Photochemical Isomerization of *trans*-Dichlorotetrakis(dimethylphenylphosphine)osmium(II)

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Photochemical isomerization of *trans*-dichlorotetrakis-(dimethylphenylphosphine)osmium(II) to its *cis*-form was confirmed by NMR and IR spectroscopy. The quantum yield of isomerization was 0.9 at 410 nm which was much larger than that (0.03 at 410 nm) of *trans*-dichlorobis(diphenylphosphinoethane)osmium(II).

While trying to study the crystal structure of osmium complexes with phosphine ligands, in particular, *trans*-dichlorotetrakis(dimethylphenylphosphine)osmium(II), referred to here as complex 1, only *cis*-form was crystallized from the crude complex. It is reasonable to think that the isomerization of *trans*-form to *cis*-form took place during the recrystallization process. The isomerization of complex 1 was originally reported by Coombe et al.,[1] and later, Champness et al.[2] who described that the reaction rate was slower when the ligand was trimethylphosphine and no isomerization occurred when the ligand was arsine or stibine. *Cis* to *trans* geometric isomerization of complexes with core structures consisting of OsS_4P_2 can be induced electrochemically.[3] Details of *trans* to *cis* isomerization, however, are still unknown. We tried to obtain kinetic data of the isomerization of complex 1 but obtained results which indicate that the isomerization of complex 1 is a photochemical reaction.

Complex 1 was prepared by modification of the method described by Sanders.[4] A deoxygenated ethanol (30 ml) solution of OsO_4 (1.0g, 3.9 mM) and concentrated hydrochloric acid (1.5 ml) was refluxed with dimethylphenylphosphine (4.4 ml, 30 mM) under argon for 28 h. Yellow crystals were obtained from a dichloromethane/hexane solution and were subjected to hexane washing and then dried under vacuum.

Ten mg of complex 1 were placed in an NMR tube (4 mm O.D., borosilicate glass) and were dissolved in 0.4 cm^3 of CD_2Cl_2 and then subjected to degassing by freeze and thaw cycles, and finally, the tube was sealed by fusing. The 4 mm NMR tube was inserted into another NMR tube (5 mm O.D., borosilicate glass) to be measured by a JEOL alpha 400 spectrometer at 298 K. The chemical shift was recorded against TMS for ^1H or an 85% H_3PO_4 solution for ^{31}P-$\{^1H\}$NMR.

The $^{31}P\{^1H\}$NMR spectrum of complex 1 in CD_2Cl_2 gave a broad signal[5] at -52.8 ppm that agreed with the value reported [1]; therefore, the configuration of the complex 1 is *trans*. After several days, a sharp singlet signal[6] at -43.2 ppm became predominant. This value of the chemical shift is identical with that of the authentic[7] *cis*-dichlorotetrakis(dimethylphenylphosphine)osmium(II) in CD_2Cl_2. In $CDCl_3$, the same complex gave two triplet signals at -43.3 and -44.5 ppm that clearly shows the configuration of the *cis*-form. Upon isomerization, the ^1H-NMR spectra also changed; a signal at 1.59 ppm, assigned as *trans*-form methyl protons, decreased in intensity, and signals at 1.49 ppm and 1.68 ppm, *cis*-form methyl protons, increased instead. These results indicate that complex 1 isomerized in CD_2Cl_2.

An experiment was performed to measure the reaction rate of complex 1's isomerization. Complex 1 was charged in the NMR tube in the same manner described above and placed in the spectrometer for two continuous days in order to obtain the time course of the isomerization. In spite of our expectations, there was no sign of isomerization within this period. This result contradicted our preliminary experiment which indicated that, under these conditions, isomerization would be completed in a few days. The only difference between these two experiments was light exposure. For the preliminary experiment, the sample tube was placed in the spectrometer only when it was being measured. The rest of the time the sample was kept on a bench illuminated by ceiling fluorescent lamps. In the second experiment, the sample remained inside the spectrometer for the entire period (two days), cut off from all light. Therefore, the sample tube was removed from the spectrometer, placed under the ceiling lamps and the reaction was monitored again. Complex 1 began to isomerize which indicates that the isomerization of complex 1 requires light.

Clarifying the effect of light, complex 1 was charged in the NMR tube in the same manner described above but this time two tubes were prepared and one, the control, was covered with aluminum foil to cut off light. Both NMR tubes were irradiated by a 500 W Xe lamp through Toshiba IRA-25S and Toshiba Y-43 filters to eliminate infrared light and light shorter than 400 nm. In the sample that was not covered by

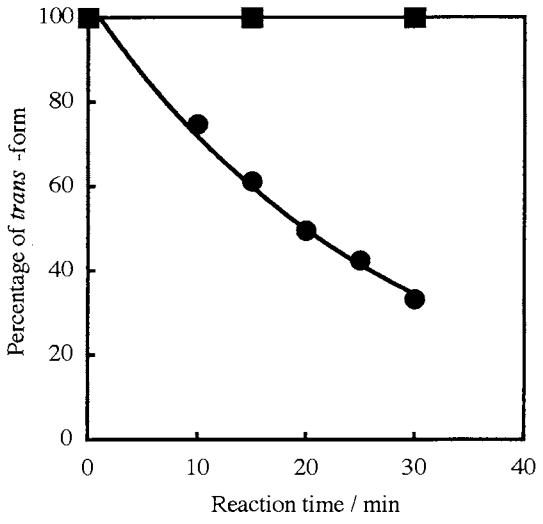

Figure 1. Isomerization of *trans*- dichlorotetrakis(dimethylphenylphosphine)osmium(II) to its *cis* -form in CD_2Cl_2 under illumination (●) and control (■).

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aluminum foil, the isomerization into *cis*-form was detected by ^{1}H-NMR spectroscopy; however, no change was observed in the control (Figure 1). In addition, formation of the *cis*-form was confirmed by IR spectroscopy (406, 420 cm^{-1}). These results indicate that the isomerization reaction of complex 1 is a photochemical reaction.

To study the irradiation time dependence of the isomerization, change of the *trans*-form to the *cis*-form was monitored by ^{1}H-NMR spectroscopy. After 25 min of irradiation, all of complex 1 isomerized to the *cis*-form which was then confirmed by ^{31}P-{^{1}H}NMR spectroscopy. In addition, the sum of methyl protons of the *cis*-form and the *trans*-form remained constant in each experiment. From these results, the reaction was expressed by using the ratio of the methyl protons of the *trans*-form and the sum of methyl protons of the *trans*-form and the *cis*-form as follows:

$$\ln[(\textit{trans}\text{-form} + \textit{cis}\text{-form}) / \textit{trans}\text{-form}] = kt$$

Plots of the ratio against the reaction time or the irradiation time resulted in a straight line that intercepts near zero. The result indicates that in the time period, 0 to 20 min (98% conversion), the photo chemical isomerization follows the first order rate expression. The amount of incident photons were measured by iron (III) oxalate[9] and the quantum yield of the reaction was determined to be 0.9 at 410 nm (Toshiba IRA-25S, Toshiba L-39, and Kenko BP-40).

In order to study the effect of ligands, bis(diphenylphosphinoethane), reffered to here as DPPE, was chosen as a bidentate ligand; consequently, *trans*-$Cl_2(DPPE)_2Os(II)$ was prepared[10] in a way similar to that reported by Chatt et al.[11] When *trans*-$Cl_2(DPPE)_2Os(II)$ was irradiated as described above, ^{31}P-{^{1}H}NMR signal at 8.43 ppm assigned to the *trans*-form decreased with irradiation time and the triplet signals assigned to the *cis*-form (7.24 and 3.84 ppm) increased. The quantum yield was 0.03 at 410 nm which is much smaller than that of dimethylphenylphosphine complex. The difference between dimethylphenylphosphine and DPPE may be attributed to the chelate effect of the ligand.

This photochemical isomerization process is a promising way of *cis*-synthesis which is much easier than the sophisticated five-step route developed by Bell et al.[11] Mechanistic study of this reaction is now underway.

References and Notes

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6 Coombe et al.[1] reported that in CD_2Cl_2 the ^{31}P-{^{1}H}NMR spectrum of the *cis*-form is a singlet due to accidental degeneracy of the P resonances.

7 *Cis*-complex was prepared as described by Bell et al.,[8] and a single crystal was obtained from a dichlorometahane/hexane solution. The X-ray structure was determined and the data are in preparation for publication.

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10 $[OsCl_6][N(n\text{-}Bu)_4]_2$ and bis(diphenylphosphinoethane) was charged in the flask that was covered with aluminum-foil and then dissolved in 1,1,2-trichlroroethane under argon and was refluxed for 24 h. Pale yellow precipitate was obtained upon evaporation of the solvent and was washed by acetone. A single crystal was obtained from a dichloromethane/hexane solution. An X-ray crystallographic study of the crystal confirmed *trans*-structure and the results are in preparation for publication.

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