Inorganica Chimica Acta, *134* (1987) 185–186

Reaction between 1,2-Bis(diphenylphosphino)methaneplatinum(II) chloride, $(Ph_2PCH_2PPh_2)PtCl_2$ and Ethynylbenzene in the Presence of Hydrazine Hydrate

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(Received April 10, 1987)

Complexes of platinum(II) and ethylnylbenzene (phenylacetylene) are known [1]. This class of compounds involves either σ-Pt–C or π-Pt–C bonds. In this communication we report a reaction between $(Ph_2PCH_2PPh_2)PtCl_2$ and ethynylbenzene, $PhC{\equiv}CH$ which yields a platinum(I) dimeric complex involving two σ-Pt–C bonds.

Experimental

$(Ph_2PCH_2PPh_2)PtCl_2$ (**I**) was prepared according to the method of Hewerstone and Watson [2] and used in an analytically pure form. Ethynylbenzene (BDH) was of reagent grade and was repurified by distillation. It was deuterated according to the method of Jenny and Roberts [3]. Potassium cyanide (BDH) was of analar grade and used without further purification. Hydrazine hydrate (99% purity, BDH) was used without further purification.

(i) Reaction Between I and PhC≡CH in the Presence of Hydrazine Hydrate

Hydrazine hydrate (0.4 cm^3) was added to a suspension of $(Ph_2PCH_2PPh_2)PtCl_2$ (**I**) (0.40 g, 0.62 mmol) in dry ethanol (10 cm^3) at room temperature. The suspension was warmed (35–40 °C) until it completely dissolved. The resulting solution was filtered under nitrogen and enthynylbenzene (0.10 cm^3) and in dry ethanol (1.0 cm^3) was added. The mixture was stirred continuously at room temperature for about 48 h during which time a bright yellow solid precipitated.

After filtration the solid was washed with dry ethanol (3×10 cm^3) and dried *in vacuo*. *Anal.* Found: C, 59.84; H, 4.35; P, 8.90. Relative molecular mass in benzene, 1173. Calc. for dimer $[(Ph_2PCH_2PPh_2)PtC{\equiv}CPh]_2$ (**II**): C, 58.22; H, 4.01; P, 9.10%. Relative molecular mass, 1361.26.

In the infrared spectrum (KBr disc and Nujol mull) **II** gives a strong sharp absorption band at 2100 cm^{-1}. Its high field ^1H NMR ($10{-}40\tau$) shows no signal which is assignable to Pt–H.

(ii) Reaction Between I and Deuterated Ethynylbenzene in the Presence of Hydrazine Hydrate

The procedure used in reaction (i) was followed. The same yellow product was isolated from the reaction mixture. The infrared spectrum of the product showed no shift in the position of the absorption band at 2100 cm^{-1}.

(iii) Reaction Between the Dimer II and Potassium Cyanide

The yellow solid (**II**) (0.041 g, 0.030 mmol) in ethanol (10 cm^3) was refluxed with potassium cyanide (0.43 g) for 8 h. Distilled water (10 cm^3) and ethoxyethane (ether) (10 cm^3) were then added to the cooled mixture. After separation of the aqueous and organic phases, the aqueous phase gave unreacted KCN and a pale yellow solid which gave two infrared absorption bands at 2020 and 2135 cm^{-1}. A colourless viscous liquid was isolated from the ethereal layer after fractional distillation but its identity was not confirmed.

Results and Discussion

On the basis of elemental analysis and relative formula mass determination, product **II** can be considered to be a dimer corresponding to the formula $[(Ph_2PCH_2PPh_2)PtC{\equiv}CPh]_2$. This formulation implies that platinum is in the low oxidation of one. Platinum(I) compounds are known [4, 5]. The absorption band at 2100 cm^{-1} in the infrared spectrum of **II** and the absence of a signal assignable to a proton bonded to the platinum atom in the high field ^1H NMR spectrum indicates that the compound consists of a σ-Pt–C≡C– unit rather than a π-Pt–C≡C– unit. If a Pt–H unit was present, use of $PhC{\equiv}CD$ would have resulted in a shift of $(2100\sqrt{2})$ cm^{-1} in the band at 2100 which was not observed, assuming that the H atom is derived from $PhC{\equiv}CH$. Therefore the band at 2100 cm^{-1} can be assigned unambiguously to ν(C≡C) of the σ-Pt–C≡C– unit.

On the basis of the evidence available, the dimer is assigned the structure given in Fig. 1. The proposed structure is preferred to that which Glockling and

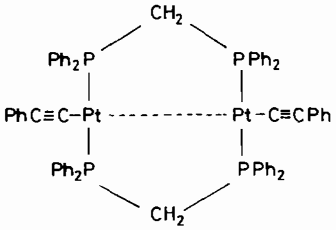

Fig. 1. Structure of dimer **II**.

0020-1693/87/$3.50

Pollock [5] assigned the chloro dimer, $[(Ph_2PCH_2PPh_2)PtCl]_2$, and was found to be incorrect by Puddephat and his co-workers [4] on the basis of its ^{31}P NMR spectrum. The proposed structure is one which eliminates much of the strain in the otherwise 4-membered ring.

An attempt was made to obtain the X-ray crystal structure of the dimer **II** by growing suitable crystals in tetrachloromethane. Brickshaped very pale yellow crystals were obtained which on analysis yielded much lower carbon, hydrogen and phosphorus content than the original yellow solid (**II**). Preliminary X-ray analysis* revealed that the crystals were a mixture of two compounds; a platinum(0) compound consisting of two chelating phosphine ligands only with a triclinic unit cell and a platinum(II) compound containing two ethyne ligands and having a monoclinic unit cell. The shortest Pt–Pt length was found to be 0.39 nm. This suggests that in tetrachloromethane **II** undergoes disproportionation which is perhaps expected of a platinum(I) compound.

The reaction between **II** and potassium cyanide was intended to test the possibility of replacing the –C≡CPh moieties with –C≡N groups. Although a reaction appeared to have taken place, it turned out to be a rather complex reaction and as a result no product from the reaction mixture has been definitely identified.

Acknowledgements

The author wishes to thank Dr S. Cameron for the preliminary X-ray work, the Queen's University of Belfast and Makerere University for financial and material support.

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*The X-ray analysis was carried out at the University of Ulster, Coleraine, N. Ireland by Dr S. Cameron.