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Synthesis, spectroscopic properties and structural characterisation of Pd(II) and Pt(II) complexes with 1,3,5-pyrazole derived ligands. Rotation around the metal–N bond

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Abstract

Reactions of ligands 1-ethyl-5-methyl-3-phenyl-1H-pyrazole ($\mathbf{L^1}$) and 5-methyl-1-octyl-3-phenyl-1H-pyrazole ($\mathbf{L^2}$) with $[PdCl_2(CH_3CN)_2$ and K_2PtCl_4 gave complexes *trans*-$[MCl_2(\mathbf{L})_2]$ (L = L^1, L^2). The new complexes were characterised by elemental analyses, conductivity measurements, infrared, ^1H and $^{13}C\{^1H\}$ NMR spectroscopies and X-ray diffraction. The NMR study of the complex $[PdCl_2(\mathbf{L^1})_2]$, in $CDCl_3$ solution, is consistent with a very slow rotation of ligands around the Pd–N bond, so that two conformational isomers can be observed in solution (*syn* and *anti*). Different behaviour is observed for complexes $[PdCl_2(\mathbf{L^2})_2]$ and $[PtCl_2(\mathbf{L})_2]$ (L = L^1, L^2), which present an isomer in solution at room temperature (*anti*). The crystal structure of $[PdCl_2(\mathbf{L^1})_2]$ complex is described, where the Pd(II) presents a square planar geometry with the ligands coordinated in a *trans* disposition.

Keywords: Pyrazole ligands; Palladium complexes; Platinum complexes; Crystal structure

1. Introduction

Research on the coordination chemistry of pyrazole-derived ligands has progressed very rapidly over the last two decades. Mukherjee published an extensive review in [1], which complements those presented by La Monica and Ardizzoia in [2] and by Trofimenko in [3–6].

The N1-substituted pyrazolic ligands have been extensively investigated in our laboratory in recent years: *N*-aminoalkylpyrazoles [7–12], *N*-phosphinoalkylpyrazoles [13–15], *N*-thioetherpyrazoles [16–22], *N*-hydroxyalkylpyrazoles [23–25] and *N*-polyetherpyrazoles [26–29].

In particular, we have reported the synthesis and structural characterisation of new palladium(II) and platinum(II) compounds with 1-hydroxyalkyl-3,5-dimethylpyrazole [23,24] and 1-hydroxyalkylpyrazole ligands [24,25]. A similar study has been carried out with complexes with N1-polyether-3,5-dimethylpyrazole ligands [26]. NMR studies of these complexes have proved the existence of conformational diastereoisomers in solution, *anti* and *syn*, due to the relative disposition of the hydroxyalkylic or polyether chains, in which the ratio of both isomers was shown to be dependent on steric factors caused by the lengths of the N1-substituent [23,25,26].

In order to see whether the hindered rotation around the metal–N bond solution is caused by the bulk substituents in 3,5-disposition, by the lengths of the N1-substituents or by the nature of the metal, the related Pd(II) and Pt(II) complexes with N1-alkyl-5-methyl-3-phenylpyrazole were prepared and studied.

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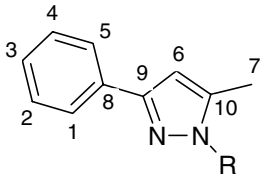

$\mathbf{L^1}$: R= ethyl
$\mathbf{L^2}$: R= octyl

Fig. 1. Pyrazole derived ligands and the atom numbering scheme.

The syntheses of 1-ethyl-5-methyl-3-phenyl-1H-pyrazole ($\mathbf{L^1}$) and 5-methyl-1-octyl-3-phenyl-1H-pyrazole ($\mathbf{L^2}$) have previously been reported in the literature [30] (Fig. 1), and it is with these ligands that we obtained and fully characterised the dichlorocomplexes with the formula $[MCl_2(\mathbf{L})_2]$ (M = Pd(II), L = L^1 (**1**); M = Pd(II), L = L^2 (**2**); M = Pt(II), L = L^1 (**3**); M = Pt(II), L = L^2 (**4**)). The crystal structure of **1** is also reported.

2. Experimental

2.1. General details

All reactions were carried out with the use of vacuum line and Schlenk techniques. All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled by standard methods.

The elemental analyses (C, N, H) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelons on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature (r.t.) 10^{-3} M in acetone solutions employing a Crison, micro CM 2200 conductimeter. Infrared spectra were run on a Perkin–Elmer FT spectrophotometer series 2000 cm^{-1} as KBr pellets or polyethylene films in the range 4000–100 cm^{-1} under a nitrogen atmosphere. The ^1H NMR, $^{13}C\{^1H\}$ NMR, HMQC, and NOESY spectra were run on a NMR-FT Bruker 250 MHz spectrometer (mixing time: 500 ms). Chemical shifts (δ) are given in ppm.

Samples of $[PdCl_2(CH_3CN)_2]$ [31] and K_2PtCl_4 were prepared as described in the literature. 1-ethyl-5-methyl-3-phenyl-1H-pyrazole ($\mathbf{L^1}$) and 5-methyl-1-octyl-3-phenyl-1H-pyrazole ($\mathbf{L^2}$) were prepared according to the published methods [30] (Fig. 1).

2.2. Synthesis

2.2.1. $[PdCl_2(L)_2]$ ($L = L^1$ (**1**), L^2 (**2**))

A solution of 0.32 mmol (0.083 g) of $[PdCl_2(CH_3CN)_2]$ in 20 ml of acetonitrile was treated with a solution of 0.64 mmol (0.121 g of $\mathbf{L^1}$, 0.176 g of $\mathbf{L^2}$) dissolved in 5 ml of acetonitrile. After 48 h of stirring at room temperature, the solution was concentrated until a crystalline precipitate appeared. The complex precipitate as a orange needles, which were recrystallised in a dichloromethane + hexane mixture. The solid was filtered off, washed with diethyl ether (5 ml) and dried in vacuo.

1: (yield: 69%) *Anal.* Calc. for $C_{24}H_{28}Cl_2N_4Pd$: C, 52.42; H, 5.10; N, 10.19. Found: C, 52.31; H, 4.93; N, 10.12%. Conductivity ($\Omega^{-1}\,cm^2\,mol^{-1}$, 1.1×10^{-3} M in acetone): 6. IR: (KBr, cm^{-1}): 3080 (νC–H)$_{ar}$, 2979 (νC–H)$_{al}$, 1557 (νC=C, νC=N)$_{ar}$, 1452 (δC=C, δC=N)$_{ar}$, 768 (δC–H)$_{oop}$; (polyethylene, cm^{-1}) 492 ν(Pd–N), 341 ν(Pd–Cl). ^1H NMR ($CDCl_3$ solution, 250 MHz) δ: isomer *syn*: 7.93 [d, ^3J = 7.2 Hz, 2H, H_1, H_5], 7.64–7.54 [m, 3H, H_2, H_3, H_4], 5.89 [s, 1H, H_6], 5.44, 5.32 [m, 2H, CH_2–CH_3], 2.04 [s, 3H, H_7], 1.15 [t, ^3J = 7.2 Hz, 3H, CH_2–CH_3] ppm. Isomer *anti*: 8.21[d, ^3J = 7.7 Hz, 2H, H_1, H_5], 7.64–7.54 [m, 3H, H_2, H_3, H_4], 6.15 [s, 1H, H_6], 4.86 [q,, ^3J = 7.0 Hz, 2H, CH_2–CH_3], 2.32 [s, 3H, H_7], 1.47 [t, ^3J = 7.0 Hz, 3H, CH_2–CH_3] ppm. ^{13}C NMR ($CDCl_3$ solution, 62.9 MHz): isomer *syn*: 153.6 (C_9), 142.9 (C_{10}), 132.5 (C_8), 130.0–128.8 (C_1–C_5), 107.4 (C_6), 45.6 (CH_2–CH_3), 15.2 (CH_2–CH_3), 12.0 (C_7) ppm. Isomer *anti*: 153.7 (C_9), 142.9 (C_{10}), 133.3 (C_8), 130.0–128.8 (C_1–C_5), 108.4 (C_6), 46.1 (CH_2–CH_3), 15.4 (CH_2–CH_3), 12.1 (C_7) ppm.

2: (yield: 63%) *Anal.* Calc. for $C_{36}H_{52}Cl_2N_4Pd$: C, 60.22; H, 7.25; N, 7.80. Found: C, 60.28; H, 7.55; N, 7.67%. Conductivity ($\Omega^{-1}\,cm^2\,mol^{-1}$, 1.2×10^{-3} M in acetone): 3. IR: (KBr, cm^{-1}): 3061 (νC–H)$_{ar}$, 2924 (νC–H)$_{al}$, 1554 (νC=C, νC=N)$_{ar}$, 1456 (δC=C, δC=N)$_{ar}$, 772 (δC–H)$_{oop}$; (polyethylene, cm^{-1}) 494 ν(Pd–N), 348 ν(Pd–Cl). ^1H NMR ($CDCl_3$ solution, 250 MHz) δ: isomer *anti*: 8.21 [d, ^3J = 6.8 Hz, 2H, H_1, H_5], 7.61–7.49 [m, 3H, H_2, H_3, H_4], 6.14 [s, 1H, H_6], 4.79 [t, ^3J = 7.3 Hz, 2H, CH_2–$(CH_2)_6$–CH_3], 2.31 [s, 3H, H_7], 1.86 [m, 2H, CH_2–CH_2–$(CH_2)_5$–CH_3], 1.33–1.07 [m, 10H, CH_2–CH_2-$(CH_2)_5$–CH_3], 0.92 [t, ^3J = 6.5 Hz, 3H, $(CH_2)_7$–CH_3] ppm. ^{13}C NMR ($CDCl_3$ solution, 62.9 MHz) δ: isomer *anti* 154.3 (C_9), 143.5 (C_{10}), 133.3 (C_8), 130.0–128.9 (C_1–C_5), 108.4 (C_6), 51.3 (CH_2–$(CH_2)_6$–CH_3), 32.2–23.1 (CH_2-$(CH_2)_6$–CH_3) 14.5 ($(CH_2)_7$–CH_3), 12.5 (C_7) ppm.

2.2.2. $[PtCl_2(L)_2]$ ($L = L^1$ (**3**), L^2 (**4**))

A solution of 0.32 mmol (0.135 g) of K_2PtCl_4 in 10 ml of HCl 0.1 M was treated with a solution of 0.64 mmol of the corresponding ligand (0.121 g of $\mathbf{L^1}$, 0.176 g of $\mathbf{L^2}$) dissolved in 5 ml of H_2O. After 72 h of stirring at room temperature, the solution was concentrated until a crystalline solid appeared. This precipitate was filtered off, washed twice with diethyl ether (5 ml) and dried in vacuo.

3: (yield: 55%) *Anal.* Calc. for $C_{24}H_{28}Cl_2N_4Pt$: C, 45.13; H, 4.39; N, 8.78. Found: C, 45.09; H, 4.48; N,

8.98%. Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.1×10^{-3} M in acetone): 13. IR (KBr, cm^{-1}): 3058 (νC–H)$_{ar}$, 2925 (νC–H)$_{al}$, 1522 (νC=C, νC=N)$_{ar}$, 1466 (δC=C, δC=N)$_{ar}$, 769 (δC–H)$_{oop}$; (polyethylene, cm^{-1}) 494 ν(Pt–N), 312 ν(Pt–Cl). ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ: isomer *anti*: 7.97 [d, ^3J = 6.8 Hz, 2H, H_1, H_5], 7.52–7.42 [m, 3H, H_2, H_3, H_4], 6.52 [s, 1H, H_6], 4.74 [q, ^3J = 6.8 Hz, 2H, CH_2–CH_3], 2.44 [s, 3H, H_7], 1.62 [t, ^3J = 6.8 Hz, 3H, CH_2–CH_3] ppm. ^{13}C NMR ($CDCl_3$ solution, 62.9 MHz) δ: isomer *anti*: 152.6 (C_9), 140.2 (C_{10}), 132.6 (C_8), 127.3–130.9 (C_1–C_5), 104.5 (C_6), 45.06 (CH_2–CH_3), 15.8 (CH_2–CH_3), 11.5 (C_7) ppm.

4: (yield: 59%) *Anal*. Calc. for $C_{36}H_{52}Cl_2N_4Pt$: C, 53.59; H 6.45; N 6.95. Found: C, 53.19; H, 5.99; N, 6.60%. Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.0×10^{-3} M in acetone): 26. IR (KBr, cm^{-1}): 3060 (νC–H)$_{ar}$, 2929 (νC–H)$_{al}$, 1551 (νC=C, νC=N)$_{ar}$, 1470 (δC=C, δC=N)$_{ar}$, 763 (δC–H)$_{oop}$; (polyethylene, cm^{-1}) 507 ν(Pt–N), 309 ν(Pt–Cl). ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ: isomer *anti*: δ: 7.88 [d, ^3J = 7.0 Hz, 2H, H_1, H_5], 7.51–7.35 [m, 3H, H_2, H_3, H_4], 6.43 [s, 1H, H_6], 4.30 [t, ^3J = 7.3 Hz, 2H, CH_2–$(CH_2)_6$–CH_3], 2.37 [s, 3H, H_7], 1.95–1.87 [m, 2H, CH_2–CH_2–$(CH_2)_5$–CH_3], 1.38–1.31 [m, 10H, CH_2–CH_2-$(CH_2)_5$–CH_3], 0.91 [t, ^3J = 7.0 Hz, 3H, $(CH_2)_7$–CH_3] ppm. ^{13}C NMR ($CDCl_3$ solution, 62.9 MHz) δ: isomer *anti* 149.2 (C_9), 141.5 (C_{10}), 138.3 (C_8), 129.1–126.6 (C_1-C_5), 103.5 (C_6), 49.7 (CH_2–$(CH_2)_6$–CH_3), 32.2–23.0 (CH_2-$(CH_2)_6$–CH_3) 14.6 ($(CH_2)_7$–CH_3), 11.7 (C_7) ppm.

2.3. X-ray crystal structure analyses

Suitable crystals for X-ray diffraction of compound *trans*-[$PdCl_2$(**L**^{1})$_2$] (**1**) were obtained through crystallisation from $CHCl_3$. One crystal was mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($12 < \theta < 21$) and refined by least-squares method. Intensities were collected with graphite monochromatised Mo Kα radiation (λ = 0.71069 Å), using $\omega/2\theta$ scan-technique. 3555 reflections were measured every two hours as orientation and intensity control, significant intensity decay was not observed. Lorentz-polarisation but no absorption corrections were made. The structure was solved by Patterson synthesis, using SHELXS computer program [32], and refined by full-matrix least-squares method with SHELX 97 computer programs [33] using 3555 reflections (very negative intensities were not assumed). The function minimised was $\sum w\|F_o|^2 - |F_c|^2|^2$, where $\omega = [\sigma^2(I) + (0.0664P)^2 + 0.0341P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. All H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. The final $R(F)$ factor and R_w (F^2) values as well as the number of parameters and other details concerning the refinement of the crystal structure are gathered in Table 1.

Table 1
Crystallographic data for *trans*-[$PdCl_2$(**L**^{1})$_2$] (**1**)

Formula	$C_{24}H_{28}Cl_2N_4Pd$
Formula weight	549.80
Temperature (K)	293(2)
Wavelength (Å)	0.71073
System, space group	triclinic, $P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	7.378(3)
b (Å)	8.747(2)
c (Å)	10.141(3)
α (°)	72.91(2)
β (°)	77.16(3)
γ (°)	83.76(2)
U (Å^3)	609.3(3)
Z	1
D_{calc} (g cm^{-3})	1.499
μ (mm^{-1})	0.999
$F(000)$	280
Crystal size (mm^3)	$0.1 \times 0.1 \times 0.2$
hkl Ranges	−10 to 10, −11 to 12, 0 to 14
2θ Range (°)	2.14–29.97
Reflections collected/unique [R_{int}]	3555/3555 [0.0000]
Completeness to θ = 29.97	100.0%
Absorption correction	None
Data/restraints/parameters	3555/0/198
Goodness-of-fit on F^2	1.074
Final R indices [$I > 2\sigma(I)$] R_1, w_2	0.0314, 0.0814
R indices (all data) R_1,w_2	0.0320, 0.0819
Largest diff. peak and hole (e Å^{-3})	0.676 and −0.439

3. Results and discussion

3.1. Synthesis and spectroscopic properties of the complexes

The complexes *trans*-[MCl_2(**L**)$_2$] (M = Pd(II): L = L^1 (**1**), L^2 (**2**); M = Pt(II): L = L^1 (**3**), L^2 (**4**)) were obtained by reaction of [$PdCl_2(CH_3CH)_2$] or K_2PtCl_4 with the corresponding pyrazolic ligand (**L**), in an acetonitrile solution in the case of Pd(II) or in a H_2O/0.1 M HCl solution with Pt(II) and in the 1M:2L ratio for both cases. The ability of L^1 and L^2 to coordinate Pd(II) and Pt(II) is comparable to that of the *N*-hydroxyalkylpyrazoles and *N*-polyetherpyrazoles [23–26]. The elemental analyses are consistent with the formula [MCl_2(**L**)$_2$] for the four compounds. Conductivity measurements in acetone (between 3 and 26 Ω^{-1} cm^2 mol^{-1}) show the non-ionic behaviour of the complexes **1**–**4** (conductivity values for a non-electrolyte are below 100 Ω^{-1} cm^2 mol^{-1} in acetone solution) [34,35].

The IR spectra in the range of 4000–400 cm^{-1} show that the ligands are coordinated to the Pd(II) or Pt(II). The ν(C=C), ν(C=N) and δ(C–H)$_{oop}$ bands of the pyrazolic ligands increase its frequency when are part of the complex [30].

The IR spectra of [MCl_2(**L**)$_2$] complexes in the region 600–100 cm^{-1} were also measured. The presence of bands at 500 cm^{-1} assigned to ν(Pd–N) or ν(Pt–N)

confirms the coordination of the ligand to the metallic atom. These complexes display one well-defined ν(Pd–Cl) band at 341 cm^{-1} (**1**) and 348 cm^{-1} (**2**), and ν(Pt–Cl) bands at 312 cm^{-1} (**3**) and 309 cm^{-1} (**4**), respectively. These bands clearly indicate that the chlorine atoms are coordinated *trans* to the Pd(II) and Pt(II) [36].

The NMR spectra of **1**–**4** were acquired using $CDCl_3$ as a solvent.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **1** show two sets of signals for many protons, suggesting the presence of conformational isomers in solution, in an intensity ratio of approximately 1:1. Our previous work also proved that the two species proposed in this case are the *anti* and the *syn* isomers (respectively), concerning the position of the hydroxyalkyl or polyether chains [23,25,26] (Fig. 2).

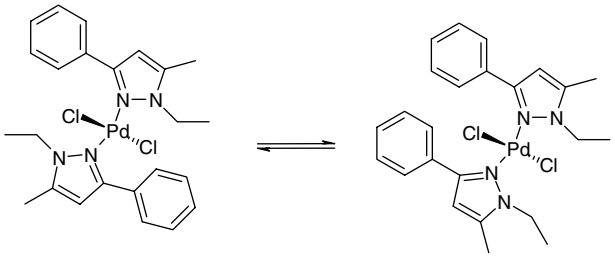

Fig. 2. The conformational isomers existing in solution due to a hindered rotation around the Pd–N bond at room temperature for compound (**1**).

A different behaviour is observed in complex **2**, which shows a unique NMR signal for each type of proton and carbon. The only specie present is the *anti* conformational isomer, which was confirmed by NOESY experiment. The presence of two conformers in complex **1** and one (*anti)* in complex **2** can be explained by the bulk of alkylchain. Thus, when the N1-alkyl chain increases its length, the less stable isomer (*syn*) decreases its concentration in solution.

The presence of two isomers in solution is not observed in complexes $[PtCl_2(\mathbf{L})_2]$ ($L = L^1$ (**3**), L^2 (**4**)) which show unique set of signals for each type of ^1H and $^{13}C\{^1H\}$ corresponding the *anti* conformational isomer. The ^1H NMR spectrum of $[PdCl_2(\mathbf{L^2})_2]$ at variable temperature (243 K) did not show any splitting or broadening of signals, which is in agreement with the existence of one specie in solution. The *anti* nature of the isomers was confirmed by a NOESY experiment, which shows NOE interaction between $\mathbf{H_1}$ and $-\mathbf{CH_2}-\mathbf{CH_2}-(CH_2)_5-CH_3$ (Fig. 3). In these compounds, the rotation around the Pt–N bond seems not to be possible due to higher Pt–N bond stability in comparison with Pd–N bonds.

The hindrance to rotation around metal–ligand bonds is predominantly controlled by steric factor but the influence of metal is not negligible [37]. It is well known that Pd(II) is more reactive than Pt(II) in substitution reactions but, interestingly, the palladium complexes are found to interconvert more readily than platinum analogues. [38]. NMR studies of rotational

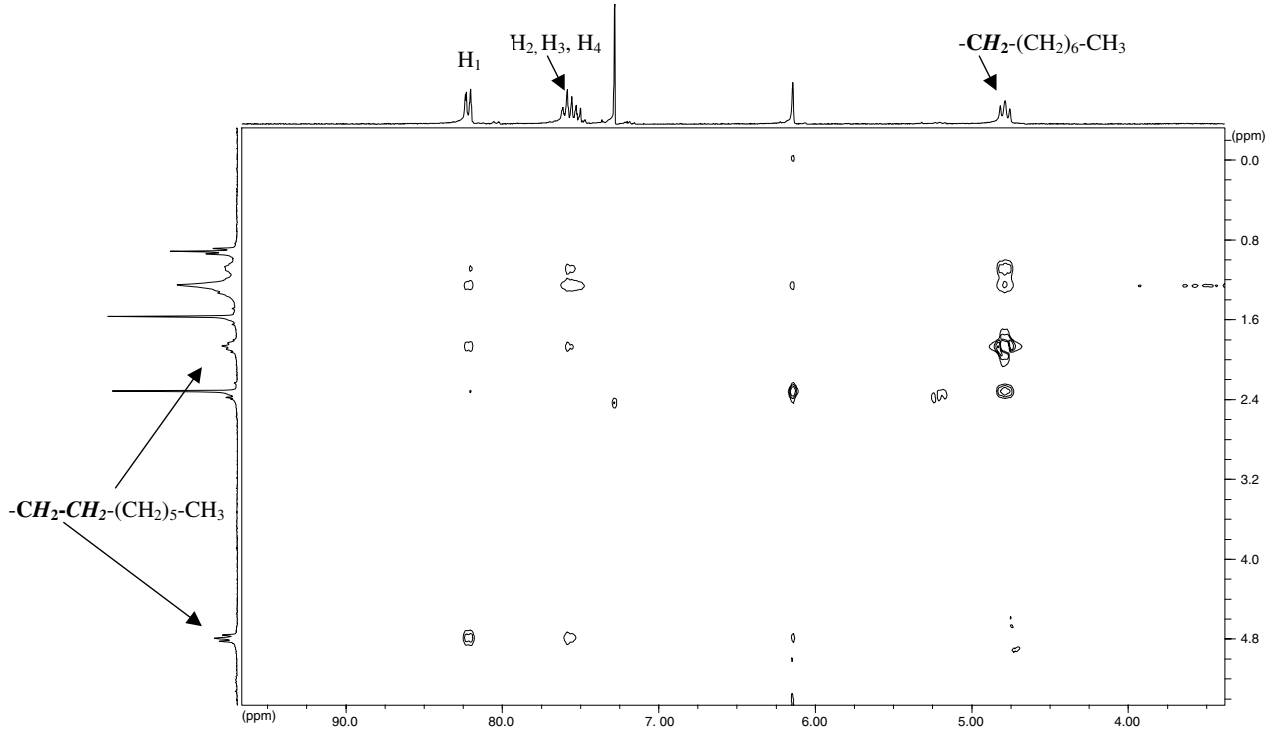

Fig. 3. The 250 MHz 2D NOESY spectrum of $[PdCl_2(\mathbf{L^2})_2]$ (**2**) in $CDCl_3$ at room temperature.

barriers for metal–N complexes have shown that in Pt(II) complexes are higher than in Pd(II) complexes [39]. These experimental observations were supported by ab initio calculations of model complexes containing Pd–N and Pt–N bonds, which reveal that the nitrogen metal π–σ interaction is stronger for Pt(II) complexes, resulting in a higher energy rotation barrier [39]. Despite the fact that pyrazole ligands are poor π-acceptors [40] and weaker π-acceptors than pyridine derivatives (largely studied in rotational dynamic processes) [41], the experimental findings suggest that the π-effects can be significant in the control of the preferential formation of the rotational diastereoisomers.

Precedents in the literature show that the reactivity of pyrazolic ligands with Pt(II) yields different results to those obtained with Pd(II) [23–25].

3.2. Crystal and molecular structure of complex *1*

The crystal structure of **1** consists of discrete centrosymmetric $[PdCl_2(\mathbf{L^1})_2]$ molecules linked by van der Waals forces. Table 2 lists selected distances and angles for this complex. The molecular structure is illustrated in Fig. 4.

The crystal structure is a monomeric molecule containing Pd(II) coordinated in a square planar environment, by two *trans* chlorides and two nitrogen atoms in the pyrazolic rings. The angles N–Pd–N and Cl–Pd–Cl are exactly 180°, which means that the metallic atoms lie in the centre of the plane determined by the two nitrogen atoms and the two chlorides. The N1-substituting alkyl chains is in an *anti* disposition. *Cis* angles N–Pd–Cl deviate from the ring angle in ≈1° the deviation in the equivalent complexes *trans*-$[MCl_2(HL)_2]$ (HL = 1-(2-hydroxyethyl)pyrazole [25]) and 1-[2-(2-methoxyethoxymethoxy)ethyl]-3,5-dimethylpyrazole [26] is ≈1°, however for the ligands 1-(2-hydroxyethyl)-3,5-dimethylpyrazole [23] and 1-[2-[2-(2-methoxyethoxy)-ethoxy]ethyl]-3,5-dimethylpyrazole [26] are only around 0.5° and 0°, respectively.

Table 2
Selected bond lengths (Å) and bond angles (°) for *trans*-$[PdCl_2(\mathbf{L^1})_2]$ (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Pd–N(1)	2.0281(16)
Pd–Cl	2.3078(9)
N(1)–Pd–N(1)#1	180.00(12)
N(1)–Pd–Cl#1	88.72(5)
N(1)–Pd–Cl	91.28(5)
Cl#1–Pd–Cl	180.00

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z$.

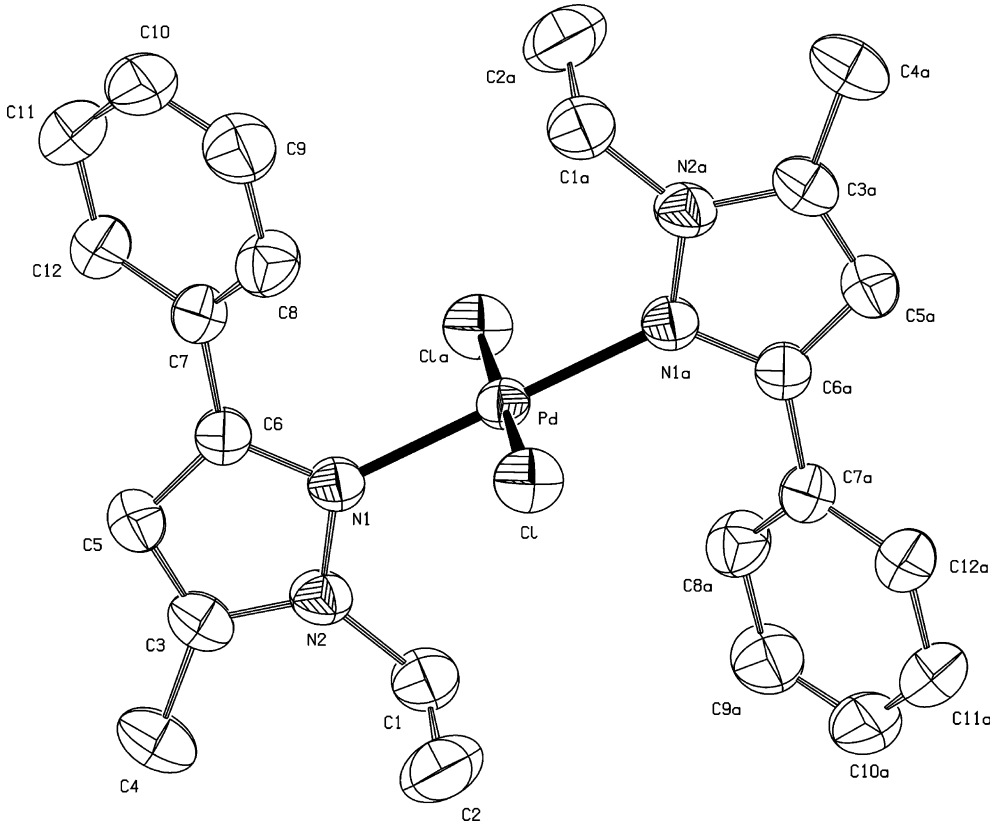

Fig. 4. ORTEP drawing of the complex $[PdCl_2(\mathbf{L^1})_2]$ (ellipsoids are shown at the 50% probability level).

The ligand ($\mathbf{L^1}$) is not planar. The phenyl group twisted with respect to the pyrazole. The angle dihedral between ph and pz is 35.06°.

The X-ray powder diffraction spectrum of **1** corroborates the presence of the single *anti* conformer in the solid state.

The $[PdCl_2(N_{pz})_2]$ *core* (containing terminal chlorine ions) is found in 21 complexes described in the literature (thirteen of the complexes found had *trans* geometry and eight were *cis*) [16,22,23,25,26,42–56]. Both the Pd–N distances (2.0281(16) Å) and the Pd–Cl distances (2.3078(9) Å) bond lengths are on the some order as those found in the literature (2.002–2.039 for Pd–N; 2.290–2.307 for Pd–Cl) [56]. Other distances and ring sizes are also in the normal ranges.

4. Conclusions

The ligands L^1 and L^2 (L) react with Pd(II) and Pt(II) ions to give new 1,3,5-pyrazole-derived compounds.

The study of the coordination of (**L**) ligands to Pd(II) and Pt(II) has revealed the formation of *trans*-$[MCl_2(\mathbf{L})_2]$ (M = Pd(II), Pt(II)). When M = Pd(II) and $L = L^1$ the NMR study is consistent with a very slow rotation around the Pd–N bond, so that two conformational isomers can be observed in solution, the intensity ratio observed for the two species is approximately 1:1. However, in the solid state only the *anti* isomer is obtained. In complex *trans*-$[PdCl_2(\mathbf{L^2})_2]$, a unique conformational isomer is observed (*anti*). The length of the N1-substituting alkyl chain increases the ratio of the *anti* isomer with respect to the *syn* isomer.

A different behaviour is observed in the complexes *trans*-$[PtCl_2(\mathbf{L})_2]$ ($L = L^1, L^2$), which shows a unique signal for each type of proton and carbon. The species present in solution is *anti*. The presence of a single conformational isomer is due to the higher stability of the Pt–N bond in comparison with Pd–N bond.

On the basis of the present work, we can establish that the presence of the *syn* and *anti* conformational isomers is controlled by steric factors coming from the size of alkyl groups and the nature of the metal. Phenyl and methyl groups at positions 3 and 5, respectively, do not modify the results obtained previously by our group [23,25,26].

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 255641 for compound $[PdCl_2(\mathbf{L^1})_2]$ (**1**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.htpp://ccdc.cam.ac.uk).

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