DOI: 10.1002/ejic.200700478

Tetranuclear Complexes of Pd^{II} with Tridentate [*C*,*N*,*O*] and [*O*,*N*,*O*] Ligands: Synthesis, Reactivity and Structural Isomerism

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Keywords: Palladium / Cyclometallation / Metallacycles / Tridentate [*C*,*N*,*O*] ligands / C–H activation

Treatment of the Schiff base ligand 2,3,4-(MeO)$_3$C$_6$H$_2$C(H)=N[2-(OH)-5-*t*BuC$_6$H$_3$] (**a**) with palladium(II) acetate in toluene gave the cyclometallated complex [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N(2-O-5-*t*BuC$_6$H$_3$)}]$_4$ (**1a**) with the tridentate ligand [*C*,*N*,*O*]. The complex showed a tetranuclear arrangement of the cyclometallated monomers with a P$_4$O$_4$ core. Reaction of 2,6-(Me)$_2$C$_6$H$_3$C(H)=N[2-(OH)C$_6$H$_4$] (**b**) and 2,5-(Me)$_2$C$_6$H$_3$C(H)=N[2-(OH)C$_6$H$_4$] (**c**) with palladium(II) acetate under similar conditions yielded the tetranuclear complexes [Pd{6-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}]$_4$ (**1b**) and [Pd{5-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}]$_4$ (**1c**), respectively, in which the tridentate [*C*,*N*,*O*] ligand is bound through the aliphatic methyl carbon. Treatment of 2,4-(Me)$_2$C$_6$H$_3$C(H)=N[2-(OH)C$_6$H$_4$] (**d**) with palladium(II) acetate yielded a mixture of isomers, [Pd{4-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}]$_n$[Pd{2,4-(Me)$_2$C$_6$H$_2$C(H)=N(2-OC$_6$H$_4$)}]$_{4-n}$ (n = 0–4), also bearing a tetranuclear structure. However, the tetramer was assembled by two types of mononuclear Pd(ligand) building blocks: the ligand is coordinated through the aliphatic methyl carbon in one and through the aromatic *ortho* carbon in the other. The crystal structure of one such isomer confirmed the spectroscopic data. Treatment of 2-(OH)-4,6-(MeO)$_2$C$_6$H$_2$C(H)=N[2-(OH)C$_6$H$_4$] (**e**) and 2-(OH)C$_6$H$_4$C(H)=N[2-(OH)C$_6$H$_4$] (**f**) with palladium(II) acetate yielded the tetranuclear complexes [Pd{2-O-4,6-(MeO)$_2$C$_6$H$_2$C(H)=N(2-OC$_6$H$_4$)}]$_4$ (**1e**) and [Pd{2-OC$_6$H$_4$C(H)=N(2-OC$_6$H$_4$)}]$_4$ (**1f**), respectively, after double deprotonation of the ligand, which coordinates to the metal through the two phenoxy oxygen atoms and the imine nitrogen atom in these complexes. Reaction of compounds **1a**–**1f** with tertiary phosphanes in acetone gave mono- and dinuclear complexes, after cleavage of the tetranuclear structure. In these complexes, the tertiary phosphane is bonded *trans* to the nitrogen atom. The crystal structures for **1a**, **1c**, **1e**, **1d**/**1d′** are reported; they show the characteristic Pd$_4$O$_4$ core.

Introduction

Cyclometallated compounds have been extensively surveyed,[1–5] and they exhibit a good number of applications related to organic as well as to organometallic compounds, metallomesogens and catalytic materials;[6–13] they also promote unusual coordination environments.[14] The more common cyclometallated complexes encountered in the literature are the palladium(II) five-membered ring species after activation of aromatic C(sp^2) atoms. Analogous compounds containing alkyl C(sp^3)–Pd bonds are also known although these are more scarce.[15–19]

On the other hand, the building of supramolecular assemblies has also attracted much attention in the past years,[20–24] and among these, examples containing square-planar palladium(II) units have been of great interest in view of their potential applications.[25] Nevertheless, few examples of supramolecular species with cyclometallated building blocks have been reported,[26–31] many of which correspond to tetrameric assemblies derived from palladium(II) cyclometallated complexes with [*C*,*N*,*X*] (*X* = *O*, *S*) tridentate ligands. Thus, for the [*C*,*N*,*S*] species, thiosemicarbazones give tetranuclear structures with an eight-membered Pd$_4$S$_4$ core,[32–34] and tetranuclear cluster complexes derived from benzothiazolines[35,36] are also known. As for the [*C*,*N*,*O*] derivatives,[37–40] they also exhibit an analogous tetranuclear structure with a Pd$_4$O$_4$ core. In order to attain neutrality the ligand is usually deprotonated in the complex, at the hydrazine nitrogen atom, at the benzothiazoline nitrogen atom or at the phenol oxygen atom. Even when there is no metal–carbon bond formation, the tetranuclear structure is reached only after deprotonation, as has been reported for a coordination compound derived from a [*N*,*N*,*S*] ligand.[41]

The purpose of this paper is twofold: first, to study the activation of aromatic carbon atoms against aliphatic carbon atoms by checking the bonding possibilities of *N*-phenol Schiff base ligands, and secondly, to determine the

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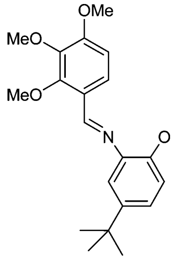
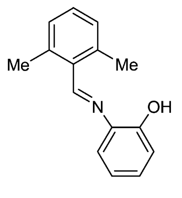
structural particularity of the resulting complexes in terms of their polynuclear nature.

Results and Discussion

The ligands employed provide several coordination approaches as a function of the substitution pattern of the phenyl ring. Thus, only **a**, **c**, **d** and **f** have available aromatic sp^2 carbon atoms suitable for metallation, as well as MeO, Me and OH substituents liable to carbon–metal and oxygen–metal bond formation. On the other hand, **b** and **e** may bind to the metal only through the MeO or OH groups; accordingly, different alternatives of palladation were found. Hence, in **a** the metal atom was found to be bonded exclusively through the C-6 atom, with no sign of metallation of the C-2 methoxy group, resulting in the formation of a five-membered palladated ring. For **b** and **c**, either the C-2 Me group or the C-6 Me group was metallated to render a six-membered palladated ring in each case. Metallation of the C-6 carbon atom in ligand **c** was not observed, quite possibly because of the steric hindrance imposed by the neighbouring C-5 Me group. The reaction of ligand **d** with palladium acetate provided a mixture of products, one rendering metallation at the aromatic C-6 atom, and another one at the aliphatic C-2 Me group, yielding $-CH_2-$Pd bond formation. Most outstanding for the tetranuclear structure of the **d** species was that, as opposed to the [*C*,*N*,*S*] or [*C*,*N*,*O*] tetramers previously reported where the four cyclometallated moieties were identical, the present case poses an unprecedented example of a tetranuclear structure with two distinct palladated groups having five and six-membered metallated rings. As for **e** and **f**, *C*-metallation was not accomplished in any instance; the deprotonation of both phenoxy groups favoured the coordination of the ligands as [*O*,*N*,*O*]. In all the cases depicted above the resulting products after palladation of the ligands were tetranuclear compounds, irrespective of the metallated atom, including the [*O*,*N*,*O*] bonded ligands.



a



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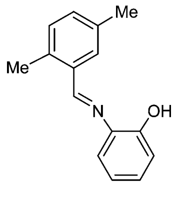

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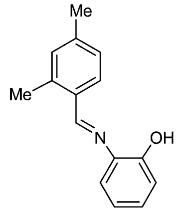

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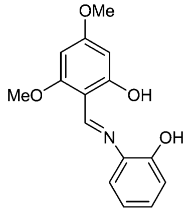

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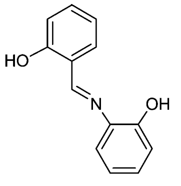
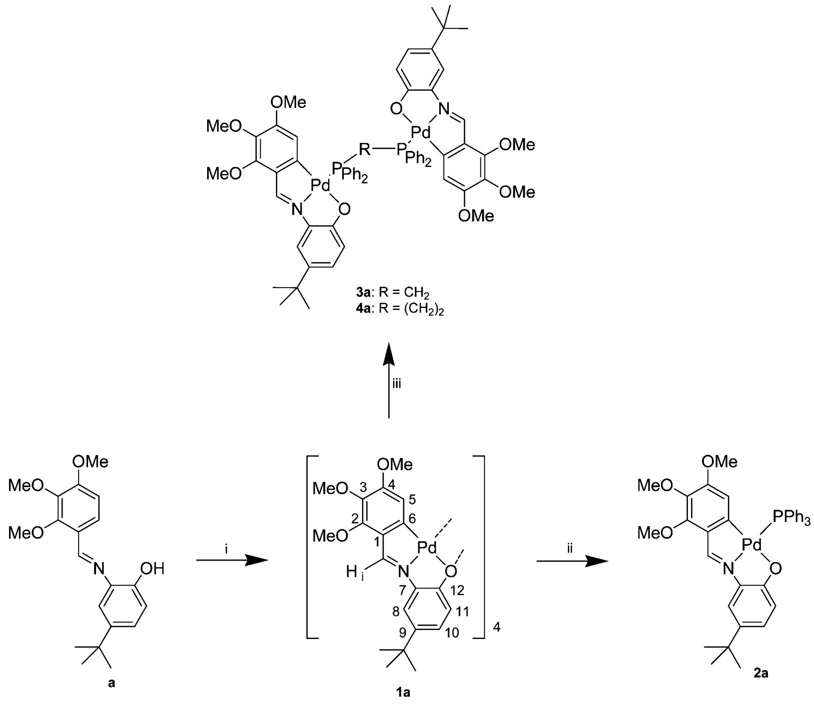


f

For the convenience of the reader the compounds and reactions are shown in Schemes 1, 2, 3 and 4. The compounds described in this paper were characterized by elemental analysis (C, H, N), by IR and ^1H, $^{31}P\{^1H\}$ NMR spectroscopy, and, in part, by FAB mass spectrometry and single-crystal X-ray diffraction (Experimental Section).



Scheme 1. (i) $Pd(AcO)_2$, (toluene); (ii) PPh_3 (acetone, 1:4 molar ratio); (iii) diphosphane (acetone, 1:2 molar ratio).

The reaction of **a** with palladium(II) acetate in toluene at 60 °C gave [Pd{2,3,4-$(MeO)_3C_6HC(H)=N(2$-O-5-tBu$C_6H_3)$}]$_4$ (**1a**) as an air-stable solid, which was fully characterized. The IR spectrum showed the shift of the ν(C=N) stretch toward lower wavenumbers from the free ligand value, because of nitrogen coordination of the imine,[42,43] and the absence of the ν(O–H) stretch, as compared to the ligand (3427 cm^{-1}), in accordance with loss of the –OH proton. In the ^1H NMR spectrum the *H*C=N and 5-H resonances were high-field shifted, as compared to the uncoordinated ligand, by 1.43 and 0.9 ppm, respectively; the low δ values in these cases were due to the structure of the complexes, which puts the *H*C=N and 5-H protons in the proximity of the shielding zone of the phenyl rings of a neighbouring metallated ligand.[32,33,37,39] Likewise, absence of the O*H* resonance in the ^1H NMR spectrum confirmed deprotonation.

The FAB mass spectra showed the cluster of peaks characteristic of the $[MH]^+$ fragment centred at 1792 uma; the isotopic pattern was in good agreement with the tetrameric formulation.

Crystal Structure of 1a

Suitable crystals were grown by slowly evaporating chloroform from a solution. Crystal data are given in Table 1. The ORTEP illustration of complex **1a**·H_2O is shown in Figure 1. The core of the tetrameric molecule consists of an eight-membered ring of alternating palladium and oxygen atoms. Each palladium atom is bonded to the ligand through an aryl carbon, a C=N nitrogen, and a phenoxy oxygen atom, and also to a bridging oxygen atom of a neighbouring cyclometallated ligand monomer, in a slightly distorted square-planar arrangement. The mean deviations from the least-squares plane are: Pd1, C1, N1, O1, O9, 0.0215 Å; Pd2, C21, N2, O5, O13, 0.0208 Å; Pd3, C41, N3, O5, O9, 0.0166 Å; Pd4, C69, N4, O1, O13, 0.0300 Å. The bond lengths at palladium are within the expected values.[37–40] The resulting cluster has approximate C_2 symmetry; the C_2 axis is perpendicular to and bisects Pd1···Pd2 and Pd3···Pd4. The Pd1···Pd2 and Pd3···Pd4 distances of 3.378(1) and 3.412(1) Å, respectively, preclude any Pd–Pd interactions. Two of the quasi-planar Pd ligand units are parallel and almost orthogonal to the other two parallel monomer moieties.

Table 1. Selected bond lengths [Å] and angles [°] for complex **1a**.

Pd1–C1	1.958(14)	Pd3–C41	1.966(13)
Pd1–N1	1.967(10)	Pd3–N3	1.953(10)
Pd1–O1	2.144(9)	Pd3–O5	2.047(8)
Pd1–O9	2.045(8)	Pd3–O9	2.134(8)
Pd2–C21	1.965(13)	Pd4–C61	1.953(13)
Pd2–N2	1.951(10)	Pd4–N4	1.961(10)
Pd2–O5	2.122(8)	Pd4–O1	2.034(8)
Pd2–O13	2.052(9)	Pd4–O13	2.138(9)
Pd1–Pd2	3.3776(14)	Pd3–Pd4	3.4120(14)
C1–Pd1–N1	82.6(6)	N3–Pd3–C41	82.4(5)
C1–Pd1–O9	96.6(5)	C41–Pd3–O5	96.8(4)
N1–Pd1–O1	81.6(4)	N3–Pd3–O9	81.8(4)
O9–Pd1–O1	99.3(3)	O5–Pd3–O9	99.1(3)
C21–Pd2–N2	82.8(5)	C61–Pd4–N4	82.2(5)
C21–Pd2–O13	96.8(5)	C61–Pd4–O1	96.0(5)
N2–Pd2–O5	81.5(4)	N4–Pd4–O13	81.7(4)
O13–Pd2–O5	99.0(3)	O1–Pd4–O13	100.0(3)
Pd4–O1–Pd1	115.4(4)	Pd3–O5–Pd2	116.0(4)
Pd1–O9–Pd3	119.0(4)	Pd2–O13–Pd4	114.5(4)

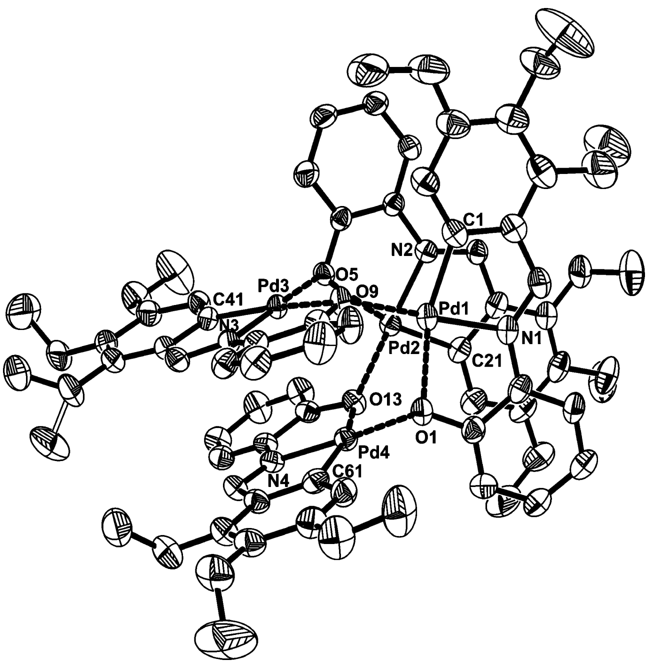
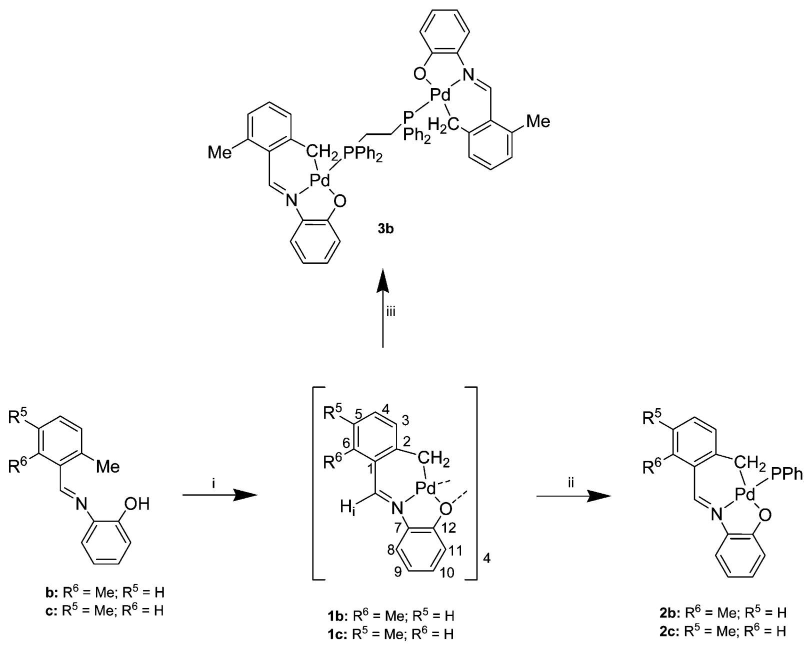


Figure 1. Molecular structure of [Pd{2,3,4-$(MeO)_3C_6HC(H)=N(2$-O-5-tBu$C_6H_3)$}]$_4$ (**1a**). *t*Bu groups have been omitted for clarity. Ellipsoids drawn at 40% level.

Treatment of **1a** with triphenylphosphane or diphosphanes (dppm, dppe) gave the mononuclear [Pd{2,3,4-$(MeO)_3$-$C_6HC(H)=N(2$-O-5-tBu$C_6H_3)$}(PPh_3)] (**2a**) or dinuclear [{Pd(2,3,4-{MeO}$_3C_6HC${H}=N{2-O-5-tBuC_6H_3})}$_2$(μ-$PPh_2CH_2PPh_2$)] (**3a**) and [{Pd(2,3,4-{MeO}$_3C_6HC${H}=N{2-O-5-tBuC_6H_3})}$_2${μ-$PPh_2(CH_2)_2PPh_2$}] (**4a**) species, as air-stable solids, which were fully characterized (Experimental Section), with opening of the polynuclear structure after P–$O_{bridging}$ bond cleavage; the Pd–$O_{chelating}$ bond remained intact in all cases. The ^1H NMR spectrum of **2a** showed the resonances of the 5-H and *H*C=N protons as doublets, coupled to the ^{31}P nucleus of the phosphane ligand ($J_{H,P}$ = 3.4 and 10.7 Hz, respectively), and the $^{31}P\{^1H\}$ NMR spectrum showed the phosphorus resonance as a singlet at δ = 34.2 ppm; these findings were in agreement with an arrangement in which the phosphorus atom is *trans* to the nitrogen atom.[44–47] The *H*C=N proton resonance, at δ = 8.14 ppm, showed a smaller high-field shift than that in compound **1a**, as compared to the free ligand, in agreement with the opening of the polynuclear structure.[39] Only one singlet was observed in the $^{31}P\{^1H\}$ NMR spectra of **3a** and **4a** for the two equivalent phosphorus nuclei.

The reaction of **b** and **c** with palladium(II) acetate in toluene at 60 °C gave the tetranuclear complexes [Pd{6-Me-2-$CH_2C_6H_3C(H)=N(2$-$OC_6H_4)$}]$_4$ (**1b**) and [Pd{5-Me-2-



Scheme 2. (i) $Pd(AcO)_2$, (toluene); (ii) PPh_3 (acetone, 1:4 molar ratio); (iii) diphosphane (acetone, 1:2 molar ratio).

$CH_2C_6H_3C(H)=N(2\text{-}OC_6H_4)\}]_4$ (**1c**), respectively, as air-stable solids which were fully characterized (Experimental Section). Bonding of the metal was attained through a methyl group in both cases; the integration for the multiplet signals in the ^1H NMR spectrum of **1c** showed that the C-6 atom was not metallated. The spectroscopic data was in agreement with nitrogen coordination of the C=N group and deprotonation of the phenoxy group, vide supra (Scheme 2, see the Experimental Section). The resonances at $\delta \approx 3.5$ ppm and $\delta \approx 2.5$ ppm were assigned to the AB system of the two nonequivalent methylene protons ($J_{H,H}$ = 13.6 and 14.1 Hz for **1b** and **1c**, respectively). Their diastereotopic nature follows from the tetrameric structure of the complex, which renders both methylene protons, on either side of the metallated moiety, magnetically nonequivalent (see the crystal structure of **1c**). The singlet resonance at $\delta = 2.28$ ppm (**1b**) and $\delta = 2.44$ ppm (**1c**) were assigned to the nonmetallated methyl groups. An interesting feature in the ^1H NMR spectrum of **1c** is the presence of weak signals, four low-intensity doublets ascribed to the 11-H and CH_2 protons were identified, which could be indicative of the presence of other species in solution. However, we were unable to isolate the minor components of the mixture by column chromatography or by any other methods. The ^1H NMR spectrum of **1c** recorded at 323 K displayed the same weak signals with no appreciable difference in either the chemical shift or in the relative intensities. When **1c** was treated with triphenylphosphane to give the mononuclear complex **2c**, vide infra, only the signals corresponding to this complex appeared in its spectrum; this seems to suggest that the weak resonances mentioned above could be due to a different grouping of the cyclometallated monomer fragments in the polynuclear structure, which when cleaved only yields **2c** in solution. The presence of weak and poorly resolved signals has been observed earlier in a similar complex.[37]

The synthesis of **1c** is one of the rare examples where activation of an aliphatic carbon, rather than an aromatic carbon, is preferred for metallation.[15–19] This is particularly interesting because activation of the aliphatic carbon implies the formation of a six-membered chelate ring as opposed to the more stable five-membered one.

Crystal Structure of 1c

Suitable crystals were grown by slowly evaporating chloroform from a solution. Crystal data are given in Table 2. The ORTEP illustration of complex **1c** is shown in Figure 2. Compound **1c** shows as tetranuclear structure with a Pd_4O_4 core similar to that described for **1a**; the most noticeable difference being the metallated carbon, which in this case was an sp^3 CH_2 carbon as opposed to the aromatic sp^2 carbon atom in **1a**. The coordination geometry about the palladium atoms is slightly distorted square-planar. The mean deviations from the least-squares plane are: Pd1, C14, N1, O1, O2, 0.0271 Å; Pd2, C34, N2, O2, O1#1, 0.0342 Å. The bond lengths and angles are in the range of those previously reported.[16,18,37–40] Another central feature of this complex is the planar disposition of the six-membered cyclometallated ring.

Several structures of cyclometallated complexes derived from Schiff bases in which the ligand is coordinated through a CH_2 carbon have been described previously; however, with the exception of a recent example reported by us,[48] in the remaining cases the six-membered cyclo-

Table 2. Selected bond lengths [Å] and angles [°] for complex **1c**.

Pd1–C14	1.985(9)	Pd2–C34	1.997(10)
Pd1–N1	1.976(6)	Pd2–N2	1.967(7)
Pd1–O1	2.123(5)	Pd2–O2	2.124(5)
Pd1–O2	2.077(6)	Pd2–O1#1	2.057(6)
Pd1–Pd1#1	3.2441(12)	Pd2–Pd2#1	3.2241(12)
N1–Pd1–C14	95.1(3)	N2–Pd2–C34	95.3(4)
N1–Pd1–O1	82.1(2)	N2–Pd2–O2	82.0(2)
C14–Pd1–O2	89.6(3)	C34–Pd2–O1#1	88.8(3)
O2–Pd1–O1	93.2(2)	O1#1–Pd2–O2	93.9(2)
Pd1–O2–Pd2	119.3(3)	Pd2#1–O1–Pd1	120.3(3)

Symmetry transformations used to generate equivalent atoms: # 1 – *x* – 1/2, –*y* + 1/2, *z*

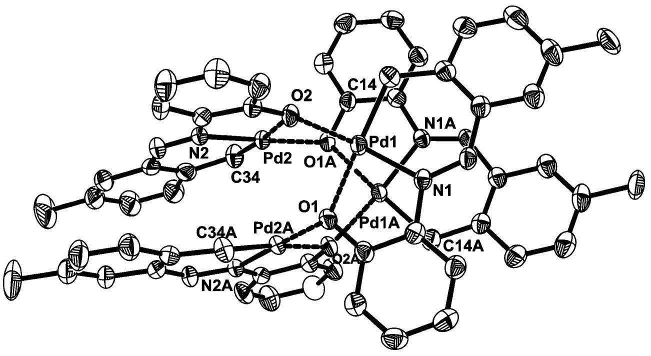


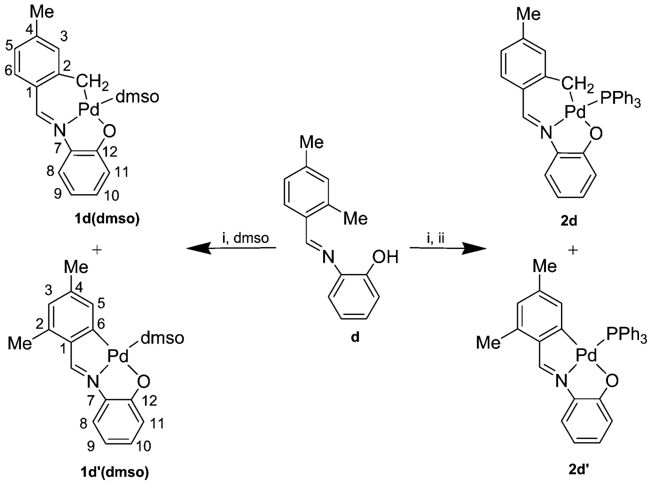
Figure 2. Molecular structure of [Pd{5-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}]$_4$ (**1c**). Ellipsoids drawn at the 40% level.

metallated ring showed a nonplanar geometry with a boat-like structure.[16,18,49–53] We believe that in **1c** the tetranuclear structure brings close two of the cyclometallated ligands, thus imposing planarity of the ring in order to avoid mutual steric repulsion.

Treatment of **1b** and **1c** with triphenylphosphane yielded the mononuclear complexes **2b** and **2c**, respectively, upon cleavage of the P–O$_{\text{bridging}}$ bond. The ^{1}H NMR spectra showed a doublet resonance assigned to the two equivalent CH$_2$ protons, consequent on splitting of the tetranuclear structure, coupled to the ^{31}P nucleus, δ = 2.96 ppm ($^3J_{\text{P,H}}$ = 5.8 Hz) and δ = 2.93 ppm ($^3J_{\text{P,H}}$ = 5.8 Hz) for **2b** and **2c**, respectively.

The reaction of **1b** with the tertiary diphosphane Ph$_2$P(CH$_2$)$_2$PPh$_2$ (dppe) gave the dinuclear cyclometallated complex, [{Pd(6-Me-2-CH$_2$C$_6$H$_3$C{H}=N{2-OC$_6$H$_4$})}$_2${µ-PPh$_2$(CH$_2$)$_2$PPh$_2$}] (**3b**), which was fully characterized. The ^{1}H NMR spectrum showed only one set of signals for the two cyclometallated moieties, and a singlet at δ = 33.2 ppm in the ^{31}P{^{1}H} NMR spectrum was assigned to the two equivalent phosphorus nuclei.

Treatment of **d** with palladium(II) acetate, under the same conditions as those used for the synthesis of **1a**–**1c**, yielded a mixture of isomers, [Pd{4-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}]$_n$ and [Pd{2,4-(Me)$_2$C$_6$H$_2$C(H)=N(2-OC$_6$H$_4$)}]$_{4-n}$ (n = 0–4), featuring dissimilar cyclometallated units arising from the different metallation site chosen by the metal: aromatic sp^2 phenyl carbon atoms or aliphatic sp^3 methyl carbon atoms. The ^{1}H NMR spectrum in CDCl$_3$ showed extended overlapping of the signals as expected for a complex mixture, as an outcome of which only five partially overlapped doublets, of the ten required, were assigned to the CH$_2$ protons at $\delta \approx$ 3.5–4.0 ppm. The signals corresponded to the isomers bearing a metallated methyl group, [Pd{4-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}]$_n$[Pd{2,4-(Me)$_2$C$_6$H$_2$C(H)=N(2-OC$_6$H$_4$)}]$_{4-n}$ (n = 1, 3, 4) and two isomers with n = 2, depending on whether the two cyclometallated monomers [Pd{4-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}] were opposite or adjacent in the tetranuclear arrangement (a sixth isomer is possible when metallation is through the C-6 carbon atom: [Pd{2,4-(Me)$_2$C$_6$H$_2$C(H)=N(2-OC$_6$H$_4$)}(PPh$_3$)]$_4$). Surprisingly, the ^{1}H NMR spectrum recorded in a donor solvent such as [D$_6$]dmso showed two singlet signals at δ = 8.82 ppm and δ = 8.41 ppm assigned to two chemically different *H*C=N protons, putting forward the existence of only two species in the solution in the aftermath of the tetranuclear structure break-up caused by coordination of the solvent, which yielded the mononuclear fragments [Pd{4-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}([D$_6$]dmso)], **1d**(dmso), and [Pd{2,4-(Me)$_2$C$_6$H$_2$C(H)=N(2-OC$_6$H$_4$)}([D$_6$]dmso)], **1d′**(dmso), with C(sp^3)–Pd and C(sp^2)–Pd bonds, respectively (see Scheme 3). Hence, only one singlet was observed for the CH$_2$ protons at 3.26 ppm, as opposed to the AB system in the tetranuclear structure, vide supra. The relative molar ratio of the complexes in solution was 1:0.5 [**1d**(dmso)/**1d′**(dmso)]. Regardless of the reaction time and temperature used in the synthesis, the final relative molar ratio remained unchanged.



Scheme 3. (i) Pd(AcO)$_2$, (toluene); (ii) PPh$_3$ (acetone, 1:4 molar ratio).

We suggest that in nondonor solvents such as chloroform the [Pd{4-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}] and [Pd{2,4-(Me)$_2$C$_6$H$_2$C(H)=N(2-OC$_6$H$_4$)}] building blocks were randomly arranged into tetranuclear moieties. Therefore, four isomers were present in the solution (vide supra), in addition to the two "pure" complexes [Pd{4-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}]$_4$ and [Pd{2,4-(Me)$_2$C$_6$H$_2$C(H)=N(2-OC$_6$H$_4$)}]$_4$. However, when the mixture was dissolved in a donor solvent the tetranuclear structure was cleaved, and the two distinct mononuclear moieties could be isolated. Another approach to the separation of the mononuclear isomers was treatment of the complex mixture with triphenylphosphane in acetone, which yielded complexes [Pd{4-Me-2-$CH_2C_6H_3C(H)=N(2-OC_6H_4)$}($PPh_3$)] (**2d**) and [Pd{2,4-$(Me)_2C_6H_2C(H)=N(2-OC_6H_4)$}($PPh_3$)] (**2d′**), which were fully characterized (Experimental Section). The above-mentioned assumption was confirmed by the crystal structure of one of the isomers.

Crystal Structure of the Mixture of [Pd{4-Me-2-$CH_2C_6H_3C(H)=N(2-OC_6H_4)$}]$_3$[Pd{2,4-$(Me)_2$-$C_6H_2C(H)=N(2-OC_6H_4)$}]

Crystal data are given in Table 3, and the ORTEP illustration is shown in Figure 3. A single crystal was isolated from a chloroform solution of the mixture of isomers and its resolved crystal and molecular structure showed the characteristic tetranuclear arrangement described for **1a** and **1c** bearing a central Pd_4O_4 core. Each palladium atom was coordinated to the ligand **d** through the C=N nitrogen, and to two phenoxy oxygen atoms, one of the latter two pertaining to a neighbouring metallated unit. However, the fourth coordination position was occupied by the C46 aromatic carbon for the Pd3 atom and by the C67 methylene carbon atom for Pd4. The ligand coordinated to Pd1 was found to be disordered, the major component (70%) corresponded to a ligand coordinated through the C7A methylene carbon and the minor component through the C6B aromatic carbon. The ligand coordinated to Pd2 was also disordered (50% for each component) and coordinated through the C26B aromatic or the C27A aliphatic carbon atoms, respectively, for each component.

Table 3. Selected bond lengths [Å] and angles [°] for complex **1d**/**d′**.

Pd1–C7A	1.941(10)	Pd3–C46	1.948(5)
Pd1–N1	1.962(5)	Pd3–N3	1.954(4)
Pd1–C6B	1.99(3)	Pd3–O1	2.067(4)
Pd1–O4	2.052(4)	Pd3–O3	2.142(4)
Pd1–O1	2.140(4)	Pd4–C67	1.976(6)
Pd2–C26B	1.926(16)	Pd4–N4	1.978(5)
Pd2–N2	1.976(4)	Pd4–O2	2.063(4)
Pd2–C27A	2.006(10)	Pd4–O4	2.124(4)
Pd2–O3	2.034(3)		
Pd2–O2	2.136(4)		
Pd1–Pd2	3.4385(9)	Pd3–Pd4	3.2368(9)
C7A–Pd1–N1	90.8(3)	C46–Pd3–N3	81.8(2)
N1–Pd1–C6B	86.0(6)	C46–Pd3–O1	98.7(2)
C7A–Pd1–O4	92.3(3)	N3–Pd3–O3	80.93(15)
C6B–Pd1–O4	97.1(6)	O1–Pd3–O3	98.64(14)
N1–Pd1–O1	81.93(18)	C67–Pd4–N4	93.9(2)
O4–Pd1–O1	95.02(17)	C67–Pd4–O2	89.8(2)
C26B–Pd2–N2	75.7(5)	N4–Pd4–O4	82.40(18)
N2–Pd2–C27A	96.4(3)	O2–Pd4–O4	93.96(15)
C26B–Pd2–O3	106.7(5)	Pd3–O1–Pd1	123.8(2)
C27A–Pd2–O3	86.3(3)	Pd4–O2–Pd2	119.15(19)
N2–Pd2–O2	81.65(18)	Pd2–O3–Pd3	116.79(17)
O3–Pd2–O2	95.74(15)	Pd1–O4–Pd4	115.5(2)

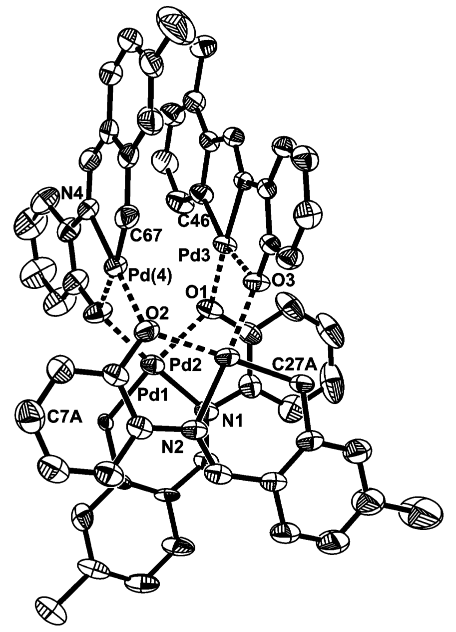
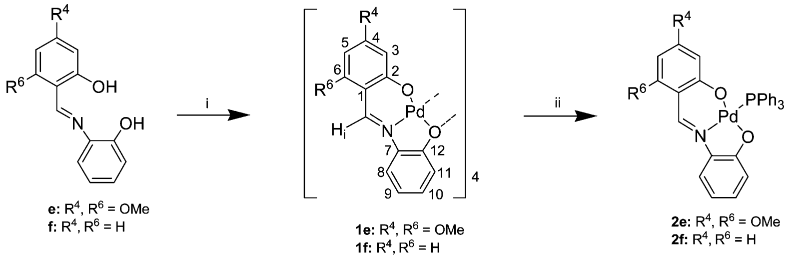


Figure 3. Molecular structure of the mixture of [Pd{4-Me-2-$CH_2C_6H_3C(H)=N(2-OC_6H_4)$}]$_n$ and [Pd{2,4-$(Me)_2C_6H_2C(H)=N$-$(2-OC_6H_4)$}]$_{4-n}$ (n = 3). Minor components of the disordered structure have been omitted for clarity. Ellipsoids drawn at the 40% level.

The reaction of **e** and **f** with palladium(II) acetate in toluene gave the non-cyclometallated complexes [Pd{2-O-4,6-$(MeO)_2C_6H_2C(H)=N(2-OC_6H_4)$}]$_4$ (**1e**) and [Pd{2-$OC_6H_4C(H)=N(2-OC_6H_4)$}]$_4$ (**1f**) as yellow and red air-stable solids, respectively. The IR spectroscopic data was in good agreement with nitrogen coordination of the imine,[42,43] and absence of the ν(O–H) bands, indicated double deprotonation of the ligands; the latter was confirmed by the absence of the O*H* resonances in the ^1H NMR spectra. While the ^1H NMR spectrum for **1e** showed a high-field shift of the *H*C=N resonance (δ = 1.19 ppm), similar to that observed for **1a**–**1c**, the *H*C=N resonance for



Scheme 4. (i) $Pd(AcO)_2$, (toluene); (ii) PPh_3 (acetone, 1:4 molar ratio).

1f appeared at δ = 8.94 ppm (shifted by 0.24 ppm), putting forward that the *H*C=N proton was not in the shielding area of the phenyl ring of an adjacent metallated ligand, probably because of cleavage of the tetranuclear structure caused by the coordination of [D$_6$]dmso used as the NMR solvent (vide supra). The IR, NMR and mass spectra of these complexes did not definitely establish their tetranuclear nature; nevertheless, resolution of the molecular structure of **1e** evidenced the tetrameric arrangement of the palladated fragments (Scheme 4).

Whereas for ligand **e** coordination is only possible through the phenoxy oxygen atoms, ligand **f** holds two coordination sites, the C-6 carbon and the phenoxy oxygen atoms; however, regardless of the reaction conditions used, the cyclometallated complex was not obtained in any case.

Crystal Structure of 1e·2CH$_2$Cl$_2$

Suitable crystals were grown by slowly evaporating dichloromethane from a solution. Crystal data are given in Table 4, and the ORTEP illustration of complex **1e** is shown in Figure 4. The molecular structure of **1e**·2CH$_2$Cl$_2$ showed a [Pd(ligand)]$_4$ tetrameric structure, in which each palladium atom was coordinated in a slightly distorted square-planar geometry through the two deprotonated phenoxy oxygen atoms, the C=N nitrogen and an oxygen atom from another Pd(ligand) unit. The mean deviations from the least-squares plane are: Pd1, O1, O2, O14, N1, 0.0091 Å; Pd2, O5, O6, O10, N2, 0.0015 Å; Pd3, O2, O9, O10, N3, 0.0285 Å; Pd4, O6, O13, O14, N4, 0.0074 Å. The core was formed by an eight-membered Pd$_4$O$_4$ ring of similar geometry to those described above. Each palladium atom belongs to two fused five- and six-membered rings, which are planar, and coplanar with the two phenol rings. The four units are arranged as parallel pairs in two sets at nearly right angles. Bond lengths and angles are within the expected values.[16,18,37–40]

Table 4. Selected bond lengths [Å] and angles [°] for complex **1e**.

Pd1–O1	1.965(4)	Pd3–O9	1.953(4)
Pd1–O2	2.013(4)	Pd3–O10	2.008(4)
Pd1–O14	2.074(4)	Pd3–O2	2.076(3)
Pd1–N1	1.940(4)	Pd3–N3	1.940(4)
Pd2–O5	1.953(4)	Pd4–O13	1.953(4)
Pd2–O6	1.999(3)	Pd4–O14	2.031(3)
Pd2–O10	2.068(4)	Pd4–O6	2.057(4)
Pd2–N2	1.940(4)	Pd4–N4	1.933(4)
Pd1–Pd2	3.0695(8)	Pd3–Pd4	3.1011(7)
N1–Pd1–O1	95.05(16	N3–Pd3–O9	95.33(16)
N1–Pd1–O2	83.87(16)	N3–Pd3–O10	83.96(16)
O1–Pd1–O14	87.81(15)	O9–Pd3–O2	86.65(14)
O2–Pd1–O14	93.25(14)	O10–Pd3–O2	94.10(14)
N2–Pd2–O5	94.98(17)	N4–Pd4–O13	95.28(16)
N2–Pd2–O6	84.50(16)	N4–Pd4–O14	83.89(16)
O5–Pd2–O10	87.90(14)	O13–Pd4–O6	86.32(15)
O6–Pd2–O10	92.62(14)	O14–Pd4–O6	94.51(14)
Pd1–O2–Pd3	121.28(17)	Pd3–O10–Pd2	120.78(18)
Pd2–O6–Pd4	116.87(17)	Pd4–O14–Pd1	118.98(17)

The reaction of **1e** and **1f** with triphenylphosphane yielded the mononuclear complexes [Pd{2-O-4,6-(MeO)$_2$-C$_6$H$_2$C(H)=N(2-OC$_6$H$_4$)}(PPh$_3$)] (**2e**) and [Pd{2-OC$_6$H$_4$C-(H)=N(2-OC$_6$H$_4$)}(PPh$_3$)] (**2f**) after cleavage of the tetranuclear structure, as air-stable solids, which were fully characterized. The ^{31}P NMR spectroscopic data were in accordance with an arrangement in which the phosphorus atom is *trans* to the nitrogen atom. Contrary to the case of five-membered ring palladacycles, the 3-H protons and (in **2e**) the C-4 MeO group were not affected by shielding from the phosphane phenyl rings; expansion of the metallated ring to six members places these nuclei away form the appropriate shielding zone.

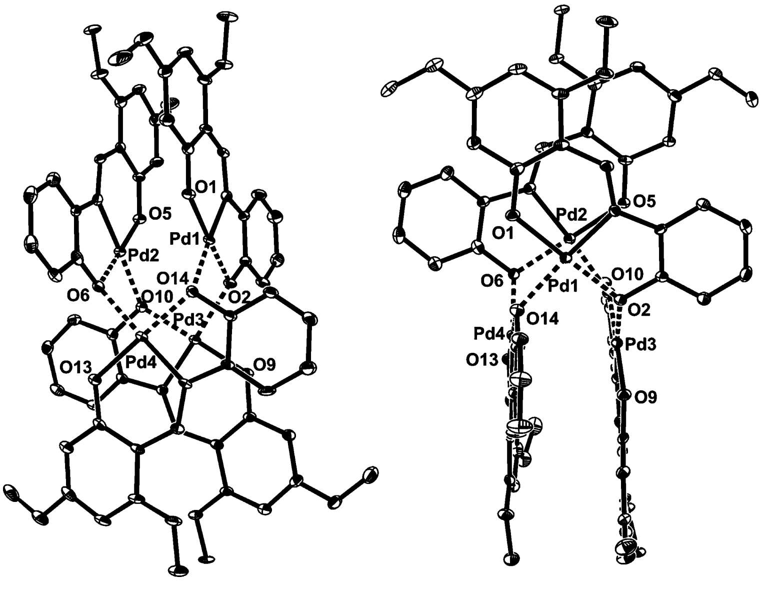


Figure 4. Molecular structure of [Pd{2-O-4,6-(MeO)$_2$C$_6$H$_2$C(H)=N(2-OC$_6$H$_4$)}]$_4$, (**1e**). Ellipsoids drawn at the 40% level.

Conclusions

We have shown that Schiff base ligands derived from 2-aminophenol offer different bonding modes to palladium(II) because of the various donor atoms they possess, behaving as tridentate [*C*,*N*,*O*] or [*O*,*N*,*O*] ligands. In all cases, tetranuclear compounds were formed upon reaction of the ligand with the metal salt through metallation of a substituted phenyl ring. As with the tridentate [*C*,*N*,*S*] thiosemicarbazones, formation of the central eight-membered Pd_4O_4 core seems to favour tetranuclear clusters, as opposed to the dinuclear moieties obtained from didentate [*C*,*N*] Schiff bases. Where choice was possible, five-membered ring metallacycles were preferred over six-membered ones; nevertheless, the latter may be obtained when substituents hinder attack of the metal atom on the phenyl ring. In the case of ligand **d**, where metallation may proceed through a phenyl or a methyl carbon atom, mixed five- and six-membered palladated moieties build up the tetrameric structure, thus constituting an unprecedented example of a tetranuclear cyclopalladated compound.

Experimental Section

General Procedures: Solvents were purified by standard methods.[54] Chemicals were reagent grade. The phosphanes PPh_3, $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2P(CH_2)_2PPh_2$ (dppe) were purchased from Aldrich Chemie. Microanalyses were carried out with a Carlo Erba Elemental Analyzer, Model 1108. IR spectra were recorded by using Nujol mulls or KBr discs with a Perkin–Elmer 1330 and a Mattson spectrophotometer. NMR spectra were obtained in $CDCl_3$ solutions and referenced to $SiMe_4$ [^{1}H, or 85% H_3PO_4 $^{31}P\{^1H\}$]; they were recorded with a Bruker AC-2005 spectrometer. All chemical shifts were reported downfield from the standards. The FAB mass spectra were recorded by using a Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol (3-NBA) was used as the matrix.

Syntheses

2,3,4-(MeO)$_3$C$_6$H$_2$C(H)=N[2-(OH)-5-*t*BuC$_6$H$_3$] (a): 2,3,4-(MeO)$_3$-C$_6$H$_2$COH (1.000 g, 6.06 mmol) was added to a solution of 2-amino-4-*tert*-butylphenol (1.188 g, 6.06 mmol) in dry chloroform (50 cm^3). The solution was heated under reflux in a Dean–Stark apparatus for 4 h. After cooling to room temperature the chloroform was removed, and a brown solid was obtained. Yield: 1850 mg, 89%. $C_{20}H_{25}NO_4$ (343.18): calcd. C 69.9, H 7.3, N 4.1; found C 68.5, H 7.0, N 3.8. IR: $\tilde{\nu}$ = 3427 (m, ν_{O-H}), 1589 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.13 (s, 9 H, *t*Bu), 3.92, 3.95, 4.02 (s, 9 H, MeO), 6.80 (d, $^3J_{H5,H6}$ = 8.3 Hz, 1 H, 5-H), 7.92 (d, $^3J_{H5,H6}$ = 8.3 Hz, 1 H, 6-H), 6.95 (d, $^2J_{H,H}$ = 8.3 Hz, 11 H), 7.4 (m, 2 H, 8-H, 10-H), 8.76 (s, 1 H, OH) (resonance taken from a spectrum recorded in [D$_6$]dmso), 8.97 (s, 1 H, H$_i$) ppm. FAB-MS: *m*/*z* = 344 [MH]$^+$.

Schiff base ligands **b**–**d** were prepared similarly as brown solids.

2,6-(Me)$_2$C$_6$H$_3$C(H)=N[2-(OH)C$_6$H$_4$] (b): Yield: 1214 mg, 89%. $C_{15}H_{15}NO$ (225.12): calcd. C 79.9, H 6.7, N 6.2; found C 68.5, H 7.0, N 3.8. IR: $\tilde{\nu}$ = 3396 (m, ν_{O-H}), 1621 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.64 (s, 6 H, Me), 7.2 (m, 7 H), 9.1 (s, 1 H, H$_i$), 10.8 (br, 1 H, OH) ppm.

2,5-(Me)$_2$C$_6$H$_3$C(H)=N[2-(OH)C$_6$H$_4$] (c): Yield: 1188 mg, 88%. $C_{15}H_{15}NO$ (225.12): calcd. C 79.9, H 6.7, N 6.2; found C 79.8, H 6.7, N 6.1. IR: $\tilde{\nu}$ = 3375 (s, ν_{O-H}), 1608 (sh, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.41, 2.59 (s, 6 H, Me), 6.95 (dt, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.06 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.3 (m, 5 H), 7.91 (s, 6-H), 8.9 (s, 1 H, H$_i$), 9.8 (br, 1 H, OH) ppm.

2,4-(Me)$_2$C$_6$H$_3$C(H)=N[2-(OH)C$_6$H$_4$] (d): Yield: 1589 mg, 97%. $C_{15}H_{15}NO$ (225.12): calcd. C 79.9, H 6.7, N 6.2; found C 79.4, H 6.4, N 6.1. IR: $\tilde{\nu}$ = 3043 (m, ν_{O-H}), 1619 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40, 2.61 (s, 6 H, Me), 6.5 (br, 1 H, OH), 6.94 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H), 7.3 (m, 5 H), 7.91 (d, $^3J_{H6,H5}$ = 7.8 Hz, 1 H, 6-H), 8.97 (s, 1 H, H$_i$) ppm.

Schiff base **e** was prepared similarly as a yellow solid.

2-(OH)-4,6-(MeO)$_2$C$_6$H$_2$C(H)=N[2-(OH)C$_6$H$_4$] (e): Yield: 1523 mg, 93%. $C_{15}H_{15}NO_4$ (273.10): calcd. C 65.9, H 5.5, N 5.1; found C 65.8, H 5.5, N 5.1. IR: $\tilde{\nu}$ = 3430 (m, ν_{O-H}), 3385 (sh), 1625 (sh, m, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.85, 3.84 (s, 6 H, MeO), 5.6 (br, 1 H, OH), 5.9, 6.1 (s, 2 H, 3-H, 5-H), 7.0 (m, 4 H), 8.9 (s, 1 H, H$_i$), 10.8 (br, 1 H, OH) ppm.

Schiff base **f** was prepared similarly as a red solid.

2-(OH)C$_6$H$_4$C(H)=N[2-(OH)C$_6$H$_4$] (f): Yield: 1176 mg, 92%. $C_{13}H_{11}NO_2$ (213.08): calcd. C 73.2, H 5.2, N 6.6; found C 73.1, H 5.0, N 6.3. IR: $\tilde{\nu}$ = 3500 (m, ν_{O-H}), 1630 (m, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.7 (br, 1 H, OH), 7.2 (m, 8 H), 8.7 (s, 1 H, H$_i$), 12.2 (br, 1 H, OH) ppm.

[Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N(2-O-5-*t*BuC$_6$H$_3$)}]$_4$ (1a): A pressure tube containing 2,3,4-(MeO)$_3$C$_6$H$_2$C(H)=N[2-(OH)-5-*t*BuC$_6$H$_3$] (0.456 mg, 1.33 mmol), palladium acetate (0.300 g, 1.33 mmol) and dry toluene (20 cm^3) was sealed under argon. The resulting mixture was heated at 60 °C for 24 h. After cooling to room temperature the solution was filtered through Celite to remove the small amount of black palladium formed. The solvent was removed under vacuum to give a red oil, which was recrystallized from dichloromethane/hexane to give the desired product as a red solid. Yield: 1191 mg, 50%. $C_{80}H_{92}N_4O_{16}Pd_4$ (1791.28): calcd. C 53.6, H 5.2, N 3.1; found C 53.0, H 5.1, N 3.1. IR: $\tilde{\nu}$ = 1571 (sh, m, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.24 (s, 9 H, *t*Bu), 3.38, 3.81, 4.03 (s, 9 H, MeO), 5.81 (s, 1 H, 5-H), 6.75 (d, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, 8-H), 6.99 (dd, $^3J_{H10,H11}$ = 8.8 Hz, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, 10-H), 7.35 (d, 1 H, 11-H), 7.54 (s, 1 H, H$_i$) ppm. FAB-MS: *m*/*z* = 1792 [MH]$^+$, 896 [M/2]$^+$.

Compound **1b** was prepared similarly as a brown solid.

[Pd{6-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}]$_4$ (1b): Yield: 98 mg, 30%. $C_{60}H_{52}N_4O_4Pd_4$ (1318.75): calcd. C 54.4, H 4.3, N 4.2; found C 53.9, H 4.1, N 4.1. IR: $\tilde{\nu}$ = 1583 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, Me), 2.60, 3.49 (d, $J_{gem(H,H)}$ = 13.6 Hz, 2 H, -CH$_2$-), 6.51 (dt, $^3J_{H9,H8}$ = 8.3 Hz, $^3J_{H10,H9}$ = 7.2 Hz, $^4J_{H11,H9}$ = 1.3 Hz, 1 H, 9-H), 6.80 (d, $^3J_{H5,H4}$ = 7.6 Hz, 1 H, 5-H), 6.86 (m, 2 H, 8-H, 4-H), 7.04 (d, $^3J_{H4,H3}$ = 7.4 Hz, 1 H, 3-H), 7.5 (dt, $^3J_{H10,H9}$ = 7.2 Hz, $^3J_{H11,H10}$ = 8.3 Hz, $^4J_{H10,H8}$ = 1.3 Hz, 1 H, 10-H), 7.84 (dd, $^3J_{H11,H10}$ = 8.3 Hz, $^4J_{H11,H9}$ = 1.3 Hz, 1 H, 11-H), 8.13 (s, 1H, H$_i$) ppm. FAB-MS: *m*/*z* = 331 [(M/4)H]$^+$.

Compound **1c** was prepared similarly as a red solid.

[Pd{5-Me-2-CH$_2$C$_6$H$_3$C(H)=N(2-OC$_6$H$_4$)}]$_4$ (1c): Yield: 40 mg, 45%. $C_{60}H_{52}N_4O_4Pd_4$ (1318.75): calcd. C 54.4, H 4.3, N 4.2; found C 54.2, H 4.3, N 4.1. IR: $\tilde{\nu}$ = 1582 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.44 (s, 3 H, Me), 2.45 (d, $J_{gem(H,H)}$ = 14.1 Hz, 1 H, -CH$_2$-), 3.59 (d, $J_{gem(H,H)}$ = 14.1 Hz, 1 H, -CH$_2$-), 6.50 (dt, $^3J_{H9,H8}$ = 7.8 Hz, $^4J_{H11,H9}$ = 0.9 Hz, 1 H, 9-H), 6.8 (m, 3 H), 7.2 (m, 3 H), 7.13 (s, 1 H, H$_i$), 7.74 (dd, $^3J_{H11,H10}$ = 8.3 Hz, $^4J_{H11,H9}$ = 0.9 Hz, 1 H, 11-H) ppm.

[Pd{4-Me-2-$CH_2C_6H_3$C(H)=N(2-OC_6H_4)}]$_n$[Pd{2,4-(Me)$_2C_6H_2$C(H)=N(2-OC_6H_4)}]$_{4-n}$ (*n* = 0–4): The mixture was prepared by following a procedure similar to that used for **1a**, but with reaction times of 5 h, 24 h and 3 d and reaction temperatures of 40, 60 and 80 °C. The components of the mixture could not be separated by column chromatography or by other methods. Yield: 30 mg, 30%. $C_{60}H_{52}N_4O_4Pd_4$ (1318.75): calcd. C 54.4, H 4.3, N 4.2; found C 54.3, H 4.3, N 4.0. IR: $\tilde{\nu}$ = 1598 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.62 (d, $J_{\mathrm{gem(H,H)}}$ = 13.5 Hz, 1 H, -CH_2-), 3.53 (d, $J_{\mathrm{gem(H,H)}}$ = 14.0 Hz, 1 H, -CH_2-), 3.83 (d, $J_{\mathrm{gem(H,H)}}$ = 13.0 Hz, 1 H, -CH_2-), 3.84 (d, $J_{\mathrm{gem(H,H)}}$ = 14.0 Hz, 1 H, -CH_2-), 3.92 (d, $J_{\mathrm{gem(H,H)}}$ = 13.7 Hz, 1 H, -CH_2-) ppm. ^{1}H NMR (200 MHz, [D_6]dmso): δ = 2.14 (s, 3 H, Me), 2.34, 2.35 (s, 6 H, Me′), 3.26 (s, 2 H, -CH_2-), 8.41 (s, 1 H, H_i), 8.82 (s, 1 H, H_i) ppm.

Compound **1e** was prepared similarly as a yellow solid.

[Pd{2-O-4,6-(MeO)$_2C_6H_2$C(H)=N(2-OC_6H_4)}]$_4$ (1e): Yield: 117 mg, 75%. $C_{60}H_{52}N_4O_{16}Pd_4$ (1510.75): calcd. C 47.7, H 3.5, N 3.7; found C 47.5, H 3.4, N 3.5. IR: $\tilde{\nu}$ = 1612 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.70, 3.82 (s, 6 H, MeO), 5.57, 5.73 (d, H5, $^{4}J_{H5,H3}$ = 1.9 Hz, 2 H, 3-H), 6.59 (t, $^{3}J_{H9,H8}$ = 7.5 Hz, 1 H, 9-H), 7.09 (m, 2 H, 8-H, 10-H), 7.71 (s, 1 H, H_i), 8.33 (d, $^{3}J_{H11,H10}$ = 8.3 Hz, 1 H, 11-H) ppm.

Compound **1f** was prepared similarly as a red solid. Different reaction times (5 h, 24 h and 5 d) were used with similar yields.

[Pd{2-OC_6H_4C(H)=N(2-OC_6H_4)}]$_4$ (1f): Yield: 118 mg, 86%. $C_{52}H_{36}N_4O_8Pd_4$ (1270.75): calcd. C 49.2, H 2.8, N 4.4; found C 48.9, H 2.8, N 4.3. IR: $\tilde{\nu}$ = 1609 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, [D_6]dmso): δ = 7.17 (m, $^{3}J_{H10,H11}$ = 8.3 Hz, $^{3}J_{H10,H9}$ = 7.0 Hz, $^{4}J_{H10,H8}$ = 1.3 Hz, 1 H, 10-H), 7.30 (m, $^{3}J_{H,H}$ = 8.0 Hz, $^{3}J_{H,H}$ = 6.8 Hz, $^{4}J_{H,H}$ = 1.3 Hz, 1 H), 7.34 (dd, H8, $^{3}J_{H9,H8}$ = 8.3 Hz, 1 H), 7.57 (dd, $^{3}J_{H,H}$ = 8.7 Hz, $^{4}J_{H,H}$ = 1.3 Hz, 1 H), 7.60 (m, $^{4}J_{H,H}$ = 1.3 Hz, 1 H, 9-H), 7.93 (m, $^{3}J_{H,H}$ = 8.6 Hz, $^{3}J_{H,H}$ = 6.8 Hz, $^{4}J_{H,H}$ = 1.8 Hz, 1 H), 8.18 (dd, $^{3}J_{H,H}$ = 8.0 Hz, $^{4}J_{H,H}$ = 1.8 Hz, 1 H), 8.33 (dd, 1 H, 11-H), 8.94 (1 H, H_i) ppm. FAB-MS: *m*/*z* = 637 [M/2]$^+$.

[Pd{2,3,4-(MeO)$_3C_6$HC(H)=N(2-O-5-*t*BuC_6H_3)}(PPh_3)] (2a): PPh_3 (6.99 mg, 0.026 mmol) was added to a suspension of **1a** (12 mg, 0.006 mmol) in acetone (15 cm^3). The mixture was stirred for 12 h, and the solvent was removed to give a violet solid, which was recrystallized from acetone/hexane. Yield: 15 mg, 80%. $C_{38}H_{38}NO_4PPd$ (710.11): calcd. C 64.3, H 5.4, N 1.9; found C 64.3, H 5.3, N 1.8. IR: $\tilde{\nu}$ = 1544 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.27 (s, 9 H, *t*Bu), 2.92, 3.73, 3.98 (s, 9 H, MeO), 5.49 (d, $^{4}J_{H5,P}$ = 3.4 Hz, 1 H, 5-H), 6.45 (d, $^{3}J_{H10,H11}$ = 8.7 Hz, 1 H, 11-H), 6.96 (dd, $^{3}J_{H10,H11}$ = 8.7 Hz, $^{4}J_{H8,H10}$ = 1.9 Hz, 1 H, 10-H), 7.05 (d, $^{4}J_{H8,H10}$ = 1.9 Hz, 1 H, 8-H), 8.14 (d, $^{4}J_{H_i,P}$ = 10.7 Hz, 1 H, H_i) ppm. ^{31}P{^{1}H} NMR (80.96 MHz, $CDCl_3$): δ = 34.2 (s) ppm.

Compounds **2b**–**2f** were prepared similarly as red or brown (**2b**) solids.

[Pd{6-Me-2-$CH_2C_6H_3$C(H)=N(2-OC_6H_4)}(PPh_3)] (2b): Yield: 10 mg, 60%. $C_{33}H_{29}NOPPd$ (592.98): calcd. C 66.8, H 4.9, N 2.4; found C 66.5, H 4.7, N 2.3. IR: $\tilde{\nu}$ = 1581 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.55 (s, 3 H, Me), 2.96 (d, $^{3}J_{CH_2,P}$ = 5.8 Hz, 2 H, -CH_2-), 6.43 (t, $^{3}J_{H10,H9}$ = 7.3 Hz, 1 H, 10-H), 6.52 (t, $^{4}J_{H_5,CH_2}$ = 4.4 Hz, 1 H, 2-H), 6.92 (m, 3 H), 7.09 (t, $^{3}J_{H,H}$ = 7.8 Hz, 1 H), 8.69 (d, $^{4}J_{H_i,P}$ = 12.7 Hz, 1 H, H_i) ppm. ^{31}P{^{1}H} NMR (80.96 MHz, $CDCl_3$): δ = 33.4 (s) ppm.

[Pd{5-Me-2-$CH_2C_6H_3$C(H)=N(2-OC_6H_4)}(PPh_3)] (2c): Yield: 29 mg, 60%. $C_{33}H_{29}NOPPd$ (592.98): calcd. C 66.8, H 4.9, N 2.4; found C 66.4, H 4.8, N 2.3. IR: $\tilde{\nu}$ = 1581 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, Me), 2.93 (d, $^{3}J_{CH_2,P}$ = 5.8 Hz, 2 H, -CH_2-), 6.43 (t, $^{3}J_{H10,H9}$ = 7.5 Hz, 1 H, 10-H), 6.66 (d, $^{3}J_{H3,H4}$ = 7.8 Hz, 1 H, 3-H), 6.89 (m, 2 H, 4-H, 11-H), 7.09 (t, $^{3}J_{H9,H8}$ = 7.5 Hz, $^{4}J_{H11,H9}$ = 1.5 Hz, 1 H, 9-H), 7.25 (d, $^{3}J_{H9,H8}$ = 7.5 Hz, 1 H, 8-H), 7.27 (s, 1 H, 6-H), 8.32 (d, $^{4}J_{H_i,P}$ = 12.7 Hz, 1 H, H_i) ppm. ^{31}P{^{1}H} NMR (80.96 MHz, $CDCl_3$): δ = 33.8 (s) ppm. FAB-MS: *m*/*z* = 592 [M]$^+$.

Compounds **2d** and **2d′** were prepared by a similar procedure to the one described for **2a** using as starting material the mixture of isomers **1d/1d′**. The compounds were obtained as a mixture [in a 1:0.5 (**2d/2d′**) molar ratio] from which the pure compounds could not be isolated by column chromatography or by other methods.

[Pd{4-Me-2-$CH_2C_6H_3$C(H)=N(2-OC_6H_4)}(PPh_3)] (2d) and [Pd{2,4-(Me)$_2C_6H_2$C(H)=N(2-OC_6H_4)}(PPh_3)] (2d′): Yield: 23 mg, 50%. $C_{33}H_{29}NOPPd$ (592.98): calcd. C 66.8, H 4.9, N 2.4; found C 66.3, H 4.7, N 2.3. IR: $\tilde{\nu}$ = 1581 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.67 (s, 6 H, Me′), 2.25 (s, 3 H, Me), 2.93 (d, $^{3}J_{CH_2,P}$ = 5.8 Hz, 2 H, -CH_2-), 5.67 (d, $^{4}J_{H5,P}$ = 3.4 Hz, 1 H, 5′-H), 8.20 (d, $^{4}J_{H_i,P}$ = 10.3 Hz, 1 H, H_i′), 8.32 (d, $^{4}J_{H_i,P}$ = 12.7 Hz, 1 H, H_i) ppm. ^{31}P{^{1}H} NMR (80.96 MHz, $CDCl_3$): δ = 34.6 (**2d′**), 33.8 (s) (**2d**) ppm.

[Pd{2-O-4,6-(MeO)$_2C_6H_2$C(H)=N(2-OC_6H_4)}(PPh_3)] (2e): Yield: 29 mg, 60%. $C_{33}H_{28}NO_4PPd$ (639.97): calcd. C 61.9, H 4.4, N 2.2; found C 61.5, H 4.1, N 2.0. IR: $\tilde{\nu}$ = 1611 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.67, 3.88 (s, 6 H, MeO), 5.63, 5.78 (d, $^{4}J_{H5,H3}$ = 2.2 Hz, 2 H, 3-H, 5-H), 6.64 (t, $^{3}J_{H10,H9}$ = 7.5 Hz, 1 H, 10-H), 6.90 (d, $^{3}J_{H11,H10}$ = 7.5 Hz, 1 H, 11-H), 7.03 (t, 1 H, 9-H), 7.72 (d, $^{3}J_{H9,H8}$ = 8.3 Hz, 1 H, 8-H), 9.12 (d, $^{4}J_{H_i,P}$ = 18.1 Hz, 1 H, H_i) ppm. ^{31}P{^{1}H} NMR (80.96 MHz, $CDCl_3$): δ = 23.4 (s) ppm. FAB-MS: *m*/*z* = 639 [M]$^+$.

[Pd{2-OC_6H_4C(H)=N(2-OC_6H_4)}(PPh_3)] (2f): Yield: 25 mg, 66%. $C_{31}H_{24}NO_2PPd$ (579.92): calcd. C 64.2, H 2.4, N 4.2; found C 64.3, H 2.3, N 4.0. IR: $\tilde{\nu}$ = 1603 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.61 (d, $^{3}J_{H5,H4}$ = 8.5 Hz, 1 H, 5-H), 6.7 (m, 2 H, 3-H, 10-H), 6.92 (dd, $^{3}J_{H11,H10}$ = 8.3 Hz, $^{3}J_{H11,H9}$ = 1.2 Hz, 1 H, 11-H), 7.08 (dt, $^{3}J_{H10,H9}$ = 6.9 Hz, $^{3}J_{H9,H8}$ = 8.3 Hz, 1 H, 9-H), 7.22 (dt, $^{3}J_{H5,H4}$ = 8.6 Hz, $^{3}J_{H4,H3}$ = 6.8 Hz, $^{3}J_{H4,H2}$ = 1.8 Hz, 1 H, 4-H), 7.74 (dd, $^{3}J_{H9,H8}$ = 8.3 Hz, $^{4}J_{H10,H8}$ = 1.4 Hz, 1 H, 8-H), 8.61 (dd, $^{4}J_{H_i,P}$ = 17.1 Hz, 1 H, H_i) ppm. ^{31}P{^{1}H} NMR (80.96 MHz, $CDCl_3$): δ = 23.3 (s) ppm. FAB-MS: *m*/*z* = 579 [M]$^+$.

Compounds **3a** and **4a** were obtained as violet solids by a similar procedure, but with a 1:2 complex **1a/** diphosphane molar ratio.

[{Pd(2,3,4-{MeO}$_3C_6$HC{H}=N{2-O-5-*t*BuC_6H_3})}$_2$(μ-$PPh_2CH_2PPh_2$)] (3a): Yield: 19 mg, 60%. $C_{65}H_{68}N_2O_8P_2Pd_2$ (1280.03): calcd. C 60.9, H 5.3, N 2.2; found C 60.2, H 5.2, N 2.1. IR: $\tilde{\nu}$ = 1544 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.32 (s, 9 H, *t*Bu), 2.89, 3.70, 3.95 (s, 9 H, MeO), 5.39 (d, $^{4}J_{H5,P}$ = 4.3 Hz, 1 H, 5-H), 6.46 (d, $^{3}J_{H10,H11}$ = 9.2 Hz, 1 H, 11-H), 7.1 (m, 2 H, 10-H, 8-H), 7.99 (d, $^{4}J_{H_i,P}$ = 10.7 Hz, 1 H, H_i) ppm. ^{31}P{^{1}H} NMR (80.96 MHz, $CDCl_3$): δ = 25.6 (s) ppm.

[{Pd(2,3,4-{MeO}$_3C_6$HC{H}=N{2-O-5-*t*BuC_6H_3})}$_2${μ-$PPh_2(CH_2)_2PPh_2$}] (4a): Yield: 21 mg, 65%. $C_{66}H_{70}N_2O_8P_2Pd_2$ (1294.06): calcd. C 61.3, H 5.4, N 2.1; found C 61.1, H 5.3, N 2.0. IR: $\tilde{\nu}$ = 1544 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.30 (s, 9 H, *t*Bu), 2.85, 3.72, 3.97 (s, 9 H, MeO), 5.38 (s, 1 H, 5-H), 6.51 (d, $^{3}J_{H10,H11}$ = 8.7 Hz, 1 H, 11-H), 7.01 (dd, $^{3}J_{H10,H11}$ = 8.7 Hz, $^{4}J_{H8,H10}$ = 1.9 Hz, 1 H, 10-H), 7.09 (d, $^{4}J_{H8,H10}$ = 1.9 Hz, 1 H, 11-H) ppm. ^{31}P{^{1}H} NMR (80.96 MHz, $CDCl_3$): δ = 35.0 (s) ppm.

Compound **3b** was obtained following a similar procedure as a brown solid.

Table 5. Crystal and structure refinement data.

	1a·H_2O	**1c**	**1d/d′**	**1e**·$4CH_2Cl_2$
Chemical formula	$C_{80}H_{94}N_4O_{17}Pd_4$	$C_{60}H_{52}N_4O_4Pd_4$	$C_{60}H_{52}N_4O_4Pd_4$	$C_{64}H_{60}Cl_8N_4O_{16}Pd_4$
Formula weight	1809.19	1318.66	1318.66	1850.36
T [°C]	293(2)	293(2)	293(2)	120(2)
λ	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$C2/c$	$Fdd2$	$P\bar{1}$	$C12/c1$
a [Å]	23.371(1)	9.311(2)	12.334(3)	31.233(6)
b [Å]	23.254(1)	27.305(6)	13.728(3)	17.500(3)
c [Å]	30.721(1)	39.281(8)	17.537(5)	27.541(5)
α [°]			75.770(4)	
β [°]	94.635(1)		81.472(4)	113.864(3)
γ [°]			81.208(4)	
V [Å^3]	16641(1)	9986(4)	2825(1)	13766(4)
Z	8	8	2	8
μ [mm^{-1}]	1.444	1.472	1.300	1.408
$2\theta_{max}$ [°]	56.58	52.88	52.88	52.92
Refln. collected	53553	2611	31767	77225
Refln. independent	19987 (R_{int} = 0.068)	2210 (R_{int} = 0.035)	11533 (R_{int} = 0.031)	14150 (R_{int} = 0.088)
R_1[a]	0.0598	0.0311	0.0432	0.0401
wR_2[b]	0.1891	0.0808	0.1332	0.0969

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [$F > 4\sigma(F)$]. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, all data.

[{Pd(6-Me-2-CH$_2$C$_6$H$_3$C{H}=N{2-OC$_6$H$_4$})}$_2${μ-PPh$_2$(CH$_2$)$_2$PPh$_2$}] (3b): Yield: 23 mg, 70%. $C_{56}H_{50}N_2O_2P_2Pd_2$ (1057.80): calcd. C 63.6, H 4.8, N 2.6; found C 63.6, H 4.7, N 2.6. IR: $\tilde{\nu}$ = 1581 (s, $\nu_{C=N}$) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 2.55 (s, 3 H, Me), 2.90 (d, $^3J_{CH_2,P}$ = 9.1 Hz, 2 H, -CH$_2$-), 6.43 (t, $^3J_{H10,H9}$ = 6.8 Hz, 1 H, 10-H), 6.74 (t, $^4J_{H_3,CH_2}$ = 2.3 Hz, 1 H, 3-H), 6.84 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 0.9 Hz, 1 H), 6.94 (d, $^3J_{H,H}$ = 4.9 Hz, 1 H), 7.10 (dt, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.4 Hz, 1 H), 8.71 (m, 1 H, H$_i$) ppm. ^{31}P{^{1}H} NMR (80.96 MHz, CDCl$_3$): δ = 33.2 (s) ppm.

X-ray Crystallographic Study: Three-dimensional, room temperature X-ray data were collected with a Siemens Smart CCD diffractometer by the ω scan method with graphite-monochromated Mo-K_α radiation (Table 5). All the measured reflections were corrected for Lorentz and polarisation effects and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. The C60 atom of **1a** was disordered over two positions with occupancies of approximately 50%. The C1–C9 and C21–C28 carbon atoms, corresponding to the benzal phenyls of two of the cyclometallated ligands in complex **1d/d′** were found to be disordered over two positions (with occupancies of approximately 70% [C1–C9] and 50% [C21–C28] for the major components). The refinement was carried out by taking into account the minor components. Refinement converged at a final R = 0.0598, 0.0311, 0.0432 and 0.0401 (for complexes **1a**, **1c**, **1d/d′** and **1e**, respectively, observed data, F) and wR_2 = 0.1891, 0.0808, 0.1332 and 0.0909 (for complexes **1a**, **1c**, **1d/d′** and **1e**, respectively, unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out by using the program package SHELX-97.[55]

CCDC-608700 (for **1a**), -608701 (for **1c**), -608702 (for **1d/d′**) and -608703 (for **1e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank the Ministerio de Educación y Ciencia (Project CTQ2006-15621-C02-01/BQU) for financial support.

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Received: May 2, 2007