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Palladium(0) Nanoparticle Catalyzed Cross-Coupling of Allyl Acetates and Aryl and Vinyl Siloxanes

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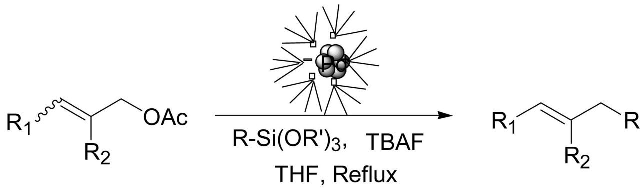


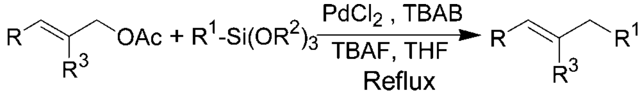
R_1 = H, Ar; R = Ph, Tol, Vinyl
R_2 = H, CO_2Me, CO_2Bu^n; R' = Me, Et

65 - 82%
7 - 10 h

The cross-coupling of allyl acetates and aryl and vinyl siloxanes proceeds readily by the catalysis of in situ generated palladium(0) nanoparticles. The reactions are stereoselective, and (*E*)-coupling products are obtained both from *cis* and *trans* allyl acetates. The coupling with vinyl siloxanes provides a novel protocol for the synthesis of 1,4-pentadienes.

The palladium-catalyzed cross-coupling reaction is a powerful tool for the formation of carbon−carbon bonds and has wide applications in organic synthesis.[1] The most frequently used methods to perform this operation are Stille,[2] Suzuki,[3] and Hiyama[4] reactions using organotin, organoborane, and organosilane coupounds, respectively. Although all three reactions provide comparable results with regard to yields and stereoselectivity, the toxicity and tedious separation of tin reagents and difficulties in the preparation and purification of Suzuki boron reagents are the disadvantages associated with Stille and Suzuki couplings. On the other hand, the ease of preparation and low toxicity of organosilane reagents has made Hiyama coupling more attractive. Although the Hiyama coupling of aryl halides and organosilanes is well-documented,[4] surprisingly the Hiyama coupling of allyl alcohol derivatives and silanes is less explored.[4c,5] Besides Hiyama's own work[4c] Deshong demonstrated coupling of cyclo-allylic benzoates with hypervalent silicon complexes,[5a−c] and Kabalka reported cross-coupling of activated allylic acetates and organosilanes.[5d] Nevertheless, several reports of allylation by allyl alcohol derivatives using Stille[6] and Suzuki[7] procedures are well-known. In view of the versatile synthetic utility of allyl moiety and advantages of Hiyama coupling, we report here a very simple and efficient cross-coupling of both unactivated and activated open-chain allylic acetates with organosiloxanes catalyzed by palladium(0) nanoparticles (Scheme 1).

SCHEME 1. Cross-Coupling Reaction of Allyl Acetate and Organo Silane Catalyzed by Pd Nanoparticles



The use of palladium nanoparticles as efficient catalysts in organic reactions has attracted considerable interest as nanoparticles provide a larger number of active sites per unit area compared to their homogeneous counterparts.[8] Our interest and continuing program to explore the novel applications of metal nanoparticles[9] led us to investigate this Hiyama cross-coupling of allyl acetates.

The experimental procedure is very simple. A mixture of allyl acetate and organosiloxane in THF was stirred at 65 °C in the presence of palladium chloride, tetrabutylammonium bromide, and tetrabutylammonium fluoride for a required period of time (TLC). Standard workup provided the product.

To determine the optimum reaction conditions for an efficient coupling, the reaction was studied with variation of reactions parameters as summarized in Table 1. The best results were obtained using 2 mol % of $PdCl_2$, 25 mol % of TBAB, and 1.1 equiv of TBAF in THF at 65 °C (entry 5, Table 1).

To determine the active catalytic species in this reaction, the reaction of cinnamyl acetate and phenyltrimethoxysilane was studied by UV (THF) spectroscopy. For comparison, the spectra of a solution of $PdCl_2$ in THF was recorded as reference. The reaction mixture after 1 min, 10 min, 30 min, 1.5 h, 3 h, and

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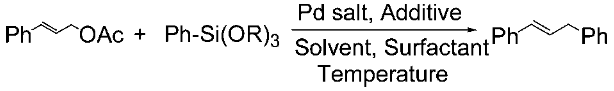
TABLE 1. Standardization of Reaction Conditions for Hiyama Cross-Coupling Reaction[a]



entry	surfactant	Pd salt	additive	solvent	temp (°C)	yield (%)
1	SDS	1	NaOH	H_2O	85	10
2	SDS	1	TBAF	H_2O	85	10
3	SDS, TBAB	1	TBAF	THF	65	76
4	TBAB	1	TBAF	THF	65	74
5	**TBAB**	**2**	**TBAF**	**THF**	**65**	**76**
6	TBAB	2	TBAF	THF	rt	20
7	TBAB	2	K_2CO_3	THF	65	10
8	TBAB	2	TBAF	toluene	100	20
9	TBAB	2	TBAF	DMF	100	15
10	TBAB	2	TBAF	NMP	100	15

[a] Pd salt 1 = Na_2PdCl_4, SDS = sodium dodecyl sulfate. Pd Salt 2 = $PdCl_2$, TBAB = tetrabutyl ammonium bromide.

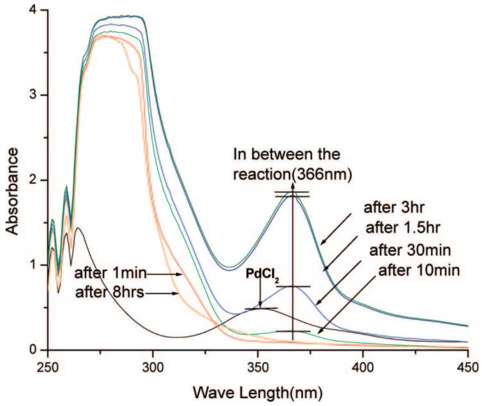


FIGURE 1. UV spectra monitoring of reaction.

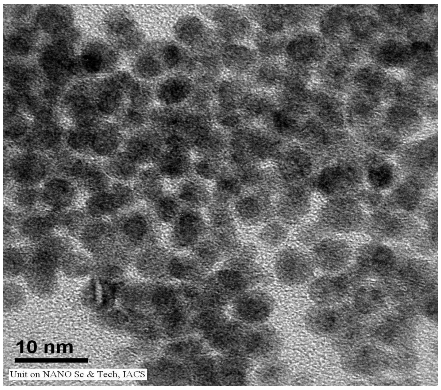


FIGURE 2. TEM image of Pd nanoparticles.

8 h showed the absence of the corresponding peak of $PdCl_2$ at 350 nm; however, a new peak at 366 nm appeared after 10 min and became maximum after 1.5 h (Figure 1). This peak remained even after 3 h and disappeared when recorded after 8 h. The new peak at 366 nm is possibly due to the formation of π-allyl Pd(II) complex with the progress of the reaction, and this peak disappeared after reductive elimination showing the formation of Pd(0) after the completion of reaction. The TEM (transmission electron microscopy) image (Figure 2) and EDS (energy dispersive X-ray spectroscopy) (Figure 3) confirmed the presence of Pd nanoparticles (3−5 nm). It is suggested that Pd(II) was reduced by allyl acetate to Pd(0) and TBAB served as stabilizer for the Pd nanoparticles.

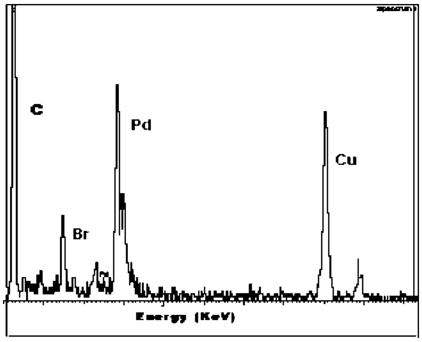


FIGURE 3. EDX spectra of Pd nanoparticles.

Several structurally varied substituted allyl acetates underwent couplings with phenyl, tolyl,[10] and vinyl siloxanes by this procedure to produce the corresponding allylated products. The results are reported in Table 2. Both unactivated (Table 2, entries 1−15) and activated acetates (Baylis−Hillman acetate adducts, Table 2, entries 16−18) participated in this reaction. The activated acetates coupled faster than unactivated ones. The reactions were highly regioselective, providing straight chain olefins through coupling from the less substituted carbon atom. Only one reaction (Table 2, entry 4) furnished a mixture of regioisomeric coupled products with a small amount (15%) of branched olefin. The stereoselectivity achieved in these reactions is also very good. Very interestingly, both *trans* (Table 2, entries 1−3, 5−8, 10) and *cis* (Table 2, entries 12−14) allyl acetates produced the (*E*)-coupled products. No *cis* product was isolated or found. The Hiyama coupling of *cis* allyl acetates was not addressed earlier. The stereochemistry of the products was established by comparison of ^{1}H NMR chemical shifts and coupling constants (*J* values) of the olefinic protons with those reported. The use of vinylsiloxanes in the Hiyama coupling of allylic acetates was not reported earlier, and this reaction presents a novel protocol for the synthesis of 1,4-dienes (Table 2, entries 7−11, 13, 18). The product obtained by the coupling of vinylsiloxane and Baylis−Hillman acetate adduct listed in entry 18, Table 2 is of high potential, having three useful functionalities for manipulation.

It is suggested that the reaction proceeds via a pathway outlined in Scheme 2. As Pd(0) nanoparticle is the active catalytic species, a cycle involving Pd(0) to Pd(II) is most likely. Oxidative addition of allyl acetate to Pd(0) generates π-allylpalladium acetate complex **1**, which undergoes transmetalation by arylsiloxane in presence of TBAF to produce an intermediate **2**. Possibly, this process operates straightway in case of *trans* allyl acetate complex. However, for *cis* allyl acetates two alternative routes may be considered. In path a the η^3-complex **1** may change its heptacity from 3 to 1 to form an intermediate complex, losing its *cis* stereochemistry,[15] which then couples with aryl siloxane to form **2**. Path b considers the possibility of a branched isomer as intermediate. However, in a blank experiment it was observed that no branched isomer was formed

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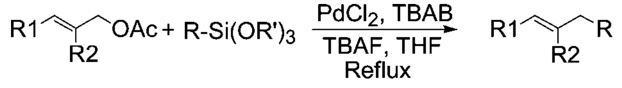
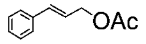
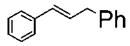
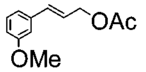
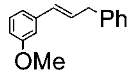
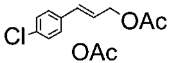
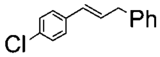
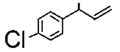
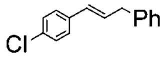
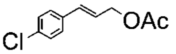
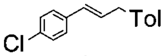
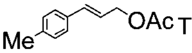
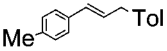
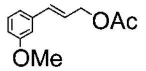
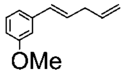
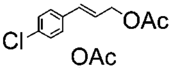
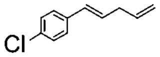
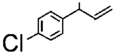
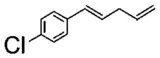
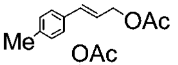
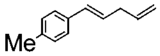
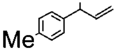
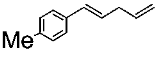
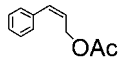
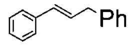
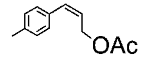
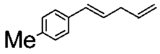
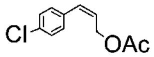
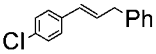
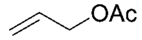
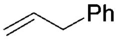
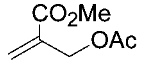
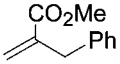
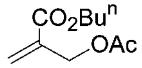
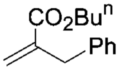
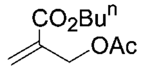
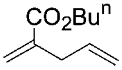
TABLE 2. Pd Nanoparticles Catalyzed Hiyama Cross-Coupling of Allyl Acetates and Aryl/Vinyl Silanes



entry	allyl acetate	R	R'	time (h)	product	yield (%)[a]	ref.
1		Ph	Me	8		75	5c
2		Ph	Me	9		74	11
3		Ph	Me	8		77	12
4		Ph	Me	8		70[b]	12
5		Tol	Et	9		70	
6		Tol	Et	9		71	
7		Vinyl	Et	8		75	
8		Vinyl	Et	7		80	7f
9		Vinyl	Et	7		80	7f
10		Vinyl	Et	8		78	7f
11		Vinyl	Et	8		74	7f
12		Ph	Me	8		74	5c
13		Vinyl	Et	8		78	7f
14		Ph	Me	8		80	12
15		Ph	Me	10		72	7a
16		Ph	Me	7		80	13
17		Ph	Me	7		81	14
18		Vinyl	Et	7		85	

[a] Yields refer to those of purified products characterized by IR and ^{1}H and ^{13}C NMR spectroscopic data. [b] Associated with branch isomer (15%).

from *cis* allyl acetate, and thus path b was eliminated. The reductive elimination of aryl group from **2** through the less hindered side (terminal position) leads to product.

In general, the reactions are clean. All of the products were obtained in high yields and high purities. The Pd nanoparticles were recovered after reaction and were reused for subsequent runs. It was found that for up to three runs the catalysts are appreciably active (Figure 4; recyclability chart); however every time during exposure the PdNP catalysts show a tendency to undergo agglomerization as observed by TEM image (Figure 5; particle size 10−12 nm in place of starting 3−5 nm) taken before second cycle. Thus they suffer gradual loss of activity with increase of particle size in subsequent runs.

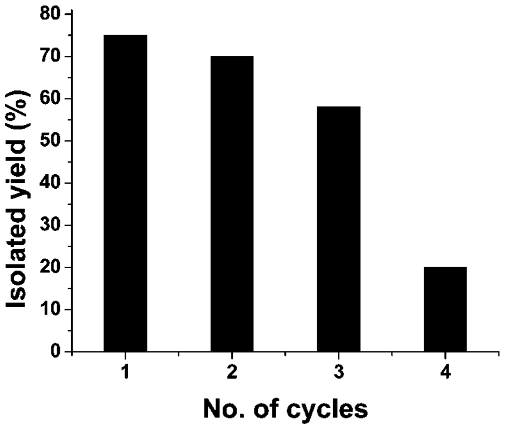


FIGURE 4. Recyclability chart.

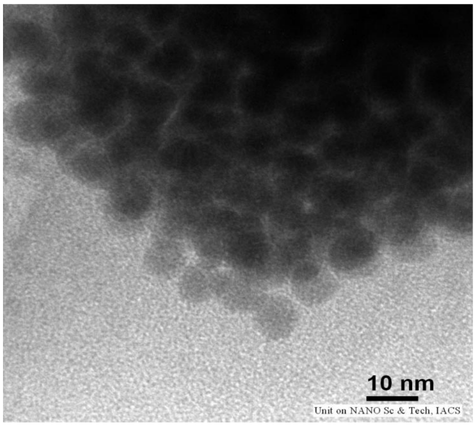
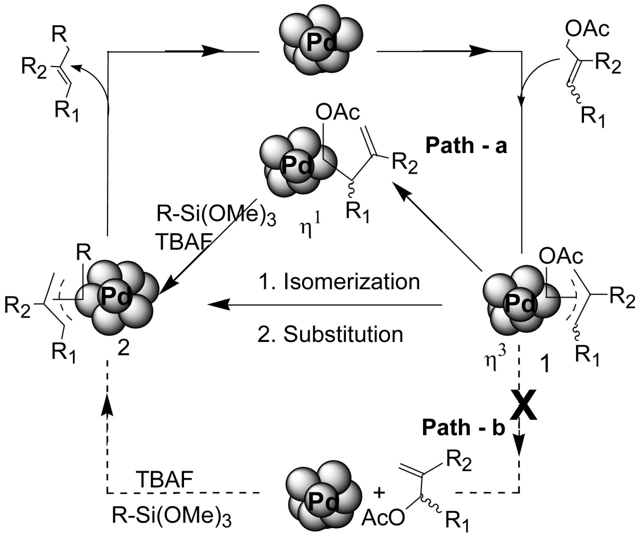


FIGURE 5. TEM image of Pd nanoparticles after first cycle.

SCHEME 2. Possible Reaction Pathway



In conclusion, we have developed a convenient and efficient one-pot procedure for Hiyama coupling of allyl acetates and aryl/vinyl siloxanes catalyzed by in situ generated palladium(0) nanoparticles. In addition to excellent regio- and stereoselectivity, good yields of products, simple operation, and general applicability to a variety of allyl acetates and organosiloxanes, this methodology provides an easy access to functionalized 1,4-dienes. The formation of (*E*)-coupled product from *trans* as well as *cis* allyl acetate is of much significance. To the best of our knowledge, this is the first report of Pd(0) nanoparticles catalyzed cross-coupling of allyl acetates and organosiloxanes, particularly vinylsiloxanes.

Experimental Section

General Experimental Procedure for Cross-Coupling Reactions. Representative Procedure for Coupling of Cinnamyl Acetate and Phenyl Trimethoxysilane (Table 2, entry 1). A mixture of cinnamyl acetate (176 mg, 1 mmol), phenyl trimethoxysilane (240 mg, 1.2 mmol), $PdCl_2$ (4 mg, 2 mol %), tetrabutylammonium bromide (80 mg, 25 mol %), and tetrabutylammonium fluoride (1 M solution in THF, 1.2 mL, 1.2 mmol) in THF (3 mL) was heated under reflux for 8 h (TLC). The reaction mixture was extracted with dry Et_2O (3 × 10 mL), and the ether extract was washed with brine and water and dried (Na_2SO_4). Evaporation of solvent left the crude product, which was purified by column chromatography over silica gel (hexane/ether 98:2) to give 1,3-diphenyl propene as a colorless oil (146 mg, 75%). The spectroscopic data (IR, ^{1}H NMR, and ^{13}C NMR) are in good agreement with the reported values.[5c]

After extraction with dry ether, the residual black Pd nanoparticles were further washed with dry ether and dried. These was reused in subsequent runs.

This procedure was followed for all of the reactions listed in Table 2. Although the representative procedure was based on a 1 mmol scale, gram quantities also provided similar results. Many of these products are known compounds and were easily identified by comparison of their spectroscopic data with those reported (see references in Table 2). The unknown compounds were properly characterized by their spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, HRMS). The purity of all compounds was also checked by ^{1}H NMR, ^{13}C NMR, and elemental analysis.

Acknowledgment. This investigation has enjoyed the financial support of DST, New Delhi by a grant [SR/S5/GC-02/2006]. R.D. and K.C. are thankful to CSIR for their fellowships.

Supporting Information Available: Characterization data (IR, ^{1}H and ^{13}C NMR, spectroscopic data and elemental analysis report) of the products in entries 5−7 and 18 in Table 2. Copies of ^{1}H and ^{13}C NMR spectra of all products listed in Table 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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