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Note

# Synthesis of diphenylphosphine palladium complexes

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#### Abstract

The synthesis of  $Pd(PPh_2H)_2Cl_2$  is achieved by reaction of  $Pd(PhCN)_2Cl_2$  with  $PPh_2H$  in toluene at room temperature.  $Pd(PPh_2H)_2Cl_2$  spontaneously transforms into  $[PdCl(\mu-PPh_2)(PPh_2H)]_2$  when let in solution and affords  $Pd(PPh_2H)_4$  when treated with two equivalents of  $PPh_2H$  in ethanol. © 1999 Elsevier Science S.A. All rights reserved.

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# 1. Introduction

The reaction of palladium salts with diphenylphosphine has been described for the first time by Issleib and Wenschuh [1] who suggested, on the basis of elemental analyses and of molecular weight measurements, complex 1 as the only product.

Further studies conducted by Hayter, showed that, depending on reaction conditions,  $PdCl_2$  or  $Na_2PdCl_4$  react with  $PPh_2H$  to form two different complexes, **2** and **3** [2]. Complex **2** was the same compound described as **1** by Issleib and reformulated as phosphido-bridged (instead that chloro-bridged) by Hayter. Complex **3** was successively recognised as the zerovalent  $Pd(PPh_2H)_4$  species **4** [3].

$$\begin{array}{c} Cl \\ Pd \\ Pd \\ Pd \\ PPh_2 \\ Pd \\ Ph_2 \\ Cl \\ \underline{3} \\ \underline{2} \end{array}$$

$$\begin{array}{c} Pd \\ Pd \\ Pd \\ Ph_2 \\ Cl \\ \underline{3} \\ \underline{3} \\ \underline{3} \\ Pd \\ \underline{3} \\ \underline$$

From both studies stems the conclusion that  $PdCl_2(PPh_2H)_2$  is unstable and not isolable at the purity state. In the paper of Hayter, however, there is a mention to an unstable intermediate complex whose colour and decomposition behaviour indicate as  $PdCl_2(PPh_2H)_2$ . In the course of our studies on secondary phosphine complexes of VIII

group metals we here describe the synthesis, the characterisation and the reactivity of  $PdCl_2(PPh_2H)_2$  (5).

# 2. Experimental

#### 2.1. Materials and apparatus

All manipulations were carried out under a pure dinitrogen atmosphere, using freshly distilled and oxygen-free solvents.

Diphenylphosphine was purchased from Strem. Samples for melting point determinations were sealed in capillary tubes under nitrogen. IR spectra were recorded on a Perkin Elmer 883 spectrometer. The UV–Vis spectra in solution were recorded on a Kontron Uvikon 942 spectrophotometer. Elemental analyses were carried out by using a Carlo Erba Elemental analyser mod. EA 1108. The NMR spectra were recorded on a Varian XL200 or on a Bruker AM400 spectrometer at 297 K, <sup>31</sup>P shifts being measured with respect to external 85% H<sub>3</sub>PO<sub>4</sub>. Simulated NMR spectra were calculated using the WINDAISY program. GC/MS analyses of the reaction solutions were performed using a HP 5890 chromatograph (30 m SE30 column) coupled with a mass selective detector HP 5970B, 70 eV.

#### 2.2. Dichlorobis(diphenylphosphino)palladium(II) (5)

#### 2.2.1. From $PdCl_2(PhCN)_2$

A toluene solution of PPh<sub>2</sub>H (1.94 g, 10.4 mmol in 10 ml) was added dropwise to a toluene solution of PdCl<sub>2</sub>(PhCN)<sub>2</sub> (2.0 g, 5.2 mmol in 30 ml) under stirring. The stirring was

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prolonged for about 2 h at room temperature causing the precipitation of a yellow solid which was filtered, washed with toluene and dried under vacuum. (2.8 g, yield 98%).

The compound is air stable in the solid state but sensitive in solution, soluble in  $CH_2Cl_2$  and slightly soluble in aromatic solvents. *Anal.* calc. for  $C_{24}H_{22}Cl_2P_2Pd$ : C, 52.44; H, 4.03; P, 11.27; Cl, 12.9; Pd, 19.36. Found: C, 52.12; H, 4.10; P, 11.12; Cl, 12.7; Pd, 19.30%. M.p. = 190°C (decompn).

UV–Vis (dichloromethane,  $1.4 \times 10^{-5} \text{ mol } \text{dm}^{-3}$ ):  $\lambda_{\text{max}}$ (nm) = 228 ( $\epsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) = 79 500), 267 (53 000), 333 (13 500). IR (nujol mull):  $\nu_{\text{max}}$  (cm<sup>-1</sup>) = 2345 (m, PH stretching), 1480 (vs), 1458 (vs), 1434 (vs), 1376 (s), 1332 (m), 1101 (vs), 1068 (s), 1026 (s), 996 (vs), 739 (vs), 689 (vs), 502 (vs), 472 (s), 453 (s), 288 (s).  $\delta^{31}$ P{H} in CDCl<sub>3</sub>: 7.41 (s).  $\delta^{-1}$ H in CDCl<sub>3</sub>: 6.13 (d,  $J_{\text{PH}}$ =404 Hz, 2H), 7.05– 7.80 (m, 20H).

## 2.2.2. From $H_2PdCl_4$

 $PdCl_2$  (0.39 g, 2.2 mmol) was dissolved in HCl 37% (7.0 ml) and the resulting dark red solution was diluted with 10 ml of ethanol. To this solution, 8.0 ml of an ethanol solution containing 0.82 g of  $PPh_2H$  (4.4 mmol) was added, causing the precipitation of a yellow solid which was filtered, washed with water and dried under vacuum (obtained 1.1 g, yield 91%).

# 2.3. Trans-dichlorobis(μ-diphenylphosphide) bis(diphenylphosphine)dipalladium(II) (2)

 $PdCl_2(PPh_2H)_2$  (200 mg, 0.36 mmol) was suspended in 8 ml of ethanol under vigorous stirring. After 5 h the solvent was evaporated and the residue was dissolved in 8 ml of fresh ethanol. This operation was repeated three times until the ethanol phase resulted neutral at the litmus paper test. After the last evaporation 5 ml of water was added to the residue affording a pale orange solid, which was filtered, washed with water, and dried under vacuum (obtained 175 mg, yield 95%).

UV–Vis (dichloromethane,  $1.1 \times 10^{-5} \text{ mol dm}^{-3}$ ):  $\lambda_{\text{max}}$ (nm) = 229 ( $\epsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) = 73 500), 327 (26 300), 377 (sh).

IR (nujol mull):  $\nu_{max}$  (cm<sup>-1</sup>) = 2348 (m, PH stretching), 1582 (m), 1571 (m), 1376 (s), 1307 (m), 1184 (m), 1160 (m), 1095 (s), 1069 (m), 1026 (s), 1998 (s), 1907 (s), 848 (vs), 739 (vs), 690 (vs), 503 (vs), 462 (vs), 410 (s), 288 (s).

 $δ^{-31}$ P{H} in CDCl<sub>3</sub>: -2.8 (m, terminal phosphines), -132.7 (m, bridging phosphides);  $J_{AX} = J_{A'X'} = 423.8$  Hz;  $J_{AX'} = J_{A'X} = 26.0$  Hz;  $J_{XX'} = 262.0$  Hz;  $J_{AA'} = -3.0$  Hz.  $δ^{-1}$ H in CDCl<sub>3</sub>: 4.98 (dm,  $J_{PH}$ =356 Hz, 2H), 7.00–7.80 (m, 40H).

## 2.4. Tetrakis(diphenylphosphine)palladium(0) (4)

Diphenylphosphine (298 mg, 1.6 mmol) was added to an ethanol suspension of PdCl<sub>2</sub>(PPh<sub>2</sub>H)<sub>2</sub> (180 mg, 0.33 mmol

in 6 ml) causing the immediate formation of a red-brown solution that slowly lightened. After 1 day, the reaction solution became pale yellow and a grey-orange solid formed which was isolated by filtration, washed with ethanol and dried under vacuum.

UV–Vis (dichloromethane,  $3.9 \times 10^{-5} \text{ mol dm}^{-3}$ ):  $\lambda_{\text{max}}$ (nm) = 230 ( $\epsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) = 47 400), 330 (sh), 390 (8900), 520 (4050).

IR (nujol mull):  $\nu_{max}$  (cm<sup>-1</sup>) = 2267 (m, PH stretching), 1580 (vs), 1568 (s), 1431 (vs), 1376 (s), 1304 (s), 1175 (s), 1155 (s), 1090 (vs), 1065 (s), 1024 (s), 999 (s), 930 (s), 911 (vs), 898 (vs), 852 (m), 823 (vs), 745 (vs), 730 (vs), 694 (vs), 497 (vs), 459 (s), 428 (s), 409 (vs), 305 (m).  $\delta^{31}$ P{H} in CD<sub>2</sub>Cl<sub>2</sub>: -18.1 (s);  $\delta^{1}$ H in CD<sub>2</sub>Cl<sub>2</sub>: 5.65 (d,  $J_{PH}$  = 285 Hz, 4H), 7.0–7.8 (m, 40H).

## 3. Results and discussion

The idea followed to succeed in isolating PdCl<sub>2</sub>(PPh<sub>2</sub>H)<sub>2</sub> was to avoid to carry out the synthesis at temperature higher than room temperature (r.t.) or in protic solvents. Therefore, a toluene solution of PdCl<sub>2</sub>(PhCN)<sub>2</sub> was added to a toluene solution of PPh<sub>2</sub>H at r.t. affording immediately a yellow solid insoluble in aromatic solvents whose elemental analysis and spectroscopic features indicate it as PdCl<sub>2</sub>-(PPh<sub>2</sub>H)<sub>2</sub>. The complex is yellow, soluble in halogenated solvents, indefinitely stable in the solid state but slowly decomposes in solution. Its proton decoupled <sup>31</sup>PNMR spectrum consists of a singlet at 7.5 ppm, whereas the coupled spectrum gives a doublet centred at 7.5 ppm with  $J_{\rm PH}$  of 420 Hz. The resonance of the P–H in the <sup>1</sup>H NMR spectrum falls at 6.13 ppm and shows the expected coupling constant with the phosphorus atom. The electronic spectrum (see Section 2) is consistent with a monomeric square planar structure, common in this kind of complexes.

The immediate precipitation of  $PdCl_2(PPh_2H)_2$  from the reaction medium is observed also when  $PPh_2H$  is added to  $PdCl_2$  solution in ethanol/HCl<sup>1</sup>.

When a CD<sub>2</sub>Cl<sub>2</sub> solution of PdCl<sub>2</sub>(PPh<sub>2</sub>H)<sub>2</sub> was left to stand overnight, the initially clean <sup>31</sup>P NMR spectrum became complicated for the presence of new peaks in the region of coordinated phosphines and of bridging phosphides substantiating the formation of the dimeric species *trans*-[PdCl( $\mu$ -PPh<sub>2</sub>)(PPh<sub>2</sub>H)]<sub>2</sub> (**2**). Spectrum simulation gave the parameters reported in the experimental part. The high field resonance of the bridging diphenylphosphides ( $\delta = -132.7$  ppm) rules out the presence of a Pd–Pd bond [4] whereas the appearance of an AA'XX'

 $<sup>^1</sup>$  Hayter reported in Ref. 2 [PdCl( $\mu\text{-PPh}_2)(\text{PPh}_2\text{H})]_2$  as the only product of the reaction of H\_2PdCl\_4 with two equivalents PPh\_2H after crystallisation from ethanol. Our study demonstrates that the dinuclear complex [PdCl( $\mu\text{-PPh}_2)(\text{PPh}_2\text{H})]_2$  found by Hayter after crystallisation derives from reaction of the initially formed PdCl\_2(PPh\_2H)\_2 when dissolved in ethanol.



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spectrum (instead of an  $ABX_2$  one) substantiates the *trans*geometry. The transformation of **5** into **2** (Eq. (1)) occurs with concomitant evolution of HCl every time the monomeric complex **5** is dissolved in the organic solvents, the rate of the reaction increasing with the polarity of the medium. The synthesis of **2** can thus be achieved in quantitative yield by repeated cycles of dissolution of **5** in ethanol and evaporation under vacuum of the resulting solution containing HCl.

$$2PdCl_2(PPh_2H)_2 \rightarrow (trans-[PdCl(\mu-PPh_2)(PPh_2H)]_2 + 2HCl$$
(1)

The reaction of **5** with excess diphenylphosphine in ethanol gave rise to a slow formation of a grey–orange solid along

with HCl (acidimetric and argentimetric analysis) and diphenylphosphineoxide (GC/MS analysis). The solid was characterised as  $Pd(PPh_2H)_4$  (4) and its formation can be accounted for as the result of a redox process between the palladium and the free phosphine according to Eq. (2):

$$\begin{split} & PdCl_2(PPh_2H)_2 + 3PPh_2H + H_2O \\ & \rightarrow Pd(PPh_2H)_4 + 2HCl + OPPh_2H \end{split} \tag{2}$$

The behaviour of PdCl<sub>2</sub>-diphenylphosphine complexes is summarised in Scheme 1.

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