

Synthesis, Molecular Structure, and Reactivity of the Tetranuclear Complex [NBu₄]₂[Pd₄(μ-PPh₂)₂(μ-Cl)₄(C₆F₅)₄]. Molecular Structure of [Pd₂(μ-PPh₂)(C₆F₅)₂(bipy)₂][ClO₄·C₆H₁₄][‡]

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Anionic tetranuclear complexes with the molecular formula [NBu₄]₂[Pd₄(μ-PPh₂)₂(μ-X)₄(C₆F₅)₄] [X = Cl (**1**), Br (**2**)] were obtained by reaction of [NBu₄]₂[Pd₂(μ-PPh₂)₂(C₆F₅)₄] and PdCl₂ (or K₂[PdCl₄]) in acetone, followed by reaction with KBr for **2**. The reactions of **1** with neutral monodentate (L) or bidentate (L-L) ligands afford the dinuclear derivatives [Pd₂(μ-PPh₂)(μ-Cl)(C₆F₅)₂L₂] [L = PPh₃ (**3**), py (**4**)] or [Pd₂(μ-PPh₂)(C₆F₅)₂(L-L)₂]ⁿ [n = 1–, L-L = acac (**6**); n = 1+, L-L = bipy (**7**) or phen (**8**)]. The structures of complexes **1** and **7** were determined by single-crystal X-ray diffraction studies. The bis(acetone) solvate of complex **1**, [NBu₄]₂[Pd₄(μ-PPh₂)₂(μ-Cl)₄(C₆F₅)₄]·2C₃H₆O, crystallizes in the monoclinic system, space group *P*2₁/*c*, with *a* = 11.679(5) Å, *b* = 16.552(7) Å, *c* = 23.868(8) Å, β = 101.10(3)°, *V* = 4527.6(15) Å³, and *Z* = 2. The central core of the anion has the shape of a rectangle with the four Pd atoms in the corners. The hexane solvate of complex **7**, [Pd₂(μ-PPh₂)(C₆F₅)₂(bipy)₂][ClO₄·C₆H₁₄], crystallizes in the monoclinic system, space group *P*2₁/*n*, with *a* = 16.214(3) Å, *b* = 10.311(2) Å, *c* = 28.380(6) Å, β = 100.82(3)°, *V* = 4660(2) Å³, and *Z* = 4. In both complexes, the long Pd···Pd distances (>3.1 Å) clearly point to the absence of any Pd–Pd interaction.

Introduction

Phosphido (PR₂[–]) groups are excellent bridging ligands able to strongly support metal centers in polynuclear derivatives. Their flexibility allows them to bridge a range of metal–metal distances within the polynuclear framework so that the metal centers may or may not be involved in metal–metal bonds.^{1–4} Phosphido bridging systems are very stable, and the polynuclear complexes that contain these ligands are able to participate in many chemical reactions in which the bridging framework is maintained.⁵

In the course of our current research, we have prepared several polynuclear homo- or heterometallic palladium(II) or platinum(II) pentafluorophenyl complexes containing bridging diphe-

nylphosphido ligands.^{1–3,6} These complexes have been used as precursors in the synthesis of derivatives of higher nuclearity.^{1–3,6} Thus, the complexes [NBu₄]₂[(C₆F₅)₂M(μ-PPh₂)₂M'(C₆F₅)₂] (M, M' = Pd or Pt) react with an aqueous solution of HCl (1:2 molar ratio), yielding the tetranuclear derivatives [NBu₄]₂[(C₆F₅)₂M(μ-PPh₂)₂M'(μ-Cl)₂M'(μ-PPh₂)₂M(C₆F₅)₂].⁶ These tetranuclear derivatives can also be obtained by reacting Li₂[*cis*-M(C₆F₅)₂(PPh₂)₂] with PtCl₂ in THF at 0 °C (1:1 molar ratio).

The structure of these tetranuclear species, established by spectroscopic techniques, seems to be a succession of four square-planar Pd or Pt centers connected through double bridging (μ-PPh₂)₂ or (μ-Cl)₂ groups and terminal pentafluorophenyl ligands. The ³¹P{¹H} NMR spectra indicate that the phosphido ligands are not supporting M–M' bonds, in agreement with the electron counting of the whole anion.⁷

It is known that the reaction of mononuclear halo or organo palladium or platinum(II) complexes with MCl₂ (M = Pd, Pt) affords the corresponding dinuclear complexes with a double halide bridging system “M(μ-Cl)₂M”.⁸

Our interest in the synthesis of polynuclear palladium and platinum complexes^{1–3,6} prompted us to study the reaction of [NBu₄]₂[M₂(μ-PPh₂)₂(C₆F₅)₄] with M'Cl₂ (1:1 or 1:2 molar; M,

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[⊗] Polynuclear Homo- or Heterometallic Palladium(II)–Platinum(II) Pentafluorophenyl Complexes Containing Bridging Diphenylphosphido Ligands. 5.

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M' = Pd, Pt) aiming to prepare other homo- or heteropolynuclear derivatives with bridging PPh₂ and Cl ligands. Such reactions, the results of which are the subject of this paper, allow the preparation of a new type of tetranuclear phosphido palladium complex of stoichiometry [NBu₄]₂[Pd₄(μ -PPh₂)₂(μ -Cl)₄(C₆F₅)₄].

Experimental Section

C, H, and N analyses were performed with a Perkin-Elmer 240B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 4000–200 cm⁻¹). NMR spectra were recorded on a Varian Unity 300 instrument with SiMe₄, CCl₄, and 85% H₃PO₄ as external references for ¹H, ¹⁹F, and ³¹P, respectively. Conductivities (solvent acetone, $c \approx 5 \times 10^{-4}$ M) were measured with a Philips PW 9509 conductometer. Mass spectra were recorded on a VG-Autospec spectrometer operating at 30 kV, using the standard Cs ion FAB gun and 3-nitrobenzyl alcohol (3-NOBA) as matrix. Literature methods were used to prepare the starting complex [NBu₄]₂[(C₆F₅)₂Pd(μ -PPh₂)₂-Pd(C₆F₅)₂].⁶

Safety Note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Preparation of [NBu₄]₂[Pd₂(μ -Cl)₂(μ -PPh₂)₂(C₆F₅)₄] (1). (a) To a solution of [NBu₄]₂[Pd₂(μ -PPh₂)₂(C₆F₅)₄] (0.100 g, 0.057 mmol) in acetone (20 mL) was added PdCl₂ (0.021 g, 0.118 mmol) and the mixture was heated to reflux for 3 h. The suspension was filtered to eliminate a small amount of black solid, and the filtrate was evaporated almost to dryness. The resulting residue was treated with CHCl₃ (4 mL) and partially evaporated. After the sample was cooled to -20 °C, a yellow solid precipitated, which was filtered off, washed with cold CHCl₃ (2 × 1 mL), and air-dried (**1**, 0.040 g, 34% yield).

(b) To a solution of [NBu₄]₂[Pd₂(μ -PPh₂)₂(C₆F₅)₄] (0.500 g, 0.288 mmol) in acetone (50 mL) was added K₂[PdCl₄] (0.188 g, 0.576 mmol) dissolved in H₂O (6 mL), and the mixture was stirred at room temperature for 3 h. The suspension was filtered to eliminate a black solid. The filtrate was evaporated to 6 mL and a solid precipitated, which was filtered off, washed with H₂O (2 × 1 mL) and then EtOH (1 mL), and dried. The solid obtained was recrystallized from acetone/CHCl₃ (**1**, 0.300 g, 50% yield).

IR (cm⁻¹): C₆F₅ X-sensitive⁹ 786; ν (Pd–Cl) 250. $\Lambda_M = 179 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Anal. Found (calcd for C₈₀Cl₄F₂₀H₉₂N₂P₂Pd₄): C, 46.49 (45.95); H, 4.61 (4.43); N, 1.36 (1.34). FAB⁻ MS: m/z 803 (C₂₄-Cl₂F₁₀H₁₀PPd₂). ³¹P{¹H} NMR (deuterioacetone): δ 48.9 (s) ppm.

Preparation of [NBu₄]₂[Pd₄(μ -Br)₄(μ -PPh₂)₂(C₆F₅)₄] (2). To a solution of **1** (0.118 g, 0.056 mmol) in acetone (15 mL) was added KBr (0.500 g, 4.202 mmol). The mixture was stirred at room temperature for 20 h and evaporated to dryness. The residue was extracted with CH₂Cl₂ (20 mL) and the solution evaporated almost to dryness. CHCl₃ (10 mL) was added with stirring, and a yellow solid crystallized, which was filtered off, washed with CHCl₃ (2 × 1 mL), and air-dried (**2**, 0.089 g, 70% yield).

IR (cm⁻¹): C₆F₅ X-sensitive 782. $\Lambda_M = 159 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Anal. Found (calcd for Br₄C₈₀F₂₀H₉₂N₂P₂Pd₄): C, 41.89 (42.35); H, 4.33 (4.09); N, 1.21 (1.23). FAB⁻ MS: m/z 893 (Br₂C₂₄F₁₀H₁₀PPd₂). ³¹P{¹H} NMR (deuterioacetone): δ 49.9 (s) ppm.

Preparation of [Pd₂(μ -PPh₂)(μ -X)(C₆F₅)₂L₂] (a) X = Cl, L = PPh₃ (3). To an acetone solution (10 mL) of **1** (0.036 g, 0.017 mmol) was added PPh₃ (0.018 g, 0.069 mmol), and the mixture was stirred at room temperature for 2.5 h. The solution was concentrated almost to dryness, and ⁱPrOH (10 mL) was added with stirring, causing a yellow solid to precipitate, which was filtered off, washed with ⁱPrOH (2 × 1 mL), and air-dried (**3**, 0.033 g, 75% yield).

IR (cm⁻¹): C₆F₅ X-sensitive 789; ν (Pd–Cl) 275. Anal. Found (calcd for C₆₀ClF₁₀H₄₀P₃Pd₂): C, 55.38 (55.78); H, 3.00 (3.12). FAB⁺ MS: m/z 1292 (C₆₀ClF₁₀H₄₀P₃Pd₂). ³¹P{¹H} NMR (deuteriochloroform): δ -2.0 (PPh₂), 18.2 (PPh₃) ppm; J(PPh₂-PPh₃) = 350.2 Hz.

(b) X = Cl, L = py (**4**). A similar procedure was used for the preparation of complex **4**. The reaction of **1** (0.060 g, 0.029 mmol) and 24 μ L (0.298 mmol) of py gives a very pale yellow solid (**4**, 0.038 g, 71% yield).

IR (cm⁻¹): C₆F₅ X-sensitive 785; ν (Pd–Cl) 279. Anal. Found (calcd for C₃₄ClF₁₀H₂₀N₂PPd₂): C, 43.83 (44.12); H, 2.12 (2.18); N, 3.22 (3.03). FAB⁺ MS: m/z 926 (C₃₄ClF₁₀H₂₀N₂PPd₂). ³¹P{¹H} NMR (deuterioacetone): δ 23.8 (s) ppm.

(c) X = Br, L = PPh₃ (**5**). To a solution of **3** (0.120 g, 0.093 mmol) in 15 mL of acetone was added KBr (0.400 g, 3.361 mmol), and the mixture was stirred for 27 h at room temperature. The mixture was evaporated to dryness and extracted with 20 mL of CH₂Cl₂. The yellow solution was evaporated to ca. 1 mL, and ⁱPrOH (10 mL) was added. The solid obtained was filtered off, washed with ⁱPrOH (2 × 1 mL), and dried at 90 °C for 90 min (**5**, 0.112 g, 90% yield).

IR (cm⁻¹): C₆F₅ X-sensitive 788. Anal. Found (calcd for BrC₆₀-F₁₀H₄₀P₃Pd₂): C, 54.14 (53.92); H, 3.20 (3.02). FAB⁺ MS: m/z 1336 (BrC₆₀F₁₀H₄₀P₃Pd₂). ³¹P{¹H} NMR (deuteriochloroform): δ -3.4 (PPh₂), 19.0 (PPh₃) ppm; J(PPh₂-PPh₃) = 349.9 Hz.

Preparation of [NBu₄]₂[Pd₂(μ -PPh₂)(acac- κ^2 -O,O')(C₆F₅)₂] (6). To a solution of **1** (0.100 g, 0.048 mmol) in acetone (10 mL) was added Ti(acac) (0.072 g, 0.237 mmol). After 2 h of stirring in the dark, the suspension was filtered off and the filtrate concentrated almost to dryness. Treatment of the resulting residue with ⁱPrOH (10 mL) caused the precipitation of a pale yellow solid, which was filtered off, washed with ⁱPrOH (2 × 1 mL), and air-dried (**6**, 0.060 g, 53% yield).

IR (cm⁻¹): C₆F₅ X-sensitive 781; acac ν (C=O) 1587, ν (C=C) 1509, ν (C–H) 768. $\Lambda_M = 81 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Anal. Found (calcd for C₇₀F₁₀H₆₀NO₄PPd₂): C, 51.14 (51.21); H, 5.13 (5.16); N, 1.27 (1.20). FAB⁻ MS: m/z 931 (C₃₄H₂₄O₄PPd₂). ¹H NMR (deuterioacetone), acac: δ 1.7 (s, 3H), 1.8 (s, 3H), 5.2 (s, 1H) ppm. ³¹P{¹H} NMR (deuterioacetone): δ 46.2 (s) ppm.

Preparation of [Pd₂(μ -PPh₂)(C₆F₅)₂(bipy)₂][ClO₄] (7). To a solution of **1** (0.052 g, 0.025 mmol) in acetone (10 mL) was added 2,2'-bipy (0.016 g, 0.102 mmol). After 10 min of stirring at room temperature, the solution was evaporated to ca. 1 mL. Treatment of the solution with ⁱPrOH (5 mL) and NBu₄ClO₄ (0.020 g, 0.058 mmol) and partial evaporation resulted in a yellow solid, which was filtered off, washed with ⁱPrOH (3 × 1 mL), and air-dried (**7**, 0.050 g, 87% yield).

IR (cm⁻¹): C₆F₅ X-sensitive 789. $\Lambda_M = 115 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Anal. Found (calcd for C₄₄ClF₁₀H₂₆N₄O₄PPd₂): C, 45.60 (46.20); H, 2.35 (2.29); N, 4.48 (4.90). FAB⁺ MS: m/z 1045 (C₄₄F₁₀H₁₀N₄PPd₂). ¹H NMR (deuterioacetone), bipy: δ 10.9 (s broad, H_α, 1H), 7.6 (d, H_β, 1H), 8.5 (d, H_δ, 1H), 8.3 (td, H_γ, 1H), 8.2 (td, H_γ, 1H), 7.9 (m, H_α, 1H), 7.6 (m, H_β, 1H), 7.5 (m, H_β, 1H) ppm; J_{αγ} = 1.6, J_{α'γ'} = 1.5, J_{γδ} = J_{βγ} = 8.1, J_{γ'δ'} = J_{β'γ'} = 8.1 Hz. ³¹P{¹H} NMR (deuterioacetone): δ 52.0 (s) ppm.

Preparation of [Pd₂(μ -PPh₂)(C₆F₅)₂(phen)₂][ClO₄] (8). Complex **8** was prepared in a similar way using **1** (0.050 g, 0.024 mmol), 1,10-phen-H₂O (0.019 g, 0.096 mmol), and NBu₄ClO₄ (0.020 g, 0.058 mmol). Yield of **8**: 0.030 g, 48%.

IR (cm⁻¹): C₆F₅ X-sensitive 786. $\Lambda_M = 125 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Anal. Found (calcd for C₄₈ClF₁₀H₂₆N₄O₄PPd₂): C, 48.50 (48.37); H, 2.28 (2.20); N, 4.53 (4.70). FAB⁺ MS: m/z 1093 (C₄₈F₁₀H₂₆N₄PPd₂). ¹H NMR (deuterioacetone), phen: δ 11.4 (s broad, 1H, H_α'), 9.0 (d, 1H, H_γ), 8.6 (d, 1H, H_γ'), 8.3 (m, 2H, H_α + H_β), 8.1 (d, 1H, H_δ), 8.0 (dd, 1H, H_β), 7.6 (dd, 1H, H_β') ppm; J_{αβ} = 5.4, J_{βγ} = 7.5, J_{δδ'} = 8.9, J_{αβ'} = 5.0, J_{β'γ'} = 7.7 Hz. ³¹P{¹H} NMR (deuterioacetone): δ 51.8 (s) ppm.

Preparation of Crystals of 1 and 7 for X-ray Structure Determinations. Suitable crystals of **1** and **7** for diffraction purposes were obtained by slow diffusion of *n*-hexane into a solution of 0.025 g of [NBu₄]₂[Pd₄(μ -PPh₂)₂(μ -Cl)₄(C₆F₅)₄] in acetone (4 mL) and [Pd₂(μ -PPh₂)(C₆F₅)₂(bipy)₂][ClO₄] in 1,2-dichloroethane (3 mL), respectively, at 4 °C.

Crystal Structure Determination of [NBu₄]₂[Pd₄(μ -PPh₂)₂(μ -Cl)₄(C₆F₅)₄] \cdot 2C₂H₆O (1**).** Table 1 lists pertinent crystallographic details. All measurements were made on an Enraf-Nonius CAD4 diffractometer with Mo K α X-radiation at 291 K. Unit cell parameters were

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Table 1. Crystallographic Data and Structure Refinement Details for **1** and **7**

	1·2C ₃ H ₆ O	7·C ₆ H ₁₄
empirical formula	C ₈₆ H ₁₀₄ Cl ₄ F ₂₀ N ₂ O ₂ P ₂ Pd ₄	C ₅₀ H ₄₀ ClF ₁₀ N ₄ O ₄ PPd ₂
mol wt	2207.1	1230.1
space group	P2 ₁ /c	P2 ₁ /n
<i>a</i> , Å	11.679(5)	16.214(3)
<i>b</i> , Å	16.552(7)	10.311(2)
<i>c</i> , Å	23.868(8)	28.380(6)
β, deg	101.10(3)	100.82(3)
<i>V</i> , Å ³	4528(2)	4660(2)
<i>T</i> , K	291	150
<i>Z</i>	2	4
λ, Å	0.710 73	0.710 73
ρ _{calc} , g cm ⁻³	1.62	1.75
μ(Mo Kα), cm ⁻¹	10.23	9.55
<i>R</i> indices	<i>R</i> = 0.038,	<i>R</i> = 0.0398,
(obs data) ^a	<i>R</i> _w = 0.062	<i>wR</i> ₂ = 0.0829
<i>R</i> indices	<i>R</i> = 0.072,	<i>R</i> = 0.0698,
(all data) ^a	<i>R</i> _w = 0.106	<i>wR</i> ₂ = 0.0875

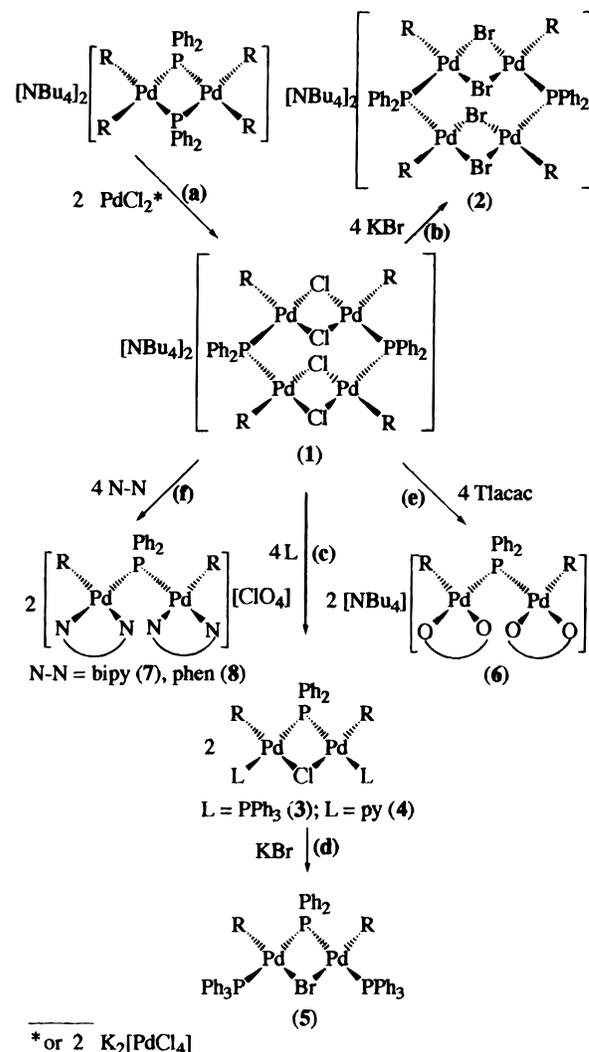
^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

determined by the least-squares refinement of the setting angles of 25 reflections, $11 \leq \theta \leq 13^\circ$. Diffracted intensities were measured in a quadrant of reciprocal space for $4.0 < 2\theta < 50.0^\circ$ ($-13 \leq h \leq 13$, $0 \leq k \leq 19$, $0 \leq l \leq 28$). Of the 8142 intensity data collected, 7936 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences (R_{int} 0.0778); of these, there were 4876 with $I > 3\sigma(I)$.

The structure was solved by direct methods and developed and refined in a series of alternating difference Fourier maps and least-squares analysis. An empirical absorption correction (DIFABS) was applied.¹⁰ All non-hydrogen atoms, except for those of the solvent, were refined with anisotropic thermal factors. The hydrogen atoms, except for those of the solvent, were placed in calculated positions and refined as riding atoms (C–H distance 0.96 Å) with a common thermal parameter. The atoms of the acetone molecule appeared disordered over two sites related by an inversion center and were refined with occupancy 0.5 except for two carbon atoms that were in common positions for the two molecules and were refined with occupancy 1. The computer program package SHELXTL PLUS¹¹ was used for all crystallographic work. In the final stages of refinement, data were weighted such that $w^{-1} = \sigma^2|F_o| + g|F_o|^2$, where $g = 0.000 01$. Final difference electron density maps showed no peaks above $1 \text{ e } \text{Å}^{-3}$ (largest difference peak 0.44; largest difference hole -1.13).

Crystal Structure Determination of [Pd₂(μ-PPh₂)₂(C₆F₅)₂(2,2'-bipy)₂][ClO₄]₂·C₆H₁₄ (7**).** Table 1 gives details of the crystallographic study, which employed an Enraf-Nonius FAST diffractometer. Unit cell parameters were determined by least-squares refinement of the setting angles of 247 reflections and updated every 15° of ω rotation. Almost one complete sphere of reciprocal space in the range $4.2 < 2\theta < 50.2^\circ$ was measured at 150 K ($-17 \leq h \leq 18$, $-8 \leq k \leq 11$, $-27 \leq l \leq 31$). Of the 18 297 intensity data collected, 7104 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences (R_{int} 0.0765); of these, there were 2951 with $I > 2\sigma(I)$.

The structure of complex **7** was solved by direct methods and refined by full-matrix least-squares procedures (SHELXTL¹²). Following isotropic convergence, an empirical absorption (DIFABS¹⁰) was applied to the data set. All atoms were positionally refined, except for H atoms (phenyl and bipy rings), set in idealized positions (C–H = 0.93 Å) with isotropic displacement parameters riding at 1.2U(C). The ClO₄⁻ anion was disordered over two sites (50:50) and was refined subject to a Cl–O distance of 1.50(5) Å. In addition, residual electron density believed to be *n*-hexane was located and modeled by (5 × 1) + (2 × 0.5) carbon atoms (no H atoms included). All non-H atoms except those of the *n*-hexane molecule and one of the half-perchlorate anions

Scheme 1. Representation of the Reactions Leading to Complexes **1–8**

were eventually refined with anisotropic displacement parameters. In the final stages of refinement data were weighted such that $w^{-1} = \sigma^2(F_o^2) + (0.0304P)^2$, where $P = [\max(F_o^2 \text{ or } 0) + 2F_c^2]/3$. Final difference electron density maps showed no peaks above $1 \text{ e } \text{Å}^{-3}$ (largest difference peak 0.79; largest difference hole -0.53).

Results and Discussion

Reaction of [NBu₄]₂[Pd₂(μ-PPh₂)₂(C₆F₅)₄] and PdCl₂. The reaction between [NBu₄]₂[Pd₂(μ-PPh₂)₂(C₆F₅)₄]⁶ and PdCl₂ in acetone (molar ratio 1:1; reflux 3 h or room temperature 50 h) results in the formation of a small amount of a black solid and a yellow solution from which a deep-yellow solid is obtained. The yellow solid is, in fact, a mixture of the starting material [NBu₄]₂[Pd₂(μ-PPh₂)₂(C₆F₅)₄] and the product [NBu₄]₂[Pd₄(μ-PPh₂)₂(μ-Cl)₄(C₆F₅)₄] (**1**), thus indicating that the reaction between the dinuclear [NBu₄]₂[Pd₂(μ-PPh₂)₂(C₆F₅)₄] and PdCl₂ requires a higher proportion of PdCl₂ to reach completion. When the reaction is carried out under similar conditions, but in a 1:2 molar ratio, only **1** is obtained as a deep-yellow solid, although in low yield (34%) (Scheme 1, step a). A small amount of palladium metal is also obtained, even if the reaction is carried out at room temperature, indicating that reaction takes place with partial decomposition.

Elemental analyses, conductivity, and mass spectral data (see Experimental Section) allow us to formulate **1** as [NBu₄]₂[Pd₄(μ-PPh₂)₂(μ-Cl)₄(C₆F₅)₄]. Furthermore, the formation of a tetranuclear anion is in agreement with the fact that the reaction requires a 1:2 molar ratio.

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(11) SHELXTL-PLUS Software Package for the Determination of Crystal Structures, Release 4.0; Siemens Analytical X-ray Instruments, Inc.; Madison, WI, 1990.

(12) SHELXTL PC, version 5.0; Siemens Analytical Instruments Inc.; Madison, WI, 1994.

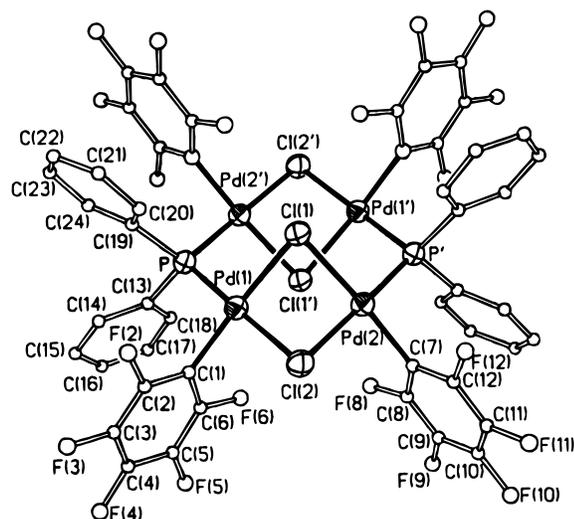


Figure 1. Molecular structure of the anion of **1** showing the full atom-labeling scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for [NBu₄]₂[Pd₄(μ -Cl)₄(μ -PPh₂)₂(C₆F₅)₄]·2C₃H₆O (**1**·2C₃H₆O)

Distances			
Pd(1)–C(1)	1.992(6)	Pd(2)–C(7)	1.997(6)
Pd(1)–Cl(1)	2.417(1)	Pd(2)–Cl(1)	2.424(2)
Pd(1)–Cl(2)	2.431(2)	Pd(2)–Cl(2)	2.441(2)
Pd(1)–P	2.256(2)	Pd(2)–P'	2.258(2)
Angles			
C(1)–Pd(1)–Cl(1)	173.5(2)	C(7)–Pd(2)–Cl(1)	175.3(2)
C(1)–Pd(1)–Cl(2)	89.0(2)	C(7)–Pd(2)–Cl(2)	90.5(2)
C(1)–Pd(1)–P	90.7(2)	C(7)–Pd(2)–P'	90.1(2)
Cl(1)–Pd(1)–Cl(2)	85.3(1)	Cl(1)–Pd(2)–Cl(2)	84.9(1)
Cl(1)–Pd(1)–P	95.2(1)	Cl(1)–Pd(2)–P'	94.5(1)
Cl(2)–Pd(1)–P	175.1(1)	Cl(2)–Pd(2)–P'	176.7(1)
Pd(1)–Cl(1)–Pd(2)	80.1(1)	Pd(1)–Cl(2)–Pd(2)	79.6(1)
Pd(1)–P–Pd(2')	105.6(1)		

Similarly, [NBu₄]₂[Pd₂(μ -PPh₂)₂(C₆F₅)₄] reacts with K₂[PdCl₄] (1:2 molar ratio), rendering a small amount of palladium and **1** in better yield (50%).

Aiming to prepare the analogous heteropolynuclear Pd/Pt derivative, we have carried out the reaction between [NBu₄]₂[Pd₂(μ -PPh₂)₂(C₆F₅)₄] and PtCl₂ under similar conditions. However, in this case a higher quantity of a black solid (metals) and a very small amount of **1**, the homonuclear palladium derivative, are obtained.

On the other hand, the reaction between [NBu₄]₂[(C₆F₅)₂Pt(μ -PPh₂)₂](C₆F₅)₂]⁶ and K₂[PtCl₄] does not yield the analogous tetranuclear platinum derivative but a mixture of compounds, which we have not been able to identify.

Structure Characterization of [NBu₄]₂[Pd₄(μ -PPh₂)₂(μ -Cl)₄(C₆F₅)₄]·2C₃H₆O (1**·2C₃H₆O).** **Crystal Structure.** The structure of the anion of complex **1** together with the atom labeling scheme is shown in Figure 1. Selected bond distances and angles are listed in Table 2. The complex anion in **1** is a tetrametallic unit and can be regarded as formed by two (non-coplanar) dinuclear palladium subunits “(C₆F₅)Pd(μ -Cl)₂Pd(C₆F₅)”, these subunits being held together by two bridging PPh₂ groups. The halves of the molecule are related by an inversion center, and the palladium atoms lie at the corners of a rectangle. The intermetallic distances are long enough [Pd(1)···Pd(2) 3.119(1) Å; Pd(1)···Pd(2') 3.596(1) Å] to preclude the possibility of metal–metal bonding.

The square-planar environment of each palladium atom comprises a pentafluorophenyl group, two mutually *cis* chlorine bridges to one adjacent metal center, and a diphenylphosphido ligand bridging to another palladium atom. The angles around

the metal are very close to 90°, Cl–Pd–Cl being the smallest, *ca.* 85°, as previously reported for complexes with “Pd(μ -Cl)₂Pd” bridging systems.¹³ The Pd–C⁹ and Pd–Cl¹³ distances are similar to those found in other complexes involving Pd–C₆F₅ and Pd–Cl bonds. The Pd–P distances are 2.256(2) and 2.258(2) Å, and the Pd–P–Pd angle is 105.6(1)°, consistent with the lack of a Pd–Pd bond.¹⁴

The “Pd(μ -Cl)₂Pd” bridging system is not planar, as is usually found, but is bent likely because of the existence of the diphosphido bridge. The dihedral angle between the Pd(1) and Pd(2) square-planar environments is 118.2(1)°. The four palladium centers, the phosphorus, and the Cl(2) and Cl(2') atoms lie in an almost perfect plane. The Pd–Cl(1), Pd–Cl(1'), and Pd–C lines and the perpendicular to this plane subtend angles of about 50°. Finally, the C₆F₅ rings are planar and nearly perpendicular to the respective coordination planes of the metal centers to which they are bonded [88.0° Pd(1) and 84.8° Pd(2)]. All the spectroscopic data agree with the solid state structure.

Spectroscopic Data. The IR spectrum of **1** shows only one absorption due to the X-sensitive mode [mainly ν (M–C) character] of the C₆F₅ group⁹ [786 cm⁻¹]. The ¹⁹F NMR spectrum of **1** at room temperature is not informative since it shows only two very broad signals, one in the *o*-F atom region and the other in the *m*-F and *p*-F region. When the spectrum is recorded at –80 °C, five signals of equal intensity (see Table 3) appear, indicating that **1** contains only one type of C₆F₅ ligand and that the halves of the C₆F₅ rings are not equivalent on the NMR time scale. The ³¹P{¹H} NMR spectrum shows only one signal (δ 48.9 ppm), indicating the equivalence of both PPh₂ groups. However, this signal appears at much lower field than the resonances found for systems containing the fragments “M-(μ -PPh₂)₂M” {*e.g.*, for [(C₆F₅)₂M(μ -PPh₂)₂M'(C₆F₅)₂]²⁻: M = M' = Pd (δ –105.6 ppm); M, M' = Pd, Pt (δ –128.2 ppm); M = M' = Pt (δ –146.9 ppm)}⁶ or “M(μ -PPh₂)(μ -Cl)M” {*e.g.*, for [(C₆F₅)₂Pt(μ -PPh₂)₂M(μ -Cl)(μ -PPh₂)Pt(PPh₃)₂]: M = Pd (δ 2.37 ppm); M = Pt (δ 1.39 ppm)}.³ Although in many cases the ³¹P resonances in phosphido complexes permit the inference that the metal centers supported by the bridging phosphido ligand are involved in metal–metal bonding, the value observed in this case is in the borderline region.⁷

Reactivity of [NBu₄]₂[Pd₄(μ -PPh₂)₂(μ -Cl)₄(C₆F₅)₄] (1**).** Substitution of the bridging chlorides in the tetranuclear complex [NBu₄]₂[Pd₄(μ -PPh₂)₂(μ -Cl)₄(C₆F₅)₄] (**1**) can easily be achieved. Thus, complex **1** reacts with an excess of KBr in acetone at room temperature, yielding the corresponding bromo derivative **2** (Scheme 1, step b). There is no evidence for the formation of the anionic [Pd₂(μ -PPh₂)Br₄(C₆F₅)₂]³⁻, which would be the result not only of substitution but also of bridge cleavage, even

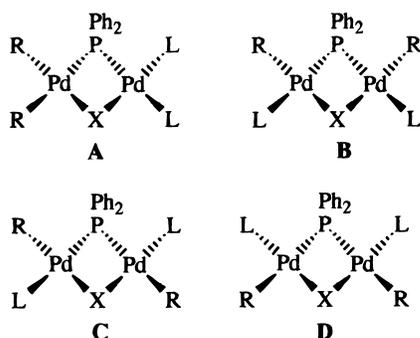
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Table 3. ^{19}F NMR Data [δ (ppm)] for complexes 1–8

complex	T , $^{\circ}\text{C}$	$\delta(\text{F}_{ortho})$	$\delta(\text{F}_{meta})$	$\delta(\text{F}_{para})$
$[\text{NBu}_4]_2[\text{Pd}_4(\mu\text{-Cl})_4(\mu\text{-PPh}_2)_2(\text{C}_6\text{F}_5)_4]$ (1) ^a	–80	–112.9 (1F), –118.8 (1F)	–164.8 (1F), –167.8 (1F)	–165.9 (1F)
$[\text{NBu}_4]_2[\text{Pd}_4(\mu\text{-Br})_4(\mu\text{-PPh}_2)_2(\text{C}_6\text{F}_5)_4]$ (2) ^a	–80	–111.5 (1F), –116.3 (1F)	–163.1 (1F), –166.1 (1F)	–164.4 (1F)
$[\text{Pd}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{C}_6\text{F}_5)_2(\text{PPh}_3)_2]$ (3) ^a	20	–113.9 (2F)	–163.4 (2F)	–163.1 (1F)
$[\text{Pd}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{C}_6\text{F}_5)_2(\text{py})]$ (4) ^a	–80	–114.4 (2F)	–162.6 (2F)	–162.3 (1F)
	20	–110.2 (2F)	–156.0 (2F)	–156.2 (1F)
$[\text{Pd}_2(\mu\text{-Br})(\mu\text{-PPh}_2)(\text{C}_6\text{F}_5)_2(\text{PPh}_3)_2]$ (5) ^b	–80	–115.5 (2F)	–162.0 (2F)	–160.4 (1F)
	20	–115.2 (2F)	–163.7 (2F)	–162.9 (1F)
$[\text{NBu}_4][\text{Pd}_2(\mu\text{-PPh}_2)(\text{acac})_2(\text{C}_6\text{F}_5)_2]$ (6) ^a	–55	–115.4 (2F)	–163.1 (2F)	–162.3 (1F)
	20	–114.4 (2F)	–166.0 (2F)	–165.7 (1F)
$[\text{Pd}_2(\mu\text{-PPh}_2)(\text{C}_6\text{F}_5)_2(\text{bipy})_2][\text{ClO}_4]$ (7) ^a	–80	–114.4 (2F)	–165.1 (2F)	–164.4 (1F)
	55	–117.0 (1F), –119.0 (1F)	–160.4 (1F), –162.8 (1F)	–160.5 (1F)
$[\text{Pd}_2(\mu\text{-PPh}_2)(\text{C}_6\text{F}_5)_2(\text{phen})_2][\text{ClO}_4]$ (8) ^a	20	–117.2 (1F), –119.1 (1F)	–160.3 (1F), –162.7 (1F)	160.4 (1F)
	55	–116.9 (1F), –118.3 (1F)	–160.5 (1F), –162.8 (1F)	–160.5 (1F)
	20	–117.1 (1F), –118.5 (1F)	–160.4 (1F), –162.7 (1F)	–160.4 (1F)
	–80	–117.5 (1F), –117.9 (1F)	–160.3 (1F), –161.8 (1F)	–160.1 (1F)

^a Measured in deuterioacetone. ^b Measured in deuteriochloroform. ^c Broad signals.

**Figure 2.** Possible isomers of complexes of stoichiometry $[\text{Pd}_2\text{Cl}(\text{C}_6\text{F}_5)_2\text{L}_2(\text{PPh}_2)]$.

when a great excess of NBu_4Br is used. The spectroscopic data indicate that **2** has a structure similar to that of **1**.

Treatment of **1** with neutral monodentate ligands such as PPh_3 or py , in a 1:4 molar ratio in acetone, results in the formation of the dinuclear species $[\text{Pd}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{C}_6\text{F}_5)_2\text{L}_2]$ ($\text{L} = \text{PPh}_3$ (**3**), py (**4**)) (Scheme 1, step c) (for elemental analysis and mass spectra, see Experimental Section).

Spectroscopic data indicate that only one of the four possible isomers (A–D) (see Figure 2) has been obtained in both cases.

The IR spectra of **3** and **4** show only one absorption assignable to the X-sensitive mode of the C_6F_5 groups,⁹ and thus structure A can be ruled out.

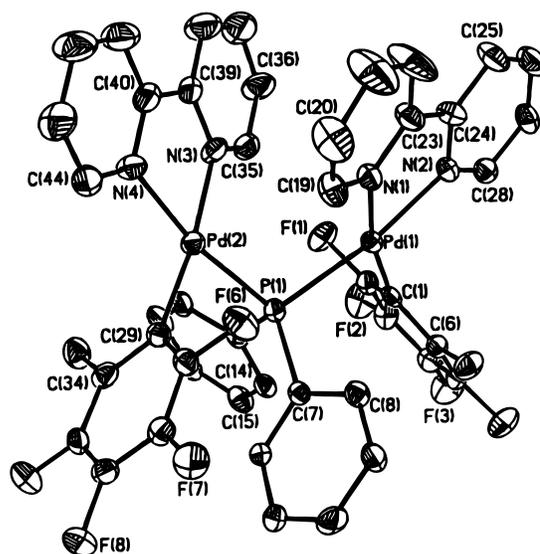
The ^{19}F NMR spectra (at room and low temperature) show three resonances due to *o*-F, *p*-F, and *m*-F atoms in a 2:1:2 ratio, respectively (see Table 3). This pattern (AA'MM'X spin system) indicates that only one type of C_6F_5 group is present in both cases and allows elimination of structure C.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** consists of eight lines corresponding to a typical pattern of an AB_2 spin system. The value of $^2J(\text{PPh}_2\text{-PPh}_3)$ (350.2 Hz) seems to indicate that PPh_2 and PPh_3 are mutually *trans*, *i.e.* that complex **3** displays the structure B. The spectrum of complex **4** shows, as expected, a singlet, although from the spectroscopic data it is not possible to infer whether **4** has structure B or D.

If it is assumed that the “ $\text{Pd}(\mu\text{-PPh}_2)\text{Pd}$ ” bridging system is preserved in the course of the reaction, initial bridge cleavage and bridge formation with concomitant halide elimination have to occur in the formation of the neutral complexes **3** and **4** (Scheme 1, step c).

When complex **3** is reacted with an excess of PPh_3 in acetone, with the intention of cleaving the “ $\text{Pd}(\mu\text{-Cl})(\mu\text{-PPh}_2)\text{Pd}$ ” bridging system, no reaction takes place, indicating the strength of that bridging system.

On the other hand, the reaction of **3** with excess KBr in acetone produces the substituted derivative **5** (Scheme 1, step

**Figure 3.** Molecular structure for the cation of **7** showing the full atom labeling scheme.

d), for which a structure similar to that of **3** can be inferred from spectroscopic data.

Finally, the elimination of all bridging halides can be achieved by using bidentate chelating ligands. Thus, the reactions of **1** with $\text{Ti}(\text{acac})$ or *N*–*N* ligands (*N*–*N* = *bipy* or *phen*), in a 1:4 molar ratio, result in the formation of the corresponding anionic (**6**) or cationic (**7** and **8**) dinuclear complexes (Scheme 1, steps e and f) with only one PPh_2 ligand bridging both metal centers. Elemental analysis, conductivity measurements in solution, and FAB mass spectra are consistent with this formulation (see Experimental Section).

Structure Characterization of Complexes 7–9. Crystal Structure of $[\text{Pd}_2(\mu\text{-PPh}_2)(\text{C}_6\text{F}_5)_2(\text{bipy})_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_{14}$ (7**· C_6H_{14}).** The structure of the cation of **7** is shown in Figure 3, and selected bond distances and angles are given in Table 4. The cation consists of two “ $\text{Pd}(\text{C}_6\text{F}_5)_2(\text{bipy})$ ” moieties which are held together by a bridging PPh_2 ligand. The long $\text{Pd}\cdots\text{Pd}$ distance [3.670(1) Å] and the consequent wide Pd-P-Pd angle [106.11(6) $^{\circ}$] clearly point to the absence of any Pd-Pd interaction.

The Pd atoms are located in nearly square-planar environments with the metal centers displaced 0.114 Å [Pd(1)] and 0.112 Å [Pd(2)] from the best (least-squares) coordination plane. The dihedral angle between these coordination planes is 131.9 $^{\circ}$. The pentafluorophenyl rings are almost perpendicular to the palladium coordination plane, the dihedral angles being 86.9 $^{\circ}$ [Pd(1)] and 83.6 $^{\circ}$ [Pd(2)]. Finally, the chelating *bipy* ligands are not perfectly planar since each pyridine ring is slightly

Table 4. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for [Pd₂(μ -PPh₂)(C₆F₅)₂(2,2'-bipy)] [ClO₄]·C₆H₁₄ (7·C₆H₁₄)

Distances					
Pd(1)–C(1)	2.004(5)	Pd(1)–N(2)	2.108(4)	Pd(1)–N(1)	2.115(4)
Pd(1)–P(1)	2.304(2)	Pd(2)–C(29)	2.019(5)	Pd(2)–N(4)	2.108(4)
Pd(2)–N(3)	2.113(4)	Pd(2)–P(1)	2.289(2)	P(1)–C(7)	1.827(5)
P(1)–C(13)	1.832(5)				
Angles					
C(1)–Pd(1)–N(2)	94.4(2)	C(1)–Pd(1)–N(1)	169.4(2)	N(2)–Pd(1)–N(1)	77.4(2)
C(1)–Pd(1)–P(1)	88.5(2)	N(2)–Pd(1)–P(1)	170.93(12)	N(1)–Pd(1)–P(1)	100.72(13)
C(29)–Pd(2)–N(4)	96.7(2)	C(29)–Pd(2)–N(3)	173.0(2)	N(4)–Pd(2)–N(3)	78.2(2)
C(29)–Pd(2)–P(1)	88.3(2)	N(4)–Pd(2)–P(1)	168.32(13)	N(3)–Pd(2)–P(1)	97.53(13)
C(7)–P(1)–C(13)	104.1(2)	C(7)–P(1)–Pd(2)	114.4(2)	C(13)–P(1)–Pd(2)	108.8(2)
C(7)–P(1)–Pd(1)	108.9(2)	C(13)–P(1)–Pd(1)	114.7(2)	Pd(2)–P(1)–Pd(1)	106.11(6)
C(6)–C(1)–Pd(1)	120.7(4)	C(2)–C(1)–Pd(1)	125.0(4)	C(34)–C(29)–Pd(2)	120.0(4)
C(30)–C(29)–Pd(2)	124.8(4)				

twisted about the C–C bond {C(23)–C(24) [10.0°], C(39)–C(40) [7.1°]}.

The Pd–P distances in **7** are slightly longer than the corresponding ones found in **1**, and the Pd–N distances are in the range of other Pd–N distances.¹⁵

It seems reasonable that complexes **6** and **8** display a structure similar to the one found for **7**.

Spectroscopic Data. The ¹⁹F NMR spectrum of complex **6** (at room and low temperature) shows three signals in a 2:1:2 ratio pointing to only one type of C₆F₅ group, in which both *o*-F (and both *m*-F) atoms are equivalent (see Table 3).

The ¹⁹F NMR spectra of complexes **7** and **8** show five signals of equal intensity (even at 50 °C), indicating that the N–N ligands are more sterically demanding than the acac ligand and that neither are the coordination planes of the palladium atoms symmetry planes (on the NMR time scale) nor are the C₆F₅ groups free to rotate around the Pd–C_{ipso} bonds even at 50 °C.

The ¹H NMR spectrum of **6** shows three signals, in a 1:3:3 ratio, as expected for equivalent acac ligands. Eight signals of equal intensity, due to the bipy or phen ligands, are observed in the ¹H NMR spectra of **7** and **8**. The complete assignments of the chemical shifts and coupling constants (see Experimental Section) have been carried out by ¹H–¹H COSY experiments.

The ³¹P{¹H} NMR spectra of complexes **6–8** show only a singlet, in accordance with the proposed formulation. The positions of the respective resonances (≈50 ppm; see Experimental Section) are similar to that of complex **1**. These types of complexes in which the two metal centers are linked solely *via* one PPh₂ bridging ligand are scarce, since in most previously reported complexes metal–metal bonds and/or other bridging ligands are also present.^{4e,4g,16}

Concluding Remarks

In this paper, we present the synthesis, structural characterization, and reactivity studies of polynuclear pentafluorophenyl Pd complexes containing the ligand diphenylphosphide acting as a bridge. It is well-known that the bridging “M(μ -PPh₂)₂M” systems are very stable and the reactions of complexes containing this bridging system usually involve the other ligands present in the molecule. Nevertheless, complex **1** is formed in a process in which the integrity of the polynuclear “Pd(μ -PPh₂)₂Pd” is not maintained. The mechanism of the formation of **1** cannot be established but implies a severe rearrangement of the ligands

in which the starting material [Pd₂(μ -PPh₂)₂(C₆F₅)₄]²⁻ acts as an arylating agent toward PdCl₂.

As a consequence of this rearrangement process, the increase in the nuclearity of the final product (complex **1**) results not in a linear chainlike structure of Pd square-planar environments linked by PPh₂ and Cl ligands but in a rectangular closed structure. This kind of disposition is not unknown for Pd or Pt complexes, but in most previous cases, the metal centers are involved in metal–metal bonds.¹⁷ The Pd–Pd distances in **1** preclude any kind of intermetallic interaction. A few examples of tetranuclear Pd(II) or Pt(II) derivatives with the metal centers in a tetrahedral array and without metal–metal bonds were also reported recently.¹⁸

The phosphido bridging system in **1** is very stable, since it is not cleaved by the addition of ligands such as Br⁻, PPh₃, py, acac⁻, bipy, or phen. In all cases, the “Pd(μ -PPh₂)Pd” unit remains intact and it is the chloride ligands which undergo substitution or cleavage reactions. For complexes **6–8**, PPh₂ is the only ligand responsible for the link between both Pd centers (no Pd–Pd bond is present), an unusual situation which proves the stability of the “Pd(μ -PPh₂)Pd” system.

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Supporting Information Available: Tables of crystallographic data, full atomic positional and equivalent isotropic displacement parameters, anisotropic displacement parameters, full bond distances and bond angles, and hydrogen coordinates and isotropic displacement parameters for **1** (10 pages). A X-ray crystallographic file, in CIF format, for complex **7** is available on the Internet only. Ordering and access information is given on any current masthead page.

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