment in the presence of exogenous hydrogen.

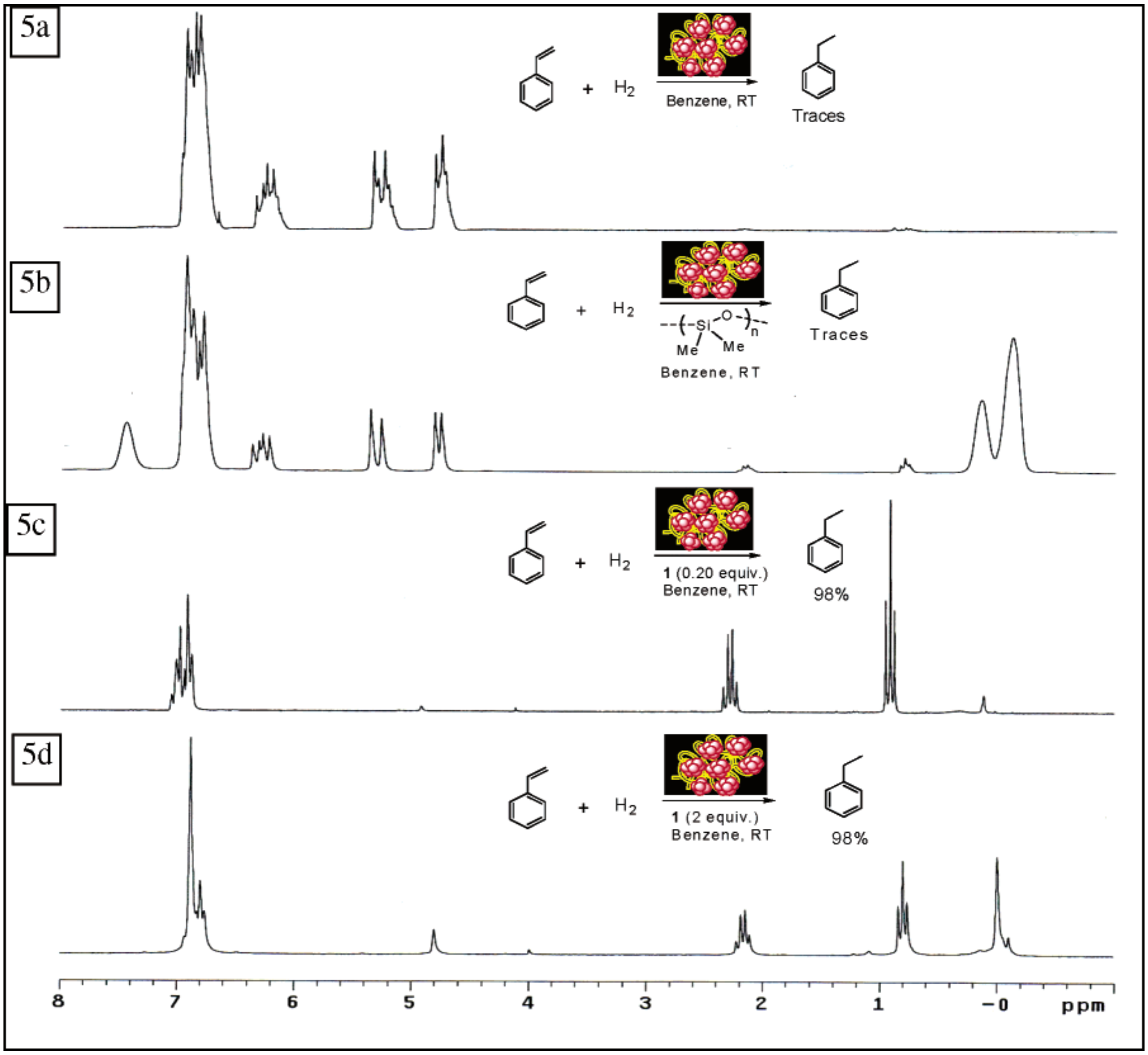


Figure 5. NMR analysis of the reduction reactions carried out with or without PMHS in the presence of hydrogen (1 atm, balloon).

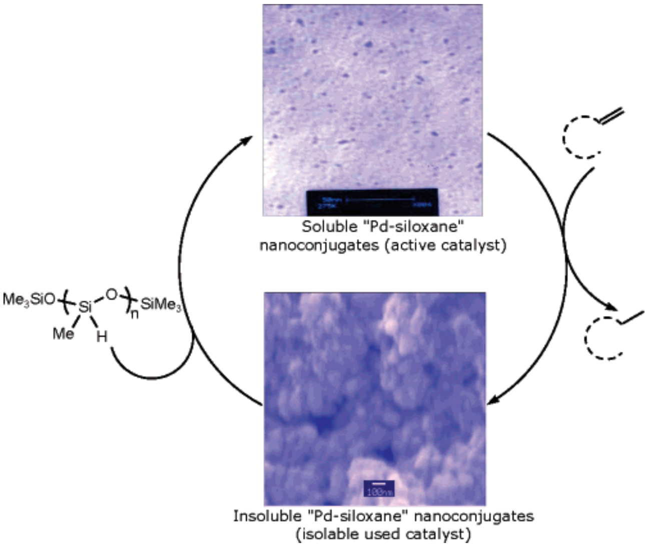
the presence of **1** (0.20 equiv to styrene), but H_2 was still used as a primary reducing agents; and (d) finally, the reaction was carried out in the presence of both **1** and H_2.

All of the experiments (a−d) were monitored by NMR to probe the product formation, and by UV−vis and TEM analysis to authenticate the presence of soluble nanoparticles. The following results were obtained: (a) TEM and UV analysis of the reaction mixtures resulting from experiments a and b showed that nanoparticles were not present in the reaction mixture, and NMR analysis indicated only traces of the reduction product (Figure 5a and 5b) were formed even after 5 h of reaction. This experiment indicated that suspended bigger "Pd"-particles do not redissolve to produce catalytically active soluble nanoparticles. It should be pointed out that under identical reaction conditions, complete reduction of styrene was achieved when $Pd(OAc)_2$ was used as catalyst. In experiments c and d, the color of the reaction mixtures changed after addition of **1,** and complete conversion to the corresponding reduced product was obtained (Figure 5c and 5d). TEM and UV analysis of the reaction mixtures showed the presence of ∼2−4 nm size "Pd"-nanoparticles during the course of the reaction. It should be pointed out that in experiment c, the abundance of nanoparticles was low (TEM analysis) in comparison to experiment d. The results of experiments c and d strongly suggest that redispersion of "Pd"-nanoparticles and subsequent color change occur only when Si−H-containing polysiloxanes are added to the reaction mixture.

On the basis of these results, we can roughly elucidate the polysiloxane-induced regeneration (decrease in size) and stabilization process as follows: Addition of PMHS (i.e., Si−H bonds) to the reaction mixture containing insoluble bigger "Pd"-nanoparticles triggers the oxidative addition and reductive elimination sequence with Si−H bonds of PMHS (Scheme 3). During this process, large particles are broken into small particles, which, due to the steric protection provided by chemoabsorbed PMHS, become stable and soluble. These polysiloxane-stabilized 2−3 nm particles remain active, stable, and soluble until substantial amounts of Si−H bonds are present in the reaction mixture. When Si−H bonds are consumed, smaller nanoparticles aggregate to become larger particles (Oswald ripening) and precipitate out from the reaction mixture. Although extracting preformed nanoparticles into polymer matrices is a known process and an effective strategy for dispersing the nanoparticles in polymer composites, in-situ regeneration, decomposition, and growth of catalytically active nanoparticles is unprecedented.

Scope and Limitations of "Pd"-Polysiloxane-Catalyzed Reductions. The chemoselective reduction of aromatic group-

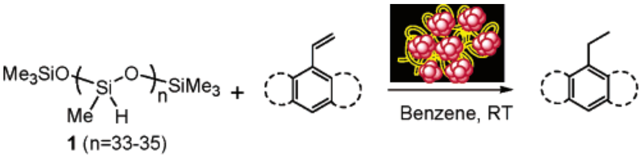
Scheme 3. Proposal for the Regeneration of Smaller "Pd Nanoparticles" in the Presence of PMHS

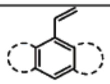
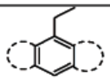
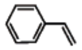
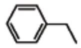
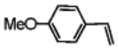
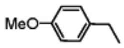
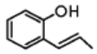
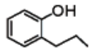
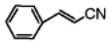
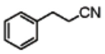
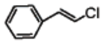
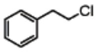
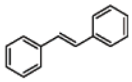
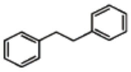
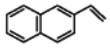
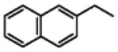
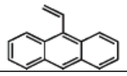
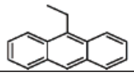


substituted conjugated alkenes was performed in benzene with 2 equiv of polymethyhydrosiloxane (PMHS), **1**, in the presence of "Pd"-nanoclusters at room temperature. In most cases, complete conversion to the corresponding reduction product was achieved in 3−6 h of reaction. Although Pd-based catalysts are known to catalyze hydrosilylation and rearrangement reactions, to our surprise, these side reactions were not observed. As is evident from the list in Table 1, excellent chemoselectivity toward hydrogenation of external C═C was achieved in the present system. The products were isolated simply by filtration from the siloxane-supported palladium nanoclusters followed by drying and removal of the solvent in vacuo. No further purification was necessary to afford pure material. The scope and limitations of the "Pd"-nanocluster-catalyzed reductions of alkenes containing functionalities such as aromatic C═C are summarized in Table 2. The limitations of the process were examined by investigating the hydrogenation of vinylic moieties containing functionalities such as aromatic C═C (entries 1−7, Table 2), OMe (entry 2, Table 2), OH (entry 3, Table 2), CN (entry 4, Table 2), and Cl (entry 5, Table 2). In all of the cases, selective reduction of vinylic functionality was observed without any detectable amounts of side products. It should be pointed out that functional groups such as alcohols (entry 3, Table 2) are particularly susceptible toward facile side reactions such as alcoholysis of silanes. The bulky substituent also does not hinder the reactivity appreciably, because alkenes such as vinyl naphthalene (entry 7, Table 2) and vinyl anthracene (entry 8, Table 2) underwent reduction reactions at room temperature. The presence of functional groups after the reduction reactions was confirmed by FT-IR and ^{1}H and ^{13}C NMR spectroscopy and was compared to authentic samples.

To further investigate the utility of this mild, high-yielding process, reduction reactions of conjugated enones were examined. Table 3 lists the reductions of conjugated enones with **1** and catalytic amounts of "Pd"-polysiloxane nanocomposite at ambient temperature. All runs demonstrated complete 1,4-selectivity to provide the corresponding ketones. No significant differences were observed in the reactivity of cyclic and acyclic systems. Commonly observed possible byproducts such as allylic alcohols were detected in the reaction mixture.[1a]

Table 2. Selective Reduction of Conjugated Aromatic Alkenes Catalyzed by "Pd-PMHS" Nanocomposite



Entry		Reaction Conditions[a]		Yield (%)
1		4h/Benzene/RT		95[b]
2		3h/Benzene/RT		95
3		4h/Benzene/RT		96
4		5h/Benzene/RT		90
5		6h/Benzene/RT		85
6		4h/Benzene/RT		94
7		4h/Benzene/RT		96[b]
8		6h/Benzene/RT		92

[a] All of the reactions were performed with 2:1 molar equivalents of **1**:alkene and were stirred under argon or nitrogen atmosphere. Reaction progress was monitored by ^{1}H NMR and/or FT-IR spectroscopy. [b] Isolated yields.

To our surprise, facile reduction of vinyl ferrocene was cleanly achieved at room temperature (Scheme 4). The corresponding reduction product was isolated in 85% yield. This transformation is noteworthy, because vinylferrocene has been reported to undergo hydrosilylation reactions with linear and cyclic polysiloxanes in the presence of single-metal-complex catalysts.[10]

Effect of the Solvents. To gain more insight into the catalysis, the course of a representative hydrogenation reaction was examined in common organic solvents under identical reaction conditions and molar ratios (Figure 6). The factors such as reaction medium, solvent coordination ability, and solvent polarity can drastically alter the reaction outcome via influencing the stability and durability of the catalyst (nanoclusters). The hydrogenation reaction of the styrene was conducted in common organic solvents under identical reaction conditions and molar ratios. In all of the solvents studied, the reaction begins after an induction period of 10−15 min. The graphs were plotted after the induction period. In THF and benzene, quantitative conversion to reduction product was achieved approximately

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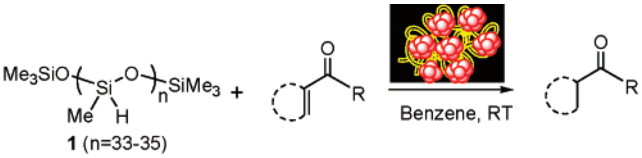
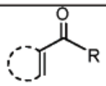
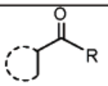
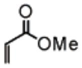
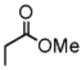
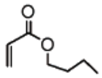
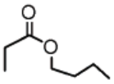
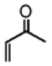
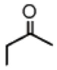
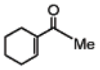
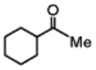
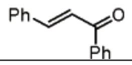
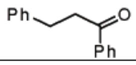
(10) For an excellent review, see: Casado, C. M.; Cuadrado, I.; Moran, M.; Alonso, B.; Barranco, M.; Losada, J. *Appl. Organomet. Chem.* **1999**, *13*, 245 and references therein.

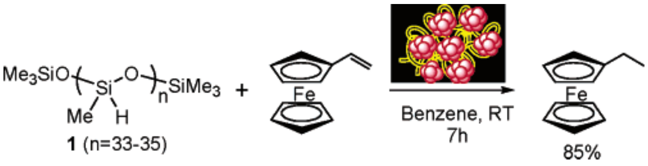
Table 3. Selective Reductions of Conjugated Enones Catalyzed by "Pd-PMHS" Nanocomposite



Entry		Reaction Conditions [a]		Yield (%)
1		4h/Benzene/RT		96
2		4h/Benzene/RT		94[b]
3		5h/Benzene/RT		95[b]
4		5h/Benzene/RT		97
5		6h/Benzene/RT		95

[a] All of the reactions were carried out with 2:1 molar equivalents of **1**:enones and were stirred under argon or nitrogen atmosphere. Reaction progress was monitored by ^{1}H NMR and/or FT-IR spectroscopy. [b] Isolated yields.

Scheme 4. "Pd"-Nanoparticle-Catalyzed Reduction of Vinylferrocene



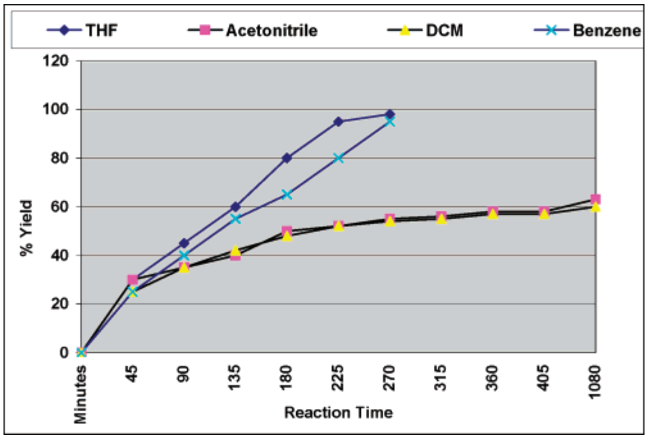


Figure 6. Plot of yield versus reaction time for reduction of styrene at room temperature.

after 4 h of reaction. However, in acetonitrile and dichloromethane, total conversion to desired product was not observed even after 24 h of reaction.

Conclusions

We have demonstrated the first example of recyclable highly active "Pd"-polysiloxane nanocomposites as selective catalysts for hydrogenation reactions. Controlled poisoning experiments in conjunction with electron microscopy studies confirm "Pd"-nanoclusters as the real catalytic species. We also established that, in addition to their role as reducing agents, in this catalysis polysiloxane serves multiple functions, for example, as a stabilizer for keeping the nanoparticles from aggregating; provides desired functional interfaces between the nanoparticles and the bulk of the materials; and facilitates the self-assembling and processing of the composites. In conclusion, we have shown that "Pd"-polysiloxane nanocomposites offer the selectivity of homogeneous single-metal-complex catalysts, and activity as well as recyclability of traditional heterogeneous catalysts.

Experimental Section

General Information. All of the experiments and manipulations were performed under a positive pressure of argon or nitrogen atmosphere using standard Schlenk-tube techniques. Solvents were purchased from EM science (Merck) and distilled over sodium/benzophenone. PMHS ($M_w \approx 2000$, 33−35 Si−H units) and Pd(OAc)$_2$ were obtained from Aldrich and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded in CDCl$_3$ on a Varian Unity NMR instrument (200 MHz). A Varian Unity NMR instrument (300 MHz) was used to carry out the CP/MAS ^{29}Si NMR spectroscopy experiments. Proton spectra were referenced internally to protonated solvent shifts. All of the peaks in the NMR spectra were reported in ppm. UV−vis spectra were recorded on a Varian Cary model 50 UV spectrophotometer. Infrared spectra were measured on the neat compounds with an FT Infrared Nicolet Mx-1 spectrophotometer. Scanning electron microscope Amray 1910 (SEM) was used to conduct the morphological studies of the solid materials. The solid was mounted on the carbon tab and coated with carbon vapors before analyzing the sample. Philips CM 100-transmission electron microscope (TEM) was applied to examine the liquid samples for the presence of "Pd"-nanoclusters during the reaction. Typically, TEM pictures of each sample were taken at three different magnifications to obtain information about the sample in general, plus a closer visualization of the clusters. A few drops of the reaction mixture were taken out with a syringe and were directly deposited on a carbon-Formvar-coated copper grid at room temperature. The solvent was allowed to evaporate from the grid under normal temperature and pressure for 1 h before TEM examination of the grid. A number of control experiments were done which provided good evidence that results are truly representative of the sample (i.e., save any crystallization in the electron beam) and that the sample is not otherwise perturbed by application of the TEM beam [e.g., controls showing that varying the sample spraying method (in air or under N$_2$) or depositing the sample as a drop and letting it dry did not change the results; controls showing that changing the beam voltage or changing the exposure time did not change the images]. The particle size analysis of the "Pd"-nanoclusters was carried out manually on the TEM images, using "Scion Image Software". Around 200−250 particles were measured manually using the software on each TEM image before plotting the "particle size analysis" graph.

Experimental Procedure for Investigations of the Nature of the True Catalyst. Pd(OAc)$_2$ (0.02 mmol, 0.005 g) or Pd colloids (0.010 g), PMHS (2.00 mmol, 0.12 mmol), and styrene (1.00 mmol, 0.12 mmol) were added together at room temperature in 2.5 mL of freshly dried and distilled benzene. Evolution of a gas (presumably hydrogen) was observed while the mixture was stirred at room temperature. The progress of the reactions was monitored by ^{1}H, ^{13}C NMR, FT-IR, and UV spectroscopy. Stirring was stopped after 4 h. The reaction mixture was centrifuged, and the filtrate was passed through a silica gel column to obtain pure product. In all of the cases, formation of corresponding reduction products was achieved within 3−8 h, unless noted otherwise.

(i) Mercury Poisoning Experiment. Pd $(OAc)_2$ (0.02 mmol, 0.005 g), styrene (1.00 mmol, 0.12 mL), and PMHS (2.00 mmol, 0.12 mL) were dissolved in 2.5 mL if benzene in a Schlenk tube. The reaction was allowed to stir until the presence of "Pd"-nanoclusters in the reaction mixture was confirmed by TEM and UV−vis spectroscopy. The reaction mixture turned colorless after the addition of mercury [2:1, Hg:$Pd(OAc)_2$] at room temperature. Characterization of the solution was performed by TEM and NMR spectroscopy. No nanoclusters were found during the TEM examination of the grid prepared, after the addition of mercury.

(ii) Thiol Poisoning Experiments. Pd $(OAc)_2$ (0.02 mmol, 0.005 g), styrene (1.00 mmol, 0.12 mL), and PMHS (2.00 mmol, 0.12 mL) were dissolved in 2.5 mL of benzene in a Schlenk tube. The reaction mixture was examined by TEM to verify the presence of "Pd"-nanoclusters. Dodecanethiol (0.04 mmol, 0.01 mL) was added to the reaction mixture, and the reaction mixture was allowed to stir for up to 24 h. ^{1}H NMR spectroscopy and transmission electron microscopy (TEM) were employed to monitor the progress and the presence of nanoclusters in the reaction mixture, respectively, after a regular period of 2 h.

(iii) Generation of Polysiloxane-Stabilized "Pd"-Nanoclusters. $Pd(OAc)_2$ (0.09 g, 0.4 mmol) was dissolved in 20 mL of benzene in a 50-mL round-bottom flask at room temperature. PMHS (0.72 mL, 12.00 mmol) was added to this solution. A color change from yellow to black was observed within 5−10 min of stirring with vigorous evolution of gas (H_2, presumably). Black solid was observed after stirring the solution for 2−3 h, and the reaction mixture turned colorless. The stirring was stopped at this point, the reaction mixture was filtered under vacuum, and black residue was collected after washing with an excess of toluene. The black solid obtained was characterized by CP/MAS ^{29}Si NMR spectroscopy, FT-IR spectroscopy, and scanning electron microscopy (SEM). ^{29}Si (CPMAS NMR) δ −36.15 (Me−Si−H-containing silicons), −64.74 (Me−Si−OCOR), −75.74 (Me−Si−OH), −110.94 (SiO_3). FT-IR spectra (KBr) 2162(m), 1021(b), 900.77(s), 2964.86 (m).

Experimental Details of Redispersion Studies. Independently synthesized polysiloxane-encapsulated "Pd"-nanoclusters (0.01 g), styrene (1.0 mmol, 0.12 mL), and PMHS (0.25 mmol, 0.015 mL) were mixed together in 2.5 mL of benzene in a 25 mL Schlenk tube. All of the reactions were performed at room temperature. A hydrogen balloon was used to maintain a constant positive pressure of hydrogen (H_2, gas) in the Schlenk tube during the reaction. The reaction mixture was analyzed with TEM after being stirred for 30 min at room temperature. Stirring was stopped after 5 h, and NMR spectroscopy examination of the reaction mixture was performed.

Typical Procedure for Hydrogenation of Alkenes Conjugated with Aromatic Functional Groups. $Pd(OAc)_2$ (0.02 mmol, 0.005 g) or Pd colloids (0.010 g), PMHS (2.00 mmol, 0.12 mmol), and styrene (1.00 mmol, 0.12 mL) were added together at room temperature in 2.5 mL of freshly dried and distilled benzene. Evolution of gas (presumably hydrogen) was observed during the stirring at room temperature. The progress of the reactions was monitored by ^{1}H, ^{13}C NMR, FT-IR, and UV spectroscopy. Stirring was stopped after 4 h. The reaction mixture was centrifuged, and the filtrate was passed through a silica gel column to obtain pure product. In all of the cases, the formation of the corresponding reduction products was achieved within 3−8 h, unless noted otherwise.

Ethylbenzene (Entry 1; Table 2): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.12(t), 2.53(q), 7.12(m), 7.21(m), 6.98(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 16.26, 28.75, 140.32, 127.5, 129.32, 125.45.

1-Ethyl-4-methoxybenzene (Entry 2; Table 2): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.24 (t), 2.59(q), 3.73(s), 6.72(m), 7.01(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 16.1, 28.6, 56, 114, 128.9, 132.5, 159.2.

2-Propylphenol (Entry 3; Table 2): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.88(t), 1.57(q), 2.47(t), 4.07, 6.5(m), 6.7(m), 6.91(m), 7.01(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 14.10, 23.04, 32.11, 115.27, 120.80, 127.81, 130.39.

3-Phenylpropionitrile (Entry 4; Table 2): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.09(t), 2.54(t), 6.99(m), 7.15(m), 7.62(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 18.73, 31.22, 118.78, 129.55, 130.76,137.96, 149.93; FT-IR ($CHCl_3$) 1280 (−CN), 2962 (C−H).

(2-Chloroethyl)benzene (Entry 5; Table 2): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.98(t), 3.89(t), 7.09(m), 7.16(m), 7.37(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 30.52, 52.32, 124.5, 127.32, 129.39, 144.23, 173.24; FT-IR ($CHCl_3$) 1760 (C═O), 2982 (C−H).

1,2-Diphenylethane (Entry 6; Table 2): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.73(t), 6.90(m), 7.20(m), 7.35(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 38.45, 126.12, 127.45, 129.36.

2-Ethylnaphthalene (Entry 7; Table 2): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.13(t), 2.62(q), 7.20−7.25(m), 7.42(1H, m), 7.58(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 15.49, 29.01, 124.97, 125.51, 125.78, 127.04, 131.93, 133.70, 141.71.

9-Ethylanthracene (Entry 8; Table 2): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.50(t), 3.65(q), 6.82(m), 7.30(m), 7.64(m), 7.75(m), 8.34(m), 8.39(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 16.8, 25.2, 124.4, 124.9, 125.0, 126.0, 128.2, 131.5, 132.2.

Procedure for Enone Hydrogenation. As outlined above for other alkenes, identical reaction conditions, molar ratios, and product isolation procedures were used. In all of the cases, reduction reactions were complete within 4−6 h at room temperature.

Propionic Acid Methyl Ester (Entry 1; Table 3): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.02(t), 1.72, 3.92(q); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 9.1, 26.1, 50.4, 172.0.

Propionic Acid Butyl Ester (Entry 2, Table 3): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.810(t), 1.02(t), 1.26(q), 1.50(m), 2.23(q), 3.99(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 9.15, 13.70, 19.14, 27.62, 30.71, 64.19, 174.60; FT-IR ($CHCl_3$) 1727(C═O), 3073(C−H).

Butane-2-one (Entry 3; Table 3): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.09(t), 1.85(q), 3.55; ^{13}C NMR ($CDCl_3$, 200 MHz) δ 18.24, 33.85, 51.51, 167.65; FT-IR ($CHCl_3$) 1698(C═O).

1-Cyclohexylethanone (Entry 4, Table 3): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.80(m), 1.22(m), 1.56(m), 1.70(m), 1.96(m), 2.11(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 14.28, 22.59, 25.86, 27.98, 28.65, 34.38, 51.63, 212.27; FT-IR ($CHCl_3$) 1680(C═O).

1, 3-Diphenyl Propan-1-one (Entry 5, Table 3): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.11(t), 3.33(t), 7.24(m), 7.28(m), 7.34(m), 7.47(m), 7.59(m), 8.01(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 30.05, 40.34, 126.05, 127.96, 128.25, 132.92, 136.80, 141.22, 199.03; FT-IR ($CHCl_3$) 1680(C═O), 2958(C−H).

Ethylferrocene (Scheme 4): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.09(t), 2.27(q), 4.00(m), 4.73, 6.84(m), 7.43(m), 7.64(m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 8.25, 27.26, 62.03, 63.83, 65.07, 105.65.

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Supporting Information Available: UV−vis spectra of the reaction mixture indicating the conversion of $Pd(OAc)_2$ to "Pd"-nanoclusters and a TEM image of dodecanethiol-passivated, catalytically inactive, yet soluble "Pd"-nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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