Journal of Organometallic Chemistry, 128 (1977) 85—87

A NEW GENERAL SYNTHESIS OF ZEISE'S DIMER, $[PtCl_2(C_2H_4)]_2$, AND ITS ANALOGS

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(Received August 2nd, 1976)

Summary

When ether solutions of complexes having the structure *trans*-$[PtCl_2(olefin)(L)]$, where L is a neutral base such as pyridine, are stirred with a large excess of cationic exchange resin, the L is removed and the dimer $[PtCl_2(olefin)]_2$ is formed. This procedure provides a convenient route to such dimers.

Introduction

We have shown earlier [1] that when complexes having the structure *trans*-$[PtCl_2(olefin)(L)]$, where L is a base such as pyridine, are prepared in the usual manner, free L accompanies the isolated crystalline complex. The presence of this free L leads to rapid exchange with complexed L when the complex is dissolved in solvents such as $CHCl_3$ thus complicating the interpretation of intrinsic ligand lability. The adventitious free L may be readily removed by treating solutions of the complex with a cationic exchange resin or by shaking briefly with a solution of HBF_4.

In one experiment using the above technique for removal of free pyridine, a solution of I was inadvertently left in contact with excess HBF_4 for a long period of time. Workup of the solution revealed that the acid had removed not only free pyridine, but complexed pyridine as well, giving rise to pure Zeise's dimer, II:

$$2\ t\text{-}[PtCl_2(C_2H_4)(Py)] + 2\ H^+ \rightarrow [PtCl_2(C_2H_4)]_2 + 2\ PyH^+ \qquad (1)$$

(I) (II)

This reaction provides a convenient new route to Zeise's dimer and the method can be extended to olefins other than ethylene. Zeise's dimer is usually prepared by acidifying aqueous-ethanolic solutions of Zeise's salt, $K[PtCl_3(C_2H_4)]$, and evaporating to dryness [2].

Results and discussion

The use of a sulfonic acid resin for the reaction shown in eqn. 1 gives better results than those obtained with HBF_4. The choice of solvent is important. A solution of I in CH_2Cl_2, on stirring with the resin for 20 h, gave only a trace of II; similar treatment of an ether solution of I gave almost pure II in about 1 h. The better coordinating solvent may assist the reaction by displacing the labile pyridine from the platinum whereupon it is trapped by the resin.

Analogs of II may be prepared by replacing the ethylene of I with other olefins. If the olefin displacement reaction is carried out in ether, the analog of I need not be isolated and the analog of II can be obtained in a one-step process starting from I.

Experimental

Zeise's dimer, II. An aqueous solution of Zeise's salt is treated with an equimolar amount of pyridine and the precipitated yellow complex filtered, washed with water, and vacuum dried, to give a 90% yield of I, m.p. 125—6°C. [3]

To a solution of 300 mg (0.80 mmol) of I in 20 ml ether there was added 4.0 g (9.68 meq) of Dowex 50W-X8 resin and the mixture was then stirred vigorously for 1 h. The resin was filtered, washed twice with 5 ml ether, and the combined filtrate treated again with 4.0 g of fresh resin. A third treatment was performed in the same manner. After the ether solution was dried over Na_2SO_4 at 0°C overnight, it was filtered. The Na_2SO_4 was washed with benzene (3 × 5 ml) and the combined filtrate evaporated to dryness under vacuum. A ^1H NMR spectrum gave no evidence of pyridine. This solid orange residue (190 mg, 80%) was recrystallized from benzene using 1—2 mg of charcoal to help remove a trace of colloidal Pt. On cooling the benzene solution, II precipitated. Filtration and drying gave 95 mg of pure dimer, m.p. 180—5°C (dec.).

1,3-Dichloro-μ-dichloro-2,4-bis(styrene)diplatinum(II).

To a solution of 300 mg (0.80 mmols) of I in 20 ml of ether there was added 0.093 ml (0.81 mmols) of styrene. The solution was refluxed for 30 min, cooled, and treated with the Dowex resin as described above. Evaporation of the ether solution in vacuo gave an orange solid. This solid was extracted with $CDCl_3$ in which the starting compound is quite soluble and the dimer only sparingly soluble. The ^1H NMR spectrum of the $CDCl_3$ solution showed no pyridine. The orange solid (260 mg, 90%) was recrystallized from benzene with decolorizing charcoal to give a bright orange powder, 0.164 mg, m.p. 199—201°C, lit. [4], 204°C.

This general procedure was used with *t*-[$PtCl_2$(1-Dodecene)(Py)] and with *t*-[$PtCl_2(C_2H_4)$(4-MePy)] and the dimers were readily isolated indicating the generality of the procedure.

Acknowledgement

We wish to thank Engelhard Industries, Inc. for a generous supply of platinum.

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