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Mechanism of the Uncatalyzed Dissociative Cis−Trans Isomerization of Bis(pentafluorophenyl)bis(tetrahydrothiophene): A Refinement

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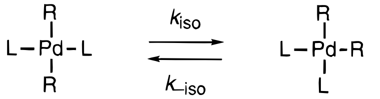
The cis−trans isomerization of complexes $[PdR_2L_2]$ is a very important reaction in organopalladium(II) chemistry (eq 1).[1]



$$\text{L}-\underset{\text{R}}{\overset{\text{R}}{\text{Pd}}}-\text{L} \underset{k_{-\text{iso}}}{\overset{k_{\text{iso}}}{\rightleftarrows}} \text{L}-\underset{\text{L}}{\overset{\text{R}}{\text{Pd}}}-\text{R} \tag{1}$$

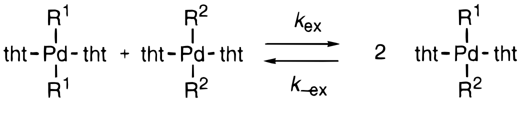
Different mechanisms have been proposed for this process depending on the nature of R and L. Thus, Yamamoto et al. have reported an autocatalytic mechanism in the case of R = Me and L = PR_3, occurring with intermolecular exchange of Me groups.[2] More recently Minniti reported an example of spontaneous intramolecular *cis−trans* isomerization for the case of R = C_6F_5 and L = tht and proposed the mechanism depicted in Scheme 1.[3]

Employing the steady-state approximation, Minniti obtained eq 2 which eventually simplifies to eq 3 in the absence of added tht.[4] He interpreted that the dissociation of tht from complex *trans*-$[Pd(C_6F_5)_2(tht)_2]$ (**1**) (via step k_1) was the rate-determining step of the process and found support for this in the high value of the enthalpy of activation ($\Delta H^{\ddagger}_{\text{iso}} = 137 \pm 6$ kJ mol^{-1}) and the large positive value of entropy of activation ($\Delta S^{\ddagger}_{\text{iso}} = 83 \pm 19$ J K^{-1} mol^{-1}) measured for the isomerization of **1** to *cis*-$[Pd(C_6F_5)_2(tht)_2]$ (**2**).

$$r_{\text{iso,ss}} = k_{\text{iso,ss}}[\mathbf{1}] = \frac{k_1k_2k_3}{(k_{-1}k_{-2} + k_2k_3) + k_{-1}k_3[\text{tht}]}[\mathbf{1}] \tag{2}$$

$$r_{\text{iso,ss}} = k_{\text{iso,ss}}[\mathbf{1}] = k_1[\mathbf{1}] \tag{3}$$

The interpretation given by Minniti appeared correct with the data available at that time. However, in the course of our investigation of the dynamic behavior in solution of bis(perhaloaryl)palladium(II) complexes we have found recently a new process, operating on the same species, which also needs the dissociation of neutral ligand tht. This is the intermolecular exchange of aryls, which can only be detected by means of crossover experiments. Indeed, **1** and *trans*-$[Pd(C_6Cl_2F_3)_2(tht)_2]$ (**3**) exchange their aryl groups giving rise to the heteroaryl complex *trans*-$[Pd(C_6Cl_2F_3)(C_6F_5)(tht)_2]$ (**5**) (eq 4).[5] This process has been shown to proceed stereoselectively, preserving the configuration of the starting complexes, and is faster than the isomerization to their corresponding cis complexes **2** and **4** (the initial reaction rate for the aryl exchange is about 4.2 × 10^{-7} mol L^{-1} s^{-1}, whereas the initial isomerization rate of **1** is 7.3 × 10^{-8} mol L^{-1} s^{-1} in $CDCl_3$ at 320.1 K using (10.0 ± 0.3) × 10^{-3} mol L^{-1} solutions). In other words, the isomerization and the aryl-exchange are two independent reactions, both involving L dissociation. In fact the addition of tht retards both processes.



$$\underset{\mathbf{1}}{\text{tht}-\underset{\text{R}^1}{\overset{\text{R}^1}{\text{Pd}}}-\text{tht}} + \underset{\mathbf{3}}{\text{tht}-\underset{\text{R}^2}{\overset{\text{R}^2}{\text{Pd}}}-\text{tht}} \underset{k_{-\text{ex}}}{\overset{k_{\text{ex}}}{\rightleftarrows}} 2\ \underset{\mathbf{5}}{\text{tht}-\underset{\text{R}^2}{\overset{\text{R}^1}{\text{Pd}}}-\text{tht}} \tag{4}$$

This affects the interpretation of the results on isomerization reported by Minniti because it is not possible that the dissociation of tht from complexes **1** or **3** controls both the isomerization and the aryl exchange, since these two processes have very different rates. Moreover, the dissociation of tht cannot be limiting the reaction rate of the trans-to-cis isomerization, which is the slower one. The same can be applied to the cis complexes, **2** and **4**, for which the differences in rate for the two processes are even higher.[6]

Thus, although the mechanism outlined in Scheme 1 is essentially correct, a revision of the kinetic approximation, and a reinterpretation of the activation parameters are needed. In our approximation, according to the experimental results, the dissociation of tht is considered to be faster than the topomerization of the three-coordinate intermediate **A**. This means that a preequilibrium will be established upon dissociation of **1**. Hence the isomerization rate is controlled by two factors, namely (1) the extension of the dissociation preequilibrium, which determines the concentration of **A**; and (2) the subsequent topological rearrangement of **A**. Considering the dissociation constant $K_{\text{eq}} = k_1/k_{-1}$, and using this assumption we obtain eq 5.[7] Equation 5 is formally similar to eq 2 and explains also the retarding effect of the addition of tht.

$$r_{\text{iso,pe}} = k_{\text{iso,pe}}[\mathbf{1}]_{\text{total}} = \frac{K_{\text{eq}}k_2}{[\text{tht}] + K_{\text{eq}}}[\mathbf{1}]_{\text{total}} \tag{5}$$

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(1) Cross, R. J. *Adv. Inorg. Chem.* **1989**, *34*, 219−292.

(2) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868−1880.

(3) Minniti, D. *Inorg. Chem.* **1994**, *33*, 2631−2634.

(4) Subscript “ss” in equations refers to the steady-state approximation, and “pe” is relative to the preequilibrium model.

(5) Casado, A. L.; Casares, J. A.; Espinet, P. *Organometallics* **1997**, *16*, 5730−5736.

(6) The cis complexes **2** and **4** exchange their aryls about 5 times faster than the trans complexes, whereas the isomerization rate in the cis-to-trans direction is about 13 times slower than in the trans-to-cis direction (as derived from the equilibrium constant value).

(7) The equilibrium is very much shifted to the cis isomer (more than 97%) and in practice can be properly considered as irreversible for the mathematical treatment. The concentration of intermediate **A** is determined by the equilibrium constant K_{eq} as

$$[\mathbf{A}] = \frac{K_{\text{eq}}}{[\text{tht}] + K_{\text{eq}}}[\mathbf{1}]_{\text{total}}$$

where $[\mathbf{1}]_{\text{total}} = [\mathbf{1}] + [\mathbf{A}]$. The reaction rate is then

$$r_{\text{iso,pe}} = -\frac{\partial[\mathbf{1}]_{\text{total}}}{\partial t} = k_2[\mathbf{A}]$$

$$r_{\text{iso,pe}} = \frac{K_{\text{eq}}k_2}{[\text{tht}] + K_{\text{eq}}}[\mathbf{1}]_{\text{total}}$$

from which the first-order isomerization constant is obtained:

$$k_{\text{iso,pe}} = \frac{K_{\text{eq}}k_2}{[\text{tht}] + K_{\text{eq}}}$$

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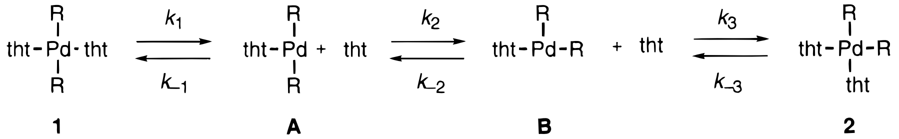
Scheme 1



It is important to realize that the actual concentration of tht in solution is $[\text{tht}] = [\text{tht}]_{\text{dis}} + [\text{tht}]_{\text{added}}$, where $[\text{tht}]_{\text{dis}}$ is the concentration arising from autodissociation. In other words, eq 5 can be rewritten as eq 6. Even in absence of added tht, the concentration of tht is not zero, but $[\text{tht}]_{\text{dis}}$. This equation can be simplified to eq 7 only for high concentrations of tht added but not when these are in the order of the concentration of tht arising from autodissociation.

$$r_{\text{iso,pe}} = k_{\text{iso,pe}}[\mathbf{1}]_{\text{total}} = \frac{K_{\text{eq}}k_2}{[\text{tht}]_{\text{dis}} + [\text{tht}]_{\text{added}} + K_{\text{eq}}}[\mathbf{1}]_{\text{total}} \quad (6)$$

$$r_{\text{iso,pe}} = k_{\text{iso,pe}}[\mathbf{1}]_{\text{total}} = \frac{K_{\text{eq}}k_2}{[\text{tht}]_{\text{added}}}[\mathbf{1}]_{\text{total}} \quad (7)$$

This can be better seen in a plot of k_{iso} vs $[\text{tht}]_{\text{added}}^{-1}$ for the values given by Minniti (Figure 1): a straight line is obtained for the range of higher concentrations of tht added, but a clear retardation is observed when the tht concentration arising from autodissociation becomes important. Thus $[\text{tht}]_{\text{dis}}$ cannot be neglected in the treatment of these data.

The values of K_{eq} and k_2 can be estimated easily: the equilibrium constant for the dissociation of **1** is defined in eq 8. Since $[\text{tht}] = [\text{tht}]_{\text{dis}} + [\text{tht}]_{\text{added}}$, and $[\mathbf{A}] = [\text{tht}]_{\text{dis}}$, this equation can be rewritten as eq 9. Finding the value of $[\text{tht}]_{\text{dis}}$ from eq 9, and taking it into eq 6, the kinetic eq 10 is obtained.[8]

$$K_{\text{eq}} = \frac{[\text{tht}][\mathbf{A}]}{[\mathbf{1}]} \quad (8)$$

$$K_{\text{eq}} = \frac{([\text{tht}]_{\text{dis}} + [\text{tht}]_{\text{added}})[\text{tht}]_{\text{dis}}}{[\mathbf{1}]_{\text{total}} - [\text{tht}]_{\text{dis}}} \quad (9)$$

$$[\text{tht}]_{\text{added}} = \frac{K_{\text{eq}}k_2}{k_{\text{iso,pe}}} - K_{\text{eq}} - \frac{k_{\text{iso,pe}}[\mathbf{1}]_{\text{total}}}{k_2} \quad (10)$$

A nonlinear fit of the experimental data in ref 3 ($[\text{tht}]_{\text{added}}$ vs k_{iso}) to eq 10 (Figure 2) affords the following values: $K_{\text{eq}} = (1.8 \pm 0.3) \times 10^{-6}$ mol L^{-1} and $k_2 = (1.4 \pm 0.2) \times 10^{-3}$ s^{-1}, for $[\mathbf{1}] = 10^{-2}$ mol L^{-1}.

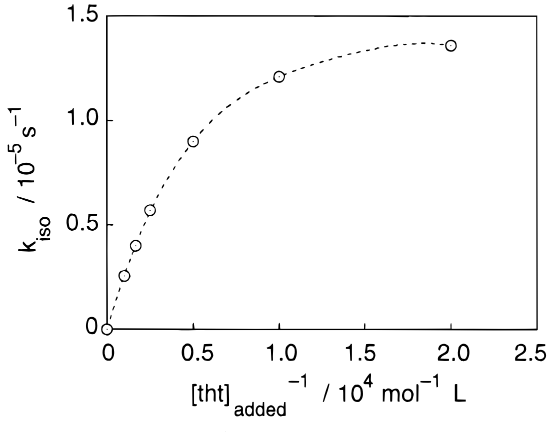


Figure 1. k_{iso} vs $[\text{tht}]_{\text{added}}^{-1}$ plot of values given in ref 3 for the isomerization of *trans*-[Pd(C$_6$F$_5$)$_2$(tht)$_2$] (**1**) to *cis*-[Pd(C$_6$F$_5$)$_2$(tht)$_2$] (**2**).

Table 1. Dissociation of tht from Complex *trans*-[Pd(C$_6$F$_5$)$_2$(tht)$_2$] (**1**) To Give Intermediate *trans*-[Pd(C$_6$F$_5$)$_2$(tht)] (**A**): Concentration of Autodissociated tht ($[\text{tht}]_{\text{dis}}$) and ratio $\alpha = [\mathbf{A}]/[\mathbf{1}]$ at Different Concentrations of Added tht[a]

$[\text{tht}]_{\text{added}}/10^{-5}$ mol L^{-1}	$[\text{tht}]_{\text{dis}}/10^{-5}$ mol L^{-1}	$[\text{tht}]/10^{-5}$ mol L^{-1}	$\alpha = [\mathbf{A}]/[\mathbf{1}]$ (%)
0	13.3	13.3	1.3
5	11.1	16.1	1.1
10	9.26	19.3	0.9
20	6.70	26.7	0.7
40	4.07	44.1	0.4
60	2.86	62.9	0.3
100	1.77	102	0.2

[a] Calculated from the value of $K_{\text{eq}} = 1.8 \times 10^{-6}$ mol L^{-1}.

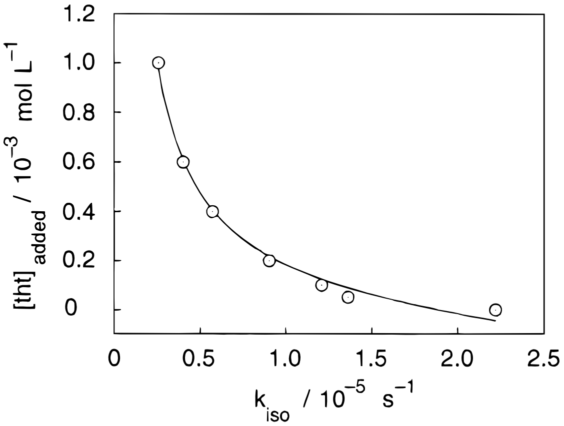


Figure 2. $[\text{tht}]_{\text{added}}$ vs k_{iso} plot of values given in ref 3 for the isomerization of *trans*-[Pd(C$_6$F$_5$)$_2$(tht)$_2$] (**1**) to *cis*-[Pd(C$_6$F$_5$)$_2$(tht)$_2$] (**2**).

Using these values it is possible to estimate the contribution of the autodissociated tht under the experimental conditions used by Minniti ($[\text{tht}]_{\text{dis}}$) as well as the ratio $\alpha = [\text{tht}]_{\text{dis}}/[\mathbf{1}] = [\mathbf{A}]/[\mathbf{1}]$ (Table 1). The results show that (1) as we had presumed, $[\text{tht}]_{\text{dis}}$ cannot be neglected with respect to $[\text{tht}]_{\text{added}}$, and (2) the value of K_{eq} is small, as expected for an unsaturated (or perhaps solvent coordinated) species. Accordingly α is small in all the range, and the dominant species is the four-coordinated **1**, not the three-coordinated **A**. The latter reaches a maximum of about 1.3% in the absence of added tht.

This analysis shows that the preequilibrium hypothesis is compatible with the experimental data. Since the preequilibrium is fast, it can be concluded that the most substantial barrier to isomerization is met in the topological rearrangement of the

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(8) The concentration of $[\text{tht}]_{\text{dis}}$ from eq 9 is

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

Taking this value into eq 6 we have:

$$k_{\text{iso,pe}} = \frac{2K_{\text{eq}}k_2}{[\text{tht}]_{\text{added}} + K_{\text{eq}}\sqrt{([\text{tht}]_{\text{added}} + K_{\text{eq}})^2 + 4K_{\text{eq}}[\mathbf{1}]_{\text{total}}}}$$

which can be rewritten as in eq 10.

T-shaped intermediate, not in the dissociative step. Moreover, this reinterpretation reconciles the experimental data with the results of a well-known theoretical study of the mechanism outlined in Scheme 1, which states that three-coordinate trans intermediates such as **A** must find a substantial topological barrier in its rearrangement to the cis-like intermediates such as **B**.[9]

Another consequence of this new view of the mechanism is that the activation parameters derived from the Eyring treatment of k_{iso} (eq 1) cannot be properly assigned to only one elementary step (i.e. they are not real, but *apparent* activation parameters).[10] According to eq 5, they most probably are contributed to a certain extent by both steps associated with k_1 and k_2. The first one would be the main contribution to the overall activation entropy, since in this step the number of particles increases. The activation enthalpy would be contributed mainly by the second step (k_2).

In summary, although the isomerization process discussed follows indeed a dissociative path, the dissociation step is not the rate-determining step. It influences the rate because a preequilibrium is established, controlling the concentration of the unsaturated species, but it is the topomerization step that presents the highest activation barrier in the process.

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