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REACTION OF COORDINATED PHOSPHINES

VI *. DIVALENT PALLADIUM PROMOTED CLEAVAGE OF CARBON—PHOSPHORUS BONDS IN TERTIARY PHOSPHINES

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Summary

The important role of divalent palladium in the cleavage of carbon—phosphorus bond of tertiary phosphines is revealed by the study of the phenylation in the $Pd(OAc)_2Ph_3P$-styrene system under various conditions; reaction atmosphere, ratio of $Ph_3P/Pd(OAc)_2$, and addition of ethanol or $Cu^{II}(OAc)_2 \cdot H_2O$.

Introduction

Tertiary phosphines are extensively used in transition metal chemistry, and their C—P bonds had been considered to be chemically stable under the usual conditions. However, cleavage of the C—P bond recently has been recognized for several transition metal complexes [1—3]. Low-valent (mostly zero-valent) metals are believed to participate in most of the reactions through an oxidative addition mechanism (eq. 1) [1,3]. We previously proposed that divalent palladium in a $Pd(OAc)_2Ph_3P$-olefin system (eq. 2) is responsible for the C—P bond cleavage and that the key step of the cleavage involves nucleophilic 1,2-migration process (eq. 3) [2c].

$$R_3P + M^{n+} \rightarrow R{-}M^{(n+2)+}{-}PR_2 \qquad (1)$$

$$\begin{aligned} Ph_3P + Pd(OAc)_2 + CH_2{=}CHPh &\xrightarrow{\text{r.t., 48 h}} \xrightarrow{\text{(i) OH}^-} \xrightarrow{\text{(ii) H}^+} \\ &PhCH{=}CHPh + PhCH{=}CH{-}OAc\ (\text{trace}) + \\ &Ph_2P(O)OH + PhP(O)(OH)_2 + H_3PO_4 + Ph_3P{=}O \qquad (2) \end{aligned}$$

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* For part V see ref. 1.

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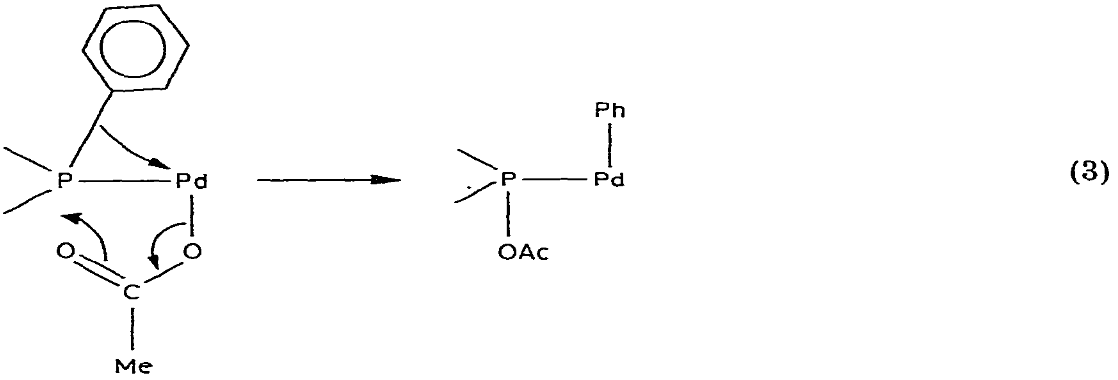
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Recently, however, an oxidative addition mechanism has been proposed for a similar system, $Pd(OAc)_2(Ph_3P)_2$-styrene, based on a kinetic study and the effect of alcohols (reducing agents for divalent palladium) on the system, which produces rate enhancement and a reduction of the induction period [4]. The results prompt us to investigate the effect of reducing agents on the phenylation under various reaction conditions. Detailed investigations of the effect of the atmosphere and the ratio of $Pd(OAc)_2$ to Ph_3P together with that of ethanol revealed again the importance of divalent palladium species in the phenylation.

Results and discussion

Effects of atmosphere and additives

The time course of the phenylation of styrene by $Pd(OAc)_2(Ph_3P)_2$ (**1**) under various conditions is shown in Fig. 1. The short induction period under typical reaction conditions is characteristic of the phenylation. If the oxidative addition mechanism were operative in the present system, the phenylation should be expected to proceed more favorably under nitrogen than under aerobic conditions. However under nitrogen the induction period drastically increased and the rate of phenylation at steady state decreased to less than 1/10 of that under aerobic conditions (Fig. 1 and Table 1). Even under nitrogen, the addition of $Cu(OAc)_2 \cdot H_2O$ eliminated the induction period and produced more than 200% of stilbene based on the $Pd(OAc)_2$ used. The addition of ethanol affected the phenylation in the opposite way depending on the atmosphere. Under aerobic conditions, ethanol increased the rate and decreased the induction period as reported previously [4]. On the other hand it severely suppressed the reaction under nitrogen. This contrary effect of ethanol, which is known to be a good reducing agent for $Pd(OAc)_2$, suggests that the reduction of divalent palladium does not lead to an active intermediate of the phenylation as suggested in the oxidative addition mechanism [4].

Effect of the $Ph_3P/Pd(OAc)_2$ ratio

A notable feature of the present phenylation is the large dependence of the progress of the reaction on the ratio $Ph_3P/Pd(OAc)_2$. When the $Ph_3P/Pd(OAc)_2$ ratio was less than 1, the phenylation proceeded without an induction period

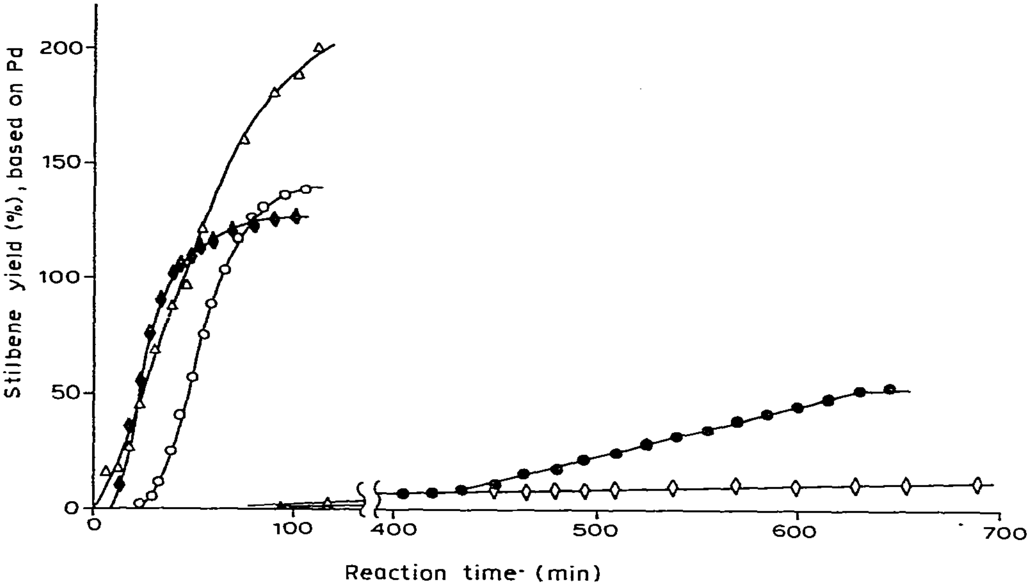


Fig. 1. Effects of atmosphere, ethanol and copper(II) acetate on the phenylation of styrene by $Pd(OAc)_2(Ph_3P)_2$ in CH_3CN at 40.0°C. $[Pd(OAc)_2(Ph_3P)_2]$ = 10 mM, [styrene] = 50 mM. —○—: air; —●—: nitrogen; —♦—: EtOH/air; —◇—: EtOH/nitrogen; —△—: $Cu(OAc)_2 \cdot H_2O$/nitrogen.

as shown in Fig. 2, even under nitrogen. Fig. 3 and 4 show the dependence of the initial rate of the phenylation (r_i) on the ratio in the range where the induction period was not observed, and under nitrogen. When the $Ph_3P/Pd(OAc)_2$ ratio was less than 0.5, the kinetics were first order in Ph_3P and zero order in $Pd(OAc)_2$, respectively. If the molar amount of Ph_3P was increased to more than a half equivalent of $Pd(OAc)_2$, the initial rate decreased inversely. These

TABLE 1

THE EFFECTS OF ATMOSPHERE, ETHANOL AND COPPER(II) ACETATE ON THE PHENYLATION BY $Pd(OAc)_2(Ph_3P)_2$ [a]

No.	Additive	Atmosphere	Induction period (min)	r_{st} (or r_i) [b] $\times 10^6$ (mol/l · s)	Final yields (%) [c] based on	
					$Pd(OAc)_2$	Ph_3P
1	none	air	32	5.3 (r_{st})	144	77
2	none	N_2	410	0.40 (r_{st})	54	27
3	$Cu(OAc)_2 \cdot H_2O$ [d]	N_2	0	3.6 (r_i)	200	100
4	EtOH [e]	air	13	8.6 (r_{st})	135	68
5	EtOH [e]	N_2	0 {0~390 min; 390 min~;	0.023 (r_i) 0.044 (r_{st})	35	17

[a] The reactions were started by the addition of 0.05 mmol of $Pd(OAc)_2(Ph_3P)_2$ to a solution of 0.25 mmol of styrene and dioctyl ether (internal standard for GLC) in 5 ml of CH_3CN at 40.0°C. [b] r_{st}: steady state rates, r_i: initial rates. [c] GLC yields. [d] One mmol of $Cu(OAc)_2 \cdot H_2O$ was added; a considerable amount of the salt remains undissolved. [e] A mixture of 1 ml of EtOH and 4 ml of CH_3CN was used as solvent.

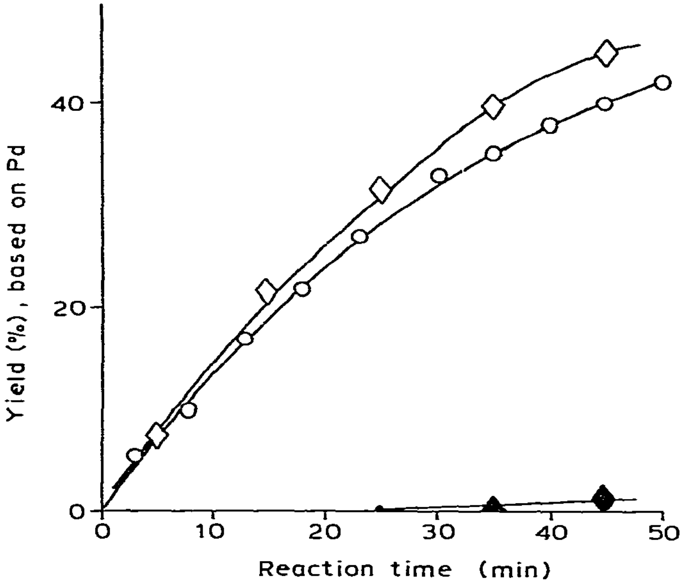


Fig. 2. Time courses of the reaction of $Pd(OAc)_2$ and Ph_3P in CH_3CN at 40.0°C. —○—: stilbene formation, $[Pd(OAc)_2] = 10$ mM, $Ph_3P/Pd(OAc)_2 = 1.03$ [styrene] = 50 mM. —◇—: bromobenzene formation in a quenching experiment by bromine. $[Pd(OAc)_2] = 10$ mM, $Ph_3P/Pd(OAc)_2 = 1.00$. —◆—: biphenyl formation in the above quenching experiment.

results suggest a dinuclear complex bearing one PPh_3 to be an active species in the presence of excess $Pd(OAc)_2$. Interestingly a dimeric species, $Pd_2(OAc)_6^{2-}$, is believed to be the most active catalytic species and to give the active dimeric π-complex, $Pd_2(OAc)_5(olefin)^{1-}$, in the olefin acetoxylation in acetic acid, while a monomeric species, $Pd(OAc)_4^{2-}$, is unreactive [5]. *Cis*-di-μ-carboxylate complexes of palladium(II) of the general types $[X(Me_2PhP)Pd(OCOR)]_2$ (X = Cl,

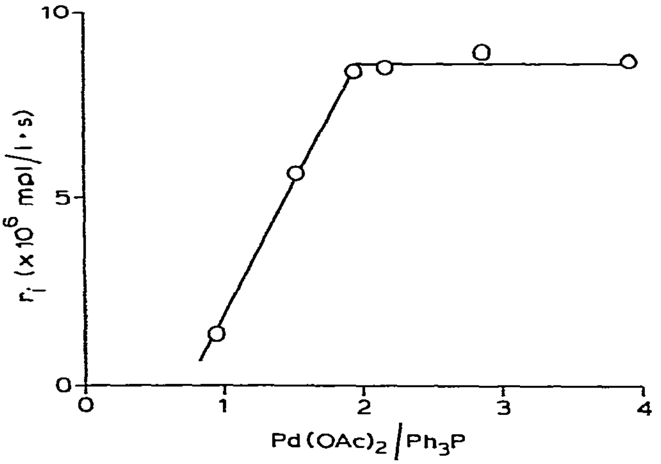


Fig. 3. Effect of the molar ratio of $Pd(OAc)_2/Ph_3P$ on the initial rate (r_i) of stilbene formation in CH_3CN at 40.0°C under nitrogen. $[Ph_3P] = 5.0$ mM (constant), [styrene] = 50 mM.

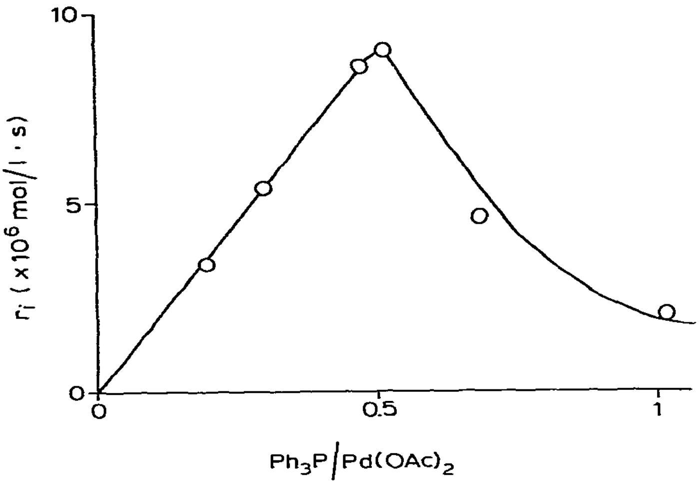
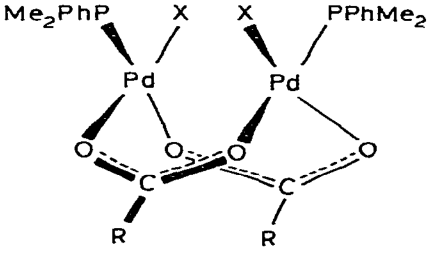


Fig. 4. Effect of the molar ratio of $Ph_3P/Pd(OAc)_2$ on the initial rate (r_i) of stilbene formation in CH_3CN at 40.0°C under nitrogen. $[Pd(OAc)_2]$ = 10 mM (constant), [styrene] = 50 mM.

Br, I) (2) have been synthesized and structurally characterized [6,7]. By the action of Ph_3P on $[Pd(OAc)_2]_3$ Wilkinson et al. isolated a similar type of the dimeric complex $[Pd(OAc)_2(Ph_3P)]_2$ (3) which possesses both bridged and unidentate carboxylate groups [8]. When $Pd(OAc)_2$ is dissolved in acetonitrile without added acetate ion it is very likely to produce the analogous neutral acetate bridged species 4. Addition of Ph_3P to the solution in the $Ph_3P/Pd(OAc)_2$ ratio of 0.5 would lead to the generation of the active species 5. The fact that the rate decreases drastically with increasing Ph_3P more than a half equivalent



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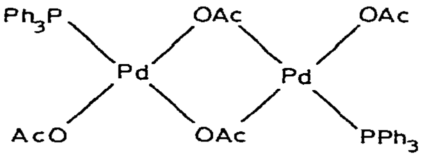

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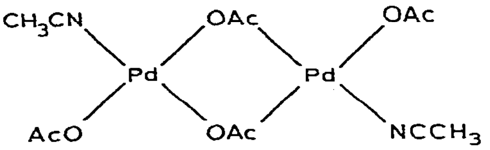

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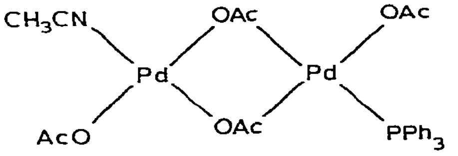
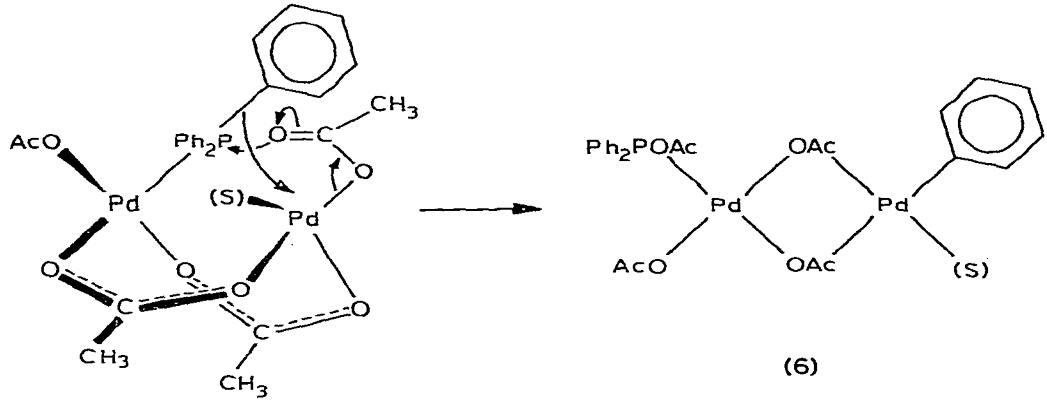


(5)

of $Pd(OAc)_2$ is reasonably attributed to the transformation of **5** to the unreactive species **3**, though formation of monomeric species could not be completely eliminated. The successful isolation of **3** [8] also supports that **3** is unreactive species. Since the C—P bond cleavage is very fast with a low molar ratio of $Ph_3P/Pd(OAc)_2$, the structure of the active species could not be elucidated.

The reason for the drastic difference of reactivity between **5** and **3** (or a monomeric species) is not clear. If the reaction goes on one palladium(II) as shown in eq. 3, **3** would be expected to be as reactive as **5**. One of the referees suggests that the higher reactivity of **5** is reasonably explained in terms of the nucleophilic attack not to the palladium(II) carrying the Ph_3P but rather to the second palladium(II) which is more electrophilic (eq. 4).



(6)

(4)

((S) = CH_3CN)

The rate of the phenylation is expected to be related to the formation of a Ph—Pd species, since it was nearly independent of the substituents and the concentration of olefin [2a,4]. The Ph—Pd species can be quenched by bromine to form bromobenzene. The time course of the formation of bromobenzene in the quenching experiment in the absence of styrene showed almost the same profile as that of the stilbene formation (Fig. 2). The results show that the rate of formation of the Ph—Pd species (r(Ph—Pd)) is a prime determinant of the phenylation irrespective of the presence of olefins, i.e., $r_i = r(\text{Ph—Pd})$. Thus, the present phenylation can be represented by eq. 5. However, any simple kinetic expressions can not be derived for the range of $Ph_3P/Pd(OAc)_2 > 0.5$.

In the range of $Ph_3P/Pd(OAc)_2 \leq 0.5$

$$r_i = r(\text{Ph—Pd}) = k_i[(\text{Pd(OAc)}_2)_2(\text{Ph}_3\text{P})] \tag{5}$$

Mechanism

All of the observations are reasonably explained in terms of the following equations. Since the mode of addition of reagents, e.g., Ph_3P to $Pd(OAc)_2$ solution (entry 10) and $Pd(OAc)_2(Ph_3P)_2$ to $Pd(OAc)_2$ solution (entry 9), does not affect the phenylation materially, the equilibrium reactions involving ligand exchange, dimerization and dissociation should be fast. Since the three phenyl groups can be utilized, Ph_3P and $Ph_2P(OAc)$ (or $PhP(OAc)_2$) may be interchangeable in the following equations. The following abbreviations are employed; $Ph_3P = \mathbf{P}$, $Ph_2P(OAc) = \mathbf{P'}$.

In the range of $Ph_3P/Pd(OAc)_2 \leq 1$:

$$Pd_2(OAc)_4(\mathbf{P})_2(\mathbf{3}) \rightleftharpoons Pd_2(OAc)_2(\mathbf{P})(\mathbf{5}) + \mathbf{P} \qquad (6)$$

$$\mathbf{5} \rightarrow Ph{-}Pd_2(OAc)_3(\mathbf{P'})(\mathbf{6}) \qquad (7)$$

$$\mathbf{6} + CH_2{=}CHPh \rightarrow PhCH{=}CHPh + H{-}Pd_2(OAc)_3(\mathbf{P'})\ (\mathbf{7}) \qquad (8)$$

$$\mathbf{7} + m\mathbf{P} \rightarrow Pd(O)(\mathbf{P})_n\,(\mathbf{8}) + Pd(OAc)_2(\mathbf{P})\ (\mathbf{9}) \quad \text{(or } \mathbf{3} \text{ or } \mathbf{5}\text{)} \qquad (9)$$

When $Pd(OAc)_2(Ph_3P)_2(\mathbf{1})$ is used as the starting complex, additional reactions, eq. 10—13, have to be considered.

$$\mathbf{1} \rightleftharpoons \mathbf{9} + \mathbf{P} \qquad (10)$$

$$\mathbf{1} + n\,\mathbf{P} \rightarrow \mathbf{8} + Ph_3P{=}O \qquad (11)$$

$$\mathbf{P} + O_2 + \mathbf{8}\ \text{(as catalyst)} \rightarrow Ph_3P{=}O \qquad (12)$$

$$\mathbf{8} + O_2 + AcOH \rightarrow \mathbf{1}\ \text{(or } \mathbf{3} \text{ or } \mathbf{5}\text{) (+ } \mathbf{P} \text{ and/or } Ph_3P{=}O\text{)} \qquad (13)$$

In the oxidative addition mechanism, the induction period is suggested to be responsible for the formation of an active palladium(0) intermediate. If the resulting zero-valent species were a decisive intermediate, the phenylation would proceed catalytically because of the regeneration of the palladium(0) species in the phenylation step (eq. 8 and 9), and should be favored by the presence of excess Ph_3P. However, the reaction proceeds at a fast rate with no induction period with a low ratio of $Ph_3P/Pd(OAc)_2$. The final yields have often exceeded the molar amount of $Pd(OAc)_2$ used under aerobic conditions, but have never exceeded those under nitrogen except in the presence of an oxidizing agent, $Cu(OAc)_2 \cdot H_2O$ (Table 1 and 2). The advantage of the oxidizing conditions strongly suggests the importance of a palladium(II) species in the phenylation.

On the basis of the marked influence of the $Ph_3P/Pd(OAc)_2$ ratio, the induction period can reasonably be correlated to a consumption of the excess Ph_3P ligand(s) to produce the active complex, **5**. The excess Ph_3P can be removed effectively through its oxidation to $Ph_3P{=}O$, a poor complexing agent. Triphenylphosphine is oxidized by oxygen, and the oxidation is accelerated markedly by the presence of small amount of palladium(0) complexes such as **8** (eq. 12) [9]. Under aerobic conditions the phenylation proved to proceed with oxygen uptake. The palladium(0) species may be initially produced through eq. 11 [10] and/or acetoxylation of styrene (the acetoxylated olefins have been observed as side products in the present phenylation [2]). It should be noted that the oxidation by oxygen removes the excess Ph_3P smoothly without any significant sacrifice of the palladium(II) species, when a catalytic amount of the palladium(0) species is formed. Moreover, the $Ph_3P{=}O$ product does not participate in the phenylation. Oxygen also serves advantageously to regenerate palladium(II) from palladium(0) formed through the phenylation.

Under nitrogen progress of the phenylation at a steady rate is believed to start after the excess Ph_3P is removed according to eq. 11. The process would

TABLE 2

THE EFFECTS OF MOLAR RATIOS OF $Pd(OAc)_2$ TO Ph_3P ON THE PHENYLATION OF STYRENE UNDER NITROGEN [a]

No	$[Pd(OAc)_2]$ (mM)	$[Ph_3P]$ (mM)	$r_i \times 10^6$ (mol/l · s)	Final yields (%) [b] based on	
				$Pd(OAc)_2$	Ph_3P
6	10	2.0	3.4	35	177
7	10	2.74	5.4	54	191
8	10	3.0	5.4	55	183
9	10 [c]	5.0 [c]	8.4	69	136
10	10	5.2	9.0	87	169
11	(10) [d]	5.2	2.1	75	144
12	10	6.8	4.0	64	93
13	10	10.3	2.0	51	49
14	4.76	5.0	1.1	58	51
15	7.62	5.0	5.7	87	133
16	10.7	5.0	8.6	65	138
17	14.1	5.0	9.1	64	181
18	19.5	5.0	8.8	47	183

[a] Unless otherwise noted the reactions were started by the addition of $Pd(OAc)_2$ (or Ph_3P) to a solution of Ph_3P (or $Pd(OAc)_2$), styrene (0.25 mmol) and dioctyl ether (internal standard) in 5 ml of CH_3CN at 40.0°C under nitrogen. [b] GLC yields. [c] The reaction was started by the addition of 0.0132 mmol of $Pd(OAc)_2(Ph_3P)_2$ to a solution of 0.0392 mmol of $Pd(OAc)_2$, styrene and dioctyl ether in 5 ml of CH_3CN. [d] Palladium(II) benzoate was used in place of $Pd(OAc)_2$.

be slow and causes inevitable decrease of palladium(II) species. Thus, the phenylation is suppressed markedly under nitrogen in the range of a higher $Ph_3P/Pd(OAc)_2$ ratio than 0.5. Copper(II) acetate works not only as an oxidizing agent but also as a carrier of the excess Ph_3P. The latter function can eliminate the induction period and the former serves to regenerate the active palladium(II) species even under nitrogen.

Reduction of palladium(II) by ethanol (eq. 14) is considered to occur at a

$$\mathbf{1} + EtOH + m\,P \rightarrow \mathbf{8} + CH_3CH{=}O + AcOH \qquad (14)$$

faster rate than that by Ph_3P. The addition of ethanol promotes the formation of **8**, which in turn facilitates the oxidation of Ph_3P under aerobic conditions, leading to the effective decrease of the induction period and an acceleration of the phenylation rate. Under nitrogen the consumption of the palladium(II) species continues without a substantial loss of Ph_3P in the presence of ethanol. Coordination of Ph_3P to the resulting palladium(0) species to form **8** may remove the excess Ph_3P to some extent, but the process is thought to become effective after a considerable amount of palladium(0) is produced, since the palladium(0) species is known to exist in solution as a triphosphine complex or a biphosphine complex bearing coordinated solvent molecules. Thus, the addition of ethanol under nitrogen suppressed the phenylation severely. In this case, the oxidative addition mechanism can not be excluded since the very slow phenylation proceeds without the induction period.

The previously proposed mechanism involved an initiatory nucleophilic attack on the coordinated phosphorus atom by acetate ion leading to phenyl transfer to palladium (eq. 3) [2]. The use of palladium benzoate in place of $Pd(OAc)_2$ in the present phenylation decreased the initial rate (entry 11) as expected by the lower nucleophilicity of benzoate ion than that of acetate ion. The results are also consistent with both the nucleophilic 1,2-migration mechanism and the electrophilic attack by the second palladium(II) with nucleophilic assistance from carboxylate (eq. 4) for the present C—P bond cleavage, although the exact active species have not been identified.

Experimental

Materials

Palladium acetate, palladium benzoate and bis(triphenylphosphine) palladium acetate were prepared by the published method [11]. Triphenylphosphine was used as received. Acetonitrile was distilled from phosphorus pentoxide (twice) and calcium hydride, and stored under nitrogen.

The time course of phenylation

The phenylation by $Pd(OAc)_2(Ph_3P)_2$; the reactions were started by the addition of 0.05 mmol of $Pd(OAc)_2(Ph_3P)_2$ to a solution of 0.25 mmol of styrene, dioctyl ether (internal standard) and 5 ml of CH_3CN, and the mixture was stirred in a thermostatted cell (40.0°C) equipped with a side arm and a serum cap. In the experiments under an aerobic condition, the side arm of the cell was kept open. When a nitrogen atmosphere was used, the cell was connected to a nitrogen line. Samples were withdrawn at appropriate time intervals by a microsyringe and directly analyzed on a GLC equipped with a flame ionization detector (10% Silicone SE-30, 2 m). The effects of ethanol were observed by the use of a mixed solvent composed of 1 ml of ethanol and 4 ml of CH_3CN.

The phenylation by the $Pd(OAc)_2$-Ph_3P systems; the reactions were started by the addition of $Pd(OAc)_2$ (or Ph_3P) to a solution of Ph_3P (or $Pd(OAc)_2$), styrene (0.25 mmol), dioctyl ether (internal standard) and 5 ml of CH_3CN, and were conducted in a thermostatted cell (40.0°C) with stirring under nitrogen. The other procedures were the same as those described above.

The initial rates were determined from the slopes of the tangent of the time course curves at 3 min after initiation.

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