

**THE REACTION OF PYRIDINE WITH *trans*-[PtCl<sub>2</sub>(*cis*-ethylene-1,2-*d*<sub>2</sub>)(pyridine)]; EVIDENCE FOR STEREOSPECIFIC ADDITION–ELIMINATION IN THE  $\pi \rightleftharpoons \sigma$  INTERCONVERSION**

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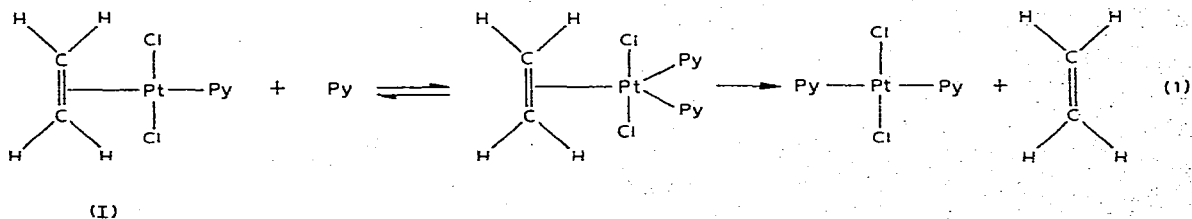
**Summary**

Treatment of *trans*-[PtCl<sub>2</sub>(*cis*-ethylene-1,2-*d*<sub>2</sub>)(pyridine)] with excess pyridine at  $-15^{\circ}\text{C}$  gives reversible formation of the carbon  $\sigma$  bonded platinum zwitterion and slow release of the complexed ethylene. Infrared analysis of the liberated gas shows no *trans*-ethylene-1,2-*d*<sub>2</sub> indicating a stereospecific addition–elimination of the pyridine.

**Introduction**

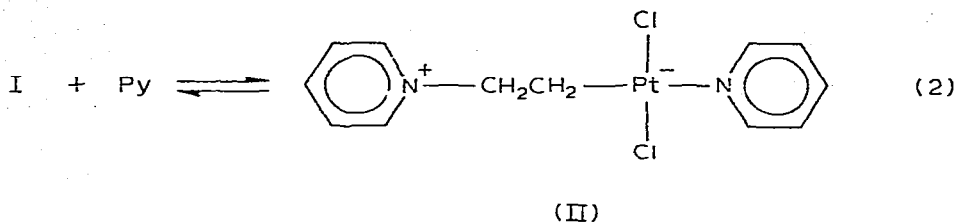
When an olefin complexed to Pt(II) is replaced by either the same or a different olefin, the displaced olefin always retains its original configuration, i.e., neither *cis*  $\rightleftharpoons$  *trans* isomerization nor double bond migration occurs [1].

Complexed olefins may also be displaced by neutral nucleophilic ligands such as pyridines [2] (Py) or phosphines [3]. Such nucleophilic displacements very likely occur by the direct attack of the ligand on the platinum with the formation of a 5-coordinate intermediate [4] (eq. 1). However, on the basis of low



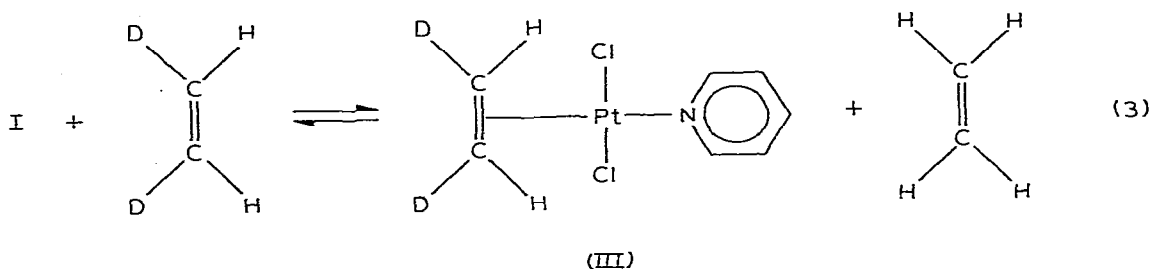
temperature <sup>1</sup>H NMR studies [5], it was postulated that pyridine may also attack the coordinated olefin to give the  $\sigma$  bonded zwitterion complex, II. Subsequently [6] related  $\sigma$  bonded complexes were actually isolated and characterized. The attack of the amines on these coordinated olefins to produce the isolable  $\sigma$  com-

plexes was demonstrated to occur by a stereospecific *trans* addition [7]. We now wish to report that formation of  $\sigma$  complex II (eq. 2) and its decomposition to regenerate the olefin proceeds by a stereospecific (*trans*) addition—elimination.



### Experimental

*trans*-[PtCl<sub>2</sub>(*cis*-ethylene-1,2-*d*<sub>2</sub>)(pyridine)] (III) was prepared by exchange of ethylene in I [8] with dideuterioethylene: The apparatus used for the exchange



is shown in Fig. 1. A solution of 0.749 g (2 mmol) of I in 20 ml of benzene was placed in the reaction flask and cooled to  $-10^\circ\text{C}$  at which temperature the con-

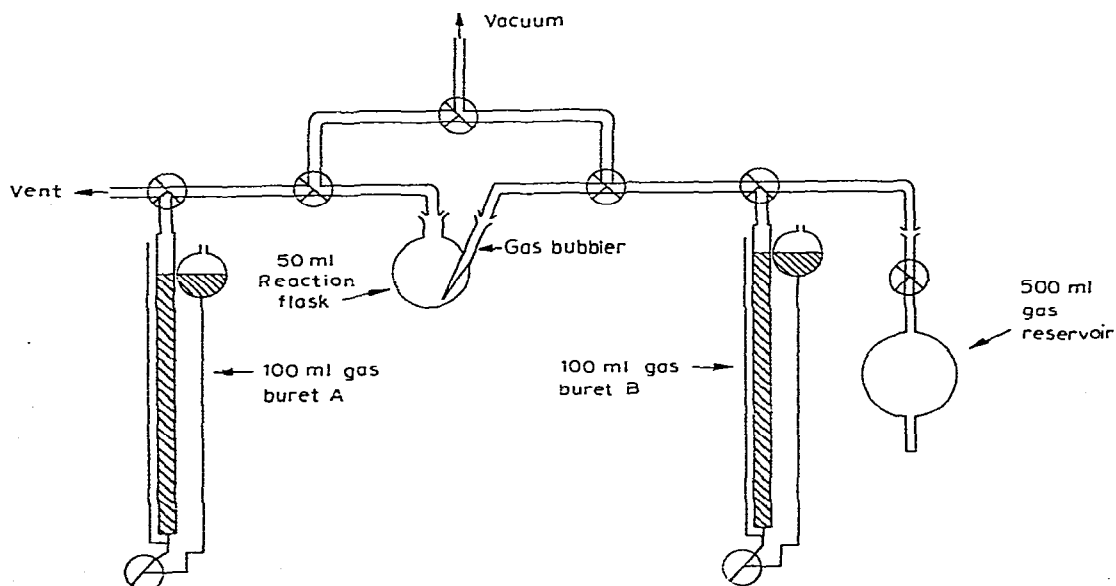


Fig. 1. Schematic diagram of the apparatus used for recycling small volumes of reaction gas.

tents are frozen solid. The apparatus was evacuated and then the reaction flask was warmed to room temperature. 25 ml (at 2 atm) of *cis*-ethylene-1,2- $d_2$  was introduced into gas buret B from the 500 ml reservoir (2 atm) and this gas was then slowly passed through the stirred solution of I and the exit gas collected in buret A. This once-through gas was then transferred back to B, bypassing the reaction flask, by appropriate manipulation of stopcocks and the leveling bulbs attached to the burets. This procedure was repeated three times. The reaction vessel was then cooled again to  $-10^\circ\text{C}$  and the system purged of gas by evacuation. A fresh 25 ml (at  $\sim 2$  atm) portion of the dideuteroethylene was then introduced into B from the reservoir. The entire procedure was repeated a total of three times. The mixture was worked up at this stage because of an accidental leak in the stopcock above the gas reservoir. The reaction mixture was removed and the benzene evaporated leaving a yellow solid m.p.  $127^\circ\text{C}$ . The mass spectrum (Perkin—Elmer Hatachi R-MV-6) of this solid indicated a mixture of starting I ( $m/e$  373) and its dideutero analog III, ( $m/e$  375); an analysis of the relative intensities of the peaks indicated the mixture contained  $\sim 75\%$  of III. Integration of the  $^1\text{H}$  NMR spectrum of the mixture in  $\text{CDCl}_3$  showed  $\sim 80\%$  of III.

#### *Reaction of trans-[PtCl<sub>2</sub>(cis-ethylene-1,2-d<sub>2</sub>)(pyridine)] with Pyridine*

A preliminary experiment was conducted in an NMR tube by adding to 0.5 ml of a 0.4 M  $\text{CDCl}_3$  solution of III a 4-fold excess of pyridine at  $-15^\circ\text{C}$ . The  $^1\text{H}$  NMR spectrum (Varian A-60, TMS standard) gave the following:  $\delta$  2.54 (doublet, 1,  $^2J(\text{PtCH}) \sim 80$  Hz,  $^3J(\text{HCCH})$  7 Hz);  $\delta$  4.67 (doublet, 1,  $^3J(\text{HCCH})$  7 Hz). Thus the NMR shows unequivocally the presence of the  $\sigma$  complex analogous to II. The spectrum also showed the presence of the  $\pi$  complex and it is estimated that at  $-15^\circ\text{C}$  the ratio of  $\pi$  to  $\sigma$  is about 1.5 : 1. The signal for the H atom on the  $\beta$  carbon in the  $\sigma$  complex and the signal for the H atom in the  $\pi$  complex overlap and thus  $^3J(\text{PtCCH})$  could not be readily determined. On standing for several days at room temperature, ethylene was liberated and a precipitate of mixed yellow and colorless crystals appeared; these probably [8] are *trans*-[PtCl<sub>2</sub>(Py)<sub>2</sub>] and [Pt(Py)<sub>4</sub>]Cl<sub>2</sub> respectively.

In a second experiment 0.475 g (1.27 mmol) of III, prepared as above, was dissolved in 5 ml of  $\text{CDCl}_3$  and to the cooled ( $-15^\circ\text{C}$ ) solution there was added 0.469 ml (5.90 mmol) of cold ( $-15^\circ\text{C}$ ) pyridine. The vessel used for the reaction consisted of a test tube sealed to a break-seal and having a side arm for introduction of reactants and for sealing of the test tube. The vessel was evacuated, sealed, and allowed to stand at  $-15^\circ\text{C}$  for one week during which time the expected yellow-white precipitate appeared in the tube. The tube was then cooled to  $-78^\circ\text{C}$ , the seal broken and the liberated ethylene was condensed into an infrared gas cell cooled to  $-196^\circ\text{C}$ . The IR spectrum (Beckman IR-12) showed bands at 844 and 953  $\text{cm}^{-1}$  in an intensity ratio of about 4 : 1 corresponding respectively to *cis*-ethylene-1,2- $d_2$  and ethylene [9]. No band at 727  $\text{cm}^{-1}$  corresponding to *trans*-ethylene-1,2- $d_2$  [9] was observed.

#### Discussion

Simple terminal olefins complexed to Pt(II) have been shown to undergo nucleophilic addition with amines to give  $\sigma$  bonded zwitterion complexes such

as II. In the case where complexed ethylene is treated with pyridine, (eq. 2) the reaction is clearly reversible. It might be assumed that internal olefins would react similarly, and providing that either the addition or the elimination were non-stereospecific, *cis-trans* isomerization might occur. However, despite many efforts in this laboratory and elsewhere, no such isomerization has been achieved. The failure to observe isomerization under conditions where the ethylene  $\sigma$  complex II is produced might be due to failure to form such complexes with internal olefins. However, it is also possible that such complexes might be formed transiently but that the addition and elimination are stereospecific in the same sense and hence no isomerization can be observed when the olefin is eventually displaced from the metal. In view of the fact that stereospecific *trans* addition of amines to complexed olefins has been demonstrated to occur for Pt(II), it might be expected that *trans* elimination also occurs. This has now been demonstrated by the observation that the  $\sigma$  complex formed from *cis*-ethylene-1,2- $d_2$  gives exclusively the *cis*-ethylene-1,2- $d_2$  when it is liberated from the platinum to which it is complexed.

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