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# Reactions of $[ReX_5(NO)]^{2-}$ with triphenylstibine. Spectroscopic investigations of $[ReX_2(NO)(SbPh_3)_3]$ , X-ray structures of $[ReCl_2(NO)(SbPh_3)_3]$ and $[ReBr_2Cl(SbPh_3)_3]$ and DFT calculations for $[ReCl_2(NO)(SbPh_3)_3]$

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# Abstract

The reactions of  $[NBu_4]_2[ReX_5(NO)]$  (X = Cl, Br) with triphenylstibine have been examined and three new rhenium complexes –  $[ReCl_2(NO)(SbPh_3)_3]$  (1),  $[ReBr_2(NO)(SbPh_3)_3]$  (2) and  $[ReBr_2Cl(SbPh_3)_3]$  (3) – have been obtained. The last one has been isolated in a low yield during slow recrystallization of the complex 2 from a mixture of chloroform and ethanol. The stibine rhenium nitrosyls have been characterized by IR and UV–vis spectroscopy. The X-ray structures of 1 and 3 have been determined. The geometric parameters of 1 have been examined using the density functional theory (DFT) method. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Rrhenium; Stibine; Nitrosyl complexes; X-ray structure; DFT calculations

# 1. Introduction

The introduction of  $\beta^-$  emitting isotopes <sup>188</sup>Re and <sup>186</sup>Re in radiotherapy, the similarity with technetium [1–5], and the key role of nitric oxide in human cardio-vascular and nervous systems and in immune response to pathogen invasion [6–9] are the main reasons of the still growing interest in rhenium nitrosyl complexes.

Previously, we reported the preparation, spectroscopic and structural characterization of rhenium nitrosyls with triphenylphosphine and triphenylarsine ligands [10–18]. The [ReOX<sub>3</sub>L<sub>2</sub>] complexes react with NO to give various products, depending on the reaction conditions: [ReX<sub>3</sub>(NO)(OPPh<sub>3</sub>)<sub>2</sub>], [ReX<sub>3</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>], [ReX<sub>2</sub>(NO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], [ReBr<sub>3</sub>(NO)(MeCN)(PPh<sub>3</sub>)], [Re-Cl<sub>3</sub>(NO)(PPh<sub>3</sub>)(OPPh<sub>3</sub>)], [ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>], [Re-Br<sub>3</sub>(NO)(dppe)][ReBr<sub>4</sub>(dppe)], [ReX<sub>3</sub>(NO)(OAsPh<sub>3</sub>)<sub>2</sub>], [ReCl<sub>4</sub>(OAsPh<sub>3</sub>)<sub>2</sub>] and [ReCl<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>] [Re-Cl<sub>4</sub>(AsPh<sub>3</sub>)<sub>2</sub>]. The reactions of [NBu<sub>4</sub>]<sub>2</sub>[ReX<sub>5</sub>(NO)] with PPh<sub>3</sub> and AsPh<sub>3</sub> lead to [ReX<sub>3</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>], [Re-Br<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>] and [ReCl<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>], [Re-Br<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>] and [ReCl<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>], [Re-Br<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>] and [ReCl<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>], [Re-Br<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>] and [ReCl<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>], [Re-Br<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>].

Now we are extending our studies to the examination of the reactivity of  $[NBu_4]_2[ReX_5(NO)]$  (X = Cl, Br) compounds towards triphenylstibine, and here we report the syntheses of the  $[ReX_2(NO)(SbPh_3)_3]$  complexes and X-ray structures of  $[ReCl_2(NO)(SbPh_3)_3]$ (1) and  $[ReBr_2Cl(SbPh_3)_3]$  (3). The latter has been

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isolated in a low yield during slow recrystallization of the  $[\text{ReBr}_2(\text{NO})(\text{SbPh}_3)_3]$  (2) complex from a mixture of chloroform and ethanol. The formation of **3** is particularly interesting since substitution reactions of the nitrosyl ligand are rarely observed [19–21]. This paper also includes the results of the DFT calculations for  $[\text{ReCl}_2(\text{NO})(\text{SbPh}_3)_3]$  based on the B3LYP functional, carried out by using the GAUSSIAN 03 program package.

Gancheff et al. [22] have performed extended tests of the ability of the B3LYP method in the LANL2DZ basis set for rhenium compounds in a geometry optimization and calculation of spectral properties. Although this is not a very extended basis set, its use with DFT has shown it to be sufficient for geometry optimization and calculation of spectral properties. It gives good agreement with the experimental data and its use is especially justified in the case of large molecules.

### 2. Experimental

## 2.1. General procedure

All the reagents used for the syntheses were commercially available and were used without further purification. The  $[t-Bu_4N]_2[ReX_5(NO)]$  (X = Cl, Br) complexes were synthesized according to the literature methods [23]. Gaseous NO was generated in the reaction: 2NaNO<sub>2</sub> + 3H<sub>2</sub>SO<sub>4</sub> + FeSO<sub>4</sub>  $\rightarrow$  2NO + 2NaH-SO<sub>4</sub> + Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 2H<sub>2</sub>O, and was purified by passing through washers with concentrated KOH solution and a column containing solid NaOH. The reactions were performed under argon atmosphere.

IR spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm<sup>-1</sup> with the samples in the form of KBr pellets. Electronic spectra were measured on a Lab Alliance UV–VIS 8500 spectrophotometer in the range 800–200 nm in deoxygenated dichloromethane solution. Magnetic susceptibilities were measured at 296 K by the Faraday method. Elemental analyses (C, H, N) were performed on a Perkin–Elmer CHN-2400 analyzer.

### 2.2. Synthesis of $[ReCl_2(NO)(SbPh_3)_3]$ (1)

A mixture of  $[t-Bu_4N]_2[ReCl_5(NO)]$  (1 g, 1.15 mmol) and SbPh<sub>3</sub> (5.3 g, 15 mmol) in ethanol (50 cm<sup>3</sup>) was refluxed for 12 h. The yellow–green precipitate thus formed was filtered and washed with ether. X-ray quality crystals were obtained by recrystallization from a mixture of chloroform and ethanol. Yield 35%.

IR (KBr, cm<sup>-1</sup>) 3049 (m), 2924 (w), 1683 (vs), 1477 (m), 1430 (s), 1333 (w), 1300 (w), 1261 (w), 1183 (w), 1157 (w), 1066 (m), 1020 (w), 995 (w), 728 (vs), 691 (vs), 449 (m).

*Anal.* Calc. for  $C_{54}H_{45}Sb_3Cl_2$  NORe: C, 48.18; H, 3.37; N, 1.04. Found: C, 48.3; H, 3.5; N, 1.1%.

# 2.3. Synthesis of $[ReBr_2(NO)(SbPh_3)_3]$ (2) and $[ReBr_2Cl(SbPh_3)_3]$ (3)

A procedure similar to that for **1** was used with  $[t-Bu_4N]_2[ReBr_5(NO)]$  (1.27 g, 1.15 mmol) and SbPh<sub>3</sub> (5.3 g, 15 mmol). A yellow-green precipitate of **2** was collected in 38% yield.

IR (KBr,  $cm^{-1}$ ) 3049 (m), 1681 (vs), 1576 (w), 1479 (m), 1431 (s), 1332 (w), 1302 (w), 1265 (w), 1186 (m), 1157 (w), 1066 (m), 1020 (w), 997 (w), 727 (vs), 692 (vs), 450 (m).

*Anal.* Calc. for C<sub>54</sub>H<sub>45</sub>Sb<sub>3</sub>Br<sub>2</sub>NORe: C, 45.19; H, 3.16; N, 0.98. Found: C, 45.3; H, 3.2; N, 1.1%.

Slow recrystallization of **2** from a mixture of chloroform and ethanol leads to the formation of the [ReBr<sub>2</sub>Cl(SbPh<sub>3</sub>)<sub>3</sub>] complex (**3**) in low yield ( $\sim$ 3%).

### 2.4. Crystal structure determinations and refinement

The X-ray intensity data of 1 and 3 were collected on a KM-4-CCD automatic diffractometer equipped with a CCD detector. 32- and 29-s exposure times were used, respectively, and all the Ewald sphere was collected up to  $\theta = 25.11^{\circ}$ . The unit cell parameters were determined from least-squares refinement of the setting angles of 16321 and 7104 strongest reflections, respectively, for 1 and 3. Details concerning crystal data and refinement are given in Table 1. Lorentz, polarization and numerical absorption corrections [24] were applied. The structures were solved by the Patterson method and subsequently completed by difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares techniques. The hydrogen atoms of the phenyl rings were treated as "riding" on their parent carbon atoms [d(C-H) = 0.96 Å] and assigned isotropic temperature factors equal to 1.2 times the value of the equivalent temperature factor of the parent carbon atom. SHELXS 97 [25], SHELXL 97 [26] and SHEL-XTL [27] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs.

#### 2.5. Computational details

The GAUSSIAN 03 program [28] was used in the calculations. The geometry optimization was carried out with the DFT method with the use of the B3LYP functional [29,30].

The LANL2DZ basis set [31] was used on the rhenium and antimony atoms, 6-31G(d) on the nitrogen, chlorine, oxygen and carbon atoms, and 6-31G basis on the hydrogen atoms in the calculations.

Table 1 Crystal data and structure refinement for 1 and 3

	1	3
Empirical formula	C54H45Sb3Cl2NORe	C54H45Sb3Br2ClRe
Formula weight	1346.26	1440.62
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	18.8063(5)	13.3916(4)
b (Å)	13.1913(3)	16.2378(5)
<i>c</i> (Å)	19.8266(5)	22.6870(9)
β (°)	91.738(2)	
Volume (Å <sup>3</sup> )	4916.3(2)	4933.3(3)
Ζ	4	4
Density (calculated) (Mg/m <sup>3</sup> )	1.819	1.940
Absorption coefficient (mm <sup>-1</sup> )	4.232	5.780
<i>F</i> (000)	2584	2736
Crystal size (mm)	$0.15 \times 0.15 \times 0.29$	$0.07 \times 0.10 \times 022$
$\theta$ range for data collection (°)	2.77–25.11	3.29–25.11
Index ranges	$-22 \leqslant h \leqslant 22$	$-15 \leqslant h \leqslant 15$
	$-15 \leq k \leq 14$	$-19 \leqslant k \leqslant 19$
	$-23 \leq l \leq 23$	$-27 \leq l \leq 21$
Reflections collected	50963	57700
Independent reflections $(R_{int})$	8760 (0.0471)	8765 (0.0566)
Completeness to $2\theta$ (%)	95.3	99.6
Data/restraints/ parameters	8760/0/587	8765/0/550
Goodness-of-fit on $F^2$	1.042	1.102
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0270$	$R_1 = 0.0426$
	$wR_2 = 0.0634$	$wR_2 = 0.0986$
R indices (all data)	$R_1 = 0.0352$	$R_1 = 0.0439$
	$wR_2 = 0.0664$	$wR_2 = 0.0994$
Absolute structure parameter		0.016(8)
Largest difference peak and hole (e/Å <sup>3</sup> )	0.751 and -0.677	1.166 and -1.577e

Natural bond orbital (NBO) calculations were performed with the NBO code [32] included in GAUSSIAN 03.

### 3. Results and discussion

The [*t*-Bu<sub>4</sub>N]<sub>2</sub>[ReX<sub>5</sub>(NO)] complexes (X = Cl, Br) react with PPh<sub>3</sub> and AsPh<sub>3</sub> to give [ReX<sub>3</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>], [ReBr<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>] and [ReCl<sub>3</sub>(NO)(AsPh<sub>3</sub>)<sub>2</sub>][Re-Cl<sub>4</sub>(AsPh<sub>3</sub>)<sub>2</sub>] [18]. The reactions of [*t*-Bu<sub>4</sub>N]<sub>2</sub>[ReX<sub>5</sub>(NO)] with triphenylstibine in ethanol lead to the [Re-X<sub>2</sub>(NO)(SbPh<sub>3</sub>)<sub>3</sub>] complexes. The smaller steric demand of SbPh<sub>3</sub> in comparison with PPh<sub>3</sub> and AsPh<sub>3</sub> explains the formation of [ReX<sub>2</sub>(NO)(SbPh<sub>3</sub>)<sub>3</sub>]. The increase of M–E and E–C (E = P, As or Sb) bond lengths in the order P > As > Sb leads to the decrease of the EPh<sub>3</sub> cone angles [33]. The yield of the  $[\text{ReX}_2(\text{NO})(\text{SbPh}_3)_3]$  complexes depends on: (i) the mole ratio of  $[\text{NBu}_4]_2[\text{ReX}_5(\text{NO})]$  to triphenylstibine (it is the highest when it is ~1:13) and (ii) the reaction time (it drops considerably when the reaction is carried out in less than 12 h). Compounds 1 and 2 were recrystallized from a mixture of CHCl<sub>3</sub>/ EtOH. The crystals of 1 were of good quality, whereas the crystals of 2 were small and badly shaped. Moreover, in the case of the bromine nitrosyl, the formation of a small amount of well-shaped yellow crystals of 3 was observed during the slow recrystallization. The oxidation reactions of rhenium complexes by halogencontaining solvents have been known for years [34]. Substitution reactions of nitrosyl ligands by halogen ligands, however, are very sparse [19–21].

The structure of 1 has been modelled with the Cl and NO ligands disordered over two sites using fractional occupancies equal to 0.45 for Cl(1), N(2), O(2) atoms and 0.55 for Cl(3), N(1) and O(1) atoms. A similar disorder of NO ligands has also been reported for iridium, rhodium and ruthenium complexes [35]. The SbPh<sub>3</sub> ligands are arranged in a *meridional* fashion, and the Cl(3) ligand is involved in weak intramolecular hydrogen bonds with the H(36) and H(54) atoms of the phenyl rings [36–38]. Fig. 1 shows a displacement ellipsoid plot of 1 and selected bond lengths and angles of this compound are summarized in Table 2.

Two groups of ligands of 3 (halide ions and stibine molecules) are arranged in a *meridional* fashion, the bromine ligands occupy a *cis* position to each other. Fig. 2 shows the molecular structure of this compound, and selected bond lengths and angles for 3 are summarized in



Fig. 1. The molecular structure of 1.

Table 2 The experimental and optimized bond lengths (Å) and angles (°) for 1

Bond lengths	Experimental	Optimized	Angles	Experimental	Optimized
Re(1)–Cl(1)	2.353(5)	2.533	N(2)-Re(1)-N(1)	178.2(9)	
Re(1)-Cl(2)	2.4443(10)	2.522	N(2)-Re(1)-Cl(1)	177.0(7)	175.35
Re(1)-Cl(3)	2.362(4)		N(1)-Re(1)-Cl(3)	177.1(7)	
Re(1) - N(1)	1.832(19)		Cl(1)-Re(1)-Cl(3)	176.3(2)	
Re(1) - N(2)	1.753(17)	1.754	N(2)-Re(1)-Cl(2)	92.3(6)	99.99
Re(1)-Sb(1)	2.6945(3)	2.762	N(1)-Re(1)-Cl(2)	86.6(7)	
Re(1)-Sb(2)	2.6640(3)	2.723	Cl(1)-Re(1)-Cl(2)	89.39(19)	84.38
Re(1)-Sb(3)	2.6758(3)	2.752	Cl(3)-Re(1)-Cl(2)	91.85(10)	
N(1)–O(1)	1.13(4)	1.195	N(2)-Re(1)-Sb(1)	84.7(6)	89.77
N(2)–O(2)	1.32(4)		N(1)-Re(1)-Sb(1)	96.5(7)	
			Cl(1)-Re(1)-Sb(1)	97.95(17)	92.46
		Cl(3)-Re(1)-Sb(1)	85.67(10)		
			Cl(2)-Re(1)-Sb(1)	84.29(3)	81.46
			Sb(2)-Re(1)-Sb(1)	94.101(10)	97.23
			Sb(3)-Re(1)-Sb(1)	169.638(10)	165.74
			N(2)-Re(1)-Sb(2)	94.8(6)	97.37
			N(1)-Re(1)-Sb(2)	86.4(7)	
			Cl(1)-Re(1)-Sb(2)	83.60(19)	78.31
			Cl(3)-Re(1)-Sb(2)	95.31(9)	
			Cl(2)-Re(1)-Sb(2)	172.52(3)	162.58
			N(2)-Re(1)-Sb(3)	89.3(6)	90.36
			N(1)-Re(1)-Sb(3)	89.3(7)	
			Cl(1)-Re(1)-Sb(3)	88.30(17)	88.48
			Cl(3)-Re(1)-Sb(3)	88.24(10)	
		Cl(2)-Re(1)-Sb(3)	87.54(3)	84.48	
			Sb(2)-Re(1)-Sb(3)	94.809(10)	96.90
			O(1) - N(1) - Re(1)	178(2)	179.1
			O(2) - N(2) - Re(1)	175(2)	



Fig. 2. The molecular structure of 3.

Table 3. The conformations of  $[ReBr_2Cl(SbPh_3)_3]$  molecules are stabilized by two weak intramolecular hydrogen bonds [35–37]. The Cl(1) ligand is involved in a

Table 3 Bond lengths (Å) and angles (°) for **3** 

Bond lengths		Angles	
Re(1)-Br(1)	2.5179(16)	Cl(1)-Re(1)-Br(1)	177.56(9)
Re(1)-Br(2)	2.5997(11)	Cl(1)-Re(1)-Br(2)	87.24(8)
Re(1)-Cl(1)	2.436(4)	Br(1)-Re(1)-Br(2)	90.49(5)
Re(1)-Sb(1)	2.6809(7)	Cl(1)-Re(1)-Sb(2)	86.72(8)
Re(1)-Sb(2)	2.6713(7)	Br(1)- $Re(1)$ - $Sb(2)$	95.54(4)
Re(1)-Sb(3)	2.6873(7)	Br(2)-Re(1)-Sb(2)	173.93(4)
		Cl(1)-Re(1)-Sb(1)	91.23(7)
		Br(1)-Re(1)-Sb(1)	87.72(4)
		Br(2)-Re(1)-Sb(1)	85.80(3)
		Sb(2)-Re(1)-Sb(1)	93.70(2)
		Cl(1)-Re(1)-Sb(3)	93.78(7)
		Br(1)-Re(1)-Sb(3)	86.90(4)
		Br(2)-Re(1)-Sb(3)	85.01(3)
		Sb(2)-Re(1)-Sb(3)	96.02(2)
		Sb(1)-Re(1)-Sb(3)	169.30(2)

weak hydrogen bond with the H(20) atom of the phenyl ring, while the Br(1) ion interacts with the H(36) atom.

Due to steric repulsion of the three bulky SbPh<sub>3</sub> molecules, the octahedral Re geometries of **1** and **3** show the expected angular distortions. The angles between *cis*-ligands vary between  $83.60(19)^\circ$  and  $97.95(17)^\circ$  for **1**, and  $85.01(3)^\circ$  and  $96.02(2)^\circ$  for **3**; the *trans*-angles are between  $169.64(1)^\circ$  and  $178.2(9)^\circ$  for **1**, and  $169.30(2)^\circ$  and  $177.56(9)^\circ$  for **3**.

There are only a few Re–Sb distances reported in the Cambridge Structural Database, with  $[ReCl_2(NO)_2 (SbPh_3)_2]$  [39] [Re–Sb: 2.711(8) and 2.710(8) Å] and  $[Re-Cl(CO)_3(SbPh_3)_2]$  [40] [Re–Sb: 2.726(1) and 2.729(2) Å] being the closest chemical examples and showing little longer Re–Sb bond lengths compared to the presented compounds (Tables 2 and 3).

Relative small C–Sb–C tetrahedral angles were found:  $94.78(17)^{\circ}$ – $102.48(17)^{\circ}$ ,  $100.2^{\circ}$  (av) for 1 and  $95.2(4)^{\circ}$ – $102.1(4)^{\circ}$ ,  $99.1^{\circ}$  (av) for 3. This is most likely due to the large Sb–C bond lengths making it possible for the phenyl rings to be compressed a little more than that which is encountered for the analogous phosphine and arsine ligands. Table 4 presents the Re–E and E–C bond lengths and C–E–C angles (E = P, As or Sb) for the selected rhenium complexes.

The average Re–NO (1.793 Å) and N–O (1.225 Å) bond lengths and the average value of the Re–N–O angle (176.5°) for **1** confirm a linear coordination of the nitrosyl group, and they are comparable with values found for phosphine and arsine rhenium nitrosyls [13–18].

A notable *trans* influence of the triphenylstibine ligand is observed in both 1 and 3; the Re–X(2) bond lengths are longer by about 0.08 Å in comparison with the corresponding Re–X distances in *cis* positions to the SbPh<sub>3</sub> ligand. A difference between Re–Cl(1) and Re–Cl(3) in 1 is a consequence of the nitrosyl disorder.

stretching frequency The nitrosyl in [Re- $X_2(NO)(SbPh_3)_3$  compounds is independent of the halogen ligand, the strong band corresponding to  $v_{NO}$ appears at  $\sim 1680 \text{ cm}^{-1}$  in the IR spectrum of the chloro (1) and bromo (2) nitrosyl. The considerable lowering of the  $v_{NO}$  for [Re<sup>I</sup>X<sub>2</sub>(NO)(SbPh<sub>3</sub>)<sub>3</sub>] complexes in comparison with the  $[Re^{II}X_3(NO)(PPh_3)_2]$  and  $[Re^{II}X_3]$ (NO)(AsPh<sub>3</sub>)<sub>2</sub>] nitrosyls [15,17,18] is consistent with the lower oxidation state of the rhenium ion. It results in an increased backdonation of electron density from the filled rhenium d-orbitals into the  $\pi^*$  antibonding orbital of the NO group.

The complexes 1 and 2 are diamagnetic, which confirms the low-spin  $d^6$  configuration of the rhenium ion in the O<sub>h</sub> field.

Table 5 presents the positions and molar absorption coefficients of the electronic bands for 1 and 2. The elec-

Table 5 Band positions and molar absorption coefficients for 1 and 2

Band position (nm)	3
Compound 1	
420.0	560
378.5	740
282.5	8440
230.0	14900
215.0	9760
Compound 2	
415.0	530
381.0	490
290.5	8200
232.0	12580
223.5	7580

 $\varepsilon$  is the molar absorption coefficient (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>).

tronic absorption spectra of both rhenium (I) complexes are very similar. They are dominated by three intense bands below 300 nm due to interligand electronic transitions of SbPh<sub>3</sub>. In addition, two less intense absorption bands appear at ~420 and ~380 nm, and they can be assigned to d–d transitions and metal-to-ligand charge transfer (MLCT) transitions from Re(I) to  $\pi^*$  ligand orbitals.

Considering the magnetic measurements, the geometry of **1** was optimized in the singlet state by the DFT method with the B3LYP functional. The optimized geometry is in quite good agreement with the experimental one, the largest differences are found for the Re–Cl and Re–Sb bond distances. A similar elongation of the rhenium–halogen bond lengths in the B3LYP with different basis sets has been found in other rhenium complexes [41].

Table 6 presents the atomic charges from the natural population analysis (NPA) for 1. The calculated charge on the nitrogen atom of the nitrosyl group is positive, whereas the oxygen atom is negatively charged. The total charge on the NO group of the title complex is negative: -0.176. The calculated charge on the rhenium atom of 1 is far from the formal charge +1. It results from charge donation from the chloride ions and triphenylstibine ligand, which act as  $\sigma$ -donors. There are large positive charges on the Sb atoms, and the charges on the chloride ions are significantly smaller than -1.

Table 4

The Re-E and E-C bond lengths and C-E-C angles (E = P, As or Sb) for the selected rhenium complexes

			-	
Complex	Re-E bond length (average, Å)	E-C bond length (average, Å)	C-E-C angle (average, °)	Reference
[Re(NO)Cl <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	2.530	1.822	104.3	[15]
[Re(NO)Br <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	2.540	1.822	104.3	[17]
[Re(NO)Cl <sub>3</sub> (AsPh <sub>3</sub> ) <sub>2</sub> ]	2.612	1.942	103.4	[18]
[Re(NO)Br <sub>3</sub> (APh <sub>3</sub> ) <sub>2</sub> ]	2.595	1.935	103.7	[18]
[ReCl <sub>2</sub> (NO) <sub>2</sub> (SbPh <sub>3</sub> ) <sub>2</sub> ]	2.711	2.114	102.5	[38]
[ReCl(CO) <sub>3</sub> (SbPh <sub>3</sub> )]	2.728	2.137	100.1	[39]
[ReCl <sub>2</sub> (NO)(SbPh <sub>3</sub> ) <sub>3</sub> ]	2.678	2.133	100.2	this work
[ReBr <sub>2</sub> Cl(SbPh <sub>3</sub> ) <sub>3</sub> ]	2.680	2.135	99.1	this work

Table 6 Atomic charges from the natural population analysis (NPA) for 1

Atom	Atomic charge		
Re(1)	-0.271		
Cl(1)	-0.515		
Cl(2)	-0.498		
N(1)	0.148		
O(1)	-0.324		
Sb(1)	1.650		
Sb(2)	1.653		
Sb(3)	1.665		

The energies and characters of several highest occupied and lowest unoccupied molecular orbitals of **1** are presented in Table 7. The selected HOMO and LUMO orbitals of **1** are depicted in Fig. 3. The investigated complex is of a large size, the number of basis functions is equal 956. Among the occupied MOs of **1** the largest numbers constitute orbitals of the phenyl rings which are not relevant for the discussion of the bonding. The others have complicated character. The percent participations of the ligand atomic orbitals in the selected HOMO and LUMO orbitals are shown in Table 7.

The bonding of NO to the rhenium center involves a synergic interaction between the nitrosyl ligand orbitals and the metal orbitals. The Re–NO bond consists of two

Table 7 The energy and character of selected molecular orbitals of **1** 

<u></u>	F(eV)	Character
HOMO - 14	-6.801	$\pi_{\rm Ph}(80.54), \ \pi_{\rm Cl}(13.99)$
HOMO - 13	-6.767	$\pi_{\mathrm{Ph}}$
HOMO - 12	-6.740	$\pi_{\mathrm{Ph}}$
HOMO – 11	-6.719	$\pi_{\mathrm{Ph}}$
HOMO - 10	-6.715	$\pi_{\mathrm{Ph}}$
HOMO – 9	-6.686	$\pi_{\mathrm{Ph}}$
HOMO – 8	-6.675	$\pi_{\mathrm{Ph}}$
HOMO - 7	-6.600	$\pi_{\mathrm{Ph}}$
HOMO – 6	-6.591	$\pi_{\mathrm{Ph}}$
HOMO – 5	-6.572	$\pi_{\mathrm{Ph}}$
HOMO - 4	-6.500	$\pi_{\text{Ph}}(59.61), \pi_{\text{Cl}}(11.93), d_{xz}(7.06) + \pi_{\text{NO}}^*(11.59)$
HOMO - 3	-6.410	$\pi_{\rm Cl}(58.88), \pi_{\rm Ph}(28.31), n_{\rm Sb}(5.69)$
HOMO - 2	-6.123	$d_{\nu z}(23.13) + \pi^*_{NO}(29.37), \pi_{Cl}(37.64)$
HOMO - 1	-5.866	$\pi_{\rm Cl}(28.15), \pi_{\rm Ph}(27.48), n_{\rm Sb}(20.03), d_{xz}(13.0)$
		$+\pi_{NO}^{*}(7.11)$
HOMO	-5.409	$d_{xy}(60.45), \pi_{Cl}(24.02)$
LUMO	-1.006	$d_{x^2-v^2}(28.52) - \sigma_{Sb}(36.07) - \sigma_{Cl}(5.82)$
LUMO + 1	-0.939	$\pi_{NO}^{*}(40.54) - d_{xz}(22.53), \pi_{Ph}^{*}(17.56)$
LUMO + 2	-0.852	$\pi^*_{NO}(18.82) - d_{\nu z}(14.96), \pi^*_{Ph}(38.75),$
		$\pi_{\rm Cl}(10.04)$
LUMO + 3	-0.809	$\pi^*_{NO}(15.77) - d_{\nu z}(17.44), \pi^*_{Ph}(30.76)$
LUMO + 4	-0.795	$\pi^*_{Ph}(30.76), \pi^*_{NO}(7.76) - d_{vz}(7.29)$
LUMO + 5	-0.572	$\pi^*_{Ph}$
LUMO + 6	-0.498	$\pi_{Ph}^*$
LUMO + 7	-0.442	$\pi_{Ph}^*$
LUMO + 8	-0.363	$\pi_{Ph}^*$
LUMO + 9	-0.306	$\pi_{Ph}^{*}$
LUMO + 10	-0.294	$\pi_{Ph}^{*}$
LUMO + 11	-0.264	$\pi_{Ph}^{*}$
LUMO + 12	-0.221	$\pi_{\mathrm{Ph}}^*$

components: (i) a donation of electron density from a  $\sigma$ type orbital on NO onto the metal orbital and (ii) a donation of electron density from the occupied metal d-orbitals into the  $\pi^*$  antibonding orbitals of the NO ligand. The occupied  $d_{yz}$  and  $d_{xz}$  rhenium orbitals participate in the back-donation from the central ion to the nitrosyl ligand in complex 1. In the occupied orbitals, the  $\pi_{NO}^*$  are distributed among several highest MOs. A substantial contribution of  $\pi_{Re-NO}$  orbitals are shown in HOMO - 4, HOMO - 2 and HOMO - 1. Percent participations of the d rhenium and  $\pi^*_{NO}$  orbitals in these MOs are very similar. The LUMO + 1, LUMO + 2 and LUMO + 3 orbitals are of  $\pi^*_{Re-NO}$  antibonding character. The LUMO + 1 orbital has prevalent NO character, whereas the LUMO + 2 and LUMO + 3 orbitals are localised almost evenly on the d rhenium and  $\pi^*_{NO}$ orbitals.

The HOMO orbital of **1** is a  $d_{xy}$  metal orbital with an admixture of chlorine  $\pi$  orbitals. The LUMO is a  $d_{x^2-y^2}$  orbital with an antibonding admixture of the chloride and antimony lone pair orbitals.

Additional information about the binding in complex 1 was obtained by NBO analysis. Table 8 presents the occupancies and natural atomic orbital compositions (NAO) of the selected NBOs for complex 1. The occupancies of the bonding and antibonding Re-N bond orbitals (BD<sub>Re-N</sub> and BD $^*_{Re-N}$  orbitals) confirms a great donation of electron density from the occupied rhenium d-orbitals into the  $\pi^*$  antibonding orbitals of the NO ligand. For compound 1, three natural bond orbitals were detected for the Re-N bond, and one orbital - for the N-O bond. The Re-N bond orbital of  $\sigma$ -character is polarized towards the nitrogen atom (ca. 73% at N) and the s- and d-orbitals of Re take part in the bonding. In the case of the Re–N bond orbitals of  $\pi$ -character, only d-orbitals of Re are included in the bonding. The N-O bond orbital is slightly polarized towards the oxygen end. In the valence-bond treatment a linear bonding mode of the nitrosyl group may be represented by the following resonance forms [42]:



The results of the NBO analysis indicate that the resonance structure D makes a significant contribution to the structure of complex 1.

It is consistent with the charges on the nitrogen and oxygen atoms of the nitrosyl group and the relatively low nitrosyl stretching frequency.

y de la companya de l		
HOMO-2	HOMO-1	НОМО
	× Co	S Cor
LUMO	LUMO+1	LUMO+2

Fig. 3. Selected HOMO and LUMO orbitals for 1. The phenyl rings are omitted for clarity, they make no contribution to the presented orbitals. Positive values of the orbital contour are represented in blue (0.04 a.u.) and negative values – in yellow (-0.04 a.u.).

Table 8 Selected results of the NBO analysis for 1

Bond orbital BD Re= $N(\sigma)$	Occupancy		NAO composition		BD*	Occupancy
	1.965	% Re % N	26.96 73.04	s(18.35%) d(81.48%) s(57.54%) p(42.44%)	$Re \equiv N(\sigma^*)$	0.419
$Re = N(\pi)$	1.944	% Re % N	48.48 51.52	d(93.84%) p(93.72%)	$Re \equiv N(\pi^*)$	0.444
$Re = N(\pi)$	1.974	% Re % N	55.55 44.45	d(99.42%) p(99.94%)	$Re \equiv N(\pi^*)$	0.469
N—O	1.996	% N % O	45.47 54.53	s(36.19%) p(63.66%) s(29.72%) p(70.14%)	N–O( $\sigma^*$ )	0.014

# 4. Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk) on request, quoting the Deposition Nos.: 254986 ( $C_{54}H_{45}Sb_3Cl_2NORe$ ) and 254987 ( $C_{54}H_{45}Sb_3Br_2ClRe$ ).

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