# Methyl/Phenyl Exchange between Palladium and a Phosphine Ligand. Consequences for Catalytic Coupling Reactions

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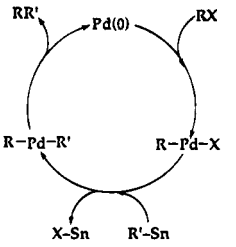
*Received August 8, 1994. Revised Manuscript Received June 8, 1995*⊗

**Abstract:** The methyl ligand of *trans*-$CH_3Pd(PPh_3)_2I$ (**1**) exchanges with a phenyl from its $PPh_3$ ligand, initially giving $PhPd(PPh_3)(PMePh_2)I$ (**4**). The $PMePh_2$ ligand of **4** then exchanges with a $PPh_3$ of **1** to give $CH_3Pd(PPh_3)(PMePh_2)I$ and with the $PMePh_2$ ligand of more **4** to give $PhPd(PPh_3)_2I$ and *trans*-$PhPd(PMePh_2)_2I$. The observed rate constant for the disappearance of **1** is about $7 \times 10^{-5}$ $s^{-1}$ at 75 °C. The rearrangement is irreversible, does not involve a free phosphonium cation, and does not require phosphine dissociation. The rearrangement competes with transmetalation when **1** is treated with tin reagents, leading to coupling products incorporating phenyls from $PPh_3$. Relatively electropositive phosphine substituents seem reluctant to rearrange onto palladium.

The palladium-catalyzed coupling of organic electrophiles with organomagnesium,[1] -zinc,[1b,2] -boron,[3] -aluminum,[4] -zirconium,[5] and particularly organotin[6] reagents has become widely used in organic synthesis. The stability of organotin reagents to air and moisture, and the fact that most functional groups are tolerant of these reagents, makes them particularly convenient nucleophiles.[6e] Both the organic moiety transferred from the tin reagent and that supplied by the electrophile are usually unsaturated (e.g., vinyl, aryl, or allyl). The electrophilic reagents are usually halides, triflates, or acetates, although fluorosulfonates, arenesulfonates, chloroformates, carbamoyl chlorides, phenyliodonium cations, and trifluoroacetic anhydride have also been used.[7]

The mechanism generally proposed[6a,b,d,8] begins with oxidative addition of the electrophilic reagent RX to Pd(0), continues with transmetalation of R′ from tin to palladium, and ends with reductive elimination of R−R′ from palladium (eq 1).




(1)

However, this mechanism requires further elaboration in order to explain recent developments. Palladium-catalyzed RX/SnR′ coupling reactions can be accelerated by (a) copper(I)[7d,9] or silver(I) catalysis,[10] (b) the coordination of an additional ligand at tin,[11,12] or (c) the replacement of the traditional triphenylphosphine ligand by tri(2-furyl)phosphine or triphenylarsine.[6e,9d,13]

Oxidative addition and reductive elimination are easily studied as individual reactions, and much is known about the way they occur in palladium-catalyzed coupling: it has recently been shown that Pd(0) is halide ligated when it adds ArX,[14] and it was earlier demonstrated that organic ligands must be cis before they can be reductively eliminated from Pd(II).[15] However, it has not proven possible to study the transmetalation step in eq 1 except as part of a multistep sequence. (Comparison[6a,b] of the relative rates at which various organotins undergo (a) Pd-

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⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1995.

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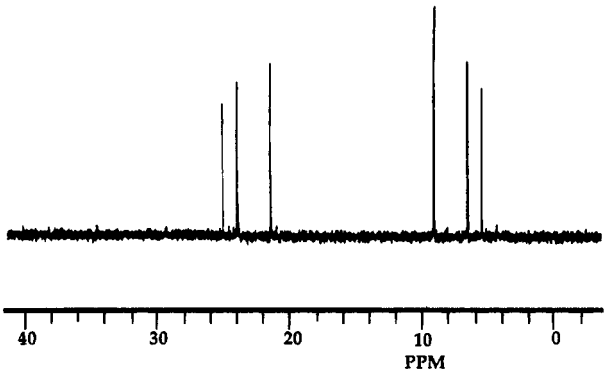
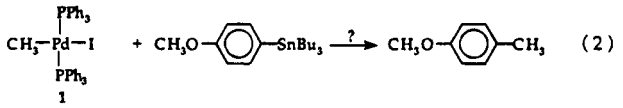



**Figure 1.** $^{31}P\{^1H\}$ NMR after an 8 mM solution of $(Ph_3P)_2PdCH_3I$ (**1**) in $C_6D_6$ was heated to 50−60 °C for 48 h.

catalyzed coupling,[16] (b) Sn-to-Pt transmetalation,[17] and (c) reaction with Hg(II)[18] suggests that transmetalation be viewed as electrophilic cleavage of the Sn−C bond.)

We have therefore examined the reaction of the simple organopalladium complex **1**[15c,19] with an aryl tin reagent (eq 2). To our surprise, we have learned that **1** undergoes a rearrangement that competes with the coupling reaction.




(2)

## Results

The nature of the rearrangement became clear from the $^{31}P\{^1H\}$ NMR spectra observed when a $C_6D_6$ solution of **1** was kept at 50 °C. As the initial singlet ($\delta$ 31.5) decreased, a singlet at $\delta$ 24.0 appeared, followed by a singlet at $\delta$ 6.7, a pair of doublets at $\delta$ 7.4 and 23.4, and a pair of doublets at $\delta$ 13.8 and 30.9; after prolonged heating only the singlets at $\delta$ 24.0 and 6.7, and the doublets at $\delta$ 7.4 and 23.4, remained (Figure 1).

The singlet at $\delta$ 24.0 agreed with that of an authentic sample of the known[20] *phenyl* complex **2**, and the singlet at $\delta$ 6.7 agreed with that of an authentic sample of known[21] *phenyl* complex **3**. As many complexes $L_2Pd(R)X$ are known to exchange phosphine ligands rapidly,[22] we suspected that the doublet of doublets

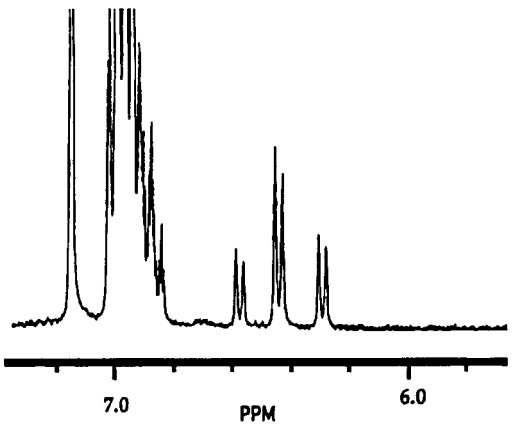
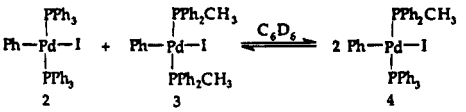


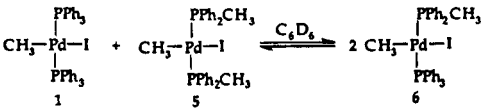

**Figure 2.** $^{31}P\{^1H\}$ NMR after a 12 mM solution of **1**-$d_6$ in $C_6D_6$ was heated to 50−60 °C for 10 h.

at 7.4 and 23.4 might belong to the mixed phosphine complex **4** and confirmed this assignment by generating **4** from a mixture of **2** and **3** (eq 3). (The equilibrium constant was unity.)



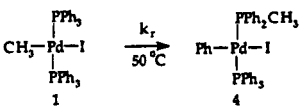

(3)

We suspected that the pair of doublets that appeared at $\delta$ 13.8 and 30.9 during the middle part of the reaction belonged to **6**, the methyl analogue of **4**, and confirmed this assignment by generating **6** from a mixture of **1** and *trans*-$CH_3Pd(PPh_2CH_3)_2I$, **5**[15c] (eq 4). (Again, the equilibrium constant was unity.)




(4)

Apparently the methyl ligand of **1** exchanges with a phenyl substituent on the phosphine ligand, forming **4** (eq 5). Phosphine exchange quickly generates **2** and **6** (eq 6). Eventually (Figure 1) only the phenyl complexes **2**, **3** (from eq 3), and **4** are present.

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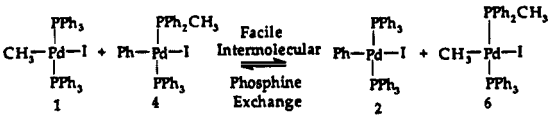
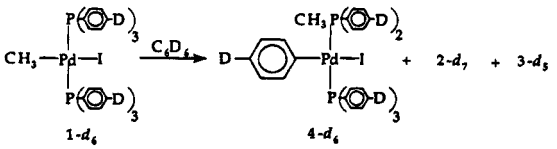



(6)

Rearrangement of the para-deuterated methyl complex **1**-$d_6$ at 50 °C gave the products in eq 7. The meta $^1H$ NMR resonances in the resulting aryl palladium complexes were all doublets ($\delta$ = 6.29, **2**; $\delta$ = 6.44, **4**; $\delta$ = 6.58, **3**) (Figure 2), showing that the deuterium labels had remained in the para position.




(7)

(16) The rate of the Pd-catalyzed coupling of the R from $Me_3SnR$ or $Bu_3SnR$ with the benzoyl from PhC(O)Cl decreases in the order alkynyl > vinyl > Ph > $PhCH_2$ > alkyl: Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6129.

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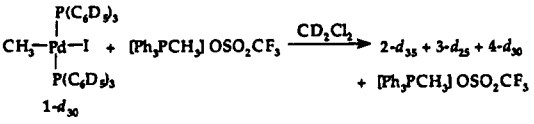
The rearrangement in eqs 5 and 7 does not involve reductive elimination of a phosphonium cation. A $^1$H NMR analysis showed no incorporation of protio phenyl groups when **1**-$d_{30}$ (0.01 M) rearranged to **2**-$d_{35}$, **3**-$d_{25}$, and **4**-$d_{30}$ at 36 °C in the presence of [$MePh_3P$]OTf (0.005 M) in $CD_2Cl_2$ (eq 8), ruling out the intermediacy of a free phosphonium cation in that solvent. (While such an experiment is impossible in aromatic solvents because of the insolubility of [$MePh_3P$]OTf, the formation of a palladium-associated phosphonium cation in such solvents should have led to the release of free $[MePh_3P]^+$ in methylene chloride.)



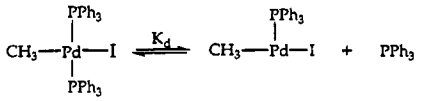
(8)

Phosphine dissociation is *not* a requirement for the rearrangement in eqs 5 and 7. Good estimates of $k_r$ can be extracted from the behavior of a solution of **1** at early reaction times, although the phosphine exchange reactions eqs 3 and 6 eventually make the system kinetically complex. $^1$H and $^{31}$P NMR show that **2** and **6** are the initial products when a solution of **1** is heated, implying that the operation of eq 6 is consuming **4** as fast as it is formed in eq 5; an additional equiv of **1** thus disappears (via eq 6) for every one that rearranges in eq 5. Under these conditions the disappearance of **1** should be first-order, with the observed rate constant given by eq 9.

$$k_{obs} \approx 2k_r \tag{9}$$

At 70 °C in $C_6D_6$, $k_{obs}$ for a solution of 0.017 M **1** is about $7 \times 10^{-5}$ s$^{-1}$, so $k_r$ must be about $3.5 \times 10^{-5}$ s$^{-1}$; the same result is obtained in the presence of 0.11 M $Ph_3P$. The $^{31}$P NMR spectra show that $PPh_3$ does not displace $PPh_2Me$ from Pd, so the added $Ph_3P$ leaves the **1** unchanged and does not affect the validity of eq 9.

Separate $^{31}$P NMR signals are observed for **1** and free $Ph_3P$ in the solution containing both. Because any phosphine dissociated from **1** would be seen, we can put an upper limit on $K_d$, the equilibrium constant for the dissociation of $Ph_3P$ from **1** (eq 10). Because no free $Ph_3P$ is observed (we estimate 5% would have been visible) when [**1**] is 0.008 M, $K_d$ must be $<2 \times 10^{-5}$ M. The presence of 0.11 M $Ph_3P$ would thus produce a substantial decrease ($>10^3$) in the rate of the rearrangement if phosphine dissociation were required.



(10)

The rearrangement in eqs 5 and 7 can compete with transmetalation. After 24 h at 50 °C in benzene, reaction 2 gives only 3% of the expected product, *p*-methylanisole; most of **1** rearranges to **4** before it reacts with the anisyl tin reagent. Reaction 2 also gives some of the aryl-phenyl coupling product **7** (8% of the initial **1**), by reductive elimination after transmetalation of **2**, **3**, or **4** (eq 11). Similarly, a styryl tin reagent gives a 6% yield of **8** (eq 12), along with a 36% yield of the methyl coupling product *trans*-β-methylstyrene; a phenylethynyl tin reagent gives a 22% yield of **9** (eq 13), along with a 22% yield of the methyl coupling product 1-phenyl-1-propyne.

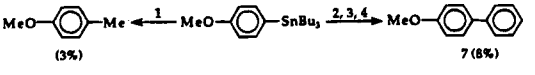
We have prepared a number of organopalladium complexes $RPdL_2X$ (L = $PPh_3$ or $AsPh_3$) and compared the ease with which they (and related compounds in the literature) undergo R/Ph exchange (eq 14) in Table 1.

**Table 1.** Ease of Rearrangement of Organopalladium Complexes (L = $PPh_3$ and X = I Unless Otherwise Specified)

| entry | Y in *p*-$YC_6H_4PdL_2X$ | conditions | rearrangement yes/no |
|---|---|---|---|
| 1 | acyl (**15**) | PhH 60 °C, 22 h | N[a] |
| 2 | $NO_2$ (**16**) | PhH 60 °C, 51 h | N[a] |
| 3 | I (**17**) | PhH 60 °C, 51 h | N[a] |
| 4 | $CF_3$ | $CDCl_3$ 50 °C, 3 h | N[b,c] |
| 5 | H | THF 50 °C | Y[d] |
| 6 | F (**18**) | PhH 60 °C, 22 h | Y[a] |
| 7 | $CH_3$ | THF 60 °C, 1 h | Y[d,e] |
| 8 | $CH_3O$ | THF 60 °C, 1 h | Y[d,e,f] |

| entry | R in $RPdL_2X$ | conditions | rearrangement yes/no |
|---|---|---|---|
| 9 | Me (**1**) | PhH 75 °C, 10 h | Y[a] |
| 10 | $CF_3CH_2$ (**19**) | PhH 50 °C, 24 h | N[a] |
| 11 | $NCCH_2$ (**20**) | PhH 50 °C, 24h | N[a,d] |
| 12 | benzyl (**21**) | PhH 60 °C, 24 h | N[a,g] |
| 13 | 2-thienyl (**22**) | PhH 60 °C, 22 h | Y[a] |
| 14 | *p*-tolyl (**23**) | PhH 60 °C, 60 h (very slow) | Y[a,h] |
| 15 | 2-furyl (**24**) | PhH 60 °C, 8 h | Y[a] |
| 16 | 3,4-methylenedioxyphenyl | PhH | Y[i] |

[a] This work. [b] Reference 25a. [c] A similar lack of reactivity was reported under catalytic conditions in DMF in ref 26. [d] Reference 23. [e] Similar reactivity was reported for the aryl bromide under catalytic conditions in DMF in ref 26. [f] Reference 24b. [g] X = Cl. [h] L = $AsPh_3$. [i] Reference 24a with X = Br.



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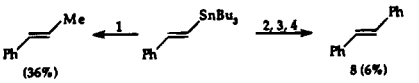

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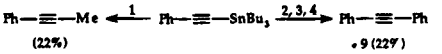

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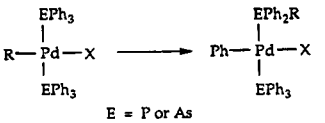


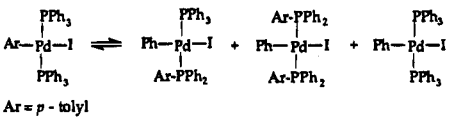
(14)

The ease with which groups exchange between palladium and a phosphine or arsine ligand varies substantially with the nature of the ligand. There is significant tolyl/phenyl exchange after 3 h when *trans*-$(Ph_3P)_2Pd(p\text{-tolyl})I$ is heated to 50 °C in benzene, but there is little rearrangement even after 6 days when *trans*-$(Ph_2MeP)_2Pd(p\text{-tolyl})I$ is heated to 60 °C in benzene. Similarly, whereas *trans*-$(Ph_3P)_2Pd(CH_3)I$ (**1**) completely rearranges to the phenyl complexes **2**, **3**, and **4** after 24 h at 60 °C, the analogous

$Ph_2MeP$ complex does not: half the initial *trans*-$(Ph_2MeP)_2Pd(CD_3)I$ (**5**-$d_3$) remains after 8 days at 50−60 °C in benzene. Furthermore, the $Ph_3As$ complex *trans*-$(Ph_3As)_2Pd(p\text{-tolyl})I$ is much slower to rearrange than the analogous $Ph_3P$ complex (see Table 1).

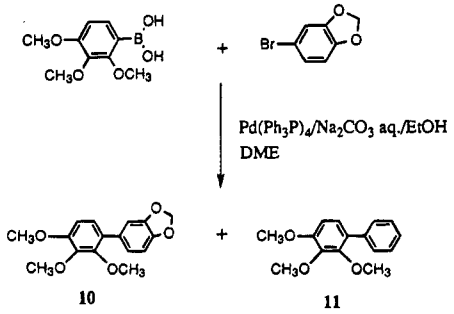
## Discussion

The related aryl-aryl exchange in eq 15 has been reported.[23] It is approximately thermoneutral.

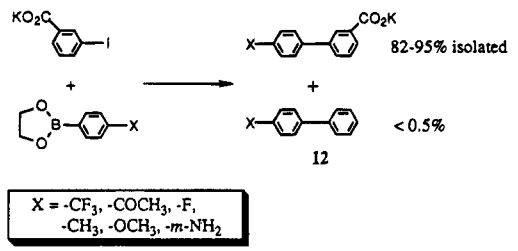



(15)

Exchange of metal- and phosphine-bound aryls has also been observed during Suzuki coupling reactions. Reaction 16 gave a 27% yield of **11** as well as a 54% yield of the expected coupling product **10**,[24] while reaction 17 gave small amounts (<0.5%) of biphenyl **12** even though extremely low catalyst concentrations were employed in aqueous solution.[25]

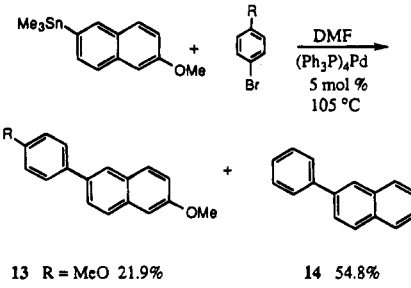



(16)




(17)

Finally, while this manuscript was being revised in response to reviewers' comments, Segelstein, Butler, and Chenard reported that the principal product of the Pd-catalyzed coupling reaction in eq 18 was the phenyl coupling product **14** instead of the aryl coupling product **13**.[26]

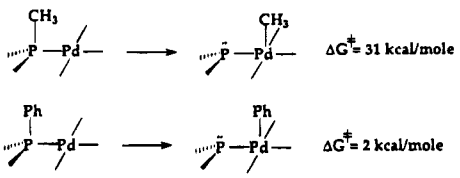



(18)

These rearrangements are undoubtedly related to reported cases where (1) a phenyl[27a] or an allyl[27b] migrates from a phosphine ligand to a metal, (2) an allyl migrates from palladium to phosphorus,[28] and (3) a phenyl from $PPh_3$ is incorporated into coupling products.[24a,29] Similar processes are surely involved in palladium-catalyzed aryl group exchange among phosphines[30] and in the breakdown of phosphine ligands in many reactions catalyzed by their complexes.[31]

The irreversibility of the rearrangement in eqs 5 and 7 shows that the Ph−Pd and Me−P bonds are collectively stronger than the Me−Pd and Ph−P bonds. The average Ph−P bond strength in $Ph_3P$ is 71 kcal/mol, while the average Me−P bond strength in $Me_3P$ is 65 kcal/mol.[32] If we assume that (1) the Me−P bond strength in $MePh_2P$ is also 65 kcal/mol, (2) the relative Ph−P ($Ph_3P$) and Me−P ($MePh_2P$) bond strengths are unaffected by coordination, and (3) the equilibrium constant for the rearrangement is at least 100, the Ph−Pd bond strength must exceed the Me−Pd bond strength by at least 9 kcal/mol. This result is consistent with the existing thermochemical data[33] and with the rearrangement of $[Re(CO)_4(CH_3)(C(O)Ph)]^-$ to $[Re(CO)_4(Ac)Ph]^-$.[34]

Extended Hückel calculations suggest that methyl migration from an $H_2PMe$ ligand to palladium is feasible, and indicate a negligible barrier to phenyl migration (eq 19).[35]




(19)

Our conclusion that the rearrangement in reactions 5 and 7 does *not* involve a phosphonium salt in $CD_2Cl_2$ or benzene is interesting in view of Segelstein, Butler, and Chenard's report[26] that a tetraaryl phosphonium salt *can* enter into the catalytic cycle with $Pd(CH_3CN)_2Cl_2$ and a stannane in DMF. No other arylating agent was present during their experiment, so it is not clear whether $Ar_4P^+$ would transfer an aryl group to palladium in the presence of a conventional substrate ArX; in any case their experiment does not establish that $Ar_4P^+$ *is formed* under catalytic conditions.

The failure of added $Ph_3P$ to inhibit reaction 5 shows that ligand *dissociation* (eq 10) either does not occur or does not increase the rate of the rearrangement. There is no obvious explanation for the difference between this result and the report of Kong and Cheng[23] that 1 equiv of $PPh_3$ led to "a nearly total inhibition of the aryl exchange" of *trans*-$(Ph_3P)_2Pd(p\text{-tolyl})I$ (eq 15).

(23) Kong, K.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6313.
(24) (a) O'Keefe, D. F.; Dannock, M. C.; Maruccio, S. M. *Tetrahedron Lett.* **1992**, *33*, 6679. A similar rearrangement has been observed during a Heck coupling reaction: (b) Hunt, A. R.; Stewart, S. K.; Whiting, A. *Tetrahedron Lett.* **1993**, *34*, 3599.
(25) (a) Wallow, T. I.; Seery, T. A. P.; Goodson III, F. E.; Novak, B. M., *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1994**, *35*, 710. (b) Wallow, T. I.; Novak, B. M. *J. Org. Chem.* **1994**, *59*, 5034.
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(35) Ortiz, J. V.; Havias, Z.; Hoffmann, R. *Helv. Chim. Acta* **1984**, *67*, 1.

The scope of such metal−ligand exchange reactions is surely important in determining the scope of palladium-catalyzed coupling. Rearrangement will not only lead to alternate coupling products (as in eqs 11−13) but may, if the rearranged complex is slower to undergo transmetalation and reductive coupling, decrease the overall coupling rate. Indeed, the coupling by the rearranged phenyl complex in reaction 11 is much slower than the corresponding coupling by its methyl palladium predecessor (reaction 2).

Table 1 combines our own observations with those elsewhere[23−26] about the exchange of various organic ligands on palladium with the phenyl groups of $Ph_3P/Ph_3As$ ligands (eq 14). It is unclear whether these observations result from kinetic or thermodynamic control, but aryl groups with more electron-withdrawing substituents seem to prefer palladium over phosphorus. (Compare for example entries 1−4 with entries 5−8.) Aryl phosphines with electron-*donating* substituents should thus be more resistant to such exchange reactions.

It is unclear whether resistance to such rearrangements is a factor in the ability of tri(2-furyl)phosphine to increase the rate of Pd-catalyzed coupling reactions.[6e,9d,13] Table 1 shows (entries 13 and 15) the migration of 2-thienyl and 2-furyl ligands from palladium to phosphorus. However, the electron-withdrawing effect of the heterocyclic substituents in tri(2-thienyl)- and tri(2-furyl)phosphine is well established,[13a,36] suggesting a preference for palladium over phosphorus. Indeed, Segelstein, Butler, and Chenard have reported[26] substantial yields of a rearrangement-derived coupling product when $(2\text{-furyl})_3P$ is used with $Pd(CH_3CN)_2Cl_2$ to effect coupling between *p*-anisyl bromide and a stannane in DMF. Probably phenyl/2-furyl exchange between Pd and P is approximately thermoneutral and can occur in either direction.

**Note Added in Proof.** Similar rearrangements that are also unaffected by added free phosphine, and thus do not involve dissociative pre-equilibria like those suggested in ref 23, have just been reported: Barañano, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937.

## Experimental Section

**General Methods.** All reactions were performed under an argon atmosphere by Schlenk techniques; the argon used was purified by passage through a column of reduced BASF R311 and then through a column of Linde 5Å molecular sieves. All NMR solvents and internal standards were dried over Na/benzophenone unless otherwise noted; $CD_2Cl_2$ was dried over $P_4O_{10}$, degassed by successive freeze−pump−thaw cycles, and vacuum transferred. Residual $^1H$ shifts in the deuterated solvents were used as the internal reference in $^1H$ NMR spectra; $^{31}P$ NMR spectra were referenced to external 85% phosphoric acid. GC experiments were run on a Hewlett-Packard Model 5890A fitted with a flame ionization detector and a Hewlett-Packard 3390A computing integrator. Mesitylene was used as an internal standard in all stock solutions. The columns were (A) 30 m × 0.25 mm internal diameter with a carbowax stationary phase having a film thickness of 0.25 $\mu$ and (B) 30 m × 0.25 mm internal diameter on a J&W Scientific column DB1301 having a film thickness of 0.25 $\mu$.

Literature procedures were used to prepare (dibenzylideneacetone)$_3Pd_2(C_6H_6)$,[37] $Pd(PPh_3)_4$,[38] $Pd(PMePh_2)_4$,[20c] *trans*-$MePd(PPh_3)_2I$ (**1**),[15c,20c,39] *trans*-$MePd(PMePh_2)_2I$ (**5**),[15c,40] *trans*-$(CD_3)Pd(PMePh_2)_2I$ (**5**-$d_3$),[15c,20a] *trans*-$PhPd(PPh_3)_2I$ (**2**),[15c,20b] *trans*-$PhPd(PMePh_2)_2I$ (**3**),[21,39] *trans*-(*p*-tolyl)$Pd(PPh_3)_2I$,[20b,39] *trans*-(*p*-tolyl)$Pd(P(C_6D_5)_3)_2I$,[20b,39] *trans*-(*p*-$IC_6H_4$)-$Pd(P(C_6D_5)_3)_2I$ (**17**),[20b] *trans*-(*p*-$O_2NC_6H_4$)$Pd(P(C_6D_5)_3)_2I$ (**16**),[20b] *trans*-(*p*-$AcC_6H_4$)$Pd(P(C_6D_5)_3)_2I$ (**15**),[20b] *trans*-(*p*-$FC_6H_4$)$Pd(P(C_6D_5)_3)_2I$ (**18**),[41] *trans*-$PhCH_2Pd(PPh_3)_2Cl$ (**21**),[42] *trans*-$NCCH_2Pd(PPh_3)_2Cl$ (**20**),[43] tri(2-furyl)phosphine,[44] *p*-iodobenzene-$d_1$ and *p*-bromobenzene-$d_1$,[45] (*p*-anisyl)tributyltin,[46] (*p*-tolyl)tributyltin,[47] phenylethynyltributyltin,[47] (*E*)-$\beta$-styryltributyltin,[48] and 4-methoxybiphenyl.[49] $Pd(P(p\text{-}C_6H_4D)_3)_4$ was prepared from $P(p\text{-}C_6H_4D)_3$ in the same way as $Pd(PPh_3)_4$ from $PPh_3$, and **1**-$d_6$ from $Pd(P(p\text{-}C_6H_4D)_3)_4$ in the same way as **1** from $Pd(PPh_3)_4$; **1**-$d_{30}$ was similarly prepared from $PPh_3$-$d_{15}$. The deuterated **2**-$d_1$ and **3**-$d_1$ were prepared from *p*-$IC_6H_4D$ and the appropriate $PdL_4$ in the same way as **2** and **3**.

NMR spectra not previously reported: for **1**, $^{31}P\{^1H\}$ ($C_6D_6$) $\delta$ 31.5 (s); for **5**, $^1H$ (corrected) ($C_6D_6$) $\delta$ .46 (t, J = 6 Hz, 3H), 2.36 (apparent triplet, spacing = 3 Hz, 3H), 7.00 (m, 12H), 7.48 (m, 8H); $^{31}P\{^1H\}$ ($C_6D_6$) $\delta$ 12.9 (s); for tri(2-furyl)phosphine, $^1H$ ($C_6D_6$) $\delta$ 5.96 (m, 3H), 6.70 (m, 3H), 7.17 (m, 3H); $^{13}C$ ($C_6D_6$) $\delta$ 110.9 (d), 121.3 (d), 147.5 (d), 149.6 (d); for *p*-$IC_6H_4D$, $^1H$ ($CDCl_3$) $\delta$ 7.12 (d, J = 8Hz, 2H), 7.39 (d, J = 8Hz, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 122.5(s), 126.6(t), 129.9-(s), 131.5(s); for *p*-$BrC_6H_4D$, $^1H$ NMR ($CDCl_3$) $\delta$ 7.01 (d, J = 8Hz, 2H), 7.62 (d, J = 8Hz, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 94.3(s), 127.1(t), 130.1(s), 137.4(s); for (*p*-anisyl)tributyltin, $^{13}C$ NMR ($CDCl_3$) $\delta$ 9.6, 13.7, 27.4, 29.1, 54.9, 113.9, 132.0, 137.5, 159.7; for (*p*-tolyl)tributyltin, $^{13}C$ NMR ($CDCl_3$) $\delta$ 9.5, 13.7, 21.4, 27.4, 29.1, 128.8, 136.4, 137.6, 137.9; for *trans*-(*p*-tolyl)$Pd(PPh_3)_2I$, $^{31}P\{^1H\}$ ($C_6D_6$): $\delta$ 23.7 (s); for **18**, $^1H$ NMR ($C_6D_6$) $\delta$ 6.09 (t, J = 9Hz, 2H), 6.59 (td, 2H), 6.97−6.99 (m, 18H), 7.66−7.73 (m, 12H); for **20**, $^{31}P\{^1H\}$ NMR ($C_6D_6$) $\delta$ 27.7 (s).

***trans*-Iodo(1,1,1-trifluoroethyl)bis(triphenylphosphine))palladium-(II) (19)** was prepared by a procedure analogous to that described in the literature.[39] $^1H$ NMR ($C_6D_6$) $\delta$ 2.02 (m, 3H), 6.89−7.06 (m, 18H), 7.87−7.94 (m, 12H). $^{31}P\{^1H\}$ NMR ($C_6D_6$) $\delta$ 27.3 (s). Anal. Calcd for $C_{38}H_{32}F_3IP_2Pd$: C, 54.28; H, 3.84; P, 7.37. Found: C, 54.15; H, 3.92; P, 7.47.

***trans*-Iodotolylbis(diphenylmethylphosphine)palladium(II)** was prepared by stirring 0.399 g (0.4 mmol) of $Pd(PMePh_2)_4$ with 0.480 g (2.2 mmol) of 4-iodotoluene in 30 mL benzene under argon for 15 min at room temperature. The pale yellow solution was evaporated under reduced pressure and the residue was washed with pentane to give 0.235 g (74%) of a white complex: $^1H$ NMR ($C_6D_6$) $\delta$ 6.45 (d, J = 8Hz, 2H), 6.81 (d, J = 8Hz, 2H), 6.99 (m, 12H), 7.56 (m, 8H); $^{31}P\{^1H\}$ NMR ($C_6D_6$) $\delta$ 6.5 (s) Anal. Calcd for $C_{33}H_{33}IP_2Pd$: C, 54.68; H, 4.59; P, 8.55. Found: C, 54.80; H, 4.63; P, 8.66.

***trans*-Iodotolylbis(triphenylarsine)palladium(II) (23)** was prepared by charging a 250 mL Schlenk flask with 0.116 g (0.5 mmol) of $(dba)_3Pd_2(C_6H_6)$ and 1.53 g (5.0 mmol) of triphenylarsine. This flask was evacuated and flushed with argon three times, and 140 mL of benzene was added by syringe. The purple solution was stirred for 30 min until a color change to yellow was complete. A solution of 1.41 g (6.5 mmol) of 4-iodotoluene in 10 mL of benzene was added by syringe to the reaction mixture. After stirring for 20 min, the transparent green solution was evaporated under reduced pressure, and the residue was washed with pentane to give 0.677 g (73%) of the product: $^1H$ NMR ($C_6D_6$) $\delta$ 1.93 (s, 3H), 1.97 (s, 3H), 6.19 (d, J = 8Hz, 2H), 6.49 (d, J = 8Hz, 2H), 6.76 (d, J = 8Hz, 2H), 6.97 (m), 7.30 (d, J = 8Hz, 2H), 7.41 (m), 7.66 (m). $^1H$ NMR ($C_6D_6$, in the presence of added $AsPh_3$ to suppress decomposition) $\delta$ 1.93 (s, 3H), 6.19 (d, J = 8Hz, 2H), 6.76 (d, J = 8Hz, 2H), 7.04 (bs), 7.38 (bs), 7.66 (bs). Anal. Calcd for $C_{43}H_{37}IAs_2Pd$: C, 55.13; H, 3.98. Found: C, 55.17; H, 3.99.

***trans*-Iodo(2-thienyl)bis(triphenylphosphine)palladium(II) (22).** A solution of 0.305 g (0.3 mmol) of $Pd(PPh_3)_4$ and 0.380 g (1.8 mmol)

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of 2-iodothiophene in 100 mL benzene under argon was stirred for 20 min at room temperature. The pale yellow solution was evaporated under reduced pressure, and the residue was washed with pentane to give 0.159 g (72%) of a yellow complex: $^1$H NMR ($C_6D_6$) $\delta$ 6.16 (d, J = 3Hz, 1H), 6.47 (t, J = 3Hz, 1H), 6.90 (d, J = 5Hz, 1H), 6.98 (m, 18H), 7.76 (m, 12H); $^{31}$P{$^1$H} NMR ($C_6D_6$) $\delta$ 22.9 (s). Anal. Calcd for $C_{40}H_{33}ISP_2Pd$: C, 57.13; H, 3.96; P, 7.37. Found: C, 57.03; H, 4.09; P, 7.27.

***trans*-Iodo(2-furyl)bis(triphenylphosphine)palladium(II) (24).** 2-Iodofuran was used instead of 2-iodothiophene in the procedure just described to give 0.156 g (62%) of a yellow complex: $^1$H NMR ($C_6D_6$) $\delta$ 5.46 (d, J = 3Hz, 1H), 5.75 (t, J = 2Hz, 1H), 7.07 (d, J = 4Hz, 1H). $^{31}$P{$^1$H} NMR ($C_6D_6$) $\delta$ 22.0 (s). Anal. Calcd for $C_{40}H_{33}IOP_2Pd$: C, 58.24; H, 4.03; P, 7.51. Found: C, 58.16; H, 4.05; P, 7.44.

**Methyltriphenylphosphonium triflate** was prepared from 0.517 g (1.9 mmol) of triphenylphosphine and 250 $\mu$L (2.2 mmol) of methyl triflate in 50 mL of hexanes. The methyl triflate was added dropwise over a period of 10 min and then allowed to stir overnight. A white solid was isolated and washed with hexanes to give 0.668 (80%) of the product: $^1$H NMR ($CD_2Cl_2$) $\delta$ 2.85 (d, J = 13Hz, 3H), 7.60−7.75 (m, 18H), 7.83−7.88 (m, 12H); $^{31}$P{$^1$H} NMR ($CD_2Cl_2$) $\delta$ 21.8 (s) [(CDCl3) $\delta$ 22.2 (s)]; $^{13}$C NMR ($CDCl_3$) $\delta$ 9.0 (d), 118.6 (d), 120.6 (q), 130.3 (d), 132.8 (d), 135.01 (d). Anal. Calcd for $C_{20}H_{18}F_3O_3PS$: C, 56.34; H, 4.26; P, 7.26. Found: C, 56.26; H, 4.30; P, 7.13.

**Tri(*p*-deuteriophenyl)phosphine.** The *p*-deuteriophenyl magnesium bromide was prepared from 5.355 g (0.03 mol) of *p*-deuteriobromobenzene and 0.913 g (0.04 mol) of magnesium turnings in 39 mL of tetrahydrofuran. The magnesium turnings were activated with several iodine crystals. The Grignard solution was cooled to −8 °C, and 950 $\mu$L (0.01 mol) of $PCl_3$ in 10 mL of THF was added dropwise. The solution then was stirred for 1 h at room temperature, quenched with 10 mL of water at 0 °C, and extracted with 2 × 50 mL diethyl ether. The organic layer was collected, dried over $MgSO_4$, and concentrated to give a white solid. Further purification by flash chromatography gave 1.09 g (38%) of the product: $^1$H NMR ($C_6D_6$) $\delta$ 7.03 (d, J = 8Hz, 2H), 7.38 (t, J = 8Hz, 2H); $^{31}$P{$^1$H} NMR ($C_6D_6$) $\delta$ −4.6 (s).

**4-(*tert*-Butyl)phenyltributyltin.** A solution of 4-*tert*-butylphenyl magnesium bromide was prepared from 4.08 g (0.02 mol) of 4-*tert*-butyltoluene and 0.52 g (0.02 mol) of magnesium turnings in 46 mL of tetrahydrofuran. The magnesium turnings were activated with several iodine crystals. To the Grignard solution was added 5.45 g (0.02 mmol) of tributyltin chloride in 20 mL of tetrahydrofuran to form a transparent tinted yellow solution. The reaction mixture was heated at the reflux temperature for 18 h. The reaction mixture was cooled and quenched with saturated aqueous ammonium chloride and then extracted with 2 × 50 mL of $NH_4Cl$ and 1 × 50 mL of brine. The organic layer was dried over $MgSO_4$, concentrated, and distilled by Kugelrohr to yield 6.48 g (80%) of (4-*tert*-butylphenyl)tributyltin: bp = 130 °C (0.005 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ .88−1.59 (m, 27H), 1.33 (s, 3H), 7.37 (d, J = 8Hz, 2H), 7.42 (d, J = 8Hz, 2H); $^{13}$C NMR ($CDCl_3$): $\delta$ 9.5, 13.7, 21.4, 27.4, 29.1, 31.3, 34.5, 124.9, 136.3, 138.2, 150.7. Anal. Calcd for $C_{22}H_{40}Sn$: C, 62.43; H, 9.53. Found: C, 62.67; H, 9.67.

**Phosphine Exchange between Palladium Complexes.** The following procedure is typical. A 50 mL Schlenk flask was charged with 0.026 g (0.03 mmol) of *trans*-$PhPd(PPh_3)_2PdI$ (**2**) and with 0.021 g (0.03 mmol) of *trans*-$PhPd(PMePh_2)_2PdI$ (**3**). The Schlenk flask was evacuated and flushed with argon three times and then brought into an inert atmosphere box. The sample was prepared in the box by adding ca. 40 mL of $C_6D_6$ to the flask. Approximately 500 $\mu$L of the mixture was removed and placed into a sealable 5 mm NMR tube. The NMR tube was removed from the glovebox and sealed under vacuum. The sample was kept frozen until the $^{31}$P{$^1$H} and $^1$H NMR spectra were acquired.

**Rearrangement of Palladium(II) Complexes.** The samples for all studies in Table 1 were prepared as for the exchange studies described above. Each was placed into a constant temperature bath from which it was periodically removed, frozen, and then thawed for $^{31}$P{$^1$H} and $^1$H NMR at room temperature.

**Positional Selectivity of the Rearrangement.** In a procedure identical to that just described, 0.029 g (0.04 mmol) of **1**-$d_6$ was dissolved in 3.3 mL of $C_6D_6$. Approximately 500 $\mu$L was transferred into a sealable NMR tube and then sealed under vacuum. The sample was placed into a constant temperature bath at 50 °C and monitored over time. The observed peaks at $\delta$ 6.7 and $\delta$ 24.1 in the $^{31}$P{$^1$H} NMR agreed with those of authentic samples of **2**-$d_1$ and **3**-$d_1$.

**Exclusion of Phosphonium Salt Mechanism. (a) Control Experiment.** A 50 mL Schlenk flask was charged with 0.001 g (0.001 mmol) of **1**-$d_{30}$. This flask was evacuated and flushed with argon three times and brought into the glovebox. The sample of **1**-$d_{30}$ was prepared in the glovebox by adding ca. 700 $\mu$L of $CD_2Cl_2$ to the flask. Approximately 500 $\mu$L of the solution of **1**-$d_{30}$ was removed by syringe and placed into a sealable NMR tube. The NMR tube was removed from the glovebox and sealed under vacuum. The NMR sample of **1**-$d_{30}$ was placed into a constant temperature bath at 36 °C and monitored over time by $^1$H and $^{31}$P{$^1$H} NMR.

**(b) Reaction of 1-$d_{30}$ in the Presence of [$Ph_3PMe$][OTf].** A 50 mL Schlenk flask was charged with 0.007 g (0.009 mmol) of **1**-$d_{30}$ and 0.002 g (0.005 mmol) of methyltriphenylphosphonium triflate. This flask was evacuated and flushed with argon three times and brought into the inert atmosphere box. A sample was prepared by adding ca. 900 $\mu$L of $CD_2Cl_2$ to the flask by syringe. Approximately 600 $\mu$L of the mixture was removed from the flask and placed into a sealable NMR tube. The NMR tube was removed from the glovebox and sealed under vacuum. The NMR sample of the mixture was placed into a constant temperature bath at 36 °C and monitored over time.

**Kinetic Procedure for Rearrangement. (a) Rearrangement with No Added Phosphine.** A 25 mL Schlenk flask was charged with 0.013 g (0.017 mmol) of **1**. The Schlenk flask was evacuated and flushed with argon three times and brought into the glovebox. A stock solution containing 4 $\mu$L of toluene in 5 mL of $C_6D_6$ was prepared, and 1 mL was transferred by syringe to the Schlenk flask containing **1**. The solution of **1** was allowed to mix, and 500 $\mu$L was placed into a sealable NMR tube by syringe. The NMR tube was removed from the glovebox, sealed under vacuum, and frozen.

The sample was thawed, and $^1$H and $^{31}$P{$^1$H} NMR spectra were recorded prior to the start of each experiment. The NMR tube of the sample of **1** was then placed into a constant temperature bath at 70 °C and periodically checked by $^1$H NMR. Each $^1$H NMR spectrum was obtained from 32 transients (32K points apiece), with a 7.5 s relaxation delay in order to obtain accurate relative intensities. The time-averaged FID was zero filled to 64K before Fourier transformation. The disappearance of **1** was monitored by following the decrease of the methyl peak of **1** relative to that of the toluene standard. The reactions showed approximate first-order behavior over 10 h, with $k = 6.5(3) \times 10^{-5}$ s$^{-1}$.

**(b) Rearrangement with Added Phosphine.** The procedure was like that just described. A 500 $\mu$L NMR sample was prepared from a 0.014 g (0.02 mmol) of **1** and 0.028 g (0.11 mmol) of $Ph_3P$ in a 1 mL stock solution of toluene in $C_6D_6$. The reactions showed approximate first-order behavior over 10 h, with $k = 7.1(3) \times 10^{-5}$ s$^{-1}$.

**Byproducts Arising from Rearrangement during Coupling Reactions.** Coupling reactions were run in a two-necked 50 mL flask with a condenser, gas inlet adapter, and a syringe inlet adapter. It was charged (for example) with 0.027 g (0.07 mmol) of 4-methoxyphenyltributyltin and then degassed by a freeze−pump−thaw cycle; 7 mL of a 0.01 M hexamethylbenzene (internal standard) stock solution was then added. A second 50 mL Schlenk flask was charged with 0.037 g (0.05 mmol) of **1**, evacuated, and flushed with argon, and 8 mL of the hexamethylbenzene stock solution in benzene was added. The solution of **1** was transferred to the reaction vessel containing the tin reagent; the flask that had contained **1** was then rinsed with 10 mL of the stock solution. After the reaction had stirred for 24 h at 50 °C, 1 mL was removed by syringe and analyzed by GC.

**Acknowledgment.** This work has been supported by NSF Grants CHE-8703218 (to J.K.S.) and CHE-9120454 (to J.R.N.). The authors are grateful to Prof. L. S. Hegedus for suggesting the phosphonium cation mechanism. The authors thank Mr. Daniel Gately and Drs. David L. Ramage and Frank Rix for their assistance in the preparation of this manuscript.

JA9426094