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# A novel mechanism for the fluxional behaviour of [Pd($\eta^2$-tetramethylethylenetetracarboxylate)(2-methylthiomethylpyridine)]

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**Abstract**

The fluxional behaviour of [Pd($\eta^2$-tmetc)(N–SMe)] (tmetc = tetramethylethylenetetracarboxylate, N–SMe = 2-methylthiomethylpyridine) in $CD_2Cl_2$ is governed by two mechanisms: (i) the concentration independent inversion at sulfur which averages the methylenic signals and collapses the four methyl signals of tmetc to two; (ii) the concentration dependent mechanism occurring via a dimeric intermediate with $C_S$ symmetry which collapses the two residual tmetc signals into a singlet. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Palladium–olefin complex; Dynamic NMR; Sulfur inversion mechanism; Dimeric $C_S$ intermediate mechanism

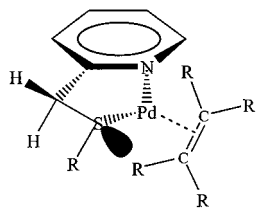
## 1. Introduction

Many organometallic compounds undergo fluxional rearrangements which are revealed by dynamic NMR spectroscopy. These rearrangements may be detected by monitoring spectra which exhibit line broadening and line collapsing, by saturation transfer experiments, or by EXSY (exchange spectroscopy) technique [1]. In most cases the fluxional behaviour is only reported without discussion of the molecular mechanism involved.

The fluxional processes of palladium(0) complexes of type [Pd($\eta^2$-olefin)(L–L′)] constitute a paradigmatic example [2]. In order to rationalise the dynamic behaviour at various temperatures exhibited by the signals of the olefin ligand and by some signals of the L–L′ ancillary ligand, the following mechanisms have been considered [2f]:

1. inversion of the configuration of coordinating atom L or L′, when this latter is $sp^3$ hybridised;
2. propeller-like olefin rotation;
3. Pd–olefin bond cleavage followed by recombination;
4. Pd–L or Pd–L′ bond cleavage followed by ligand rotation and recombination (olefin pseudo-rotation);
5. intermolecular exchange with the free olefinic ligand;
6. intermolecular exchange with the free ancillary L–L′ ligand.

The simple detection of the dynamic behaviour is no proof for any of these mechanisms. However, definitive arguments for a correct mechanistic choice may be provided by traditional line shape analysis [3] of the resonance peaks undergoing broadening and collapse and by the kinetic parameters therefrom. To this aim, we have investigated the behaviour of the palladium(0) complex [Pd($\eta^2$-tmetc)(N–SMe)] (**1**) (tmetc = tetramethylethylenetetracarboxylate, N–SMe = 2-methyl-




R = COOMe

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thiomethylpyridine) which is a stable and readily characterised species [2f].

## 2. Results and discussion

The $^1$H-NMR spectrum of **1** in $CDCl_3$ is completely 'frozen' at $-90$ °C. Because of the pyramidal arrangement around S, the methylenic protons are diastereotopic and appear as an AB system, while the tmetc methyls are non-equivalent and are represented by four distinct singlets (which are labelled 1–4 in decreasing frequency sequence). A dynamic process shows up between $-90$ and $-20$ °C, which monitors the collapse of the AB system into a singlet and the melting of the four-singlet system of tmetc into a two-singlet system. Subsequently, at higher temperatures (from $-20$ to 30 °C), the two remaining singlets undergo a further collapse to a single peak.

The two low-temperature phenomena (collapse of the AB quartet and reduction from four to two of the tmetc methyl groups) occur jointly in the same temperature range, and independently of the sample concentration. They are therefore the result of a unimolecular rearrangement or rearrangements. It is tempting to identify this rearrangement with mechanism 1. As a matter of fact, the inversion at sulfur results in the loss of diastereotopism of the methylenic protons and at the same time in the exchange of the chemical environments of geminal tmetc methyls (mechanism 1 in Fig. 1).

We could perform correct line shape simulations for the two exchanging systems with the DNMR5 program [4]. Figs. 2 and 3 document the accuracy of the simulations.

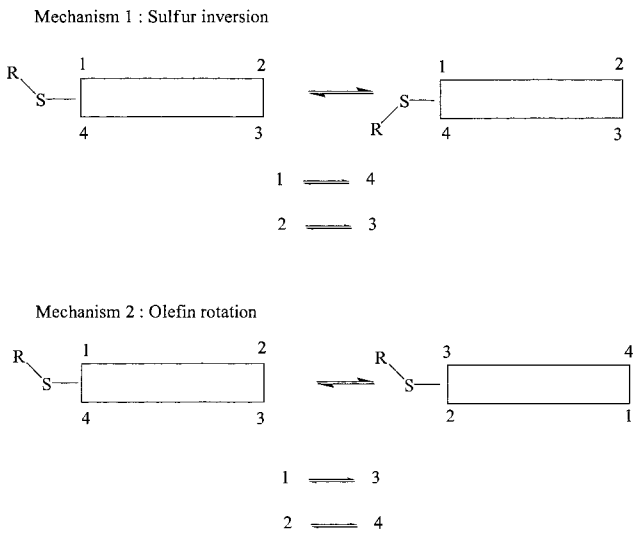


Fig. 1. Proposed unimolecular mechanisms for the collapse of the methyl resonances of the tmetc (tetramethylethylenetetracarboxylate) moiety of **1**. The tmetc unit is represented by the rectangle, where the corners designate the methyl groups.

A correct simulation of the tmetc signals could be accomplished only assuming the interchange between methyls 1 and 4 on one side and methyls 2 and 3 on the other (in the exchange matrix, $k_{1,4} = k_{2,3}$ are determined from simulation, while the remaining constants are kept to 0). Thus, signals 1 and 4 belong to one set of geminal tmetc methyls and signals 2 and 3 to the other. However, it is not possible to establish the location of the two-geminal groups (i.e. on which side of the coordinating atom, either N or S), or their relative orientation.

More important, the Eyring analysis of the kinetic constants obtained from the two low temperature phenomena, reported in Table 1, gives values for the activation enthalpy $\Delta H^{\neq}$ and activation entropy $\Delta S^{\neq}$ which are to be considered equal within the statistical error. Of particular relevance are the small absolute values of $\Delta S^{\neq}$. Because of the intrinsically great errors in the evaluation of the entropy parameter, obtained from the intercept of the Eyring plot, and therefore from a long-drawn extrapolation, $\Delta S^{\neq}$ values are to be taken with care. Thus our small $\Delta S^{\neq}$ value is to be considered virtually zero. The meaning of this result will be dealt with later.

The high temperature collapse of the two residual methyl peaks into a single resonance has been analysed under different mechanistic hypotheses. The propeller like olefin rotation (mechanism 2 in Fig. 1) will interchange methyl 1 with methyl 3 and methyl 2 with methyl 4. Thus the identical values for $k_{1,4}$ and $k_{2,3}$ ($k_{1,4} = k_{2,3}$) are extrapolated values from the Eyring plot of the low-temperature process, $k_{1,3}$ and $k_{2,4}$ values ($k_{1,3} = k_{2,4}$) are determined by shape simulation, and $k_{1,2}$ and $k_{3,4}$ are kept to 0. Other processes (which may be described by mechanisms 3, 4, 5 or 6) will cause the synchronous interchange of all tmetc methyls and will require $k_{1,4} = k_{2,3}$ as extrapolated values, and $k_{1,3} = k_{2,4} = k_{1,2} = k_{3,4}$ from shape simulation. It turned out that the two hypotheses are indistinguishable, as the same simulated spectra are obtained when the rate constants for the first hypothesis are twice the rate constants for the second one. The high-temperature simulation will also require the knowledge of the exact chemical shifts of the interconverting methyls at the investigated temperatures. These values cannot be obtained from shape simulation (these parameters and the first-order interconversion constants are correlated) but are extrapolated from linear plots of the chemical shifts versus $1/T$ (measured at low temperatures).

The correct identification of the mechanism stems from the rationalisation of the following experiments.

The $k$ values obtained from shape simulation at 20 °C (under either hypothesis) are linearly correlated with the concentration of **1** (Fig. 4). Thus the mechanism is bimolecular: the slope gives the second order rate constant $k_2 = 440 \pm 2$ s$^{-1}$ mol$^{-1}$ dm$^3$. The inter-

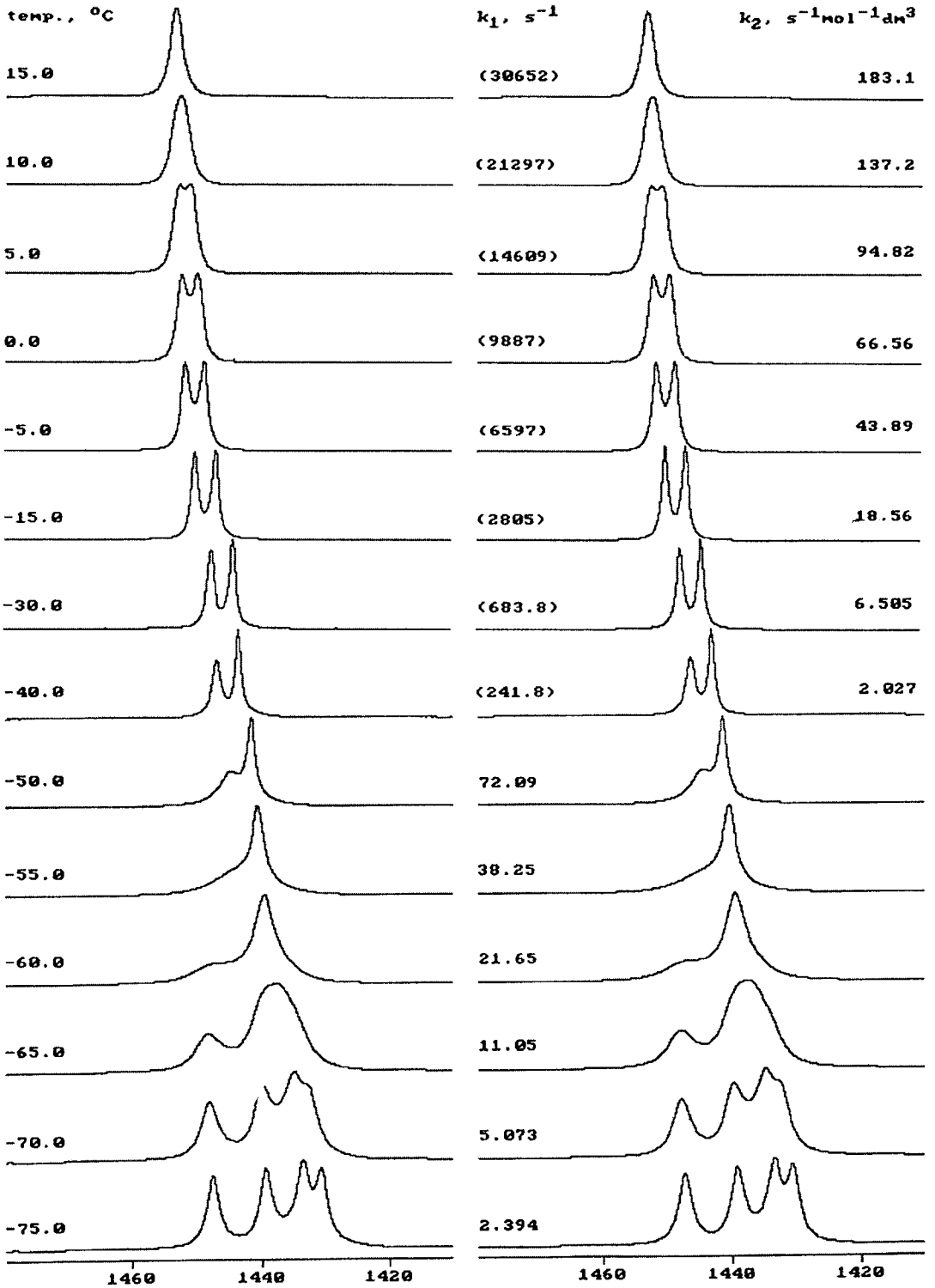


Fig. 2. Experimental (left) and simulated (right) spectra of tmetc methyls at the reported temperatures. The unimolecular $k_1$ kinetic constants are calculated under the hypothesis of the mechanism of inversion at sulfur ($k_{1,4} = k_{2,3}$, while all other $k$ values are kept to 0). The bimolecular $k_2$ constants are obtained from the pseudo first-order constants calculated under the hypothesis of the intermediacy of complex **2** with $C_S$ symmetry ($k_{1,3} = k_{2,4} = k_{1,2} = k_{3,4}$, while $k_{1,4} = k_{2,3}$ are extrapolated $k_1$ values [in parentheses]). The concentration of **1** is $2.7 \times 10^{-2}$ mol dm$^{-3}$.

cept, although small, is statistically significant and the value ($k_1 = 0.40 \pm 0.04$ s$^{-1}$) will suggest the occurrence also of a less important unimolecular mechanism ($k_1$ vs. $k_2$ is about $10^{-3}$).

The following further experiments, detailed in Table 2, rule out the possibility that the concentration dependence may be due to the adventitious presence of free tmetc ligand or of free N–SMe ancillary ligand (their

concentrations, in the dilution experiment in Fig. 4, would be proportional to that of **1**). The proven participation of these ligands in the rearrangement process would validate mechanisms 5 or 6.

Tmetc is indeed present as an impurity at about 1% (from the integrated NMR signals) in the solution of **1**. However, while the doubling of the concentration of **1** doubles the kinetic rate constant (see Fig. 4), the addition of a similar amount of tmetc has no effect (see Table 2). On the contrary, the N–SMe ancillary ligand does participate in the rearrangement process, as the addition enhances the kinetic rate constant (Table 2). In

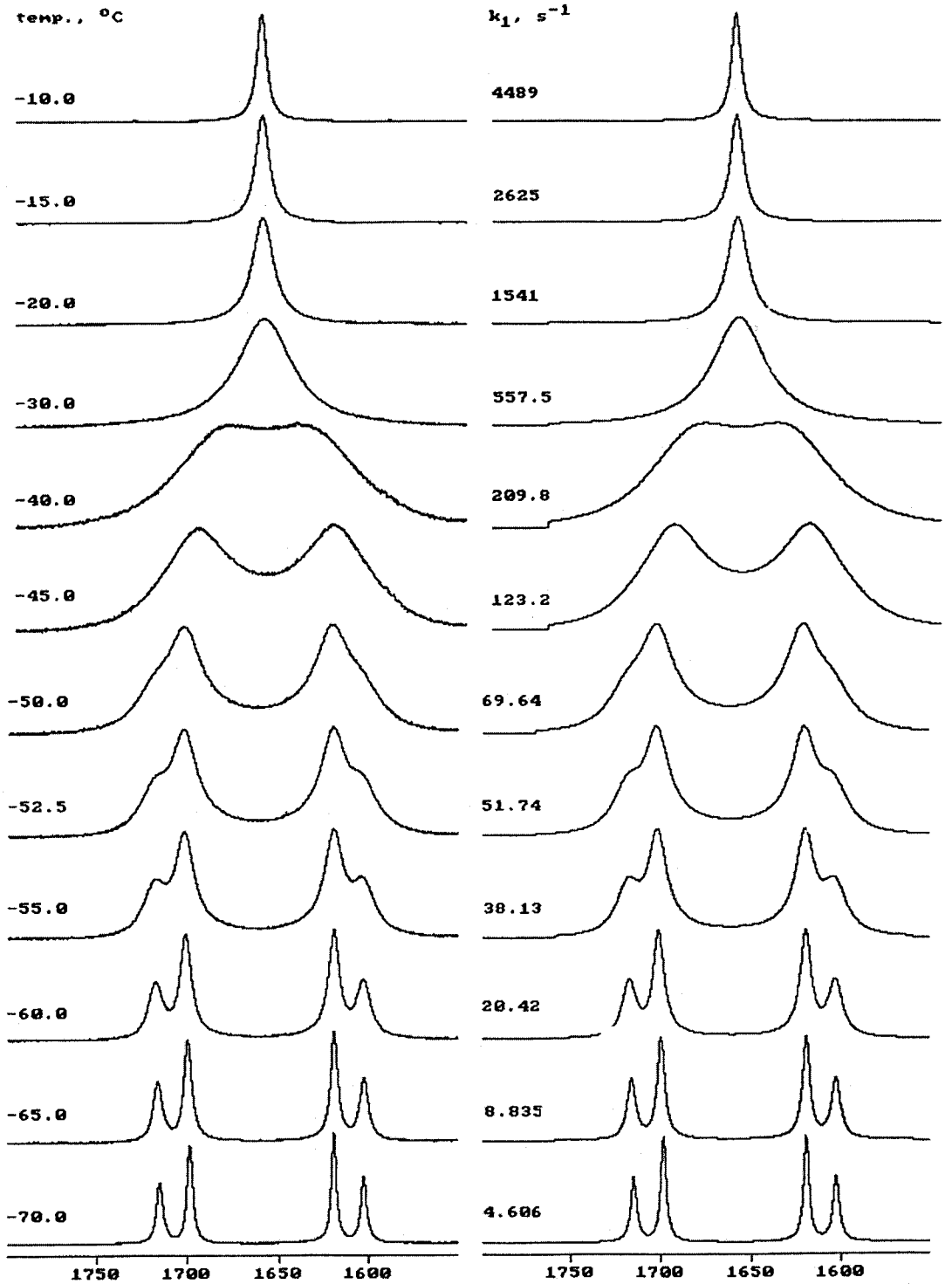


Fig. 3. Experimental (left) and simulated (right) spectra for the collapse of the AB system of the methylenic protons of **1** into a singlet.

Table 1
Calculated activation parameters (Eyring equation) for the fluxional rearrangements of **1**

| Mechanism | Monitored group | $\Delta H^{\neq}$ (Kcal mol$^{-1}$) | $\Delta S^{\neq}$ (cal mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|
| Sulfur inversion | $CH_2S$ | $11.5 \pm 0.1$ | $2.0 \pm 0.3$ |
| Sulfur inversion | $CH_3$ (tmetc) | $11.3 \pm 0.1$ | $1.1 \pm 0.5$ |
| Intermediacy of **2** | $CH_3$ (tmetc) | $10.2 \pm 0.2$ | $-12.8 \pm 0.6$ |

Table 2
Pseudo first-order constants (calculated by simulation of the tmetc resonances) at 20 °C of **1**, in the absence or presence of added tmetc and N–SMe ancillary ligand

| **1** (mol dm$^{-3}$) | tmetc (mol dm$^{-3}$) | N–SMe (mol dm$^{-3}$) | $k$ (s$^{-1}$) |
|---|---|---|---|
| $4.8 \times 10^{-3}$ | $5.5 \times 10^{-5}$ [a] | | 2.51 |
| $4.8 \times 10^{-3}$ | $2.7 \times 10^{-3}$ | | 2.48 |
| $4.8 \times 10^{-3}$ | $5.5 \times 10^{-5}$ [a] | $1.8 \times 10^{-2}$ | 78.9 |

[a] Present as an impurity.

this situation the intermolecular mechanism 6 will take place, as is also revealed by the incipient broadening of the methylenic resonances of **1** and of the free ligand. There is, however no proof of the presence of this ligand as impurity: no signal attributable to it is detected in the low temperature spectra of **1**, and the methylenic resonance of **1** shows no line width variation in the concentration interval of Fig. 4.

Since the ancillary ligand is absent and the tmetc ligand is present but not contributing, the concentration dependence phenomenon must only be related to the palladium complex **1** itself. We will therefore propose a different mechanism, not yet reported in the literature, which describes the formation of the intermediate dimeric complexes **2** and **3**, with $C_S$ and $C_2$ symmetry, respectively, deriving from different approaches of the two monomeric units **1** (Fig. 5).

In the complex **2** the $C_S$ symmetry makes the geminal groups of every tmetc ligand equivalent, thus bringing about the collapse of the respective resonances. The Eyring plot of the second order constants (from the first order constants obtained by line shape analysis and divided by the concentration of **1**: $2.7 \times 10^{-2}$ mol dm$^{-3}$) confirms this mechanistic hypothesis. The activation entropy $\Delta S^{\neq}$ (reported in Table 1) is significantly negative, as required by a mechanism centred on the formation of a dimeric intermediate complex.

Dimeric intermediates of similar nature have been invoked in order to rationalise the second order dependence found in other processes monitored by dynamic NMR spectroscopy [5].

The activation enthalpy $\Delta H^{\neq}$ for the mechanism of inversion at sulfur is low, and indeed much lower than the values reported for the inversion at tri-bound sulfo-

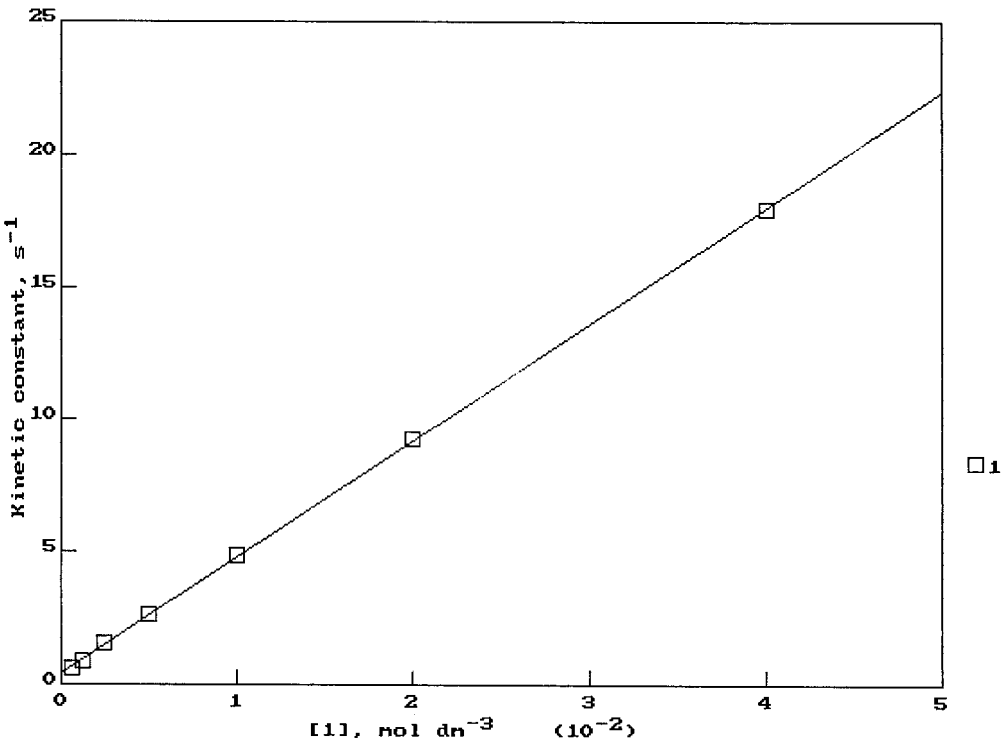


Fig. 4. Correlation between the concentration of **1** and the pseudo first-order constants (obtained from shape simulation at 20 °C under the hypothesis of the intermediacy of **2**).

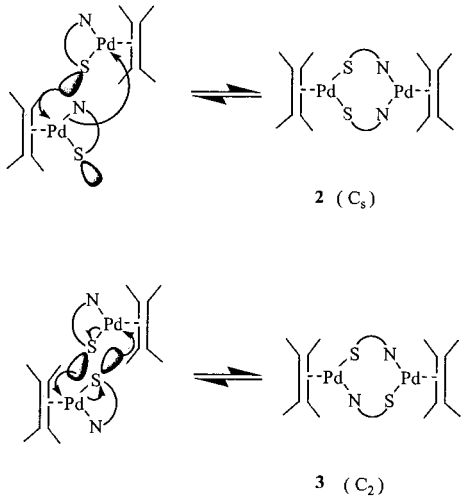


Fig. 5. Bimolecular intermediates **2** and **3** derived from different approaches of two molecules of **1**. The intermediate **2**, with $C_S$ symmetry, mixes the chemical environments of the collapsed (by the mechanism of sulfur inversion) methyls 1, 4 and 2, 3.

nium sulfur [6]. It is generally postulated that such low values, usually encountered for the inversion at sulfur in organometallic compounds, are rather to be associated with the rupture of the S–metal bond, followed by the formation of a new bond with the other lone pair of sulfur (an $S_N1$-like mechanism) [2b,7]. The value near to zero for the activation entropy will suggest a mechanism with synchronous rupture and formation of bonds, an $S_N2$-like mechanism triggered by the presence of the lone pair at sulfur. It is perhaps significant that also the bimolecular mechanism by the dimeric intermediate **2** may be thought of as initiated by the lone pair at sulfur.

The exclusion of mechanisms 2 and 3, which would imply the cleavage of one or both σ and π Pd–tmetc bonds, is indicative of the particular strength of these bonds (particularly of the σ bond, as mechanism 2 may also be hindered by the steric demand of tmetc). This conclusion is in agreement with the kinetic order found in the exchange reactions of other Pd–tmetc complexes with several olefins [2b,2f]. The olefin exchange reactions, when tmetc is involved, are indeed slow with respect to the NMR time scale (no line broadening is observed upon addition of tmetc to **1**) and show only a second order dependence (no hints of dissociative path are observable in the olefin exchange reactions) since they apparently occur via mechanism 5, mechanism 3 being by far a more energetic process.

## 3. Experimental

The complex **1** was synthesised as reported [2f]. The variable temperature spectra were run in $CD_2Cl_2$ on a Varian Unity 400 spectrometer. The uncertainty in the temperature measurement is estimated at $\pm 1$ K. The iterative fitting of the experimental spectra by the DNMR5 program [4] gives the kinetic constants together with the relative errors. The estimated and the computed errors are considered by the linear fitting of the Eyring equation.

### *3.1. [Pd(η²-tetramethylethylenetetracarboxylate)-(2-methylthiomethylpyridine)] (**1**)*

$^1$H-NMR ($CD_2Cl_2$, 400 MHz, $-90$ °C), $\delta$: 8.85 (d, pyridine, $J = 5.3$), 7.80 (t, pyridine, $J = 7.7$), 7.48 (d, pyridine, $J = 7.7$), 7.32 (dd, pyridine, $J = 7.7$, 5.4), 5.32 (s, SC$H_3$), 4.26 and 4.03 (AB system, C$H_2$, $J = 16.8$), 3.61, 3.59, 3.57 and 3.56 (singlets, tmetc C$H_3$).

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