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A cyclometallated Pd(II) complex containing a cytosine model nucleobase

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Abstract

The acetate bridges in a cyclometallated, dinuclear complex **3** of Pd(II) with the 3,8-dinitro-6-phenylphenanthridine ligand can be substituted by the deprotonated model nucleobase 1-methylcytosine to give a doubly bridged 1-methylcytosinato complex **4**. **4** has a folded structure as concluded from ^{1}H NMR spectroscopy. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cyclometallated complex; Pd(II) complex; Nucleobase; 1-methylcytosine

1. Introduction

The interaction of palladium (II) amine complexes with nucleobases, the constituents of nucleic acids, is a field of current interest. [1–3] This is mainly due to the fact that Pd(II) species display considerable faster kinetics than Pt(II) species (ca. 10^5 times) while producing analogous products in general. Among others, we have made extensive use of the model nucleobase 1-methylcytosine (1-MeC) in preparing metal–nucleobase complexes. [3] This nucleobase may act principally as a monodentate ligand through N3 or as a bidentate ligand through N3 and the deprotonated N4. [4] Only occasionally have others binding patterns been observed, e.g. binding exclusively to N4 [5] or binding to C5 in conjunction with N3 and N4. [6] In the case of N3,N4 bridging, two metal atoms are linked in a way similar to cyclometallated complexes containing acetate bridges [7–10].

In the present study, our initial aim was to synthesize and characterize cyclometallated complexes of Pd(II) and Pt(II) derived from 3,8-dinitro-6-phenylphenanthridine and to investigate their reactions with a representative nucleobase, namely 1-MeC. 3,8-dinitro-6-phenylphenanthridine was chosen on the bases that we are interested in cyclometallated compounds with ligands having intrinsic pharmacological properties. [11,12] We have been able to obtain a compound that has been characterized by spectroscopy where deprotonated 1-MeC (1-MeC$^-$) bridges two palladium atoms. To our knowledge, this compound represents the first example of a Pd(II) cyclometallated complex with two 1-MeC$^-$ nucleobases acting as bridges through N3 and N4 of the nucleobase. It has not been possible to synthesize the mononuclear Pd(II):1-methylcytosine complex containing neutral 1-MeC. It should be pointed out that even with an excess of 1-MeC we have always obtained the dinuclear bis-(1-methylcytosinate) product. Moreover, we have been unable to synthesize the analogous Pt(II) complex.

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Table 1
Characteristic IR frecuencies for the ligand **1** and complexes **2**–**6**

	C=N	N–O	C=O	M–C	M–N	M–Cl
1	1619, 1592	1508, 1345	—	—	—	—
2	1616, 1577	1518, 1344	—	623	465	323, 303
3	1618, 1576	1516, 1346	1562, 1414[a]	622	458	—
4	1616, 1576, 1548, 1521[c]	1520, 1345	1652[b]	620	459	—
5	1616, 1578	1515, 1344	—	620	458	319
6	1617, 1577	1517, 1345	—	619	458	—

M: Pd or Pt.
[a] Bridging-acetate.
[b] Amide.
[c] 1-MeC.

2. Results and discussion

2.1. Synthesis and characterization of the complexes

The reaction between K_2PtCl_4 and the ligand 3,8-dinitro-6-phenylphenanthridine (**1**), (1:1.1) in AcOH, for 10 days yielded the corresponding complex **2**. This complex is insoluble in most organic solvents and only soluble in DMSO and DMF.

The IR spectrum of this complex (Table 1), shows the corresponding Pt–C (623 cm^{-1}) and Pt–N (465 cm^{-1}) stretching modes which suggests that cycloplatination has taken place. Two new bands corresponding to the Pt–Cl stretching vibrations at 323 and 303 cm^{-1} can also be observed, which suggests a dinuclear structure for this complex.

The ^1H NMR spectra for the ligand **1** and complex **2** are listed in Table 2. The general procedure to assign these spectra was as follows. First, the ^1H NMR spectrum was tentatively assigned on the basis of chemical shift and spin–spin coupling information. Second, the assignments were then unambiguosly confirmed by two-dimensional homonuclear correlation spectroscopy (COSY and/or NOESY) [13,14].

Fig. 1 shows the aromatic region of the ^1H NMR spectra of the ligand and of complex **2**. Spin–spin coupling constants of these protons allow us to identify the two double doublets corresponding to H2 and H9 protons (at 8.52 and 8.90 ppm), the doublets corresponding to H1 and H10 protons, with only one *ortho* coupling constant (at 9.12 and 9.26 ppm), and the doublets corresponding to H4 and H7 protons, with *meta* coupling constant (at 9.53 and 9.60 ppm). On the other hand, we can distinguish the double doublets of H11 and H14 (at 8.01 and 8.31 ppm) and the double triplets of H12 and H13 (at 7.34 and 7.40 ppm) which are due to the cyclometallated ring. However distinction within each pair is not possible from these spectra.

Fig. 2 shows the COSY spectrum of this complex, including the normal (1D) spectrum for comparison. From the off-diagonal connectivities, the protons corresponding to each of the phenanthridine rings and coupled pairs in the metallated ring can be distinguished.

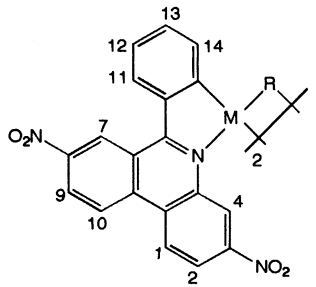
The difference NOE spectrum obtained by irradiation of the signal at 9.53 ppm (corresponding to H4 or H7) shows a significant enhancement of the signal at 8.01 ppm which identifies this signal to the H11 proton, the closest in space to the H7 proton being irradiated.

In general, we can observe a deshielding effect for all the protons of the phenanthridine ring with respect to that of the free ligand. We observe the disappearance of the multiplet corresponding to the phenyl ring protons and the appearance of four signals corresponding to the four different protons, H11–H14. These features confirms the cyclometallation. H14 is deshielded after cycloplatination despite the back-bonding character of the metal, which could be a consequence of the steric effect to the metallated substituent at C15. The shielding observed for H12 ($\Delta\delta = -0.28$ ppm) *para* with respect to the Pt–C bond, clearly indicates some metal-ligand back-bonding [15]. The deshielding effect at H11 and H7 ($\Delta\delta = 0.18$ and 0.72 ppm, respectively) must be a consequence of the change in the spatial arrangement after cyclometallation. On the other hand, it is interesting to point out that there was not observed any reaction between the chloro-bridged cycloplatinated compound and 1-methylcytosine.

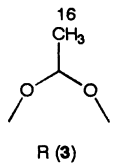
The reaction between $Pd(AcO)_2$ (1 equiv.) and 3,8-dinitro-6-phenylphenanthridine (**1**; 1.1 equiv.) in refluxing glacial AcOH under argon for 3 h, yields the corresponding acetate-bridged complex **3** (Scheme 1).

The microanalytical data are consistent with the empirical formula, LPdAcO. The IR spectrum (Table 1) shows two bands at 1562 and 1414 cm^{-1}, which are typical of bridging acetates [16]. Moreover, there are two bands for the C=N stretching mode. Only one of them is shifted to lower frequency, from 1592 cm^{-1} in **1** to 1576 cm^{-1} in **3**, which indicates coordination through the nitrogen atom. The presence of the Pd–N band at 458 cm^{-1} and a new band at 622 cm^{-1}, assigned to a Pd–C vibration mode, indicates that the cyclometallation has taken place.

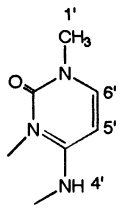
Table 2
^{1}H NMR Data (δ, ppm) for ligand **1** and complexes **2**–**6**



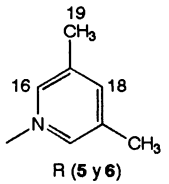
M = Pd (**3**, **4**, **5** y **6**)
M = Pt (**2**)



R (**3**)



R (**4**)



R (**5** y **6**)

	1	**1**[a]	**2**	**3**	**4**	**5**[a]	**6**[a]
H1	9.17, d, 1H $J = 9.1$	8.81, d, 1H $J = 9.1$	9.12, d, 1H $J = 9.0$	8.84, m, 1H	8.80, d, 1H $J =$ 8.9	8.63, d, 1H $J = 9.1$	8.61, d, 1H $J = 9.5$
H2	8.51, dd, 1H $J = 2.3$ and 9.1	8.56, dd, 1H $J = 2.3$ and 9.1	8.52, dd, 1H $J = 2.2$ and 9.0	8.31, m, 1H	8.20, m[b]	8.48, dd, 1H $J = 2.2$ and 9.1	8.45, d, 1H $J = 9.5$
H4	8.85, d, 1H $J = 2.3$	9.17, d, 1H $J = 2.3$	9.60, d, 1H $J = 2.2$	9.33, m, 1H	9.33, s, 1H	10.36, d, 1H $J = 2.2$	10.34, s, 1H
H7	8.81, d, 1H $J = 2.3$	9.13, d, 1H $J = 2.3$	9.53, d, 1H $J = 2.2$	8.29, m, 1H	8.19, m[b]	9.76, s, 1H	9.75, s, 1H
H9	8.74, dd, 1H $J = 2.3$ and 9.1	8.75, dd, 1H $J = 2.3$ and 9.1	8.90, dd, 1H $J = 2.2$ and 9.1	8.52, m, 1H	8.49, d, 1H $J =$ 8.9	8.85, m, 1H	8.85, s, 1H
H10	9.26, d, 1H $J = 9.1$	8.92, d, 1H $J = 9.1$	9.26, d, 1H $J = 9.1$	8.94, m, 1H	8.91, d, 1H $J =$ 8.9	8.85, m, 1H	8.85, s, 1H
H11	7.83, m, 1H	7.79, m, 1H	8.01, d, 1H $J = 7.7$	6.73, m, 1H	6.63, d, 1H $J =$ 4.2	7.85, d, 1H $J = 7.1$	7.85, d, 1H $J = 7.5$
H12	7.68, m, 2H	7.67, m, 2H	7.40, t, 1H $J = 7.7$	6.48, m, 1H	6.38, m, 2H	7.30, t, 1H $J = 7.1$	7.31, t, 1H $J = 7.5$
H13	7.68, m, 2H	7.67, m, 2H	7.34, dt, 1H $J = 1.2$ and 7.7	6.55, m, 1H	6.38, m, 2H	7.12, t, 1H $J = 7.1$	7.14, t, 1H $J = 7.5$
H14	eq. H12	eq. H12	8.31, dd, 1H $J = 1.2$ and 7.7	6.83, m, 1H	6.81, d, 1H $J =$ 7.6	6.45, d, 1H $J = 7.1$	6.37, d, 1H $J = 7.5$
H16				2.16, s, 3H		8.67, s, 2H	8.68, s, 2H
H18						7.52, s, 1H	7.52, s, 1H
H19						2.41, s, 6H	2.40, s, 6H
H6′					7.08, d, 1H $J =$ 7.3		
H5′					5.87, d, 1H $J =$ 7.3		
H4′					6.52, s, 1H		
H1′					3.09, s, 3H		

[a] $CDCl_3$.
[b] Overlapped signal. J (^{1}H–^{1}H) en Hz. s: singlet; d: doublet; m: multiplet; dd: double–doublet. δ (ppm) of 1-MeC free: H6′, 7.55; H5′, 5.60. δ (ppm) of 3,5-Lutidine free: H16, 7.64; H18, 6.49; H19, 1.53.

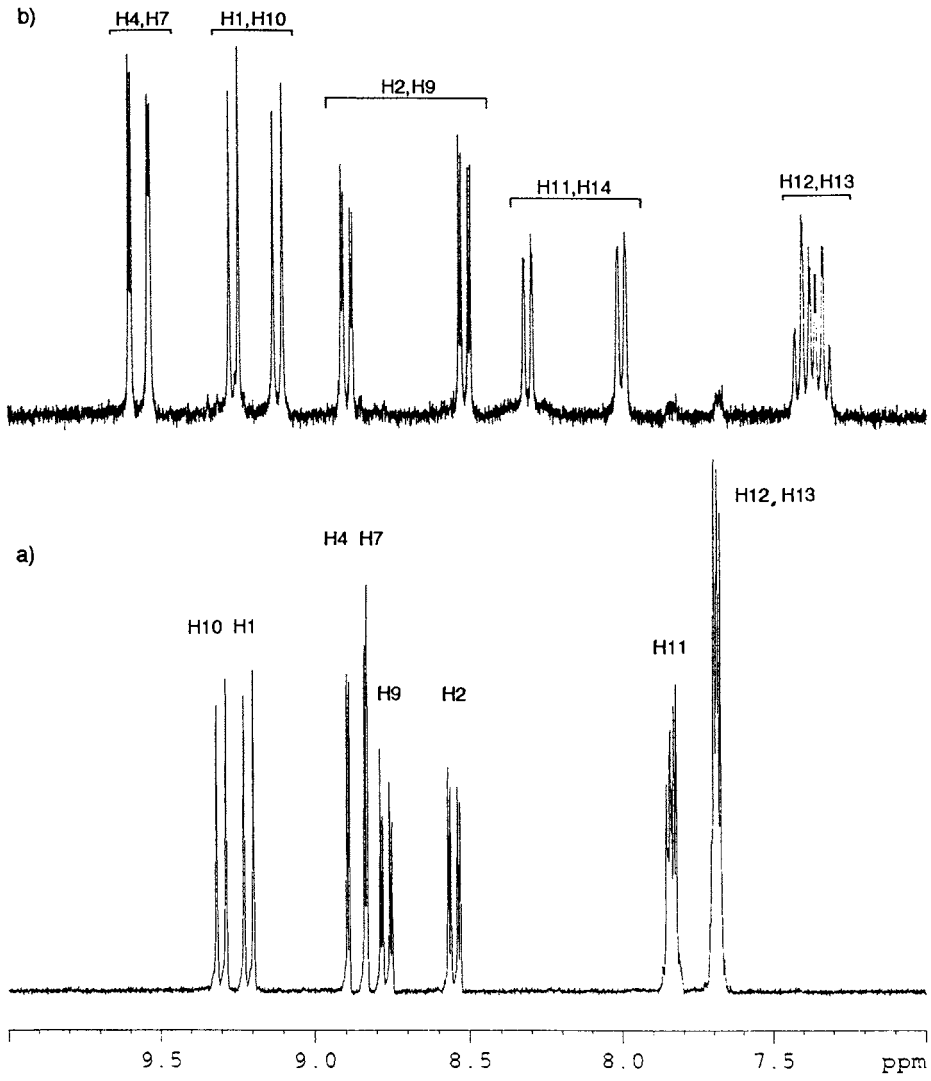


Fig. 1. Sections of proton NMR spectra of Ligand (a) and complex **2** (b) in DMSO-d_6.

The low solubility of this complex in most organic solvents, even in DMSO (1 mg ml^{-1}) made it difficult to record the NMR spectra. The ^1H NMR spectral data for the ligand, **1**, and complex **3** are shown in Table 2. Only one signal appears for the acetate-bridged methyl group at δ 2.16 ppm which suggests a *trans* arrangement of the ligands. [7]

The slight broadening and upfield shift of the aromatic signals of complex **3** (except for H4) could be due to anisotropic effects between the aromatic rings as a consequence of the folded shape for this complex [7]. Moreover, four different and strongly shifted signals appear for the phenyl ring, thus confirming that the cyclometallation has taken place in this ring. The strong shift to higher field observed for these protons could be due to the flow of charge from the electron-rich (d^8) metal atom into the aromatic ring (π-back-bonding) [17] and/or simply a consequence of ligand deprotonation.

The reaction of the acetate-bridged complex **3** with 1-MeC in 1:1 ratio at 37°C for 6 h led to complex **4**. This complex is insoluble in most organic solvents and only slightly soluble in DMSO and DMF.

The IR spectrum of compound **4** (Table 1) exhibits two broad bands at 1548 and 1521 cm^{-1}, typical of anionic, N3,N4 bridging 1-methylcytosine ligands (1-MeC$^-$–N3,N4). [3]c The bands at 620 and 459 cm^{-1}, can be assigned to ν(Pd–C) and ν(Pd–N) respectively, which indicates that the cyclometallated structure has been maintained.

The ^1H NMR of compound **4** is, as far as the phenanthridine moiety is concerned, similar to the folded acetate-bridged complex **3**, suggesting a similar structure for both complexes. The comparison of the chemical shifts observed for the aromatic 1-MeC protons in **4** (5.87 and 7.08 ppm for H5′ and H6′) and free 1-MeC (5.60 and 7.55 ppm for H5′ and H6′, respectively) are consistent with 1-MeC acting as a bridge ligand through N3 and N4 nitrogen atoms. [3]c In

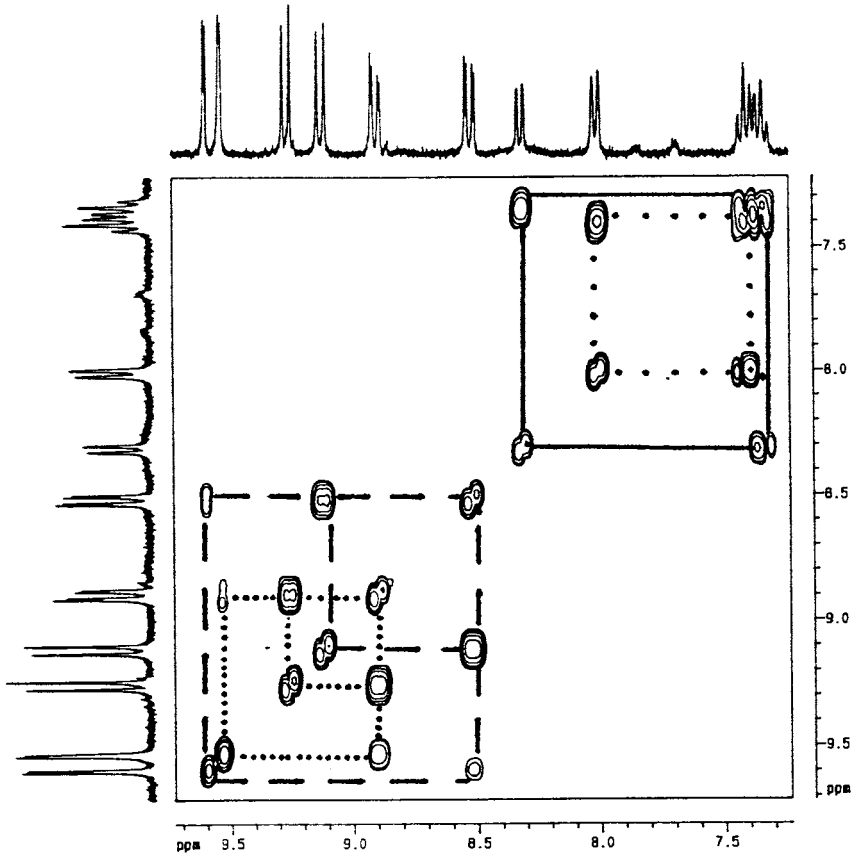


Fig. 2. Homonuclear two-dimensional correlation spectrum of complex **2** in DMSO-d_6.

particular, the upfield shift of the H6′ proton is indicative of anion formation of 1-MeC. The relative intensity of the singlet at 6.52 ppm, assigned to NH4′, further supports this interpretation.

The FAB mass spectrum of **4** shows a peak at $m/z = 1151$ corresponding to the molecular formula $[LPd(1\text{-}MeC^-)]_2$. Moreover, peaks at $m/z = 1026$, 681 and 574 corresponding to $[Pd_2L_2(1\text{-}MeC^-)]$, $[Pd_2L(1\text{-}MeC^-)]$ and $[PdL(1\text{-}MeC^-)]$, respectively, can also be observed, thereby confirming the dimeric nature of this complex.

The reaction of the μ-acetate complex **3** with 1-MeC at a 1:2-ratio in the presence of LiBr or LiCl does not lead to the corresponding monomer, as observed in the reaction with 3,5-lutidine (see below). The fact that 1-MeC does not form an analogous compound as lutidine may have something to do with the polarity of 1-MeC.

The reaction of complex **3** with 3,5-lutidine and LiBr in CH_2Cl_2 for 24 h at room temperature yields the corresponding halo-complex **6** (Scheme 1). When NaCl is used instead of LiBr, the reaction is slower, requiring refluxing for 48 h to obtain the halide-complex **5**. Both complexes, **5** and **6**, are soluble in most organic solvents. The study of these complexes allows us to determine the NMR parameters of the cyclometallated complexes (see below).

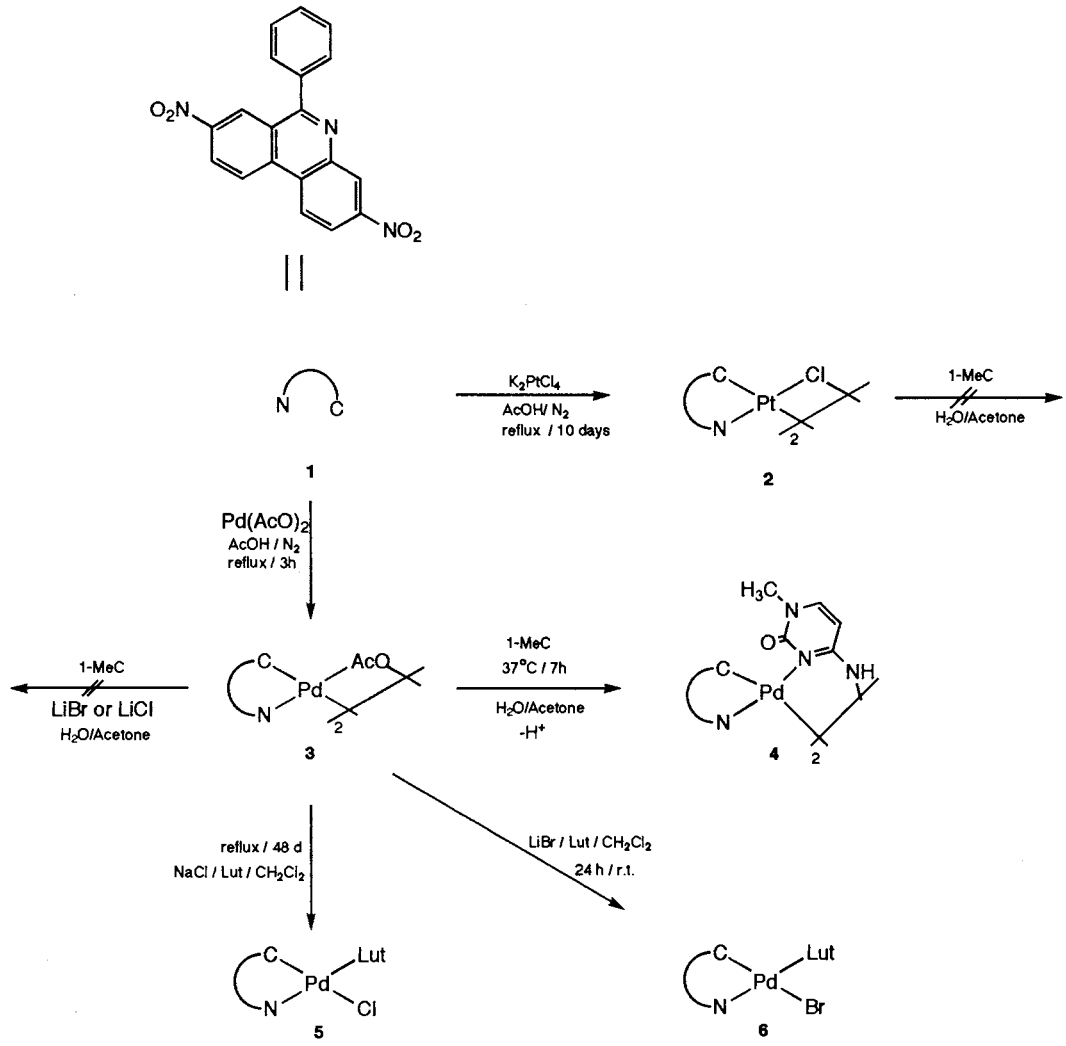
The microanalytical data for **5** and **6** are consistent with the formula [LPd(Lut)X] (X = Cl, **5**; X = Br, **6**). The FAB mass spectra of these complexes show similar fragmentation patterns, which include the loss of the halogen atom and later on of the lutidine ligand.

The IR spectrum of complex **5** (Table 1) shows only one Pd–Cl band at 286 cm^{-1} indicating that only one isomer has been formed, probably with chloride *trans* to the Pd–C bond. [15] This should be also true for [Pd(Lut)Br] (**6**), but in this case the Pd–Br stretching vibration cannot be observed.

The ^1H NMR data for complexes **5** and **6** are shown in Table 2. Difference NOE spectra obtained by irradiation of H14 (6.45 ppm in **5** and 6.37 ppm in **6**), show a significant enhancement of the signal intensities at 8.67 ppm in **5** and at 8.68 ppm in **6**, which are due to the lutidine-proton H16. This fact confirms that in both complexes the lutidine is *trans* to the nitrogen atom.

We note that the NMR parameters are similar for both complexes, i.e. the halogen atoms (Br or Cl) have not influence on the chemical shift of the rest of the protons of the ligand, except on H14, probably due to the difference in *trans* effect of these two atoms.

The phenyl-metallated ring protons are shielded with respect to the ligand, except H11. Thus, H14 is strongly upfield shifted ($\Delta\delta = \Delta\delta_{complex} - \Delta\delta_{ligand} = -1.22$ and



Scheme 1.

-1.30 ppm for **5** and **6**, respectively), probably due to space shielding induced by the lutidine ring. [18] The shielding observed for H12 *para* with respect to Pd–C bond ($\Delta\delta = -0.37$ and -0.36 ppm for **5** and **6**, respectively) indicates metal-ligand π-back bonding. [17] H11 is almost unchanged ($\Delta\delta = 0.06$ for **5** and **6**), probably due to the coplanarity with the phenanthridine ring which should produce a deshielding effect, compensating the upfield shift observed for the other protons of this ring.

2.2. Comparative ^1H NMR study of the cyclometallated complexes

The differences found on the ^{1}H NMR parameters for the phenanthridine cyclometallated derivative complexes could be attributed to the different solvents used (DMSO-d_6 and $CDCl_3$) or to the different metal. However, we found some similarities between the cycloplatinated dimer **2** and the palladium monomer complexes, **5** and **6**, (recorded in DMSO-d_6 and $CDCl_3$, respectively). On the other hand, there are large differences between these flat complexes (**2**, **5** and **6**) and **3** and **4**, which have a folded structure. We think that these differences are probably a consequence of the different structure of the complexes rather than a consequence of different solvent or metal used.

Table 3 shows the $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$ for the cyclometallated complexes. The dimeric complexes with a folded structure, **3** and **4**, show the same shielding effect with respect to the ligand, except for the H4, which may be attributed to anisotropy effects between the aromatic rings as a consequence of the folded shape of these complexes. The same effect is even observed for H7 and H11, where the coplanarity imposed by the cyclometallation should produce a deshielding effect.

The deshielding observed for H4 for all the complexes could be attributed to the delocalization of charge produced in this ring as a consequence of the aromaticity provoked in the cyclometallated ring. [8] The larger deshielding effect observed for this proton in complexes **5** and **6** could be due to the halogen bound to the palladium atom.

The proton H14, *ortho* to the Pd–C bond, appears upfield shielded in complexes **5** and **6**, probably due to the shielding effect of the lutidine ring. The same effect is observed for proton H14 in complexes **3** and **4**, which may be attributed to a charge flow as a consequence of the open-book shape (with interaction between the aromatic rings of the ligands).

3. Experimental

3.1. General procedures

The infrared spectra were recorded in Nujol mulls and KBr pellets in the 4000–200 cm^{-1} range using a Perkin–Elmer Model 283 spectrophotometer. NMR spectra were recorded on a Bruker AMX-300 spectrometer in DMSO-d_6 and in $CDCl_3$ with TMS as internal standard. The C, H and N analyses were carried out with a Perkin–Elmer 2400 microanalyzer. The mass spectra were recorded in a V. G. AUTODPEC high resolution spectrometer, using m-NBA or H_2SO_4 as a matrix, depending on the compound.

The analytical data are within the limits of experimental error ($\pm 0.4\%$)

All solvents were purified, prior to use, by standard methods. Palladium (II) and Platinum (II) salts and 3,8-dinitro-6-phenylphenanthridine were purchased from Johnson Matthey and Aldrich respectively. 1-Methylcytosine was prepared according to the literature [19].

3.2. Synthesis of $[LPtCl]_2$ (2)

In a Schlenk, 1.1 equiv. of **1** (0.38 gr, 1.1 mmol) and 1 equiv. of K_2PtCl_4 (0.415 gr, 1 mmol) were added to 10 ml of glacial AcOH under argon in reflux. After 10 days, the mixture was cooled to room temperature, filtered off and washed with water, CH_2Cl_2 and diethyl ether. The solid obtained was dried in vacuo (yield: 42%). MP: >300°C.

Table 3
^{1}H-NMR ($\Delta\delta = \delta_{complex} - \delta_{ligand}$) of the Complexes

	Dimers			Monomers	
	Folded		Unfolded		
	3	**4**	**2**	**5**	**6**
H1	−0.33	−0.37	−0.05	−0.18	−0.20
H2	−0.20	−0.31	+0.01	−0.08	−0.11
H4	+0.48	+0.48	+0.75	+1.19	+1.17
H7	−0.52	−0.62	+0.72	+0.63	+0.62
H9	−0.22	−0.25	+0.16	+0.10	+0.10
H10	−0.32	−0.35	0	−0.07	−0.07
H11	−1.10	−1.20	+0.18	+0.06	+0.06
H12	−1.20	−1.30	−0.28	−0.37	−0.36
H13	−1.13	−1.30	−0.34	−0.55	−0.53
H14	−0.85	−0.87	+0.63	−1.22	−1.30

3.3. Synthesis of $[LPd(AcO)]_2$ (3)

A mixture of $Pd(AcO)_2$ (0.224 gr, 1 mmol) with the ligand (**1**) (0.380 gr, 1.1 mmol) was refluxed in glacial AcOH (10 ml) under argon for 3 h. The mixture was then cooled. The solid obtained was filtered, washed with CH_2Cl_2 and diethyl ether and dried in vacuo (yield: 97%). MP: >300°C, with decomposition.

3.4. Synthesis of $[LPd(1\text{-}MeC^-)]_2$ (4)

A solution of 1 equiv. of 1-metylcytosine (0.249 gr, 2 mmol) in water, was added to a suspension of compound **3** (0.102 gr, 1 mmol) in acetone. The mixture was stirred for 6 h at 37°C. The solid obtained was filtered off, washed with water, acetone and diethyl ether, and dried in vacuo, yielding **4** (68%). MP: 288–291°C with decomposition. FAB-MS: 1151, 1026, 681, 574.

3.5. Synthesis of [LPdLutCl] (5)

To a suspension of compound **3** (0.102 gr, 1 mmol) in 10 ml CH_2Cl_2, 8 equiv. of 3,5-lutidine (0.858 gr, 8 mmol) and NaCl (0.468 gr, 8 mmol) were added. After 2 days of refluxing, a yellow solution was obtained. The solution was cooled, and concentrated. When petroleum ether was added, the product immediately precipitated out as a yellow solid. The solid obtained was filtered and washed with petroleum ether and dried in vacuo (yield: 93%). MP: 263–265°C with decomposition. FAB-MS: 592; 557; 450.

3.6. Synthesis of compound [LPdLutBr] (6)

To a suspension of compound **3** (0.102 gr, 1 mmol) in 10 ml CH_2Cl_2, 3,5-Lutidin (0.429 gr, 4 mmol) and LiBr (0.347 gr, 4 mmol) were added. After stirring for 5 h at room temperature the orange suspension changed to a yellow solution. The solution was then stirred for 24 h. Addition of petroleum ether gave a yellow solid. The solid obtained was filtered and washed with petroleum ether and dried in vacuo (yield: 79%). MP: 258–260°C with decomposition. FAB-MS: 638; 557; 450.

Acknowledgements

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