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Synthesis and characterization of a homologous series of mononuclear palladium complexes containing different cyclometalated ligands

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Abstract

New mononuclear palladium(II) complexes formed by with 2-hydroxy-4-(*n*-hexyloxybenzylidene)-4'-*n*-hexylaniline (**HL**) and 2-phenylpyridine (**I**), benzo[h]quinoline (**II**), azobenzene (**III**), 2-benzoylpyridine (**IV**) or phenyl-2-pyridylketone-2,4-dinitrophenylhydrazine (**V**) have been synthesized and characterized by analytical and spectroscopic methods and the single-crystal structures of [(IVa)Pd(L)] and [(Va)Pd(L)] have been established. The spectroscopic and diffractometric data account for molecular structures wherein the palladium(II) center is part of two chelate rings involving **HL** and one of the **I–V** ligands which form a five-member N,C{[(Ia)Pd(L)], [(IIa)Pd(L)] and [(IIIa)Pd(L)]}, a six-member N,C{[(IVa)Pd(L)]}, or a six-member N,N' {[(Va)Pd(L)]} metallacycle. The electronic spectra of [(IIIa)Pd(L)] and [(Va)Pd(L)] show an absorption maxima, at 495 ($\epsilon \sim 3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 531 nm ($\epsilon \sim 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), respectively, which results are significantly affected by the polarity of the solvent. These chromophores should therefore be of interest for the preparation of nonlinear optical materials. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopalladate complexes; Schiff base complexes; Crystal structures; Palladium complexes

1. Introduction

The great interest in materials which feature physical properties of potential use in new technologies presently drives many new investigations into organometallic and coordination compounds. In particular, with reference to applications for optoelectronic devices, research has been focused on the synthesis of materials with nonlinear optical [1], photorefractive [2,3] or electroluminescent [4] properties and the promising results reported to date confirm that the incorporation of a metal center into a molecular structure plays an important role.

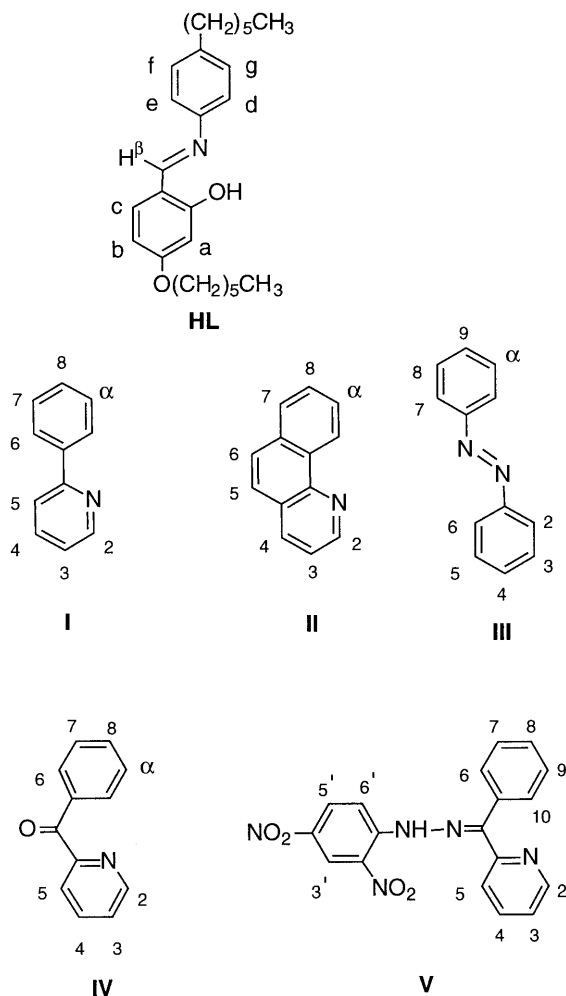
In a recent study the influence of palladium(II) or platinum(II) ions involved in rings formed by or-

thometalation of imines has been considered. Thus, comparing the uncomplexed ligands with their dinuclear or mononuclear complexes, it has been observed that the nonlinearity of these systems increases when a strong donor group is located in the cyclometalated ring [1c]. Moreover, it has been shown that the five-membered metalacycle of orthopalladated species exhibits a certain degree of aromaticity [5]. Hence, the electro-optical properties, which arise from the metal containing molecular fragment should ultimately depend on both the nature and electronic environment experienced by the different atoms which are part of the palladacycle. In this context we planned to synthesize new mononuclear cyclopalladated complexes in order that they be subsequently tested for nonlinear optical properties and/or photorefractivity.

The ligands we selected are the salicylideneaniline **HL** and the species **I–V** shown in Scheme 1. We report here on the synthesis, characterization and spectroscopic

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Scheme 1. Aromatic protons numbering scheme and molecular structure of the reacted ligands, HL and I–V.

properties of the homologous series of mononuclear complexes [(Ia–Va)Pd(L)] which contain the palladacycles [(Ia–Va)Pd], Ia–Va and L standing for the deprotonated form of I–V and HL, respectively. The crystal structures of complexes [(IVa)Pd(L)] and [(Va)Pd(L)] are also described.

2. Results and discussion

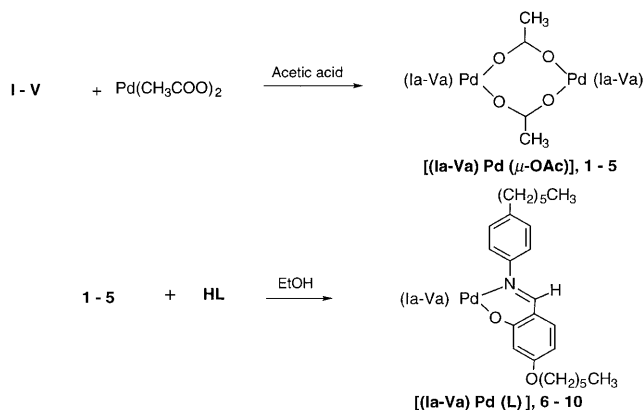
2.1. Synthesis and structures

The commercially unavailable ligands HL and V were prepared through the reaction of 2-hydroxy-4-(n-hexyloxy)benzaldehyde [6] with 4-n-hexylaniline and IV with 2,4-dinitrophenylhydrazine [7], respectively (Section 3). Both products are solids, which give the expected analytical and spectroscopic data. Moreover, HL displays thermotropic mesomorphism (Section 3) which consists in an enantiotropic smectic C (SmC) and a nematic (N) mesophases [8].

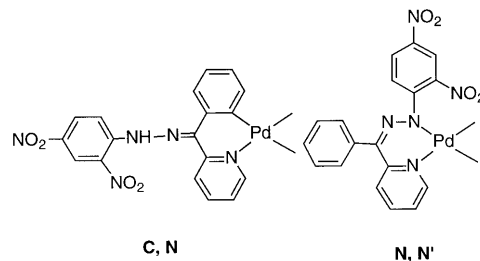
On treating the I–V ligands with palladium(II) acetate, the dimeric species [(Ia–Va)Pd(μ-OAc)] (1–5) in Scheme 2, were obtained (Section 3). The I–V substrates were selected because of their ability to undergo the orthometalation process. In complexes 1 [9], 2 [10], 3 [11] and 4 [12], the occurrence of the expected N,C metalacycle was confirmed by comparison with the literature data. In complex 5, unlike 1–4, both C,N, and N,N' six-membered metalacycle formation (Scheme 3) can take place [13]. However, the N,N' coordination mode was inferred from both the IR spectrum, which lacks the absorption attributable to N–H stretching, and the molecular structure of complex 10 (Scheme 2 and Fig. 2).

Compounds [(Ia–Va)Pd(L)] (6–10), have been obtained from complexes 1–5 by a subsequent bridge splitting reaction performed with HL. The L coordination (Scheme 2) was proved by inspection of the IR and ¹H NMR spectra. In particular, the shifts of the C=N stretching [14] and of the imine proton (H^β) resonance [15] with respect to the homologous HL signals, are both accounted for by the occurrence of the metal complexation (Section 3).

In complexes 6–10 the palladium coordination sphere consists of two chelate systems with an C,N and O,N (6–9) or an N,N' and O,N (10) set of bonding atoms. In principle, products 6–10 can be isomeric mixtures of *N,N-trans* or *cis* isomers. However, for



Scheme 2. Synthesis of complexes 1–10.



Scheme 3. Possible cyclopalladation modes of ligand V.

similar cyclopalladated salicylideneaminato species, it has been shown previously that such isomers, if any, differ in the position of the imine hydrogen signal in the ^1H NMR spectrum [16]. In the present case, the ^1H NMR spectra of all the **6–10** synthesized species show a single imine proton resonance. Therefore **6–10** are pure complexes and their molecular geometries, which are N,N-*trans* and N,N-*cis* in **9** and **10**, respectively (Figs. 1 and 2), are N,N-*trans* in **6–8** [16].

The molecular structure of complexes **9** and **10**, [(IVa)Pd(L)] and [(Va)Pd(L)], respectively, was determined by single crystal X-ray analysis. A perspective view of complex **9** is shown in Fig. 1. Selected bond distances and angles are given in Table 1. The palladium atom is coordinated in a slightly distorted square planar geometry with a *trans* arrangement of the N donor atoms. The two chelating organic ligands give rise, upon coordination to the palladium atom, to two six-membered rings at a dihedral angle of $29.7(2)^\circ$.

The ring obtained from chelation of the salicylideneaminato ligand **HL**, of type $\text{Pd-NC}_3\text{O}$, is essentially planar, with a maximum deviation from the mean plane of $0.046(4)$ Å at N(1). The torsion angles for the $\text{Pd-NC}_3\text{O}$ cycle are reported in Table 1. The bond lengths and angles agree well with those found for palladium bis-salicylideneaminato complexes [17]. However, the Pd–O(1) bond distance of $2.069(4)$ Å is found to be slightly longer than *trans* to oxygen atoms, because of the *trans* effect of the σ -bonded C atom. This feature is found to be similar in complex [*N*-(phenyl)-2-salicylideneaminato]-[4'-(methoxyphenyl)-*NNO*-azoxy-*N*²]-4-methoxyphenyl-2-ato] palladium(II) [14]. The N-bonded phenyl ring is tilted by $60.6(2)^\circ$ with respect to the salicylideneaminato plane. Both the alkyl and alkoxy chains of the salicylideneaminato ligand include one *gauche* bond [C(14)–C(15) and C(22)–C(23)] with torsion angles of $-70(1)$ and $45(5)^\circ$,

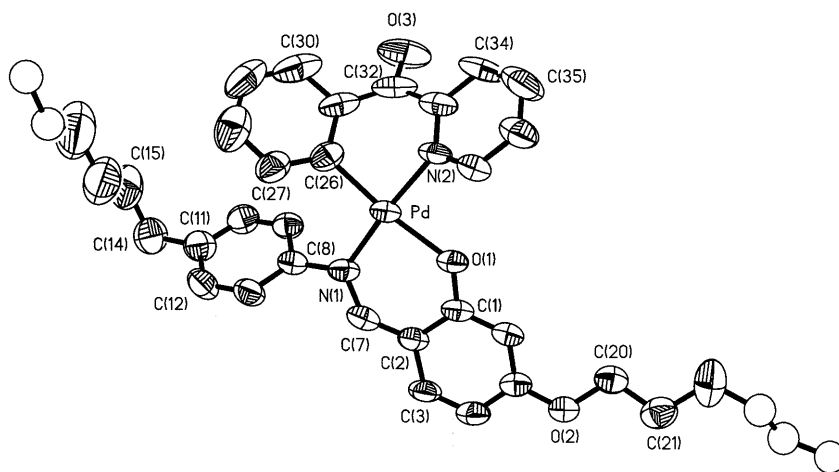


Fig. 1. Molecular structure and atomic labeling scheme (50% probability thermal ellipsoids) of complex **9**, [(IVa)Pd(L)]. Hydrogen atoms omitted for clarity.

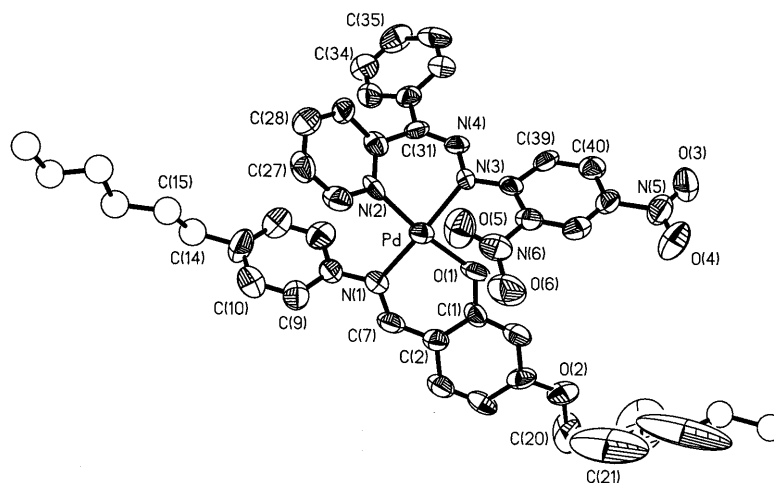


Fig. 2. Molecular structure and atomic labeling scheme (50% probability thermal ellipsoids) of complex **10**, [(Va)Pd(L)]. Hydrogen atoms omitted for clarity.

Table 1
Selected bond distances (Å), angles (°) and torsion angles (°) for complex **9**, [(IVa)Pd(L)]

Pd–O(1)	2.069(4)	Pd–N(1)	2.051(5)
Pd–N(2)	2.029(5)	Pd–C(26)	1.986(7)
O(1)–C(1)	1.301(7)	C(1)–C(2)	1.439(9)
C(2)–C(7)	1.389(9)	N(1)–C(7)	1.318(8)
C(26)–C(31)	1.415(10)	C(31)–C(32)	1.469(12)
C(32)–C(33)	1.491(12)	N(2)–C(33)	1.350(9)
O(3)–C(32)	1.230(10)		
C(26)–Pd–N(2)	87.4(3)	C(26)–Pd–N(1)	97.0(3)
N(2)–Pd–N(1)	174.1(2)	C(26)–Pd–O(1)	172.3(2)
N(2)–Pd–O(1)	84.95(19)	N(1)–Pd–O(1)	90.73(18)
Pd–O(1)–C(1)–C(2)	–5.2(9)	O(1)–C(1)–C(2)–C(7)	5.9(10)
C(1)–C(2)–C(7)–N(1)	0.7(11)	C(2)–C(7)–N(1)–Pd	–6.8(10)
C(7)–N(1)–Pd–O(1)	5.4(5)	N(1)–Pd–O(1)–C(1)	0.1(5)
Pd–C(26)–C(31)–C(32)	–11.7(10)	C(26)–C(31)–C(32)–C(33)	–35.7(10)
C(31)–C(32)–C(33)–N(2)	31.1(10)	C(32)–C(33)–N(2)–Pd	19.2(9)
C(33)–N(2)–Pd–C(26)	–49.1(6)	N(2)–Pd–C(26)–C(31)	43.5(6)

Table 2
Selected bond distances (Å), angles (°) and torsion angles (°) for complex **10**, [(Va)Pd(L)]

Pd–O(1)	1.966(8)	Pd–N(1)	2.067(10)
Pd–N(2)	1.975(10)	Pd–N(3)	2.058(9)
O(1)–C(1)	1.326(14)	C(1)–C(2)	1.416(16)
C(2)–C(7)	1.412(17)	N(1)–C(7)	1.287(15)
N(2)–C(30)	1.349(15)	C(30)–C(31)	1.495(16)
N(4)–C(31)	1.265(13)	N(3)–N(4)	1.358
O(1)–Pd–N(2)	170.3(3)	O(1)–Pd–N(3)	88.6(3)
N(2)–Pd–N(3)	82.4(4)	O(1)–Pd–N(1)	92.3(4)
N(2)–Pd–N(1)	97.0(4)	N(3)–Pd–N(1)	171.8(4)
Pd–O(1)–C(1)–C(2)	8.5(17)	O(1)–C(1)–C(2)–C(7)	0.0(2)
C(1)–C(2)–C(7)–N(1)	1.0(2)	C(2)–C(7)–N(1)–Pd	–8.7(19)
C(7)–N(1)–Pd–O(1)	–11.5(10)	N(1)–Pd–O(1)–C(1)	–12.1(8)
Pd–N(2)–C(30)–C(31)	–6.0(19)	N(2)–C(30)–C(31)–N(4)	–33.9(18)
C(30)–C(31)–N(4)–N(3)	6.8(16)	C(31)–N(4)–N(3)–Pd	50.1(11)
N(4)–N(3)–Pd–N(2)	–64.9(7)	N(3)–Pd–N(2)–C(30)	43.1(8)

respectively, and show some evidence of disorder as indicated by their thermal factors.

The second six-membered ring, $\text{Pd-NC}_3\text{C}$, obtained from cyclometallation of ligand IV is in a boat conformation (Table 1) with the Pd and C(32) atoms lying (0.903(4) and 0.355(6) Å) above the mean plane through N(2), C(26), C(31) and C(33) atoms, respectively. The conformation as well as the bond distances and angles within the cycle are found to be in agreement with those observed in other palladium(II) complexes containing similar six-membered rings [18].

The crystal structure of complex **10** [(Va)Pd(L)], with the pertinent atom-labeling scheme, is shown in Fig. 2. Selected bond lengths and angles are listed in Table 2. The palladium atom is in a distorted square planar geometry, coordinated from one side to the nitrogen and oxygen atoms of the salicylideneaminato ligand **HL**. The ligand **V** completes the coordination to the palladium atom behaving as an N,N bidentate monoanionic ligand. As in complex **9**, the palladium atom is part of two six-membered rings, tilted with respect to each other by 32.4(5)°. The Pd–NC₃O cycle from the salicylideneaminato ligand **HL** is planar to within 0.06 Å (torsion angles in Table 2). Unlike complex **9**, the Pd–O(1) bond distance of 1.966(8) Å is in the range of values found for palladium bis-salicylideneaminato complexes [17]. The other bond lengths and the bond angles agree with those found for complex **9**. The rotationally free phenyl ring of **HL** is tilted by 55.3(2)° with respect to its best mean plane. While the conformation of the hexyl chain is almost completely *trans*-planar, the hexyloxy chain shows one *gauche* bond [C(20)–C(21)] with torsion angle of –70(3)°.

Ligand **V** upon cyclopalladation forms a six-membered ring, Pd–NC₃NN, using the N_{py} atom and the deprotonated nitrogen atom N(3). The ring conformation is a half-twist, with the N(3), N(4), C(30) and C(31) atoms lying approximately on the same plane (within 0.02 Å). Some differences in terms of bond distances and angles within the Pd–NC₃NN cycle are found with respect to the only example of a palladium(II) complex containing a similar type of six-membered chelate ring reported up to now [13]. On the other hand, the bond lengths and angles of ligand **V** compare favorably with those found in a structurally characterized hydrazone ligand [19].

2.2. UV–Vis spectroscopy of complexes **6–10**

The electronic absorption spectra of the cyclometallated species **6–10**, recorded in dichloromethane solutions, exhibit two bands peaking at about 300 and 400 nm (Table 3). The higher energy band is attributable to intense π – π^* transitions ($\epsilon > 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) centered on both the **HL** and **I–V** ligands. The lower energy band is less intense ($\epsilon < 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and can be assigned to a CT transition involving, most likely, the palladium-bonded oxygen atom, as suggested by the presence of this center in all complexes [20]. Comparison of the spectroscopic properties with the molecular structures (Scheme 2) allows some tentative assignment to be made. Complexes **6** and **7** show a band, at 360 ($\epsilon \sim 10\,900 \text{ M}^{-1} \text{ cm}^{-1}$) and 378 nm ($\epsilon \sim 10\,800 \text{ M}^{-1} \text{ cm}^{-1}$) respectively, which can likely due to transitions involving the cyclometallated 2-phenylpyridine **I** in **6** or benzo[h]quinoline **II** in **7** [20]. For **8**, a band at 344 nm is present, which could be of π – π^* origin, arising from the orthopalladated azobenzene fragment [21].

Table 3
Spectroscopic data ^a of complexes **6–10**, [(Ia–Va)Pd(L)]

Complexes	Absorption λ (ϵ M ⁻¹ cm ⁻¹)		
	Toluene ^b	Dichloromethane ^b	Acetone ^b
6	314 (25000) 405 (6430)	314 (19850) 360 (10940) 402 (8340)	324 (9040) 362 (5430) 402 (4350)
7	293:313 (20950:20590) 382 (10650)	294:312 (23300:23040) 378 (10820)	330 (12540) 379 (10290)
8	310 (27260) 344 (25790) 500 (3030)	310 (25160) 344 (20970) 495 (3310)	344 (17350) 494 (2900)
9	292 (23460) 390 (8810)	301 (20100) 394 (11200)	393 (9680)
10	308 (26250) 396 (14980) 537 (18340)	305 (29670) 391 (14710) 531 (20130)	388 (12070) 523 (17460)

^a Room temperature.

^b Static dielectric constant ϵ : toluene, 2.4; dichloromethane, 9.1; acetone, 20.7.

Finally, **8** and **10** display absorption maxima at 495 ($\epsilon \sim 3 \times 10^3$ M⁻¹ cm⁻¹) and 531 nm ($\epsilon \sim 2 \times 10^4$ M⁻¹ cm⁻¹), respectively. The nature of these bands is not easily identified, but in **10** the presence of the stronger electron acceptor dinitro substituted hydrazone ligand, **V**, suggest $\pi - \pi^*$ transitions which might be affected by CT interactions.

It is known that molecules exhibiting solvatochromism usually display second-order nonlinear optical properties [22]. For this reason, the spectra of the synthesized complexes were recorded in solvents with different polarity (Table 3). Noteworthy, the lowest energy band of complexes **8** and **10** is moderately affected by the polarity of the solvent (Table 3 and Fig. 3). Thus, interesting nonlinear optical properties should also be expected for compounds **8** and **10**.

Investigations using the electric-field-induced second harmonic generation (EFISH) method are now under way.

3. Experimental

3.1. Materials and procedures

All the commercially available chemicals were purchased from Aldrich Chemical Co. and were used without further purification.

¹H NMR spectra were recorded on a Bruker WM-300 (CDCl₃ solutions, Me₄Si internal standard) and IR spectra with a Perkin–Elmer 2000 FT-IR (KBr pellets). Elemental analyses were performed with a Perkin–Elmer 2400 analyzer. Solutions room-temperature absorption spectra were recorded with a Perkin–Elmer Lambda 9 spectrometer.

3.2. Syntheses of the ligands

The 2-hydroxy-4-(*n*-hexyloxy)benzaldehyde, intermediate for the synthesis of **HL**, was prepared as reported in the literature [6]. The ligand **V** [7] was prepared according to the reported procedure modified as follows.

3.2.1. 2-Hydroxy-4-(*n*-hexyloxybenzylidene)-4'-*n*-hexylaniline (**HL**)

A solution of 4-*n*-hexylaniline (1.34 ml, 6.97 mmol) in ethanol (5 ml) was added slowly to a stirred solution of 2-hydroxy-4-(*n*-hexyloxy)benzaldehyde (1.550 g, 6.97 mmol) in ethanol (25 ml). Immediately, the solution turned yellow. After stirring for 4 h under reflux, the yellow precipitate, which formed at room temperature, was collected by filtration, washed with a small amount of ethanol and vacuum dried. The analytically pure product was obtained as a yellow solid upon recrystallization from chloroform–methanol. Yield 0.645 g, 75%. M.p. (°C) 43 (SmC) 82 (N) 94 (I). Found: C, 78.69; H, 9.19; N, C₂₅H₃₅NO₂ requires: C, 78.70; H, 9.25; N, 3.71%. ν_{\max} (KBr, cm⁻¹) 2362–2342 (OH), 1615 (C=N). δ (CDCl₃, ppm) 13.93 (1H, s, OH), 8.52 (1H, s, H^b), 7.20 (5H, m, H^{c,d,e,f,g}), 6.47 (2H, m, H^{a,b}), 3.99 (2H, t, O–CH₂), 2.61 (2H, t, Ph–CH₂).

3.2.2. Phenyl-2-pyridylketone-2,4-dinitrophenylhydrazone (**V**)

A 1.0 g (5.05 mmol) sample of 2,4-dinitrophenylhydrazine was suspended in ethanol (15 ml) and the red–orange mixture heated to 50°C. Concentrated hydrochloric acid (0.2 ml) was then added with stirring. The mixture turned dark red in a few seconds. A solution of 2-benzoylpyridine (**IV**) (0.924 g, 5.05 mmol)

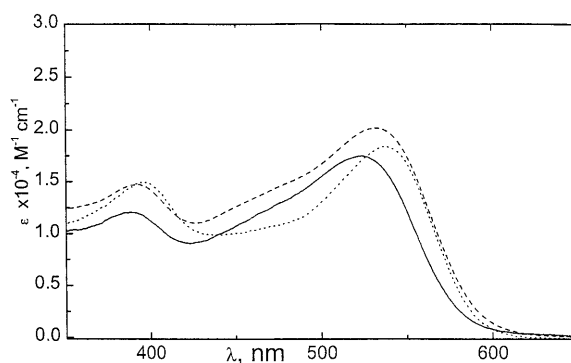


Fig. 3. Electronic spectrum of **10** in toluene (···), dichloromethane (---) and acetone (—).

in ethanol (10 ml) was then added. A red–orange suspension was obtained after approximately 5 min. After being stirred for 30 min at 50°C, the mixture was dilute with water (5 ml) and the so formed orange–yellow solid filtered off at room temperature and recrystallized from concentrated acetic acid. Yield 0.740 g, 40%. M.p. 208–210°C. Found: C, 59.33; H, 4.00; N, 19.28. $C_{18}H_{13}N_5O_4$ requires: C, 59.50; H, 3.61; N, 19.28%. ν_{\max} (KBr, cm^{-1}) 3096 (N–H), 1582 (C=N). δ (CDCl_3 , ppm) 11.94 (1H, s, N–H), 9.16 (1H, d, H^3), 9.01 (1H, m, H^2), 8.32 (1H, dd, H^5), 8.24 (1H, d, H^6), 7.85 (1H, td, H^4), 7.65 (2H, m, $H^{6,10}$), 7.51 (3H, m, $H^{7,8,9}$), 7.49 (1H, m, H^3), 7.45 (1H, m, H^5).

3.3. Syntheses of the acetato-bridged complexes (1–5)

The complexes $[(Ia)Pd(\mu-OAc)]_2$ (1) [9], $[(IIa)Pd(\mu-OAc)]_2$ (2) [10], $[(IIIa)Pd(\mu-OAc)]_2$ (3) [23] and $[(IVa)Pd(\mu-OAc)]_2$ (4) [12], were prepared according to the reported procedures modified as follows.

3.3.1. $[(Ia)Pd(\mu-OAc)]_2$ (1)

To a stirred hot solution of palladium(II) acetate (0.50 g, 2.23 mmol) in 80 ml of acetic acid, the stoichiometric amount of 2-phenylpyridine (I) (0.32 ml, 2.23 mmol) was added and the resulting dark orange solution stirred at 50°C for 3.5 h. The brown cloudy suspension formed after that time, was filtered at room temperature through a short Celite column to separate a small amount of black insoluble solid. The solvent was removed from the filtrate under reduced pressure. The crude product was dissolved in acetone and the addition of ethanol gave green–yellow microcrystals. The solid was collected by filtration and dried under vacuum. Yield 0.680 g, 95%. M.p. (dec.) 294–296°C. Found: C, 48.85; H, 3.41; N, 4.69. $C_{26}H_{22}N_2O_4Pd_2$ requires: C, 48.45; H, 3.47; N, 4.38%. ν_{\max} (KBr, cm^{-1}) 1571 (asym. C=O), 1416 (sym. C=O). δ (CDCl_3 , ppm) 7.87 (1H, dd, H^2), 7.37 (1H, td, H^4), 7.08 (1H, d, H^5), 6.92 (1H, dd, H^{α}), 6.84 (3H, m, $H^{6,7,8}$), 6.44 (1H, m, H^3), 2.27 (3H, s, CH_3).

3.3.2. $[(IIa)Pd(\mu-OAc)]_2$ (2)

The complex palladium(II) acetate (2.23 mmol, 0.50 g) was dissolved in hot acetic acid (70 ml) and an excess of solid benzo[h]quinoline (II) (2.54 mmol, 0.455 g) was added in one portion with stirring. The suspension, which turned dark red in few minutes, was stirred overnight under N_2 at reflux and a yellow solution formed. The yellow suspension obtained by addition of water (120 ml) was extracted with dichloromethane. Extracts were combined, dried over anhydrous Na_2SO_4 and filtered. Partial evaporation of the solvent under reduced pressure and addition of ethyl acetate afforded a gold yellow solid precipitate which was filtered off and dried under vacuum. Yield 0.555 g, 72%. M.p.

(dec.) 275–276°C. Found: C, 52.79; H, 3.24; N, 4.32. $C_{30}H_{22}N_2O_4Pd_2$ requires: C, 52.42; H, 3.23; N, 4.08%. ν_{\max} (KBr, cm^{-1}) 1565 (asym. C=O), 1411 (sym. C=O). δ (CDCl_3 , ppm) 7.87 (1H, dd, H^2), 7.50 (1H, dd, H^4), 7.30 (3H, m, $H^{\alpha,6,7}$), 7.14 (1H, dd, H^8), 7.04 (1H, d, H^5), 6.28 (1H, dd, H^3), 2.45 (3H, s, OCH_3).

3.3.3. $[(IIIa)Pd(\mu-OAc)]_2$ (3)

A sample of azobenzene (III) (0.405 g, 2.23 mmol) was added to a solution of palladium(II) acetate (0.50 g, 2.23 mmol) in acetic acid (80 ml) and the dark mixture, resulting after stirring for 6 h at 50°C, was filtered at room temperature through a short Celite column. The filtrate was concentrated under reduced pressure and the addition of methanol afforded a red dark solid after cooling at -10°C . Yield 0.705 g, 91%; M.p. (dec.) 200–205°C. Found: C, 48.52; H, 3.39; N, 8.03. $C_{28}H_{24}N_4O_4Pd_2$ requires: C, 48.50; H, 3.49; N, 8.08%. ν_{\max} (KBr, cm^{-1}) 1560 (asym C=O), 1415 (sym. C=O). δ (CDCl_3 , ppm) 7.71 (1H, dd, H^7), 7.35 (2H, m, $H^{2,6}$), 7.25 (3H, m, $H^{3,4,5}$), 7.14 (1H, td, H^8), 6.81 (1H, td, H^9), 6.49 (1H, dd, H^{α}), 2.06 (3H, s, CH_3).

3.3.4. $[(IVa)Pd(\mu-OAc)]_2$ (4)

A slight excess of 2-benzoylpyridine (IV) (0.489 g, 2.67 mmol) was added to a stirred solution of palladium(II) acetate (0.50 g, 2.23 mmol) in acetic acid (75 ml) and the resulting orange solution stirred at 50°C. The solution immediately turned yellow and cloudy. A creme solid by-product was removed by filtration and washed with dichloromethane while the yellow filtrate, after evaporation of the solvent, gave a yellow viscous oil which was extracted by dichloromethane. Extracts were combined and dried over anhydrous Na_2SO_4 . A slow addition of hexane induced the precipitation of a pale yellow powder. This product was filtered, washed with hexane and dried under vacuum. Yield 0.630 g, 81%. M.p. (dec.) 271–275°C. Found: C, 48.06; H, 3.13; N, 3.86. $C_{28}H_{22}N_2O_6Pd_2$ requires: C, 48.37; H, 3.19; N, 4.03%. ν_{\max} (KBr, cm^{-1}) 1665 (C=O ketone), 1578 (asym. C=O acetate) 1423 (sym. C=O acetate). δ (CDCl_3 , ppm) 8.28 (1H, d, H^2), 7.85 (1H, d, H^5), 7.81 (1H, d, H^4), 7.44 (1H, d, H^6), 7.15 (1H, td, H^3), 6.99 (1H, td, H^7), 6.87 (1H, td, H^8), 6.84 (1H, dd, H^{α}), 2.07 (3H, s, CH_3).

3.3.5. $[(Va)Pd(\mu-OAc)]_2$ (5)

To a solution of palladium(II) acetate (0.50 g, 2.23 mmol) in 50 ml of hot acetic acid was added a stoichiometric amount of the phenyl-2-pyridylketone-2,4-dinitrophenylhydrazone (V) (0.809 g, 2.23 mmol). The mixture was stirred for 1 h at 50°C and after cooling to room temperature the bordeaux solid which formed was filtered off and suspended in dichloromethane. The dark red solid was removed by filtration and diethyl

ether was added to the dark red filtrate. Cooling overnight at -10°C led to a red bordeaux microcrystalline solid which was filtered and dried under vacuum. Yield 0.480 g, 40%. M.p. (dec.) $273\text{--}275^{\circ}\text{C}$. Found: C, 45.36; H, 2.66; N, 13.21. $\text{C}_{40}\text{H}_{30}\text{N}_{12}\text{O}_{12}\text{Pd}_2$ requires: C, 45.51; H, 2.86; N, 13.27%. ν_{max} (KBr, cm^{-1}) 1596 ($\text{C}=\text{N}$), 1559 (asym. $\text{C}=\text{O}$), 1440 (sym. $\text{C}=\text{O}$).

3.4. Synthesis of the mononuclear complexes 6–10

A typical preparation is reported for **6**; all analogous complexes, **7–10**, were prepared using the same synthetic procedure. Color, yield, melting point, elemental analyses, IR and ^1H NMR data are as follows.

3.4.1. [(Ia)Pd(L)] (6)

The ligand **HL** (0.150 g, 0.393 mmol) was suspended in ethanol and added to 0.125 g (0.196 mmol) of $[(\text{Ia})\text{Pd}(\mu\text{-OAc})_2]$ (**1**), in one portion with stirring. A pale orange precipitate formed in approximately 15 m. After stirring for 24 h at room temperature, the cream yellow solid which was obtained was filtered off, suspended in chloroform and the suspension filtered through a short Celite column. The solvent was partially evaporated under reduced pressure and ethanol added dropwise. The resulting yellow solid was filtered off and dried under vacuum. Yield 0.211 g, 84%. M.p. $177\text{--}182^{\circ}\text{C}$. Found: C, 67.19; H, 6.68; N, 3.97. $\text{C}_{36}\text{H}_{42}\text{N}_2\text{O}_2\text{Pd}$ requires: C, 67.44; H, 6.60; N, 4.37%. ν_{max} (KBr, cm^{-1}) 1612 ($\text{C}=\text{N}$). δ (CDCl_3 , ppm) 9.31 (1H, d, H^2), 7.99 (1H, s, H^b), 7.81 (1H, td, H^4), 7.62 (1H, d, H^5), 7.44 (2H, d, $\text{H}^{\text{d,e}}$), 7.35 (1H, d, H^a), 7.25 (1H, m, H^3), 7.14 (2H, d, $\text{H}^{\text{f,g}}$), 7.12 (1H, d, H^c), 6.88 (1H, t, H^8), 6.56 (1H, t, H^7), 6.44 (1H, d, H^a), 6.20 (1H, dd, H^b), 5.78 (1H, d, H^6), 4.00 (2H, t, $\text{O}-\text{CH}_2$), 2.63 (2H, t, $\text{Ph}-\text{CH}_2$).

3.4.2. [(IIa)Pd(L)] (7)

Greenish–yellow solid. Yield 0.202 g, 77%. M.p. $161\text{--}168^{\circ}\text{C}$. Found: C, 68.44; H, 6.48; N, 3.89. $\text{C}_{38}\text{H}_{42}\text{N}_2\text{O}_2\text{Pd}$ requires: C, 68.62; H, 6.36; N, 4.21%. ν_{max} (KBr, cm^{-1}) 1610 ($\text{C}=\text{N}$). δ (CDCl_3 , ppm) 9.50 (1H, dd, H^2), 8.28 (1H, dd, H^4), 8.00 (1H, s, H^b), 7.68 (1H, d, H^6), 7.59 (1H, dd, H^3), 7.54 (1H, d, H^5), 7.47 (2H, d, $\text{H}^{\text{d,e}}$), 7.39 (1H, d, H^a), 7.19 (2H, d, $\text{H}^{\text{f,g}}$), 7.15 (1H, d, H^c), 6.94 (1H, t, H^8), 6.52 (1H, d, H^a), 6.23 (1H, dd, H^b), 5.75 (1H, d, H^7), 4.04 (2H, t, $\text{O}-\text{CH}_2$), 2.68 (2H, t, $\text{Ph}-\text{CH}_2$).

3.4.3. [(IIIa)Pd(L)] (8)

Bordeaux solid. Yield 0.155 g, 58%. M.p. $100\text{--}104^{\circ}\text{C}$. Found: C, 66.77; H, 6.37; N, 5.93. $\text{C}_{37}\text{H}_{43}\text{N}_3\text{O}_2\text{Pd}$ requires: C, 66.51; H, 6.49; N, 6.29%. ν_{max} (KBr, cm^{-1}) 1611 ($\text{C}=\text{N}$). δ (CDCl_3 , ppm) 7.98 (1H, s, H^b), 7.92 (2H, m, $\text{H}^{2,6}$), 7.86 (1H, m, H^7), 7.54 (3H, d, $\text{H}^{3,4,5}$), 7.35 (2H, d, $\text{H}^{\text{d,e}}$), 7.17 (2H, d, $\text{H}^{\text{f,g}}$),

7.10 (1H, d, H^c), 7.04 (1H, t, H^8), 6.69 (1H, m, H^9), 6.20 (1H, dd, H^b), 6.16 (1H, d, H^a), 5.60 (1H, d, H^c), 3.93 (2H, t, OCH_2), 2.66 (2H, t, $\text{Ph}-\text{CH}_2$).

3.4.4. [(IVa)Pd(L)] (9)

Yellow solid. Yield 0.203 g, 77%. M.p. $185\text{--}187^{\circ}\text{C}$. Found: C, 66.42; H, 6.24; N, 4.52. $\text{C}_{37}\text{H}_{42}\text{N}_2\text{O}_3\text{Pd}$ requires: C, 66.41; H, 6.33; N, 4.19%. ν_{max} (KBr, cm^{-1}) 1663 ($\text{C}=\text{O}$ ketone), 1612 ($\text{C}=\text{N}$). δ (CDCl_3 , ppm) 9.26 (1H, d, H^2), 8.16 (1H, dd, H^5), 8.02 (1H, td, H^4), 7.98 (1H, s, H^b), 7.61 (1H, td, H^3), 7.54 (1H, dd, H^a or H^6), 7.16 (1H, d, H^c), 6.88 (2H, d, $\text{H}^{\text{d,e}}$), 6.81 (1H, d, H^7 or H^8), 6.78 (2H, d, $\text{H}^{\text{f,g}}$), 6.73 (1H, d, H^7 or H^8), 6.48 (1H, td, H^a or H^6), 6.37 (1H, d, H^a), 6.24 (1H, dd, H^b), 4.00 (2H, t, $\text{O}-\text{CH}_2$), 2.44 (2H, t, $\text{Ph}-\text{CH}_2$).

3.4.5. [(Va)Pd(L)] (10)

Bordeaux solid. Yield 0.152 g, 45%. M.p. (dec.) $220\text{--}223^{\circ}\text{C}$. Found: C, 60.40; H, 5.31; N, 10.02. $\text{C}_{43}\text{H}_{47}\text{N}_6\text{O}_6\text{Pd}$ requires: C, 60.74; H, 5.57; N, 9.88%. ν_{max} (KBr, cm^{-1}) 1611 ($\text{C}=\text{N}$), 1594 ($\text{C}=\text{N}$ hydrazone). δ (CDCl_3 , ppm) 8.84 (1H, d, H^3), 8.50 (1H, d, H^6), 8.13 (1H, dd, H^5), 7.90 (1H, d, H^2), 7.74 (1H, dd, H^7 or H^8), 7.53 (6H, m, $\text{H}^{\text{B},4,6,7}$ or $\text{H}^{8,9,10}$), 7.29 (1H, d, H^3), 7.06 (2H, d, $\text{H}^{\text{d,e}}$), 7.01 (1H, d, H^c), 6.93 (2H, d, $\text{H}^{\text{f,g}}$),

Table 4

Crystallographic data for complexes **9** and **10**

	[(IVa)Pd(L)] (9)	[(Va)Pd(L)] (10)
Empirical formula	$\text{C}_{37}\text{H}_{42}\text{N}_2\text{O}_3\text{Pd}$	$\text{C}_{43}\text{H}_{46}\text{N}_6\text{O}_6\text{Pd}$
Formula weight	669.13	849.26
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (\AA)	22.503(9)	12.331(4)
b (\AA)	10.125(2)	13.780(5)
c (\AA)	14.709(5)	14.178(6)
α ($^{\circ}$)	90	103.33(3)
β ($^{\circ}$)	91.45(3)	104.78(3)
γ ($^{\circ}$)	90	109.82(3)
V (\AA^3)	3350(2)	2054(1)
Z	4	2
$F(000)$	1392	880
D_{calc} (g cm^{-3})	1.327	1.373
Absorption coefficient (mm^{-1})	0.591	0.506
Transmission factors	0.989/0.719	1.00/0.873
Temperature (K)	298	298
Total number of reflections	5539	4692
Number of unique reflections	5293	4492
	$[R_{\text{int}} = 0.0343]$	$[R_{\text{int}} = 0.0460]$
Data/restraints/parameters	3808	2892
	$[I > 2\sigma(I)]/2/363$	$[I > 2\sigma(I)]/10/465$
$R_1^a [I > 2\sigma(I)]$	0.065	0.082
wR_2^b	0.177	0.211
Goodness-of-fit (F^2)	1.041	1.078

$$^a R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$^b wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$$

6.80 (1H, m, H⁵), 6.21 (1H, dd, H^b), 5.87 (1H, d, H^a), 3.87 (2H, t, O–CH₂), 2.48 (2H, t, Ph–CH₂).

3.5. Structure determinations of **9**, [(IVa)Pd(L)], and **10**, [(Va)Pd(L)]

Details of the data collection, structure analysis and refinement are listed in Table 4. Diffraction measurements were carried out on a Siemens R3m/V automated four-circle diffractometer equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Cell dimensions for each analysis were determined from the setting-angle values of centered reflections. The data were corrected for Lorentz, polarization and X-ray absorption effects. A semi-empirical absorption correction was applied using a method based upon azimuthal (Ψ) scan data [24] (transmission coefficients min/max of 0.719/0.989 for **9** and 0.873/0.998 for **10**). The structures were solved by heavy-atom (Patterson and Fourier difference) by using the SHELXTL [25] computer program and refined by full-matrix least-squares against F^2 . All the non-hydrogen atoms were refined anisotropically with exception of some C atoms of the aliphatic and alkoxy chains assigned with isotropic displacement parameters [C(17), C(18), C(19), C(23), C(24) and C(25) for complex **9**; from C(14) to C(19), C(24) and C(25) for complex **10**]. As a result of a disorder, similarity constraints were applied to the C–C bond distances between these carbon atoms and even so in some cases the geometry was not readily modeled. The hydrogen atoms were included as idealized atoms riding on the respective carbon atoms with C–H bond lengths appropriate to the carbon atom hybridization. Calculations were made with programs of the SHELXL-97 package [26].

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