



Synthesis and characterisation of palladium compounds with new polyetherpyrazole ligands

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Abstract

The present report is on the synthesis of new 3,5-dimethylpyrazolic derived ligands that are N1-substituted by polyether chains: 1-(2-methoxyethoxymethyl)-3,5-dimethylpyrazole (**L**¹), 1-[2-(2-methoxyethoxymethoxy)ethyl]-3,5-dimethylpyrazole (**L**²) and 1-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]-3,5-dimethylpyrazole (**L**³). These ligands form complexes with the formula [PdCl₂L₂] when reacting with [PdCl₂(CH₃CN)₂] in the ratio 1M:2L. Two crystalline structures have been resolved with ligands **L**¹ and **L**³, where the Pd(II) presents a square planar geometry with the ligands co-ordinated in a *trans* disposition. NMR studies prove the existence of two conformational diastereoisomers for each complex in solution, as a consequence of the slow rotation around the Pd–N bond: *syn* and *anti*. The reaction of ligands **L**¹, **L**² and **L**³ with [PdCl₂(CH₃CN)₂] in presence of AgBF₄ yields the compounds [PdClL₃]BF₄, characterised by elemental analysis, conductivity measurements, ¹H NMR, ¹³C{¹H} NMR, infrared spectra, and FIA ES(+)/MS. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metal pyrazolic derived ligand complexes have recently attracted considerable interest due not only to their extensive co-ordination chemistry, but also to their catalytic and biological properties [1–3].

Some N1 polyetherpyrazolic ligands are already described in the literature. The 1,2-bis[3-(pyrazol-1-yl)-2-oxapropyl]benzene co-ordinates first row metals such as Cu(II), Co(II) and Zn(II) [4]. Other cyclic polyetherpyrazolic ligands appear to act as macrocycles with alkali or alkaline earth metals and also with ammonium derivatives [5,6]. No palladium complexes with this type of ligands have been described.

In our laboratory, different N1-substituted pyrazolic ligands have been prepared and complexed to metallic atoms: *N*-aminoalkylpyrazoles have been co-ordinated

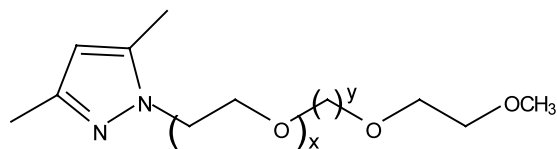
to Rh(I) [7–11], *N*-phosphinoalkylpyrazoles to Ru(II) [12] and *N*-tioetherpyrazoles to Pd(II) [13]. Here, and as a continuation of our previous studies concerned with the reactivity of *N*-hydroxyalkylpyrazole ligands towards palladium [14], we are interested in evaluating the behaviour of polyetherpyrazole ligands in the presence of the same metal.

The 1-(2-methoxyethoxymethyl)-3,5-dimethylpyrazole (**L**¹), 1-[2-(2-methoxyethoxymethoxy)ethyl]-3,5-dimethylpyrazole (**L**²) and the 1-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]-3,5-dimethylpyrazole (**L**³) have not previously been reported in the literature (Fig. 1), and it is with these ligands, that we obtained and fully characterised the dichlorocomplexes with the formula [PdCl₂L₂] (**L** = **L**¹ (**1**), **L**² (**2**), **L**³ (**3**)). The crystal structures of **1** and **3** are also reported.

The reaction of ligands **L**¹, **L**² and **L**³ with the complex [PdCl₂(CH₃CN)₂] in the presence of AgBF₄ (in the ratio 4L:1M:2AgBF₄) yields the compounds [PdClL₃]BF₄ (**L** = **L**¹ (**4**); **L**² (**5**); **L**³ (**6**)).

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L¹: x = 0; y = 1

L²: x = 1; y = 1

L³: x = 1; y = 2

Fig. 1. Pyrazole derived ligands.

2. Experimental

2.1. General methods

All reactions were performed under a nitrogen atmosphere with the use of vacuum line and standard Schlenk techniques. All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled under N₂ by standard methods just before use.

Elemental analyses (C, N, H) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature (r.t.) in 10⁻³ M acetonitrile, employing a CyberScan CON 500 (Eutech Instruments) conductimeter. Infrared spectra were run on a Perkin Elmer FT spectrophotometer, serie 2000 cm⁻¹ as KBr, NaCl or polyethylene pellets in the range 4000–100 cm⁻¹. ¹H NMR and ¹³C{¹H} NMR spectra were recorded on a NMR-FT Bruker 250 MHz spectrometer. All chemical shifts values (δ) are given in ppm. Electronic impact mass spectra were measured on a Hewlett–Packard HP-5989 A apparatus (CG/MS). Liquid chromatography/Electrospray mass spectrometry experiments were performed by the Scientifictechnics Services of the Universitat de Barcelona on a Shimadzu Ad VP chromatography instrument and API 150 (Applied Biosystems) mass spectrometer. The carrier was CH₃CN at a 0.2 ml min⁻¹ flow rate. The samples were dissolved in CH₃CN at a concentration of 0.4 mg ml⁻¹ and 5 μl of each solution injected on line. In the case of electrospray interface, whole flow was introduced in the capillary source and nebulised AT a 12 (arbitrary units) nitrogen flow. The auxiliary gas was nitrogen at 7000 cc min⁻¹ flow rate. The main electrical conditions for the positive electrospray were: capillary at 4200 V; potentials: DP = 20 and 60 V; FP = 200 V; EP = -10 V. The mass range measured was between 100 and 950 uma in full scan mode, cycle time was 2 s. The 1-(2-hydroxyethyl)-3,5-dimethylpyrazole [15] and PdCl₂(CH₃CN)₂ [16] have been prepared according to published procedures.

2.2. Synthesis of ligands

2.2.1. Preparation of 1-(2-methoxyethoxymethyl)-3,5-dimethylpyrazole (L¹)

To a solution of 1.68 g (17 mmol) of 3,5-dimethylpyrazole in 15 ml of dichloromethane, 2.47 g of methoxyethoxymethyl chloride (19 mmol) was added dropwise. To the resulting solution 2.71 g (27 mmol) of triethylamine was also slowly added, while cooling the solution in an ice-water bath. The mixture was stirred for 30 min at r.t. 15 ml of water was added twice to dissolve the ammonium salt. The dichloromethane was separated and dried over sodium sulphate anhydrous and filtered. The solution was then evaporated to dryness under vacuum leaving a pale yellow oil (yield: 3.03 g, 95%). C₉H₁₆N₂O₂: Anal. Calc.: C, 58.70; H, 8.70; N 15.22. Found: C, 57.81; H, 8.41; N, 14.71%. IR: (NaCl, cm⁻¹): 2924–2819 (νC–H)_{al}, 1562 (νC=C, νC=N), 1456 (δCH₃)_{as}, 1423 (δC=C, δC=N), 1378–1360 (δCH₃)_s, 1089 (νC–O–C)_{as}, 800 (δC–H)_{oop}. ¹H NMR (CDCl₃ solution, 250 MHz) δ: 5.85 [s, 1H, CHpz], 5.38 [s, 2H, NCH₂O], 3.61 [m, ²J = 9.0 Hz, ³J = 2.4 Hz, ³J = 6.4 Hz, ³J = 6.2 Hz, ³J = 3.4 Hz, 2H, OCH₂], 3.46 [m, ²J = 9.1 Hz, ³J = 2.4 Hz, ³J = 6.2 Hz, ³J = 6.4 Hz, ³J = 3.4 Hz, 2H, OCH₂], 3.35 [s, 3H, OCH₃], 2.29 [s, 3H, CH₃], 2.20 [s, 3H, CH₃]. ¹³C{¹H} NMR (CDCl₃ solution, 62.9 MHz) δ: 147.6 (CCH₃), 139.7 (CCH₃), 106.3 (CHpz), 77.7 (NCH₂O), 71.1 (OCH₂), 67.2 (OCH₂), 58.6 (OCH₃), 13.1 (CH₃), 10.3 (CH₃). MS (EI): m/z: 185 [MH⁺, <1], 125 [pzCH₂O⁺, 40], 109 [pzCH₂⁺, 100], 96 [pzH⁺, 36], 59 [CH₃OCH₂CH₂⁺, 12].

2.2.2. Preparation of 1-[2-(2-methoxyethoxymethoxy)ethyl]-3,5-dimethylpyrazole (L²)

To a solution of 1.65 g (12 mmol) of 1-(2-hydroxyethyl)-3,5-dimethylpyrazole in 20 ml of THF, 5.2 ml of 2.5 M butyllithium (13 mmol) was added in a water-ice bath. The mixture was stirred for 15 min at 0 °C. Methoxyethoxymethyl chloride (1.50 g, 12 mmol) was added dropwise to the suspension of the lithium salt (at 0 °C). The mixture was stirred at r.t. for 1 h, THF was removed under reduced pressure. The ligand was dissolved in dichloromethane. LiCl was filtrated and the solution was evaporated to dryness giving the ligand as yellow oil (yield 2.42 g, 90%). C₁₁H₂₀N₂O₃: Anal. Calc.: C, 57.89; H, 8.77; N, 12.28. Found: C, 57.70; H, 8.78; N, 11.94%. IR: (NaCl, cm⁻¹): 2926–2881 (νC–H)_{al}, 1553 (νC=C, νC=N), 1461–1426 ((δCH₃)_{as}, (δC=C, δC=N)), 1395–1386 (δCH₃)_s, 1117–1045 (νC–O–C)_{as}, 777 (δC–H)_{oop}. ¹H NMR (CDCl₃ solution, 250 MHz): δ 5.67 [s, 1H, CHpz], 4.53 [s, 2H, OCH₂O], 4.05 [t, ³J = 5.8 Hz, 2H, NCH₂], 3.78 [t, ³J = 5.8 Hz, 2H, OCH₂], 3.41 [m, 4H, OCH₂], 3.27 [s, 3H, OCH₃], 2.15 [s, 3H, CH₃], 2.11 [s, 3H, CH₃]. ¹³C{¹H} NMR (CDCl₃ solution, 62.9 MHz): δ 147.4 (CCH₃),

139.6 (CCH₃), 104.7 (CHpz), 95.2 (OCH₂O), 71.6 (OCH₂), 66.5 (OCH₂), 58.8 (OCH₃), 48.3 (NCH₂), 13.3 (CH₃), 10.9 (CH₃). MS (EI): *m/z*: 229 [MH⁺, 1], 153 [pzCH₂CH₂O⁺, 20], 123 [pzCH₂CH₂⁺, 17], 109 [pzCH₂⁺, 16], 96 [pzH⁺, 96], 89 [CH₃OCH₂CH₂OCH₂⁺, 100], 59 [CH₃OCH₂CH₂⁺, 85].

2.2.3. Preparation of 1-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]-3,5-dimethylpyrazole (**L**³)

3,5-Dimethylpyrazole (0.80 g (8.3 mmol)) was deprotonated with 0.56 g (8.3 mmol) of sodium ethoxide in ethanol, under a N₂ atmosphere. The mixture was stirred at r.t. overnight. The solvent was then removed under vacuum. Toluene (20 ml) was added to the white resulting solid. 1-[2-[2-(2-Methoxyethoxy)ethoxy]ethyl] chloride (1.53 g, 8.3 mmol) was added dropwise to the suspension and the solution was refluxed overnight. The NaCl was filtered and the solution was dried under vacuum. Colourless oil was obtained (yield: 1.87 g, 94%). C₁₂H₂₂N₂O₃: *Anal.* Calc.: C, 59.50; H, 9.09; N, 11.57. Found: C, 59.13; H, 8.49; N, 11.24%. IR: (NaCl, cm⁻¹): 2925–2879 (νC–H)_{al}, 1553 (νC=C, νC=N), 1464 (δCH₃)_{as}, 1424 (δC=C, δC=N), 1387–1352 (δCH₃)_s, 1109 (νC–O–C)_{as}, 774 (δC–H)_{oop}. ¹H NMR (CDCl₃ solution, 250 MHz): δ 5.64 [s, 1H, CHpz], 4.02 [t, ³J = 5.5 Hz, 2H, NCH₂], 3.69 [t, ³J = 5.5 Hz, 2H, OCH₂], 3.44 [m, 8H, OCH₂], 3.26 [s, 3H, OCH₃], 2.14 [s, 3H, CH₃], 2.09 [s, 3H, CH₃]. ¹³C{¹H} NMR (CDCl₃ solution, 62.9 MHz): δ 147.3 (CCH₃), 139.7 (CCH₃), 104.6 (CHpz), 71.8 (OCH₂), 70.5 (OCH₂), 70.4 (OCH₂), 70.3 (OCH₂), 70.2 (OCH₂), 58.8 (OCH₃), 48.4 (NCH₂), 13.3 (CH₃), 10.9 (CH₃). MS (EI): *m/z*: 243 [MH⁺, <1], 167 [pzCH₂CH₂OCH₂CH₂⁺, 29], 123 [pzCH₂CH₂⁺, 66], 109 [pzCH₂⁺, 91], 96 [pzH⁺, 100], 59 [CH₃OCH₂CH₂⁺, 31].

2.3. Synthesis of the metal complexes

2.3.1. Complexes [PdCl₂(L)₂] (where L = L¹ (**1**); L² (**2**); L³ (**3**))

To a solution of 0.080 g (0.30 mmol) of PdCl₂(CH₃CN)₂ in 15 ml of dichloromethane, 0.60 mmol of the appropriate ligand L (L¹, 0.110 g; L², 0.137 g; L³, 0.145 g) dissolved in 5 ml of the same solvent was added. The orange solution turned yellow. The mixture was stirred at r.t. overnight. For **1**, two-thirds of the solvent was then removed under vacuum and the concentrated solution was kept in the fridge for a few days. The complex precipitated as orange needles, which were recrystallised in a dichloromethane+diethyl ether mixture. For **2** the solvent was completely removed and the yellow oil was washed twice with 5 ml of diethyl ether. The solvent was removed until a precipitate appeared in the case of **3**. The yellow solid was filtered, washed twice with 5 ml of diethyl ether and recrystallised in a dichloromethane+diethyl ether mixture.

1 (yield: 79%). C₁₈H₃₂N₄O₄Cl₂Pd: *Anal.* Calc.: C, 39.61; H, 5.87; N, 10.27. Found: C, 39.92; H, 5.86; N, 10.25%. Conductivity (Ω⁻¹ cm² mol⁻¹, 1.10 × 10⁻³ M in acetonitrile): 11. IR: (KBr, cm⁻¹): 2998–2823 (νC–H)_{al}, 1560, 1559 (νC=C, νC=N), 1468 (δCH₃)_{as}, 1419 (δC=C, δC=N), 1363 (δCH₃)_s, 1117–1094 (νC–O–C)_{as}, 828 (δC–H)_{oop}; (polyethylene, cm⁻¹): 332 (νPd–Cl). ¹H NMR (CDCl₃ solution, 250 MHz) δ: isomer **1a**: 6.27 [s, 4H, NCH₂O], 5.95 [s, 2H, CHpz], 3.88 [m, 4H, OCH₂], 3.55 [m, 4H, OCH₂], 3.36 [s, 6H, OCH₃], 2.85 [s, 6H, CH₃], 2.33 [s, 6H, CH₃]. Isomer **1b**: 6.25 [s, 4H, NCH₂O], 5.94 [s, 2H, CHpz], 3.88 [m, 4H, OCH₂], 3.55 [m, 4H, OCH₂], 3.35 [s, 6H, OCH₃], 2.85 [s, 6H, CH₃], 2.33 [s, 6H, CH₃]. ¹³C{¹H} NMR (CDCl₃ solution, 62.9 MHz) δ: isomer **1a**: 151.2 (CCH₃), 144.7 (CCH₃), 108.8 (CHpz), 78.8 (NCH₂O), 71.7 (OCH₂), 68.6 (OCH₂), 59.0 (OCH₃), 15.3 (CH₃), 11.6 (CH₃). Isomer **1b**: 151.0 (CCH₃), 144.6 (CCH₃), 108.7 (CHpz), 78.6 (NCH₂O), 71.5 (OCH₂), 68.2 (OCH₂), 59.0 (OCH₃), 15.1 (CH₃), 11.6 (CH₃).

2 (yield: 96%). C₂₂H₄₀N₄O₆Cl₂Pd: *Anal.* Calc.: C, 58.84; H, 4.45; N, 6.24. Found: C, 58.55; H, 4.39; N, 5.97%. Conductivity (Ω⁻¹ cm² mol⁻¹, 9.47 × 10⁻³ M in acetonitrile): 5. IR: (NaCl, cm⁻¹): 2986–2818 (νC–H)_{al}, 1558 (νC=C, νC=N), 1471 (δCH₃)_{as}, 1364 (δCH₃)_s, 1115–1045 (νC–O–C)_{as}, 789 (δC–H)_{oop}; (polyethylene, cm⁻¹): 336 (νPd–Cl). ¹H NMR (CDCl₃ solution, 250 MHz) δ: isomer **2a**: 5.81 [s, 2H, CHpz], 4.95 [t, ³J = 5.1 Hz, 4H, NCH₂], 4.64 [s, 4H, OCH₂O], 4.48 [t, ³J = 5.1 Hz, 4H, OCH₂], 3.55 [m, 4H, OCH₂], 3.46 [m, 4H, OCH₂], 3.30 [s, 6H, OCH₃], 2.80 [s, 6H, CH₃], 2.24 [s, 6H, CH₃]. Isomer **2b**: 5.81 [s, 2H, CHpz], 4.89 [t, ³J = 5.5 Hz, 4H, NCH₂], 4.39 [t, ³J = 5.5 Hz, 4H, OCH₂], 3.55 [m, 4H, OCH₂], 3.46 [m, 4H, OCH₂], 3.30 [s, 6H, OCH₃], 2.72 [s, 6H, CH₃], 2.31 [s, 6H, CH₃]. ¹³C{¹H} NMR (CDCl₃ solution, 62.9 MHz) δ: isomer **2a**: 150.0 (CCH₃), 144.4 (CCH₃), 107.3 (CHpz), 95.5 (OCH₂O), 71.6 (OCH₂), 66.8 (OCH₂), 66.3 (OCH₂), 58.8 (OCH₃), 49.5 (NCH₂), 14.8 (CH₃), 11.9 (CH₃). Isomer **2b**: 149.6 (CCH₃), 144.3 (CCH₃), 107.2 (CHpz), 95.5 (OCH₂O), 71.6 (OCH₂), 66.8 (OCH₂), 66.2 (OCH₂), 58.8 (OCH₃), 49.5 (NCH₂), 14.8 (CH₃), 11.9 (CH₃).

3 (yield: 89%). C₂₄H₄₄N₄O₆Cl₂Pd: *Anal.* Calc.: C, 43.55; H, 6.65; N, 8.46. Found: C, 43.33; H, 6.63; N, 8.51%. Conductivity (Ω⁻¹ cm² mol⁻¹, 1.06 × 10⁻³ M in acetonitrile): 9. IR: (KBr, cm⁻¹): 2960–2852 (νC–H)_{al}, 1558 (νC=C, νC=N), 1470 (δCH₃)_{as}, 1350 (δCH₃)_s, 1102 (νC–O–C)_{as}, 820 (δC–H)_{oop}; (polyethylene, cm⁻¹): 341 (νPd–Cl). ¹H NMR (CDCl₃ solution, 250 MHz) δ: isomer **3a**: 5.85 [s, 2H, CHpz], 4.98 [t, ³J = 5.0 Hz, 4H, NCH₂], 4.47 [t, ³J = 5.0 Hz, 4H, OCH₂], 3.57 [broad signal, 16H, OCH₂], 3.36 [s, 6H, OCH₃], 2.77 [s, 6H, CH₃], 2.31 [s, 6H, CH₃]. Isomer **3b**: 5.85 [s, 2H, CHpz], 4.91 [t, ³J = 5.0 Hz, 4H, NCH₂], 4.37 [t, ³J = 5.0 Hz, 4H, OCH₂], 3.52 [broad signal, 16H,

OCH₂], 3.36 [s, 6H, OCH₃], 2.85 [s, 6H, CH₃], 2.31 [s, 6H, CH₃]. ¹³C{¹H} NMR (CDCl₃ solution, 62.9 MHz) δ: 149.7 (CCH₃), 144.7 (CCH₃), 107.5 (CHpz), 72.0 (OCH₂), 70.9 (OCH₂), 70.5 (OCH₂), 69.7 (OCH₂), 69.6 (OCH₂), 59.1 (OCH₃), 50.2 (NCH₂), 15.0 (CH₃), 12.2 (CH₃).

2.3.2. Complexes [PdCl(L)₃](BF₄) (where L = L¹ (4); L² (5); L³ (6))

To a solution of 0.078 g (0.30 mmol) of PdCl₂(CH₃CN)₂ in 15 ml of acetonitrile, 0.117 g (0.60 mmol) of AgBF₄ dissolved in 5 ml of methanol was added. The solution was stirred at r.t. and lightprotected for 30 min. The orange solution was then filtered through a pad of Celite and 1.20 mmol of L (L¹, 0.221 g; L², 0.274 g; L³, 0.290 g) dissolved in 5 ml of acetonitrile was added, while cooling the mixture in a ice-water bath. The solution was stirred for 2 h. A precipitated appeared, which was filtered (over Celite) and separated from the solution. The solvent was removed under vacuum yielding yellow oils.

4: C₂₇H₄₈BF₄N₆O₆ClPd: Anal. Calc.: C, 41.50; H, 6.15; N, 10.76. Found: C, 41.69; H, 6.13; N, 10.74%. Conductivity (Ω⁻¹ cm² mol⁻¹, 1.02 × 10⁻³ M in acetonitrile): 155. IR: (NaCl, cm⁻¹): 2982–2820 (νC–H)_{al}, 1559 (νC=C, νC=N), 1464 (δCH₃)_{as}, 1423 (δC=C, δC=N), 1361 (δCH₃)_s, 1130–1057 (νC–O–C_{as}, νB–F), 801 (δC–H)_{oop}; (polyethylene, cm⁻¹): 340 (νPd–Cl). ¹H NMR (acetone-d₆ solution, 250 MHz) δ: 5.94 [s, 3H, CHpz], 5.39 [s, 6H, NCH₂O], 3.56 [t, ³J = 4.7 Hz, 6H, OCH₂], 3.41 [t, ³J = 4.7 Hz, 6H, OCH₂], 3.24 [s, 9H, OCH₃], 2.31 [s, 9H, CH₃], 2.15 [s, 9H, CH₃]. ¹³C{¹H} NMR (acetone-d₆ solution, 62.9 MHz) δ: 148.7 (CCH₃), 141.6 (CCH₃), 107.1 (CHpz), 78.6 (NCH₂O), 72.2 (OCH₂), 68.3 (OCH₂), 58.7 (OCH₃), 13.8 (CH₃), 10.7 (CH₃). ES(+) MS (m/z): 693 [PdCl(L¹)₃]⁺ [M⁺], 511 [PdCl(L¹)₂]⁺, 325 [PdClL¹]⁺ and 294 [PdCl(dmpzCH₂O(CH₂)₂)⁺ (100%).

5: C₃₃H₆₀BF₄N₆O₉ClPd: Anal. Calc.: C, 43.39; H, 6.57; N, 9.20. Found: C, 43.11; H, 6.36; N, 9.20%. Conductivity (Ω⁻¹ cm² mol⁻¹, 1.01 × 10⁻³ M in acetonitrile): 146. IR: (NaCl, cm⁻¹): 2930–2818 (νC–H)_{al}, 1557 (νC=C, νC=N), 1459 (δCH₃)_{as}, 1423 (δC=C, δC=N), 1398 (δCH₃)_s, 1115–1046 (νC–O–C_{as}, νB–F), 847 (δC–H)_{oop}; (polyethylene, cm⁻¹): 347 (νPd–Cl). ¹H NMR (acetone-d₆ solution, 250 MHz) δ: 6.16 [s, 3H, CHpz], 4.62 [s, 6H, OCH₂O], 4.49 [t, ³J = 5.0 Hz, 6H, NCH₂], 3.91 [t, ³J = 5.0 Hz, 6H, OCH₂], 3.45 [m, 12H, OCH₂], 3.24 [s, 9H, OCH₃], 2.39 [s, 9H, CH₃], 2.34 [s, 9H, CH₃]. ¹³C{¹H} NMR (acetone-d₆ solution, 62.9 MHz) δ: 147.5 (CCH₃), 144.4 (CCH₃), 107.2 (CHpz), 95.9 (OCH₂O), 72.5–66.7 (OCH₂), 58.7 (OCH₃), 50.2 (NCH₂), 12.0 (CH₃), 11.3 (CH₃). ES(+) MS (m/z): 825 [PdCl(L²)₃]⁺ [M⁺ < 1%], 559 [PdCl[dmpz(CH₂)₂O]₃]⁺ and 251 [PdCl(dmpzCH₂)⁺ (100%) (dmpz = 3,5-dimethylpyrazole).

6: C₃₆H₆₆BF₄N₆O₉ClPd: Anal. Calc.: C, 45.25; H, 6.91; N, 8.80. Found: C, 45.37; H, 6.82; N, 8.67%. Conductivity (Ω⁻¹ cm² mol⁻¹, 1.01 × 10⁻³ M in acetonitrile): 158. IR: (NaCl, cm⁻¹): 2919–2879 (νC–H)_{al}, 1554 (νC=C, νC=N), 1464 (δCH₃)_{as}, 1423 (δC=C, δC=N), 1353 (δCH₃)_s, 1102–1058 (νC–O–C_{as}, νB–F), 849–824 (δC–H)_{oop}; (polyethylene, cm⁻¹): 343 (νPd–Cl). ¹H NMR (acetone-d₆ solution, 250 MHz) δ: 6.07 [s, 3H, CHpz], 4.40 [t, ³J = 5.0 Hz, 6H, NCH₂], 3.85 [t, ³J = 5.0 Hz, 6H, OCH₂], 3.48 [m, 24H, OCH₂], 3.27 [s, 9H, OCH₃], 2.36 [s, 9H, CH₃], 2.30 [s, 9H, CH₃]. ¹³C{¹H} NMR (acetone-d₆ solution, 62.9 MHz) δ: 152.3 (CCH₃), 148.2 (CCH₃), 106.2 (CHpz), 72.1–70.3 (OCH₂), 58.3 (OCH₃), 50.0 (NCH₂), 13.5 (CH₃), 10.9 (CH₃). ES(+) MS (m/z): 867 [PdCl(L³)₃]⁺ [M⁺], 627 [PdCl(L³)₂]⁺, 385 [PdClL³]⁺ and 352 [PdCl(dmpz(CH₂CH₂O)₂CH₂CH₂)⁺ (100%).

2.4. X-ray crystal structure analyses

Suitable crystals for X-ray diffraction experiments of compounds **1** and **3** were obtained through recrystallisation from a CH₂Cl₂+diethyl ether mixture. Data for **1** were collected on a MAR345 diffractometer. For **3**, the crystal was mounted on an Enraf–Nonius CAD4 diffractometer. Both were measured at r.t. using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Intensities were collected using the ω–2θ scan-technique. The structures were solved by direct methods (SHELXS-97) [17] and refined by full-matrix least-square method with (SHELXL-97) [18].

For complex **1** all H atoms were computed and refined, using a riding model with an overall isotropic temperature factor equal to 1.2 time the equivalent temperature factor of the atom, which are linked. For compound **3**, 14 H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and 8 H atoms were computed and refined with an overall isotropic temperature factor. The final R (on F) and R_w(F²) values as well as the number of parameters refined and other details concerning the refinement of the crystal structures are presented in Table 1.

3. Results and discussion

3.1. Synthesis and spectroscopic properties of the complexes

The three new ligands (Fig. 1) are readily obtained from the reaction of the corresponding chloride (ClCH₂OCH₂CH₂OCH₃ for L¹ and L² and ClCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃ for L³) with the 3,5-dimethylpyrazole (for L¹) or the 3,5-dimethylpyr-

Table 1
Crystal data for **1** and **3**

Compound	1 [PdCl ₂ (L ¹) ₂]	3 [PdCl ₂ (L ³) ₂]
Formula	C ₁₈ H ₃₂ Cl ₂ N ₄ O ₄ Pd	C ₂₄ H ₄₄ Cl ₂ N ₄ O ₆ Pd
<i>M</i>	545.78	661.93
System	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>a</i>
Unit cell dimensions		
<i>a</i> (Å)	9.3590(10)	8.392(3)
<i>b</i> (Å)	16.1550(10)	15.980(9)
<i>c</i> (Å)	15.9220(10)	11.703(2)
β (°)	95.24(2)	92.21(2)
<i>U</i> (Å ³)	2397.3(3)	1568.3(1)
<i>Z</i>	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.512	1.402
μ (mm ⁻¹)	1.026	0.803
<i>F</i> (000)	1120	688
Crystal size (mm ³)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
<i>hkl</i> Ranges	0 to 10, 0 to 17, –18 to 18	–11 to 11, 0 to 22, –4 to 16
2 θ Range (°)	1.80–25.02	2.16–29.96
Reflections collected/unique	12041, 3859	4758/ 4535
	[<i>R</i> (int) = 0.0344]	[<i>R</i> (int) = 0.0252]
Data, restraints, parameters	3859, 0, 265	4535, 0, 233
Final <i>R</i> ₁ , <i>wR</i> ₂	0.0508, 0.1091	0.0522, 0.0990
<i>R</i> ₁ (all data), <i>wR</i> ₂ ^a	0.0786, 0.1205	0.1386, 0.1208
Largest difference peak and hole	+0.581 and –0.411	+0.834 and –0.811
(e Å ⁻³)		

^a The function minimized was $\sum w((F_o)^2 - (F_c)^2)^2$, where $w = [\sigma^2(I) + (aP)^2]^{-1}$, and $P = (F_o^2 + 2F_c^2)/3$.

azole sodium salt (for L³) or with the 1-hydroxyethyl-3,5-dimethylpyrazole lithium salt (for L²).

The three ligands were fully characterised. However, the ¹H NMR spectrum of L¹ shows a complex group of signals in the methylene region. In order to determine both their ¹H–¹H coupling constants and chemical shifts, a simulated spectrum has been obtained using gNMR program [19]. The two NCH₂ protons are almost isochronous (as shown in the chemical shifts in Section 2). Each one has three different coupling constants with the other NCH₂ proton and with the two CH₂O protons. This is what makes the signal appear as a multiplet. The same thing occurs with the protons of the CH₂O.

Other syntheses of polyetherpyrazole ligands (all of them containing two pyrazolic rings with N1 substituting polyether chains, either cyclic or linear) have been already described in the literature [5,6].

The ability of L¹, L² and L³ to co-ordinate to Pd(II) is comparable to that of the *N*-hydroxyalkylpyrazoles, as neither the alcohol nor the ether groups participate in the ligation. Concerning the dichloropalladium complexes (**1–3**), they were readily obtained from the reaction of [PdCl₂(CH₃CN)₂] with the corresponding ligand in the ratio 1M:2L. The elemental analyses correspond to the stoichiometry [PdCl₂L₂]. The neutral-

ity of the compounds is evident after their conductivity measurements (compared with tabulated values [20]): between 5 and 11 Ω⁻¹ cm² mol⁻¹ in acetonitrile. The IR spectra in the range of 4000–400 cm⁻¹ show that the ligands are co-ordinated to the Pd(II). The (δC–H)_{oop} band of the pyrazolic ligand increases its frequency when it is part of the complex. No significant change is observed in the (νC=C, νC=N) bands. The ¹H NMR (and ¹³C NMR in complex **1** and **2**) spectra show two sets of signals for many protons, suggesting the presence of conformational isomers in solution, in an intensity ratio of approximately 1:1 in the case of **1**, 1:0.8 for **2**, and 1:0.7 in **3**. As our previous work showed [14], the two species proposed in this case are the *anti* and the *syn* isomers (respectively), concerning the position of the two carbon chains (Fig. 2). Each isomer would undergo a very slow rotation (slower than the NMR acquisition time) to give the other one. Taking into account the intensity ratios of both complexes, we can say that in the case of **1** the stability of both conformations is similar, but not in the case of **2** and **3**. The position of such a long N1 substituting chain determines that one of the two isomers (the *anti*) is less hindered, and the two ligands can better accommodate. Thus when the N1 polyether chain increases its length, the less stable isomer (*syn*) decreases its concentration in solution.

When the [PdCl₂(CH₃CN)₂] reacts with an excess of ligand in the presence of AgBF₄, complexes with the formula [PdClL₃]BF₄ (**4–6**) are obtained (the stoichiometry is confirmed by elemental analyses). The conductivity measurements in acetonitrile show that the complexes behave as electrolytes 1:1 in solution [20], which is consistent with its monocationic nature. In the IR spectra, the band (δC–H)_{oop} again increases the frequency with respect to the free ligand and also to the dichlorocomplexes. The presence of one chloride co-ordinated to the palladium atom is also shown through the IR spectra in the range of 600–100 cm⁻¹, with the presence of one band in each spectrum around 340 cm⁻¹ corresponding to the (νPd–Cl) [21]. In the NMR spectra of complexes [PdClL₃](BF₄) one species only can be seen. The steric hindrance due to the co-ordination of three ligands to Pd(II), makes that only one isomer is stable (the position of the polyether chains is determined by steric aspects).

To confirm the existence of these species electrospray mass spectra were recorded. The positive ionisation spectrum of **1** and **3** when measured gave peaks with *m/z* values of 693 and 867, respectively (molecular peak of the cation). In the spectrum of **2** the molecular peak (825) was observed in an intensity lower than 1%, probably due to the easy cleavage of the polyether chain. It is well known that the cleavage of the methylene α-diether is quite easy (even used as a protecting group for alcohols). But the ES(+) MS

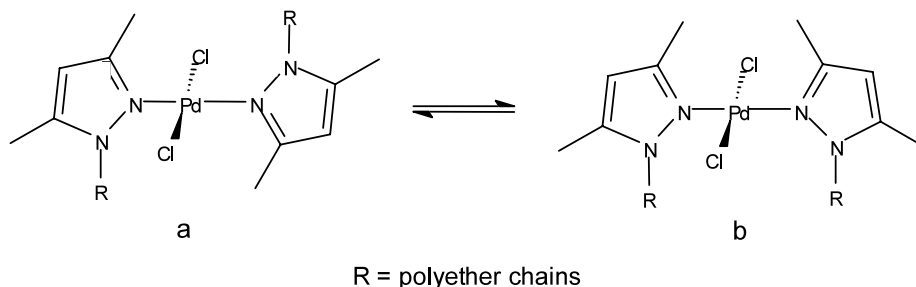


Fig. 2. Scheme of the conformational isomers existing in solution due to a hindered rotation around the Pd–N bond at room temperature.

does show many fragmentation peaks, thus confirming the existence of the species.

3.2. Crystal and molecular structure of complexes **1** and **3**

Complexes **1** and **3** appear to be structurally similar, consisting of monomeric $[\text{PdCl}_2(\text{L})_2]$ molecules and having a square planar geometry around the metal atom. The environment consists of two chlorides coordinated *trans* to the Pd(II) and two nitrogen atoms in the pyrazolic rings. Selected bond lengths and angle data for **1** and **3** are gathered in Table 2. The angles N–Pd–N and Cl–Pd–Cl in both complexes 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 polyether chains are in both cases in an *anti* disposition. Thus, in the solid state only one isomer is observed and the structures correspond to **1a** and **3a** (Fig. 2). **1a** crystallises with two independent molecules per unit cell. Fig. 3 shows one of the molecules. Both molecules present the same geometry. No interesting distances around the metal are observed in the first independent molecule (the one containing Pd(1)). But in the second one (molecule with Pd(2)) the ligand seems to fall onto the metallic atom giving a short intramolecular distance between Pd(2)···O(1A) of 3.090(3) Å (which falls in the palladium co-ordination sphere of 3.6 Å).

Fig. 4 shows complex **3a** (the major isomer of **3** observed in solution). The X-ray powder diffraction

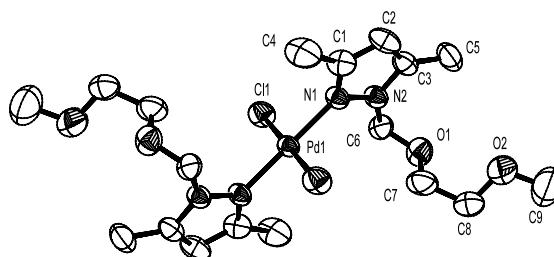


Fig. 3. Structure of **1** showing the numbering scheme; ellipsoids are drawn at the 50% probability level.

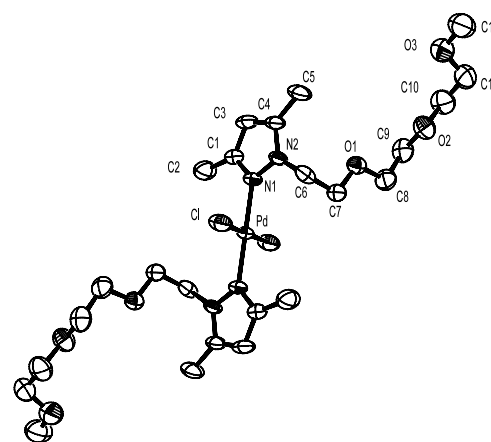


Fig. 4. Structure of **3** showing the numbering scheme; ellipsoids are drawn at the 50% probability level.

Table 2

Selected bond lengths (Å) and bond angles ($^\circ$) for **1** and **3** with estimated standard deviations (e.s.d.s) in parentheses

1		3	
<i>Bond lengths</i>			
Pd1–N1	2.011(4)	Pd–N1	2.016(3)
Pd2–N1A	2.009(4)	Pd–Cl	2.2980(14)
Pd1–Cl1	2.2998(15)		
Pd2–Cl2	2.3035(15)		
<i>Bond angles</i>			
N1a ⁱ –Pd1–Cl1	88.61(13)	N1–Pd–Cl	90.28(9)
N1A–Pd2–Cl2	89.19(13)		

Pd atoms are located in an inversion center. $i = -x, -y, -z$.

spectra of **1** and **3** corroborate the presence of the unique *anti* conformer in the solid state.

The pyrazolyl–nitrogen and chloride to palladium distances are slightly different in both complexes but are in the range found for similar compounds [1.927–2.102 Å for Pd–N [22–27] and 2.276–2.304 Å for Pd–Cl [24,25,27]. If we compare these distances with those observed in the equivalent *N*-hydroxyalkylpyrazole palladium complexes [14], we can see that the increase of the Pd–N bond length in $[\text{PdCl}_2(\text{HL}^1)_2]$ ($\text{HL}^1 = 1$ -hydroxymethyl-3,5-dimethylpyrazole) due to a higher electronic localisation in the N–N bond does not happen in the case of **1**, although in both cases there is only one carbon bonded to the nitrogen. Bond lengths between **3** and $[\text{PdCl}_2(\text{HL}^2)_2]$ ($\text{HL}^2 = 1$ -(2-hydro-

xyethyl)-3,5-dimethylpyrazole) are also comparable. The bond lengths between the metal and each coordinated ligand atom are, as expected, equal within experimental errors in each molecule.

4. Conclusions

In contrast to the well studied *N*-alkylaminopyrazoles [7–11] and *N*-thioetherpyrazoles [13], this type of new ligands contain many hard oxygen atoms not expected to co-ordinate to Pd(II), which is considered a metal of medium hardness. In complexes [PdCl₂L₂], NMR observes two conformational isomers: the *syn* and the *anti*, due to a slow rotation around the Pd–Npz bond. The length of the N1-substituting polyether chain makes the complexes exhibit a different behaviour. The higher length of the polyether chain increases the ratio of the *anti* isomer with respect to the *syn*. It was possible to accommodate three ligands around the metallic atom when removing one chloride leading to the complexes [PdClL₃](BF₄).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 190305 and 190306 for compounds **1** and **3**, 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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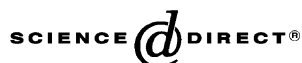
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New dinuclear Pd(II) complex with pyrazolate bridges. Synthesis and crystal structure of $[\text{Pd}(\mu\text{-pz})(\text{pzH})_2]_2(\text{BF}_4)_2$ (pzH = pyrazole)

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Abstract

Dinuclear pyrazolate-bridged Pd(II) complex $[\text{Pd}(\mu\text{-pz})(\text{pzH})_2]_2(\text{BF}_4)_2$ has been prepared by treatment of pyrazole (pzH), sodium ethoxide, and $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$. The new complex has been characterised by elemental analyses, IR, ¹H NMR, ¹³C{¹H} NMR, and single crystal X-ray diffraction methods. This structure shows two palladium atoms bridged by two pyrazolate ligands. The square-planar geometry of each Pd atom is completed by two pyrazole ligands. The six-membered dipalladacycle formed by the two Pd atoms and the two bridging pyrazolate ligands adopt a distorted boat-like conformation. This compound is the first example of a dinuclear Pd(II)–pyrazolate homoleptic complex.

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Keywords: Palladium complex; Dinuclear complex; Pyrazolate complex; Crystal structure

1. Introduction

Multidentate nitrogen-donor ligands were designed with the aim of preparing polynuclear compounds with an appropriate metal–metal separation, which is very important in studies of functional models for bimetallic biosites [1]. Such ligands are extensively used for the assembly of cyclic supermolecules. Pyridyl [2–8], imidazolyl [9–11], and particularly pyrazolyl [1,12–14] derivatives have been incorporated into the design and construction of novel polynuclear complexes.

In particular, the pyrazolate coordination chemistry has recently received a major injection of structurally unprecedented and exciting compounds [1,12,14–17]. Previously, our group has published a dinuclear palladium(II) complex connected by bridging pyrazolate ligands, with various pyrazolic ligand linkers [18].

Several studies have provided some homoleptic rare-earth pyrazolate polynuclear complexes [19,20]. In the platinum group metals, the majority of the pyrazolate containing compounds are heteroleptic. Two examples

of homoleptic dinuclear [21] and trinuclear [22] platinum compounds have been reported in the literature. To our knowledge, the title compound $[\text{Pd}(\mu\text{-pz})(\text{pzH})_2]_2(\text{BF}_4)_2$ (pzH = pyrazole; pz = pyrazolate) is the first example of dinuclear Pd(II)–pyrazolate homoleptic complex.

Here, we describe the preparation, crystal structure, and spectroscopic properties of this dinuclear palladium(II) complex in which the square-planar coordination of each palladium atom is completed by two pyrazole ligands.

2. Experimental

2.1. General

All reactions were performed under nitrogen atmosphere with the use of standard Schlenk techniques and vacuum line. All starting materials were commercially available and used as purchased. All solvents were dried and distilled under N₂ by standard methods just before use.

Microanalyses (C, H, and N) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-

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1108 instrument. Conductivity data were measured in c. 10^{-3} M methanol solutions, using a CyberScan CON 500 (Eutech Instruments) conductimeter. Infrared spectra were run on a Perkin Elmer FT spectrophotometer series 2000 cm^{-1} as KBr pellets and polyethylene films in the range 4000–100 cm^{-1} under a nitrogen atmosphere. ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, HMQC, and NOESY (mixing time 500 ms) spectra were recorded on a NMR-FT Bruker 250 MHz. All chemical shift values (δ) are given in ppm.

2.2. Complex $[\text{Pd}(\mu\text{-pz})(\text{pzH})_2]_2(\text{BF}_4)_2$, where pzH = pyrazole

A solution of 0.57 mmol (0.039 g) of pyrazole (pzH) and 0.19 mmol (0.013 g) of sodium ethoxide in CH_2Cl_2 (20 ml) was stirred for 1 h. To the resulting suspension 0.19 mmol (0.083 g) of $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ was added. The mixture was stirred at room temperature overnight. A white solid precipitated, was filtered off, washed with 5 ml of CH_2Cl_2 , and dried under vacuum. The product was recrystallised from acetone (yield 97%).¹

3. Results and discussion

Reaction in a dichloromethane solution of pyrazole with $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ in the ratio 3:1 (when one third of the ligands are deprotonated with sodium ethoxide), a new dinuclear complex $[\text{Pd}(\mu\text{-pz})(\text{pzH})_2]_2(\text{BF}_4)_2$ was obtained. This product is yellow and gives satisfactory C, H, and N elemental analyses. The formation of such a dimer is achieved, thanks to the pyrazolate units that can coordinate the two palladium atoms through both N in the heterocyclic rings in an exodentate mode.

Conductivity data in methanol are in accord with a 1:2 electrolyte [23,24].

The IR spectrum shows two signals $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ (1626 and 1539 cm^{-1}) and two $\delta(\text{CH})_{\text{oop}}$ (792 and 766 cm^{-1}) in accordance with the two types of coordination of the pyrazolic ligands. Signals at 1626 and 766 cm^{-1} correspond to bridged pyrazolate ligands and signals at 1539 and 792 cm^{-1} to monodentate pyrazolic

units. As some of the pyrazoles are not deprotonated, the $\nu(\text{N}-\text{H})$ band is also observed [25].

The NMR spectra of the dimer show that in solution of acetone- d_6 , half of the complex is symmetrical to the other half. That is to say, there are three types of pyrazole units that give rise to different NMR signals. The bridged pyrazolate can be clearly distinguished from the other two monodentate pyrazoles. This means that the four neutral ligands are not equivalent, but they are equivalent two to two. Particularly, in the ^1H NMR spectrum, the signal corresponding to the CH in the bridged ligand (CH_b) appears as a triplet at higher fields in comparison with the other two triplets from the same proton in the terminal ligands (CH_t). Both NCH protons in the pyrazolate are symmetrically equivalent, yielding only a doublet at 7.11 ppm. Three doublets corresponding to the NCH protons in the terminal pyrazolic ligands are displayed at higher chemical shifts: one of them includes two protons from different pyrazolic units that turn out to be isochronous. The phase sensitive bidimensional NOESY spectrum shows two cross peaks that correlate the two doublets at 8.27 and 8.07 with the triplet at 6.60 ppm, which means that they all correspond to the same ring. The same thing occurs with the three signals in the other terminal heterocycle. Moreover, a cross peak is observed between the most de-shielded NCH_t proton at 8.27 ppm and the NCH_b. That explains why the mentioned proton is on the side of the bridged ligand and why it is the closest in space to the NCH in the pyrazolate unit.

The $^{13}\text{C}\{^1\text{H}\}$ NMR signal assignment was made based on the HMQC experiment. Signals corresponding to the CH protons appear in the same order as they previously did in the ^1H NMR spectrum. However, the signals of the NCH group in the deprotonated ligand are observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in the middle of the two sets of carbon signals NCH in the neutral ligands (one set assigned to the carbon next to the NH and the other to the N coordinated to Pd(II)) [25,26].

Suitable crystals for X-ray diffraction were obtained from acetone solution. The structure of the complex was unequivocally determined by single crystal X-ray diffraction.²

¹ Analysis found: C, 27.21%; H, 2.83%; N, 21.33%. Calculated for $\text{C}_{18}\text{H}_{22}\text{N}_{12}\text{Pd}_2\text{B}_2\text{F}_8$: C, 27.26%; H, 2.78%; N, 21.20%. Conductivity ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, 9.2×10^{-4} M in methanol): 200. IR (KBr): $\nu(\text{N}-\text{H})$ 3358; $\nu(\text{C}-\text{H})_{\text{ar}}$ 3143; $\nu(\text{C}=\text{C})_{\text{b}}$, $\nu(\text{C}=\text{N})_{\text{b}}$ 1626; $\nu(\text{C}=\text{C})_{\text{t}}$, $\nu(\text{C}=\text{N})_{\text{t}}$ 1539; $\nu(\text{B}-\text{F})$ 1073; $\delta(\text{C}-\text{H})_{\text{oop(t)}}$ 792, $\delta(\text{C}-\text{H})_{\text{oop(b)}}$ 766; $\nu(\text{Pd}-\text{N})_{\text{as}}$ 520, 477 cm^{-1} ; IR (polyethylene): $\nu(\text{Pd}-\text{N})_{\text{s}}$ 245, 238 cm^{-1} . ^1H NMR (250 MHz, acetone- d_6 , ppm): δ = 8.27 [2H, d, 3J = 2.1 Hz, NCH_{t(1)}]; 8.07 [4H, d, 3J = 2.2 Hz, NCH_{t(1)}, NCH_{t(2)}]; 7.92 [2H, d, 3J = 2.4 Hz, NCH_{t(2)}]; 7.11 [4H, d, 3J = 2.4 Hz, NCH_b]; 6.60 [2H, t, 3J = 2.1 Hz, CH_{t(1)}]; 6.55 [2H, t, 3J = 2.4 Hz, CH_{t(2)}]; 6.04 [2H, t, 3J = 2.4 Hz, CH_b]. $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, acetone- d_6 , ppm): δ = 143.3 [NCH_{t(1)}]; 142.9 [NCH_{t(2)}]; 140.9 [NCH_b]; 135.1 [NCH_{t(1)}]; 134.4 [NCH_{t(2)}]; 108.5 [CH_{t(1)}]; 108.4 [CH_{t(2)}]; 107.2 [CH_b].

² X-ray structure determination and refinement of complex $[\text{Pd}(\mu\text{-pz})(\text{pzH})_2]_2(\text{BF}_4)_2$. Crystal data: crystals were grown from acetone $\text{C}_{18}\text{H}_{22}\text{N}_{12}\text{Pd}_2\text{B}_2\text{F}_8$, $M = 792.90$, pale yellow, crystal size $0.1 \times 0.1 \times 0.2$ (mm); orthorhombic, space group $\text{Pc}2_1\text{b}$, $a = 9.3630(10)$, $b = 16.5300(10)$, $c = 18.2300(10)$ Å, $V = 2821.5$ (4) Å³, $Z = 4$, $D_c = 1.867$ Mg m⁻³, $F(000) = 1552$, $\mu(\text{Mo}-\text{K}\alpha) = 1.361$ mm⁻¹. Data collection and processing: data collected on a MAR 345 diffractometer with an image plate detector. 17,727 reflections were measured in the range $2.74^\circ < \theta < 31.60^\circ$ ($R_{\text{int}}(I) = 0.032$). 3608 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Solution (direct methods) and refinement program: (SHELXS-97 and SHELXL-97) [30]. For all reflections $R(F) = 0.056$ and $R_w(F^2) = 0.141$. Final R indices [$I > 2\sigma(I)$] $R(F) = 0.048$ and $R_w(F^2) = 0.135$.

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Table 1
Selected bond lengths (Å) and angles (°)

Pd(1)··Pd(2)	3.4539(7)		
Pd(1)–N(1)	1.974(6)	Pd(2)–N(2)	1.985(5)
Pd(1)–N(3)	2.002(7)	Pd(2)–N(4)	1.995(7)
Pd(1)–N(5)	2.016(6)	Pd(2)–N(11)	2.000(6)
Pd(1)–N(7)	2.041(7)	Pd(2)–N(9)	2.006(8)
N(1)–Pd(1)–N(3)	87.9(3)	N(2)–Pd(2)–N(4)	88.6(3)
N(1)–Pd(1)–N(5)	92.2(3)	N(2)–Pd(2)–N(11)	177.4(3)
N(3)–Pd(1)–N(5)	175.5(3)	N(4)–Pd(2)–N(11)	89.8(3)
N(1)–Pd(1)–N(7)	177.0(3)	N(2)–Pd(2)–N(9)	90.9(3)
N(3)–Pd(1)–N(7)	92.3(3)	N(4)–Pd(2)–N(9)	177.7(2)
N(5)–Pd(1)–N(7)	87.8(3)	N(11)–Pd(2)–N(9)	90.9(3)

The molecular structure of the complex consists of discrete $[\text{Pd}_2(\mu\text{-pz})_2(\text{pzH})_4]^{2+}$ cations and BF_4^- anions.

The cation complex is dinuclear. Table 1 lists selected bond distances and angles. In the cation, two $[\text{Pd}(\text{pzH})_2]$ moieties are bridged by two pyrazolate ligands in an exodidentate fashion (Fig. 1). The central six-membered $[\text{Pd}(\mu\text{-pz})_2\text{Pd}]$ core is non-planar with Pd–N_{pz} distances between 1.974(6) and 2.002(7) Å and N–Pd–N angles of ca. 88° between the pyrazolate groups. The metal atoms are positioned at the vertices of a boat conformation $\Delta C_5(\text{Pd}) = 0.954(2)^\circ$, derived from the mean plane defined by the remaining four atoms, see Fig. 2, as in previously reported Pd(II) and μ -pyrazolate dimers [18,27–29]. The Pd(1)··Pd(2) separation of 3.4539(7) Å, which is comparable to $[\text{Pd}_2(\eta^3\text{-C}_4\text{H}_7)(\text{C}_6\text{F}_5)_2(\mu\text{-pz})_2]$ (3.493 Å) [27], is longer than the corresponding metal–metal distance in $[\text{Pd}(\mu\text{-dmpz})(\eta^3\text{-C}_3\text{H}_4)]_2$ (dmpz = 3,5-dimethylpyrazole) (3.343 Å) [28], $[\text{PdCl}(\text{PMe}_2\text{Ph})(\mu\text{-dmpz})_2]$ (3.115(1) Å) [29], and $[\text{Pd}(\text{L}^1)_4]_2$ ($\text{L}^1 = 3$ -phenyl-5-(6-methyl)-(2-pyridyl)pyrazole) (3.097(2) Å) [18]. Comparable bond lengths within the pyrazolate rings suggest substantial delocalisation upon deprotonation. The bow angles between the planes N1–N2–N3–N4 and N2–Pd2–N4, N1–Pd1–N3 are 41.9(5)° and 42.0(5)°, respectively.

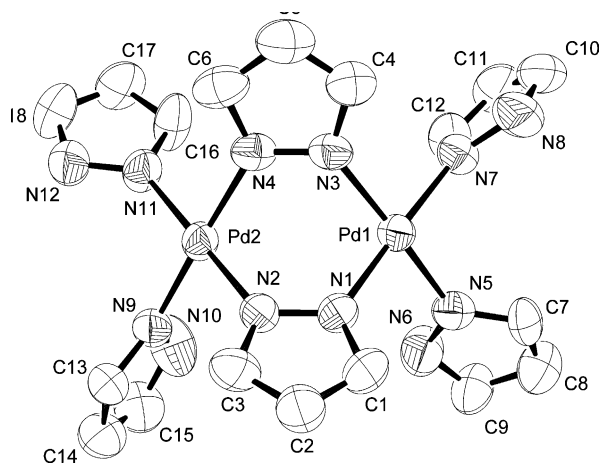


Fig. 1. Structure and adopted numbering scheme of $[\text{Pd}(\mu\text{-pz})(\text{pzH})_2]^{2+}$.

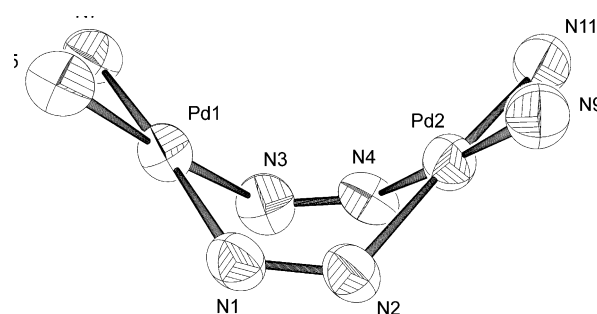


Fig. 2. Drawing of dipalladacycle in $[\text{Pd}(\mu\text{-pz})(\text{pzH})_2]^{2+}$ showing its information.

The coordination around Pd atoms is square-planar. The deviations of the Pd atoms from the least-squares plane defined by Pd and N atoms are 0.635 Å. The dihedral angle between the two planes defined around Pd atoms is 84.4(3)°.

The dihedral angles between the monodentate pyrazole ligands N5–N6–C9–C8–C7 and N7–N8–C10–C11–C12, and N9–N10–C15–C14–C13 and N11–N12–C18–C17–C16 are 73.3(7)° and 86.5(7)°, respectively.

Hydrogen bonds were found between the cations and anions. Only one BF_4^- is bonded to one cation by N(10)–H and F(3) (the N(10)–H bond length was geometrically fixed in the refinement (0.86 Å) and the contact parameters between N(10)–H and F(3) are H··F(3), 2.35 Å; N(10)··F(3), 3.15(2) Å; N(10)–H··F(3), 155°).

Supplementary material

Addition of material, consisting of fractional atomic coordinates, displacement parameters, observed and calculated structure factors, and complete lists of bond distances and bond angles are available from CCDC, deposition number 206826. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44- 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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Reaction of platinum(II) derivatives with 1-hydroxyalkyl-3,5-dimethylpyrazole ligands. Cleavage of the N(pz)–C(sp³) bond. X-ray crystal structure of *cis*-[PtCl₂(HL²)₂] (HL² = 1-(2-hydroxyethyl)-3,5-dimethylpyrazole) and *trans*-[PtCl₂(dmpz)₂] (dmpz = 3,5-dimethylpyrazole)

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Abstract

The reactions of 1-hydroxymethyl-3,5-dimethylpyrazole (HL¹) and 1-(2-hydroxyethyl)-3,5-dimethylpyrazole (HL²) with several platinum starting materials ([PtCl₂(CH₃CN)₂], *cis*- and *trans*-[PtCl₂(PhCN)₂], PtCl₂ and K₂PtCl₄) under different conditions have been examined and compared with those obtained from the reactions with Pd(II). *cis* and *trans* Pt(II) adducts are obtained in a different ratio depending on the metallic starting complex. The reaction of HL¹ with any of the Pt(II) complexes differs from that with Pd(II) and also from the equivalent reaction of HL² with Pt(II). This reaction implies the rupture of the ligand: the cleavage of the N(pz)–C(sp³) bond leads to [PtCl₂(dmpz)₂] (dmpz = 3,5-dimethylpyrazole). For comparison, the direct reaction of dmpz with Pt(II) has also been studied. The crystal structure of *cis*-[PtCl₂(HL²)₂] and *trans*-[PtCl₂(dmpz)₂] are here reported.

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Keywords: Platinum complexes; Pyrazole complexes; Alcohol ligand complexes

1. Introduction

The coordination properties of pyrazolic ligands have been extensively studied and reported in the literature [1–5]. In the last 5 years, our research group has focused on this subject, especially on the synthesis of 3,5-dimethylpyrazole derivative ligands N1 substituted [6–15]. We have reported the reactivity of some 1-hydroxyalkyl-3,5-dimethylpyrazole [16] and 1-polyether-3,5-dimethylpyrazole [17] ligands with Pd(II).

As for most of the 4d metals, the similarity of their chemistry to that of their 5d congeners (in this case palladium to platinum) is well known, we were, therefore, interested in evaluating the behaviour of the

aforementioned 1-hydroxyalkyl-3,5-dimethylpyrazole ligands (HL) with Pt(II) in order to compare results.

Precedents in the literature show that the reactivity of pyrazolic ligands with Pt(II) yields different results to those obtained with Pd(II) [18]. It is also known that palladium is much more reactive than platinum. Concerning the isomery of palladium complexes of the type [PdCl₂L₂], isomers can exist in either the *cis* or *trans* form, but isomerisation often occurs readily in solution (probably via a five-coordinate intermediate, which usually involves a solvent molecule). Thus, for the ligands studied in this paper only the *trans*-[PdCl₂(HL)₂] complexes were obtained (both crystal structures were confirmed by X-ray diffraction) when reacting with [PdCl₂(CH₃CN)₂] [16]. In the case of Pt(II) complexes, in general, both *cis* and *trans* dichloroplatinum complexes are more easily obtained separately (depending on the experimental conditions) due to platinum's

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higher stability in front of isomerisation. These selective syntheses of the two independent isomers have already been studied, focusing on the antitumoural and cytotoxic activity of the compounds [19–21].

Therefore, reactions of $[\text{PtCl}_2(\text{CH}_3\text{CN})_2]$, *cis*- and *trans*- $[\text{PtCl}_2(\text{PhCN})_2]$, PtCl_2 and K_2PtCl_4 with ligands HL^1 (1-hydroxymethyl-3,5-dimethylpyrazole) and HL^2 (1-(2-hydroxyethyl)-3,5-dimethylpyrazole) (Fig. 1) under various conditions have been tested and described in this paper. For comparison, the reaction of the 3,5-dimethylpyrazole (dmpz) with platinum complexes was also tried.

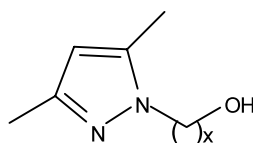
The crystal structures of *cis*- $[\text{PtCl}_2(\text{HL}^2)_2]$ and *trans*- $[\text{PtCl}_2(\text{dmpz})_2]$ have been determined by X-ray diffraction and are here reported.

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. Ligands 1-hydroxymethyl-3,5-dimethylpyrazole (HL^1) [22] and 1-(2-hydroxyethyl)-3,5-dimethylpyrazole (HL^2) [23] (Fig. 1) and compounds $[\text{PtCl}_2(\text{CH}_3\text{CN})_2]$ [24] and $[\text{PtCl}_2(\text{PhCN})_2]$ [25] were prepared according to published procedures. *Cis* and *trans* isomers of $[\text{PtCl}_2(\text{PhCN})_2]$ were separated by chromatography as described in the literature [18]. All solvents were dried and distilled by standard methods.

The elemental analyses (C, N, H) were carried out by the staff of the Chemical Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in ca. 10^{-3} M methanol, employing a CyberScan CON 500 (Eutech Instruments) conductivity meter. 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} . ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR and COSY spectra were obtained on a Bruker AC-250 MHz and the NOESY spectrum on a NMR-FT Bruker 500 MHz instrument (mixing time 500 ms). All chemical shift



$x = 1$ HL^1

$x = 2$ HL^2

Fig. 1. Pyrazole derived ligands HL^1 and HL^2 .

values (δ) are given in parts per million and are referenced with respect to residual protons in the solvent for proton spectra and to solvent signals for $^{13}\text{C}\{^1\text{H}\}$ spectra.

2.2. Synthesis

2.2.1. Reactions of HL^1 , HL^2 and dmpz with K_2PtCl_4

To a solution of 0.13 mmol (0.056 g) of K_2PtCl_4 in 10 ml of water, was added 0.26 mmol of the corresponding ligand (0.034 g of HL^1 , 0.038 g of HL^2 or 0.026 g of dmpz) dissolved in 5 ml of water. The mixture was stirred in a hot water bath (60–70 °C) for 3 h (when heating the solution over 80–90 °C, Pt(II) is reduced to Pt(0)). The reddish solution started turning yellow. The mixture was left under stirring at room temperature for 7 days (until the red colour of the starting material K_2PtCl_4 had completely disappeared). For HL^1 and dmpz, a white–yellow solid precipitated and was filtered off, washed twice with 5 ml of cold water and dried in vacuum. For HL^2 secondary products and the free ligand were extracted with dichloromethane. The platinum complexes rested in the aqueous solution. Water was removed under reduced pressure yielding a yellow solid, which was washed twice with 5 ml of dichloromethane and dried in vacuum.

2.2.2. Reactions of HL^2 and dmpz with K_2PtCl_4 in 0.1 M HCl

To a solution of 0.19 mmol (0.078 g) of K_2PtCl_4 in 10 ml of 0.1 M HCl was added 0.38 mmol of the corresponding ligand (0.053 g of HL^2 or 0.037 g of dmpz). The solution was stirred for 3 days at room temperature. In the synthesis with ligand HL^2 the solution was left air opened. Red needles of K_2PtCl_4 and white squared crystals of KCl were formed at the bottom of the flask. Complex *cis*- $[\text{PtCl}_2(\text{HL}^2)_2]$ was separated from the crystals by solving it with 5 ml of dichloromethane. The solvent was evaporated to dryness leaving a yellow solid. For ligand dmpz a white solid corresponding to *cis*- $[\text{PtCl}_2(\text{dmpz})_2]$ precipitated in the reaction mixture, which was filtered off, washed with 5 ml of cold water and dried in vacuum.

2.2.3. Reactions of HL^1 , HL^2 and dmpz with PtCl_2

To 0.21 mmol (0.055 g) of PtCl_2 was quickly added 15 ml of chloroform. 0.42 mmol of the corresponding ligand (0.052 g of HL^1 , 0.058 g of HL^2 or 0.040 g of dmpz) was added to the resulting suspension. The mixture was refluxed for a week (except with ligand dmpz, for which the reaction took only 24 h at room temperature to occur). The yellowish solution was filtered to separate Pt(0) and the starting material PtCl_2 . Complexes were extracted from the organic phase with water. Water was evaporated under vacuum, yielding pale yellow solids.

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2.2.4. Reactions of HL¹, HL² and dmpz with [PtCl₂(CH₃CN)₂]

To a solution of 0.14 mmol (0.050 g) of [PtCl₂(CH₃CN)₂] in 15 ml of acetonitrile was added 0.28 mmol of the corresponding ligand (0.036 g of HL¹, 0.040 g of HL² or 0.028 g of dmpz) dissolved in 5 ml of the same solvent. The mixture was refluxed for more than 40 h. From the yellow solution the solvent was evaporated to dryness. Fifteen millilitre of dichloromethane was added to the residue until complete dissolution. Four to five millilitre of diethyl ether was then added to the resulting yellow solution. A solid precipitated (white for HL¹ and dmpz, yellow for HL²), which was filtered off, washed with 5 ml of diethyl ether and dried in vacuum.

2.2.5. Reactions of HL¹, HL² and dmpz with [PtCl₂(PhCN)₂]

To a solution of 0.11 mmol (0.050 g) of [PtCl₂(PhCN)₂] in 10 ml of chloroform was added 0.22 mmol of the corresponding ligand (0.028 g of HL¹, 0.031 g of HL² or 0.021 g of dmpz) dissolved in 5 ml of the same solvent. The mixture was refluxed for several hours (44 h for HL¹, 85 h for HL² and 29 h for dmpz). From the yellow solution the solvent was evaporated to dryness yielding yellow solids. [PtCl₂(HL²)₂] was not obtained through this method; the platinum starting material and the free ligand were recovered unaltered.

Reactions with *cis*-[PtCl₂(PhCN)₂] and *trans*-[PtCl₂(PhCN)₂] were tried with ligand HL¹ and dmpz in the same ratios and under the same conditions described above and refluxing the mixtures for 5 days. From the *cis*-[PtCl₂(PhCN)₂], yellow solutions were obtained. From the *trans*-[PtCl₂(PhCN)₂], the resulting dark yellow solutions were filtered over Celite. The solvent was evaporated to dryness and washed with 5 ml of diethyl ether yielding yellow solids.

2.2.5.1. [PtCl₂(HL²)₂] (2). C₁₄H₂₄N₄O₂Cl₂Pt: Anal. Calc: C, 30.76; H, 4.39; N, 10.25; Found: C, 30.37; H, 4.25; N, 9.85%. Conductivity (Ω⁻¹ cm² mol⁻¹, 1.03 10⁻³ M in methanol): 12. IR (KBr, cm⁻¹): 3495–3437 (νO–H), 3129 (νC–H)_{ar}, 2923 (νC–H)_{al}, 1554 (νC=C, νC=N), 1465 (δCH₃)_{as}, 803 (δC–H)_{oop}. (Polyethylene, cm⁻¹): Isomer **2a** (*cis*): 442 (νPt–N), 328, 324 (νPt–Cl)_t. Isomer **2b** (*trans*): 457 (νPt–N), 335 (νPt–Cl)_t. ¹H NMR (D₂O solution, 250 MHz) δ: Isomer **2a** (*cis*): 6.26 [2 H, s, CH pyrazole], 4.32 [4 H, t, ³J = 5.1 Hz, NCH₂], 3.92 [4 H, t, ³J = 5.1 Hz, CH₂OH], 2.38 [6 H, s, CH₃], 2.34 [6 H, s, CH₃]. Isomer **2b** (*trans*): 6.08 [2 H, s, CH pyrazole], 4.84 [4 H, t, ³J = 5.6 Hz, NCH₂], 4.41 [4 H, t, ³J = 5.6 Hz, CH₂OH], 2.68 [6 H, s, CH₃], 2.41 [6 H, s, CH₃]. ¹³C{¹H} NMR (D₂O solution, 62.9 MHz) δ: Isomer **2a** (*cis*): 147.0 [CCH₃], 145.7 [CCH₃], 107.8 [CH pyrazole], 59.5 [CH₂OH], 50.6 [NCH₂], 10.6 [CH₃], 10.4

[CH₃]. Isomer **2b** (*trans*): 150.5 [CCH₃], 145.1 [CCH₃], 106.9 [CH pyrazole], 59.2 [CH₂OH], 50.2 [NCH₂], 13.8 [CH₃], 11.1 [CH₃].

2.2.5.2. [PtCl₂(dmpz)₂] (3). (C₁₀H₁₆N₄Cl₂Pt) 0.25(CH₄O) Anal. Calc: C, 26.82; H, 3.73; N, 11.92; Found: C, 26.31; H, 3.38; N, 11.94%. Conductivity (Ω⁻¹ cm² mol⁻¹, 1.05 10⁻³ M in methanol): 15. IR (KBr, cm⁻¹): 3207 (νN–H), 3146 (νC–H)_{ar}, 1577 (νC=C, νC=N), 810 (δC–H)_{oop}. (Polyethylene, cm⁻¹): Isomer **3a** (*cis*): 444 (νPt–N), 335, 327 (νPt–Cl)_t. Isomer **3b** (*trans*): 457 (νPt–N), 340 (νPt–Cl)_t. ¹H NMR (CDCl₃ solution, 250 MHz) δ: Isomer **3a** (*cis*): 5.75 [2 H, s, CH pyrazole], 2.38 [6 H, s, CH₃], 2.12 [6 H, s, CH₃]. Isomer **3b** (*trans*): 5.75 [2 H, s, CH pyrazole], 2.64 [6 H, s, CH₃], 1.99 [6 H, s, CH₃]. ¹³C{¹H} NMR (CDCl₃ solution, 62.9 MHz) δ: Isomer **3a** (*cis*): 150.8 [CCH₃], 142.2 [CCH₃], 105.3 [CH pyrazole], 14.4 [CH₃], 10.3 [CH₃]. Isomer **3b** (*trans*): 151.1 [CCH₃], 143.4 [CCH₃], 106.0 [CH pyrazole], 14.5 [CH₃], 11.1 [CH₃].

2.2.5.3. [PtCl₂(dmpz)]₂ (4). (C₁₀H₁₆N₄Cl₄Pt₂) Anal. Calc: C, 16.57; H, 2.21; N, 7.73; Found: C, 16.44; H, 2.18; N, 7.63%. Conductivity (Ω⁻¹ cm² mol⁻¹, 1.01 10⁻³ M in methanol): 24. IR (KBr, cm⁻¹): 3203 (νN–H), 3146 (νC–H)_{ar}, 1584 (νC=C, νC=N), 792 (δC–H)_{oop}. IR (Polyethylene, cm⁻¹): 461, 457 (νPt–N), 385 (νPt–Cl)_t, 318, 249 (νPt–Cl)_b. ¹H NMR (CDCl₃ solution, 250 MHz) δ: 5.78 [2 H, s, CH pyrazole], 2.64 [6 H, s, CH₃], 2.36 [6 H, s, CH₃]. ¹³C{¹H} NMR (CDCl₃ solution, 62.9 MHz) δ: 150.5 [CCH₃], 142.2 [CCH₃], 105.5 [CH pyrazole], 14.4 [CH₃], 10.3 [CH₃].

2.3. Crystallography

Crystals of **2a** and **3b** suitable for X-ray diffraction experiments were obtained from a dichloromethane/acetonitrile and methanol/acetonitrile mixture, respectively. Data were collected on an Enraf-Nonius CAD4 four-circle diffractometer (for **2a**) using ω/2θ scan technique and on a MAR345 diffractometer (for **3b**), using ϕ scan technique. In both cases the measurements were at room temperature with monochromatized Mo Kα radiation (λ = 0.71069 Å), using ω/2θ scan-technique. The structures were solved by direct methods (SHELXS-97) [26] and refined by full-matrix least-squares methods (SHELXL-97) [27]. All H atoms were computed and refined, using a riding model with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom linked to the hydrogen atom, which are linked to. The final R(on F) factor and wR(on F²) values as well as the number of parameters refined and other details concerning the refinement of the crystal structures are gathered in Table 1.

Table 1
Crystal data for **2a** and **3b**

	<i>cis</i> -[PtCl ₂ (HL ²) ₂] (2a)	<i>trans</i> -[PtCl ₂ (dmpz) ₂] (3b)
Formula	C ₁₄ H ₂₄ Cl ₂ N ₄ O ₂ Pt	C ₁₀ H ₁₆ Cl ₂ N ₄ Pt· 0.5(CH ₃ OH)
<i>M</i>	546.36	474.28
System, space group	monoclinic, <i>C2/c</i>	monoclinic, <i>P2₁/a</i>
<i>a</i> (Å)	28.712(5)	14.3310(10)
<i>b</i> (Å)	8.873(8)	13.0300(10)
<i>c</i> (Å)	14.596(6)	17.7320(10)
β (°)	102.48(2)	102.2660(10)
<i>U</i> (Å ³)	3631(4)	3235.6(4)
<i>Z</i>	8	8
<i>D</i> _{calc} (g cm ⁻³)	1.999	1.947
μ (mm ⁻¹)	8.037	8.996
<i>F</i> (0 0 0)	2112	1800
Crystal size (mm)	0.2 × 0.1 × 0.2	0.1 × 0.1 × 0.2
<i>h k l</i> Ranges	−40 to 39, 0–12, 0–20	−17 to 18, 0–14, 0–25
2 θ Range (°)	2.41–30.00	1.96–31.59
Reflexions collected/unique	5495/5277 [<i>R</i> _{int} = 0.0683]	16151/6578 [<i>R</i> _{int} = 0.0388]
Data, restraints, parameters	5277, 0, 208	6578, 4, 321
Final <i>R</i> ₁ , <i>wR</i> ₂	0.0436, 0.0829	0.0505, 0.1252
<i>R</i> ₁ (all data), <i>wR</i> ₂	0.1647, 0.1071	0.0775, 0.1364
<i>a</i> ^a	0.0347	0.1029
Largest difference peak and hole (e Å ⁻³)	+0.838, −0.963	+0.869, −0.566

^a The function minimized was $\Sigma w((F_o)^2 - (F_c)^2)^2$, where $w = [\sigma^2(I) + (aP)^2]^{-1}$, and $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussion

Reactions of HL¹ and HL² (Fig. 1) with several platinum starting materials such as [PtCl₂(CH₃CN)₂], *cis*- and *trans*-[PtCl₂(PhCN)₂], PtCl₂ and K₂PtCl₄ are developed under different conditions (Scheme 1). In general, and in contrast to the palladium complexes, these reactions take a longer time and need higher temperatures to occur. Moreover, yields are much lower (10–20%).

The resulting products of these reactions have been characterised by elemental analyses, conductivity measurements, and infrared and NMR spectra. As not all the reactions yielded to pure products, the elemental analyses and the infrared spectra have been acquired from the pure ones. The ratio of the *cis* and *trans* isomers has been calculated through NMR experiments, which were also useful to determine the presence of other products or even the free ligand. As described in the literature for many other ligands [19,20], the *cis* isomers can be obtained from the reaction of the ligand with K₂PtCl₄ in 0.1 M HCl; therefore, the ¹H and ¹³C{¹H} NMR spectra of the *cis* isomers were determined from this reaction, and the *trans* isomers were characterised by comparison with the spectra of a mixture of both adducts.

The NMR spectra shows that for HL², in stoichiometric conditions, the greater part of the free ligand rests unaltered in solution. For HL¹ the expected complex [PtCl₂(HL¹)₂] was not isolated, nor was there any evidence of the free ligand in the reaction mixture. But the [PtCl₂(dmpz)₂] adduct (characterised by comparison with the ¹H NMR spectrum of the direct reaction between Pt(II) and the commercial ligand dmpz) and some other products (usually complex [PtCl₂(dmpz)₂] (**4**)) have been found, meaning that a cleavage of N(pz)–C(sp³) bond has occurred. Thus, two types of behaviour have been observed between ligands HL¹ and HL².

3.1. Reactions with HL²

Reaction of HL² with K₂PtCl₄ in 0.1 M HCl at room temperature for 3 days, leads to the obtaining of the *cis* isomer only (16% yield). When HL² reacts with K₂PtCl₄ in water, either at room temperature or through refluxing, a mixture of the *cis* and the *trans* isomers formed, in a ratio of ca. 1:1. The reaction of the ligand HL² with [PtCl₂(CH₃CN)₂] in acetonitrile and PtCl₂ in chloroform refluxing for 4 days yields *trans*-[PtCl₂(HL²)₂] (16 and 12% yield, respectively). No reaction is observed between the [PtCl₂(PhCN)₂] and this ligand even if the solution is kept refluxing for almost 7 days.

3.2. Reactions with HL¹

Reaction of HL¹ with [PtCl₂(CH₃CN)₂] leads to the *trans*-[PtCl₂(dmpz)₂] complex (14% yield). In contrast, when the ligand reacts either with K₂PtCl₄, *cis*-[PtCl₂(PhCN)₂], *trans*-[PtCl₂(PhCN)₂] or the mixture of the *cis* and the *trans* isomers of [PtCl₂(PhCN)₂] the *cis*-[PtCl₂(dmpz)₂] is mainly obtained (ratios *cis:trans* around 1:0.5). In addition, reactions with any of the [PtCl₂(PhCN)₂] isomers give rise to the obtaining of [PtCl₂(dmpz)₂]. When HL¹ reacts with PtCl₂, there is no signal corresponding to the *trans*-[PtCl₂(dmpz)₂]. Isomer *cis*-[PtCl₂(dmpz)₂] is the minor product among a mixture of unknown species.

3.3. Reactions with dmpz

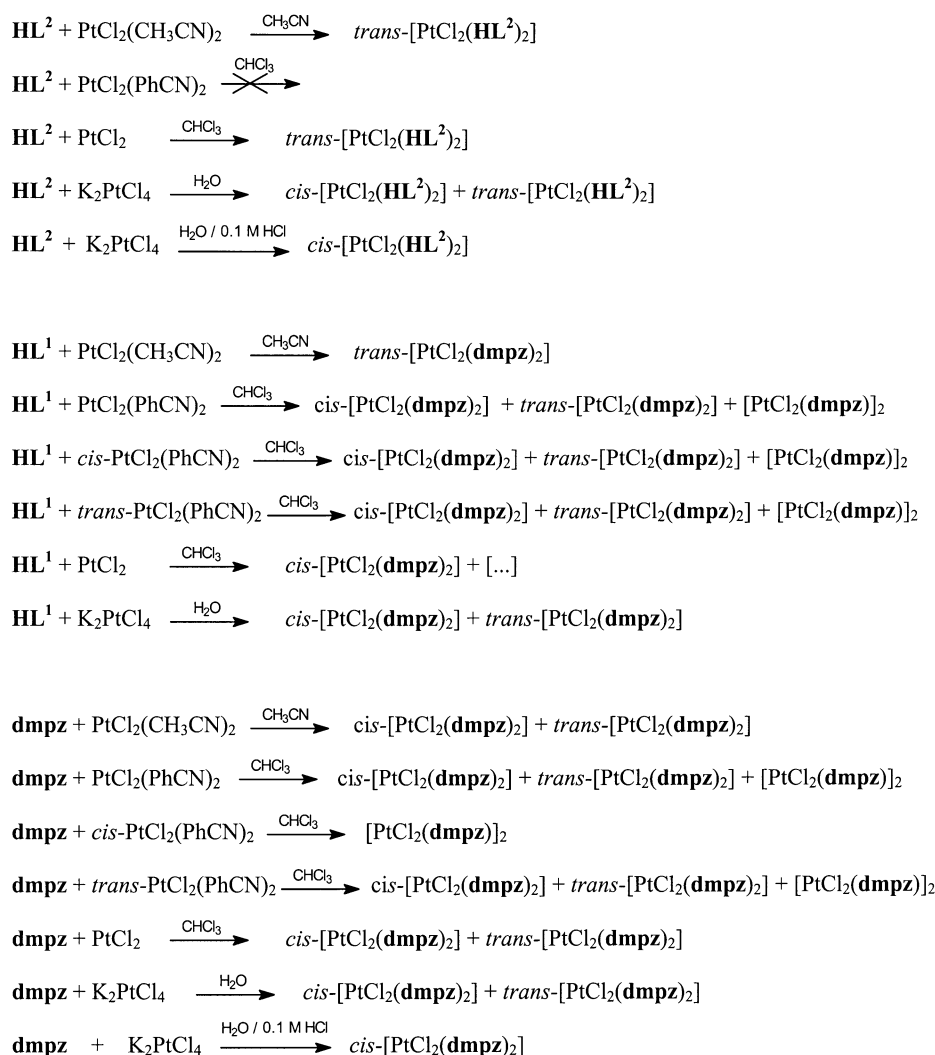
In order to compare this last reactivity of HL¹ with Pt(II) to that of the dmpz with this metal, the same reactions have been examined. A few differences have been observed.

With complex [PtCl₂(CH₃CN)₂] under the same experimental conditions, the *trans*-[PtCl₂(dmpz)₂] is mainly formed, although the presence of the *cis* isomer is also found (ratio 1:0.3). As it happened with HL¹ the *cis*-[PtCl₂(dmpz)₂] is mainly obtained when the dmpz reacts with K₂PtCl₄ and PtCl₂—in the ratio 1:0.1

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Scheme 1.

(although in the case of PtCl_2 no other unidentified products appear in the ^1H NMR spectrum). But the reactions with $\text{trans-}[\text{PtCl}_2(\text{PhCN})_2]$ or with the mixture of $[\text{PtCl}_2(\text{PhCN})_2]$ isomers yield a mixture of almost the 50% of the *cis* and the *trans-}[\text{PtCl}_2(\text{dmpz})_2]. However, in both reactions complex $[\text{PtCl}_2(\text{dmpz})]_2$ is mainly obtained. This dimer is purely isolated through reaction of *dmpz* with $\text{cis-}[\text{PtCl}_2(\text{PhCN})_2]$. Reaction of *dmpz* with K_2PtCl_4 in 0.1 M HCl at room temperature for 3 days, leads to the obtaining of only the *cis* isomer (19% yield).*

Elemental analyses are consistent with the formula $[\text{PtCl}_2(\text{HL}^2)_2]$ for compound **2**. Its neutrality is demonstrated by conductivity measurements ($12 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in ca. 10^{-3} M in methanol corresponds to a non-electrolyte species—below $80 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ [28,29]). Moreover, in the IR spectrum the ($\nu\text{O-H}$) band at $3495\text{--}3437 \text{ cm}^{-1}$ indicates the presence of the alcohol group and thus the presence of the unaltered ligand [30,31]. Coordination to platinum is demon-

strated in the IR spectra between 500 and 100 cm^{-1} of both *cis* and *trans* compounds: the unique absorption at 335 cm^{-1} in the spectrum for isomer $\text{trans-}[\text{PtCl}_2(\text{HL}^2)_2]$ is assigned to the ($\nu\text{Pt-Cl}$) and indicates that the chloride ions are coordinated *trans* to the Pt(II). The $\text{cis-}[\text{PtCl}_2(\text{HL}^2)_2]$ isomer presents two bands at 328 and 324 cm^{-1} due to the *cis* ligation [32]. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra corroborate the obtaining of **2**. One signal for each proton and each carbon is observed. The chemical shifts of the coordinated ligand clearly increase with respect to the free ligand (especially in the *trans* isomer).

Elemental analyses of **3** and the ones obtained for the compound coming from the synthesis with HL^1 are equivalent and are consistent with the formula $[\text{PtCl}_2(\text{dmpz})_2]$. This can also be seen in the IR spectrum of the reaction with HL^1 , where a ($\nu\text{N-H}$) band is observed at 3207 cm^{-1} instead of the expected ($\nu\text{O-H}$) band at about 3400 cm^{-1} [30,31]. IR spectra between 500 and 100 cm^{-1} allow the distinction between the

coordination *cis* and *trans* of the 3,5-dimethylpyrazole: *cis*-[PtCl₂(dmpz)₂] shows two bands ($\nu_{\text{Pt-Cl}}$) at 335 and 327 cm⁻¹, whereas *trans*-[PtCl₂(dmpz)₂] presents only one band at 340 cm⁻¹ [32]. Conductivity measurements are in agreement with a non-electrolyte (15 Ω⁻¹ cm² mol⁻¹ in ca. 10⁻³ M in methanol [28,29]). NMR spectra of the two syntheses are also the same. As it happened in complex **2**, signals appear at lower fields, which also proves the coordination of the ligand. In the case of the reaction with ligand HL¹, the absence of the protons corresponding to the methylene group (CH₂OH) in the ¹H NMR spectrum and the carbon of the same chemical group in the ¹³C{¹H} NMR spectrum, together with the already described elemental analyses and IR, are the determining proofs of the cleavage of the N(pz)-C(sp³) bond for the obtaining of compound **3** instead of [PtCl₂(HL¹)₂].

The presence of the new complex **4** was observed in many ¹H and ¹³C{¹H} NMR spectra. However, the compound was purely isolated when dmpz was treated with *cis*-[PtCl₂(PhCN)₂]. As spectra did not coincide with any of the two isomers *cis*-[PtCl₂(dmpz)₂] or *trans*-[PtCl₂(dmpz)₂] but they displayed only one signal for each proton or carbon, respectively, we thought of a simple compound that contained all the heterocyclic rings symmetrically bonded to Pt(II). Elemental analyses were consistent with the empirical formula 'PtCl₂(dmpz)' and conductivity measurements indicated that it was a non-electrolyte species [28,29]. Among the various species proposed, the one that gathered all these characteristics is the dimer [PtCl₂(dmpz)₂]. Two chloride atoms bridge the two metals. The square planar coordination around Pt(II) is completed by two terminal chlorides and two pyrazolic ligands. The IR spectrum between 500 and 100 cm⁻¹ are also in agreement with this species as two type of bands for both terminal and bridged Pt-Cl bonds (($\nu_{\text{Pt-Cl}}$)_t and ($\nu_{\text{Pt-Cl}}$)_b, respectively) are observed.

3.4. Cleavage of the C(sp³)-N(pz) bond

In spite of some little differences between reactions with HL¹ and the dmpz itself, it can be proved that 3,5-dimethylpyrazole (dmpz) is formed from 1-hydroxy-methyl-3,5-dimethylpyrazole (HL¹) in the presence of Pt(II). As it happens with a rutenium(II) complex when it reacts with HL¹ [33], the cleavage of the N(pz)-C(sp³) bond, in this case, might be catalysed by the platinum complex itself. 3,5-Dimethylpyrazole and formaldehyd (the starting products of the synthesis of HL¹) were recovered. To clarify this point, reactions with deuterated solvents were under taken in order to detect formaldehyd. In deuterium oxide reaction of HL¹ with K₂PtCl₄ displayed, a part from the signals of the corresponding [PtCl₂(dmpz)₂] complex, one signal at 82.1 ppm in the ¹³C{¹H} NMR spectrum. The signal is

assigned to the methylenic carbon of CH₂(OD)₂, the protonated form of methandiol achieved from hydration of formaldehyd in aqueous solution [34]. Formaldehyd was also observed in the ¹H and ¹³C{¹H} NMR spectra when [PtCl₂(PhCN)₂] reacts with HL¹ in a CDCl₃ solution. A broad band at 9.73 ppm (in the ¹H NMR spectrum) and a small signal at 194.5 ppm (in the ¹³C{¹H} NMR spectrum) confirmed the presence of the formaldehyd. A similar process is described in the literature when the bis(pyrazolyl)propane (L-L) reacts with Pt(II) complexes. Cleavage of this bond yields the [PtCl₂(pzH)₂] complexes (pzH = pyrazole)—the *cis* or the *trans* isomer depends on the experimental conditions—instead of the expected [PtCl₂(L-L)] [18].

3.5. *Cis* and *trans* isomers

The presence of two different species in solution in the reaction of HL² with K₂PtCl₄ was confirmed by COSY and NOESY NMR experiments (the cross peaks showed which signals came from the same product, through the coupling constants and also through their closeness in space). Fig. 2 shows a part of the two-dimension NOE spectrum. The NOE cross peaks were found to interconnect the CH protons at 6.26 ppm with the two methyl groups at 2.38 and 2.34 ppm. Two other cross peaks are observed for the other CH groups at 6.08 ppm, which are near methyls at 2.68 and 2.41 ppm. Two more peaks appear to interconnect the methylene groups: the CH₂ at 4.84 ppm with the one at 4.41 ppm, and the CH₂ at 4.32 with the one at 3.92 ppm. Also, the mentioned CH₂ at 4.84 ppm is close in space to the methyl at 2.41 ppm, giving one more cross peak in the spectrum. All those cross peaks clearly indicate that two different isomers coexist in solution. Thanks to the NOE experiments, signals corresponding to each isomer were fully assigned. However, no differential peaks due to the different disposition in space of the *cis* and the *trans* isomer were observed in the NOE experiments. Thus the isomers could not be characterised by this method.

Trials of separation of both isomers by chromatography were unsuccessful. The product degraded inside the silica column.

Differentiation between the *cis* and the *trans* isomers were made on the basis of the NMR spectra with the help of the methods described in the literature for the synthesis of the *cis* isomer [19,20]. It is known that the reaction between K₂PtCl₄ and many heterocyclic ligands (such as 3,5-dimethylpyrazole, diisopropylpyrazole, 3,5-pyrazoledicarboxylic acid, thiazole. . .) in the presence of hydrochloric acid (0.1 M), leads to the obtaining of the *cis* isomer. Using this information, the NMR spectra of **2** and **3**, when the ligands react with K₂PtCl₄ in water, were understood as a mixture of the *cis* and *trans* isomers, since half of them (either in the ¹H NMR or

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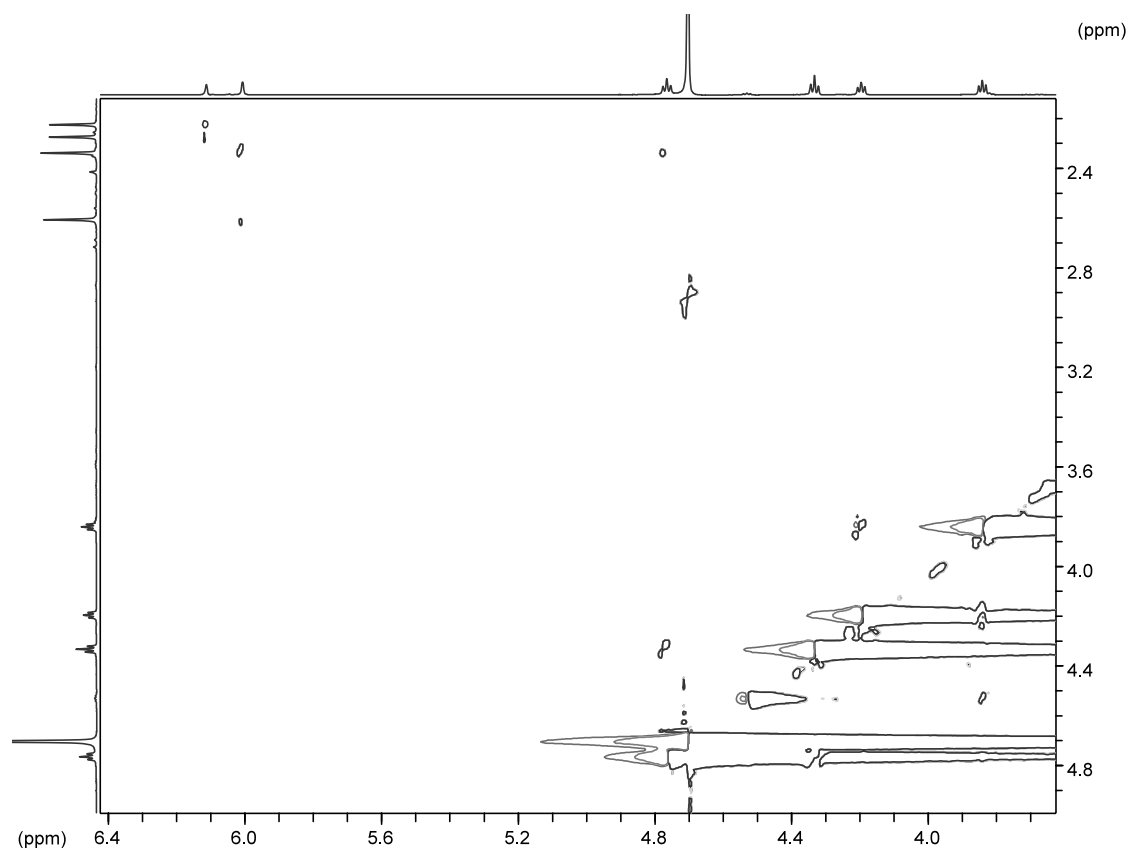


Fig. 2. Part of the two-dimension NOE spectrum of a mixture of *cis*-[PdCl₂(HL²)₂] and *trans*-[PdCl₂(HL²)₂].

¹³C{¹H} NMR) coincided with the ones observed in the spectra of the same complex coming from the synthesis of the *cis* stereoisomer. The other half were assigned to the *trans* adduct.

NMR chemical shifts for every complex (included each isomer) are shown in Section 2.

3.6. Crystal and molecular structure of complexes **2a** and **3b**

The crystal structures of **2a** (Fig. 3) and **3b** (Fig. 4) consist of molecules with the formula [PtCl₂(HL)₂] (HL = 1-(2-hydroxyethyl)-3,5-dimethylpyrazole (**2a**) and 3,5-dimethylpyrazole (**3b**)). **2a** is a monomeric molecule in the solid state, while **3b** turns out to be a dimer due to the existence of four hydrogen bonds N–H...Cl. Moreover, this last structure contains 0.5 methanol molecules from the solvent used in the crystallisation. The Pt(II) atom, in both cases, has a square planar geometry (with a tetrahedral distortion, in which the platinum atoms lie 0.018(2) Å (for structure **2a**) and 0.016(2) Å and 0.027(2) Å (for structure **3b**) out of the coordination plane) coordinated to two chlorides and two nitrogen atoms from the pyrazolic rings. The two chlorides are in a *cis* disposition in compound **2a** and in a *trans* disposition in complex **3b**. Selected bond lengths

and bond angles are gathered in Tables 2 and 3, respectively.

Bond lengths in both structures are comparable and also similar with reported values for Pt–N and Pt–Cl in similar compounds. Pt–N distances in compound **2a** (2.021(8) and 2.016(9) Å) are very similar to those found in compound *cis*-[PtCl₂(dpzm)]₂ (dpzm = 4,4'-dipyrazolymethane (2.016(8) Å and 2.020(7) Å) [35]. They do not differ significantly from those in compounds *cis*-[PtCl₂(dphpz)] (dphpz = 3,5-diphenylpyrazole) (1.994(7) Å and 2.019(7) Å) [36], *cis*-[PtCl₂(pzH)₂] (pzH = pyrazole) (1.934(8) Å and 1.966(8) Å) [18] and the same metallic unit in [Pt(pzH)₄][PtCl₄][*cis*-PtCl₂(pzH)₂]₂ (1.99(2) Å and 1.97(2) Å) [19]. Pt–Cl bond lengths (2.292(2) and 2.311(3) Å) are also comparable to the ones found in compounds described above (range 2.276(3)–2.303(2) Å) [19,18,35,36].

Pt–N distances in compound **3b** are a few shorter, especially in the first molecule of the dimer (1.978(5) and 1.982(5) Å). No *trans* complexes with crystal structures that contain two pyrazolic ligands and two halides have been found in the literature to compare. However, the related compound *trans*-[PtCl₂(Tz)₂] (Tz = thiazole) has been determined by X-ray diffraction [35]. Its Pt–N distances (2.02(2) Å and 2.08(2) Å) are slightly longer than in compound **3b** but the Pt–Cl ones (2.300(5) Å) are comparable.

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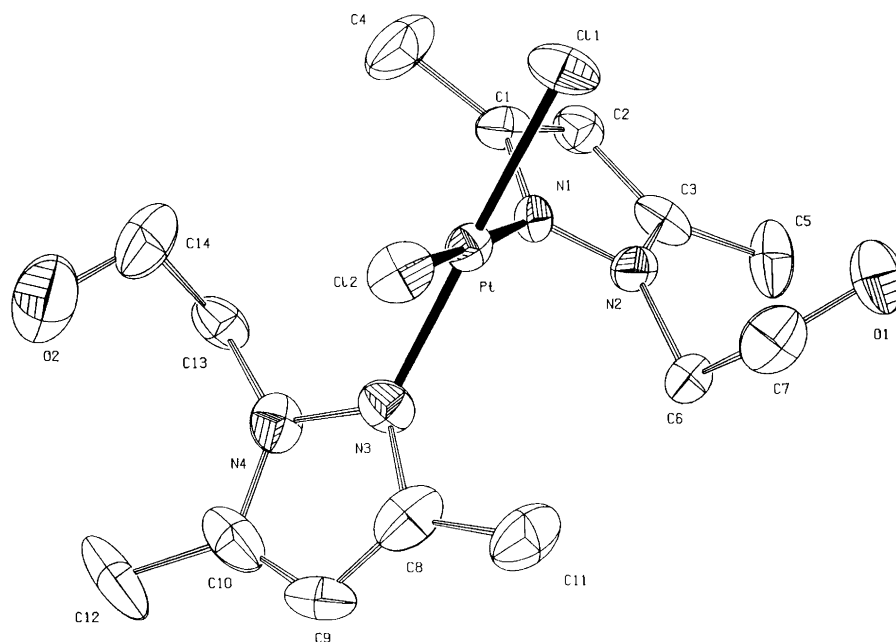
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Fig. 3. Structure of **2a** showing the numbering scheme; ellipsoids are drawn at the 50% probability level.

In compound **2a**, the two hydroxyalkyl N1 substituting chains are in an *anti* disposition to decrease the intramolecular steric hindrance due to the *cis* isomery.

As a consequence of these steric factors due to the *cis* disposition of the two pyrazolic ligands, the *cis* angle N(1)–Pt–N(3) deviates almost 6° from the right angle.

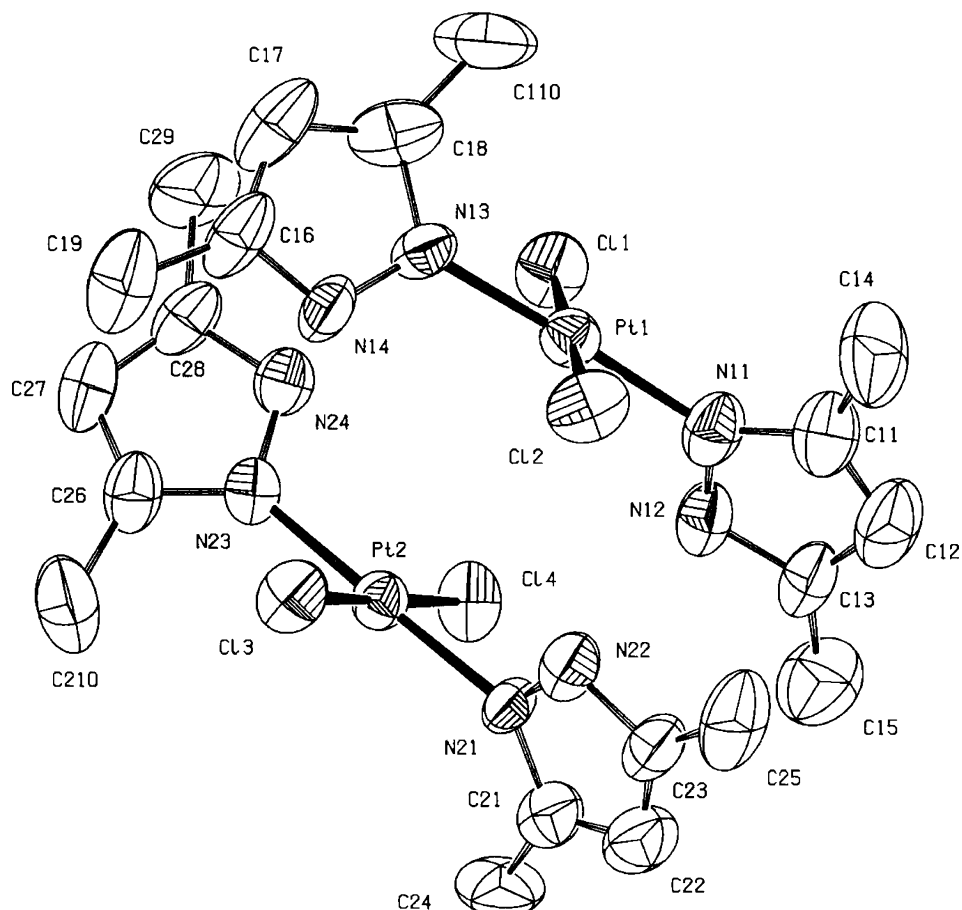


Fig. 4. Structure of **3b** showing the numbering scheme; ellipsoids are drawn at the 50% probability level.

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Table 2
Selected bond lengths (Å) and angles (°) for **2a** with estimated standard deviations (e.s.d.s.) in parentheses

Bond lengths			
Pt–N(1)	2.021(8)	Pt–Cl(1)	2.311(3)
Pt–N(3)	2.016(9)	Pt–Cl(2)	2.292(2)
Bond angles			
N(1)–Pt–N(3)	95.8(3)	N(3)–Pt–Cl(2)	86.8(2)
N(1)–Pt–Cl(2)	177.4(2)	N(3)–Pt–Cl(1)	175.8(2)
N(1)–Pt–Cl(1)	88.1(2)	Cl(1)–Pt–Cl(2)	89.32(9)

Table 3
Selected bond lengths (Å) and angles (°) for **3b** with e.s.d.s. in parentheses

Bond lengths			
Pt(1)–N(11)	1.978(5)	Pt(2)–N(21)	2.009(5)
Pt(1)–N(13)	1.982(5)	Pt(2)–N(23)	2.015(5)
Pt(1)–Cl(1)	2.2800(18)	Pt(2)–Cl(4)	2.2958(16)
Pt(1)–Cl(2)	2.3130(19)	Pt(2)–Cl(3)	2.2962(16)
Bond angles			
N(11)–Pt(1)–N(13)	178.0(2)	N(21)–Pt(2)–N(23)	178.0(2)
N(11)–Pt(1)–Cl(1)	89.26(17)	N(21)–Pt(2)–Cl(4)	90.71(15)
N(13)–Pt(1)–Cl(1)	91.74(18)	N(23)–Pt(2)–Cl(4)	90.08(15)
N(11)–Pt(1)–Cl(2)	91.02(18)	N(21)–Pt(2)–Cl(3)	89.22(15)
N(13)–Pt(1)–Cl(2)	87.98(17)	N(23)–Pt(2)–Cl(3)	89.95(15)
Cl(1)–Pt(1)–Cl(2)	179.71(7)	Cl(4)–Pt(2)–Cl(3)	178.84(6)

Thus the Cl–Pt–Cl is slightly narrower than 90° (89.32(9)°). However, in the literature, *cis* angles Cl–Pt–Cl are a bit wider than the ones determined in our structure **2a**. For *cis*-[PtCl₂(pzH)₂] the value of this angle is 90.9(1)° [18] and for the same metallic unit in [Pt(pzH)₄][PtCl₄][*cis*-PtCl₂(pzH)₂]₂ is 91.6(2)° [19]. For compound *cis*-[PtCl₂(dphpz)₂] the angle is 91.8(1)° [36]. This might be explained by a higher steric hindrance of the methyl groups in ligand HL². The *trans* isomer of **3b** has *cis* angles N–Pt–Cl very close to 90° (the widest is 91.7(2) Å). Although we still have the methyl groups, the *trans* disposition allows a better accommodation of the two ligands. In this compound the pyrazolic rings are at dihedral angles of 57.8(5)° and 64.0(4)°, for the two molecules, while in compound **2a** the angle between the two heterocyclic rings is 73.0(6)°.

One intermolecular hydrogen bond is observed in crystal structure **2a** between the O–H bond of one hydroxyethyl chain of one molecule and a chloride from another molecule (data are collected at Table 4), thus yielding infinite chains parallel to the crystallographic vector *b*. The structure of **3b** is very similar to that found for *trans*-[PdCl₂(dmpz)₂] [37] where each N–H bond in a molecule points towards a chloride from the other molecule, yielding four N–H···Cl hydrogen bonds (Table 4). These interactions are, in both cases, the driving force of the dimerisation. The distance between Pt(1) and Pt(2) is 3.7610(4) Å. The two five-membered

Table 4
Distances and angles related to hydrogen bonding (Å, °)

Donor–H···acceptor	D–H	H···A	D···A	D–H···A
Compound 2a				
O(1)–H(1O)···Cl(1) ^{a,b}	0.82	2.43	3.238(9)	171.0(2)
Compound 3b				
N(12)–H(12N)···Cl(4) ^b	0.86	2.36	3.214(6)	172.5(2)
N(14)–H(14N)···Cl(3) ^b	0.86	2.39	3.249(6)	173.5(2)
N(22)–H(22N)···Cl(2) ^b	0.86	2.40	3.223(6)	161.9(2)
N(24)–H(24N)···Cl(1) ^b	0.86	2.42	3.262(6)	167.4(2)

^a Symmetry codes: 1/2–*x*, –1/2+*y*, 1/2–*z*.

^b O–H and N–H distances have been fixed.

heterocyclic ring centroids (one above the other in the two different coordination planes) are separated 3.884(6) and 4.008(6) Å. The two best fit planes of the platinum coordination in the dimer (Pt1, N11, Cl1, N13, Cl2 and Pt2, N21, Cl3, N23, Cl4) are almost parallel to each other: the dihedral angle between them is 1.72(4)°.

4. Conclusion

3,5-Dimethylpyrazole derivative platinum complexes with the formula [PtCl₂(HL)₂] (HL = pyrazolic ligand) have been synthesised. With the ligand 1-(2-hydroxyethyl)-3,5-dimethylpyrazole (HL²) both isomers *cis* and *trans* are obtained depending on the platinum starting material. Ligand 1-hydroxymethyl-3,5-dimethylpyrazole (HL¹) showed a different and more complex behaviour. In spite of obtaining complexes [PtCl₂(HL¹)₂], the equivalent 3,5-dimethylpyrazole (dmpz) adducts are found. This effect is due to the cleavage of the Npz–C(sp³) bond of the aromatic ligand in the presence of Pt(II). The same compounds are also obtained when the dmpz itself reacts with the platinum compounds. The ratio of isomer *cis* and *trans* is also dependent on the starting platinum complex. Although both isomers were present in solution only the *cis*-[PtCl₂(HL²)₂] (**2a**) and the *trans*-[PtCl₂(dmpz)₂] (**3b**) crystallised and were resolved by X-ray diffraction. When working with HL¹ and dmpz, the compound [PtCl₂(dmpz)₂] has also been observed in many cases and it was even possible its isolation and characterisation.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 206909 for **2a** and 206910 for **3b**. 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-

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Reactivity of the ligand bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether (L_1) with Pd(II) and Pt(II). Crystal structure of *cis*-[PtCl₂(L_1)]

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Abstract

The coordination chemistry of the ligand bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether (L_1) was tested in front of Pd(II) and Pt(II). Complexes *cis*-[MCl₂(L_1)] (M = Pd(II) and Pt(II)) were obtained, due to the chelate condition of the ligand and the formation of a stable ten-membered ring. The crystal structure of *cis*-[PtCl₂(L_1)] was resolved by X-ray diffraction. Treatment of [PdCl₂(L_1)] or [Pd(CH₃CN)₄](BF₄)₂ with AgBF₄ in the presence of L_1 gave the complex [Pd(L_1)₂](BF₄)₂. The initial *cis*-[PdCl₂(L_1)] was recovered by reacting [Pd(L_1)₂](BF₄)₂ with an excess of NEt₄Cl. Reaction of [Pt(CH₃CN)₄](BF₄)₂ (generated *in situ* from [PtCl₂(CH₃CN)₂] and AgBF₄ in acetonitrile) with ligand L_1 yields complex [Pt(L_1)₂](BF₄)₂.

Keywords: Palladium complexes; Platinum complexes; Ether-pyrazole ligand; Crystal structure.

1. Introduction

The d⁸ electronic configuration of Pd(II) and Pt(II) complexes tends to give them a square planar geometry. Both metals are considered as rather soft centres, which tend to coordinate easily with soft donor atoms. Of these, N-containing heterocycles such as pyrazole-based ligands have already been tested. Moreover, their coordination chemistry with those metallic centres (among others) has also been well documented in six recently published reviews [1,6]. Dichloropalladium complexes with two monodentate pyrazolic ligands have usually a *trans* isomery [7-17]. Both *cis* and *trans* isomers are initially formed but the *cis* – *trans* isomerisation readily occurs in solution,

probably through five-coordinated species, which incorporates one solvent molecule [18]. In the case of Pt(II), both isomers are stable in solution and the achievement of the final *cis* or *trans* isomer depends on the platinum starting material and the reaction conditions [19]. As an example, 1-hydroxyalkyl-3,5-dimethylpyrazole ligands (HL) [7] react with Pd(II) to form only the *trans*-[PdCl₂(HL)₂], but when they coordinate with Pt(II), both *cis* and *trans* isomers are formed [20].

When the ligand has a chelating behaviour, the *cis* isomer is often easily achieved either with Pd(II) or Pt(II) (*trans* isomers may also be obtained with big chelating rings) [21].

Here, as an extension of our studies on pyrazole-ether derived ligands [8], we report the coordination behaviour of the ligand bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether (**L**₁) (Fig. 1) to Pd(II) and Pt(II). The coordination chemistry of this ligand has already been studied with Cu(I) [22], Co(II) [23] and Cd(II) [24], in which the ligand adopts a κ^3N,O,N coordination mode of bonding. In our group a previous study with **L**₁ was performed with Rh(I) [25]. This study illustrates the ability of the ligand to adopt different conformations and coordination modes when associated with Rh(I): κ^3N,O,N and κ^2N,N . Complexes *cis*-[MCl₂(**L**₁)] (M = Pd(II) (**1**) and Pt(II) (**2**)) are synthesised and characterised. The crystal structure of *cis*-[PtCl₂(**L**₁)] is also reported. Reactivity of **1** with an excess of ligand and in the presence of AgBF₄ yields [Pd(**L**₁)₂](BF₄)₂ (**3**). It was also possible to obtain (**3**) and [Pt(**L**₁)₂](BF₄)₂ (**4**) starting with [M(CH₃CN)₄](BF₄)₂ (M = Pd(II) or Pt(II)) and **L**₁ with a 1M:4**L**₁ ratio). The reverse reaction to recover *cis*-[PdCl₂(**L**₁)] is also described using NEt₄Cl as the chloride source.

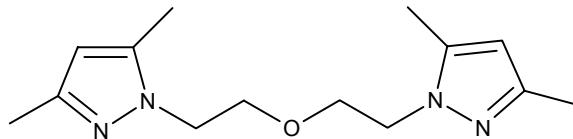


Fig. 1. Ligand bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether (**L**₁).

2. Experimental

2.1. General methods

All reactions were performed under a nitrogen atmosphere with the use of vacuum line and standard Schlenk techniques. All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled under N₂ by standard methods just before use. The bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether (**L**₁) [22], [PdCl₂(CH₃CN)₂] [26], [PtCl₂(CH₃CN)₂] [27] and [Pt(CH₃CN)₄](BF₄)₂ [28] were prepared according to published procedures.

Elemental analyses (C, N, H) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in ca. 10⁻³ M acetonitrile or methanol, employing a CyberScan CON 500 (Euthech Instruments) 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} . ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a NMR-FT Bruker 250 MHz spectrometer. Variable temperature ^1H NMR spectra were recorded on a NMR-FT Bruker 500 MHz spectrometer. All chemical shifts values (δ) are given in ppm. Mass spectra were obtained with an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics.

2.2. Synthesis of the metal complexes

2.2.1. Complex *cis*-[PdCl₂(L₁)] (1)

To a solution of 0.070 g (0.27 mmol) of [PdCl₂(CH₃CN)₂] in 20 ml of CH₂Cl₂ was added 0.071 g (0.27 mmol) of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether (L₁) dissolved in 5 ml of the same solvent. The orange solution turned yellow. The mixture was stirred at room temperature overnight. The solvent was completely removed. The orange solid was recrystallised by column chromatography using a CH₂Cl₂/acetone 9:1 mixture as eluent (yield: 88%).

C₁₄H₂₂N₄OCl₂Pd: *Anal.* Calc.: C, 38.24; H, 5.01; N, 12.75 %; Found: C, 38.49; H, 5.25; N, 12.51 %. **Conductivity** ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, 1.10 10^{-3} M in acetonitrile): 8. **IR**: (KBr, cm^{-1}): 2955-2870 ($\nu\text{C-H}$)_{al}, 1558 ($\nu\text{C}=\text{C}$, $\nu\text{C}=\text{N}$)_{ar}, 1471 (δCH_3)_{as}, 1423 ($\delta\text{C}=\text{C}$, $\delta\text{C}=\text{N}$)_{ar}, 1402 (δCH_3)_s, 1119 ($\nu\text{C-O-C}$)_{as}, 797 ($\delta\text{C-H}$)_{oop}; (polyethylene, cm^{-1}): 504 ($\nu\text{Pd-N}$); 367, 339 ($\nu\text{Pd-Cl}$). **^1H NMR** (CDCl₃ solution, 250 MHz) δ : 5.91 [s, 2 H, CHpz], 5.18 [t, $^3J=7.2$ Hz, 4 H, NCH₂], 4.42 [t, $^3J=7.2$ Hz, 4 H, OCH₂], 2.89 [s, 6 H, CH₃], 2.28 [s, 6 H, CH₃]. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (CDCl₃ solution, 62.9 MHz) δ : 150.5 (CCH₃), 143.6 (CCH₃), 108.0 (CHpz), 68.6 (OCH₂), 49.0 (NCH₂), 15.1 (CH₃), 11.9 (CH₃).

2.2.2. Complex *cis*-[PtCl₂(L₁)] (2)

To a solution of 0.070 g (0.17 mmol) of K₂PtCl₄ in 7 ml of distilled water was added 0.044 g (0.17 mmol) of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether (L₁) suspended in 10 ml of the same solvent. The suspension was refluxed for 2 h. An undesirable orange solid precipitated and was filtered off. The aqueous phase was extracted twice with 10 ml of CH₂Cl₂. Water was removed under reduced pressure yielding a white solid (yield: 19%).

C₁₄H₂₂N₄OCl₂Pt: *Anal.* Calc.: C, 31.82; H, 4.17; N, 10.61 %; Found: C, 31.94; H, 4.11; N, 10.08 %. **Conductivity** ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, 9.47 10^{-3} M in methanol): 11. **IR**: (KBr, cm^{-1}): 2962, 2927 ($\nu\text{C-H}$)_{al}, 1557 ($\nu\text{C}=\text{C}$, $\nu\text{C}=\text{N}$)_{ar}, 1466 (δCH_3)_{as}, 1415 ($\delta\text{C}=\text{C}$, $\delta\text{C}=\text{N}$)_{ar}, 1393 (δCH_3)_s, 1102 ($\nu\text{C-O-C}$)_{as}, 802 ($\delta\text{C-H}$)_{oop}; (polyethylene, cm^{-1}): 516 ($\nu\text{Pt-N}$); 342, 326 ($\nu\text{Pt-Cl}$). **^1H NMR** (CDCl₃ solution, 250 MHz) δ : 6.97 [m, $^2J=15.9$ Hz, $^3J=12.4$ Hz, $^3J=3.4$ Hz, 2 H, NCHH], 5.96 [s, 2 H, CHpz], 4.25 [m, $^2J=13.4$ Hz, $^3J=12.4$ Hz, $^3J=2.4$ Hz, 2 H, OCHH], 4.24 [m, $^2J=15.9$ Hz, $^3J=2.4$ Hz, $^3J=1.9$ Hz, 2 H, NCHH], 4.10 [m, $^2J=13.4$ Hz, $^3J=3.4$ Hz, $^3J=1.9$ Hz, 2 H, OCHH], 2.81 [s, 6 H, CH₃], 2.30 [s, 6 H, CH₃]. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (CDCl₃ solution, 62.9 MHz) δ : 150.6 (CCH₃), 142.5 (CCH₃), 108.8 (CHpz), 72.4 (OCH₂), 52.1 (NCH₂), 16.1 (CH₃), 12.4 (CH₃).

2.2.3. Complex $[Pd(L_1)_2](BF_4)_2$ (3)

Method 1:

To a solution of 0.051 g (0.12 mmol) of $[Pd(CH_3CN)_4](BF_4)_2$ in 15 ml of acetonitrile (cooled in an ice-water bath) was added 0.060 g (0.23 mmol) of L_1 in 5 ml of the same solvent. The pale yellow solution turned dark yellow. The solution was stirred for one hour at 0°C and overnight at room temperature. The solvent was removed under reduced pressure leaving a dark yellow solid, which was washed twice with diethyl ether and dried *in vacuo*. The solid was recrystallised in a mixture of CH_2Cl_2 and diethyl ether (yield: 85%).

Method 2:

To a solution of 0.117 g (0.27 mmol) of $[PdCl_2(L_1)]$ in 15 ml of a mixture of CH_2Cl_2 /methanol (1:1) was added 0.070 g of L_1 and 0.104 g (0.53 mmol) of $AgBF_4$ in 10 ml of methanol. The solution was stirred at r.t. and protected from light for 30 min. The $AgCl$ precipitated and was filtered off. The yellow solution was then filtered through a pad of Celite. The solvent was removed under reduced pressure yielding a dark yellow solid, which was recrystallised in a mixture of CH_2Cl_2 and diethyl ether (yield: 68%).

$C_{28}H_{44}B_2F_8N_8O_2Pd$: Anal. Calc.: C, 41.79; H, 5.47; N, 13.93 %; Found: C, 41.40; H, 5.71; N, 13.44 %. **Conductivity** ($\Omega^{-1}cm^2mol^{-1}$, $1.01 \cdot 10^{-3}$ M in acetonitrile): 236. **IR:** (KBr, cm^{-1}): 2922-2871 ($\nu C-H$)_{al}, 1554 ($\nu C=C$, $\nu C=N$)_{ar}, 1466 (δCH_3)_{as}, 1425 ($\delta C=C$, $\delta C=N$)_{ar}, 1390 (δCH_3)_s, 1117 ($\nu C-O-C$)_{as}, 1059 ($\nu B-F$), 820-786 ($\delta C-H$)_{oop}. **1H NMR** (acetone d_6 solution, 250 MHz) δ : 6.01 [s, 4 H, $CHpz$], 4.35 [t, $^3J=4.7$ Hz, 8 H, NCH_2], 3.79 [t, $^3J=4.7$ Hz, 8 H, OCH_2], 2.27 [s, 12 H, CH_3], 2.26 [s, 12 H, CH_3]. **$^{13}C\{^1H\}$ NMR** (acetone d_6 solution, 62.9 MHz) δ : 149.1 (CCH_3), 142.7 (CCH_3), 106.6 ($CHpz$), 71.1 (OCH_2), 50.1 (NCH_2), 14.4 (CH_3), 11.2 (CH_3). **ES(+)**MS m/z : 665 $[Pd(L_1)_2Cl]^+$, 263 $[L_1+H]^+$.

2.2.4. Complex $[Pt(L_1)_2](BF_4)_2$ (4)

To a solution of 0.072 g (0.21 mmol) of $[PtCl_2(CH_3CN)_2]$ in 15 ml of acetonitrile was added 0.083 g (0.42 mmol) of $AgBF_4$. The solution was refluxed for 4 hours protected from light. $AgCl$ precipitated, which was filtered off over celite. 0.108 g (0.42 mmol) of L_1 in 5 ml of acetonitrile was then added. After stirring for 6 days at room temperature, the solution was evaporated to dryness and the residue was washed with diethyl ether (yield: 78%).

$C_{28}H_{44}B_2F_8N_8O_2Pt$: Anal. Calc.: C, 37.64; H, 4.93; N, 12.55 %; Found: C, 37.36; H, 4.92; N, 12.25 %. **Conductivity** ($\Omega^{-1}cm^2mol^{-1}$, $1.01 \cdot 10^{-3}$ M in acetonitrile): 223. **IR:** (KBr, cm^{-1}): 2925-2871 ($\nu C-H$)_{al}, 1554 ($\nu C=C$, $\nu C=N$)_{ar}, 1465 (δCH_3)_{as}, 1426 ($\delta C=C$, $\delta C=N$)_{ar}, 1392 (δCH_3)_s, 1111 ($\nu C-O-C$)_{as}, 1060 ($\nu B-F$), 822-774 ($\delta C-H$)_{oop}. **1H NMR** (acetone d_6 solution, 250 MHz) δ : 6.01 [s, 4 H, $CHpz$], 4.36 [t, $^3J=4.7$ Hz, 8 H, NCH_2], 3.79 [t, $^3J=4.7$ Hz, 8 H, OCH_2], 2.27 [s, 12 H, CH_3], 2.26 [s, 12 H, CH_3]. **$^{13}C\{^1H\}$ NMR** (acetone d_6 solution, 62.9 MHz) δ : 149.1 (CCH_3), 142.6 (CCH_3), 106.5 ($CHpz$), 71.1 (OCH_2), 50.1 (NCH_2), 14.5 (CH_3), 11.2 (CH_3). **ES(+)**MS m/z : 754 $[Pt(L_1)_2Cl]^+$, 456 $[Pt(L_1)-H]^+$.

2.2.5. Synthesis to recover *cis*-[PdCl₂(L₁)] (1) from [Pd(L₁)₂](BF₄)₂ (3)

To a solution of 0.076 g (0.09 mmol) of **3** in 6 ml of CH₂Cl₂ was added 0.31 g (1.87 mmol) of NEt₄Cl (previously dried in the heater for dehydration) in 6 ml of absolute ethanol. The mixture was refluxed for 5 days. The NEt₄Cl and NEt₄BF₄ were extracted twice from the organic solution with 10 ml of water. The CH₂Cl₂/EtOH (1:1) solution was dried in *vacuo* yielding a yellow solid, which was characterised as a mixture of *cis*-[PdCl₂(L₁)] (53%), [Pd(L₁)₂](BF₄)₂ (18%), the free ligand and other secondary products.

2.3. X-ray crystal structure analyses

Suitable crystals for X-ray diffraction experiments of compound **2** were obtained through recrystallisation from a CH₂Cl₂/diethyl ether (1:1) mixture. Data were collected on a MAR345 diffractometer and measured at room temperature (293(2) K) using graphite-monochromatized Mo-K_α radiation (λ = 0.71069 Å). The structure was solved by direct methods (SHELXS 97) [29] and refined by full-matrix least square methods (SHELXL 97) [30].

Table 1.
Crystal data for compound *cis*-[PtCl₂(L₁)] (2)

Formula	C ₁₄ H ₂₂ Cl ₂ N ₄ OPt
M	528.35
System	Monoclinic
Space group	P2 ₁ /c
<i>a</i> (Å)	12.8140(10)
<i>b</i> (Å)	9.3120(10)
<i>c</i> (Å)	16.4010(10)
β (°)	113.37(1)
<i>U</i> (Å ³)	1796.5(3)
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	1.953
μ (mm ⁻¹)	8.114
F(000)	1016
Crystal size (mm ³)	0.1 x 0.1 x 0.2
<i>hkl</i> Ranges	-18 to 18, 0 to 13, -22 to 22
2θ Range (°)	2.78-31.61
Reflections collected/unique	17165, 5313 [R(int)=0.0229]
Data, restraints, parameters	5313, 0, 204
Final <i>RI</i> , <i>wR2</i>	0.0305, 0.0660
<i>RI</i> (all data), <i>wR2</i>	0.0390, 0.0698
Largest diff. Peak, hole (e Å ⁻³)	+0.899, -0.913

All H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 time the equivalent temperature factor of the atom,

which are linked. The weight was $\omega = [\sigma^2(I) + (0.0200 P)^2 + 5.2042 P]^{-1}$ where $P = (|F_o|^2 + 2|F_c|^2)/3$. The final $R(\text{on } F)$ and $R_w(F^2)$ values as well as the number of parameters refined and other details concerning the refinement of the crystal structure are presented in Table 1.

3. Results and discussion

3.1. Synthesis and spectroscopic properties of the complexes

Ligand bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether (L_1) reacts with the starting material (either $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ or $[\text{K}_2\text{PtCl}_4]$) in the molar ratio 1:1 to give the neutral chlorocomplexes *cis*- $[\text{MCl}_2(L_1)]$ ($M = \text{Pd(II)}$ (**1**), Pt(II) (**2**)), confirmed by elemental analyses and conductivity measurements (its non-ionic behaviour is determined by values of 8 and 11 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ [31, 32]). The IR spectra in the range of 4000-400 cm^{-1} show that the ligand is coordinated to the Pd(II) and Pt(II). The most striking bands of the pyrazolic ligands ($\nu\text{C}=\text{C}, \nu\text{C}=\text{N}$)_{ar} and ($\delta\text{C}-\text{H}$)_{oop} increase their frequency when they are part of the complex (from 1553 to 1558 and 1557 cm^{-1} and from 784 to 797 and 802 cm^{-1} , respectively) [33, 34]. In the IR spectra in the region 600-100 cm^{-1} the ($\nu\text{M}-\text{N}$) ($M = \text{Pd(II)}$, Pt(II)) bands are observed at 504 and 516 cm^{-1} , respectively. Moreover, the spectra display two bands corresponding to the stretching ($\nu\text{Pd}-\text{Cl}$) in compound **1** (at 367 and 339 cm^{-1}) and ($\nu\text{Pt}-\text{Cl}$) in compound **2** (at 342 and 326 cm^{-1}), which are typical of compounds with a *cis* disposition of the chloro ligands around the metal [35]. Both complexes were also fully characterised by NMR experiments. The ^1H NMR spectrum of complex **1** shows two well-defined triplets of the methylenic protons (at 5.18 and 4.42 ppm) with a $^3J = 7.2$ Hz and three sharp singlets corresponding to the methyl groups and the aromatic *CH*_{pz} protons in the heterocycle. This fact indicates that the molecule of complex **1** possesses higher symmetry in solution due to the occurrence of a fluxional process involving the deformation of the methylenic chains in ligand L_1 , which was investigated by variable-temperature ^1H NMR experiments at 500 MHz in acetone d_6 .

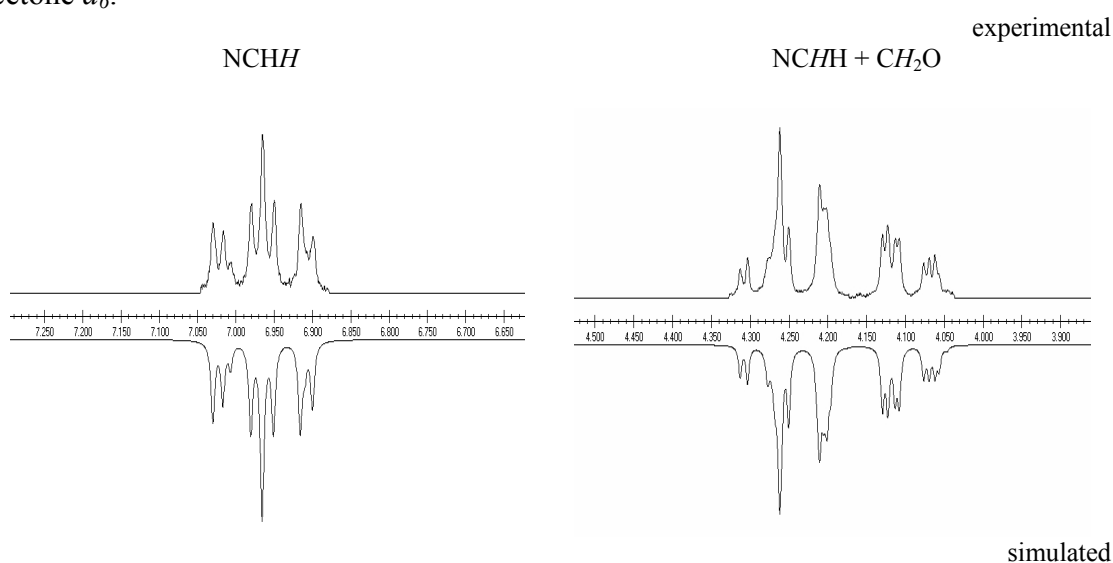


Fig. 2. The 250 MHz ^1H NMR and the simulated gNMR spectrum for the methylenic protons of *cis*- $[\text{PtCl}_2(L_1)]$ (**2**).

Lowering the temperature to 183 K does not induce any broadening or splitting of the methylenic signals, meaning that this fluxional phenomenon has a very low activation energy barrier impossible to block by NMR. However, the ^1H NMR spectrum of **2** presents a complex group of signals in the methylene region assigned to a AA'BB' spin system at room temperature. In order to determine both their ^1H - ^1H coupling constants and chemical shifts (see Experimental Section), a simulated spectrum was obtained using the gNMR program [36] (the real and the simulated spectra are shown in Fig. 2).

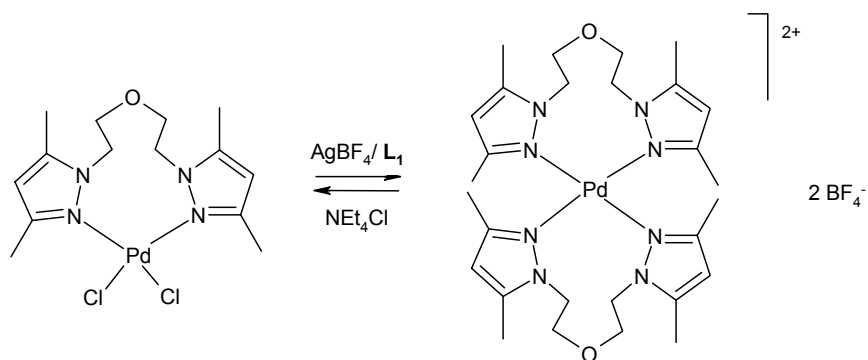
The protons at 6.97 and 4.24 ppm correspond to the methylene group linked to the N. The most deshielded H has a big coupling constant with one of the CH_2O protons but small constant with the other proton. The proton at 4.24 ppm has two small coupling constants with both CH_2O protons. Thus signals at 4.25 and 4.10 ppm are assigned to the CH_2O group. These observations are consistent with a rigid conformation of the bonded ligand L_1 in complex **2**, which renders non-equivalent the methylene protons. However, the CHpz and the CH_3 protons of the aromatic cycles are not significantly affected and remain as singlets. The structure of **2** was further investigated by X-ray diffraction.

Complexes $[\text{M}(\text{L}_1)_2](\text{BF}_4)_2$ ($\text{M} = \text{Pd}(\text{II})$ (**3**), $\text{Pt}(\text{II})$ (**4**)) are obtained by reacting one equivalent of $[\text{M}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (when $\text{M} = \text{Pt}(\text{II})$ the starting compound is generated *in situ* from the reaction of $[\text{PtCl}_2(\text{CH}_3\text{CN})_2]$ and AgBF_4 in acetonitrile [28]) with the ligand L_1 in the ratio 1:2. The elemental analyses are consistent with the formula of complexes. The conductivity values of 236 and 223 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ in acetonitrile solution prove that they are electrolytes 2:1 (range found for 2:1 electrolyte species in acetonitrile: 220-260 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ [31, 32]). The IR spectra of the compounds show as the most striking features the presence of strong and broad bands at about 1060 cm^{-1} corresponding to the ($\nu\text{B-F}$) absorption [33, 34]. The positive ionisation Electrospray Mass Spectra of **3** and **4** have been recorded. In the spectrum of both complexes the molecular peaks ($m/z = 315$ and 359.5, respectively) are not observed. However the peaks corresponding to the cations $[\text{Pd}(\text{L}_1)_2\text{Cl}]^+$ ($m/z = 665$) and $[\text{Pt}(\text{L}_1)_2\text{Cl}]^+$ ($m/z = 755$) are displayed, probably as a consequence of the ionisation technique, corroborating the existence of complexes.

In the two complexes both ligands are symmetrically bonded to the metal as only one signal for each proton and carbon are observed in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, respectively. In the ^1H NMR spectra two triplets are assigned to the methylenic chain $\text{NCH}_2\text{CH}_2\text{O}$ meaning that all the CH_2 protons are equivalent. Three singlets for the CHpz and the CH_3 are observed.

By treatment of complex **1** with AgBF_4 in the presence of the ligand L_1 (ratio 1:2:1) in methanol solution, the compound $[\text{Pd}(\text{L}_1)_2](\text{BF}_4)_2$ has also been obtained (yield: 68%). This yield is lower than that obtained when the reaction was carried out with $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (see Experimental Section). Due to the low yield of the synthesis of *cis*- $[\text{PtCl}_2(\text{L}_1)]$ (**2**), the formation of the compound $[\text{Pt}(\text{L}_1)_2](\text{BF}_4)_2$ from **2** was monitored only by ^1H NMR spectroscopy.

The compound *cis*- $[\text{PdCl}_2(\text{L}_1)]$ may be recovered by treating compound **3** with an excess of NEt_4Cl (ratio 1:20) in $\text{CH}_2\text{Cl}_2/\text{ethanol}$ (1:1) solution refluxing for 5 days (Scheme 1).



scheme 1

^1H NMR experiments confirmed the presence of *cis*- $[\text{PdCl}_2(\text{L}_1)]$ (53%), as well as the free ligand. However, the reaction was not completed; therefore the presence of complex $[\text{Pd}(\text{L}_1)_2](\text{BF}_4)_2$ (18%) and other secondary products were also observed. In contrast, the use of the same reaction conditions with compound $[\text{Pt}(\text{L}_1)_2](\text{BF}_4)_2$ gave decomposition products.

3.2. Crystal and molecular structure of complex 2

The crystal structure of complex **2** consists of monomeric *cis*- $[\text{PtCl}_2(\text{L}_1)]$ molecules (Fig. 3). The platinum centre has a square planar geometry (with a slight tetrahedral distortion, in which the metallic atom lies 0.014(1) Å out of the coordination plane).

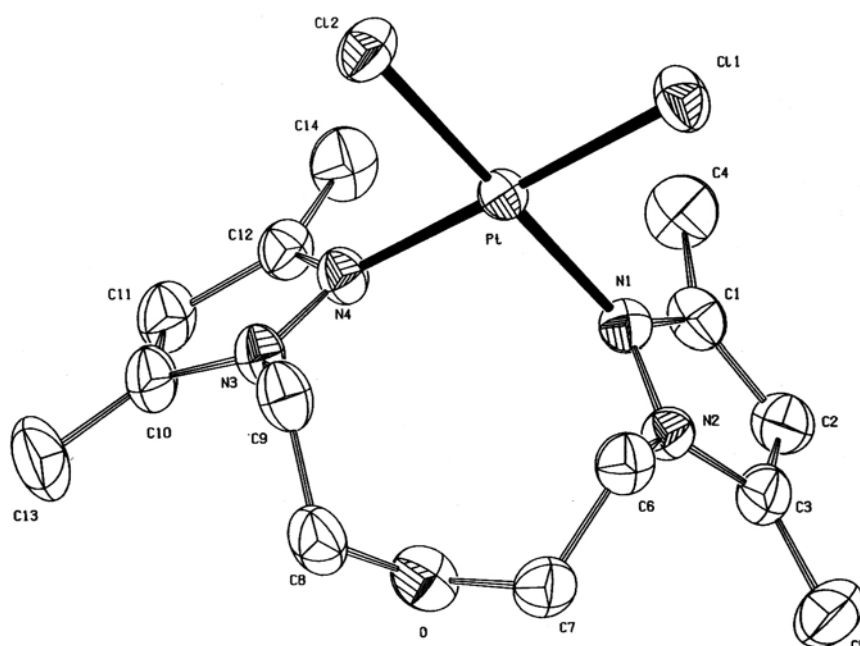


Fig. 3. Structure of **2** showing the numbering scheme; ellipsoids are drawn at the 50% probability level.

The environment consists of two chlorides in *cis* disposition to the metal and two nitrogen atoms in the pyrazolic rings. This *cis*- $\text{PtCl}_2(\text{Npz})_2$ core is already found in the literature as a part of five-crystal structures with ligands 1-(2-hydroxyethyl)-3,5-dimethylpyrazole [20], 4,4'-di(1-pyrazolyl)methane [37], 3,5-diphenylpyrazole [38] and

pyrazole [19,39]. The Pt-Cl (2.2868(10) and 2.3000(10) Å) distances in complex **2** are typical of platinum square-planar complexes and of the same order as the ones in the structures found (Pt-Cl from 2.276(3) Å to 2.303(2) Å [19, 20, 37-39]). However, the Pt-Npz (2.032(3) and 2.026(3) Å) bond lengths are the longest reported so far (Pt-Npz from 1.93(4) Å to 2.021(8) Å) [19, 20, 37-39]. All the complexes described above have a *cis* disposition of the pyrazolic ligands, therefore angles N-Pt-N and Cl-Pt-Cl are also likely to be compared. In most of the cases, the Cl-Pt-Cl angle appears to be wider than the N-Pt-N angle, often by more than 2°. In structure **2** and in complex *cis*-[PtCl₂(HL²)₂] (HL² = 1-(2-hydroxyethyl-3,5-dimethylpyrazole), *cis* angles N-Pt-N are clearly wider and deviate in almost 4° and 6°, respectively, from the right angle (93.8(1)° in **2** and 95.8(3)° in *cis*-[PtCl₂(HL²)₂] [20]). Other bond lengths of interest and angle data are gathered in Table 2.

Table 2.
Selected bond lengths (Å) and angles (°) for **2** with estimated standard deviations (e.s.d.s) in parentheses

Pt-N1	2.032(3)	Pt-Cl1	2.2868(10)
Pt-N4	2.026(3)	Pt-Cl2	2.3000(10)
N1-Pt-N4	93.8(1)	N1-Pt-Cl1	87.31(9)
N4-Pt-Cl1	178.76(10)	N1-Pt-Cl2	177.64(9)
N4-Pt-Cl2	87.32(10)	Cl1-Pt-Cl2	91.59(4)

The N1 substituting ether chain is placed above the coordination plane. However, the platinum centre does not interact with the oxygen atom of the ether group (Pt-O = 4.058(9) Å). Thus the ligand **L**₁ adopts a κ^2N,N bonding mode.

When ligand **L**₁ coordinates to Rh(I) in the complex [Rh(COD)(**L**₁)](BF₄) (COD = 1,5-cyclooctadiene) the ligand shows the same coordination mode of bonding κ^2N,N [25]. However, ligand **L**₁ usually exhibits a stable “T-shaped” coordination mode, in which the ligand is bonded to the metal ion through both N in the pyrazolic ring and the O of the ether function (κ^2N,O,N). This mode of bonding is illustrated in the crystal structures of [Rh(CO)(**L**₁)](BF₄) [25], [Cu(**L**₁)](BF₄) [22] and [M(NO₃)₂(**L**₁)] (M = Co(II) [23] and Cd(II) [24]).

4. Conclusion

The ¹H NMR studies discussed in the present paper show that ligand **L**¹ presents a higher symmetry in complex *cis*-[PdCl₂(**L**₁)] due to a fluxional process occurring in solution, while it adopts a rigid conformation in complex *cis*-[PtCl₂(**L**₁)]. The crystal structure of *cis*-[PtCl₂(**L**₁)] is reported here and illustrates the κ^2 coordination mode of **L**₁, where the ligand coordinates to Pt(II) only through the N in the pyrazolic rings. The O of the ether group does not participate in the ligation. Thus, the didentate κ^2N,N character yields the *cis* ligation around the metallic centre and implies the formation of a ten-member N-M-N ring (M = Pd(II) and Pt(II)) that appears to be thermodynamically stable.

When L_1 reacts with $[M(CH_3CN)_4](BF_4)_2$ ($M = Pd(II)$ and $Pt(II)$) complexes $[M(L_1)_2](BF_4)_2$ are obtained. In this case, the 1H NMR spectra show that the ligand is symmetrically bonded to the metal in both complexes.

The initial compound *cis*- $[PdCl_2(L_1)]$ may be partially recovered by treating $[Pd(L_1)_2](BF_4)_2$ with an excess of NEt_4Cl (ratio 1:20, aprox.) under reflux, in $CH_2Cl_2/EtOH$ (1:1).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC n°:213956 for **2**. 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@aacd.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>].

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Study of the bonding properties of the bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether toward Rh(I): an hemilabile ligand exhibiting $\kappa^3 N, N, O$ meridional or facial coordination mode

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Abstract

The bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether ligand (L_1) reacts with $[Rh(COD)(THF)_2][BF_4]$ generated in situ, giving $[Rh(COD)(L_1-\kappa^2 N, N)][BF_4]$ (**1**)[BF_4]. The 1,5-cyclooctadiene ligand is displaced by carbon monoxide to generate $[Rh(CO)_2(L_1)][BF_4]$ (**2**)[BF_4] in which in the solid state, the ligand L_1 adopts a facial $\kappa^3 N, N, O$ bonding mode. This is the first example of such a coordination mode for this ligand, which generally prefers a 'T-shaped' meridional bonding mode. In solution **2**[BF_4] exists as a mixture of two isomers in rapid equilibrium on the NMR time scale, $[Rh(CO)_2(L_1-\kappa^2 N, N)]^+$ (**2a**)⁺ and the major compound $[Rh(CO)_2(L_1-\kappa^3 N, N, O)]^+$ (**2b**)⁺. **2**[BF_4] loses easily one molecule of carbon monoxide at room temperature leading to $[Rh(CO)(L_1-\kappa^3 N, N, O)][BF_4]$ (**3**)[BF_4] in which L_1 adopts a 'T-shaped' meridional bonding mode. Carbon monoxide addition in solution regenerates rapidly **2**[BF_4]. The single-crystal X-ray structures of **1**[BF_4], **2b**[BF_4] and **3**[BF_4] are reported. © 2003 Elsevier B.V. All rights reserved.

Keywords: Rhodium(I) complexes; Ether–pyrazole ligand; Hemilabile ligand; Tridentate ligand

1. Introduction

In a recent publication some of us have shown that the bis[2-(3,5-dimethyl-1-pyrazolyl)methyl]ethylamine (**L**) is a very flexible ligand in Rh(I) complexes, through the possibility of $\kappa^2 N, N$ or $\kappa^3 N, N, N$ bonding mode depending on the electronic configuration and the steric constraints around the metal [1]. The hemilabile centre of the ligand is logically, the nitrogen atom of the amine function. As an extension of that work, it was tempting to consider ligands similar to **L**, but containing a harder donor centre than the nitrogen atom of the amine group, such as the oxygen of an ether group, and to investigate

the incidence of such a modification on the bonding properties of the ligand.

Most of known ligands associating pyrazole rings and one (or more) ether groups consist of two pyrazolyl rings linked together through both N1 atoms by an ether or a polyether chain [2,3]. These ligands were mainly designed for the capture and selective complexation of alkaline, ammonium or calcium cations. The bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether (**L**₁, Fig. 1) has retained our attention. Its coordination chemistry involving first and second row metals such as Cu(I) [4], Co(II) [5] and Cd(II) [6] has been studied and in all cases the ligand has been shown to adopt a meridional κ^3 bonding mode. For our part, we have investigated the bonding properties of the ligand **L**₁ toward Rh(I), which is a softer metallic centre, and in the present paper we disclose the synthesis, the behaviour in solution and the crystal structures of $[Rh(COD)(L_1-\kappa^2 N, N)][BF_4]$ (**1**)[BF_4], $[Rh(CO)_2(L_1-\kappa^2 N, N)][BF_4]$ (**2**)[BF_4] and

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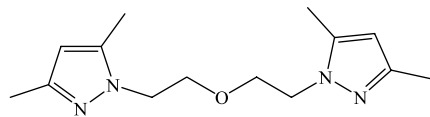


Fig. 1. Structure of the bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether ligand (L_1).

$[\text{Rh}(\text{CO})(L_1-\kappa^3N,N,O)][\text{BF}_4]$ ($[3][\text{BF}_4]$) complexes
(COD = 1,5-cyclooctadiene).

2. Results and discussion

The bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether reacts at room temperature with $[\text{Rh}(\text{COD})(\text{THF})_2][\text{BF}_4]$, generated in situ from the reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ and AgBF_4 in THF, to give the complex $[\text{Rh}(\text{COD})(L_1-\kappa^2N,N)][\text{BF}_4]$ ($[1][\text{BF}_4]$) in 87% yield. This complex, which crystallizes as yellow needles, was characterised by elemental analyses and spectroscopic methods. At room temperature, the compound shows a well resolved but complex ^1H NMR spectrum. Signals assigned to the olefinic protons of the cyclooctadiene ligand are observed at 3.90 and 3.71 ppm as two broad peaks in a 1:1 ratio. These chemical shifts are in full agreement with the presence of nitrogen atoms in a *trans* position [1]. The non-equivalence of the olefinic hydrogens atoms reveals a rigid conformation of the bonded ligand L_1 . Corroborating the rigidity of the ligand, the methylene protons of the $\text{OCH}_2\text{CH}_2\text{N}$ chain exhibit a diastereotopic character and appear as three groups of signals at 4.26, 4.48 and 6.28 ppm, which integrate as 4, 2 and 2 protons. The spin system, which can be analysed as two identical AA'BB' spin systems, has been simulated using the gNMR program [7]. Finally, the pyrazolic methyl and CH groups give singlets at 2.21, 2.80 and 5.93 ppm, respectively. From these data it was not possible, however, to ascertain whether the ligand L_1 in $[1]^+$ was κ^2N,N or κ^3N,N,O bonded to rhodium. The structure of $[1][\text{BF}_4]$ was further investigated in the solid state by X-ray diffraction.

The complex crystallizes with two independent ion pairs per unit cell. The two cations $[1]^+$ present the same geometry, all the corresponding distances and angles being equal within the experimental errors. A perspective view of one of the two independent cations $[1]^+$ (cation A) is shown on Fig. 2. Selected bond lengths and angles are provided in Table 1. The distance between the rhodium and the oxygen atom ($\text{Rh}(1\text{A})-\text{O}(8\text{A}) = 4.146(5)$ Å; $\text{Rh}(1\text{B})-\text{O}(8\text{B}) = 4.145(5)$ Å) is clearly longer than the sum of the van der Waals radii (3.37 Å), probing that there is no interaction between the two atoms. The rhodium atom is located slightly above the mean plane defined by the two pyrazolic nitrogen atoms and the centroid of the C=C bonds (0.021 Å for molecule A, 0.029 Å for molecule B). The Rh–N

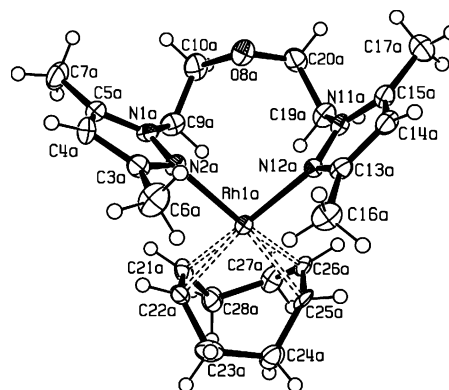


Fig. 2. Crystal structure of the cation $[1]^+$ showing the numbering scheme; ellipsoids are drawn at the 30% probability level.

Table 1

Selected bond lengths (Å) and bond angles (°) for $[1][\text{BF}_4]$, $[2b][\text{BF}_4]$ and $[3][\text{BF}_4]$

	$[1][\text{BF}_4]$ Molecule A	$[1][\text{BF}_4]$ Molecule B	$[2b][\text{BF}_4]$	$[3][\text{BF}_4]$
<i>Bond lengths</i>				
C(21)–C(22)	1.377(8)	1.410(9)		
C(25)–C(26)	1.415(8)	1.370(8)		
C(21)–Rh(1)	2.151(5)	2.128(5)		
C(22)–Rh(1)	2.150(5)	2.167(5)		
C(25)–Rh(1)	2.172(5)	2.148(5)		
C(26)–Rh(1)	2.142(5)	2.165(5)		
N(2)–Rh(1)	2.128(5)	2.138(5)	2.1264(19)	2.032(4)
N(12)–Rh(1)	2.145(5)	2.141(5)	2.1033(19)	2.042(4)
C(1)–Rh(1)			1.843(3)	1.795(5)
C(2)–Rh(1)			1.856(2)	
O(8)–Rh(1)	4.146(5)	4.146(5)	2.764(2)	2.116(3)
<i>Bond angles</i>				
C(10)–O(8)–C(20)	116.6(5)	116.1(5)	113.13(16)	113.2(4)
C(10)–O(8)–Rh(1)				123.4(3)
C(20)–O(8)–Rh(1)				123.4(3)
C(21)–Rh(1)–C(25)	89.7(2)	97.0(2)		
C(21)–Rh(1)–C(26)	81.8(2)	81.7(2)		
C(22)–Rh(1)–C(25)	81.3(2)	80.8(2)		
C(22)–Rh(1)–C(26)	97.3(2)	89.2(2)		
C(21)–Rh(1)–N(2)	90.0(2)	87.9(2)		
C(22)–Rh(1)–N(2)	88.0(2)	91.5(2)		
C(25)–Rh(1)–N(2)	162.6(2)	160.0(2)		
C(26)–Rh(1)–N(2)	158.2(2)	162.3(2)		
C(21)–Rh(1)–N(12)	166.4(2)	161.4(2)		
C(22)–Rh(1)–N(12)	156.0(2)	159.9(2)		
C(25)–Rh(1)–N(12)	91.5(2)	88.30(2)		
C(26)–Rh(1)–N(12)	90.8(2)	92.2(2)		
N(2)–Rh(1)–N(12)	92.8(2)	93.2(2)	90.03(7)	173.2(2)
N(2)–Rh(1)–O(8)			83.40(8)	86.5(2)
N(12)–Rh(1)–O(8)			80.47(8)	86.8(2)
C(1)–Rh(1)–O(8)				179.0(2)
C(2)–Rh(1)–O(8)				
C(1)–Rh(1)–N(12)			91.91(9)	92.7(2)
C(2)–Rh(1)–N(2)			87.83(9)	
C(1)–Rh(1)–N(2)			166.49(10)	94.1(2)
C(2)–Rh(1)–N(12)			177.77(8)	
C(1)–Rh(1)–C(2)			90.02(10)	

distances are equal within the experimental errors and with an average value of 2.14 Å, they are slightly longer than those found in related complexes associating bis(pyrazolyl)alkylamines [1], bis(pyrazolyl)alkanes [8], tris(pyrazolyl)alkanes [9], or tris(pyrazolyl)hydridoborate [10,11] to rhodium ($2.082 < \text{Rh}-\text{N} < 2.133$ Å).

It thus appears that, by contrast to the ligand bis[(3,5-dimethyl-1-pyrazolyl)methyl]ethylamine ligand **L** in $[\text{Rh}(\text{COD})(\text{L}-\kappa^3\text{N},\text{N},\text{N})][\text{BF}_4]$ [1], the ligand **L**₁ in $[\mathbf{1}]^+$ adopts a $\kappa^2\text{N},\text{N}$ bonding mode.

In order to evaluate further the coordination properties of **L**₁ toward a rhodium(I) centre of different steric and electronic environment, the 1,5-cyclooctadiene in $[\mathbf{1}]^+$ was substituted for carbon monoxide. This was readily achieved by bubbling carbon monoxide through a solution of $[\mathbf{1}][\text{BF}_4]$ in dichloromethane at room temperature to give $[\text{Rh}(\text{CO})_2(\text{L}_1)][\text{BF}_4]$ ($[\mathbf{2}][\text{BF}_4]$). The IR spectrum of $[\mathbf{2}]^+$ in solution shows four bands in the νCO region, two weak bands at 2105 and 2042 cm^{-1} and two strong bands at 2090 and 2022 cm^{-1} , suggesting the presence of two isomers in solution, namely $[\mathbf{2a}]^+$ for the minor complex, and $[\mathbf{2b}]^+$ for the major one. Similar observations have been made in the case of $[\text{Rh}(\text{CO})_2(\text{L})][\text{BF}_4]$ and it was shown that the weakest bands correspond to the isomer in which the ligand **L** was $\kappa^2\text{N},\text{N}$ -bonded to rhodium [1]. As the CO absorption bands of a given 18 valence electron complex are expected to appear at lower frequencies as compared to a 16 electron one, it can be deduced that in the major isomer, $[\mathbf{2b}][\text{BF}_4]$, the oxygen of the ether group is bonded to rhodium. Suitable crystals for X-ray diffraction of $[\mathbf{2}][\text{BF}_4]$ were obtained by crystallisation under a CO atmosphere. Infrared spectrum in KBr dispersion showed that these crystals corresponded to the major isomer of $[\mathbf{2}][\text{BF}_4]$, $[\mathbf{2b}][\text{BF}_4]$ (νCO : 2082, 2009 cm^{-1}). Fig. 3 depicts cation $[\mathbf{2b}]^+$. Selected bond lengths and angles are collected in Table 1. The complex $[\mathbf{2b}]^+$ presents a distorted square pyramid geometry around rhodium: the nitrogen atoms N(2) and N(12) of the pyrazolyl ligands and the two carbon atoms C(1) and C(2) of the carbonyl ligands constitute the basis of the

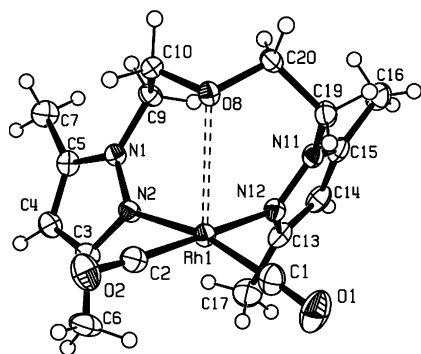


Fig. 3. Crystal structure of the cation $[\mathbf{2b}]^+$ showing the numbering scheme; ellipsoids are drawn at the 30% probability level.

pyramid, while the oxygen atom O(8) of the ether arm figures its summit. The rhodium atom lays 0.122 Å out of basis of the pyramid, toward the oxygen atom O(8). The Rh–O(8) distance of 2.764(2) Å is shorter than the sum of the van der Waals radii (3.37 Å) and this is consistent with a bonding interaction between the two atoms. It is worth noting, however, this Rh–O bond is one of the longest reported so far [12]. Due to the steric strains, the Rh–O(8) bond is bent over the ligand **L**₁ ($\text{O}(8)-\text{Rh}-\text{N}(2) = 83.40(8)^\circ$, $\text{O}(8)-\text{Rh}-\text{N}(12) = 80.43(8)^\circ$). It thus appears that in the solid state the ligand **L**₁ adopts a facial $\kappa^3\text{N},\text{N},\text{O}$ bonding mode. This is the first example of such a coordination mode for this ligand, which generally prefers a ‘T-shaped’ meridional coordination mode [5].

The ^1H NMR spectrum of $[\mathbf{2}]^+$ at 295 K shows sharp resonances for the CH and CH₃ groups of the pyrazolyl cycles but ill defined broad signals in the region where the methylene resonances are expected (4–5 ppm). This suggests the occurrence of a fluxional process, which was investigated further by variable-temperature ^1H -NMR experiments at 500 MHz. At 240 K the signals of the methylene protons are well defined giving an AA’BB’ spin system at 4.87 and 4.09 ppm, and 4.21 and 3.99 ppm, respectively (Fig. 4). Coupling constants and chemical shifts have been determined by comparing the ^1H -NMR spectrum of this region with a simulated spectrum using the gNMR program [7]. Besides the CH and CCH₃ groups of the pyrazolyl cycles are not significantly affected and their resonances remain as singlet upon cooling. Lowering the temperature does not

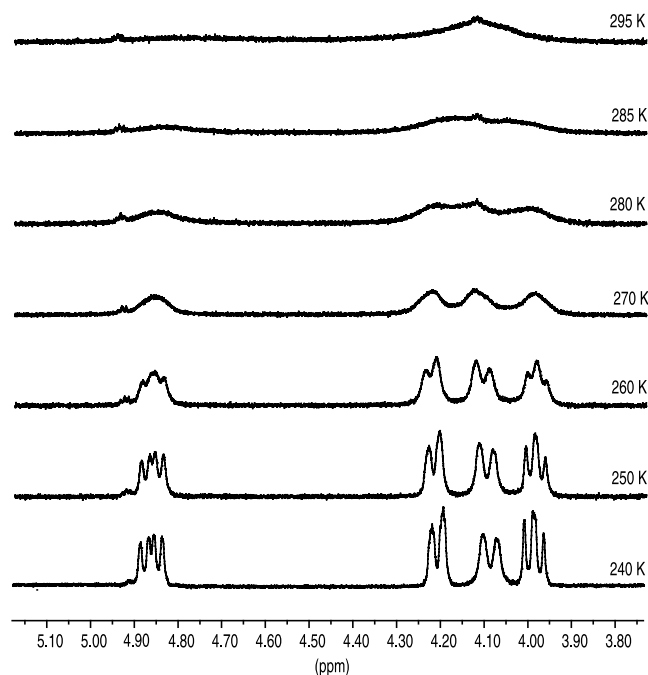


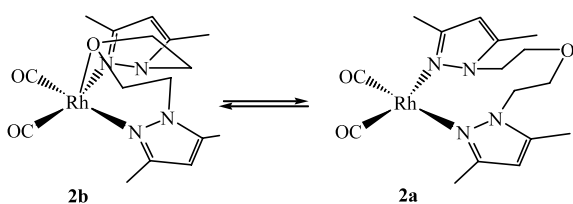
Fig. 4. 500 MHz ^1H -NMR variable temperature spectra (from 295 to 240 K) of the methylene region of cation $[\mathbf{2}]^+$ in $(\text{CD}_3)_2\text{CO}$ solution.

induce further significant change, except a slight broadening of the methylene resonances. These observations are consistent with a reversible opening of the Rh–O bond and imply, in accordance with the IR data, the existence in solution of both $[\text{Rh}(\text{CO})_2(\text{L}_1-\kappa^2\text{N},\text{N})]^+$ (**[2a]**⁺) and $[\text{Rh}(\text{CO})_2(\text{L}_1-\kappa^3\text{N},\text{N},\text{O})]^+$ (**[2b]**⁺) species in solution in a fast (NMR-time scale) equilibrium (Scheme 1). However, at 240 K the concentration of **[2a]**⁺ is certainly low as it has not been clearly detected by NMR.

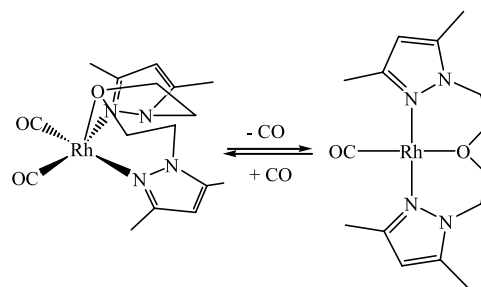
Attempts to crystallize **[2][BF₄]** under a nitrogen atmosphere led to $[\text{Rh}(\text{CO})(\text{L}_1-\kappa^3\text{N},\text{N},\text{O})][\text{BF}_4]$ (**[3][BF₄]**) in a nearly quantitative yield. Noticeably, this shows that **[2][BF₄]** is more easily decarbonylated than the parent complex $[\text{Rh}(\text{CO})_2(\text{L}_1-\kappa^3\text{N},\text{N},\text{N})][\text{BF}_4]$ as the later species requires refluxing conditions in THF to give $[\text{Rh}(\text{CO})(\text{L}_1-\kappa^3\text{N},\text{N},\text{N})][\text{BF}_4]$ **[1]**. Bubbling carbon monoxide through a solution of **[3][BF₄]** regenerates quantitatively **[2][BF₄]** (Scheme 2). The infrared spectrum of **[3][BF₄]** in dichloromethane solution shows a νCO absorption at 1994 cm^{-1} .

The solid state structure of **[3]**⁺ is shown on Fig. 5. Bond lengths and angles of interest are gathered in Table 1. The cation **[3]**⁺ exhibits a square planar geometry around Rh. Like in the known Cu(I), and Cd(II) complexes the ligand **L₁** adopts a ‘T-shaped’ coordination mode with a N(2)–Rh–N(12) angle of $173.2(2)^\circ$. The Rh–O(8) bond distance of $2.116(3)\text{ \AA}$ is very similar to the corresponding Rh–O bond distance in the related species $[\text{Rh}(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{PPh}_2)][\text{PF}_6]$ ($2.112(8)\text{ \AA}$) [13]. The Rh–N bond distances are significantly shorter than in **[1]**⁺ and **[2b]**⁺ but compares well with the corresponding Rh–N bond distances found in $[\text{Rh}(\text{CO})_2(\text{L}_1-\kappa^3\text{N},\text{N},\text{N})][\text{BF}_4]$ **[1]**. Finally, the distance Rh–C(1) of $1.795(5)\text{ \AA}$ is significantly shorter than the Rh–C(carbonyl) distances in **[2b]**⁺ ($1.843(3)$ and $1.856(2)\text{ \AA}$). Such a shortening can be attributed to a *trans* influence of the ether function.

Considering the solid state structure of the cation **[3]**⁺ it appears that the molecule possesses only a (non crystallographic) *C*₂ symmetry, the *C*₂ axis passing through the Rh(1) and O(8) atoms. This is apparently incompatible with the room temperature ¹H NMR data, which indicates that the molecule possesses higher symmetry in solution, the methylene groups giving rise to two triplets. As a matter of fact, lowering the temperature of the NMR experiments induces a pro-



Scheme 1.



Scheme 2.

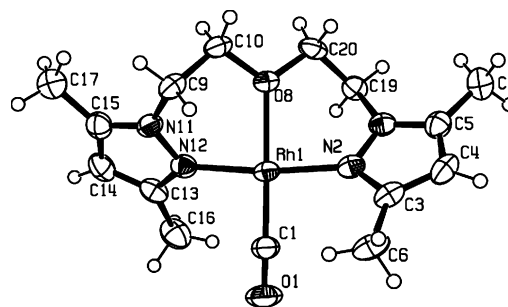


Fig. 5. Crystal structure of the cation **[3]**⁺ showing the numbering scheme; ellipsoids are drawn at the 30% probability level.

gressive broadening of the signals of the methylene groups until 230 K, a temperature at which two broad peaks at 3.96 and 4.85 ppm are observed. Further lowering to 190 K induces the appearance of a well-defined AA'BB' spin systems consistent with the solid-state structure. The coalescence behaviour of the AA'BB' systems yields an activation energy barrier of 44 kJ mol^{-1} for the observed dynamic process.

This low energy fluxional phenomenon, which renders equivalent the hydrogen atoms inside each methylene group, is certainly a conformational equilibrium of the six-membered chelate ring due to the rocking of the pyrazolyl cycles around the Rh–N bonds without any metal–ligand bond breaking. This has to be contrasted with the fluxional process observed for **[2]**⁺ due to the reversible opening of the Rh–O bond (*vide supra*) which is a higher energy process.

3. Conclusion

This study illustrates the ability of the ligand **L₁** to adopt different conformations and coordination modes when associated with rhodium(I). Notably, a facial $\kappa^3\text{N},\text{N},\text{O}$ mode of coordination has been evidenced in solid state structure of $[\text{Rh}(\text{CO})_2(\text{L}_1-\kappa^3\text{N},\text{N},\text{O})][\text{BF}_4]$ (**[2b][BF₄]**) and this constitutes the first example of such a bonding mode for that ligand. **L₁** exhibits hemilabile properties as in solution, **[2]**⁺ exists as a mixture of two isomers in which **L₁** is either $\kappa^2\text{N},\text{N}$ or $\kappa^3\text{N},\text{N},\text{O}$ -bonded to Rh. Due to the chelating properties

of L_1 and its preference for a meridional κ^3N,N,O bonding mode, decarbonylation of $[2]^+$ occurs easily at room temperature to produce $[Rh(CO)(L_1-\kappa^3N,N,O)][BF_4]$ ($[3][BF_4]$). As compared to the ligand L , the ligand L_1 shows a lower propensity to adopt a κ^3 mode of bonding due to the hardest nature of the oxygen of ether function. Indeed, the ligand L adopts a κ^3 mode of bonding in $[Rh(COD)(L-\kappa^3N,N,N)][BF_4]$ in spite of severe steric strains with the COD ligand $[1]$, whereas L_1 shows a κ^2 bonding mode in $[Rh(COD)(L_1-\kappa^2N,N)][BF_4]$ even though the steric strains are expected to be lower due to the longer chain between the pyrazole ring and the heteroatom donor.

4. Experimental

4.1. General remarks

All reactions were carried out under a nitrogen atmosphere with the use of vacuum line and standard Schlenk techniques. All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled before use by standard methods. The ligand bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether $[4]$ and $[Rh(COD)Cl]_2$ $[14]$ were prepared according to the published procedures. Routine NMR spectra were obtained on Bruker AC200 or AC250 spectrometers. The 1H -NMR variable temperature spectra were recorded on a Bruker DRX500 spectrometer. All chemical shift values (δ) are given in ppm and are referenced with respect to residual protons in the solvent for 1H spectra and to solvent signals for ^{13}C spectra. Elemental analyses (C, N, H) were performed by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Infrared spectra were recorded on a Perkin Elmer 2000 FT spectrophotometer.

4.2. Synthesis of $[Rh(COD)(L_1)][BF_4]$ ($[1][BF_4]$)

$AgBF_4$ (79 mg, 0.40 mmol) was added to a solution of $[Rh(COD)Cl]_2$ (100 mg, 0.20 mmol) in THF (20 ml). The solution was stirred for half an hour at room temperature (r.t.) and light protected. The orange solution turned yellow and $AgCl$ precipitated. The solution was filtered and L_1 (105 mg, 0.40 mmol) was then added. After stirring overnight, the solution was evaporated to dryness and the residue was re-crystallized at $-20^\circ C$ from a dichloromethane–ether mixture to yield yellow crystals in 87% yield. Anal. Calc. for $C_{22}H_{34}BF_4N_4ORh$ (560.25): C, 47.17; H, 6.07; N, 10.01. Found: C, 46.77; H, 6.11; N, 9.69%. 1H -NMR ($CDCl_3$ solution, 250 MHz) δ : 6.28 [m, $^2J = 15.9$ Hz, $^3J = 2.5$ Hz, $^3J = 11.8$ Hz, 2H, NCHH], 5.93 [s, 2H, CH pyrazole], 4.48 [m, $^2J = 15.9$ Hz, $^3J = 2.4$, $^3J = 0.6$, 2H,

NCHH], 4.26 [m, $^2J = 12.5$ Hz, $^3J = 2.5$ Hz, $^3J = 2.4$ Hz, 2H, OCHH], 4.14 [m, $^2J = 12.5$ Hz, $^3J = 11.8$ Hz, $^3J = 0.6$ Hz, 2H, OCHH], 3.90 [b, 2H, CH cod], 3.71 [b, 2H, CH cod], 2.90 [m, 2H, CHH_{exo} cod], 2.80 [s, 6H, CH_3], 2.56 [m, 2H, CHH_{exo} cod], 2.21 [s, 6H, CH_3], 1.89 [m, 4H, CHH_{endo} cod]. $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 62.9 MHz) δ : 148.4 (CCH_3), 142.9 (CCH_3), 108.9 (CH pyrazole), 84.4 (d, $J_{Rh-C} = 12$ Hz, =CH), 83.7 (d, $J_{Rh-C} = 12$ Hz, =CH), 72.9 (OCH_2), 54.0 (NCH $_2$), 30.6–30.1 (CH_2 cod), 16.0 (CH_3), 11.9 (CH_3).

4.3. Synthesis of $[Rh(CO)_2(L_1)][BF_4]$ ($[2][BF_4]$)

Carbon monoxide was bubbled for 2 h through a solution of $[1][BF_4]$ (100 mg) dissolved in dichloromethane (20 ml). The yellow solution turned dark yellow. The solution was then evaporated to dryness in vacuum to leave a dark yellow powder, which was re-crystallized in a dichloromethane–ether mixture under a CO atmosphere by cooling at $-20^\circ C$. Orange crystals corresponding to the isomer $[2b]^+$ were obtained in 60% yield. Anal. Calc. for $C_{16}H_{22}BF_4N_4O_3Rh$ (508.10): C, 37.82; H, 4.33; N, 11.03. Found: C, 37.57; H, 4.49; N, 10.43%. IR (CH_2Cl_2 solution) $\nu(CO)$: isomer $[2a]^+$: 2105(w), 2042(w) cm^{-1} ; isomer $[2b]^+$: 2090(s), 2022(s) cm^{-1} . 1H NMR ($(CD_3)_2CO$ solution at 240 K, 500 MHz) δ : 6.26 (s, 2H, CH pyrazole), 4.87 [dd, $^2J = 15.8$ Hz, $^3J = 9.5$ Hz, 2H, NCHH], 4.21 [d, $^2J = 12.0$ Hz, 2H, OCHH], 4.09 [d, $^2J = 15.8$ Hz, 2H, NCHH], 3.99 [dd, $^2J = 12.0$ Hz, $^3J = 9.5$ Hz, 2H, OCHH], 2.48 [s, 6H, CH_3], 2.38 [s, 6H, CH_3]. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$ solution, 62.9 MHz) δ : 182.8 (d, $J_{Rh-C} = 70.5$ Hz, CO), 152.4 (CCH_3), 145.9 (CCH_3), 108.9 (CH pyrazole), 71.4 (OCH_2), 51.2 (NCH $_2$), 16.2 (CH_3), 12.6 (CH_3).

4.4. Synthesis of $[Rh(CO)(L_1)][BF_4]$ ($[3][BF_4]$)

$[2][BF_4]$ was crystallized at $-20^\circ C$ in a dichloromethane–ether mixture under N_2 . Crystals of $[3][BF_4]$ were obtained as yellow needles. Anal. Calc. for $C_{15}H_{22}BF_4N_4O_2Rh$ (480.09): C, 37.52; H, 4.59; N, 11.67. Found: C, 37.30; H, 4.46; N, 11.24%. IR (CH_2Cl_2 solution) $\nu(CO)$: 1994(s) cm^{-1} . 1H NMR ($(CD_3)_2CO$ solution, 200 MHz) δ : 6.22 [s, 2H, CH pyrazole], 4.92 [t, $^3J = 4.5$ Hz, 4H, NCH $_2$], 4.09 [t, $^3J = 4.5$ Hz, 4H, OCH_2], 2.42 [s, 6H, CH_3], 2.37 [s, 6H, CH_3]. (CD_2Cl_2 solution at 190 K, 500 MHz) δ : 6.03 [s, 2H, CH pyrazole], 4.83 [dd, $^2J = 15.7$ Hz, $^3J = 11.6$ Hz, 2H, NCHH], 4.50 [d, $^2J = 15.7$ Hz, 2H, NCHH], 3.98 [d, $^2J = 9.5$ Hz, 2H, OCHH], 3.79 [dd, $^2J = 9.5$ Hz, $^3J = 11.6$ Hz, 2H, OCHH], 2.31 [s, 6H, CH_3], 2.30 [s, 6H, CH_3]. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$ solution, 62.9 MHz) δ : 186.2 (d, $J_{Rh-C} = 89.3$ Hz, CO), 152.7 (CCH_3), 144.5 (CCH_3), 108.4 (CH pyrazole), 73.1 (OCH_2), 48.6 (NCH $_2$), 15.3 (CH_3), 11.5 (CH_3).

4.5. X-ray crystallographic study

Crystals of [1][BF₄], [2b][BF₄] and [3][BF₄] suitable for X-ray diffraction were obtained through re-crystallization from dichloromethane–ether mixtures (under a CO atmosphere for [2b][BF₄]). Data were collected on a STOE IPDS diffractometer at 160 K for [1][BF₄] and [2b][BF₄] and at 293 K for [3][BF₄]. Full crystallographic data for the three complexes are gathered in Table 2. All calculations were performed on a personal computer using the WINGX system [15]. The structures were solved by using the SIR-92 program [16], which revealed in each instance the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses by using the SHELXS-97 program [17]. Atomic scattering factors were taken from the usual tabulations [18]. Anomalous dispersion terms for Rh atoms were included in Fc [19]. All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms were set in idealized position (R₃CH, C–H = 0.96 Å; R₂CH₂, C–H = 0.97 Å; RCH₃, C–H = 0.98 Å; C(sp²)–H = 0.93 Å; U_{iso} 1.2 or 1.5 times greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached).

Complex [1][BF₄] was found to crystallize with two independent pairs of ions per unit cell. The structure was best refined considering a racemic twin with a 0.41268/0.58732 relative contribution of the twin components. In addition, one of the BF₄ counter-anion was found to be disordered; a suitable model was found considering a rotation of ca. 30° of the F₄ tetrahedron around one of the B–F axis. In the structure of complex [3][BF₄] also the BF₄ counter-anion was found to be disordered; a suitable model was refined considering a head-to-tail arrangement of pairs of BF₄ units sharing a face of the F₄ tetrahedrons along an axis parallel to *a* axis. In addition, two strong residual peaks were observed in the final difference Fourier maps; these peaks were finally attributed to water molecule statistically distributed over two different sites in channels parallel to the *a* axis.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 208789–208791 for compounds [1][BF₄], [2b][BF₄] and [3][BF₄], respectively. Copies of this information may be obtained free of

Table 2
Crystal data for [1][BF₄], [2b][BF₄] and [3][BF₄]

Compound	[1][BF ₄]	[2b][BF ₄]	[3][BF ₄]
Empirical formula	C ₄₄ H ₆₈ B ₂ F ₈ N ₈ O ₂ Rh ₂	C ₃₂ H ₄₄ B ₂ F ₈ N ₈ O ₆ Rh ₂	C ₁₅ H ₂₂ BF ₄ N ₄ O ₃ Rh
Molecular weight (g)	1120.50	1016.19	480.09
Temperature (K)	160(2)	160(2)	293(2)
Wavelength (Å)	0.71073	–	–
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>Pca</i> 2 ₁ (no. 29)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)
Unit cell dimensions			
<i>a</i> (Å)	27.684(5)	8.1696(12)	4.6776(5)
<i>b</i> (Å)	7.942(5)	9.9445(15)	12.4521(15)
<i>c</i> (Å)	21.712(5)	12.8477(19)	17.720(2)
α (°)	90	87.839(18)	97.584(14)
β (°)	90	89.683(17)	92.555(13)
γ (°)	90	77.286(17)	99.906(13)
<i>V</i> (Å ³)	4774(3)	1017.5(3)	1005.4(2)
<i>Z</i>	4	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.559	1.658	1.639
μ (mm ⁻¹)	0.769	0.900	0.908
<i>F</i> (000)	2304	512	500
θ Range (°)	2.56–26.24	2.10–26.09	2.17–26.04
Index ranges	–34 ≤ <i>h</i> ≤ 34, –9 ≤ <i>k</i> ≤ 9, –26 ≤ <i>l</i> ≤ 26	–9 ≤ <i>h</i> ≤ 10, –12 ≤ <i>k</i> ≤ 12, –15 ≤ <i>l</i> ≤ 15	–5 ≤ <i>h</i> ≤ 5, –15 ≤ <i>k</i> ≤ 15, –21 ≤ <i>l</i> ≤ 21
Reflections collected	36028	8815	9936
Independent reflections	9369 [<i>R</i> _{int} = 0.0539]	3621 [<i>R</i> _{int} = 0.0223]	3668 [<i>R</i> _{int} = 0.0412]
Completeness to θ_{\max} (%)	98.4	89.7	91.3
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	9335/73/631	3621/0/266	3640/70/275
Goodness of fit on <i>F</i> ²	1.058	0.999	1.049
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0493, <i>wR</i> ₂ = 0.1240	<i>R</i> ₁ = 0.0261, <i>wR</i> ₂ = 0.0655	<i>R</i> ₁ = 0.0448, <i>wR</i> ₂ = 0.1136
<i>R</i> (all data)	<i>R</i> ₁ = 0.0509, <i>wR</i> ₂ = 0.1263	<i>R</i> ₁ = 0.0273, <i>wR</i> ₂ = 0.0662	<i>R</i> ₁ = 0.0576, <i>wR</i> ₂ = 0.1200
Residual electron density (e Å ⁻³)	2.497 and –0.826	0.842 and –0.614	1.120 and –0.568

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: http://www.ccdc.cam.ac.uk).

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Aqua(η^4 -1,5-cyclooctadiene)[1-(2-methoxyethoxymethyl)-3,5-dimethylpyrazole]rhodium(I) tetrafluoroborate

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å

R factor = 0.043

wR factor = 0.117

Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex, $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_2)(\text{H}_2\text{O})](\text{BF}_4)$ or $[\text{Rh}L(\text{COD})(\text{H}_2\text{O})](\text{BF}_4)$, is a monomer in the solid state. The Rh^{I} centre is in a square-planar arrangement. The four coordination sites are occupied by the N atom of the pyrazole ligand, the O atom from a water molecule and the centroids of the two cyclooctadiene olefin bonds. The structure is stabilized by hydrogen bonds between the coordinated water molecule and the two O atoms of the ether groups of the pyrazole ligand and one of the F atoms of the BF_4 unit.

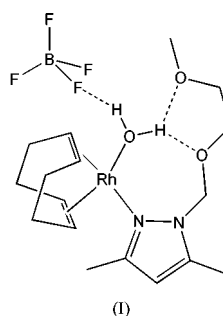
Received 17 July 2003

Accepted 22 July 2003

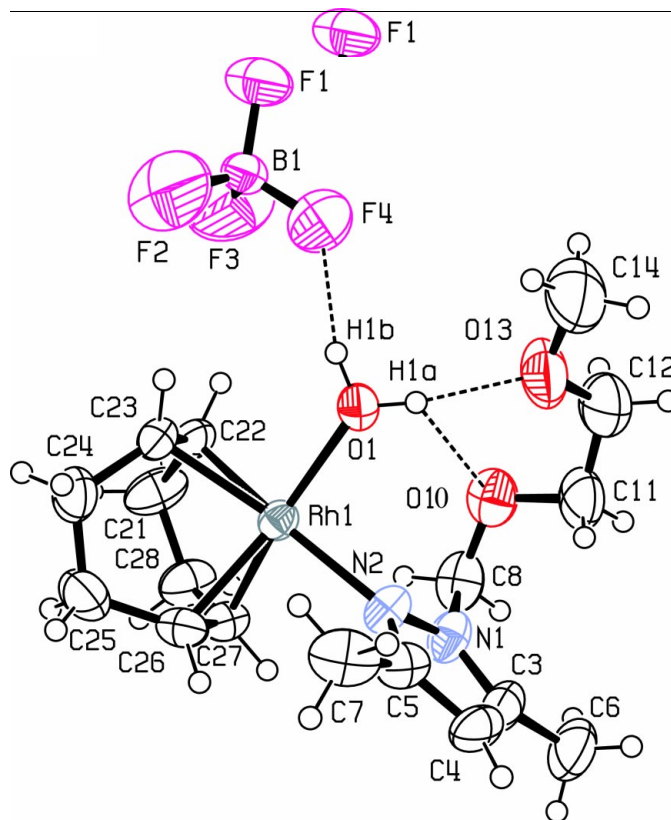
Online 31 July 2003

Comment

The organic compound 1-(2-methoxyethoxymethyl)-3,5-dimethylpyrazole (*L*) is a potential polydentate ligand that can coordinate to a metal centre by the unsubstituted N atom and by the O atoms of the ether groups. The reactivity of this ligand toward $[\text{RhCl}(\text{COD})]_2$ has been investigated with the aim of proving its chelating ability. This led to the formation of the title compound, $[\text{Rh}L(\text{COD})(\text{H}_2\text{O})](\text{BF}_4)$, (I).



The rhodium complex has a square-planar geometry (Fig. 1 and Table 1), the metal centre being linked to the four olefin C atoms of the 1,5-cyclooctadiene ligand, to the non-substituted N atom of the pyrazole ring, and to the O atom of a coordinated water molecule. The Rh atom lies 0.0052 (3) Å out of the coordination plane. It thus appears that *L* acts as a monodentate ligand, since the O atoms of the ether groups do not participate in the ligation to the metal centre. Intramolecular hydrogen bonds are observed between atoms O10 and O13 of the pendant ether arm and the coordinated water molecule [$\text{O10}\cdots\text{H1a} = 2.64$ (3) Å and $\text{O13}\cdots\text{H1a} = 1.89$ (2) Å]. As a result of these intramolecular interactions, a stable seven-membered ring including Rh1 is formed. In addition, a hydrogen bond between one of the F atoms of the BF_4 unit and the water molecule is also observed [$\text{F4}\cdots\text{H1b} = 1.91$ (2) Å]. The Rh1–N2 bond length in (I) [2.103 (3) Å] is equal, within experimental error, to the Rh–N bond length



The structure of the title compound, showing the numbering scheme.

Figure 1 displacement ellipsoids drawn at the 30% probability level.

The structure of the title compound, showing the numbering scheme, with displacement ellipsoids drawn at the 30% probability level.

[2.109 (9) Å] found in the parent compound

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yellow solution, *L* (0.061 g, 0.34 mmol) was added. The solution was stirred overnight at room temperature. The solvent was then removed

under reduced pressure, yielding a yellow oil. The oil was dissolved in

a dichloromethane/diethyl ether mixture and small yellow crystals of

the complex $[\text{Rh}(\text{COD})(\text{H}_2\text{O})(\text{BF}_4)]$ were obtained upon standing

at room temperature. $^1\text{H NMR}$ (250 MHz, CDCl_3 , p.p.m.): δ 6.05 (s,

2H, NCH_2O), 5.93 (s, 1H, CH (pyrazole)), 4.07 (br, 2H, H_2O), 3.75

(s, 3H, OCH_3), 2.76 (s, 3H, CCH_3), 2.51 (br, 2H, $\text{CH}_2(\text{COD})$), 2.32 (s,

2H, NCH_2O), 1.93 (s, 1H, CH (pyrazole)), 1.47 (br, 2H, H_2O), 1.32

(s, 3H, OCH_3), 2.76 (s, 3H, CCH_3), 2.51 (br, 2H, $\text{CH}_2(\text{COD})$), 2.32

(s, 2H, NCH_2O), 1.93 (s, 1H, CH (pyrazole)), 1.47 (br, 2H, H_2O), 1.32

(s, 3H, OCH_3), 2.76 (s, 3H, CCH_3), 2.51 (br, 2H, $\text{CH}_2(\text{COD})$), 2.32

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(s, 2H, NCH_2O), 1.93 (s, 1H, CH (pyrazole)), 1.47 (br, 2H, H_2O), 1.32

metal-organic papers

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1a...O10	0.852 (18)	2.64 (3)	3.166 (4)	121 (3)
O1—H1a...O13	0.852 (18)	1.89 (2)	2.729 (5)	167 (4)
O1—H1b...F4	0.845 (18)	1.91 (2)	2.731 (5)	164 (4)

H atoms attached to C atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (CH), 0.97 (CH₂) and 0.97 Å (CH₃), and an isotropic displacement parameter equal to 1.2 times U_{eq} of the parent atom. The H atoms of the water molecule were located at the final stage of the refinement using the program *HYDROGEN* (Nardelli, 1999); their isotropic displacement parameters were set to 1.2 times U_{eq} of the O atom and they were held fixed during the final refinement.

Data collection: *IPDS* (Stoe & Cie, 2000); cell refinement: *IPDS*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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