A Novel Reversible Aryl Exchange Involving Two Organometallics: Mechanism of the Gold(I)-Catalyzed Isomerization of *trans*-[PdR_2L_2] Complexes (R = Aryl, L = SC_4H_8)

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[AuR^1(tht)] (**3a**) (R^1 = 3,5-$C_6Cl_2F_3$, tht = tetrahydrothiophene) very efficiently catalyzes the isomerization of *trans*-[$Pd(R^1)_2(tht)_2$] (**1a**) to *cis*-[$Pd(R^1)_2(tht)_2$] in $CDCl_3$. The ^{19}F NMR kinetic study leads to the first-order rate law $r_{iso} = k_{iso}$[**1a**] = ($k_{spo} + k_{cat}$[**3a**])[**1a**], where $k_{spo} = (1.50 \pm 0.03) \times 10^{-6}$ s^{-1} and $k_{cat} = a/(b + [tht])$ with $a = (1.32 \pm 0.07) \times 10^{-4}$ s^{-1} and $b = (3.0 \pm 0.2) \times 10^{-5}$ mol L^{-1} (at 304.4 K). The reaction of **1a** and [$Au R^2$(tht)] ($R^2 = C_6F_5$) yields *cis*-[$PdR^1R^2(tht)_2$] and **3a**, evidencing that the catalyzed isomerization takes place with aryl-group exchange between Pd(II) and Au(I). An associative mechanism passing through R-bridged intermediates [(tht)$(R^1)_2$Pd(μ-R^2)Au(tht)] and a donor−acceptor activated complex [(tht)$(R^1)_2(R^2)$Pd→Au(tht)]‡ is proposed. The results suggest that the associative displacement of tht from **1a** by the nucleophilic arylgold(I) complex to give [(tht)$(R^1)_2$Pd(μ-R^2)Au(tht)] is the rate-determining step (k_1). This is supported by the typical bimolecular activation parameters that were found: $\Delta H_1^‡ = 56.4 \pm 1.6$ kJ mol^{-1} and $\Delta S_1^‡ = -46 \pm 6$ J K^{-1} mol^{-1}.

Introduction

Group transfer between organometallics is a critical step in most organic reactions assisted by organotransition-metal complexes, such as the widely used palladium-catalyzed coupling of organic electrophiles RX and organometallics MR′.[1] In catalytic cycles, the intermediate [$PdRXL_2$], produced by fast oxidative addition of RX to [PdL_2] species,[2] can undergo two exchange processes with MR′. The X for R′ exchange (eq 1) leads, after reductive elimination, to the cross-coupling product RR′, whereas the R for R′ exchange (eq 2) seems to be responsible for the formation of homocoupling products.[3]

$$[PdRXL_2] + MR' \rightarrow [PdRR'L_2] + MX \qquad (1)$$

$$[PdRXL_2] + MR' \rightarrow [PdR'XL_2] + MR \qquad (2)$$

Additionally, other group exchanges between organometallic intermediates have been detected under catalytic conditions,[4] which can affect the reaction selectivity. Thus, the understanding of such exchange mechanisms is fundamental for the control of the coupling efficacy. Surprisingly, despite the importance of the topic, rigorous and detailed kinetic studies to support the mechanistic proposals are scarce, probably due to the difficulty introduced by the instability and reactivity of many transition-metal organometallics, particularly, in our case, those of Pd.

In the past few years, we have shown the advantages of pentafluorophenyl as a ligand to study palladium complexes. This aryl group allows one to isolate some otherwise unstable intermediates, slows down some reactions, and facilitates the identification of the compounds and the monitoring of the reactions using ^{19}F NMR in place of ^1H NMR spectroscopy. We have applied this to the study of the Heck reaction,[5] Pd migration processes,[6] the oxidative addition of ArI to Pd(0)[2] and recently to prove the operation and mechanisms of exchange processes involving some polydentate ligands.[7]

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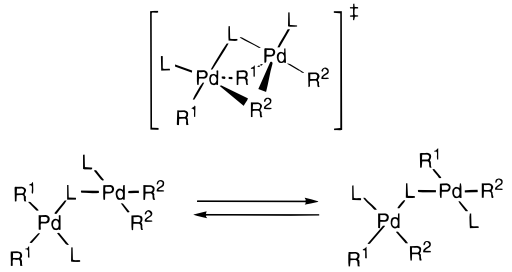
Scheme 1[a]



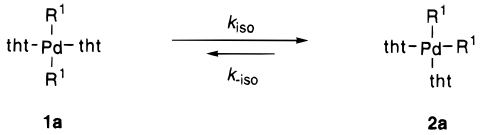
[a] $R^1 = C_6Cl_2F_3$, $R^2 = C_6F_5$, L = tht.

More recently, we have introduced the use of $C_6Cl_2F_3$ (3,5-dichlorotrifluorophenyl) in connection with that of C_6F_5. The availability of these two groups, chemically very similar but spectroscopically very different, allows us to carry out exchange studies similar to those sometimes carried out by isotopic labeling.[8] Thus, we have reported a novel type of exchange between halogenoless organopalladium complexes: $[Pd(C_6Cl_2F_3)_2(tht)_2]$ (tht = tetrahydrothiophene) and $[Pd(C_6F_5)_2(tht)_2]$ exchange their aryls reversibly, yielding $[Pd(C_6Cl_2F_3)(C_6F_5)(tht)_2]$.[9] The exchange takes place with full retention of the cis−trans configuration of the starting complexes. This exchange occurs exclusively with neutral ligands L possessing lone electron pairs (such as thioethers, not with phosphines or pyridines) via the formation of L-bridged intermediates, helping the formation of the electron-deficient aryl bridges needed for the aryl exchange to occur (Scheme 1, henceforth $R^1 = C_6Cl_2F_3$ and $R^2 = C_6F_5$).

The cis−trans isomerization also occurs, but as an independent and much slower process.[10] However, we have now discovered that this isomerization can be catalyzed by Au(I) complexes. Moreover, the kinetic study of this process reveals that this catalyzed isomerization takes place by a reversible double-aryl exchange between Pd(II) and Au(I). Thus, the reaction becomes relevant in connection with synthetic processes cocatalyzed by two or more different metals (e.g., the Stille reaction assisted by CuI).[11]

Results

Isomerization of *trans*-$[Pd(C_6Cl_2F_3)_2(tht)_2]$ Catalyzed by $[Au(C_6Cl_2F_3)(tht)]$. The spontaneous isomerization of *trans*-$[Pd(C_6Cl_2F_3)_2(tht)_2]$ (**1a**) to *cis*-$[Pd(C_6Cl_2F_3)_2(tht)_2]$ (**2a**) in $CDCl_3$ is very slow, and the equilibrium is reached after days at room temperature (eq 3, about 97% cis).[10,12] However, the isomerization



1a **2a** (3)

is complete within seconds when 1 equiv of $[Au(C_6Cl_2F_3)(tht)]$ (**3a**) is added, evidencing an extraordinary catalytic effect of the Au(I) complex. Using smaller amounts of **3a**, the rate of isomerization can be controlled to be adequate for its kinetic study by ^{19}F NMR (Figure 1).

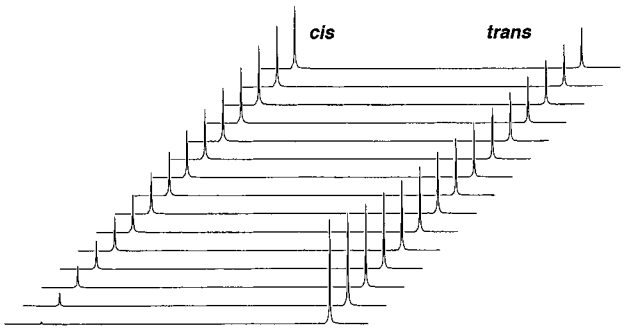


Figure 1. ^{19}F NMR (282 MHz) spectral sequence (12 min invervals) of the isomerization of *trans*-$[Pd(C_6Cl_2F_3)_2(tht)_2]$ (**1a**) to *cis*-$[Pd(C_6Cl_2F_3)_2(tht)_2]$ (**2a**) catalyzed by $[Au(C_6Cl_2F_3)(tht)]$ (**3a**) in $CDCl_3$ at 320.3 K. $[\mathbf{1a}]_0 = (1.00 \pm 0.03) \times 10^{-2}$ mol L^{-1}, $[\mathbf{3a}] = (9.9 \pm 0.5) \times 10^{-6}$ mol L^{-1} (0.1 mol %).

The Au(I)-catalyzed isomerization of **1a** followed good first-order kinetics (eq 4) when the experiments were carried out with addition of tht. In the experiments

$$\ln\left(\frac{[\mathbf{1a}]}{[\mathbf{1a}]_0}\right) = k_{iso}t \qquad (4)$$

without added tht, a small retardation was observed as the reaction proceeded, due to catalyst decomposition.[13] Therefore, we measured the initial (up to 10% conversion) isomerization rate of **1a** (r_0). The results obtained under different conditions are given in Table 1.[14]

The reaction is first order with respect to the concentration of catalyst **3a**. The isomerization rate is proportional to [**3a**] as shown in Figure 2a, the slope being $(4.52 \pm 0.11) \times 10^{-2}$ s^{-1}. Therefore, the rate law follows eq 5, which shows two contributions: One accounts for the spontaneous (k_{spo}) and the other for the catalyzed isomerization (k_{cat}). The latter is by far the most

$$r_{iso} = k_{iso}[\mathbf{1a}] = (k_{spo} + k_{cat}[\mathbf{3a}])[\mathbf{1a}] \qquad (5)$$

important contribution. For 0.1 mol % of **3a**, the isomerization mainly runs (97%) via the catalytic path-

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(14) Since the equilibrium in eq 3 is shifted far toward the cis side and the measurements have been made at the earlier stages of the reaction, the r_0 values given for the isomerization of **1a** to **2a** are hardly affected by the opposite reaction, that of **2a** to **1a**.

Table 1. Initial Rates for the [Au($C_6Cl_2F_3$)(tht)] (3a)-Catalyzed Isomerization of *trans*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (1a) to *cis*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (2a) in $CDCl_3$[a]

T/K	[**3a**]/10^{-5} mol L^{-1}	[tht]$_{added}$/10^{-4} mol L^{-1}	r_0/10^{-6} mol L^{-1} s^{-1}
304.4 ± 0.2	0	0	0.0150 ± 0.0003
304.4	0.99 ± 0.05	0	0.54 ± 0.03
304.4	0.99	1.54 ± 0.04	0.0596 ± 0.0008
304.4	1.97 ± 0.05	0	1.00 ± 0.04
304.4	1.97	1.54	0.146 ± 0.004
304.4	3.94 ± 0.05	0	1.71 ± 0.09
304.4	3.94	1.54	0.290 ± 0.003
304.4	5.91 ± 0.05	0	2.6 ± 0.2
304.4	5.91	0.386 ± 0.010	1.20 ± 0.02
304.4	5.91	0.772 ± 0.016	0.824 ± 0.004
304.4	5.91	1.16 ± 0.03	0.559 ± 0.007
304.4	5.91	1.54	0.431 ± 0.005
304.4	5.91	1.93 ± 0.04	0.358 ± 0.004
304.4	7.88 ± 0.06	0	3.54 ± 0.08
304.4	7.88	1.54	0.578 ± 0.005
304.4	9.85 ± 0.06	0	4.6 ± 0.2
304.4	9.85	1.54	0.769 ± 0.007
310.3	0.99 ± 0.05	0	0.80 ± 0.3
315.2	0.99	0	1.07 ± 0.05
320.3	0.99	0	1.59 ± 0.09
326.3	0.99	0	2.42 ± 0.12
331.9	0.99	0	3.81 ± 0.06

[a] Up to 10% conversion. [**1a**]$_0$ = (1.00 ± 0.03) × 10^{-2} mol L^{-1}.

way, whereas more than 1 mol % of catalyst leads to isomerization rates too fast for NMR monitoring at 304.4 K.

A similar behavior was obtained in the presence of added tht, but the rates were much slower. The slope in Figure 2b is (7.8 ± 0.2) × 10^{-3} s^{-1} for [tht]$_{added}$ = (1.54 ± 0.04) × 10^{-4} mol L^{-1}. Clearly, tht retards the Au-catalyzed isomerization. Experiments carried out with 0.6 mol % of catalyst **3a** reveal that the reaction is minus first order with respect to the concentration of tht.[15] The plot of r_0^{-1} vs [tht]$_{added}$ is a straight line (Figure 3) whose slope is (1.27 ± 0.04) × 10^{10} L^2 s mol^{-2} and the intercept is very close to the value of r_0^{-1} measured without addition of tht. The dependence of k_{cat} on the concentration of added tht is given in eq 6, with a = (1.32 ± 0.07) × 10^{-4} s^{-1} and b = (3.0 ± 0.2) × 10^{-5} mol L^{-1}, at 304.4 K.

$$k_{cat} = \frac{a}{b+[\text{tht}]} \qquad (6)$$

Equations 5 and 6 are consistent with the first-order kinetics observed in the experiments carried out with added tht. In the absence of added tht, the catalyst decomposition makes the term [**3a**] in eq 5 decrease with time, diminishing k_{iso} along the isomerization.[13]

The temperature dependence of the isomerization rate has been studied in the absence of added tht and is analyzed later (see Discussion). Finally, the temperature dependence of the equilibrium constant K_{eq} = [**2a**]/[**1a**] in $CDCl_3$ has been also measured using **3a**-catalysis in order to reach equilibrium within minutes. The results are given in Table 2 and afford the following thermodynamic parameters: $\Delta H°$ = −12.7 ± 0.5 kJ mol^{-1} and $\Delta S°$ = −12.7 ± 1.6 J K^{-1} mol^{-1}.

(15) With 0.6 mol % of **3a**, the catalyzed pathway contributes 99.4% to the total isomerization rate, then $k_{iso} \approx k_{cat}$.

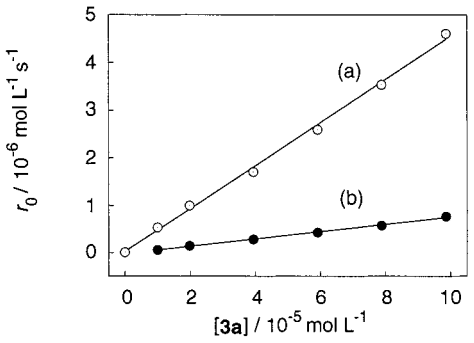


Figure 2. Catalytic effect of [Au($C_6Cl_2F_3$)(tht)] (**3a**) on the isomerization of *trans*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (**1a**) to *cis*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (**2a**) in $CDCl_3$ at 304.4 K: (a) without addition of tht; (b) with [tht]$_{added}$ = (1.54 ± 0.04) × 10^{-4} mol L^{-1} (1.6 mol %). [**1a**]$_0$ = (1.00 ± 0.03) × 10^2 mol L^{-1}. r_0 is the initial isomerization rate.

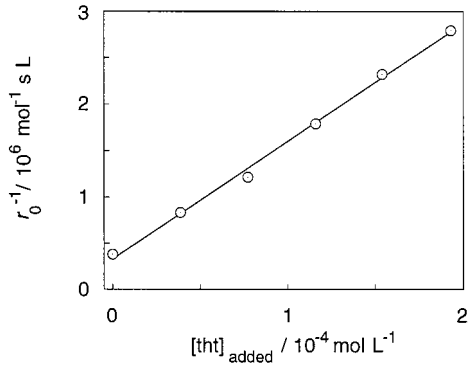


Figure 3. Retardation effect by addition of tht on the [Au($C_6Cl_2F_3$)(tht)] (**3a**)-catalyzed isomerization of *trans*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (**1a**) to *cis*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (**2a**) in $CDCl_3$ at 304.4 K. [**1a**]$_0$ = (1.00 ± 0.03) × 10^{-2} mol L^{-1}, [**3a**] = (5.91 ± 0.05) × 10^{-5} mol L^{-1} (0.6 mol %). r_0 is the initial isomerization rate.

Table 2. Temperature Dependence of the Equilibrium Constant K_{eq} for the Isomerization of *trans*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (1a) to *cis*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (2a) in $CDCl_3$[a]

T/K	K_{eq}
332.5	22.0
326.0	23.5
320.6	25.2
316.5	27.1
311.9	30.2
306.0	32.7
300.4	36.0
296.1	37.4

[a] Catalyzed by [Au($C_6Cl_2F_3$)(tht)] (**3a**). [**1a**]$_0$ = [**3a**] = (1.00 ± 0.03) × 10^{-2} mol L^{-1}.

Aryl-Group Scrambling between Au(I) and Pd(II) during the Au(I)-Catalyzed Isomerization. Experiments carried out mixing $C_6Cl_2F_3$ and C_6F_5 complexes have revealed that the Au(I)-catalyzed isomerization takes place with aryl exchange between Au(I) and Pd(II). For example, the reaction between *trans*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (**1a**) and [Au(C_6F_5)(tht)] (**3b**) (1:1) produces *cis*-[Pd($C_6Cl_2F_3$)$_{2-n}$(C_6F_5)$_n$(tht)$_2$] (n = 0 (**2a**), 1 (**2c**), 2 (**2b**)) and [Au($C_6Cl_2F_3$)(tht)] (**3a**). Concentration−time profiles of this reaction, retarded by addition of tht to make ^{19}F NMR monitoring possible, are shown in Figure 4.

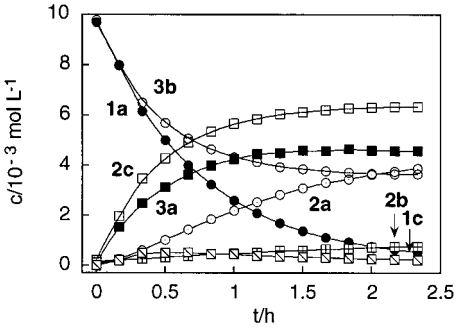
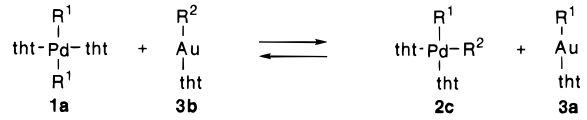


Figure 4. Concentration−time plots for the reaction between *trans*-[Pd($C_6Cl_2F_3$)$_2$(tht)$_2$] (**1a**) with [Au(C_6F_5)(tht)] (**3b**) in the presence of tht (6×10^{-2} mol L^{-1}) in $CDCl_3$ at 322.6 K. The products are *cis*-[Pd($C_6Cl_2F_3$)$_{2-n}$(C_6F_5)$_n$(tht)$_2$] (n = 0 (**2a**), 1 (**2c**), 2 (**2b**)), *trans*-[Pd($C_6Cl_2F_3$)(C_6F_5)(tht)$_2$] (**1c**), and [Au($C_6Cl_2F_3$)(tht)] (**3a**).

Table 3. Product Distribution at Equilibrium of the Reaction in Figure 4

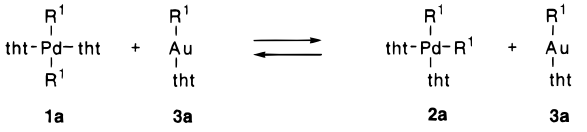
complex	$c_{found}/10^{-3}$ mol L^{-1}	$c_{calcd}/10^{-3}$ mol L^{-1}
1a	0.18	0.17
1b	~0	0.04
1c	0.17	0.17
2a	4.4	4.3
2b	1.2	1.1
2c	4.1	4.3
3a	6.6	6.7
3b	3.4	3.3

Complexes **2c** and **3a** are initially formed by the aryl exchange shown in eq 7.[16] Once some **3a** has been



(7)

formed, it can react with **1a** to give **2a** (as in eq 8). The



(8)

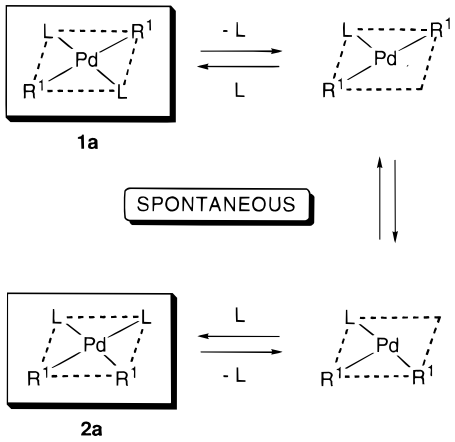
rest of the products are generated by similar exchange processes. Thus, from this experiment it is clear that *the Au(I)-catalyzed isomerization in Pd(II) complexes takes place with simultaneous aryl exchange between both organometallics*.

At the end of the reaction in Figure 4, the concentrations of the complexes correspond to a statistical distribution of the aryls between Pd(II) and Au(I) (Table 3),[17] as expected from the chemical similarity of the $C_6Cl_2F_3$ and C_6F_5 groups.

(16) The cis−trans configuration of heteroaryl Pd(II) complexes **1c** and **2c** have been assigned by comparison of their ^{19}F NMR chemical shifts with those of the homoaryl complexes cis (**1a**,**b**) and trans (**2a**,**b**). Moreover, in the case of the cis complex **2c**, $^{19}F-^{19}F$ through−space couplings between the $C_6Cl_2F_3$ and C_6F_5 rings produce a typical fine structure in the F_{ortho} resonances, see: Albéniz, A. C.; Casado, A. L.; Espinet, P. *Organometallics* **1997**, *16*, 5416−5423.

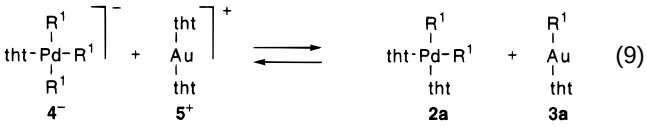
(17) The statistical distribution in Table 3 has been calculated by resolving a system with eight variables (concentration of eight complexes) and eight relationships (first, balance of Pd; second, balance of Au; third, balance of $C_6Cl_2F_3$ group; fourth to sixth, K_{iso} = [cis]/[trans] = 97/3, for each pair of cis−trans isomers; and seventh to eighth, K_{ex} = [hetero]^2/([homo−C_6F_5][homo−$C_6Cl_2F_3$]) = 4, for *cis* and *trans* configurations.

Scheme 2



Reactions between tht and Au(I) Catalyst. [Au($C_6Cl_2F_3$)(tht)] (**3a**) was checked for possible reactions with tht which could inhibit its catalytic activity. The addition of free tht to **3a** (2:1 mol, in $CDCl_3$) produced fluxionality in the ^1H NMR spectrum, indicating a fast free-for-coordinated tht exchange, but not in the ^{19}F NMR spectrum. This result discards the formation of any [Au($C_6Cl_2F_3$)(tht)$_n$] (n > 1) in appreciable amount. Thus, the inhibition observed under catalytic conditions (where the concentration of free tht is much lower) is not due to the formation of three-coordinate gold(I) species.

Arylation of Cationic Au(I) by Anionic Pd(II) Complexes. To support a step in our mechanistic proposal, the reaction of (NBu_4)[Pd($C_6Cl_2F_3$)$_3$(tht)] (NBu_4·**4**) and [Au(tht)$_2$](ClO_4) (**5**·ClO_4) in $CDCl_3$ was studied. As expected from closely related studies in the literature,[18] the anionic Pd complex arylated the cationic Au(I) one (eq 9).



(9)

Discussion

The spontaneous isomerization of *trans*-[Pd(C_6F_5)$_2$(tht)$_2$] (**1b**) to *cis*-[Pd(C_6F_5)$_2$(tht)$_2$] (**2b**) has been reported and is slow. A dissociative mechanism (Scheme 2) has been proposed from the retardation effect of the addition of tht and from the values of the activation parameters: $\Delta H^{\ddagger} = 137 \pm 6$ kJ mol^{-1} and $\Delta S^{\ddagger} = 83 \pm 19$ J K^{-1} mol^{-1}.[10] The very positive $\Delta S^{\ddagger}$ value agrees with an increase in the number of particles through the isomerization. Nevertheless, as we have recently shown,[12] the high value of $\Delta H^{\ddagger}$ is mainly contributed by the topomerization step of the three-coordinate intermediate.[19]

The Au(I)-catalysis of this cis−trans isomerization is an unreported process. Its most significant features are (i) The Au(I)-catalyzed isomerization involves aryl exchange between Pd(II) and Au(I); and (ii) there is a retardation effect by addition of neutral ligand. The

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

Scheme 3

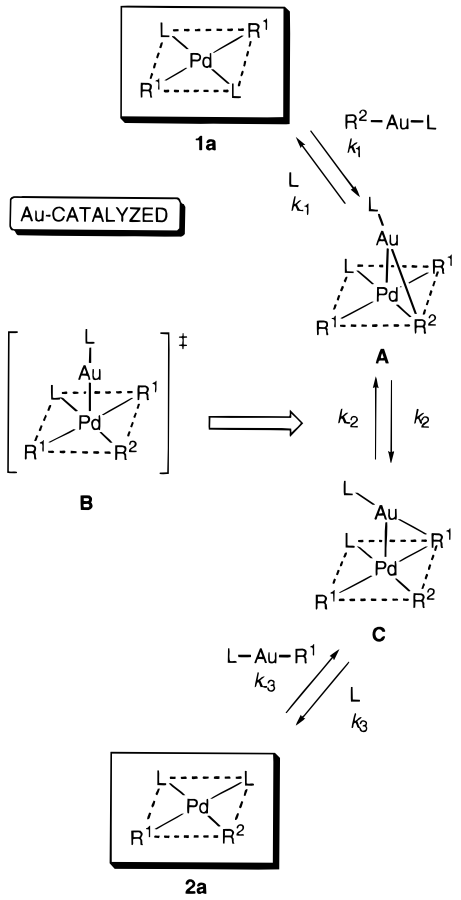
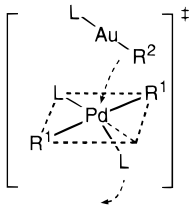


Chart 1



mechanism outlined in Scheme 3 is consistent with these observations. It starts with a nucleophilic attack of the electron-rich complex **3a** to **1a** (Chart 1), to produce an L-for-R^2 associative substitution, leading to an aryl-bridged intermediate **A** (step k_1).[20] In the coordination sphere of Pd, the fragment Au(tht) can slide from one R^2 to any R^1 (step k_2), most probably through a high-energy intermediate or activated complex **B**, to give **C**, which is finally cleaved by tht (step k_3) producing the net effect of a change of the geometry at the Pd center with aryl exchange.

The existence of some kind of intermediate **A** (and **C**, both in undetectable concentration) is required by the kinetic results.[21] The structure proposed is identical to that found by X-ray diffraction for the hydrido-bridged cation $[(PEt_3)_2(C_6F_5)Pt(\mu\text{-}H)Au(PPh_3)]^+$ (Figure 5a).[22]

(20) Associative ligand substitutions on Pd(II) species take usually place with preservation of the geometry, see: Cross, R. J. *Adv. Inorg. Chem.* **1989**, *34*, 219−292.

(21) A direct transformation through a single activated complex (for instance a species with the Au and Pd centers bridged by the two exchanging groups) would yield a rate law independent of [L].

(22) Albinati, A.; Lehner, H.; Venanzi, L. M.; Wolfer, M. *Inorg. Chem.* **1987**, *26*, 3933−3939.

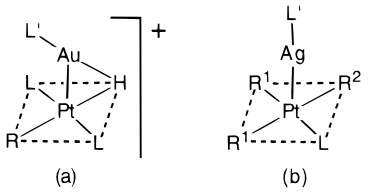


Figure 5. Simplified drawings for the X-ray difraction structures of (a) $[(PEt_3)_2C_6F_5)Pt(\mu\text{-}H)Au(PPh_3)]^+$ and (b) $[(tht)(C_6Cl_5)(C_6F_5)_2Pt\rightarrow Ag(PPh_3)]$. From refs 22 and 18, respectively.

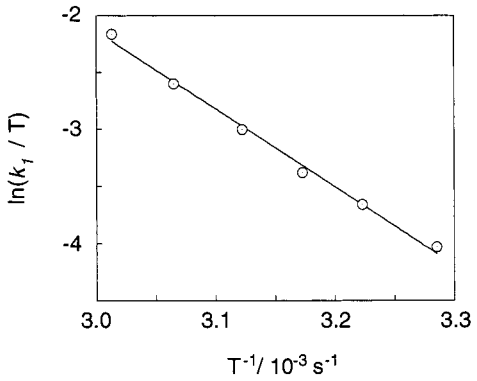


Figure 6. Eyring representation of k_1 values derived from the $[Au(C_6Cl_2F_3)(tht)]$ (**3a**)-catalyzed isomerization of *trans*-$[Pd(C_6Cl_2F_3)_2(tht)_2]$ (**1a**) to *cis*-$[Pd(C_6Cl_2F_3)_2(tht)_2]$ (**2a**). $[\mathbf{2a}]_0 = (1.00 \pm 0.03) \times 10^{-2}$ mol L^{-1}, $[\mathbf{3a}] = (9.9 \pm 0.5) \times 10^{-6}$ mol L^{-1} (0.1%), $CDCl_3$.

Also, the activated complex **B** has an even closer model characterized by X-ray diffraction, the complex $[(tht)(C_6Cl_5)(C_6F_5)_2Pt\rightarrow Ag(PPh_3)]$ (Figure 5b), where there is a donor−acceptor Pt→Ag bond.[18] For both kinds of complexes, a greatly reduced stability is expected when Pt is substituted for Pd and in fact the gold complex $\mathbf{5}^+$ is arylated by the anionic tris-arylated Pd complex $\mathbf{4}^-$, as shown in eq 9.

The mechanism in Scheme 3 leads to the theoretical rate law given in eq 10 (see Appendix). Comparing both

$$k_{cat} = \frac{k_1 k_2 [\mathbf{3a}]}{k_2 + k_{-1}[tht]} \qquad (10)$$

equations, the following values are obtained: $k_1 = 4.4 \pm 0.3$ mol^{-1} L s^{-1} and $k_2/k_{-1} = (3.0 \pm 0.2) \times 10^{-5}$ mol L^{-1} in $CDCl_3$ at 304.4 K.

In the absence of added tht and neglecting the small contribution of the uncatalyzed isomerization,[15] the reaction rate can be simplified to eq 11, where the isomerization rate seems to be controlled by the bimolecular interaction between Au and Pd complexes (step k_1 in Scheme 3). Applying eq 12, values of k_1 can be estimated from those of r_0 measured in the absence of added tht (Table 1).

$$r_{iso} = k_{cat}[\mathbf{1a}] = k_1[\mathbf{3a}][\mathbf{1a}] \qquad (11)$$

$$k_1 = \frac{r_0}{[\mathbf{3a}][\mathbf{1a}]_0} \qquad (12)$$

The activation parameters derived from a Eyring treatment of these k_1 values (Figure 6) are $\Delta H_1^{\ddagger} = 56.4 \pm 1.6$ kJ mol^{-1} and $\Delta S_1^{\ddagger} = -46 \pm 6$ J K^{-1} mol^{-1}. They are in sharp contrast with those found for the spontane-

ous isomerization and clearly indicate a bimolecular step, k_1, as postulated in Scheme 3. A classical associative substitution of tht in **1a** (k_1) through a pentacoordinate activated complex (Chart 1) is compatible with the negative activation entropy and the low activation enthalpy observed.[23]

Conclusions

In this paper, we have described a novel aryl exchange between [AuRL] and [PdR_2L_2] complexes (R = perhalophenyl, L = neutral ligand), which takes place with cis−trans isomerization of the latter. The mechanism involves associative substitution of the neutral ligand L in *trans*-[PdR_2L_2] by the nucleophilic Au(I) complex and formation of an aryl-bridged intermediate *trans*-[$LR_2Pd(\mu$-R)AuL]. The subsequent AuL-fragment migration to terminal R groups leads to *cis*-[$LR_2Pd(\mu$-R)AuL], which is finally cleaved by free L yielding *cis*-[PdR_2L_2]. This novel isomerization pathway is enabled by the use of the electron-rich Au(I) center, which makes its R group nucleophilic enough to initiate the reaction via nucleophilic attack to the electrophilic Pd center.

Experimental Section

General methods were as reported elsewhere.[9] The complexes [AuCl(tht)],[24] *trans*-[$Pd(C_6Cl_2F_3)_2(tht)_2$] (**1a**),[25] *trans*-[$Pd(C_6F_5)_2(tht)_2$] (**1b**),[26] *cis*-[$Pd(C_6Cl_2F_3)_2(tht)_2$] (**2a**),[25] *cis*-[$Pd(C_6F_5)_2(tht)_2$] (**2b**),[26] [$Au(C_6F_5)(tht)$] (**3b**),[27] $(NBu_4)_2[Pd(C_6Cl_2F_3)_4]$,[25] $[Au(tht)_2](ClO_4)$ (**5**),[28] and $[Li(C_6Cl_2F_3)]$,[25] were prepared as reported in the literature.

[$Au(C_6Cl_2F_3)(tht)$] (3a). To a solution of $[Li(C_6Cl_2F_3)]$ (5.15 mmol) in diethyl ether (80 mL) at −78 °C was added finely ground [AuCl(tht)] (1.50 g, 4.68 mmol). The mixture was stirred for 2 h, allowing the temperature to increase slowly. Stirring was continued at room temperature for an additional 15 min. The resulting white suspension was treated with water (60 mL), and the organic layer was separated, washed with water (2 × 20 mL), dried over anhydrous $MgSO_4$, and concentrated to ca. 5 mL. Upon cooling at −28 °C, white needles of **3a** separated, which were filtered, washed with cold diethyl ether (3 × 1 mL), and air-dried (yield 1.98 g, 87%): IR (KBr) 1435 (vs), 1403 (vs), 1055 (s), 1037 (s), 773 (vs), 713 (m), 704 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.44 (s, br, SCH_2), 2.23 (s, br, CCH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ −90.28 (s, *o*-C*F*), −116.62 (s, *p*-C*F*). Anal. Calcd for $C_{10}H_8AuCl_2F_3S$: C, 24.76; H, 1.66. Found: C, 24.84; H, 1.73.

[NBu_4][$Pd(C_6Cl_2F_3)_3(tht)$] (NBu_4·4). A solution of $(NBu_4)_2[Pd(C_6Cl_2F_3)_4]$ (204 mg, 0.147 mmol) and **1a** (110, 0.161 mmol) in THF (6 mL) was stirred at 50 °C for 5 h. The yellow solution was filtered to remove traces of black palladium, and evaporated to dryness. The residue was treated with diethyl ether (5 mL) to give a white solid (NBu_4)·**4** which was separated, washed with diethyl ether (2 × 1 mL) and air-dried (yield 0.204 g, 67%): IR (KBr) 2965 (s), 1425 (vs), 1396 (vs), 1040 (vs), 770 (vs); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.25 (m, CH_2), 2.64 (m, SCH_2), 1.82 (m, $SCCH_2$), 1.70 (m, CH_2), 1.45 (m, CH_2), 1.01 (t, CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ −81.56 (q, $^{\text{through-space}}J_{FF}$ = 6.8 Hz, 2F, *o*-C*F*), −83.13 (t, $^{\text{through-space}}J_{FF}$ = 6.8 Hz, 4F, *o*-C*F*), −118.99 (s, 2F, *p*-C*F*), −120.52 (s, F, *p*-C*F*). Anal. Calcd for $C_{38}H_{44}Cl_6F_9PdNS$: C, 44.02; H, 4.28; N, 1.35. Found: C, 44.23; H, 4.32; N, 1.41.

Kinetics on the [$Au(C_6Cl_2F_3)(tht)$]-Catalyzed Isomerization of *trans*-[$Pd(C_6Cl_2F_3)_2(tht)_2$]. NMR tubes (5 mm) were charged with **1a** (4.1 ± 0.1 mg, 6.00 ± 0.15 μmol) and suitable aliquots of two $CDCl_3$ solutions, one with tht ((5.80 ± 0.10) × 10^{-4} mol L^{-1}) and the other with **3a** ((5.91 ± 0.03) × 10^{-4} mol L^{-1}). Both solutions had been previously titrated by ^{1}H NMR using naphthalene as the internal standard. The mixtures were dissolved, in $CDCl_3$ at room temperature (293 K), to a fixed volume of 600 ± 5 μL and placed into a thermostated probe. Concentration vs time data were then acquired by comparing the ^{19}F NMR signal areas of complexes **1a** and *cis*-[$Pd(C_6Cl_2F_3)_2(tht)_2$] (**2a**) (Figure 1). Attempts at fitting the data points to a first-order law, eq 4, were satisfactory only for experiments carried out with free tht. Alternatively, initial reaction rates (in mol L^{-1} s^{-1}) were measured by fitting the initial data points (up to 10% of conversion) to a Taylor equation $[\mathbf{1a}] = a_0 + a_1t + a_2t^2$, from which the initial reaction rate is $r_0 = (\partial[\mathbf{1a}]/\partial t)_{t=0} = a_1$. Measurements of the equilibrium constant, $K_{eq} = [\mathbf{2a}]/[\mathbf{1a}]$, were carried out on a samples with $[\mathbf{1a}]_0 = [\mathbf{3a}] = (1.00 \pm 0.03) \times 10^{-2}$ mol L^{-1}.

Reactions of *trans*-[$Pd(C_6Cl_2F_3)_2(tht)_2$] (1a) with [$Au(C_6F_5)(tht)$] (3b). A sample with $[\mathbf{1a}]_0 = [\mathbf{3b}] = (1.00 \pm 0.03) \times 10^{-2}$ mol L^{-1} and [tht] = 6 × 10^{-2} mol L^{-1}, prepared as described above, was allowed to react at 322.6 K. The reaction was followed by ^{19}F NMR, calculating the concentrations of the products (Figure 4). ^{19}F NMR (282 MHz, $CDCl_3$) data for heteroaryl products are given.[9] **1c**: δ −92.67 (s, *o*-$C_6Cl_2F_2F$), −117.10 (s, *p*-$C_6Cl_2F_2F$), −119.34 (m, *o*-$C_6F_2F_3$), −158.90 (m, *p*-C_6F_4F), −161.63 (m, *m*-$C_6F_2F_3$). **2c**: 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 (m, *p*-C_6F_4F), −162.84 (m, *m*-$C_6F_2F_3$).

Reactions of [$Au(C_6Cl_2F_3)(tht)$] (3a) with tht. A (10.0 ± 0.03) × 10^{-3} mol L^{-1} sample in **3a** and (5.0 ± 0.2) × 10^{-3} mol L^{-1} in tht, prepared as described above, was examined by NMR. The ^{19}F NMR spectrum showed only signals from **3a** without changes in δ. The ^{1}H NMR (300 MHz, $CDCl_3$) spectrum showed very broad (fluxional) signals at δ 2.83 (SCH_2), 1.95 (CCH_2).

Error Analysis. Errors were estimated as reported before.[9]

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Appendix

Derivation of Rate Eq 10. The steady-state concentration of intermediates **A** and **C** in Scheme 3 are

$$[\mathbf{A}] = \frac{k_1[\mathbf{3a}][\mathbf{1a}] + k_{-2}[\mathbf{C}]}{k_{-1}[\text{tht}] + k_2} \tag{13}$$

$$[\mathbf{C}] = \frac{k_2[\mathbf{A}] + k_{-3}[\mathbf{2a}][\mathbf{3a}]}{k_3[\text{tht}] + k_{-2}} \tag{14}$$

$$[\mathbf{A}] = \frac{k_1(k_{-2} + k_3[\text{tht}])[\mathbf{1a}][\mathbf{3a}] + k_{-2}k_{-3}[\mathbf{2a}][\mathbf{3a}]}{\{k_1(k_{-2} + k_3[\text{tht}])\}[\text{tht}]} \tag{15}$$

The reaction rate is

(23) Other observations further support the proposed mechanism. For example, isomerizations on similar Pt(II) complexes are much slower than for Pd, in agreement with the different behavior of these two metals in associative substitutions (see ref 20). This and other results will be reported in a forthcoming paper.

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$$r_{\mathrm{iso,cat}} = -\frac{\partial[\mathbf{1a}]}{\partial t} = k_1[\mathbf{1a}][\mathbf{3a}] - k_{-1}[\mathbf{A}] \quad (16)$$

$$r_{\mathrm{iso,cat}} = \frac{k_1k_2k_3[\mathbf{1a}][\mathbf{3a}] - k_{-1}k_{-2}k_{-3}[\mathbf{2a}][\mathbf{3a}]}{k_{-1}k_{-2} + k_2k_3 + k_{-1}k_3[\mathrm{tht}]} \quad (17)$$

Equation 17 holds for the reversible reaction. However, it can be simplified to an irreversible isomerization of **1a** since eq 3 is shifted far toward the cis isomer and our measurements have been made at the early stages of the isomerization of **1a** to **2a**. This means that [**2a**] is small and $k_{-1}k_{-2} \ll k_2k_3$, giving

$$r_{\mathrm{iso,cat}} = k_{\mathrm{cat}}[\mathbf{1a}] = \frac{k_1k_2[\mathbf{3a}]}{k_2 + k_{-1}[\mathrm{tht}]}[\mathbf{1a}] \quad (10)$$

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