Uncatalyzed *Cis–Trans* Isomerization of Bis(pentafluorophenyl)bis(tetrahydrothiophene)palladium(II) Complexes in Chloroform: Evidence for a Dissociative Mechanism

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The complexes *cis*- and *trans*-[$Pd(C_6F_5)_2(tht)_2$] (tht = tetrahydrothiophene) spontaneously isomerize in chloroform to a *cis–trans* equilibrium mixture, where the *cis* isomer is the predominant species. The first-order forward rate constant, k_{tc}, and the equilibrium constant, K_{eq}, have been measured at different temperatures by proton NMR. The isomerization suffers mass-law retardation by added tht and is characterized by a high value of the enthalpy of activation ($\Delta H_{tc}^{\ddagger} = 137 \pm 6$ kJ mol^{-1}) and a large positive value of the entropy of activation ($\Delta S_{tc}^{\ddagger} = 83 \pm 19$ J K^{-1} mol^{-1}). In contrast, the substitution of tht by 2-methylpyridine in *trans*-[$Pd(C_6F_5)_2(tht)_2$] is characterized by a low enthalpy of activation ($\Delta H_N^{\ddagger} = 51 \pm 2$ kJ mol^{-1}) and a negative entropy of activation ($\Delta S_N^{\ddagger} = -114 \pm 4$ J K^{-1} mol^{-1}). These findings are consistent with the usual associative mode of activation for the substitution reaction, while for the isomerization a mechanism is suggested involving the dissociative loss of tht and the interconversion of two geometrically distinct three-coordinate intermediates.

Introduction

Detailed kinetic studies of *cis–trans* isomerization of complexes of the type *cis*-[$Pt(PEt_3)_2(R)X$] (R = alkyl or aryl group; X = halide ion)[1] and of displacement of sulfur-bonded ligands L from *cis*-[PtR_2L_2] (L = sulfoxide or thioether) by nitrogen chelating ligands[2,3] have shown that three-coordinate T-shaped intermediates (i.e., 14-electron species) are formed in both processes through dissociatively activated pathways. In these substrates, the presence of Pt–C σ bonds seems to be a prerequisite for the promotion of a unimolecular process involving ligand dissociation.

Organometallic complexes of palladium(II) play an important role in a number of palladium-catalyzed organic reactions,[4] and the creation of a vacant coordination site on the metal by loss of one ligand is often proposed as a fundamental step for the occurrence of the catalytic process.[5] These considerations prompted us to investigate the nucleophilic substitution reactions of organopalladium complexes analogous to the species [PtR_2L_2]. During preliminary experiments on the stability in solution of the complexes *cis*- and *trans*-[$Pd(C_6F_5)_2(tht)_2$] (tht = tetrahydrothiophene) it was found that each isomer spontaneously converts to a *cis–trans* equilibrium mixture in chloroform or benzene, with the *cis* isomer predominant at equilibrium.

The kinetic study of the observed geometrical interconversion is of interest in that the majority of isomerization studies have been carried out on inorganic square planar d^8 complexes of the type [MX_2L_2][6] and reports concerning the isomerization reactions of corresponding organopalladium compounds [PdR_2L_2] are still scarce.[7] The isomerization of this type of organometallic complex was investigated in the framework of thermal decomposition of *trans*- and *cis*-dialkylbis(tertiary phosphine)palladium(II) complexes. It was demonstrated that a *trans*-dimethylbis(tertiary phosphine)palladium complex isomerizes to a *cis*-dimethyl complex before giving the reductive elimination product. However, the results of mechanistic studies of the isomerization of these substrates were conflicting. Stille[7a] proposed an associative mechanism assisted by coordinating solvent or phosphine involving the pseudorotation of five-coordinate intermediates, while Yamamoto et al.[7b] supported a mechanism involving dissociation of the phosphine ligand followed by an intermolecular methyl-transfer reaction.

In this paper we report the kinetic study of the observed uncatalyzed *cis–trans* isomerization of [$Pd(C_6F_5)_2(tht)_2$] complexes in deuteriochloroform solution. A dissociative mechanism is proposed which involves the conversion of two geometrically distinct three-coordinate intermediates [$Pd(C_6F_5)_2(tht)$]. The displacement of tht of *cis*- and *trans*-[$Pd(C_6F_5)_2(tht)_2$] by nucleophiles was also investigated to gain further information on the reactivity of the two isomers. The kinetics of the reaction between the *trans* complex and 2-methylpyridine were consistent with the usual associative mechanism in square planar substitution. A comparison can be made between dissociative and associative pathways in the same substrate.

Experimental Section

***trans*- and *cis*-Bis(pentafluorophenyl)bis(tetrahydrothiophene)palladium(II).** A sample of *trans*-[$PdCl_2(tht)_2$] (2.41 g, 6.82 mmol) was added with stirring to a solution of LiC_6F_5 (15 mmol) in dry diethyl ether (50 cm^3) at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 4 h. The mixture was hydrolyzed with aqueous ether and evaporated under vacuum to a small volume. Ethanol was added (50 cm^3) to give *trans*-[$Pd(C_6F_5)_2(tht)_2$] (0.95 g). Anal. Calcd for $C_{20}H_{16}F_{10}S_2Pd$: C, 38.94; H, 2.61; F, 30.8. Found: C, 39.05; H, 2.67; F, 30.6. Partial evaporation of ethanol (ca. 20 cm^3) and crystallization at −20 °C gave a mixture of *trans*- and *cis*-[$Pd(C_6F_5)_2(tht)_2$] (0.18 g). The solution was filtered, and the filtrate was reduced

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under vacuum to ca. 5 cm³. White crystals of *cis*-[Pd(C_6F_5)$_2$(tht)$_2$] (0.52 g) were obtained from this solution by cooling. Anal. Calcd for $C_{20}H_{16}F_{10}S_2Pd$: C, 38.94; H, 2.61; F, 30.8. Found: C, 38.91; H, 2.53; F, 31.0.

***trans*-Bis(pentafluorophenyl)(2-methylpyridine)(tetrahydrothiophene)palladium(II).** To a solution of *trans*-[Pd(C_6F_5)$_2$(tht)$_2$] (0.123 g, 0.2 mmol) in chloroform was added 2-methylpyridine (2 mmol). The reaction mixture was stirred for 4 h and evaporated to dryness. Addition of petroleum ether (bp 40–60 °C) gave white crystals of *trans*-[Pd(C_6F_5)$_2$(2-pic)(tht)]. Anal. Calcd for $C_{22}H_{15}F_{10}NSPd$: C, 42.50; H, 2.43; F, 30.55. Found: C, 42.38; H, 2.40; F, 30.4.

Apparatus. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer FT 1720X instrument; ^{1}H NMR spectra, on a Bruker AMX R300 spectrometer equipped with a variable-temperature probe. Chemical shifts are reported in ppm downfield from internal tetramethylsilane.

All reactions involving organometallic compounds were carried out under nitrogen by using standard techniques for handling air-sensitive compounds. Diethyl ether was dried by distillation from sodium benzophenone. Other compounds were the best available commercial materials and were used without further purification.

Kinetics of Isomerization of *trans*-[Pd(C_6F_5)$_2$(tht)$_2$]. Solutions of the complex (0.01–0.05 mol dm^{-3}) in $CDCl_3$ were prepared at room temperature. These solutions were sealed in 5-mm NMR tubes under vacuum, after degassing three times by the freeze–pump–thaw technique. The samples were placed in a thermostated oil bath, and portions were removed at intervals for NMR measurements. The variable-temperature probe was calibrated prior to each measurement by using a platinum resistance thermometer. The extent of isomerization was determined without need for an internal standard by measuring the areas of the peak of CH_2S of the *trans* or *cis* isomer relative to the total amount of the areas of CH_2 of both isomers.

Kinetics of the Substitution Reactions of *trans*-[Pd(C_6F_5)$_2$(tht)$_2$]. Chloroform was dried by standard methods and distilled prior use. 2-Methylpyridine was distilled under vacuum from KOH pellets. The kinetic data were obtained on a Perkin-Elmer Lambda 5 spectrophotometer equipped with a constant-temperature cell holder. Absorbance readings were taken in the wavelength region 300–350 nm or at a selected wavelength (314 nm). The reactions were started by adding a weighed sample of the complex to a prethermostated standardized solution of the nucleophile and shaking the solution rapidly. Runs were carried out under pseudo-first-order conditions, and observed rate constants k_{obsd} were calculated from the slopes of plots of $\ln(A_t - A_\infty)$ vs time. Such plots were linear for more than 3 half-lives of the reaction.

The activation parameters for the isomerization and substitution reactions were obtained from conventional Eyring plots of $\ln(k/T)$ vs $1/T$. Thermodynamic values for the isomerization were obtained by standard least-squares analyses of plots of $\log(K_{eq})$ vs $1/T$.

Results

Uson et al. reported that in the reaction of *trans*-[PdCl$_2$(tht)$_2$] with LiC_6F_5 in a 1:2.2 molar ratio only the complex *trans*-[Pd(C_6F_5)$_2$(tht)$_2$] was obtained.[8] Repeating this procedure gave a mixture of *trans*-[Pd(C_6F_5)$_2$(tht)$_2$] and *cis*-[Pd(C_6F_5)$_2$(tht)$_2$]. Each isomer was separated by fractional crystallization. Satisfactory indications of the stereochemistry of the two isomers came from their IR spectra. The *cis* complex showed two bands at 789 and 780 cm^{-1} while the *trans* isomer had a single band at 772 cm^{-1}. These absorptions are attributable to "X-sensitive" vibrations involving mainly M–C stretching and have already been used for structural elucidation.[8] The ^{1}H NMR spectrum of *trans*-[Pd(C_6F_5)$_2$(tht)$_2$] in $CDCl_3$ showed a multiplet at δ(CH_2S) 2.68 and a multiplet at δ(CH_2) 1.86. The corresponding multiplets of the methylene groups of the tht ligand of the *cis* isomer were observed at δ 2.91 and 1.88.

(a) Uncatalyzed Isomerization. When the complex *trans*-[Pd(C_6F_5)$_2$(tht)$_2$] was dissolved in $CDCl_3$ or C_6D_6, it was found to isomerize spontaneously to an equilibrium mixture of the two isomers. The same is true for the *cis* isomer. Figure 1 illustrates the typical changes in the ^{1}H NMR spectra for the isomerization

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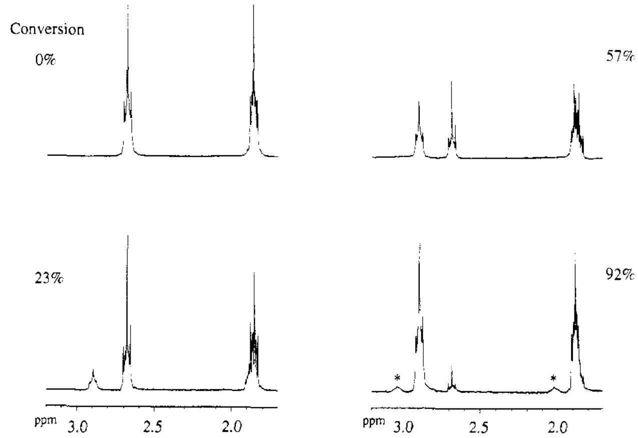

Figure 1. Proton NMR spectral changes for the isomerization of *trans*-[Pd(C_6F_5)$_2$(tht)$_2$] in $CDCl_3$ at 60 °C. Asterisks denote decomposition products Pd(tht)$_n$.

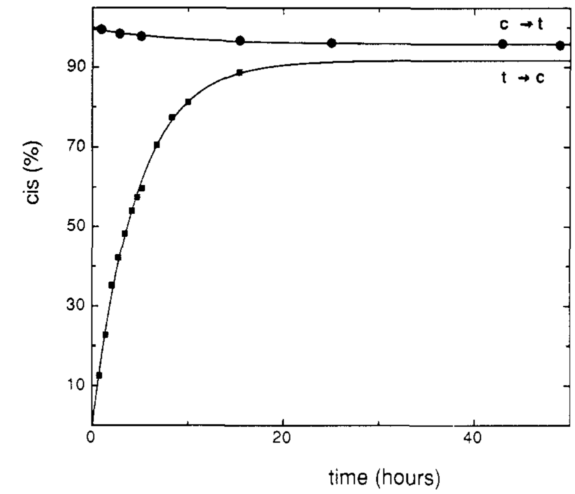

Figure 2. Time-conversion curves of isomerization of the complexes [Pd(C_6F_5)$_2$(tht)$_2$] (*trans*, **t**; *cis*, **c**) in $CDCl_3$ at 60 °C.

of *trans*-[Pd(C_6F_5)$_2$(tht)$_2$] to *cis*-[Pd(C_6F_5)$_2$(tht)$_2$] in $CDCl_3$ at 60 °C. In this temperature, a slight darkening of the solution was observed at the final stage of the geometrical conversion. However, the isomerization was free from thermal decomposition up to ca. 85% conversion and decomposition was of less importance or absent at lower temperatures.

Proton NMR spectroscopy represents a convenient way of studying the isomerization of the species [Pd(C_6F_5)$_2$(tht)$_2$]. The CH_2S signal was selected for the kinetic studies. This signal due to the *trans* isomer clearly decreases with time, matching the increase of the corresponding resonance of the *cis* isomer. Typical time-conversion curves for the *trans* to *cis* and *cis* to *trans* isomerizations in $CDCl_3$ at 60 °C are illustrated in Figure 2 (time-conversion data are available as supplementary material (Table SI)). These curves show that there is a true equilibrium (eq 1) and that both forward and reverse reactions are first-

$$trans\text{-}[Pd(C_6F_5)_2(tht)_2] \underset{k_{ct}}{\overset{k_{tc}}{\rightleftarrows}} cis\text{-}[Pd(C_6F_5)_2(tht)_2] \quad (1)$$

order in the concentration of the complexes. For this reversible reaction the followng rate expression is derived:[9]

$$\frac{[c]_{eq}}{[t]_0} \ln \frac{[c]_{eq}}{[c]_{eq} - [c]} = k_{tc}t \quad (2)$$

In the eq 2 $[t]_0$ represents the initial concentration of the *trans*

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Table 1. Kinetic and Thermodynamic Data for the Uncatalyzed Isomerization of $[Pd(C_6F_5)_2(tht)_2]$ Complexes in Deuteriochloroform

T, K	10^5k_{tc},[a] s^{-1}	10^5k_{ct},[b] s^{-1}	K_{eq}[c]
313.16	0.233	0.0169	13.8
318.16	0.448	0.034	13.1
323.16	1.17	0.096	12.2
328.16	2.22	0.19	11.7
333.16	5.83	0.51	11.4

[a] $\Delta H_{tc}^{\ddagger} = 137 \pm 6$ kJ mol^{-1}; $\Delta S_{tc}^{\ddagger} = 83 \pm 19$ J K^{-1} mol^{-1}. [b] $\Delta H_{ct}^{\ddagger} = 145 \pm 6$ kJ mol^{-1}; $\Delta S_{ct}^{\ddagger} = 88 \pm 19$ J K^{-1} mol^{-1}. [c] $\Delta H^{\circ} = -8.6 \pm 0.7$ kJ mol^{-1}; $\Delta S^{\circ} = -6 \pm 2$ J K^{-1} mol^{-1}.

Table 2. Effect of tht on the Rates of the Uncatalyzed Isomerization of $[Pd(C_6F_5)_2(tht)_2]$ Complexes in Deuteriochloroform at 55 °C

10^4[tht], mol dm^{-3}	$10^5k_{tc\ obsd}$, s^{-1}	$10^5k_{ct\ obsd}$, s^{-1}	10^4[tht], mol dm^{-3}	$10^5k_{tc\ obsd}$, s^{-1}	$10^5k_{ct\ obsd}$, s^{-1}
0.0	2.22	0.19	4.0	0.57	0.049
0.5	1.36	0.12	6.0	0.40	0.035
1.0	1.21	0.10	10.0	0.256	0.022
2.0	0.90	0.077			

isomer, $[c]_{eq}$ is the concentration of the *cis* isomer at equilibrium, and [c] is the concentration of the *cis* isomer at time *t*. All plots gave straight lines for at least 2–3 half-lives. The equilibrium constant $K_{eq} = k_{tc}/k_{ct} = [c]_{eq}/[t]_{eq}$ was obtained by integration of the ^{1}H NMR CH_2S resonances of the two isomers after 6 or 7 half-lives. Hence, by combining k_{tc} with the equilibrium constant, we obtained k_{ct}. The data for the temperature effect on the rate of the forward and reverse reactions and on the equilibrium constant are collected in Table 1. The values of k_{tc} and K_{eq} were averaged over five independent experiments and were reproducible to better than ±5%.

The rates of interconversion of the isomers are very slow, and the equilibrium lies on the side of the *cis* form. Addition of small amounts of tht to a solution of *trans*-$[Pd(C_6F_5)_2(tht)_2]$ resulted a depression of the rate of isomerization, as shown by the values of the first-order rate constants in Table 2. The plot of $1/k_{tc,obsd}$ vs [tht] is linear with a finite intercept, which is identical with the value of $1/k_{tc}$ obtained in the absence of tht. This result indicates a rate law of the form

$$k_{tc,obsd} = a/(b[\text{tht}] + c) \quad (3)$$

(b) Nucleophilic Substitution. The reactions of *trans*- and *cis*-$[Pd(C_6F_5)_2(tht)_2]$ with pyridine (py) have been qualitatively examined by proton NMR. When an excess of py (1 mol dm^{-3}) was added to a solution of the *trans* isomer (0.05 mol dm^{-3}) in $CDCl_3$ at 20 °C, the NMR spectra showed that the displacement of tht occurs in two consecutive steps, the first being fast. The signal of free tht [$\delta(CH_2S)$ 2.82] is observed immediately after mixing, together with a signal of equivalent intensity of coordinated tht [$\delta(CH_2S)$ 2.72], reasonably assigned to the complex *trans*-$[Pd(C_6F_5)_2(py)(tht)]$. This species changed with time into a second species, since only the signal of free tht was observed 1 h after the mixing. Upon the addition of petroleum ether (bp 40–60 °C) to this solution, a white precipitate was obtained. This was isolated and analytically and spectroscopically identified as *trans*-$[Pd(C_6F_5)_2(py)_2]$.[10] The signals of the ^{1}H NMR spectrum in deuteriochloroform are assigned as follows: δ 7.24 (2 H, m, $H^{3,5}$), 7.65 (1 H, m, H^4), 8.74 (2 H, m, $H^{2,6}$).

The reaction of *cis*-$[Pd(C_6F_5)(tht)_2]$ with an excess of py was fast with respect to the NMR time scale, and only the signals of free tht were observed after mixing. The complex *cis*-$[Pd(C_6F_5)_2(py)_2]$ was isolated from this solution. The resonances of the aromatic protons are assigned as follows: δ 7.32 (2 H, m, $H^{3,5}$), 7.74 (1 H, m, H^4), 8.55 (2, H, m, $H^{2,6}$). These substitution reactions occur with retention of the geometry, and the *cis* isomer is found to react faster than the *trans* isomer. The observed reactivity agrees with the greater *trans* effect of the C_6F_5 group compared with that of py.

When the complex *trans*-$[Pd(C_6F_5)_2(tht)_2]$ (0.02 mol dm^{-3}) was reacted with an excess of 2-methylpyridine (2-pic; 0.4 mol dm^{-3}), the ^{1}H NMR spectra showed that the rate of the first stage had slowed down. The intensity of the signal of free tht is equivalent to that of coordinated tht of the monosubstituted species [$\delta(CH_2S)$ 2.72] 20 min after mixing. No further spectral variation was observed after 12 h at room temperature. From the reaction mixture the complex *trans*-$[Pd(C_6F_5)_2(2\text{-pic})(tht)]$ was isolated. The *trans* geometry is inferred from its IR spectrum showing a single band at 770 cm^{-1}. The signals of the proton NMR spectrum in deuterated chloroform are assigned as follows: δ 1.91 (4 H, m, CH_2), 2.72 (4 H, m, CH_2S), 2.99 (3 H, s, CH_3), 7.11 (1 H, m, H^4), 7.14 (1 H, dd, H^3), 7.53 (1 H, td, H^5), 8.96 (1 H, br d, H^6).

These findings suggest that the reaction between *trans*-$[Pd(C_6F_5)_2(tht)_2]$ and 2-pic proceeds according to eq 4.

$$\textit{trans}\text{-}[Pd(C_6F_5)_2(tht)_2] + 2\text{-pic} \xrightarrow{k_N} \textit{trans}\text{-}[Pd(C_6F_5)_2(2\text{-pic})(tht)] + \text{tht} \quad (4)$$

The kinetics of this reaction was studied at different temperatures by conventional spectrophotometric methods in chloroform under pseudo-first-order conditions. The k_{obsd} values, available as supplementary material (Table SII), when plotted against the concentration of the nucleophile, gave straight lines, which passed through the origin within the limits of experimental error. The substitution reaction follows the rate equation

$$k_{obsd} = k_N[L] \quad (5)$$

The second-order rate constant k_N refers to the associative attack of the nucleophile on the substrate. The values of k_N, obtained from linear regression analysis of the rate law, are listed in Table 3 (uncertainties are standard errors of estimates).

Table 3. Temperature Dependence of the Rate Constants for the Substitution Reaction of Eq 4[a]

T, K	10^2k_N, mol^{-1} dm^3 s^{-1}	*T*, K	10^2k_N, mol^{-1} dm^3 s^{-1}
293.16	0.676 ± 0.014	308.16	1.88 ± 0.12
298.16	0.952 ± 0.022	313.16	2.61 ± 0.11
303.16	1.28 ± 0.05	318.16	3.78 ± 0.15

[a] $\Delta H_N^{\ddagger} = 51 \pm 1$ kJ mol^{-1}; $\Delta S_N^{\ddagger} = -114 \pm 4$ J K^{-1} mol^{-1}.

Discussion

A number of mechanisms have been proposed for isomerization of d^8 complexes,[6,11] including association to give ionic or five-coordinate intermediates, dissociation to give three-coordinate species, and involvement of tetrahedral intermediates.

Mass-law retardation of the isomerization of the complexes $[Pd(C_6F_5)_2(tht)_2]$ by added tht suggests that the rate-determining step must involve the reversible release of tht.

The mechanism that properly accounts for the kinetic and thermodynamic data is shown in Scheme 1.

This mechanism involves a dissociative path in which the breaking of the bond between the metal and the sulfur atom of the tht ligand gives a neutral three-coordinate "*trans*-like" intermediate. This interconverts into its "*cis*-like" analogue that eventually undergoes the reentry of tht to yield *cis*-$[Pd(C_6F_5)_2(tht)_2]$. We assume that the two geometrically distinct intermediates have T-shaped stereochemistry. MO calculations

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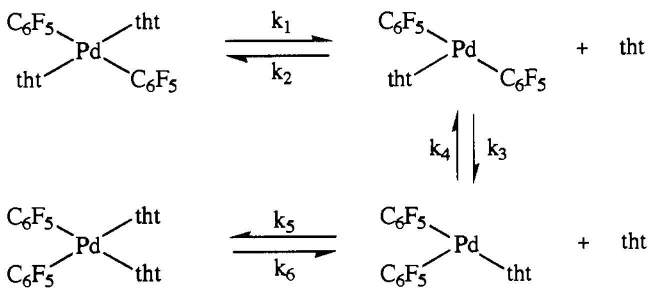
Scheme 1



provide theoretical support for the configurational stability of T-shaped three-coordinated species and the energetic scheme for their conversion.[12]

Employing the steady-state approximation, we determine the rate law for the mechanism of Scheme 1 as

$$-d[trans\text{-}Pd(C_6F_5)_2(tht)_2]/dt = k_{tc}[trans\text{-}Pd(C_6F_5)_2(tht)_2] - k_{ct}[cis\text{-}Pd(C_6F_5)_2(tht)_2] \quad (6)$$

where

$$k_{tc,obsd} = \frac{k_1k_3k_5}{(k_2k_4 + k_3k_5) + k_2k_5[tht]} \quad (7)$$

and

$$k_{ct,obsd} = \frac{k_2k_4k_6}{(k_2k_4 + k_3k_5) + k_2k_5[tht]} \quad (8)$$

This mechanism is in agreement with all experimental findings. Equation 6 shows that $k_{tc}/k_{ct} = K_{eq} = [cis\text{-}Pd(C_6F_5)_2(tht)_2]/[trans\text{-}Pd(C_6F5)_2(tht)_2]$. The *cis* isomer is enthalpy favored. The *trans* to *cis* isomerization is exothermic ($\Delta H° = -8.6 \pm 0.7$ kJ mol^{-1}). In fact, the *cis* geometry avoids placing two ligands of high *trans*-influence (the C_6F_5 group) opposite to each other and allows a greater amount of palladium–sulfur π back-donation. The negative value of entropy ($\Delta S° = -6 \pm 2$ J K^{-1} mol^{-1}) agrees with the expectation that the solvent shell is more ordered for the polar *cis* isomer.

The rate law of eq 7 is in agreement with eq 3 since it predicts a linear plot of $1/k_{tc,obsd}$ vs [tht]. When no tht is added, if $k_2k_4 < k_3k_5$, eq 7 reduces to $k_{tc} = k_1$, and hence the rate constant, k_1, of palladium–sulfur bond breaking can be obtained either from the intercept of the mass-law retardation plot or, more simply, by carring out the isomerization in neat solvent. The value of the ratio k_2/k_3 can also be calculated from the linear plot of $1/k_{tc,obsd}$ vs [tht]. This ratio measures the efficiency of tht in capturing the unsaturated *trans*-like intermediate in competition with the process leading to the *cis* isomer. The calculated value (k_2/k_3 $= 7 \times 10^3$) shows that reassociation of the *trans*-like intermediate with tht (1 mol dm^{-3}) is at least 10^3 times faster than its conversion to the *cis*-like intermediate. This result is consistent with a theoretical study of the isomerization of the complexes *trans*-[$PdMe_2L_2$] (L = tertiary phosphines).[12] It has been shown that the T-shaped *trans*-like PdR_2L, arising from dissociation of L from *trans*-[PdR_2L_2], will encounter a consistent energy barrier to its rearrangement to the *cis*-like species.

The suggested rate-determining bond cleavage in Scheme 1 is supported from the high value of the enthalpy of activation ($\Delta H_{tc}^{\ddagger} = 137 \pm 6$ kJ mol^{-1}) and the large positive value of entropy of activation ($\Delta S_{tc}^{\ddagger} = 83 \pm 19$ J K^{-1} mol^{-1}). The activation parameters for the isomerization are in sharp contrast with the low enthalpy ($\Delta H_N^{\ddagger} = 51 \pm 2$ kJ mol^{-1}) and the negative entropy of activation ($\Delta S_N^{\ddagger} = -114 \pm 4$ J K^{-1} mol^{-1}) obtained for the substitution reaction of *trans*-[$Pd(C_6F_5)_2(tht)_2$]. The comparison of the data for the isomerization (Table 1) and for the substitution reaction (Table 3) shows unambiguously that the associative mechanism remains the favored pathway for substitution and the dissociative mechanism, while being present, normally gives a negligible contribution to the reactivity of these organopalladium complexes. The values of the activation parameters for the isomerization of the complexes [$Pd(C_6F_5)(tht)_2$] compare well with those obtained for the dissociative substitution of sulfur donor ligands from *cis*-[$Pt(C_6H_5)_2(Me_2S)_2$] ($\Delta H^{\ddagger} = 101$ kJ mol^{-1}, $\Delta S^{\ddagger} = 42$ J K^{-1} mol^{-1}) by a nitrogen chelating ligand,[13] where the key intermediates is a coordinatively unsaturated 14-electron species of the type [PtR_2L]. Therefore, it is reasonable to think that the same factors influencing the stability of the coordinatively unsaturated platinum(II) species are involved in the stabilization of [PdR_2L] species. It was recently demonstrated[14] that the promotion of a dissociative pathway is mainly a combined result of a ground-state destabilization and stabilization of the three-coordinate intermediate by extensive electron transfer from the σ-donor ligands to the metal. In connection with this, it is noteworthy that the complexes *trans*-[$PdCl_2$(thioether)$_2$] are stable in a chloroform solution and there is no evidence of *cis*–*trans* isomerization.[15] Perhaps a kinetic investigation of the effect of changing the nature of L on the isomerization of complexes of the type [$Pd(C_6F_5)_2L_2$] could add important information regarding the role of ancillary ligands in the dissociative mechanism of organopalladium complexes.

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Supplementary Material Available: Table SI, giving time-conversion data for the isomerization, and Table SII, giving pseudo-first-order rate constants (k_{obsd}, s^{-1}) for the substitution reaction (4 pages). Ordering information is given on any current masthead page.

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