

Synthesis and characterization of $[\text{Rh}^{\text{III}}\text{Cl}_2(\eta^1\text{-C}_6\text{H}_5)(\text{PYR})_2(\text{SbPh}_3)]$, $[\text{Rh}^{\text{III}}\text{Cl}_2(\eta^1\text{-C}_6\text{H}_5)(\text{PY})_2(\text{THZ})]$, $[\text{Rh}^{\text{III}}\text{Cl}_2(\eta^1\text{-C}_6\text{H}_5)(\text{PY})_2(\text{PYR})]$, and $[\text{Rh}^{\text{III}}\text{Cl}_2(\eta^1\text{-C}_6\text{H}_5)(\text{CEP})(\text{SbPh}_3)_2]$ [PYR = pyrazine; PY = pyridine; THZ = thiazole; CEP = N-(2-cyanoethylpyrrole)]. Crystal and molecular structure of $[\text{Rh}^{\text{III}}\text{Cl}_2(\eta^1\text{-C}_6\text{H}_5)(\text{PYR})_2(\text{SbPh}_3)]$ and $[\text{Rh}^{\text{III}}\text{Cl}_2(\eta^1\text{-C}_6\text{H}_5)(\text{PY})_2(\text{THZ})]$

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Abstract—The mononuclear compounds *trans*-dichloro(η^1 -phenyl)*cis*-bis(pyrazine)(triphenylstibine)rhodium(III) (**1**), and *trans*-dichloro(η^1 -phenyl){N-(2-cyanoethylpyrrole)}*trans*-bis(triphenylstibine)rhodium(III) (**3**) were prepared from *trans*-dichloro(η^1 -phenyl)tris(triphenylstibine)rhodium(III) in ethanol. The mononuclear compounds *trans*-dichloro(η^1 -phenyl)*trans*-bis(pyridine)(thiazole)rhodium(III) (**2**) and *trans*-dichloro(η^1 -phenyl)*trans*-bis(pyridine)(pyrazine)rhodium(III) (**4**) were obtained from *trans*-dichloro(η^1 -phenyl)tris(pyridine)rhodium(III) in methanol. Compounds **1** and **2** were analysed *via* X-ray diffraction techniques from single crystals. The four compounds were characterized by spectroscopy and elemental analysis. The coordination sphere geometry for all the complexes is octahedral; the *trans* influence exerted by the phenyl ligand is responsible for a long Rh—N bond distance (2.263(3) Å) and of large downfield shifts for ¹H NMR signals. The pyrazine ligands are monodentate in both **1** and **4**. In the solid state the pyrazine ligands do not bridge the metal centres. Compounds **1** and **2** are barely stable in solution at room temperature. The thiazole molecule of **2** binds the metal through the nitrogen atom whereas sulfur does not show any donating ability. An extended-Hückel analysis shows that the pyrazine ligands contribute significantly to the frontier unoccupied molecular orbitals. The atomic charges on the non-metal bound nitrogen atoms of pyrazine ligands is −0.175 e in agreement with a bridging ability between two metal centres for this ligand. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: rhodium; antimony; pyrazine; thiazole; pyrrole; pyridine; phenyl.

Rhodium complexes with pyridines and their analogues have attracted the curiosity of many groups for a variety of reasons, some of which are: the ability to act as intercalators for nucleic acids [1] and to be involved in supramolecular interactions with bio-

logical systems [2], the photochemical and photophysical properties [3], the catalytic activities [4], the antimicrobial and anticancer activities [5].

The synthesis and the characterisation of $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{SbPh}_3)_3]$ from the reaction of RhCl_3 and excess triphenylstibine performed in this laboratory a few years ago [6,7], opened an interesting route for the preparation of a variety of organometallic compounds

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of rhodium(III) and pyridine (or its analogues). The preparation of different organometallic compounds through a few step-high yield syntheses from $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{SbPh}_3)_3]$ is mostly due to the different degree of removability of the three triphenylstibine molecules from the coordination sphere because of the differences in the *trans*-effects and -influences of $\eta^1\text{-Ph}$ and SbPh_3 . On continuing the investigation of new coordination and organometallic compounds of rhodium we succeeded in the synthesis and characterisation of new derivatives obtained from $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{SbPh}_3)_3]$. Here we report on the synthesis, X-ray structural characterisation, spectroscopy and molecular orbital analysis of the title compounds.

EXPERIMENTAL

Materials

$\text{RhCl}_3 \times \text{H}_2\text{O}$ (Janssen or Aldrich); $\text{Ag}(\text{CF}_3\text{SO}_3)$, triphenylstibine (SbPh_3 , Fluka); pyridine (PY, Erba); pyrazine (PYR, Aldrich); thiazole (THZ, Janssen) and *N*-(2-cyanoethylpyrrole) (CEP, Janssen) were used without any further purifications. $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{SbPh}_3)_3]$ and $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{PY})_3]$ were obtained by following the procedure reported in refs [6] and [7].

Synthesis

$[\text{RhCl}_2(\eta^1\text{-Ph})(\text{PYR})_2(\text{SbPh}_3)]$ (1). A mixture of $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{SbPh}_3)_3] \times \text{C}_2\text{Cl}_4$ (0.17 mmol, 0.250 g) and excess PYR (0.51 mmol, 0.750 g) in absolute ethanol (50 mL) was refluxed, under stirring, for 1 h: a yellow solution was obtained. A red microcrystalline solid formed by cooling to room temperature; it was filtered off, washed with cold ethanol, ether and then air dried. Yield, 52 mg, 40%. Found: C, 49.77; H, 3.63; N, 7.28. Calc. for $\text{C}_{32}\text{H}_{28}\text{Cl}_2\text{N}_4\text{RhSb}$, $[\text{RhCl}_2(\text{C}_6\text{H}_5)\{\text{Sb}(\text{C}_6\text{H}_5)_3\}(\text{C}_4\text{H}_4\text{N}_2)_2]$ (Mw, 764.1): C, 50.29; H, 3.69; N, 7.33.

^1H NMR data (CDCl_3): δ = 9.22 (2H, *ortho* protons of PYR *trans* to Ph), 8.95 (2H, *ortho* protons of PYR *cis* to Ph), 8.58 (2H, *meta* protons of PYR *trans* to Ph), 8.32 (2H, *mc*, *meta* protons of PYR *cis* to Ph); 8.55, free PYR.

The solid is soluble, at least, in ethanol, acetone and ethylacetate, but is stable in solution only if free pyrazine is present. Red single crystals suitable for a X-ray diffraction analysis, were obtained by slow evaporation, at room temperature, of a solution of the crude compound and free PYR in ethylacetate.

$[\text{RhCl}_2(\eta^1\text{-Ph})(\text{PY})_2(\text{THZ})]$ (2). A boiling solution of $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{PY})_3]$ (0.7 mmol, 0.340 g) in absolute ethanol (100 mL), was mixed with THZ (35 mmol, 3.0 g); the final yellow solution was refluxed and stirred for 2 h. On concentration, the solution produced big yellow needles, suitable for X-ray diffraction analysis. The crystals were separated from the solution, washed with ethanol and then air dried. Yield,

138 mg, 40%. Found: C, 47.13; H, 3.60; N, 8.58. Calc. for $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{N}_3\text{RhS}$, $[\text{RhCl}_2(\text{C}_6\text{H}_5)(\text{C}_5\text{H}_5\text{N})_2(\text{C}_3\text{H}_3\text{NS})]$ (Mw, 494.4): C, 46.15; H, 3.67; N, 8.50. ^1H NMR data (CDCl_3): δ = 9.54 (1H, H(2) THZ), 8.53 (1H, H(5)), 7.49 (1H, H(4)), 8.54–8.52 (4H, *ortho*, PY), 7.69–7.61 (4H, *meta*) 7.11–7.04 (2H, *para*); 8.88 (H(2)), 7.98 (H(5)), 7.42 (H(4)), free THZ; 8.59 (*ortho*), 7.66 (*para*), 7.27 (*meta*), free PY.

$[\text{RhCl}_2(\eta^1\text{-Ph})(\text{PYR})(\text{PY})_2]$ (3). A mixture of $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{PY})_3]$ (0.7 mmol, 0.340 g), PYR (12 mmol, 0.960 g) and EtOH (30 mL) was refluxed for 1 h under stirring and then cooled to room temperature. The crystalline yellow precipitate was filtered, washed with EtOH and Et_2O and then stored in the air and finally under vacuum at 25°C. Yield, 137 mg, 40%. Found: C, 49.48; H, 3.67; N, 11.18. Calc. for $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{N}_4\text{Rh}$ (Mw, 489.2): C, 49.10; H, 3.92; N, 11.45.

^1H NMR data (CDCl_3): δ = 8.86 (4H, PYR, broad), 8.57–8.54 (4H, *ortho*), 7.75–7.67 (4H, *meta*), 7.16–7.10 (2H, *para*).

$[\text{RhCl}_2(\eta^1\text{-Ph})(\text{CEP})(\text{SbPh}_3)_2]$ (4). A suspension of $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{SbPh}_3)_3] \times \text{C}_2\text{Cl}_4$ (0.34 mmol, 0.500 g) and CEP (58 mmol, 7 g) in MeOH (150 mL) was refluxed under stirring for 1 h. A crystalline yellow solid formed. The mixture was cooled to room temperature and the solid was filtered, washed with MeOH and Et_2O and then stored in the air and finally under vacuum. Yield, 197 mg, 60%. Found: C, 53.52; H, 4.00; N, 2.46. Calc. for $\text{C}_{49}\text{H}_{53}\text{Cl}_2\text{N}_2\text{RhSb}_2$ (Mw, 965.7): C, 54.06; H, 4.02; N, 2.60.

^1H NMR data (CDCl_3): δ = 6.56 (2H), 6.14 (2H), 3.77 (2H), 2.41 (2H); 6.70 (2H), 6.19 (2H), 4.14 (2H), 2.71 (2H) free CEP.

Crystal structure determination

$[\text{RhCl}_2(\eta^1\text{-Ph})(\text{PYR})_2(\text{SbPh}_3)]$ (1). A well formed red prism (0.10 × 0.20 × 0.20 mm) was selected and mounted on a glass fibre for the X-ray data collection. Crystallographic data are reported in Table 1. Unit-cell parameters were obtained by least-squares refinement of the values of 36 carefully centered and randomly selected reflections ($9 < 2\theta < 40^\circ$). The intensities were corrected for Lorentz, polarization and absorption effects (ψ -scan technique).

The structure solution and refinement were performed through Patterson and Fourier methods. All the atoms (including hydrogen atoms) were located through the Fourier-difference map. The Rh, Sb, Cl, N and C atoms were treated anisotropically; the isotropic thermal parameters of the H atoms were fixed at 1.2 times the values of $U(\text{eq})$ of the C atoms to which they are linked. The scattering factors were those of SHELX86 [8] and SHELX93 [9]. All the calculations were carried out on VAX 6610 and OLIDATA-Pentium machines, using SHELXs and PARST [10] computer packages.

$[\text{RhCl}_2(\text{Ph})(\text{PY})_2(\text{THZ})]$ (2). A yellow needle

Table 1. Crystal data and structure refinement for 1 and 2

Empirical formula	C ₃₂ H ₂₈ Cl ₂ N ₄ RhSb	C ₁₉ H ₁₈ Cl ₂ N ₃ RhS
Formula weight	764.14	494.23
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Tetragonal
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>I</i> 4 ₁ /acd
<i>a</i> (Å)	9.791(2)	15.672(3)
<i>b</i> (Å)	27.082(2)	15.672(3)
<i>c</i> (Å)	11.5610(10)	16.959(6)
β (°)	96.760(10)	
Volume (Å ³)	3044.2(7)	4165(2)
<i>Z</i>	4	8
<i>D_c</i> (Mg/m ³)	1.667	1.576
Abs. Coeff. (mm ⁻¹)	1.633	1.184
<i>F</i> (000)	1512	1984
Crystal size (mm)	0.10 × 0.20 × 0.20	0.90 × 0.80 × 0.70
$\theta_{\min}$ (°)	2.58	3.14
$\theta_{\max}$	24.99	25.00
Index ranges	0 ≤ <i>h</i> ≤ 11, 0 ≤ <i>k</i> ≤ 32, -13 ≤ <i>l</i> ≤ 13	0 ≤ <i>h</i> ≤ 18, 0 ≤ <i>k</i> ≤ 18, 0 ≤ <i>l</i> ≤ 20
Reflections collected	5682	1759
Independent reflections	5357 [<i>R</i> (int) = 0.0137]	923 [<i>R</i> (int) = 0.0692]
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5341/0/452	912/5/60
Goodness-of-fit on <i>F</i> ²	1.060	1.074
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0289, <i>wR</i> 2 = 0.0609	<i>R</i> 1 = 0.0411, <i>wR</i> 2 = 0.0916
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0441, <i>wR</i> 2 = 0.0676	<i>R</i> 1 = 0.0879, <i>wR</i> 2 = 0.1160
Largest diff. peak and hole (e Å ⁻³)	0.593 and -0.565	0.602 and -0.491

(0.20 × 0.20 × 0.70 mm) was selected and mounted on a glass fiber for the X-ray crystallographic analysis (see Table 1 for details). The unit-cell parameters were obtained by least squares refinement of the values of 51 randomly selected reflections ($9 < 2\theta < 40^\circ$). The intensities were corrected for Lorentz, polarization and absorption effects (ψ -scan technique).

The structure was solved using a 'trial and error' procedure to locate the metal atom in a special position. The Rh atom was located at the crossing point of three two-fold axis; thus there is a statistical disorder in the crystal lattice. The scattering factors of all the equatorial donors were assigned the value relevant to nitrogen. The occupancy factors (S.O.F.) of the equatorial ligands atoms were fixed as follows: 1, C(2) and C(6); 0.75, C(3), C(4) and C(5); 0.25, S(1) and C(7). The atoms Rh, Cl, N, C(2), C(4), C(6) were treated anisotropically. All the H atoms were set in calculated positions *via* the AFIX options of SHELX93; H(7) was not located because of the disorder. The thermal parameters of the H atoms were fixed at 1.2 times the *U*(eq) value of the C atom to which they are linked. The distances S(1)—C(2), S(1)—C(7) and C(4)—C(3), C(4)—C(5), C(6)—C(7) were fixed at 1.70(1) and 1.39(1) Å, respectively.

Spectroscopy

The IR spectra were recorded through the KBr pellet technique on a FT-IR Perkin-Elmer model 1600

spectrometer. The ¹H NMR spectra were recorded at 200 MHz by a Brüker AC-200 spectrometer.

EH-MO Calculations

A molecular orbital investigation carried out through the extended-Hückel method implemented in the INPUTC&ICONC [11] package was performed for compound 1. The parameters used were those standard in the program. The distance-dependent weighted Wolfsberg-Helmholz formula [11,12] was used. The molecular geometry was that obtained *via* X-ray diffraction at the solid state and it was not optimized. The axis set has been reported below (Results and Discussion). The graphics results were obtained *via* the package CACAO [13] implemented on an OLIDATA-Pentium computer.

Molecular mechanics

Molecular mechanics calculations were carried out *via* the MacroModel 3.0 package [14] implemented on a VAX6610 computer connected to an Evans & Sutherland graphic terminal. The strain energy was computed as the sum $E_{\text{tot}} = E_b + E_\theta + E_\phi + E_{\text{nb}} + E_{\text{hb}}$ (stretching, bending and torsional deformations, non bonding and hydrogen bonding interactions, respectively). The force field used was AMBER [15] included

in the MacroModel package properly modified to simulate the coordination spheres of Rh and Sb. Other details for the procedure used in this work as well as the force field parameters relevant to Rh and Sb atoms are those reported in ref [7].

RESULTS AND DISCUSSION

X-ray crystallography

Bond lengths and angles for **1** and **2** are reported in Table 2 and Table 3, respectively. The coordination sphere is pseudo-octahedral for both the compounds (see also Figs 1 and 2). The metal center is linked to two chloride ions *trans* to each other (axial positions) and to a η^1 -phenyl ligand. The other three equatorial positions are occupied by a SbPh_3 and two PYR ligands in **1**, and by a THZ and two PY ligands in **2**.

The largest deviation from idealised values of 180 and 90° for the coordination sphere of **1** is shown by the N(12)—Rh—Sb angle [170.75(8)°]; correspondingly N(12) deviates 0.400(3) Å from the least squares plane of Cl(1)/Cl(2)/Sb/N(12). The Rh atom deviates of 0.3059(3) Å from the least-squares plane defined by N(12)/C(22)/C(32)/N(42)/C(52)/C(62).

The Rh—Cl bond distances average 2.349(1) and 2.345(2) Å for **1** and **2**, respectively, in good agreement with previously reported values for analogues compounds [7,16,17] and for other rhodium(III) complexes such as $[\text{RhCl}_3(\text{DMSO})_3]$ (2.312(1)–2.342(2) Å) [18] and $[\text{Rh}_2\text{Cl}_6(\text{PEt}_3)_4]$ (average, 2.330(5) Å) [19].

The Rh—C and Rh—Sb bond lengths for **1** are 2.042(3) and 2.5313(5) Å, respectively, also in good agreement with the values found for $[\text{Rh}^{\text{III}}\text{Cl}_2(\eta^1\text{-Ph})(\text{NCMe})(\text{SbPh}_3)_2]$ [16] and $[\text{Rh}^{\text{III}}\text{Cl}_2(\eta^1\text{-Ph})(\text{SbPh}_3)_3]$ (2.09(2); 2.58(2) Å, Sb *trans* to Sb) [6]. The Rh—C(N) bond length for **2** is 2.0845(5) (Å 2.088(4) Å for $[\text{RhCl}_2(\eta^2\text{-Ph})(\text{PY})_3]$) [6]. These values for Rh^{III} —C bond distances compare well with those previously reported for $[\text{Rh}\{2\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O}\}_2\text{Cl}(\text{CO})]$ (1.984(4), *trans* to O; 2.041(3), *trans* to Cl) [20]. Rh—C bond distances of 2.01(1) and 2.08(1) Å (C *trans* to C) have been reported for $[\text{Rh}^{\text{III}}(\text{C}_6\text{F}_5)_3(\text{PEt}_3)_2]$ [21].

The Rh—N bond lengths for **1** are 2.263(3) [N(11)] and 2.155(3) [N(12)], and show that the *trans*-influence of $\eta^1\text{-Ph}$ is larger than that attributable to Sb. It has to be noted that Rh—N(sp²) bonds *trans* to other nitrogen donors are much shorter: 2.020(8) Å (average) for $[\text{Rh}(2,9\text{-diamino-4,7-diazadecane})(9,10\text{-phenanthrenequinonediimine})]^{3+}$ [1] and 2.07(2) Å (average) for $[\text{RhCl}_3(\text{oxazolinylpyridine})]$ [4c]. Both the PYR molecules are strictly planar [largest deviation, 0.008(5) Å for C(32)] and the angle between the two planes is 69.6(1)°. The two PYR ligands are in a staggered position with respect to the Rh—Cl bonds; Cl(1)—Rh—N(11)—C(61) and Cl(1)—Rh—N(12)—C(62) torsion angles are 24.0(1) and −30.7(1)°, respectively.

Table 2. Selected bond lengths (Å) and angles (°) for **1**

Rh—C(1)	2.042(3)
Rh—N(12)	2.155(3)
Rh—N(11)	2.263(3)
Rh—Cl(1)	2.3410(10)
Rh—Cl(2)	2.3564(10)
Rh—Sb	2.5313(5)
Sb—C(1P2)	2.125(4)
Sb—C(1P1)	2.127(4)
Sb—C(1P3)	2.136(4)
N(11)—C(61)	1.334(5)
N(11)—C(21)	1.334(5)
N(12)—C(22)	1.327(5)
N(12)—C(62)	1.330(5)
N(41)—C(51)	1.314(7)
N(41)—C(31)	1.321(8)
N(42)—C(52)	1.317(5)
N(42)—C(32)	1.325(6)
C(1)—C(6)	1.390(5)
C(1)—C(2)	1.392(5)
C(2)—C(3)	1.379(6)
C(3)—C(4)	1.371(6)
C(4)—C(5)	1.374(6)
C(5)—C(6)	1.385(6)
C(22)—C(32)	1.361(6)
C(52)—C(62)	1.384(6)
C(21)—C(31)	1.383(7)
C(51)—C(61)	1.393(7)
C(1)—Rh—N(12)	86.33(12)
C(1)—Rh—N(11)	178.70(13)
N(12)—Rh—N(11)	92.72(11)
C(1)—Rh—Cl(1)	90.90(10)
N(12)—Rh—Cl(1)	91.18(8)
N(11)—Rh—Cl(1)	88.23(9)
C(1)—Rh—Cl(2)	93.08(10)
N(12)—Rh—Cl(2)	92.75(8)
N(11)—Rh—Cl(2)	87.84(9)
Cl(1)—Rh—Cl(2)	174.58(4)
C(1)—Rh—Sb	84.96(10)
N(12)—Rh—Sb	170.75(8)
N(11)—Rh—Sb	96.04(8)
Cl(1)—Rh—Sb	92.07(3)
Cl(2)—Rh—Sb	84.63(3)
C(1P2)—Sb—C(1P1)	102.48(14)
C(1P2)—Sb—C(1P3)	100.35(14)
C(1P1)—Sb—C(1P3)	101.51(14)
C(1P2)—Sb—Rh	117.27(10)
C(1P1)—Sb—Rh	116.65(10)
C(1P3)—Sb—Rh	115.98(10)
C(61)—N(11)—C(21)	116.1(4)
C(61)—N(11)—Rh	121.5(3)
C(21)—N(11)—Rh	122.3(3)
C(22)—N(12)—C(62)	115.5(3)
C(22)—N(12)—Rh	124.2(3)
C(62)—N(12)—Rh	119.8(2)
C(51)—N(41)—C(31)	115.1(5)
C(52)—N(42)—C(32)	114.2(4)
C(6)—C(1)—C(2)	116.8(3)
C(6)—C(1)—Rh	123.4(3)
C(2)—C(1)—Rh	119.8(3)
C(3)—C(2)—C(1)	121.6(4)
C(4)—C(3)—C(2)	120.3(4)
C(3)—C(4)—C(5)	119.6(4)

Table 2. *Continued*

C(4)—C(5)—C(6)	119.9(4)
C(5)—C(6)—C(1)	121.6(4)
N(12)—C(22)—C(32)	122.0(4)
N(42)—C(32)—C(22)	123.7(4)
N(42)—C(52)—C(62)	123.3(4)
N(12)—C(62)—C(52)	121.3(4)
N(11)—C(21)—C(31)	121.0(5)
N(41)—C(31)—C(21)	123.6(5)
N(41)—C(51)—C(61)	123.0(5)
N(11)—C(61)—C(51)	121.2(5)
C(2P1)—C(1P1)—Sb	121.2(3)
C(6P1)—C(1P1)—Sb	119.9(3)
C(6P2)—C(1P2)—Sb	121.9(3)
C(2P2)—C(1P2)—Sb	119.7(3)
C(2P3)—C(1P3)—Sb	121.1(3)
C(6P3)—C(1P3)—Sb	119.8(3)

Table 3. Selected bond lengths (Å) and angles (°) for **2**

Rh—N	2.084(5)
Rh—Cl	2.345(2)
N—C(2)	1.348(8)
N—C(6)	1.373(8)
C(2)—C(3)	1.359(14)
C(2)—S	1.754(9)
C(3)—C(4)	1.403(9)
C(4)—C(5)	1.381(9)
C(5)—C(6)	1.345(11)
C(6)—C(7)	1.403(10)
C(7)—S	1.697(10)
N#1—Rh—N	178.7(3)
N—Rh—Cl	90.6(2)

Symmetry transformations used to generate equivalent atoms: #1 $-y+3/4$, $-x+3/4$, $-z+3/4$.

The bond distances N(1)—C(2) and N(1)—C(6) for the two PYR molecules average 1.331(6) Å, whereas N(4)—C(3) and N(4)—C(5) average 1.319(9) and the mean value of C(2)—C(3) and C(5)—C(6) bond distance is 1.380(7) Å. These parameters are in excellent agreement with the values of 1.348(13), 1.319(16), 1.381(17) Å, recently found for N(1)—C(2), C(3)—N(4), C(2)—C(3) for [Ru^{II}Cl(PY)₄(PYR)]⁺ [22].

Sb—C bond distances [mean value, 2.129(4) Å], C—Sb—C [101.4(1)°] and Rh—Sb—C [116.1(1)°] bond angles are in agreement with values previously reported for analogues Rh(III) complexes [6,7,16]. The PY, THZ and Ph ligands of **2** are strictly planar and the largest deviation is that of C(7) from the plane of N(3)/C(23)/S(3)/C(63)/C(73) [0.10(4) Å].

Selected intermolecular H-bonds for **1** can be listed as follows: C(2)(η^1 -Ph) $\cdots$ Cl(2), 3.256(4); C(6)(η^1 -Ph) $\cdots$ Cl(1), 3.199(4); C(22) $\cdots$ Cl(2), 3.302(4); C(6P1) $\cdots$ Cl(1), 3.439(5); angles at the H atoms range 111–118°.

The analysis of the crystal packing for **1** (Fig. 3) shows that the complex molecules are stacked along the *z*-axis and interact *via* H-bonds which involve pyrazine and chloride ligands (C(52) $\cdots$ Cl(2) ($x+1/2, y+1/2, z+1/2$), 3.565(5) Å) or η^1 -Ph and chloride ligands (Cl(1) $\cdots$ C(3) ($x+1/2, -y+1/2, z+1/2$), 3.481(4) Å; the angles at the H atoms are about 150°).

Molecular orbital

The molecular orbital analysis carried out for **1** shows that occupied frontier orbitals have an high character of d_{xz} , d_{yz} and $d_{x^2-y^2}$ atomic orbital of rhodium (see Table 4 and Fig. 4; the axis set is: *x* vector bisects the N—Rh—N angle, *z* vector is along the

Table 4. Selected MOs for **1**

Mo#	AOs (% and sign) ^a	E/eV
96	Rh px (5+), N(11) py(7+), N(11) px(6), N(41) px(9+), N(41) py (9-)	-11.935
95	Rh x^2-y^2 (29-), N(42) py(7+)	-11.878
94	Rh x^2-y^2 (29-), C(1)P(2)py(7+)	-11.762
93	Rh xz (44-), Rh yz (26-), Cl1 px(8+), Cl1 py(5+), C(12) px(7-)	
92	Rh xz (25-), Rh yz (43+), Cl(1) py(7-), Cl(2)py(6+)	-11.213
HOMO		
91	N(11) px(5+), N(11) py(6+), N(41) px(6+), N(42)py(6-)	-9.894
90	N(11) px(6-), N(12) px(8-), N(41) px(5-), N(42)px(7-)	-9.808
89	C(1)P(1) py(11-), C(3)P(1) py(16+), C(4)P(1) py(9-), C(6)P(1) py(20+)	-8.298
88	C(3)P(3)px(17-), C(6)P(3)px(18-)	-8.245
79	Rh z^2 (25+), Rhxy(22+)	-6.088

^aThe values below 5% have been ignored.

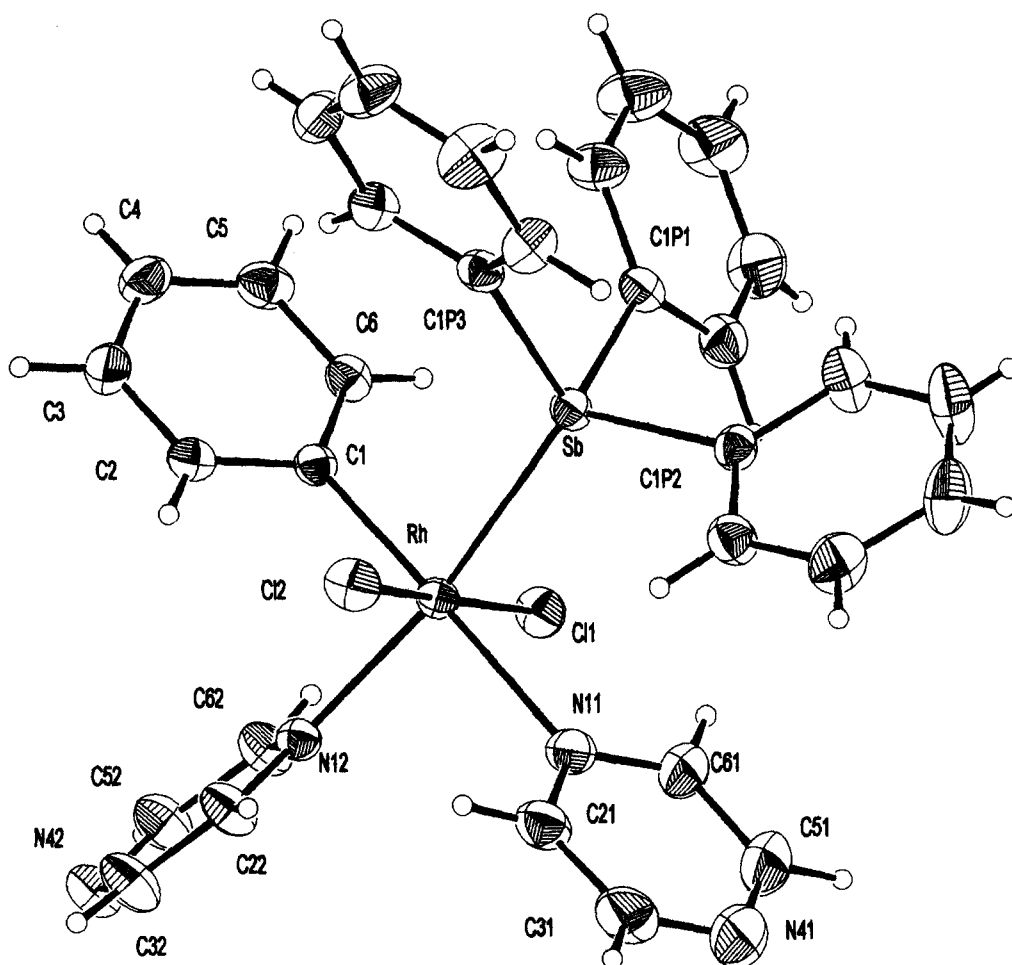


Fig. 1. Drawing of the molecular structure of **1**. The labelling of some atoms of SbPh_3 was omitted for clarity. Ellipsoids enclose 30% probability.

Rh—Cl bonds); HOMO ($-1081.91 \text{ kJ mol}^{-1}$, Fig. 4) being mainly d_{xz} (25%) and d_{yz} (43%) rhodium orbitals. The unoccupied frontier orbitals, excluding the LUMO, have high character of d_{xy} and d_{z^2} orbitals of rhodium. This is in agreement with the splitting of the d orbitals of the metal by an octahedral crystal field.

It has to be noted that LUMO ($-954.64 \text{ kJ mol}^{-1}$, Table 4, Fig. 4) has large contributions from the p atomic orbitals of both the PYR ligands. The HOMO-LUMO gap is relatively small (-127 kJ mol^{-1}) when compared to the corresponding value previously found for $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{SbPh}_3)(\text{THZ})_2]$ (-338 kJ mol^{-1}) [7]. LUMO for $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{SbPh}_3)(\text{THZ})_2]$ is much more destabilised than that for **1** and consists mainly of p atomic orbitals from phenyl groups of SbPh_3 [7].

The existence of two unoccupied MOs at relatively low energy for the PYR derivative, means that metal-to-ligand-charge-transfer phenomena should be easier for **1** than for $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{SbPh}_3)(\text{THZ})_2]$. This is in agreement with the well known capability of PYR to give binuclear complexes of second row transition metals in which (PYR acts as a bridge) the oxidation state of the two metal centres is different and can

be easily changed or interchanged (see Creutz-Taube compounds) [23]. It has to be noted that a π mixing of d -orbitals from Ru and p orbitals from pyrazine was previously computed for $[(\text{NH}_3)_5\text{Ru}(\text{PYR})\text{Ru}(\text{NH}_3)_5]^{5+}$ [23b].

The analysis of the atomic charges for **1** (Table 5) and for $[\text{RhCl}_2(\eta^1\text{-Ph})(\text{SbPh}_3)(\text{THZ})_2]$ shows that, whereas S atom of coordinated THZ is largely positive ($+0.36e$) [24], the N(4) atoms of PYR of **1** are highly negative (-0.71). This result suggests that the coordinated PYR molecule can probably compete with free ligands to link to another metal centre, so behaving as a bridge. It has to be noted that THZ has never been found to coordinate through the sulfur atom at least for this class of rhodium compounds. It has also to be recalled that CDCl_3 solutions of **1** show a facile loss of PYR unless excess PYR is present. Single crystals of **1** could be prepared only if excess PYR was present (in a solution of ethylacetate).

Spectroscopy

The ^1H NMR spectrum of **1** from CDCl_3 , even in the case of very fresh solutions, shows four broad signals at

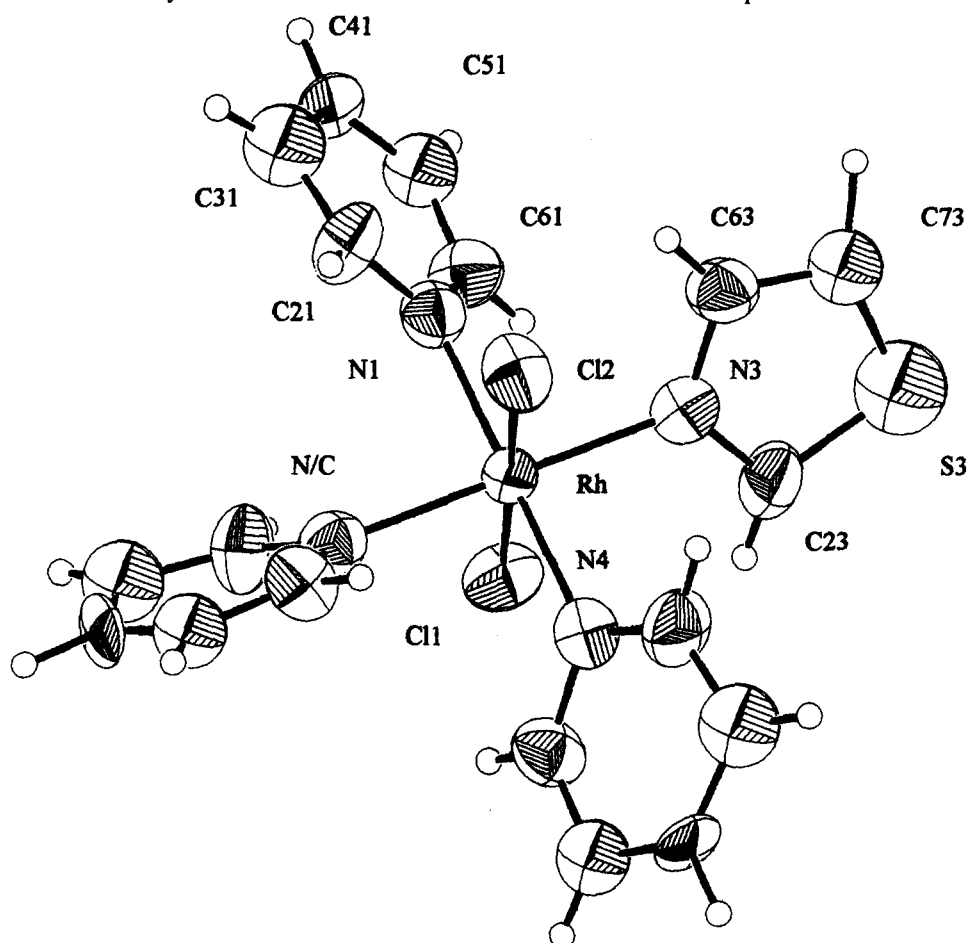


Fig. 2. The diagram shows the molecular structure of **2**. Ellipsoids enclose 30% probability.

Table 5. Selected atomic charged (e) for **1** as obtained by the molecular orbital calculations performed at the Extended-Hückel level

Rh	0.211
Sb	0.066
Cl(1)	-0.548
Cl(2)	-0.543
N(11)	-0.343
N(12)	-0.298
N(41)	-0.703
N(42)	-0.733
C(1)	-0.218
C(2)	-0.132
C(3)	-0.051
C(4)	-0.124
C(5)	-0.065
C(6)	-0.137
C(21)	0.223
C(31)	0.269
C(51)	0.288
C(61)	0.220
C(22)	0.251
C(32)	0.292
C(52)	0.306
C(62)	0.257

9.22, 8.95, and 8.59 and 8.32 ppm (8.55, free PYR) attributable to the protons ortho and meta of the two independent ligand molecules, respectively. The shape of the bands and their evolution with time indicate that the species undergoes reactions in solution. Within two hours from the mixing, the signals at 9.3–9.2 and that at 8.32 are much more broadened, whereas the signal at 8.59 is shifted to 8.55 ppm. This suggests that the formation of a binuclear PYR-bridged complex and the release of free PYR is probable.

The ^1H NMR spectrum of **4** from fresh CDCl_3 solutions has a broad signal at 8.86 ppm (4H) attributable to the protons of PYR ligand. The doublet at 8.57–8.54 (4H) is attributable to the ortho protons of the two PY ligands. The triplet at 7.75, 7.71, 7.67 ppm (2H) comes from the para protons of PY, whereas the system at 7.16, 7.13, 7.10 (4H) is due to the meta protons. Finally the system centered at 6.98 (5H) is attributable to the protons of $\eta^1\text{-Ph}$.

The ^1H NMR spectrum of **2** has a doublet at 9.54, 9.53 (1H) attributable to H(2) of THZ. The signal at 7.50–7.47 (1H) is attributable to H(4) of THZ and the system centered at 6.96 (5H) comes from η^1 -Ph protons. The signal from H(5) must be overlapping with one of the signals from PY protons, probably H(*ortho*)(8.53) or H(*para*)(7.64 ppm).

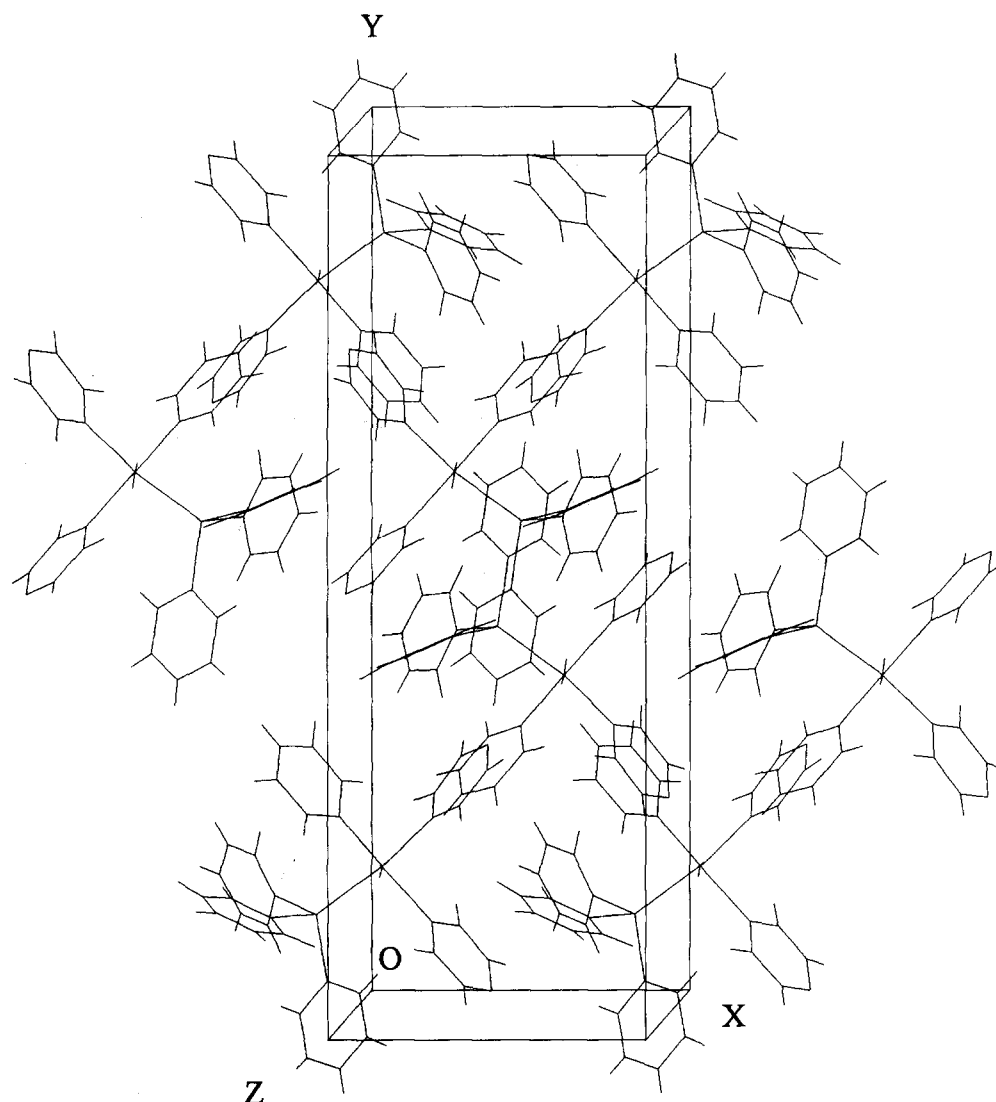


Fig. 3. The diagram shows the packing of selected molecules of **1** related to the cell boundary.

All IR spectra show bands at about 350 and 1570 cm^{-1} , attributable to Rh—Cl [25] and phenyl C—C [25] stretching vibrations, respectively. The absorption at 860 cm^{-1} in the spectrum of free THZ previously attributed to out of plane deformation of the N atom of THZ coupled to C—S stretching [26] is no longer present in the spectrum of **2** in agreement with the Rh—N(THZ) bond formation.

Molecular mechanics

The computed distances and angles for the ligand moieties of **1** deviate from the experimental (solid state, X-ray diffraction) ones less than 0.03 Å and 3°, respectively. As regards the coordination sphere parameters the agreement is good too; the largest deviations being those relevant to Rh—N (*trans* to C), 0.05 Å ($d_{\text{calcd}} - d_{\text{exp}}$) and Sb—Rh—N (*cis* to C), 7.5°

($\theta_{\text{calcd}} - \theta_{\text{exp}}$). One of the Ph rings of SbPh₃ and PYR(**1**) ligand have short C···C contacts (3.78–3.21 Å) in the computed molecule of [RhCl₂(η^1 -Ph)(PYR)₂(SbPh₃)]; so, it is reasonable to assume the presence of stacking interaction between the two rings, at the gas phase. Packing forces must be responsible for the absence of intramolecular stacking interactions at the solid state.

In conclusion this work produced the synthesis and structural characterisation of new organometallic compounds of rhodium(III). The octahedral geometry around the metal centre is much influenced by the bulky SbPh₃ molecule and by the high trans-influence of η^1 -Ph and SbPh₃. The *trans*-Rh^{III}Cl₂ function has shown to be very inert at least in alcohol and chloroform up to the solvent boiling points in aerobic conditions. A significant role of a π -donation from chlorine which stabilizes the Rh—Cl bonds has been revealed by EH—MO calculations.

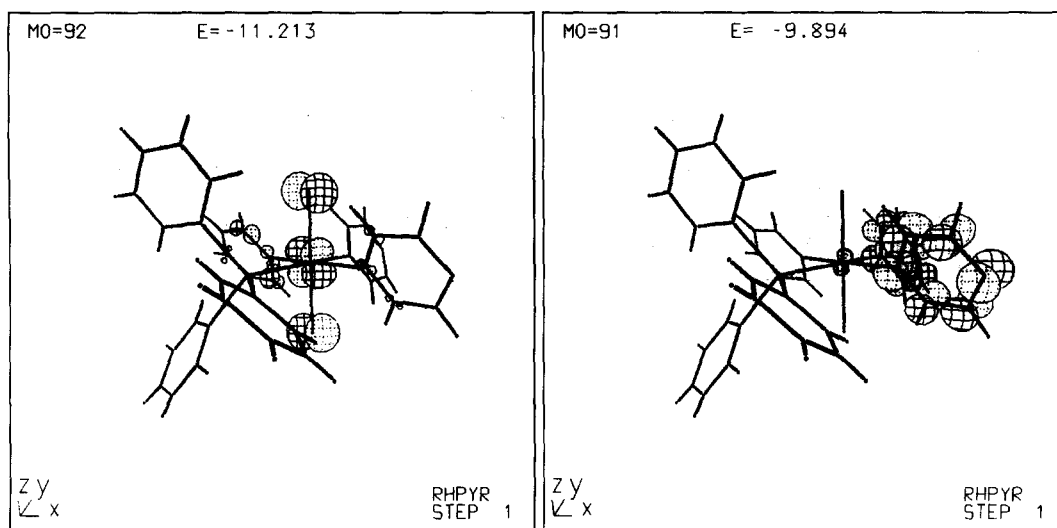


Fig. 4. Drawings of HOMO and LUMO for 1 (= RHPYR).

The synthesis, the analysis of the structures and the molecular orbital study for the PYR derivatives (**1** and **4**) suggest to plan the preparation of new binuclear complexes containing bridging pyrazine molecules; efforts in this field are in progress in this laboratory.

Finally, the experimental structures obtained from this work allowed to confirm the rightness of the force field previously set up for this class of compounds [7].

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