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Preliminary communication

LIGAND EXCHANGE REACTIONS IN THE PREPARATION OF *trans*-$[PtCl_2(Olefin)(L)]$ COMPLEXES

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Summary

In the usual preparation of *trans*-$[PtCl_2(olefin)(L)]$ complexes, where L is a neutral base such as isoquinoline or pyridine, adventitious free L contaminates the complex. It is important to remove the free base before meaningful ^1H NMR spectra can be obtained. This can be achieved by treatment of a solution of the complex with a cationic exchange resin, or more conveniently, by extraction of the solution with HBF_4.

Introduction

Perhaps the most convenient procedure for the preparation of *trans*-$[PtCl_2(olefin)(L)]$ (I) where L is a neutral base such as isoquinoline, pyridine, or related compounds, consists of adding stoichiometric quantities of L to an aqueous solution of $K[PtCl_3(olefin)]$. Examination of the ^1H NMR spectra of freshly prepared $CDCl_3$ solutions of such complexes frequently show no $^3J(Pt—NCH)$ [1—3]. The failure to observe such coupling is obviously due to rapid exchange of L, but it has not been clear whether such exchange occurs with L or with solvent or with both. Because stoichiometric (or smaller) quantities of L are used in the preparation, solvolysis usually has been implicated [3]. We now wish to report that the failure to observe $^3J(Pt—NCH)$ in freshly prepared $CDCl_3$ solutions of I is due to the presence of adventitious free L. The free ligand may be conveniently removed either by extraction with HBF_4 or by treatment with a cationic exchange resin.

Results and discussion

The preparation of *trans*-$[PtCl_2(C_2H_4)(isoquinoline)]$ was carried out by the usual procedure. When 1 mmole of this complex was dissolved in 5 ml $CDCl_3$ and the NMR spectrum examined, no $^3J(Pt—NCH)$ was observed. After shaking the solution with 1 g of Dowex 50W-8X resin, the filtered solution was again examined in the NMR spectrometer and now the coupling was clearly discernible. The filtered resin was washed with 200 ml $CHCl_3$ and dried. The resin was then extracted with 5 ml of 1/1 CH_3OH/conc. aq. NH_4OH. The resulting extract was shaken with an equal volume of hexane. The UV spectrum of this hexane solution was identical to the reported [4] spectrum of pure isoquinoline.

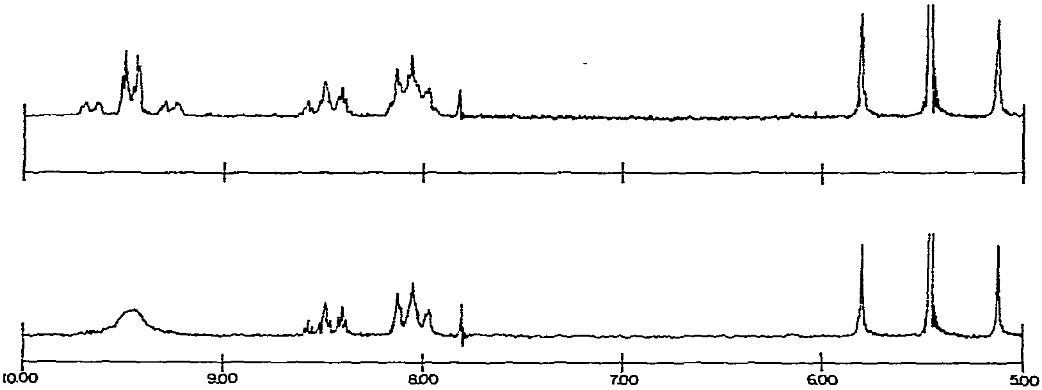

Fig.1. (Bottom) 90 MHz ^1H NMR spectrum of a 0.2 *M* freshly prepared $CDCl_3$ solution of *trans*-$[PtCl_2(C_2H_4)(C_5H_5N)]$. (Top) 90 MHz ^1H NMR spectrum of the above solution after contact with resin.

A freshly prepared $CDCl_3$ solution of *trans*-$[PtCl_2(C_2H_4)(C_5H_5N)]$, prepared by the above procedure, gave the ^1H NMR spectrum shown in Fig. 1 (bottom). As expected, no ^3J(Pt—NCH) was observed. After treatment with the exchange resin, the spectrum of the solution was again examined. The new spectrum, Fig. 1 (top), clearly shows this coupling. Thus when free ligand is removed, a fresh $CDCl_3$ solution of the complex, contrary to previous reports [3] does show coupling.

The complex I (L = 4-carbomethoxypyridine; olefin = C_2H_4) prepared in the usual manner and dissolved in $CDCl_3$ showed no ^3J(Pt—NCH). Extraction of the $CDCl_3$ solution with HBF_4 (aq) and examination of the $CDCl_3$ solution now showed ^3J(Pt—NCH). The UV spectrum of the aqueous HBF_4 solution indicated the presence of uncomplexed 4-carbomethoxypyridine. The same behavior was observed for the complex *trans*-$[PtCl_2$(*cis*-2-butene)(4-methylpyridine)$]$. The aqueous HBF_4 extraction is very conveniently carried out in the NMR tube or a small test tube.

The above observations suggest that caution must be exercised before reaching conclusions regarding ligand lability in Pt^{II} complexes based on ^1H NMR interpretations. The complexes prepared by the known procedures usually have traces of free ligand present and this may be responsible for the fast exchange (no ^3J(Pt—NCH)) observed in $CDCl_3$ solutions. Free ligand must be removed before solvolytic reactions are considered.

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