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Kinetic Resolution of Dichlorobis(pyridine)(1-phenylpropan-1,3-diyl)platinum(IV). Experimental Demonstration of its Equilibrium with Dichlorobis(pyridine)(2-phenylpropan-1,3-diyl)platinum(IV)

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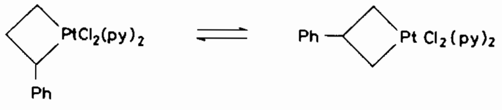
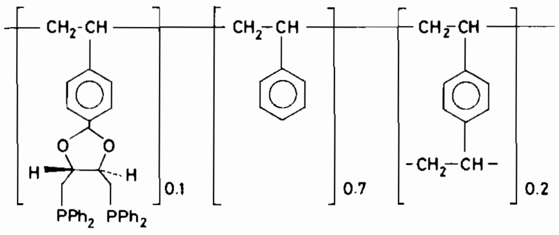
Considerable interest has been generated in the mechanism by which dichlorobis(pyridine)(1-phenylpropan-1,3-diyl)platinum(IV), 1, rearranges to dichlorobis(pyridine)(2-phenylpropan-1,3-diyl)platinum(IV), 2 [1–3]. A number of labeling experiments and stereochemical probes have been used to investigate this reaction. The α-isomer, 1, is prepared from Zeise's dimer* and phenyl-cyclopropane. If 1 is heated to 60 °C in $CHCl_3$ for 1 h one obtains a mixture of 1 and 2 in an approximate ratio of 1:4 [1–3]. The structural distinctions between 1 and 2 were made by ^{13}C-NMR [1] and the structure of 1 has now been confirmed by X-ray crystallography [4]. While the mechanism remains unknown, it is commonly felt that the rearrangement of 1 to 2 is an overall equilibrium process with 2 representing the thermodynamically more stable isomer. The rearrangement of 1 to 2 does seem to exhibit the characteristics of a fast equilibrium but this hypothesis has yet to be demonstrated experimentally. We report in this communication the first demonstration of an equilibrium between 1 and 2. We are also reporting on the first preparation of an optically-active platinacyclobutane. Our method should be general for the preparation of other optically-active platinacyclobutanes and thus offers a new probe by which to examine platinacyclobutane reactions.



1 2

If 1 and 2 are indeed in equilibrium, then, optically active 1 should convert to racemic by virtue of its passage through achiral 2. In order to test this concept it became necessary to prepare optically active 1. Unfortunately the achiral nature of the starting materials made a synthetic approach to this problem unlikely. We have previously established that chiral cyclopropanes could be kinetically resolved by first converting them to their corresponding platinacyclobutanes followed by decomposition with optically active phosphines and olefins [5]. This implies that the undecomposed platinacyclobutane would be optically active. However the recovery of optically active platinacyclobutane from a solution containing phosphine-chelated platinum would be tedious and probably result in substantial loss of the desired compound. The tenuous stability of 1 relative to 2 in addition to the small scale of reaction, made any separation by chromatographic methods impractical.

These problems were overcome by employing the insoluble, optically-active polymer 3 reported by Stille. This polymer has a polystyrene backbone which has been 20% cross-linked with divinylbenzene and incorporates a 10% DIOP-equivalent unit into the polymer. The use of this polymer gives an ideal resolving agent in that the quantity of platinacyclobutane which is decomposed forms phosphine-chelated platinum that is removable by simple filtration. The resolution can be effected in ethanol. Filtration and subsequent crystallization from the filtrate offers a simple yet effective method of preparing optically active 1.



3

The resolution of 1 was carried out in a vacuum atmosphere dry box containing a nitrogen atmosphere. To a 50-ml Erlenmeyer containing 20 ml of absolute ethanol were added 270 mg of racemic 1 and 350 mg of 3. The solution was stirred for 5 min during which time a distinct fading of the characteristic yellow color of 1 occurred. The solution was filtered and the filtrate was removed from the dry box whereupon 0.5 ml of water was added. Crystallization occurred soon thereafter and 100 mg of optically active 1 was recovered. The crystals of 1 recovered in this fashion had an $[\alpha]^{26}_{D}$ + 30.0° (*c* 1.0, $CHCl_3$). While the degree of resolution is unknown, the magnitude of rotation was sufficient to carry out the rearrangement experiment. A ^{13}C-NMR of the resolved 1 confirmed that it was not contaminated with 2.

We initially attempted to follow the rearrangement of 1 to 2 by observing optically active 1 in a heated

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*Zeise's dimer is di-μ-chloro-dichloro(η^2-ethene)diplatinum(II).

polarimetry cell. However, this proved to be impractical as the optical rotation changed first with changing temperature and then began decreasing as rearrangement commenced. This decrease in the optical rotation began before the polarimetry cell had thermally equilibrated. More satisfying and reproducible results were obtained by using the specific rotation value above as the initial value. A standardized sample of optically active 1 in $CHCl_3$ was maintained in an equilibrated bath at 60 °C. Samples were withdrawn at 5 min intervals and cooled by immersion in a dry ice-acetone bath and then warmed to 26 ± 1 °C whereupon polarimetry readings were obtained. While such manipulations do not afford an opportunity to make any realistic kinetic measurements it was quite clear that the optical activity of the platinacyclobutane solution was decreasing and after only 20 min the solution no longer showed any optical rotation*. A ^{13}C-NMR analysis of the 20 min solution established that both 1 and 2 were present in about equal quantities. Thus mere dilution of 1 by its conversion to 2 should have only reduced the optical activity by 50% whereas no optical activity was observed. Thus, optically-active 1 had been converted to racemic 1. The most reasonable explanation for this observation would be the establishment of an equilibrium between 1 and 2 as part of the rearrangement process.

In summary, we have prepared optically-active 1 by a kinetic resolution employing 3 and have demonstrated the loss of this optical activity, presumably by an equilibrium process, under conditions which effect the rearrangement of 1 to 2.

Acknowledgement

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*An ETL-NPL automatic polarimeter was used. Readings of ±0.0005 are attainable on this instrument.