

New dinuclear diphenylphosphido-bridged palladium(I) derivatives and the X-ray crystal and molecular structures of the mononuclear homoleptic diphenylphosphine complexes $\text{Pd}(\text{PPh}_2\text{H})_4$ and $[\text{Pd}(\text{PPh}_2\text{H})_4](\text{BF}_4)_2$

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday and in recognition of his fundamental contributions to the advancement of inorganic and organometallic chemistry.

Abstract

By reacting $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$ with PPh_2H we isolated the doubly bridged dinuclear complex $[\text{Pd}_2(\mu\text{-PPh}_2)_2(\text{PPh}_2\text{H})_3]$ (**1**). This reacts with HBF_4 yielding the mono-phosphido-bridged cationic derivative $[\text{Pd}_2(\mu\text{-PPh}_2)(\text{PPh}_2\text{H})_4]\text{BF}_4$ (**2**), arising from the protonation of one of the bridging phosphides. Contrary to our previous data on the parent *t*-butyl systems, a mononuclear homoleptic phosphine complex is not an intermediate in the formation of **1**. $\text{Pd}(\text{PPh}_2\text{H})_4$ (**3**), was in fact prepared by an independent route and was shown to decompose thermally to another (uncharacterized) polynuclear derivative; fluoboric acid reacts with **3** yielding its palladium(II) analogue $[\text{Pd}(\text{PPh}_2\text{H})_4](\text{BF}_4)_2$ (**3**)(BF_4)₂, with dihydrogen evolution. We also report the crystal and molecular structures of **3** and (**3**)(BF_4)₂, the first homoleptic transition metal complexes of diphenylphosphine to be structurally characterized. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Dinuclear; Homoleptic; Palladium; Phosphido-bridged; Secondary phosphine

1. Introduction

Doubly bridged hetero- [1] and homobimetallic [2] phosphides $[\text{L}_n\text{M}(\mu\text{-PR}_2)_2\text{M}'\text{L}'_m]$ of several transition metals have been described. Restricting the field to homonuclear systems, the relatively few examples containing early transition metals are mainly bis- [2a,c] or monocyclopentadienyls [2d] of Group 4, but niobium [2e], vanadium [2f] or lanthanide (Sm [2g]) derivatives are also known. Moving toward the central triads (Groups 6–8), molybdenum [3a,c] and iron [3d,h] complexes have been more extensively investigated, but others containing Cr [3i], W [3a], Mn [3i–n], Ru [3o–q] and Os [3r] have been reported.

Late transition metal complexes [4,5] are by far the most numerous. With $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$ [4], these are mainly $[\text{CpM}(\mu\text{-PR}_2)_2]$ and derivatives, studied by Werner and coworkers [4a–d], and $[\text{L}_2\text{M}(\mu\text{-PR}_2)_2]$ ($\text{L} = \text{CO}, \text{PR}_3$) and derivatives, developed by Jones and coworkers [4e–h].

Most derivatives [5] of Group 10 metals have the general formula $[\text{LM}(\mu\text{-PR}_2)_2]$ ($\text{L} =$ mainly phosphines, [5a–c]) with two $\text{M}(\text{I})$ centers, or $[(\text{R}_3\text{P})(\text{X})\text{M}(\mu\text{-PR}_2)]_2^{n+}$ ($n = 0, \text{X} = \text{Cl}, \text{Br}; n = 2, \text{X} = \text{PR}_3$, [5d–g]) with two $\text{M}(\text{II})$ centers.

The structural features of these systems have been thoroughly investigated, and the $\text{M}_2(\mu\text{-P})_2$ core has shown a remarkable flexibility. The $\text{M}-\text{P}_\mu-\text{M}$ and $\text{P}_\mu-\text{M}-\text{P}_\mu$ bond angles vary through a wide range (60–125°), thus allowing variable $\text{M}-\text{M}$ bond distances (2.375–4.3 Å) and orders (0–3) [2–5]. The central core

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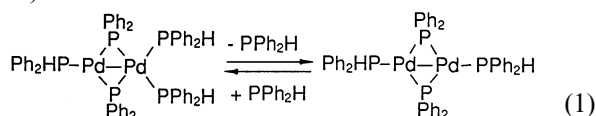
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was most frequently found to be planar or nearly planar, with rare exceptions of folded structures with dihedral (flap) angles in the range 105–135°; this folding is often due to the presence of a third bridging (or semi-bridging) ligand [1c,2c,g,3b,h,4d].

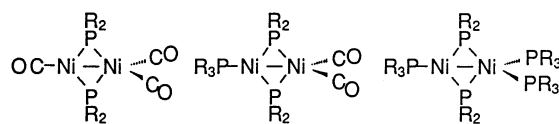
Our group is involved in the search for synthetic methods for new doubly bridged phosphido derivatives of palladium [6] and platinum [7] and in the study of their reactivity. This report deals with the synthesis of $[\text{Pd}_2(\mu\text{-PPh}_2)_2(\text{PPh}_2\text{H})_3]$ (**1**), which has been protonated to give the mono-phosphido bridged cationic derivative $[\text{Pd}_2(\mu\text{-PPh}_2)(\text{PPh}_2\text{H})_4]\text{BF}_4$ (**2**) BF_4 . Attempting to clarify the mechanism of formation of **1** we prepared and characterized the mononuclear binary Pd(0) and Pd(II) derivatives, $\text{Pd}(\text{PPh}_2\text{H})_4$ (**3**) and $[\text{Pd}(\text{PPh}_2\text{H})_4](\text{BF}_4)_2$ (**3**)(BF_4)₂, whose crystal and molecular structures are also reported.

2. Results and discussion

By adding at -45°C an acetone solution of $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$ to a 10-fold molar excess of PPh_2H dissolved in the same solvent, a red powder precipitated out in a few minutes. After work-up the solid was collected and characterized by IR, showing two ν_{PH} absorptions at 2342 and 2368 cm^{-1} due to non-equivalent PPh_2H molecules, and NMR spectroscopies. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum (CDCl_3 , 293 K) exhibits only two broad singlets at 164 and -8.2 ppm , the latter splitting into two broad singlets (-5.8 and -9.9 ppm) at 233 K. Although the lack of information due to rapid exchange, also in the low temperature spectra, precludes an unequivocal assignment, we tentatively assigned the structure $[\text{Pd}_2(\mu\text{-PPh}_2)_2(\text{PPh}_2\text{H})_3]$ (**1**), to the new complex, assuming its rapid equilibration with $[\text{Pd}_2(\mu\text{-PPh}_2)_2(\text{PPh}_2\text{H})_2]$, by loss of a PPh_2H molecule (Eq. 1).



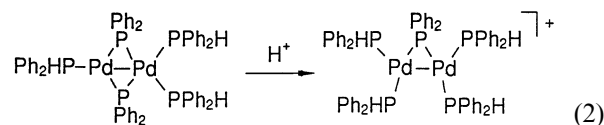
Elemental analyses confirm structure **1**, which has been observed in Ni(I) [5a,8] derivatives (Chart A), but is unprecedented for palladium(I).



(Chart A)

A further support to structure **1** comes from the result of its reaction with acids. In fact, a red chloroform solution of complex **1** reacts with an excess of $\text{HBF}_4\text{Et}_2\text{O}$; the solution turns immediately deep violet, then slowly red, orange and, finally, yellow.

The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of a sample of the solution shows the complete disappearance of **1** and the formation of a new complex with minor amounts of another two. The main component was isolated in 60% yield and identified as $[\text{Pd}_2(\mu\text{-PPh}_2)(\text{PPh}_2\text{H})_4]\text{BF}_4$ (**2**) BF_4 , which can be presumed to form by protonation of one of the bridging phosphides (Eq. 2).



The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of (**2**) BF_4 (CD_2Cl_2 , 293 K) exhibits a low field (222.4 ppm) and two high field (-2.07 and -12.3 ppm) resonances, respectively assigned to the bridging phosphide (X), and to the magnetically non-equivalent couples of phosphines pseudo-*cis* (AA') and pseudo-*trans* (MM') to the first nucleus (spin system AA'MM'X). The spectrum was satisfactorily simulated by the following set of parameters: $\delta_X = 222.38$, $\delta_{AA'} = -2.08$, $\delta_{MM'} = -12.3\text{ ppm}$; $^2J_{MX} = 270$, $^2J_{AX} = 6$, $^3J_{MM'} = 18$, $^2J_{AM} = 46$, $^3J_{AM'} = 2$, $^3J_{AA'} = 53\text{ Hz}$ (see Fig. 1).

2.1. Preparation of $\text{Pd}(\text{PPh}_2\text{H})_4$ (**3**)

As shown in our preceding reports, $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$ reacts with either $\text{P}^t\text{Bu}_2\text{H}$ [9] or PCy_2H [10] yielding the corresponding dinuclear derivative $[\text{Pd}(\mu\text{-PR}_2)(\text{PR}_2\text{H})_2]$. It was also established that the mechanism of these transformations is strongly dependent upon the secondary phosphine. With suitable modifications of the reaction procedures the different key intermediates, i.e. the mononuclear Pd(0) homoleptic $\text{Pd}(\text{P}^t\text{Bu}_2\text{H})_3$ in the first case [9b], or the dinuclear $\text{Pd}_2(\mu\text{-PCy}_2)(\mu, \eta^3\text{-C}_3\text{H}_5)(\text{PCy}_2\text{H})_2$ in the latter [10], were isolated and characterized (Scheme 1).

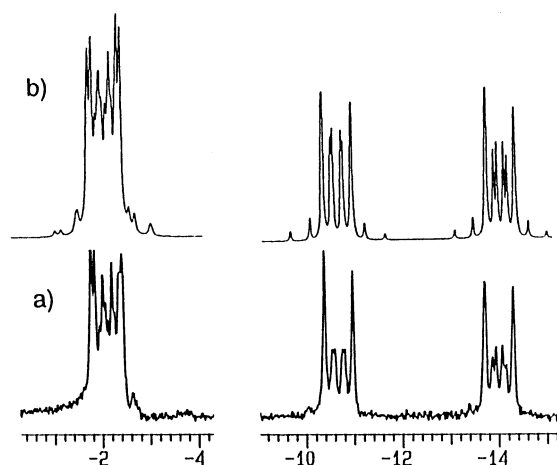
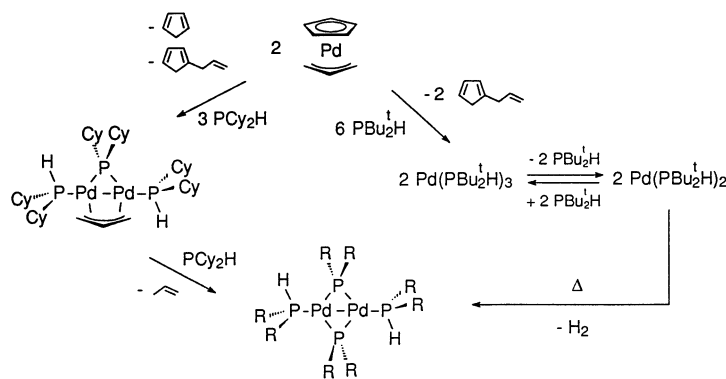


Fig. 1. High field region of the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum (CD_2Cl_2 , 293 K) of (**2**) BF_4 : (a) experimental; (b) calculated.



Scheme 1.

The different type of mechanism can be attributed to differences in the reactivity of the $\text{Pd}(\text{PR}_2\text{H})_n$ homoleptic derivative which, when $\text{R} = \text{Cy}$, should react with $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$ as soon as it is formed, yielding the allyl-bridged intermediate shown in Scheme 1.

We could not isolate or even observe any intermediate preceding the formation of **1** from $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$ and PPh_2H , and decided to attempt an alternative route to a potential candidate, i.e. a mononuclear $\text{Pd}(0)$ derivative $\text{Pd}(\text{PPh}_2\text{H})_n$. A successful synthetic procedure was found by reacting the known [9b] $\text{Pd}(\text{P}^t\text{Bu}_2\text{H})_3$ with a 10-fold excess of PPh_2H in toluene at -20°C . After work-up the tetrakis-substituted $\text{Pd}(\text{PPh}_2\text{H})_4$ (**3**), was isolated in 86% yield [11]. Complex **3** was isolated as a yellow crystalline solid which shows a single ν_{PH} absorption at 2268 cm^{-1} in the IR spectrum and a singlet at -9.8 ppm in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum (-80°C). It is thermally stable as a solid and can be stored at room temperature for weeks without decomposition, but its solutions are stable only in the presence of an excess of the phosphine. Crystals suitable for the diffractometric determination (see Section 2.2) could be obtained only by recrystallization from toluene/ Et_2O mixtures in the presence of a 10-fold excess of PPh_2H . In the absence of added phosphine the yellow solutions of **3** become rapidly red at room temperature while new $^{31}\text{P}\{^1\text{H}\}$ -NMR resonances grow at 227 and 237 ppm. These can be assigned to bridging phosphides of di- or polynuclear systems different from **1** ($\delta_{\text{P}} = 164\text{ ppm}$), which were not further characterized, thus ruling out the intermediacy of a binary PPh_2H complex of $\text{Pd}(0)$ from the possible mechanisms of formation of **1** from $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$.

Complex **3** reacts with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ with dihydrogen evolution yielding, as the main product, the corresponding palladium(II) derivative $[\text{Pd}(\text{PPh}_2\text{H})_4](\text{BF}_4)_2$ (**3**)(BF_4)₂, which was isolated in 55% yield. Single crystals of this complex were obtained by recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixtures and were analyzed by X-ray diffractometry (see Section 2.2). The IR spectrum (Nujol, KBr) of (**3**)(BF_4)₂ shows ν_{PH} and ν_{BF} absorp-

tions at 2365 and 1030 cm^{-1} , respectively. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum exhibits a singlet at 3.5 ppm which splits, in the corresponding proton coupled spectrum, into a six-line signal typically found in derivatives containing the *trans*-(PR_2H)₂M subunit [9b,12].

2.2. Crystal structures

Although the chemistry of palladium phosphine complexes has been extensively investigated, the number of crystallographic studies concerning homoleptic derivatives is rather limited. In the case of palladium(0) tetrasubstituted derivatives of monodentate tertiary phosphines, up to now only $\text{Pd}(\text{PPh}_3)_4$ [13], $\text{Pd}[\text{P}(\text{C}\equiv\text{C}-\text{Ph})_3]_4$ [14], $\text{Pd}[\text{P}(\text{CH}_2\text{OH})_3]_4$ [15] and $[\text{Pd}(\text{P}_4)](\text{Cl})_4$ [16] have been described.

The number is somewhat increased by including some derivatives of chelating diphosphines: $\text{Pd}(\text{dippe})_2$ [17], $\text{Pd}(\text{dppp})_2$ [18], $\text{Pd}(\text{dcpe})(\text{dppe})$ [19], $\text{Pd}(\text{PP})_2$ [20]. Structures of palladium(II) PdL_4 complexes are limited to those with polydentate or macrocyclic phosphines: $[\text{Pd}(\text{PP})_2]^{2+}$ [21–24] and $[\text{Pd}(\text{P}_4)]^{2+}$ [25–27].

Therefore complexes **3** and **3**²⁺ constitute the first structurally characterized homologue pair of $\text{Pd}(0)$ and Pd(II)ML_4 derivatives. The unit cell of **3** contains four molecules, each with a metal placed on the $\bar{4}$ axis. The operation $\bar{4}$ on the asymmetric unit $[\text{Pd}(\text{PPh}_2\text{H})]$ makes the coordination around the metal almost ideally tetrahedral ($\text{P}-\text{Pd}-\text{P} = 108.705(15)$ and $111.02(3)^\circ$).

The whole molecule may be inscribed in a cube of approximately $9\text{ \AA}$ edge length, with the P–H bonds pointing alternatively in opposite directions, as imposed by the site symmetry. The structures of **3** and of cation **3**²⁺ are shown, respectively in Figs. 2 and 3, and significant bond distances and angles are given in the captions. The square coordination ($\text{P}-\text{Pd}-\text{P} = 89.912(7)^\circ$) around palladium in **3**²⁺ is not strictly planar, since the metal is slightly out of the phosphorus atoms plane ($0.092\text{ \AA}$). The 4-fold axis constrains all the P–H hydrogens to point towards the same direction. The less disordered anion is placed just on this side, 3.7

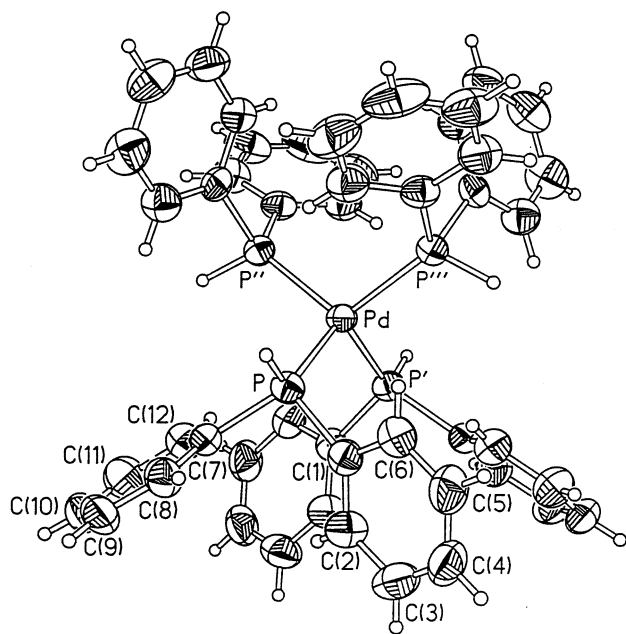


Fig. 2. ORTEP view of complex **3** (thermal ellipsoids are at 50% probability, hydrogens are omitted for clarity). Pd–P 2.3213(6), P–C 1.833(2) Å; P–Pd–P' 111.02(3), P–Pd–P'' 108.705(15)°. Symmetry transformations used to generate equivalent atoms: ' = $-x+1, -y+3/2, z$; '' = $y-1/4, -x+5/4, -z+1/4$; ''' = $-y+5/4, x+1/4, -z+1/4$.

Å above. The second one is placed on the other side, 5.7 Å below. Ligand crowding in the square plane makes the Pd–P bonds slightly longer (0.02 Å) than in **3**, in spite of the metal radius reduction due to oxidation. The bulkiness of the cation and its 4-fold symmetry constrains the crystal packing and produces a tetragonal structure although its symmetry operators

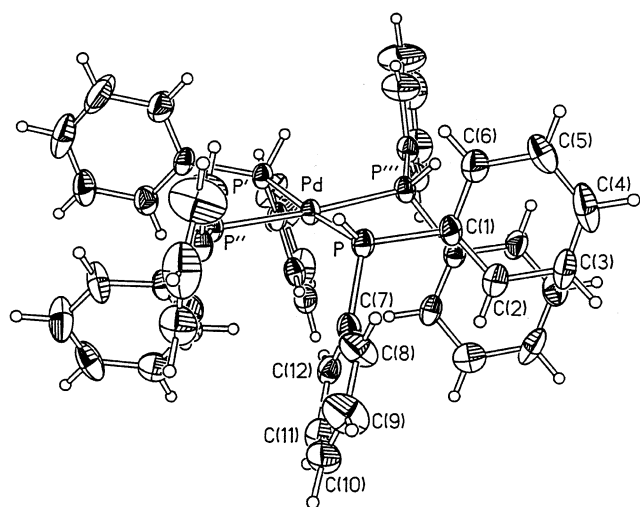


Fig. 3. ORTEP view of cation 3^{2+} (thermal ellipsoids are at 30% probability, hydrogens are omitted for clarity). Pd–P 2.340(3), P–C 1.813(12) Å; P–Pd–P' 175.5(2), P–Pd–P'' 89.91(1)°. Symmetry transformations used to generate equivalent atoms: ' = $-x+1/2, -y+1/2, z$; '' = $-y+1/2, x, z$; ''' = $y, -x+1/2, z$.

are inconsistent with the point symmetry of the small tetrafluoroborate anion.

Bond distances and angles of both structures compare well with the corresponding ones for the structures cited above. As far as we know only two structures of complexes containing a Pd–PPh₂H bond [Pd(μ-PPh₂)Cl(PPh₂H)]₂, and PdCl(PPh₂H){[PPh₂(O)]₂H} [28] have been reported.

3. Conclusions

This paper reports the preparation of a new palladium derivative which was suggested to be the doubly bridged phosphide [Pd₂(μ-PPh₂)₂(PPh₂H)₃] (**1**). As shown in our previous works [29], the presence of two phosphido ligands, although reinforcing the dinuclear structure in Group 10 metal complexes, have some drawbacks if one is interested in the reactivity of the system. Particularly if one searches for the cooperation of the two metals in binding and activation, which can be precluded by steric crowding and/or metal orbital occupancy due to the presence of the bridging phosphides. We have also shown that protonation, either if it goes at phosphorus [6] or at one of the metals [29b], eventually removes one of the bridging ligands and affords mono-phosphido-bridged cationic derivatives which can exhibit metal cooperation in ligand bonding.

Since the previous synthetic procedures yielded derivatives with the central [M₂(μ-PR₂)]⁺ core (M = Pd, Pt) with *t*-butyl or cyclohexyl substituents at phosphorus, the protonation of **1**, shown here to produce [Pd₂(μ-PPh₂)(PPh₂H)₄](BF₄)₂ (**2**)(BF₄), will offer the possibility to investigate about steric and electronic effects on the bonding capabilities of the Pd₂ core. Finally, the achievement of Pd(PPh₂H)₄ (**3**), and [Pd(PPh₂H)₄](BF₄)₂ (**3**)(BF₄)₂, the first structurally characterized homologue pair of Pd(0) and Pd(II) binary phosphine complexes, allowed us to compare their solid state features. As reported above, the crystallographic study has shown that ligand crowding in the cation 3^{2+} makes the Pd–P bonds longer than in **3**, in spite of the metal radius reduction due to oxidation.

4. Experimental

All manipulations were performed under an atmosphere of purified nitrogen or carbon monoxide by using standard Schlenk techniques. Solvents were dried by standard procedures and freshly distilled under nitrogen. Deuterated solvents were used as purchased and stored on molecular sieves under an inert atmosphere. CpPd(η³-C₃H₅) [30], PPh₂H [31] and Pd(P^{*i*}Bu₂H)₃ [9b] were prepared as previously described. IR spectra were registered with a Perkin–

Elmer FT-IR 1725X spectrophotometer and NMR spectra with a Varian Gemini 200BB spectrometer.

4.1. Preparation of $[Pd_2(\mu-PPh_2)_2(PPh_2H)_3]$ (**1**)

A red acetone (10 ml) solution of $CpPd(\eta^3-C_3H_5)$ (300 mg, 1.4 mmol) was slowly dropped at $-45^\circ C$ into an acetone (10 ml) solution of PPh_2H (2.5 ml, 14.1 mmol). A red solid precipitated out in a few minutes; the suspension was stirred for 30 min while the flask was warmed at room temperature. The solid **1** was filtered, washed with acetone, and vacuum dried (567 mg, 70% yield). Anal. Found: C, 64.0, H, 4.73. $C_{60}H_{53}P_5Pd_2$ requires: C, 63.1, H, 4.68. IR (Nujol, KBr): 2342, 2268 (ν_{PH}) cm^{-1} .

4.2. Preparation of $[Pd_2(\mu-PPh_2)(PPh_2H)_4]BF_4$ (**2**) BF_4

Two equivalents of HBf_4Et_2O were added to a red THF (10 ml) solution of **1** (180 mg, 0.158 mmol). The color of the solution turned immediately violet and then slowly (12 h) orange, and by addition of Et_2O (**2**) BF_4 precipitated out as a yellow powder which was filtered, washed with Et_2O , and vacuum dried (116 mg, 60%). Anal. Found: C, 58.2, H, 4.50. $C_{60}H_{54}BF_4P_5Pd_2$ requires: C, 58.6, H, 4.43. IR (Nujol, KBr) 2360 w br (ν_{PH}), 1030 s br (ν_{BF}), cm^{-1} .

4.3. Preparation of $Pd(PPh_2H)_4$ (**3**)

A toluene (15 ml) solution of $Pd(P^tBu_2H)_3$ (1.29 g, 2.36 mmol) was dropped at $-20^\circ C$ into a toluene (25 ml) solution of PPh_2H (5 ml, 28.7 mmol). The solution was stirred 30 min while the flask was heated to room temperature. Most of the solvent was evaporated and a pale yellow solid was precipitated by addition of Et_2O (20 ml). The solid was filtered, washed with Et_2O , vacuum dried and stored in the dark (1.735 g, 86%). Anal. Found: C, 66.9, H, 5.26. $C_{48}H_{44}P_4Pd$ requires: C, 67.7, H, 5.21. IR (Nujol, KBr) 2268 (ν_{PH}) cm^{-1} .

4.4. Preparation of $[Pd(PPh_2H)_4](BF_4)_2$ (**3**) $(BF_4)_2$

A 10-fold excess of HBf_4Et_2O was added at $-70^\circ C$ to a yellow CH_2Cl_2 (15 ml) solution of complex **3** (145 mg, 0.170 mmol). The solution was slowly allowed to reach room temperature and stirred until the evolution of dihydrogen (GC analysis) was complete (5 h). Most of the solvent was evaporated and *n*-hexane (10 ml) was added. The pale yellow oil that precipitated out was recrystallized from a CH_3CN/Et_2O . The pale yellow solid obtained was filtered and vacuum dried (95 mg, 54.6% yield). Anal. Found: C, 56.7; H, 4.35. $C_{48}H_{44}B_2F_8P_4Pd$ requires: C, 56.3; H,

4.33. IR (Nujol, KBr) 2365 w (ν_{PH}) and 1030 vs (ν_{BF}) cm^{-1} .

4.5. Preparation of $[Pd(PPh_2H)_4](CF_3SO_3)_2$ (**3**) $(CF_3SO_3)_2$

A 10-fold excess of CF_3SO_3H was added at $-70^\circ C$ to a yellow DME (20 ml) solution of complex **3** (160 mg, 0.188 mmol). The solution was slowly allowed to reach room temperature and stirred until the evolution of dihydrogen (GC analysis) was complete (5 h). Most of the solvent was evaporated and Et_2O (15 ml) was added. A colorless solid precipitated out and was filtered and vacuum dried (155 mg, 72% yield). Anal. Found: C, 52.0; H, 3.82. $C_{50}H_{44}F_6O_6P_4PdS_2$ requires: C, 52.2; H, 3.86. IR (Nujol, KBr) 2362 w (ν_{PH}) and 1270 vs, 1144 s, 1030 s and 639 s cm^{-1} vs (uncoordinated triflate) [32] cm^{-1} .

4.6. X-ray diffraction study

Some single crystals of **3** and $3(BF_4)_2 \cdot C_6D_6$, obtained as described in the paragraph before, were selected in air and glued at the end of glass fibers. All the X-ray diffraction measurements were done on a Siemens P4 four-circle diffractometer, equipped with graphite monochromatized $Mo-K_\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All data collections were made in $\omega/2\theta$ scan mode. Three standard reflections were measured every 97 measurements, to control the absence of decay and equipment stability. Data reductions were made by means of the XSCANS [33] program.

4.7. Crystal structure determination of **3**

Crystals of **3** are light yellow tetragonal prisms. One of them was mounted on the diffractometer at room temperature and the cell parameters listed in the second column of Table 1 were obtained. The diffraction symmetry and systematic absences indicated the tetragonal $I4_1/a$ space group. A redundant set of data was measured collecting a total of 2484 reflections. They were corrected for Lorentz and polarization effects and for absorption by using the ψ -scan method and obtaining 0.444 and 0.513 as the minimum and the maximum transmission factors. After merging the equivalents ($R_{int} = [\sum |F_o^2 - F_{mean}^2| / \sum (F_o^2)] = 0.0276$), a set 1874 unique reflections was obtained. The structure was solved by the automatic statistical procedure contained in the SHELXTL [34] program and was refined by the least-squares method contained in the same program. The hydrogen atoms were introduced in calculated positions and during the refinement were let ride on the connected carbon atoms. The final refinement cycle with anisotropic thermal factors for all the non-hydrogen atoms gave the reliability factors listed in Table 1.

Table 1
Crystal data and structure refinement

Compound	3	3(BF₄)₂·C₆D₆
Empirical formula	C ₄₈ H ₄₄ P ₄ Pd	C ₅₄ H ₅₀ B ₂ F ₈ P ₄ Pd
Formula weight	851.11	1102.84
Temperature (K)	293(2)	293(2)
Crystal system	Tetragonal	Tetragonal
Space group	I4 ₁ /a (n.88)	P4/ncc (n.130)
Unit cell dimensions		
<i>a</i> (Å)	19.061(1)	12.530(2)
<i>b</i> (Å)	19.061(1)	12.530(2)
<i>c</i> (Å)	11.631(1)	33.122(7)
<i>V</i> (Å ³)	4225.8(5)	5200.2(15)
<i>Z</i>	4	4
<i>D</i> _{calc} (Mg m ^{−3})	1.338	1.409
Absorption coefficient (mm ^{−1})	0.623	0.544
<i>F</i> (000)	1752	2248
Crystal size (mm ³)	0.62 × 0.48 × 0.25	0.44 × 0.36 × 0.20
θ range for data collection	2.05–24.97°	2.04–22.49°
Index ranges	−1 ≤ <i>h</i> ≤ 22 (1 ≤ <i>k</i> ≤ 22 (1 ≤ <i>l</i> ≤ 13	−1 ≤ <i>h</i> ≤ 13 (1 ≤ <i>l</i> ≤ 35
Reflections collected	2484	4173
Independent reflections	1874 [<i>R</i> _{int} = 0.0276]	1718 [<i>R</i> _{int} = 0.0522]
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1874/0/140	1718/0/158
Goodness-of-fit ^a on <i>F</i> ²	1.034	1.259
Final <i>R</i> indices ^a [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0263, <i>wR</i> ₂ = 0.0607	<i>R</i> ₁ = 0.0748, <i>wR</i> ₂ = 0.2229
<i>R</i> indices ^a (all data)	<i>R</i> ₁ = 0.0365, <i>wR</i> ₂ = 0.0654	<i>R</i> ₁ = 0.1261, <i>wR</i> ₂ = 0.2507
<i>A</i> ; <i>B</i> (<i>w</i>) ^a	0.0307; 2.51	0.1126; 9.87
Largest diff. peak and hole (e Å ^{−3})	0.242 and −0.262	1.029 and −0.616

^a Goodness-of-fit = $[\sum [w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$, where *N*, *P* are the numbers of observations and parameters, respectively, $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [\text{MAX}(F_o^2, 0) + 2F_c^2]/3$.

4.8. Crystal structure determination of **3(BF₄)₂ · C₆D₆**

A yellow prism with square section of **3(BF₄)₂ · C₆D₆** was selected for the diffractometric study and the lattice parameters listed in Table 1 were observed. The diffraction symmetry and systematic absences suggested the tetragonal *P4/ncc* space group. The intensity of 2484 reflections having θ between 3.22 and 25.0° were collected and were corrected for Lorentz and polarization effects and for absorption by using the ψ -scan method yielding 0.232 and 0.273 as the minimum and the maximum transmission factors. After merging the equivalents (*R*_{int} = 0.0522), a set of 1718 unique reflections was obtained.

The structure solution was found by direct methods through the SIR92 [35] program. Cation **3**²⁺ was located on the 4-fold axis with the Pd atom at 0.25, 0.25, 0.63. A successive difference Fourier synthesis showed

two groups of maxima on both sides of the cation at *z* = 0.74 and *z* = 0.46. They were interpreted as being due to the disorderly distribution of BF₄[−] groups among several possible positions. We therefore placed an 'ideal' BF₄[−] group with the central atom at 0.25, 0.25, 0.742 and occupancy of 0.25. To account for the larger disorder of the anion on the other side, two further 'ideal' BF₄[−] groups were introduced with the central atoms at 0.25, 0.25, 0.455 and 0.25, 0.25, 0.460 with occupancy 0.125 + η and 0.125 − η , respectively.

The successive least-squares refinement cycles gave a distribution of the BF₄[−] anions better fitting experimental data, within the constraints of tetrahedral geometric ideality. Other diffused maxima, placed around the $\bar{4}$ axis at 0.75, 0.25, *z*, then became present in the difference Fourier map. They were attributed to a disordered molecule of C₆D₆ (crystals were grown in a solution previously used in NMR spectra, where a few drops of C₆D₆ had been added for the lock signal capture and the field homogeneity optimization operations). The refinement of this last model gave the reliability factors listed in the last column of Table 1.

5. Supplementary material

Crystallographic data for the structural analyses has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 115355 for complex **3** and No. 115356 for **(3)(BF₄)₂·C₆D₆**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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