

Mass spectrometric and structural studies of some platinum-group metal complexes: the crystal and molecular structure of *trans*-[Ru(NO)Cl₃(SbPh₃)₂]

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Abstract—The ruthenium triphenylstibine complexes [RuCl₂(SbPh₃)₃] and [RuCl₂(SbPh₃)₄], and the nitrosyl complexes [Ru(NO)Cl₃(EPh₃)₂] for E = Sb, As, P; [Rh(NO)Cl₂(EPh₃)₂] for E = As, P, have been investigated using electrospray mass spectrometry. The mass spectrometric evidence suggests that [RuCl₂(SbPh₃)₄] is formed and not [RuCl₂(SbPh₃)₃] as previously reported. *In situ* derivatisation in the presence of alkali metal ions gave simple spectra for the ruthenium nitrosyl complexes but not the rhodium complexes. The crystal and molecular structure for the ruthenium complex [Ru(NO)Cl₃(SbPh₃)₂] has been determined by single crystal X-ray diffraction. There is a crystallographically imposed centre of inversion and the NO and chlorides are disordered. The triphenylstibine ligands are coordinated in the *trans* configuration (Ru–Sb = 2.649(1) Å). © 1998 Elsevier Science Ltd. All rights reserved

Keywords: ruthenium; nitrosyl; rhodium; triphenylstibine; electrospray mass spectrometry X-ray structure.

The preparation, reaction, and structural chemistries of nitrosyl-organopnictide and nitrosyl organochalcogenide complexes of platinum-group metals of the form [M(NO)X₃L₂] for M = Ru, Os, X = halide, L = organopnictide or organochalcogenide, and [M(NO)X₂L₂] for M = Rh, Ir, X = halide, L = organopnictide have been reported by us and other workers [1–18]. The chemistry of complexes with tertiary stibine and arsine ligands is in general much less well developed compared with their phosphine analogues despite the fact that they are good donor ligands. One reason for this may be the lack of suitable analytical probes for these ligands. Tertiary phosphines are conveniently studied using ³¹P NMR spectroscopy, but there are no readily accessible NMR active nuclei available for the arsine and stibine ligands. There have been a number of X-ray structural investigations of these complexes, but again most of the studies have been carried out on organophosphine complexes with

little data available for organoarsine or organostibine complexes [15,19–28].

The versatile new soft ionisation technique available in electrospray mass spectrometry [ESMS] is well suited to studying such complexes [29–30]. The soft ionisation process used in ESMS typically results in simple patterns in which the molecular ion peak or a simple adduct is clearly evident. At low cone voltage fragmentation is usually very limited, and fragmentation can easily be investigated by raising the cone voltage.

For neutral transition metal complexes good spectra can often be obtained by *in situ* derivatisation. For example this may involve the formation of adducts in which a halide or other negative ligand has been replaced by a neutral donor ligand that is present in the solvent. Common donor ligands include acetonitrile, water, and ammonia, and replacement of a halide ion by these ligands results in the formation of adducts with a single positive charge.

Here we have investigated the reported preparation of the complex [RuCl₂(SbPh₃)₃] using ESMS. In

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addition we report ESMS for the complexes $[\text{Ru}(\text{NO})\text{Cl}_3(\text{EPh}_3)_2]$ for $\text{E} = \text{P}, \text{As}, \text{Sb}$, and the five coordinate rhodium analogues, $[\text{Rh}(\text{NO})\text{Cl}_2(\text{EPh}_3)_2]$ for $\text{E} = \text{P}, \text{As}$. During our studies of ruthenium organostibine complexes we isolated crystals of $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$. Because of the paucity of data for organostibine complexes we have determined the structure by single crystal X-ray diffraction.

EXPERIMENTAL

The complexes $[\text{RuCl}_2(\text{SbPh}_3)_3]$, $[\text{RuCl}_2(\text{SbPh}_3)_4]$, $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$, $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$, $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$, $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$, and $[\text{Rh}(\text{NO})\text{Cl}_2(\text{AsPh}_3)_2]$, were prepared by literature methods [1–3,7]. Recrystallisation by the slow evaporation of a chloroform solution produced red-orange, bipyramidal crystals of $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$ suitable for X-ray analysis. Spectroscopic and analytical data for the recrystallised material were as observed previously for the bulk sample [1]: IR KBr disk $\nu(\text{NO})$ 1840 cm^{-1} ; ^1H NMR (δ ppm) 7.45 3-H, m; 7.75 2-H, m. Anal: found; C, 45.77; H, 3.19%; calc. for $\text{C}_{36}\text{H}_{30}\text{Cl}_3\text{NORuSb}_2$: C, 45.83; H, 3.20%.

Electrospray mass spectra were recorded in positive-ion mode on a VG Platform II instrument, using methanol as the mobile phase. No precautions were taken to exclude oxygen from the system. The samples were introduced via a microlitre syringe and a 10 μl sample loop fitted to a Rheodyne injector, with the mobile phase being delivered to the mass spectrometer by a Spectra System P1000 LC pump, at a flow rate of 0.01 ml min^{-1} . Nitrogen was employed both as the nebulising and drying gas. Fragmentation was investigated by varying the skimmer cone voltage, typically from 10 to 80 V. Spectra were typically acquired as 10 to 12 scans, and subsequently averaged. Isotope patterns for major species were recorded, and compared with calculated patterns obtained using the Isotope simulation program [31].

The crystal data, data collection parameters, and structure refinement details are summarised in Table 1. The unit cell parameters were determined by the least square refinement of 25 accurately centred high angle reflections. The data were collected at 168 K on a Siemens R3m Four-circle X-ray diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using θ -scans to a maximum angle of $2\theta = 54^\circ$. Reflection intensities were corrected for Lorentz and polarisation effects, and crystal stability was monitored by observation of three standard reflections after every 100 reflections: no movement or decay was observed. The absorption correction was based on ψ -scans and an ellipsoidal model, and the structure was solved in the centrosymmetric space group $P\bar{1}$ using the direct methods. The structure has been modelled with the chlorides and NO disordered over all four sites using a fractional occupancy [1/4 NO + 3/4 Cl] as recommended by the crystallographic

Table 1. Crystal data and structure refinement for $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$

Empirical formula	$\text{C}_{36}\text{H}_{30}\text{Cl}_3\text{NORuSb}_2$
Formula weight	943.53
Temperature	168(2) K
Wavelength	0.71073 \AA
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
<i>a</i>	9.842(4) \AA
<i>b</i>	9.850(2) \AA
<i>c</i>	10.419(4) \AA
α	111.450(10) $^\circ$
β	109.52(3) $^\circ$
γ	92.44(3) $^\circ$
Volume	870.3(5) \AA^3
<i>Z</i>	1
Density (calculated)	1.800 mg/m^3
Absorption coefficient	2.229 mm^{-1}
Absorption correction	ψ -scans, ellipsoid model
Min/max transmission	0.477/0.531
<i>F</i> (000)	458
Crystal size	0.44 \times 0.42 \times 0.36 mm
Crystal colour/morphology	red-orange/bipyramid
θ range for data collection	2.24–27.00 $^\circ$
Index ranges	–12 $\leq h \leq$ 2; –11 $\leq k \leq$ 11, –12 $\leq l \leq$ 12
Reflections collected	4540
Independent reflections	3682 [$R_{\text{int}} = 0.0141$]
Independent reflections [$I > 2\sigma(I)$]	3283
Refinement method	Full-matrix least-squares on F^2
Data/constraints/parameters	3682/12/208
Goodness-of-fit on F^2	1.028
Final <i>R</i> indices [$I > 2\sigma(I)$]	R_1 0.0548, wR_2 0.1458
<i>R</i> indices (all data)	R_1 0.0613, wR_2 0.1517
Largest diff. peak and hole	1.98 and –1.13 e \AA^{-3}

referee. The nitrogen and oxygen atoms were inserted in calculated positions using Ru–N and N–O bond lengths taken from the literature [20]. The Ru–Cl, Ru–N, and N–O bond lengths were constrained to provide an acceptable refinement. All non-hydrogen atoms except the disordered nitrogen and oxygen atoms were modelled assuming anisotropic thermal vibration. Attempts to refine the nitrogen and oxygen atoms using isotropic thermal vibration were unsuccessful, and so these atoms were modelled using fixed temperature factors. Atomic scattering factors were taken from Crommer and Mann [32] and corrected for the effects of anomalous scattering using values from Crommer and Liberman [33]. The structure was solved using the direct methods and the refinement was carried out using a full-matrix least squares refinement procedure based on F^2 . The final cycle of refinement based on 3283 unique observed data [$I > 2\sigma(I)$] and 208 variables converged with an

Table 2. Selected bond lengths [\AA] and angles [$^\circ$] for $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$

Ru(1)—Cl(1)	2.277(3)
Ru(1)—Cl(2)	2.345(2)
Ru(1)—Sb(1)	2.649(1)
Sb(1)—C(36)	2.095(8)
Sb(1)—C(16)	2.126(8)
Cl(1)—Ru(1)—Cl(2)	89.2(1)
Cl(2)—Ru(1)—Sb(1)	90.8(7)
C(31)—C(36)—Sb(1)	115.5(7)

$R = 0.0548$ and $R_w = 0.0613$, where the functions minimised are: $R = \Sigma(|F_o| - |F_c|) / \Sigma(|F_o|)$ and $R_w = \sqrt{[\Sigma w|F_o| - |F_c|^2] / \Sigma w|F_o|^2}$. The data were processed and the structure solution and refinement carried out using the SHELXTL system of programs [34].

Selected atomic distances and angles are given in Table 2.

RESULTS AND DISCUSSION

Stephenson and Wilkinson (1966) [35] have reported that the reaction of hydrated ruthenium chloride with triphenylstibine at room temperature or under reflux results in the formation of the complex $[\text{RuCl}_2(\text{SbPh}_3)_3]$. Champness *et al.* (1993) have disputed the formation of $[\text{RuCl}_2(\text{SbPh}_3)_3]$ and their attempts to prepare this complex resulting in the formation of the complex $[\text{RuCl}_2(\text{SbPh}_3)_4]$ characterised by single-crystal X-ray diffraction [19]. As pointed out it is sometimes difficult to discriminate convincingly between these complexes on the basis of elemental analytical data or other spectroscopic evidence [19]. Although much structural information is provided by single-crystal X-ray studies, this does not provide information about the bulk material.

In this work the reaction of ruthenium chloride with excess triphenylstibine [6:1] under reflux gave a pink powder. The ESMS for this powder in the presence of a trace amount of CH_3CN contained evidence for the parent ion $[\text{RuCl}_2(\text{SbPh}_3)_4]^+$ [$M^+ = 1584$] and the adduct: $[\text{RuCl}_2(\text{SbPh}_3)_3(\text{CH}_3\text{CN})]^+$ [$M^+ = 1273$]. A small peak assigned to the $[\text{RuCl}_2(\text{SbPh}_3)_3]^+$ ion [$M^+ = 1232$] was observed, but only a high cone voltage [>80 V]. It is likely that this species has appeared as a result of fragmentation of the parent ion $[\text{RuCl}_2(\text{SbPh}_3)_4]^+$.

The product of the reaction of ruthenium chloride with triphenylstibine at room temperature gave a different, more complex, spectrum. The complexity of the spectrum indicated that a mixture of compounds had been produced in this reaction. There was no evidence for parent ions $[\text{RuCl}_2(\text{SbPh}_3)_3]^+$, $[\text{RuCl}_2(\text{SbPh}_3)_4]^+$, or any simple adducts of these ions.

Hence our studies support those of Champness *et al.* (1993), and it seems there is some doubt over the existence of $[\text{RuCl}_2(\text{SbPh}_3)_3]$.

The nitrosyl complexes $[\text{Ru}(\text{NO})\text{Cl}_3(\text{EPh}_3)_2]$ for $\text{E} = \text{Sb}, \text{As}, \text{P}$ were also investigated using ESMS. None of the complexes gave simple spectra when measured in the presence of neutral donor species. Other workers have reported good ESMS for neutral metal carbonyl complexes by *in situ* derivatisation in the presence of anionic or cationic species [29–30]. For complexes containing basic carbonyl ligands, good spectra were obtained using Ag^+ ions. Non-polar, poorly basic carbonyl complexes required the presence of a nucleophile such as the methoxylate ion. This derivatisation reaction resulted in the formation of negative ion adducts of the form $[\text{M} + \text{OMe}]^-$.

In this work good spectra were obtained for ruthenium nitrosyl complexes in the presence of traces of alkali metal ions. The spectra for the complex $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$ together with the isotope pattern and simulated spectra are shown in Fig. 1. Similar spectra were obtained for the triphenylphosphine and triphenylarsine complexes. The spectra suggest that simple 1:1 adducts are formed between the nitrosyl

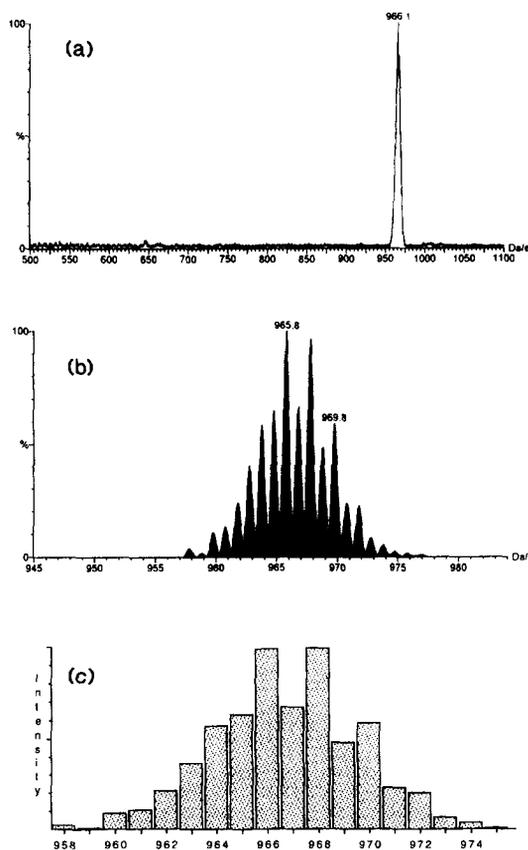


Fig. 1. Electrospray mass spectrum for $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2] + \text{Na}^+$. (a) Mass spectrum; (b) isotope pattern for $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2] + \text{Na}^+$; (c) simulated mass spectrum for $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2] + \text{Na}^+$.

complex and the alkali metal ions. Good spectra were obtained using Li^+ , Na^+ or K^+ ions, but not with Cs^+ or Rb^+ . We also repeated our ESMS investigation of the complexes $[\text{RuCl}_2(\text{SbPh}_3)_3]$, and $[\text{RuCl}_2(\text{SbPh}_3)_4]$ in the presence of alkali metal ions, but were unable to obtain good spectra. Thus it seems likely that the nitrosyl oxygen is the basic centre despite the fact that the NO is bound in the linear fashion. Previous X-ray photoelectron studies have suggested that there is greater electron density on the nitrosyl ligand when it is coordinated in the bent fashion [36–42]. In view of this we also investigated some five-coordinate rhodium analogues: i.e. complexes of the form $[\text{Rh}(\text{NO})\text{Cl}_2(\text{EPh}_3)_2]$. However, we were unable to obtain good spectra of parent ions or using any of the *in situ* derivatisation techniques described above. Previous studies have shown that the coordinated NO in these complexes is particularly labile and hence it seems likely that it is lost under the experimental conditions employed [1].

A view of the structure of $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$ is shown in Fig. 2. Based on statistical analysis of the data and the recommendation of Brock and Dunitz (1994) [43] we have solved the structure in the centrosymmetric space group $P\bar{1}$, despite the fact that this imposes disorder.

The ruthenium atom lies on the origin and hence the structure has a crystallographically imposed centre of inversion and because of this, the NO and chlorides are disordered. The structure has been modelled with the chlorides and NO disordered over all four sites using a fractional occupancy of $[1/4 \text{ NO} + 3/4 \text{ Cl}]$ and constrained bond lengths [see Experimental]. Crystallographically imposed disorder in NO complexes has also been reported for the related five-coordinated iridium and rhodium triphenylphosphine complexes $[\text{Ir}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$, and $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ [4–5]. The triphenylstibine ligands in $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$ are in the more common *trans* configuration as

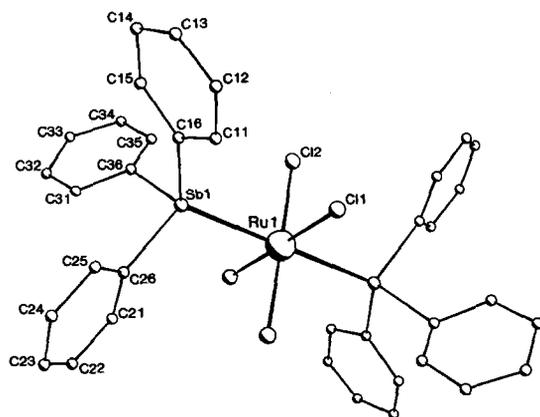


Fig. 2. Perspective view of the structure of $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$. The disordered NO has been omitted for clarity.

reported for other similar structures [4–5,9,12–13]. Few complexes are known in which the organonitride or organochalcogenide ligand are coordinated in the *cis* configuration [1,15–18]. In fact the *cis* arrangement of the organonitride ligands is only seen for complexes containing less bulky ligands such as Me_2PPh and Me_2AsPh [1,17].

The structures for two analogous complexes have been reported previously: $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ [12] and more recently $[\text{Ru}(\text{NO})\text{Cl}_3(\text{AsPh}_3)_2]$ [20]. The triphenylphosphine and triphenylarsine analogues are isostructural with each other and with the related complex $[\text{Os}(\text{NH}_3)\text{Cl}_3(\text{PPh}_3)_2]$ [21]. All of these structures were solved in the space group $C2/c$. Close examination of the crystalline sample of $[\text{Ru}(\text{NO})\text{Cl}_3(\text{SbPh}_3)_2]$ revealed that the sample contained crystals of two different morphologies: red thin plates, and red-orange bipyramids. We investigated both crystal types extensively and found no difference in unit cell parameters or any evidence for a unit cell similar to that seen for the phosphine or arsine analogues. Furthermore, there is no evidence in the spectra or analytical figures for the presence of any other compounds.

There are few reports of X-ray structural determinations of platinum group metal complexes containing organostibine ligands. Almost all of the reported complexes were carbonyl complexes [19,20–28] and the only closely comparable complexes are *mer*- $[\text{OsBr}_3(\text{SbPh}_3)_3]$ [23] and $[\text{RuCl}_2(\text{SbPh}_3)_4]$ [19]. The Ru—Sb bond length of 2.649(1) Å found in this work is at the long end of the range compared with the reported values [range 2.579(1)–2.654(2) Å]. Two of the values reported for $[\text{OsBr}_3(\text{SbPh}_3)_3]$ [2.640(2), 2.644(2) Å] are a little shorter than found in this work. The third bond length reported for $[\text{OsBr}_3(\text{SbPh}_3)_3]$ [2.654(2) Å] is unusually long when compared with this work and the other reported values. This is somewhat surprising considering the osmium atom is formally in the +3 oxidation state whereas most of the other complexes are in the +2 or lower oxidation states. Interestingly the M—Sb bond lengths seen in the ruthenium (II) complex $[\text{RuCl}_2(\text{SbPh}_3)_4]$ [range 2.625(1)–2.632(1) Å] are significantly shorter than seen in either of $[\text{OsBr}_3(\text{SbPh}_3)_3]$ or in the present work, although they are similar to the other reported values. This difference may indicate a higher degree of metal-to-ligand π -back-bonding in the complex $[\text{RuCl}_2(\text{SbPh}_3)_4]$ due to the presence of the soft Ru(II) metal ion. In view of the disorder and constraints imposed upon the Ru—Cl bond lengths during refinement, comparisons with other data are unlikely to be meaningful. The C—Sb and C—C bond lengths in the ligands are similar to other reported values [9,11–13,19,21–28].

Supplementary material

Isotropic thermal parameters, atomic coordinates, a complete list of bond distances and angles, together

with observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre.

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