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The Syntheses, Crystal, Molecular and Electronic Structures of $[ReBr_3(py)_3]_{0.42}[ReBr_2(NO)(py)_3]_{0.58}$, *trans*-$[ReBr_4(OPPh_3)_2]$ and Orthorhombic Polymorph of *mer-cis*-$[ReBr_3(NO)(OPPh_3)_2]$

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$[ReBr_3(py)_3]_{0.42}[ReBr_2(NO)(py)_3]_{0.58}$ (**1**), *trans*-$[ReBr_4(OPPh_3)_2]$ (**2**), $[ReBr(NO)(dppe)_2]Br$ (**3**) and orthorhombic polymorph of *mer-cis*-$[Re(NO)Br_3(OPPh_3)_2]$ (**4**) complexes have been synthesized by reactions of monoclinic polymorph of *mer-cis*-$[Re(NO)Br_3(OPPh_3)_2]$ with pyridine, bis(diphenylophosphino)ethane, 2,2′-bipyridine, 1,10-phenanthroline. The NO group in **1** and **4** is coordinated in a linear way. Due to nitrosyl/bromine compositional disorder, the shortening of Re–NO distance [1.68(5) Å] and the elongation of N–O bond length [1.38(10) Å] are observed in **1**. The N–O bond length in **4** is extremely short [0.94(1) Å], which results probably from steric interactions of two mutually *cis* $OPPh_3$ molecules and a large discrepancy of Re–O–P angle values.

Key words: rhenium, nitrosyl, X-ray structure, electronic structure

The widespread contemporary interest in the development of technetium and rhenium radiopharmaceuticals [1–5] has fostered an expansion of the coordination chemistry of these metals. Due to a key role of nitric oxide in human cardiovascular and nervous systems and in immune response to pathogen invasion, rhenium nitrosyl complexes are of special importance. Nitrosyl compounds are considered as potential deliverers of NO to biological targets upon demand either by thermal reactions or by photochemical excitation [6–9].

We investigated the reactivity of $[ReOX_3L_2]$ compounds containing P-, As- and N-donor monodentate and bidentate ligands (L) towards gaseous nitric oxide [10–20]. The $[ReOX_3(PPh_3)_2]$ and $[ReOX_3(AsPh_3)_2]$ complexes (X = Cl, Br) react with NO to give various products, depending on the reaction conditions: $[ReX_3(NO)(OPPh_3)_2]$, $[ReX_3(NO)(PPh_3)_2]$, $[ReX_2(NO)_2(PPh_3)_2]$, $[ReBr_3(NO)(MeCN)(PPh_3)]$, $[ReCl_3(NO)(PPh_3)(OPPh_3)]$, $[ReCl_4(PPh_3)_2]$, $[ReX_3(NO)(OAsPh_3)_2]$, $[ReCl_4(OAsPh_3)_2]$ and $[ReCl_3(NO)(AsPh_3)_2][ReCl_4(AsPh_3)_2]$. The $[ReOBr_3(dppe)]$ complex reacts with NO only in the presence of a large excess of PPh_3 to give $[ReBr_3(NO)(dppe)][ReBr_4(dppe)]$, whereas the reactions of $[ReOBr_3(bipy)]$ and $[ReOBr_3(phen)]$ with NO lead to the isolation of the starting material.

Intending to obtain the nitrosyls containing pyridine (py), bis(diphenylphosphino)ethane (dppe), 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen), we have examined the reactions of *mer-cis*-[$ReBr_3(NO)(OPPh_3)_2$] with py, dppe, bipy and phen, expecting that mutually *cis* $OPPh_3$ molecules of the starting compound will be replaced by the P- and N-donor ligands. However, the reactions of *mer-cis*-[$ReBr_3(NO)(OPPh_3)_2$] with py and dppe are disproportion reactions, and they afford [$ReBr_3(py)_3$]$_{0.42}$[$ReBr_2(NO)(py)_3$]$_{0.58}$ (**1**), *trans*-[$ReBr_4(OPPh_3)_2$] (**2**), [ReBr(NO)(dppe)$_2$]Br (**3**), whereas refluxing of *mer-cis*-[Re(NO)$Br_3(OPPh_3)_2$] with bipy or phen in chloroform leads only to conversion of the starting monoclinic form of *mer-cis*-[Re(NO)$Br_3(OPPh_3)_2$] into an orthorhombic polymorph (**4**).

EXPERIMENTAL

Triphenylphosphine, bis(diphenylophosphino)ethane, 2,2′-bipyridine, 1,10-phenanthroline and ammonium perrhenate were purchased from Aldrich Chemical Co., and used without further purification. Solvents were obtained from commercial sources and thoroughly deoxygenated prior to use. The reactions were performed under argon atmosphere. The monoclinic polymorph of *mer-cis*-[$ReBr_3(NO)(OPPh_3)_2$] was prepared according to [19]. Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000÷400 cm^{-1} with the samples in the form of potassium bromide pellets. Electronic spectra were measured on a spectrophotometer Lab Alliance UV-VIS 8500 in the range 800÷220 nm in deoxygenated dichloromethane solution. Magnetic susceptibilities were measured at 296 K by the Faraday method.

Preparation of [$Re^{III}Br_3(py)_3$]$_{0.42}$[$Re^{I}Br_2(NO)(py)_3$]$_{0.58}$ *(1)*: The [$ReBr_3(NO)(OPPh_3)_2$] complex (0.40 g, 0.4 mmol) was heated in dry pyridine (8 ml) at reflux for 4 h. The solution was evaporated to 3 ml and an excess of diethyl ether was added. The dark red solid, which precipitated, was recrystallized from a mixture CH_2Cl_2/C_2H_5OH to give prismatic crystals (0.2 g, 70%). IR (KBr, cm^{-1}) 3030 (m), 3007 (s), 2873 (m), 1666 (s), 1606 (m), 1479 (m), 1444 (s), 1391 (w), 1214 (m), 1152 (w), 1066 (m), 1012 (w), 758 (s) 725 (m), 694 (s), 619 (w). Elemental analysis confirmed the composition.

Preparation of trans-[$ReBr_4(OPPh_3)_2$] *(2) and* [ReBr(NO)(dppe)$_2$]Br *(3)*: [$ReBr_3(NO)(OPPh_3)_2$] (0.5 g, 0.5 mmol) was added to a solution of dppe (1 g, 2.5 mmol) in benzene (75 ml) and dichloromethane (25 ml) and was refluxed for 48 hours. The colour changed gradually from green to yellow. The resulting solution was evaporated to dryness and the residue was extracted with diethyl ether (200 ml) to remove an excess of dppe and $OPPh_3$ liberated in the reaction. The yellow crude product was filtered and treated with methanol (60 ml). The yellow precipitate of *trans*-[$ReBr_4(OPPh_3)_2$] undissolved in MeOH was filtered (yield 35%). The volume of methanol solution was condensed to 8 ml and upon cooling to 4°C, yellow microcrystalline solid of [ReBr(NO)(dppe)$_2$]Br was isolated (Yield 33%). X-ray quality crystals of *trans*-[$ReBr_4(OPPh_3)_2$] were obtained by recrystallization from CH_2Cl_2-MeOH. IR of **2** (KBr, cm^{-1}) 3052 (m), 1484 (m), 1436 (s), 1337 (w), 1314 (w), 1122 (vs), 1074 (s), 1026 (m), 747 (m), 726 (s) 690 (s), 533 (s), 528 (s), 475 (w). Elemental analysis confirmed the composition. IR of **3** (KBr, cm^{-1}) 3047 (w), 2894 (w), 2828 (w), 1705 (vs), 1480 (m), 1435 (s), 1319 (w), 1192 (w), 1158 (w), 1097 (m), 876 (w), 824 (w), 749 (s), 702(s) 689 (s), 531 (s), 514 (s), 481 (m). Elemental analysis confirmed the composition.

Preparation of orthorhombic polymorph of mer-cis-[$ReBr_3(NO)(OPPh_3)_2$] *(4)*: Monoclinic polymorph of *mer-cis*-[$ReBr_3(NO)(OPPh_3)_2$] (0.5 g, 5 mmol) was added to a solution of 2,2′-bipyridine (0.39 g, 2.5 mmol) in chloroform (50 ml). The green solution thus formed was refluxed for 48 h. The volume was condensed to 5 ml and upon slow cooling to room temperature green microcrystalline solid was isolated from the chloroform solution. X-ray quality crystals of **4** were obtained by recrystallization from $CHCl_3$-MeOH. (Yield 85%). The orthorhombic polymorph of *mer-cis*-[$ReBr_3(NO)(OPPh_3)_2$] was also isolated in the reaction of the monoclinic polymorph of *mer-cis*-[$ReBr_3(NO)(OPPh_3)_2$] (0.5 g, 5 mmol) with 1,10-phenanthroline (0.5 g, 2.5 mmol). IR of **4** (KBr, cm^{-1}) 3059 (w), 2961 (w), 2922 (w), 1754 (vs), 1485 (m), 1437 (s), 1261 (w), 1195 (m), 1182 (s), 1123 (vs), 1066 (s), 1025 (w), 755(w), 724 (s), 691 (s), 537 (s), 475 (w), 455 (w). Elemental analysis confirmed the composition.

Crystal structure determination and refinement. The three-dimensional X-ray intensity data were collected on a Kuma KM-4 diffractometer, using Mo$K\alpha$ radiation (graphite monochromator) in the ω-2θ scan mode, at room temperature. Details concerning crystal data and refinement are given in Table 1. Lorentz, polarization and empirical absorption corrections were applied. The structure was solved by the Patterson and Fourier methods. Bromine/nitrosyl compositional disorder was observed in **1**, the unaccounted electron density was present, when it was modelled as pure nitrosyl. Both components of the disorder were refined anisotropically and the site occupancies refined to 0.58 and 0.42 for NO and Br, respectively. TWIN refinement was used for **2** and two carbon atoms (C15 and C33) of **2** were refined isotropically. All the other non-hydrogen atoms in **1**, **2** and **4** were refined anisotropically, using full-matrix, least-squares technique. 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 and refined with individual isotropic temperature factor equal 1.2 times the value of equivalent temperature factor of the parent carbon atom and the C–H distance free to refine. SHELXL93, SHELXL97 and SHELXTL programs [21–23] were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs. The relatively high R values for these complexes (Table 1) result from poor-quality crystals but we were not able to obtain better ones.

RESULTS AND DISCUSSION

The complex **1** has been obtained in the reaction of *mer-cis*-$[Re^{II}Br_3(NO)(OPPh_3)_2]$ with pyridine and the yield of this reaction strongly depends on two factors: – the purity of pyridine; the presence of moisture in the pyridine leads to drastic decrease in the product yield, – the reaction time; the yield of **1** is considerably lower when the reaction is carried out for less than four hours.

It is a disproportion reaction, what confirms the presence of two kinds of molecules $[Re^{III}Br_3(py)_3]$ (**1-I**) and $[Re^{I}Br_2(NO)(py)_3]$ (**1-II**) in molar ratio equal to ≈ 1:1 in crystals of **1**. Considering the *cis*-arrangement of two triphenylphosphine oxide ligands in *mer-cis*-$[ReBr_3(NO)(OPPh_3)_2]$, it can be predicted that the replacement of $OPPh_3$ molecules in $[ReBr_3(NO)(OPPh_3)_2]$ by potential bidentate ligands – dppe, bipy and phen – will easily occur. However, according to our research, the reaction of $[Re^{II}Br_3(NO)(OPPh_3)_2]$ with dppe, similarly to the reaction with pyridine, is a disproportion reaction and affords **2** and **3**:

$$2[Re^{II}Br_3(NO)(OPPh_3)_2]+2dppe \rightarrow [Re^{IV}Br_4(OPPh_3)_2]+[Re^{I}Br(NO)(dppe)_2]Br+2OPPh_3+NO.$$

2,2′-Bipyridine and 1,10-phenanthroline do not replace phosphine ligands in starting *mer-cis*-$[Re(NO)Br_3(OPPh_3)_2]$. Refluxing of *mer-cis*-$[Re(NO)Br_3(OPPh_3)_2]$ with bipy or phen in chloroform leads only to conversion of starting monoclinic form of *mer-cis*-$[Re(NO)Br_3(OPPh_3)_2]$ into orthorhombic polymorph **4**.

The accurate cell parameters, crystal data and details concerning the structure for **1**, **2** and **4** are given in Table 1.

Complex **1** with nitrosyl/bromine compositional disorder (Fig. 1a) belongs to the $P2_1/n$ space group. The molecules of $[ReBr_3(py)_3]$ (**1-I**) are packed together with molecules of $[ReBr_2(NO)(py)_3]$ (**1-II**) in a proportion 0.42:0.58 (≈1:1). In both molecules, **I** and **II**, the rhenium atom has a distorted octahedral coordination with pyridine ligands in a *meridional* geometry. The numbering scheme of **1-I** and **1-II** molecules are shown in Figure 1b and 1c, respectively.

Table 1. Crystal data and structure refinement for **1**, **2** and **4**.

	1	**2**	**4**
Empirical formula	$C_{15}H_{15}Br_{2.42}N_{3.58}O_{0.58}Re$	$C_{36}H_{30}P_2O_2Br_4Re$	$C_{36}H_{30}P_2O_2Br_3NO_3Re$
Formula weight	634.16	1062.38	1012.48
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1$	$P2_12_12_1$
Unit cell dimensions			
a (Å)	9.178(2)	10.048(2)	10.932(2)
b (Å)	12.923(3)	15.390(3)	16.855(3)
c (Å)	15.602(3)	12.010(2)	19.746(4)
α (°)	90	90	90
β (°)	91.01(3)	101.09(3)	90
γ (°)	90	90	90
Volume (Å^3)	1850.2(7)	1822.5(6)	3638.4(12)
Z	4	2	4
Density (calc., Mg/m^3)	2.277	1.936	1.848
Abs. coefficient (mm^{-1})	11.792	7.837	6.758
F(000)	1177	1014	1948
Crystal dimensions (mm)	0.23×0.10×0.03	0.21×0.18×0.05	0.44×0.18×0.16
θ range for data collection (°)	2.05 to 25.06	1.73 to 27.06	1.59 to 25.80
Index ranges	$-10 \le h \le 10$ $-15 \le k \le 2$ $0 \le l \le 18$	$-12 \le h \le 0$ $-19 \le k \le 2$ $-15 \le l \le 15$	$0 \le h \le 13$ $0 \le k \le 20$ $-24 \le l \le 24$
Reflections collected	4010	4805	7608
Completeness to 2 theta	94.8%	97.5%	100.0%
Absorption correction	empirical	empirical	empirical
Max. and min. transmissions	0.749 and 0.169	0.695 and 0.290	0.411 and 0.155
Independent reflections	3259(R_{int} = 0.0613)	4652(R_{int} = 0.0619)	6997(R_{int} = 0.0403)
Data/restraints/parameters	3259/0/219	4652/1/397	6997/0/416
Goodness-of-fit on F^2	1.161	1.163	1.242
Final R indices [$I>2\sigma(I)$]	R1 = 0.0838 wR2 = 0.1618	R1 = 0.0784 wR2 = 0.1235	R1 = 0.0706 wR2 = 0.0982
R indices (all data)	R1 = 0.1429 wR2 = 0.1854	R1 = 0.1450 wR2 = 0.1524	R1 = 0.1206 wR2 = 0.1126
Largest diff. peak and hole (e Å^{-3})	1.673 and –1.753	1.374 and –3.452	0.656 and –0.951

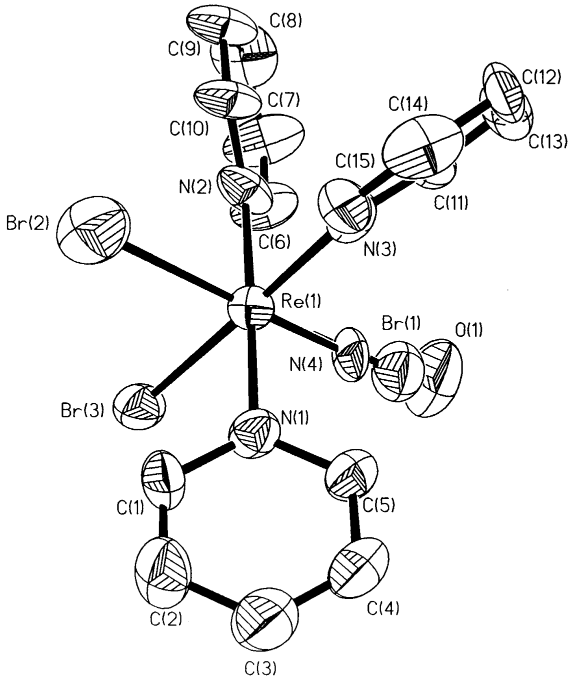

Figure 1a. The molecular structure of the disordered [$\mathrm{ReBr_{2.42}(NO)_{0.58}(py)_3}$] compound. The thermal ellipsoids are drawn at 50% probability level.

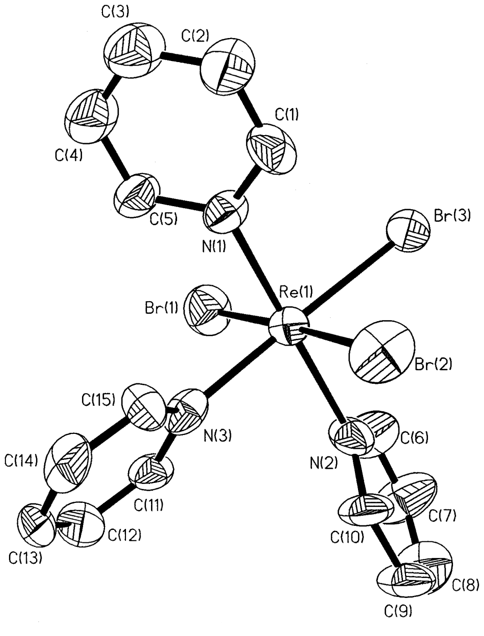

Figure 1b. The molecular structure of the [$\mathrm{ReBr_3(py)_3}$] complex (**1**–**I**).

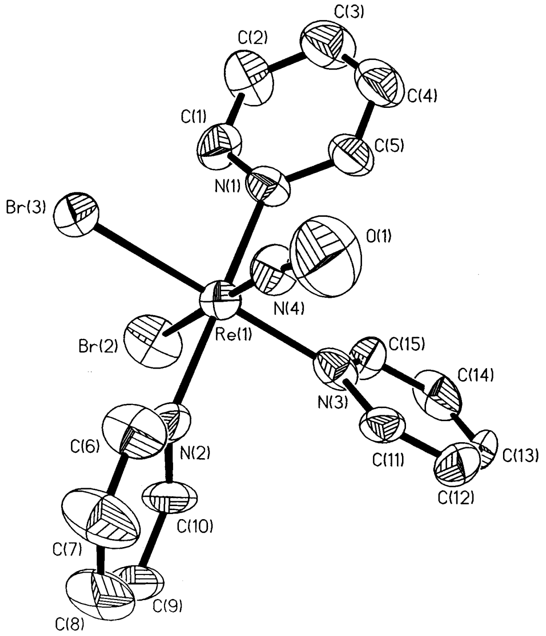

Figure 1c. The molecular structure of the [ReBr$_2$(NO)(py)$_3$] complex (**1**–**II**).

The molecules of **1** are linked *via* C(2)–H(2A)···O(1)(-x+1/2,y+1/2,-z+1/2) intermolecular weak hydrogen bonds (D···A distance equals 3.256(3) Å and D–H···A angle 129°). The conformations of molecules of compound **1** are stabilized by three weak intramolecular hydrogen bonds: C(1)-H(1A)···Br(2) [D···A distance equals to 3.360(8) Å and D–H···A angle 115°], C(10)-H(10A)···Br(2) [D···A distance equals to 3.359(1) Å and D–H···A angle 114°] and C(5)-H(5A)···N(4) [D···A distance equals to 2.925(3) Å and D–H···A angle 104°].

2 belongs to the $P2_1$ space group and consists of [ReBr$_4$(OPPh$_3$)$_2$] molecules linked *via* C(36)–H(36A)···Br(3)(-x+2,-y-1/2,-z+2) weak intermolecular hydrogen bonds (D···A distance equals to 3.808(5) Å and D–H···A angle 161°). Moreover, the conformations of molecules of compound **2** are stabilized by two weak intramolecular hydrogen bonds C(8)–H(8A)···O(1) and C(32)–H(32A)···O(2) (D···A distances equal to 2.980(2) and 2.059(8) Å, respectively; D–H···A angle for the both is equal to 106°).

The geometry around the Re(IV) ion is defined by four bromine donors and two *trans* oxygen atoms of the two triphenylphosphine oxide ligands. The molecular structure of **2** is presented in Figure 2.

4 belongs to the $P2_12_12_1$ space group and consists of isolated *mer-cis*-[ReBr$_3$(NO)(OPPh$_3$)$_2$] molecules. Only two weak intramolecular hydrogen bonds: C(12)–H(12A)···Br(3) [D···A distance equals to 3.8473 Å and D–H···A angle 168°] and C(32)–H(32A)···O(2) [D···A distance equals to 3.010 Å and D–H···A angle 106°] can be found in the compound **4**, providing slight stabilization to the molecule.

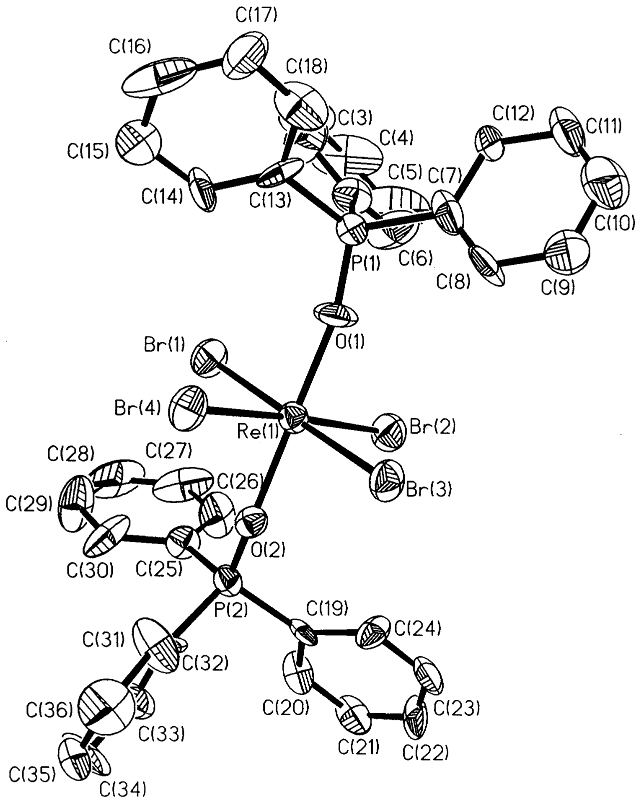

Figure 2. The molecular structure of the *trans*-[$ReBr_4(OPPh_3)_2$] complex.

The synthesis, crystal, molecular and electronic structure of monoclinic form of *mer-cis*-[$Re(NO)Br_3(OPPh_3)_2$] have been presented in paper [19]. The unit cell volume of orthorhombic polymorph **4** is smaller in comparison with the monoclinic form, so **4** is denser. In the monoclinic polymorph, the rhenium atom occupies special position *e* of space group *C*2/*c* with multiplicity 4 and the site symmetry 2, whereas all atoms of orthorhombic polymorph occupy the general positions. The packing diagrams of the monoclinic and orthorhombic polymorphs are given in Figs 3 and 4, respectively.

In the polymorphs, the rhenium atom has a distorted octahedral environment with bromine ligands in *meridional* geometry and linear nitrosyl group *trans* to one of two mutually *cis* $OPPh_3$ molecules (Fig. 5).

The most important bond lengths and angles for **1**, **2** and **4** are reported in Table 2.

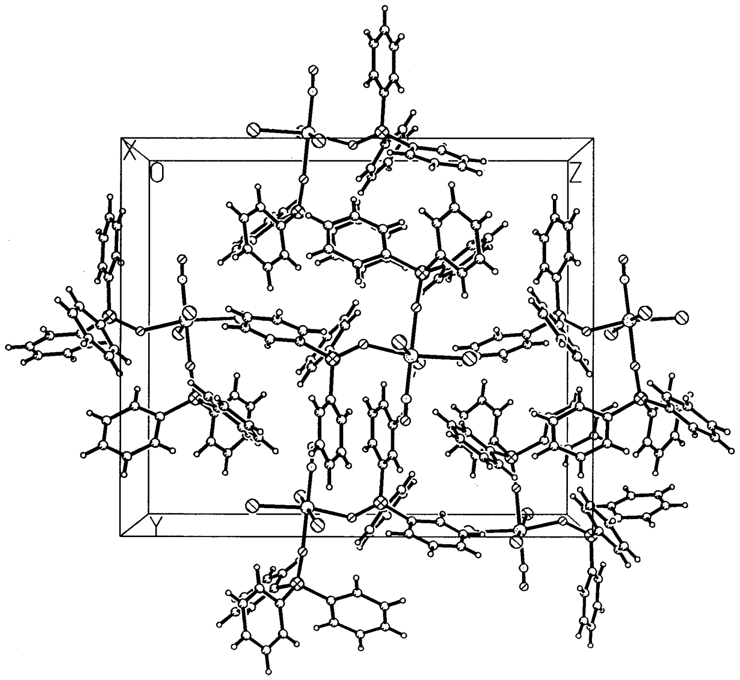

Figure 3. The packing diagram of the orthorhombic polymorph of *mer-cis*-[ReBr$_3$(NO)(OPPh$_3$)$_2$].

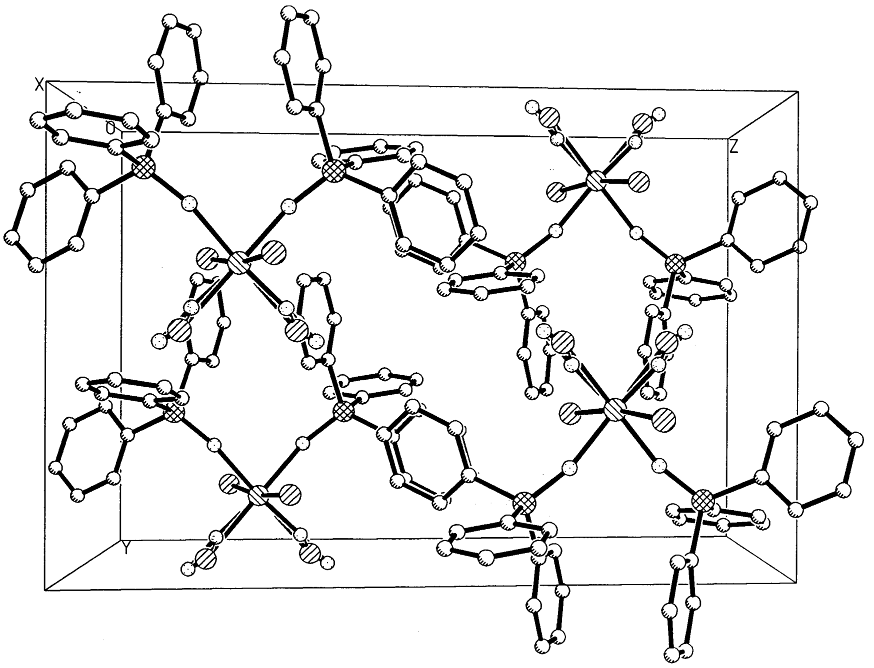

Figure 4. The packing diagram of the monoclinic polymorph of *mer-cis*-[ReBr$_3$(NO)(OPPh$_3$)$_2$].

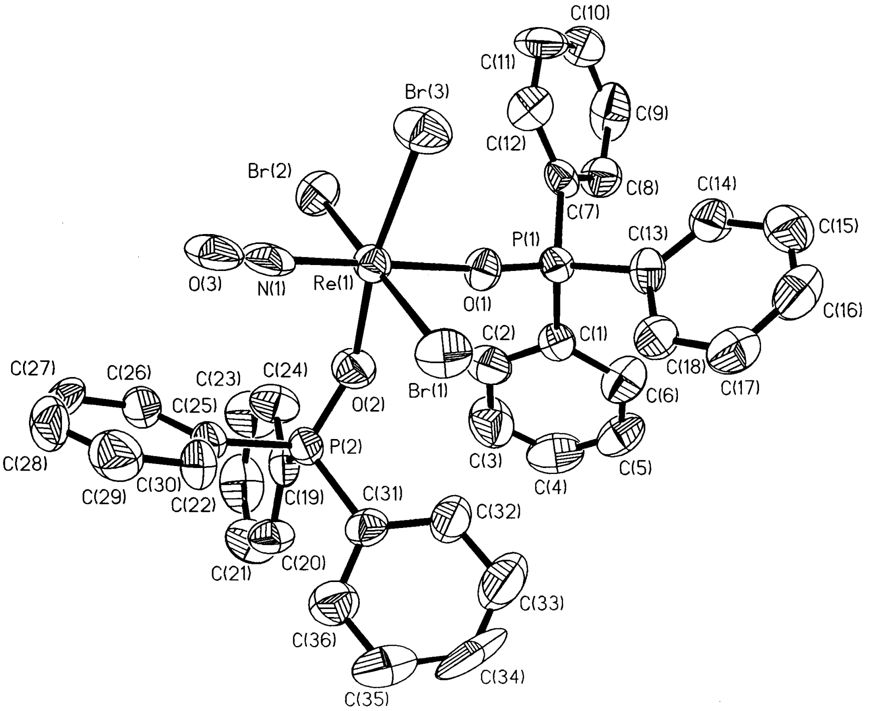

Figure 5. The molecular structure of orthorhombic polymorph of *mer-cis*-[ReBr$_3$(NO)(OPPh$_3$)$_2$].

Table 2. Selected bond lengths [Å] and angles [°] for **1**, **2** and **4**.

Bond lengths	**1**	**2**	**4**
Re(1)–Br(1)	2.49(2)	2.479(4)	2.511(2)
Re(1)–Br(2)	2.548(3)	2.505(4)	2.534(2)
Re(1)–Br(3)	2.571(2)	2.518(4)	2.473(2)
Re(1)–Br(4)		2.508(4)	
Re(1)–N(1)$_{py}$	2.13(2)		
Re(1)–N(2)$_{py}$	2.16(2)		
Re(1)–N(3)$_{py}$	2.14(2)		
Re(1)–N$_{NO}$	1.68(5)		1.87(2)
O–N	1.38(10)		0.94(1)
Re(1)–O(1)		2.00(2)	2.076(7)
Re(1)–O(2)		2.03(2)	2.071(9)
P(1)–O(1)		1.51(2)	1.497(8)
P(2)–O(2)		1.49(2)	1.533(9)
Angles			
O(1)–Re(1)–O(2)		177(1)	80.5(3)
O(1)–Re(1)–Br(1)		89.5(7)	86.8(2)
O(2)–Re(1)–Br(1)		92.6(6)	88.4(3)
O(1)–Re(1)–Br(2)		91.7(7)	87.2(2)
O(2)–Re(1)–Br(2)		90.2(5)	86.2(3)
Br(1)–Re(1)–Br(2)	177.5(3)	90.5(1)	172.51(6)

Table 2 (continuation)

O(1)–Re(1)–Br(4)		90.8(7)	
O(2)–Re(1)–Br(4)		87.3(5)	
Br(1)–Re(1)–Br(4)		90.8(1)	
Br(2)–Re(1)–Br(4)		177.2(1)	
O(1)–Re(1)–Br(3)		89.2(7)	88.3(2)
O(2)–Re(1)–Br(3)		88.7(6)	168.8(3)
Br(1)–Re(1)–Br(3)	91.4(3)	178.7(1)	91.36(6)
Br(2)–Re(1)–Br(3)	91.0(1)	89.7(1)	92.92(6)
Br(4)–Re(1)–Br(3)		89.1(1)	
P(1)–O(1)–Re(1)		162(2)	174.1(6)
P(2)–O(2)–Re(1)		154(1)	140.4(6)
N(1)–Re(1)–O(1)			179.2(5)
N(1)–Re(1)–O(2)			99.2(4)
N(1)–Re(1)–Br(1)	91.0(5)		92.4(5)
N(1)–Re(1)–Br(2)	89.9(5)		93.6(5)
N(1)–Re(1)–Br(3)	89.1(5)		92.0(3)
O–N–Re(1)	172(5)		175(1)
N(4)–Re(1)–N(1)	89(1)		
N(4)–Re(1)–N(3)	90(1)		
N(1)–Re(1)–N(3)	91.2(6)		
N(4)–Re(1)–N(2)	92(1)		
N(1)–Re(1)–N(2)	178.4(7)		
N(3)–Re(1)–N(2)	88.7(6)		
N(3)–Re(1)–Br(1)	89.5(5)		
N(2)–Re(1)–Br(1)	90.5(6)		
N(4)–Re(1)–Br(2)	178(1)		
N(3)–Re(1)–Br(2)	88.2(4)		
N(2)–Re(1)–Br(2)	88.5(6)		
N(3)–Re(1)–Br(3)	179.1(4)		
N(2)–Re(1)–Br(3)	90.9(4)		
N(4)–Re(1)–Br(3)	91(1)		

The departures from the ideal octahedron of **1** and **2** are very limited (the *cis*- and *trans*-angles are near to 90 and 180°, respectively), whereas the angles between *cis*-ligands in **4** vary between 80.5(3) and 99.2(4)° and the *trans*-angles are between 179.2(5) and 168.8(3)°. The angular deformation around the rhenium in **4** is larger in comparison with the monoclinic form, in which the *cis* angles deviate from 90° by ≤ 4.7° and *trans* angles – by 7.62°. The significant departure from the ideal octahedron in orthorhombic polymorph is connected with large discrepancy of Re–O–P angle values: Re–O–P = 140.4(6) and 174.1(6)°, what is in accordance with sizeable steric interactions of two mutually *cis* $OPPh_3$ molecules. In monoclinic polymorph, the position of the second O atom is generated by symmetry operation, so the Re–O–P angles are identical and they are 158.0(3)°.

Due to nitrosyl/bromine compositional disorder in **1**, we observe the shortening of Re–NO distance [1.68(5) Å] and the elongation of N–O bond length [1.38(10) Å] in comparison with other rhenium nitrosyl complexes. In monoclinic polymorph of *mer-cis*-$[ReBr_3(NO)(OPPh_3)_2]$, the Re–NO bond length is 1.76(1) Å and N–O distance is 1.26(1) Å [19], in $[ReBr_4(NO)(EtOH)]^-$ the Re–NO bond length is 1.72(2) and N–O distance is 1.19(2) Å [24], and in *mer*-$[ReCl_2(NO)(PMePh_2)_3]$ they are 1.78(1), 1.18(1) Å respectively [25]. The N–O bond length in the orthorhombic polymorph is very short [0.94(1) Å]. Such a short N–O distance in nitrosyl transition metal complexes is very rare but similar shortening of N–O bond is observed in $[NEt_4][ReBr_4(NO)(MeCN)]$ [0.99(2) Å] [26], *mer*-$[RuCl_3(NO)(PPh_2(CH_2)_3PPh_2)]$ [0.907(7) Å] [27] and *trans*-$[RuCl(NO)(dppe)_2]^{2+}\cdot[RuCl_4(NO)(H_2O)]\cdot\frac{1}{2}[RuCl_6]^{4+}\cdot 2H_2O$ [0.927(7) Å] [28]. In the case of **4** the shortening of N–O bond length results probably from steric interactions of two mutually *cis* $OPPh_3$ molecules and large discrepancy of Re–O–P angle values. The Re–N–O angles [172(5)° for **1** and 175.2(14)° for **4**] indicate approximately linear coordination of the nitrosyl ligand in **1** and **4**.

The shortening of the Re–Br(1) distance in **1** [2.49(2) Å] in comparison with Re–Br(2) [2.548(3) Å] is the consequence of nitrosyl/bromine compositional disorder and the elongation of Re(1)–Br(3) bond length in comparison with Re–Br(2) results from *trans* effect of pyridine. The *trans* effect of pyridine-like ligands is often observed, in the *mer*-$[ReCl_3(3,5\text{-lut})_3]$ complex (where 3,5-lut = 3,5-dimethylpyridine) the chloride ligand *trans* to the 3,5-dimethylpyridine bond is lengthened by 0.04 Å compared to the mutually *trans*-ones [29]. The $Re–N_{py}$ bond lengths in **1** (in the range 2.13(2)÷2.16(2) Å, mean 2.145 Å) are comparable to those found for similar complexes: *mer*-$[ReCl_3(3,5\text{-lut})_3]$ – 2.12÷2.13 Å [29], *trans*-$[ReO_2(py)_4]^+$ – 2.14÷2.17 Å [30], $[ReOCl_2(OEt)(py)_2]$ – 2.13 and 2.14 Å [31] and *trans*-$[ReO_2(4\text{-picoline})_4]^+$ – 2.11÷2.15 Å [32].

In **4**, the Re–Br(3) bond length [2.473(2) Å] in *trans* position to $OPPh_3$ molecule is shorter than Re–Br(1) = 2.511(2) Å and Re–Br(2) = 2.534(2) Å. A similar trend is observed in monoclinic form of *mer-cis*-$[Re(NO)Br_3(OPPh_3)_2]$, in which the Re–Br distance *trans* to $OPPh_3$ is 2.462(3) Å and the others are 2.4988(7) Å.

Comparison with other rhenium complexes containing $OPPh_3$ shows that the Re–O and P–O bond lengths and Re–O–P angles in **2** and **4** (see Table 2) are not unusual: in $[ReCl_3(NO)(OPPh_3)_2]$ Re–O = 2.055(6) Å, P–O = 1.493(6) Å, Re–O–P = 157.8(4)° [16] and in $[ReBr_{2.5}Cl_{1.5}(OPPh_3)_2]$ Re–O = 2.030(7) Å, P–O = 1.459(8) Å, Re–O–P = 158.1(5)° [33]. The Re–O [2.087(7) Å] and P–O [1.523(8) Å] distances in $[ReCl_4(dppom\text{-}P,O)]$ [dppom = $Ph_2PCH_2P(=O)Ph_2$] are slightly longer and the Re–O–P angle [130.1(1)°] far smaller in comparison with **2** and **4**, but it results from the bidentate nature of the dppom ligand [34].

The IR spectra of the **1**, **3** and **4** show ν(NO) at 1666, 1705 and 1754 cm^{-1}, respectively. These values are consistent with the linear NO range of Haymore and Ibers [ν(NO) above 1620–1610 cm^{-1} were assigned to linear M–N–O systems, while ν(NO) below 1610 cm^{-1} were assigned to bent M–N–O systems] [35]. Most nitrosyl rhenium(I) complexes of type $[ReX_2(NO)L_3]$, where L is nitrogen or phosphorus donor ligands, show a ν(NO) very close to 1660 cm^{-1}, for example: $[ReCl_2(NO)(PMe_2Ph)_3]$ 1665 cm^{-1}, $[ReCl_2(NO)(PEt_2Ph)_3]$ 1660 cm^{-1}, $[ReCl_2(NO)(py)(PPh_3)_2]$ 1670 cm^{-1} [25], $[ReBr_2(NO)(4\text{-picoline})_3]$ 1660 cm^{-1} [36]. The complexes $[ReX(NO)(dppe)_2]X$ (X = Cl, HSO_4 and F), $[ReF(NO)(dppe)_2][BF_4]$ and $[ReCl(NO)(dppe)_2][BF_4]$ [37,38], analogous to **3**, were isolated as yellow solids with a strong ν(NO) band at *ca.* 1670$\div$1710 cm^{-1}. As a consequence of shortening of the N–O distance in **4**, the strong band corresponding to the stretch of the nitrosyl group appears at higher frequencies in comparison with **1**, **3** and monoclinic polymorph.

The presence of two strong bands corresponding to ν(O=P) at 1123 and 1182 cm^{-1} in spectrum of **4** confirms the *cis* geometry of two coordinated $OPPh_3$ molecules, whereas a strong single band at 1122 cm^{-1} in spectrum of **2** indicates the *trans* positions of $OPPh_3$ ligands. These values are comparable with those that have been found for *cis*-$[Re(NCS)_4(PPh_3)(OPPh_3)]$ – 1116 cm^{-1} [39], $[ReCl_3(NO)(OPPh_3)_2]$ – 1136 and 1159 cm^{-1} [16], monoclinic polymorph of $[ReBr_3(NO)(OPPh_3)_2]$ – 1122 and 1159 cm^{-1} [19] and $[ReCl_3(NO)(PPh_3)(OPPh_3)]$ – 1120 cm^{-1} [15].

2 is paramagnetic with an effective magnetic moment of μ_{eff} = 4.20 B.M. corresponding to three unpaired electrons.

The positions and molar absorption coefficients of electronic bands for **1–4** complexes and the electronic transitions assigned to the bands are shown in Table 3. The interpretation of absorption bands gathered in Table 3 is based on earlier papers [40–43].

Re(I) and Re(III) ions, having similar symmetry and nearly identical coordination sphere, showing absorption bands corresponding to the same electron transitions, except for charge transfer from Re(I) to π*NO and π^{b}Re–Br to d orbitals of Re(III) ion. The $b_2 \rightarrow \pi^*$NO transition is confirmed by Table 2 data, because the Re–N(O) bond length (1.68 Å) is significantly shorter than the Re–N_{py} distance (2.132 Å). Lower part of $e \rightarrow \pi^*$NO transition in band at 18750 cm^{-1} (as in the case of band at 24690 cm^{-1}) is connected with symmetry of e and b_2 orbitals towards NO ligand, placed in xy plane. Higher intensity of 24690 cm^{-1} band and the bands at 18790 and 22920 cm^{-1} indicates higher π-acceptor ability of NO as py. However, two transitions connected with $d_{Re} \rightarrow \pi^*_{py}$ charge transfer confirm longer $d_{N=C}$ = 1.36 Å in Re(I) and Re(III) complexes, in comparison with $d_{N=C}$ = 1.33 Å in free pyridine. Transitions of $d_{Re} \rightarrow \pi^*_{py}$ type in Re(I) and W(0) complexes with pyridine were discussed in earlier works [40–43].

The magnetic moment of **2** and its pseudo-octahedral symmetry are confirmed by absorption bands, both d→d and charge transfer ones. Low intensity of the band at 20780 cm^{-1} indicates an intercombination character of the quartet-doublet electron transition, related with spin-orbital coupling. Considering C_{4v} symmetry of complex **3**, the band at 26330 cm^{-1} has a low intensity, and the one at 38460 cm^{-1}, as symmetrically allowed, is significantly more intensive.

The monoclinic and orthorhombic polymorphs, dissolved in dichloromethane, give identical UV-VIS spectra so the electronic structure of the both polymorphs is the same. The electronic structure of monoclinic polymorph of *mer-cis*-$[ReBr_3(NO)(OPPh_3)_2]$ has been discussed in detail in [19].

Table 3. Band positions, molar absorption coefficients and assignments for **1**–**4** complexes.

$[ReBr_3(py)_3]_{0.42}[ReBr_2(NO)(py)_3]_{0.58}$ (**1**)				*trans*-$[ReBr_4(OPPh_3)_2]$ (**2**)			$[ReBr(NO)(dppe)_2]Br$ (**3**)			*mer-cis*-$[ReBr_3(NO)(OPPh_3)_2]$ (**4**)		
Band Position $[cm^{-1}]$	ε	Assignment		Band Position $[cm^{-1}]$	ε	Assignment	Band Position $[cm^{-1}]$	ε	Assignment	Band Position $[cm^{-1}]$	ε	Assignment
		$[ReBr_2(NO)(py)_3]$	$[ReBr_3(py)_3]$									
18750	5950	$e \rightarrow \pi^{*}_{py}$ $e \rightarrow \pi^{*}_{NO}$	$e \rightarrow \pi^{*}_{py}$ $b_2 \rightarrow e$	20780	87	${}^4A_{2g} \rightarrow {}^2T_{2g}$	26330	230	$b_2 \rightarrow \pi^{*}_{NO}$	14510	40	$d_{xy} \rightarrow d_{xz}$
22920	5930	$b_2 \rightarrow \pi^{*}_{py}$ $e \rightarrow b_1$	$b_2 \rightarrow \pi^{*}_{py}$ $e \rightarrow b_1$	23600	1410	${}^4A_{2g} \rightarrow {}^4T_{2g}$	27030	260	$e \rightarrow b_2$	15460	65	$d_{xy} \rightarrow d_{yz}$
24690	7565	$b_2 \rightarrow \pi^{*}_{NO}$ $b_2 \rightarrow b_1$	$b_2 \rightarrow b_1$	25600	4110	${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ $\pi^{0}_{O=P} \rightarrow b_{2g}$	38460	46510	$e \rightarrow \pi^{*}_{NO}$ $e \rightarrow a_1$	23260	1690	$\pi^{0}_{O=P} \rightarrow d_{xy}$
38820	10950	$\pi \rightarrow \pi^{*}_{py}$	$\pi \rightarrow \pi^{*}_{py}$ $\pi^{b}_{Re\text{-}Br} \rightarrow d_{Re}$	30150	6670	${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ $\pi^{b}_{Re\text{-}Br} \rightarrow b_{2g}$	42050	20340	$\pi^{b}_{C_6H_5} \rightarrow 3dp$	25170	4660	$d_{xy} \rightarrow \pi^{*}_{NO}$
				37735	12830	$\pi^{b}_{Re\text{-}Br} \rightarrow e_g$ $\pi^{0}_{O=P} \rightarrow e_g$				31150	1910	$d_{xy} \rightarrow d_{x^2-y^2}$
				43290	17780	$\pi^{b}_{C_6H_5} \rightarrow 3dp$				36490	6860	$\pi^{b}_{Re\text{-}Br} \rightarrow d_{xz}$
										37310	7625	$\pi^{b}_{Re\text{-}Br} \rightarrow d_{yz}$
										38170	7030	$\pi^{0}_{O=P} \rightarrow d_{xz}$
										42220	11840	$\pi^{b}_{C_6H_5} \rightarrow 3dp$

ε = molar absorption coefficient $[dm^3 \cdot mol^{-1} \cdot cm^{-1}]$.

CONCLUSIONS

Refluxing *mer-cis*-[Re(NO)$Br_3(OPPh_3)_2$] with 2,2′-bipyridine or 1,10-phenanthroline in chloroform leads only to conversion of starting monoclinic form of *mer-cis*-[Re(NO)$Br_3(OPPh_3)_2$] into orthorhombic polymorph – bipy and phen do not replace phosphine ligands. The *mer-cis*-[Re(NO)$Br_3(OPPh_3)_2$] complex reacts with bis(diphenylphosphine)ethane to yield two products *trans*-[$ReBr_4(OPPh_3)_2$] and [ReBr(NO)$(dppe)_2$]Br, whereas the reaction of *mer-cis*-[$ReBr_3(NO)(OPPh_3)_2$] with pyridine leads to $[ReBr_3(py)_3]_{0.42}[ReBr_2(NO)(py)_3]_{0.58}$.

Supplementary data. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the depositions numbers: 198110 ($[ReBr_3(py)_3]_{0.42}[ReBr_2(NO)(py)_3]_{0.58}$), 198111 (*trans*-[$ReBr_4(OPPh_3)_2$]), 198112 (orthorhombic polymorph of *mer-cis*-[$ReBr_3(NO)(OPPh_3)_2$]).

REFERENCES

1. Jurisson S.S. and Lydon J.D., *Chem. Rev.*, **99**, 2205 (1999).
2. Liu S. and Edwards D.S., *Chem. Rev.*, **99**, 2235 (1999).
3. Volkert W.A. and Hoffmann T.J., *Chem. Rev.*, **99**, 2269 (1999).
4. Volkert W., Goeckeler W.F., Ehrhardt G.J. and Ketring A.R., *J. Nucl. Med*, **32**, 174 (1991).
5. Deutsch E.A., Libson K., Vanderheyden J.L., Technetium and Rhenium in Chemistry and Nuclear Medicine 3, Eds.: M. Nicolini, G. Bandoli and U. Mazzi, Raven Press, NY, 1990, p. 13–22.
6. Palmer R.M.J., Ferrige A.G. and Moncada S., *Nature*, **327**, 524 (1987).
7. Moncada S., Palmer R.M.J. and Higgs E.A., *Pharmacol. Rev.* **43**, 109 (1991).
8. Feldman P.L., Griffith O.W. and Stuehr D.J., *Chem. Eng. News*, **71**, 26 (1993).
9. Feeelish M. and Stamler J.S., Eds. Methods in Nitric Oxide Research; J. Wiley and Sons; Chichester, England, 1996, and references therein.
10. Dzięgielewski J.O., Filipek K. and Machura B., *Polyhedron*, **14**, 555 (1995).
11. Dzięgielewski J.O., Machura B. and Kupka T., Spectroscopy of Biological Molecules, Eds.: J.C. Merlin, S. Turrell, J.P. Huvenne, Kluver Academic Publishers, Dordrecht 1995, p. 589.
12. Dzięgielewski J.O., Machura B. and Marek J., *Polyhedron*, **15**, 3713 (1996).
13. Dzięgielewski J.O., Machura B. and Bartczak T.J., *Polyhedron*, **15,** 2813 (1996).
14. Bartczak T.J., Czurak W., Dzięgielewski J.O. and Machura B., *Polish J. Chem.*, **72**, 633 (1998).
15. Dzięgielewski J.O., Machura B., Kupka T., Bartczak T.J. and Czurak W., *Polish J. Chem.*, **72**, 1009 (1998).
16. Dzięgielewski J.O., Machura B., Bartczak T.J., Czurak W., Kusz J. and Warczewski J., *J. Coord. Chem.*, **48**, 125 (1999).
17. Bartczak T.J., Czurak W., Dzięgielewski J.O., Machura B., Jankowska A., Kusz J. and Warczewski J., *Polyhedron*, **18**, 2313 (1999).
18. Bartczak T.J., Czurak W., Dzięgielewski J.O., Machura B., Kusz J. and Warczewski J., *Polish J. Chem.*, **74**, 265 (2000).
19. Bartczak T.J., Czurak W., Dzięgielewski J.O., Machura B., Jankowska A., Kusz J. and Warczewski J., *J. Coord. Chem.*, **52**, 361 (2001).
20. Machura B., Dzięgielewski J.O., Michalik S., Bartczak T.J., Kruszynski R. and Kusz J., *Polyhedron*, **21**, 2617 (2002).
21. Sheldrick G.M., SHELXL93. Program for the Solution and Refinement of Crystal Structures. University of Göttingen, Germany, 1993.
22. Sheldrick G.M., SHELXL97. Program for the Solution and Refinement of Crystal Structures. University of Göttingen, Germany, 1997.
23. Sheldrick G.M., SHELXTL: release 4.1 for Siemens Crystallographic Research Systems, 1990.
24. Ciani G., Giusto D., Manassero M. and Sansoni M., *J. Chem. Soc., Dalton Trans.*, 2156 (1975).

25. Adams R.W., Chatt J., Hoope N.E. and Leigh G.J., *J Chem. Soc., Dalton Trans.,* 1075 (1974).
26. Ciani G., Giusto D., Manassero M. and Sansoni M., *J. Chem. Soc*., *Dalton Trans*., 2156 (1975).
27. Batista A.A., Pereira C., Queiroz S.L. de Oliveira L.A.A., de A. Santos R.H. and de P. Gambardella M.T., *Polyhedron*, **16**, 927 (1997).
28. Zampieri R.C.L., Poelhsitz G., Batista A.A, Nascimento O.R., Ellena J. and Castellano E.E., *J. Inorg. Biochem.*, **92**, 82 (2002).
29. Tisato F., Refosco F., Dolmella A. and Bandoli G., *Polyhedron*, **17**, 3947 (1998).
30. Brewer J.C., Thorp H.H., Slagle K.M., Brudvig G.W. and Gray H.B., *J. Am. Chem. Soc*., **113**, 3171 (1991).
31. Lock C.J.L. and Turner G., *Acta Cryst.*, **B34**, 923 (1978).
32. Schmid S. and Strähle J., *Z. Kristallogr.*, **198**, 49 (1992).
33. Harben S.M., Smith P.D., Beddoes R.L., Helliwell M., Collinson D. and Garner C.D., *Acta. Cryst*., **C54**, 941 (1998).
34. Rossi R., Marchi A., Marvelli L., Magon L., Peruzzini M., Casellato U. and Graziani R., *Inorg. Chim. Acta*, **204**, 63 (1993).
35. Haymore B.L. and Ibers I.A., *Inorg. Chem*., **14**, 3060 (1975).
36. Ciani G., Giusto D., Manassero M. and Sansoni M., *Gazz. Chim. Ital.*, **107**, 429 (1977).
37. Wang Y., da Silva J.J.R.F., Pombeiro A.J.L., Pellinghelli M.A. and Tiripicchio A., *J. Organomet. Chem.*, **430**, C56 (1992).
38. Wang Y., da Silva J.J.R.F., Pombeiro A.J.L., Pellinghelli M.A. and Tiripicchio A., *J. Organomet. Chem.*, **476**, C9 (1994).
39. Hübener R. and Abram U., *Inorg. Chim. Acta*, **211**, I21 (1993).
40. Wrighton M.S. and Morse D.L., *J. Am. Chem. Soc.*, **96**, 337 (1974).
41. Giordano P.J. and Wrighton M.S., *J. Am. Chem. Soc.*, **101**, 2888 (1979).
42. Wrighton M.S., *Chem. Rev.*, **74**, 401 (1974).
43. Abrahmson H.B. and Wrighton M.S., *Inorg. Chem.*, **17**, 3385 (1978).