

Synthesis, X-ray structures and solution studies of new organo–rhodium(III) complexes with stibine, pyridine and pyrimidine derivatives

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Abstract

The synthesis, X-ray structure and spectroscopic characterization of new organo–rhodium(III) compounds is reported. From the reaction of RhCl_3 with SbPh_3 ($\text{Ph} = -\text{C}_6\text{H}_5$, 1:3–4 molar ratio), in boiling ethanol, a mixture of [*trans*- $\text{RhCl}_2(\text{Ph})(\text{SbPh}_3)_3$] (**1**) and [*mer*- $\text{RhCl}_3(\text{SbPh}_3)_3$] (**2**) was obtained. A previous hint on this reaction is given by R. Cini, G. Giorgi and E. Periccioli, *Acta Crystallogr., Sect. C*, 47 (1991) 716. The separation of **1** and **2** was carried out by recrystallizing the mixture from acetone: $1 \cdot (\text{CH}_3)_2\text{CO}$ precipitates first. **1** was separated from **2** also through chromatographic techniques (SiO_2 column, CH_2Cl_2 eluent). High yield preparation of **1** was carried out on adding $\text{Ag}(\text{CF}_3\text{SO}_3)$ to the suspension obtained by refluxing a mixture of RhCl_3 and SbPh_3 ($\text{Rh}/\text{Sb}/\text{Ag}$ molar ratio of 1:4:1). High yield synthesis of **2** was obtained by refluxing an ethanol mixture of RhCl_3 and SbPh_3 (1:3) in the presence of an excess of Cl^- , or by refluxing a mixture of RhCl_3 and SbPh_3 (1:10) in ethanol solvent. Orange crystals of $1 \cdot 0.45(\text{CH}_3)_2\text{CO}$ belong to the triclinic system, space group $P\bar{1}$ (No. 2) with $a = 12.686(2)$, $b = 14.906(2)$, $c = 15.523(3)$ Å, $\alpha = 107.73(2)$, $\beta = 95.10(2)$, $\gamma = 93.62(2)^\circ$, $Z = 2$, $D_c = 1.60 \text{ g cm}^{-3}$. The structure was refined to $R = 0.0594$ and $R_w = 0.0651$. The complex molecule consists of an octahedrally coordinated Rh(III) center linked to two *trans* Cl^- ions, and to a Ph and to three SbPh_3 ligands in the basal plane. A Rh–Sb bond is much lengthened by a strong *trans* influence from the Ph ligand. **1** reacted with an excess of pyridine (Py) and 3,5-dimethylpyridine (3,5-lutidine, Lu) in refluxing methanol to produce [*trans*- $\text{RhCl}_2(\text{Ph})(\text{Py})_3$] (**3**) and [*trans*- $\text{RhCl}_2(\text{Ph})(\text{Lu})_3$] (**4**), respectively. **1** reacted also with boiling CH_3CN to produce [$\text{RhCl}_2(\text{Ph})(\text{CH}_3\text{CN})(\text{SbPh}_3)_2$] **3** reacted with an excess of 4-methylpyrimidine (Mp) in refluxing methanol to produce [*trans*- $\text{RhCl}_2(\text{Ph})(\text{Py})_2(\text{Mp})$] (**5**). Yellow needles of **3** belong to the tetragonal system, space group $I4_1/acd$ (No. 142), with $a = 15.660(2)$, $c = 17.044(2)$ Å, $Z = 8$, $D_c = 1.55 \text{ g cm}^{-3}$. The structure was refined to $R = 0.0402$ and $R_w = 0.0446$. Yellow prisms of **4** belong to the tetragonal system, $P4/nnc$ (No. 126), $a = 11.522(3)$, $c = 10.289(2)$ Å, $Z = 2$, $D_c = 1.39 \text{ g cm}^{-3}$. The structure was refined to $R = 0.0579$ and $R_w = 0.0601$. Both **3** and **4** contain two Cl^- ligands *trans* to each other, a Ph group and three Py or Lu molecules in the equatorial sites. Their ^1H NMR spectra show large downfield shifts for the signals relevant to the Py or Lu ligand molecule *trans* to Ph. The ^1H NMR spectrum of **5** shows that the two Py ligands are *trans* to each other and that Mp is coordinated through N(1), which occupies the position *trans* to Ph. The complex molecules of **3**, **4** and **5** are stable in CHCl_3 solution, at room temperature for periods of hours. The reaction of **2** with an excess of Py in refluxing methanol produced the well known complex [*trans*- $\text{RhCl}_2(\text{Py})_4$] $^+$.

Introduction

Although the chemistry of rhodium(III)–tertiary phosphine complexes has been documented in a large number of scientific reports, comparatively few complexes of monodentate tertiary arsine and virtually

no tertiary stibine complexes are described in the literature [1].

The class of complexes of the type $[\text{RhX}_3\text{L}_3]$, where L is a ligand with heavier group V donor and X is a halogenide ion, is a very populous one, with *meridional* (*mer*) isomers being normally the rule [1]. The main preparative way to this kind of complexes is the direct reaction of the ligand with rhodium trihalogenide. A large variety of reactions on the $[\text{RhX}_3\text{L}_3]$ complexes allows to prepare many other rhodium(III) compounds [1].

On the other hand it has to be pointed out that the preparation of metal complexes with potential ability

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to bind nucleobases (and their derivatives) has become an area of considerable interest in the last two decades (some of the works are listed in ref. 2). The growing research efforts in the field of antineoplastic and antiviral activity of some heavy metal complexes has shown that the primary target of the drugs are usually the endocyclic nitrogen atoms of nucleic acid heteroaromatic bases which bind to the metal center [2]. It has often been found that metal complexes with anticancer activity are neutral, a property which facilitates the crossing of the cell membrane; once inside the cell the complex molecule can release one (or some) of the donor atoms, and the free sites can then bind to the nucleobases. Such a kind of mechanism is invoked for the anticancer activity of the well known $[cis-PtCl_2(NH_3)_2]$ [3].

General nucleophilic substitution reactions at the metal center are modulated by a series of factors like *trans* influence, steric hindrance, concentration of the ligands [4].

Therefore, it is of primary interest to investigate the influence of different ligands on the nucleophilic substitution at the metal center which directs the formation of metal-heteroaromatic base bonds. We reasoned that the insertion of η^1 -bound phenyl (Ph) groups in the Rh coordination sphere could open new promising synthetic routes to complexes with potential anticancer properties, by taking advantage from the high *trans* influence exerted by the Ph ligand itself. Furthermore the preparation of new rhodium(III) complexes containing different ligands such as stibines, nitriles, heteroaromatic bases and possibly Ph can give more impetus to the studies on photosensitivity, kinetic, thermodynamic, spectroscopy, and catalysis of rhodium compounds.

It happened to us to find that the reaction of $RhCl_3 \cdot 3H_2O$ with $SbPh_3$, in refluxing ethanol, produced the insertion of a Ph group into the coordination sphere of rhodium(III). The Ph ligand was then able to modulate the nucleophilic substitution on the metal through its *trans* influence. Nucleophilic agents like nitriles are able to displace just the donor *trans* to Ph but not the other ligands [5]. That finding prompted us to investigate the products of the reaction of $RhCl_3$ with $SbPh_3$ as well as the reactivity of the complexes formed with heteroaromatic bases. The field nicely merges with our project to synthesize new metal compounds with heteroaromatic bases (particularly nucleobases) and their derivatives [2p-t].

This work reports on the reaction of $RhCl_3$ with $SbPh_3$, the structures of its main products, i.e. the neutral complex molecules $[trans-RhCl_2(Ph)(SbPh_3)_3]$ (**1**) and $[mer-RhCl_3(SbPh_3)_3]$ (**2**), on the reactivity of **1** and **2** with heteroaromatic bases, and on the solid and solution state structures of the neutral complexes $[trans-RhCl_2(Ph)(Py)_3]$ (Py = pyridine) (**3**), and

$[trans-RhCl_2(Ph)(Lu)_3]$ (Lu = 3,5-dimethylpyridine = 3,5-lutidine) (**4**). This work reports also on the isolation and characterization of the product of the reaction of **3** with the nucleobase analogous 4-methylpyrimidine (Mp): $[trans-RhCl_2(Ph)(Py)_2(Mp)]$ (**5**).

Experimental

Materials

$RhCl_3 \cdot 3H_2O$ and $SbPh_3$ were reagent grade from Merck or Aldrich, and Ega Chemie or Fluka, respectively. $Ag(CF_3SO_3)$ was from Gmbh.

Absolute ethanol, methanol, diethyl ether and dichloromethane were analytical grade Merck or Bdh products; Py, Lu and Mp were Aldrich products. Analytical grade HCl (37%) was from Merck. All the solvents, Py, Lu, Mp and $SbPh_3$ were carefully tested for the presence of free benzene through standard gas-chromatographic techniques. The experiments gave negative results.

Synthesis

$[RhCl_2(Ph)(SbPh_3)_3]$ (**1**)

Procedure A. 2×10^{-3} mols (0.527 g) of $RhCl_3 \cdot 3H_2O$ were dissolved in 8 ml of warm absolute ethanol. The solution was filtered and then added to a mixture containing 8×10^{-3} mols (2.824 g) of $SbPh_3$ and 30 ml of absolute ethanol. After few minutes heating, a yellow crystalline solid precipitated. The suspension was refluxed under stirring for 3 h. After cooling down to room temperature the suspension was filtered and the crystalline solid was washed with hot ethanol. The crude product was recrystallized from CH_2Cl_2/C_2H_5OH (1:10 vol./vol.).

Chromatographic (CR) tests (SiO_2/CH_2Cl_2) showed the presence of two major species in the purified solid. The species which migrates slowly shows to be alterable during the CR experiments. On repeating many times the recrystallization procedure no improvement in the separation of the two components was achieved, even though the percentage of the components of the CH_2Cl_2/C_2H_5OH mixture was varied.

The same result as that above described was obtained when the $RhCl_3/SbPh_3$ molar ratio in the starting mixture was 1:3.

The separation of **1** was obtained by passing the mixture through a column of SiO_2 (230–400 mesh, 30 cm) with CH_2Cl_2 as eluent. The first yellow fraction was collected and brought to dryness. Yield 30%. *Anal.* Found: C, 54.65; H, 3.62; Cl, 5.60. Calc. for $C_{60}H_{50}Cl_2RhSb_3$: C, 55.01; H, 3.85; Cl, 5.41%.

A second method for separating the two major components of the reaction of $RhCl_3$ with $SbPh_3$ was as

follows. An amount of 300 mg of the crude solid was added to 200 ml of acetone. The mixture was heated up to reflux for 5 min. The resulting orange solution was filtered and then allowed to cool down to room temperature. Orange prisms grew overnight. They were filtered off and washed with acetone. After drying in the air at room temperature for half a day the crystals were collected and stored at 0 °C. Elemental and X-ray analysis, as well as infrared spectroscopy agreed with the presence of free acetone. Yield 30%. *Anal.* Found: C, 55.20; H, 4.28; Cl, 4.95. Calc. for $1 \cdot (\text{CH}_3)_3\text{CO}$, $\text{C}_{63}\text{H}_{56}\text{OCl}_2\text{RhSb}_3$: C, 53.31; H, 4.13; Cl, 5.18%.

Some efflorescence of the free acetone occurs when the crystals are stored at room temperature for a period of some days (as shown by the decreasing of the infrared absorption band at 1710 cm^{-1} , C=O stretching vibration).

Procedure B. The yellow suspension obtained by refluxing (3 h) the mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and SbPh_3 (1:4 molar ratio, 2×10^{-3} mols of RhCl_3 , see procedure A) in ethanol was mixed with a solution containing 2×10^{-3} mols (0.514 g) of $\text{Ag}(\text{CF}_3\text{SO}_3)$ and 6 ml of absolute ethanol. The suspension was refluxed for 3 h in the dark and then it was allowed to cool down to room temperature. The yellow crystalline solid was filtered and washed with ethanol. The crude product was mixed with CH_2Cl_2 . AgCl was filtered off and the solution was treated with ethanol. The solid was then purified through recrystallization from acetone. Yield 60%.

$[\text{RhCl}_3(\text{SbPh}_3)_3]$ (2)

Procedure A. The mother acetone solution from which $1 \cdot (\text{CH}_3)_2\text{CO}$ was filtered off (1, procedure A), produced (on concentrating at room temperature) yellow crystals (thin plates, as yet not suitable for single crystal X-ray analysis) of 2. They were collected and washed with ethanol. Yield 35%. *Anal.* Found: C, 51.00; H, 3.71; Cl, 8.58. Calc. for $\text{C}_{54}\text{H}_{45}\text{Cl}_3\text{RhSb}_3$: C, 51.13; H, 3.58; Cl, 8.39%.

Procedure B. 2×10^{-3} mols (0.527 g) of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ were dissolved in 8 ml of warm ethanol. The solution was filtered and mixed with 1 ml of concentrated (37%) HCl. The resulting solution was added to a mixture of 6×10^{-3} mols (2.118 g) of SbPh_3 and 22 ml of ethanol. After few minutes heating, a yellow solid precipitated. The suspension was refluxed under stirring for 4 h, then it was allowed to cool down to room temperature. The solid was filtered off and washed with ethanol at room temperature. The crude product was recrystallized from $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$ (1:10 vol./vol.). Yield 70%.

Procedure C. 2×10^{-3} mols of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ were dissolved in 8 ml of warm ethanol. The solution was filtered and mixed with a mixture containing 20×10^{-3} mols of SbPh_3 and 50 ml of absolute ethanol. The mixture was refluxed for 3 h. After cooling down to room temperature the suspension was washed with ethanol. The crude product was recrystallized from $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$. Yield 70%.

$[\text{RhCl}_2(\text{Ph})(\text{Py})_3]$ (3) and $[\text{RhCl}_2(\text{Ph})(\text{Lu})_3]$ (4)

An amount of 1×10^{-3} mol (1.37 g) of 1 was mixed with 50 ml of methanol. The suspension was treated with 5 ml of the base (Py or Lu). The mixture was refluxed under stirring for 2 h. The pale yellow solution was allowed to cool to room temperature and to concentrate. Yellow needles (3) and yellow prisms (4) grew in a period of 2–3 days. Yield 60%. *Anal.* 3: Found: C, 51.54; H, 4.09; N, 8.27; Cl, 14.60. Calc. for $\text{C}_{21}\text{H}_{20}\text{N}_3\text{Cl}_2\text{Rh}$: C, 51.66; H, 4.13; N, 8.61; Cl, 14.52%. *Anal.* 4: Found: C, 56.50; H, 5.75; N, 7.10; Cl, 12.52. Calc. for $\text{C}_{27}\text{H}_{32}\text{N}_3\text{Cl}_2\text{Rh}$: C, 56.66; H, 5.63; N, 7.34; Cl, 12.39%.

$[\text{RhCl}_2(\text{Ph})(\text{Py})_2(\text{Mp})]$ (5)

1×10^{-3} mols (0.49 g) of 3 were mixed with 30 ml of methanol; the resulting suspension was treated with 6 ml of Mp and then refluxed for 2 h. A pale yellow solution was obtained, which produced a yellow crystalline solid when cooled to room temperature. The solid was collected and washed with cold CH_3OH . Yield 60%. *Anal.* Found: C, 49.72; H, 4.43; N, 11.4; Cl, 14.2. Calc. for $\text{C}_{21}\text{H}_{21}\text{N}_4\text{Cl}_2\text{Rh}$: C, 50.12; H, 4.21; N, 11.14; Cl, 14.10%.

$[\text{RhCl}_2(\text{Py})_4]\text{Cl} \cdot 5\text{H}_2\text{O}$ (6)

1×10^{-3} mols (1.27 g) of 2 were added to 30 ml of methanol. 3 ml of Py were added to the suspension; the mixture was then refluxed for 2 h. The resulting pale yellow solution was filtered and allowed to cool down to room temperature. The solvent was reduced to one third. Ten volumes of diethyl ether were suddenly added to the solution, under stirring. A crystalline pale yellow solid precipitated; it was filtered off, washed with ether and dried in the air, and then stored under vacuum, at room temperature. Yield 60%. *Anal.* Found: C, 38.63; H, 4.98; N, 9.12; Cl, 17.0. Calc. for $\text{C}_{20}\text{H}_{20}\text{N}_4\text{Cl}_3\text{Rh} \cdot 5\text{H}_2\text{O}$: C, 39.01; H, 4.91; N, 9.10; Cl, 17.32%.

Spectroscopic measurements

IR spectra were measured on a Perkin-Elmer model 597 spectrometer. UV-Vis spectra were recorded with a Perkin-Elmer model 200 spectrophotometer equipped with a Hitachi recorder. ^1H NMR spectra were recorded

TABLE 1. Experimental details for the X-ray data collections for compounds 1, 3 and 4

	1	3	4
Formula	$C_{61.33}H_{52.70}O_{0.45}Cl_2Sb_3Rh$	$C_{21}H_{20}N_3Cl_2Rh$	$C_{27}H_{32}N_3Cl_2Rh$
<i>M</i>	1336.2	488.2	572.4
Crystal system	triclinic	trigonal	trigonal
Space group	$P\bar{1}$ (No. 2)	$I4_1/acd$ (No. 142)	$P4/mnc$ (No. 126)
Unit cell determination	25, randomly selected, high θ reflections	25, randomly selected, high θ reflections	25, randomly selected, high θ reflections
<i>a</i> (Å)	12.686(2)	15.660(2)	11.522(3)
<i>b</i> (Å)	14.906(2)	17.044(2)	10.289(2)
<i>c</i> (Å)	15.523(3)		
α (°)	107.73(2)		
β (°)	95.10(2)		
γ (°)	93.62(2)		
<i>V</i> (Å ³)	2772(1)		
<i>D_c</i> (g cm ⁻³)	1.60		
<i>Z</i>	2		
<i>F</i> (000)	1310		
Crystal form	orange prism,	yellow needle	yellow prism
Crystal size (mm)	0.125 × 0.100 × 0.125	0.52 × 0.15 × 0.075	0.15 × 0.20 × 0.15
μ (Mo K α) (cm ⁻¹)	18.78	10.72	8.30
Diffractometer	Enraf-Nonius, CAD4	Enraf-Nonius, CAD4	Phillips, PW1100
λ (Å)	0.71069, graphite monochromatized	0.71069, graphite monochromatized	0.71069, graphite monochromatized
Scan range (°)	5 < 2 θ < 45	5 < 2 θ < 55	4 < 2 θ < 60
Scan type	$\pm h, \pm k, l$	h, k, l	h, k, l
Reflections collected	three standard reflections	three standard reflections	two standard reflections
Intensity control parameters	periodically measured, 2 h	periodically measured, 2 h	periodically measured, 100 min
No. data collected at 22 °C	6033	2014	2292
Data reduction	Lorentz-polarization effects and empirical absorption corrections	Lorentz-polarization effects and empirical absorption corrections	Lorentz-polarization effects and empirical absorption corrections
No. independent observed reflections with $F > 3\sigma(F)$	4176	630	439
Structure solution	Patterson and Fourier methods	Fourier method	Fourier method
Refinement	Rh, Sb, Cl atoms: anisotropic; C, O atoms: isotropic for the free acetone molecule	Rh, Cl, N, C atoms: anisotropic; H atoms: isotropic	Rh, Cl, N, C atoms: anisotropic; H atoms: isotropic
Calculations	SHELX-76 [6a] and SHELX-86 [6b] programs on a VAX/750 computer	SHELX-76 [6a] program on a VAX/750 computer	SHELX-76 [6a] program on a VAX/750 computer
Scattering factors	SHELX-76 [6a] program and International Tables of Crystallography [6c]	SHELX-76 [6a] program and International Tables of Crystallography [6c]	SHELX-76 [6a] program and International Tables of Crystallography [6c]
<i>R</i> ($= \sum F_o - F_c / \sum F_o $)	0.0594	0.0402	0.0579
<i>R_w</i> ($= \sum w F_o - F_c / \sum (F_o \sqrt{w})$)	0.0651	0.0446	0.0601
Weighting scheme	$w = 1 / \{ \sigma^2(F) + 0.01F^2 \}$	$w = 1 / \{ \sigma^2(F) + 0.0557F^2 \}$	$w = 1 / \{ \sigma^2(F) + 0.00257F^2 \}$
No. parameters refined	308	80	49

with a Varian XL 200 spectrometer operating at 200 MHz.

Conductivity measurements

The conductivity measurements were carried out with a Radiometer conductivity-meter type CDM2d connected to a cell maintained at 25 °C. The cell was calibrated with a 0.1 M KCl solution.

Mass spectrometry measurements

The mass spectrometry (MS) measurements were performed on a VG 70-250S double-focusing instrument operating in the ionization mode at 70 eV, with an ion source temperature of 200 °C and an accelerating voltage of 8 kV. The resolution was 5000 M/ Δ M (10% of valley definition). The samples were introduced via the direct inlet system.

X-ray data collection and structure solution

Experimental details for the X-ray data collection of **1**, **3** and **4** are listed in Table 1. Single crystals of **1** were grown from acetone solution; those of **3** and **4** were obtained from methanol solution.

The structure of **1** was solved with Patterson and Fourier techniques. The Rh, Sb and Cl atoms were refined anisotropically; C and O atoms were treated isotropically. The molecule of acetone was constrained during the refinement with the C–C distances fixed at 1.52 ± 0.03 Å and the C–O distance fixed at 1.21 ± 0.01 Å. The isotropic thermal parameters of the acetone atoms were fixed at $U = 0.05$ Å². The occupancy of the acetone molecule was refined to 0.45(2).

The structure of **3** was solved by a trial-and-error procedure which located the Rh atom in the special positions. The Rh, Cl, N and C atoms were refined anisotropically whereas the isotropic thermal parameters for all the hydrogen atoms were refined to $U = 0.0679$ (95) Å². Owing to the statistical disorder of the complex molecule, it was not possible to discriminate between Ph and Py systems. The equatorial donor linked to Rh was given the scattering factor of nitrogen atom; however 1/4 of the positions are occupied by carbon atom.

The structure of **4** was also solved by following the trial-and-error procedure used for **3**. All the non-hydrogen atoms were refined anisotropically. Owing to the statistical disorder of the complex molecule, the occupancy of the carbon atom linked to position 3 (*meta*) of the Lu ligand, was fixed at 0.75. The equatorial donor linked to Rh was assigned the scattering factor of nitrogen atom.

Atomic coordinates, bond distances and angles are listed in Tables 2, 3 and 4, respectively. See also 'Supplementary material'.

TABLE 2. Atomic coordinates ($\times 10^4$) with e.s.d.s

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	SOF ^a
[Rh(III)Cl ₂ (C ₆ H ₅)(Sb(C ₆ H ₅) ₃) ₃]·0.45(CH ₃) ₂ CO (1)				
Rh	2304(1)	2605(1)	2302(1)	1.0
Sb(1)	647(1)	2089(1)	3088(1)	1.0
Sb(2)	1261(1)	3491(1)	1351(1)	1.0
Sb(3)	3689(1)	1768(1)	3021(1)	1.0
Cl(1)	2048(5)	1185(4)	1071(4)	1.0
Cl(2)	2371(4)	3987(4)	3562(3)	1.0
C(1)	3670(17)	3091(15)	1856(15)	1.0
C(2)	4291(20)	3841(17)	2372(17)	1.0
C(3)	5218(21)	4193(18)	2070(17)	1.0
C(4)	5489(23)	3745(21)	1269(20)	1.0
C(5)	4907(24)	2959(22)	663(20)	1.0
C(6)	3903(21)	2647(19)	976(18)	1.0
C(111)	−446(17)	814(15)	2545(14)	1.0
C(112)	−1365(20)	779(18)	2994(17)	1.0
C(113)	−2052(22)	−58(20)	2663(18)	1.0
C(114)	−1852(23)	−770(20)	1945(19)	1.0
C(115)	−953(24)	−711(21)	1491(20)	1.0
C(116)	−226(21)	121(19)	1816(17)	1.0
C(121)	−584(16)	3049(14)	3412(14)	1.0
C(122)	−532(20)	3711(18)	4288(16)	1.0
C(123)	−1360(22)	4280(20)	4468(19)	1.0
C(124)	−2108(23)	4259(21)	3823(20)	1.0
C(125)	−2163(23)	3641(20)	2960(19)	1.0
C(126)	−1428(22)	2974(19)	2749(18)	1.0
C(131)	1059(18)	1999(16)	4437(15)	1.0
C(132)	1823(20)	2708(18)	5016(17)	1.0
C(133)	2165(23)	2668(20)	5890(19)	1.0
C(134)	1728(26)	1933(23)	6206(22)	1.0
C(135)	967(26)	1219(23)	5563(22)	1.0
C(136)	647(21)	1302(19)	4731(18)	1.0
C(211)	−267(17)	2890(15)	707(14)	1.0
C(212)	−1006(22)	3492(19)	481(18)	1.0
C(213)	−2003(21)	3064(19)	31(18)	1.0
C(214)	−2253(23)	2133(21)	−233(19)	1.0
C(215)	−1542(23)	1502(21)	−41(19)	1.0
C(216)	−491(19)	1898(18)	449(16)	1.0
C(221)	978(19)	4903(17)	2016(15)	1.0
C(222)	1430(28)	5652(26)	1789(24)	1.0
C(223)	1268(30)	6594(26)	2247(25)	1.0
C(224)	680(25)	6733(22)	2964(21)	1.0
C(225)	210(21)	6031(19)	3217(18)	1.0
C(226)	391(20)	5115(18)	2757(17)	1.0
C(231)	1887(18)	3715(16)	176(15)	1.0
C(232)	2885(22)	4246(19)	350(19)	1.0
C(233)	3310(24)	4419(22)	−407(21)	1.0
C(234)	2709(29)	4096(25)	−1245(24)	1.0
C(235)	1684(28)	3647(25)	−1365(23)	1.0
C(236)	1284(22)	3461(20)	−615(19)	1.0
C(311)	4762(19)	1063(17)	2133(16)	1.0
C(312)	5631(22)	1550(19)	1953(18)	1.0
C(313)	6294(23)	1108(21)	1387(19)	1.0
C(314)	6111(24)	168(22)	928(20)	1.0
C(315)	5286(29)	−350(25)	1068(24)	1.0
C(316)	4546(25)	83(22)	1677(21)	1.0
C(321)	4857(17)	2523(15)	4112(14)	1.0
C(322)	4630(24)	3404(22)	4670(21)	1.0
C(323)	5489(26)	3969(23)	5386(21)	1.0
C(324)	6364(23)	3541(21)	5486(19)	1.0
C(325)	6590(25)	2635(22)	4906(21)	1.0

(continued)

TABLE 2. (continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>SOF</i> ^a
C(326)	5767(28)	2162(24)	4193(23)	1.0
C(331)	3078(18)	653(16)	3479(15)	1.0
C(332)	3476(20)	595(18)	4349(17)	1.0
C(333)	3036(27)	-146(24)	4646(22)	1.0
C(334)	2207(27)	-794(24)	4100(22)	1.0
C(335)	1882(27)	-722(24)	3279(23)	1.0
C(336)	2278(22)	22(19)	2950(18)	1.0
C(1A) ^a	5078(35)	8261(24)	3185(20)	0.45
C(2A) ^a	4671(31)	7474(16)	2315(20)	0.45
C(3A) ^a	4107(34)	7766(24)	1554(22)	0.45
O(A) ^a	4642(24)	6651(17)	2283(19)	0.45
[Rh(III)Cl₂(C₆H₅)(C₅H₅N)₃] (3)				
Rh	0	7500	3750	0.25
Cl	1059(1)	6445(1)	3750	0.5
N(C)	670(3)	8164(3)	4616(3)	1.0
C(2)	1034(4)	7748(4)	5222(3)	1.0
C(3)	1476(5)	8190(5)	5796(4)	1.0
C(4)	1569(4)	9047(4)	5762(4)	1.0
C(5)	1205(4)	9466(4)	5152(4)	1.0
C(6)	755(3)	9020(4)	4594(3)	1.0
H(2)	1099(39)	7160(47)	5238(33)	1.0
H(3)	1768(47)	7929(51)	6101(36)	1.0
H(4)	1797(53)	9344(53)	6168(33)	1.0
H(5)	1172(41)	9979(46)	5217(35)	1.0
H(6)	520(38)	9196(39)	4155(37)	1.0
[Rh(III)Cl₂(C₆H₅)(C₇H₅N)₃] (4)				
Rh	2500	2500	2500	0.125
Cl	2500	2500	210(3)	0.25
N(C)	1224(5)	1224(5)	2500	0.5
C(1)	1286(7)	294(8)	1709(9)	1.0
C(2)	470(9)	-579(7)	1708(10)	1.0
C(3)	-469(6)	-469(6)	2500	0.5
C(22)	671(12)	-1606(11)	843(13)	0.75
H(1)	1947(97)	291(92)	1348(83)	1.0
H(3)	-880(80)	-880(80)	2500	0.5
H(221)	-38(12)	-2212(11)	948(13)	0.75
H(222)	1474(12)	-2025(11)	1111(13)	0.75
H(223)	722(12)	-1320(11)	-156(13)	0.75

^aThe site occupation factor (*SOF*) for the acetone molecule was refined to 0.45(2) whereas the thermal parameter for its atoms was fixed at $U=0.05 \text{ \AA}^2$. The atomic distances for the acetone molecule were constrained (see 'Experimental').

Results and discussion

Solid state structure

The structure of **1** (Fig. 1) consists of a complex molecule which has the Rh(III) centre linked to three Sb(Ph₃)₃ molecules and to two *trans* chloride ions. The octahedral coordination sphere is completed with a carbon atom from a Ph ring. The acetone molecule does not show any bonding interaction to the metal centre. The Rh–Cl bond lengths average 2.361(5) Å and the Rh–Sb bond distances relevant to two Sb atoms *trans* to each other average 2.588(2) Å in agreement with values previously found in [RhCl₂(Ph)(CH₃CN)–(SbPh₃)₂] [5] or in other Rh(III) complexes [8–10].

TABLE 3. Selected bond lengths (Å) with e.s.d.s

[Rh(III)Cl₂(C₆H₅)(Sb(C₆H₅)₃)₃]·0.45(CH₃)₂CO (1)	
Rh–Sb(1)	2.706(2)
Rh–Sb(2)	2.594(2)
Rh–Sb(3)	2.582(2)
Rh–Cl(1)	2.362(5)
Rh–Cl(2)	2.360(5)
Rh–C(1)	2.090(22)
Sb(1)–C(111)	2.174(21)
Sb(1)–C(121)	2.174(20)
Sb(1)–C(131)	2.159(22)
Sb(2)–C(211)	2.109(21)
Sb(2)–C(221)	2.112(23)
Sb(2)–C(231)	2.159(22)
Sb(3)–C(311)	2.119(24)
Sb(3)–C(321)	2.124(21)
Sb(3)–C(331)	2.127(22)
C(1)–C(2)	1.32(3)
C(2)–C(3)	1.43(3)
C(3)–C(4)	1.31(4)
C(4)–C(5)	1.38(4)
C(5)–C(6)	1.50(4)
C(6)–C(1)	1.39(3)
[Rh(III)Cl₂(C₆H₅)(C₅H₅N)₃] (3)	
Rh–Cl	2.340(2)
Rh–N(C)	2.088(4)
N(C)–C(2)	1.346(7)
N(C)–C(6)	1.347(7)
C(2)–C(3)	1.386(9)
C(3)–C(4)	1.351(8)
C(4)–C(5)	1.356(8)
C(5)–C(6)	1.374(8)
[Rh(III)Cl₂(C₆H₅)(C₇H₅N)₃] (4)	
Rh–Cl	2.356(3)
Rh–N(C)	2.080(7)
N(C)–C(1)	1.347(9)
C(1)–C(2)	1.377(11)
C(2)–C(3)	1.360(11)
C(2)–C(22)	1.499(15)

The Sb atom *trans* to the Ph ligand shows a Rh–Sb bond length of 2.706(2) Å, in agreement with a large *trans* influence of the Ph ligand [4].

Significant deviations from ideal octahedral values are found for the Sb(2)–Rh–Sb(3), Sb(3)–Rh–C(1) and Cl(1)–Rh–Cl(2) angles which are 166.6(1), 80.9(6) and 173.8(2)°, respectively.

The Cl(1)–Rh–C(1)–C(6) torsion angle is 13.8(5)°, so the Ph and Cl[−] ligands are in an almost eclipsed conformation. The distance between the *ortho* carbon atoms of Ph and the Cl[−] ligands are about 3.15 Å. As a consequence the two Cl[−] ligands point away from the Ph ligand and the Cl(1)–Rh–Cl(2) angle is smaller than 180°.

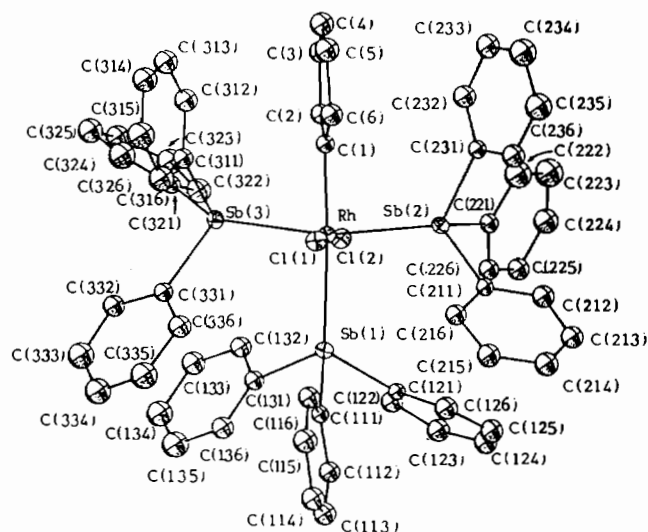
Intramolecular stacking interaction exists between the Ph ligand and the C(311)–C(316) ring (angle between the two plane normals: 31.3°; shortest C–C contact = 3.34 Å). This interaction accounts for the low values of the Sb(2)–Rh–Sb(3) and

TABLE 4. Selected bond angles ($^{\circ}$) with e.s.d.s

[Rh(III)Cl₂(C₆H₅)₃(Sb(C₆H₅)₃)₃]·0.45(CH₃)₂CO (1)	
Sb(1)–Rh–Sb(2)	97.3(1)
Sb(1)–Rh–Sb(3)	95.8(1)
Sb(1)–Rh–Cl(1)	92.7(1)
Sb(1)–Rh–Cl(2)	81.5(1)
Sb(1)–Rh–C(1)	173.0(6)
Sb(2)–Rh–Sb(3)	166.6(1)
Sb(2)–Rh–Cl(1)	91.4(2)
Sb(2)–Rh–Cl(2)	87.5(1)
Sb(2)–Rh–C(1)	86.3(6)
Sb(3)–Rh–Cl(1)	85.5(2)
Sb(3)–Rh–Cl(2)	96.8(1)
Sb(3)–Rh–C(1)	80.9(6)
Cl(1)–Rh–Cl(2)	173.8(2)
Cl(1)–Rh–C(1)	93.2(6)
Cl(2)–Rh–C(1)	92.8(6)
Rh–Sb(1)–C(111)	126.9(6)
Rh–Sb(1)–C(121)	117.9(5)
Rh–Sb(1)–C(131)	114.7(6)
C(111)–Sb(1)–C(121)	95.3(8)
C(111)–Sb(1)–C(131)	98.7(8)
C(121)–Sb(1)–C(131)	97.8(8)
Rh–Sb(2)–C(211)	118.0(6)
Rh–Sb(2)–C(221)	117.6(6)
Rh–Sb(2)–C(231)	120.2(6)
C(211)–Sb(2)–C(221)	101.9(9)
C(211)–Sb(2)–C(231)	97.2(8)
C(221)–Sb(2)–C(231)	98.0(9)
Rh–Sb(3)–C(311)	114.9(6)
Rh–Sb(3)–C(321)	122.3(6)
Rh–Sb(3)–C(331)	116.2(6)
C(311)–Sb(3)–C(321)	96.5(9)
C(311)–Sb(3)–C(331)	100.8(9)
C(321)–Sb(3)–C(331)	102.3(8)
Rh–C(1)–C(2)	122(2)
Rh–C(1)–C(6)	119(2)
C(2)–C(1)–C(6)	119(2)
C(1)–C(2)–C(3)	122(2)
C(2)–C(3)–C(4)	120(2)
C(3)–C(4)–C(5)	124(3)
C(4)–C(5)–C(6)	115(3)
C(5)–C(6)–C(1)	120(2)
Sb(1)–C(111)–C(112)	117(2)
Sb(1)–C(111)–C(116)	119(2)
Sb(1)–C(121)–C(122)	120(1)
Sb(1)–C(121)–C(126)	119(2)
Sb(1)–C(131)–C(132)	116(2)
Sb(1)–C(131)–C(136)	123(2)
Sb(2)–C(211)–C(212)	119(2)
Sb(2)–C(211)–C(216)	119(2)
Sb(2)–C(221)–C(222)	122(2)
Sb(2)–C(221)–C(226)	121(2)
Sb(2)–C(231)–C(232)	116(2)
Sb(2)–C(231)–C(236)	120(2)
Sb(3)–C(311)–C(312)	121(2)
Sb(3)–C(311)–C(316)	119(2)
Sb(3)–C(321)–C(322)	118(2)
Sb(3)–C(321)–C(326)	118(2)
Sb(3)–C(331)–C(332)	120(2)
Sb(3)–C(331)–C(336)	119(2)
[Rh(III)Cl₂(C₆H₅)(C₇H₉N)₃] (3)	
Cl–Rh–N(C)	89.7(1)
Cl'–Rh–N(C)	90.5(1)

TABLE 4. (continued)

N(C)–Rh–N(C)'	89.9(2)
N(C)–Rh–N(C)''	90.1(2)
N(C)–Rh–N(C)'''	179.6(1)
Rh–N(C)–C(2)	120.9(4)
Rh–N(C)–C(6)	121.7(4)
C(2)–N(C)–C(6)	117.4(5)
N(C)–C(2)–C(3)	120.8(6)
C(2)–C(3)–C(4)	121.3(6)
C(3)–C(4)–C(5)	118.0(6)
C(4)–C(5)–C(6)	120.0(6)
C(5)–C(6)–N(C)	122.5(6)
[Rh(III)Cl₂(C₆H₅)(C₇H₉N)₃] (4)	
Cl–Rh–Cl'	180
Cl–Rh–N(C)	90
N–Rh–N'	90/180
N–Rh–C	90/180
Rh–N(C)–C(1)	121.7(4)
C(1)–N(C)–C(1')	116.7(9)
C(1)–C(2)–C(3)	118.3(8)
C(1)–C(2)–C(22)	118.1(9)
C(3)–C(2)–C(22)	123.6(9)
C(2)–C(3)–C(2')	120.6(8)

Fig. 1. ORTEP [7] drawing of the complex molecule of **1** with the labelling of the atoms. The view is almost parallel to the Cl(1)–Rh axis. Ellipsoids enclose 30% of the electron density.

Sb(3)–Rh–C(1) bond angles, discussed above. Steric hindrance involving the bulky SbPh₃ molecules contributes to the deviations from the canonical octahedral values. The Sb atom has an approximate tetrahedral geometry for all the SbPh₃ ligands. The Sb–C bond distances average 2.12(2), 2.13(2) and 2.17(2) Å for Sb(2), Sb(3) and Sb(1), respectively. These distances are in agreement with the mean values of 2.145 and 2.118 Å previously found for other compounds [9, 10]. The C–Sb–C angles average 99.9(9), 99.0(9) and 97.3(8) $^{\circ}$ for Sb(3), Sb(2) and Sb(1), respectively, in agreement

(continued)

with previously reported mean values of the C–Sb–C angle for SbPh_3 ligand: 101.0° [9] and 102.3° [10].

The three Rh–Sb(2)–C angle values are very close to each other and average $118.6(6)^\circ$. However the Rh–Sb(3)–C and Rh–Sb(1)–C angle values range from $114.9(6)$ to $122.3(6)$ and $114.7(6)$ to $126.9(6)^\circ$, respectively. The steric hindrance between the two Cl^- donors and the Sb(1)–C(111)····C(116) group (which are almost coplanar) is presumably responsible for the opening of the Rh–Sb(1)–C(111) angle up to $126.9(6)^\circ$.

The structure of **3** (Fig. 2) consists of neutral molecules in which the Rh(III) ion is linked to three Py molecules and to a Ph ligand in the equatorial plane. The two Cl^- ligands occupy the axial positions. The Rh(III) centre lays on three two-fold axes, whereas the two Cl^- ions and the metal centre are on the same two-fold axis. The molecules of **3** have a statistical disorder in the crystal lattice as required by symmetry elements, so that all the equatorial positions are crystallographically equivalent.

The Rh–Cl distance of $2.340(2)$ Å is normal. The Rh–N(C) distance of $2.088(4)$ Å is in agreement with other Rh(III)–N(Py) distances [8, 11], as well as with the Rh–C(Ph) distance found in **1** and in $[\text{RhCl}_2(\text{Ph})(\text{CH}_3\text{CN})(\text{SbPh}_3)_3]$ [5], or in previously reported investigation [9, 12].

The Py(Ph) plane is tilted with respect to the equatorial plane, the Cl–Rh–N(C)–C(2) torsion angle being $-41.9(5)^\circ$.

The structure of **4** (Fig. 3) is similar to that of **3**. The Rh–Cl and Rh–N(C) distances of $2.356(3)$ and $2.080(7)$ Å, respectively, are in agreement with the values found for **1** and **3**. The Rh(III) ion is located in a special position where a four-fold axis (which passes through the Cl–Rh–Cl group) and four two-fold axes cross each other. As a consequence a statistical disorder exists in the crystal lattice. The Lu(Ph) plane is tilted with respect to the equatorial plane, the Cl–Rh–N(C)–C(1) torsion angle being 44.8° .

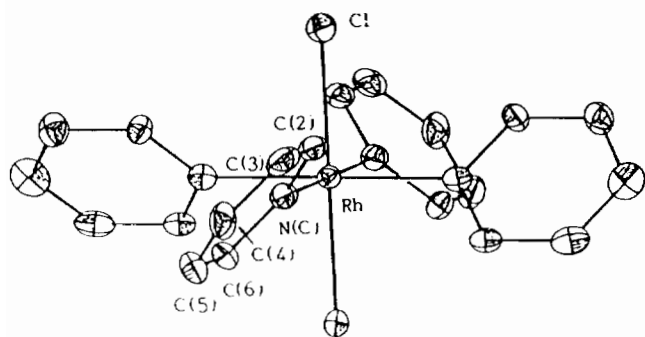


Fig. 2. ORTEP [7] drawing of the complex molecule of **3** with the labelling scheme. The view is almost parallel to the basal plane. Ellipsoids enclose 30% probability.

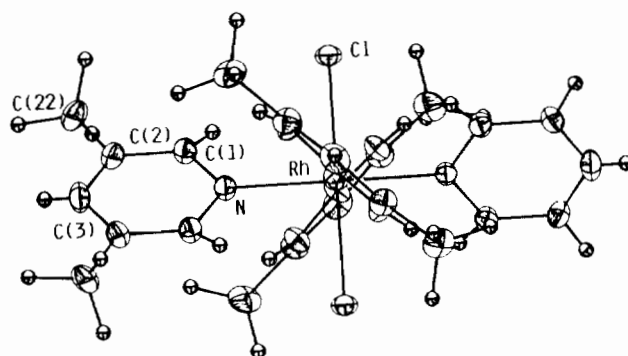


Fig. 3. ORTEP [7] drawing of the complex molecule of **4** showing also the labelling of the atoms. The view is almost parallel to the N(Lu)–Rh–N(Lu) axis. Ellipsoids enclose 30% probability.

UV–Vis spectra

The spectrum of **1** shows absorption bands at λ_{max} (nm) (CH_2Cl_2), 390.0 (shoulder = sh, $\epsilon = 570 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$); 303.4 (3660); 250.0 (sh, 10 920). The spectrum of **2** (in CH_2Cl_2) is in excellent agreement with that reported in ref. 13. Absorption bands are at 392.4 (21 560); 313.8 (19 300); 260 (sh, 24 300). It has to be pointed out that the highest energy bands are red-shifted for **2** when compared with **1**. Moreover the molar absorbance of **2** is far higher than for **1**.

The spectrum of **3** (in CH_2Cl_2) shows absorption bands at 410.0 (120); 273.0 (10 700); 267.0 (11 690); 262.0 (11 636).

The spectrum of **5** (in CH_2Cl_2) shows absorption bands at 415 (81); 273 (sh, $\sim 11 000$); 265.5 (11 145).

The spectrum of **6** (in CH_3OH) shows maxima at 410 (86); 270 (sh, 9850); 262 (13 500); 256 (13 670).

A small red-shift is found for the high energy bands of **3** with respect to that of **6**; however, it has to be noted that the spectrum of **6** was recorded from CH_3OH solutions whereas all the other compounds were studied from CH_2Cl_2 solutions.

^1H NMR spectra

The spectrum of **3** (in CDCl_3 , Fig. 4) shows well defined signals centered at 8.97, 8.59, 7.85 and 7.70 ppm from tetramethylsilane (TMS). Other signals occur in the region 7.40–6.90 ppm. The free Py molecule absorbs at 8.59 (*ortho*), 7.66 (*para*) and 7.27 (*meta*) ppm. The ratio of the integrals of the peak systems at 8.97 and 8.59 ppm, as well as the ratio of the integrals of the signals at 7.85 and 7.70 ppm is 1:2. The signals at 8.97 and 8.59 ppm are assigned to the *ortho* protons of the Py ligands *trans* and *cis* to the Ph ligand, respectively. The signals at 7.85 and 7.70 ppm are attributable to the *para* protons of the Py molecules, again located *trans* and *cis* to the Ph ligand, respectively.

So the *ortho* proton signal relevant to the Py molecule *trans* to Ph shows the highest downfield shift on com-

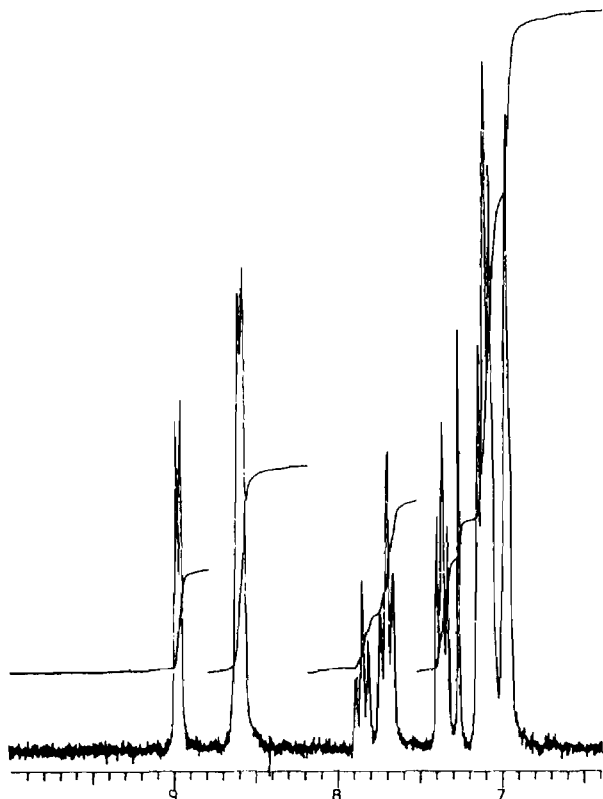


Fig. 4. 200 MHz ^1H NMR spectrum of **3** in CDCl_3 solvent, showing the downfield region from TMS.

plexation, whereas the *ortho* proton signal of the Py molecules *cis* to Ph undergoes a minor effect. The *para* proton signal for the *trans* Py molecule is also shifted more than that relevant to the *cis* ligand.

The spectrum of **4** (in CDCl_3 , Fig. 5) shows two sets of peaks attributable to the *ortho* and *para* protons of Lu at 8.523 and 7.437 ppm, and 8.169 and 7.273 ppm from TMS, respectively. They correspond to the Lu molecules *trans* and *cis* to the Ph ligand, respectively. The CH_3 protons absorb at 2.250 and 2.153 ppm for the Lu ligand *trans* and *cis* to Ph, respectively. The free base spectrum shows three singlets at 8.209, 7.256 and 2.254 ppm from TMS. So the signals of the *ortho* and *para* protons of Lu *trans* to Ph show large downfield shift, whereas those relevant to the ring protons of Lu *cis* to Ph are practically unaffected.

The spectrum of **5** (in CDCl_3 , Fig. 6), shows peaks at 9.41 ppm (singlet, H(2) Mp), 8.95 (doublet, H(6) Mp), 8.60 (doublet, H(*ortho*) Py), 7.71 (triplet, H(*para*) Py), 7.24–6.93 (system of signals relevant to all the other aromatic protons), 2.63 (singlet, CH_3 - Mp) ppm. The signals relevant to the H(2) and H(6) protons of Mp undergo a downfield shift of 0.38 and 0.43 ppm, respectively, upon complexation. The corresponding downfield shift for the CH_3 - proton signal of Mp is 0.15 ppm. On the basis of these data it is evident that

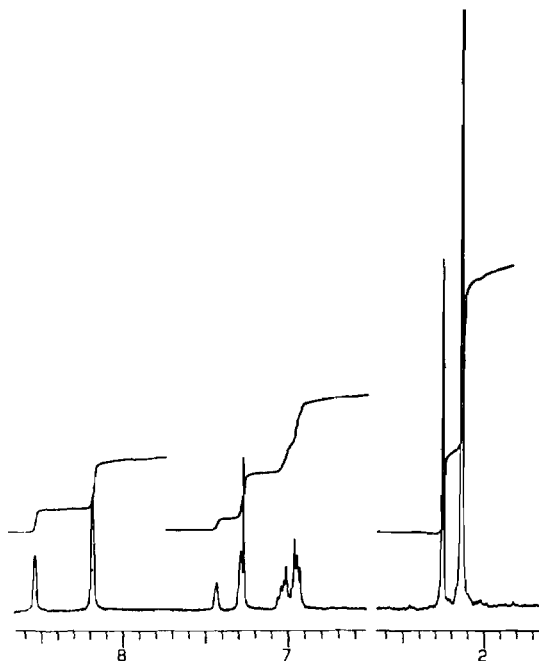


Fig. 5. 200 MHz ^1H NMR spectrum of **4** in CDCl_3 solvent, showing the chemical shift scale based on TMS.

the N(1) atom of Mp behaves as donor. This conclusion is in agreement with the steric hindrance exerted by the CH_3 - group in position 4, which excludes N(3) from the coordination sphere.

The spectrum of **6** (in CD_3OD , Fig. 7) shows three systems of signals centered at 8.57, 8.17 and 7.57 ppm from TMS, with integrals of a 2:1:2 ratio. These signals can be assigned to the *ortho*, *para* and *meta* protons of the Py molecule, respectively. All the signals of the Py ligand are downfield shifted on complexation, the largest effect being experienced by the *para* proton.

The spectrum shows that the four ligand molecules are magnetically equivalent. This datum is in agreement with an octahedral coordination structure containing the nitrogen atoms in the equatorial plane and two Cl^- ions in the axial positions.

Conductivity

The molar conductivity (Λ_M) of **6** in methanol solution, at 25 °C, is $80.5 \pm 0.2 \text{ ohm}^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$ in agreement with an electrolyte of the type A^+B^- [14]. All the analytical, spectroscopic (for IR data see below) and conductivity data bring to the conclusion that **6** is $[\text{trans-RhCl}_2(\text{Py})_4]\text{Cl} \cdot 5\text{H}_2\text{O}$ [15]. The structure of **6** suggests that **2** has a *mer* geometry instead of a *facial* (*fac*) one. It could be argued that, starting from the *mer* isomer, just one of the Cl^- ligands should be removed by a Py molecule, owing to the *trans* influence exerted by SbPh_3 [1, 4]. In fact it has been shown that the halogenide *trans* to the ternary phosphine of $[\text{mer-RhX}_3\text{L}_3]$ complexes is more labile than the other two. The three

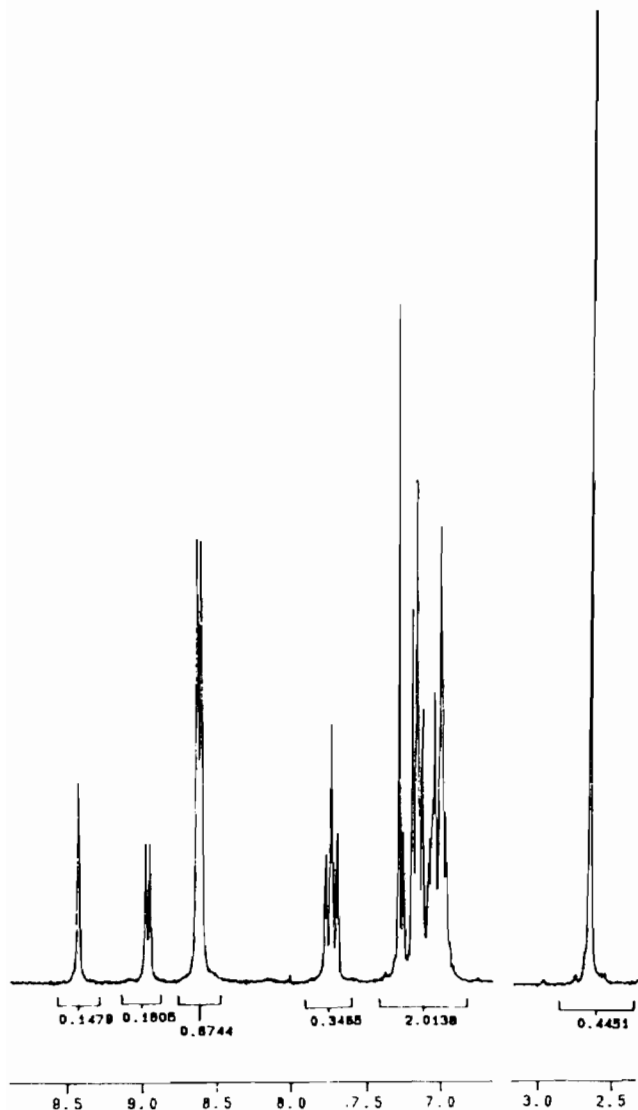


Fig. 6. 200 MHz ^1H NMR spectrum of **5** in CDCl_3 solvent with the chemical shift scale based on TMS and the integral of the signals.

SbPh_3 ligands are also replaced by Py molecules. From a *fac* isomer, the substitution of all the Cl^- ligands should be expected as all of them experience the same *trans* influence from Sb donors, and $[\text{Rh}(\text{Py})_6]^{3+}$ should be the product. However, whether two Cl^- ions are removed, the $[\text{RhCl}(\text{Py})_5]^{2+}$ derivative should be expected. Finally, in the case just a Cl^- ion is removed, the product should be $[\text{cis-RhCl}_2(\text{Py})_4]^+$. However, it has to be noted that previous attempts to prepare $[\text{Rh}(\text{Py})_6]^{3+}$ and $[\text{RhCl}(\text{Py})_5]^{2+}$ were unsuccessful [15]. Moreover the isolation of $[\text{cis-RhCl}_2(\text{Py})_4]^+$ has never been reported in the literature, at our knowledge. It seems probable that some steric hindrance preclude the formation of these three species [15]. Taking into account the catalytic activity exerted by ethanol (and primary alcohol in general) on rhodium(III)-Py com-

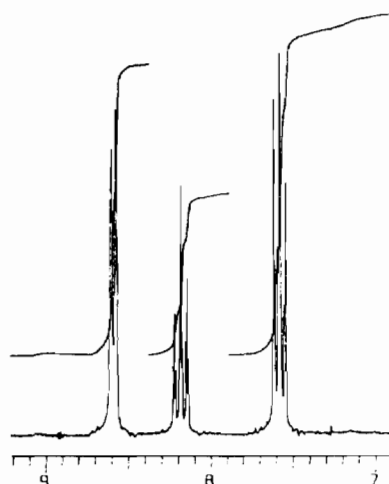


Fig. 7. 200 MHz ^1H NMR spectrum of **6** in CD_3OD solvent with the chemical shifts scale from TMS.

plexes [1, 15], some rearrangement, able to produce $[\text{trans-RhCl}_2(\text{Py})_4]^+$ from $[\text{fac-RhCl}_3(\text{SbPh}_3)_3]$, cannot be ruled out.

The formation of just $[\text{mer-RhCl}_3(\text{SbPh}_3)_3]$ from the reaction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with SbPh_3 was previously reported [13]. The assignment of the geometry was made on the basis of spectroscopic data. However, no mention to the formation of $[\text{RhCl}_2(\text{Ph})(\text{SbPh}_3)_3]$ or other products was made in that paper [13]. The *mer* geometry for **2** can be expected on the basis of the serious steric hindrance between the bulky SbPh_3 molecules which should occur in the *fac* isomer. It has to be noted that just small tertiary phosphines were found able of forming *fac* isomers [1].

IR spectra

The spectrum of $\mathbf{1} \cdot (\text{CH}_3)_2\text{CO}$ in the solid state (KBr pellets) shows an absorption band at 1710 cm^{-1} attributable to the $\text{C}=\text{O}$ stretching vibration of free acetone [16]. Strong sharp bands at 1560 , 1465 and 1380 cm^{-1} and a sharp medium band at 1215 cm^{-1} in the spectrum of $\mathbf{1} \cdot (\text{CH}_3)_2\text{CO}$ are not found in the spectrum of free SbPh_3 and acetone. On the other hand those absorption bands are present in the spectrum of $[\text{RhCl}_2(\text{Ph})(\text{CH}_3\text{CN})(\text{SbPh}_3)_2]$ [5]. It is reasonable that such absorptions are due to vibrations of coordinated Ph [16]. Bands at 1580 , 1465 and 1380 cm^{-1} are found in the spectra of both **3** and **4**. The spectrum of **3** shows the presence of a strong sharp band at 1600 cm^{-1} which can be attributed to $\text{C}=\text{N}$ stretching vibrations of Py ligand [16]. A similar band is found at the same wavelength in the spectrum of **4** and at 1610 cm^{-1} in the spectrum of **6**.

The spectrum of **6** shows bands at: 3410 (broad, strong=s), 1485 (weak=w), 1450 (s), 1215 (s), 1155 (w), 1070 (s), 1020 (s), 765 (s), 698 (s) cm^{-1} .

MS spectra

MS experiments carried out on the fresh mother liquor which produced **1** and **2** from the reaction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with SbPh_3 (1:4 molar ratio) showed the presence of ClSbPh_2 . In fact the MS spectrum contains the signal relevant to the molecular ion $[\text{ClSbPh}_2]^{++}$ at $m/z=310$ and the characteristic fragment ion $[\text{ClSbPh}]^+$ at $m/z=233$ due to the loss of the Ph radical. Both the peaks are multiplets and show the characteristic isotope clusters of molecules containing one atom both of Sb and Cl. MS experiments on ethanol solution of the commercial SbPh_3 did not reveal any traces of ClSbPh_2 .

Conclusions

In conclusion it has to be emphasized that the reaction of RhCl_3 with SbPh_3 in a molar ratio of about 1:3–4, in boiling ethanol produces a mixture of **1** and **2**.

1 proved to be a suitable starting material to insert nitrile [5] and pyridine derivatives in a coordination sphere containing a η^1 -bound Ph ligand, and to produce **3** and **4**.

3 was able to react with a nucleobase analogous such as Mp. This suggests that **3** may react with nucleic acids; tests for anticancer activity on this complex should be worthwhile. Much more work should be carried out to have a clear picture of the reaction mechanism which brings to **1** and **2** from the reaction of RhCl_3 and SbPh_3 in ethanol. The experiments listed below shed some light about this reaction. The $\text{RhCl}_3/\text{SbPh}_3$ molar ratio was 1:3–4 unless otherwise specified.

(1) The solution of the reactants in ethanol was refluxed under an atmosphere of air, and under ultrapurified nitrogen; in both the cases the same mixture of **1** and **2** was obtained.

(2) Particular care was devoted to use reactants and solvents free from benzene or benzene derivatives (see 'Experimental'). On the contrary, for some tests, an excess of benzene was added to the reaction mixture. The product was the same mixture of **1** and **2**, for all the trials.

(3) The reaction was carried out either in the dark or under the light emitted by a 100 W (tungsten) lamp. The product was the same mixture of **1** and **2** in both the cases.

(4) Ag^+ was added to a mixture of **1**, **2** ($\text{Rh}/\text{Sb}/\text{Ag}$ overall molar ratio of 1:4:1, see 'Experimental') and ethanol. The suspension produced **1** in high yield.

(5) An excess of Cl^- ions was added to the mixture of RhCl_3 , SbPh_3 and ethanol; on refluxing, **2** was produced in high yield (see 'Experimental').

(6) On refluxing a suspension of **2** in ethanol for 3–4 h a mixture of **1** and **2** was obtained.

(7) On refluxing a solution of **2** in CHCl_3 , a mixture of **1** and **2** was obtained.

(8) The reaction of RhCl_3 with a tenfold excess of SbPh_3 produced **2** in high yield (see 'Experimental').

(9) ClSbPh_2 was produced from the reaction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with SbPh_3 (1:4 molar ratio, see 'Results and discussion').

The influence of O_2 is excluded by experiment (1). Free benzene is not responsible for producing **1**: Ph ligand must come from SbPh_3 (experiment (2)). Visible light does not exert any relevant influence on the reaction (experiment (3)). The removal of the Cl^- ligand *trans* to SbPh_3 facilitates the insertion of Ph (experiment (4) and (5)). Solvent molecules seem to take a part in the formation of **1** and **2** on the basis of experiments (6)–(8).

At this stage of the work it seems reasonable to assume that the reaction of RhCl_3 with SbPh_3 in ethanol first produces **2** (*mer* isomer). The Cl^- donor which experiences a strong *trans* influence from Sb is then replaced by a Ph group coming from a SbPh_3 molecule, whereas a ClSbPh_2 molecule is formed.

Supplementary material

List of thermal parameters, bond lengths and bond angles involving the Ph rings of PPh_3 and the H atoms as well as the calculated and observed structure factors are available from the Cambridge Crystallographic Data Centre.

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