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Reaction of Coordinated Phosphines. IV. Mechanism of Carbon-Phosphorus Bond Cleavage in Triarylphosphines and Trialkylphosphines by Palladium(II) Acetate

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Reaction of triphenylphosphine with an equimolar amount of $Pd(OAc)_2$ in acetic acid at room temperature in the presence of styrene gave *trans*-stilbene(94%), H_3PO_4(0.8%), $PhP(O)(OH)_2$(40%), $Ph_2P(O)(OH)$(19%), and $Ph_3P{=}O$(35%). Reactions of tributyl- and trioctylphosphine with $Pd(OAc)_2$ in acetic acid at 90 °C yielded butene(20%) and octene(1-; 22%, 2-; 17%), respectively, as main products. The phenylation of some olefins with triphenylphosphine in acetic acid-*d*, as well as other features of the reaction lead to the conclusion that nucleophilic attack on coordinated phosphorus atom is the most probable pathway for the formation of the phenylation agent (phenylpalladium species) in the reaction system among the others, *ortho*-metallation and oxidative addition.

Tertiary phosphines have been used as versatile and useful ligands in various phases of the chemistry and reactions of transtion-metal complexes, and are considered to bear carbon-phosphorus bond being stable under usual reaction conditions. Only a few has been known about the reaction of tertiary phosphines coordinated to transition metals,[2)] except for *ortho*-metallation to arylphosphines and metallation of carbon-hydrogen bond in alkylphosphines which leads to five membered metal cycles.[3)] Thus, degradation of the phosphines themselves in the metal complexes has hitherto been ignored or overlooked as a minor side reaction. Recent studies, however, indicated that the degradation of such ligands can take place under suitable conditions with surprising ease.[1,2)] These findings suggest that detailed informations of this type of degradation would not only serve for a full understanding of the chemical transformation of transition-metal complexes in general, but also may shed light on a specific problem such as the mechanism of catalyst decay where the transformationof the ligands may result in a significant loss of its activity after repeated reaction cycles.

Previously, we reported that $Pd(OAc)_2(PPh_3)_n$ ($n=1$ or 2) served as an arylating reagent of various kinds of olefins, and proposed a tentative mechanism involving a facile cleavage of the carbon-phosphorus bond assisted by nucleophilic attack to the phosphorus with acetate ion, mostly based on the effect of *p*-substituents in the aryl groups and the nature of the products.[4)] Moreover, a related C–A bond fission in APh_n–PdX_2 system (A=As, Sb, Bi, Se, or Te, $n=2$ or 3, X=OAc or halogen) evidenced that the behavior of PPh_3–$Pd(OAc)_2$ system was clearly different from those containing Bi, Sb, (or Hg), which proceeded *via* a simple electrophilic attack by bivalent palladium (or metal exchange) without the assistance of acetate ion.[1)] Present paper deals with the studies on a stoichiometry of the phosphorus compound and deuterium labeling to substantiate the mechanistic features of the arylation. An analogous carbon-phosphorus bond cleavage of some trialkylphosphines assisted by $Pd(OAc)_2$ is also presented.

Results and Discussion

Reaction of Triphenylphosphine with $Pd(OAc)_2$. A mixture of triphenylphosphine and 1 or 4 equivalents of $Pd(OAc)_2$ in acetic acid was allowed to react at room temperature in the presence of excess styrene. After removal of organic compounds except for phosphorus containing compounds, chromatography of the chloroform extract from aqueous phase afforded triphenylphosphine oxide and the other phosphorus compounds (Reaction 1 and Table 1).

$$PPh_3 + Pd(OAc)_2 + CH_2{=}CHPh \xrightarrow{\text{AcOH, room temp, 48 h}}$$
$$PhCH{=}CHPh(\mathbf{1}) + PhCH{=}CHOAc(\mathbf{2}) + Ph_3P{=}O(\mathbf{3})$$
$$+ Ph_2P(O)OH(\mathbf{4}) + PhP(O)(OH)_2(\mathbf{5}) + H_3PO_4(\mathbf{6}) \quad (1)$$

In view of the results that in the absence of $Pd(OAc)_2$ most of triphenylphosphine was recovered unchanged except for oxidation to its oxide, the formation of these compounds are reasonably understood in terms of aerobic oxidation and hydrolysis of probable intermediates acetoxyphenylphosphines, $Ph_n(OAc)_{3-n}P$ ($n=3$—1), in the treatment. It is to be noted that despite of the recovery of some amount of triphenylphosphine (as its oxide), much of the products was obtained as phenylphosphonic acid, especially in the presence

Table 1. Reaction of triphenylphosphine with $Pd(OAc)_2$ in the presence of styrene in acetic acid[a)]

Run	Molar ratio	Yield(%) based on PPh_3[b)]					Yield(%) based on Pd
	PPh_3 : $Pd(OAc)_2$: Styrene	**1**	**3**	**4**	**5**	**6**	**2**[c)]
1	1 : 1 : 4	94	35	19	40	0.8	trace
2	1 : 4 : 16	200	14	8	70	2.0	30

a) At room temp for 2 days. b) Moles of product per moles of PPh_3 utilized. c) The product is contaminated with a small amount of acetophenone and other carbonyl compounds.

of excess $Pd(OAc)_2$. The results in Table 1 indicate that two of the three phenyl groups (and some of the third one) are effectively utilized in the phenylation, and the diphenylphosphine intermediate is more reactive than triphenylphosphine in the present phenyl transfer. The marked depression of the amount of acetoxylated product(**2**) may be explained in terms of decrease of associated palladium(II) species in the presence of the phosphine ligand by considering the recent mechanistic study[5] on olefin-acetoxylation describing that dimeric palladium acetate was the most reactive species. The specific role of $Pd(OAc)_2$ is supported by the observations that none of the phenylated olefins or biphenyl was produced in the reactions of triphenylphosphine with $PdCl_2$ or other transition metal salts, $RhCl_3\cdot 3H_2O$, $RuCl_3$, $CoCl_2$, $NiCl_2$, and $Ni(OAc)_2\cdot 4H_2O$, but the systems of $PdCl_2$–NaOAc or $RhCl_3\cdot 3H_2O$–AgOAc with PPh_3 gave rise to phenylated olefins (54% and a trace amount, respectively, based on PPh_3).

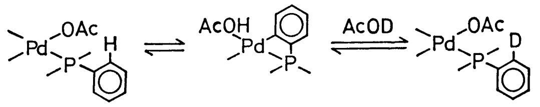
Reaction of Trialkylphosphine with Pd(OAc)$_2$. Although an attempted alkylation of styrene with some trialkylphosphines in place of triphenylphosphine failed under the same conditions described above and even at temperature up to 50 °C, heating of an equimolar mixture of $Pd(OAc)_2$ and tributyl- or trioctylphosphine in acetic acid at 90 °C gave a considerable amount of olefins and a small amount of oxidation product (Reactions 2 and 3) accompanied by precipitation of a considerable amount of palladium black.

$$P(n\text{-}Bu)_3 + Pd(OAc)_2 \xrightarrow{\text{AcOH, 90 °C, 3 h}} \text{1-butene}(20\%) + \text{2-butanone}(2.5\%) + \text{2-butenes(traces)} + \text{butane(trace)} \qquad (2)$$

$$P(n\text{-}C_8H_{17})_3 + Pd(OAc) \xrightarrow{\text{AcOH, 90 °C, 20 h}} \text{1-octene}(22\%) + \text{2-octene}(17\%) + \text{octane}(0.2\%) + \text{2-octanone}(2.2\%) + \text{octenyl acetates}(2.1\%) \qquad (3)$$

Carbon-phosphorus bond cleavage could not be found in the absence of $Pd(OAc)_2$ under the same reaction conditions. Only traces of cyclohexene and cyclohexanone were formed from tricyclohexylphosphine. The formation of the olefins could be explained in terms of alkyl transfer from phosphorus to palladium to form an alkylpalladium species which decomposed to the olefins and palladium hydrides. The low reactivity of the alkylphosphines for the carbon-phosphorus bond cleavage can be understood by considering larger electron donating ability of the alkyl groups as compared to phenyl group and steric effect, especially for tricyclohexylphosphine, if one assumes that nucleophilic attack of acetate ion on the coordinated phosphine is operative in the reaction as proposed previously.[1,4]

*Reaction of Triphenylphosphine or Triphenylphosphine-*d$_{15}$ *with Pd(OAc)*$_2$ *in Acetic Acid*-d. *ortho*-Metallation to coordinated triarylphosphines has been widely observed in transition-metal complexes.[2a,3,6] Furthermore, Nyholm *et al.*[7] reported that in the reaction with osmium carbonyl cluster complex triphenylphosphine was subjected to cleavage of carbon-phosphorus bond to produce a benzyne complex as one of the products. When a solution of $Pd(OAc)_2(PPh_3)_2$ in acetic-d_3 acid-d was allowed to stand at room temperature for 11 days, the NMR spectrum showed that 1.2 hydrogens per mole of triphenylphosphine were exchanged. The exchange can be reasonably interpreted by the process which involves the formation of an *ortho*-metallated intermediate as delineated in Reaction 4. This observation led us to inquire the mechanistic relation between the arylation and the *ortho*-metallation.



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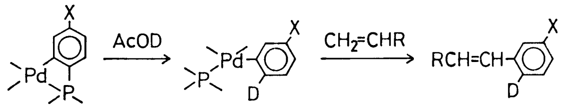
If the *ortho*-metallation were operative as a crucial step in the formation of a phenylpalladium species, either directly or through a benzyne complex, the arylation with *p*-substituted triphenylphosphine would give rise to the product carrying the substituent(X) at a *meta* position or a mixture of phenylated olefins with *meta* and *para* substituent, as formally shown in Reactions 5, 6, and 7. Similarly *meta*-substituted triphenylphosphine would give rise to a mixture of *ortho*, *meta*, and *para* substituted products.



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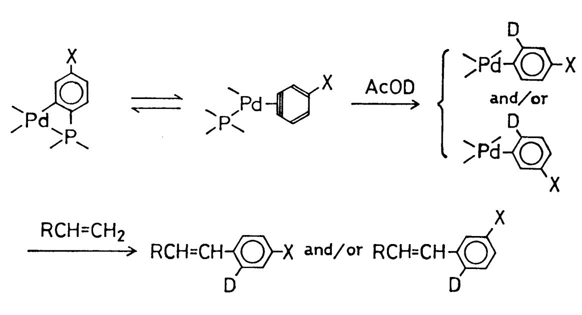

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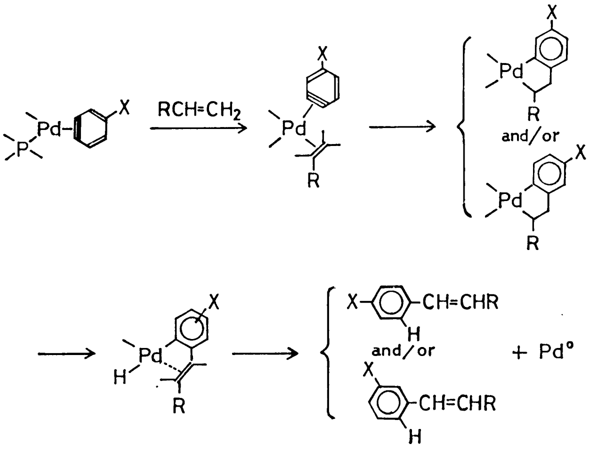

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However, this was not the case for the current arylation, and only *p*-substituted products were obtained in the reactions with several *p*-substituted triphenyl-

Table 2. Phenylation of 1-octene and styrene by PPh_3 or PPh_3-d_{15} with $Pd(OAc)_2$ in acetic acid-*d*

Run	Phosphine and ratio to $Pd(OAc)_2$		Olefin	Conditions temp (°C),	*t* (h)	Deuterium content in phenylated olefin[a]
6	PPh_3	2	1-Octene	40	4	$C_6H_{13}CH{=}CH\text{-}Ph\text{-}d_{0.15}$
7	PPh_3	2	Styrene	40	4	Stilbene-$d_{0.13}$
8	PPh_3	1	Styrene	r.t.	2	Stilbene-$d_{0.0}$
9	PPh_3-d_{15}	1	Styrene	r.t.	2	Stilbene-$d_{5.08}$

a) Deuterium content was estimated by MS measurement for Runs 6, 7, and 8, and by NMR measurement for Run 9.

phosphines.[4] The regiospecificity of the position where olefin is introduced was further evidenced by the fact that only ethyl *m*-methylcinnamate was formed in the reaction of tri-*m*-tolylphosphine with $Pd(OAc)_2$ in the presence of excess ethyl acrylate. In order to obtain further information relating to the role of the *ortho*-metallation, phenylation of olefins with triphenylphosphine and $Pd(OAc)_2$ in acetic acid-*d* was carried out. The reaction with triphenylphosphine-d_{15} in the same solvent was also conducted to differentiate between the usual route *via* phenylpalladium and the other which might occur through the benzyne intermediate, if it formed (Reactions 6 and 7). As shown in Table 2, when one equivalent of triphenylphosphine or triphenylphosphine-d_{15} was utilized, the phenyl group in the starting phosphines transferred as such without being subjected to any H–D exchange. On the other hand, the presence of another mole of triphenylphosphine gave rise to incorporation of deuterium in the products, though it is to a small extent. It is to be mentioned here that the ratio of triphenylphosphine to $Pd(OAc)_2$ affects the rate of the phenylation as shown in Fig. 1. The reverse relationship between the rate of phenylation and the extent of the H–D exchange strongly suggests that the exchange became recognized only because of the decrease of the phenylation rate and that the *ortho*-metallation (Reaction 4) does not contribute to the formation of the phenylpalladium species for phenylation of olefins.

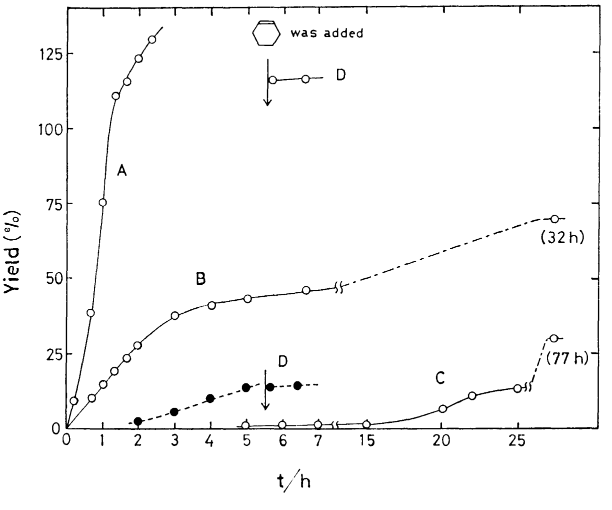
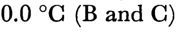
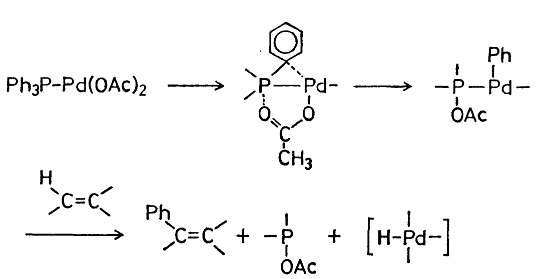


Fig. 1 Time course of phenylation of cyclohexene in acetonitrile. $[Pd(OAc)_2]=0.1$ M, $[PPh_3]=0.05$ M (A), 0.1 M (B), 0.2 M (C), 0.05 M (D), = 0.2 M. Temp: 25.0 °C (A and D), 30.0 °C (B and C). Yields are based on PPh_3.
—○—: Phenylcyclohexenes, —●—: Ph–Ph.

Mechanism of the Arylation. Previously we proposed the tentative mechanism for the facile carbon-phosphorus bond cleavage, which involved an initiatory nucleophilic attack on the coordinated phosphorus atom by acetate ion leading to phenyl transfer to palladium.[4]



(8)

Recently, Fahey and Mahan[8] have described reversible oxidative addition of triphenylphosphine to zero-valent nickel and palladium complexes (Reaction 9).

$$C_6F_5\text{-}PPh_2 + Pd(0) \longrightarrow C_6F_5\text{-}Pd(II)\text{-}PPh_2 \qquad (9)$$

This fact introduces an alternative pathway to be considered for the formation of the phenylpalladium species in the present phenylation, since the reaction proceeds with accompanied formation of zero-valent palladium. If the oxidative addition route is operative in the present system the phenylation should be expected to proceed more favorably under nitrogen atmosphere than under aerobic conditions. The effect of the atmosphere examined in the reaction of $Pd(OAc)_2(PPh_3)_2$ with 1-octene (Table 3) shows that under nitrogen the yield of phenylated olefins decreased remarkably, whereas the addition of an oxidizing agent, $Cu(OAc)_2 \cdot 2H_2O$, increases the yield even under nitrogen. Since the phenylation in the system of phenylmercury(II) acetate–$Pd(OAc)_2$ is known to be little affected by the atmosphere,[9] the results can be considered to indicate that the atmosphere influences the step of the formation of the phenylpalladium species, and divalent palladium is principally responsible for the present carbon-phosphorus bond cleavage.

Another feature of the current phenylation is the marked effect of the ratio of triphenylphosphine to $Pd(OAc)_2$ on the reaction rate (Fig. 1). The increase in triphenylphosphine/Pd ratio depressed both the rate and yield of the phenylation. Particularly, the use of double moles of triphenylphosphine to $Pd(OAc)_2$ introduced a long induction period (curve C), and the presence of excess triphenylphosphine substantially

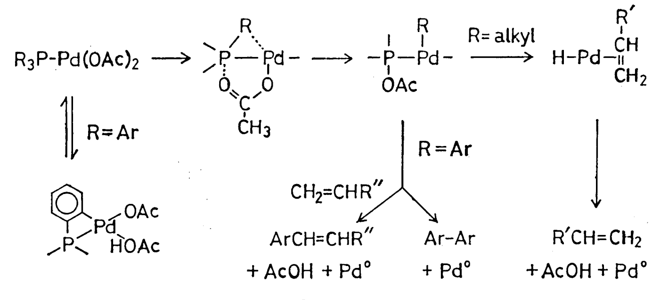
Table 3. The effect of atmosphere on the phenylation of 1-octene by $Pd(OAc)_2(PPh_3)_2$ in acetic acid

Run	Atmosphere	Additive	Conditions t (h),	(temp, °C)	Phenylated olefins (%)[a]	Acetoxylated olefins (%)[b]
3	air	—	9	(50)	97	3
4	nitrogen	—	70	(50)	35	5
5	nitrogen	$Cu(OAc)_2 \cdot 2H_2O$	22	(50)	113	2

a) 1- and 2-Phenyl-1-octenes and -2-octenes. Yields are based on the Pd complex. b) A mixture of isomeric octenyl acetates and octan-2-one. Yields are the sum of those of the acetates and the ketones.

inhibited the reaction.[4] It would be unreasonable to consider that the rate of the oxidative addition (Reaction 9) reduces in such a manner as shown in Fig. 1 even in the presence of one or two equivalents of triphenylphosphine. It is most probable that coordination of two phosphine molecules to $Pd(OAc)_2$ somehow prevents the phenyl migration from phosphorus to palladium (Reaction 8). Under aerobic conditions the phosphine is extruded from the coordination sphere by oxidation to the phosphine oxide, thus leaving a vacant site in the palladium complex which serves for the phenyl migration to take place. Under nitrogen atmosphere, such process obviously is not available, and cupric acetate is needed as oxidant or more probably as carrier of the "excess" triphenylphosphine. The reasoning for the formation of the phenylpalladium species directly from $Pd(OAc)_2$ and triphenylphosphine was further evidenced by the following experiment. The reactions A and D in Fig. 1 were carried out under the same conditions except for the mode of addition of cyclohexene. In the reaction A, the olefin was applied to a solution of $Pd(OAc)_2$ just before the addition of triphenylphosphine. When a mixture of triphenylphosphine and $Pd(OAc)_2$ in acetonitrile was allowed to react for 5.5 h, a small amount of biphenyl was detected before the addition of cyclohexene (Reaction D). On addition of the olefin to the mixture, the formation of phenylcyclohexenes took place very rapidly and was completed within 5 min. Nevertheless, the yield (120 %) was comparable to those under the condition A. The results strongly supports the conclusion that the phenylpalladium species are formed to a considerable extent even in the absence of olefins and the presence of zero-valent palladium species is unnecessary for the production of phenylating agent in the present reaction system.

All of the observations are consistent with the following reaction scheme which involves an nucleophilic attack by acetate on the coordinated phosphorus atom. The similar mechanism could be applied for the migration of the second and the third phenyl groups from phosphorus to palladium, though no direct evidence is available at present.



Scheme.

Experimental

Materials. Palladium acetate and bis(triphenylphosphine)palladium(II) acetate were prepared by the method of Wilkinson *et al.*[10] Triphenylphosphine and tributylphosphine were of commercial origin and were used without further purification. Triphenylphosphine-d_{15} was prepared from pentadeuterophenyl magnesium bromide and phosphorus trichloride.[11] Trioctylphosphine was prepared by the similar method described above; bp 183—187 °C/1 mmHg (lit,[12] 173—178 °C/0.3 mmHg). Olefins and solvents were of commercial origin and were used after distillation. Acetic acid was refluxed with potassium permanganate before distillation.

Reaction of Trialkylphosphine with $Pd(OAc)_2$. The solution of trialkylphosphine(5 mmol) and $Pd(OAc)_2$(5 mmol) in acetic acid (20 ml) was heated at 90 °C under stirring for 3 to 20 h. Evolution of gas (24 ml at 15 °C) was observed for tributyl phosphine. The gas was consisted of 1-butene(98%), 2-butene(1%) and butane(1%) according to the analysis with GLC (20% dibenzyl ether on Celite 545). Palladium black deposited was removed by filtration and organic products in the reaction mixture were extracted with ether, neutralized with aq sodium hydrogencarbonate, washed three times with aq sodium chloride and dried. The products were identified by comparison with those of authentic samples and with decane as an internal standard on GLC. The peak assigned to ketones disappeared by the treatment of the ethereal solution with 2,4-dinitrophenylhydrazine.

Reaction of Triphenylphosphine with $Pd(OAc)_2$ in the Presence of Styrene. In a 100 ml flask were placed 1.31 g(5 mmol) of triphenylphosphine, 1.12 g(5 mmol) of $Pd(OAc)_2$, 2.08 g (20 mmol) of styrene and 10 ml of acetic acid. The mixture was stirred at room temperature for 48 h. Excess styrene and acetic acid were evaporated under vacuum at room temperature, and then styrene derivatives were steam-distilled from the residue. The distillate was extracted with ether. Stilbene, acetoxylated styrene and acetophenone in the extract was separated by column chromatography on silica gel (Wakogel, C-100). The residue was extracted with chloroform, and the chloroform layer gave triphenylphosphine oxide and diphenylphosphinic acid after chromatography on silica gel. $Ph_2P(O)OH$, mp 188—192 °C(lit,[13] 194—195 °C). Phenylphosphonic acid was obtained from the aq layer, mp 145—150 °C(without purification, lit,[14] 158—161 °C). A small portion of aq layer was used for the analysis of phosphoric acid.[15] All the phosphorus compounds obtained in the present reaction were identified by comparison of the IR with those of authentic samples except for phosphoric acid. The assignment of the phenylated and acetoxylated products was described previously.[4,16]

*Reaction of Tri-*m*-tolylphosphine with Pd(OAc)$_2$ in the Presence of Ethyl Acrylate.* To a mixture of Pd(OAc)$_2$(5 mmol) and ethyl acrylate(20 mmol) in acetonitrile(30 ml) was added tri-*m*-tolylphosphine at room temperature and stirred for 12 h. Palladium metal deposited was removed by filtration and a distillation of the filtrate gave 0.60 g of ethyl *m*-methylcinnamate(bp 120 °C/5 mmHg). The structure of the product was identified by comparison of IR, NMR, and the retention time on GLC (Reoplex 400, 1.5 m, 140 °C) with an authentic sample. The IR and GLC analysis excluded the formation of ethyl *p*-methylcinnamate.

*Phenylation in Acetic Acid-*d. Reaction procedure in acetic acid-*d* was similar to that in acetic acid except for the protection from the moisture by a calcium chloride tube. *trans*-1-Phenyl-1-octene was separated by preparative GLC as described previously[4] and was analyzed by MS: *m/e*, 188(M$^+$), relative intensities of isotope peaks; M+1=35.7 (%), M+2=7.15(%) (values from lit[17] for $C_{14}H_{20}$, M+1=15.45, M+2=1.11). Stilbene was isolated in the same way as described above. The relative intensities were as follows. Run 7: *m/e*, 180(M$^+$); M+1=30.92, M+2=5.01. Run 8: M+1=15.27. Run 9: M+1=15.0 (values from lit,[17] for $C_{14}H_{12}$, M+1=15.32, M+2=1.09). Stilbene from the run 9 was hydrogenated over Pd/BaCO$_3$ to 1,2-diphenylethane. PMR of the product showed two singlets placed at δ 2.86(methylene protons) and 7.12(aromatic protons). The ratio of the peak area of the aromatic to aliphatic protons was 1.23(an average from five measurements) which showed the presence of 5.08 of deuterium in a molecule. The deuterium calcd from MS was 4.83.

Determination of Time Course of Phenylation. Runs A and B: To a solution of Pd(OAc)$_2$(0.5 mmol) in acetonitrile containing an internal standard (diethyleneglycol dibutyl ether), cyclohexene (1.0 mmol) triphenylphosphine (0.25 or 0.5 mmol) were added and stirred in a thermostated cell. Samples were withdrawn at appropriate time intervals by a microsyringe and directly analyzed on GLC equipped with flame ionization detector. Rection procedure for Runs C and D was similar to the above except for the way of addition of cyclohexene and triphenylphosphine. Thus, in Run C, bis(triphenylphosphine)palladium acetate was used and in Run D, triphenylphosphine was allowed to react with Pd(OAc)$_2$ for 5.5 h before the addition of cyclohexene.

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