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## Phase-transfer catalyzed base hydrolysis of $\text{Pt}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{Cl}_2$ . Synthesis and crystal structure of the trinuclear compound $[\text{Pt}_3(\mu_3\text{-O})(\mu\text{-}\eta^2\text{-PPh}_2\text{O})_3(\text{PPh}_2\text{Me})_3]\text{PF}_6 \cdot \text{CHCl}_3$

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### Abstract

Base hydrolysis of  $\text{Pt}(\text{dppm})\text{Cl}_2$ , ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), under phase-transfer-catalysis (PTC) conditions gave the triplatinum compound  $[\text{Pt}_3(\mu_3\text{-O})(\mu\text{-}\eta^2\text{-PPh}_2\text{O})_3(\text{PPh}_2\text{Me})_3]\text{PF}_6$ . This trinuclear compound can be transformed to  $\{\text{Pt}(\text{PPh}_2\text{Me})(\text{PPh}_2(\text{OH}))\text{Cl}_2\}$ , which upon treating with aqueous NaOH under PTC conditions produced a dimeric compound  $[\text{Pt}(\mu\text{-OH})(\text{PPh}_2\text{Me})(\text{PPh}_2\text{O})]_2$ . The trinuclear compound has been characterized by various spectroscopic methods and X-ray crystallography.

### Introduction

The use of phase-transfer-catalysis (PTC) in organometallic chemistry has received much attention [1]. We have recently reported [2] that the reaction of  $\text{Pt}(\text{dppm})\text{Cl}_2$  ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) with  $[\text{S}(\text{O})\text{Me}_3]\text{Cl}$  under basic PTC conditions gives the complex  $\{\text{Pt}(\text{PPh}_2\text{Me})(\text{PPh}_2(\text{OH}))[(\text{CH}_2)_2\text{S}(\text{O})\text{Me}]\}\text{Cl}$ , in which a  $\text{dppm}$  ligand is hydrolyzed to produce  $\text{PPh}_2\text{Me}$  and  $\text{PPh}_2(\text{OH})$  ligands. We have also noted that the base hydrolysis of  $\text{Pt}(\text{dppm})\text{Cl}_2$  also occurs under PTC conditions, and more than two products have been observed. Base hydrolysis of  $\text{dppm}$  is an important chemistry for Pt- $\text{dppm}$  complexes, especially under mild PTC conditions. Recently it has been reported [3] that the reaction of  $\text{Pt}(\text{dppm})\text{Cl}_2$  with aqueous  $\text{OH}^-$  in  $\text{dmsO}$ ,  $\text{MeCN}$  or water produced *cis* and *trans*  $[\text{Pt}(\mu\text{-OH})(\text{PPh}_2\text{O})(\text{PPh}_2\text{Me})]_2$ , **3**. Since we have obtained a novel trinuclear species instead of **3** upon the hydrolysis of  $\text{Pt}(\text{dppm})\text{Cl}_2$  under PTC/ $\text{OH}^-$  conditions, we wish to report our preliminary results on this matter [4\*].

\* Reference number with asterisk indicates a note in the list of references.

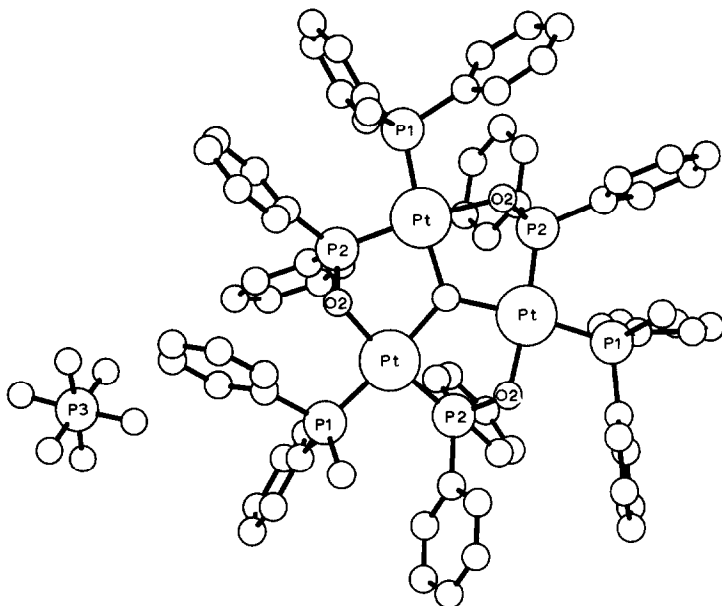


Fig. 1. The molecular structure of compound 1.

## Experimental

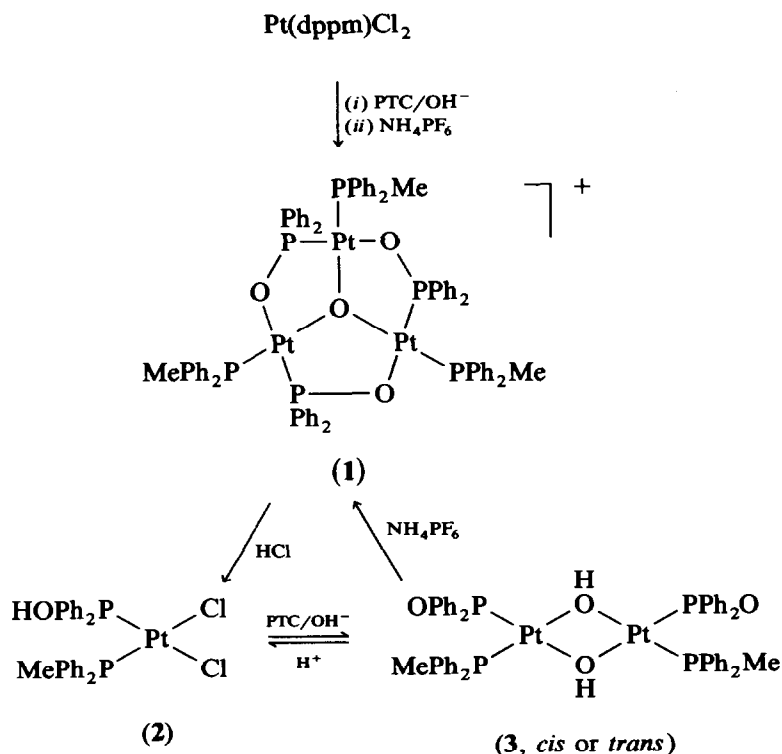
Compound  $[\text{Pt}_3(\mu_3\text{-O})(\mu\text{-}\eta^2\text{-PPh}_2\text{O})_3(\text{PPh}_2\text{Me})_3]\text{PF}_6 \cdot \text{CHCl}_3$ , **1**, was obtained (45% yield as crystalline material) from the reaction of  $\text{Pt}(\text{dppm})\text{Cl}_2$  (0.35 mmol in 15 ml  $\text{CH}_2\text{Cl}_2$ ) with aqueous KOH (1.8 N, 5 ml) in the presence of  $n\text{-Bu}_4\text{NCl}$ , followed by anion exchange with  $\text{NH}_4\text{PF}_6$  and recrystallization from  $\text{CHCl}_3$ . The rate of hydrolysis reaction depends on the amount of phase-transfer (PT) catalyst and the concentration of KOH. This PT catalyzed dppm hydrolysis reaction is facile and the workup is easy. Compound **1** has been characterized. Anal. Found: C, 43.77; H, 3.40.  $\text{C}_{75}\text{H}_{69}\text{F}_6\text{O}_4\text{P}_7\text{Pt}_3 \cdot \text{CHCl}_3$  calcd: C, 44.11; H, 3.38%. FAB mass spectrum 1804 [ $M - (\text{PF}_6 + \text{CHCl}_3)$ ]. M.p. 189–192°C.  $\lambda_{\text{M}} \text{CHCl}_3$  was 82  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ .  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$  shows the typical 1 : 1 : 4 : 1 : 1 signal assignable to the coordinated  $\text{PPh}_2\text{Me}$ .  $^{31}\text{P}\{^1\text{H}\}$  spectrum of **1** shows two doublets ( $\delta = 7.75$  and 88.12 ppm, relative to 85%  $\text{H}_3\text{PO}_4$ ,  $J = 16.7$  Hz) with  $^{195}\text{Pt}$  satellite ( $J = 3687$  and 4113 Hz respectively). The small  $^{31}\text{P} - ^{31}\text{P}$  coupling constant and large  $^{31}\text{P} - ^{195}\text{Pt}$  coupling constant suggest that  $\text{PPh}_2\text{Me}$  is *cis* to  $\text{PPh}_2\text{O}$ . The molecular structure of **1** was further characterized by single crystal X-ray structure analysis. The colorless crystal is trigonal, space group  $R3c$  with  $a = 15.434(2)$ ,  $c = 54.436(6)$  Å;  $V = 11229.04$  Å<sup>3</sup>;  $M_r = 2072.13$ ;  $Z = 6$ ;  $D_c = 1.839$  g/cm<sup>3</sup>,  $F(000) = 6010.74$ ;  $\text{Cu-K}\alpha$  radiation,  $\lambda = 1.54056$  Å,  $\mu = 134$  cm<sup>-1</sup>. Anisotropic least squares refinement for 2108 independent reflections with  $I_o \geq 2.0\sigma(I_o)$  gives  $R = 0.026$ . An ORTEP plot of the molecular structure is shown in Fig. 1.

## Results and discussion

The molecular geometry of compound **1** consists of three platinum atoms and each platinum atom has square planar geometry. The three planes are triply bridged

by an oxygen atom in a propeller arrangement, and each platinum atom is further bridged consecutively by two P–O fragments, thus forming a large cyclic compound. The triply bridging Pt–O1 distance (2.088(1) Å) is comparable to the P–O bridging Pt–O2 distance (2.079(7) Å). The P2–O2 distance (1.545(12) Å) is longer than the P=O bond reported for  $[\text{Pt}(\mu\text{-NH}_2)(\text{PPh}_2\text{O})(\text{PPh}_3)]_2$  (1.526(11) Å) [5]. A compound consisting of three platinum atoms triply bridged by an oxygen atom in the centre has been reported [6], and a bridging P–O is also known for other metals [7]. However, to our knowledge, this is the first platinum complex containing a planar  $\text{Pt}_3\text{O}$  moiety with bridging P–O ligand, and this is the first such type of molecule obtained by the PTC technique.

Treating compound **1** with concentrated HCl gives the monomeric compound  $\{\text{Pt}(\text{PPh}_2\text{Me})[\text{PPh}_2(\text{OH})\text{Cl}_2]\}$ , **2**. Treating compound **2** with aqueous NaOH under PTC conditions produces compound **3** [3], which upon the addition of  $\text{NH}_4\text{PF}_6$  produces compound **1** again. The interconversion of compounds **1**, **2** and **3** under various conditions are depicted in Scheme 1. Compound **1** also reacts readily with ligands such as dithiolates and phosphines. It is a convenient way to synthesize complexes containing different phosphine ligands. An extensive chemistry is expected and is currently under investigation.



Scheme 1.

Pt(dppm)Cl<sub>2</sub> is a very common compound both as a starting material and as a catalyst. The facile base hydrolysis under mild PTC conditions and the rich chemistry expected for compound **1** deserve attention.

### Acknowledgements

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