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Synthesis and reactivity of acetylacetonato-C^{γ} complexes of M^{II} (M = Pd or Pt): X-ray crystal structure of $[Pd(C_6F_5)(OOCPh)(bipy)] \cdot CHCl_3$

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Abstract

Acetylacetonato-C^{γ} complexes of stoichiometry $[M(C_6X_5)(acac-C^{\gamma})(N-N)]$ (M = Pd; X = F or Cl; N–N = 1,10-phenanthroline or 2,2′-bipyridine) (M = Pt; X = F; N–N = 1,10-phenanthroline (phen), or 2,2′-bipyridine (bipy)) have been obtained by treatment of the acetylacetonato-O,O' complexes $[M(C_6X_5)(acac-O,O')(tht)]$ (tht = tetrahydrothiophene) with the corresponding N–N base in 1/1 molar ratio. Complexes $[Pd(C_6F_5)(acac-C^{\gamma})(phen)]$ (**1**) and $[Pd(C_6F_5)(acac-C^{\gamma})(bipy)]$ (**2**) react with organic substrates containing acidic hydrogen atoms [HR], yielding the corresponding complexes $[Pd(C_6F_5)(R)(N-N)]$ (R = CF_3COO, CH_3COO, PhCOO, PhS or $P(S)Ph_2$). However, the reaction of **2** with $HPPh_2$ affords the dinuclear phosphido-bridged complex $[\{Pd(\mu\text{-}PPh_2)(C_6F_5)(HPPh_2)\}_2]$. All complexes have been characterized by spectroscopic methods (IR and ^1H, ^{19}F and $^{31}P\{^1H\}$NMR) and the molecular structure of $[Pd(C_6F_5)(OOCPh)(bipy)] \cdot CHCl_3$ (**12**) has been determined by X-ray diffraction methods.

Keywords: Palladium; Platinum; Acetylacetonate-C$^{\gamma}$ complexes; Pentafluorophenyl; Pentachlorophenyl; Carboxylate

1. Introduction

Acetylacetonato complexes in which this ligand is O,O'-chelating coordinated have been widely studied [1] because of their applications as reagents for NMR spectroscopy, vapour-phase chromatography, solvent extraction techniques etc. However, in spite of the extensive work, the chemistry of the acetylacetonato-C^{γ} derivatives, in which the acac group is σ bonded to the metal centre through the C^{γ} atom, has received much less attention [1,2].

During our work on the synthesis of perhalophenyl complexes of Pd(II) and Pt(II) with polyfunctional ligands such as $[Ph_2P-CH-PPh_2]^-$, $[C(PPh_2)_3]^-$ and $[SPPh_2]^-$, acetylacetonato-O,O' complexes were very useful starting materials [3]. As an extension of the chemistry of Pd(II) and Pt(II) with the acetylacetonate ligand, we describe here the synthesis of some new M–acac–C^{γ} complexes (M = Pd or Pt) and the reactivity of two palladium derivatives towards organic substrates containing acidic hydrogen atoms, as RCOOH, RSH, $HP(S)Ph_2$ and $HPPh_2$. These displace the $acac^-$ group as Hacac with coordination of the anionic fragment $RCOO^-$, RS^-, $[SPPh_2]^-$ and $[PPh_2]^-$.

2. Results and discussion

2.1. Acetylacetonato-C^{γ} complexes of Pd(II) and Pt(II)

The reaction between $[M(C_6X_5)(acac-O,O')(tht)]$ (M = Pd, X = F or Cl) (M = Pt; X = F) and the bidentate basis ligands N–N (N–N = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy)) in 1/1 molar ratio causes the displacement of the tht and the isomerization of the acac O,O' into the C^{γ}-coordinated form, affording the neutral derivatives $[M(C_6X_5)(acac-C^{\gamma})(N-N)]$:

$$[M(C_6X_5)(acac-O,O')(tht)] + N-N \longrightarrow [M(C_6X_5)(acac-C^{\gamma})(N-N)] + tht \quad (1)$$

M = Pd, X = F, N–N = phen (**1**) or bipy (**2**)

M = Pd, X = Cl, N–N = phen (**3**) or bipy (**4**)

M = Pt, X = F, N–N = phen (**5**) or bipy (**6**)

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The process takes place in CH_2Cl_2 at room temperature for the Pd complexes and in refluxing benzene for the platinum complexes.

Complexes **1–6** have satisfactory elemental analysis and their IR spectra (see Section 4) show the following characteristic absorptions:

(a) for all complexes, a very strong absorption in the 1690–1670 cm^{-1} region together with a second absorption (less intense) around 1630 cm^{-1} indicate the C^{γ}-coordination mode of the acac group [4]. Moreover, the disappearance of the in-plane and out-of-plane bending mode π(C–H) at around 800 cm^{-1} in the acac–*O,O'* compounds confirms the C^{γ} coordination [5].

(b) Absorptions in the 1500, 1060, 950 and 790 (X-sensitive) cm^{-1} regions show the presence of coordinated pentafluorophenyl groups [6] and absorptions in the 1350–1280 cm^{-1} region and around 830 and 670 cm^{-1} indicate coordinated C_6Cl_5 ligands [7].

(c) Finally, characteristic absorptions of the *N,N*-chelating coordinated 1,10-phenanthroline and 2,2'-bipyridine were also observed [8].

The ^1H NMR spectra of **1–6** (Table 1) show, in the low field region, eight complex resonances (sometimes overlapping) corresponding to the eight chemically inequivalent protons of 1,10-phenanthroline or 2,2'-bipyridine. The complete assignment of the chemical shifts and coupling constants (Fig. 1 and Table 1) has been made taking into account the similar patterns of resonances of **1–6** and those found for **7–16**, and the ^1H–^1H COSY and NOESY experiments performed for **9** and **10** (see below).

In addition, the ^1H NMR spectra show a singlet resonance at about 2.2 ppm corresponding to the methyl groups of acac and a singlet resonance in the 4.2–4.9 ppm region corresponding to the C*H* group of acac, which shows ^{195}Pt satellites in **5** and **6** and confirms the C^{γ} coordination. This resonance shifts upfield from the acac–*O,O'* compounds (5.42 ppm for $[Pd(C_6F_5)(acac)(tht)]$ and 5.47 ppm for its Pt analogue) to the acac–C^{γ} complexes (4.2–4.9 ppm), related to the hybridization change in the C^{γ} atom ($sp^2 \rightarrow sp^3$) and the *C* coordination.

The ^{19}F NMR spectra of **1**, **2**, **5** and **6** (Table 2) show a set of three signals (AA'MM'X spin system), corresponding to the *ortho*-F (with ^{195}Pt satellites in **5** and **6**), *para*-F and *meta*-F. All these data are consistent with the structure for these compounds depicted in Fig. 1.

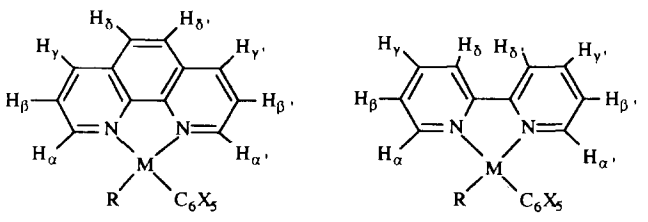

Fig. 1.

2.2. Reactivity of $[Pd(C_6F_5)(acac-C^{\gamma})(N-N)]$ towards acidic reactants HR

The acac–*O,O'* can be easily displaced as Hacac by a variety of organic molecules containing acidic hydrogen atoms, the resulting anion remaining coordinated to the Pd(II) [3]. In the same way, the complexes $[Pd(C_6F_5)(acac-C^{\gamma})(N-N)]$ (N–N = phen (**1**) or bipy (**2**)) react with the organic substrates H–R (R = CF_3COO^-, CH_3COO^-, $PhCOO^-$, PhS^- or $P(S)Ph_2^-$) to give the corresponding neutral complexes $[Pd(C_6F_5)(R)(N-N)]$ (**7–16**):

$$[Pd(C_6F_5)(acac-C^{\gamma})(N-N)] + HR \longrightarrow [Pd(C_6F_5)(R)(N-N)] + Hacac \quad (2)$$

R = CF_3COO, N–N = phen (**7**) or bipy (**8**)
R = CH_3COO, N–N = phen (**9**) or bipy (**10**)
R = PhCOO, N–N = phen (**11**) or bipy (**12**)
R = PhS, N–N = phen (**13**) or bipy (**14**)
R = $P(S)Ph_2$, N–N = phen (**15**) or bipy (**16**)

The reactions were carried out in refluxing dichloromethane for **7–12** and in dichloromethane at room temperature for **13–16**. All complexes showed satisfactory elemental analysis (see Section 4). The IR spectra of all complexes showed the disappearance of the absorptions due to the C^{γ}-bonded acac and contain similar patterns of absorptions due to the C_6F_5 and N–N ligands, as described for the acetylacetonato derivatives **1** and **2**. New absorptions were observed as a consequence of the presence of the different R substituents; for **7–12**, which contain a carboxylate ligand, a very strong absorption in the 1710–1620 cm^{-1} region was found, attributed to the $\nu_{asym}(CO_2)$ stretching mode [9]. The $\nu_{sym}(CO_2)$ stretching mode overlaps other aromatic resonances falling in the range 1500–1400 cm^{-1}, precluding their unambiguous assignment. For **13** and **14**, weak absorptions due to the phenyl rings of the SPh were observed (1580–1630 cm^{-1}). Finally, **15** and **16** showed characteristic absorptions of the *P*-coordinated $P(S)Ph_2$ (630–600 cm^{-1}), assigned to the stretching $\nu_{P=S}$ [10].

The ^1H NMR spectra of **7–16**, in the low field region, showed eight different resonances (sometimes overlapping) corresponding to the eight chemically inequivalent protons of 1,10-phenanthroline or 2,2'-bipyridine. For **9** and **10**, two singlet resonances at about 2.00 ppm indicated the presence of acetate and, for **11–16**, unresolved resonances between 6.9 and 7.5 ppm were attributed to the Ph rings.

Table 1
^{1}H NMR data for **1–17**

Complex	δ (ppm)							$^3J_{\alpha\beta}$ (Hz)	$^4J_{\alpha\gamma}$ (Hz)	$^3J_{\beta\gamma}$ (Hz)	$^4J_{\beta\delta}$ (Hz)	$^3J_{\gamma\delta}$ (Hz)	$^3J_{\alpha'\beta'}$ (Hz)	$^4J_{\alpha'\gamma'}$ (Hz)	$^3J_{\beta'\gamma'}$ (Hz)	$^4J_{\beta'\delta'}$ (Hz)	$^3J_{\gamma'\delta'}$ (Hz)	$^3J_{\delta\delta'}$ (Hz)	Other data	
	H_α	$H_{\alpha'}$	H_β	$H_{\beta'}$	H_γ	$H_{\gamma'}$	$H_\delta + H_{\delta'}$													
1	10.33	7.86	8.03	7.61	8.44	8.43	7.93, 7.88	5.22	1.38	8.20			5.05	1.25	9.82			8.70	2.19 [a]	4.26 [b]
2	9.96	7.55	7.72	7.30	7.98	7.96	8.04, 8.02	5.63	1.11	6.46	2.51	OR	5.16	BR	7.19	1.59	OR		2.16 [a]	4.37 [b]
3	10.16	7.94	8.02	7.67	8.47	8.47	7.97, 7.92	5.22	1.41	8.14			4.97	1.45	8.20			8.84	2.22 [a]	4.35 [b]
4	9.34	7.84	7.62	7.43	OR	OR	OR	5.25	NR	7.14	1.86	OR	5.43	NR	5.73	2.91	OR		2.21 [a]	4.51 [b]
5	10.55	8.31 [c]	8.07	7.65	8.56	8.53	7.95, 7.90	5.31	1.26	8.20			5.20	1.09	8.18			8.81	2.18 [a]	4.96 [b,d]
6	10.21	OR	7.77	7.34	OR	OR	OR	4.98	NR	7.38	1.59	OR	5.67	OR	7.29	1.62	OR		2.16 [a]	4.81 [b,d]
7	8.76	8.28	7.96	7.71	8.61	8.56	8.05, 8.00	5.02	1.44	8.26			5.18	1.21	8.21			8.84		
9	8.69	8.13	7.82	7.57	8.51	8.48	7.93, 7.88	4.88	1.07	8.50			5.07	0.88	8.20			8.83	2.06 [e]	
10	8.45	7.94	7.52	7.31	8.08	8.04	8.17, 8.14	5.30	1.56	6.70	1.28	7.65	5.53	1.53	7.30	1.34	8.00		2.00 [e]	
11	8.79	8.31	7.81	7.67	8.54	8.52	8.02, 7.96	4.96	1.37	8.27			5.05	1.33	8.25			8.86	7.41–7.31 [f]	
12	8.38	7.97	OR	OR	OR	OR	8.35, 8.26	5.28				7.90	5.13				7.89		7.40–7.23 [f]	
13	9.38	8.28	7.86	7.71	8.52	8.50	8.00 7.97	5.02	1.48	8.13			4.84	1.35	8.19			8.81	7.57–6.89 [g]	
14	9.13	7.97	7.52	7.38	8.08	8.04	7.50, 7.49	5.02	1.10	8.03	2.26	7.15	5.24	NR	7.09	NR	7.66		6.90–6.88 [g]	
15	7.97	7.92	7.66		8.43		7.96	5.11		8.20										
17																			5.40 [h]	[i]

Complex **8** was too insoluble for NMR measurements. Complex **16** had all resonances overlapping.
OR, overlapping resonances; BR; broad resonance; NR, not resolved.
[a] CH_3–acac.
[b] CH–acac.
[c] $^3J_{Pt-H} = 28.96$ Hz.
[d] $^2J_{Pt-H} = 128$ Hz.
[e] CH_3–COO.
[f] *Ph*COO.
[g] *Ph*S(h) $^1J_{P-H} = 356.74$ Hz.
[i] 7.0–7.2 ppm P*Ph*$_2$.

Table 2
^{19}F and $^{31}P\{^1H\}$ NMR data for **1–17**

Complex	δ (ppm)			$^3J_{Pt-o-F}$	δ (ppm)		$^4J_{P-o-F}$
	o-F_o	*m*-F_m	*p*-F_p	(Hz)	CF_3	P	(Hz)
1	−117.1	−162.3	−159.7				
2	−117.2	−162.3	−159.7				
5	−118.5	−162.7	−160.3	410.5			
6	−118.6	−162.7	−160.4	406.0			
7	−120.8	−162.5	−158.9		−74.3		
9	−119.8	−162.7	−159.8				
10	−120.0	−162.7	−159.9				
11	−120.1	−162.8	−159.9				
12	−120.2	−162.7	−159.9				
13	−117.3	−163.1	−161.2				
14	−117.4	−163.1	−161.2				
15	−115.2	−162.2	−160.6			57.61	11.2
16	−115.4	−162.1	−160.4			57.83	10.2
17	−113.9	−163.5	−162.2			$\delta(P_a) = -115.44$ ppm, $\delta(P_x) = 0.24$ ppm, $^2J_{ax} = 341.45$ Hz, $^2J_{aa'} = 206.21$ Hz, $^2J_{ax'} = -4.84$ Hz	

In order to obtain an accurate assignment of the resonances of the 1,10-phenanthroline and 2,2′-bipyridine groups, $^1H-^1H$ COSY measurements were carried out for $[Pd(C_6F_5)(OOCCH_3)(phen)]$ (**9**) and $[Pd(C_6F_5)(OOCCH_3)(bipy)]$ (**10**), since they were the most soluble in $CDCl_3$. The correlations allow a distinction to be

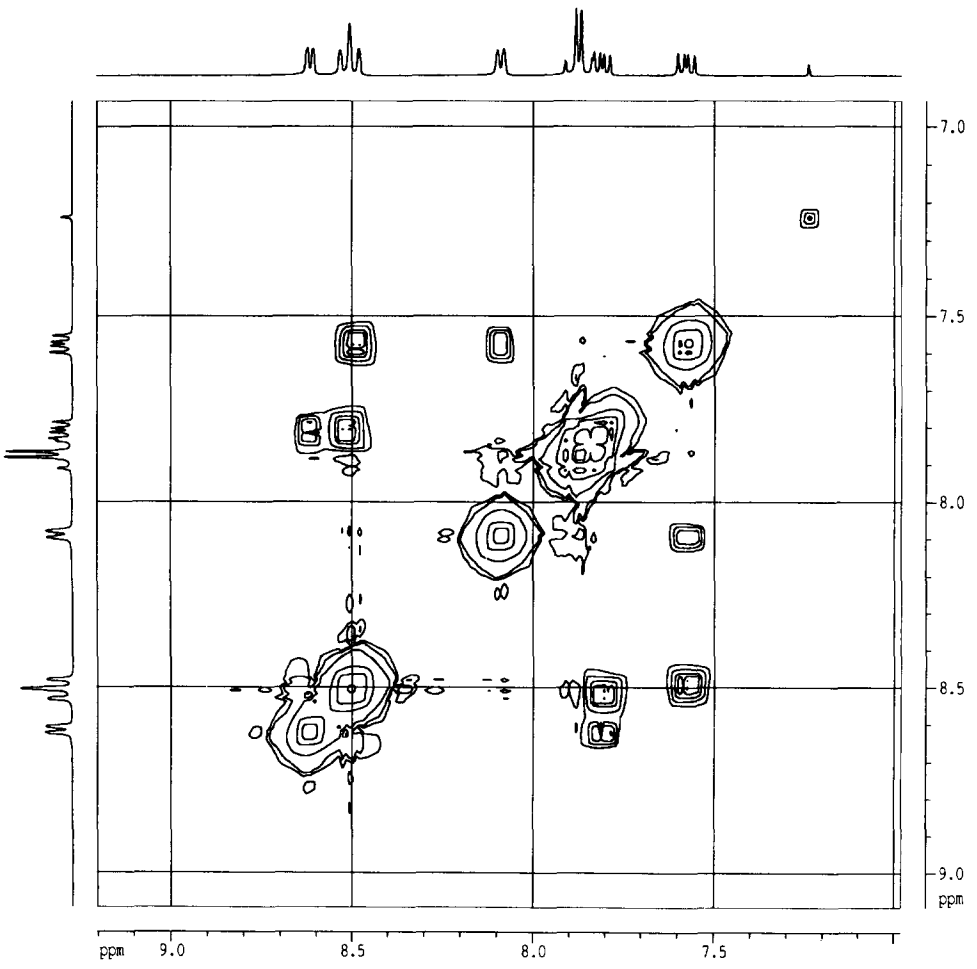

Fig. 2.

made between the resonances of each half of the N–N ligands: (H_α, H_β, H_γ) and ($H_{\alpha'}$, $H_{\beta'}$, $H_{\gamma'}$). The resonances due to H_δ and $H_{\delta'}$ were indistinguishable. They form an AB system without other coupling in the phen complexes, and in the bipy compounds they overlap the resonances of H_γ and $H_{\gamma'}$. Fig. 2 shows the ^1H–^1H COSY spectrum of **9**.

To complement the ^1H–^1H COSY spectra, ^1H–^1H NOESY experiments were performed for the same compounds **9** and **10** under the same conditions (see Section 4). The resonance at lowest field and attributed to H_α in both compounds shows a strong nuclear Overhauser effect interaction with the resonance because the methyl group of the acetate ligand, indicating the proximity of the interacting nuclei. From these data, a complete assignment of the resonances due to phen and bipy can be derived (Fig. 1). The similarity in the observed pattern of signals for complexes containing phen and bipy (including the acac–C^γ complexes) allows us to extend these assignments to **1–16**. Fig. 3 show the ^1H–^1H NOESY spectrum of **9**.

The ^{19}F NMR spectra of **7–16** (see Table 2) all showed a set of three signals (AA'MM'X spin system), corresponding to *ortho*-F, *para*-F and *meta*-F, indicating that both halves of the C_6F_5 group are equivalent. For **7** an additional singlet resonance due to CF_3COO is also observed.

The $^{31}P\{^1H\}$ NMR spectra of **15** and **16** (see Table 2) show a single resonance for $P(S)Ph_2$ at 57 ppm, with a triplet structure due to the coupling with the *ortho*-F atoms of the C_6F_5 group. This confirms the *P* coordination of the $P(S)Ph_2$ ligand.

The X-ray crystal structure determination of $[Pd(C_6F_5)(OOCPh)(bipy)]$ (**12**) completes the characterization of this kind of compound.

2.3. *X-ray structure of* $[Pd(C_6F_5)(OOCPh)(bipy)] \cdot CHCl_3$ (**12**) $\cdot CHCl_3$)

A drawing of the structure of **12** is presented in Fig. 4. Selected bond distances and angles are collected in Table 3. Positional parameters and their estimated standard deviations are listed in Table 4.

The mononuclear complex **12** contains a palladium

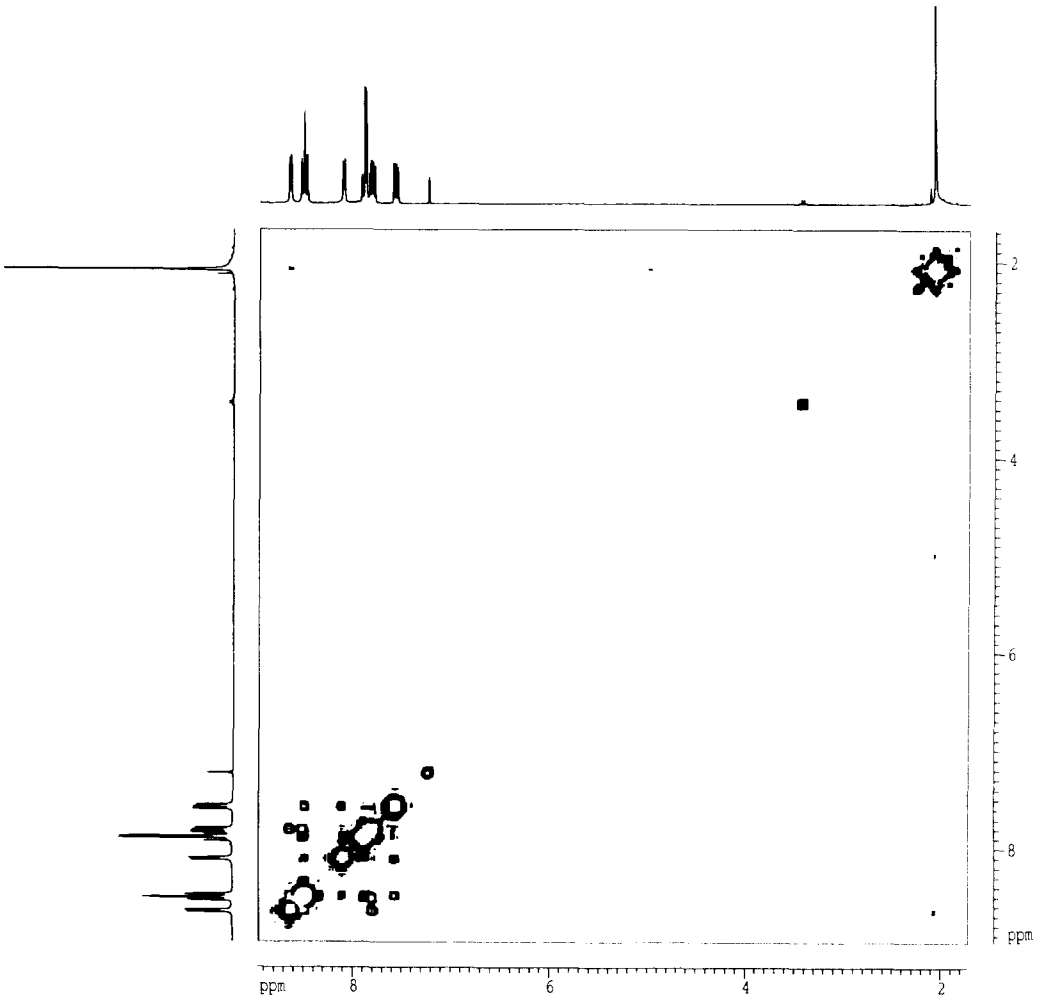

Fig. 3.

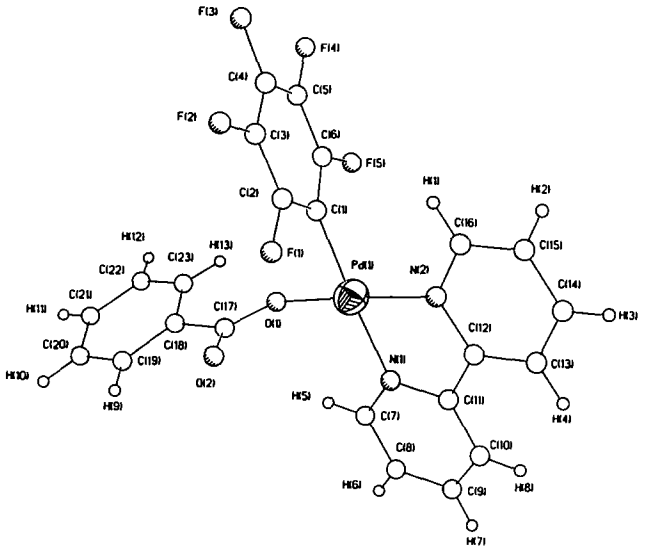

Fig. 4.

atom located in a distorted square planar environment, formed by the two nitrogen atoms of the chelating bipy ligand, the C_{ipso} of the C_6F_5 group and one oxygen atom of the benzoate ligand, which is monodentate. The Pd–C(C_6F_5), Pd–N(bipy) and Pd–O(benzoate) bond distances are in the usual range found in the literature [3b,c,9,11]. The different Pd–N distances (Pd(1)–N(1), 2.031(4) Å; Pd(1)–N(2) 2.004(4) Å) are in accord with the higher *trans* influence of C_6F_5 compared with benzoate [12]. Both C–O distances in benzoate are equal within the experimental error: C(17)–O(1), 1.266(8) Å; C(17)–O(2), 1.248(8) Å. The Pd(1)–O(2) (non-coordinated oxygen) distance is 3.089(5) Å. The value for the chelate angle N(1)–Pd(1)–N(2)(80.2(1)°) is similar to that in other values in palladium complexes with bipy chelating [13]. Both pentafluorophenyl and benzoate are planar, and the dihedral angles formed by these planes and the best least-squares plane defined by Pd(1)–C(1)–O(1)–N(1)–N(2) (coordination plane) are 78.3(2)° and 75.5(1)° respectively [14].

Table 3
Selected bond lengths (Å) and angles (°) for **12**

Bond lengths			
Pd(1)–C(1)	1.999(5)	Pd(1)–N(1)	2.031(4)
Pd(1)–N(2)	2.004(4)	Pd(1)–O(1)	2.003(4)
O(1)–C(17)	1.266(8)	O(2)–C(17)	1.248(8)
C(17)–C(18)	1.494(8)		
Bond angles			
C(1)–Pd(1)–N(1)	176.9(2)	C(1)–Pd(1)–N(2)	97.2(2)
N(1)–Pd(1)–N(2)	80.2(1)	C(1)–Pd(1)–O(1)	87.4(2)
N(1)–Pd(1)–O(1)	95.1(1)	N(2)–Pd(1)–O(1)	174.6(1)
Pd(1)–C(1)–C(2)	124.1(4)	Pd(1)–C(1)–C(6)	121.7(4)
Pd(1)–N(1)–C(7)	125.4(1)	Pd(1)–N(1)–C(11)	114.6(1)
Pd(1)–N(2)–C(16)	125.5(1)	Pd(1)–N(2)–C(12)	114.5(1)
Pd(1)–O(1)–C(17)	120.8(4)	O(1)–C(17)–O(2)	125.1(6)
O(1)–C(17)–C(18)	115.1(5)	O(2)–C(17)–C(18)	119.7(5)
C(17)–C(18)–C(19)	120.6(3)	C(17)–C(18)–C(23)	119.4(3)

Table 4
Atomic coordinates for **12**

	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)
Pd(1)	6782(1)	4396(1)	−565(1)
C(1)	7251(4)	3327(3)	−953(3)
C(2)	6984(3)	2518(3)	−804(3)
C(3)	7317(4)	1778(3)	−1069(3)
C(4)	7945(4)	1852(4)	−1499(3)
C(5)	8259(5)	2626(4)	−1651(4)
C(6)	7892(5)	3352(4)	−1387(3)
F(1)	6360(3)	2408(2)	−378(2)
F(2)	7010(3)	1004(2)	−917(2)
F(3)	8267(3)	1126(2)	−1774(2)
F(4)	8872(3)	2688(3)	−2080(3)
F(5)	8218(3)	4117(3)	−1568(3)
C(7)	6647(2)	6031(2)	241(2)
C(8)	6242	6778	436
C(9)	5471	6992	173
C(10)	5104	6459	−286
C(11)	5509	5712	−481
N(1)	6280	5498	−218
C(16)	5578(3)	3929(2)	−1635(2)
C(15)	4841	4041	−1981
C(14)	4300	4708	−1821
C(13)	4496	5262	−1316
C(12)	5233	5149	−971
N(2)	5774	4483	−1130
O(1)	7790(3)	4429(2)	3(2)
O(2)	7181(3)	3675(3)	786(2)
C(17)	7789(4)	4058(4)	546(3)
C(19)	8636(3)	3873(3)	1552(2)
C(20)	9394	3913	1879
C(21)	10114	4164	1554
C(22)	10076	4375	902
C(23)	9318	4335	575
C(18)	8598	4084	900
C(24)	3439(5)	7814(5)	−1573(4)
Cl(1)	3568(7)	7147(6)	−2320(5)
Cl(2)	4480(10)	8106(11)	−1316(8)
Cl(3)	3010(8)	8803(8)	−1757(7)
Cl(1′)	3863(4)	7238(3)	−2205(3)
Cl(2′)	4247(6)	8438(6)	−1193(4)
Cl(3′)	2720(5)	8571(5)	−1886(3)
Cl(1″)	4133(8)	7313(7)	−1983(6)
Cl(2″)	3918(12)	8554(12)	−1115(9)
Cl(3″)	2502(8)	8231(9)	−1954(7)

2.4. Reaction of [Pd(C_6F_5)(acac-C^γ)(bipy)] with $HPPh_2$

Finally, we have studied the reaction of [Pd(C_6F_5)-(acac-C^γ)(bipy)] with $HPPh_2$ in tetrahydrofuran (THF) (molar ratio, 1/1), to prepare the corresponding palladium compound with a terminal phosphido ligand [15]. However, the expected complex [Pd(C_6F_5)(PPh_2)(bipy)] is not obtained but the binuclear derivative [Pd(μ-PPh_2)(C_6F_5)($HPPh_2$)]$_2$ (**17**) is although with a very low yield (20%). By increasing the amount of $HPPh_2$ (molar ratio, 1/2), **17** can be isolated with a higher yield

(50%). The reaction is schematized as follows and involves the displacement not only of acetylacetone but also of bipy:

$$[Pd(C_6F_5)(acac\text{–}C^{\gamma})(bipy)] + 2HPPh_2 \longrightarrow \tfrac{1}{2}[Pd(\mu\text{-}PPh_2)(C_6F_5)(HPPh_2)]_2 \quad (3)$$

17

+ Hacac + bipy

The formation of **17** is a clear indication of the high tendency of the phosphido groups to act as bridging ligands, and this must be the driving force for the displacement of the typically chelating bipy. It should also be noted that the reaction of $[Pd(C_6F_5)(acac\text{–}C^{\gamma})(N\text{–}N)]$ with $Ph_2P(S)H$ (another usually bridging ligand) does not result in the displacement of the bipy but in the formation of the mononuclear complexes **15** and **16** with terminal $P(S)Ph_2$. Complex **17** shows satisfactory elemental analysis (see Section 4) and its IR spectrum shows characteristic absorptions of P-coordinated $HPPh_2$ [16] and of C_6F_5 [6], together with several absorptions in the phosphine regions (770–700 and 570–470 cm^{-1}). The $^{31}P\{^1H\}$ NMR spectrum of **17** (see Table 2) shows two resonances at 0.2 and −115.4 ppm characteristic of an AA′XX′ spin system. A similar spin system and values of the chemical shifts have been found for the related neutral phosphido-bridged complexes $[\{Pd(\mu\text{-}PR_2)(X)(PR'_3)\}_2]$ [17]. The high value of the coupling constant $^2J_{P_A-P_X} = {}^2J_{P_{A'}-P_{X'}} = 341$ Hz, indicates a *trans* arrangement of the P_A and P_X atoms [18]. The ^{19}F NMR spectrum showed one type of C_6F_5 group and the ^1H NMR spectrum showed signals due to the Ph groups and a doublet of multiplets, centred at 5.4 ppm and attributed to the H atom of $HPPh_2$. All these data, together with the observation in the IR spectrum of a single absorption in the C_6F_5 X-sensitive zone, are consistent with the structure shown in Fig. 5.

3. Conclusion

The synthesis of acetylacetonato-C^{γ} complexes of M(II) (M = Pd or Pt) can be accomplished by treatment of acetylacetonato-O,O' derivatives, containing a weakly coordinated tht group, with chelating N–N. The protonation of these acac–C^{γ} complexes by acidic organic substrates [HR] causes the displacement of the acetylacetonate group as Hacac and the coordination of the anionic fragment $[R]^-$.

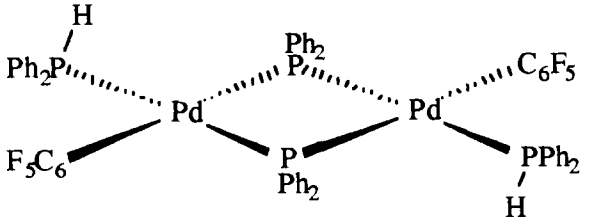

Fig. 5.

4. Experimental section

4.1. General procedures

Solvents were dried and distilled under dinitrogen by standard methods. IR spectra (4000–200 cm^{-1}) were recorded on a Perkin–Elmer 883 spectrophotometer in Nujol mulls. ^1H, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature on a Bruker ARX-300 spectrometer in $CDCl_3$ solution. Elemental analyses were carried out on a Perkin–Elmer 240-B microanalyser. The starting compounds $[M(C_6X_5)(acac\text{–}O,O')(tht)$ [3a] and $HP(S)Ph_2$ [19] were prepared according to published methods.

4.2. Synthesis of acac–C^{γ} complexes $[M(C_6X_5)(acac\text{–}C^{\gamma})(N\text{–}N)]$ (1–6)

$[Pd(C_6F_5)(acac\text{–}C^{\gamma})(phen)]$ (**1**). To a solution of $[Pd(C_6F_5)(acac\text{–}O,O')(tht)]$ (0.200 g, 0.434 mmol) in CH_2Cl_2 (20 ml) was added 1,10-phenanthroline–H_2O (0.093 g, 0.434 mmol) and the solution was stirred at ambient temperature for 24 h. During this time a pale-yellow solid precipitated. The precipitation was completed by partial evaporation (4 ml) and Et_2O addition (20 ml). The solid was filtered off and washed with Et_2O (3 × 10 ml) (**1**) (yield, 85% (0.200 g)). Anal. Found: C, 49.57; H, 2.56; N, 5.18. $C_{23}H_{15}F_5N_2O_2Pd$ Calc.: C, 49.97; H, 2.73; N, 5.06%. IR: ν 1680vs, 1633s ($\nu_{C=O}$, acac), 1606m, 1594m, 1586m (phen), 1502vs, 1061vs, 954vs (C_6F_5), 851vs (phen), 791s (C_6F_5, X-sensitive) cm^{-1}.

Complexes **2**, **3** and **4** were obtained similarly. $[Pd(C_6F_5)(acac\text{-}C^{\gamma})(bipy)]$ (**2**). $[Pd(C_6F_5)(acac\text{–}O,O')(tht)]$ (0.255 g, 0.554 mmol) reacts with 2,2′-bipyridine (0.086 g, 0.554 mmol) to give **2** as a pale-yellow solid (yield, 72% (0.211 g)). Anal. Found: C, 47.30; H, 2.99; N, 5.38. $C_{21}H_{15}F_5N_2O_2Pd$ Calc.: C, 47.70; H, 2.86; N, 5.29%. IR: ν 1679vs, 1640s ($\nu_{C=O}$, acac), 1602m (bipy), 1504vs, 1062vs, 952vs (C_6F_5), 790s (C_6F_5, X-sensitive), 763vs (bipy) cm^{-1}.

$[Pd(C_6Cl_5)(acac\text{–}C^{\gamma})(phen)]$ (**3**). $[Pd(C_6Cl_5)(acac\text{–}O,O')(tht)]$ (0.095 g, 0.175 mmol) reacts with 1,10-phenanthroline–H_2O (0.037 g, 0.175 mmol) to give **3** as a pale-yellow solid (yield, 43% (0.050 g)). Anal. Found: C, 43.40; H, 2.66; N, 4.02. $C_{23}H_{15}Cl_5N_2O_2Pd$ Calc.: C, 43.50; H, 2.38; N, 4.41%. IR: ν 1685vs, 1630s ($\nu_{C=O}$, acac), 1605m, 1590m, 1585m (phen), 1330vs, 1320vs, 1295vs (C_6Cl_5), 847vs (phen), 830s (C_6Cl_5, X-sensitive), 673 (C_6Cl_5) cm^{-1}.

$[Pd(C_6Cl_5)(acac\text{-}C^{\gamma})(bipy)]$ (**4**). $[Pd(C_6Cl_5)(acac\text{–}O,O')(tht)]$ (0.095 g, 0.175 mmol) reacts with 2,2′-bi-

pyridine (0.027 g, 0.175 mmol) to give **4** as a yellow solid (yield, 40% (0.043 g)). Anal. Found: C, 41.61; H, 2.72; N, 4.45. $C_{21}H_{15}Cl_5N_2O_2Pd$ Calc.: C, 41.28; H, 2.47, N, 4.58%. IR: ν 1677vs, 1624s ($\nu_{C=O}$, acac), 1597m (bipy), 1323vs, 1313vs, 1288vs (C_6Cl_5), 835s (C_6Cl_5, X-sensitive), 760vs (bipy), 670 (C_6Cl_5) cm^{-1}.

[$Pt(C_6F_5)$(acac–C^γ)(phen)] (**5**). To a solution of [$Pt(C_6F_5)$(acac–*O*,*O*′)(thf)] (0.300 g, 0.546 mmol) in benzene (20 ml) was added 1,10-phenanthroline–H_2O (0.117 g, 0.546 mmol). The resulting solution was heated under reflux for 7 h and cooled; then the solvent evaporated to dryness. The residue was extracted with CH_2Cl_2 (30 ml) and filtered, and the resulting solution was evaporated to dryness. Treatment of the residue with Et_2O (20 ml) gave **5** as a yellow solid (yield, 40% (0.140 g)). Anal. Found: C, 44.06; H, 1.96; N, 4.81. $C_{23}H_{15}F_5N_2O_2Pt$ Calc.: C, 43.06; H, 2.35; N, 4.36%. IR: ν 1688vs, 1645s ($\nu_{C=O}$, acac), 1605m, 1586m (phen), 1509vs, 1069vs, 952vs (C_6F_5), 844vs (phen), 804s (C_6F_5, X-sensitive) cm^{-1}.

[$Pt(C_6F_5)$(acac-C^γ)(bipy)] (**6**). Complex **6** was obtained following a work-up similar to that described for **5**: [$Pt(C_6F_5)$(acac–*O*,*O*′)(tht)] (0.300 g, 0.546 mmol) reacts with 2,2′-bipyridine (0.081 g, 0.546 mmol) to give **6** as a yellow solid (yield, 45% (0.152 g)). Anal. Found: C, 41.09; H, 2.40; N, 4.72. $C_{21}H_{15}F_5N_2O_2Pt$ Calc.: C, 40.85; H, 2.44; N, 4.53%. IR: ν 1688vs, 1649s ($\nu_{C=O}$, acac), 1606m (bipy), 1506vs, 1066vs, 953vs (C_6F_5), 804s (C_6F_5, X-sensitive), 764vs (bipy) cm^{-1}.

4.3. Synthesis of complexes of stoichiometry [Pd(C_6F_5)(R)(N–N)] (7–16)

[$Pd(C_6F_5)(OOCCF_3)$(phen)] (**7**). To a suspension of [$Pd(C_6F_5)$(acac–C^γ)(phen)] (**1**) (0.150 g, 0.271 mmol) in CH_2Cl_2 (25 ml) was added CF_3COOH (21 μl, 0.280 mmol). The resulting colourless solution was heated under reflux for 5 h. After cooling, the solvent was evaporated to dryness and the residue treated with 25 ml of Et_2O, giving (**7**) as an off-white solid (yield, 95% (0.146 g)). Anal. Found: C, 42.03; H, 1.49; N, 4.64. $C_{20}H_{18}F_8N_2O_2Pd$ Calc.: C, 42.39; H, 1.42; N, 4.94%. IR: ν, 1708vs ($\nu_{C=O}$, acetate), 1603m, 1585m, 1572m (phen), 1506vs, 1065vs, 957vs (C_6F_5), 846vs (phen), 797s (C_6F_5, X-sensitive) cm^{-1}.

[$Pd(C_6F_5)(OOCCF_3)$(bipy)] (**8**). Complex **8** was obtained similarly: [$Pd(C_6F_5)$(acac–C^γ)(bipy)] (**2**) (0.250 g, 0.473 mmol) reacts with CF_3COOH (38 μl, 0.500 mmol) to give **8** as a yellow solid (yield, 86% (0.220 g)). Anal. Found: C, 39.67; H, 1.51; N, 5.10. $C_{18}H_{18}F_8N_2O_2Pd$ Calc.: C, 39.84; H, 1.48; N, 5.16%. IR: ν 1700vs ($\nu_{C=O}$, acetate), 1607m (bipy), 1504vs, 1061vs, 956vs (C_6F_5), 789s (C_6F_5, X-sensitive), 769vs (bipy) cm^{-1}.

[$Pd(C_6F_5)(OOCCH_3)$(phen)] (**9**). To a suspension of [$Pd(C_6F_5)$(acac–C^γ)(phen)] (**1**) (0.250 g, 0.452 mmol) in CH_2Cl_2 (25 ml) was added CH_3COOH (27 μl, 0.460 mmol) and the mixture was heater under reflux for 5 h. The initial suspension gradually dissolved and gave a pale-yellow solution. After cooling, the solvent was evaporated to dryness and the residue was treated with 25 ml of Et_2O, giving **9** as a pale-yellow solid (yield, 97% (0.225 g)). Anal. Found: C, 46.32; H, 2.14; N, 5.49. $C_{20}H_{11}F_5N_2O_2Pd$ Calc: C, 46.85; H, 2.16; N, 5.46%. IR: ν 1630vs, 1602vs ($\nu_{C=O}$, acetate), 1504vs, 1061vs, 952vs (C_6F_5), 849vs (phen), 795s (C_6F_5, X-sensitive) cm^{-1}.

[$Pd(C_6F_5)(OOCCH_3)$(bipy)] (**10**). Complex **10** was obtained similarly. [$Pd(C_6F_5)$(acac–C^γ)(bipy)] (**2**) (0.250 g, 0.473 mmol) reacts with CH_3COOH (28 μl, 0.480 mmol) to give **10** as a pale-yellow solid (yield, 95% (0.220 g)). Anal. Found: C, 44.26; H, 2.21; N, 5.75. $C_{18}H_{11}F_5N_2O_2Pd$ Calc.: C, 44.24; H, 2.27; N, 5.73%. IR: ν 1622vs, 1604vs ($\nu_{C=O}$, acetate), 1502vs, 1060vs, 957vs (C_6F_5), 792s (C_6F_5, X-sensitive), 763vs (bipy) cm^{-1}.

[$Pd(C_6F_5)$(OOCPh)(phen)] (**11**). [$Pd(C_6F_5)$(acac–C^γ)(phen)] (**1**) (0.150 g, 0.271 mmol) reacts with PhCOOH (0.033 g, 0.280 mmol) to give **11** as a pale-yellow solid (yield, 93% (0.145 g)). Anal. Found: C, 51.76; H, 2.14; N, 4.80. $C_{25}H_{13}F_5N_2O_2Pd$ Calc: C, 52.24; H, 2.27; N, 4.87%. IR: ν 1635vs, 1620vs ($\nu_{C=O}$, acetate), 1600m, 1578m (phen), 1504vs, 1064vs, 953vs (C_6F_5), 853vs (phen), 794s (C_6F_5, X-sensitive) cm^{-1}.

[$Pd(C_6F_5)$(OOCPh)(bipy)] (**12**). [$Pd(C_6F_5)$(acac–C^γ)(bipy)] (**2**) (0.250 g, 0.473 mmol) reacts with PhCOOH (0.115 g, 0.480 mmol) to give **12** as a pale-yellow solid (yield, 83% (0.216 g)). Anal. Found: C, 50.29; H, 2.86; N, 4.92. $C_{23}H_{13}F_5N_2O_2Pd$ Calc.: C, 50.15; H, 2.38; N, 5.08%. IR: ν 1643vs, 1626vs ($\nu_{C=O}$, acetate), 1604 (bipy), 1501vs, 1059vs, 958vs (C_6F_5), 792s (C_6F_5, X-sensitive), 764vs (bipy) cm^{-1}.

[$Pd(C_6F_5)$(SPh)(phen)] (**13**). To a suspension of [$Pd(C_6F_5)$(acac–C^γ)(phen)] (**1**) (0.250 g, 0.452 mmol) in CH_2Cl_2 (25 ml) was added PhSH (47 μl, 0.460 mmol). The initial yellow suspension became orange after stirring for 6 h. The solid was filtered off and washed with 100 ml of Et_2O (**13**) (yield, 83% (0.210 g)). Anal. Found: C, 50.94; H, 2.40; N, 4.98; S, 5.15. $C_{24}H_{13}F_5N_2PdS$ Calc.: C, 51.21; H, 2.33; N, 4.97; S, 5.69%. IR: ν 1629m, 1579m (Ph), 1603m, 1582m, 1563m (phen), 1504vs, 1063vs, 952vs (C_6F_5), 847vs (phen), 794s (C_6F_5, X-sensitive) cm^{-1}.

[$Pd(C_6F_5)$(SPh)(bipy)] (**14**). Complex **14** was obtained similarly: [$Pd(C_6F_5)$(acac–C^γ)(bipy)] (**2**) (0.250 g, 0.473 mmol) reacts with PhSH (51 μl, 0.500 mmol) to give **14** as an orange solid (yield, 91% (0.232 g)). Anal. Found: C, 48.41; H, 2.60; N, 5.12; S, 5.97. $C_{22}H_{13}F_5N_2PdS$ Calc.: C, 49.04; H, 2.43; N, 5.20; S, 5.95%. IR: ν 1636m, 1578m (Ph), 1600m (bipy),

1504vs, 1061vs, 952vs (C_6F_5), 794s (C_6F_5, X-sensitive), 763vs (bipy) cm^{-1}.

[$Pd(C_6F_5)\{P(S)Ph_2\}$(phen)] (**15**). To a suspension of [$Pd(C_6F_5)$(acac–C^γ)(phen)] (**1**) (0.150 g, 0.271 mmol) in CH_2Cl_2 (20 ml) was added $HP(S)Ph_2$ (0.059 g, 0.271 mmol) and the mixture was stirred at ambient temperature for 3 h. The resulting deep-yellow solution was evaporated to dryness and the residue was treated with Et_2O (20 ml), giving a deep-yellow solid **15** (yield, 82% (0.152 g)). Anal. Found: C, 53.84; H, 2.74; N, 4.21; S, 4.73. $C_{30}H_{18}F_5N_2PPdS$ Calc.: C, 53.70; H, 2.70; N, 4.17; S, 4.78%. IR: ν 1630m (Ph), 1605m, 1595m, 1585m (phen), 1503vs, 1060vs, 950vs (C_6F_5), 845vs (phen), 790s (C_6F_5, X-sensitive), 630s, 610s, 600s, 520vs ($SPPh_2$) cm^{-1}.

[$Pd(C_6F_5)\{P(S)Ph_2\}$(bipy)] (**16**) was obtained similarly. [$Pd(C_6F_5)$(acac–C^γ)(bipy)] (**2**) (0.150 g, 0.284 mmol) reacts with $HP(S)Ph_2$ (0.062 g, 0.284 mmol) to give **15** as an orange solid (yield, 61% (0.112 g)). Anal. Found: C, 51.98; H, 3.15; N, 4.03; S, 4.88. $C_{28}H_{18}F_5N_2PPdS$ Calc.: C, 50.98; H, 3.80; N, 4.33; S, 4.95%. IR: ν 1630m (Ph), 1605m (bipy), 1500vs, 1065vs, 955vs (C_6F_5), 792s (C_6F_5, X-sensitive), 765vs (bipy), 630s, 610s, 605s, 520vs ($SPPh_2$) cm^{-1}.

4.4. Synthesis of [{Pd(μ-PPh_2)(C_6F_5)($HPPh_2$)}$_2$] (17)

To a suspension of [$Pd(C_6F_5)$(acac–C^γ)(bipy)] (**2**) (0.250 g, 0.473 mmol) in dry THF (20 ml) under dinitrogen was added $HPPh_2$ (0.172 ml, 1.0 mmol). The initial pale-yellow solid dissolved immediately and gave a deep orange solution. This solution was stirred at room temperature for 15 min and then the solvent evaporated to dryness. Addition of dry Et_2O (30 ml) and continuous stirring gave **17** as a deep-yellow solid (yield, 50% (0.154 g)). Anal. Found: C, 56.38; H, 2.94. $C_{60}H_{42}F_{10}P_4Pd_2$ Calc.: C, 55.88; H, 3.28%. IR: ν 2340m (ν_{P-H}, $HPPh_2$), 1497vs, 1055vs, 948vs (C_6F_5), 855s, 845s ($HPPh_2$), 769s (C_6F_5, X-sensitive), 505vs, 494vs, 461vs ($HPPh_2$ + μ-PPh_2) cm^{-1}.

4.5. ^1H–^1H COSY and NOESY measurements for 9 and 10

The experiments were performed at a measuring frequency of 300.13 MHz. The data were acquired into a 256 × 1024 matrix and then transformed into 1024 × 1024 points using a sine window in each dimension. For the NOESY measurements the mixing time was 400 ms.

4.6. Crystal structure determination

Suitable crystals of **12** were obtained by slow diffusion of hexane into a $CHCl_3$ solution of the crude product at room temperature. Intensity data were recorded at room temperature using graphite-monochromated Mo Kα X-radiation on a Siemens Stoe AED 2 diffractometer ($4° \leqslant 2\theta \leqslant 47°$). Accurate lattice parameters were determined from the position of 18 reflections ($24° \leqslant 2\theta \leqslant 28°$). Intensity data were corrected for Lorentz and polarization effects. Absorption corrections were based on Ψ-scan solutions (rescaled minimum and maximum transmission factors of 0.612 and 0.663, respectively).

4.7. Crystal data

$C_{24}H_{14}Cl_3F_5N_2O_2Pd$ (**12**); $M = 670.13$; orthorhombic; space group, *Pbca*; $a = 16.058$ (3) Å, $b = 15.601$ (3) Å and $c = 20.766$ (4) Å; $V = 5202.35$ Å^3; $Z = 8$; $D_c = 1.71$ g cm^{-3}; $F(000) = 2648$; $\mu = 10.8$ cm^{-1}; 3817 unique data; 3008 observed data ($(F > 4.0\sigma(F))$ for the refinement of 303 parameters; scan method, ω–θ; $w^{-1} = \sigma^2(F) + 0.0003F^2$; $R = 0.0472$; $wR = 0.0515$; $\Delta/\sigma = 0.001$; largest difference peaks 0.57 and −0.68 electrons Å^{-3}.

4.8. Structure solution and refinement

The structure was solved by the use of Patterson and Fourier methods. All calculations were carried out with SHELXTL-PLUS [20]. All non-hydrogen atoms were refined with anisotropic thermal parameters, except for the atoms of the disordered crystallization solvent. The Ph groups were refined as rigid rings. Hydrogen atoms were introduced in calculated positions and refined with a unique thermal parameter. Calculations by the full-matrix least-squares method were performed on a Micro-Vax 4000-300 computer.

5. Supplementary material available

Tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK. Structure factors are available from the authors.

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References

[1] (a) R.C. Mehrotra, R. Bohra and D.P. Gaur, *Metal β-diketonates and Allied Derivatives*, Academic Press, London, 1978;

(b) A.R. Siedle, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry* Vol. 2, Pergamon, Oxford, 1987, p. 365.
[2] S. Kawaguchi, *Coord. Chem. Rev., 70* (1986) 51.
[3] (a) J. Forniés, R. Navarro and E.P. Urriolabeitia, *J. Organomet. Chem., 390* (1990) 257; (b) J. Forniés, F. Martínez, R. Navarro and E.P. Urriolabeitia, *Polyhedron, 9* (1990) 2181; (c) J. Forniés, F. Martínez, R. Navarro, E.P. Urriolabeitia and A.J. Welch, *J. Chem. Soc., Dalton Trans.,* (1993) 2147; (d) J. Forniés, F. Martínez, R. Navarro, M. Tomás and E.P. Urriolabeitia, *J. Chem. Soc., Dalton Trans.,* (1994) 505.
[4] B. Bock, K. Flatau, H. Junge, M. Khur and H. Musso, *Angew. Chem.,Int. Edn. Engl., 10* (1971) 225.
[5] D. Gibson, *Coord. Chem. Rev., 4* (1969) 225.
[6] R.Usón and J. Forniés, *Adv. Organomet. Chem., 28* (1988) 219, and references cited therein.
[7] (a) E. Maslowsky, Jr., *Vibrational Spectra of Organometallic Compounds,* Wiley, New York, 1977, p. 437; (b) J. Casabó, J.M. Coronas and J. Sales, *Inorg. Chim. Acta, 65* (1982) L161.
[8] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 2nd edn., 1970, p. 229, and references cited therein.
[9] G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev., 33* (1980) 227.
[10] (a) D.M. Anderson, E.A.V. Ebsworth, T.A. Stephenson and M.D. Walkinshaw, *J. Chem. Soc., Dalton Trans.,* (1982) 2343; (b) E. Lindner and C.P. Krieg, *J. Organomet. Chem., 269* (1984) 65; (c) M.T. Pinillos, M.P. Jarauta, D. Carmona, L.A. Oro, M.C. Apreda, C. Foces-Foces and F.H. Cano, *J. Chem. Soc., Dalton Trans.,* (1989) 1987.
[11] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.,* (1989) S1.
[12] M.L. Tobe, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. 1, Pergamon, Oxford, 1987, p. 315, and references cited therein.
[13] P.C. Chieh, *J. Chem. Soc., Dalton Trans.,* (1972) 1643.
[14] M. Nardelli, *Comput. Chem., 7* (1983) 95.
[15] (a) A.J. Blake, R.W. Cockman, E.A.V. Ebsworth, S.G.D. Henderson, J.H. Holloway, N.J. Pilkington and D.W.H. Rankin, *Phosphorus Sulphur, 30* (1987) 143; (b) A. Handler, P. Peringer and E.P. Müller, *J. Chem. Soc., Dalton Trans.,* (1990) 3275.
[16] J. Forniés, C. Fortuño, R. Navarro, F. Martínez and A.J. Welch, *J. Organomet. Chem., 394* (1990) 643.
[17] J.B. Brandon and K.R. Dixon, *Can. J. Chem., 59* (1981) 1188.
[18] R. Usón, J. Forniés, P. Espinet, R. Navarro and C. Fortuño, *J. Chem. Soc., Dalton Trans.,* (1987) 2077.
[19] G. Peters, *J. Am. Chem. Soc., 82* (1960) 4751.
[20] G.M. Sheldrick, *SHELXT-PLUS, Software Package for the Determination of Crystal Structure, Release 4.0,* Siemens Analytical X-Ray Instruments, Madison, WI, 1990.