Inorganica Chimica Acta, *208* (1993) 189–194

Ruthenium(II) and (III) complexes of triphenylstibine: a reinvestigation and the X-ray structure of *trans*-$RuCl_2(SbPh_3)_4$

Neil R. Champness, William Levason* and Michael Webster

Department of Chemistry, University of Southampton, Southampton SO9 5NH (UK)

(Received December 24, 1992; revised February 11, 1993)

Abstract

The reaction of $RuCl_3 \cdot nH_2O$ with $SbPh_3$ under a variety of conditions produced *trans*-$RuCl_2(SbPh_3)_4$, which was characterised by a single crystal X-ray study. The crystals are monoclinic, space group $C2$ (No. 5) with $a = 26.50(4)$, $b = 26.49(5)$, $c = 20.16(1)$ Å, $\beta = 109.73(9)°$, $Z = 8$. The structure was refined to $R = 0.041$ using 5106 reflections with $F > 4\sigma(F)$. Ru–Sb = 2.625(1)–2.632(1), Ru–Cl = 2.408(2)–2.439(1) Å. The complexes $RuBr_2(SbPh_3)_4$, *trans*-$[RuX_2(SbPh_3)_4]BF_4$ (X = Cl or Br) have been prepared and characterised by analysis, IR and UV–Vis spectroscopies, magnetic and conductance measurements, and by cyclic voltammetry. All attempts to obtain the reported $RuCl_2(SbPh_3)_3$ or *mer*-$RuCl_3(SbPh_3)_3$ have been unsuccessful.

Introduction

The reaction of hydrated ruthenium trichloride with triphenylstibine in organic solvents has been reported to produce a deep pink solid variously formulated as $RuCl_2(SbPh_3)_3$ or $RuCl_2(SbPh_3)_4$ [1–4]. A pink $RuCl_2(SbPh_3)_3$ has been reported from the reduction of ruthenium trichloride with zinc amalgam in alcohol, followed by addition of $SbPh_3$ [5]. Ruthenium(II) bromides, $RuBr_2(SbPh_3)_n$ ($n = 3$ or 4) have also been reported although with very limited data [2, 3].

The ruthenium(II) triphenylphosphine complexes $RuCl_2(PPh_3)_3$ and $RuCl_2(PPh_3)_4$ are well established [6], and the former has been shown to be a square pyramid by an X-ray study [7]. The nature of $RuCl_2(PPh_3)_4$ is less clear, since its solution chemistry is often indistinguishable from that of the tris(phosphine) species, and some workers regard it as $RuCl_2(PPh_3)_3 \cdot PPh_3$ with the fourth phosphine not coordinated to the ruthenium [8]. In contrast osmium(II) only forms *trans*-$OsX_2(SbPh_3)_4$ (X = Cl or Br) [9, 10]. Here we report a reinvestigation of the RuX_2–$SbPh_3$ system including an X-ray study of the title complex, and new ruthenium(III) complexes.

Experimental

Hydrated ruthenium trichloride was obtained from Johnson Matthey and used as received. Ruthenium tribromide was made by repeatedly treating the chloride with 48% aqueous hydrobromic acid and evaporating the mixture to dryness. Physical measurements were made as described previously [11].

Ruthenium(II) complexes

$RuCl_2(SbPh_3)_4$ was prepared by the method of Stephenson and Wilkinson [1]. $RuCl_3 \cdot xH_2O$ (0.53 g, 2.0 mmol) was refluxed with $SbPh_3$ (5.5 g, 14 mmol) in methanol (30 ml) for 1 h. A pink solid precipitated and was filtered off, washed with acetone (100 ml) and diethyl ether (10 ml), and dried *in vacuo* (yield 0.85 g, 27%). *Anal.* Found: C, 54.2; H, 3.8. Calc. for $C_{72}H_{60}Cl_2RuSb_4$: C, 54.6; H, 3.8%.

$RuBr_2(SbPh_3)_4 \cdot CH_2Cl_2$ was prepared similarly from $RuBr_3 \cdot xH_2O$ in 2-methoxyethanol, and recrystallised from CH_2Cl_2. *Anal.* Found: C, 49.2; H, 3.4. Calc. for $C_{73}H_{62}Br_2Cl_2RuSb_4$: C, 49.7; H, 3.4%.

Ruthenium(III) complexes

$[RuCl_2(SbPh_3)_4]BF_4$. $RuCl_2(SbPh_3)_4$ was suspended in 40% HBF_4 (15 ml) and concentrated HNO_3 was added dropwise (2 ml in total) and the mixture stirred for 5 min. The light brown solid was filtered off, washed with water (10 ml) and diethyl ether (2×10 ml) and dried *in vacuo*. *Anal.* Found: C, 47.3; H, 3.4; Cl, 4.4. Calc. for $C_{72}H_{60}BCl_2F_4RuSb_4$: C, 51.7; H, 3.6; Cl, 4.3%.**

---

*Author to whom correspondence should be addressed.

**Analyses for carbon obtained from different laboratories for different samples of these two complexes were consistently a few percent low. The spectroscopic and electrochemical data revealed no impurities, and we believe this is a further example of the difficulties sometimes experienced in obtaining good carbon analyses on compounds containing Sb and F in combination with a heavy transition metal.

0020-1693/93/$6.00

$[RuBr_2(SbPh_3)_4]BF_4$ was prepared analogously from $RuBr_2(SbPh_3)_4$. *Anal.* Found: C, 46.0; H, 3.5; Br, 9.7. Calc. for $C_{72}H_{60}BBr_2F_4RuSb_4$: C, 49.1; H, 3.4; Br, 9.0%.

X-ray structure determination

Small air-stable red crystals of *trans*-$RuCl_2(SbPh_3)_4$ were obtained by vapour diffusion of diethyl ether into a dichloromethane solution of the complex. The crystals formed as very small square plates. Data were collected using an Enraf-Nonius FAST area detector diffractometer equipped with Mo radiation and a graphite monochromator. Cell dimensions were obtained from 250 reflections using a room temperature (293 K) crystal (0.1×0.1×0.03 mm) mounted in a glass capillary. The intensity data for 20602 reflections were collected from approximately one hemisphere of reciprocal space based on a primitive triclinic cell and corrected for the Lorentz and polarisation factors using the diffractometer software [12]. The Niggli matrix [13] strongly suggested a C-centered monoclinic cell and transformation of the cell followed by inspection of the Laue symmetry supported this choice of crystal system. The systematic absences ($hkl, h+k=2n$ only) indicated the space groups $C2$, Cm or $C2/m$ and observation of a small number of reflections of type $h0l$ with l odd eliminated space groups Cc or $C2/c$ (see later). The structure was solved in the space group $C2$. Inspection of the Patterson function revealed a convincing set of vectors for the $RuSb_4Cl_2$ group (*trans* octahedral) and SHELXS86 [14] produced one solution with a low figure of merit in this space group. The trial model showed two crystallographically independent $RuSb_4Cl_2$ fragments and subsequent structure factor and electron-density syntheses over several iterations located all 24 phenyl rings. Full-matrix least-squares refinement [15] on F minimising $\Sigma w\Delta^2$ {anisotropic (Ru, Sb) and isotropic (Cl, C) atoms, rigid phenyl groups (d(C–C) = 1.395 Å), $w^{-1}=\sigma^2(F)$, |max. shift/error| = 0.17} converged to R of 0.041. The residual electron density was in the range 2.93 to −0.98 e Å^{-3}. No H atoms were included in the model and no absorption correction was applied. Complex neutral atom scattering factors were taken from SHELX76 (Cl, C) and ref. 16 (Ru, Sb). Further details are provided in Table 1 and Table 2 gives the final atomic coordinates.

A unit cell diagram viewed down c showed that the Ru, Sb and Cl atoms of the two independent molecules in $C2$ are nearly related by a c glide plane and with a change of origin conform to the space group $C2/c$. However inclusion of the carbon atoms shows that the glide plane does not extend to these atoms and thus the structure should properly be described in space group $C2$. See 'Supplementary material'.

Crystals of *trans*-$OsCl_2(SbPh_3)_4$ were also prepared and diffraction data measured. The data are of inferior quality but were sufficient to establish that the two materials had essentially the same cell dimensions and the same structure. Thus using as a starting point the atomic coordinates for the ruthenium compound the 3487 observed reflections ($F>4\sigma(F)$) gave $R=0.069$. See 'Supplementary material'.

TABLE 1. Crystal data and structure solution parameters

Formula	$C_{72}H_{60}Cl_2RuSb_4$
Formula weight	1584.25
Crystal system	monoclinic
Space group	$C2$ (No. 5)
a (Å)	26.50(4)
b (Å)	26.49(5)
c (Å)	20.16(1)
β (°)	109.73(9)
V (Å^3)	13321(34)
Z	8
$F(000)$	6192
D_{calc} (g/cm^3)	1.580
μ (Mo Kα) (cm^{-1})	19.2
λ (Mo Kα) (Å)	0.71069
Reflections measured	20602 (2θ(max.) = 50.7°)
Unique reflections	13931 ($R_{int}=0.075$)
Observed reflections ($F>4\sigma(F)$)	5106
No. parameters	394
R	0.041
R_w	0.053

$R=\Sigma(\|F_o\|-\|F_c\|)/\Sigma\|F_o\|$; $R_w=[\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$.

Results and discussion

The reaction of hydrated ruthenium trichloride* with $SbPh_3$ in a 1:>5 molar ratio in refluxing methanol, gave a dark pink solid. On washing with copious amounts of acetone a brown–green solution was formed, leaving a paler pink solid. Unfortunately the reported C, H and Cl analyses do not discriminate convincingly between $RuCl_2(SbPh_3)_3$ (calc.: C, 52.7; H, 3.7; Cl, 5.75%) and $RuCl_2(SbPh_3)_4$ (calc.: C, 54.6; H, 3.8; Cl, 4.48%) formulations, which is no doubt one reason for the conflicting literature. The identity of the pale pink solid has been established by a single crystal X-ray study.

Structure of trans-$RuCl_2(SbPh_3)_4$

The structure of $RuCl_2(SbPh_3)_4$ consists of discrete *trans* octahedral molecules with the two crystallographically independent groups having very similar conformations (see Fig. 1). The angles at Ru show small distortions of up to 13° away from the idealised 90/180° angles. The nature of this is most clearly illustrated

---

*Despite the name 'hydrated ruthenium trichloride', the material mostly contains Ru(IV) with 'trichloride' reflecting the 3:1 Cl:Ru ratio [17].

TABLE 2. Atomic coordinates for *trans*-[$RuCl_2(SbPh_3)_4$]

Atom	x/a	y/b	z/c
Ru(1)	0.2478(1)	−0.0902	−0.0012(1)
Sb(1)	0.3471(1)	−0.0649(1)	0.0144(1)
Sb(2)	0.2703(1)	−0.1854(1)	−0.0149(1)
Sb(3)	0.1544(1)	−0.1145(1)	0.0091(1)
Sb(4)	0.2206(1)	0.0055(1)	−0.0139(1)
Cl(1)	0.2802(3)	−0.0934(4)	0.1263(4)
Cl(2)	0.2149(3)	−0.0906(4)	−0.1281(4)
Ru(2)	0.2504(1)	0.0382(1)	0.4998(1)
Sb(5)	0.2353(1)	−0.0591(1)	0.5113(1)
Sb(6)	0.3443(1)	0.0205(1)	0.4867(1)
Sb(7)	0.2730(1)	0.1350(1)	0.5187(1)
Sb(8)	0.1494(1)	0.0569(1)	0.4823(1)
Cl(3)	0.2815(3)	0.0364(3)	0.6282(4)
Cl(4)	0.2192(3)	0.0395(3)	0.3717(3)
C(111)	0.4095(7)	−0.1130(7)	0.0817(9)
C(112)	0.4335(7)	−0.1504(7)	0.0537(9)
C(113)	0.4735(7)	−0.1809(7)	0.0985(9)
C(114)	0.4896(7)	−0.1740(7)	0.1712(9)
C(115)	0.4657(7)	−0.1366(7)	0.1993(9)
C(116)	0.4256(7)	−0.1061(7)	0.1545(9)
C(121)	0.3783(8)	0.0014(7)	0.0752(10)
C(122)	0.4205(8)	0.0275(7)	0.0642(10)
C(123)	0.4426(8)	0.0696(7)	0.1052(10)
C(124)	0.4224(8)	0.0856(7)	0.1573(10)
C(125)	0.3802(8)	0.0595(7)	0.1683(10)
C(126)	0.3582(8)	0.0173(7)	0.1272(10)
C(131)	0.3752(8)	−0.0529(8)	−0.0718(9)
C(132)	0.3391(8)	−0.0344(8)	−0.1347(9)
C(133)	0.3565(8)	−0.0235(8)	−0.1912(9)
C(134)	0.4100(8)	−0.0312(8)	−0.1848(9)
C(135)	0.4461(8)	−0.0498(8)	−0.1219(9)
C(136)	0.4287(8)	−0.0606(8)	−0.0654(9)
C(211)	0.3240(7)	−0.2028(8)	−0.0730(10)
C(212)	0.3256(7)	−0.1693(8)	−0.1257(10)
C(213)	0.3561(7)	−0.1808(8)	−0.1681(10)
C(214)	0.3851(7)	−0.2258(8)	−0.1578(10)
C(215)	0.3835(7)	−0.2593(8)	−0.1051(10)
C(216)	0.3530(7)	−0.2478(8)	−0.0627(10)
C(221)	0.3055(7)	−0.2362(8)	0.0743(8)
C(222)	0.3440(7)	−0.2166(8)	0.1346(8)
C(223)	0.3715(7)	−0.2488(8)	0.1897(8)
C(224)	0.3606(7)	−0.3004(8)	0.1846(8)
C(225)	0.3221(7)	−0.3199(8)	0.1243(8)
C(226)	0.2946(7)	−0.2878(8)	0.0692(8)
C(231)	0.2057(7)	−0.2295(8)	−0.0812(10)
C(232)	0.1730(7)	−0.2594(8)	−0.0555(10)
C(233)	0.1310(7)	−0.2868(8)	−0.1020(10)
C(234)	0.1216(7)	−0.2845(8)	−0.1744(10)
C(235)	0.1542(7)	−0.2546(8)	−0.2001(10)
C(236)	0.1963(7)	−0.2271(8)	−0.1536(10)
C(311)	0.1511(9)	−0.1824(7)	0.0693(10)
C(312)	0.1975(9)	−0.1992(7)	0.1216(10)
C(313)	0.1957(9)	−0.2418(7)	0.1615(10)
C(314)	0.1475(9)	−0.2676(7)	0.1491(10)
C(315)	0.1011(9)	−0.2508(7)	0.0968(10)
C(316)	0.1029(9)	−0.2082(7)	0.0569(10)
C(321)	0.0829(7)	−0.1283(8)	−0.0774(9)
C(322)	0.0892(7)	−0.1497(8)	−0.1374(9)
C(323)	0.0442(7)	−0.1643(8)	−0.1938(9)
C(324)	−0.0070(7)	−0.1574(8)	−0.1902(9)
C(325)	−0.0133(7)	−0.1360(8)	−0.1302(9)
C(326)	0.0317(7)	−0.1215(8)	−0.0738(9)
C(331)	0.1273(8)	−0.0645(7)	0.0738(10)
C(332)	0.1498(8)	−0.0696(7)	0.1468(10)
C(333)	0.1345(8)	−0.0370(7)	0.1910(10)
C(334)	0.0968(8)	0.0007(7)	0.1622(10)
C(335)	0.0743(8)	0.0059(7)	0.0892(10)
C(336)	0.0895(8)	−0.0267(7)	0.0450(10)
C(411)	0.2307(7)	0.0557(8)	0.0744(8)
C(412)	0.2263(7)	0.0339(8)	0.1352(8)
C(413)	0.2295(7)	0.0640(8)	0.1933(8)
C(414)	0.2371(7)	0.1159(8)	0.1905(8)
C(415)	0.2415(7)	0.1378(8)	0.1298(8)
C(416)	0.2382(7)	0.1077(8)	0.0717(8)
C(421)	0.2546(8)	0.0515(8)	−0.0780(10)
C(422)	0.2311(8)	0.0462(8)	−0.1508(10)
C(423)	0.2527(8)	0.0717(8)	−0.1957(10)
C(424)	0.2976(8)	0.1024(8)	−0.1678(10)
C(425)	0.3210(8)	0.1077(8)	−0.0950(10)
C(426)	0.2995(8)	0.0823(8)	−0.0501(10)
C(431)	0.1385(6)	0.0263(8)	−0.0746(9)
C(432)	0.1106(6)	−0.0076(8)	−0.1272(9)
C(433)	0.0575(6)	0.0022(8)	−0.1681(9)
C(434)	0.0323(6)	0.0459(8)	−0.1564(9)
C(435)	0.0602(6)	0.0797(8)	−0.1038(9)
C(436)	0.1133(6)	0.0699(8)	−0.0629(9)
C(511)	0.2041(7)	−0.1112(7)	0.4254(8)
C(512)	0.2202(7)	−0.1040(7)	0.3669(8)
C(513)	0.2047(7)	−0.1384(7)	0.3112(8)
C(514)	0.1732(7)	−0.1800(7)	0.3141(8)
C(515)	0.1571(7)	−0.1871(7)	0.3726(8)
C(516)	0.1726(7)	−0.1527(7)	0.4282(8)
C(521)	0.3059(6)	−0.1034(7)	0.5701(8)
C(522)	0.3491(6)	−0.0807(7)	0.6215(8)
C(523)	0.3932(6)	−0.1096(7)	0.6601(8)
C(524)	0.3941(6)	−0.1613(7)	0.6473(8)
C(525)	0.3510(6)	−0.1840(7)	0.5958(8)
C(526)	0.3069(6)	−0.1550(7)	0.5572(8)
C(531)	0.1906(7)	−0.0838(8)	0.5767(9)
C(532)	0.2173(7)	−0.0896(8)	0.6489(9)
C(533)	0.1892(7)	−0.1054(8)	0.6925(9)
C(534)	0.1344(7)	−0.1156(8)	0.6639(9)
C(535)	0.1077(7)	−0.1099(8)	0.5917(9)
C(536)	0.1358(7)	−0.0940(8)	0.5481(9)
C(611)	0.3731(8)	0.0749(7)	0.4287(10)
C(612)	0.3378(8)	0.1062(7)	0.3786(10)
C(613)	0.3576(8)	0.1417(7)	0.3424(10)
C(614)	0.4127(8)	0.1457(7)	0.3563(10)
C(615)	0.4480(8)	0.1144(7)	0.4063(10)
C(616)	0.4282(8)	0.0789(7)	0.4425(10)
C(621)	0.3505(8)	−0.0404(7)	0.4205(10)
C(622)	0.3692(8)	−0.0883(7)	0.4460(10)
C(623)	0.3745(8)	−0.1255(7)	0.3998(10)
C(624)	0.3610(8)	−0.1148(7)	0.3282(10)
C(625)	0.3422(8)	−0.0670(7)	0.3027(10)
C(626)	0.3370(8)	−0.0298(7)	0.3489(10)
C(631)	0.4179(6)	0.0099(7)	0.5739(8)
C(632)	0.4248(6)	0.0340(7)	0.6379(8)
C(633)	0.4731(6)	0.0293(7)	0.6935(8)
C(634)	0.5146(6)	0.0005(7)	0.6851(8)

(*continued*)

TABLE 2. (*continued*)

Atom	*x/a*	*y/b*	*z/c*
C(635)	0.5078(6)	−0.0236(7)	0.6211(8)
C(636)	0.4594(6)	−0.0189(7)	0.5655(8)
C(711)	0.2321(7)	0.1766(7)	0.5769(9)
C(712)	0.2174(7)	0.1534(7)	0.6298(9)
C(713)	0.1935(7)	0.1817(7)	0.6696(9)
C(714)	0.1844(7)	0.2332(7)	0.6563(9)
C(715)	0.1990(7)	0.2564(7)	0.6034(9)
C(716)	0.2229(7)	0.2280(7)	0.5636(9)
C(721)	0.3518(6)	0.1568(8)	0.5889(10)
C(722)	0.3620(6)	0.1602(8)	0.6614(10)
C(723)	0.4122(6)	0.1762(8)	0.7059(10)
C(724)	0.4521(6)	0.1888(8)	0.6780(10)
C(725)	0.4418(6)	0.1854(8)	0.6055(10)
C(726)	0.3917(6)	0.1694(8)	0.5610(10)
C(731)	0.2622(7)	0.1889(7)	0.4341(8)
C(732)	0.2936(7)	0.2323(7)	0.4426(8)
C(733)	0.2846(7)	0.2663(7)	0.3870(8)
C(734)	0.2442(7)	0.2569(7)	0.3228(8)
C(735)	0.2128(7)	0.2136(7)	0.3143(8)
C(736)	0.2218(7)	0.1795(7)	0.3699(8)
C(811)	0.1111(7)	0.1188(7)	0.4145(10)
C(812)	0.0893(7)	0.1096(7)	0.3422(10)
C(813)	0.0607(7)	0.1475(7)	0.2970(10)
C(814)	0.0540(7)	0.1946(7)	0.3240(10)
C(815)	0.0759(7)	0.2037(7)	0.3963(10)
C(816)	0.1044(7)	0.1658(7)	0.4415(10)
C(821)	0.1168(8)	0.0645(8)	0.5670(9)
C(822)	0.1392(8)	0.0356(8)	0.6277(9)
C(823)	0.1187(8)	0.0389(8)	0.6828(9)
C(824)	0.0758(8)	0.0711(8)	0.6772(9)
C(825)	0.0534(8)	0.1000(8)	0.6165(9)
C(826)	0.0739(8)	0.0967(8)	0.5614(9)
C(831)	0.0925(7)	0.0019(7)	0.4233(10)
C(832)	0.1026(7)	−0.0270(7)	0.3713(10)
C(833)	0.0643(7)	−0.0613(7)	0.3318(10)
C(834)	0.0159(7)	−0.0667(7)	0.3443(10)
C(835)	0.0058(7)	−0.0378(7)	0.3963(10)
C(836)	0.0441(7)	−0.0035(7)	0.4358(10)

C atoms are labelled C(IJK) where I (1–8) is the same as the bonded Sb atom, J (1–3) indicates the particular ring, and L (1–6) denotes the atoms of one ring. C(IJ1) is always bonded to Sb(I).

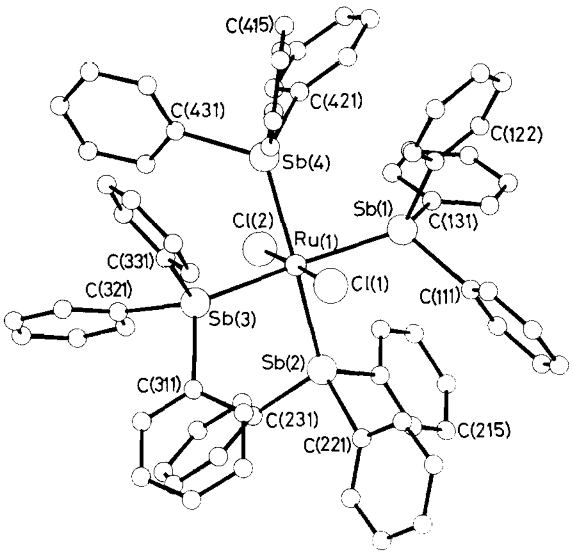

Fig. 1. View of one of the two molecules in the asymmetric unit showing the geometry and the atom labelling scheme. The second molecule is very similar.

TABLE 3. Selected bond lengths (Å) and angles (°) for *trans*-$[RuCl_2(SbPh_3)_4]$

Ru(1)–Cl(1)	2.422(2)	Ru(2)–Cl(3)	2.439(1)
Ru(1)–Cl(2)	2.408(2)	Ru(2)–Cl(4)	2.430(1)
Ru(1)–Sb(1)	2.629(1)	Ru(2)–Sb(5)	2.632(1)
Ru(1)–Sb(2)	2.625(1)	Ru(2)–Sb(6)	2.630(1)
Ru(1)–Sb(3)	2.632(1)	Ru(2)–Sb(7)	2.632(1)
Ru(1)–Sb(4)	2.625(1)	Ru(2)–Sb(8)	2.627(1)
Sb–C	2.130(3) (min.) to 2.190(3) (max.)		
C–C (fixed)	1.395		
Cl(1)–Ru(1)–Cl(2)	177.7(1)	Cl(3)–Ru(2)–Cl(4)	179.6(1)
Sb(1)–Ru(1)–Sb(2)	90.2(1)	Sb(5)–Ru(2)–Sb(6)	90.7(1)
Sb(1)–Ru(1)–Sb(3)	169.2(1)	Sb(5)–Ru(2)–Sb(7)	167.4(1)
Sb(1)–Ru(1)–Sb(4)	89.8(1)	Sb(5)–Ru(2)–Sb(8)	91.0(1)
Sb(2)–Ru(1)–Sb(3)	91.6(1)	Sb(6)–Ru(2)–Sb(7)	90.6(1)
Sb(2)–Ru(1)–Sb(4)	169.0(1)	Sb(6)–Ru(2)–Sb(8)	167.4(1)
Sb(3)–Ru(1)–Sb(4)	90.5(1)	Sb(7)–Ru(2)–Sb(8)	90.4(1)
Cl(1)–Ru(1)–Sb(1)	84.3(1)	Cl(3)–Ru(2)–Sb(5)	83.9(1)
Cl(1)–Ru(1)–Sb(2)	93.8(1)	Cl(3)–Ru(2)–Sb(6)	96.4(1)
Cl(1)–Ru(1)–Sb(3)	85.0(1)	Cl(3)–Ru(2)–Sb(7)	83.5(1)
Cl(1)–Ru(1)–Sb(4)	97.1(1)	Cl(3)–Ru(2)–Sb(8)	96.2(1)
Cl(2)–Ru(1)–Sb(1)	96.8(1)	Cl(4)–Ru(2)–Sb(5)	95.8(1)
Cl(2)–Ru(1)–Sb(2)	84.2(1)	Cl(4)–Ru(2)–Sb(6)	83.8(1)
Cl(2)–Ru(1)–Sb(3)	94.0(1)	Cl(4)–Ru(2)–Sb(7)	96.8(1)
Cl(2)–Ru(1)–Sb(4)	84.9(1)	Cl(4)–Ru(2)–Sb(8)	83.6(1)
Ru–Sb–C	114.5(1) (min.) to 125.8(1) (max.)		
C–Sb–C	92.8(2) (min.) to 102.4(2) (max.)		
C–C–C (fixed)	120		

by examining the Cl(1)–Ru(1)–Sb angles, where the angles to Sb(1) and Sb(3) are less than 90° (84.3, 85.0) and the angles to Sb(2) and Sb(4) are greater than 90° (93.8, 97.1) (see Table 3). These angles and the conformation of the phenyl rings presumably minimise intramolecular repulsions between the bulky ligands and a similar distortion has been noted in the *trans*-$[OsCl_2(PMe_3)_4]^+$ cation [9]. The Ru–Cl bond distances (2.408–2.439 Å) are a little longer than those found in the five-coordinate Ru(II) complex $RuCl_2(PPh_3)_3$ (2.39 Å) [7]. Among SbR_3 complexes the triphenyl derivative has been examined most frequently and the geometry reported here is unexceptional. The Ru–Sb distances (2.625–2.632 Å) accord well with $Ru(CO)_4(SbPh_3)$ (2.623 Å) [18] and $Ru(CO)_4(SbMe_3)$ (2.619 Å) [19]. A few examples of tris-triphenylantimony octahedral metal complexes have been reported including *mer*-$OsBr_3(SbPh_3)_3$ [20] and $RhCl_2(Ph)(SbPh_3)_3$ [21], but the only other tetrakis derivative is an Au(I) compound with a tetrahedrally coordinated metal atom [22].

Spectroscopic data and reactions

The physical data on *trans*-$RuCl_2(SbPh_3)_4$ in Table 4 are much as expected for a low-spin d^6 metal centre in an essentially D_{4h} environment. In particular, the two bands in the visible spectrum are assignable as the d–d transitions $^1A_{1g} \rightarrow {}^1E_g$, and $^1A_{1g} \rightarrow {}^1A_{2g}$. The complex obeys the Beer–Lambert law in CH_2Cl_2 solution over the concentration range 10^{-3}–10^{-4} mol dm^{-3}, and has a normal molecular weight in $CHCl_3$ solution [4], which rule out the possibility of any significant dissociation to $RuCl_2(SbPh_3)_3$ and $SbPh_3$ in solution. The $RuBr_2(SbPh_3)_4$ made in a similar reaction from ruthenium tribromide is clearly analogous.

Cyclic voltammetry showed that both complexes undergo reversible 1*e* oxidations in CH_2Cl_2 solution to the Ru(III) cations at potentials *c*. 0.3 V more positive than those reported for *trans*-$OsX_2(SbPh_3)_4$ [9], reflecting the usual trends between Ru(III) and Os(III) [9, 23]. The oxidations were also achieved chemically with nitric acid, and the orange–brown *trans*-$[RuX_2(SbPh_3)_4]BF_4$ isolated from aqueous HBF_4 solutions. In the solid state the Ru(III) complexes decompose back to Ru(II) over several weeks, and decomposition occurs in days in chlorocarbon solutions. The *trans*-$[RuX_2(SbPh_3)_4]BF_4$ are paramagnetic (Table 4) with $\mu \sim 2$ BM as expected for low-spin d^5 Ru(III) [24]. The UV–Vis spectra are assignable by comparison with those of the Os(III) analogues [23], and are dominated by charge transfer transitions, with the very low energy of the $\sigma(Sb) \rightarrow Ru$ transitions (*c*. 11 000 cm^{-1}) being notable.

Other ruthenium–SbPh₃ complexes

Following the detailed characterisation of *trans*-$RuCl_2(SbPh_3)_4$ above, we carried out the reaction of $RuCl_3 \cdot nH_2O$ with $SbPh_3$ in a variety of alcohols (ethanol, n-butanol and 2-methoxyethanol) and in different ratios (Ru:$SbPh_3$ 1:3–1:6) in attempts to obtain a tris complex, but in every case isolated only the tetrakis complex, usually contaminated with varying amounts of green–brown material (A), which was removed by washing with acetone. We also repeated the reported [5] reduction of $RuCl_3 \cdot nH_2O$ with zinc amalgam in ethanol, and treated the blue product with $SbPh_3$. We found that the product was *trans*-$RuCl_2(SbPh_3)_4$ containing larger amounts of the same acetone soluble green–brown complex A*.

Apart from the nitrido complex $RuNCl_3(SbPh_3)_2$ [25], the only other $SbPh_3$ ruthenium halide complex reported is *mer*-$RuCl_3(SbPh_3)_3$. This is said [26] to be formed along with $Ru(NO)Cl_3(SbPh_3)_2$ by reaction of $RuCl_3 \cdot nH_2O$, $SbPh_3$ and NOCl in CH_2Cl_2, although no data were reported, and it is not clear if the products were separated. In our hands [27] this reaction gave a mixture of $Ru(NO)Cl_3(SbPh_3)_2$ [28], *trans*-$RuCl_2(SbPh_3)_4$ and Ph_3SbCl_2, along with very small amounts of other uncharacterised products. Our attempts to 'intercept' the reduction of $RuCl_3 \cdot nH_2O$ with $SbPh_3$ at the Ru(III) stage were unsuccessful, only *trans*-$RuCl_2(SbPh_3)_4$ being formed consistent with literature reports [1, 4]. Cautious chlorination of *trans*-$RuCl_2(SbPh_3)_4$ in CH_2Cl_2 in the hope of removing one ligand,

TABLE 4. Selected physical data

Complex	Colour	ν(Ru-X)^a (cm^{-1})	E_{max} (10^3 cm^{-1}) (ϵ_{mol} (dm^3 mol^{-1} cm^{-1}))^b	E°^{c} (V)	$\Lambda_M{}^d$ (Ω^{-1} cm^2 mol^{-1})	μ^e (BM)
$RuCl_2(SbPh_3)_4$	pink	315	18.6 (960); 23.3 (950); 33.0 (50870)	+0.75 (ox)		diamagnetic
$RuBr_2(SbPh_3)_4$	dark pink	n.o.	17.9 (520); 22.7 (620)(sh); 31.5 (22970)	+0.77 (ox)		diamagnetic
$[RuCl_2(SbPh_3)_4]BF_4$	orange–brown	325	11.6 (530); 21.9 (2340)(sh); 28.1 (32040); 32.0 (12940)(sh)	+0.75 (red)	15	2.09
$[RuBr_2(SbPh_3)_4]BF_4$	brown	n.o.	10.8 (1370); 15.5 (360); 21.1 (2710)(sh); 26.8 (30000); 31.0 (18130)	+0.77 (red)	13	2.17

^{a}Nujol mulls, n.o. not observed due to strong ligand modes. ^{b}CH_2Cl_2 solutions. ^{c}Recorded in CH_2Cl_2 standardised to the $(Cp)_2Fe/(Cp)_2Fe^+$ couple at +0.57 V. ^{d}10^{-3} mol dm^{-3} solutions in 1,2-dichloroethane, 1:1 electrolytes have values in the range 10–24 Ω^{-1} cm^2 mol^{-1}. ^{e}±0.1 BM.

---

*Complex A has not been fully identified. It contains ruthenium(III) and $SbPh_3$ but has not been obtained in crystalline form which would permit X-ray characterisation. The analysis (C = 58.0; H = 7.5; Cl = 2.5%), particularly the high C/Cl ratio suggests it may contain fragmented ligand, cf. $RhCl_2(Ph)(SbPh_3)_3$ [21].

gave *trans*-$[RuCl_2(SbPh_3)_4]^+$, identified *in situ* by its UV–Vis spectrum. On the basis of these experiments we have no evidence for the existence of the *mer*-$RuCl_3(SbPh_3)_3$ complex. The osmium analogue, the green *mer*-$OsCl_3(SbPh_3)_3$ is well known [11].

Supplementary material

Lists of thermal parameters, bond lengths and angles as well as the observed and calculated structure factors are available from the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank the SERC for financial support (N.R.C.), M. R. Davis for experimental assistance and Professor M. B. Hursthouse for the X-ray data collection by the SERC service.

References

1 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem., 28* (1966) 945.
2 D. Gussoni, G. Mercati and F. Morazzoni, *Gazz. Chim. Ital., 109* (1979) 545.
3 B. E. Prater, *J. Organomet. Chem., 34* (1972) 379.
4 A. Araneo and S. Martinengo, *Rend. Ist. Lomb. Accad. Sci. Lett. A, 99* (1965) 829; *Chem. Abstr., 65* (1966) 1748d.
5 M. M. T. Khan and R. Mohiuddin, *Polyhedron, 2* (1983) 1247.
6 F. Jardine, *Prog. Inorg. Chem., 31* (1984) 265.
7 S. J. La Placa and J. A. Ibers, *Inorg. Chem., 4* (1965) 778.
8 P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc., 97* (1975) 4221.
9 N. R. Champness, W. Levason, R. A. S. Mould, D. Pletcher and M. Webster, *J. Chem. Soc., Dalton Trans.,* (1991) 2777.
10 A. Araneo and C. Bianchi, *Gazz. Chim. Ital., 97* (1967) 885.
11 R. A. Cipriano, W. Levason, R. A. S. Mould, D. Pletcher and M. Webster, *J. Chem. Soc., Dalton Trans.,* (1990) 2609.
12 M. B. Hursthouse, A. I. Karaulov, M. Ciechanowicz-Rutkowska, A. Kolasa and W. Zankowska-Jasinska, *Acta Crystallogr., Sect. C, 48* (1992) 1257.
13 P. M. de Wolff and B. Gruber, *Acta Crystallogr., Sect. A, 47* (1991) 29.
14 G. M. Sheldrick, *SHELXS86,* program for crystal structure solution, University of Göttingen, Germany, 1986.
15 G. M. Sheldrick, *SHELX76,* program for X-ray structure determination, University of Cambridge, UK, 1976.
16 *International Tables for X-ray Crystallography,* Vol. 4, Kynoch, Birmingham, UK, 1974, pp. 99, 149.
17 J. A. Rard, *Chem. Rev., 85* (1985) 1.
18 E. J. Forbes, D. L. Jones, K. Paxton and T. A. Hamor, *J. Chem. Soc., Dalton Trans.,* (1979) 879.
19 L. R. Martin, F. W. B. Einstein and R. K. Pomeroy, *Inorg. Chem., 24* (1985) 2777.
20 C. C. Hinckley, M. Matusz and P. D. Robinson, *Acta Crystallogr., Sect. C, 44* (1988) 1829.
21 R. Cini, G. Giorgi and L. Pasquini, *Inorg. Chim. Acta, 196* (1992) 7.
22 P. G. Jones, *Acta Crystallogr., Sect. C, 48* (1992) 1487.
23 N. R. Champness, W. Levason, D. Pletcher and M. Webster, *J. Chem. Soc., Dalton Trans.,* (1992) 3243.
24 B. N. Figgis and J. Lewis, *Prog. Inorg. Chem., 6* (1964) 37.
25 W. P. Griffith and D. Pawson, *J. Chem. Soc., Dalton Trans.,* (1975) 417.
26 K. C. Jain, K. K. Pandey, R. Prasad, T. Singh and U. C. Agarwala, *Ind. J. Chem., 19A* (1980) 1089.
27 M. R. Davis, unpublished work, 1992.
28 M. B. Fairey and R. J. Irvine, *J. Chem. Soc. A,* (1966) 475.