Inorg. Chem. **1980**, *19*, 3551–3552

Correspondence

Uncatalyzed Isomerization and Substitution Reactions of Sterically Crowded Pt(II) Complexes

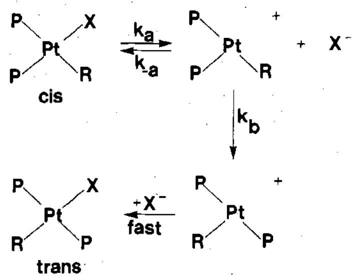
Sir:

We wish to draw your attention to a recent paper[1] concerning the uncatalyzed cis to trans isomerization and methanol solvolysis of arylplatinum complexes. Romeo and co-workers[1] present arguments, in addition to those stated previously,[2–5] in favor of a dissociative mechanism (Scheme I) for the spontaneous isomerization and an associative mechanism for the solvolysis (halide substitution) of *cis*-Pt(PEt_3)$_2$(R)X, where X ≡ a halide ion and R ≡ an alkyl or substituted aryl group. However, the reported evidence[1–5] is by no means conclusive, and a number of anomalies, which will be discussed, remain unsolved.

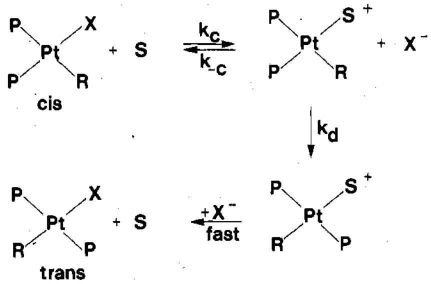
Romeo and co-workers[4] reported similar rate parameters for the uncatalyzed isomerization and methanol solvolysis of the most sterically crowded complex in the series (viz., R ≡ mesityl) and extended their arguments to favor a dissociative solvolysis mechanism for the latter complex. This is in contrast to the generally accepted associative mode of substitution for the complexes containing the less sterically crowded substituents in particular[1,4] and for Pt(II) complexes in general.[6] The rate and activation parameters,[7,8] including values for $\Delta V^{\ddagger}$ for the cis to trans isomerization and methanol solvolysis reactions of *cis*- and *trans*-Pt(PEt_3)$_2$(mesityl)Br, clearly illustrate that the mechanism of these reactions had the common feature of a rate-determining solvolysis step, which is beyond any doubt *associative* in character. A recent study[9] of the solvent dependence of the substitution reactions of *cis*-Pt(PEt_3)$_2$(mesityl)Br further underlined this conclusion. The k_1 path in such reactions (substitution via solvolysis) depends strongly on the nature of the solvent, which is not expected to be the case for a dissociative solvolysis mechanism as suggested before.[4]

We[7] have, therefore, developed an alternative explanation for the findings of Romeo and co-workers[4] and suggested that the mechanism for both processes includes an associative solvolysis step (Scheme II) but that a switch in rate-determining step occurs from k_c to k_d (i.e., from a steady-state to a preequilibrium approximation) in going from a more to a less sterically crowded Pt(II) complex. Since the mesityl complex is the most sterically hindered one studied to date, it is difficult to visualize why the less sterically hindered complexes must isomerize according to the dissociative mechanism[1–5] outlined in Scheme I and cannot undergo an initial associative solvolysis step prior to isomerization as outlined in Scheme II. Furthermore, evidence for an initial solvolysis step and the above-mentioned crossover of rate-determining step was found in a recent high-pressure study[8] of the uncatalyzed cis to trans isomerization of Pt(PEt_3)$_2$(R)X complexes.

Scheme I



Scheme II



By coincidence, Romeo and co-workers[1] also very recently considered the possibility of a rapid initial solvolysis step (as in Scheme II) but rejected it on the basis of a number of observations. For example, the rate law for the isomerization process involving a rapid preequilibrium is given by the equation[7]

$$k_{obsd} = k_d K_c/([X^-] + K_c) \qquad K_c = k_c/k_{-c}$$

which reduces to $k_{obsd} = k_d$ at $[X^-] = 0$, i.e., in the absence of added X^-. Since k_d describes the isomerization of the solvolytic intermediate species, it should be independent of the nature of X^-. However, they[1] found k_d to depend on the nature of X^- for the isomerization of *cis*-Pt(PEt_3)$_2$(C_6H_5)X and therefore rejected this mechanism (Scheme II) in favor of the dissociative mechanism in Scheme I. A closer look at their data[1] reveals that the graphical representation in Figure 1 of ref 1 is rather misleading since it only covers a limited range of $[X^-]$. If this plot is modified (see Figure 1) to include all the data (in Table III of ref 1), the intercepts of the lines (k_d^{-1}) for various X^- are indeed very close, especially when the large range of k_{obsd}^{-1} values is taken into account. This was further illustrated by a least-squares fit of the data, which yields values for k_d^{-1} (intercept) of (1.8 ± 0.2) × 10^2, (7.0 ± 0.9) × 10^2, and (16.3 ± 10.2) × 10^2 s for X = Cl, Br, and I, respectively. A similar result was found in a recent study[10] of the isomerization of *cis*-Pt(PEt_3)$_2$(C_6H_5)X in methanol, for which k_d turned out to be (2.1 ± 0.1) × 10^{-3}, (3.9 ± 3.9) × 10^{-3}, and (1.9 ± 2.1) × 10^{-3} s^{-1} at 40 °C for X = Cl, Br, and I, respectively. The error limits on the values of k_d for X = Cl are significantly smaller than those for X = Br and I. This is due to the smaller slope of the k_{obsd}^{-1} vs. $[X^-]$ plot for X = Cl (than those for X = Br and I), which results in a more accurate determination of the intercept in this case (see Figure 1). It follows that k_d is within experimental error limits constant for the above series, and we, therefore, favor the associative mechanism outlined in Scheme II.

Further arguments used by Romeo and co-workers[1] against the associative mechanism in Scheme II concern the lack of spectrophotometric and conductometric evidence of the presence of the preequilibrium solvolysis step. The UV absorption spectra of the *cis*-Pt(PEt_3)$_2$(C_6H_5)X species are very similar for all X and only exhibit a weak shoulder around 250

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(1) Romeo, R.; Minniti, D.; Lanza, S. *Inorg. Chem.* **1979**, *18*, 2362.
(2) Faraone, G.; Ricevuto, V.; Romeo, R.; Trozzi, M. *J. Chem. Soc. A* **1971**, 1877.
(3) Romeo, R.; Minniti, D.; Trozzi, M. *Inorg. Chim. Acta* **1975**, *14*, L15.
(4) Romeo, R.; Minniti, D.; Trozzi, M. *Inorg. Chem.* **1976**, *15*, 1134.
(5) Romeo, R. *Inorg. Chem.* **1978**, *17*, 2040.
(6) Tobe, M. L. *Inorg. React. Mech.* **1972**, 63.
(7) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 572.
(8) Kelm, H.; Louw, W. J.; Palmer, D. A. *Inorg. Chem.*, **19**, 843 (1980).
(9) Palmer, D. A.; van Eldik, R.; Kelm, H. *Z. Anorg. Allg. Chem.*, in press.
(10) Louw, W. J.; van Eldik, R.; Kelm, H. *Inorg. Chem.* **1980**, *19*, 2878.

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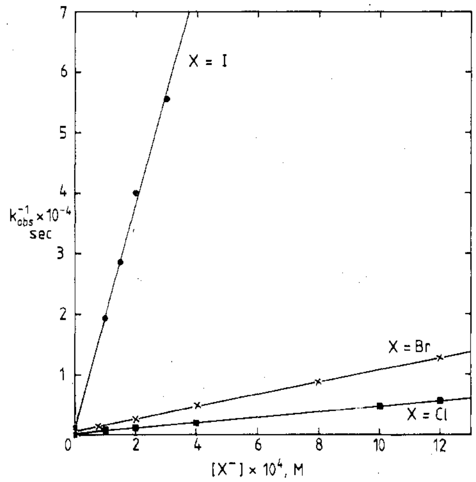

Figure 1. Plot of k_{obsd}^{-1} vs. $[X^-]$ for the cis to trans isomerization of $Pt(PEt_3)_2(C_6H_5)X$ in methanol at 30 °C.

nm. A possible shift in equilibrium (K_c in Scheme II) upon the addition of LiX will be difficult to observe spectrophotometrically.[11] In fact, since the nature of the absorption spectrum of *cis*-$Pt(PEt_3)_2(C_6H_5)S^+$ is not known, the possibility that it is similar to that of the *cis*-$Pt(PEt_3)_2(C_6H_5)X$ species cannot be ruled out, thereby making such spectrophotometric equilibrium measurements meaningless. Conductometric measurements of K_c, in the manner outlined elsewhere,[1] strongly depend on the assumed value of Λ_∞ for a 1:1 electrolyte in methanol. Furthermore, such measurements are bound to result in too low values for K_c due to deviations from ideality. An alternative procedure[10] resulted in values for K_c of the same order of magnitude as those observed kinetically and underlines the validity of the mechanism in Scheme II.

To sum up, we conclude that the available evidence is in agreement with our suggested mechanism (Scheme II). We continue to believe that the initial step in the isomerization process is indeed an associative solvolysis reaction, in contrast to the formation of the three-coordinate intermediate as suggested by Romeo and co-workers.[1-5] Furthermore, our mechanism (Scheme II) also provides a sound basis for explaining the observed switchover in mechanism in the case of the largest substituent, viz., mesityl, which definitely does not fit in with the suggestions of Romeo and co-workers.[1-5] It then follows that the solvolysis reactions of both *cis*- and *trans*-$Pt(PEt_3)_2(R)X$ and the isomerization reaction of *cis*-$Pt(PEt_3)_2(R)X$ all proceed via the same solvolysis reaction. In the presence of an added substituent, the solvento intermediate rapidly undergoes substitution with retention of configuration. However, in the absence of such an added substituent, the solvento intermediate can undergo a slow rate-determining isomerization step which could in fact be dissociative in nature as emphasized before.[8]

Registry No. *cis*-$Pt(PEt_3)_2(C_6H_5)I$, 56553-44-7; *cis*-$Pt(PEt_3)_2(C_6H_5)Br$, 15702-94-0; *cis*-$Pt(PEt_3)_2(C_6H_5)Cl$, 15702-92-8.

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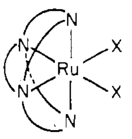
[11] van Eldik, R.; Louw, W. J., unpublished results.

Additions and Corrections

1980, Volume 19

Stephan S. Isied: Complexes of Ruthenium(III) and Ruthenium(II) with 1,4,8,11-Tetraazacyclotetradecane (Cyclam): Cis and Trans Isomers.

Page 911. The correct figure for *cis*-[Ru(cyclam)Cl_2]Cl is



Page 912. In Figure 1B, the *y* axis should read ϵ (M^{-1} cm^{-1}) × 10^{-2}.—Stephan S. Isied

David C. Calabro and Dennis L. Lichtenberger*: Comments on Koopmans' Theorem and Electron Relaxation with Valence Ionization.

Page 1732. In the abstract line 4 should read, "the relatively large E_R for ionization of 3d electrons is associated with the 3d shielding of 3s and 3p electrons".

Page 1733. Equation 3 should be: $E_R = (N_{valence} - 1)(0.35/n)^2$. In the next paragraph, sentence 4 should read, "The change in E_R between atoms of successive groups is indicated to be $(0.35/n)^2$."—Dennis L. Lichtenberger

Keith F. Purcell,* Stephen F. Clark, and John D. Petersen*: Theoretical Prediction and Experimental Confirmation of Trans to Cis Photoisomerization in d^6 Transition-Metal Complexes.

Page 2185. In line 11, "λ < or > 0" should read "λ > or < 0".—Keith F. Purcell