

## Note

 Photo-assisted formation of a chelating diphos ligand from  $\text{PPh}_3$  and a cyclometallated  $[\text{P}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2]^-$  ligand. Crystal structure of  $\text{Pd}\{\eta^2\text{-}o\text{-}[\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{C}_6\text{H}_4)\}\text{Br}_2$ 

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Dedicated to Professor F.A. Cotton on his 70th birthday

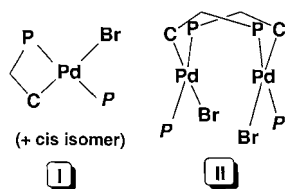
## Abstract

The cyclometallated palladium compound,  $\text{Pd}[\eta^2\text{-}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}[\text{P}(\text{C}_6\text{H}_5)_3]$  (**1**), in the solid state by action of light, evolves to give  $\text{Pd}\{\eta^2\text{-}o\text{-}[\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{C}_6\text{H}_4)\}\text{Br}_2$  (**2**). This compound contains the diphosphine,  $o\text{-}[\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{C}_6\text{H}_4)$ , as chelated ligand that is formed by a couple reaction of the metallated ligand  $\eta^2\text{-}[(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]^-$  and the coordinated arylphosphine. A study by NMR spectroscopy confirms that the *o*-phenylene bridge in the diphosphine ligand in **2** comes from the metallated phosphine ligand in **1**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Cyclometallation; P–C bond breaking

## 1. Introduction

In recent papers [1,2] we have described the synthesis and characterization of new palladium(II) compounds of general formula *cis,trans*- $\text{Pd}[\eta^2\text{-}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}[\text{P}]$  that contain a metallated phosphine ligand  $[(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]^-$ , (PC), forming a four-atom metallocycle (type I in Scheme 1). The stability of these compounds was related to the concept of geometrical



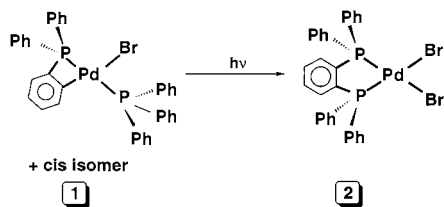
Scheme 1.

rigidity [3] associated with a sterically congested situation due to the bulkiness of the auxiliary ligand *P*, usually a triarylphosphine. An observation supporting this interpretation was that compounds of type I with small-size phosphines as  $\text{PMe}_3$  or  $\text{PMe}_2\text{Ph}$  are not stable and undergo evolution to form dinuclear species of type II,  $\{\text{Pd}[\mu\text{-}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}[\text{P}]\}_2$  (Scheme 1) [2]. In this transformation the metallated ligand rearranges from chelating to bridging coordination mode. The reverse process, from bridging to chelating mode, seems to be very favorable for compounds with bulky phosphines [1,2].

We report in this paper additional results concerning the reactivity of the cyclometallated compound mixture, *cis,trans*- $\text{Pd}[\eta^2\text{-}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}[\text{P}(\text{C}_6\text{H}_5)_3]$  (**1**). These compounds in the solid state slowly form, among other unidentified species, the compound  $\text{Pd}\{\eta^2\text{-}o\text{-}[\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{C}_6\text{H}_4)\}\text{Br}_2$  (**2**). This reaction, which is promoted by light, involves coupling of the metallated ligand PC and the coordinated triphenylphosphine.

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Scheme 2.

## 2. Results and discussion

The cyclometallated compound *cis,trans*-Pd[η<sup>2</sup>-(C<sub>6</sub>H<sub>4</sub>)P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]Br[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>] (**1**) is readily available from the reaction of the tetranuclear compound {Pd[μ<sup>2</sup>-(C<sub>6</sub>H<sub>4</sub>)P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]Br}<sub>4</sub> [**1**] with stoichiometric amounts of triphenylphosphine. In solution, this compound is present as a mixture of *cis* and *trans* isomers in equilibrium. We have observed that **1** in the solid state and exposed to light slowly changed from pale yellow to an orange color. Simultaneously in the <sup>31</sup>P-NMR spectrum two new doublet signals at 42.6 and 53.4 ppm (*J*<sub>P-P</sub> = 27 Hz) and one new singlet at 64.2 ppm appeared with increasing intensity. After long irradiation (ca. 5 days) the evolution was completed and from this reaction mixture, we were able to isolate single crystals of a product of formula Pd{η<sup>2</sup>-*o*-[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)}Br<sub>2</sub> (**2**), confirmed by X-ray methods. Compound **2** was also synthesized by reaction of *o*-[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>) with PdCl<sub>2</sub> and NaCl; the Pd{η<sup>2</sup>-*o*-[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)}Cl<sub>2</sub> (**3**) obtained, easily exchanged the halogen ligand by reaction with Bu<sub>4</sub>NBr in excess to give **2**. The <sup>1</sup>H-NMR spectrum of **2** shows signals centered at 7.42, 7.50, 7.58 and 7.76 ppm of relative intensities 8:4:4:8. From the COSY spectrum we can assign these signals to protons of the compound and we observe that the signal at 7.58 ppm corresponds to four protons of the *o*-phenylene bridge and the other three signals are due to the protons of terminal phenyl rings. Compounds **2** and **3** had been prepared previously from [PdCl<sub>4</sub>]<sup>2-</sup> [4].

We have confirmed that light irradiation is necessary to produce the chemical reaction of the process. The formation of **2** is remarkable because it takes place in the solid state at room temperature and it involves P–C bond cleavage and bond formation as well as extensive ligand rearrangement (Scheme 2). We have performed two independent experiments to conclude that the *o*-[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>) ligand is formed by coupling of the metallated PC group and one 'P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>' group from the triphenylphosphine. The first of these experiments consisted of irradiating the compound Pd[η<sup>2</sup>-(C<sub>6</sub>H<sub>4</sub>)P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]Br[P(C<sub>6</sub>D<sub>5</sub>)<sub>3</sub>] (**1d**) in the same conditions already described for **1**. From the resulting

reaction mixture a new species named as **2d** was isolated. The <sup>31</sup>P{<sup>1</sup>H} spectrum of **2d** showed only one signal at 64.1 ppm. The <sup>1</sup>H-NMR spectrum showed the same four groups of signals at 7.42, 7.50, 7.58 and 7.76 ppm but in this case the relative intensities were 4:2:4:4. The fact that the signal at 7.58 ppm assigned to the four protons in the bridging *o*-phenylene group was still present in **2d** supports that this fragment comes from the metallated phosphine ligand [(C<sub>6</sub>H<sub>4</sub>)P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sup>-</sup> and not from the coordinated triphenylphosphine. Consequently, compound **2d** was formulated as Pd[η<sup>2</sup>-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)P(C<sub>6</sub>D<sub>5</sub>)<sub>2</sub>]Br<sub>2</sub>.

When the compound Pd[η<sup>2</sup>-(C<sub>6</sub>H<sub>4</sub>)P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]Br[P(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>] (**4**) was similarly irradiated, a new compound, **5** was obtained. The <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum showed a typical AB system ( $\delta_A = 64.3$ ,  $\delta_B = 63.9$  ppm, <sup>2</sup>*J*<sub>P-P</sub> = 16 Hz) and the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra confirmed the presence of only one type of CH<sub>3</sub> in the molecule. These data confirm that also in the formation of compound **5**, the whole PC ligand was incorporated to form the bidentate ligand. Consequently compound **5** was formulated as Pd[η<sup>2</sup>-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)P(*p*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>]Br<sub>2</sub>.

The nature of the other product or products resulting from this reaction is not clear to us yet. Additional studies will be performed oriented to investigate this point and also further mechanistic details of this particular reaction.

### 2.1. The crystal structure

The structure of **2** (Fig. 1) was determined by X-ray diffraction, and corresponds to the Pd[η<sup>2</sup>-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-

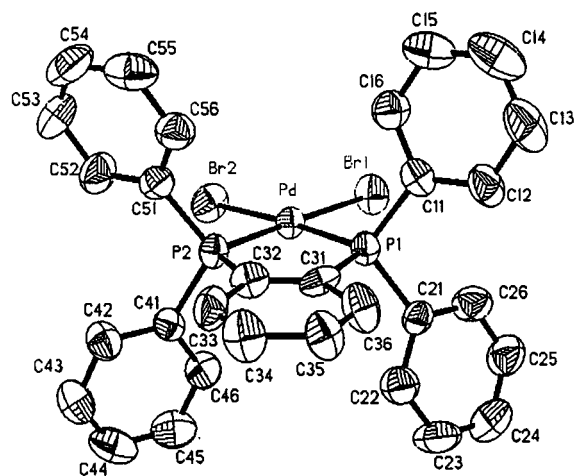


Fig. 1. ORTEP drawing of compound Pd{η<sup>2</sup>-*o*-[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)}Br<sub>2</sub>. Selected distances are Pd–P2 = 2.213(2), Pd–P1 = 2.2366(19), Pd–Br1 = 2.4607(10), Pd–Br2 = 2.4734(10), P1–C21 = 1.804(8), P2–C41 = 1.800(8) Å. Selected angles are P2–Pd–P1 = 87.03(7), P2–Pd–Br1 = 176.62(6), P1–Pd–Br1 = 89.68(6), P2–Pd–Br2 = 88.97(6), P1–Pd–Br2 = 175.57(6), Br1–Pd–Br2 = 94.35(4)°.

$\text{P}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2\text{Br}_2$  compound. The palladium is bonded to two bromines and two phosphorus atoms of the diphosphine,  $(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2$ , in a square planar coordination. The Pd–P distances are 2.237(2) and 2.213(2) Å and the P–Pd–P angle, 87.01(7)° has a value between the observed ones in similar compounds with diphosphines that contain a central *o*-phenylene group with *ortho* substituents, (83.4(3)–87.79(4)°) [5].

### 3. Experimental

All reactions were carried out in an argon atmosphere, using standard Schlenk techniques.  $\text{PdCl}_2$ , NaCl, *o*- $[\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{C}_6\text{H}_4)$ ,  $\text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{P}(\text{C}_6\text{D}_5)_3$  and  $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$  were purchased from commercial sources. Solvents were degassed and used without further purification. *Cis,trans*- $\text{Pd}[\eta^2\text{-}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}[\text{P}(\text{C}_6\text{H}_5)_3]$  (**1**), *cis,trans*- $\text{Pd}[\eta^2\text{-}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}[\text{P}(\text{C}_6\text{D}_5)_3]$  (**1d**) and *cis,trans*- $\text{Pd}[\eta^2\text{-}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}[\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3]$  (**4**) were prepared by the literature procedures [1,2]. Elemental analyses were performed by Servicio de Microanálisis Elemental, Universidad Complutense de Madrid. NMR spectra were recorded on Bruker AC-200 and Varian Unity-400 spectrometers. Chemical shifts ( $\delta$ ) are given in ppm, relative to TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ), or 85%  $\text{H}_3\text{PO}_4$  aqueous solution ( $^{31}\text{P}$ ). Coupling constants (*J*) are given in Hz.

#### 3.1. Preparation of compounds

##### 3.1.1. $\text{Pd}\{\eta^2\text{-}o\text{-}[\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{C}_6\text{H}_4)\}\text{Br}_2$ (**2**)

A suspension of 0.150 g of *cis,trans*- $\text{Pd}[\eta^2\text{-}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}[\text{P}(\text{C}_6\text{H}_5)_3]$  (0.211 mmol) in  $\text{CH}_2\text{Cl}_2$  extended in a Petri plate was irradiated with light from an Osram-200 bulb for 5 days. In a few minutes  $\text{CH}_2\text{Cl}_2$  was evaporated and during the total process the compound evolved from a pale yellow solid to a brown one. The brown solid was dissolved in 2 ml of  $\text{CH}_2\text{Cl}_2$ , and 10 ml of ethyl ether was added. The solution was maintained at  $-20^\circ\text{C}$  for 2 days, crystallizing a light yellow solid that was filtered off and washed with ether (0.044 g, 59% yield). Anal. Calc. for  $\text{C}_{30}\text{H}_{24}\text{Br}_2\text{P}_2\text{Pd}$ : C, 50.56; H, 3.39. Found: C, 49.87; H, 3.71%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.42 ppm (t, *J* = 6 Hz, 8H, H *meta* to P in phenyl rings), 7.50 ppm (m, 4H, H *para* to P in phenyl rings), 7.58 ppm (aromatics, m, 4H, *o*-phenylene bridge) and 7.76 ppm (dd, *J* = 12, *J* = 8 Hz, 8H, H *ortho* to P in phenyl rings).  $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ), 64.2 ppm.

##### 3.1.2. $\text{Pd}\{\eta^2\text{-}o\text{-}[\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{C}_6\text{H}_4)\}\text{Cl}_2$ (**3**)

A 0.020 g (0.113 mmol) sample of  $\text{PdCl}_2$  and 0.014 g (0.240 mmol) of NaCl were suspended in 5 ml of ethanol and stirred at room temperature for 12 h. The

resulting red–brown solution was filtered and 0.051 g (0.114 mmol) of *o*- $[\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{C}_6\text{H}_4)$  were added, precipitating a light yellow solid which was filtered after 30 min of stirring. The solid was recrystallized from a  $\text{CH}_2\text{Cl}_2$ –ethanol solution giving  $\text{Pd}\{\eta^2\text{-}o\text{-}[\text{P}(\text{C}_6\text{H}_5)_2]_2(\text{C}_6\text{H}_4)\}\text{Cl}_2$ , (0.064 g, 91% yield). Anal. Calc. for  $\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{P}_2\text{Pd}$ : C, 57.76; H, 3.88. Found: C, 57.20; H, 3.61%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.46 ppm (m, 8H), 7.54 ppm (m, 4H), 7.65 ppm (m, 4H) and 7.80 ppm (dd, *J* = 11, *J* = 9 Hz, 8H).  $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ), 64.4 ppm.

##### 3.1.3. $\text{Pd}[\eta^2\text{-}o\text{-}(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{D}_5)_2]\text{Br}_2$ (**2d**)

A 0.080 g (0.110 mmol) sample of a mixture of *cis,trans*- $\text{Pd}[\eta^2\text{-}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}[\text{P}(\text{C}_6\text{D}_5)_3]$  (**1d**) was suspended in 3 ml of  $\text{CH}_2\text{Cl}_2$  and the same procedure described for compound **2** was followed. A 0.034 g sample of  $\text{Pd}[\eta^2\text{-}o\text{-}(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{D}_5)_2]\text{Br}_2$  (**2d**) was obtained (85%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.42 ppm (t, *J* = 6 Hz, 4H, H *meta* to P in phenyl rings), 7.50 ppm (m, 2H, H *para* to P in phenyl rings), 7.58 ppm (m, 4H, *o*-phenylene bridge) and 7.76 ppm (dd, *J* = 12, *J* = 8 Hz, 4H, H *ortho* to P in phenyl rings).  $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ), 64.2 ppm (pseudotriplet).

##### 3.1.4. $\text{Pd}[\eta^2\text{-}o\text{-}(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_2]\text{Br}_2$ (**5**)

A 0.095 g (0.126 mmol) sample of a mixture of *cis,trans*- $\text{Pd}[\eta^2\text{-}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}[\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3]$  (**4**) was suspended in 3 ml of  $\text{CH}_2\text{Cl}_2$  and the same procedure described for compound **2** was followed, giving 0.021 g of  $\text{Pd}[\eta^2\text{-}o\text{-}(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_2]\text{Br}_2$  (45%). Anal. Calc. for  $\text{C}_{32}\text{H}_{28}\text{Br}_2\text{P}_2\text{Pd}$ : C, 51.89; H, 3.51. Found: C, 51.50; H, 3.51%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 2.36 ppm ( $\text{CH}_3$ , s, 6H), 6.8–8.0 ppm (aromatics, m, 22H).  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ): 21.6 ppm ( $\text{CH}_3$ , s), 127–136 ppm (aromatics, m), 143 ppm (aromatics, s).  $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ):  $\delta_A = 64.2$ ,  $\delta_B = 63.9$  ppm ( $^2J_{\text{P-P}} = 16$  Hz).

#### 3.2. X-ray structure determination

An Enraf–Nonius CAD4 diffractometer was employed for data collection on compound **2**. The structure was solved by direct methods using the SIR92 program, followed by Fourier synthesis and refined on  $F^2$  for all reflections except for 308 with very negative  $F^2$  or flagged for potential systematic errors (SHELXL-93). All non-H atoms were refined anisotropically. Yellow monocystals were grown in  $\text{CH}_2\text{Cl}_2$ –hexane.  $\text{Pd}[\text{P}_2\text{C}_{30}\text{H}_{24}]\text{Br}_2$ : crystal size:  $0.2 \times 0.25 \times 0.3$  mm<sup>3</sup>, *M* = 712.65, monoclinic, space group  $P2_1/n$  ( $\# 14$ ) with *a* = 9.9307(7), *b* = 15.170(3), *c* = 18.459(2) Å,  $\beta$  = 97.611(7)°, *V* = 2756.3(7) Å<sup>3</sup> and *Z* = 4 (*D*<sub>calc</sub> = 1.717 g cm<sup>-3</sup>; Mo–K $\alpha$  radiation  $\lambda$  = 0.71069 Å), giving *R*(*F*) = 0.058 and *R*<sub>w</sub>(*F*<sup>2</sup>) = 0.159 by using 4821 observed reflections with *I* > 2σ(*I*).

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 133153 for compound **2**.

#### Acknowledgements

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