

Note

Cationic palladium(II)-allyl-complexes containing 2-pyridyldiphenylphosphine: X-ray crystal structure of the binuclear complex $[\text{Pd}(\eta^3\text{-2-Me-allyl})(\mu\text{-Ph}_2\text{PPy})]_2(\text{BF}_4)_2$. Detection of an intramolecular C(allyl)–H···phenyl ring π -interaction

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Abstract

Reaction of $[\text{PdCl}(\eta^3\text{-2-Me-allyl})(\text{Ph}_2\text{PPy})]$ (**1**) with AgBF_4 affords the new dinuclear cationic complex $[\text{Pd}(\eta^3\text{-2-Me-allyl})(\mu\text{-Ph}_2\text{PPy})]_2(\text{BF}_4)_2$ (**2**). The X-ray structural analysis of **2** shows that the 2-pyridyldiphenylphosphine ligands adopt a binucleating role through the P and N atoms bridging two independent palladium centres to form an eight-membered metallocyclic ring. One of the *anti* hydrogen atoms of the allyl moiety was located very close to a phenyl ring of Ph_2PPy indicating the occurrence of a CH/ π interaction. Addition of one equivalent of Ph_2PPy to complex (**2**) affords the mononuclear cationic complex $[\text{Pd}(\eta^3\text{-2-Me-allyl})(\text{Ph}_2\text{PPy})_2](\text{BF}_4)$ (**3**). © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

The chemistry of η^3 -allyl palladium complexes continues to receive much attention since they are used as catalysts or catalyst precursors in several different catalytic processes [1]. In particular, the chemistry of cationic η^3 -allyl complexes has been deeply investigated because these species are the key intermediates in asymmetric allylic alkylation [2]. In this connection, it is worth to note that even though a wide range of ancillary ligands have been used in order to direct and control the reactivity of the Pd–allyl moiety, the studies dealing with palladium–allyl complexes containing 2-pyridyldiphenylphosphine are rare [3–5] and the chemistry of these species remains almost unexplored. This lack of interest appears somehow anomalous

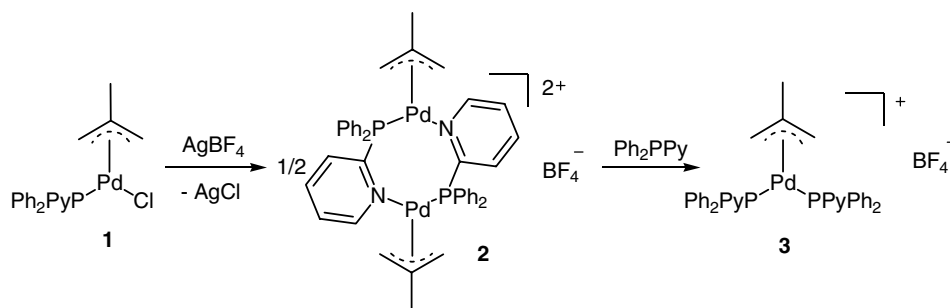
because 2-pyridyldiphenylphosphine is a potentially P–N bidentate ligand which, for instance, in combination with $\text{Pd}(\text{OAc})_2$ gives a highly efficient catalytic system for alkyne carbonylation reactions [6,7].

We wish to report here the synthesis and the characterization of a novel cationic dinuclear η^3 -allyl–palladium complex in which Ph_2PPy bridges two independent palladium atoms.

2. Results and discussion

Complex $[\text{PdCl}(\eta^3\text{-2-Me-allyl})(\text{Ph}_2\text{PPy})]$ (**1**) was synthesised by reacting $[\text{PdCl}(\eta^3\text{-2-Me-allyl})]_2$ with Ph_2PPy according to the literature [4]. Addition of one equivalent of AgBF_4 to a dichloromethane solution of **1** induces the immediate precipitation of AgCl . Dilution of the filtrate with diethyl ether leads to precipitation of the dinuclear cationic complex **2** as a pale yellow powder (Scheme 1).

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Scheme 1.

Single-crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **2**. The molecular structure of **2** is shown in Fig. 1 and selected bond lengths and angles are reported in Table 1.

The X-ray analysis of complex **2** showed that 2-pyridyldiphenylphosphine ligands adopt a binucleating role through the P and N atoms bridging two independent palladium centres to form an eight-membered metallocyclic ring. In fact, the distance between the two palladium atoms (3.944(8)) Å is out of the range found for Pd–Pd bonds [8]. Examples of dinuclear palladium species in which two Ph₂PPy ligands bridge two Pd atoms in head-to-tail [8] or in head-to-head [9] mode are known; however, to the best of our knowledge, no example of cyclic species having no palladium–palladium bond such as **2** has been previously reported. The Pd(1)–Py–P(2) and Pd(2)–Py–P(1) moieties are essentially planar, with a dihedral angle between the two planes of 35.3(1)°. The orientations around the central

metals are distorted square planar configurations with C(11)–Pd(1)–C(13), N(1)–Pd(1)–P(1) angles of 67.7(5)° and 96.5(2)°, and C(15)–Pd(2)–C(17), N(2)–Pd(2)–P(2) angles of 67.2(4)° and 98.0(2)°, respectively. The allyl ligands are bonded to the palladium atoms in asymmetric η³-fashion as indicated by the almost equal Pd(1)–C(12) (2.207(8) Å), Pd(1)–C(13) (2.214(9) Å), Pd(2)–C(16) (2.211(8) Å) and Pd(2)–C(17) (2.207(9) Å) bond lengths, which are significantly larger than the Pd(1)–C(11) (2.132(8) Å) and Pd(2)–C(15) (2.126(9) Å) ones, while the carbon–carbon bond lengths of the η³-allyl groups are nearly equal (Table 1). The two methyl groups (C(14) and C(18)) on the central atom are not in the same plane of the other three carbon atoms and are bent towards the palladium by a distance of 0.30(1) Å from the C(11)–C(12)–C(13) and C(15)–C(16)–C(17) planes, respectively, as similarly observed for other palladium(II) derivatives containing the η³-2-Me-allyl ligand [10]. The Pd(1)–P(1) and Pd(2)–P(2) distances of 2.307(2) Å and 2.295(2) Å,

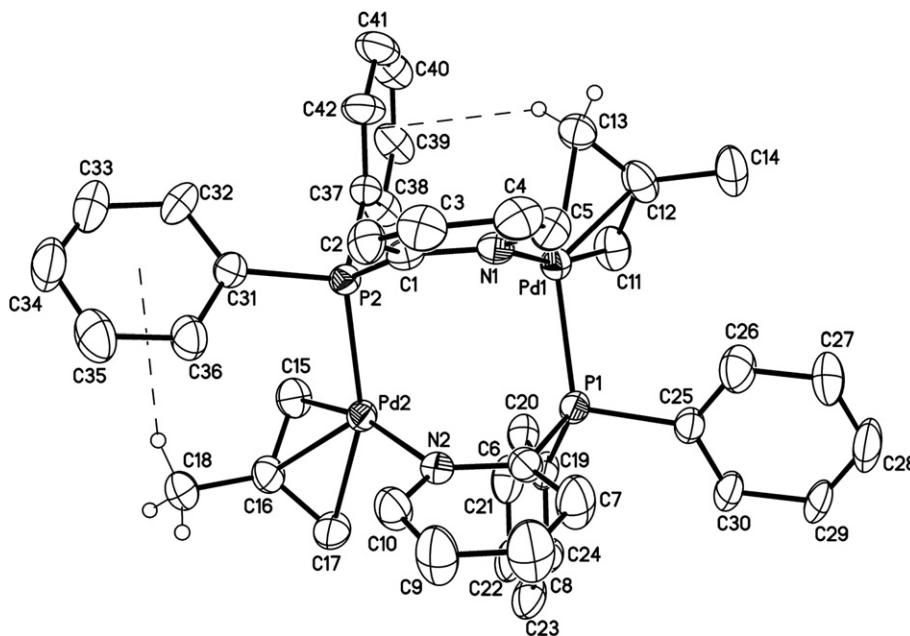


Fig. 1. Ortep view of the solid state structure of the dinuclear palladium complex **2**. The broken lines show: (i) the interaction between the *anti* allyl proton linked to C13 and the [C(37), C(38), C(39), C(40), C(41), C(42)] phenyl ring and, (ii) the close contact between the hydrogen atoms of C(18) methyl group and the [C(31), C(32), C(33), C(34), C(35), C(36)] phenyl ring.

Table 1
Selected bond distances (Å), angles (°) and non-bonding distances (Å) for [Pd₂(η³-C₄H₇)₂(Ph₂PPy)₂](BF₄)₂ (**2**)

Bond distances			
Pd(1)–P(1)	2.307(2)	Pd(2)–P(2)	2.295(2)
Pd(1)–N(1)	2.152(5)	Pd(2)–N(2)	2.164(7)
Pd(1)–C(11)	2.132(9)	Pd(2)–C(15)	2.126(9)
Pd(1)–C(12)	2.207(8)	Pd(2)–C(16)	2.211(8)
Pd(1)–C(13)	2.214(9)	Pd(2)–C(17)	2.207(9)
P(1)–C(6)	1.840(9)	P(2)–C(1)	1.850(7)
N(1)–C(1)	1.37(1)	N(2)–C(6)	1.35(1)
C(11)–C(12)	1.43(2)	C(15)–C(16)	1.43(1)
C(12)–C(13)	1.42(2)	C(16)–C(17)	1.42(1)
C(12)–C(14)	1.53(1)	C(16)–C(18)	1.51(1)
Bond angles			
P(1)–Pd(1)–N(1)	96.5(2)	P(2)–Pd(2)–N(2)	98.0(2)
P(1)–Pd(1)–C(11)	96.4(4)	P(2)–Pd(2)–C(15)	95.6(3)
P(1)–Pd(1)–C(13)	161.0(3)	P(2)–Pd(2)–C(17)	159.0(3)
N(1)–Pd(1)–C(11)	166.7(4)	N(2)–Pd(2)–C(15)	166.2(3)
N(1)–Pd(1)–C(12)	129.3(4)	N(2)–Pd(2)–C(16)	129.7(4)
N(1)–Pd(1)–C(13)	99.0(3)	N(2)–Pd(2)–C(17)	99.0(4)
C(11)–Pd(1)–C(13)	67.7(5)	C(15)–Pd(2)–C(17)	67.2(4)
Pd(1)–N(1)–C(1)	125.3(4)	Pd(2)–N(2)–C(6)	124.4(6)
N(1)–C(1)–P(2)	114.8(5)	N(2)–C(6)–P(1)	116.9(6)
C(11)–C(12)–C(13)	116.1(9)	C(15)–C(16)–C(17)	114.8(9)
C(11)–C(12)–C(14)	121.6(9)	C(15)–C(16)–C(18)	122.7(9)
C(13)–C(12)–C(14)	121.3(9)	C(17)–C(16)–C(18)	121.0(9)
Non-bonding distances			
H(13A)···Q(1) ^a	2.66(2)		
H(17A)···Q(2) ^b	2.80(6)		
H(18B)···Q(3) ^c	3.27(8)		

^a Q(1) is the centroid of the six-membered ring [C(37), C(38), C(39), C(40), C(41), C(42)].

^b Q(2) is the centroid of the six-membered ring [C(19), C(20), C(21), C(22), C(23), C(24)].

^c Q(3) is the centroid of the six-membered ring [C(31), C(32), C(33), C(34), C(35), C(36)].

respectively, are normal for phosphine–palladium complexes.

The head-to-tail coordination mode of the two P–N ligands found in the solid state is retained in solution. In fact, inspection of the ¹³C{¹H} NMR spectrum of **2** reveals that many resonances appear as second order AXX' multiplets (see for instance Fig. 2) indicating that the relevant

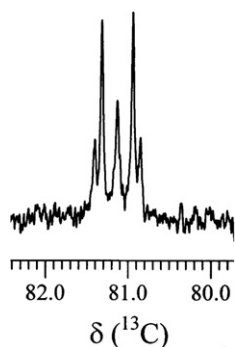


Fig. 2. Section of the ¹³C NMR spectrum of complex **2** showing the second order AXX' multiplet due to the terminal allyl carbon atom *trans* to the phosphorus atom.

carbon atoms are coupled with two chemically but not magnetically equivalent phosphorus atoms [9,11,12]. In particular, as far as the carbon atoms of the allyl moiety are concerned, it is worth to note that the signals due to the central (at δ 139.6) and the terminal carbon atoms *trans* to the phosphorus (at δ 81.1) are AXX' multiplets, while the resonance of the terminal carbon atoms *cis* to the phosphorus (at δ 59.9) is a singlet. Furthermore, the ¹³C{¹H} NMR spectrum of **2** indicates that the eight-membered ring is rigid showing two separate sets of resonances for the carbon atoms of the phenyl rings of the ligands. A detailed analysis of the heterocorrelated ¹H, ¹³C-HMQC bidimensional measurement allows to find all the aromatic proton chemical shift values, confirming the magnetic non-equivalence of the two phosphine phenyl rings (see Section 3 for a comprehensive list of chemical shifts).

The ¹H NMR spectrum of complex **2** displays, along with the signals due to 2-pyridyldiphenylphosphine, five separate resonances at δ 3.91 (m), δ 3.32 (s), δ 2.92 (s), δ 1.50 (s), and δ 1.05 (d, $J_{H,P} = 10.1$ Hz). These signals integrate in the 2:2:2:6:2 ratio with respect to the phosphine protons and are to be attributed to the protons of the methallyl moiety (see Table 2).

In particular, in the NOESY experiment, dipolar correlations with the CH₃ resonance indicate that the signals at δ 3.91 and δ 3.32 are due to the two *syn* protons of the methallyl group. Moreover, the ¹H, ¹³C-HMQC heteronuclear correlation measurement indicates that the hydrogen atoms which resonate at δ 3.91 and δ 1.05 are linked to the carbon atom resonating at δ 81.1 and that the hydrogen atoms whose signals occur at δ 3.32 and δ 2.92 are connected to the carbon resonating at δ 59.9. In keeping with this findings, the signals at δ 3.91 and δ 1.05 are to be attributed to H_c and H_d (see Fig. 3 for the allyl protons numbering scheme), the *syn* hydrogen and the *anti* hydrogen *trans* to P, respectively; the signal at δ 1.05 is an AA'X multiplet since H_d couples with both phosphorus atoms as confirmed by the fact that the resonance becomes a singlet in the ¹H{³¹P} NMR spectrum. Hence, the signals at δ 3.32 and δ 2.92 are to be attributed to H_a and H_b, the *syn* hydrogen and the *anti* hydrogen in *cis* position to phosphine ligand: the close proximity between these protons and the phosphorus atom was finally confirmed by ³¹P–¹H HOESY measurements. According to the above assignments, the ¹H NMR spectrum of **2** looks very intriguing since the resonance of H_d as well as that of the methyl protons appear markedly upfield (1.05 and 1.50 ppm, respectively) with respect to the chemical shifts usually found for this type

Table 2
Chemical shifts of allyl protons in complexes **1–3**^a

Complex	CH ₃	H _b	H _a	H _d	H _c
1	1.96	2.76	3.06	3.56	4.48
2	1.50	2.92	3.32	1.05	3.91
3	1.89	3.21	3.82	3.21	3.82

^a In CD₂Cl₂ at 298 K.

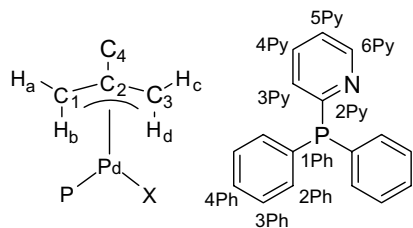


Fig. 3. Numbering scheme for the allyl moiety and Ph₂PPy.

of hydrogen atoms in other cationic [Pd(η^3 -allyl)(P–N)]⁺ complexes [13–16] (compare also with the ¹H NMR data for complexes **1** and **3** reported in Table 2). Anomalous ¹H upfield shifts generally occur when proton nuclei reside in a strongly shielding zone, e.g. over the ring currents of an aromatic moiety.

Accordingly, inspection of the crystal structure of **2** reveals that the structure of the dinuclear dication forces the allyl ligand close to the phenyl rings of the P-ligand and that the *anti*-H(13A) proton is located at a very short distance, viz., 2.66(2) Å, from the centroid of the [C(37), C(38), C(39), C(40), C(41), C(42)] ring (see Fig. 1). Similarly, the distance between H(17A) and the centroid of the [C(19), C(20), C(21), C(22), C(23), C(24)] ring is 2.80(6) Å. Such short distances are significantly smaller than the sum of the relevant van der Waals radii [17]. In the last decade several examples of such close CH/ π contacts have been reported in organometallic and coordination chemistry and it is generally accepted that these interactions are attractive, albeit weak [17]. Although this kind of interaction is not rare in organometallic compounds [17], the present case is worthy of note because it involves a terminal hydrogen atom of an allyl moiety.

The close proximity of H_d to the phenyl ring found in the solid state structure is retained in solution as confirmed by its above-mentioned ring current induced anomalous chemical shift and also by the NOESY experiment in which the *anti* proton H_d exhibits a NOE contact with the protons of the phenyl at δ 7.655.

A very similar situation was found [18] in the case of *anti*-homo-bimetallic complexes of 2,7-dimethyl-*as*-indacene-diide with two Rh(cyclo-octa-1,5-diene)₂ or Ir(cyclo-octa-1,5-diene)₂ groups, where an olefinic proton of the coordinated cycloolefin is located at about 2.5–2.7 Å above an arene ring and its resonance undergoes a comparable upfield shift in the ¹H NMR spectrum.

The anomalous upfield shift of the resonance of the methyl protons of the methallyl units may be similarly justified taking into account the ring current effect due to the proximity of the CH₃ group bearing the H(18A), H(18B) and H(18C) hydrogens to the centroid of the [C(31), C(32), C(33), C(34), C(35), C(36)] phenyl ring found in the crystal structure (Fig. 1), e.g. this distance for H(18B) is 3.27(8) Å. Accordingly, a NOE contact was observed between the methyl resonance and the aromatic protons at δ 7.410.

In order to ascertain the stability of the eight-membered ring, complex **2** was treated with one equivalent of 2-pyridyldiphenylphosphine. The reaction leads to selective breaking of the palladium–nitrogen bond affording in almost quantitative yield the cationic complex **3** in which the two Ph₂PPy behave as monodentate P-donors (Scheme 1). In fact, in the proton allyl region, the ¹H NMR spectrum of **3** presents only three separate and sharp resonances centered at δ 1.89 (s, CH₃), δ 3.21 (m, allyl *anti* protons) and δ 3.82 (br s, allyl *syn* protons) in keeping with the presence of a symmetry plane bisecting the allyl moiety. The equivalence of the two phosphorus atoms is confirmed by the ³¹P NMR spectrum of **3** which consists of a singlet at δ 26.4. Conclusive evidence for the symmetrical structure of **3** is given by the ¹³C NMR spectrum where the terminal allyl carbon atoms appear as the A part of an AXX' spin system, while the central carbon atom is an 1:2:1 triplet owing to the coupling with two equivalent phosphorus atoms.

The allyl moiety of complex **3** appears to be rigid and no sign of dynamic behaviour was detected by NMR spectroscopy at room temperature.

3. Experimental

Reactions were performed under argon atmosphere using standard Schlenk techniques. Solvents (J.T. Baker) were purified as described in the literature [19]. 2-Pyridyldiphenylphosphine was purchased from Aldrich. [PdCl(η^3 -2-Me-allyl)]₂ [20] and [PdCl(η^3 -2-Me-allyl)(Ph₂PPy)] [4] were prepared according to the literature.

¹H, ¹³C and ³¹P NMR spectra were obtained as CDCl₃ or CD₂Cl₂ solutions on a Bruker DRX-400 spectrometer operating at 400.13, 100.61 and 161.98 MHz, respectively, and equipped with a BVT2000 temperature controller. The chemical shift values are given in δ units with reference to internal Me₄Si for ¹H and ¹³C, and to external 85% H₃PO₄ for ³¹P. Suitable integral values for the proton spectra were obtained by a pre-scan delay of 10 s to ensure a complete relaxation for all the resonances. The proton assignments were performed by standard chemical shift correlations as well as by 2D COSY, TOCSY, and NOESY experiments. The ¹³C chemical shift values were assigned through 2D-heteronuclear correlation experiments (heteronuclear multiple quantum correlation, HMQC, with bilinear rotation-decoupling, BIRD, sequence [21] and quadrature along F1 achieved using the time-proportional receiver phase incrementation, TPPI, method [22] for the H-bonded carbon atoms, and heteronuclear multiple bond correlation, HMBC [23] for the other ¹³C nuclei).

3.1. [PdCl(η^3 -2-CH₃-C₃H₄)(Ph₂PPy)] (**1**)

A solution of 2-pyridyldiphenylphosphine (670 mg, 2.56 mmol) in dichloromethane (20 mL) was added dropwise to a solution of [Pd(η^3 -2-CH₃-C₃H₄)Cl]₂ (500 mg, 1.28 mmol) in dichloromethane (20 mL). The resulting

solution was stirred for 1 h, then concentrated under reduced pressure. Addition of diethyl ether caused the precipitation of complex **1** as a white solid (1.10 g, 95% yield). ^1H NMR (CD_2Cl_2): $\delta = 1.96$ (s, 3H, CH_3), 2.76 (s, 1H, H_b *anti*), 3.06 (s, 1H, H_a *syn*), 3.56 (d, 1H, H_d *anti*, $J_{\text{H,P}} = 9.9$ Hz), 4.48 (m, 1H, H_c *syn*, $J_{\text{H,P}} = 6.7$ Hz), 7.34 (m, 1H, H-5Py), 7.36–7.55 (m, 6H, arom), 7.64–7.80 (m, 6H, arom), 8.75 (m, 1H, H-6Py, $J_{\text{H-5Py,H-6Py}} = 5.0$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 26.0$ (s). ^{13}C NMR (CDCl_3) $\delta = 157.7$ (d, C-2Py, $J_{\text{C,P}} = 61.5$ Hz), 150.2 (d, C-6Py, $J_{\text{C,P}} = 14.8$ Hz), 135.9 (d, C-4Py, $J_{\text{C,P}} = 8.7$ Hz), 134.3 (d, C-2Ph, $J_{\text{C,P}} = 13.2$ Hz), 132.9 (d, C-2all, $J_{\text{C,P}} = 4.9$ Hz), 132.0 (d, C-1Ph, $J_{\text{C,P}} = 42.3$ Hz), 130.4 (s, C-4Ph), 130.0 (d, C-3Py, $J_{\text{C,P}} = 25.2$ Hz), 128.5 (d, C-3Ph, $J_{\text{C,P}} = 10.4$ Hz), 123.8 (s, C-5Py), 78.0 (d, C-3all, $J_{\text{C,P}} = 32.4$ Hz), 61.3 (s, C-1all), 23.2 (s, C-4all).

3.2. $[\text{Pd}_2(\eta^3\text{-}2\text{-CH}_3\text{-C}_3\text{H}_4)_2(\mu\text{-Ph}_2\text{PPy})_2](\text{BF}_4)_2$ (**2**)

To a solution of **1** (500 mg, 1.10 mmol) in dichloromethane (20 mL) was added dropwise a solution of AgBF_4 (210 mg, 1.10 mmol) in CH_3OH (5 mL). The resulting suspension was stirred for 1 h at room temperature, then filtered to eliminate AgCl . Addition of diethyl ether to the filtrate caused the precipitation of complex **2** as a pale yellow solid (512 mg, yield 92%). ^1H NMR (CD_2Cl_2): $\delta = 1.05$ (d, 2H, H_d *anti*, $J_{\text{H,P}} = 10.1$ Hz), 1.50 (s, 6H, CH_3), 2.92 (s, 2 H_b *anti*), 3.32 (m broad, 2 H_a *syn*), 3.91 (m, 2 H_c *syn*, $J_{\text{H,P}} = 2.8$ Hz), 7.31–7.48 (m, 3H, arom), 7.50–7.65 (m, 4H, arom), 7.68–7.87 (m, 4H, arom), 9.00 (d, 2H, H-6Py, $J_{\text{H-5Py,H-6Py}} = 5.1$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 27.27$ (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 158.2$ (AA'X m, 1C, C-2Py), 155.6 (AA'X m, 1C, C-6Py), 139.6 (AA'X m, 1C, C-2all), 139.1 (AA'X m, 1C, C-4Py), 137.0 (AA'X m, 2C, C-2Ph), 134.8 (AA'X m, 1C, C-4Ph), 132.8 (AA'X m, 2C, C-2Ph), 132.4 (AA'X m, 1C, C-4Ph), 131.3 (AA'X m, 2C, C-3Ph), 131.1 (d, 1C, $J_{\text{C,P}} = 5$ Hz, C-3Py), 130.5 (AA'X m, 2C, C-3Ph), 129.8 (AA'X m, 1C, C-1Ph), 126.7 (s, 1C, C-5Py), 125.7 (AA'X m, 1C, C-1Ph), 81.1 (AA'X m, 1C, C-3all), 59.9 (s, 1C, C-1all), 22.3 (s, 1C, C-4all). Anal. Calc. for $\text{C}_{42}\text{H}_{42}\text{B}_2\text{F}_8\text{N}_2\text{P}_2\text{Pd}_2$: C, 49.30; H, 4.14. Found: C, 49.10; H, 4.10%.

3.3. $[\text{Pd}(\eta^3\text{-}2\text{-CH}_3\text{-C}_3\text{H}_4)(\text{Ph}_2\text{PPy})_2]^+(\text{BF}_4)^-$ (**3**)

A solution of 2-pyridyldiphenylphosphine (307 mg, 1.17 mmol) in dichloromethane (20 mL) was added to a solution of **2** (600 mg, 0.58 mmol) in dichloromethane (30 mL). The resulting solution was stirred for 1 h at room temperature then concentrated to small volume under reduced pressure. Addition of diethyl ether afforded complex **3** as a pale yellow solid (720 mg, 80% yield). ^1H NMR (CD_2Cl_2): $\delta = 1.89$ (s, 6H, CH_3), 3.21 (AA'XX' m, 4H, H_{anti}), 3.82 (br s, 4H, H_{syn}), 7.06 (d, 2H, H-3Py, $J_{\text{H-3Py,H-4Py}} = 8.0$ Hz), 7.20 (m, 2H, H-5Py), 7.28–7.54 (m, 22 H_{arom}), 8.44 (d, 2H, H-6Py, $J_{\text{H-5Py,H-6Py}} = 4.5$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 26.4$ (s). $^{13}\text{C}\{^1\text{H}\}$ NMR

(CD_2Cl_2): $\delta = 156.9$ (AA'X m, 2C, C-2Py), 150.6 (AA'X m, 2C, C-6Py), 138.2 (t, 1C, C-2all, $J_{\text{C,P}} = 4.9$ Hz), 136.6 (AA'X m, 2C, C-4Py), 134.0 (AA'X m, 8C, C-2Ph), 131.4 (d, 4C, C-4Ph, $J_{\text{C,P}} = 9.9$ Hz), 130.9 (AA'X m, 4C, C-1Ph), 129.1 (AA'X m, 8C, C-3Ph), 128.0 (AA'X m, 2C, C-3Py), 124.8 (s, 2C, C-5Py), 76.91 (AA'X m, 2C, C-1all and C-3all), 23.4 (C-4all). Anal. Calc. for $\text{C}_{38}\text{H}_{36}\text{BF}_4\text{N}_2\text{P}_2\text{Pd}$: C, 58.82; H, 4.68. Found: C, 58.79; H, 4.62%.

3.4. X-ray measurements and structure determination

Crystal data for $\{[\text{Pd}_2(\eta^3\text{-C}_4\text{H}_7)_2(\text{Ph}_2\text{PPy})_2]^{2+}[(\text{BF}_4)_2]^{2-}\} \cdot \text{H}_2\text{O}$ (**2**). $\text{C}_{42}\text{H}_{42}\text{P}_2\text{N}_2\text{B}_2\text{F}_8\text{OPd}_2$: $M = 1041.18$, monoclinic, space group Cc , $a = 11.501(2)$ Å, $b = 26.360(3)$ Å, $c = 16.581(3)$ Å, $\beta = 92.42(3)^\circ$, $V = 5022(1)$ Å³, $Z = 4$, $D_c = 1.374$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu(\text{Mo K}\alpha) = 8.40$ mm⁻¹, $F(000) = 2088$.

Crystal was lodged in Lindemann glass capillary and centered on a four circle Philips PW1100 diffractometer using graphite monochromated Mo K α radiation (0.71073 Å), following the standard procedures at room temperature. All intensities were corrected for Lorentz polarization and absorption [24].

The structures were solved by standard direct methods [25]. Refinement was carried out by full-matrix least-squares procedures (based on F_o^2) using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions in their described geometries and during refinement were allowed to ride on the attached carbon atoms with fixed isotropic thermal parameters ($1.2U_{\text{equiv}}$) of the parent carbon atom. The Flack parameters [26] have been refined for the structure. For a total of 533 parameters, $wR' = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.128$, $S = 1.182$, and conventional $R = 0.047$, based on the F values of 6023 reflections having $I \geq 2 \sigma(I)$. Structure refinement and final geometrical calculations were carried out with SHELXL-97 [27] program, implemented in the WinGX package [28].

4. Supplementary material

CCDC 635915 contains the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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