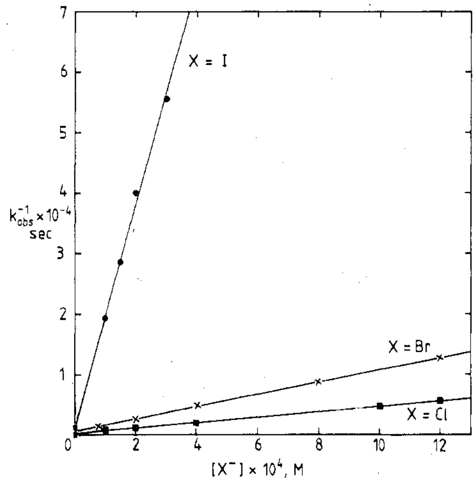

Figure 1. Plot of k_{obsd}^{-1} vs. $[X^-]$ for the cis to trans isomerization of $Pt(PEt_3)_2(C_6H_5)X$ in methanol at 30 °C.

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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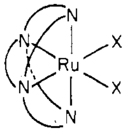
(11) van Eldik, R.; Louw, W. J., unpublished results.

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, "$\lambda <$ or > 0" should read "$\lambda >$ or < 0".—Keith F. Purcell