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Synthesis and X-ray Crystallographic Characterization of (μ-(Diphenylphosphino)phenyl-C^2,P)palladium Bromide. A Novel Tetranuclear Metalated Compound

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Introduction

Transition metal compounds with bridging metalated ligands are often restricted to compounds with metal−metal bonds.[1] There are some examples of binuclear platinum(II) complexes containing bridging *o*-$C_6H_4PPh_2$ or *o*-$C_6H_4P(Ph)CH_2CH_2P(Ph)_2$ ligands in which there is no formal metal−metal bond.[2] Even though a large number of cyclometalated palladium compounds have been reported, palladium compounds with bridging metalated phosphines are rare.[3a,b] A recent publication reports a tetranuclear palladium(II) species with a metalated 2-[*N*-(1-naphthylmethylidene)amino]benzenethiolate ligand (C,N,S). In this compound, the Pd(C,N,S) fragments resulting from metalation of the pendant side arm are bridged by the sulfur atoms.[3c] We describe here the ability of a metalated ligand, $[P(C_6H_4)Ph_2]^-$ (PC), to exhibit chelating and bridging coordination modes in a quite reversible way. We also describe the preparation and characterization of a tetranuclear metalated palladium compound with interesting structural features.

Experimental Section

All reactions were carried out in argon atmosphere, using standard Schlenk techniques. P(*o*-BrC_6H_4)Ph_2 (PCBr) was purchased from commercial sources (Organometallics). Solvents were degassed and used without further purification. $Pd(dba)_2$ [dba = $(C_6H_5)CH{=}CH{-}C(O){-}CH{=}CH(C_6H_5)$] was prepared by the literature procedure.[4] Elemental analyses were performed by ICMA, University of Zaragoza. NMR spectra were recorded in Bruker AC-200 and Varian Unity-400 spectrometers.

Preparation of Compounds. [Pd{$P(C_6H_4)(C_6H_5)_2$}Br]$_4$ (1). To a suspension of 0.300 g of $Pd(dba)_2$ (0.52 mmol) in toluene (3 mL) was added PCBr (0.180 g, 0.52 mmol). The mixture was stirred at room temperature for 45 min, and the resulting dark brown solution was refluxed for 10 min, giving a yellow-green solid and a yellow solution. After the solution was cooled, the solid was separated by filtration and dissolved in a minimum amount of dichloromethane, giving a yellow solution and a black residue, which was discarded. Addition of acetone to the filtered solution resulted in the formation of **1**, a yellow powder, which was washed with acetone and dried in vacuo (0.173 g, 0.097 mmol, 73% yield). Anal. Calcd for $C_{72}H_{56}Br_4P_4Pd_4$: C, 48.30; H, 3.15. Found: C, 48.13; H, 2.04. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.74 ppm.

[Pd{$P(C_6H_4)(C_6H_5)_2$}Br(PCBr)] (2). To a suspension of 0.300 g of $Pd(dba)_2$ (0.52 mmol) in toluene (3 mL) was added PCBr (0.360 g, 1.05 mmol). The mixture was stirred at room temperature for 45 min. During this time, a dark brown solution was formed, which was refluxed for 10 min. The resulting yellow solution was filtered and evaporated to dryness. The residue was extracted twice with 5 mL of acetone, and the extracts were evaporated to dryness. Crystallization of the residue from a dichloromethane−ethyl ether mixture gave pale yellow crystals that were washed with ethyl ether and dried in vacuo, resulting in the formation of 0.219 g of **2** as a cis/trans mixture of isomers (0.28 mmol, 53% yield). Anal. Calcd for $C_{36}H_{28}Br_2P_2Pd$: C, 54.82; H, 3.58. Found: C, 55.56; H 3.56. $^{31}P\{^1H\}$ NMR ($CDCl_3$): cis isomer δ 19.85 (P_a), −81.74 (P_b) ppm ($^2J_{P-P}$ = 12 Hz); trans isomer δ 26.73 (P_a), −88.43 (P_b) ppm ($^2J_{P-P}$ = 460 Hz). Cis/trans ratio = 0.80 from integration of the signals in the ^{31}P NMR spectrum.

Reaction of 2 and Pd(dba)$_2$. To a solution of 0.150 g of **2** (0.20 mmol) in toluene (3 mL) was added $Pd(dba)_2$ (0.109 g, 0.19 mmol). The mixture was stirred at room temperature for 45 min and refluxed for 10 min, giving a yellow solution and a dark solid. Further crystallization of this solid from CH_2Cl_2−acetone gave **1** in the pure form (0.080 g, 0.045 mmol, 48% yield).

Thermal Reaction of 2 in Toluene. A 0.100 g sample of **2** (0.13 mmol) (mixture of cis and trans isomers), dissolved in 5 mL of toluene, was heated at 100 °C for 1 h. The ^{31}P NMR spectrum of the solution confirmed the presence of a substantial amount of free PCBr. The solution was evaporated to dryness, and the residue was crystallized from dichloromethane−acetone mixture, yielding **1** (0.022 g, 0.012 mmol, 37% yield).

Another 0.100 g sample of **2** (0.13 mmol) and 0.015 g of PCBr (0.03 mmol), dissolved in 5 mL of toluene, were treated as described above, yielding **1** (0.008 g, 0.004 mmol, 12% yield).

Synthesis of Compounds Pd{$P(C_6H_4)(C_6H_5)_2$}Br(PR_3). PR_3 = PPh_3. To a suspension of 0.050 g (0.028 mmol) of **1**, in 15 mL of degassed CH_2Cl_2, was added 0.029 g (0.111 mmol) of PPh_3. The mixture changed from yellow to a pale yellow solution after 10 min. The resulting solution was stirred at room temperature for 30 min and evaporated to dryness. Crystallization of the residue from a 1:2 CH_2Cl_2−hexane mixture gave a pale yellow crystalline mixture of *cis*/*trans*-Pd{$P(C_6H_4)(C_6H_5)_2$}Br(PPh_3) isomers **3** (0.067 g, 85% yield). Anal. Calcd for $C_{36}H_{29}BrP_2Pd\cdot{}^1/_4CH_2Cl_2$: C, 59.55; H, 4.07. Found: C, 59.33; H, 3.28. ^1H NMR ($CDCl_3$): δ 6.3 (aromatics, t, J = 8 Hz), 6.8 (aromatics, t, J = 7 Hz), 6.9−7.6 (aromatics, m), 7.7 (aromatics, t, J = 8 Hz) and 8.0 (aromatics, dd, J = 12 Hz, J = 7 Hz), 5.3 ppm (CH_2Cl_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): cis isomer δ 16.0 (P_a), −79.8 (P_b) ppm ($^2J_{P-P}$ = 16 Hz); trans isomer δ 30.9 (P_a), −85.8 (P_b) ppm ($^2J_{P-P}$ = 462 Hz). Cis/trans ratio =0.30.

PR_3 = PCy_3. To a suspension of 0.040 g of **1** (0.022 mmol) in 5 mL of CH_2Cl_2 was added PCy_3 (0.025 g, 0.089 mmol). The mixture was stirred at room temperature for 30 min, and the resulting pale yellow solution was evaporated to dryness. Crystallization of the residue from a CH_2Cl_2−hexane mixture gave a pale yellow compound, *trans*-Pd{$P(C_6H_4)(C_6H_5)_2$}Br(PCy_3) (**4**) (0.051 g, 79% yield). Anal. Calcd for $C_{36}H_{47}BrP_2Pd$: C, 59.39; H, 6.51. Found: C, 59.41; H, 6.87. ^1H NMR ($CDCl_3$): δ 1.30 (cyclohexyl, m, 9H), 1.64 (cyclohexyl, d, J = 12 Hz, 6H), 1.71 (cyclohexyl, d, J = 12 Hz, 3H), 1.80 (cyclohexyl, d, J = 10 Hz, 6H), 2.05 (cyclohexyl, d, J = 10 Hz, 6H), 2.52 (cyclohexyl, d, J = 14 Hz, 3H), 7.20 (aromatics, m, 2H), 7.26 (aromatics, m, 2H), 7.41 (aromatics, m, 6H), 7.92 ppm (aromatics, dd, J = 11 Hz, J = 8 Hz, 4H). $^{13}C\{^1H\}$ NMR: 26.43 (cyclohexyl, s), 27.63 (cyclohexyl, d, J_{C-P} = 10 Hz), 30.25 (cyclohexyl, s), 32.88 (cyclohexyl, d, J_{C-P} = 17 Hz), 125.47 (aromatics, d, J_{C-P} = 8 Hz), 128.69 (aromatics, dd, J_{C-P}= 10 Hz, J_{C-P} = 5 Hz), 129.73 (aromatics,

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Table 1. Crystallographic Data for $[Pd\{P(C_6H_4)(C_6H_5)_2\}Br]_4$

formula: $C_{72}H_{56}Br_4P_4Pd_4$
fw: 1790.38
space group: *Fddd*
cell dimensions (16 °C):
$a = 18.195(2)$ Å
$b = 20.873(3)$ Å
$c = 34.712(7)$ Å
$V = 13183.20$ Å^3
$Z = 8$

$D_{calcd} = 1.804$ g cm^{-3}
$T = 289$ K
diffractometer: CAD4
radiation: Mo Kα (0.717 03 Å)
μ(Mo Kα) = 10.14 cm^{-1}
$R^a = 0.0387$
$R_w^b = 0.0518$

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) in $[Pd\{P(C_6H_4)(C_6H_5)_2\}Br]_4$

Pd−Br	2.505(1)	Pd′−Br	2.567(1)
Pd−P′	2.232(2)	Pd−Cl	2.023(8)
Br−Pd−Br′	85.25(3)	Br−Pd−P′	177.30(7)
Br−Pd−Cl	91.1(2)	Br′−Pd−P′	95.81(6)
Br′−Pd−Cl	171.0(2)	P′−Pd−Cl	87.4(2)

s), 130.35 (aromatics, m), 130.62 (aromatics, d, $J_{C-P} = 6$ Hz), 131.02 (aromatics, d, $J_{C-P} = 6$Hz), 133.11 (aromatics, t, $J_{C-P} = 7$ Hz), 133.76 (aromatics, dd, $J_{C-P} = 12$ Hz, $J_{C-P} = 2$ Hz), 140.04 (aromatics, d, $J_{C-P} = 17$ Hz), 148.12 ppm (aromatics, dd, $J_{C-P} = 47$ Hz, $J_{C-P} = 4$ Hz) . $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.91 (P_a), −87.00 (P_b) ppm, ($^2J_{P-P} = 440$ Hz).

NMR Study of Pd(dba)(PCBr)$_2$ in Solution. Samples of Pd(dba)(PCBr)$_2$ were prepared *in situ* by reacting Pd(dba)$_2$ and PCBr in toluene in a 1:2 molar ratio and stirring the mixture at room temperature for 45 min. ^{31}P NMR spectra were recorded at different temperatures in the range from −55 to +25 °C. High-temperature spectra were recorded in a separate experiment, using a new sample that was heated at 45 °C for 30 min, and after the sample was allowed to equilibrate at room temperature for 10 min, a new spectrum was recorded. The experiment was repeated after heating at 55, 65, and 75 °C.

X-ray Structure Determination. Yellow prisms were grown by vapor diffusion of acetone in a solution of **1** in CH_2Cl_2. A summary of the fundamental crystal data is given in Table 1. Cell constants were obtained from 25 reflections ($4 < 2\theta < 50°$). Space group was obtained from systematic absences and subsequent least-squares refinement. The structure was solved by standard heavy atom techniques with the Molen/Vax package.[5] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated and added to the structure factor calculations but were not refined. Scattering factors and $\Delta f'$ and $\Delta f''$ values were taken from the literature.[6] Selected bond lengths (Å) and angles (deg) are given in Table 2.

Results and Discussion

The reaction of the orthohalogenated phosphine PCBr and Pd(dba)$_2$ (1:1 molar ratio) results in the formation of the tetranuclear palladium compound **1** in high yield (Scheme 1, reaction i). This compound can be described as a palladium(II) species resulting from insertion of the palladium(0) into the C−Br bond of the phosphine.

The structure of **1** (Figure 1), determined by X-ray diffraction, consists of a parallelogram of four palladium atoms, with alternate sides bridged either by two orthometalated phosphines or by two bromides. The metalated phosphines are in a head-to-tail arrangement. Each palladium has a square planar coordination, bound to one carbon, one phosphorus, and two bromines. The distances between nonbonded palladium atoms across the metalated ligands are considerably shorter (Pd···Pd′ 3.09 Å) than those across the Pd_2Br_2 bridge (Pd···Pd″ 3.64 Å). The bromine bridges are not symmetric: Pd−Br 2.505(1) and Pd−Br′ 2.567(1) Å. This trend in Pd−Br distances is consistent with the trans influences of PR_3 and σ-aryl.

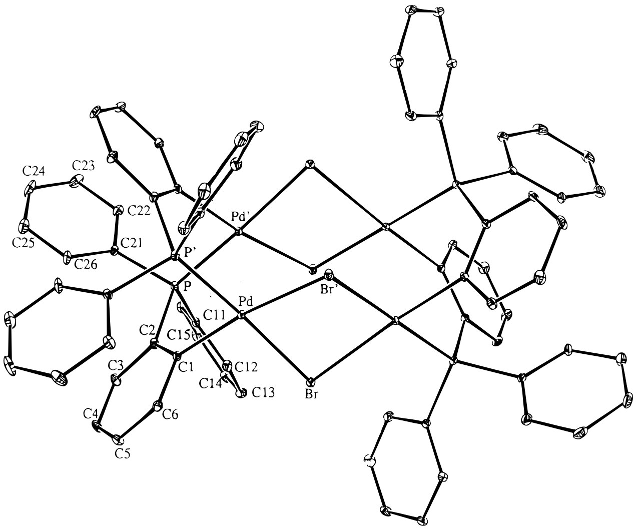
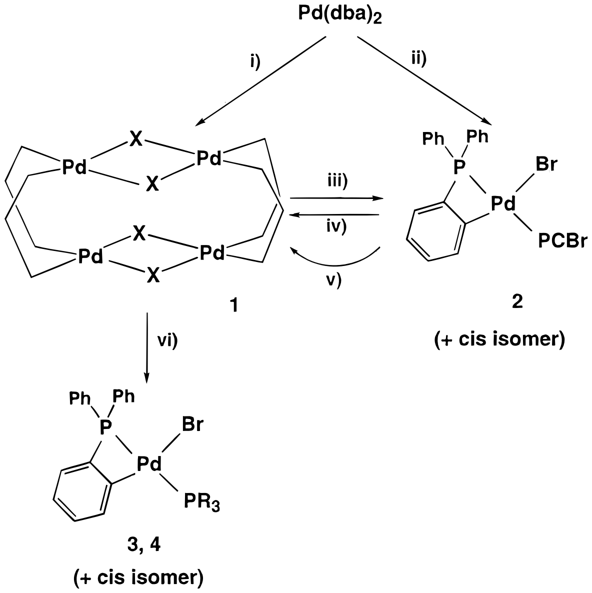


Figure 1. ORTEP view of **1** with the atom labeling scheme. Hydrogens are omitted for clarity.

Scheme 1



Several examples of tetranuclear palladium compounds have been described in the literature.[7] The arrangement of the palladium atoms seems to be very much dependent on the nature of the auxiliary ligands. Particularly in those compounds with palladium in oxidation state II, the metal atoms can have a distorted tetrahedral arrangement,[7a−c] a butterfly shape,[7g] or a square arrangement with different bridging ligands conecting the metal atoms in a pairwise manner.[7i−k] The palladium−palladium distances are significantly longer for the palladium(II) compounds, consistent with the existence of only weak metal−metal interactions. To our knowledge, there is only one species, $Na_2[Pd_4(\mu\text{-}Cl)_4(\mu\text{-pcp})_2(\text{pcpH})_2]$, with a similar structure (Figure 2A). In this compound, the four palladium atoms are bridged by chlorines and PCP (methylenebis(phosphinic acidate)) ligands.[7k] The nonbonded Pd···Pd distances across the bridging pcp and pcpH ligands are considerably longer (3.332 Å) than the analogous distances in **1** across the metalated

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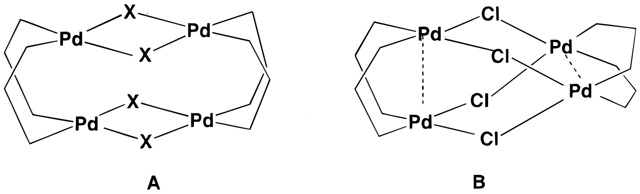
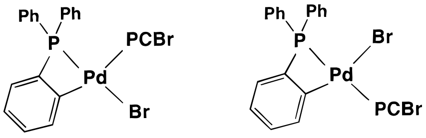


Figure 2. Metal arrangements observed for tetranuclear palladium compounds: (A) planar and (B) tetrahedral.



2-cis **2- trans**

Figure 3. Schematic structure for **2-cis** and **2-trans** isomers.

phosphine ligand (3.09 Å). To our knowledge, **1** is the first example of a palladium compound with bridging metalated phosphines. It is interesting to compare the structure of **1** with that of $[PdCl(ArNNNAr)]_4$ (ArNNNAr = 1,3-di(*p*-tolyl)-triazenide).[7c] In this case, the palladium atoms adopt a distorted tetrahedral arrangement (Figure 2B) rather than a square arrangement. The factors that control these structural details are not clear at this time.

If $Pd(dba)_2$ is reacted with an excess of the orthohalogenated phosphine PCBr (P:Pd molar ratio 2 or higher), **2** is the main reaction product, but **1** is still formed in low yield (<15%) (Scheme 1, reaction ii). The ^{31}P NMR spectrum of **2** shows two blocks of signals of equal intensity and is consistent with the formula $Pd(\eta^2\text{-PC})Br(\eta^1\text{-PCBr})$ for **2**. The high-field signals at *ca.* −80 ppm, characteristic of a four-atoms M−P−C−C metallocycle,[8] are assigned to the metalated phosphine, and the signals at *ca.* 20 ppm are assigned to the η^1-PCBr ligand. The observed $^2J_{P-P}$ coupling constants of 12 and 460 Hz indicate that **2** is present as a mixture of two isomers, **2-cis** and **2-trans** (Figure 3), with a cis/trans ratio of 0.80. It is generally accepted that the arrangement of a phosphine trans to an aryl group is much less favorable than the cis arrangement in palladium(II) compounds.[9] In this context, the observation of the **2-cis** isomer as a result of a thermal reaction is remarkable.

It was noticeable that, even in the presence of an excess of PCBr, **1** was obtained in moderate or low yield. This is due to the equilibrium reaction shown in Scheme 1 involving **1**, **2**, and free PCBr ligand. The occurrence of reaction iv has been confirmed by ^{31}P NMR spectroscopy as **2**, in halogenated solvents, slowly forms **1**, leaving PCBr in solution. At room temperature, this rearrangement is very slow, and it is only noticeable after 7 h, but it is fast in boiling 1,2-dichloroethane (bp 83 °C). This equilibrium can be minimized by adding free PCBr to the solution.

The reverse reaction (reaction iii) can be completed only after long standing of **1** and PCBr in solution at room temperature. No significant cluster cleavage (<10%) is observed after boiling in 1,2-dichloroethane for 2 h. However, **2** readily reacts with 1 equiv of $Pd(dba)_2$ (reaction v), to give **1** as the major reaction product.

These results suggest that substantial Pd−P dissociation occurs in **2** at high temperature. However, we do not have any evidence of a dinuclear species such as $(PC)Pd(\mu^2\text{-Br})_2Pd(PC)$ formed in solution from the "Pd(PC)Br" fragments resulting from Pd−P dissociation in **2**. If such a species is formed in solution, it probably undergoes rearrangement of the metalated ligand from chelating to bridging coordinated mode to generate **1**.

The tetranuclear unit of **1** is readily cleaved by other phosphines of different cone angles allowing the isolation of the mononuclear species Pd(PC)BrP (P = PPh_3 (**3**), PCy_3 (**4**)) in high yield (reaction vi). Based on the ^{31}P NMR spectra, we consider these compounds structurally similar to **2** (see Experimental Section). In the case of PCy_3, only the trans isomer is formed, but some isomerisation to the cis isomer (up to 20%) is observed after 24 h in dichloromethane at room temperature. The ^{13}C NMR spectrum of a freshly prepared sample of **4** gave the 10 expected signals for the metalated phosphine in the chemical shift range of 125−149 ppm. The DEPT spectrum allow us to assign the signal at 131.02 ppm to the carbon bonded to the palladium. For **3**, a cis/trans isomeric ratio close to 0.3 is observed.

The Chemical Reaction. We have monitored the reaction of $Pd(dba)_2$ and PCBr, looking for some intermediates that might give information about the mechanistic aspects of the metalation process. After stirring a mixture of PCBr and $Pd(dba)_2$ (2:1 P:Pd molar ratio) in toluene at room temperature, a dark brown solution is formed. The reaction is completed in about 30−40 min according to the $^{31}P\{^1H\}$NMR data. The resulting solution exhibits two resonances of equal intensity at 29.2 and 24.8 ppm. Similar spectroscopic results have been reported for $Pd(dba)(PPh_3)_2$ isolated from the reaction of $Pd(dba)_2$ and PPh_3.[10] Based on these results, we assume that $Pd(dba)(PCBr)_2$ is formed in solution before the metalation reaction occurs. This is also the only P-containing complex in solution when $Pd(dba)_2$ and PCBr are mixed in a 1:1 or 1:3 molar ratio.

We have obtained some variable temperature $^{31}P\{^1H\}$ NMR spectra of $Pd(dba)(PCBr)_2$ in toluene solution. The two resonances, already broad at room temperature, become broader at higher temperature and collapse to a single resonance at ca. 70 °C. Addition of 1 equimolar amount of free PCBr did not produce any significant modification of the line shape of the spectra. At 75 °C, the metalation reaction is completed in 5 h,

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and signals due to **1**, **2**, and free PCBr are observed in the $^{31}P\{^1H\}$NMR spectrum. No other resonances due to intermediate species were observed.

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Supporting Information Available: Tables giving details of the crystal structure determination, bond distances and angles, and refined and calculated atomic coordinates and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.

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