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Syntheses, characterization and X-ray structure of palladium(II) and nickel(II) complexes of tetradentate pyrrole containing ligands

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Abstract

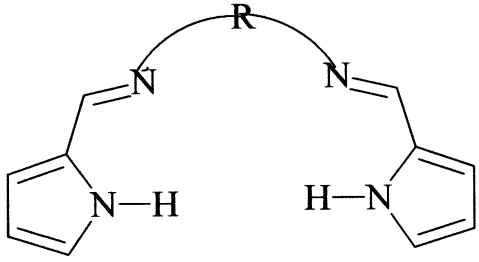
Palladium(II) and nickel(II) complexes with tetradentate ligands derived from pyrrole 2-carboxaldehyde and various diamines have been synthesized and characterized. The complexes are neutral and the coordination around the metal is square-planar; they are able to activate the molecular hydrogen and to catalyse the homogenous hydrogenation of phenylacetylene. The X-ray structures of *N,N′*-cycloexylenebis(pyrrol-2-ylmethyleneamine) (**H_2L4**), **PdL4** and **PdL3** (**H_2L3**, *N,N′*-propylenebis(pyrrol-2-ylmethyleneamine)) are discussed.

Keywords: Shiff-base complexes; Nickel complexes; Palladium complexes; Hydrogenation

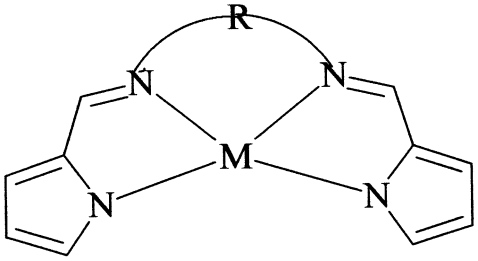
1. Introduction

'Salen' (salen, *N,N′*-bis(salicyldene)ethylenediamine) or 'salen-type' ligands and their complexes have received continuous and intensive attention in many fields of research. For example, [Pd(salen)] was proposed as a model of the active site of the enzyme hydrogenase [1] and it is a well known hydrogenation catalyst [1,2], chiral [metal(salen)] complexes are used in asymmetric catalysis [3], some of its nickel(II), copper(II) and VO^{2+} complexes are metallomesogens [4], nickel(II) and manganese(III) derivatives exhibit interesting NLO response [5].

On the contrary, little is known about the ligand behaviour of the analogous compounds derived from pyrrole 2-carboxaldehyde and about the properties of their complexes [6,7]. In this paper, some N_2N_2' ligands, obtained precisely from pyrrole 2-carboxaldehyde and diverse aromatic (**H_2L1**, Scheme 1) and aliphatic (**H_2L2**–**H_2L4**, Scheme 1) diamines, are synthesized and characterized, together with their Ni(II) and Pd(II) complexes. The diprotic ligands behave as tetradentate, when they are deprotonated (Scheme 2); their coordination behaviour is unequivocally established also by



Scheme 1. Presentation of the ligands (R=C_6H_5: **H_2L1**; R=$(CH_2)_2$: **H_2L2**; R=$(CH_2)_3$: **H_2L3**; R=*trans*-C_6H_{10}: **H_2L4**).



Scheme 2. Presentation of the complexes (M=Ni, Pd).

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means of the X-ray diffraction analysis carried out on **PdL3**, **H_2L4·H_2O** and **PdL4**. Finally, the complexes are tested as catalysts in the homogeneous hydrogenation of phenylacetylene.

2. Experimental

2.1. General procedures

The reagents of commercial quality were used without further purification, with the exception of phenylacetylene, that was distilled and stored under nitrogen. Physical measurements and the general procedure for the hydrogenation of phenylacetylene were made as described elsewhere [8]; thermogravimetric analysis was carried out with a TGA Perkin–Elmer Delta in the range 30–200 °C (5° min^{-1}). GC analyses were performed on a DANI HP 3800 flame-ionization gas-chromatograph (OV 101 on CHP capillary column). All new compounds gave satisfactory elemental analyses.

2.2. Synthesis and characterization

2.2.1. Ligands

The ligands were prepared according to the method already described [1], which involved a condensation reaction of pyrrole 2-carboxaldehyde and diamine in a 2:1 molar ratio, with EtOH as solvent.

*2.2.1.1. N,N′-Phenylenebis(pyrrol-2-ylmethyleneamine) (**H_2L1**).* Yield: 80%. M.p.: 200 °C (dec.) (lit. [6] 204 °C). ^{1}H NMR ($CDCl_3$): δ 6.07 (t, 2H, H pyrrole β); 6.30 (s, br, 2H, H pyrrole γ) 6.46 (d, 2H, H pyrrole α); 7.13 (q, 2H, H phenyl *meta*); 7.30 (q, 2H, H phenyl *ortho*); 7.75 (s, 2H, H imine); 12.30 (s, br, 2H, D_2O exchangeable, NH). FT-IR (cm^{-1}, KBr): 3400 w, br, ν(NH); 3077 m, $\nu(CH_{ar.})$; 1616 sh, ν(C=N).

*2.2.1.2. N,N′-Ethylenebis(pyrrol-2-ylmethyleneamine) (**H_2L2**).* Yield: 95%. M.p.: 179–180 °C (dec.) (lit. 178–180 °C [1]). ^{1}H NMR ($CDCl_3$): δ 3.81 (s, 4H, CH_2); 6.26 (q, 2H, H pyrrole β); 6.50 (q, 2H, H pyrrole γ); 6.91 (m, br, 2H, H pyrrole α); 7.29 (s, 2H, H imine); 8.07 (s, br, 2H, D_2O exchangeable, NH). FT-IR (cm^{-1}, KBr): 3176 s, br ν(NH); 2942–2868 s, ν(CH alkyl.); 1642 sh, ν(C=N).

*2.2.1.3. N,N′-Propylenebis(pyrrol-2-ylmethyleneamine) (**H_2L3**).* Yield: 64%. M.p.: 119–120 °C (dec.) (lit. 119–120 °C [6]). ^{1}H NMR ($CDCl_3$): δ 1.95 (m, 2H, $CH_2CH_2CH_2$); 3.60 (t, 4H, $CH_2CH_2CH_2$); 6.22 (t, 2H, H pyrrole β); 6.46 (t, 2H, H pyrrole γ); 6.85 (s, br, 2H, H pyrrole α); 8.02 (s, 2H, H imine); 9.27 (s br, 2H, D_2O exchangeable, NH). FT-IR (cm^{-1}, KBr): δ 3400 w, ν(NH); 3061 m, ν(CH pyrrole); 2944–2850 s, $\nu(CH_2$ alkyl.); 1638 sh, ν(C=N).

*2.2.1.4. N,N′-Cycloexylenebis(pyrrol-2-ylmethyleneamine) (**H_2L4·H_2O**).* M.p.: 203 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.30–1.77 (m br, 8H, CH_2); 3.00 (m, 2H, CH); 6.18 (t, 2H, H pyrrole β); 6.34 (q, 2H, H pyrrole γ); 6.79 (s, br, 2H, H pyrrole α); 7.66 (s, 2H, H imine); 10.41 (s, br, 2H, D_2O exchangeable, NH). FT-IR (cm^{-1}, KBr): 3400 w, ν(NH); 3066 m, ν(CH pyrrole); 2932–2857 s, $\nu(CH_2)$; 1633 sh, ν(C=N).

2.2.2. Complexes

The ligand and the nickel acetate are dissolved in the minimum amount of EtOH; the resulting solution is stirred at room temperature (r.t.) until a precipitate appears. The solid is filtered, washed with absolute EtOH and recrystallized from CH_2Cl_2/n-C_6H_{14}.

*2.2.2.1. **Ni(L1)**.* Reaction time: 1 h. Colour: dark red. M.p.: ≈290 °C (dec.). Yield: 97%. ^{1}H NMR ($CDCl_3$): δ 6.22 (d, br, 2H, H pyrrole β); 6.78 (d, 2H, H pyrrole γ); 6.82 (s, br, 2H, H pyrrole α); 7.02 (m, 2H, H phenyl *meta*); 7.16 (m, 2H, H phenyl *ortho*); 7.56 (s, 2H, H imine). FT-IR (cm^{-1}, KBr): 3030–3100 w, $\nu(CH_{ar.})$; 1550 sh, ν(C=N). The same product is obtained from the template reaction between $Ni(CH_3COO)_2$, pyrrole 2-carboxaldehyde and *o*-phenylenediamine.

*2.2.2.2. **Ni(L2)**.* Reaction time: 4 h. Colour: yellow–orange. M.p.: 214 °C (dec.). Yield: 87%. ^{1}H NMR ($CDCl_3$): δ 3.58 (s, 4H, H alkyl.); 6.10 (s, br, 2H, H pyrrole β); 6.55 (s, br, 2H, H pyrrole γ); 6.78 (s, br, 2H, H pyrrole α); 7.13 (s, 2H, H imine). FT-IR (cm^{-1}, KBr): 3070 m, ν(CH pyrrole); 2919 s, ν(CH alkyl.); 1589 sh, ν(C=N).

*2.2.2.3. **Ni(L3)**.* Reaction time: 3 h. Colour: red. M.p.: >300 °C. Yield: 96%. ^{1}H NMR ($CDCl_3$): δ 1.79–1.80 (m, br, 2H, $CH_2CH_2CH_2$); 3.12 (t, 4H, $CH_2CH_2CH_2$); 6.13 (d, br, 2H, H pyrrole β); 6.59 (d, 2H, H pyrrole γ); 6.93 (s, br, 2H, H pyrrole α); 7.19 (s, 2H, H imine). FT-IR (cm^{-1}, KBr): 3100 w, ν(CH pyrrole); 2924 s, ν(CH alkyl.); 1594 sh, ν(C=N).

*2.2.2.4. **Ni(L4)**.* Reaction time: 1 h. Colour: yellow. M.p.: 272 °C (dec.). Yield: 95%. ^{1}H NMR ($CDCl_3$): δ 1.20 (d, 4H, CH_2); 1.74 (s, br, 2H, CH_2); 2.11 (s, br, 2H, CH_2); 3.48 (s, br, 2H, CH); 6.10 (s, br, 2H, H pyrrole β); 6.53 (d, 2H, H pyrrole γ); 6.76 (s, br, 2H, H pyrrole α); 7.05 (s, 2H, H imine). FT-IR (cm^{-1}, KBr): 3070 w, ν(CH pyrrole); 2850–2939 s, ν(CH alkyl.); 1579 sh, ν(C=N).

The Pd complexes are obtained in the same way as Ni ones, but palladium acetate is dissolved in MeCN.

2.2.2.5. ***Pd(L1)***. Reaction time: 4 h. Colour: red. Recrystallization solvent: $C_6H_5CH_3$. M.p.: 288 °C (dec.). Yield: 70%. ^{1}H NMR ($CDCl_3$): δ 6.26 (q, 2H, H pyrrole β); 6.83 (d, 2H, H pyrrole γ); 6.93 (s, br, 2H, H pyrrole α); 7.07 (m, 2H, H phenyl *meta*); 7.18 (m, 2H, H phenyl *ortho*); 7.54 (s, 2H, H imine). FT-IR (cm^{-1}, KBr): 3030–3100 w, ν($CH_{ar.}$); 1546 sh, ν(C=N).

2.2.2.6. ***Pd(L2)***. Reaction time: 4 h. Colour: yellow. Recrystallization solvent: $CHCl_3$/n-C_6H_{14} (1/1 v/v). M.p.: >300 °C (dec.). Yield: 83%. FT-IR (cm^{-1}, KBr): 3070 w, ν(CH pyrrole); 2900 m, ν(CH alkyl.); 1589 sh, ν(C=N). The low solubility of the complex in the common deuterated solvents prevented the recording of the ^{1}H NMR spectrum.

2.2.2.7. ***Pd(L3)***. Reaction time: 4 h. Colour: light yellow. Recrystallization solvents: $CHCl_3$/n-C_6H_{14}. M.p.: >300 °C (dec.). Yield: 74%. ^{1}H NMR ($CDCl_3$): δ 1.93 (m, 2H, $CH_2CH_2CH_2$); 3.34 (t, 4H, $CH_2CH_2CH_2$); 6.21 (q, 2H, H pyrrole β); 6.67 (d, 2H, H pyrrole γ); 7.14 (s, br, 2H, H pyrrole α); 7.39 (s, 2H, H imine). FT-IR (cm^{-1}, KBr): 3070 w, ν(CH pyrrole); 2915 m, ν(CH alkyl.); 1591 sh, ν(C=N).

2.2.2.8. ***Pd(L4)***. Reaction time: 4 h. Colour: green–yellow. Recrystallization solvent: absolute EtOH. M.p.: 287–288 °C (dec.). Yield: 60%. ^{1}H NMR ($CDCl_3$): δ 1.26 (d, 4H, CH_2); 1.81 (d, br, 2H, CH_2); 2.18 (d, br, 2H, CH_2); 3.80 (s, br, 2H, CH); 6.18 (q, 2H, H pyrrole β); 6.64 (d, 2H, H pyrrole γ); 6.99 (s, br, 2H, H pyrrole α); 7.25 (s, 2H, H imine). FT-IR (cm^{-1}, KBr): 3070 w, ν(CH pyrrole); 2939 s, ν(CH alkyl.).

2.3. Crystal structure determination of ***H_2L4·H_2O***, ***PdL4*** *and* ***PdL2***

Crystal data and details of structure refinement are given in Table 1. A crystal of **H_2L4·H_2O** was mounted on a Siemens AED three circle diffractometer (graphite-monochromated Mo Kα radiation) and used to measure cell dimensions and diffraction intensities. The crystal belongs to the orthorhombic system. The cell dimensions and diffraction intensities of the crystals of **PdL4** and **PdL3** were measured at r.t. on a Philips PW 1100 diffractometer (graphite-monochromated Mo Kα radiation). They belong to the monoclinic system; the correctness of the $P2_1/a$ space group was tested by LE PAGE program [9]. No decay in the intensity of standard reflections was noticed over the course of data collections. The intensity data were measured following a modified version [10] of the method of profile analysis by Lehmann and Larsen [11] and were corrected for Lorentz, polarization and, for **PdL4** and **PdL3**, absorption effects using a ψ-scan technique. The structures were solved by direct methods [12] and refined by full-matrix least-squares techniques based on F^2 [13]. Anisotropic thermal parameters were employed for non-hydrogen atoms. In **H_2L4·H_2O** and **PdL4** all the hydrogen atoms were located from ΔF maps and included in the refinement with isotropic parameters. In **PdL3**, only a part of the hydrogen atoms was located in the Fourier maps, the other was put in calculated position and constrained to ride on their carrying atoms. Neutral scattering factors [14] were employed and the anomalous dispersion terms for all atoms were included in Fc. The calculations were performed on a Digital Alpha 255 workstation at the 'Centro di Studio per la Strutturistica Diffrattometrica del CNR' in Parma. The molecular geometry was analyzed with the PARST program [15], and the drawings were made with ORTEP [16].

3. Results and discussion

The synthesis and the spectroscopic characterization of the ligands **H_2L1**–**H_2L4** do not show any remarkable features (see Section 2). **H_2L4** crystallizes with a water molecule, which is not lost before decomposition, as results from the thermogravimetric analysis.

The Ni(II) and Pd(II) acetates react with an ethanol solution of the ligands giving red or yellow–orange products. They have common spectroscopic features: in the IR spectra the ν(NH) bands disappear, while the ν(C=N) bands are shift to lower wavenumbers. The ^{1}H NMR spectra confirm the deprotonation; the ring protons result deshielded compared with those in the free ligands and the imine protons have undergone a large upfield shift. The coordination around the metal clearly involves the two imine and the two pyrrole nitrogens, as, on the other hand, the X-ray analysis carried out on **PdL4** and **PdL3** has confirmed. The narrow peaks of the ^{1}H NMR spectra induce to think that the nickel complexes are diamagnetic, with a square-planar N_2N_2' coordination around the metal, as the palladium ones. The titration of a $CDCl_3$ solution of the nickel species with d_6-DMSO and d_5-pyridine was followed by ^{1}H NMR: the metal ion does not increase its coordination number by adding molecules of solvent in the apical positions, in contrast with analogous N_2O_2 complexes [17]. The recording of the ^{1}H NMR spectrum of **PdL2** is prevented by its low solubility in the common solvents. **PdL2** is also the only complex unstable under hydrogen (see the hydrogenation experiments), so the possibility that its structure is different from the other ones—i.e. a polymeric structure as proposed for the green form of [Pd(salen)] [18]—cannot be ruled out.

Table 1
Crystal data and summary of intensity data collection and structure refinement for compounds **H_2L4·H_2O**, **PdL4** and **PdL3**

Compound	**H_2L4·H_2O**	**PdL4**	**PdL3**
Empirical formula	$C_8H_{11}N_2O_{0.5}$	$C_{16}H_{18}N_4Pd$	$C_{13}H_{14}N_4Pd$
Formula weight	143.19	372.74	332.68
Data collection method	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
Space group	$P22_12_1$	$P2_1/c$	$P2_1/a$
Unit cell dimensions			
a (Å)	8.839(5)	7.087(2)	37.298(9)
b (Å)	16.547(5)	19.239(6)	16.953(5)
c (Å)	5.569(5)	11.211(4)	8.120(3)
β (°)		98.42(3)	90.69(2)
V (Å^3)	814.5(9)	1512.1(8)	5134(3)
Z	4	4	16
D_{calc} (g cm^{-3})	1.168	1.637	1.722
Absorption coefficient (mm^{-1})	0.076	1.226	1.433
Crystal size (mm)	0.28 × 0.29 × 0.42	0.32 × 0.38 × 0.39	0.13 × 0.16 × 0.46
θ Range (°)	3.37–30.06	3.09–26.98	3.21–30.02
Reflections collected	4743	6465	15922
Independent reflections	2389 [$R_{int} = 0.0329$]	3288 [$R_{int} = 0.0379$]	14988 [$R_{int} = 0.0723$]
Parameters	142	262	759
Final R indices R_1 [$I > 2\sigma(I)$]	$R_1 = 0.0498$, $wR_2 = 0.1343$	$R_1 = 0.0297$, $wR_2 = 0.0488$	$R_1 = 0.0362$, $wR_2 = 0.0433$
R indices (all data)	$R_1 = 0.0978$, $wR_2 = 0.1506$	$R_1 = 0.0673$, $wR_2 = 0.0555$	$R_1 = 0.2169$, $wR_2 = 0.0691$
Goodness-of-fit on F^2	0.805	0.848	0.688
Extinction coefficient	0.107(14)		
Absolute structure parameter	0(3)		
Largest difference peak and hole (e Å^{-3})	0.221 and −0.169	1.083 and −0.676	0.901 and −0.658

3.1. Crystal structure discussion

The molecular structure of the ligand **H_2L4·H_2O** and of the complexes **PdL4** and **PdL3** has been determined. The ORTEP drawings of the molecules, with the atom labelling scheme, are shown in Figs. 1–3. In Fig. 1, the A labelled atoms of **H_2L4·H_2O** are related to the other ones by a twofold axis, passing through the midpoint of the C6–C6A and C8–C8A bonds. The organic moiety crystallizes with a water molecule, lying on the twofold axis, that plays an important role in the molecular geometry. In fact, the oxygen atom of the water molecule acts as a donor of a hydrogen bond with N2 (O···N2 = 2.783(3); H···N2 1.75(4) Å; O–H–N2 = 164(3)°) and as an acceptor towards N1 (N1···O = 2.868(2); H···O 2.00(2) Å; N1–H–O = 159(2)°). The same is valid for N2A and O1 ($x, y, z+1$). These interactions are probably responsible of the planarity of this part of the molecule. Effectively, the ligand can

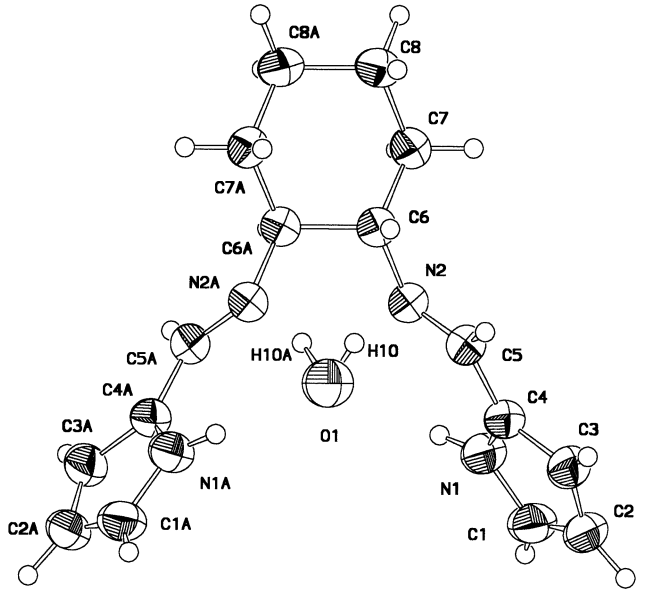

Fig. 1. ORTEP view of **H_2L4·H_2O**, with thermal ellipsoids at the 40% probability level.

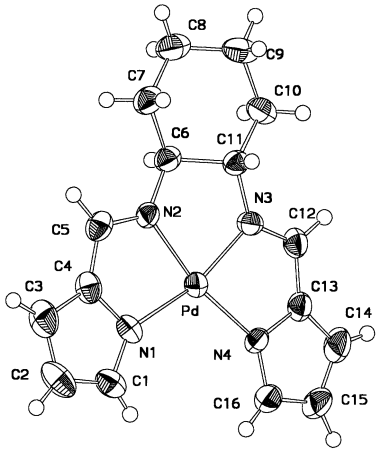

Fig. 2. ORTEP view of **PdL4**, with thermal ellipsoids at the 40% probability level.

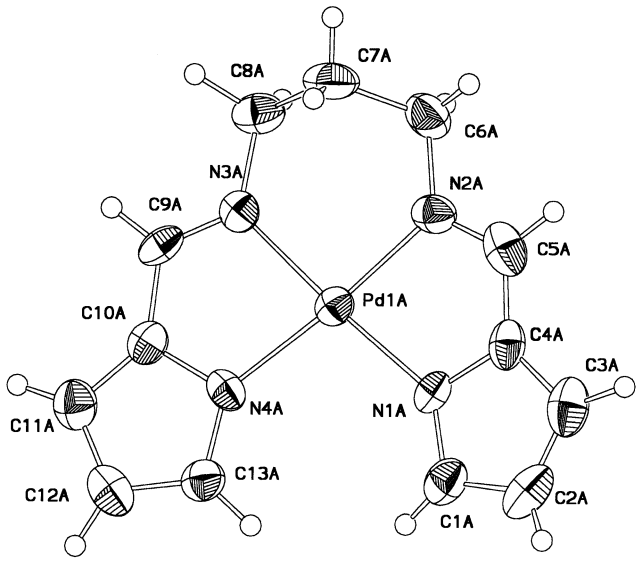

Fig. 3. ORTEP view of **PdL3** (molecule A), with thermal ellipsoids at the 40% probability level.

be described by two mean planes: one containing the imine bond and pyrrole ring, with a maximum deviation of −0.018(2) Å for C5, and the other containing the cyclohexane ring; these planes form a dihedral angle of 77.0(1)°. Around the imine bond, the configuration is *E*; the conformer is the *syn* one: the H6C6N2C5 torsional angle is −19(1)°, in accordance with the results of the MMX calculation on the analogous compound *N,N′*-dibenzylidene-(1*R*, 2*R*)-1,2-diaminocyclohexane (−18°) [19].

In the palladium complex **PdL4**, the ligand is bi-deprotonated and N_2N_2' tetradentate through the pyrrole and imine nitrogens. The coordination induces the formation of three five-membered chelate rings. The stereochemical constraints, imposed by the ligand, produce a puckering of the central chelate ring and, as a consequence, the distortion of the square-planar geometry. The tetrahedral twist, defined by the dihedral angle between the N1PdN2 and N3PdN4 planes, is 5.8°. The N2···N1 and N3···N4 rings deviate slightly from planarity (maximum deviation 0.023(4) and 0.030(4) Å for C5 and C13, respectively). The third chelate ring, which contains the alkyl bridge, is necessarily not planar: the N2–C6–C11–N3 torsion angle is 44.9(4)°. While the N1···C4 pyrrole ring is almost coplanar with the respective chelate ring (0.9(1)°), N4···C13 forms a dihedral angle of 4.2(1)°. The dihedral angles between the N_2N_2' plane and the pyrrole rings are 3.6(1) and 6.8(1)°, respectively; the angle between the ring planes is 9.5(2)°. The Pd–N(pyrrole) distances are significantly longer than the Pd–N(imine) distances.

The **PdL3** complex crystallizes with four crystallographically independent molecules (A–D) in the asymmetric unit. The four molecules are quite similar, then only A is reported in Fig. 3; the principal differences are summarized in Table 3. The coordination around palladium atoms is square-planar, with the formation of two five-membered and one six-membered chelate rings. **H_2L3** too is bi-deprotonated and N_2N_2' donor. The four nitrogen atoms deviate from the least-square plane, but in different way, and in fact the sum of $(\Delta/\sigma)^2$ is 6.644 for A, 27.141 for B, 8.237 for C and 50.024 for D molecule. The palladium atom deviates from the plane formed by the four nitrogens, in particular PdA 0.055(1), PdB −0.044(1), PdC 0.056(1), PdD −0.047(1) Å. This displacement is probably due to the long contacts PdA–PdB and PdC–PdD (3.90(1) and 3.85(1) Å, respectively). An analogous situation was found in the structure of [*N,N′*-propylenebis(2-pyrrolylmethyleneaminato)nickel(II)] (Ni–Ni 3.787(2) Å) [20]. The comparison of the four molecules two by two with the aid of SYMMOL [21] reveals only pseudo symmetry elements. In particular, there is a pseudo centre of symmetry at $x = 0.4401(1)$, $y = 0.2339(1)$, $z = -0.0953(1)$ between A and B, and a pseudo centre of symmetry at $x = 0.690(1)$, $y = 0.278(1)$, $z = 0.409(1)$ between C and D.

It might be interesting to compare the differences in the distances and angles at the palladium atom in both complexes. In **PdL4** the Pd–N(imine) distances are comparable and shorter than the Pd–N(pyrrole) ones (see Table 2). In **PdL3** the four averaged Pd–N distances are similar, as anticipated by ab initio studies [22], even if the situation results more complicated considering the molecules one by one (Table 3). A significant difference in coordination geometry is observed for the N–Pd–N angles. In the compound **PdL4**, the N(pyrrole)–Pd–N(pyrrole) angle is 114.0(1)° and the N(imine)–Pd–N(imine) is 83.9(1)°; in **PdL3** the same angles range between 102.8(2) and 103.4(2)°, and 94.7(2) and 95.9(2)°, respectively. The differences are comprehensible, since the propyl bridge in **PdL3** is less strained than the ethyl bridge in **PdL4**.

Table 2
Selected bond lengths (Å) and angles (°) for compounds **H_2L4·H_2O**, **PdL4** and **PdL3**, with e.s.d.s in parenthesis

	H_2L4·H_2O	**PdL4**		**PdL3**
Bond lengths				
Pd–N1		2.046(3)		2.012(2) (av.)
Pd–N2		1.959(3)		2.008(7)
Pd–N3		1.962(3)		2.004(3)
Pd–N4		2.046(3)		2.011(3)
N1–C1	1.367(3)	1.339(4)		1.352(6)
N1–C4	1.352(3)	1.386(4)		1.380(4)
C4–C5	1.442(3)	1.425(5)		1.423(4)
N2–C5	1.276(3)	1.285(4)		1.263(5)
N2–C6	1.459(3)	1.483(4)		1.469(8)
N3–C11		1.462(4)	N3–C8	1.455(6)
N3–C12		1.292(4)	N3–C9	1.289(5)
C12–C13		1.427(5)	C9–C10	1.410(4)

Table 3
Significant differences in the four independent molecules of **PdL3**, with e.s.d.s in parenthesis

	A	B	C	D
Bond lengths				
Pd–N1	2.008(5)	2.011(5)	2.016(4)	2.012(5)
Pd–N4	2.006(5)	2.013(5)	2.018(5)	2.008(5)
Pd–N2	2.027(5)	2.001(5)	1.995(5)	2.008(5)
Pd–N3	2.000(5)	2.010(5)	2.001(5)	2.005(5)
N1–C1	1.354(7)	1.365(7)	1.355(6)	1.339(6)
N4–C13	1.347(8)	1.314(8)	1.344(7)	1.337(7)
N2–C5	1.254(6)	1.273(7)	1.269(7)	1.257(7)
N3–C9	1.290(7)	1.281(8)	1.303(8)	1.283(8)
N2–C6–C7	112.0(6)	114.7(6)	112.4(6)	112.9(5)
C6–C7–C8	116.5(6)	112.8(7)	115.7(7)	116.0(6)
Dihedral angles (°) formed by the planes				
N1 C1C2 C3 C4 ^ N1 C4 C5 N2 Pd	2.2(2)	2.8(2)	3.9(2)	4.3(2)
N4 C13–C12–C11–C10 ^ N3 C9 C10 N4 Pd	7.5(2)	6.5(2)	5.3(2)	5.6(2)

3.2. Catalysis

All the complexes are tested as catalysts in the homogeneous hydrogenation of phenylacetylene under mild conditions, by using methanol or DMF as solvents. The methanol solutions result stable under hydrogen atmosphere in presence as well as in absence of the organic substrate. Only **PdL2** is completely reduced to palladium black in a few hours. At the end of the reactions, the complexes are precipitated by adding diethyl ether and their unchanged nature is confirmed by IR analysis. It is known that [Pd(salen)] is able to activate molecular hydrogen by heterolytic split, resulting in the protonation of the ligand and formation of a palladium hydride; the subsequent step is the transfer of the hydrogen to the substrate to give the hydrogenated product. The reaction is very sensible to the acid–base properties of the solvent and it is base catalysed [1]. In consideration of this, **PdL3**, **NiL3**, **PdL4** and **NiL4** are tested in DMF solution; **PdL4** and **NiL4** are also used in the presence of variable amounts of NaOH ([catalyst] = 5×10^{-4} M; [NaOH]/[cat.] = 10, 25). The results of the gas-chromatographic analysis of the reaction mixtures are reported in Tables 4 (reactions in methanol and DMF) and 5 (reactions in methanol with NaOH). Both Ni(II) and Pd(II) complexes are able to activate molecular hydrogen to give styrene and ethylbenzene in variable amount. In the DMF solutions, the palladium complexes are significantly more active than in methanol, while the opposite is true for the corresponding nickel complexes. Even if there are no NMR evidences, it is possible that in solution the apical positions of the nickel complexes are occupied by the coordinating solvent, slowing down the catalyst activity. Finally, by adding NaOH, the activity of the palladium complexes is reinforced. In the case of the nickel catalysts, the effects depend on the base concentration:

Table 4
Products of the hydrogenation of phenylacetylene in methanol and in DMF (%)

	1	5	24 h		1	5	24 h
PdL1				**NiL1**			
CH_3OH	87 phen.	50	4	CH_3OH	84	26	6
	12 sty.	41	15		15	65	58
	1 ethyl	9	81		1	9	36
PdL2				**NiL2**			
	not stable			CH_3OH	85	19	1
					13	44	8
					2	37	91
PdL3				**NiL3**			
CH_3OH	92	56	–	CH_3OH	94	68	–
	8	41	64		6	31	82
	–	3	36		–	1	18
DMF	87	14	–	DMF	96	85	50
	13	82	6		4	15	12
	–	4	94		–	–	38
PdL4				**NiL4**			
CH_3OH	96	85	13	CH_3OH	94	66	1
	4	15	24		6	33	90
	–	–	63		–	1	9
DMF	87	15	–	DMF	95	90	70
	13	81	–		5	10	28
	–	4	100		–	–	2

Phen, phenylacetylene; sty, styrene; ethyl, ethylbenzene.

there is a positive effect with [catalyst]/[NaOH] = 1/10, but a slow down of the reaction rate with a 1/25 ratio. Nickel is not very studied as catalyst in homogenous hydrogenation [23], even if it is known that, for example, the active site of the enzyme hydrogenase contains nickel. The mechanism of action is known even less. [Ni(saloph)] (saloph, bis(salicylaldehyde)-*o*-phenylenediamine) is used in the hydrogenation of cyclohexane

Table 5
Products of the hydrogenation of phenylacetylene in methanol, with increasing amount of NaOH ([catalyst]/[NaOH] = 1/10, 1/25)

PdL4	1	2	3	5	24 h	**NiL4**	1	2	3	5	24 h
1/10	89	76	57	21	1	1/10	91	71	55	19	1
	11	23	41	72	32		9	27	42	73	51
	–	1	2	7	67		–	2	3	8	48
1/25	85	66	40	7	–	1/25	93	83	72	57	11
	15	33	56	56	18		6	16	26	40	73
	–	1	4	37	82		1	1	2	3	16

and cyclooctene. In the proposed mechanism, the hydrogen molecule is activated by oxidative addition to give a Ni(IV) dihydride intermediate [24]. By means of ^{1}H NMR, it has not been possible to have any evidence of such a specie in our nickel solutions, maintained under hydrogen in a sealed tube. Anyway, any speculation about the reaction mechanism is, at this stage, premature.

4. Supplementary material

A full list of crystal data and refinement have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 181669–181671 for **H_2L4·H_2O**, **PdL4** and **PdL3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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