An Aryl Exchange Reaction with Full Retention of Configuration of the Complexes: Mechanism of the Aryl Exchange between [PdR_2L_2] Complexes in Chloroform (R = Pentahalophenyl, L = Thioether)

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The complexes [$Pd(3,5\text{-}C_6Cl_2F_3)_2L_2$] and [$Pd(C_6F_5)_2L_2$] (L = SC_4H_8 (tht), or SMe_2) react in CCl_3D to give a mixture also containing the heteroaryl products [$Pd(3,5\text{-}C_6Cl_2F_3)(C_6F_5)L_2$], whereas for L = PPh_3, $AsPh_3$, 2-picoline, 4-picoline, or $^1/_2$COD, this exchange is not observed. The ^{19}F NMR kinetic study supports that the scrambling of the aryl groups takes place with retention of configuration at both Pd centers via a triply-bridged binuclear activated complex [$L(C_6Cl_2F_3)Pd(\mu\text{-}C_6Cl_2F_3)(\mu\text{-}C_6F_5)(\mu\text{-}L)Pd(C_6F_5)L$]‡. The aryl double bridge is supported by a bridging S-donor ligand facilitating an otherwise difficult exchange (not observed for other weak L ligands, such as picolines, lacking a second lone pair). This constitutes the first reported example of reversible migration of σ-C-bonded groups between bis-organo Pd(II) complexes proceeding without *cis*−*trans* isomerization. The isomerization process is also observed, occurring at a much slower rate.

Introduction

The alkyl or aryl transfer from main-group or transition-metal organometallics to transition-metal halo complexes has been known for many years and is used as a preparative method of σ-C organopalladium(II) complexes.[1] The process is also involved in the Pd-assisted cross-coupling reactions of organic halides RX and main-group organometallics MR′ (Scheme 1, main cycle) *via* $PdRR'L_2$ (**II**), which eventually reductively eliminates the cross-coupling product R−R′.[2]

Aryl-for-aryl and aryl-for-alkyl exchanges have been detected between $PdRXL_2$ complexes (**I**) and arylating main-group reagents.[2e,3] These processes seem to be responsible for the formation of undesired homocoupling products RR or R′R′ in the cross-coupling reactions, as they give rise to PdR_2L_2 or PdR'_2L_2 complexes (**IV**) (Scheme 1, side path).

Other exchanges between organopalladium(II) intermediates affecting the selectivity of the coupling process have been reported. Thus, Yamamoto *et al.* have found the exchange of R groups in the reaction between [PdR_2L_2] and PdR′XL_2 (L = phosphine),[2c,3b] as well as in the *trans*−*cis* spontaneous isomerization of $PdMe_2(PR_3)_2$ complexes, which was studied by isotopic labeling.[4] $MgR_2(ether)_n$ reagents also exchange with [PdR_2L_2] and simultaneously promote the isomerization of the Pd(II) complex.[5] In each case, a dissociation of a neutral ligand is proposed prior to the formation of a binuclear complex of the types **V**−**VII** (Chart 1).

The methyl-for-halogen exchange was studied by Puddephatt *et al.* in a systematic study of the symmetrization reactions of PtX_2L_2 and PtR_2L_2.[6] A mechanism without ligand dissociation involving intermediate **VIII** (Chart 2) was established for phosphine

Scheme 1

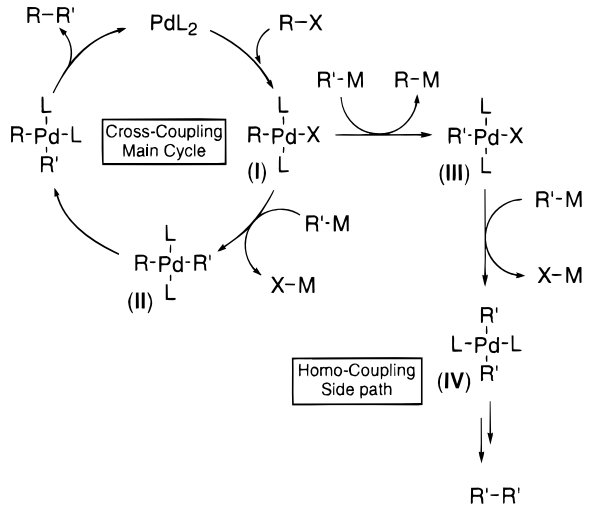

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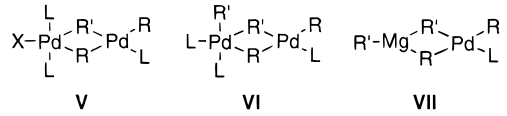
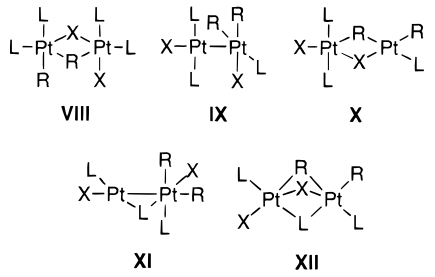
Chart 1



V VI VII

Chart 2



VIII IX X XI XII

complexes, whereas prior ligand dissociation was proposed for SMe_2 complexes. In the latter case, it was not possible to decide between several probable intermediates **IX**−**XII**.

In the course of our investigation of the dynamic behavior in solution of bis(perhaloaryl)palladium(II) complexes, we found that the complexes $[Pd(C_6Cl_2F_3)_2(tht)_2]$ ($C_6Cl_2F_3$ = 3,5-dichlorotrifluorophenyl; tht = tetrahydrothiophene) and $[Pd(C_6F_5)_2(tht)_2]$ react reversibly in $CDCl_3$ solution to give $[Pd(C_6Cl_2F_3)(C_6F_5)(tht)_2]$ *without* isomerization. The process is much faster than the spontaneous *trans*-to-*cis* isomerization found in $[Pd(C_6F_5)_2(tht)_2]$ (for which a dissociative mechanism has been proposed),[7] suggesting a new type of aryl exchange in the chemistry of d^8 square-planar complexes. Here, we report a detailed mechanistic study on the aryl-exchange reaction between complexes $[PdR_2L_2]$ (R = C_6F_5, $C_6Cl_2F_3$). The stability of these complexes toward other possible reactions, e.g., reductive elimination,[8] facilitates this study.

Results

The complexes $[PdR_2L_2]$ (L = tht) undergo three processes in $CDCl_3$: (i) neutral ligand exchange (within seconds); (ii) aryl exchange (within hours); and (iii) *trans*−*cis* isomerization (within days). This difference in rate allowed us to carry out kinetic studies on the second process using NMR techniques.

Exchange of R Groups between Complexes $[PdR_2L_2]$. Mixtures of $[Pd(C_6Cl_2F_3)_2(tht)_2]$ and $[Pd(C_6F_5)_2(tht)_2]$ (whether *cis* or *trans*) evolve in $CDCl_3$ to a mixture containing also the heteroaryl products $[Pd(C_6Cl_2F_3)(C_6F_5)(tht)_2]$. The most noticeable feature in these reactions is that the aryl-exchange process occurs with retention of the *trans*−*cis* configuration at Pd. Figure 1 shows the concentration−time plot of three independent experiments involving different configurations of the starting complexes.

The reaction of a mixture of complexes *cis*-$[Pd(C_6Cl_2F_3)_2(tht)_2]$ (**1a**) and *cis*-$[Pd(C_6F_5)_2(tht)_2]$ (**1b**) (Figure 1a) shows the formation of *cis*-$[Pd(C_6Cl_2F_3)(C_6F_5)(tht)_2]$ (**1c**) only (eq 1, henceforth $R^1 = C_6Cl_2F_3$ and $R^2 = C_6F_5$).[9] The equilibrium concentrations are practically those expected from statistical considerations: 25% of **1a** + 25% of **1b** + 50% of **1c**.

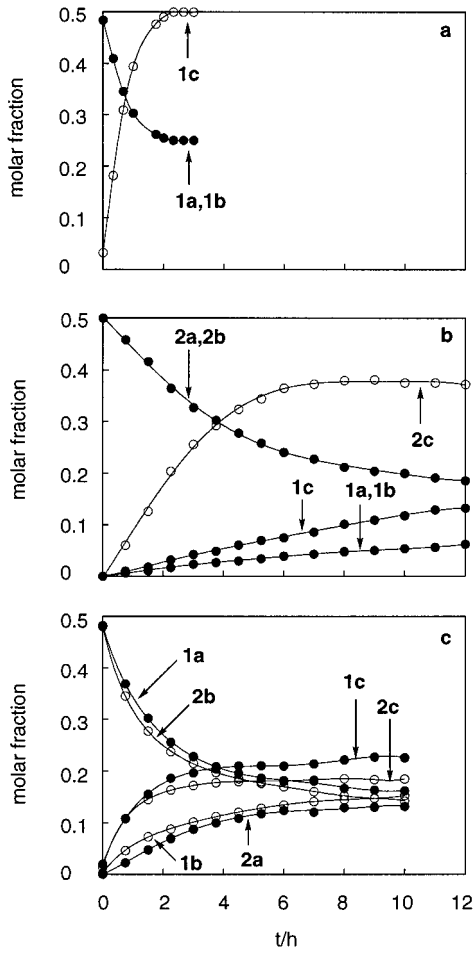
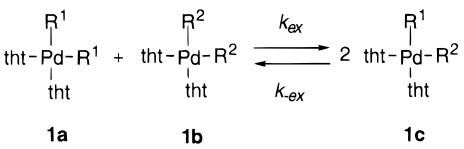
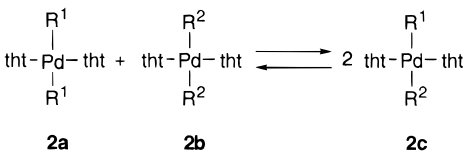


Figure 1. Concentration−time plots for the reactions between (a) *cis*-$[Pd(C_6Cl_2F_3)_2(tht)_2]$ (**1a**) and *cis*-$[Pd(C_6F_5)_2(tht)_2]$ (**1b**); (b) *trans*-$[Pd(C_6Cl_2F_3)_2(tht)_2]$ (**2a**) and *trans*-$[Pd(C_6F_5)_2(tht)_2]$ (**2b**); and (c) **1a** and **2b**. Initial concentration in each complex was 10.0 ± 0.7 mM (imposed by the low solubility of the *trans* complexes), $CDCl_3$, 320.1 ± 0.2 K. The products are *cis*-$[Pd(C_6Cl_2F_3)(C_6F_5)(tht)_2]$ (**1c**) and *trans*-$[Pd(C_6Cl_2F_3)(C_6F_5)(tht)_2]$ (**2c**).



1a **1b** **1c** (1)

The *trans* complexes **2a** and **2b** (Figure 1b and eq 2) yield *trans*-$[Pd(C_6Cl_2F_3)(C_6F_5)(tht)_2]$ (**2c**) first.[9] As the



2a **2b** **2c** (2)

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(9) The structures of **1c** and **2c** have been assigned by comparison of the ^{19}F NMR chemical shift values with those of the *cis* (**1a**,**b**) and *trans* (**2a**,**b**) complexes. Moreover, in the case of the *cis* complex **1c**, through-space $^{19}F-^{19}F$ couplings between the $C_6Cl_2F_3$ and C_6F_5 rings produce multiplet signals for the F_{ortho} nuclei, which is not observed in *trans*-**2c**. See: Albéniz, A. C.; Casado, A. L.; Espinet, P. *Organometallics* **1997**, *16*, 5416.

Table 1. Second-Order Rate Constants k_{ex} for the Exchange of Aryl Groups between *cis*-[Pd(C$_6$Cl$_2$F$_3$)$_2$(tht)$_2$] (1a) and *cis*-[Pd(C$_6$F$_5$)$_2$(tht)$_2$] (1b)[a]

entry	[**1a**]/10^{-3} mol L^{-1}	*T*/K	[tht]$_{added}$/10^{-3} mol L^{-1}	k_{ex}/10^{-3} L mol^{-1} s^{-1}
1	40.0 ± 0.4	330.8 ± 0.2	0	7.5 ± 0.4
2	40.0	324.8	0	3.65 ± 0.18
3	40.0	320.1	0	1.90 ± 0.09
4	40.0	320.1	2.94 ± 0.09	0.096 ± 0.005
5	40.0	320.1	3.43 ± 0.10	0.084 ± 0.004
6	40.0	320.1	4.90 ± 0.13	0.055 ± 0.003
7	40.0	320.1	7.8 ± 0.2	0.0350 ± 0.0017
8	40.0	314.4	0	1.04 ± 0.05
9	40.0	309.6	0	0.77 ± 0.04
10	30.0 ± 0.4	320.1	0	3.4 ± 0.2
11	20.0 ± 0.3	320.1	0	6.0 ± 0.3
12	15.0 ± 0.3	320.1	0	12.0 ± 0.7
13	10.0 ± 0.3	320.1	0	20.5 ± 1.4
14	10.0	320.1	0	11.8 ± 0.9[c]
15	10.0	320.1	0	4.2 ± 0.3[d]

[a] Equimolecular mixtures in CCl_3D. [b] Estimated from the initial reaction rate between **1a** and **2b**. [c] The same for **2a** and **2b**.

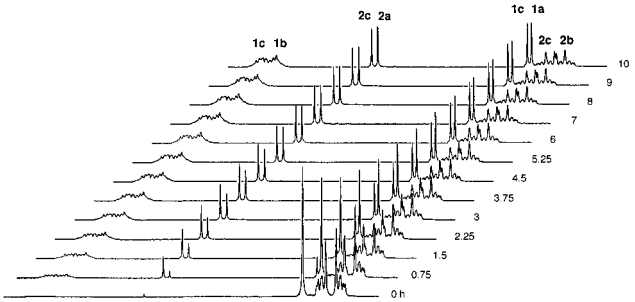
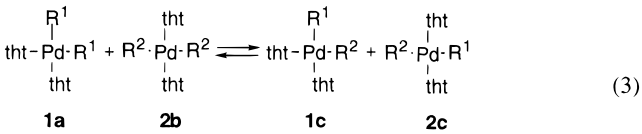


Figure 2. ^{19}F 282 MHz NMR spectra sequence (−116 to −119 ppm region) for the reaction of *cis*-[Pd(C$_6$Cl$_2$F$_3$)$_2$(tht)$_2$] (**1a**, 10^{-2} M) and *trans*-[Pd(C$_6$F$_5$)$_2$(tht)$_2$] (**2b**, 10^{-2} M) in CCl_3D at 320.1 K.

reaction progresses, the initial *trans* mixture slowly isomerizes and *cis* products (**1a**, **1b**, and **1c**) are detected. This clearly shows that the isomerization is a slower process that occurs independently from the aryl exchange.[7]

Finally, a mixture of **1a** (*cis*) and **2b** (*trans*) generates **1c** and **2c** at similar rates at an early stage of the reaction (Figure 1c, Figure 2). Later, the isomerization products **1b** and **2a** are formed. Note that the *trans* complex **2a** is produced faster than expected from direct *cis*−*trans* isomerization of **1a** (this isomerization is undetectable, as shown in Figure 1a). These observations suggest the occurrence of three concurrent exchanges with retention of configuration (eq 3−5). As



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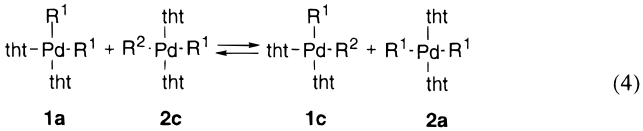

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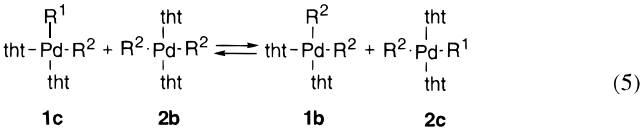


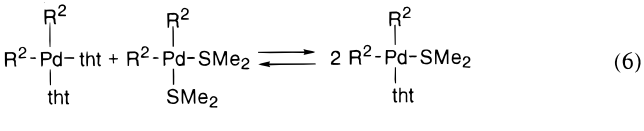
(5)

shown in Table 1 (entries 13−15), the tht *cis* complexes **1** exchange faster than the *trans* complexes **2** and the *cis* (**1**) + *trans* (**2**) mixture shows a rate almost halfway between the other two.

The complexes *cis*-[Pd(C$_6$Cl$_2$F$_3$)$_2$(SMe$_2$)$_2$] (**3a**) and *cis*-[Pd(C$_6$F$_5$)$_2$(SMe$_2$)$_2$] (**3b**) exchange their aryl groups giving *cis*-[Pd(C$_6$Cl$_2$F$_3$)(C$_6$F$_5$)(SMe$_2$)$_2$] (**3c**) at a rate clearly faster than the tht complexes. On the contrary, no aryl exchange was found between *cis*-[Pd(C$_6$Cl$_2$F$_3$)$_2$L$_2$] (L = 2-pic, **4a**; 4-pic, **5a**; 1,5-cyclooctadiene (COD), **6a**) and *cis*-[Pd(C$_6$F$_5$)$_2$L$_2$] (L = 2-pic, **4b**; 4-pic, **5b**; COD, **6b**) or between *trans*-[Pd(C$_6$Cl$_2$F$_3$)$_2$L$_2$] (L = 4-pic, **7a**; PPh$_3$, **8a**; AsPh$_3$, **9a**) and *trans*-[Pd(C$_6$F$_5$)$_2$L$_2$] (L = 4-pic, **7b**; PPh$_3$, **8b**; AsPh$_3$, **9b**). This suggests a clear-cut influence of the ancillary ligand L on the aryl-exchange process.

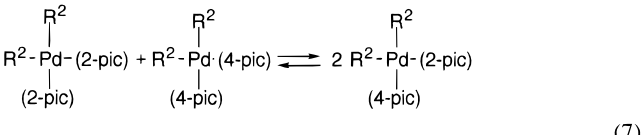
Ligand dissociation is likely to be needed in order to allow for the formation of R bridges. In fact, the addition of tht slowed down the reaction between **1a** and **1b** (Table 1). The ease of ligand dissociation was tested by checking the ease of L exchange between neutral complexes.

In the case of the thioether complexes, the neutral ligand dissociation is clearly faster than the aryl groups exchange. In reaction 6, the exchange of thioether, which necessarily involves ligand dissociation, takes place immediately after both reagents are mixed whereas the aryl exchange between the same complexes needs hours for completion. Also, the picoline complexes **4** and



(6)

5 exchange their neutral ligands quite fast (eq 7, the *ca.* 1:1:2 equilibrium is reached in about 1 h at room temperature) but, as stated above, they do not exchange aryl groups.



(7)

In summary, whereas the neutral ligand exchange is a process common to picoline and thioether complexes,

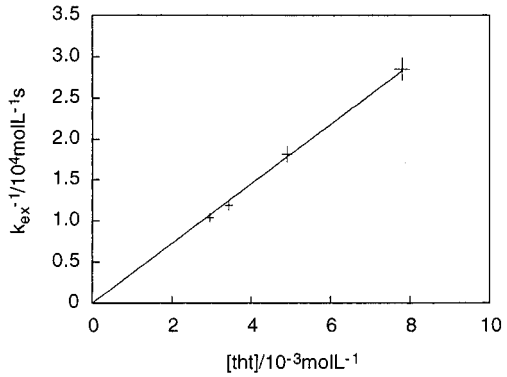
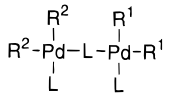


Figure 3. Retardation effect of the addition of tht on the aryl-exchange rate *cis*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (**1a**, 4×10^{-2} mol L^{-1}) and *cis*-[Pd(C_6F_5)$_2$(tht)$_2$] (**1b**, 4×10^{-2} mol L^{-1}) in CCl_3D at 320.1 K.

Chart 3



A

the aryl exchange occurs only in the latter. This supports the idea that easy neutral ligand dissociation is not the only requirement for the aryl exchange to occur, but the intermolecular exchange of the aryl groups requires the availability of a second electron pair on the ancillary ligand (e.g. S-donors) in order to form L-bridged **A**-like intermediates (Chart 3). This hypothesis has been investigated further by carrying out a kinetic study on reaction 1 between tht complexes.

Kinetics on Aryl Exchange between Complexes 1a and 1b. The *cis* complexes were chosen for the kinetic studies. The reaction between *cis*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (**1a**) and *cis*-[Pd(C_6F_5)$_2$(tht)$_2$] (**1b**) in CCl_3D (eq 1) was monitored by ^{19}F NMR spectroscopy. It follows a good second-order law until the equilibrium is reached (see Experimental Section).[10] The second-order rate constants k_{ex} measured under different experimental conditions are listed in Table 1.

The aryl exchange is retarded by the addition of free tht (entries 4−7), and the reaction follows an order minus one with respect to the concentration of added tht (the slope of the ln(k_{ex}) *vs* ln([tht]$_{added}$) plot is −1.0).[10] A linear correlation between k_{ex}^{-1} and [tht]$_{added}$ is then obtained (Figure 3), the slope being $(3.63 \pm 0.09) \times 10^6$ s (for 4×10^{-2} mol L^{-1} solutions of both complexes at 320.1 K). On the other hand, the reaction rate constant k_{ex} notably decreases with the total concentration of the complexes, [Pd] = [**1a**]$_0$ + [**1b**]$_0$, when working in the absence of added tht (entries 3, 10−13). The slope of the ln(k_{ex}) *vs* ln([Pd]) plot is −1.7 (∼−3/2). Accordingly, a linear correlation between k_{ex} and $[Pd]^{-3/2}$ is obtained (Figure 4), the slope being $(6.1 \pm 0.3) \times 10^{-5}$ mol$^{1/2}$ $L^{-1/2}$ s^{-1} (at 320.1 K). Finally, the dependence on the temperature (entries 1−3, 8−9) of 4×10^{-2} mol L^{-1} samples was also analyzed by means of an Eyring plot (ln(k_{ex}/T) *vs* T^{-1}), giving the following apparent activation parameters: $\Delta H^{\ddagger}_{ex} = 91 \pm 7$ kJ mol^{-1}; and $\Delta S^{\ddagger}_{ex} = -15 \pm 25$ J K^{-1} mol^{-1}.[11]

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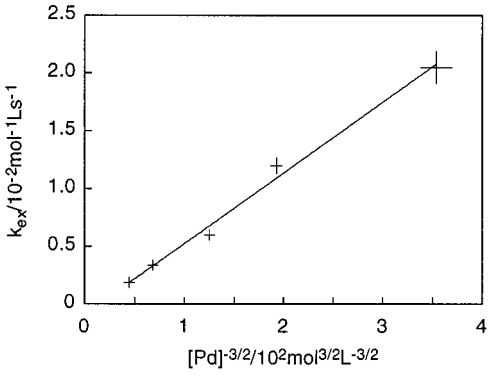
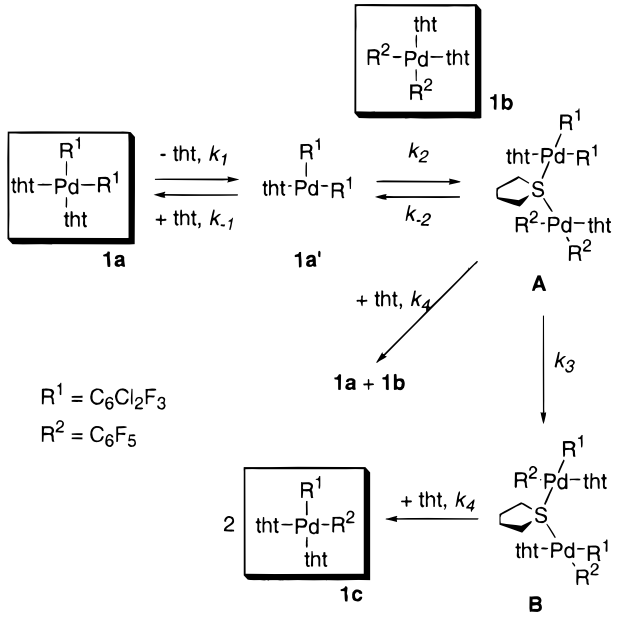


Figure 4. Self-retardation effect of the total concentration of the palladium complexes, [Pd], on the aryl-exchange rate of *cis*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (**1a**) and *cis*-[Pd(C_6F_5)$_2$(tht)$_2$] (**1b**) in CCl_3D at 320.1 K. [Pd] = [**1a**]$_0$ + [**1b**]$_0$.

Scheme 2



Discussion

The study of mixtures of [Pd(C_6F_5)$_2$L$_2$] and [Pd($C_6Cl_2F_3$)$_2$L$_2$] has revealed the occurrence of a exchange process unobservable on solutions of the pure complexes. It consists of the intermolecular exchange of aryl groups, which occurs between organopalladium(II) complexes containing thioethers (tht or SMe_2) as ancillary ligands L, but not for other ligands such as COD, phosphines, arsines, or picolines.

The mechanism given in Scheme 2 accounts for the experimental kinetic results. The dissociation of tht from complex **1a** generates a three-coordinate intermediate **1a′**, which is quickly captured by a tetracoordinate complex **1b** giving intermediate **A**. Aryl scrambling in **A** produces intermediate **B**, which is finally cleaved by tht yielding two molecules of the product, **1c**. Obviously

(11) Since the absolute value of $\Delta S^{\ddagger}$ is small, this discounts a rate-determining step purely associative (characterized by very negative $\Delta S^{\ddagger}$, see ref 7) or purely dissociative (positive values $\Delta S^{\ddagger}$, see ref 15) and suggests that several steps contribute to the observed $\Delta S^{\ddagger}_{ex}$ and $\Delta H^{\ddagger}_{ex}$ values. Under the circumstances, these values are far from having a clear interpretation (see ref 9a, Chapter 7.1). Strictly speaking, activation parameters can be calculated only for elemental steps, and for this reason we refer to them as *apparent* $\Delta S^{\ddagger}_{ex}$ and $\Delta H^{\ddagger}_{ex}$. Alternatively, the Arrhenius treatment gives the activation energy $E_a = 94 \pm 7$ kJ mol^{-1}.

the reaction can start at **1b**, but the parallel steps have not been drawn for simplicity. It should be noted that the aryl exchange is a reversible process which also takes place between molecules that are identical to each other, but it can be detected only when different aryl groups are involved.

The theoretical rate equation, eq 8, has been obtained under the steady-state assumption (see Appendix),[10] [Pd] being the total concentration of the complexes ([Pd] = [**1a**] + [**1b**] + [**1c**] = [**1a**]$_0$ + [**1b**]$_0$).

$$r_{ex} = k_{ex}[\mathbf{1a}][\mathbf{1b}], \text{ with } k_{ex} = \frac{2k_1k_2k_3}{(k_2k_4[\mathrm{Pd}] + k_{-1}k_{-2} + k_{-1}k_3)[\mathrm{tht}] + k_2k_3[\mathrm{Pd}]} \quad (8)$$

Equation 8 agrees with the experimental order minus one with respect to the concentration of tht shown in Figure 3. The concentration of tht is never zero in eq 8. In effect, if it happened to be zero, then $k_{ex} = 2k_1/[\mathrm{Pd}]$ and the aryl exchange would be controlled by the tht dissociation step (k_1) only, but we have found in the experiments carried out on neutral ligand exchange (eqs 6 and 7) that the neutral ligand dissociation is much faster than the aryl exchange. In fact, complexes **1** dissociate some tht ([tht]$_{dis}$), and the apparent [Pd]$^{-3/2}$ dependence of k_{ex} in the absence of added tht is satisfactorily explained if [tht]$_{dis} = m$[Pd]$^{1/2}$.[12] Putting this into eq 8 and assuming that the contribution of the other terms can be neglected, we obtain eq 9, which agrees with the experimental results in Figure 4.

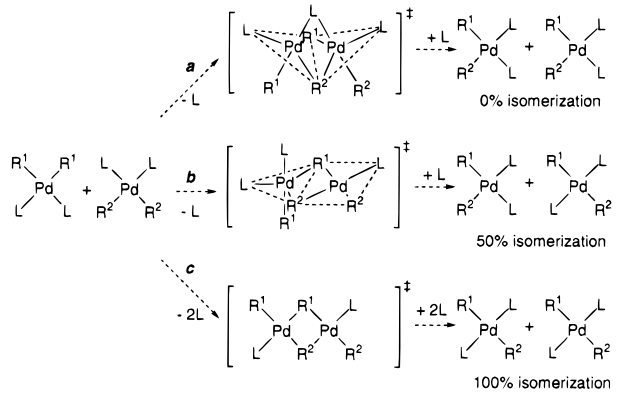
$$k_{ex} = \frac{2k_1k_3}{mk_4[\mathrm{Pd}]^{3/2}} \quad (9)$$

Analysis of Figure 4 using eq 9 gives $m = 3.6 \times 10^{-4}$ mol$^{1/2}$ L$^{-1/2}$. This indicates that the concentration of tht autodissociated from complexes **1** ([Pd] = 8×10^{-2} mol L^{-1}) is 10^{-4} mol L^{-1}, that is 0.13 mol %.

The [tht] and [Pd] terms in the denominator of eq 8 reflect two retarding effects, one due to [Pd] and the other due to [tht]. The three-coordinate intermediate **1a′** can be captured either by reagents **1a** and **1b** or by product **1c** at step k_2 ([Pd] term). Only when the **1a′** is captured by **1b** is the aryl exchange productive (via k_3) and generates **1c**. In the other cases, **1c** is not formed and the capture of **1a′** only reduces its concentration (the same applies to intermediate **1b′**). On the other hand, the effect of the addition of tht is mostly to reduce the concentration of intermediate **A** at step k_4 ([tht] term), before it rearranges to **B** (step k_3).

The preservation of the geometry along the aryl-exchange process is a very clear indication of the nature of the activated complex at which the exchange takes place. Scheme 3 shows the three different possible activated complexes for the exchange of two aryl groups. Only the first pathway, path a, passing through an activated complex formed by two pentacoordinate Pd(II) centers sharing a face explains the full preservation of the *cis* (or eventually the *trans*) geometry in both organopalladium moieties.[13] Moreover, this pathway requires a good bridging ligand L, as is the case of thioethers. The alternative paths would produce full (Scheme 3, path c) or half isomerization (Scheme 3, path b), which was not observed.

Scheme 3



Yamamoto *et al.* have proposed an exchange of the type shown in path 3b (L = PPh_3, $R^1 = R^2$ = Me) in the auto-catalyzed *cis*−*trans* isomerization of [$PdMe_2(PPh_3)_2$] complexes.[4] Most likely, the fluorophenyl complexes with ancillary ligands L other than thioethers (phosphines, arsines, picolines) could react similarly but this was not detected, meaning that their reaction is extremely slow. This suggests that the initial formation of a L-bridged intermediate **A** facilitates the formation of R-bridges for R groups that otherwise would not react at a reasonable rate by paths b or c in Scheme 3. Perhaloaryl double bridges have been previously described in stable organopalladium(II) and -platinum(II) species.[14] Bridging S-donor ligands are also well-known.[15] It is not unreasonable that other potential bridging groups containing lone pairs, such as halogen atoms,[6] might be able to play a role similar to that of tht.

The rate of exchange has a complex dependence on several steps,[16] as revealed by the appearance of several k_i in the expression for k_{ex}. The measured activation parameters must then include contributions from these steps.[11] It is found that the aryl exchange is faster between two *cis* complexes than for the *cis* and *trans* case, whereas two *trans* complexes give the slowest exchange. This can be related to the two main influences on the exchange rate. The tht dissociation (associated to k_1) must be easier for the *cis* complexes (because the tht ligand is trans to an R ligand having a high *trans* influence).[17−19] On the other hand, the scrambling of the R groups in **A** (associated with k_3) must be controlled by the energy of the transition state **‡3**. The latter depends on the position of the ligands attached to the pentacoordinate Pd(II) centers: It has

(12) For a given dissociation reaction, C = C′ + L, the equilibrium constant is $K_{dis} = x^2/([\mathbf{C}]_0 - x)$. If x is low, it reduces to $K_{dis} = x^2/[\mathbf{C}]_0$ and [L] = $x = \sqrt{K_{dis}[\mathbf{C}]_0}$. Then, the proposed square root dependence of [tht]$_{dis}$ on [Pd] is acceptable.

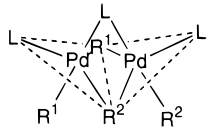
(13) For associative mechanisms on Pd(II) complexes, see: Cross, R. J. *Adv. Inorg. Chem.* **1989**, *34*, 219−292.

(14) (a) Usón, R.; Forniés, J.; Falvello, L. R.; Tomás, M.; Casas, J. M.; Martín, A.; Cotton, F. A. *J. Am. Chem. Soc.* **1994**, *116*, 7160−7165. (b) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R.; Feng, X. *J. Am. Chem. Soc.* **1993**, *115*, 4145−4154. (c) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Navarro, P. *J. Chem. Soc., Dalton Trans.* **1989**, 169−172. (d) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M. *Organometallics* **1988**, *7*, 2279−2285.

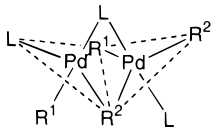
(15) Some examples of tht-bridged complexes are given, see: (a) Usón, R.; Forniés, J.; Falvelo, L. R.; Tomás, M.; Casas, J. M.; Martin, A. *Inorg. Chem.* **1993**, *32*, 5212−5215. (b) Usón, R.; Forniés, J.; Tomás, M.; Ara, I. *J. Chem. Soc., Dalton Trans.* **1989**, 1011−1016.

(16) Several definitions of the rate-determining (or controlling) step (rds or rcs) have been proposed. A brief discussion is available in ref 9a, Chapter 4.5, or ref 9b, Chapter 2.3.

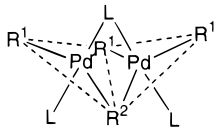
Chart 4



‡**3** from **1a** (*cis*) + **1b** (*cis*)



‡**3** from **1a** (*cis*) + **2b** (*trans*)



‡**3** from **2a** (*trans*) + **2b** (*trans*)

been shown that in trigonal-bipyramidal d^8 pentacoordinate transition metal complexes, the stronger σ donors prefer the axial sites.[20] Hence, the transition states ‡**3** (Chart 4) with the R groups (stronger donors than tht) in the axial positions must be lower in energy and more easily accessible. Thus, both effects contribute in the same sense to the reaction rates observed: *cis* + *cis* > *cis* + *trans* > *trans* + *trans*

Conclusions

The presence of ligands with two electron pairs (such as tht or SMe_2) seems to open a novel lower energy pathway for aryl exchange, which occurs with retention of configuration at both Pd centers differently from other pathways previously proposed. This occurs because the ancillary ligand helps in the formation of a triply-bridged binuclear activated complex where the aryl double bridge is supported by a bridging S-donor ligand. The possibility for halogen ligands to be playing a similar third-bridge role in exchanges between halogen-containing organometallic complexes should be considered. Also, it might be worth testing the possibility to induce exchanges with retention of configuration in other systems by the use of lone-pair-containing ligands in place of phosphines.

Experimental Section

All reactions involving organolithium reagents were carried out under N_2. Commercial 2-pic (2-picoline) and 4-pic (4-picoline) were used without further purification. Solvents were distilled using standard methods; deuteriochloroform for the kinetic samples was treated with anhydrous $MgSO_4$ and Na_2CO_3. Infrared spectra (cm^{-1}, Nujol−polyethylene) were recorded on a Perkin-Elmer FT 1720 X spectrophotometer. Combustion CHN analyses were made on a Perkin-Elmer 2400 CHN microanalyzer. ^1H and ^{19}F NMR spectra were recorded on a Bruker ARX 300 instrument equipped with a VT-100 variable-temperature probe. The temperature (± 0.2 K) was calibrated using MeOH and ethylene glycol ^1H NMR standard methods. Chemical shifts are reported in ppm from tetramethylsilane (^1H) or CCl_3F (^{19}F) in CCl_3D solutions at 293 K.

The complexes *cis*-[$PdR_2(tht)_2$] (R = $C_6Cl_2F_3$, **1a**; C_6F_5, **1b**), *trans*-[$PdR_2(tht)_2$] (R = $C_6Cl_2F_3$, **2a**; C_6F_5, **2b**), *cis*-[$PdR_2(SMe_2)_2$] (R = $C_6Cl_2F_3$, **3a**; C_6F_5, **3b**), *cis*-[PdR_2(COD)] (R = $C_6Cl_2F_3$, **6a**; C_6F_5, **6b**), *trans*-[$PdR_2(PPh_3)_2$] (R = $C_6Cl_2F_3$, **8a**; C_6F_5, **8b**), and *trans*-[$Pd(C_6F_5)_2(AsPh_3)_2$] (**9b**) were prepared as previously reported.[21,22] NMR data (some not previously reported) are as follows. **1a**: ^1H NMR δ 2.87 (m, SCH_2), 1.86 (m, CCH_2); ^{19}F NMR δ −89.98 (s, *o*-C*F*), −118.23 (s, *p*-C*F*). **1b**: ^1H NMR δ 2.90 (m, SCH_2), 1.87 (m, CCH_2); ^{19}F NMR δ −116.46 (m, *o*-C*F*), −160.20 (t, *p*-C*F*), −162.93 (m, *m*-C*F*). **2a**: ^1H NMR δ 2.66 (m, SCH_2), 1.85 (m, CCH_2); ^{19}F NMR δ −92.65 (s, *o*-C*F*), −117.16 (s, *p*-C*F*). **2b**: ^1H NMR δ 2.68 (m, SCH_2), 1.85 (m, CCH_2); ^{19}F NMR δ −118.41 (m, *o*-C*F*), −158.86 (t, *p*-C*F*), −161.64 (m, *m*-C*F*). **3a**: ^1H NMR δ 2.15 (s, SCH_3); ^{19}F NMR δ −90.70 (s, *o*-C*F*), −118.04 (s, *p*-C*F*). **3b**: ^1H NMR δ 2.17 (s, SCH_3); ^{19}F NMR δ −117.00 (m, *o*-C*F*), −159.86 (t, *p*-C*F*), −162.56 (m, *m*-C*F*). **6a**: ^1H NMR δ 5.79 (s, C*H*), 2.75 (s, CH_2); ^{19}F NMR δ −91.20 (s, *o*-C*F*), −117.30 (s, *p*-C*F*). **6b**: ^1H NMR δ 5.83 (s, C*H*), 2.76 (s, CH_2); ^{19}F NMR δ −117.40 (m, *o*-C*F*), −159.20 (t, *p*-C*F*), −162.40 (m, *m*-C*F*). **8a**: ^1H NMR δ 7.5−7.2 (m, C*H*); ^{19}F NMR δ −88.10 (t, J_{PF} = 4.8 Hz, *o*-C*F*), −118.23 (t, J_{PF} = 2 Hz, *p*-C*F*); $^{31}P\{^1H\}$ NMR δ 22.54 (m). **8b**: ^1H NMR δ 7.5−7.2 (m, C*H*); ^{19}F NMR δ −113.91 (m, *o*-C*F*), −162.38 (m, *p*-CF), −163.41 (m, *m*-C*F*); $^{31}P\{^1H\}$ NMR δ 22.73 (m). **9b**: ^1H NMR δ 7.4−7.1 (m, C*H*); ^{19}F NMR δ −113.87 (m, *o*-C*F*), −161.39 (m, *p*-CF), −163.20 (m, *m*-C*F*).

***cis*-[PdR_2L_2] (R = $C_6Cl_2F_3$, L = 2-pic (4a) and 4-pic (5a); R = C_6F_5, L = 2-pic (4b) and 4-pic (5b)).** To a solution of *cis*-[PdR_2(COD)] (**9**) (0.2 mmol) in CH_2Cl_2 (20 mL) was added an excess of L (0.5 mmol), and the mixture was stirred for 30 min. The resulting colorless solution was evaporated to dryness to give white *cis*-[PdR_2L_2] (**4** and **5**), which was washed with *n*-hexane (3 × 4 mL) and air-dried (quantitative yields). **4a**: IR 1050 vs, 1030 vs, 774 vs, 758 vs, 699 s, 688 s; ^1H NMR δ 8.86 (m, H, C*H*), 7.57 (dt, H, C*H*), 7.16 (m, 2H, C*H*), 3.10 (s, 3H, CH_3); ^{19}F NMR δ −91.19 (fluxional, *o*-C*F*), −120.08 (s, *p*-C*F*). Anal. Calcd for $C_{24}H_{14}Cl_4F_6N_2Pd$: C, 41.62; H, 2.04; N, 4.05. Found: C, 41.30; H, 2.22; N, 4.01. **4b**: IR 1059 vs, 958 vs, 795 s, 783 s, 765 s; ^1H NMR δ 8.90 (m, H, C*H*), 7.59 (dt, H, C*H*), 7.20 (m, 2H, C*H*), 3.10 (s, 3H, CH_3); ^{19}F NMR δ −117.65 (fluxional, *o*-C*F*), −161.37 (t, *p*-C*F*), −164.37 (m, *m*-C*F*). Anal. Calcd for $C_{24}H_{14}F_{10}N_2Pd$: C, 45.99; H, 2.25; N, 4.47. Found: C, 45.77; H, 2.27; N, 4.34. **5a**: IR 1069 s, 1050 s, 1040 s, 813 s, 700 m, 690 m; ^1H NMR δ 8.35 (m, 2H, C*H*), 7.09 (m, 2H, C*H*), 2.33 (s, 3H, CH_3); ^{19}F NMR δ −91.21 (s, *o*-C*F*), −120.10 (s, *p*-C*F*). Anal. Calcd for $C_{24}H_{14}Cl_4F_6N_2Pd$: C, 41.62; H, 2.04; N, 4.05. Found: C, 41.76; H, 2.10, N, 3.87. **5b**: IR 1056 s, 1040 s, 956 vs, 812 s, 808 s, 796 s, 786 s; ^1H NMR δ 8.35 (m, 2H, C*H*), 7.09 (m, 2H, C*H*), 2.34 (s, 3H, CH_3); ^{19}F NMR δ −117.61 (m, *o*-C*F*), −162.00 (t, *p*-C*F*), −164.34 (m, *m*-C*F*). Anal. Calcd for $C_{24}H_{14}F_{10}N_2Pd$: C, 45.99; H, 2.25; N, 4.47. Found: C, 45.75; H, 2.17; N, 4.34.

***trans*-[PdR_2L_2] (R = $C_6Cl_2F_3$, L = 4-pic (7a) and $AsPh_3$ (9a); R = C_6F_5, L = 4-pic (7b)).** To a solution of *trans*-[$PdR_2(tht)_2$] (**2**; 0.2 mmol) in CH_2Cl_2 (10 mL) was added an excess of L (1.0 mmol), and the mixture was stirred for 60 min. The resulting colorless solution was evaporated to dryness to give white complexes **7** or **9a**, which were washed with diethyl ether (3 × 2 mL) and air-dried (quantitative yields). **7a**: IR 1039 s, 1022 m, 816 m, 774 s, 672 m; ^1H NMR δ 8.54 (m, 2H, C*H*), 7.03 (m, 2H, C*H*), 2.30 (s, 3H, CH_3); ^{19}F NMR δ −97.16 (s, *o*-C*F*), −119.45 (s, *p*-C*F*). Anal. Calcd for $C_{24}H_{14}Cl_4F_6N_2$-

(17) For dissociative mechanisms in Pd(II) complexes, see: (a) Frey, U.; Helm, L.; Merbach, A.; Romeo, R. *J. Am. Chem. Soc.* **1989**, *111*, 8161−8165. (b) Casares, J. A.; Coco, S.; Espinet, P.; Lin, Y.-S. *Organometallics* **1995**, *14*, 3058−3067 and references therein.

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(19) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857−1867.

(20) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365−374.

(21) Usón, R.; Forniés, J.; Martínez, F.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1980**, 888−893.

(22) Espinet, P.; Martínez-Ilarduya, J. M.; Pérez-Briso, C.; Casado, A. L.; Alonso, M. A. *J. Organomet. Chem.*, in press.

Pd: C, 41.62; H, 2.04; N, 4.05. Found: C, 41.26; H, 2.09, N, 4.00. **7b**: IR 1064 s, 1043 s, 950 vs, 812 vs, 768 s, 504 s; ^{1}H NMR δ 8.53 (m, 2H, C*H*), 7.01 (m, 2H, C*H*), 2.18 (s, 3H, CH_3); ^{19}F NMR δ −122.50 (m, *o*-C*F*), −161.20 (t, *p*-C*F*), −163.10 (m, *m*-C*F*). Anal. Calcd for $C_{24}H_{14}F_{10}N_2Pd$: C, 45.99; H, 2.25; N, 4.47. Found: C, 45.72; H, 2.43; N, 4.25. **9a**: IR (KBr) 1590 s, 1484 s, 1436 vs, 1428 vs, 1397 vs, 1045 vs, 1032 vs, 777 vs, 746 vs, 738 vs, 693 vs, 677 s, 480 vs, 472 s, 462 s; ^{1}H NMR δ 7.4−7.2 (m, C*H*); ^{19}F NMR δ −88.13 (s, *o*-C*F*), −119.98 (s, *p*-C*F*). Anal. Calcd for $C_{48}H_{30}As_2Cl_4F_6Pd$: C, 51.53; H, 2.70. Found: C, 51.33; H, 2.78.

Kinetics on the Aryl-Group Exchange between [PdR$_2$(tht)$_2$] (Table 1). NMR tubes (5 mm) were charged with equimolar solid mixtures of complexes and aliquots of a tht solution in CCl_3D ($30.7 \pm 0.7 \times 10^{-3}$ mol L^{-1}). The samples were dissolved at room temperature in CCl_3D to a fixed volume of 600 ± 5 μL and placed into a thermostated probe. The evolution of selected signals of the complexes (in the range from −116 to −119 ppm, see Figure 2) was monitored by ^{19}F NMR. Conversion-time data were fitted to an integrated reversible second-order equation $\ln[1 - ([\mathbf{1c}]/[\mathbf{1a}]_0)] = -2k_{ex}[\mathbf{1a}]_0 t$,[10] giving k_{ex} (standard deviations are also given). ^{19}F NMR data for heteroaryl products **1c**: δ −89.83 (m, *o*-$C_6Cl_2F_2F$), −116.34 (m, *o*-$C_6F_2F_3$), −118.20 (s, *p*-$C_6Cl_2F_2F$), −160.18 (t, *p*-C_6F_4F), −162.84 (m, *m*-$C_6F_2F_3$). **2c**: δ −92.67 (s, *o*-$C_6Cl_2F_2F$), −117.10 (s, *p*-$C_6Cl_2F_2F$), −118.34 (m, *o*-$C_6F_2F_3$), −158.90 (t, *p*-C_6F_4F), −161.63 (m, *m*-$C_6F_2F_3$).

Reactions of [PdR$_2$L$_2$] Complexes. Appropriate mixtures of complexes in CCl_3D ($10.0 \pm 0.7 \times 10^{-3}$ mol L^{-1} in each one) were placed into a thermostated bath (±1 K). The evolution of the reaction mixtures was examined by ^{1}H and ^{19}F NMR. The NMR data for products are given as follows. *cis*-[Pd($C_6Cl_2F_3$)(C_6F_5)(SMe_2)$_2$] (**3c**): ^{1}H NMR δ 2.14 (s, SCH_3), 2.16 (s, SCH_3); ^{19}F NMR δ −90.70 (m, 2F, *o*-$C_6Cl_2F_2F$), −116.09 (m, 2F, *o*-$C_6F_2F_3$), −118.03 (s, F, *p*-$C_6Cl_2F_2F$), −159.86 (t, F, *p*-C_6F_4F), −162.50 (m, 2F, *m*-$C_6F_2F_3$). *cis*-[Pd(C_6F_5)$_2$(tht)(SMe_2)] (**10**): ^{1}H NMR δ 2.91 (m, 2H, SCH_2), 2.17 (s, 3H, CH_3), 1.88 (m, 2H, CCH_2). *cis*-[Pd(C_6F_5)$_2$(2-pic)(4-pic)] (**11**): ^{1}H NMR δ 8.93 (m, 1H, C*H*), 8.26 (m, 2H, C*H*), 7.61 (t, 1H, C*H*), 7.15 (m, 4H, C*H*), 3.08 (s, 3H, CH_3), 2.32 (s, 3H, CH_3); ^{19}F NMR δ −117.95 (br, 2F, *o*-C*F*), −161.89 (t, 1F, *p*-C*F*), −162.10 (t, 1F, *p*-C*F*), −164.30 (m, 2F, *m*-C*F*), −164.50 (m, 2F, *m*-C*F*).

Error Analysis. Errors σ_{x_i} of directly measured magnitudes x_i were taken as determined by the error of the apparatus. Errors of magnitudes extracted from least-squares linear regression were taken as the standard deviation of respective coefficient. Errors σ_y of mathematically calculated values $y = f(x_i)$ were estimated as $(\sigma_y)^2 = \sum_i [(\partial y/\partial x_i)\sigma_{x_i}]^2$.

Acknowledgment. Financial support by the Dirección General de Investigación Científica y Técnica (Project No. PB96-0363) and the Junta de Castilla y León (Project No. VA40-96) and a fellowship to A.L.C. from the Ministerio de Educación y Ciencia are very gratefully acknowledged.

Appendix. Derivation of Rate Equation 8. For simplicity, we have considered that complexes **1a** and **1b** react at similar rates in Scheme 2. This seems a reasonable approximation considering their chemical similarity. Although the aryl exchange is reversible, we will develop the steady-state approximation for the forward reaction only (k_{ex}). The steady-state concentrations of intermediates **1′** and **A** are

$$\frac{\partial[\mathbf{1a'}]}{\partial t} = k_1[\mathbf{1a}] + k_{-2}[\mathbf{A}] - k_{-1}[\mathbf{1a'}][\mathrm{tht}] - k_2[\mathbf{1a'}][\mathbf{1a}] - k_2[\mathbf{1a'}][\mathbf{1b}] - k_2[\mathbf{1a'}][\mathbf{1c}] = 0$$

$$\frac{\partial[\mathbf{1a'}]}{\partial t} = k_1[\mathbf{1a}] + k_{-2}[\mathbf{A}] - k_{-1}[\mathbf{1a'}][\mathrm{tht}] - k_2[\mathbf{1a'}][\mathrm{Pd}] = 0$$

$$[\mathbf{1a'}] = \frac{k_1[\mathbf{1a}] + k_{-2}[\mathbf{A}]}{k_{-1}[\mathrm{tht}] + k_2[\mathrm{Pd}]}$$

where [Pd] is the total amount of the complexes ([Pd] = [**1a**] + [**1b**] + [**1c**] = [**1a**]$_0$ + [**1b**]$_0$).

Similarly, for [**1b′**]

$$[\mathbf{1b'}] = \frac{k_1[\mathbf{1b}] + k_{-2}[\mathbf{A}]}{k_{-1}[\mathrm{tht}] + k_2[\mathrm{Pd}]}$$

Only the intermediates **A** formed by one moiety of **1a** and one moiety of **1b** can yield aryl exchange:

$$\frac{\partial[\mathbf{A}]}{\partial t} = k_2[\mathbf{1a'}][\mathbf{1b}] + k_2[\mathbf{1a}][\mathbf{1b'}] - k_{-2}[\mathbf{A}] - k_4[\mathbf{A}][\mathrm{tht}] - k_3[\mathbf{A}] = 0$$

$$[\mathbf{A}] = \frac{k_2[\mathbf{1a'}][\mathbf{1b}] + k_2[\mathbf{1a}][\mathbf{1b'}]}{k_4[\mathrm{tht}] + k_{-2} + k_3}$$

$$[\mathbf{A}] = \frac{2k_1k_2[\mathbf{1a}][\mathbf{1b}]}{(k_4[\mathrm{tht}] + k_3)(k_{-1}[\mathrm{tht}] + k_2[\mathrm{Pd}]) + k_{-1}k_{-2}[\mathrm{tht}]}$$

Then the reaction rate for the forward direction r_{ex} is

$$r_{ex} = k_3[\mathbf{A}] = \frac{2k_1k_2k_3}{(k_4[\mathrm{tht}] + k_3)(k_{-1}[\mathrm{tht}] + k_2[\mathrm{Pd}]) + k_{-1}k_{-2}[\mathrm{tht}]}[\mathbf{1a}][\mathbf{1b}] \quad (10)$$

This equation can be simplified considering that [tht]^2 in the denominator is very small:

$$r_{ex} = \frac{2k_1k_2k_3}{(k_2k_4[\mathrm{Pd}] + k_{-1}k_{-2} + k_{-1}k_3)[\mathrm{tht}] + k_2k_3[\mathrm{Pd}]}[\mathbf{1a}][\mathbf{1b}]$$

and the second-order rate constant is

$$k_{ex} = \frac{2k_1k_2k_3}{(k_2k_4[\mathrm{Pd}] + k_{-1}k_{-2} + k_{-1}k_3)[\mathrm{tht}] + k_2k_3[\mathrm{Pd}]} \quad (8)$$

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