Note

Rhodium(III) ditertiary stibine complexes

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Abstract

The rhodium(III) distibine complexes trans-[Rh(L–L)$_2$X$_2$]Y (L–L = Ph$_2$Sb(CH$_2$)$_3$SbPh$_2$ or o-C$_6$H$_4$(SbMe$_2$)$_2$; X = Cl, Br or I; Y = X or BF$_4$) have been prepared and studied by UV–Vis, ^{1}H and ^{103}Rh NMR spectroscopies and electrospray mass spectrometry. The ^{103}Rh NMR spectroscopic data are reported and compared with data on related phosphine and arsine complexes. The single crystal X-ray structure of trans-[Rh{Ph$_2$Sb(CH$_2$)$_3$SbPh$_2$}$_2$Cl$_2$][ClO$_4$] is reported (Rh–Sb = 2.594(2), 2.611(2); Rh–Cl = 2.369(7) Å). © 1998 Elsevier Science S.A.

Keywords: Rhodium complexes; Stibine complexes

1. Introduction

The chemistry of bi- and poly-dentate antimony ligands remains little explored [1]. In the case of rhodium(III) the complexes [Rh{Ph$_2$Sb(CH$_2$)$_3$SbPh$_2$}$_2$X$_2$]X were reported some years ago [2], but characterised only by analysis and UV–Vis spectroscopy, and one tridentate stibine complex fac-[Rh{MeC(CH$_2$SbPh$_2$)$_3$}Cl$_3$] has been described [3]. More recently in connection with studies of various phosphine and arsine complexes by ^{103}Rh NMR spectroscopy [4,5], we became interested in some distibine analogues and report here their spectroscopic properties.

2. Results and discussion

The complexes trans-[Rh{o-C$_6$H$_4$(SbMe$_2$)$_2$}$_2$X$_2$]BF$_4$ (X = Cl, Br or I) were obtained by reaction of the ligand with the appropriate rhodium(III) halide in ethanol. The addition of HBF$_4$ gave rise to orange powders for the chloride and bromide derivatives or a dark red solid for the iodide. The complexes [Rh{Ph$_2$Sb(CH$_2$)$_3$SbPh$_2$}$_2$X$_2$]X, (X = Cl, Br or I) may be prepared similarly [2]. A convenient alternative synthesis is reaction of [Rh(H$_2$O)$_6$]$^{3+}$ with the ligand and the appropriate KX in a 1:2: ~4 molar ratio in ethanol–H$_2$O.

which allows easy introduction of the anion of choice. All six complexes were identified as trans by the spectroscopic and structural studies described below. For the diphosphine or diarsine analogues cis isomers are obtainable [4,6,7]. For example they may be synthesised from the trans by sequential reaction with Li$_2$CO$_3$ and HX, but attempts to apply this route to the distibine complexes failed.

The complexes are air-stable in both the solid state and solution and dissolve readily in organic solvents. Their compositions were established by analysis and confirmed by electrospray mass spectrometry which showed major peaks with characteristic isotope distribution patterns corresponding to [Rh(L–L)$_2$X$_2$]$^+$ fragments; an example of trans-[Rh{o-C$_6$H$_4$(SbMe$_2$)$_2$}$_2$Cl$_2$]$^+$ is reproduced in Fig. 1.

The UV–Vis spectra are typical of six-coordinate Rh(III) species [4], and the presence of singlet δ(Me) resonances in the ^{1}H NMR spectra of the [Rh{o-C$_6$H$_4$(SbMe$_2$)$_2$}$_2$X$_2$]BF$_4$ complexes identifies them as trans isomers. The redox properties of the complexes were investigated by cyclic voltammetry in CH$_2$Cl$_2$ solution, calibrated against the Fc/Fc$^+$ couple at 0.57 V. No oxidative processes were observed <2 V and irreversible reductions, presumably to Rh(I) occurred in the range −0.48 to −0.61 V. Repeated attempts to grow single crystals of any of the [Rh{Ph$_2$Sb(CH$_2$)$_3$SbPh$_2$}$_2$X$_2$]$^+$ complexes with either halide or BF$_4^-$ counterions failed. A single crystal of modest quality was however obtained by the addition of 70% perchloric acid to an acetonitrile solution of [Rh{Ph$_2$Sb(CH$_2$)$_3$SbPh$_2$}$_2$Cl$_2$]Cl.

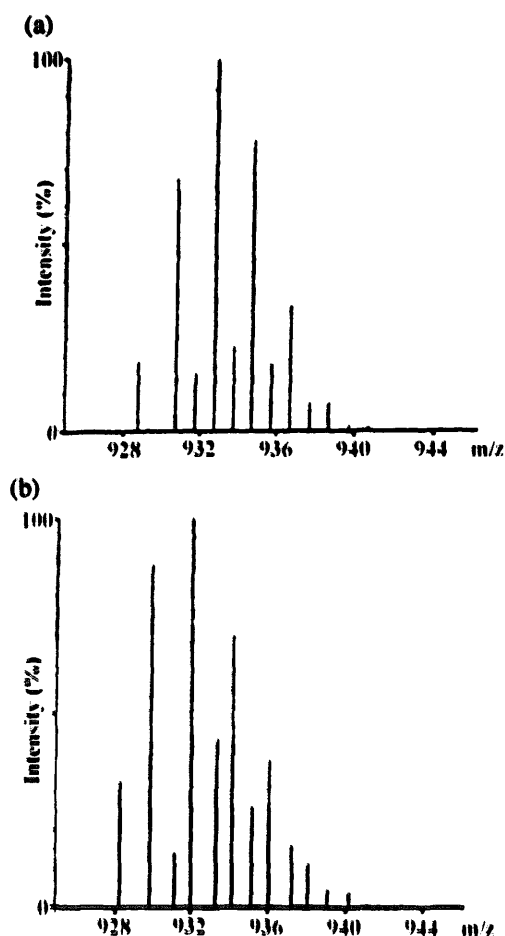* Corresponding author. Tel.: +44-1703-595 000; fax: +44-1703-593 781.

(a)

(b)

Fig. 1. Part of the electrospray mass spectrum of *trans*-|Rh(*o*-C₆H₄-(SbMe₂)₂)₂Cl₂|⁺ showing (a) the calculated pattern of the ion and (b) the experimental isotope pattern.

2.1. *Structure of |Rh(Ph₂Sb(CH₃)₃SbPh₃)₂Cl₂||ClO₄|*

The structure consists of discrete centrosymmetric cations and disordered perchlorate anions (Fig. 2 and Table 1). The *trans* octahedral Rh geometry confirms the spectroscopic conclusions for the solution species and the structure represents the first example of this ligand to be characterised by X-ray methods. The majority of the Sb–Rh distances in the literature refer to the ligand Ph₃Sb, however the present distances (Table 1) are in good agreement with the Rh–Sb(*trans* Sb) found [8] in |RhCl₂Ph(Ph₃Sb)₃| (2.582(2), 2.594(2) Å), the same compound providing a comparator Rh–Cl(*trans* Cl) distance (2.361 av. Å) which is also in good agreement with that found here. A useful summary of Sb–Rh distances is provided by Cavaglioni and Cini [9]. The six-membered chelate ring is best described as an unsymmetrical 'boat' conformation and with the Sb–C and C–C distances being unexceptional.

2.2. *¹⁰³Rh NMR studies*

The ¹⁰³Rh isotope has $I = 1/2$ and is 100% abundant, but its low resonance frequency (3.16 MHz) and long relaxation

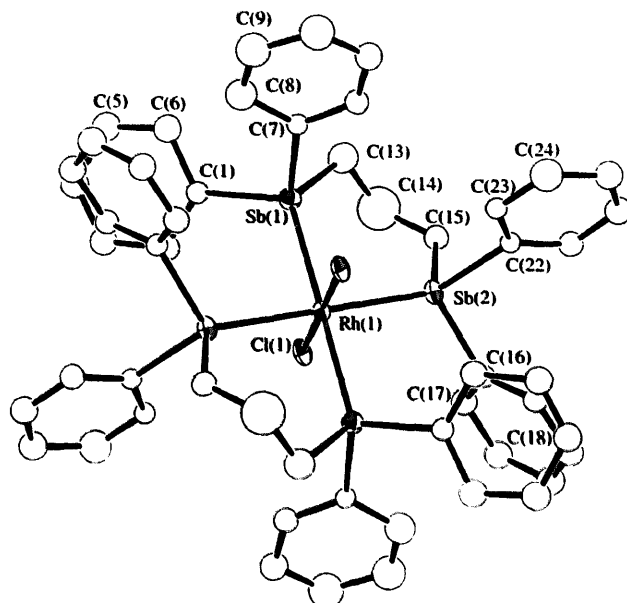Fig. 2. The centrosymmetric cation in |Rh(Ph₂Sb(CH₂)₃SbPh₂)₂Cl₂|-|ClO₄| showing the atom numbering scheme. Thermal ellipsoids/spheres are drawn at the 50% probability level.

Table 1
Selected bond lengths (Å) and angles (°) for |Rh(Ph₂Sb(CH₂)₃-SbPh₂)₂Cl₂||ClO₄|

Rh(1)–Sb(1)	2.594(2)	C(13)–C(14)	1.57(5)
Rh(1)–Sb(2)	2.611(2)	C(14)–C(15)	1.46(5)
Rh(1)–Cl(1)	2.369(7)		
Sb–C		2.09(3)–2.17(3)	
C–C (phenyl)		1.34(4)–1.48(4)	
Sb(1)–Rh(1)–Sb(2)	87.86(6)	Sb(1)–C(13)–C(14)	114(2)
Sb(1)–Rh(1)–Cl(1)	88.0(2)	C(13)–C(14)–C(15)	120(4)
Sb(2)–Rh(1)–Cl(1)	80.8(2)	C(14)–C(15)–Sb(2)	120(2)
Rh–Sb–C		114.2(7)–122.8(7)	
C–Sb–C		98(1)–106(1)	
C–C–C (phenyl)		116(3)–126(3)	

times, especially in high symmetry environments limited NMR studies for many years [10]. We have recently reported ¹⁰³Rh NMR data for a range of phosphorus and arsenic donor ligand complexes [4,5], and comparison of data from the present complexes is clearly of interest. The rhodium(III) distibine complexes gave sharp singlet ¹⁰³Rh NMR resonances (Table 2), although due to the moderate solubility of the complexes long accumulations (typically 50–80 000 transients) were necessary. In the case of *trans*-|Rh(*o*-C₆H₄(SbMe₂)₂)₂Cl₂|BF₄ poor solubility was a problem: no resonance was observed from saturated CH₂Cl₂ solutions, and the complex appeared to decompose slowly in dimethylsulf-oxide. In *N,N*-dimethylformamide solution a very weak resonance was observed (reproducibly) at δ +2165 which may be the resonance of the cation, but due to its weakness the assignment remains tentative. The shifts are dominated by the donor set and only slightly influenced by the ligand substituents. Fig. 3 compares the shifts of the present com-
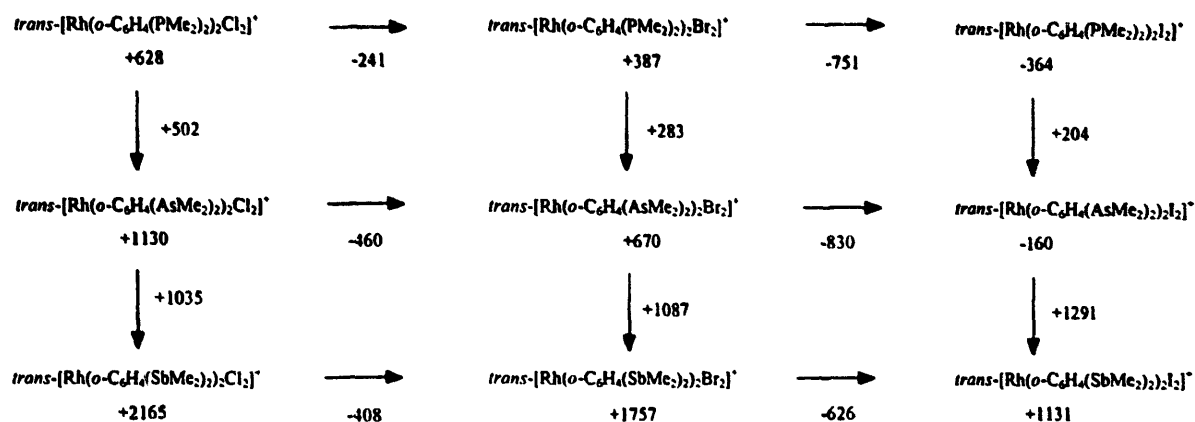
trans-[Rh(o-C₆H₄(PMe₂)₂)₂Cl₂]⁺ ——→ trans-[Rh(o-C₆H₄(PMe₂)₂)₂Br₂]⁺ ——→ trans-[Rh(o-C₆H₄(PMe₂)₂)₂I₂]⁺
+628   −241   +387   −751   −364

│ +502   │ +283   │ +204

trans-[Rh(o-C₆H₄(AsMe₂)₂)₂Cl₂]⁺ ——→ trans-[Rh(o-C₆H₄(AsMe₂)₂)₂Br₂]⁺ ——→ trans-[Rh(o-C₆H₄(AsMe₂)₂)₂I₂]⁺
+1130   −460   +670   −830   −160

│ +1035   │ +1087   │ +1291

trans-[Rh(o-C₆H₄(SbMe₂)₂)₂Cl₂]⁺ ——→ trans-[Rh(o-C₆H₄(SbMe₂)₂)₂Br₂]⁺ ——→ trans-[Rh(o-C₆H₄(SbMe₂)₂)₂I₂]⁺
+2165   −408   +1757   −626   +1131

Fig. 3. ¹⁰³Rh NMR shifts of trans-[Rh(L–L)₂X₂]⁺ as a function of ligand.

Table 2
¹⁰³Rh NMR data [a]

Complex ion	L–L	
	Ph₂Sb(CH₂)₃SbPh₂ [c]	o-C₆H₄(SbMe₂)₂
[Rh(L–L)₂Cl₂]⁺	+2104	+2165 [b,d]
[Rh(L–L)₂Br₂]⁺	+1535	+1757 [c]
[Rh(L–L)₂I₂]⁺	+1265	+1131 [c]

[a] Spectra were recorded at 300 K in the solvent indicated. The chemical shifts are to high frequency of Ξ = 3.16 MHz.
[b] Solution in HCONMe₂.
[c] Solution in CH₂Cl₂.
[d] Assignment tentative, see text.

plexes with those of the trans-[Rh(L–L)₂X₂]⁺ (L–L = o-C₆H₄(PMe₂)₂ and o-C₆H₄(AsMe₂)₂) [4]. As can be seen the shifts move to low frequency as the donor atoms are changed Cl → Br → I and Sb → As → P. For the phosphine and arsine ligands cis-[Rh(L–L)₂X₂]⁺ isomers are obtainable and these have lower frequency shifts than the trans analogues [4]. The factors which influence ¹⁰³Rh chemical shifts have been discussed in some detail by Mann [10]. Two major factors operating within the [Rh{o-C₆H₄(EMe₂)₂}₂X₂]⁺ (E = P, As or Sb; X = Cl, Br or I) are from the Ramsey equation, the inverse dependence of δ upon the d–d transition energies in the electronic spectra and a nephelauxetic effect. The observed chemical shift trends are consistent with this model.

3. Experimental

Physical measurements were made as described previously [4,5,11]. Analytical data were obtained from the Microanalytical Laboratory of Imperial College, London. The ligands were made by literature methods [12,13]. The source of [Rh(H₂O)₆]³⁺ was the rhodium electroplating solution made by Johnson Matthey Ltd. as RJ-100 electroplating solution; ¹⁰³Rh NMR studies showed hexaaquorhodium(III) to be the predominant species, with minor amounts of aquo-sulfato species present.

3.1. Synthesis

3.1.1. [Rh{Ph₂Sb(CH₂)₃SbPh₂}₂X₂]X (X = Cl, Br or I)

To a solution of Ph₂Sb(CH₂)₃SbPh₂ (1.0 mmol), dissolved in a mixture of abs. alcohol (20 cm³) and dichloromethane (20 cm³), the rhodium plating solution was added (0.5 mmol Rh). The reaction mixture was heated to reflux and an excess of the appropriate potassium halide (chloride, bromide or iodide) was added and stirring was continued for 48 h at room temperature. The orange (chloride or bromide) or red–black (iodide) solid that precipitated from the solution was isolated by filtration and recrystallised from dichloromethane and hexane. Yields: ~70%.

3.1.1.1. [Rh{Ph₂Sb(CH₂)₃SbPh₂}₂Cl₂]Cl

Anal. Found: C, 46.3; H, 3.5. Calc. for C₅₄H₅₂Cl₃RhSb₄: C, 46.4; H, 3.7%. UV–Vis (E_max/10³cm⁻¹ (ε_mol/dm³mol⁻¹ cm⁻¹), CH₂Cl₂): 26.7 (7440), 21.7 (sh). ¹H NMR (CDCl₃): 1.65–1.80 (m), 7.0–7.6 (m).

3.1.1.2. [Rh{Ph₂Sb(CH₂)₃SbPh₂}₂Br₂]Br

Anal. Found: C, 42.0; H, 3.3. Calc. for C₅₄H₅₂Br₃RhSb₄: C, 42.4; H, 3.4%. UV–Vis (E_max/10³cm⁻¹ (ε_mol/dm³mol⁻¹ cm⁻¹), CH₂Cl₂): 26.8 (8145), 24.2 (1510). ¹H NMR (CDCl₃): 1.50–1.65 (m), 7.0–7.6 (m).

3.1.1.3. [Rh{Ph₂Sb(CH₂)₃SbPh₂}₂I₂]I

Anal. Found: C, 39.0; H, 3.2. Calc. for C₅₄H₅₂I₃RhSb₄: C, 38.8; H, 3.1%. UV–Vis (E_max/10³ cm⁻¹ (ε_mol/dm³ mol⁻¹ cm⁻¹), CH₂Cl₂): 26.6 (5715), 21.1 (5210). ¹H NMR (CDCl₃): 1.45–1.55 (m), 7.0–7.6 (m).

3.1.2. trans-[Rh{o-C₆H₄(SbMe₂)₂}₂X₂]BF₄ (X = Cl, Br or I)

A solution of RhX₃·nH₂O (X = Cl, Br or I) (0.5 mmol) in ethanol (50 cm³) was treated with ligand (1.5 mmol). The mixture was refluxed for 3 h before an excess of HBF₄ (10 cm³, 40%) was added and refluxing continued for 1 h. On cooling the reaction mixture a solid was precipitated from solution, this was isolated by filtration, rinsed with diethyl ether (3×10 cm³), recrystallised from CH₂Cl₂–Et₂O, and dried in vacuo. Yields: ~40%.

3.1.2.1. trans-[Rh{o-C₆H₄(SbMe₂)₂}₂Cl₂]BF₄

Anal. Found: C, 24.0; H, 3.0. Calc. for C₂₀H₃₂B-Cl₂F₄RhSb₄: C, 23.5; H, 3.1%. UV–Vis ($E_{max}/10^3$ cm⁻¹ ($\epsilon_{mol}/$dm³ mol⁻¹ cm⁻¹), CH₂Cl₂): 32.4 (1700), 24.6 (457). ¹H NMR (CDCl₃): 1.77 (s), 7.0–7.6 (m).

3.1.2.2. trans-[Rh{o-C₆H₄(SbMe₂)₂}₂Br₂]BF₄

Anal. Found: C, 21.3; H, 2.4. Calc. for C₂₀H₃₂B-Br₂F₄RhSb₄: C, 21.7; H, 2.9%. UV–Vis ($E_{max}/10^3$ cm⁻¹ ($\epsilon_{mol}/$dm³ mol⁻¹ cm⁻¹), CH₂Cl₂): 31.6 (14 540), 26.3 (2590), 21.3 (sh). ¹H NMR (CDCl₃): 1.90 (s), 6.9–7.7 (m).

3.1.2.3. trans-[Rh{o-C₆H₄(SbMe₂)₂}₂I₂]BF₄

Anal. Found: C, 19.8; H, 2.4. Calc. for C₂₀H₃₂BF₄I₂RhSb₄: C, 20.0; H, 2.7%. UV–Vis ($E_{max}/10^3$ cm⁻¹ ($\epsilon_{mol}/$dm³ mol⁻¹ cm⁻¹), CH₂Cl₂): 28.5 (9300), 22.9 (9180). ¹H NMR (CDCl₃): 2.11 (s), 7.0–7.6 (m).

3.2. Structure determination of [Rh{Ph₂Sb(CH₂)₃SbPh₂}₂Cl₂][ClO₄]

Addition of a few drops of HClO₄ (70%) to a MeCN solution of the chloride salt followed by refrigeration gave yellow crystals of the required compound. The selected crystal was mounted on a glass fibre using the oil-film technique and held at 150 K during the experiment.

C₅₄H₅₂Cl₃O₄RhSb₄, M_r = 1461.27, monoclinic, space group P2/n (No. 13), a = 16.070(3), b = 10.427(5), c = 17.614(3) Å, β = 99.30(1)°, V = 2912.7(1.5) Å³, T = 150 K, D_{calc} = 1.666 g cm⁻³, Z = 2, $F(000)$ = 1416.

Using a Rigaku AFC7S diffractometer fitted with graphite monochromator and Mo Kα radiation (λ = 0.71069 Å), ω-2θ scans (2θ max, 48.4°), 4232 reflections were collected of which 4064 were unique (R_{int} = 0.086). There was no significant decay of the standard reflections and the data were corrected for absorption (ψ-scan) and Lorentz and polarisation effects. The data processing lead to the space group P2/n or Pn of which the former was favoured by the N(z) test.

The structure was solved in the centrosymmetric space group using direct methods [14] to locate the heavy atoms and subsequent structure-factor and electron-density maps located the lighter atoms. The Rh atom was positioned on a centre of symmetry. No H atoms were included in the model and the C atoms were retained with isotropic thermal parameters to retain an acceptable observations-to-parameter ratio. The disordered perchlorate whilst showing four O atoms gave a poor geometry and it was refined using a common isotropic

O thermal parameter and restraints in the Cl–O distance (to 1.45 Å). Full-matrix least-squares refinement on F using 1890 reflections ($I > 3\sigma(I)$) [15] converged to R = 0.068 (R_w = 0.087). The rather large residual peaks in the electron density maps (3.35 e Å⁻³) were near the ClO₄⁻ anion.

4. Supplementary material

Atomic coordinates, thermal parameters and bond length and angle data have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

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