

Thermal Stability, Decomposition Paths, and Ph/Ph Exchange Reactions of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}]$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{F}$, and HF_2)

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Complexes of the type $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}]$, where $\text{X} = \text{I}$ (**1**), Br (**2**), Cl (**3**), F (**4**), and HF_2 (**5**), possess different thermal stability and reactivity toward the Pd–Ph/P–Ph exchange reactions. While **1** decomposed (16 h) in toluene at 110 °C to $[\text{Ph}_4\text{P}]\text{I}$, Pd metal, and Ph_3P , complexes **2** and **3** exhibited no sign of decomposition under these conditions. Kinetic studies of the aryl–aryl exchange reactions of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}_6\text{D}_5)\text{X}]$ in benzene- d_6 demonstrated that the rate of exchange decreases in the order $\mathbf{1} > \mathbf{2} > \mathbf{3}$, the observed rate constant ratio, $k_{\text{I}}:k_{\text{Br}}:k_{\text{Cl}}$, in benzene at 75 °C being ca. 100:4:1 for **1-d**₅, **2-d**₅, and **3-d**₅. The exchange was facilitated by a decrease in the concentration of the complex, polar media, and a Lewis acid, e.g., $\text{Et}_2\text{O}\cdot\text{BF}_3$. Unlike $[\text{Bu}_4\text{N}]\text{PF}_6$, which speeded up the exchange reaction of **2-d**₅, $[\text{Bu}_4\text{N}]\text{Br}$ inhibited it due to the formation of anionic four-coordinate $[(\text{Ph}_3\text{P})\text{Pd}(\text{C}_6\text{D}_5)\text{Br}_2]^-$. The latter and its iodo analogue were generated in dichloromethane and benzene upon addition of $[\text{Bu}_4\text{N}]\text{X}$ or PPN Cl to $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-X})_2]$ ($\text{X} = \text{I}, \text{Br}, \text{or Cl}$) and characterized in solution by ^1H and ^{31}P NMR spectral data. The mechanism of the aryl–aryl exchange reactions of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}_6\text{D}_5)\text{X}]$ in noncoordinating solvents of low polarity may not require Pd–X ionization but rather involves phosphine dissociation, the ease of which decreases in the order $\text{X} = \text{I} > \text{Br} > \text{Cl}$, as suggested by crystallographic data. Two mechanisms govern the thermal reactions of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{F}]$, **4**. One of them is similar to the aryl–aryl exchange and decomposition path for **1–3**, involving a tight ion pair intermediate, $[\text{Ph}_4\text{P}][(\text{Ph}_3\text{P})\text{PdF}]$, within which two processes were shown to occur. At 75 °C, the C–P oxidative addition restores the original neutral complex (**4**). At 90 °C, reversible fluoride transfer from Pd to the phosphonium cation resulted in the formation of covalent $[\text{Ph}_4\text{PF}]$ and $[(\text{Ph}_3\text{P})\text{Pd}]$, which was trapped by PhI to produce $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-I})_2]$. The other decomposition path of **4** leads to the formation of $[(\text{Ph}_3\text{P})_3\text{Pd}]$, Pd, Ph_2 , Ph_3PF_2 , and $\text{Ph}_2\text{P–PPh}_2$ as main products. Unlike the aryl–aryl exchange, this decomposition reaction is *not* inhibited by free phosphine. The formation of biphenyl was shown to occur due to PdPh/PPh coupling on the metal center. Mechanisms accounting for the formation of these products are proposed and discussed. The facile (4 h at 75 °C) thermal decomposition of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})(\text{FHF})]$ (**5**) in benzene resulted in the clean formation of PhH, Ph_3PF_2 , Pd metal, and $[(\text{Ph}_3\text{P})_3\text{Pd}]$.

Introduction

Complexes of the general formula $[(\text{R}_3\text{P})_2\text{Pd}(\text{Ar})\text{X}]$ ($\text{X} = \text{halogen}$) and related organopalladium compounds are key intermediates in numerous Pd-catalyzed reactions of aryl halides, such as the Heck arylation of olefins, the Kharasch-Fields, Stille, Suzuki, and Sonogashira coupling reactions, and various nucleophilic displacement and carbonylation reactions.¹ High temperatures (100–200 °C) are frequently required for conducting some of these reactions, e.g., when inert ArCl substrates are employed.^{1c} Quite often, however, precipitation of Pd metal and, as a consequence, fast termination of the catalytic process are observed at elevated temperatures needed for the reaction to occur at a satisfactory rate. Identifying mechanisms that govern the thermal decomposition of $[(\text{R}_3\text{P})_2\text{Pd}(\text{Ar})\text{X}]$

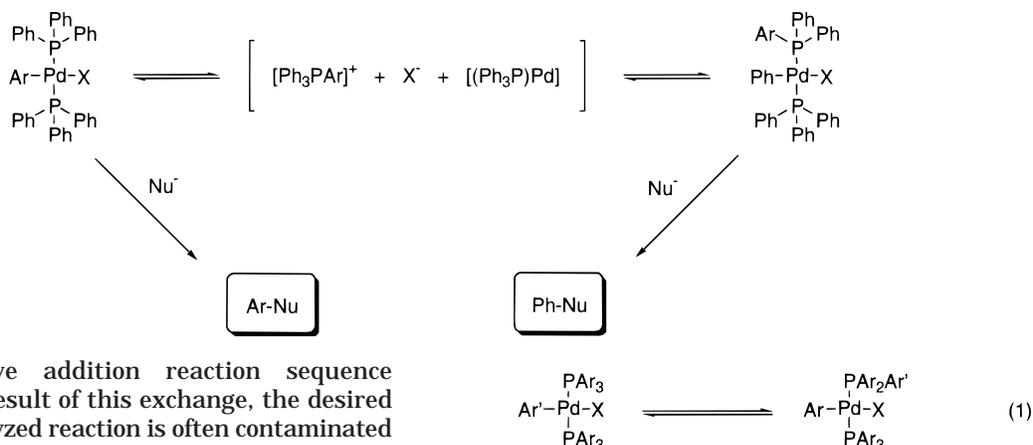
may be critical for successful use and further development of the catalytic chemistry of aryl halides. In this paper, we report on the thermal stability and decomposition paths of palladium aryls containing the most conventional Ph_3P and different halogen ligands. Some mechanistic aspects of the closely related aryl–aryl exchange reactions of such complexes were also studied and are presented in this work.

Results and Discussion

Thermal Stability of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}]$ ($\text{X} = \text{I}, \text{Br}$, and Cl). Surprisingly little has been reported on the thermal stability and decomposition patterns of these complexes.² It has been shown that at temperatures above 50 °C $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ar})\text{I}]$,^{3,4} $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ar})\text{Br}]$,⁵ and $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ar})\text{Cl}]$ ⁶ undergo the peculiar Pd–aryl/P–aryl exchange (eq 1) that likely occurs via a tetraarylphosphonium intermediate involved in the C–P reductive

[†] Contribution No. 7972.

Scheme 1

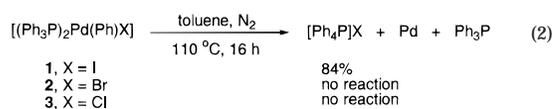


elimination–oxidative addition reaction sequence (Scheme 1).^{4,5} As a result of this exchange, the desired product of a Pd-catalyzed reaction is often contaminated with a similar compound derived from the aryl originally bound to the phosphorus and eventually transferred to the metal during the course of the catalytic run (Scheme 1).^{4,5,7}

Sakamoto, Shimizu, and Yamamoto⁸ reported the formation of $[\text{Ph}_4\text{P}]\text{I}$ in ca. 30% yield from $[(\text{Ph}_3\text{P})_2\text{Pd}$

$(\text{Ph})\text{I}]$, **1**, in refluxing dichloromethane (40 °C).⁹ However, no formation of tetraarylphosphonium salts was observed when **1** and similar complexes were heated in THF-*d*₈ or CDCl_3 at higher temperatures (50–60 °C).^{3,4,6} Goodson, Wallow, and Novak⁴ pointed to the remarkable ability of chlorinated solvents to promote the formation of phosphonium salts from $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ar})\text{I}]$,¹⁰ but no rationale for this effect was offered.⁴ Vicente and co-workers^{9b,c} also reported that the formation of phosphonium cations from cyclopalladated aromatics was very facile in dichloromethane but not in acetone.

We found that $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{I}]$ slowly (16 h) decomposed in toluene under nitrogen at 110 °C (oil bath) to give Pd metal, triphenylphosphine, and tetraphenylphosphonium iodide in high yield (eq 2).



As no dibenzyl was found among the reaction products (GC–MS), a free-radical mechanism for the reaction can be ruled out. Remarkably, *no sign of decomposition* was observed after $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{Br}]$, **2**, and $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{Cl}]$, **3**, were heated at the same temperature for the same period of time (¹H and ³¹P NMR).¹¹ Because the thermal decomposition and aryl–aryl exchange reactions of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ar})\text{X}]$ are closely related (Scheme 1), the significant difference in the thermal stability of the iodo complex **1** and its bromo and chloro counterparts **2** and **3** (eq 2) prompted us to study the dependence of aryl–aryl exchange rate (eq 1) on the nature of X.

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(10) In the presence of extra phosphine, however, the formation of tetraarylphosphonium salts from $[(\text{Ar}_3\text{P})_2\text{Pd}(\text{Ar}')\text{I}]$ occurred in THF-*d*₆ at 50 °C.⁴ For the Pd-catalyzed formation of tetraarylphosphonium salts from haloarenes and triarylphosphine, see: Ziegler, C. B.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2941. Migita, T.; Nagai, T.; Kiuchi, K.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2869.

(11) Herrmann et al.⁶ mentioned that $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{Cl}]$ decomposed very slowly in toluene at 120 °C to produce small quantities of Pd metal. The reaction time was not specified, and other products were not reported.⁶

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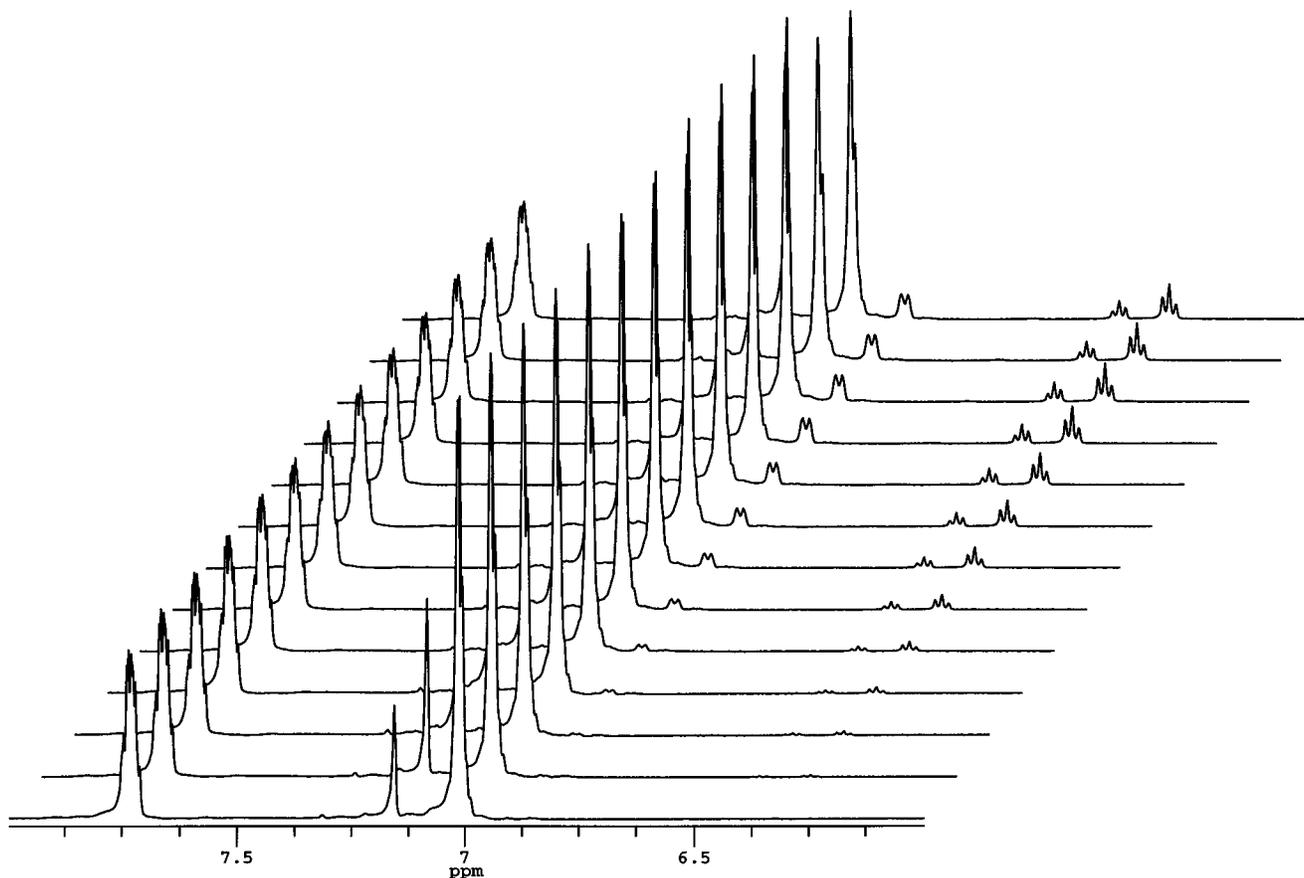
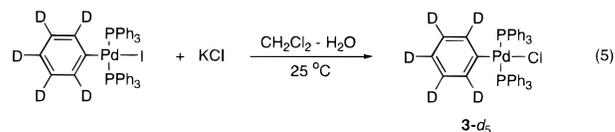
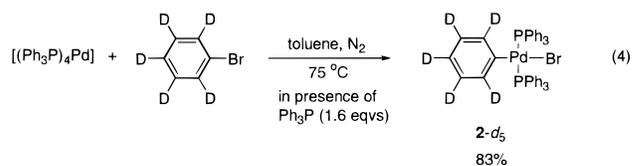
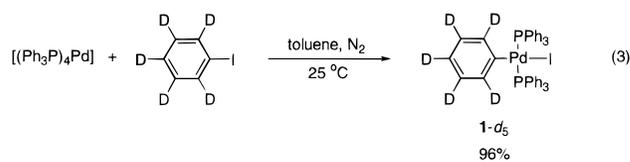


Figure 1. Aryl–aryl exchange reaction of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}_6\text{D}_5)\text{Br}]$ ($\mathbf{2-d}_5$) in benzene- d_6 ($C = 1.1 \times 10^{-2}$ M) at 75°C , as monitored by ^1H NMR spectroscopy. Bottom: $t = 0$ min. Top: $t = 540$ min. Time to full Pd- C_6D_5 /Pd- C_6H_5 equilibration = 7 h. The residual solvent peak appears as a singlet resonance at 7.1 ppm.

Obtaining this information was important because in the catalytic reactions,¹ intermediates $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ar})\text{X}]$ are formed from the corresponding ArX , of which the halogen X can be varied if it helps avoid or suppress the undesirable aryl–aryl exchange processes.

Aryl–Aryl Exchange Reactions of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}_6\text{D}_5)\text{X}]$ ($\text{X} = \text{I}, \text{Br}, \text{and Cl}$). Model compounds for these studies were $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}_6\text{D}_5)\text{X}]$, where $\text{X} = \text{I}$ ($\mathbf{1-d}_5$), Br ($\mathbf{2-d}_5$), and Cl ($\mathbf{3-d}_5$). Complexes $\mathbf{1-d}_5$ and $\mathbf{2-d}_5$ were prepared by the oxidative addition reaction of $\text{C}_6\text{D}_5\text{I}$ and $\text{C}_6\text{D}_5\text{Br}$, respectively, to $[(\text{Ph}_3\text{P})_4\text{Pd}]$ (eqs 3 and 4).^{12,13} The chloro complex $\mathbf{3-d}_5$ was synthesized via the biphasic halide–halide exchange¹⁴ between $\mathbf{1-d}_5$ and KCl (eq 5).

All exchange reactions were run under nitrogen in standard 5-mm NMR tubes with rigorously anhydrous, oxygen-free solvents. After the tubes were placed in a thermostated oil bath ($\pm 1^\circ\text{C}$) or the VT probe of an NMR spectrometer, the exchange was frequently monitored by ^1H NMR spectroscopy. In benzene- d_6 , the proton Pd- C_6H_5 resonances appeared at 6.3 (2H, *meta*), 6.45 (1H, *para*), and 6.9 (2H, *ortho*) ppm, whereas two multiplet signals at 7.0 (18H, *meta* and *para*) and 7.7 (12H, *ortho*) were from the phenylphosphine ligands. As the exchange occurred, the originally absent Pd- C_6H_5 resonances first appeared and then grew in intensity until the Pd- C_6D_5 and Pd- C_6H_5 species equilibrated (Figure 1). At that point, the integral intensity ratio of the Ph-P to Ph-Pd resonances was 6, indicating complete scrambling of the C_6D_5 group over the Pd and P centers; most accurate measurements were obtained



by integrating the signals at 6.3 ppm (2H, *m*- $\text{C}_6\text{H}_5\text{Pd}$) and 7.7 ppm (12H, *o*- $\text{C}_6\text{H}_5\text{P}$). Results of these studies are summarized in Table 1. It was found that the exchange was more facile for dilute rather than concentrated solutions of the complexes; for example, at 75°C in benzene- d_6 , the $\text{C}_6\text{D}_5/\text{C}_6\text{H}_5$ exchange in $\mathbf{2-d}_5$ was

(12) The reaction of $\text{C}_6\text{D}_5\text{I}$ occurred rapidly and cleanly at room temperature. To avoid the aryl–aryl exchange during the addition of less reactive¹³ $\text{C}_6\text{D}_5\text{Br}$ to the Pd(0) complex at 75°C , the reaction was run in the presence of 2 equiv of Ph_3P . It has been demonstrated^{3,4} that the addition of free phosphine ligand suppresses the aryl–aryl exchange reactions of $[(\text{R}_3\text{P})_2\text{Pd}(\text{Ar})\text{I}]$.

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Table 1. C_6H_5 – C_6D_5 Exchange Reactions of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}_6\text{D}_5)\text{X}]$, where X = I (**1-d₅**), Br (**2-d₅**), and Cl (**3-d₅**), at 75 °C ($C = 1.1 \times 10^{-2}$ M)

entry no.	X	solvent	additive (equiv)	time to Pd– C_6D_5 /Pd– C_6H_5 equilibration (h)	decomposition
1	I	benzene- d_6	none	0.3	none
2	I	benzene- d_6	$[\text{Bu}_4\text{N}]^+\text{I}^-$ (1)	0.5	none
3	I	DMF- d_7	none	<0.1	15%
4	Br	benzene- d_6	none	7	none
5	Br	benzene- d_6	$\text{Et}_2\text{O}\cdot\text{BF}_3$ (0.01)	0.1	none
6	Br	benzene- d_6	$\text{Et}_2\text{O}\cdot\text{BF}_3$ (1)	exchanges at 25 °C	10%
7	Br	benzene- d_6	$[\text{Bu}_4\text{N}]^+\text{PF}_6^-$ (0.5)	0.7	none
8	Br	benzene- d_6	$[\text{Bu}_4\text{N}]^+\text{PF}_6^-$ (1.5)	0.6	none
9	Br	benzene- d_6	$[\text{Bu}_4\text{N}]^+\text{PF}_6^-$ (3)	0.3	none
10	Br	benzene- d_6	$[\text{Bu}_4\text{N}]^+\text{Br}^-$ (3)	15	none
11	Br	benzene- d_6	$[\text{Bu}_4\text{N}]^+\text{I}^-$ (1.5)	2	none
12	Br	DMSO- d_6	none	<1	35%
13	Br	DMF- d_7	none	0.2	5%
14	Cl	benzene- d_6	none	30	none
15	Cl	DMSO- d_6	none	<1	15%

complete after 4 and 10 h for $[\mathbf{2-d}_5] = 3.6 \times 10^{-3}$ and 4.6×10^{-2} M, respectively.¹⁵ Each of these and all other experiments (Table 1) were successfully reproduced 2–6 times. Because of the concentration effect observed, all exchange reactions listed in Table 1 were run with a standard concentration of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}_6\text{D}_5)\text{X}] = 1.1 \times 10^{-2}$ M.

Due to the multiple exchange (one Ph on Pd and six on the P ligands) reliable and precise kinetic data for this reaction can be obtained only at low conversions. As it is clear that sufficiently accurate integration (¹H NMR) is impossible at such conversions, the alternative “time to equilibration” technique was employed. Although absolute rate constants cannot be obtained this way, the design of all experiments (see above) allowed for the reliable quantitative determination of the rate constant ratio, a critical parameter needed to gain insight into the mechanism of the thermal decomposition and aryl–aryl exchange reactions of the Pd aryls.

As seen from Table 1, the rate of exchange is dependent on the nature of X, the observed rate constant ratio, $k_{\text{Br}}:k_{\text{I}}:k_{\text{Cl}}$, in benzene being ca. 100:4:1 for **1-d₅**, **2-d₅**, and **3-d₅**, respectively (entries 1, 4, and 14). No sign of any reaction other than the aryl–aryl exchange was noticed in benzene at 75 °C. In contrast, after the iodo complex **1-d₅** was heated in CDCl_3 at 60 °C for 40 min, ca. 5–10% of the complex decomposed to produce $[\text{Ph}_4\text{P}]^+$ and small amounts of $[(\text{Ph}_3\text{P})_2\text{PdI}_2]$ (³¹P NMR: 12.1 ppm) among several other products. The initial exchange rate in chloroform was faster than in benzene at the same temperature (60 °C), but as the decomposition in CDCl_3 took place, the exchange reaction decelerated considerably. As a result, after 2 h 40 min, **1-d₅** had not yet fully equilibrated in chloroform, whereas complete Ph- d_5 scrambling was observed for the benzene sample. The exchange reactions in DMF- d_7 and DMSO- d_6 (Table 1, entries 3, 12, 13, and 15) were considerably faster than in benzene; side reactions always occurred when DMF and DMSO solvents were used.

A significant acceleration of the exchange for the bromo complex **2-d₅** was observed in the presence of a

Lewis acid, $\text{Et}_2\text{O}\cdot\text{BF}_3$ (Table 1, entries 4, 5, and 6). In benzene- d_6 at 75 °C, the reaction proceeded ca. 40 times faster when only 0.01 equiv of $\text{Et}_2\text{O}\cdot\text{BF}_3$ was added. The addition of an equimolar amount of $\text{Et}_2\text{O}\cdot\text{BF}_3$ resulted in an even more pronounced effect; that is, **2-d₅** began to exchange its phenyls at ambient temperature. After 1 h at 25 °C, more than 50% of the C_6D_5 groups in **2-d₅** were replaced with the phenyls of the PPh_3 ligands. The ³¹P NMR spectrum of the sample exhibited singlets at 23.0, 23.1, and 23.2 ppm from different isotopomers of deuterated **2** and two minor resonances at 21.9 and 22.0 ppm, presumably from two isotopomers of the orange cationic complex formulated as $[(\text{Ph}_3\text{P})_2\text{PdPh}]^+$ ($\delta = 21.7$).¹⁶ This spectral line assignment was corroborated by the slow formation of a microcrystalline orange precipitate during the experiment.

Consistent with the salt effect reported by Goodson, Wallow, and Novak,⁴ the exchange reaction of **2-d₅** in benzene- d_6 solutions speeded up considerably in the presence of tetrabutylammonium hexafluorophosphate.¹⁷ Faster rates were observed with higher concentrations of $[\text{Bu}_4\text{N}]\text{PF}_6$, as exemplified by entries 4 and 7–9 in Table 1. For instance, in the presence of 3 equiv of $[\text{Bu}_4\text{N}]\text{PF}_6$, the reaction was approximately 20 times faster (entries 4 and 9). However, when this experiment was repeated with $[\text{Bu}_4\text{N}]\text{Br}$ instead of $[\text{Bu}_4\text{N}]\text{PF}_6$ (entries 9 and 10), a retardation effect rather than acceleration of the exchange was observed. In the presence of $[\text{Bu}_4\text{N}]\text{I}$, the exchange reaction of **1-d₅** was only slightly slower (entry 2). Importantly, tetrabutylammonium *iodide* also promoted the exchange reaction of the *bromo* complex **2-d₅**, albeit not as efficiently as the hexafluorophosphate salt (entries 4, 8, and 11).

Mechanism of the Aryl–Aryl Exchange in Media of Low Polarity. Anionic Complexes $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}_2]^-$. The aryl–aryl exchange reaction of $[(\text{Ar}_3\text{P})_2\text{Pd}(\text{Ar}')\text{X}]$ (eq 1) involves C–P reductive elimination of $[\text{Ar}_3\text{PAR}']^+$ from the metal center, followed by oxidative addition of the phosphonium cation back to the Pd(0) species generated (Scheme 1).^{4,5} Evidence has been presented for phosphine dissociation^{3,4} and/or Pd–X ionization⁴ being the first key step of the exchange. Either process would result in coordinative unsaturation of the Pd(II) center, thus promoting C–P reductive

(15) It has been reported⁴ that the aryl–aryl exchange reaction of $\{[(4\text{-FC}_6\text{H}_4)_3\text{P}]_2\text{Pd}(\text{I})(4\text{-C}_6\text{H}_4\text{OMe})\}$ was first order in the complex. This exchange reaction was run in THF- d_6 , a much more coordinating solvent in comparison with benzene- d_6 employed in our studies. In addition, the use of dibromomethane as the internal standard⁴ may not be justified for studying kinetics of reactions mediated by highly reactive, electron-rich, coordinatively unsaturated Pd(0) species. Such zerovalent complexes react with chlorinated solvents (see ref 4 and main text above and below), which are less electrophilic than CH_2Br_2 .

(16) Amatore, C. A.; Carré, E.; Jutand, A.; M'Barki, M. A.; Meyer, G. *Organometallics* **1995**, *14*, 5605.

(17) $[\text{Bu}_4\text{N}]^+\text{PF}_6^-$, $[\text{Bu}_4\text{N}]^+\text{Br}^-$, and $[\text{Bu}_4\text{N}]^+\text{I}^-$ are all moderately soluble in benzene at 75 °C (5–10 mg/mL).

elimination.¹⁸ While the addition of free phosphine strongly inhibits the aryl–aryl exchange reactions of $[(\text{Ar}_3\text{P})_2\text{Pd}(\text{Ar}')\text{I}]^{3,4}$ and $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}_6\text{D}_5)\text{F}]$ (see below), the decelerating effect of extra halide is significantly less pronounced (see ref 4 and Table 1) and insufficiently understood.

Our results demonstrate that the rate of the aryl–aryl exchange reaction of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}_6\text{D}_5)\text{X}]$ is dependent on the nature of X trans to the σ -aryl, decreasing in the order $\text{I} > \text{Br} > \text{Cl}$ (Table 1). Given the fact that polar media promote the reaction, it would be tempting to propose Pd–X ionization to be a requirement for the exchange to occur.⁴ Indeed, the exchange reaction of **2-d₅** was faster in the presence of a Lewis acid, $\text{Et}_2\text{O}\cdot\text{BF}_3$ (Table 1, entries 5 and 6), possibly due to the Pd–Br bond ionization caused by the boron trifluoride.¹⁹ Furthermore, it has been demonstrated that in polar solvents such as DMF the Pd–X bond is ionized, with the affinity of the metal center for X increasing in the order $\text{I} < \text{Br} < \text{Cl}$.^{16,20} The same order for the binding ability of the halide anions to $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})]^+$ ($\text{I} < \text{Br} < \text{Cl} < \text{F}$) has been observed for significantly less polar solvents (CH_2Cl_2 and CHCl_3).^{14,21} However, in such solvents and especially in benzene and toluene, which were used in this work, substantial ionization of the Pd–X bond is unlikely.²² The values of 5.9×10^{-4} , 2.8×10^{-4} , and 5×10^{-5} mol dm⁻³ have been obtained for Pd–X dissociation constants (K_D) of **1**, **2**, and **3**, respectively, in DMF at 293 K.²⁰ In benzene, however, these complexes show much less ionization.²² For comparison, ionic tetrabutylammonium salts are 2–4 orders of magnitude more dissociated in DMF²³ than the Pd–X bond of **1**, **2**, and **3**.²⁰ In benzene, however, $[\text{Bu}_4\text{N}]\text{X}$ are strongly associated, forming large clusters consisting of tight ion pairs.²⁴ For instance, Everaert and Persoons^{24b} estimated K_D for tetrabutylammonium picrate in benzene to be ca. 6.5×10^{-18} at 298 K. Therefore, at least a few orders of magnitude lower values might be

expected for K_D of **1**, **2**, and **3** in benzene or toluene solutions. These considerations suggest that Pd–X ionization is unlikely a requirement for the aryl–aryl exchange reactions of **1–3** to occur in media of low polarity, such as benzene or toluene. If so, the two questions arise: (1) Why does the exchange rate depend on the nature of halogen X? and (2) Why is the exchange reaction of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}]$ in benzene speeded up in the presence of $[\text{Bu}_4\text{N}]\text{PF}_6$ but inhibited by $[\text{Bu}_4\text{N}]\text{X}$?

The mechanism shown in Scheme 2 does not involve the Pd–X ionization step while readily accounting for all observations made in this and previous^{3,4} works. It is to be stressed that the concept of Pd–X ionization is *not* challenged when the exchange is run in the presence of a Lewis acid or in polar media, where the Pd–X bond can ionize more easily. On the other hand, the catalytic effect of BF_3 observed in our studies (see above) might be due to its complexation with both the halide and phosphine.^{19c}

Comparison of the P–Pd bond distances in the crystal structures of **1** ($[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{I}]$; P–Pd = 2.342(1) and 2.338(1) Å), **2** ($[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{Br}]$; P–Pd = 2.327(2) and 2.322(2) Å), and **3** ($[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{Cl}]$; P–Pd = 2.324(1) and 2.316(1) Å)¹⁴ predicts that ease of phosphine dissociation from these complexes and hence the aryl–aryl exchange efficiency would follow the trend **3** < **2** < **1**, other things being equal. This is exactly the order that was observed (Table 1). The variation in the Pd–P bond distances for complexes **1–3** is probably best rationalized in terms of different field effects (electronegativities) of the halogens.

Phosphine dissociation from $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}]$ produces tricoordinate $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}]$, which then undergoes reversible reductive elimination of tetraphenylphosphonium cation.^{4,5a} The tricoordinate intermediate probably exists in equilibrium with its dimer, $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-X})_2]$. It has been shown⁸ that $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-I})_2]$, a better precursor for $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{I}]$, decomposes in CH_2Cl_2 more readily than $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{I}]$, to give $[\text{Ph}_4\text{P}]\text{I}$ in a much higher, almost quantitative yield. The formation of the key tricoordinate intermediate $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}]$ should be favored at lower concentrations of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}]$, as suggested by the equilibria between the two and also between $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}]$ and its dimer (Scheme 2). Indeed, we observed that the exchange reaction of **2-d₅** proceeded more readily at lower concentrations of the complex (see above).

We proposed that in the presence of $[\text{Bu}_4\text{N}]\text{X}$ the reductive elimination of $[\text{Ph}_4\text{P}]\text{X}$ from the tricoordinate complex $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}]$ might be inhibited owing to its reaction with the halide of the ammonium salt, to form saturated, square-planar $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}_2]^-$.²⁵ To check this assumption, reactivity of $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-X})_2]$ toward $[\text{Bu}_4\text{N}]\text{X}$ (X = Br or I) was studied. We found that while both $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-I})_2]$ and $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-Br})_2]$ are poorly soluble in benzene and

(18) Reductive elimination reactions are often facilitated by ligand pre-dissociation. See: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 322. Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; John Wiley and Sons: New York, 1994; p 151. Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice Hall: Upper Saddle River, NJ, 1996; p 178.

(19) (a) It is noteworthy that Lewis acids can abstract a tertiary phosphine from its Pd complexes. Kayaki, Shimizu, and Yamamoto^{19b} have demonstrated that the addition of 1 equiv of AgBF_4 to $[(\text{Me}_3\text{P})_2\text{Pd}(\text{R})\text{X}]$ furnishes $[(\text{Me}_3\text{P})_2\text{Pd}(\text{R})(\text{solvent})]^+$, whereas $[(\text{Me}_3\text{P})\text{Pd}(\text{R})(\text{solvent})_2]^+$ is formed when excess AgBF_4 is employed. The formation of a 1:1 complex of Ph_3P with BF_3 is well-documented.^{19c} (b) Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn* **1997**, *70*, 1135. (c) Spitsyn, V. I.; Kollí, I. D.; Sadykova, E. M.; Nesterenko, R. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, 45. Romm, I. P.; Sadykova, E. M.; Gur'yanova, E. N.; Kollí, I. D. *Zh. Obshch. Khim.* **1973**, *43*, 728. Fluck, E.; Weber, D. Z. *Naturforsch. B* **1974**, *29*, 603. Muylle, E.; Van Der Kelen, G. P.; Claeys, E. G. *Spectrochim. Acta A* **1976**, *32*, 1149.

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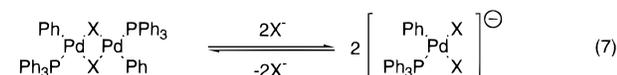
(21) Grushin, V. V. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 994.

(22) (a) Jutand and Mosleh^{22b} have reported that triflate complexes $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ar})\text{OTf}]$ exhibited no conductivity in toluene, while being ion-paired. (b) Jutand, A.; Mosleh, A. *Organometallics* **1995**, *14*, 1810.

(23) (a) Szejgis, A.; Bald, A.; Gregorowicz, J. *Phys. Chem. Liq.* **1997**, *35*, 165, and references therein. (b) Islam, N.; Zaidi, S. B. A.; Ansari, A. A. *Bull. Chem. Soc. Jpn* **1989**, *62*, 309. (c) Tsentovskii, V. M.; Mochalov, K. N.; Barabanov, V. P.; Tumasheva, N. A. *Zh. Obshch. Khim.* **1974**, *44*, 1338. (d) Levitskaya, N. K.; Tkachenko, L. I.; Shkodin, A. M. *Elektrokhimiya* **1974**, *10*, 580.

(24) (a) Ivashkevich, A. N.; Kostynuk, V. P. *Zh. Fiz. Khim.* **1991**, *65*, 948, and references therein. (b) Everaert, J.; Persoons, A. *J. Phys. Chem.* **1981**, *85*, 3930. (c) Barker, C.; Yarwood, J. *Faraday Symp. Chem. Soc.* **1977**, 136.

(25) (a) A closely related anionic Pd complex, $[(\text{Ph}_3\text{P})\text{PdCl}_3]^-$,^{25b–f} forms reversibly upon addition of $[\text{Bu}_4\text{N}]^+\text{Cl}^-$ to $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Cl})_2(\mu\text{-Cl})_2]^{25b}$ or $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]^{25f}$. (b) Goodfellow, R. J.; Goggins, P. L.; Duddell, D. A. *J. Chem. Soc. A* **1968**, 504. (c) Dillon, K. B.; Waddington, T. C.; Younger, D. J. *Chem. Soc., Dalton Trans.* **1975**, 790. (d) Bardi, R.; Piazzesi, A. M.; Del Pra, A.; Cavinato, G.; Toniolo, L. *Inorg. Chim. Acta* **1983**, *75*, 15. (e) Tollari, S.; Demartin, F.; Cenini, S.; Palmisano, G.; Raimondi, P. *J. Organomet. Chem.* **1997**, *527*, 93. (f) Amatore, C.; Jutand, A.; Mottier, L. *Eur. J. Inorg. Chem.* **1999**, 1081.



X	K_{eq} ($\text{mol}^{-1} \text{dm}^3$) in CD_2Cl_2
I	0.2
Br	10
Cl	11

While readily establishing within the time of mixing, equilibrium 7 is slow on the NMR time scale at room temperature, allowing for equilibrium constant measurements, using ^{31}P NMR spectroscopy. Thus, in CD_2Cl_2 at 25 °C, K_{eq} was estimated to be 10 and 0.2 $\text{mol}^{-1} \text{dm}^3$ for $\text{X} = \text{Br}$ and I , respectively, with the initial concentrations of the reagents used being $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-Br})_2] = 1.2 \times 10^{-3}$, $[\text{Bu}_4\text{NBr}] = 9.5 \times 10^{-3}$, $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-I})_2] = 4.3 \times 10^{-3}$, and $[\text{Bu}_4\text{NI}] = 6.5 \times 10^{-2}$ M. Similar observations were made with solutions of $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-Cl})_2]$ and PPNCl in dichloromethane; $K_{\text{eq}} = 11 \text{ mol}^{-1} \text{dm}^3$ for $\text{X} = \text{Cl}$ was measured, using $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-Cl})_2]$ and PPNCl in CD_2Cl_2 at the initial concentrations of 1.7×10^{-3} and 8.0×10^{-2} M, respectively. Since the complexes $[\text{Bu}_4\text{N}]\text{X}$ ($\text{X} = \text{Br}, \text{I}$) and PPNCl involved in eq 7 are strongly associated in low polar solvents, the equilibrium constants were calculated in the approximation that all activity coefficients were close to unity. In accord with the order of halide anion affinity for $\text{Pd}(\text{II})$ in media of low polarity,^{14,21} the inertness of the anionic complex increases when going from $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{I}_2]^-$ ($K_{\text{eq}} = 0.2$) to $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{Br}_2]^-$ ($K_{\text{eq}} = 10$), and further to $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{Cl}_2]^-$ ($K_{\text{eq}} = 11$).

It is clear that in the presence of $[\text{Bu}_4\text{N}]\text{X}$ or PPNCl the tricoordinate intermediate $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}]$, which is prone to reductive elimination, would equilibrate with $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}_2]^-$, which is a coordinatively saturated anion and is therefore less inclined to reductively eliminate $[\text{Ph}_4\text{P}]^+$ (Scheme 2).³⁰ A transition state with substantial separation of charges for the reductive elimination from neutral $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}]$ accounts for the solvent effect observed. Indeed, the aryl–aryl exchange occurs faster in media of higher polarity, which stabilizes the polar transition state, thus lowering the activation energy barrier to the formation of $[\text{Ph}_4\text{P}]^+$ and $[\text{PdX}]^-$. The latter (or more likely $[(\text{Ph}_3\text{P})\text{PdX}]^-$ emerging from the phosphine addition, as shown in Scheme 2) and the phosphonium cation form a tight ion pair, within which the reverse process, oxidative addition, occurs. We obtained strong evidence for the halide ligand remaining on the metal during the exchange when conducted at 75 °C in benzene and toluene (see below). The X ligand not only stabilizes the $\text{Pd}(0)$ species but also enhances the reactivity of the metal center

(30) There may be an alternative path^{25a,f} for the formation of $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}_2]^-$ that involves nucleophilic attack of the halide on $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}]$, followed by phosphine elimination from the resulting five-coordinate anionic complex $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}_2]^-$. As the aryl–aryl exchange reactions occurred, neither $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}_2]^-$ nor $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}_2]^-$ were observed by the ^{31}P NMR technique.

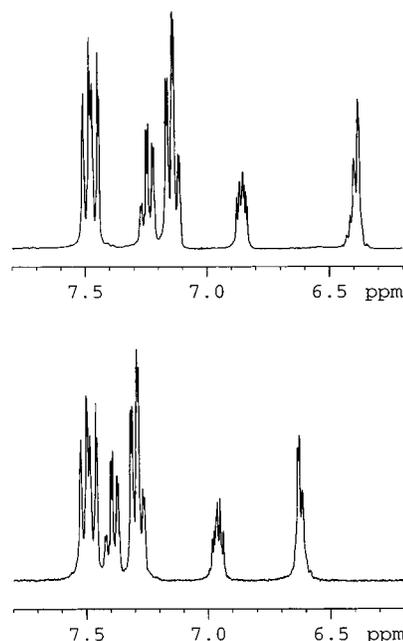


Figure 2. ^1H NMR spectra (CD_2Cl_2 , 20 °C) of $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-Br})_2]$ (bottom) and $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{Br}_2]^-$ generated by the addition of $[\text{Bu}_4\text{N}]\text{Br}$ (50 equiv per Pd) to $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-Br})_2]$ (top).

Table 2. ^{31}P and ^1H NMR Data for Complexes $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-X})_2]$ and $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}_2]^-$, Where $\text{X} = \text{I}, \text{Br}, \text{Cl}$, Obtained for Solutions in CD_2Cl_2 and C_6D_6 at 25 °C (see text)

nucleus	$[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-X})_2]$		$[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}_2]^-$	
	δ (CD_2Cl_2)	δ (C_6D_6)	δ (CD_2Cl_2)	δ (C_6D_6)
^{31}P				
X = Cl	31.6	n.a. ^a	30.9	n.a. ^a
X = Br	30.4	30.7	29.9	30.5
X = I	27.3	27.6	28.2	28.0
$^1\text{H}^b$				
3,4- $\text{C}_6\text{H}_5\text{Pd}$	6.7	6.6	6.4	6.5
2- $\text{C}_6\text{H}_5\text{Pd}$	7.0	7.3	6.9	7.4
3- $\text{C}_6\text{H}_5\text{P}$	7.3		7.15	
4- $\text{C}_6\text{H}_5\text{P}$	7.4		7.25	
3,4- $\text{C}_6\text{H}_5\text{P}$		6.9		7.0
2- $\text{C}_6\text{H}_5\text{P}$	7.5	7.6	7.5	7.9

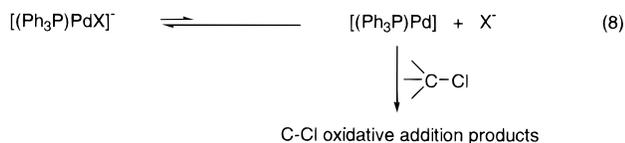
^a Not available. ^b ^1H NMR chemical shift and signal shape parameters of these complexes are identical for $\text{X} = \text{I}$ and Br . No ^1H NMR data are available for $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{Cl}_2]^-$.

toward oxidative addition,³¹ in this case of the tetraphenylphosphonium cation.

At higher temperatures and/or in polar solvents, the $\text{Pd}-\text{X}$ bond of the anionic zerovalent Pd complexes ionizes to produce $[\text{Ph}_4\text{P}]\text{X}$ and unstable low-ligated neutral $\text{Pd}(0)$ species (Scheme 2). In chlorinated solvents, such as dichloromethane, 1,2-dichloroethane, and chloroform, the $\text{Pd}-\text{X}$ ionization should be more facile than in benzene or toluene. Moreover, the $\text{C}-\text{Cl}$ bonds of these solvents may react with coordinatively unsaturated neutral $\text{Pd}(0)$ species, thus driving the equilibrium between $[(\text{Ph}_3\text{P})\text{PdX}]^-$ and $[(\text{Ph}_3\text{P})\text{Pd}]$ (eq 8) toward the latter. This is why $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{I}]$ and especially $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-I})_2]$ readily decompose in chlorinated

(31) (a) Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1338. (b) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 8375. (c) Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254, and references therein.

solvents to give $[\text{Ph}_4\text{P}]\text{I}^{4,8}$ (see also our results described above).

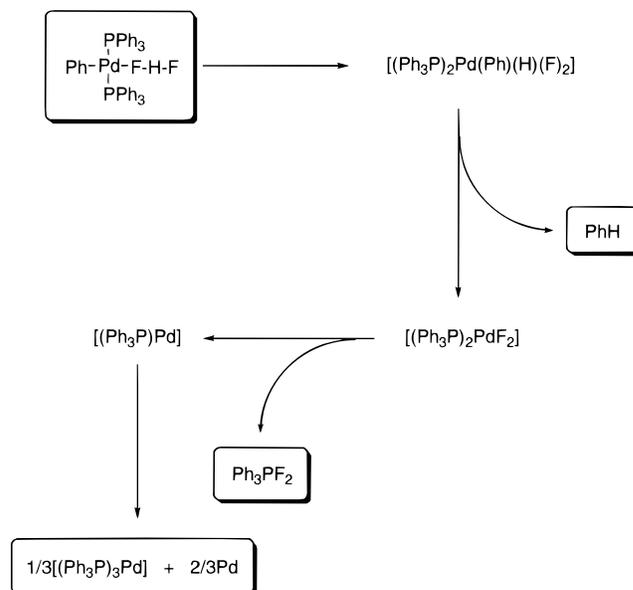


An increase in K_{eq} for eq 8 in the order $\text{X} = \text{Cl} < \text{Br} < \text{I}$ (for solvents of low polarity but not for polar solvents, such as DMF^{31b,c}) is perfectly consistent with the observed order of thermal stability of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}]$, $\text{X} = \text{I} < \text{Br}, \text{Cl}$. Bromo and chloro complexes **2** and **3** are less prone to decompose to $[\text{Ph}_4\text{P}]\text{X}$ and also to exchange its aryls for a number of reasons. First, as we already mentioned, the Pd–P bond weakens when going from **3** to **2** and further to **1**. As a result, the ability of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}]$ to eliminate a phosphine ligand to produce the reactive tricoordinate intermediate, $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}]$, increases in the order $\text{X} = \text{Cl} < \text{Br} < \text{I}$. Second, the capability of $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}]$ to reductively eliminate $[\text{Ph}_4\text{P}]^+$ should increase in the same sequence due to the well-established order of the π -donating ability of halogens $\text{F} > \text{Cl} > \text{Br} > \text{I}$.³² While symmetry forbidden for *square-planar* Pd(II) complexes,³² $p_{\pi} \rightarrow d_{\pi}$ interactions between X and Pd in *tricoordinate* $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}]$ are allowed, resulting in partial electron/coordinative saturation of the metal center and consequently a higher activation energy barrier to reductive elimination. On the contrary, the reverse process, C–P oxidative addition within the tight ion pair (Scheme 2), is expected to be faster for Pd(0) species ligated with chloride rather than bromide and iodide.^{31b,c}

Thermal Decomposition of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{X}]$ ($\text{X} = \text{F}$ and HF_2). These and similar organopalladium fluoro complexes have been recently synthesized in our laboratories,^{33–35} primarily in order to explore the possibility of reductive elimination of ArF as a key step for the metal-catalyzed synthesis of fluoroarenes. Thus, thermal decomposition reactions of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{F}]$, **4**, $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})(\text{FHF})]$, **5**, and analogous compounds have been of special interest to us. All experiments involving **4** and **5** were conducted in a nitrogen atmosphere under rigorously anhydrous conditions, in Teflon liners placed inside standard 5-mm glass NMR tubes. For heat-transfer purposes, the space between the liner and the glass tube was filled with the pure solvent that was used for the reaction.

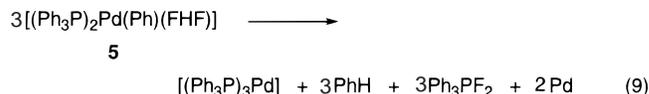
Bifluoride **5** was found to be substantially less thermally stable than its fluoro counterpart **4**. After a toluene solution of **5** was kept at 75 °C for 4 h, the decomposition of the complex was complete, resulting in a yellow solution and a black precipitate of Pd metal. Benzene was found in the liquid phase (GC–MS). Only one resonance, a doublet at –38 ppm with $J_{\text{P-F}} = 666$ Hz, was present in the ¹⁹F NMR spectrum of the sample. The ³¹P NMR spectrum exhibited two signals, a triplet at –56.7 ppm ($J_{\text{P-F}} = 666$ Hz) and a singlet at 21.3 ppm, their integral intensity ratio being 1:3. Both the doublet

Scheme 3



(¹⁹F NMR) and triplet (³¹P NMR) with the same coupling constant were from Ph_3PF_2 .³⁶ To assign the ³¹P NMR singlet at 21.3 ppm, iodobenzene was added to the sample. As a result, the yellow solution decolorized within 15 s, and the signal at 21.3 ppm disappeared. Two new singlet resonances were observed instead, at –5.5 ppm (Ph_3P) and 22.3 ppm ($[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{I}]$) in a 1:2 integral ratio. Bubbling CO through the colorless solution converted the $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})\text{I}]$ to $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{COPh})\text{I}]$ (18.9 ppm).³⁷ These experiments allowed for the unambiguous assignment of the singlet at 21.3 ppm to $[(\text{Ph}_3\text{P})_3\text{Pd}]$.

Equation 9 describes the stoichiometry of the decomposition of **5**. The mechanism of this reaction likely involves the formation of an unstable Pd(IV) hydride³⁸ via oxidative addition of HF, followed by reductive elimination of benzene and the formation of $[(\text{Ph}_3\text{P})_2\text{PdF}_2]$. The latter is also unstable, decomposing³⁹ immediately to Ph_3PF_2 and a zerovalent palladium complex, $[(\text{Ph}_3\text{P})\text{Pd}]$, which disproportionates to $[(\text{Ph}_3\text{P})_3\text{Pd}]$ and Pd metal (Scheme 3).

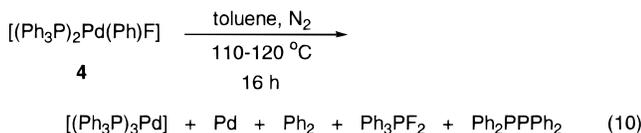


Fluoro complex **4** did not decompose under these conditions. At 110–120 °C, however, a slow (16 h) decomposition of **4** in toluene was observed, leading to biphenyl, Pd metal, $[(\text{Ph}_3\text{P})_3\text{Pd}]$, Ph_3PF_2 , and $\text{Ph}_2\text{P-PPh}_2$ (eq 10) and also small (5–15%) amounts of a few other P-containing products that were not identified.

In a separate series of similar experiments carried out in toluene at 110 °C, it was found that conducting the decomposition in the presence of 2.5 equiv of Ph_3P had no influence on the reaction rate. The reaction

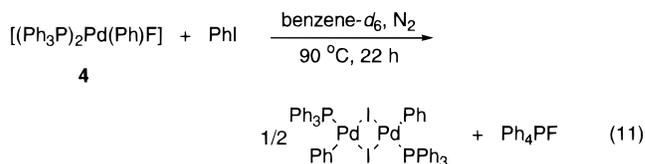
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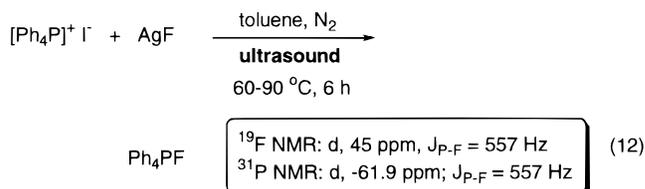


mixtures were analyzed as described above,⁴⁰ the diphosphine being identified by its characteristic ³¹P NMR chemical shift of -14.3 ppm.⁴¹ Fluorobenzene (¹⁹F NMR; GC-MS) and dibenzyl (GC-MS) were not found among the reaction products, which indicated that neither C-F reductive elimination⁴² nor free-radical processes took place during the thermal decomposition of **4**. It was tempting to propose that **4** decomposed via a mechanism involving its disproportionation to a 1:1 mixture of [(Ph₃P)₂Pd(Ph)₂] and [(Ph₃P)₂PdF₂]. The former would rapidly undergo reductive elimination of biphenyl,⁴³ while the latter would decompose to Pd(0) and Ph₃PF₂.³⁹ (see Scheme 3). To test this hypothesis, [(Ph₃P)₂Pd(4-C₆H₄NO₂)F],^{34,35} **6**, was decomposed under similar conditions (toluene, 110° C, N₂, 16 h). The choice of **6** was dictated by the inability^{3,4,6} of complexes of the type [(Ph₃P)₂Pd(4-C₆H₄Y)X] to produce [(Ph₃P)Pd(Ph₂P(4-C₆H₄Y))(Ph)X] via aryl-aryl exchange when Y is a strong electron acceptor (eq 1). GC-MS analysis of the reaction mixture obtained upon decomposition of **6** revealed the presence of only the *monosubstituted* biphenyl 4-NO₂C₆H₄-C₆H₅ and absence of (4-NO₂C₆H₄)₂. Two conclusions can be drawn from this observation. First, the proposed mechanism that involved the disproportionation of **4** to the diphenyl and difluoro complexes should be ruled out. Second, the biphenyl emerged from the thermal decomposition of **4** must have been formed via coupling of the *σ*-phenyl with a phenyl of the Ph₃P ligands, somehow occurring on the metal center.

In an attempt to trap Pd(0) intermediates, the thermal decomposition of **4** was carried out in the presence of iodobenzene, which is known¹³ to readily undergo oxidative addition to zerovalent Pd complexes. When **4** was decomposed at 90 °C in the presence of 1.5 equiv of PhI, a totally different set of products formed (eq 11), namely, an organopalladium dimer [(Ph₃P)₂Pd₂(Ph)₂(μ-I)₂] and fluorotetraphenylphosphorane, with only a

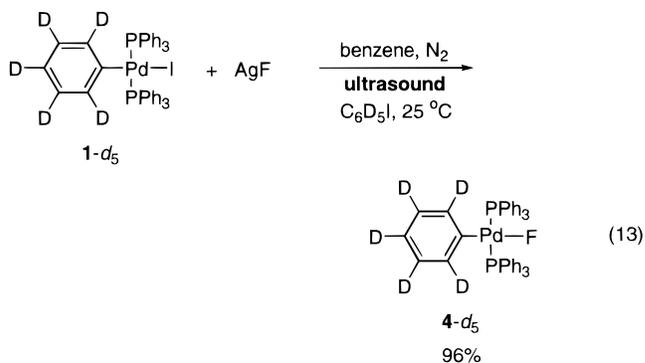


small amount (<10%) of Ph₃PF₂ being produced. The dimer (³¹P NMR: 27.6 ppm) eventually precipitated out of the reaction mixture and was found identical with an authentic sample.²⁹ Although the phosphorane, Ph₄PF (the sublimable covalent form of tetraphenylphosphonium fluoride), has been reported,⁴⁴ its NMR parameters in benzene and toluene have not been. We generated Ph₄PF in solution by sonicating a suspension of [Ph₄P]I and AgF in anhydrous toluene under N₂ at 60–90 °C for 6 h (eq 12). The ¹⁹F and ³¹P NMR spectra



of the resulting solution exhibited doublets with *J*_{P-F} = 557 Hz at 45 ppm (¹⁹F) and -61.9 ppm (³¹P). Consistent with the formulation Ph₄PF, these doublet resonances were identical with those observed in the NMR spectra of the reaction mixture obtained by the thermolysis of **4** in benzene-*d*₆ in the presence of PhI.

Aryl-Aryl Exchange Reactions of [(Ph₃P)₂Pd-(C₆D₅)F]. We also studied the aryl-aryl exchange reaction of [(Ph₃P)₂Pd(C₆D₅)F], **4-d**₅, which we synthesized via the ultrasound-promoted I/F exchange^{33,34} between **1-d**₅ and AgF in benzene (eq 13). At 75 °C in



benzene-*d*₆, the deuterated phenyl on the metal in **4-d**₅ equilibrated with the phenyls on the P ligands after 9 h. This exchange reaction appeared to be autocatalytic, exhibiting an induction period of ca. 0.5–1 h at 75 °C. This was not the case for the aryl-aryl interchange reactions of **1-d**₅, **2-d**₅, and **3-d**₅ (see above). The observed time to equilibration for the exchange reaction of **4-d**₅ was noticeably longer than for the iodo complex **1-d**₅, slightly longer than for the bromide **2-d**₅, but shorter than for the chloride **3-d**₅ (see Table 1). Unlike

(40) Misleading data may be obtained when GC or GC-MS techniques are used for analysis of solutions containing [(Ph₃P)_nPd] for benzene and biphenyl. We found that when a toluene solution of pure [(Ph₃P)₄Pd] was injected in a GC-MS instrument, the complex decomposed in the injector port (250 °C) to produce Ph₃P along with considerable quantities of benzene, biphenyl, and *o*-terphenyl. Hence, before performing the analysis of such solutions for benzene/biphenyl, all [(Ph₃P)_nPd] species present should be somehow converted to stable products that are neither PhH/Ph₂ nor compounds capable of producing PhH/Ph₂ upon injection in the instrument. In a series of control tests it was found that air oxidation of the zerovalent Pd complex did not provide a solution for the problem. Satisfactory results were obtained after toluene solutions of [(Ph₃P)₄Pd] had been shaken with excess 30% H₂O₂ under nitrogen. After 3–10 h at room temperature, the complex was completely oxidized to an inorganic form of Pd and Ph₃PO which did not decompose in the injector port.

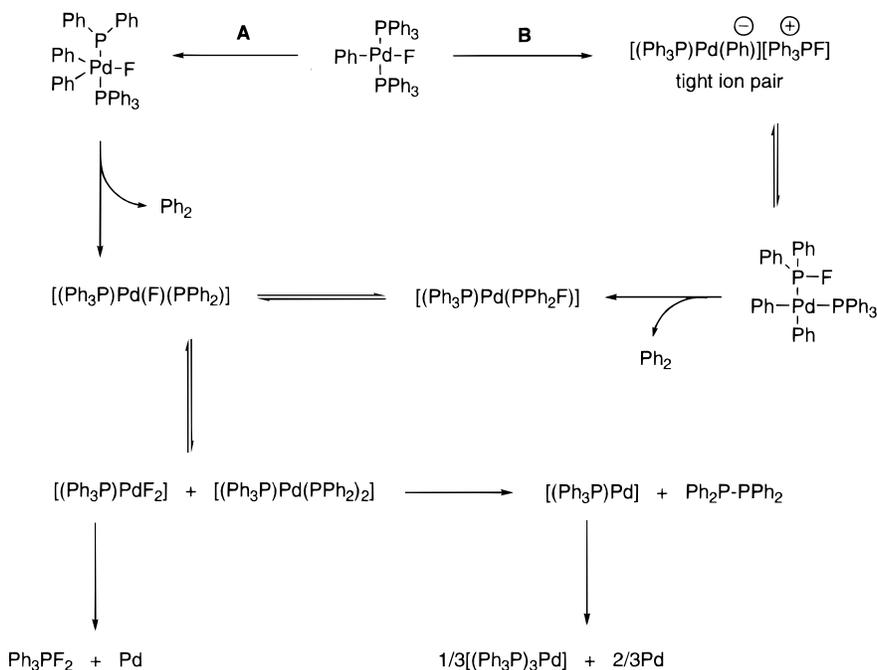
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Scheme 5



to produce biphenyl and $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph}_2\text{P})\text{F}]$. The latter may equilibrate with $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph}_2\text{P})_2]$ and $[(\text{Ph}_3\text{P})\text{PdF}_2]$, which would reductively eliminate $\text{Ph}_2\text{P-PPh}_2$ and Ph_3PF_2 , respectively, to produce Pd(0). It is also conceivable that $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph}_2\text{P})\text{F}]$ rearranges to $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph}_2\text{PF})]$. In fact, as the decomposition of **4** occurred, the formation and eventual disappearance of two species was observed (major, ^{19}F NMR, doublet, 2 ppm; ^{31}P NMR, doublet, -68.5 ppm; $J_{\text{P-F}} = 630$ Hz) and (minor, ^{19}F NMR, doublet, 3 ppm; ^{31}P NMR, doublet, -69.7 ppm; $J_{\text{P-F}} = 648$ Hz), which can be assigned to Pd complexes containing Ph_2PF ligand(s).⁴⁸ It has been shown^{48b,c,49} that Ph_2PF readily disproportionates below 100°C to give a mixture of $\text{Ph}_2\text{P-PPh}_2$ and Ph_2PF_3 . The latter may be reduced by the Pd(0) species to Ph_2PF via a series of oxidative addition and reductive elimination reactions.

Path B (Scheme 5) differs from path A in that the biphenyl reductively eliminates from a Pd(II) complex which is formed via P-F reductive elimination of $[\text{Ph}_3\text{P}(\text{Ph})\text{PF}]^+$,⁵⁰ followed by oxidative addition of one of its Ph-P bonds to the Pd(0) complex. Both paths A and B lead to coordinatively unsaturated *neutral* Pd(0) species which trap avidly the phosphine molecules emerging from the predissociation step that is required for the aryl-aryl exchange to occur (Schemes 2 and 4). As a result, the aryl-aryl exchange, reaction of **4-d**₅ is autocatalytic, exhibiting an induction period needed to produce the coordinatively unsaturated Pd species (Scheme 5) that catalyze the aryl-aryl exchange process. This autocatalytic effect disappears, or at least diminishes substantially, when the exchange reaction is run in the presence

of iodobenzene (see above), an efficient scavenger for the Pd(0) complexes which readily add PhI, thus gaining coordinative saturation. For instance, PhI readily reacts with $[(\text{Ph}_3\text{P})\text{Pd}]$ generated in situ, to give $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ph})_2(\mu\text{-I})_2]$,²⁹ the latter possessing much lower affinity for Ph_3P than the former.

Concluding Remarks

Results obtained in this work bear several implications for catalysis. The leaving group X of the aromatic substrate, ArX, used for a Pd-catalyzed reaction has been long known^{1,13} to determine the reactivity of the C-X bond toward catalytically active zerovalent palladium. Oxidative addition of aryl halides or triflates to Pd(0) is the first key step which frequently but not always determines the overall rate of the catalytic reaction, the well-established order of reactivity being $\text{ArI} > \text{ArBr} \approx \text{ArOTf} \gg \text{ArCl} \gg \text{ArF}$. At the same time, little is known about the influence of the ligand X on successive steps of the catalytic cycle. It had been thought that after the oxidative addition that results in the formation of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Ar})\text{X}]$ the halogen X becomes more or less a spectator rather than an active player for the rest of the catalytic cycle. In recent years, however, information has begun to accrue, suggesting that the nature of X can sometimes strongly control such critical catalytic steps as olefin or CO coordination, ligand exchange, migratory insertion, reductive elimination, and so forth.^{1c} Our data clearly demonstrate that catalytically active Pd species forming in a reaction using iodoarenes will be less thermally stable and more prone to undergo P-aryl/Pd-aryl exchange reactions than analogous complexes mediating the same catalytic process that employs similar bromoarenes. To suppress the highly undesired aryl-aryl exchange reactions, one might consider conducting the process in media of low polarity in the presence of extra phosphine ligand and/

(48) (a) NMR parameters of free Ph_2PF : ^{19}F NMR = -202 ppm; ^{31}P NMR = 168 ppm; $J_{\text{P-F}} = 905$ Hz;^{48b} ^{19}F NMR = -195.9 ppm; ^{31}P NMR = 162.3 ppm; $J_{\text{P-F}} = 883$ Hz.^{48c} (b) Brown, C.; Murray, M.; Schmutzler, R. *J. Chem. Soc. C* **1970**, 878. (c) Riesel, L.; Haenel, J. Z. *Anorg. Allg. Chem.* **1991**, 603, 145.

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(50) (a) ^{19}F NMR = -129.1 ppm; ^{31}P NMR = -93.7 ppm; $J_{\text{P-F}} = 998$ Hz. (b) Seel, F.; Bassler, H.-J. *Z. Anorg. Allg. Chem.* **1975**, 418, 263.

or a halide source.⁵¹ Running the process at the highest possible Pd catalyst concentration may also help avoid the aryl–aryl interchange reactions. Although no panacea is offered in this work to cure the aryl–aryl exchange “disease”, it is hoped that our data and mechanistic considerations may help develop some “preventive measures” that will broaden the scope and reduce the limitations of the catalytic chemistry of aromatic halides.

Experimental Section

All manipulations were done in a glovebox under nitrogen, unless otherwise noted. Solvents used for the decomposition and exchange studies were dried and stored over freshly activated molecular sieves (4 Å). Teflon liners for standard 5-mm glass NMR tubes were supplied by the Wilmad Company. All chemicals were purchased from Aldrich, Kodak, Strem, and Organometallics Chemical Companies. Complexes **1**,¹³ **2**,¹³ **3**,¹⁴ **4**,^{33,34} **5**,³⁴ **6**,^{34,35} and $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-D})_2]$ ²⁹ were prepared as described in the literature. NMR spectra were obtained with a Bruker Avance DPX 300 spectrometer. A Hewlett-Packard 6890 Series GC-MS instrument was used for GC-MS analysis.

Synthesis of 1-d₅. Iodobenzene-d₅ (Aldrich, 98% D; 0.17 g; 0.81 mmol) was added to a stirring mixture of $[(\text{Ph}_3\text{P})_4\text{Pd}]$ (Strem, 99.9%; 0.85 g; 0.74 mmol) and toluene (15 mL). After the mixture was stirred at room temperature for 18 h, the product was isolated in air. The white precipitate was separated, washed with toluene (3 × 1 mL) and hexanes (5 × 10 mL), and dried under vacuum. This gave 0.55 g of the product. Combining the mother liquor with the toluene and hexane washings resulted in precipitation of 0.04 g of pure **1-d₅**. Total yield: 0.59 g (96%). ¹H NMR (CD₂Cl₂, 20 °C), δ: 7.3 (m, 2H, 3-C₆H₅P), 7.4 (m, 1H, 4-C₆H₅P), 7.6 (m, 2H, 2-C₆H₅P). ³¹P NMR (CD₂Cl₂, 20 °C), δ: 22.2 (s).

Synthesis of 2-d₅. A mixture of $[(\text{Ph}_3\text{P})_4\text{Pd}]$ (Strem, 99.9%; 0.55 g; 0.48 mmol), bromobenzene-d₅ (Aldrich, 99.5% D; 0.55 g; 3.4 mmol), Ph₃P (0.20 g; 0.76 mmol), and toluene (5 mL) was stirred at 75 °C (oil bath) for 5 h. The mixture was cooled to room temperature. After 2 h the product was isolated in air. The solid was separated, washed with hexanes (5 × 5 mL), recrystallized from dichloromethane–ether, and dried under vacuum. The yield of the white crystalline **2-d₅** was 0.31 g (83%). ¹H NMR (CD₂Cl₂, 20 °C), δ: 7.3 (m, 2H, 3-C₆H₅P), 7.4 (m, 1H, 4-C₆H₅P), 7.6 (m, 2H, 2-C₆H₅P). ³¹P NMR (CD₂Cl₂, 20 °C), δ: 22.8 (s).

Synthesis of 3-d₅. This complex was prepared under biphasic conditions from **1-d₅** and KCl in CH₂Cl₂–H₂O, according to the literature method for the synthesis of **3**.¹⁴ The reaction, isolation, and purification of the product were carried out in air. The complex was purified by three recrystallizations from dichloromethane–ether. ¹H NMR (CD₂Cl₂, 20 °C), δ: 7.3 (m, 2H, 3-C₆H₅P), 7.4 (m, 1H, 4-C₆H₅P), 7.6 (m, 2H, 2-C₆H₅P). ³¹P NMR (CD₂Cl₂, 20 °C), δ: 23.9 (s).

Synthesis of 4-d₅. A mixture of **1-d₅** (0.20 g; 0.24 mmol), AgF (0.04 g; 0.31 mmol), PhI-d₅ (Aldrich, 98% D; 0.01 g; 0.05 mmol), and benzene (7.5 mL) was sonicated under N₂ at 20–25 °C for 3.5 h (monitored by ³¹P NMR spectroscopy). The product was isolated in air. The benzene solution was filtered through a Celite plug. The solids were thoroughly extracted with warm (45 °C) benzene. After filtration of the extracts through the same Celite plug, all benzene solutions were combined, reduced in volume to ca. 3 mL, and treated with

hexanes (10 mL). The white crystals were separated and dried under vacuum. The yield of spectroscopically pure **4-d₅** was 0.15 g (86%). The complex was brought into a drybox, where it was recrystallized from anhydrous dichloromethane–ether and dried. ¹H NMR (C₆D₆, 20 °C), δ: 7.0 (m, 3H, 3,4-C₆H₅P), 7.9 (m, 2H, 2-C₆H₅P). ³¹P NMR (C₆D₆, 20 °C), δ: 18.7 (d, *J*_{P–F} = 13 Hz).

Synthesis of $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-Br})_2]$. This complex was prepared and isolated in air. To a clear colorless solution of $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-OAc})_2]$ ⁵² (0.095 g; 0.09 mmol) and $[\text{Bu}_4\text{N}]\text{-Br}$ (0.076 g; 0.24 mmol) in CH₂Cl₂ (1 mL) were added acetone (10 mL) and water (0.2 mL). After 3 h the pale lemon-yellow crystalline solid was separated, thoroughly washed with acetone and dichloromethane, and dried under vacuum. The yield of the bromo dimer was 0.093 g (94%). Anal. Calcd for C₄₈H₄₀Br₂P₄D₂: C, 54.8; H, 3.8; Br, 15.2. Found: C, 55.1; H, 3.7; Br, 15.6. For NMR parameters of the complex, see Table 2.

Synthesis of $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-Cl})_2]$. This complex was also prepared and isolated in air. To a clear colorless solution of $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-OAc})_2]$ ⁵² (0.170 g; 0.16 mmol) and PPN Cl (0.203 g; 0.34 mmol) in CH₂Cl₂ (5 mL) were added acetone (20 mL) and water (1 mL). After 15 min the white crystals of $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-Cl})_2]$ were separated, thoroughly washed with acetone, and dried under vacuum. The yield of the spectroscopically pure²⁸ chloro dimer was 0.140 g (86%).

Thermal Decomposition of 1–3. A mixture of **1** (0.16 g; 0.19 mmol) and toluene (10 mL) was stirred under reflux (N₂) for 16 h. A palladium mirror formed. ³¹P NMR analysis of the brown liquid phase indicated the presence of Ph₃P (br s, –0.1 ppm), small quantities (ca. 10%) of unreacted **1** (s, 22.4 ppm), and trace amounts (ca. 1%) of $[(\text{Ph}_3\text{P})_2\text{Pd}_2]$ (s, 12.5 ppm). Both the shape (broadened) and the chemical shift of the Ph₃P resonance suggested exchange with phosphine Pd(0) complexes present in low concentration. The solids were extracted with CH₂Cl₂ (3 × 5 mL). The combined extracts were filtered, reduced in volume to ca. 3 mL, and treated with ether (30 mL). The white precipitate of $[\text{Ph}_4\text{P}]\text{I}$ was separated, washed with ether, and dried under vacuum. The product (0.075 g; 84%) was identical with a commercial sample of tetraphenylphosphonium iodide. Under similar conditions, complexes **2** and **3** exhibited no sign of decomposition (¹H and ³¹P NMR).

Preparation of Samples for Aryl–Aryl Exchange and Thermal Decomposition Studies. NMR tubes and Teflon liners were kept under vacuum (5 × 10^{–3} mm) for 12 h prior to use. All complexes, tetrabutylammonium salts, and anhydrous solvents were kept under nitrogen in a drybox. Teflon liners were used to prepare samples for reactions of bifluoro or fluoro Pd complexes. After charged NMR tubes were capped with 5-mm rubber septum stoppers and sealed with Parafilm, the samples were taken out of the drybox. To speed up dissolution of solid complexes and tetrabutylammonium salts in benzene-d₆, sonication and/or gentle heating (25–40 °C) were applied. Once all solids dissolved, the sample was placed in a preheated oil bath or VT probe of the NMR spectrometer.

Generation of $[(\text{Ph}_3\text{P})\text{Pd}(\text{Ph})\text{X}_2]^-$ from $[(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{Ph})_2(\mu\text{-X})_2]$ and $[\text{Bu}_4\text{N}]\text{X}$ (X = I and Br) or PPN Cl. (a) A mixture of a dinuclear complex, $[\text{Bu}_4\text{N}]\text{X}$ (or PPN Cl), and a dry deuterated solvent was prepared in the drybox, as described above. The mixture was shaken and/or slightly heated until the solids dissolved (3–5 min), after which the sample was analyzed by NMR (Table 2). (b) A solution (suspension) of a dinuclear complex was placed in an NMR tube capped with a rubber septum. Separately, a solution of known concentration of $[\text{Bu}_4\text{N}]\text{X}$ or PPNCl was prepared in a GC vial. Both the tube and the vial were taken out of the drybox. The salt solution was added, portionwise, to the NMR tube containing the complex with a microsyringe. NMR spectra

(51) Running such reactions in the presence of extra halide might suppress the formation of cationic Pd intermediates, which can be crucial for successful catalysis. See: Yamamoto, A. *J. Organomet. Chem.* **1995**, *500*, 337. Kayaki, Y.; Yamamoto, A. *Yuki Gosei Kagaku Kyokaiishi* **1998**, *56*, 96. Yamamoto, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1027.

(52) Grushin, V. V.; Besimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3259.

were taken after each addition. A representative experiment is described below.

A solution of [Bu₄N]Br (92 mg) in CD₂Cl₂ (0.5 mL) was prepared in a standard GC vial. Using a microsyringe, 10 μL of this solution was added to a septum-capped NMR tube containing [(Ph₃P)₂Pd₂(Ph)₂(μ-Br)₂] (3 mg) in CD₂Cl₂ (0.5 mL). After the tube was shaken for 5 min at 25 °C, a small amount of the undissolved dinuclear complex still remained in the mixture. Both ³¹P and ¹H NMR spectra of the mixture indicated that the liquid phase contained the unreacted dimer (δ_P = 30.4 ppm) and [Bu₄N][(Ph₃P)Pd(Ph)Br₂] (δ_P = 29.9 ppm) in a 1:2 ratio. Because counterion exchange between the latter and excess [Bu₄N]Br is fast on the NMR time scale, one type of butyl group was observed in the ¹H NMR spectrum. Integration of the butyl proton resonances against the aromatic signals allowed for calculation of the concentrations of the dimer, [Bu₄N]Br, and the anionic complex at equilibrium to

be 0.8×10^{-3} , 8.7×10^{-3} , and 0.8×10^{-3} M, respectively ($K_{\text{eq}} \approx 10 \text{ mol}^{-1} \text{ dm}^3$).

Ultrasound-Promoted Reaction of [Ph₄P]I with AgF in Toluene. A suspension of [Ph₄P]I (0.06 g; 0.13 mmol) and AgF (0.09 g; 0.71 mmol) in dry toluene (0.3 mL) was sonicated in a Teflon liner placed in a standard 5-mm NMR tube under N₂ at 60 °C for 2 h. The sample was analyzed by ³¹P and ¹⁹F NMR: δ_P = -61.9 ppm (d, $J_{\text{P-F}} = 557 \text{ Hz}$); δ_F = 45 ppm (d, $J_{\text{P-F}} = 557 \text{ Hz}$). After sonication for an additional 4 h at 90 °C the conversion to Ph₄PF somewhat increased.

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