Atropisomerization in *cis*-[Pd(2-C_6BrF_4)$_2$$L_2$] (L = Thioether): A Dual Mechanism Involving Ligand-Dissociative and Nondissociative Competitive Pathways

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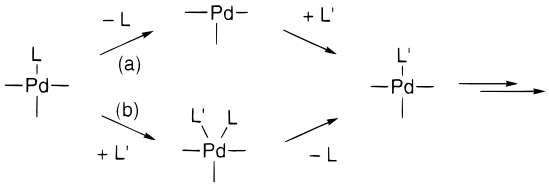
Interconversion of the syn and anti rotational isomers of *cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$] (**1**) (tht = tetrahydrothiophene) takes place very fast in $CDCl_3$ solution. The process has been studied by ^{19}F NMR magnetization transfer experiments. The first-order syn-to-anti atropisomerization rate constant k_{ab} decreases with the addition of tht until it reaches an asymptotic value (1.419 ± 0.012 s^{-1} at 299.1 K). This behavior reveals a dual mechanism involving two competitive pathways: the rotation of the aryl group in the four-coordinate complex **1** and the rotation in a three-coordinate species formed by tht dissociation from **1**. The latter is a clear-cut example of a mechanism starting with a neutral ligand dissociation in an organopalladium(II) complex. The activation parameters associated to each of these two pathways are $\Delta H^{\ddagger} = 83 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = 37 \pm 10$ J K^{-1} mol^{-1}, for the nondissociative path, and $\Delta H^{\ddagger} = 77 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = 28 \pm 10$ J K^{-1} mol^{-1} for the dissociative contribution. Similar energy is required (at 293 K) for the aryl rotation directly in the four-coordinate complex **1** ($\Delta G^{\ddagger} = 72 \pm 4$ kJ mol^{-1}) or via tht dissociation ($\Delta G^{\ddagger} = 70 \pm 4$ kJ mol^{-1}); hence, the two pathways make noticeable contributions to the atropisomerization process.

Introduction

A dissociation (usually of a neutral ligand) is often proposed as the initial step in many reactions involving Pd(II) and other square planar d^8 organometallic complexes. This dissociation enables subsequent β-H elimination,[1a−c] isomerization,[1d−j] reductive elimination,[1d−i] or exchange reactions.[1k] Support for the dissociation step comes mostly from observation of a rate retarding effect by addition of ligand. For instance, in multistep reactions involving an initial ligand substitution, it is usually assumed that the observation of a retardation effect upon addition of excess of neutral ligand L indicates a dissociative (unimolecular) step, in which an organopalladium(II) complex loses L (Scheme 1a);[1h,2] then, the vacant coordination site is occupied by an incoming ligand L′ in a fast process. However, such retardation effect can also be compatible with an associative (bimolecular) ligand substitution (Scheme 1b).[3] Hence, the proposal of a dissociative mechanism needs to be supported by additional data other than the ligand retardation effect, for example, values of the activation parameters.[4]

Scheme 1



On the other hand, it is important to realize that ligand substitution processes (which are probably the most studied kinetically) are very unlikely to be dissociative in Pd(II). In fact, to the best of our knowledge there is not a single example so far which has been proved to be dissociative. The reason is that, in the presence of an incoming ligand or solvent, the alternative associative substitution is much faster. Only in Pt(II), where associative substitutions are much slower than in Pd(II) and the dissociative mechanisms are less disfavored, have the latter been demonstrated.[5] Thus the search for unambiguous dissociative processes in Pd(II) should be better focused on processes other than ligand substitutions.

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Table 1. Data for the Atropisomerization of *syn*,*cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$] (**1a**) into *anti*,*cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$] (**1b**):[a] Equilibrium Constant (K_{eq}), Rate Constant (k_{ab}), and Nondissociative (k_1) and Dissociative (k_{Dis}) Contributions to k_{ab}

T/K	K_{eq}	$[tht]_{added}$/ 10^{-4} mol L^{-1}	k_{ab}/s^{-1}	k_1/s^{-1}	k_{dis}/s^{-1}
276.7 ± 0.2	3.19 ± 0.04	0	0.661 ± 0.006	0.0744 ± 0.0006	0.587 ± 0.005
282.3	3.13 ± 0.05	0	1.181 ± 0.009		
287.7	3.02 ± 0.08	0	2.15 ± 0.03	0.395 ± 0.003	1.76 ± 0.03
293.1	2.95 ± 0.03	0	3.95 ± 0.06	0.732 ± 0.008	3.22 ± 0.05
299.1	2.91 ± 0.05	0	8.11 ± 0.09	1.419 ± 0.012	6.69 ± 0.06
293.1*b*		0	8.36 ± 0.16		
299.1[c]		0	5.05 ± 0.10		
299.1		1.00 ± 0.02	6.02 ± 0.09		
299.1		1.25 ± 0.03	5.47 ± 0.09		
299.1		1.67 ± 0.04	4.94 ± 0.06		
299.1		2.50 ± 0.04	4.08 ± 0.05		
299.1		5.00 ± 0.05	2.76 ± 0.03		
299.1		110 (∞)	1.419 ± 0.012		
305.0	2.77 ± 0.02	0	14.10 ± 0.19	2.99 ± 0.04	11.11 ± 0.15
311.3	2.75 ± 0.03	0	27.5 ± 0.6		
317.7	2.64 ± 0.02	0	60 ± 3	9.21 ± 0.2	51 ± 3

[a] $[\mathbf{1}]_{total} = (2.00 \pm 0.07) \times 10^{-2}$ mol L^{-1} in $CDCl_3$. [b] Using CaH_2-dried $CDCl_3$. [c] Using $CDCl_3$-saturated with water.

The thermodynamic data in the literature for dissociative processes in Pd(II) are very scarce.[6] Sen et al. have determined the values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the reaction Pd(COCOPh)Cl$(PPh_3)_2$ = Pd(COCOPh)Cl(PPh_3) + PPh_3.[6a] $\Delta G^{‡}$ values have been reported on the mechanism of apparent rotation in (π-allyl)−palladium complexes with bidentate nitrogen ligands, which seems to occur via cleavage of a Pd−N bond, although some aspects remain obscure.[6b] Finally, as a result of the study of the thermolysis behavior of *trans*-[PdEt(OAc)$(PMe_3)_2$], the following values were obtained for the dissociation of AcO^- in EtOH: $\Delta H^{‡}$ = 41.4 kJ mol^{-1} and $\Delta S^{‡}$ = −171.4 J K^{-1} mol^{-1}.[6c] The large negative $\Delta S^{‡}$ value was interpreted as the dissociation of the acetate being assisted by solvent coordination.

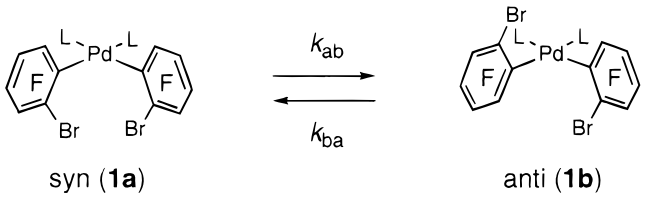
Whenever a dissociation process is followed by subsequent steps leading to products different from the starting materials (e.g., isomers, coupling products in a thermal decomposition, products of a ligand exchange), there is some uncertainty whether the activation parameters determined are related to the dissociative step (assumed to be the rate-determining step) or to a subsequent step in the whole process (if that assumption is not correct). Thus we have recently shown that the $\Delta H^{‡}$ and $\Delta S^{‡}$ values measured in a study of the cis−trans isomerization of [Pd$(C_6F_5)_2$(tht)$_2$] (tht = tetrahydrothiophene), which had been assigned to the initial tht dissociation step,[7] are very much influenced by the subsequent topomerization step of the three-coordinate intermediate.[8] Also the intermolecular aryl exchange reaction in [PdR_2L_2] complexes involves initial L dissociation, but again the parameters measured do not correspond to the dissociation step, which is fast.[9]

To avoid these uncertainties, it is necessary to carry out studies on systems offering the dissociation as isolated as possible from other subsequent processes, preferably as the only one occurring. We have found that the study of the hindered rotation of some aryls in palladium complexes offers this opportunity. For example, the rotation of C_6F_5 in [Pd(C_6F_5)X(SPPy$_2$Ph)-*N*,*S*] (X = Cl, Br, I; Py = pyridin-2-yl) in chloroform occurs in a dissociated contact ion pair [Pd(C_6F_5)(SPPy$_2$Ph)-*N*,*S*]·X and allows measurement of the parameters for the dissociation of halides.[10] In other cases the aryl rotation can take place without dissociation.[11]

In this paper we report the atropisomerization of *cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$],[12] which we believe is the most unambiguous example of a dissociative mechanism operating in a Pd(II) complex and involving dissociation of a neutral ligand.

Results

Atropisomerization in *cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$]. The interconversion of the syn and anti rotational isomers of *cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$] (**1**) in $CDCl_3$ solution (eq 1) is very fast



syn (**1a**) anti (**1b**)

compared to the preparative time scale, and the compound is obtained as an equilibrium mixture of the syn (**1a**) and the anti (**1b**) forms in approximate ratio 1:3 (see Table 1 for K_{eq} at different temperatures).[12]

The atropisomerization rate at a given temperature can be measured by ^{19}F NMR magnetization transfer techniques (see the Experimental Section). A typical experiment, inverting the F^6 signal of **1b**, is shown in Figure 1. The data analysis has been made by applying eqs 2 and 3 (derivation of these equations is available as Supporting Information),[13] where a_t corresponds to the peak area of **1a** atropisomer and b_t to that of the **1b** one.

(6) (a) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148−156, and literature cited in ref 10 in this paper. (b) Gogoll, A.; Örnebro, J.; Grennberg, H.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1994**, *116*, 3631−3632. (c) Kawataka, S.; Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Organometallics* **1994**, *13*, 3517−3524.
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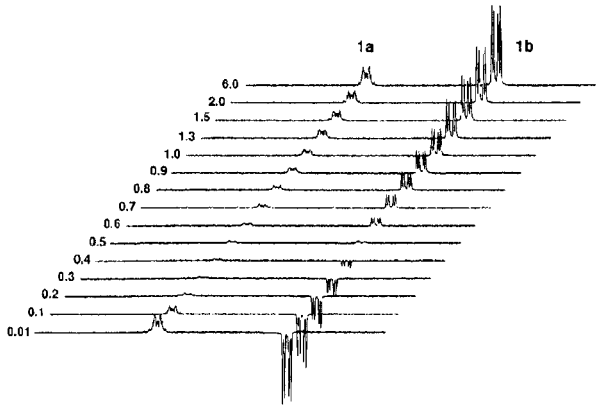

Figure 1. ^{19}F NMR magnetization transfer experiment (282 MHz, F^6 signals) between the syn (**1a**) and the anti (**1b**) atropisomers of *cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$]. $[\mathbf{1}]_{total} = (2.00 \pm 0.07) \times 10^{-2}$ mol L^{-1} in $CDCl_3$ at 293.5 K. The magnetization transfer delay t is given in seconds.

$$\ln\{[a_\infty + b_\infty] - [a_t + b_t]\} = -R_1 t + C \qquad (2)$$

$$\ln\left(a_t - \frac{a_\infty}{b_\infty}\right) = \left[-R_1 - k_{ab}\left(1 + \frac{a_\infty}{b_\infty}\right)\right]t + C \qquad (3)$$

Fitting the experimental values to eqs 2 and 3 we obtain the relaxation rate R_1 (making the assumption that it is the same for both isomers) and the first-order rate constant for the syn-to-anti atropisomerization, k_{ab}.

The atropisomerization rate constant for the opposite direction (i.e., anti-to-syn), k_{ba}, can be measured similarly by inverting the signal of **1a** in Figure 1. Nevertheless, it is easier to calculate it from the equilibrium constant (K_{eq}) defined in eq 4,

$$K_{eq} = \frac{[\mathbf{1b}]}{[\mathbf{1a}]} = \frac{k_{ab}}{k_{ba}} \qquad (4)$$

which is measured in the ^{19}F NMR spectrum of the equilibrium mixture. The rate constants k_{ab} and the equilibrium constants at different temperatures are given in Table 1.

The kinetic results reveal that the atropisomerization rate is retarded by addition of free tht, although this retardation has a limit (Figure 2): the first-order rate constant k_{ab} diminishes by the addition of tht until an asymptotic value is reached (1.419 $\pm$ 0.012 s^{-1} at 299.1 K). Further additions of tht do not change k_{ab}. Thus, there are two independent pathways leading to atropisomerization, one retarded by addition of tht and one unaffected which remains productive even at high concentration of tht. On the other hand, the atropisomerization is not catalyzed by the addition of water. On the contrary, it is slightly retarded (Table 1).

The temperature dependence of the equilibrium constant (Table 1) leads to the following thermodynamic parameters for the syn-to-anti direction: $\Delta H^\circ = -3.34 \pm 0.17$ kJ mol^{-1} and $\Delta S^\circ = -2.4 \pm 0.6$ J K^{-1} mol^{-1}.[14]

Atropisomerization in *cis*-[Pd(2-C_6BrF_4)$_2$(3,5-Me_2py)$_2$]. *cis*-[Pd(2-C_6BrF_4)$_2$(3,5-Me_2py)$_2$] (**2**) also gives an equilibrium mixture of two atropisomers, where the anti predominates (K_{eq} = 1.30). The syn-to-anti atropisomerization rate measured by ^{19}F NMR magnetization transfer was $k_{ab} = 2.08 \pm 0.07$ s^{-1} at 328.0 K. In contrast to the previous case, here this value does not change upon addition of free 3,5-dimethylpyridine.

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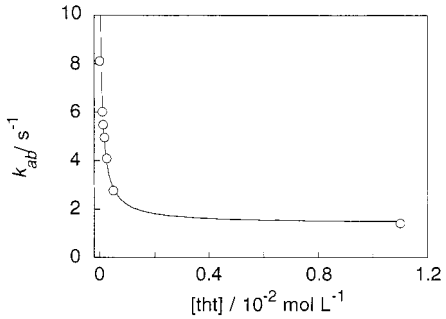
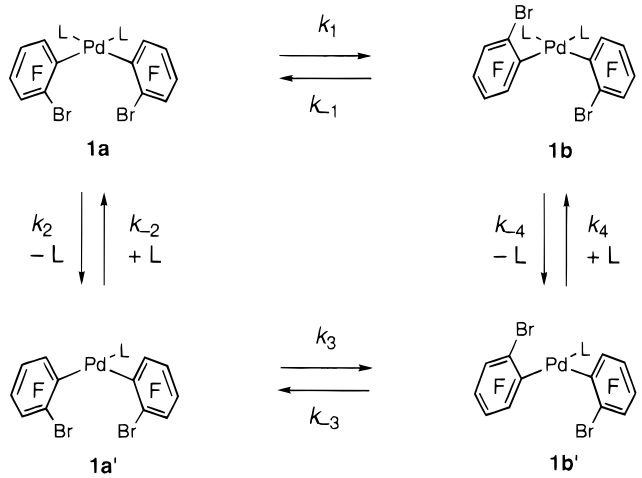


Figure 2. Retarding effect of the addition of tht on the atropisomerization of *syn,cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$] (**1a**) into *anti,cis*-[Pd(2-C_6BrF_4)$_2$-(tht)$_2$] (**1b**). $[\mathbf{1}]_{total} = (2.00 \pm 0.07) \times 10^{-2}$ mol L^{-1} in $CDCl_3$ at 299.1 K.

Scheme 2



Discussion

Mechanisms of Atropisomerization. The interconversion between the atropisomers *syn,cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$] (**1a**) and *anti,cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$] (**1b**) shows a remarkable kinetic effect: the atropisomerization is retarded by the addition of tht until a limiting value is reached. This behavior can be understood by considering the simultaneous occurrence of the two atropisomerization pathways shown in Scheme 2: (1) The *direct conversion* by rotation of the aryl group in the four-coordinate complexes **1a** and **1b** and (2) the *dissociative conversion*, by rotation in three-coordinate species **1a′** and **1b′** formed by dissociation of tht form **1a** and **1b**, respectively. For the complex *cis*-[Pd(2-C_6BrF_4)$_2$(3,5-Me_2py)$_2$] (**2**), no dissociative contribution is detected. Obviously, the labile tht in **1** greatly facilitates the dissociative pathway, contribution of which is negligible for complexes with better ligands such as pyridines.

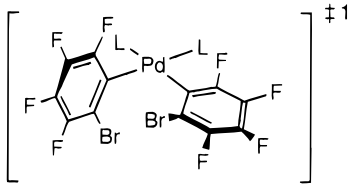
Applying the steady-state approximation to the mechanism in Scheme 2 we get the expressions for k_{ab} and k_{ba} given in eqs 5 and 6 (the derivation of these equations is available as Supporting Information).

$$k_{ab} = k_1 + \frac{k_2 k_3 k_4}{k_{-2}(k_{-3} + k_4[\text{tht}]) + k_3 k_4} \qquad (5)$$

$$k_{ba} = k_{-1} + \frac{k_{-2} k_{-3} k_{-4}}{k_{-2}(k_{-3} + k_4[\text{tht}]) + k_3 k_4} \qquad (6)$$

The atropisomerization equilibrium constant K_{eq}, which is independent of the concentration of tht, is related to the observed

Chart 1



rate constants (k_{ab} and k_{ba}) and to the elementary rate constants of the two contributing mechanisms in Scheme 2, as shown in eq 7:

$$K_{eq} = \frac{k_{ab}}{k_{ba}} = \frac{k_1}{k_{-1}} = \frac{k_2 k_3 k_4}{k_{-2} k_{-3} k_{-4}} \quad (7)$$

Equation 5 is consistent with our kinetic results (Table 1). There are two contributions to the observed syn-to-anti atropisomerization rate constant k_{ab} (the same applies to k_{ba}). One is independent of the tht concentration and accounts for the aryl rotation in the four-coordinate complex **1a**, via k_1. It can be measured for very high concentration of added tht, when it is the only contributing pathway. The other term decreases with [tht] and is assigned to the aryl rotation in a three-coordinate complex **1a′**. Accordingly, it has been labeled k_{dis} (eq 8). This contribution can be calculated as the difference between the observed rate constant k_{ab} and k_1 (eq 9).

$$k_{dis} = \frac{k_2 k_3 k_4}{k_{-2}(k_{-3} + k_4[\text{tht}]) + k_3 k_4} \quad (8)$$

$$k_{dis} = k_{ab} - k_1 \quad (9)$$

Thus, the contributions of the two competitive pathways, via k_1 and via k_{dis}, can be separated at each temperature, and the corresponding values are given in the last two columns of Table 1.

Atropisomerization in the Four-Coordinate Complex. An Eyring treatment of the k_1 values yields the following activation parameters: $\Delta H^{\ddagger}_1 = 83 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger}_1 = 37 \pm 10$ J K^{-1} mol^{-1}. These values suggest an activated complex very sterically hindered and disordered along step k_1, as outlined in Chart 1. The rotation in **1a** probably requires an elongation of the Pd−SC_4H_8 and Pd−aryl bonds and some angle deformations. We have shown previously that the hindrance to rotation is mostly determined by the interference of the ortho substituent in the aryl group with the donor atom of the ligands cis to it.[11] Here two possible rotation directions can be envisaged as a consequence of the asymmetry of the aryl group. However, rather than a complete rotation, it seems easier that the atropisomerization takes place by half-rotations in both senses, always with the F atom toward the S-donor ligand L (as in Chart 1) since this produces less steric hindrance in the activated complex.

Atropisomerization in the Three-Coordinate Complex. An Eyring treatment of the k_{dis} values affords the following activation parameters: $\Delta H^{\ddagger}_{dis} = 77 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger}_{dis} = 28 \pm 10$ J K^{-1} mol^{-1}. The interpretation of these values is not as simple as before, since they cannot be directly assigned to only one elemental step. In fact, only for [tht] = 0 would eq 8 simplify to $k_{dis} = k_2$ (assuming that $k_{-2}k_{-3} \ll k_3k_4$), and only then would the activation parameters correspond to the dissociation of tht from **1a**. However, as we have shown previously,[8,9] even in absence of added tht the actual concentration of ligand ([tht]) is not zero but a finite value arising from autodissociation of both **1a** and **1b**, which can be labeled as $[\text{tht}]_{dis}$. This can be better seen in Figure 3a: the plot of k_{dis}^{-1} vs $[\text{tht}]_{added}$ is not a straight line (as it should be expected if [tht] = $[\text{tht}]_{added}$ in eq 8) but a curve. This curvature is due to the fact that [tht] is underestimated in the low range of $[\text{tht}]_{added}$, where $[\text{tht}]_{dis}$ cannot be neglected. A more correct treatment of the system needs to consider that [tht] = $[\text{tht}]_{added}$ + $[\text{tht}]_{dis}$. An exact mathematical solution of the system is not possible, as the unknown magnitudes are more than experimental data and some approximations are needed.

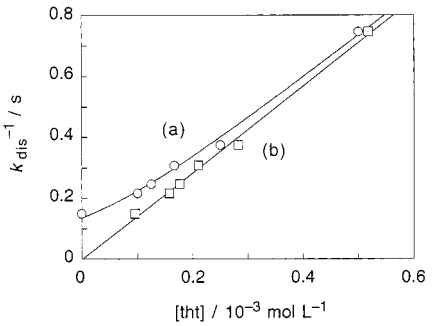


Figure 3. Plots of k_{dis} vs $[\text{tht}]_{added}$ (a) and k_{dis} vs [tht] (b). Note that the curvature in plot a is corrected in plot b by considering the autodissociation, i.e., [tht] = $[\text{tht}]_{added}$ + $[\text{tht}]_{dis}$.

First, we assume that, even in the absence of added tht, the reassociation steps in Scheme 2 are faster than the aryl rotation in the three-coordinate intermediates (hence $k_4[\text{tht}] \gg k_{-3}$, and $k_{-2}[\text{tht}] \gg k_3$). In other words, this means that a preequilibrium (defined by $K_2 = k_2/k_{-2}$) is established. Then eq 8 is simplified to eq 10.

$$k_{dis} = \frac{k_2 k_3}{k_{-2}([\text{tht}]_{added} + [\text{tht}]_{dis})} = \frac{K_2 k_3}{[\text{tht}]_{added} + [\text{tht}]_{dis}} \quad (10)$$

The second reasonable approximation we make is to consider that both atropisomers **1a** and **1b** dissociate tht similarly; i.e., K_2 (for **1a**) = K_4 (for **1b**) = K_{dis} (for **1** total). Thus the dissociation of **1** can be defined as a whole by eq 11,[15] which reduces to eq 12 when $[\text{tht}]_{dis}$ is small. Plugging the value of $[\text{tht}]_{dis}$ from eq 12 into eq 10 we obtain eq 13.

$$K_{dis} = \frac{[\mathbf{1}']_{total}[\text{tht}]}{[\mathbf{1}]_{total} - [\mathbf{1}']_{total}} = \frac{[\text{tht}]_{dis}([\text{tht}]_{added} + [\text{tht}]_{dis})}{[\mathbf{1}]_{total} - [\text{tht}]_{dis}} \quad (11)$$

$$K_{dis} = \frac{[\text{tht}]_{dis}([\text{tht}]_{added} + [\text{tht}]_{dis})}{[\mathbf{1}]_{total}} \quad (12)$$

$$k_{dis} = \frac{k_3}{2[\mathbf{1}]_{total}}\{\sqrt{[\text{tht}]_{added}^{\,2} + 4K_{dis}[\mathbf{1}]_{total}}) - [\text{tht}]_{added}\} \quad (13)$$

$$k_{dis}^{-1} = \frac{2[\mathbf{1}]_{total}}{k_3}\{\sqrt{[\text{tht}]_{added}^{\,2} + 4K_{dis}[\mathbf{1}]_{total}}) - [\text{tht}]_{added}\}^{-1} \quad (14)$$

A nonlinear least-squares analysis of the experimental leading to Figure 3a using eq 14 gives the following values: $K_{dis} = (4.3 \pm 0.8) \times 10^{-7}$ M and $k_3 = 1700 \pm 300$ s^{-1} ($r = 0.998$).[16]

(15) Where $[\mathbf{1}]_{total} = [\mathbf{1a}] + [\mathbf{1b}]$, and $[\mathbf{1}']_{total} = [\mathbf{1a}'] + [\mathbf{1b}']$.

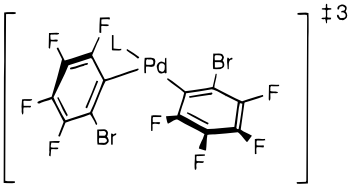
(16) The use of eq 14 is mathematically preferred to that of eq 13 for a least-squares fitting because the dispersion of k_{dis}^{-1} values is more regular than that of k_{dis}.

Table 2. Estimation of the Autodissociation of tht in *cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$] (**1**)

$[tht]_{added}/10^{-4}$ mol L^{-1}	$[tht]_{dis}/10^{-5}$ mol L^{-1}	$[tht]/10^{-4}$ mol L^{-1}	k_{dis}/s^{-1}
0	9.3	0.93	6.60
1.00	5.5	1.55	4.60
1.25	4.9	1.74	4.05
1.67	4.1	2.08	3.52
2.50	3.1	2.81	2.66
5.00	1.7	5.17	1.34

[a] $[\mathbf{1}]_{total} = (2.00 \pm 0.07) \times 10^{-2}$ mol L^{-1} in $CDCl_3$, at 299.1 K.

Chart 2



With this value of K_{dis}, we have calculated [tht] for each value of $[tht]_{added}$ (Table 2). The order of dissociation (about 0.5 mol % Pd for [Pd] = 0.02 mol L^{-1}) is consistent with those estimated by us independently for the dissociation of tht in closely related systems.[8,9]

Plotting the new values of [tht] instead of those of $[tht]_{added}$, a linear correlation between k_{dis}^{-1} and [tht] is obtained with a zero intercept (Figure 3b, intercept = 0.004 ± 0.014 s, slope = 1400 ± 50, r = 0.997). This supports that the assumption initially used is acceptable; i.e., *the existence of a dissociation preequilibrium of* ***1*** *(for both the syn and anti forms) is responsible for the release of free tht, which cannot be neglected in the range of low concentration of added tht.* Consequently, the atropisomerization rate via the dissociative pathway is controlled by both the dissociation of tht and the aryl rotation in three-coordinate intermediates **1a′** and **1b′**, and both processes contribute to the activation parameters associated to k_{dis}. Likely the most important contribution to $\Delta H^{\ddagger}_{dis}$ and $\Delta S^{\ddagger}_{dis}$ must be associated with the dissociation of tht, explaining the high value of the activation enthalpy (a Pd−SC_4H_8 cleavage is needed) and the positive activation entropy (the number of particles increases).

The aryl rotation is about 1000 times faster in the three-cordinate intermediate (k_3) than in the four-coordinate complex (k_1), in agreement with the absence of the Br···S steric hindrance in **1a′** and **1b′**. However, the rotation in the three-coordinate intermediate is still slow (respect to the tht-dissociation) since the interaction F···C remains as a lower but noticeable barrier to rotation (Chart 2).

Analysis of Alternative Pathways. Other plausible mechanisms that could produce a tht-retardable atropisomerization can be discarded: (1) The retarding effect could be due to the formation of a pentacoordinated species [Pd(2-C_6BrF_4)$_2$(tht)$_3$] where the aryl rotation was slower. In the limit of high concentration of tht, all the starting complex would be in the form of this intermediate. In that case the pentacoordinate complex should be easily detected as a new species nearly 100% abundant, but no evidence of it was found by NMR. (2) The dissociative pathway could be in fact an aryl rotation in a water complex, *cis*-[Pd(2-C_6BrF_4)$_2$(tht)(OH_2)], formed upon tht substitution by traces of water present in the solvent. However, independent experiments demonstrate that water does not catalyze the aryl rotation but slightly retards it (which in fact is compatible with an eventual capture of the three-coordinate intermediate).

It is worth noting that in the context of this paper it is not meant that an unsolvated three coordinate species is preserved in solution as distinguishable from a solvent stabilized species. As a matter of fact, a differentiation between these two situations in what are considered noncoordinating solvents is difficult and of no practical consequence. It is customary to use both concepts indistinctly (three-coordinate intermediates such as the one considered here have been proposed by others previously in $CDCl_3$).[5a,7,17] Chloroform is not a coordinant solvent to Pd(II) organometallics (Pd complexes of this kind have been never reported); however, we cannot discount a weak solvent association with the three-coordinate complex. Finally, it is interesting to note that, even if the rotation attributed to a three-coordinate intermediate was occurring in the solvato complex *cis*-[Pd(2-C_6BrF_4)$_2$(tht)(ClCDCl_2)], this should have been formed via a dissociative mechanism: in effect, it is difficult to believe that $CDCl_3$ was able to induce an associative mechanism if the more coordinant and smaller OH_2 does not.

Conclusions

In this paper we have studied the very simple atropisomerization of *cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$] which follows two competitive pathways: one requires the dissociation of neutral ligand tht and the other takes place in a four-coordinate complex. Their activation free energies are very close ($\Delta G^{\ddagger}_1 = 72 \pm 4$ kJ mol^{-1} and $\Delta G^{\ddagger}_{dis} = 70 \pm 4$ kJ mol^{-1} at 293 K), and both pathways make measurable contributions to the atropisomerization. The dissociative pathway represents an unambiguous case of a mechanism initiated by dissociation of a neutral ligand in a Pd(II) complex. Nevertheless, despite the simplicity of the process, the activation parameters cannot be assigned only to the dissociation step (this is probably a quite general problem that should not be overlooked). For complexes with better ligands, the dissociative contribution seems negligible.

Experimental Section

The complexes *cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$] (**1**) and *cis*-[Pd(2-C_6BrF_4)$_2$(cod)] were prepared as previously reported.[12] Deuteriochloroform for the kinetic studies was treated with anhydrous $MgSO_4$ and Na_2CO_3. ^{19}F NMR spectra were run on a Bruker ARX-300 spectrometer equipped with a VT-100 variable-temperature unit (±0.2 K, the temperature was measured by standard methods using MeOH or ethylene glycol).

***cis*-[Pd(2-C_6BrF_4)$_2$(3,5-Me_2py)$_2$] (2).** To a solution of *cis*-[Pd(2-C_6BrF_4)$_2$(cod)] (100 mg, 0.149 mmol) in CH_2Cl_2 (5 mL) was added 3,5-Me_2py (38 μL, 0.33 mol). The mixture was stirred for 20 min and evaporated to dryness. The residue was treated with *n*-hexane, giving a white complex **2** which was washed with *n*-hexane and air-dried (quantitative yield). IR (KBr): 1482 (vs), 1423 (vs), 1156 (m), 1082 (m), 1009 (s), 822 (s), 766 (m), 705 (m). ^1H NMR ($CDCl_3$): δ 8.14 (br s, C*H*), 8.11 (br s, C*H*), 7.34 (br s, C*H*), 2.24 (s, CH_3).^{19}F NMR ($CDCl_3$): δ syn −113.21 (m, CF^6), −128.53 (m, CF^3), −159.07 (m, CF^5), −161.00 (dd, J_{34} = 21.5 Hz, J_{45} = 19.6 Hz, CF^4); anti −112.92 (m, CF^6), −128.52 (dd, J_{34} = 21.5 Hz, J_{36} = 11.0 Hz, CF^3), −159.05 (dd, J_{45} = 19.5 Hz, J_{56} = 31.3 Hz, CF^5), −161.02 (dd, J_{34} = 21.5 Hz, J_{45} = 19.5 Hz, CF^4). Anal. Calcd for $C_{26}H_{18}Br_2F_8N_2Pd$: C, 40.21; H, 2.34; N, 3.61. Found: C, 40.16; H, 2.49; N, 3.51.

Magnetization Transfer Experiments on the Atropisomerization of *cis*-[Pd(2-C_6BrF_4)$_2$(tht)$_2$] (1). NMR tubes (5 mm) were charged with **1** (8.9 ± 0.1 mg, 12.0 ± 0.2 μmol) and suitable amounts of tht (added as aliquots of a standard (30.7 ± 0.7) × 10^{-3} mol L^{-1} solution in $CDCl_3$, previously titrated by ^1H NMR using naphthalene as internal standard). The mixtures were dissolved in $CDCl_3$ to a total volume of 600 ± 5 μL, obtaining (2.00 ± 0.07) × 10^{-2} mol L^{-1} concentrations in **1**. The samples were placed in a thermostated probe. The solutions contain a

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

mixture of two atropisomers in equilibrium, syn (**1a**, minor) and anti (**1b**, major). The interconversion rate was measured by magnetization transfer experiments using ^{19}F NMR (Figure 2): The F^6 signal of **1b** (on resonance) was selectively inverted using a $90°-D_1-90°-t-90°-D_2$ sequence, where $D_1 = {}^1/_2\Delta\nu$, $\Delta\nu$ is the separation in Hz between both signals, t is the magnetization transfer delay, and D_2 the relaxation delay. Values of 90° pulse and D_1 were carefully determined at each temperature. After excitation, the signal areas of both atropisomers were measured at t intervals and fitted to eqs 2 and 3 to obtain the values of k_{ab} (Table 1). Other experiments were carried out by inverting the F^6 signal of **1a**, giving similar values for the atropisomerization rate. Experiments on **2** were carried out following a similar procedure.

Error Analysis. Errors treatment was carried out as previously reported.[9]

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Supporting Information Available: Derivation of eqs 2, 3, 5, and 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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