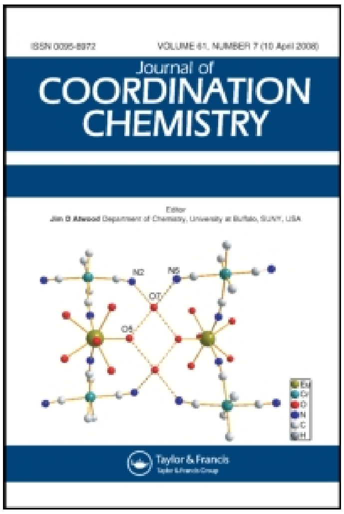

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THE SYNTHESIS, CRYSTAL, MOLECULAR AND ELECTRONIC STRUCTURES OF TRIBROMO(NITROSYL) *BIS*(TRIPHENYLPHOSPHINE OXIDE) RHENIUM(II) AND TRIBROMO(NITROSYL) *BIS*(TRIPHENYLPHOSPHINE)RHENIUM(I)

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THE SYNTHESIS, CRYSTAL, MOLECULAR AND ELECTRONIC STRUCTURES OF TRIBROMO(NITROSYL) *BIS*(TRIPHENYLPHOSPHINE OXIDE) RHENIUM(II) AND TRIBROMO(NITROSYL) *BIS*(TRIPHENYLPHOSPHINE)RHENIUM(I)

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Gaseous nitric oxide reacts with a benzene solution of $[ReOBr_3(PPh_3)_2]$ to give $[ReBr_3(NO)(OPPh_3)_2]$ (**1**). When the reaction is carried out in the presence of an excess of free triphenylphosphine, the product is $[ReBr_3(NO)(PPh_3)_2]$ (**2**). The latter is also isolated in the reaction of **1** with PPh_3. This paper, apart from the synthetic methods, presents spectroscopic and magnetochemical measurements, and crystal, molecular and electronic structures for **1** and **2**.

Keywords: Rhenium; Nitrosyl; X-ray structure; Electronic structure; Nitric oxide

INTRODUCTION

A variety of methods are available for the synthesis of transition metal nitrosyl complexes. This group of compounds can be obtained using gaseous nitric oxide, nitrosonium salts, organic and inorganic nitroso compounds, inorganic nitrites and hydroxylamine. The first of these methods is particularly attractive. Gaseous nitric oxide can be easily synthesised and purified in the laboratory and nitrosyl complexes are obtained with high

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*Corresponding author.

yield in these reactions [1–22]. The reactions may either proceed without or with ligand substitution in the coordination spheres of metals. Simple addition usually occurs when gaseous NO is passed through a solution of a coordinatively unsaturated transition metal complex. In coordinatively saturated compounds nitric oxide readily replaces such ligands as CO, tertiary phosphines and alkenes [23]. Reactions of NO with metal cluster compounds often lead to metal–metal bond cleavage, whereas reactions of nitric oxide with high oxidation state metal halides usually give low-valency nitrosyl compounds and nitrosyl halide [24–28]. The type and stability of the complexes obtained in these reactions depends on a variety of factors such as temperature, solvent, time of reaction and other ligands in the coordination sphere. Nitric oxide reacts with $[MnX_2(PR_3)]$ complexes ($R_3 = Pr_3$, Bu_3, $PhMe_2$, $PhEt_2$) both in the solid state and in THF solution. $[Mn(NO)X_2(PR_3)]$ is isolated for $X = Cl$ and Br, while for $X = I$ the product is unstable and rapidly decomposes *via* the oxidation of the phosphine [29, 30]. The reaction of NO with a solution of $[ReOCl_3(PPh_3)_2]$ in benzene affords green crystals of $[ReCl_3(NO)(OPPh_3)_2]$, whereas the same reaction carried out in methylene chloride gives a mixture of two complexes, $[ReCl_3(NO)(OPPh_3)(PPh_3)]$ (major product) and $[ReCl_4(PPh_3)_2]$ [31–33].

Here we present synthetic methods for $[ReBr_3(NO)(OPPh_3)_2]$ (**1**) and $[ReBr_3(NO)(PPh_3)_2]$ (**2**), their spectroscopic characterisation and their electronic, crystal and molecular structures.

EXPERIMENTAL

Triphenylphosphine and NH_4ReO_4 were purchased from Aldrich Chemical Co. and used without further purification. $[ReOBr_3(PPh_3)_2]$ was synthesized according to literature methods [34]. Gaseous NO, obtained in the reaction $2NaNO_2 + 3H_2SO_4 + 2FeSO_4 \rightarrow 2NO + 2NaHSO_4 + Fe_2(SO_4)_3 + 2H_2O$, was purified by passing through concentrated KOH solution and over solid NaOH. Solvents were dried and deoxygenated prior to use in the usual way. The reaction, all preparations and recrystallizations were performed under an argon atmosphere.

Preparation of $[ReBr_3(NO)(OPPh_3)_2]$ (1)

NO was passed through a vigorously stirred and refluxing solution of $[ReOBr_3(PPh_3)_2]$ (0.97 g, 1 mmol) in benzene (30 cm^3) for 6 h. The colour changed gradually from greenish-yellow to dark red. The resulting solution was evaporated to a volume of 10 cm^3 and the green precipitate formed by addition of 40 cm^3 of EtOH and was filtered off after 15 min. The product was washed with cold ether and dried *in vacuo*. Yield, 0.73 g (0.72 mmol) of [$ReBr_3(NO)(OPPh_3)_2$]. Crystals suitable for X-ray structure determination were obtained by slow evaporation of an acetonitrile solution of the nitrosyl rhenium(II) complex.

Preparation of [$ReBr_3(NO)(PPh_3)_2$] (2)

A. NO was passed through a vigorously stirred and refluxing solution of [$ReOBr_3(PPh_3)_2$] (0.97 g, 1 mmol) and PPh_3 (2 g, 7.6 mmol) in benzene (30 cm^3) for 6 h. The colour changed gradually from greenish-yellow to dark violet. The resulting solution was evaporated to a volume of 10 cm^3 and the violet precipitate formed by addition of 80 cm^3 of EtOH was filtered off after 15 min. The product was washed with ethanol and cold ether and dried *in vacuo*. Yield, 0.68 g (0.69 mmol) of [$ReBr_3(NO)(PPh_3)_2$]. Crystals suitable for X-ray structure determination were obtained by slow evaporation of an acetonitrile solution of the nitrosyl rhenium(II) complex.

B. A mixture of **1** (0.2 g, 0.2 mmol) and PPh_3 (0.6 g, 2.3 mmol) in toluene was refluxed for 5 h. The colour changed gradually from green to dark violet. The resulting solution was evaporated to a volume of 10 cm^3 and excess EtOH was added to give [$ReBr_3(NO)(PPh_3)_2$] as a violet, crystalline precipitate. The product was washed with ethanol and cold ether and dried *in vacuo*. Yield, 0.17 g (0.174 mmol) of [$ReBr_3(NO)(PPh_3)_2$].

Physical Measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the range 4000 to 400 cm^{-1} with the samples in potassium bromide pellets. Electronic spectra were measured on a Beckman 5240 spectrophotometer in the range 800 to 220 nm in deoxygenated dichloromethane solutions. ^1H and ^{31}P NMR were obtained at room temperature in $CDCl_3$ solutions using a Varian VXR300 spectrometer. In the case of the proton NMR, TMS was used as internal standard, and for phosphorus, 85% aqueous H_3PO_4 solution as external reference. Magnetic susceptibilities were measured at 296 K by the Faraday method.

Crystal Structure Determination and Refinement

Three-dimensional X-ray intensity data were collected on a Kuma KM-4 diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at room temperature. Details concerning crystal data and refinement for **1** and **2** are given in Table I. Lorentz, polarization and empirical absorption

TABLE I Crystal data and structure refinement details for **1** and **2**

	1	**2**
Empirical formula	$C_{36}H_{30}Br_3NO_3P_2Re$	$C_{36}H_{30}Br_3NOP_2Re$
Formula weight	1012.48	980.48
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
Unit cell dimensions	$a = 14.0870(10)$ Å	$a = 24.608(5)$ Å
	$b = 13.2320(10)$ Å, $\beta = 96.040(10)°$	$b = 9.590(2)$ Å, $\beta = 116.87(3)°$
	$c = 19.739(2)$ Å	$c = 16.036(3)$ Å
V	3658.9(5) Å^3	3375.8(12) Å^3
Z	4	4
Density (calculated)	1.838 Mg m^{-3}	1.929 Mg m^{-3}
Absorption coefficient	6.720 mm^{-1}	7.276 mm^{-1}
F(000)	1948	1884
Crystal size	0.63 × 0.25 × 0.25 mm	0.21 × 0.24 × 0.09 mm
θ range for data collection	2.07 to 30.06°	2.32 to 27.09°
Index ranges	$-19 \leq h < 19$; $-1 \leq k < 18$; $-1 \leq l \leq 27$	$-31 \leq h < 28$; $-2 \leq k \leq 12$; $0 \leq l \leq 20$
Reflections collected	6263	4603
Independent reflections	5351($R_{int} = 0.0300$)	3678($R_{int} = 0.0554$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5351/0/222	3632/0/202
Goodness-of-fit on F^2	1.139	1.056
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0477$, $wR2 = 0.1302$	$R1 = 0.0471$, $wR2 = 0.1497$
R indices (all data)	$R1 = 0.0595$, $wR2 = 0.1302$	$R1 = 0.1140$, $wR2 = 0.1497$

corrections were applied for **1** and **2**. The structures of the complexes were solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically using full-matrix, least-squares techniques. The hydrogen atom positions of the phenyl rings were found from subsequent difference Fourier syntheses and were treated as riding on the adjacent carbon atom [$d(\mathrm{C}-\mathrm{H}) = 0.96$ Å] and refined with individual isotropic temperature factors equal to 1.2 times the value of the equivalent isotropic temperature factor of the parent carbon atom. SHELXL97 [35] and SHELXTL [36] programs were used for all calculations. Atomic scattering factors were those incorporated in the computer programs.

RESULTS AND DISCUSSION

$[\mathrm{ReBr_3(NO)(OPPh_3)_2}]$ (**1**) complex has been obtained in a similar way to the chloro- analogue, $[\mathrm{ReCl_3(NO)(OPPh_3)_2}]$ [31]. Both complexes are products of the nitrosylation of a refluxing solution of the corresponding $[\mathrm{ReO}X_3\mathrm{(PPh_3)_2}]$ oxocomplex ($X = \mathrm{Cl}$ or Br) in benzene by nitric oxide, so the course of $[\mathrm{ReBr_3(NO)(OPPh_3)_2}]$ formation is the same as presented for $[\mathrm{ReCl_3(NO)(OPPh_3)_2}]$.

Complex **1** is isostructural with $[\mathrm{ReCl_3(NO)(OPPh_3)_2}]$. Both compounds crystallise in the monoclinic space group *C*2/*c*. The rhenium atom in **1**, just as in $[\mathrm{ReCl_3(NO)(OPPh_3)_2}]$, occupies special position *e* of space group *C*2/*c* with multiplicity 4 and the site symmetry 2. Re(1) is octahedrally surrounded by Br(1) and O(1) (of the $\mathrm{OPPh_3}$ group) atoms with site occupation factors 1.0 and by the nitrosyl group N(1)—O(2) and Br(2) atoms occupying a statistically common position with site occupation factors each of 0.5. The numbering scheme of **1** is shown in Figure 1 and the most important bond lengths and angles for **1** are reported in Table II. Table III contains atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathrm{Å}^2 \times 10^3$) for **1**.

The Re(1)—N(1)—O(1) angle [172.6(13)°] and N(1)—O(2) bond length [1.26(1) Å] indicates approximately linear coordination of the nitrosyl ligand. However, in comparison with the $[\mathrm{ReCl_3(NO)(OPPh_3)_2}]$ complex, the N—O bond length in **1** is a little longer [1.21(3) Å] in the chloro complex [31]. The Re(1)—O(1) [2.048(4) Å] and O(1)—P(1) [1.505(4) Å] bond distances in **1** are in good agreement with values found for $[\mathrm{ReCl_3(NO)(OPPh_3)_2}]$ [Re—O = 2.055(6), P—O = 1.493(6) Å].

The ^{31}P NMR spectrum of **1** consists of a broad signal at 29.83 ppm and the ^{1}H NMR spectrum of **1** shows only phenyl multiplets between 7.19 and

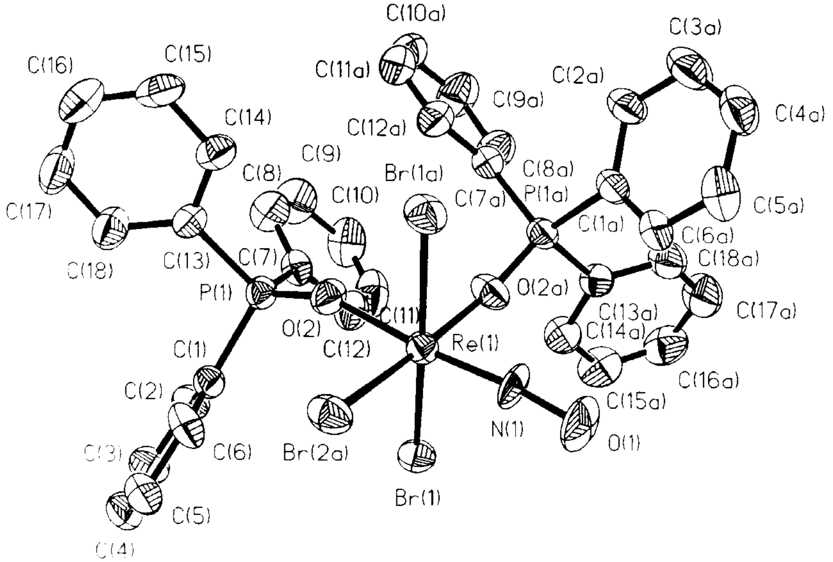

FIGURE 1 The molecular structure of **1**. Thermal ellipsoids are drawn at 30% probability.

TABLE II Selected bond lengths [Å] and angles [°] for **1**

Bond lengths		*Angles*	
Re(1)—N(1)	1.757(12)	N(1)—Re(1)—O(1)	174.5(5)
Re(1)—O(1)	2.048(4)	O(1)—Re(1)—Br(2)	176.62(13)
Re(1)—Br(2)	2.462(3)	N(1)—Re(1)—Br(1)	94.7(4)
Re(1)—Br(1)	2.4988(7)	OP(1)—Re(1)—Br(1)	87.86(12)
O(1)—P(1)	1.505(4)	Br(2)—Re(1)—Br(1)	88.81(4)
P(1)—C(13)	1.790(7)	P(1)—O(1)—Re(1)	158.0(3)
P(1)—C(1)	1.792(6)	O(1)—P(1)—C(13)	111.1(3)
P(1)—C(7)	1.796(6)	O(1)—P(1)—C(1)	108.6(3)
N(1)—O(2)	1.261(13)	C(13)—P(1)—C(1)	108.7(3)
C(1)—C(6)	1.366(10)	O(1)—P(1)—C(7)	113.2(3)
C(1)—C(2)	1.387(10)	C(13)—P(1)—C(7)	107.9(3)
C(2)—C(3)	1.400(10)	C(1)—P(1)—C(7)	107.2(3)
C(3)—C(4)	1.340(14)	O(2)—N(1)—Re(1)	172.6(13)
C(4)—C(5)	1.37(2)	C(6)—C(1)—P(1)	122.4(6)
C(5)—C(6)	1.377(11)	C(2)—C(1)—P(1)	118.4(5)
		C(1)—C(2)—C(3)	120.2(8)
		C(4)—C(3)—C(2)	118.7(9)
		C(3)—C(4)—C(5)	121.8(8)
		C(4)—C(5)—C(6)	119.8(8)
		C(1)—C(6)—C(5)	120.1(9)

7.85 ppm. One signal in the ^{31}P NMR spectrum of **1** complex indicates the presence only of one kind of phosphine ligands, $OPPh_3$, in the coordination sphere and signal broadening is caused by the paramagnetism of **1**. The

TABLE III Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$Å^2$ × 10^3] for **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	X/a	*Y/b*	*Z/c*	U_{eq}
Re(1)	0	3535(1)	2500	50(1)
O(1)	−342(3)	2391(4)	3130(2)	69(1)
P(1)	−233(1)	1680(1)	3728(1)	55(1)
Br(1)	1683(1)	3396(1)	3034(1)	73(1)
Br(2)	511(1)	4889(2)	1764(1)	75(1)
N(1)	260(9)	4439(12)	1894(6)	74(4)
O(2)	544(13)	5109(14)	1508(8)	119(7)
C(1)	−1395(4)	1401(5)	3973(3)	61(1)
C(2)	−2152(5)	1321(6)	3466(4)	79(2)
C(3)	−3063(6)	1067(8)	3634(6)	96(3)
C(4)	−3187(6)	907(8)	4289(6)	102(3)
C(5)	−2457(7)	1015(9)	4796(5)	106(3)
C(6)	−1552(6)	1236(7)	4635(4)	85(2)
C(7)	458(4)	2201(5)	4462(3)	60(1)
C(8)	1118(6)	1595(6)	4851(4)	77(2)
C(9)	1606(7)	2012(9)	5433(4)	98(3)
C(10)	1448(6)	2988(9)	5621(4)	94(3)
C(11)	820(8)	3573(7)	5226(4)	96(3)
C(12)	312(6)	3157(7)	4650(3)	83(2)
C(13)	319(5)	522(5)	3513(3)	64(1)
C(14)	−91(7)	−390(6)	3588(5)	91(2)
C(15)	401(10)	−1278(8)	3449(7)	117(4)
C(16)	1279(9)	−1220(9)	3198(6)	112(4)
C(17)	1646(8)	−313(10)	3129(5)	110(3)
C(18)	1210(5)	576(6)	3268(4)	79(2)

TABLE IV Infrared data for **1** and **2**

Band position [cm^{-1}]		
[$ReBr_3(NO)(OPPh_3)_2$]	[$ReBr_3(NO)(PPh_3)_2$]	*Assignment*
1738	1776	ν(NO)
1485	1482	δ(C—CH in plane)
1437	1436	ν(P—C_6H_5)
1159 and 1122		ν(P=O)
1082	1091	δ(C—H in plane)
750 and 725	742 and 701	δ(C—C out of plane)
690	692	δ(C—C in plane)
536	521	ν(Re—N)

magnetic moment for **1** (1.77 BM) corresponds to one unpaired electron. A strong band corresponding to the stretch of the nitrosyl group appears at 1737 cm^{-1}. Table IV gives assignments of characteristic IR bands for **1** [37]. Positions and molar absorption coefficients of electronic bands for **1** and the electronic transitions assigned to the bands are shown in Table V [38].

Absorption bands in the electronic spectrum of **1** at 14510, 15460 and 31150 cm^{-1} correspond to electron transitions between *d* orbitals split in a ligand field of C_s symmetry. The band at 27150 cm^{-1} is a result of the

TABLE V Band positions, molar absorption coefficients CD and assignments for the electronic spectra of **1** and **2**

[$ReBr_3(NO)(OPPh_3)_2$]			[$ReBr_3(NO)(PPh_3)_2$]		
Band positions [cm^{-1}]	*Molar absorption coefficients* M^{-1} cm^{-1}	*Assignments*	*Band positions* [cm^{-1}]	*Molar absorption coefficients* M^{-1} cm^{-1}	*Assignments*
14,510	39	$d_{xy} \rightarrow d_{xz}$	15,504	292	$d_{xz} \rightarrow \pi^*_{NO}$
15,460	66	$d_{xy} \rightarrow d_{yz}$	17,513	1,766	$d_{yz} \rightarrow \pi^*_{NO}$
23,260	1,686	$\pi^0_{O=P} \rightarrow d_{xy}$	21,930	906	$d_{xy} \rightarrow d_{yz}$
27,150	4,656	$d_{xy} \rightarrow \pi^*_{NO}$	23,810	908	$d_{xy} \rightarrow d_{xz}$
31,150	1,913	$d_{xy} \rightarrow d_{x^2}-y^2$	32,573	2,216	$d_{xy} \rightarrow d_{x^2-y^2}, \pi^b_{Re-Br} \rightarrow d_{xz}$
36,490	6,859	$\pi^b_{Re-Br} \rightarrow d_{xz}$	41,353	12,510	$\pi^0_{C_6H_5} \rightarrow 3d_P, d_{xy} \rightarrow \pi^*_{NO}$
37,310	7,624	$\pi^b_{Re-Br} \rightarrow d_{yz}$			
38,170	7,029	$\pi^0_{O=P} \rightarrow d_{xz}$			
42,220	11,841	$\pi^b_{C_6H_5} \rightarrow 3d_p$			

TABLE VI Values of ligand field parameters for **1** and **2**

Ligand field parameter	*Value* [cm^{-1}] [$ReBr_3(NO)(OPPh_3)_2$]	[$ReBr_3(NO)(PPh_3)_2$]
Dq	3,115	3,257
Ds	−4,494	−6,802
Dt	395	680

$d_{xy} \rightarrow \pi^*_{NO}$ transition. Bands at 23260, 36490, 37310 and 38170 cm^{-1} are charge transfer transitions connected with transition of $\pi^o_{O=P}$ or π^b_{Re-Br} electrons to suitable *d* orbitals of the rhenium ion. The highest energy band is a result of an electronic transition in the phosphine ligand molecule. Based on the data of Table V, values of ligand field parameters *Dq*, *Ds* and *Dt* have been defined and energies of molecular orbitals for **1** have been estimated. Values of ligand field parameters for **1** are given in Table VI. In **1** the Re ion is present in the +2 oxidation state, and its electronic configuration, considering splitting of *d* orbitals in C_s symmetry is $(d_{xy})^2$ $(d_{xz})^2$ $(d_{yz})^1$.

[$ReBr_3(NO)(PPh_3)_2$] (**2**) is isostructural with the chloro- analogue, [$ReCl_3(NO)(PPh_3)_2$] [39]. The Re(1) atom in **2** is octahedrally surrounded by three bromine atoms: Br(1), Br(2) and Br(2a), a nitrosyl group N(1)—O(1) and two phosphorus atoms P(1) and P(1a). The central ion, Re(1), the nitrosyl group N(1)—O(1) and one of the bromine ligands Br(1) occupy special positions on a two-fold axis. The numbering scheme of **2** is shown in Figure 2.

In the [$ReBr_3(NO)(PPh_3)_2$] complex, contrary to the [$ReBr_3(NO)(OPPh_3)_2$] complex, phosphine ligands are in the *trans* arrangement. Most important bond lengths and angles for **2** are reported in Table VII. Table VIII presents atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2**.

The Re(1)—N(1)—O(1) angle (180.00°) and N(1)—O(1) bond length [1.12(2) Å] confirm the linear coordination of nitrosyl ligand. The N(1)—O(1) bond length in **2** is slightly shorter than the value found for [$ReCl_3(NO)(PPh_3)_2$] [1.20(1) Å] [39].

Table IV contains assignments of characteristic bands in IR range for **2** [37]. A strong band corresponding to the nitrosyl stretch appears at 1776 cm^{-1}. Compound **2** is paramagnetic with a magnetic moment equal to 1.8 BM, corresponding to one unpaired electron.

The positions and molar absorption coefficients of electronic absorption bands for **2** and the electronic transitions assigned to the bands are shown in Table V [38]. The transitions $d_{xz} \rightarrow \pi^*_{NO}$ and $d_{yz} \rightarrow \pi^*_{NO}$, responsible for bands

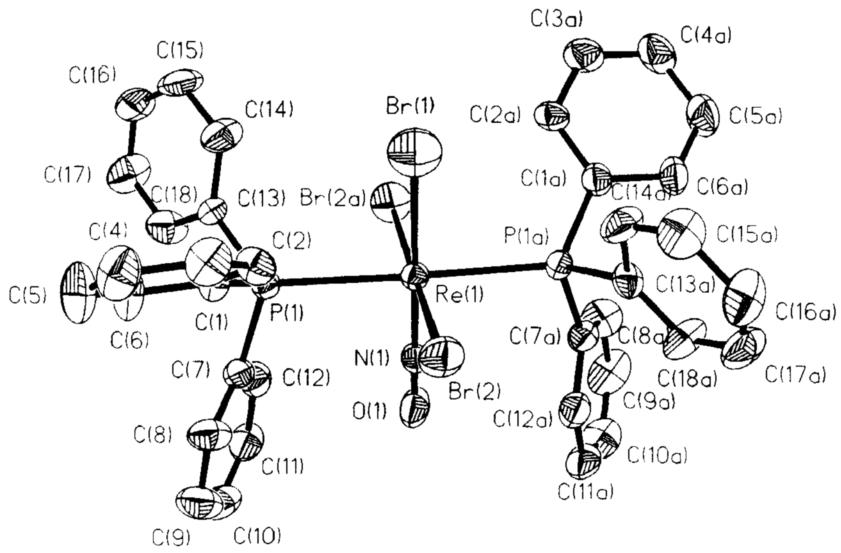

FIGURE 2 The molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability.

TABLE VII Selected bond lengths [Å] and angles [°] for **2**

Bond lengths		*Angles*	
Re(1)—N(1)	1.769(12)	N(1)—Re(1)—Br(2)	90.57(4)
Re(1)—Br(2)	2.4811(14)	N(1)—Re(1)—Br(2a)	90.57(4)
Re(1)—Br(1)	2.496(3)	N(1)—Re(1)—Br(1)	180.000(1)
Re(1)—P(1)	2.540(2)	Br(2)—Re(1)—Br(2a)	178.86(7)
N(1)—O(1)	1.12(2)	Br(2)—Re(1)—Br(1)	89.43(4)
P(1)—C(1)	1.830(10)	Br(2a)—Re(1)—Br(1)	89.43(4)
P(1)—C(7)	1.834(10)	N(1)—Re(1)—P(1a)	90.75(6)
P(1)—C(13)	1.802(10)	Br(2)—Re(1)—P(1a)	87.59(6)
		Br(2a)—Re(1)—P(1a)	92.39(6)
		Br(1)—Re(1)—P(1a)	89.25(6)
		N(1)—Re(1)—P(1)	90.75(6)
		Br(2)—Re(1)—P(1)	92.39(6)
		Br(2a)—Re(1)—P(1)	87.59(6)
		Br(1)—Re(1)—P(1)	89.25(6)
		P(1a)—Re(1)—P(1)	178.50(12)
		O(1)—N(1)—Re(1)	180.000(2)
		C(1)—P(1)—C(13)	106.1(5)
		C(1)—P(1)—C(7)	105.7(4)
		C(13)—P(1)—C(7)	101.0(5)
		C(1)—P(1)—Re(1)	106.7(3)
		C(13)—P(1)—Re(1)	119.7(3)
		C(7)—P(1)—Re(1)	116.5(3)

of low intensities at 15504 and 17513 cm^{-1}, respectively, are symmetry forbidden. The nitrosyl group lies in the *xy* plane and the donor orbitals of the rhenium atom in the *xz* and *yz* planes. The $d_{yz} \rightarrow \pi^*_{NO}$ transition includes

TABLE VIII Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	X/a	Y/b	Z/c	U_{eq}
Re(1)	0	3339(1)	2500	26(1)
Br(2)	568(1)	3313(2)	4232(1)	52(1)
Br(1)	0	736(3)	2500	75(1)
N(1)	0	5183(12)	2500	31(2)
O(1)	0	6354(12)	2500	55(3)
P(1)	975(1)	3304(3)	2324(2)	28(1)
C(1)	1233(4)	5114(10)	2420(7)	32(2)
C(2)	869(6)	6046(12)	1749(9)	44(3)
C(3)	993(6)	7454(12)	1816(10)	53(3)
C(4)	1515(8)	7934(13)	2612(11)	64(4)
C(5)	1878(7)	7046(15)	3266(10)	62(4)
C(6)	1746(6)	5576(13)	3167(9)	53(3)
C(7)	912(4)	2670(10)	1204(7)	33(2)
C(8)	731(7)	1274(11)	976(9)	51(3)
C(9)	696(7)	759(13)	133(10)	60(4)
C(10)	854(6)	1575(14)	−436(9)	56(3)
C(11)	1025(7)	2873(14)	−192(8)	57(3)
C(12)	1050(6)	3446(13)	621(8)	50(3)
C(13)	1621(5)	2320(11)	3137(7)	36(2)
C(14)	2183(5)	2387(15)	3097(9)	53(3)
C(15)	2680(6)	1644(16)	3683(10)	63(3)
C(16)	2631(6)	748(15)	4347(9)	55(3)
C(17)	2100(6)	668(13)	4406(8)	49(3)
C(18)	1593(5)	1426(10)	3821(7)	36(2)

$d_{xz} \rightarrow \pi^*_{NO}$, so the intensity of the band at 17513 cm^{-1} is a little higher than the intensity of the band at 15504 cm^{-1}. The shorter Re — N bond length and longer N — O bond length in **1** than in **2**, resulting from the stronger *trans* influence of the Br^- anion than $OPPh_3$ group (see Figs. 1 and 2), indicates more effective transition of electron density from the occupied d_{xy} rhenium orbital to π^*_{NO} in the complex with $OPPh_3$ than in $[ReBr_3(NO)(PPh_3)_2]$. The electronic band at 32573 cm^{-1} for **2**, similar to the band at 31150 cm^{-1} in **1**, corresponds to the $d_{xy} \rightarrow d_{x^2} - y^2$ electron transition, but its higher intensity results from a partial contribution of the $\pi^b_{Re-Br} \rightarrow d_{xz}$ transition. Similarly, a partial contribution of $d_{xy} \rightarrow \pi^*_{NO}$ in the band at 41510 cm^{-1}, which is mainly assigned to $\pi^b_{C_6H_5} \rightarrow 3d_P$, causes an increase of its intensity in comparison with **1**. Based on the data of Table V, values of ligand field parameters *Dq*, *Ds* and *Dt* have been defined and the energies of molecular orbitals for **2** have been estimated. Values of ligand field parameters are shown in Table VI.

In **2** the Re ion is present in the +1 oxidation state, and its electronic configuration, considering splitting of *d* orbitals in C_{2v} symmetry is $(d_{xy})^2 (d_{yz})^2 (d_{xz})^1$.

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Supplementary Material

Full crystallographic data for **1** and **2** are available on request from the authors.

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