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Study of the reactivity of tris(pyrazolyl)amine and bis(pyrazolyl)amine ligands toward Rh(I). Crystal structure of $[Rh_3Cl_3(cod)_3\mathbf{tdma}]\cdot CH_3CN$ (**tdma** = tris[(3,5-dimethyl-1-pyrazolyl)methyl]amine), a C_3-symmetric compound

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Abstract

Rh(I) compounds $[Rh_2Cl_2(cod)_2\mathbf{L}]$ (**L** = tris[(1-pyrazolyl)methyl]amine (**tpma**) (**1**), tris[2-(1-pyrazolyl)ethyl]amine (**tpea**) (**2**), tris[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (**tdea**) (**3**), bis[2-(1-pyrazolyl)ethyl]amine (**bpea**) (**4**) and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (**bdea**) (**5**)), and $[Rh_3Cl_3(cod)_3\mathbf{tdma}]$ (**tdma** = tris[3,5-dimethyl-1-pyrazolyl)methyl]amine (**6**), have been prepared, and characterised by elemental analyses, conductivity, IR, ^1H and ^{13}C NMR spectroscopy and liquid mass spectrometry (with electrospray and APCI interfaces). The ^1H NMR spectra and molar conductance of $[Rh_2Cl_2(cod)_2\mathbf{L}]$ complexes suggested the presence of 1:1 electrolyte species $[Rh(cod)\mathbf{L}]^+$ $[RhCl_2(cod)]^-$ in solution. A combined electrospray and APCI liquid mass spectrometry study confirmed the presence of both $[Rh(cod)\mathbf{L}]^+$ and $[RhCl_2(cod)]^-$ ions in solution, but the neutral molecular form of complexes in solution was not found. The crystal structure of complex $[Rh_3Cl_3(cod)_3\mathbf{tdma}]$ was resolved by X-ray diffraction. The molecular structure is unusual and consists of a ligand **tdma** coordinated to three "RhCl(cod)" units with a C_3-symmetry.

Keywords: Rhodium complexes; Pyrazole complexes; Trinuclear complex; Crystal structure; C_3-symmetry

1. Introduction

The increasing interest in chelating polydentate nitrogen-donor ligands, especially for heterocyclic compounds, is based on the occurrence of such systems in nature [1,2].

Special attention is given to pyrazole derivatives. In our laboratory, a several N1-substituted pyrazolic ligands have been prepared and complexed to metallic atoms. In particular, *N*-aminoalkylpyrazoles have been coordinated to Rh(I) [3–7].

We report here the study of a family of ligands, tris(pyrazolyl)amines and bis(pyrazolyl)amines, which have a similar configuration to that found for uninegative poly(1-pyrazolyl)borates and neutral poly(1-pyrazolyl)methanes [8–12].

A large variety of pyrazole derivatives, tris(pyrazolyl)amines and bis(pyrazolyl)amines can now be prepared though novel methods [10,13,14].

Tris(pyrazolyl)amines are tripodal and potentially tetradentate, whereas bis(pyrazolyl) amines are potentially tridentate. The coordinative properties of these ligands were studied in detail.

Tris[(1-pyrazolyl)methyl]amine (**tpma**) [13,15,16], tris[(3,5-dimethyl-1-pyrazolyl)methyl]amine (**tdma**) [16], tris[2-(1-pyrazolyl)ethyl]amine (**tpea**) [17], tris[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (**tdea**) [18], bis[2-(1-pyrazolyl)ethyl]amine (**bpea**) and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (**bdea**) [19] have been reported elsewhere (Fig. 1). The reaction of these ligands with

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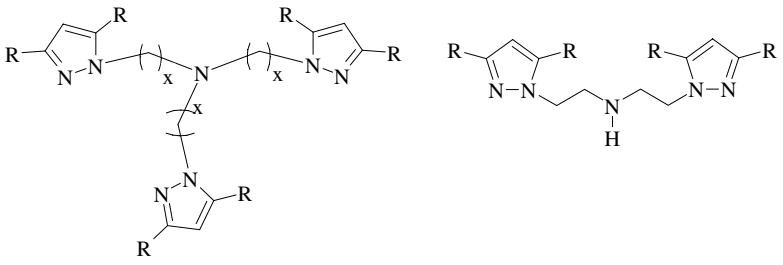

R = H, x = 1; **tpma**
R = CH_3, x = 1; **tdma**
R = H, x = 2; **tpea**
R = CH_3, x = 2; **tdea**

R = H; **bpea**
R = CH_3; **bdea**

Fig. 1. Pyrazole derived ligands.

$[RhCl(cod)]_2$ gave complexes $[Rh_2Cl_2(cod)_2\mathbf{L}]$ (**L** = **tpma** (**1**), **tpea** (**2**), **tdea** (**3**), **bpea** (**4**), **bdea** (**5**)), which were fully characterised. In contrast, for the ligand **tdma** we obtained a trichloro complex $[Rh_3Cl_3(cod)_3\mathbf{tdma}]$ (**6**). The crystal structure of complex **6** is also reported.

2. Experimental

2.1. General methods

All the reactions were performed under a nitrogen atmosphere following standard Schlenk techniques. Solvents were dried and distilled under N_2 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 methanol and acetonitrile, employing a CyberScan CON 500 (Euthech Instruments) conductimeter. Infrared spectra were run on a Perkin Elmer FT spectrophotometer, serie 2000 as KBr or polyethylene pellets in the range 4000–100 cm^{-1}. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a NMR-FT Bruker 250 MHz spectrometer in $CDCl_3$ solutions at room temperature (^1H, 250 MHz; ^{13}C, 62.9 MHz). All chemical shifts were referenced to the residual signals of the protons of the solvents and were quoted in ppm downfield from TMS. 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 CH_3CN at a 0.2 ml min^{-1} flow rate. The samples were dissolved in CH_3CN 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 were: (a) positive electrospray: capillary at 4200 V; potentials: DP = 20 V; FP = 200 V; EP = −10 V, the mass range measured was between 100 and 950 u.m.a in full scan mode, cycle time was 2 s and the source temperature 200 °C. (b) negative electrospray: capillary at −4200 V potentials: DP = −25; FP = −200 V; EP = 10 V, the mass range measured was between 50 and 500 u.m.a in full scan mode, cycle time was 1 s and the source temperature 200 °C. The $[RhCl(cod)]_2$ [20] (cod = cycloocta-1,5-diene) has been prepared according to published method.

2.2. Synthesis of the metal complexes

2.2.1. Complexes $[Rh_2Cl_2(cod)_2\mathbf{L}]$ (where **L** = **tpma** (**1**); **tpea** (**2**); **tdea** (**3**); **bpea** (**4**); **bdea** (**5**))

The coordination compounds were prepared dissolving 0.070g (0.142 mmol) of $[RhCl(cod)]_2$ in 5 ml of dichloromehane and adding this solution to a solution of the appropriate ligand **L** (0.142 mmol) (**tpma**, 0.037 g; **tpea**, 0.043 g; **tdea**, 0.056 g; **bpea**, 0.037 g; **bdea**, 0.048 g) dissolved in 5 ml of the same solvent. The mixture was stirred at r.t. for 6 h and concentrated on a vacuum line. The yellow-orange solids were filtered, washed twice with 5 ml of diethyl ether and recrystalised in a dichloromethane/hexane (1:1) mixture.

1 (yield 93%) $C_{28}H_{39}N_7Cl_2Rh_2$: *Anal. Calc.*: C, 44.82; H, 5.24; N, 13.07. Found: C, 44.30; H, 4.93; N, 12.88%. Conductivity (Ω^{-1} cm^2 mol^{-1}): 79.8 (1.10 mmol in MeOH), 29.5 (1.23 mmol in MeCN). IR: (KBr, cm^{-1}): 3093 ν(C–H)$_{ar}$, 2937–2832 ν(C–H ligand + cod)$_{al}$, 1516 ν(C=C), C=N), 1460 $\delta(CH_3)_{as}$ ligand/δCH_2) cod, 1410 δ(C=C ligand + cod, C=N), 1365 $\delta(CH_3)_s$, 1097–997 δ(C–H ligand + cod)ip, 820, 762 δ(C–H ligand + cod)$_{oop}$; (polyethylene, cm^{-1}): 352 ν(Rh–N), 279, 254 ν(Rh–Cl). ^1H NMR ($CDCl_3$ solution, 250 MHz) δ: 7.53 [b, 6H, C*H*], 6.29 [t, 3H, C*H*], 5,62 [b, 6H, NCH_2], 4.19 [b, 8H, =C*H* cod], 2.47 [b, 8H, CH*H* exo cod], 1.81 [b, 8H,

CHH_{endo} cod]. $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 62.9 MHz) δ: 140.6 (CH_{pz}), 132.6 (CH_{pz}), 107.0 (CH_{pz}), 78.8 (*C*H(cod)), 73.9 (N*C*H$_2$), 31.2 (*C*H$_2$(cod)). ES(+) MS (*m*/*z*): 468 (100%) [Rh(cod)**tpma**]$^+$; ES(−) MS (*m*/*z*): 285 (6%), 283 (35%), 281 (100%) [$RhCl_2$(cod)]$^-$.

2 (yield 65%) $C_{31}H_{45}N_7Cl_2Rh_2$: *Anal. Calc.*: C, 46.99; H, 5.72; N, 12.37. Found: C, 47.13; H, 5.86; N, 12.30%. Conductivity (Ω^{-1} cm^2 mol^{-1}): 79.5 (1.21 mmol in MeOH), 86.0 (1.17 mmol in MeCN). IR: (KBr, cm^{-1}): 3102 ν(C–H)$_{ar}$, 2938–2832 ν(C–H ligand + cod)$_{al}$, 1514 ν(C=C, C=N), 1432 $\delta(CH_3)_{as}$ ligand/$\delta(CH_2)$ cod, 1397 δ(C=C ligand + cod, C=N), 1362 $\delta(CH_3)_s$, 1091–966 δ(C–H ligand + cod)ip, 817, 753 δ(C–H ligand + cod)$_{oop}$; (polyethylene, cm^{-1}): 351 ν(Rh–N), 279, 254 ν(Rh–Cl). ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ: 7.48 [b, 6H, C*H*], 6.09 [s, 3H, C*H*], 3.88 [b, 6H, NCH_2], 4.62 [b, 8H, =C*H* cod], 2.94 [b, 6H, NCH_2], 2.42 [b, 8H, CH*H* exo cod], 1.78 [b, 8H, CHH_{endo} cod]. $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 62.9 MHz) δ: 139.8 (CH_{pz}), 131.2 (CH_{pz}), 105.2 (CH_{pz}), 85.1 (*C*H(cod)), 54.9 (N*C*H$_2$), 50.8 (N*C*H$_2$), 31.7 (*C*H$_2$(cod)), 30.7 (*C*H$_2$(cod)), 15.2 (*C*H$_3$), 10.4 (*C*H$_3$). ES(+) MS (*m*/*z*): 510 (100%) [Rh(cod)**tpea**]$^+$; ES(−) MS (*m*/*z*): 285 (14%), 283 (65%), 281 (100%) [$RhCl_2$(cod)]$^-$.

3 (yield 71%) $C_{37}H_{57}N_7Cl_2Rh_2$: *Anal. Calc.*: C, 50.70; H, 6.54; N, 11.18. Found: C, 51.27; H, 6.68; N, 11.98%. Conductivity (Ω^{-1} cm^2 mol^{-1}): 74.4 (1.35 mmol in MeOH), 59.0 (1.26 mmol in MeCN). IR: (KBr, cm^{-1}): 3136 ν(C–H)$_{ar}$, 2923–2832 ν(C–H ligand + cod)$_{al}$, 1554 ν(C=C, C=N), 1464 $\delta(CH_3)_{as}$ ligand/$\delta(CH_2)$ cod, 1426 δ(C=C ligand + cod, C=N), 1358 $\delta(CH_3)_s$, 1068–964 δ(C–H ligand + cod)ip, 818, 777 δ(C–H ligand + cod)$_{oop;}$ (polyethylene, cm^{-1}): 375 ν(Rh–N), 279, 254 ν(Rh–Cl). ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ: 5.74 [d, 3H, C*H*], 3.83 [b, 6H, NCH_2], 4.65 [b, 8H, =C*H* cod], 2.88 [b, 6H, NCH_2], 2.17 [b, 8H, CH*H* exo cod], 2.23 [s, 9H, CH_3], 2.32 [s, 9H, CH_3], 1.74 [b, 8H, CHH_{endo} cod]. $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 62.9 MHz) δ: 148.5 (CH_{pz}), 139.5 (CH_{pz}), 105.2 (CH_{pz}), 85.1 (*C*H(cod)), 55.3 (N*C*H$_2$), 47.5 (N*C*H$_2$), 33.2 (*C*H$_2$(cod)), 29.3 (*C*H$_2$(cod)), 13.8 (*C*H$_3$), 11.3 (*C*H$_3$). ES(+) MS (*m*/*z*): 594 (100%) [Rh(cod)**tdea**]$^+$; ES(−) MS (*m*/*z*): 285 (6%), 283 (53%), 281 (100%) [$RhCl_2$(cod)]$^-$.

4 (yield 75%) $C_{26}H_{39}N_5Cl_2Rh_2$: *Anal. Calc.*: C, 44.72; H, 5.63; N, 10.03. Found: C, 44.32; H, 5.35; N, 9.82%. Conductivity (Ω^{-1} cm^2 mol^{-1}): 73.3 (1.18 mmol in MeOH), 22.4 (1.43 mmol in MeCN). IR: (KBr, cm^{-1}): 3102 ν(N–H), 2932–2832 ν(C–H ligand + cod)$_{al}$, 1516 ν(C=C, C=N), 1432 $\delta(CH_3)_{as}$ ligand/$\delta(CH_2)$ cod, 1409 δ(C=C ligand + cod), δ(C=N), 1367 $\delta(CH_3)_s$, 1095–962 δ(C–H ligand + cod)ip, 818, 760 δ(C–H ligand + cod)$_{oop}$; (polyethylene, cm^{-1}): 371 ν(Rh–N), 280, 256 ν(Rh–Cl). ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ: 7.53 [d, 2H, C*H*], 7.46 [d, 2H, C*H*], 6.27 [t, 2H, C*H*], 4.64 [b, 4H, NCH_2], 4.18 [b, 8H, =C*H* cod], 3.22 [b, 4H, NCH_2], 2.43 [b, 8H, CH*H* exo cod], 1.77 [b, 8H, CHH_{endo} cod]. $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 62.9 MHz) δ: 140.3 (CH_{pz}), 129.0 (CH_{pz}), 106.9 (CH_{pz}), 80.3 (*C*H(cod)), 51.7 (N*C*H$_2$), 50.5 (N*C*H$_2$), 31.2 (*C*H$_2$(cod)), 28.4 (*C*H$_2$(cod)). ES(+) MS (*m*/*z*): 416 (100%) [Rh(cod)**bpea**]$^+$; ES(−) MS (*m*/*z*): 285 (18%), 283 (65%), 281 (100%) [$RhCl_2$(cod)]$^-$.

5 (yield 74%) $C_{30}H_{47}N_5Cl_2Rh_2 \cdot H_2O$: *Anal. Calc.*: C, 47.76; H, 6.28; N, 9.28. Found: C, 47.82; H, 6.15; N, 8.89%. Conductivity (Ω^{-1} cm^2 mol^{-1}): 76.6 (1.32 mmol in MeOH), 36.5 (1.24 mmol in MeCN). IR: (KBr, cm^{-1}): 3192 ν(N–H), 2918–2834 ν(C–H ligand + cod)$_{al}$, 1554 ν(C=C, C=N), 1437 $\delta(CH_3)_{as}$ ligand/(CH$_2$) cod, 1384 δ(C=C ligand + cod), δ(C=N), 1362 $\delta(CH_3)_s$, 977 δ(C–H ligand + cod)ip, 818, 772 δ(C–H ligand + cod)$_{oop}$; (polyethylene, cm^{-1}): 350 ν(Rh–N), 277, 259 ν(Rh–Cl). ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ: 5.80 [s, 2H, C*H*], 4.83 [b, 4H, NCH_2], 4.10 [b, 8H, =C*H* cod], 3.35 [b, 4H, NCH_2], 2.39 [b, 8H, CH*H* exo cod], 2.30 [s, 12H, CH_3], 1.74 [b, 8H, CHH_{endo} cod]. $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 62.9 MHz) δ: 148.7 (CH_{pz}), 141.3 (CH_{pz}), 106.8 (CH_{pz}), 79.6 (*C*H(cod)), 50.1 (N*C*H$_2$), 48.2 (N*C*H$_2$), 31.1 (*C*H$_2$(cod)), 28.3 (*C*H$_2$(cod)), 14.5 (*C*H$_3$), 11.8 (*C*H$_3$). ES(+) MS (*m*/*z*): 488 (100%) [Rh(cod)**bdea**]$^+$; ES(−) MS (*m*/*z*): 285 (15%), 283 (41%), 281 (100%) [$RhCl_2$(cod)]$^-$.

2.2.2. Complex [$Rh_3Cl_3(cod)_3$(**tdma**)] (**6**)

A total of 0.105 g (0.213 mmol) of [RhCl(cod)]$_2$ dissolved in 5 ml of dichloromethane, were added to a solution of 0.048 g (0.142 mmol) of **tdma** in 5 ml of dichloromethane and the mixture was stirred at r.t. for 6h. The solvent was evaporated to dryness in vacuo and the residue was washed with diethyl ether and dissolved in a minimum amount of dichloromethane. Adding hexane to the solution precipitated the compound. The yellow-orange solid was filtered off dried in vacuo washed twice with 5 ml of diethyl ether and recrystalised in a dichloromethane/hexane (1:1) mixture. This complex has also been obtained using 1M:1L and 2M:1L stoichiometries, though with smaller yields (51% and 58%, respectively, referenced to rhodium).

6 (yield 65%) $C_{42}H_{63}N_7Cl_3Rh_3$: *Anal. Calc.*: C, 46.66; H, 5.83; N, 9.07. Found: C, 46.96; H, 6.03; N, 9.04%. Conductivity (Ω^{-1} cm^2 mol^{-1}): 43.6 (1.18 mmol in MeOH), 54.3 (1.35 mmol in MeCN). IR: (KBr, cm^{-1}): 3119–3091 ν(C–H)$_{ar}$, 2915–2831 ν(C–H ligand + cod)$_{al}$, 1517 ν(C=C, C=N), 1447–1428 $\delta(CH_3)_{as}$ ligand/(CH$_2$) cod, 1386–1375 δ(C=C) ligand + cod, δ(C=N), 1366 $\delta(CH_3)_s$, 1123–906 δ(C–H ligand + cod)ip, 822, 736 δ(C–H ligand + cod)$_{oop}$; (polyethylene, cm^{-1}): 370 ν(Rh–N), 278, 254 ν(Rh–Cl). ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ: 5.78 [s, 3H, C*H*], 4.97 [s, 6H, NC*H* $_2$], 4.23 [b, 12H, =C*H* cod], 2.50 [b, 12H, CH*H* exo cod], 1.83 [s, 9H, CH_3], 2.19 [s, 9H, CH_3], 1.75 [b, 8H, CHH_{endo} cod]. $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 62.9 MHz) δ: 149.7 (CH_{pz}), 144.0 (*C* H_{pz}), 108.2 (CH_{pz}), 86.5–74.9

Table 1
Crystal data for compound [Rh_3Cl_3**tdma**] (**6**)

Formula	$C_{44}H_{66}Cl_3N_8Rh_3$
M	1122.13
System	Trigonal
Space group	$P\bar{3}$
a (Å)	13.4112(9)
b (Å)	13.4112(9)
c (Å)	15.5410(10)
γ (°)	120
U (Å^3)	2420.7(3)
Z	2
D_c (g cm^{-3})	1.539
μ (mm^{-1})	1.215
$F(000)$	1144
Crystal size (mm^3)	$0.2 \times 0.3 \times 0.2$
hkl Ranges	−18 to 18, 0 to 13, −22 to 22
2θ Range (°)	1.75–28.93
Reflections collected/unique	9854, 4143 [R(int) = 0.0432]
Data, restraints, parameters	4143, 2, 191
Final $R1$, $wR2$	0.0588, 0.1479
$R1$, (all data), $wR2$	0.0904, 0.1632
Largest diff. peak, hole (e Å^{-3})	+0.232, −0.614

(*C*H(cod)), 66.4 (N*C*H$_2$), 33.9–28.8 (*C*H$_2$(cod)), 15.2 (*C*H$_3$), 10.4 (*C*H$_3$).

2.3. X-ray crystal structure analyses

Suitable crystals for X-ray diffraction experiments of compound **6** were obtained through recrystallisation from acetonitrile. Data were collected on a MAR-345 diffractometer and measured at room temperature (293(2) K) using graphite-monochromatised Mo-Kα radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods (SHELX 97) [21] and refined by full-matrix least square methods (SHELX 97) [22].

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, which they are linked to. The weigh was $\omega = [\sigma^2(I) + (0.0917P)^2 + 0.8857P]^{-1}$ where $P = (|F_o|^2 + 2|F_c|^2)/3$. The final R(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

The reaction of the rhodium(I) [RhCl(cod)]$_2$ complex with tris(pyrazolyl)amines (**tpma**, **tpea**, **tdea**, **tdma)** and bis(pyrazolyl) amines (**bpea**, **bdea)** in a 1:1 molar ratio in CH_2Cl_2 solution led to [Rh_2Cl_2(cod)**L**] (**L** = **tpma** (**1**), **tpea** (**2**), **tdea** (**3**), **bpea(4)**, **bdea(5)**) and [Rh_3Cl_3(cod)$_3$**L**] (**L** = **tdma** (**6**). In both cases, this occurred irrespective of the molar ratio M:L used.

These compounds were characterised by elemental analyses, IR and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, conductivity measurements and electrospray mass spectrometry. The elemental analyses correspond to the stoichiometries [Rh_2Cl_2(cod)**L**] (**1**–**5**) and [Rh_3Cl_3(cod)$_3$**L**] (**6**). IR spectra of complexes in KBr pellets in the range 4000–400 cm^{-1} display absorptions of tris(pyrazolyl)amines, bis(pyrazolyl)amines and cod ligands. The characteristic ν(C=C) and ν (C=N) absorption for the pyrazolyl group in the complexes **1**–**6** appears at 1554–1514 cm^{-1} whereas the δ(C=C) and δ(C=N) bands are observed at 1426–1375 cm^{-1}, which are lower energies than in the free ligands [23,24]. The IR spectra of complexes **4**–**5** show moderated shifts of the ν(N–H) band 3102 and 3192 cm^{-1}, respectively [5,25]. The presence of chlorides coordinated to rhodium atoms is shown in the IR spectra in the range 600–100 cm^{-1}, with the appearance of two bands in each spectrum around 280 and 255 cm^{-1}, respectively, corresponding to the ν(Rh–Cl) [26].

The ^{1}H NMR spectra of complexes **1**–**6** are in accordance with the presence of tris(pyrazolyl)amine or bis(pyrazolyl)amine [13] and cod ligands [5,27]. On the other hand, the corresponding signal of the N*H* hydrogen for complexes **4**, **5** could not be assigned.

In the ^{1}H NMR spectrum of **6** only one sharp signal for each type of proton is observed, whereas for complexes **1**–**5** the signals of the ^{1}H NMR spectra are broad.

In the complexes **1**–**5** the cod resonances appear as broad signals, which could not be resolved at low temperatures. This can be attributed to the presence of different "Rh(cod)" forms in solution or a possible reorientation of the coordinated cod ligand, as has been established in pyrazolate rhodium (I) complexes [27]. The ^{13}C NMR spectra of complexes show resonances for the carbon atoms of the tris(pyrazolyl)amines or bis(pyrazolyl)amines and cod ligands. No significant differences between ^{13}C NMR spectra of the free and coordinated tris(pyrazolyl)amines and bis(pyrazolyl)amines were observed. The corresponding signals of the diolefinic ligand show the expected ^{13}C chemical shifts [5,27]. In complexes **1**–**5** molar conductivity in MeOH is between neutral molecules and 1:1 electrolytes, whereas in complex **6** molar conductivity in MeOH corresponds to a neutral molecule. The neutrality of compounds **1**–**6** is obvious in acetonitrile [28,29].

The broad signals observed in the ^{1}H NMR spectra of the [Rh_2Cl_2(cod)$_2$**L**] (**1**–**5**) complexes synthesised are consistent with the presence of both ionic [Rh(cod)**L**]$^+$ [$RhCl_2$(cod)]$^-$ and neutral forms in solution. The equilibrium between binuclear neutral and ionic forms which was suggested for related *NN*′ bidentate ligands and *NN*′*N* tridentate ligands [5,6,30–32] (Fig. 2) could not be resolved by NMR data.

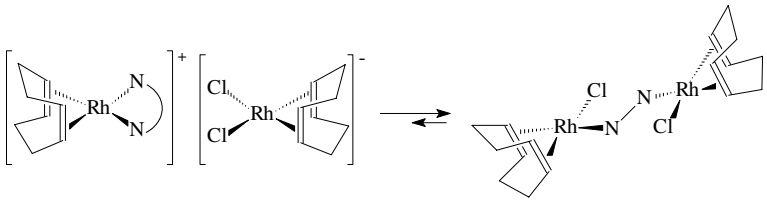

Fig. 2. Equilibrium in solution proposed for complexes **1**–**5**.

The obtention of two different stoichiometries should be caused by steric requirements of ligands. Thus, tris-pyrazolyl ligands containing an ethylenic chain between N amine and N pyrazole or those 3,5 unsubstituted, form $[Rh_2Cl_2(cod)\mathbf{L}]$ complexes. Bis-pyrazolyl ligands led to same type of products. These ligands have less steric requirements when act as chelates. On the contrary, **tdma** ligand contains a short CH_2 link between nitrogens and methyl groups in 3,5 positions also. These facts restrict chelation, leading to the formation of $[Rh_3Cl_3(cod)_3\mathbf{tdma}]$ complex, where **tdma** act as a non-chelating ligand.

Since efforts to grow crystals from solutions of complexes $[Rh_2Cl_2(cod)_2\mathbf{L}]$ were unsuccessful, we recorded electrospray mass spectra of complexes **1**–**5** in acetonitrile in order to confirm the presence of those ions in solution. This technique is effective for the study of inorganic complexes in solution, allowing ions present in solution to be observed in the mass spectra [33,34]. The positive ionisation spectra of (**1**–**5**) complexes gave peaks with *m*/*z* values of 468 $[Rh(cod)\mathbf{tpma}]^+$, 510 $[Rh(cod)\mathbf{tpea}]^+$, 594 $[Rh(cod)\mathbf{tdea}]^+$, 416 $[Rh(cod)\mathbf{bpea}]^+$, 488 $[Rh(cod)\mathbf{bdea}]^+$ (molecular peaks of the cation). The negative ionisation spectra of (**1**–**5**) complexes gave peaks with *m*/*z* values of 281, 283, 285 $[RhCl_2(cod)]^-$ (molecular peaks of the anion). In order to identify the molecular complexes of the type $[Rh_2Cl_2(cod)\mathbf{L}]$ we also recorded the APCI (atmospheric pressure chemical ionisation) mass spectra of complexes **1**–**5.** This technique shows a different peaks of some cationic and anionic species: $[Rh(cod)\mathbf{L}]^+$, $[Rh(cod)]^+$ and $[RhCl_2(cod)]^-$. Mass spectrometry also failed to show peaks corresponding to the molecular complex $[Rh_2Cl_2(cod)\mathbf{L}]$.

3.2. Crystal and molecular structure of complex $[Rh_3Cl_3(cod)_3\mathbf{tdma}]\,CH_3CN$ (**6**)

The molecular structure of the new complex was determined by X-ray diffraction (Fig. 3) and selected bond distances and angles are listed in Table 2. It is unusual and consists of a trinuclear complex containing one tris[3,5-dimethyl-1-pyrazolyl)methyl]amine (**tdma**) ligand, three diolefins (cod), three Cl^- anions and solvent acetonitrile molecule with a ternary axis through an N1, C1–N1–C1# angle of 109.9(3)°.

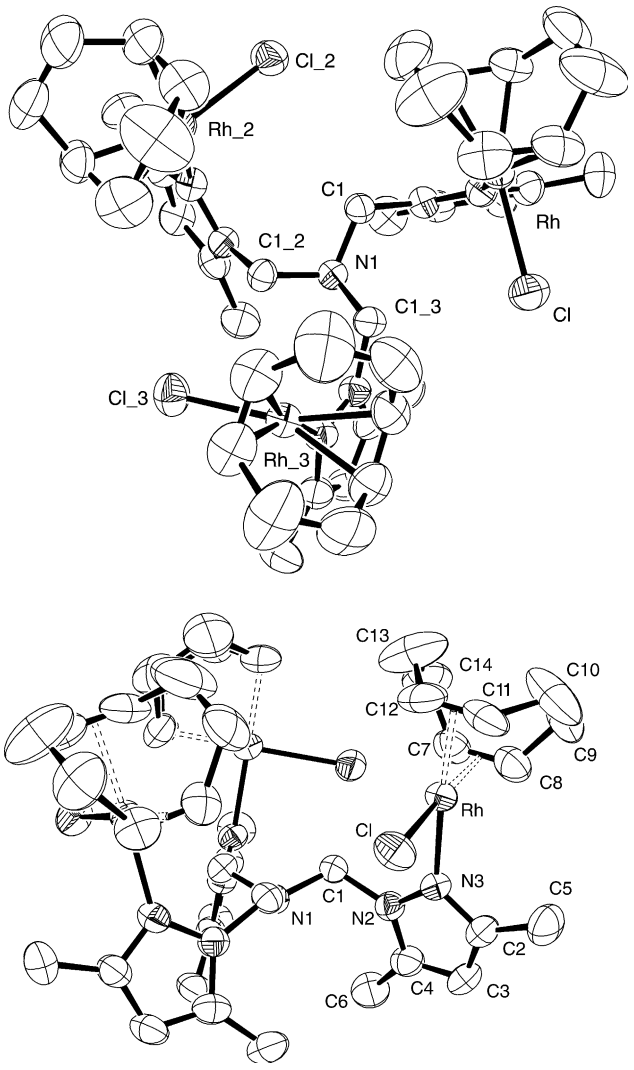

Fig. 3. Different perspectives of crystal structure of the complex $[Rh_3Cl_3(cod)_3\mathbf{tdma}]CH_3CN$ (**6**); ellipsoids are drawn at the 50% probability level.

The metal atom is surrounded by an identical *core* composed of the pyrazole nitrogen of the ligand, one chlorine atom, and one cycloocta-1,5-diene. Therefore the ligand acts in a tridentate fashion, through three pyrazole nitrogens.

A slightly distorted square-planar geometry is observed around the Rh(I) [considering the midpoints of the olefin bonds (Mp)]. The rhodium atoms deviates

Table 2
Selected bond lengths (Å) and angles (°) for **6** with estimated standard deviations (e.s.d.s) in parentheses

Rh–N(3)	2.114(4)	Rh–C(7)	2.114(5)
Rh–C(8)	2.110(5)	Rh–C(12)	2.123(5)
Rh–C(11)	2.130(5)	Rh–Cl	2.3728(13)
C(8)–Rh–N(3)	90.95(19)	C(7)–Rh–C(11)	95.1(3)
C(8)–Rh–C(7)	37.7(2)	C(12)–Rh–C(11)	37.8(3)
N(3)–Rh–C(7)	92.78(19)	C(8)–Rh–Cl	157.94(17)
C(8)–Rh–C(12)	92.8(3)	N(3)–Rh–Cl	88.52(11)
N(3)–Rh–C(12)	164.9(2)	C(7)–Rh–Cl	164.35(16)
C(7)–Rh–C(12)	81.4(3)	C(12)–Rh–Cl	93.4(2)
C(8)–Rh–C(11)	82.5(2)	C(11)–Rh–Cl	89.59(12)
N(3)–Rh–C(11)	157.2(2)		

Table 3
Cell parameters for complex **6**

	1M:1L	2M:1L	3M:1L
a (Å)	13.510(4)	13.498(2)	13.40(2)
b (Å)	13.53(2)	13.510(2)	13.42(2)
c (Å)	15.53(1)	15.516(2)	15.52(2)
γ (°)	120.005(5)	119.7(2)	119.8(1)
U (Å^3)	2458	2456	2419

from the coordination plane MClMpMp′ by −0.069 Å. The intramolecular separations Rh···Rh are 6.264(3) Å.

The Rh–N(3) [35–37], Rh–Cl [35,37–40], and Rh–C(diolefinics) (cod) [3–5,7,41] bond lengths are of the same order as those found in the literature. The Cl–Rh–N3 angle (88.52(11)°) is significantly smaller than those found in the literature for similar compounds [89.6–92.3°] [36,38].

Twelve structures of Rh(I) trinuclear complexes have been described. Three of these structures have one C_3 axis. These complexes are $[\{Rh(cod)\}_3(\mu_3\text{-}H)\{\mu_3\text{-}C(CH_2)_3\}]$ [42], $[RhCl\{Se(CH_2CH_2CH{=}CH_2)_2\}]_3$ [40], and [1,3,5,-$C_6H_3\{CH{=}C{=}RhCl(P^iPr_3)_2\}_3$] [39].

Complex **6** crystallised always as a sole product using 1M:1L, 2M:1L, and 3M:1L stoichiometries. In this way, suitable crystals for X-ray diffraction experiments were obtained for the three syntheses through crystallisation from CH_2Cl_2/diethyl ether (1:1) mixture. We measured cell parameters of one crystal from each synthesis. Cell parameters are given in Table 3.

4. Conclusions

We have synthesised new Rh(I) complexes containing tris(pyrazolyl)amine and bis(pyrazolyl)amine ligands. In both cases we obtained $[Rh_2Cl_2(cod)_2\mathbf{L}]$ (**L** = **tpma** (**1**), **tpea** (**2**), **tdea** (**3**), **bpea** (**4**), **bdea** (**5**)) except for the ligand **tdma**, for which we obtained $[Rh_3Cl_3(cod)_3\mathbf{L}]$. Differences in stoichiometry of products could be caused by steric hindrance, due to the presence in **tdma** of methyl groups in 3,5 positions and short N–CH_2–N chain between the pyrazolyl groups. Molar conductivity values suggest that complexes $[Rh_2Cl_2(cod)_2\mathbf{L}]$ are a 1:1 electrolytes in solution and NMR data agree with a bidentate coordination of the ligands. To confirm the presence of those ionic species we recorded positive and negative electrospray mass spectra of the compounds. The results confirmed the presence of $[Rh(cod)\mathbf{L}]^+$ and $[RhCl_2(cod)]^-$ in solution.

The structure of $[Rh_3Cl_3(cod)_3\mathbf{tdma}]$ was determined by X-ray diffraction, showing an unusual C_3-symmetry of complex.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 224153 for compound **6**. 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: diposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] E.C. Constable, P.J. Steel, Coord. Chem. Rev. 93 (1989) 205.
[2] H. Beinert, Coord. Chem. Rev. 33 (1980) 55.
[3] G. Esquius, J. Pons, R. Yáñez, J. Ros, X. Solans, M. Font-Bardia, J. Organomet. Chem. 605 (2000) 226.
[4] G. Esquius, J. Pons, R. Yáñez, J. Ros, X. Solans, M. Font-Bardia, Acta Crystallogr. C58 (2002) m133.
[5] G. Esquius, J. Pons, R. Yáñez, J. Ros, J. Organomet. Chem. 619 (2001) 14.
[6] R. Mathieu, G. Esquius, N. Lugan, J. Pons, J. Ros, Eur. J. Inorg. Chem. (2001) 2683.
[7] G. Esquius, J. Pons, R. Yáñez, J. Ros, R. Mathieu, B. Donnadieu, N. Lugan, Eur. J. Inorg. Chem. (2002) 2999.
[8] S. Trofimenko, Chem. Rev. 72 (1972) 497.
[9] S. Trofimenko, Adv. Chem. Ser. 150 (1976) 289.
[10] S. Trofimenko, Prog. Inorg. Chem. 34 (1986) 115.
[11] S. Trofimenko, Chem. Rev. 93 (1993) 943.
[12] N. Kitajima, W.B. Tolman, Prog. Inorg. Chem. 43 (1995) 419.
[13] W.L. Driessen, Recl. Trav. Chim. Pays-Bas 101 (1982) 441.
[14] R. Mukherjee, Coord. Chem. Rev. 203 (2000) 151.
[15] W.L. Driessen, W.G.R. Wiesmeijer, M. Schipper-Zablotskaja, R.A.G. de Graaff, J. Reedijk, Inorg. Chim. Acta 162 (1989) 233.
[16] G.J. van Driel, W.L. Driessen, J. Reedijk, Inorg. Chem. 24 (1985) 2919.
[17] T.N. Sorrell, D.J. Jameson, Inorg. Chem. 21 (1982) 1014.
[18] T.N. Sorrell, D.L. Jameson, C.J. O'Connor, Inorg. Chem. 23 (1984) 190.
[19] C.F. Martens, A.P.H.J. Schenning, M.C. Feiters, H.W. Berens, J.G.M. vander Linden, G. Admiraal, P.T. Beurskens, H. Kooijman, A.L. Spek, R.J.M. Nolte, Inorg. Chem. 34 (1995) 4735.

[20] G. Giordano, R.H. Crabtree, Inorg. Synth. 19 (1979) 218.
[21] G.M. Sheldrick, SHELXS 97. Program for Crystal Structure Determination, University of Göttingen, Germany, 1997.
[22] G.M. Sheldrick, SHELXL 97. Program for Crystal Structure Determination, University of Göttingen, Germany, 1997.
[23] J. Pons, X. López, E. Benet, J. Casabó, F. Teixidor, J.F. Sánchez, Polyhedron 9 (1990) 2839.
[24] A. Chadghan, J. Pons, A. Caubet, J. Casabó, J. Ros, A. Alvarez-Larena, J.F. Piniella, Polyhedron 19 (2000) 855.
[25] M. Hesse, H. Maier, B. Zeeh, Spectroscopic Methods in Organic Chemistry, Thieme Verlag, Berlin, Germany, 1987.
[26] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fourth ed., Wiley, New York, USA, 1986.
[27] M. Cano, J.V. Heras, M. Maeso, M. Alvaro, R. Fernández, E. Pinilla, J.A. Campo, A. Monge, J. Organomet. Chem. 534 (1997) 159.
[28] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
[29] L.K. Thompson, F.L. Lee, E.J. Gabe, Inorg. Chem. 27 (1988) 39.
[30] B. Crociani, F. di Bianca, M. Paci, T. Boschi, Inorg. Chim. Acta 145 (1988) 253.
[31] H.T. Dieck, J.J. Klaus, J. Organomet. Chem. 246 (1983) 301.
[32] E. Anzuela, M.A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla, M.A. Monge, Inorg. Chim. Acta 185 (1991) 211.
[33] W. Henderson, G.M. Olsen, Polyhedron 17 (1998) 577.
[34] J.L. Wedgwood, A.P. Hunter, R.A. Kresinski, A.W.G. Platt, B.K. Stein, Inorg. Chim. Acta 290 (1999) 189.
[35] L.A. Oro, M.T. Pinillos, C. Tejel, J. Chem. Soc., Dalton Trans. (1988) 1927.
[36] L.A. Oro, M.A. Ciriano, F. Viguri, A. Tiripicchio, M. Tiripicchio-Camellini, F.J. Lahoz, New J. Chem. (1986) 75.
[37] L.A. Oro, M.T. Pinillos, C. Tejel, C. Foces-Foces, F.H. Cano, J. Chem. Soc., Chem. Commun. (1984) 1687.
[38] L.A. Oro, M.T. Pinillos, C. Tejel, J. Chem. Soc., Dalton Trans. (1986) 1087.
[39] H. Werner, P. Bachmann, M. Laubender, O. Gevert, Eur. J. Inorg. Chem. (1998) 1217.
[40] E.W. Abel, D.G. Evans, J.R. Koe, V. Sik, M.B. Hursthouse, M. Mazid, Polyhedron 11 (1992) 401.
[41] M.A. Ciriano, J.J. Pérez-Torrente, F.J. Lahoz, L.A. Oro, J. Chem. Soc., Dalton Trans. (1992) 1831.
[42] G.E. Herberich, U. Englert, L. Wasemann, P. Hofmann, Angew. Chem. Int. Ed. Engl. 30 (1991) 313.