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Palladium(II)-catalysed H/D allylic exchange in alkenes: An intermediacy of palladium(IV)?

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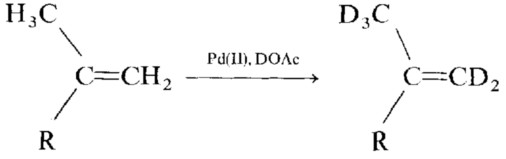
Evidence is presented that the dimeric π-allylic species $[(\eta^3\text{-allyl})PdCl]_2$ is not intermediate in the $Li_2Pd_2Cl_6$-catalysed allylic H/D exchange in alkenes. Neither H/D exchange in α-methylstyrene, nor enrichment of $[(\eta^3\text{-2-PhC}_3H_4)PdCl]_2$, was observed when the latter complex was incubated at 100°C in D_3CCOOD either in the presence or in the absence of $PhC(CH_3){=}CH_2$, respectively. The kinetics of H/D exchange in α-methylstyrene catalysed by $Li_2Pd_2Cl_6$ were studied in some detail. The exchange proceeds at highest rates when reduction of palladium(II) takes place and is much slower in the presence of 1,4-benzoquinone as a palladium reoxidant. The exchange rate is directly proportional to the alkene and catalyst concentrations and independent of the reoxidant concentration. It is suggested that the palladium(II)-catalysed exchange involves an intermediate hydride–allyl species where palladium has a formal oxidation state of IV.

Keywords: Palladium, allylic complexes, alkenes, H/D exchange, kinetics, mechanism, acidolysis

INTRODUCTION

The chemistry of π-allylpalladium(II) complexes is undoubtedly one of the most advanced areas of modern organometallic chemistry.[1–3] The very wide applicability of the complexes in synthesis,[4–6] structural[7] and mechanistic[8] studies is so impressive that it may seem unwise to doubt the basic mechanisms proposed in the late 1960s to account for the key transformations involving the compounds. One such reaction is the palladium(II)-catalysed H/D allylic exchange in alkenes which occurs in a DOAc solvent (Eqn [1]):



[1]

This has been studied in detail by Volger[9] and a two-step mechanism was proposed (Scheme 1). Note that both steps, namely the formation of η^2 and η^3 species, are reversible, and enrichment with deuterium occurs on deuterolysis of the dimeric π-allyl complex $[(\eta^3\text{-2-RC}_3H_4)PdCl]_2$. It is clear that if this mechanism is operative, the η^3 complexes formed must be labile in the solvent, and that exchange should occur in the presence of either a palladium(II) salt or a $[(\eta^3\text{-2-RC}_3H_4)PdX]_2$ complex. We have found however that exchange does not occur in the presence of the latter. In particular, the α-methylstyrene derivative, $[(\eta^3\text{-2-PhC}_3H_4)PdCl]_2$, neither incorporates deuterium if incubated in DOAc, nor catalyses the exchange in added α-methylstyrene. Consequently, the mechanism in Scheme 1 does not conform to the experimental observations. The present work was thus aimed to get a deeper understanding of the mechanism of palladium(II)-catalysed H/D allylic exchange on the basis of kinetic measurements invoking also some relevant chemical evidence.

$$RC(CH_3){=}CH_2 + PdX_4^{2-} \rightleftharpoons [(\eta_2\text{-}RC(CH_3){=}CH_2)PdX_3]^- + X^-$$

$$[(\eta^2\text{-}RC(CH_3){=}CH_2)PdX_3]^- \rightleftharpoons 1/2[(\eta^3\text{-}RC_3H_4)PdX]_2 + HX + X^-$$

Scheme 1

RESULTS AND DISCUSSION

Figure 1 shows a typical kinetic curve for H/D exchange in α-methylstyrene in D_3CCOOD solvent catalysed by palladium(II) chloride equilibrated with an equimolar amount of lithium chloride, i.e. when the catalyst exists in solution predominantly as a $Li_2Pd_2Cl_6$ dimer.[10,11] As seen, the exchange is characterized by a marked induction period, at the end of which a reduction of palladium(II) can be seen. Added as a reoxidant, 1,4-benzoquinone makes the curve strictly first-order, but slows down the exchange considerably. The reduction of palladium(II) does not now take place even at the end of the reaction. Although of unknown composition, reduced palladium species are thus more effective catalysts of allylic H/D exchange compared with palladium(II) complexes. Since we had been interested in the reactivity of palladium(II) complexes, all further kinetic runs were made in the presence of 1,4-benzoquinone. The reoxidant has no effect on the pseudo-first-order rate constants (k_{obs}) in the concentration range $(0.76–7.6) \times 10^{-2}\ mol\,dm^{-3}$. The values of k_{obs} were also independent of the total alkene concentration in the range $(3.19–25.4) \times 10^{-2}\ mol\,dm^{-3}$. The dependence of k_{obs} on $[Li_2Pd_2Cl_6]$ (Fig. 2) is almost linear, but some curvature is evident at higher concentrations. One may rationalize the deviation taking into account that the catalyst $Li_2Pd_2Cl_6$ is made from equivalent amounts of '$PdCl_2$' and LiCl, since an excess of LiCl strongly decreases the exchange rate. As a result, there is no free lithium chloride in the system and the following equilibrium must be operative (Eqn [2]):

$$3Li_2Pd_2Cl_6 + 2S \overset{K_2}{\rightleftharpoons} 2LiPd_2Cl_5S + 2Li_2PdCl_4$$

$$(S = \text{solvent; equilibrium constant} = K_2) \quad [2]$$

which is evidently a sum of the two equilibria below (Eqns [2a] and [2b]):

$$Li_2Pd_2Cl_6 \rightleftharpoons LiPd_2Cl_5S + LiCl \quad K_{eq} = K' \quad [2a]$$

$$Li_2Pd_2Cl_6 + 2LiCl \rightleftharpoons 2Li_2PdCl_4 \quad K_{eq} = K'' \quad [2b]$$

Equation [2] shows that the solvated species $LiPd_2Cl_5S$, a reactive starting material,[12] is generated together with the coordinately saturated species Li_2PdCl_4.

There are appropriate data for the corresponding sodium system to show that Eqn [2] is shifted to the left and hence $x = K_2^{1/4}[Pd(II)]_t^{3/4}$, where $[Pd(II)]_t$ is the total concentration of palladium[II] at time t and x is the equilibrium concentration of MPd_2Cl_5S and M_2PdCl_4, and $[Pd(II)]_t - 4x/3 \approx [Pd(II)]_t$. Since $K' = 2.9 \times 10^{-5}\ mol\,dm^{-3}$ and $K'' = 1.8\ mol^{-1}\,dm^3$,[11] $K_2 = (K')^2 \times (K'') = 1.5 \times 10^{-9}\ mol\,dm^{-3}$. If $[Pd(II)]_t = 2 \times 10^{-2}\ mol\,dm^{-3}$, $x = 1.9 \times 10^{-4}\ mol\,dm^{-3}$ which is much less than the concentration of $M_2Pd_2Cl_6$. Therefore, if the solvated species $LiPd_2Cl_5S$ is a true reactive species, k_{obs} should be directly proportional to $[Pd(II)]_t^{3/4}$. The inset in Fig. 2 shows this can be the case. The kinetic data obtained lead to the following rate expression: Eqns [3a] and [3b]:

$$\text{Rate} = k'_3[LiPd_2Cl_5S][\alpha\text{-methylstyrene}] \quad [3a]$$

$$= k_3[Pd(II)]_t^{3/4}[\alpha\text{-methylstyrene}] \quad [3b]$$

where $k_{obs} = k_3[Pd(II)]_t^{3/4}$. The rate constants k_3 at different temperatures together with the corresponding activation parameters $\Delta H^{\pm}$ and $\Delta S^{\pm}$ are summarized in Table 1.

To measure the kinetic isotope effect, following the enrichment of $PhC(CD_3){=}CD_2$ with protium, in H_3CCOOH, we prepared D_5-α-methylstyrene enriched by *ca* 90%. This seemed to be sufficient since k_{obs} was evaluated by plotting the logarithm of the area under the $=CH_2$ signal in the NMR spectrum against time. We were able to measure reliably the exchange rate in $PhC(CD_3){=}CD_2$ only at 97°C. Consequently, the k_H/k_D value of 3.7 ± 1.3 was also obtained at this temperature, the k_3 calculated using $\Delta H^{\pm}$ and $\Delta S^{\pm}$ from Table 1.

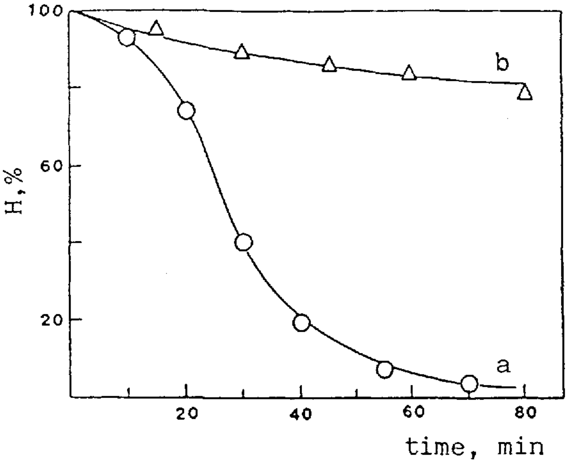


Figure 1 Kinetic curves of the H/D exchange in α-methylstyrene in the absence (a) and in the presence (b) of 1,4-benzoquinone in D_3CCOOD at 80°C, $[Li_2Pd_2Cl_6] = 0.95 \times 10^{-2}\ mol\,dm^{-3}$, $[\text{alkene}] = 6.39 \times 10^{-2}\ mol\,dm^{-3}$, $[\text{1,4-benzoquinone}] = 3.81 \times 10^{-2}\ mol\,dm^{-3}$

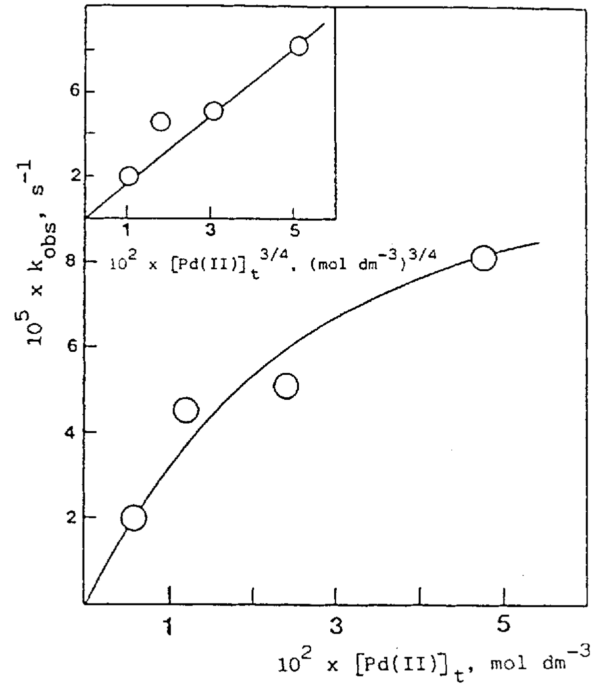


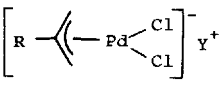
Figure 2 Dependence of k_{obs} for H/D exchange in α-methylstyrene on catalyst concentration at 80°C (for other conditions see legend to Figure 1).

The rate of deuteration of $MeOOCC(CH_3){=}CH_2$ was also measured under the same conditions. This alkene reacted half as fast as α-methylstyrene.

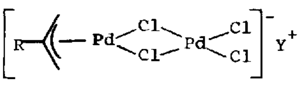
The rate equation (Eqn [3a]) is practically the same as that reported by Volger for the formation of the η^3-allyl complex directly from the alkene and chloropalladate(II)[9] and could nicely support the mechanism in Scheme 1, if it were not for two observations. The first, which has been already mentioned in the Introduction, is a complete inability of the dimeric complex $[(\eta^3\text{-2-PhC}_3H_4)PdCl]_2$ to catalyse H/D exchange in α-methylstyrene in D_3CCOOD. The enrichment of the complex itself was also not detected. The second observation showing that dimeric η^3-allylpalladium(II) chloride is not an intermediate is as follows: H/D exchange in α-methylstyrene on a preparative scale is accompanied by the formation of bis[(η^3-2-phenylallyl)-palladium(II) chloride], the degree of substitution of deuterium for hydrogen in free and η^3-complexed α-methylstyrene being drastically different. In particular, heating a solution of α-methylstyrene (0.7 mol dm^{-3}) and $Li_2Pd_2Cl_6$ (0.051 mol dm^{-3}) in D_3CCOOD at 100°C for one week afforded 13 mg of the complex (with a degree of enrichment of 20%), whilst α-methylstyrene was enriched by 80%. Evidently, this is inconsistent with the mechanism shown in Scheme 1. At the same time the value of the kinetic isotope effect clearly shows that the exchange does involve the rate-limiting cleavage of a C—H bond, and since all five alkenyl hydrogens are finally exchanged, the allylic CH_3 group must be a site of an attack of palladium(II). Therefore, a true intermediate of the exchange should contain the allylically palladated α-methylstyrene, but its structure must differ from that of $[(\eta^3\text{-2-PhC}_3H_4)PdCl]_2$. What possibilities exist? Two different mechanisms can be considered. The first is a slight modification of that in Scheme 1 where an intermediate is a neutral dimer with an allyl ligand attached to both sides of the complex ('two-sided' complex). The real intermediate may be a 'one-sided' complex such as **I** or **II** formed prior to $[(\eta^3\text{-allyl})PdCl]_2$. Note that **I** and **II** are anionic complexes and, hence, must be more reactive towards the acid compared with the neutral dimers. One might attempt to generate **I** and **II** by addition of LiCl or $Li_2Pd_2Cl_6$, respectively, to a D_1-acetic acid solution of the dimer to trigger the H/D exchange. We did not, however, observe any significant enrichment of $[(\eta^3\text{-2-PhC}_3H_4)PdCl]_2$ under these conditions. In particular, the stoichiometric amounts of the complex and lithium chloride were mixed in D_1-acetic acid and kept at 70°C for a week. The

Table 1 The rate constants (k_3) and the corresponding activation parameters of the H/D allylic exchange in alkenes in D_3CCOOD solvent

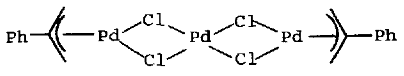
Run	Alkene	Temp. (°C)	$10^4\ k_3$ [(mol dm^{-3})$^{-3/4}$ s^{-1}]	$\Delta H^{\pm}$ (kJ mol^{-1})	$\Delta S^{\pm}$ (J mol^{-1} K^{-1})
1	α-Methylstyrene	70	5.11 ± 0.20		
2	α-Methylstyrene	80	12.5 ± 0.9	100.6 ± 5.8	−16.9 ± 2.0
3	α-Methylstyrene	90	38.1 ± 2.2		
4	Methyl methacrylate	80	6.14 ± 0.47		



I



II



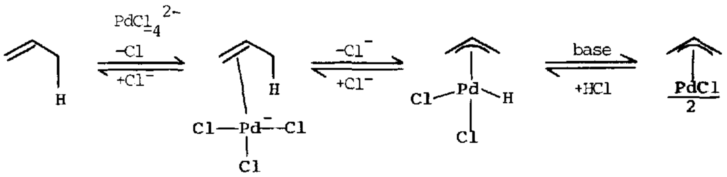
III

enrichment did not exceed 10%. For comparison, it takes 3 h to exchange completely α-methylstyrene at 80°C in the presence of $Li_2Pd_2Cl_6$. Further, the interaction of the dimer with $Li_2Pd_2Cl_6$ also did not induce the exchange, but provided trinuclear complex **III** which did not contain deuterium after refluxing in D_1-acetic acid for 24 h.

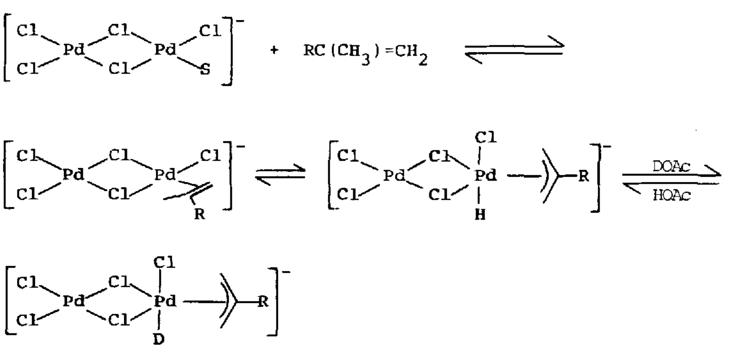
The structure of **III** was established on the basis of analytical, ^{1}H NMR and IR spectral data. Similar trinuclear η^3-allylpalladium(II) complexes were reported previously by other workers.[13] To this end, the mechanism with **I** and **II** as intermediates does not seem acceptable.

Another plausible mechanism of the exchange suggests a pathway via formation of η^3-allylpalladium complexes proposed by Trost *et al.* (Scheme 2).[14] Its main difference from that of Volger[9] is the involvement of the intermediate η^3-allylpalladium hydride. We believe that it may be a crucial intermediate of the exchange. In fact, all the data obtained correspond to the mechanism shown in Scheme 3. One must only accept that the hydrogen atom attached to palladium is rather acidic and can be exchanged with deuterium of the deuterated solvent. A collapse of the η^3-allylpalladium hydride into the precursor η^2-alkene complex is responsible for the substitution of deuterium for hydrogen in the alkene molecule. When a base is present, η^3-allylpalladium hydride is rapidly transformed into the final η^3-allylpalladium(II) complex, giving evidence that the hydrogen transferred is in fact of an acidic nature. For a long time, common criticism of such mechanisms was an involvement, at least formal, of palladium(IV) as an intermediate. Although palladium(IV) intermediates seemed very implausible in the early 1970s, they were often invoked later to account for various pathways of palladium(II)-catalysed reactions.[15] Moreover, it has been recently demonstrated that palladium(IV) species are easily produced on oxidative addition of methyl iodide to Pd(dipy)Me_2[16a] or the related complex.[16b]

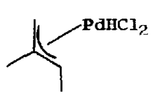
The mechanism in question is one of the three types of allylic activation by palladium disputed in the literature:[17]



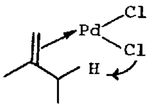
Scheme 2



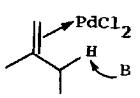
Scheme 3



A



B



C

In our view only a mechanism involving **A** can account for the exchange. In cases **B** and **C**, η^3-allypalladium(II) complexes are immediately formed after the C–H bond cleavage; hence, they cannot be intermediates. It should be pointed out on historical grounds that species such as **A** were first proposed as intermediates by Moiseev,[18,19] but from reductive decomposition of η^3-allylpalladium(II) species.

The very high stability of η^3-allylpalladium(II) complexes towards protonolysis in acetic acid solutions seemed at first confusing. The mechanism in Scheme 1 suggested that the complexes must be more active towards acetic acid. But kinetic data[20] for the acidolysis of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ by HCl indicate that in HOAc the dimers must be indefinitely stable. In particular, the second-order rate constant of the acidolysis by HCl is $1.1 \times 10^{-5}\,\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$ at 30°C. Since the pK_a of HOAc is 14.45 in this solvent,[21] the corresponding pseudo-first-order rate constant is only *ca* $3.5 \times 10^{-12}\,\text{s}^{-1}$, the half-life being *ca* 6000 years! This is, of course, a rough estimate, but despite this it convincingly shows that abstraction of hydrogen from a η^3-allyl intermediate is an impossible route to subsequent protolytic activation of the dimer formed. We attempted to cleave the η^3-allylpalladium bond in acetic acid using the tertiary phosphine derivative **IV**. It does undergo protonolysis, although very slowly, in the presence of lithium chloride according to Eqn [4] below. At 80°C the yield of the palladium complex **V** precipitated after five days was 54%. This process is similar to that found by us for the corresponding cyclopalladated complexes,[22] but the latter are much more reactive under the same conditions. These findings provide additional evidence that the η^3-allyl group is very strongly bound to palladium(II) and such species cannot be intermediates in the H/D exchange.

The observation that reduced palladium species are better catalysts than the initial chloropalladates(II) needs some comment. One could expect that insertion of palladium complexes into an allylic C–H bond is easier for reduced Pd species [probably Pd(0) or Pd(I)] than for Pd(II) derivatives (cf. oxidative addition of methyl iodide to Pd(0)[23] and Pd(II)[16] complexes). Therefore, the higher activity of the more electron-rich reduced species may be also indicative of the fact that the mechanism of the H/D allylic exchange involves the allylpalladium hydride intermediate.

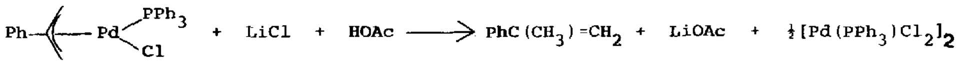
EXPERIMENTAL

^{1}H NMR spectra were obtained on a Tesla BS 467 spectrometer with hexamethyldisiloxane as an internal standard. IR spectra were recorded on a JASCO-200 spectrophotometer in KBr pellets.

Palladium(II) chloride and lithium chloride were Reakhim reagents. α-Methylstyrene and methyl methacrylate (Reakhim) were distilled before use. Acetic acid, H_3CCOOH (Reakhim), of highest available purity was additionally purified according to a standard procedure;[24] H_3CCOOD was obtained by reacting D_2O with acetic anhydride; D_3CCOOD was an Izotop reagent and used as received. D_5-α-Methylstyrene and di-μ-chlorobis[(η^3-2-phenylallyl)palladium(II)] were obtained as described.[9]

A general kinetic procedure for the H/D exchange

Stock solution of $Li_2Pd_2Cl_6$ (17.5–140 μl), obtained by mixing 0.050 g (0.282 mmol) palladium(II) chloride and 0.012 g (0.282 mmol) lithium chloride in 2 cm^3 D_3CCOOD, was added to 100–200 μl of the stock solution of 1,4-benzoquinone (0.46 mg in 0.5 cm^3 D_3CCOOD) in a 5 mm NMR ampoule. This solution was mixed with 0.077–0.62 mmol alkene (α-methylstyrene or methyl methacrylate), 60 μl hexamethyldisiloxane and 2–6 μl nitromethane as a reference. D_3CCOOD was finally added to increase the



IV V [4]

total volume to 415 μl. The solution was then transferred to the NMR spectrometer which was equipped with a temperature-control device. The H/D exchange was followed by measuring areas under the signals from vinylic and allylic protons. Addition of NaOAc to the reaction mixture after the signals had disappeared resulted in quantitative formation of the complex $[(\eta^3\text{-2-PhC}_3D_4)PdCl]_2$. Observed pseudo-first-order rate constants, k_{obs}, were evaluated by plotting $\ln A$ against time, where A is the area under the corresponding signal. Values of k_{obs} obtained were independent of the particular peak taken.

Preparation of $[(\eta^3\text{-2-PhC}_3H_4)\text{-}Pd(\mu\text{-Cl})_2Pd(\mu\text{-Cl})_2Pd(\eta^3\text{-2-PhC}_3H_4)]$ (III)

$[(\eta^3\text{-2-PhC}_3H_4)PdCl]_2$ (0.200 g, 0.386 mmol), palladium(II) chloride (0.137 g, 0.772 mmol), and lithium chloride (0.033 g, 0.772 mmol) were dissolved in 20 cm^3 acetic acid and kept at 70°C for 3 h. Slow cooling provided brown–red crystals which were filtered, washed with chloroform, and dried; yield 71% (0.190 g). M.p. 205–210°C (dec). Anal.: Found: C, 30.3; H, 2.63; Cl, 20.5%. Calcd for $C_{18}H_{18}Cl_4Pd_3$: C, 31.1; H, 2.59; Cl, 20.4%.

Preparation of $[(\eta^3\text{-2-PhC}_3H_4)PdCl(PPh_3)]$ (IV) and its LiCl-induced solvolysis by HOAc

To a solution of $[(\eta^3\text{-2-PhC}_3H_4)PdCl]_2$ (0.120 g, 0.232 mmol) in 10 cm^3 chloroform, triphenylphosphine (0.121 g, 0.464 mmol) was added. The solution was then concentrated; hexane was added on heating. The yellow crystals which precipitated were filtered and dried *in vacuo*; yield 83% (0.200 g). Anal.: Found: C, 61.9; H, 4.70; Cl, 7.06; Pd, 20.3%. Calcd for $C_{27}H_{24}ClPPd$: C, 62.2; H, 4.61; Cl, 6.81; Pd, 20.4%. The acidolysis was performed as follows. Compound **IV** (0.050 g, 0.096 mmol) was dissolved in 2 cm^3 benzene and the solution was mixed with 0.012 g (0.287 mmol) LiCl dissolved in 2 cm^3 acetic acid. The mixture was kept at 80°C for five days to produce orange–red crystals of $[PdCl_2(PPh_3)]_2$ (V). Anal.: Found: C, 49.1; H, 3.38; Cl, 16.5; Pd, 24.2%. Calcd for $C_{36}H_{30}Cl_4P_2Pd_2$: C, 49.1; H, 3.41; Cl, 16.2; Pd, 24.2%. α-Methylstyrene was detected in solution by GC.

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