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# Assembly of cyclopalladated units: synthesis, characterisation, X-ray crystal structure and study of the reactivity of the tetrametallic cyclopalladated complex $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-O)}\}]_4 \cdot 2\text{CHCl}_3$

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## Abstract

The reaction of the equimolar amounts of the Schiff base  $\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-OH)}$  (**1**) and palladium(II) acetate in refluxing methanol for 2 h produces  $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-O)}\}]_4 \cdot 2\text{CHCl}_3$  (**2**). The X-ray crystal structure of **2**·2CHCl<sub>3</sub> reveals that it contains a central non-planar eight-membered ring “Pd<sub>4</sub>O<sub>4</sub>” formed by the self-assembly of four cyclopalladated fragments in which the ligand behaves as a [C, N, O]<sup>2-</sup> terdentate ligand and the oxygen atoms act as bridges between the monomeric units. The reaction of **2** with triphenylphosphine or 1,1'-bis(diphenylphosphino)ferrocene (dppf) produces the opening of the central “Pd<sub>4</sub>O<sub>4</sub>” core and the formation of the monomeric derivative  $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-O)}\}(\text{PPh}_3)]$  (**3**)·CH<sub>2</sub>Cl<sub>2</sub> and the trimetallic complex  $[\{\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-O)}\}]_2(\mu\text{-dppf})]$  (**4**), respectively. In **3** and **4**, the ligand also behaves as a dianionic and terdentate [C, N, O]<sup>2-</sup> group, thus indicating that the Pd–O bond exhibits remarkable stability. The X-ray crystal structure of **3**·CH<sub>2</sub>Cl<sub>2</sub> confirmed the mode of binding of the Schiff base and a *trans* arrangement between the imine nitrogen and the PPh<sub>3</sub> ligand. A comparative study of the spectrochemical properties of compounds **2–4** is also reported.

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**Keywords:** X-ray crystal structures; Cyclopalladated complexes; Self-assembly

## 1. Introduction

The crystal engineering of coordination networks and of metal-based supramolecular architectures has attracted great interest in the late years [1]. In these cases, the formation of the final macromolecular array is usually achieved either using spacers (i.e. bridging ligands or metal-containing fragments) to connect several building blocks or by the self-assembly of a given number of monomeric coordination complexes [2]. Among all the examples reported so far those containing square-planar palladium(II) units have attracted special

attention due to their potential applications in different areas, including their ability as molecular receptors [3]. However, examples involving palladium(II) blocks containing a  $\sigma(\text{Pd-C})$  bond are not so common. A few articles focused on the use of bridging bidentate ligands have been described [4,5], but examples of self-assembly of cyclometallated units are scarce [5]. A few molecular polygons and boxes having Pd<sup>II</sup> and bidentate  $\{(C, N)^-$  or  $(C, O)^-\}$  or terdentate  $\{(C, N, N')^-, (N, C, N)^-, (C, N, S)^-\}$  ligands are known [5], but as far as we know, self-assembly of palladacyclic arrays with  $(C, N, O)^{2-}$  ligands are not so common [6,7]. Vila and coworkers [6] have recently postulated the formation of the polynuclear compound  $[\text{Pd}\{2,3,4\text{-(MeO)}_3\text{C}_6\text{H-CH=N-C}_6\text{H}_3\text{-2-(O)-4-R}\}]_n$  (with R = H or Me) arising from the self-assembly of cyclopalladated units, but to the best of our knowledge, only one tetrametallic complex

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containing four “Pd(C, N, O)” fragments has been structurally characterised by X-ray diffraction [7].

Here we provide conclusive evidence of the formation of the tetranuclear palladium(II) complex  $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-O)}\}]_4 \cdot 2\text{CHCl}_3$  (**2**) formed by self-assembly of four palladacycles arising from the activation of the  $\sigma(\text{C-H})$  and  $\sigma(\text{O-H})$  bonds of  $\text{C}_6\text{H}_5\text{-CH=N-(C}_6\text{H}_4\text{-2-OH)}$  (**1**). The reactivity of **2** with the phosphines: triphenylphosphine ( $\text{PPh}_3$ ) or 1,1'-bis(diphenylphosphino)ferrocene ( $\text{dppf}$ ) is also studied and reveals the low lability of the terminal Pd–O bond in **2**. A comparative study of the spectrochemical properties of **2** and **3** is also reported.

## 2. Results and discussion

Ligand **1** was prepared by condensation between benzaldehyde and  $\text{H}_2\text{N-C}_6\text{H}_4\text{-2-OH}$  using the general method described for the preparation of organic ketimines [8]. Its characterisation data (see Section 3) agreed with the proposed formulae.

Treatment of equimolar amounts of **1** and  $\text{Pd}(\text{AcO})_2$  in refluxing methanol for 2 h, followed by the removal of small amounts of the Pd(0) formed, produced  $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-O)}\}]_4 \cdot 2\text{CHCl}_3$  (**2**) (Scheme 1). Its elemental analyses (see Section 3) were consistent with the proposed formulae. The  $\text{FAB}^+$  mass spectrum of **2** showed a peak at  $m/z = 1206$ , which corresponds to  $[\{\text{M-2}(\text{CHCl}_3)\}]^+$  cation. In the MALDI-TOF spectrum, the presence of two additional peaks at  $m/z = 905$   $\{[\{\text{M-2}(\text{CHCl}_3)\}3/4]^+\}$  and  $604$   $\{[\{\text{M-2}(\text{CHCl}_3)\}2]^+\}$  suggested the fragmentation of the tetrametallic array and the formation of trimeric and dimeric units, respectively.

This compound has also been characterised by X-ray diffraction. Its molecular structure is shown in Fig. 1 and a selection of bond lengths and angles is presented in Table 1.

The crystal structure of  $2 \cdot 2\text{CHCl}_3$  confirmed the presence of the tetranuclear complex  $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-O)}\}]_4$  and  $\text{CHCl}_3$  (in a 1:2 molar ratio). The tetramer (Fig. 1A) can be visualised as formed by four nearly planar “[Pd{C<sub>6</sub>H<sub>4</sub>-CH=N-(C<sub>6</sub>H<sub>4</sub>-2-O)}]” fragments, which share the oxygen atom with the neighbouring unit, leading to a central non-planar “Pd<sub>4</sub>O<sub>4</sub>” eight-membered ring (Fig. 1B), in which all the Pd···Pd distances are greater than the sum of the van der Waals radii (3.22 Å) [9], thus suggesting that there is no direct interaction between the Pd<sup>II</sup> atoms.

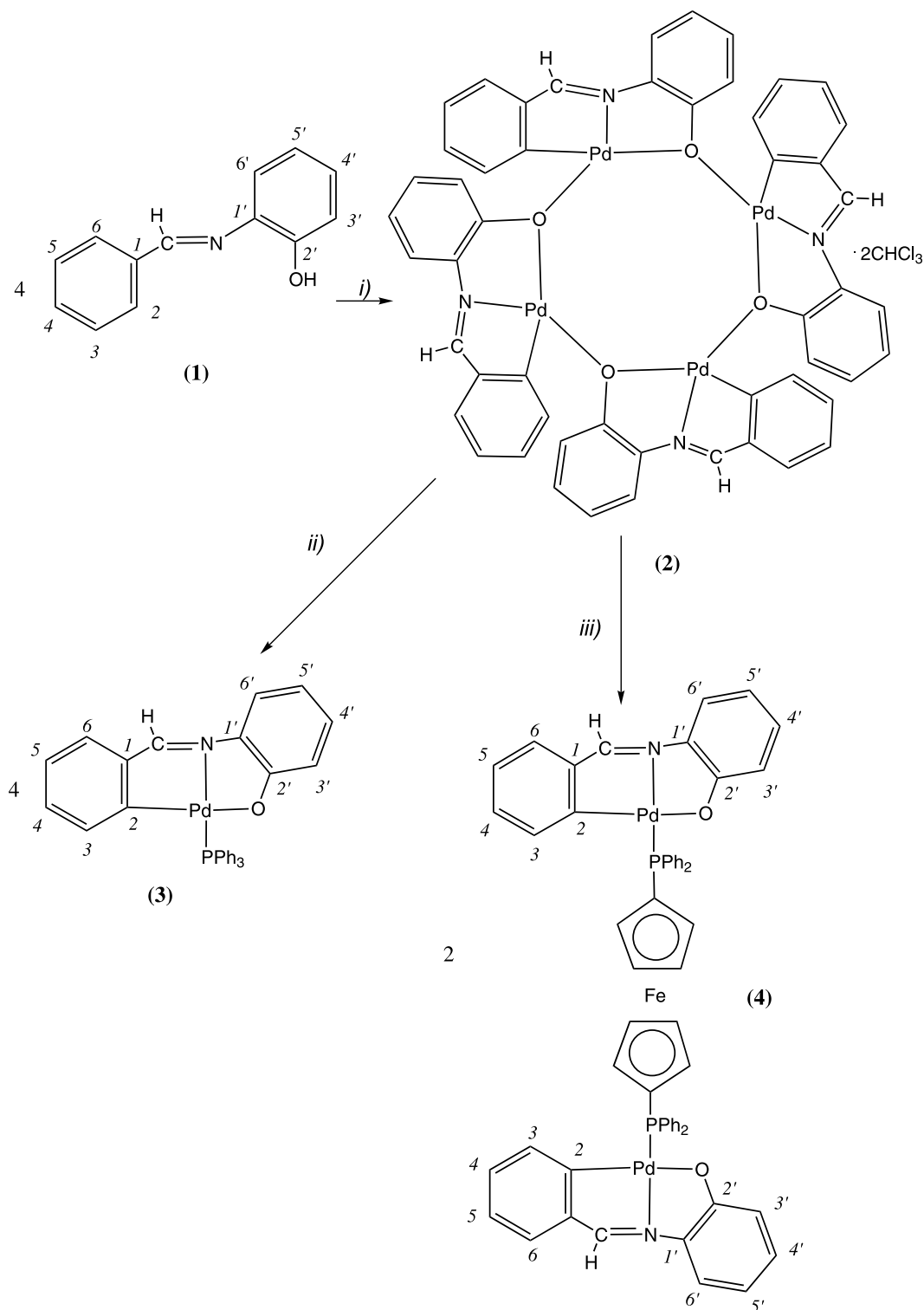
In the tetramer, each palladium is bound to the two heteroatoms (O and N) of the ligand and to the carbon adjacent to the imine group, the remaining coordination site being occupied by the oxygen atom of a neighbouring and nearly orthogonal “[Pd{C<sub>6</sub>H<sub>4</sub>-CH=N-(C<sub>6</sub>H<sub>4</sub>-2-O)}]” unit. A slightly distorted square-planar environ-

ment is the result.<sup>1</sup> As a consequence of this distribution of groups, two of the monomers, with a head-to-tail orientation, are parallel and nearly orthogonal to the other pair of “[Pd{C<sub>6</sub>H<sub>4</sub>-CH=N-(C<sub>6</sub>H<sub>4</sub>-2-O)}]” moieties which have a similar arrangement. The distances between the aryl rings belonging to each one of the “quasi-parallel” units vary from 3.79 to 3.88 Å. These values fall in the range expected for van der Waals interactions, and the shortest O···O separation in the tetramer is 3.156 Å. These findings indicate that the free space available for a host molecule to enter into the inner part of the tetramer is small and consequently, the  $\text{CHCl}_3$  solvation molecules are not included in the central part of the tetramer.

Despite the complexity of the tetrameric array of  $2 \cdot 2\text{CHCl}_3$  in the solid state, its <sup>1</sup>H-NMR spectrum at 298 K showed only nine signals, which could be easily identified with the use of two-dimensional heteronuclear <sup>1</sup>H- and <sup>13</sup>C-NMR experiments. These findings could be indicative that the tetramer is fluxional or dissociates in solution. In a first attempt to clarify this point, proton-NMR spectra of  $2 \cdot 2\text{CHCl}_3$  were registered in the range 223–298 K using a Bruker Avance 600 MHz instrument (Fig. 2A–D). In general terms, the spectra obtained at 278, 243 and 223 K (Fig. 2B–D) showed also nine signals and only tiny differences in their chemical shifts and their resolution were detected. Similar findings were also shown when the spectra were recorded with a Varian 300 MHz instrument in the same range of temperatures. The ES-mass spectrum of  $2 \cdot 2\text{CHCl}_3$  showed a peak at  $m/z = 603$  which could be indicative of the presence of a dimeric unit in solution.

Besides that, as can be easily seen in Fig. 2C and D, for the lowest temperatures (248 and 223 K) the presence of weak and poorly resolved additional signals was also detected in the <sup>1</sup>H-NMR spectra. This may be indicative of the presence of small amounts of another specie in solution. However, the low intensity of the signals and their poor resolution did not allow us to

<sup>1</sup> The least-squares equation of the plane defined by the atoms O(11), O(41), N(12) and C(113) is  $(0.5881)\text{XO} + (0.8023)\text{YO} + (-0.0278)\text{ZO} = 1.7048$  (deviations from the plane are as follows: O(11),  $-0.083$  Å; O(41),  $0.0720$  Å; N(12),  $0.1040$  Å; and C(113),  $-0.0929$  Å). The least-squares equation of the plane defined by the atoms O(11), O(21), N(21) and C(213) is  $(-0.2282)\text{XO} + (0.2740)\text{YO} + (0.9174)\text{ZO} = 3.2970$  (deviations from the plane are as follows: O(11),  $-0.017$  Å; O(21),  $-0.020$  Å; N(21),  $0.024$  Å; and C(213),  $-0.022$  Å). The least-squares equation of the plane defined by the atoms O(21), O(31), N(31) and C(313) is  $(0.4836)\text{XO} + (0.8738)\text{YO} + (-0.0508)\text{ZO} = 4.9090$  (deviations from the plane are as follows: O(21),  $-0.042$  Å; O(31),  $0.047$  Å; N(31),  $-0.058$  Å; and C(113),  $0.053$  Å). The least-squares equation of the plane defined by the atoms O(31), O(41), N(41) and C(413) is  $(-0.1875)\text{XO} + (0.2200)\text{YO} + (0.9573)\text{ZO} = 6.4110$  (deviations from the plane are as follows: O(31),  $-0.006$  Å; O(41),  $0.007$  Å; N(41),  $-0.009$  Å; and C(413),  $0.0079$  Å).



Scheme 1. i) 4 Pd(OAc)<sub>2</sub>, in refluxing methanol, 2h. ii) 4 PPh<sub>3</sub> in CDCl<sub>3</sub>. iii) dppf in CH<sub>2</sub>Cl<sub>2</sub>

clarify the nature of the minor component present in solution.

The addition of PPh<sub>3</sub> to a CHCl<sub>3</sub> solution of 2·2CHCl<sub>3</sub> gave [Pd{C<sub>6</sub>H<sub>4</sub>-CH=N-(C<sub>6</sub>H<sub>4</sub>-2-O)}(PPh<sub>3</sub>)] (3)·CH<sub>2</sub>Cl<sub>2</sub> (Scheme 1). Its <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum showed a singlet at 34.39 ppm, which is consistent with a

*cis* arrangement of the PPh<sub>3</sub> and the metallated carbon. This is the typical arrangement of groups found in related palladacycles derived from imines [10] due to the transphobia effect [11]. When larger excesses of PPh<sub>3</sub> were used (PPh<sub>3</sub>: Pd molar ratio in the range 4–12) no evidence of the cleavage of the Pd–O bond was detected

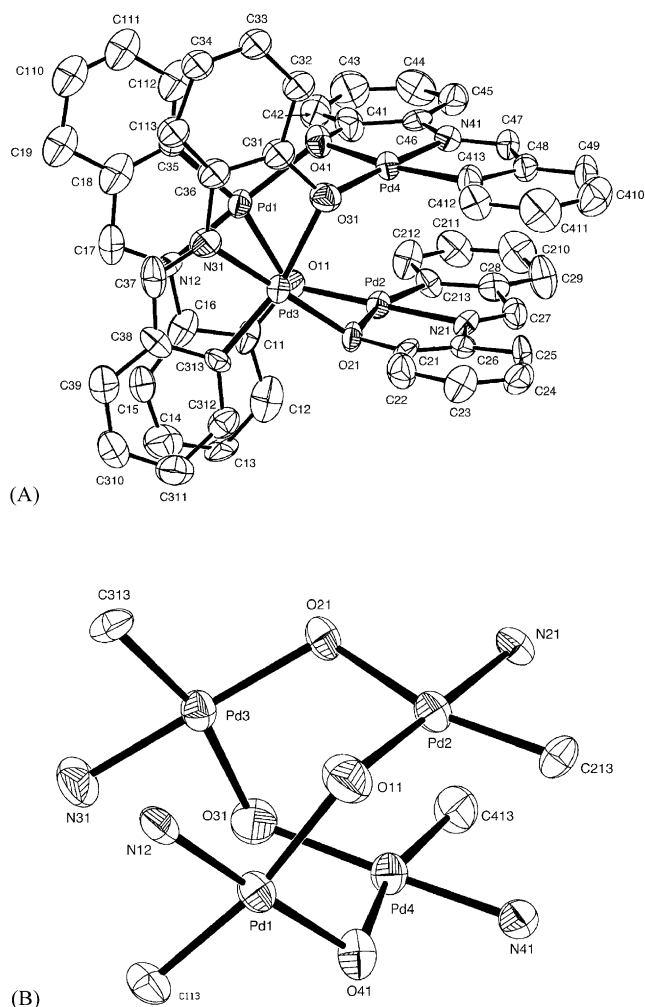


Fig. 1. (A) Molecular structure of the tetrametallic array (**2**) and atom labelling scheme. (B) A schematic view of the central “Pd<sub>4</sub>O<sub>4</sub>” core. Hydrogen atoms have been omitted for clarity.

by <sup>1</sup>H- and <sup>31</sup>P{<sup>1</sup>H}-NMR, thus suggesting a remarkable stability of the Pd–O bond.

The molecular structure of **3** is shown in Fig. 3 and a selection of bond lengths and angles is presented in Table 2.

The structure contains molecules of [Pd{C<sub>6</sub>H<sub>4</sub>–CH=N–(C<sub>6</sub>H<sub>4</sub>–2–O)}(PPh<sub>3</sub>)] and CH<sub>2</sub>Cl<sub>2</sub> in a 1:1 molar ratio. In each one of the palladium(II)-containing molecules the metal is in a slightly distorted square-planar environment,<sup>2</sup> bound to the imine nitrogen, N, the oxygen, O, and the C(13) atom of the ligand, thus confirming the [C, N, O]<sup>2-</sup> mode of binding of the imine. The remaining coordination site is occupied by the phosphorus of PPh<sub>3</sub>. The P–Pd–C(13) angle (81.4°) indicates that the metallated carbon and the PPh<sub>3</sub> are in

<sup>2</sup> The least-squares equation of the plane defined by the atoms C(13), N, O and P is (–0.4707)XO + (0.8614)YO + (–0.1909)ZO = –5.6591 (deviations from the plane are as follows: C(13), 0.026 Å; N, –0.030 Å; O, 0.024 Å and P, –0.020 Å).

Table 1  
Selected bond lengths (Å) and angles (°) for **2**·2CHCl<sub>3</sub> (standard deviation parameters are given in parenthesis)

Selected bond lengths	
Pd(1)–N(12)	1.924(9)
Pd(1)–O(41)	2.058(6)
Pd(2)–C(213)	1.976(9)
Pd(2)–O(11)	2.023(8)
Pd(3)–C(313)	1.910(11)
Pd(3)–O(31)	2.029(7)
Pd(4)–N(41)	1.943(7)
Pd(4)–O(31)	2.132(11)
O(11)–C(11)	1.348(14)
O(31)–C(31)	1.396(14)
N(12)–C(17)	1.331(14)
N(32)–C(37)	1.294(13)
Pd(1)–C(113)	1.939(14)
Pd–O(11)	2.149(9)
Pd(2)–N(21)	2.004(7)
Pd(2)–O(21)	2.191(11)
Pd(3)–N(31)	1.973(10)
Pd(3)–O(31)	2.131(7)
Pd(4)–C(413)	1.977(10)
Pd(4)–O(41)	1.943(7)
O(21)–C(21)	1.311(11)
O(41)–C(41)	1.336(12)
N(22)–C(27)	1.305(11)
N(41)–C(47)	1.261(11)
Selected bond angles	
O(41)–Pd(1)–O(11)	97.2(3)
O(21)–Pd(3)–O(31)	82.1(4)
O(11)–Pd(1)–N(12)	83.1(5)
O(31)–Pd(3)–N(31)	82.1(14)
N(12)–Pd(1)–C(113)	80.5(5)
N(31)–Pd(3)–C(313)	80.7(5)
O(11)–Pd(2)–O(21)	99.5(3)
O(31)–Pd(4)–O(41)	98.4(3)
O(21)–Pd(2)–N(21)	79.3(3)
O(41)–Pd(4)–N(41)	81.9(3)
N(21)–Pd(2)–C(213)	83.6(3)
N(41)–Pd(4)–C(413)	82.5(4)

a *cis* arrangement in good agreement with the results obtained from the NMR studies.

The Pd–C(13) bond length (1.938(8) Å) does not differ significantly from the average value found for **2** (1.95(3) Å) and agrees with the values reported for most of cyclopalladated compounds containing bidentate [C, N]<sup>–</sup> or terdentate [C, N, X]<sup>–</sup> (X = N, S or P) ligands [12], while the Pd–N bond in **3** is (1.995(6) Å) slightly larger, if significant, than in the tetranuclear derivative (average value: 1.961(3) Å). This difference could be related to the different influence of the ligand in the *trans*-position (an oxygen in **2** and a phosphorous in **3**) [13].

In the crystal structures of **2**·2CHCl<sub>3</sub> and **3**·CH<sub>2</sub>Cl<sub>2</sub>, the aryl rings of the Schiff base are planar and their main planes deviate by ca. 1.6°, 1.1°, 4.4° and 4.2° (in **2**) and by 3.1° (in **3**) from co-planarity.

In the unit cell of **3**·CH<sub>2</sub>Cl<sub>2</sub>, the [Pd{C<sub>6</sub>H<sub>4</sub>–CH=N–(C<sub>6</sub>H<sub>4</sub>–2–O)}(PPh<sub>3</sub>)] molecules are packed in such a

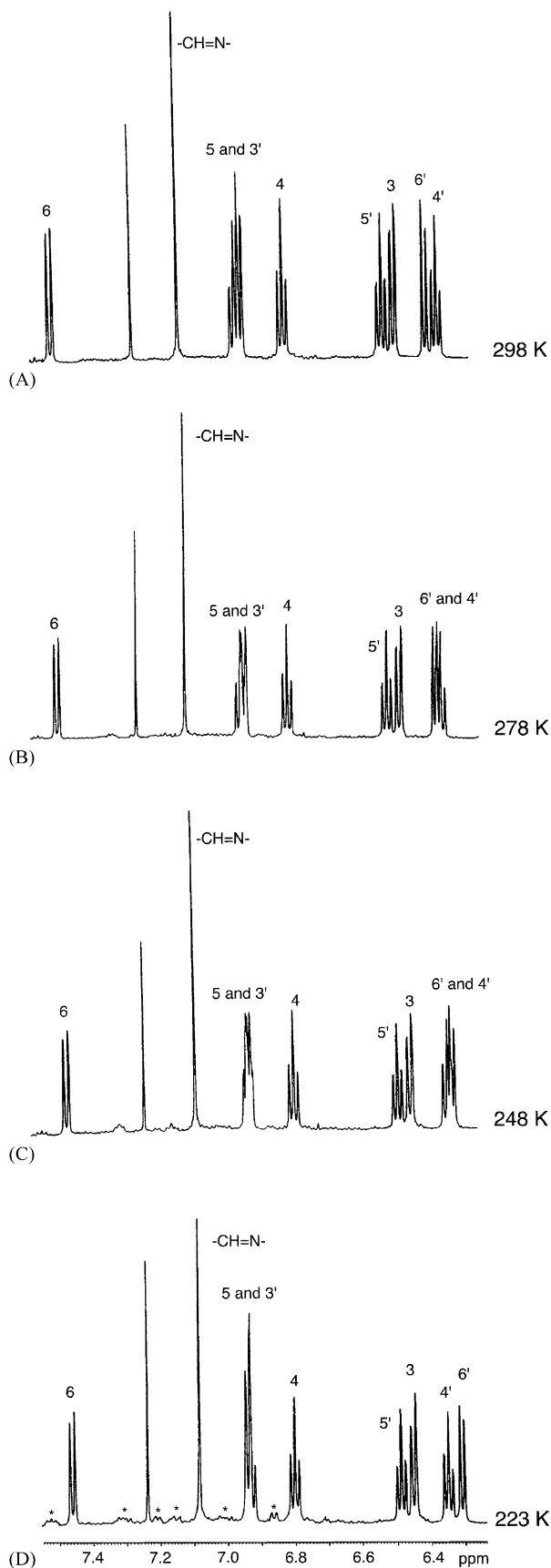


Fig. 2

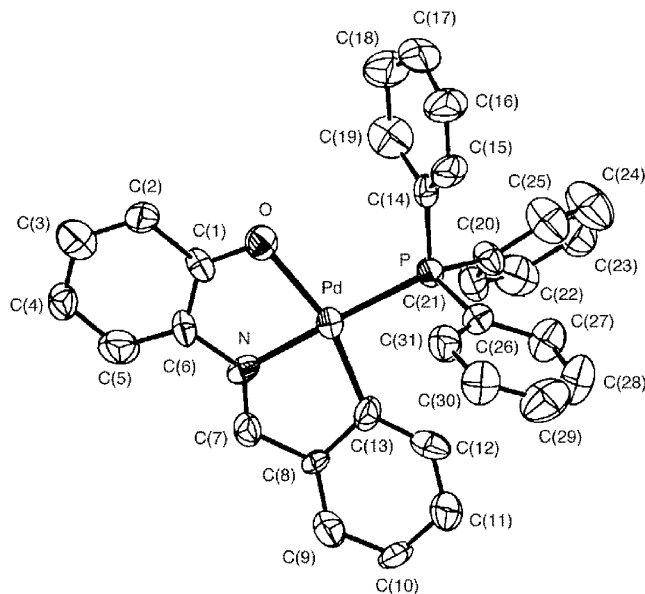


Fig. 3. Molecular structure of **3** and atom numbering scheme.  $\text{CH}_2\text{Cl}_2$  molecule as well as the hydrogen atoms have been omitted for clarity.

way that the distance between the  $\text{C}(30)\text{--H}(30\text{A})$  bond of one molecule and the phenyl ring defined by the set of atoms  $\text{C}(8)\text{--C}(13)$  (2.744 Å) of a neighbouring unit suggests, according to the literature [14], the existence of a  $\text{C--H}\cdots\pi$  interaction; a similar type of interaction is also found between the  $\text{C}(32)\text{--H}(32\text{A})$  bond of the  $\text{CH}_2\text{Cl}_2$  molecule and the  $\text{C}(14)\text{--C}(18)$  ring of the  $\text{PPh}_3$  ligand. Despite this arrangement of molecular units, the shortest intermolecular  $\text{Pd}\cdots\text{Pd}$  separation in **2** (7.10 Å) clearly exceeds the sum of their van der Waals radii [9], thus suggesting that there is no direct interaction between the two metals.

Recently, macromolecules arising from the assembly of potentially bridging ligands and monomeric palladacycles with  $[\text{C}(\text{sp}^2, \text{phenyl}), \text{N}]^-$  or  $[\text{S}, \text{C}(\text{sp}^2, \text{phenyl}), \text{S}]^-$  groups have been described [4]. In the view of these facts and the great ability of **2** to react with phosphine ligands (i.e.  $\text{PPh}_3$ ), we decided to elucidate the potential use of **2** as a supplier of building blocks for supramolecular architectures; with this aim we studied the reactivity of **2** with the diphosphine dppf.

Treatment of  $\text{CHCl}_3$  solution of  $2 \cdot 2\text{CHCl}_3$  with dppf (in a **2**: dppf molar ratio = 0.5) at room temperature (20 °C) produced after evaporation a deep-purple solid (**4**). Its elemental analyses were consistent with those expected for the heterotrimetallic compound  $[\{\text{Pd}[\text{C}_6\text{H}_4\text{--CH=N--}(\text{C}_6\text{H}_4\text{--2-O})]\}_2(\mu\text{-dppf})]$  (**4**), in

Fig. 2. Partial view of the  $^1\text{H-NMR}$  spectra (600 MHz) of  $2 \cdot \text{CHCl}_3$  in the range 6.25–7.52 ppm at different temperatures ( $T = 298, 278, 248$  and 223 K). Labelling of the signals corresponds to those shown in Scheme 1. The asterisks denote the additional weak signals detected at low temperatures (see text).

Table 2  
Selected bond lengths (Å) and angles (°) for **3**-CH<sub>2</sub>Cl<sub>2</sub> (standard deviation parameters are given in parenthesis)

Selected bond lengths	
Pd–C(13)	1.938(8)
Pd–O	2.070(5)
O–C(1)	1.360(10)
N–C(6)	1.402(9)
C(1)–C(2)	1.471(10)
C(3)–C(4)	1.334(10)
C(7)–C(8)	1.463(9)
C(9)–C(10)	1.395(10)
C(11)–C(12)	1.382(10)
C(13)–C(8)	1.460(10)
Pd–N	1.995(6)
Pd–P	2.070(5)
C(1)–C(6)	1.360(10)
N–C(7)	1.189(8)
C(2)–C(3)	1.416(11)
C(4)–C(5)	1.408(10)
C(8)–C(9)	1.367(10)
C(10)–C(11)	1.384(10)
C(12)–C(13)	1.366(10)
Selected bond angles	
C(13)–Pd–N	81.4(3)
O–Pd–P	101.33(16)
Pd–O–C(1)	108.7(5)
C(1)–C(6)–N	111.8(8)
N–C(7)–C(8)	118.5(8)
C(8)–C(13)–Pd	138.1(7)
N–Pd–O	80.5(2)
C(13)–Pd–P	96.8(3)
O–C(1)–C(6)	124.7(8)
C(6)–N–C(7)	128.8(7)
C(7)–C(8)–C(13)	110.4(7)
O–Pd–C(13)	161.9(3)

which two monomeric units “[Pd{C<sub>6</sub>H<sub>4</sub>–CH=N–(C<sub>6</sub>H<sub>4</sub>–2–O)}]” are connected by a bridging dppf ligand. The <sup>31</sup>P{<sup>1</sup>H}-NMR of **4** showed a singlet (at δ = 29.2 ppm) downfield-shifted from the free ligand, thus suggesting that the two phosphorous atoms are equivalent. The position of this signal was consistent with the values reported for related palladium(II) compounds containing a bridging dppf ligand [4a,6].

In a first attempt to elucidate the effect produced by the coordination of the Schiff base to the palladium(II) and the influence of the remaining ligands bound to the palladium upon the spectroscopic properties of the complexes, we decided to register the UV–vis spectra of the free ligand and compounds **2–4** in CH<sub>2</sub>Cl<sub>2</sub>. A summary of the results obtained from these studies is presented in Table 3.

The UV–vis spectrum of free ligand showed two intense bands centred at 276 and 352 nm which are assigned to charge transfer transitions. For compounds **3** and **4** three absorption bands were observed in the spectra. Two of them, which appeared in the range 270–350 nm, are assigned to metal-perturbed intraligand

Table 3  
UV–vis spectroscopic data for compounds under study: wavelengths (λ<sub>i</sub>, in nm) and extinction coefficients (ε<sub>i</sub>)

Compound	λ <sub>1</sub> (ε <sub>1</sub> )	λ <sub>2</sub> (ε <sub>2</sub> )	λ <sub>3</sub> (ε <sub>3</sub> )
<b>1</b>	276 (9184)	352 (8309)	–
<b>2</b> <sup>a</sup>	280 (8406)	350 (4256)	532 (2187)
<b>3</b>	291 (6638)	340 (2765)	526 (2172)
<b>4</b>	278 (9838)	334 (6584)	496 (1669)

<sup>a</sup> Additional bands at λ = 336 nm (sh) (ε = 4256) and 464 nm (ε = 2488).

transitions, while the band at lower energies (in the range 490–530 nm) with extinction coefficients (ε) greater than 10<sup>3</sup> are assigned, according to the literature [15], to metal to ligand charge transfer transitions (MLCT) from the 4d(π) orbitals of the palladium(II) to a π\* orbital of the ligand. The spectrum of **2**·2CHCl<sub>3</sub> was more complex than those of **3** and **4**, since two additional shoulders at λ = 336 and 464 nm were also detected in the spectrum. This finding may be related to the presence of smaller units in solution (i.e. dimers or trimers).

To sum up, the results presented here provide conclusive evidence of the formation of a tetranuclear cyclopalladated compound arising from the assembly of four palladacyclic blocks with a [C, N, O]<sup>2-</sup> ligand. This type of coordination, also present in **3** and **4**, is not common in the literature. On the other hand, it is well-known that some palladacycles containing planar terdentate [C, N, X]<sup>-</sup> ligands may be potentially useful from the point of view of their optical properties (i.e. their luminescence) [15]. Besides that, the presence of a σ(Pd–C) and a σ(Pd–O) bonds in **2**, **3** and **4** has an additional interest {with [C, X]<sup>-</sup> (X = N or O) ligands} due to their potential use as precursors or intermediates in organic synthesis [16] as well as in homogeneous catalysis [17].

### 3. Experimental

#### 3.1. Materials and methods

Benzaldehyde and H<sub>2</sub>N–C<sub>6</sub>H<sub>4</sub>–2–OH were obtained from Aldrich and used as received. All the solvents used in this work were dried and distilled before use. Elemental analyses (C, H and N) were carried out at the Servei de Recursos Científics i Tècnics (Universitat Rovira i Virgili, Tarragona). Infrared spectra were obtained with a Nicolet Impact-400 instrument using KBr disks. Proton and the two-dimensional NMR experiments ({<sup>1</sup>H–<sup>1</sup>H} COSY and NOESY) and the {<sup>1</sup>H–<sup>13</sup>C} heteronuclear correlations (HMBC and HSQC) were recorded with a Bruker Avance 600 MHz instrument at 20 °C using CDCl<sub>3</sub> (99.9%) as solvent and

SiMe<sub>4</sub> {for <sup>1</sup>H and <sup>13</sup>C} as reference, and the variable temperature experiments were performed in the range 223–298 K using a Bruker Avance 600 MHz and a Varian 300 MHz instruments using the same solvent as for the <sup>1</sup>H-NMR spectra at 298 K. <sup>31</sup>P{<sup>1</sup>H}-NMR spectra of **3** and **4** were obtained with a Bruker 250DRX instrument using CDCl<sub>3</sub> as solvent and trimethylphosphite as reference ( $\delta$  <sup>31</sup>P{P(OMe)<sub>3</sub>} = 140.17 ppm). Mass spectra [(FAB<sup>+</sup>) for **1–4**, ES (in CHCl<sub>3</sub>) and MALDI-TOF for **2**] were obtained with a VG-Quatro-Fissions (for FAB<sup>+</sup>) or with a Voyager DE RP Applied Biosystems (for MALDI-TOF) instruments. The matrix used in each case was 3-nitrobenzylalcohol (NBA) (for FAB<sup>+</sup> mass spectra) and 2,5-dihydroxybenzoic acid (DBA) (for MALDI-TOF).

### 3.1.1. Preparation of C<sub>6</sub>H<sub>5</sub>-CH=N-(C<sub>6</sub>H<sub>4</sub>-2-OH) (**1**)

Benzaldehyde (0.305 g, 4.35 × 10<sup>-3</sup> mol) and H<sub>2</sub>N-(C<sub>6</sub>H<sub>4</sub>-2-OH) (0.475 g, 4.35 × 10<sup>-3</sup> mol) were dissolved in ethanol (30 ml). The mixture was refluxed for 1 h and filtered out. The filtrate was concentrated to ca. 10 ml on a rotary evaporator and then allowed to evaporate at 20 °C. The solid formed was collected and air-dried (yield: 0.725 g, 84.5%). Anal. (%): C, 79.3; H, 5.7; N, 7.3; C<sub>13</sub>H<sub>11</sub>NO requires: C, 79.2; H, 5.6; N, 7.1%. MS (FAB<sup>+</sup>):  $m/z$  = 197 [M<sup>+</sup>]. IR (in cm<sup>-1</sup>): 3376 [ $\nu$ (O-H)] and 1625 [ $\nu$ (>C=N-)]. <sup>1</sup>H-NMR data [18]:  $\delta$  = 8.68 [s, 1H, -CH=N-], 7.91 [d, 2H, H<sup>2</sup> and H<sup>6</sup>, <sup>3</sup>J = 7.5 Hz], 7.50 [m, 2H, H<sup>3</sup> and H<sup>5</sup>, <sup>3</sup>J = 7.5 Hz], 7.21 [m, 1H, H<sup>4</sup>], 7.02 [d, 1H, H<sup>3</sup>, <sup>3</sup>J = 8.0 Hz], 6.90 [t, 1H, H<sup>4</sup>, <sup>3</sup>J = 8.0 Hz], 7.20 [t, 1H, H<sup>5</sup>, <sup>3</sup>J = 8.0 Hz], 7.30 [d, 1H, H<sup>6</sup>, <sup>3</sup>J = 8.0 Hz] and 7.47 [OH, partially overlapped by the signal at  $\delta$  = 7.50] ppm. <sup>13</sup>C{<sup>1</sup>H}-NMR data [18]:  $\delta$  = 157.1 [-CH=N-], 152.2 [C<sup>1</sup>], 128.7 [C<sup>2</sup> and C<sup>6</sup>], 131.4 [C<sup>3</sup> and C<sup>5</sup>], 128.8 [C<sup>4</sup>], 135.7 [C<sup>1'</sup>], 135.4 [C<sup>2'</sup>], 118.5 [C<sup>3'</sup>], 114.9 [C<sup>4'</sup>], 129.4 [C<sup>5'</sup>] and 115.6 [C<sup>6'</sup>] ppm.

### 3.1.2. Preparation of [Pd{C<sub>6</sub>H<sub>4</sub>-CH=N-(C<sub>6</sub>H<sub>4</sub>-2-O)}<sub>2</sub>]<sub>4</sub> (**2**)·2CHCl<sub>3</sub>

Pd(AcO)<sub>2</sub> (171 mg, 7.6 × 10<sup>-4</sup> mol) and **1** (150 mg, 7.6 × 10<sup>-4</sup> mol) were suspended in methanol (HPLC grade, 20 ml) and refluxed for 2 h. The solid formed was collected by filtration and air-dried. Then, it was dissolved in CHCl<sub>3</sub> (20 ml) and filtered through Celite. Evaporation of the filtrate at 20 °C gave red prisms of **2** (yield: 158 mg, 60.2%). Anal. (%): C, 45.0; H, 2.7; N, 4.0; C<sub>54</sub>H<sub>38</sub>Cl<sub>6</sub>N<sub>4</sub>O<sub>4</sub>Pd<sub>4</sub> requires: C, 44.9; H, 2.6; N, 3.9%. MS (FAB<sup>+</sup>):  $m/z$  = 1206 [{M-2(CHCl<sub>3</sub>)}]<sup>+</sup>; MS (MALDI-TOF):  $m/z$  = 1206 [{M-2(CHCl<sub>3</sub>)}]<sup>+</sup>, 905 [{M-2(CHCl<sub>3</sub>)}3/4]<sup>+</sup> and 604 [{M-2(CHCl<sub>3</sub>)}/2]<sup>+</sup>. IR (in cm<sup>-1</sup>): 1595 and 1582 [ $\nu$ (>C=N-)]. <sup>1</sup>H-NMR data [18] at 298 K:  $\delta$  = 7.11 [s, 1H, -CH=N-], 6.40 [dt, 1H, H<sup>3</sup>, <sup>3</sup>J = 7.8 and 1.2 Hz], 6.82 [td, 1H, H<sup>4</sup>, <sup>3</sup>J = 7.8 and 1.2 Hz], 6.93 [td, 1H, H<sup>5</sup>, <sup>3</sup>J = 7.8 and 1.2 Hz], 7.48 [dd, 1H, H<sup>6</sup>, <sup>3</sup>J = 7.8 and 1.2 Hz], 6.90 [dd, 1H, H<sup>3'</sup>, <sup>3</sup>J = 7.5 and 1.1 Hz], 6.34 [td, 1H, H<sup>4'</sup>, <sup>3</sup>J = 7.5 and 1.1 Hz],

6.51 [td, 1H, H<sup>5'</sup>, <sup>3</sup>J = 7.5 and 1.1 Hz] and 6.37 [d, 1H, H<sup>6'</sup>, <sup>3</sup>J = 7.8 and 1.2 Hz] ppm. <sup>13</sup>C{<sup>1</sup>H}-NMR data [18]:  $\delta$  = 162.2 [-CH=N-], 155.4 [C<sup>1</sup>], 138.6 [C<sup>2</sup>], 127.0 [C<sup>3</sup>], 132.5 [C<sup>3</sup>], 124.1 [C<sup>4</sup>], 131.0 [C<sup>5</sup>], 124.3 [C<sup>6</sup>], 151.0 [C<sup>1'</sup>], 136.2 [C<sup>2'</sup>], 127.0 [C<sup>3'</sup>], 117.2 [C<sup>4'</sup>], 127.0 [C<sup>5'</sup>] and 124.2 [C<sup>6'</sup>] ppm.

### 3.1.3. Preparation of [Pd{C<sub>6</sub>H<sub>4</sub>-CH=N-(C<sub>6</sub>H<sub>4</sub>-2-O)}<sub>2</sub>](PPh<sub>3</sub>)] (**3**)·CH<sub>2</sub>Cl<sub>2</sub>

Triphenylphosphine (22 mg, 8.4 × 10<sup>-5</sup> mol) was added to a CHCl<sub>3</sub> solution (10 ml) of **2**·2CHCl<sub>3</sub> (30 mg, 2.10 × 10<sup>-5</sup> mol). The mixture was stirred at (20 °C) for 30 min and filtered out. The filtrate was concentrated to dryness on a rotary evaporator. The residue was then treated with CH<sub>2</sub>Cl<sub>2</sub> (4 ml) and the addition of *n*-hexane ( $\approx$  2 ml) followed by the slow evaporation of the solvents produced microcrystals of **3**, which were collected and dried in vacuum (yield: 36 mg, 74%). Anal. (%): C, 66.1; H, 4.4; N, 2.6; C<sub>31</sub>H<sub>24</sub>NOPPd·CH<sub>2</sub>Cl<sub>2</sub> requires: C, 66.0; H, 4.3; N, 2.5%. MS (FAB<sup>+</sup>):  $m/z$  = [{M-CH<sub>2</sub>Cl<sub>2</sub>}]<sup>+</sup>. IR (in cm<sup>-1</sup>): 1601 [ $\nu$ (>C=N-)]. <sup>1</sup>H-NMR data [18]:  $\delta$  = 7.95 [d, 1H, -CH=N-, <sup>4</sup>J(H-P) = 8 Hz], 6.02 [dd, 1H, H<sup>3</sup>, <sup>3</sup>J = 8.0 and 1.0 Hz], 6.78 [td, 1H, H<sup>4</sup>, <sup>3</sup>J = 8.0 and 1.0 Hz], 6.91 [td, 1H, H<sup>5</sup>, <sup>3</sup>J = 8.0 and 1.0 Hz], 7.12 [dd, 1H, H<sup>6</sup>, <sup>3</sup>J = 8.0 and 1.0 Hz], 6.49 [dd, 1H, H<sup>3'</sup>, <sup>3</sup>J = 7.6 and 1.1 Hz], 6.31 [td, 1H, H<sup>4'</sup>, <sup>3</sup>J = 7.6 and 1.1 Hz], 6.81 [td, 1H, H<sup>5'</sup>, <sup>3</sup>J = 7.6 and 1.1 Hz] and 7.64 [dd, 1H, H<sup>6'</sup>, <sup>3</sup>J = 7.6 and 1.1 Hz], 5.12 [s, 1H, CH<sub>2</sub>Cl<sub>2</sub>] and 7.28–7.53 [m, 15H, aromatic protons of the PPh<sub>3</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H}-NMR data [18]:  $\delta$  = 170.2 [-CH=N-], 157.2 [C<sup>1</sup>], 137.6 [C<sup>2</sup>], 127.8 [C<sup>3</sup>], 124.1 [C<sup>4</sup>], 129.6 [C<sup>5</sup>], 126.7 [C<sup>6</sup>], 130.4 [C<sup>1'</sup>], 152.6 [C<sup>2'</sup>], 115.5 [C<sup>3'</sup>], 116.7 [C<sup>4'</sup>], 130.4 [C<sup>5'</sup>], 129.5 [C<sup>6'</sup>], 123.08, 128.4, 132.0 and 134.9 [C<sup>a</sup>, C<sup>b</sup>, C<sup>c</sup> and C<sup>d</sup> of the PPh<sub>3</sub>] ppm. <sup>31</sup>P{<sup>1</sup>H}-NMR data:  $\delta$  = 34.4 ppm, s.

### 3.1.4. Preparation of [Pd{C<sub>6</sub>H<sub>4</sub>-CH=N-(C<sub>6</sub>H<sub>4</sub>-2-O)}<sub>2</sub>]<sub>2</sub>( $\mu$ -dppf)] (**4**)

dppf (23 mg, 5.2 × 10<sup>-5</sup> mol) was added to a CHCl<sub>3</sub> solution (10 ml) containing **2**·2CHCl<sub>3</sub> (30 mg, 2.1 × 10<sup>-5</sup> mol). The reaction mixture was stirred at room temperature for 6 h. After this period the non-dissolved materials were removed by filtration and discarded and the purple filtrate was concentrated on a rotary evaporator to ca. 2 ml. Slow evaporation of the solvent produced the precipitation of violet thin needles of **4** (yield: 42 mg, 71.6%). Anal. (%): C, 62.3; H, 4.1; N, 2.5; C<sub>60</sub>H<sub>46</sub>N<sub>2</sub>O<sub>2</sub>FeP<sub>2</sub>Pd<sub>2</sub> requires: C, 62.2; H, 4.01; N, 2.4%. MS (FAB<sup>+</sup>):  $m/z$  = 1158 [M]<sup>+</sup>. IR (in cm<sup>-1</sup>): 1608 [ $\nu$ (>C=N-)]. <sup>1</sup>H-NMR data [18]:  $\delta$  = 7.90 [d, 2H, -CH=N-, <sup>4</sup>J(H-P) = 10.4 Hz], 5.95 [dd, 2H, H<sup>3</sup>, <sup>3</sup>J = 7.8 and 1.1 Hz], 6.78 [td, 2H, H<sup>4</sup>, <sup>3</sup>J = 7.8 and 1.1 Hz], 6.91 [td, 2H, H<sup>5</sup>, <sup>3</sup>J = 7.8 and 1.1 Hz], 7.10 [dd, 2H, H<sup>6</sup>, <sup>3</sup>J = 7.8 and 1.1 Hz], 6.55 [dd, 2H, H<sup>3'</sup>, <sup>3</sup>J = 8.0 and 1.0 Hz], 6.39 [td, 2H, H<sup>4'</sup>, <sup>3</sup>J = 8.0 and 1.0 Hz], 6.71 [td, 2H, H<sup>5'</sup>, <sup>3</sup>J = 8.0 and 1.0 Hz], 7.64 [dd, 2H, H<sup>6'</sup>, <sup>3</sup>J = 8.0 and

1.0 Hz], 5.16 [d, 4H, H<sup>2</sup> and H<sup>5</sup> (dppf),  $J = 1.3$  Hz], 4.23 [d, 4H, H<sup>3</sup> and H<sup>4</sup> (dppf),  $J = 1.3$  Hz] and 7.28–7.53 [m, 20H, aromatic protons of the PPh<sub>3</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H}-NMR data [18] (selected data):  $\delta = 174.0$  [–CH=N–], 157.8 [C<sup>1</sup>], 137.8 [d, C<sup>2</sup>], 138.9 [C<sup>3</sup>], 124.6 [C<sup>4</sup>], 128.1 [C<sup>5</sup>], 126.9 [C<sup>6</sup>], 130.8 [C<sup>1</sup>], 150.8 [C<sup>2</sup>], 115.9 [C<sup>3</sup>], 113.6 [C<sup>4</sup>], 131.4 [C<sup>5</sup>], 129.5 [C<sup>6</sup>], 73.1, 75.6 and 75.9 (three doublets due to the three types of <sup>13</sup>C nuclei of the dppf) ppm. <sup>31</sup>P{<sup>1</sup>H}-NMR data:  $\delta = 29.2$  ppm, s.

### 3.2. Crystallography

A prismatic crystal of **2**·2CHCl<sub>3</sub> or **3**·CH<sub>2</sub>Cl<sub>2</sub> (sizes in Table 4) was selected and mounted on a Enraf-Nonius-CAD 4 four-circle diffractometer (for **3**·CH<sub>2</sub>Cl<sub>2</sub>). Intensities were collected with graphite monochromatised Mo–K<sub>α</sub> radiation using  $\omega/2\theta$  scan technique. For **2**·2CHCl<sub>3</sub>, the number of reflections measured in the range  $2.00^\circ \leq \theta \leq 29.95^\circ$  was 8953 of which 8149 were assumed as observed applying the condition  $I > 2\sigma(I)$ , while for **3**·CH<sub>2</sub>Cl<sub>2</sub> the number of reflections measured in the range  $2.08^\circ \leq \theta \leq 30.15^\circ$  was 8383 of which 1673

were assumed as observed applying the condition  $I > 2\sigma(I)$ . Three reflections were measured every 2 h as orientation and intensity control, and no significant intensity decay was observed. Lorentz polarisation corrections were performed but absorption corrections were not.

The structures were solved by direct methods using SHELXS computer program [19] and refined by full-matrix least-squares method with the SHELXL97 computer program [20] using 8382 reflections (very negative intensities were not assumed). The function minimised was  $\sum w||F_o|^2 - |F_c|^2|^2$ , with  $w = [\sigma^2(I) + (0.0942P)^2]^{-1}$  (for **2**·2CHCl<sub>3</sub>) and  $w = [\sigma^2(I) + (0.0001P)^2]^{-1}$  (for **3**·CH<sub>2</sub>Cl<sub>2</sub>) and  $P = (|F_o|^2 + 2|F_c|^2)/3$ , and  $f$ ,  $f'$  and  $f''$  were taken from the literature [21].

For **3** all the hydrogen atoms were computed and refined using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom linked to it. The final  $R$  values as well as further details concerning the resolution and refinement of the crystal structures are presented in Table 4.

Table 4

Crystal data and details of the refinement of the crystal structures of **2**·2CHCl<sub>3</sub> and **3**·CH<sub>2</sub>Cl<sub>2</sub>

	<b>2</b> ·2CHCl <sub>3</sub>	<b>3</b> ·CH <sub>2</sub> Cl <sub>2</sub>
Empirical formula	C <sub>54</sub> H <sub>38</sub> Cl <sub>6</sub> N <sub>4</sub> O <sub>4</sub> Pd <sub>4</sub>	C <sub>32</sub> H <sub>26</sub> Cl <sub>2</sub> NO <sub>2</sub> Pd
$M_w$	1445.22	648.81
$T$	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions		
$a$ (Å)	20.690(4)	15.361(3)
$b$ (Å)	11.530(14)	8.30(2)
$c$ (Å)	21.782(7)	22.911(6)
$\alpha = \gamma$ (°)	90	90
$\beta$ (°)	93.80	98.61(2)
Volume (Å <sup>3</sup> )	5185(7)	2887(7)
$Z$	4	4
$D_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.851	1.439
$F(0\ 0\ 0)$	2832	1312
Crystal size (mm <sup>3</sup> )	$0.1 \times 0.1 \times 0.1$	$0.1 \times 0.1 \times 0.2$
Theta range for data collection (°)	2.00–29.95	2.08–30.15
Number of reflections collected	8953	8382
Number of unique reflections	8149 [ $R_{\text{int}} = 0.0641$ ]	8382 [ $R_{\text{int}} = 0.0589$ ]
Number of data	8149	8382
Number of parameters	609	343
Goodness of fit on $F^2$	0.927	0.784
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0497$ , $wR_2 = 0.1352$	$R_1 = 0.0584$ , $wR_2 = 0.0422$
$R$ indices (all data)	$R_1 = 0.1375$ , $wR_2 = 0.1685$	$R_1 = 0.3601$ , $wR_2 = 0.0715$
Largest difference peak and hole	0.979 and –1.093	0.729 and –0.645

### 4. Supplementary materials

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 196567 and 205347. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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### References

- [1] (a) J.M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995 See for example: ;  
(b) L. Fabbrizzi, A. Poggi, *Transition Metals in Supramolecular Chemistry*, vol. 448, Kluwer Academic Publishers, Dordrecht, 1994;  
(c) M. Eddaouli, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keefe, O.M. Yaghi, *Acc. Chem. Res.* 34 (2001) 319;  
(d) A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby, M. Schröder, *Coord. Chem. Rev.* 183 (1999) 117;  
(e) P.J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed.* 38 (1999) 2638.
- [2] (a) L. Carlucci, G. Ciani, F. Porta, D.M. Proserpio, L. Santagostini, *Angew. Chem. Int. Ed.* 41 (2002) 1907;  
(b) M. Fujita, K. Ogura, *Coord. Chem. Rev.* 148 (1996) 249.



- [3] J.W. Canary, B.C. Gibb, in: K.D. Karlin (Ed.), *Progress in Inorganic Chemistry*, vol. 45, Wiley, New York, 1997, p. 1.
- [4] (a) M. López-Torres, A. Fernández, J.J. Fernández, A. Suárez, S. Castro-Juiz, J.M. Vila, M.T. Pereira, *Organometallics* 20 (2001) 1350;  
(b) J.R. Hall, S.J. Loeb, G.K.H. Shimizu, G.P.A. Yap, *Angew. Chem. Int. Ed.* 37 (1998) 121.
- [5] (a) R.F. Carina, A.F. Williams, G. Bernardinelli, *Inorg. Chem.* 40 (2001) 1826;  
(b) C. Fernández-Rivas, D.J. Cárdenas, B. Martín-Matute, A. Monge, E. Gutiérrez-Puebla, M.A. Echevarren, *Organometallics* 20 (2001) 2998;  
(c) H.A. Ankersmit, P.T. Witte, H. Kooijman, M.T. Lakin, A.L. Spek, K. Goubitz, K. Vrieze, G. Van Koten, *Inorg. Chem.* 35 (1996) 6035;  
(d) C. López, A. Caubet, R. Bosque, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* 645 (2002) 146;  
(e) T. Kawamoto, I. Nagasawa, H. Kuma, Y. Kushi, *Inorg. Chem.* 35 (1996) 2427;  
(f) T. Kawamoto, I. Nagasawa, H. Kuma, Y. Kushi, *Inorg. Chim. Acta* 265 (1997) 163;  
(g) F. Hueso-Urena, N.A. Illan-Cabeza, M.N. Moreno-Carretero, A.L. Penas-Chamorro, R. Faure, *Inorg. Chem. Commun.* 2 (1999) 323;  
(h) J. Vicente, M.C. Lagunas, E. Bleuel, M.C. Ramírez de Arellano, *J. Organomet. Chem.* 648 (2001) 62.
- [6] A. Fernández, D. Vázquez-García, J.J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J.M. Vila, *New J. Chem.* 26 (2002) 398.
- [7] H. Yang, M.A. Khan, K.M. Nicholas, *Chem. Commun.* (1992) 210.
- [8] S. Pawlenko, Houben-Weyl. *Methoden der organische Chemie: organische Stickstoff Verbindungen mit einer C,N Doppelbindung*, Georg Thieme, Stuttgart (Germany), 1990, p. 222 (Band E 14/b, Teil 1; Chapter 1).
- [9] (a) A. Bondi, *J. Phys. Chem.* (1964) 441;  
(b) A.I. Kitaigorodskii, *Molecular Crystals and Molecules*, Academic Press, London, UK, 1973.
- [10] (a) J. Albert, J. Granell, J. Sales, M. Font-Bardía, X. Solans, *Organometallics* 14 (1995) 1393;  
(b) P.S. Pregosin, R.W. Kuntz, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), *<sup>31</sup>P- and <sup>13</sup>C-NMR of Transition Metal Phosphine Complexes*, Springer, Berlin, Germany, 1979;  
(c) A. Fernández, E. Pereira, J.J. Fernández, M. López-Torres, A. Suárez, R. Mosteiro, J.M. Vila, *Polyhedron* 21 (2002) 39;  
(d) X. Riera, A. Caubet, C. López, V. Moreno, E. Freisinger, M. Willemann, B. Lippert, *J. Organomet. Chem.* 629 (2001) 97.
- [11] (a) J. Vicente, J.A. Abad, A. Frankland, M.C. Ramírez de Arellano, *Chem. Eur. J.* 5 (1999) 3066;  
(b) J. Vicente, A. Arcas, D. Bautista, M.C. Ramírez de Arellano, *J. Organomet. Chem.* 663 (2002) 164.
- [12] T.H. Allen, O. Kennard, *Chem. Des. Automat. News* 8 (1993) 146.
- [13] G. Wilkinson, F.A. Stone, W.W. Abel (Eds.), *Comprehensive Organometallic Chemistry: The Synthesis, Reactions and Structures of Organometallic Compounds*, Vol. 6, Pergamon Press, New York, 1982, p. 236.
- [14] S.J. Calson, T. Lu, R.L. Luck, *Inorg. Chem. Commun.* 6 (2003) 455.
- [15] (a) M. Maestri, C. Deutsche-Cornioley, A. Von Zelewski, *Coord. Chem. Rev.* 11 (1991) 117;  
(b) F. Neve, A. Crispini, C. Di Pietro, S. Campagna, *Organometallics* 21 (2002) 3511;  
(c) D. Song, Q. Wu, A. Hook, I. Kosin, S. Wang, *Organometallics* 20 (2001) 4683.
- [16] (a) I. Omae, *Applications of Organometallic Compounds*, Wiley, Chichester, UK, 1998;  
(b) A.D. Ryabov, *Synthesis* (1985) 233 and references therein;  
(c) J. Spencer, M. Pfeffer, *Adv. Met. Org. Chem.* 6 (1998) 103;  
(d) K.E. Torraca, S.I. Kuwabe, S.L. Buchwald, *J. Am. Chem. Soc.* 122 (2000) 12907;  
(e) Q. Shelby, N. Kataoka, G. Mann, J. Hartwig, *J. Am. Chem. Soc.* 122 (2000) 10718;  
(f) J.L. Serrano (Ed.), *Metallomesogens: Synthesis, Properties and Applications*, VCH, Weinheim, Germany, 1996;  
(g) B.B. Eran, D. Singer, K. Praefcker, *Eur. J. Inorg. Chem.* (2001) 111.
- [17] P.W. Jolly, G. Wilke, W.A. Kermann, B. Cornils (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, Germany, 1996.
- [18] Labelling of the atoms correspond to that shown in the scheme.
- [19] G.M. Sheldrick, *SHELXS: A Computer Program for Determination of Crystal Structures*, University of Göttingen, Germany, 1997.
- [20] G.M. Sheldrick, *SHELX-97: A Computer Program for Determination of Crystal Structures*, University of Göttingen, Germany, 1997.
- [21] *International Tables of X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, UK, 1974, pp. 99–100.