

## NEW TRIMETHYLENEDIPHOSPHINE COMPLEXES OF PALLADIUM(II)

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(Received February 7th, 1971)

### SUMMARY

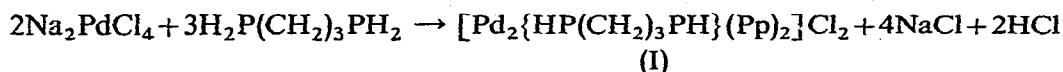
The new complex  $[\text{Pd}_2(\text{HPCH}_2\text{CH}_2\text{CH}_2\text{PH})(\text{H}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PH}_2)_2]\text{Cl}_2$  has been prepared by treatment of  $\text{Na}_2\text{PdCl}_4$  with  $\text{H}_2\text{P}(\text{CH}_2)_3\text{PH}_2$  in ethanol. This product has been treated with sodium perchlorate in ethanol to give the corresponding diperchlorate, which is very explosive.

### INTRODUCTION

In the course of attempts to prepare new complexes of palladium with alkylenediphosphines, we have isolated an explosive binuclear diperchlorate complex with trimethylenediphosphine. We describe below the route to the ligand, and the preparation of the complex.

### RESULTS AND DISCUSSION

Trimethylenediphosphine was obtained from the reaction between sodium dihydrogen phosphide and 1,3-dichloropropane in liquid ammonia and was identified by means of elementary analysis and IR spectrum; the latter exhibits a strong band at  $2280\text{ cm}^{-1}$ , characteristic of P-H stretching vibration<sup>1\*</sup>. Treatment of the diphosphine (ca. 2 moles) with  $\text{Na}_2\text{PdCl}_4$  in ethanol gave the yellow dichloride complex  $\{\text{Pd}_2[\text{HP}(\text{CH}_2)_3\text{PH}](\text{Pp})_2\}\text{Cl}_2$  (I) (Pp = diphosphine), according to the equation:

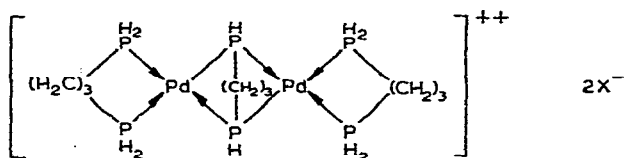


The ionic character of the compound was confirmed by conductivity measurements ( $\Lambda_M = 52\text{ ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  in ethanol solution  $1.03 \times 10^{-3}\text{ M}$  at  $22^\circ$ ).

When the ethanol solution of (I) is treated with  $\text{NaClO}_4$ , a yellow crystalline product  $\{\text{Pd}_2[\text{HP}(\text{CH}_2)_3\text{PH}](\text{Pp})_2\}(\text{ClO}_4)_2$  (II) precipitates, and its IR spectrum exhibits bands at  $1110$  and  $920\text{ cm}^{-1}$  characteristic of ionic perchlorates<sup>4</sup>. When well dried the perchlorate explodes violently on percussion or rubbing. Owing to its explosive character, this complex has not yet been fully characterized.

\* The diphosphine preparation has been previously mentioned only in patents<sup>2</sup>, which do not give much detail. Leffler and Teach mentioned its preparation in an abstract<sup>3</sup>, but gave no details.

Although we do not yet have direct evidence, the following structure can be postulated for the new compounds on the basis of the well known tendency of palladium to form binuclear complexes containing the phosphorous-bridged structure  $\text{Pd}_2\text{P}_2^{5-}$ :



## EXPERIMENTAL

The apparatus utilized in the preparation of the diphosphine is shown in Fig. 1. All the operations were carried out under dry nitrogen with rigorous exclusion of air and moisture.

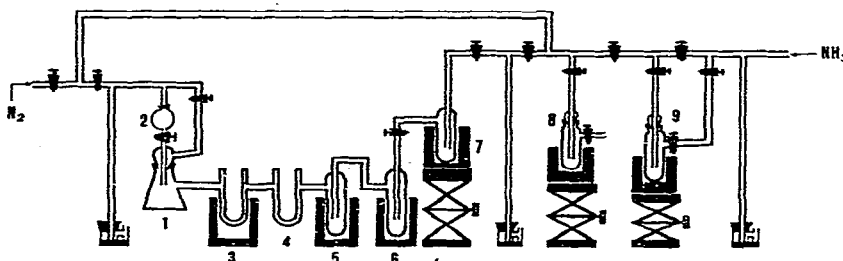


Fig. 1. 1 AIP; 2  $\text{H}_2\text{SO}_4$  (1/10); 3 Ice bath; 4 KOH; 5 and 6 Acetone/ $\text{CO}_2$  trap; 7 Liquid nitrogen; 8 Reaction vessel; 9  $\text{NH}_3$  condensation and anhydriification.

The complexes were prepared and manipulated under nitrogen by standard vacuum-line techniques. Infrared spectra were measured on a Perkin-Elmer 337 spectrometer.

### Trimethylenediphosphine $\text{H}_2\text{P}(\text{CH}_2)_3\text{PH}_2$

A stream of  $\text{PH}_3$  (obtained from 19.8 g of 58.6% AIP (0.2 moles) and dilute (1/10)  $\text{H}_2\text{SO}_4$ ) was bubbled at  $-35^\circ$  slowly with stirring into the blue solution of  $\text{NaNH}_2$  obtained from 4.6 g of sodium metal (0.2 moles) and 150 ml of liquid ammonia until the blue colour disappeared and the solution became yellow. Then 8.9 g (0.1 moles) of 1,3-dichloropropane were added slowly under vigorous stirring, with disappearance of the colour. The ammonia was allowed to evaporate off completely, and the residue was directly distilled under reduced pressure to give 8 g of a fraction boiling at  $50-55^\circ/25$  mm. The crude liquid was fractionated to give 6 g (60%) of pure diphosphine (b.p.  $46-48^\circ/24$  mm) (lit.  $129-131^\circ/725$  mm). (Found: P, 57.9.  $\text{C}_3\text{H}_{10}\text{P}_2$  calcd.: P, 57.5%.)

### $\mu$ -Trimethylenediphosphide-bis(trimethylenediphosphine)dipalladium dichloride (I)

Trimethylenediphosphine (1.1 g; 10.2 mmoles) in ethanol (5 ml) was added to a water/ethanol solution (30 ml) of sodium tetrachloropalladate(II) (1.70 g; 5.8 mmoles),

to give a yellow precipitate which redissolved on shaking. The solution was evaporated to dryness *in vacuo*, and the residue treated with the minimum amount of absolute ethanol. The sodium chloride was filtered off and the filtrate concentrated to a small volume to give a yellow crystalline product (m.p.  $> 360^\circ$ ). (Found: Cl, 11.70; P, 29.90; Pd, 34.6.  $C_9H_{28}Cl_2P_2Pd_2$  calcd.: Cl, 11.70; P, 30.06; Pd, 35.0%.)

### The perchlorate complex (II)

Complex (II) was prepared by dissolving (I) (0.5 g) in absolute ethanol (15 ml) and adding dropwise a saturated ethanolic solution of sodium perchlorate. The yellow crystalline precipitate was collected, washed and then stored under ethanol. (Found: P, 24.8; Pd, 28.5.  $C_9H_{28}Cl_2O_8P_6Pd_2$  calcd.: P, 25.3; Pd, 29.0%.) Owing to the highly explosive character of the product, its melting point and chlorine content could not be determined.

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*J. Organometal. Chem.*, 30 (1971) 431-433

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