*Inorganica Chimica Acta,* 31 (1978) L367–L368
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

# Photochemical Behaviour of $RuCl_3NOL_2$ Complexes

GIUSEPPE INNORTA and ALBERTO MODELLI

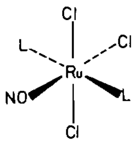
*Istituto Chimico "G. Ciamician", Università di Bologna, 40126 Bologna, Italy*

Received August 9, 1978

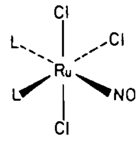
During a study [1] of ligand substitution reactions in complexes of formula $RuCl_3NOL_2$ (L = $PPh_3AsPh_3$ and $SbPh_3$) it was observed that the solutions in $CH_2Cl_2$ of such complexes were light sensitive, the phenomenon being ascertained by extensive variations of their ultraviolet spectra; it was also observed that those spectral variations seemed to be reversible when the solutions were later on kept in the dark.

This kind of behaviour suggested that formation of isomers could occur under the influence of light.

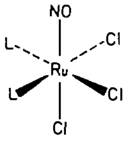
For complexes of this kind, three isomers are possible. For those cited above, however, only configuration I, with the two L ligands in *trans* position [2], has been isolated.



I



II



III

We have therefore taken into consideration the complex with L = $PMe_2Ph$, of which two of the three possible configurations (I and III) have been isolated and described [2]. We prepared and identified on the basis of their IR and NMR spectra [2] the two isomers. Both of them, in a solution of $CH_2Cl_2$, appeared thermally stable enough to allow a study of their light induced transformations. Figs. 1 and 2 show the variations that occur to the ultraviolet spectra of the isomers I and III when their solutions ($\sim 10^{-4}$ *M*) are irradiated at room temperature with a 365 nm light beam.

The formation of a new product, with identical spectral features, is evident in both the cases.

The maxima which characterize the original compounds disappear and a new maximum appears at 245 nm. Moreover, the presence of isosbestic points indicates that very likely the transformation occurs without the formation of intermediate species in sizable concentrations.

The ultraviolet spectra obtained by irradiation remain stable at room temperature for several hours. However, if the solution is refluxed, in about three hours the product is completely converted into the isomer I.

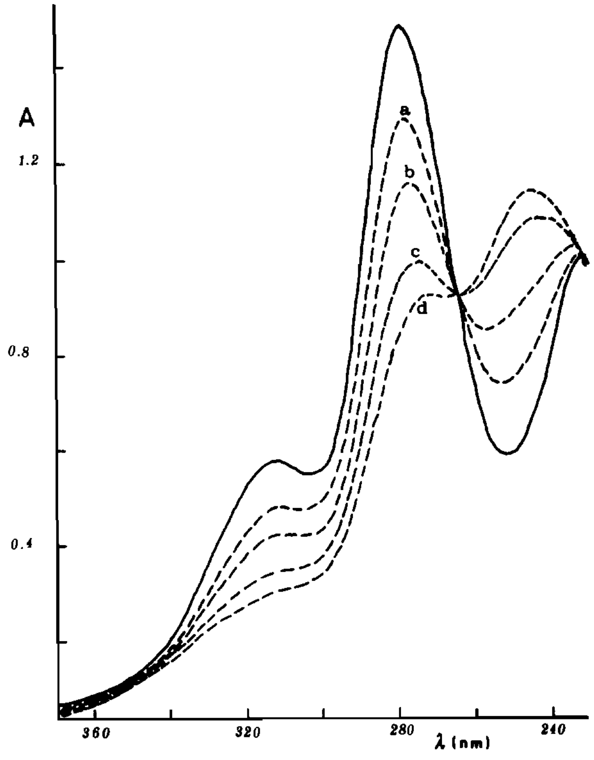


Figure 1. Variation of the ultraviolet spectrum of $RuCl_3NO(PMe_2Ph)_2$ (conf. I) induced by irradiation with a 365 nm light beam. Exposure time: continuous curve 0, (a) = 6 min, (b) = 11 min, (c) = 21 min, (d) = 31 min.

The infrared spectra of the irradiated solutions exhibit a band, due to the NO stretching, at 1866 ± 2 $cm^{-1}$ as for the isomer I but slightly higher than that of the isomer III.

Finally, the NMR spectrum of an irradiated solution of the isomer I in $CCl_3D$ shows, with a triplet due to the presence of I, two doublets centered at 2.08 and 1.40 ppm (referenced to tetramethylsilane). Such an NMR spectrum is the one expected for an isomer with the phosphinic ligands mutually *cis* [3]. On the other hand, the observed value of the chemical shift excludes the configuration III.

We suggest therefore that light induces the formation of the thermally inaccessible isomer II. Even if there is no direct evidence, it is possible to suppose that also for the complexes with $PPh_3$, $AsPh_3$ and $SbPh_3$ as ligands under irradiation, the isomer II is formed.

Some experiments have also been performed in order to investigate the mechanism of the photochemical isomerization. To this purpose, a solution of $RuCl_3NO(PMe_2Ph)_2$ (configuration I) containing $SbPh_3$ in about 5 molar excess was irradiated under the same conditions.

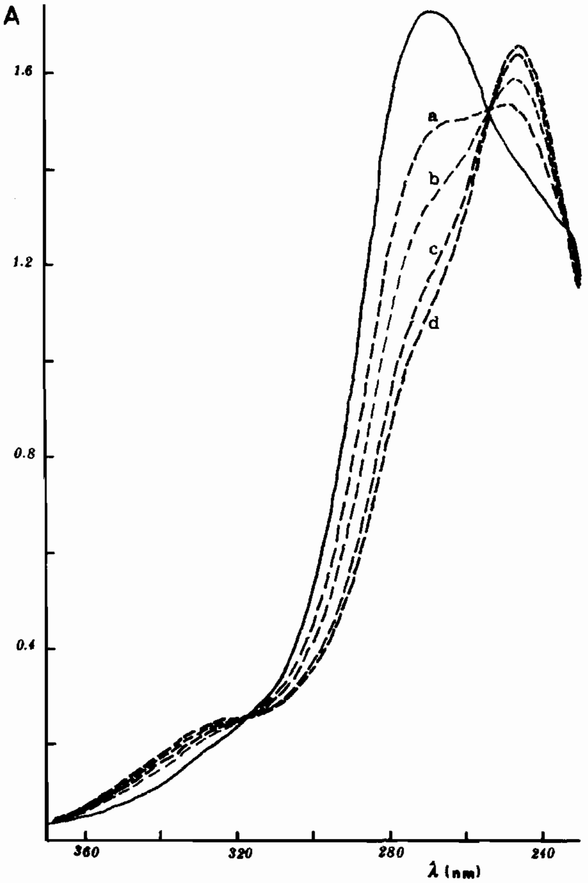


Figure 2. Variation of the ultraviolet spectrum of $RuCl_3NO(PMe_2Ph)_2$ (conf. III) induced by irradiation with a 365 nm light beam. Exposure time: continuous curve 0, (a) = 6 min, (b) = 16 min, (c) = 21 min, (d) = 31 min.

No modifications of the experimental trend, with regard to that of Fig. 1, occurred. This indicates that the photochemical conversion does not involve the cleavage of L. In this case, in fact, the attack of $SbPh_3$ on the reaction intermediate would cause the formation of a new product and, as a consequence, a modification of the ultraviolet spectrum.

It seems therefore probable that for this complex the photochemical conversion involves a nondissociative intramolecular mechanism with a different geometry of the excited complex [4].

The same experiment was performed with $RuCl_3NO(PPh_3)_2$; this complex, after irradiation in the absence of $SbPh_3$, is quickly reconverted into the original conformation I but, in the presence of $SbPh_3$, a new product originates whose ultraviolet spectrum shows a maximum at 347 nm instead of 335 nm (results of our experiment indicate that no thermal reaction occurs between this complex and $SbPh_3$ at 30 °C for 48 hours).

This kind of experiment was also made on a preparative scale: $RuCl_3NO(PPh_3)_2$ (0.3 g) and $SbPh_3$ (0.7 g) dissolved in 500 ml of $CH_2Cl_2$ were irradiated with sunlight for 1 hour. The volume of the solution was then reduced to about 50 ml and ethanol was added to precipitate a yellow complex which was washed with ethanol and n-hexane.

The ultraviolet spectrum of this complex is equal to that obtained in the previous experiment; the ESCA spectrum shows the presence of Sb and P and therefore allows the hypothesis that the formula of this complex could be $RuCl_3NO(PPh_3)(SbPh_3)$. This hypothesis is supported by the reaction that occurs between this complex and $PPh_3$ to give $RuCl_3NO(PPh_3)_2$.

The different behaviour of the two most studied complexes can therefore be summarized as follows: i) when L = $PMe_2Ph$, the photochemical reaction is not reversible at room temperature and is not modified by the presence of free $SbPh_3$; ii) when L = $PPh_3$, the photochemical reaction is reversible at room temperature. If $SbPh_3$ is present in the solution, the formation of the complex containing both the ligands occurs.

The instability of a *cis* conformation when L = $PPh_3$ may be due to a strong steric hindrance (it is to be noted that some effects due to the size of the $PPh_3$ group were pointed out for the isomer I also [5]). The stability of the conformations II and III when L = $PMe_2Ph$ can be due to the smaller size of this ligand.

The same intramolecular mechanism for the photochemical isomerization can be suggested for $RuCl_3NO(PPh_3)_2$ and $RuCl_3NO(PMe_2Ph)_2$; in this case, the different behaviour in the presence of $SbPh_3$ can be ascribed to the successive thermal isomerization.

This reaction should therefore occur via a five-coordinate intermediate obtained by loss of L. This intermediate would preferably react with $SbPh_3$ present in large excess.

## Acknowledgment

The authors wish to thank Prof. A. Foffani for helpful discussion.

## References

1 A. Foffani, G. Innorta, S. Torroni and G. Serrazanetti, in preparation.
2 R. E. Townsend and K. J. Coskran, *Inorg. Chem., 10,* 1661 (1971).
3 J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc., London,* 291 (1963).
4 J. K. Burdett, *Inorg. Chem., 15,* 212 (1976).
5 B. L. Haymore and J. A. Ibers, *Inorg. Chem., 14,* 3060 (1975).