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Mechanism of reaction of *trans*-diarylbis(diethylphenylphosphine)palladium(II) complexes with aryl iodides to give biaryls *

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Abstract

The mechanism of reaction of *trans*-$PdAr_2L_2$ ($Ar = m$-tolyl or phenyl, $L = PEt_2Ph$) with aryl iodides affording biaryls has been studied. The rate of reaction is independent of the concentration of aryl iodide but is significantly accelerated by the presence of *trans*-$PdAr(I)L_2$. Cross-over experiments on the reaction of diarylpalladium complexes with monoarylpalladium iodides reveals the occurrence of two types of intermolecular processes between the diaryl and monoaryl complexes. The first process results in a scrambling of aryl groups between the diaryl and monoaryl complexes without formation of biaryls, while the second yields the reductive elimination products, biaryls.

Introduction

The formation of C–C bond by use of organometallic compounds of main group elements and aryl halides catalyzed by nickel and palladium complexes has been widely used in organic synthesis [1]. The essential part of the reaction mechanism is generally represented by Scheme 1.The scheme is made up of two fundamental processes; one is the alkylation (arylation) of the intermediate monoarylmetal halide (I) with RM′ to give a diorganometal complex (II) (*trans*-metallation process) and the other is reductive elimination to form Ar–R with concomitant oxidative addition of ArX to regenerate the intermediate arylmetal halide species (I).

Although Scheme 1 represents the essential feature of the catalytic cross coupling reaction, the mechanistic details remain to be established. Scheme 1 does not specify

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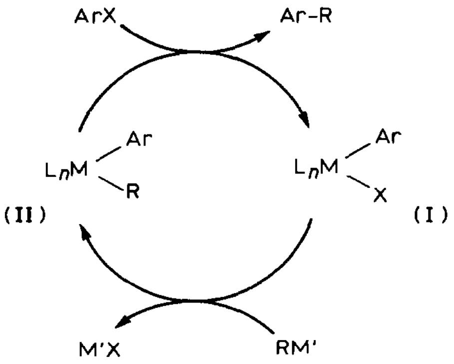
* Dedicated to Professor Luigi Sacconi in recognition of his important contributions to organometallic chemistry.



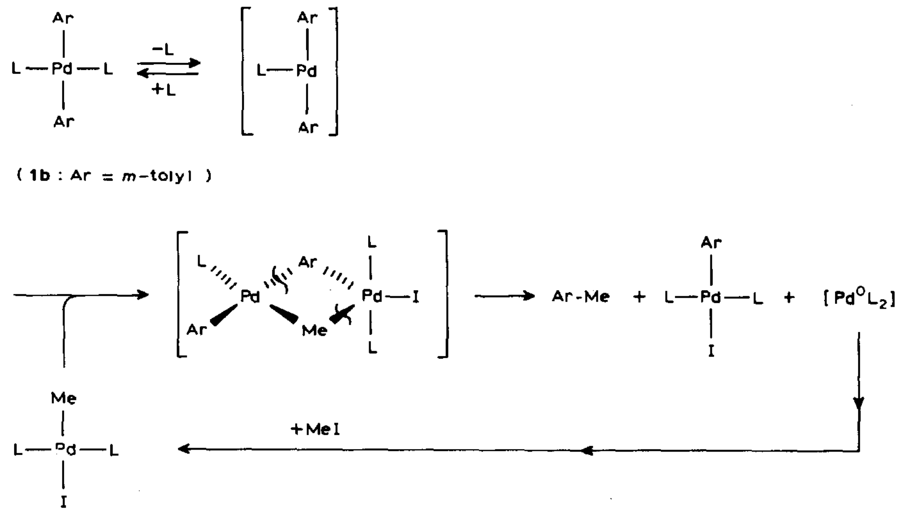
Scheme 1. Generally accepted reaction mechanism for coupling of the aryl group in aryl halide (ArX) and organometallic compounds (RM′) of main group elements catalyzed by a transition metal complex (ML_n).

the configurations of the intermediate species I and II. Detailed mechanisms of interactions of I and II with RM′ and aryl halides are not defined either. In earlier work we and Stille's group examined the thermolysis behavior of dialkylpalladium complexes having two tertiary phosphine ligands [2,3]. The interactions of the diorganopalladium complexes with alkylmagnesium compounds [4] and organic halides [2,5,6] have been also investigated. Through these studies we have established that: (1) for reductive elimination from diorganopalladium to take place, the two organic ligands must be in mutually *cis* positions; (2) the reductive elimination of alkane from dialkylpalladium complexes proceeds through a dissociative pathway involving a T-shaped *cis*-$[PdR_2L]$ type species; (3) the *trans-cis* isomerization to form the *cis*-PdR_2L_2 is promoted by methylmagnesium compounds; (4) when RLi is used as RM′ in Scheme 1, tri- and tetra-alkylpalladate species may be formed [7]; (5) the interaction of *trans*-diarylpalladium complexes, $PdAr_2L_2$, with methyl iodide involves intermolecular exchange of the organic groups.

Thus it has been shown that Scheme 1 provides an essential but oversimplified picture of the palladium-catalyzed cross-coupling reaction. A particularly important influence on the catalytic system is exerted by the interaction of the diorganopalladium complexes with the organic halides, since the catalytic reactions are usually carried out in the presence of an excess of the organic halide.

We have previously shown by kinetic and isotopic studies that the reaction of *trans*-$PdAr_2L_2$ with methyl iodide to give Ar-Me proceeds not through a generally assumed mechanism involving a Pd^{IV} species [2,6] but through a process, previously undetected, involving an intermolecular reaction between the diarylpalladium complex and *trans*-$PdMe(I)L_2$, which is formed by oxidative addition of MeI to Pd^0-tertiary phosphine complex generated in the reaction (Scheme 2) [5].

The scheme involves an intial partial dissociation of L from *trans*-$PdAr_2L_2$ to give a T-shaped three-coordinate species which interacts with *trans*-$PdMe(I)L_2$ to form a bridged intermediate that releases Ar-Me as the reductive elimination product and also gives *trans*-$PdAr(I)L_2$ and a $[Pd^0L_2]$ species. The $[Pd^0L_2]$ complex undergoes the oxidative addition reaction with MeI to form *trans*-$PdMe(I)L_2$, which interacts further with $[PdAr_2L]$ species to form Ar-Me.



Scheme 2. A proposed mechanism for production of Ar-Me in the reaction of *trans*-$PdAr_2L_2$ and methyl iodide.

Since aryl halides are usually used with organometallic compounds of main elements for cross coupling in the palladium-catalyzed process, we have extended our study to an examination of the interaction of *trans*-$PdAr_2L_2$ (**1**) with aryl iodides. We now report that the mechanism of the reaction is similar to that shown in Scheme 2; the involvement of the aryl exchange process was confirmed by monitoring the reaction system by high-resolution ^{31}P NMR spectroscopy.

Results

Kinetic study of reaction of trans-$PdPh_2L_2$ ($L = PEt_2Ph$) with phenyl iodide

Reaction of *trans*-$PdPh_2L_2$ (**1a**, 0.1 mol l^{-1}) with phenyl iodide (1.0 mol l^{-1}) in toluene at 60 °C gave quantitative yields of biphenyl and *trans*-$PdPh(I)L_2$ (**2a**).

$$\underset{(\mathbf{1a},\ L = PEt_2Ph)}{\textit{trans}\text{-}PdPh_2L_2} + PhI \xrightarrow[60\,^{\circ}C]{\text{toluene}} Ph\text{-}Ph + \underset{(\mathbf{2a})}{\textit{trans}\text{-}PdPh(I)L_2} \qquad (1)$$

In the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution measured at 60 °C, the signal due to **1a** decreased as the signal due to **2a** increased. No signals other than those from **1a** and **2a** were observed during the reaction.

The S-shaped time-yield curve (a) in Fig. 1 for the formation of biphenyl in reaction (1), which was monitored by HPLC, indicates occurrence of an autocatalytic process. Addition of a small amount of isolated **2a** to the system significantly accelerates the biphenyl formation (curve (b)). Furthermore, in the presence of more than 1 equivalent of added **2a** per **1a**, the S-shape curve is no longer observed, and the reaction is of first-order kinetics with respect to the concentration of **1a** (curves (c) and (d)) irrespective of the concentration of added **2a**. In the presence of 1 equivalent of added **2a**, the rate is also independent of the concentration of phenyl

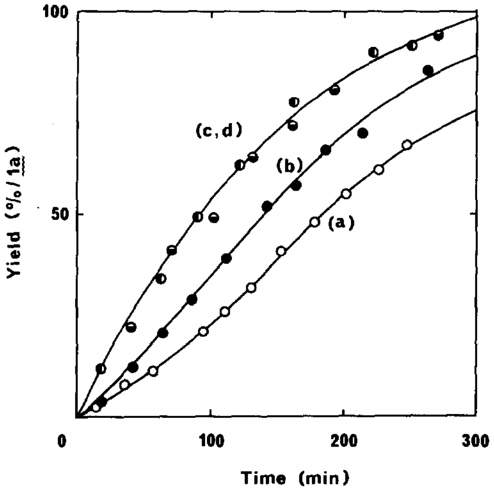


Fig. 1. Variation with time of the yield of biphenyl in the reaction of *trans*-$PdPh_2L_2$ (**1a**, 0.1 mol l^{-1}) and PhI (1.0 mol l^{-1}) in toluene at 60 °C in the absence and presence of *trans*-$PdPh(I)L_2$ (**2a**). Initial concentration of added **2a** (mol l^{-1}): a, 0.00; b, 0.01; c, 0.10; d, 0.20.

iodide *. Addition of free PEt_2Ph (in an amount equivalent to that of **1a**) to the system totally suppressed reaction.

The kinetic features described above are quite similar to those observed previously in the reaction of ditolyl complex (**1b**) with methyl iodide to give *m*-xylene (Scheme 2), in which *trans*-$PdMe(I)L_2$ accelerates the reaction.

Reaction of diarylpalladium(II) complex with aryl iodide in the presence of monoarylpalladium(II) complex

Treatment of *trans*-$Pd(m\text{-tolyl})_2L_2$ (**1b**) with *m*-tolyl iodide afforded quantitative yields of 3,3′-bitolyl and *trans*-$Pd(m\text{-tolyl})(I)L_2$ (**2b**) (Table 1, run 1). Addition of *trans*-$PdPh(I)L_2$ (**2a**) to the system resulted in formation of biphenyl and 3-methylbiphenyl in addition to 3,3′-bitolyl (runs 2 and 3). Increase in the amount of the phenylpalladium iodide complex **2a** led to increase in the yields of the biaryls containing the phenyl group(s). Similarly the reaction of the diphenyl complex **1a** with phenyl iodide gave biphenyl (run 4), but the addition of the monotolyl complex **2b** to the reaction system afforded 3-methylbiphenyl and 3,3′-bitolyl, together with biphenyl (run 5).

Treatment of the diphenyl complex (**1a**) with *m*-tolyl iodide gave biphenyl, 3-methylbiphenyl, and 3,3′-bitolyl in a molar ratio of 51/44/5 (run 6), along with the monophenyl and monotolyl comlexes **2a** and **2b**. The relative ratio of three kinds of biaryls formed in the reaction was independent of the concentration of *m*-tolyl iodide but was significantly altered by addition of the monophenyl complex **2a** to the system (run 7).

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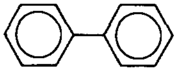
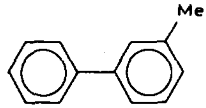
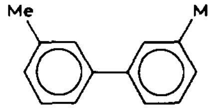
* First-order rate constants at three different concentrations of phenyl iodide are: 10^4k_{obsd}, s^{-1} ([PhI], mol l^{-1}) = 1.5 (0.2), 1.5 (1.0), 1.5 (2.0).

Table 1

Reactions of *trans*-$PdAr_2L_2$ (**1**) with ArI in the absence and presence of *trans*-$PdAr(I)L_2$ (**2**) (L = PEt_2Ph) [a]

Run	1	2	2/1 ratio	ArI (Ar)	Products (%/1)		
							
1	**1b**	–	0	*m*-tolyl	0	0	100
2	**1b**	**2a**	1	*m*-tolyl	7	40	52
3	**1b**	**2a**	3	*m*-tolyl	30	58	15
4	**1a**	–	0	phenyl	100	0	0
5	**1a**	**2b**	1	phenyl	56	38	6
6	**1a**	–	0	*m*-tolyl	51	44	5
7	**1a**	**2a**	3	*m*-tolyl	82	17	1

[a] Reaction conditions: **1** (0.1 mol l^{-1}), ArI (1.0 mol l^{-1}), in toluene at 60 °C. **1a**, *trans*-$PdPh_2L_2$; **1b**, *trans*-Pd(*m*-tolyl)$_2L_2$; **2a**, *trans*-$PdPh(I)L_2$; **2b**, *trans*-Pd(*m*-tolyl)(I)L_2.

Reaction of the diarylpalladium(II) complex with monoarylpalladium(II) complex in the absence of aryl iodide

The results described above strongly suggest that biaryl formation involves an intermolecular process between the diaryl and monoaryl complexes. Thus we next examined the reactions of the diaryl and monoaryl complexes in the absence of aryl iodides.

Reaction of *trans*-$PdAr_2L_2$ with *trans*-$PdAr'(I)L_2$ in toluene containing dimethyl maleate (dmm) * proceeded smoothly at 60 °C to give three kinds of biaryls, Ar–Ar, Ar–Ar′, and Ar′–Ar′ (Table 2), along with the Pd^0-olefin complexes $Pd(dmm)L_2$ and $Pd(dmf)L_2$ (dmf = dimethyl fumarate). Furthermore, the original monoaryl complex was converted into a mixture of two kinds of monoaryl complexes, *trans*-$PdAr(I)L_2$ and *trans*-$PdAr'(I)L_2$.

$$\begin{array}{lll} \underset{(1)}{trans\text{-}PdAr_2L_2} + \underset{(2)}{trans\text{-}PdAr'(I)L_2} & \xrightarrow[\text{toluene}]{\text{dmm}} & Ar{-}Ar + Ar{-}Ar' + Ar'{-}Ar' + \\ (L = PEt_2Ph) & & trans\text{-}PdAr(I)L_2 + trans\text{-}PdAr'(I)L_2 \\ & & + Pd(dmm)L_2 + Pd(dmf)L_2 \end{array} \quad (2)$$

The distribution of biaryls formed in reaction 2 (Table 2) indicates occurrence of a scrambling of the aryl groups in the systems.

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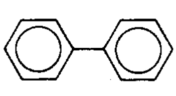
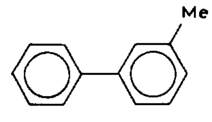
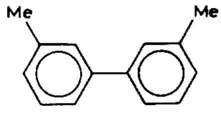
* As shown previously [5], addition of dmm to the system is essential to permit examination of the intermolecular reactions between *trans*-$PdAr_2L_2$ and *trans*-$PdR(X)L_2$ type complexes in the absence of organic halides. In the absence of dmm a coordinatively unsaturated $[Pd^0(PEt_2Ph)_2]$ species, which is formed by the reactions of diaryl- and monoorganopalladium complexes, induces rapid decomposition of the diaryl complexes to give the homocoupling product, Ar–Ar. The $[Pd^0(PEt_2Ph)_2]$ species is effectively trapped by dmm to form a Pd^0-olefin complex. Since dmm is readily isomerized to dmf in the presence of PEt_2Ph and Pd^0-PEt_2Ph species, the olefin complex was obtained as a mixture of complexes coordinated with dmm and dmf.

Table 2

Reactions of *trans*-$PdAr_2L_2$ (**1**) with *trans*-$PdAr'(X)L_2$ (**2**) ($L = PEt_2Ph$) [a]

Run	1	2	2/1 ratio	Products (%/1)		
						
1	**1a**	**2b**	2	28	49	23
2	**1b**	**2a**	1	11	45	43
3	**1b**	**2a**	3	40	49	11
4	**1b**	$PdPh(Br)L_2$	3	36	51	13
5	**1b**	$PdPh(Cl)L_2$	3	36	51	13

[a] Reaction conditions: **1** (0.1 mol l^{-1}), in toluene containing dimethyl maleate (0.2 mol l^{-1}) at 60 °C. **1a**, *trans*-$PdPh_2L_2$; **1b**, *trans*-Pd(*m*-tolyl)$_2$$L_2$; **2a**, *trans*-$PdPh(I)L_2$; **2b**, *trans*-Pd(*m*-tolyl)(I)L_2.

Figure 2 shows the progress with time of the biaryl formation in run 3, Table 2. The rate of formation of biaryls showed a first-order dependence on the concentration of diarylpalladium but was independent of the concentration of monoarylpalladium iodide ($10^4k_{obsd} = 1.0 \pm 0.1$ s^{-1} at 60 °C). The reaction was effectively retarded by addition of free PEt_2Ph. The reactions of **1b** (Ar = *m*-tolyl) with *trans*-$PdPh(X)L_2$ (X = Br and Cl) (runs 4 and 5) also showed first-order kinetics with slightly smaller rate constants (10^4k_{obsd}, $s^{-1} = 0.7$ (X = Br), 0.5 (Cl)), and afforded random scrambling products.

Figure 3 illustrates $^{31}P\{^1H\}$ NMR spectra (200 MHz) of the reaction solution (run 1, Table 2) at the early stage of the reaction. Spectrum (A) was recorded after 10 min, when the formation of biaryls was negligible. The spectrum exhibits five

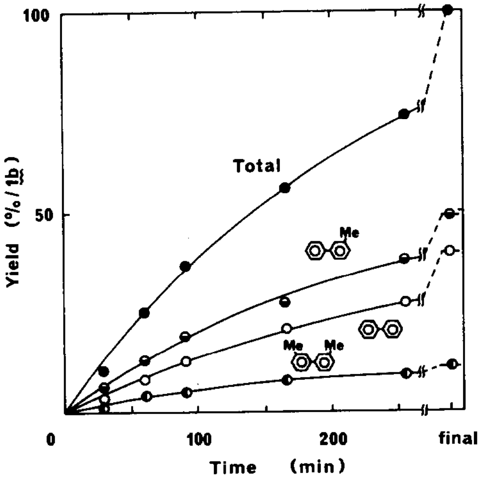


Fig. 2. Variation with time of the yield of biaryls in the reaction of *trans*-Pd(*m*-tolyl)$_2$$L_2$ (**1b**, 0.1 mol l^{-1}) and *trans*-$PdPh(I)L_2$ (**2a**, 0.3 mol l^{-1}) in toluene containing dimethyl maleate (0.2 mol l^{-1}) at 60 °C.

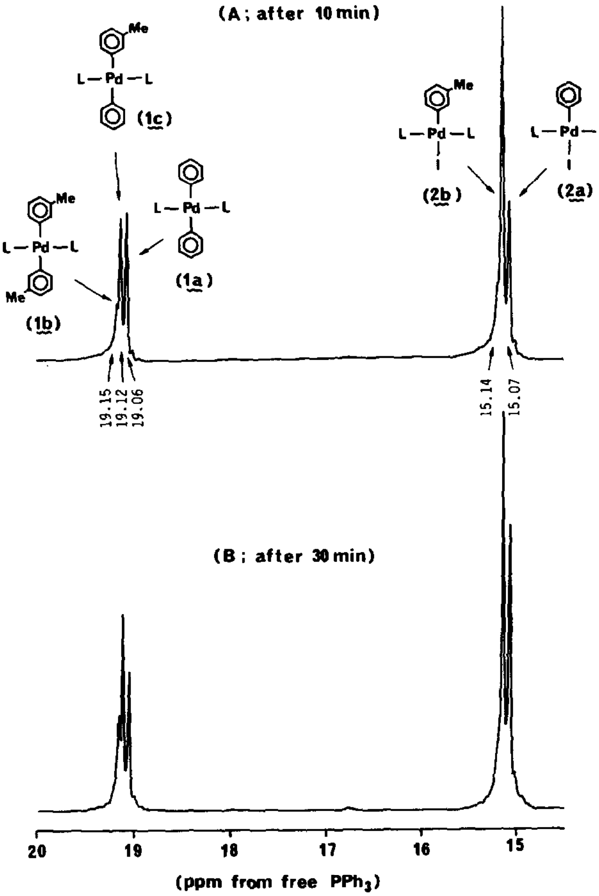


Fig. 3. $^{31}P\{^1H\}$ NMR spectra (200 MHz) of the reaction solution of *trans*-$PdPh_2L_2$ (**1a**, 0.1 mol l^{-1}) and *trans*-Pd(*m*-tolyl)(I)L_2 (**2b**, 0.2 mol l^{-1}) in toluene containing dimethyl maleate (0.2 mol l^{-1}) at 60 ° C. Reaction time (min): A, 10; B, 30.

singlets; those at 19.06 and 15.14 ppm correspond to the starting complexes **1a** and **2b**, respectively, whereas the signals at 19.15 and 15.07 ppm can be assigned to ditolylpalladium (**1b**) and monophenylpalladium (**2a**) by comparison with the spectra of authentic samples recorded under the same conditions. Another singlet at 19.12 ppm may be assigned to *trans*-Pd(*m*-tolyl)(Ph)L_2 (**1c**) on the basis of its chemical shift. After 30 min, when 10% of diarylpalladium complexes had been converted into biaryls and Pd^0-olefin complexes, the relative heights of the signals from three diaryl complexes were **1a**/**1b**/**1c** $\simeq$ 1/1/2, and those of the signals from the two monoaryl complexes **2a** and **2b** were approximately equal (spectrum (B)). On further reaction the three singlets due to the diaryl complexes simultaneously decreased with increase in the signals due to Pd^0-olefin complexes at 21.87 and 20.92 ppm, whereas the heights of the signals from to the monoaryl complexes remained almost the same.

The NMR observations clearly indicate that a rapid scrambling of aryl groups between the diaryl and monoaryl complexes takes place prior to biaryl formation.

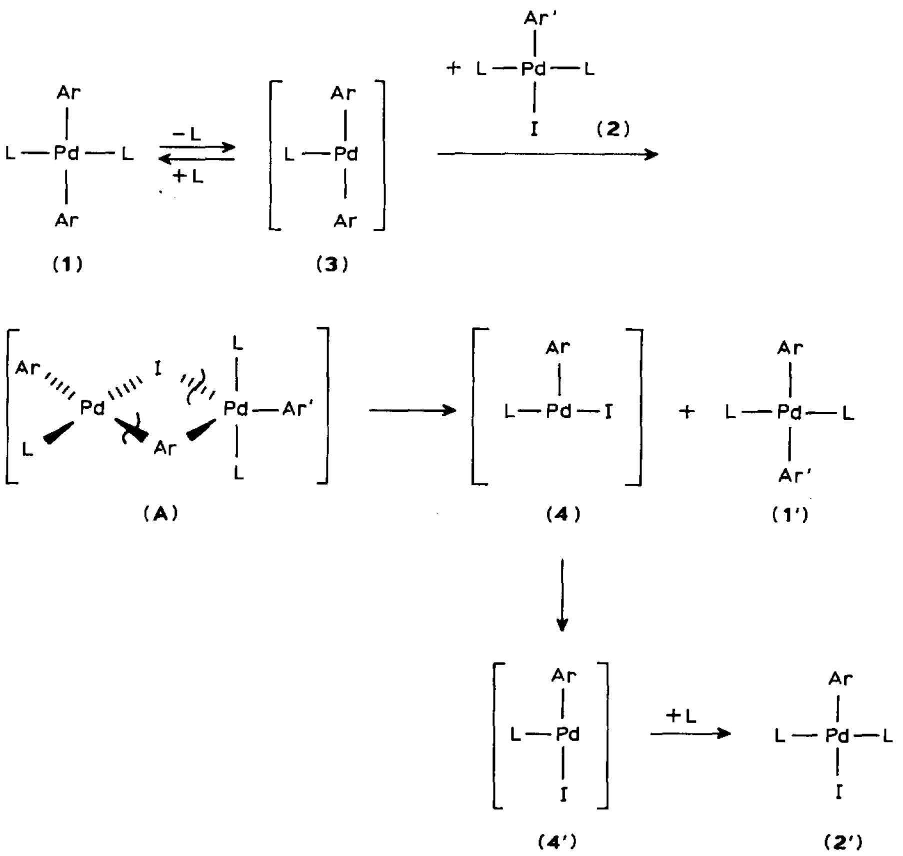
The rapid scrambling of the aryl groups was totally suppressed by addition of a small amount of PEt_2Ph (1 equiv./**1a**).

Discussion

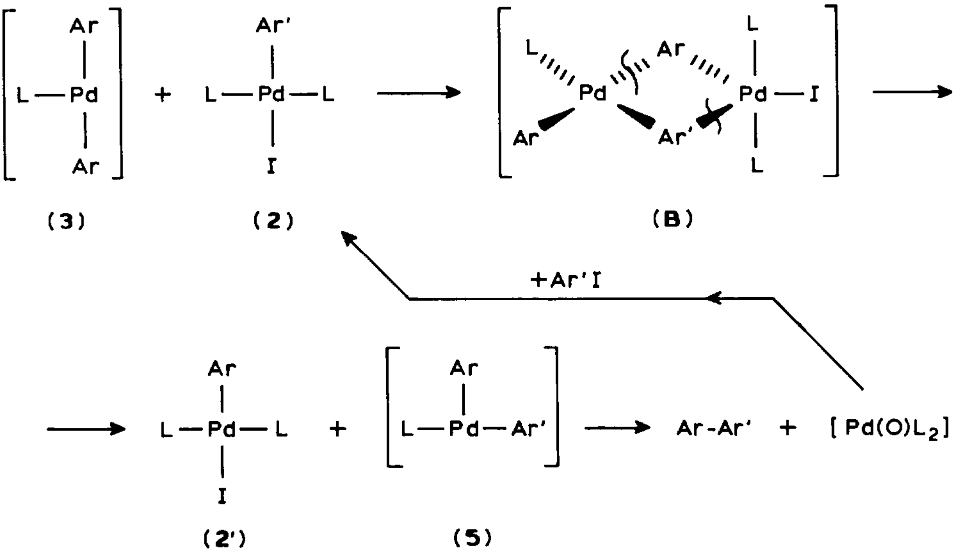
The new results clearly indicate that two types of intermolecular processes are operative in the systems. The first leads to scrambling of the aryl groups between the diaryl and monoaryl complexes whereas the second produces biaryls. The former process is much faster than the latter. Since both processes are severely retarded by addition of free PEt_2Ph to the system, they are assumed to involve dissociation of the phosphine ligands.

As the most likely process responsible for the rapid scrambling of aryl groups, we postulate the following mechanism involving a dinuclear species A containing iodide and aryl bridges.

Dissociation of L from *trans*-diarylpalladium complex (**1**) gives the three-coordinate species **3**, which forms the bridged intermediate **A** on interaction with the



Scheme 3. Proposed mechanism for the aryl group exchange in the reaction of *trans*-$PdAr_2L_2$ (**1**) and *trans*-$PdAr'(I)L_2$ (**2**).



Scheme 4. Proposed mechanism for reductive elimination of Ar–Ar′ in the reaction of *trans*-$PdAr_2L_2$ (**1**) and *trans*-$PdAr'(I)L_2$ (**2**) involving the aryl group exchange reaction.

monoaryl complex **2**. Breaking of the Pd–Ar and Pd–I bonds in **A** as shown in Scheme 3 produces *trans*-$PdAr(Ar')L_2$ (**1′**) and a three-coordinate monoaryl species **4**. Isomerization of **4** to its "*trans*" isomer **4′**, and coordination of L to **4′** gives *trans*-$PdAr(I)L_2$ (**2′**). Further reaction of **1′** with *trans*-$PdAr'(I)L_2$ (**2**) gives *trans*-$PdAr'_2L_2$.

Since halide is the most common bridging ligand in dinuclear palladium complexes, this type of reaction may smoothly proceed if the thermodynamics of the reaction are favorable. Similar intermolecular exchange processes of anionic ligands have been postulated for disproportionation and isomerization reactions of d^8 square-planar complexes [8].

The biaryl formation is accounted for by the mechanism depicted in Scheme 4, which is assumed on the basis of analogy to Schemes 2 and 3.The mechanism involves a dinuclear intermediate **B**, in which the palladium centers are bridged by the aryl groups instead of the aryl and iodide ligands in **A**. Cleavage of the Ar–Pd and Ar′–Pd bonds in **B** provides the monoarylpalladium species **2′** and the *cis*-[PdAr(Ar′)L] species (**5**), which yields biaryl by reductive elimination. The Pd^0 species generated by the reductive elimination undergoes oxidative addition of aryl iodide to regenerate the monoaryl complex. In this mechanism monoarylpalladium halide complex serves as a catalyst for the *trans-cis* isomerization of the diaryl-palladium complex. The *cis* isomer thus formed has a suitable geometry to undergo reductive elimination [2,3].

Conclusion

The results provide another example of acceleration by an added monoorganopalladium complex of reductive elimination involving the C–C bond coupling from a diorganopalladium complex. The feature in common with that of previously reported reductive elimination reactions of the diaryl complex on interaction with methyl iodide [5] and of the *trans-cis* isomerization of the dimethylpalladium complex treated with methylmagnesium compounds [4] is the involvement of the ligand dissociation from the diorganopalladium complexes and the alkyl(aryl) exchange reactions. These results have been consistently accounted for in terms of aryl(alkyl)-bridged intermediates. Further studies on the reactions of *trans-* and *cis*-aryl(alkyl)palladium complexes with organic halides are in progress and will be described elsewhere.

Experimental

All manipulations were carried out under argon or in vacuum. $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL GX-500 spectrometer; chemical shifts are relative to PPh_3 as an external standard. Quantitative analysis of biaryls formed by the reactions was carried out by HPLC (Shimadzu LC-4A, RI detector, Zorbax ODS column, $MeOH/H_2O$ (4/1)) with mesitylene as an internal standard. Diaryl and monoarylpalladium complexes were prepared by published methods [5,7].

Reaction of diarylpalladium with aryl iodide in the presence and absence of monoarylpalladium

A toluene solution of the aryl iodide (0.2–2.0 mmol) (1 ml) was added to a diaryl complex (0.1 mmol) and/or an appropriate amount of monoarylpalladium in a Schlenk tube. The tube was placed in a thermostatted bath (Haake F2) at $60.0 \pm 0.1°$C. The amounts of biaryls produced were determined at intervals by HPLC. The system was homogeneous throughout the reaction.

Reaction of diarylpalladium with monoarylpalladium in the absence of aryl iodide

A solution of dimethyl maleate (0.2 mmol) in toluene (1 ml) was added to the diarylpalladium (0.1 mmol) and an appropriate amount of monoaryl complex contained in a Schlenk tube. The tube was evacuated by pumping and then placed in a thermostatted bath ($60.0 \pm 0.1°$C). At intervals, the Schlenk tube was removed from the bath and quickly cooled with liquid N_2. After introduction of argon, the system was warmed to ca. 5°C and analyzed by HPLC. The system was again evacuated and placed in the thermostatted bath, and the reaction continued.

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