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Polyhedron 22 (2003) 2869–2875

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# The synthesis, spectroscopic characterisation, crystal and molecular structure of two novel bent oxo-bridged dimers of rhenium(V) with μ-benzotriazolate ligands

B. Machura[a], Jan O. Dziegielewski[a,*], R. Kruszynski[b,1], T.J. Bartczak[b]

[a] *Department of Inorganic and Radiation Chemistry, Institute of Chemistry, University of Silesia, 9th Szkolna Street, 40-006 Katowice, Poland*
[b] *X-ray Crystallography Laboratory, Institute of General and Ecological Chemistry, Technical University of Lódz, 116 Zeromski Street, 90-924 Lódz, Poland*

Received 4 March 2003; accepted 12 May 2003

## Abstract

Refluxing of [ReOX$_3$(PPh$_3$)$_2$] (X = Cl, Br) complexes with 4 equiv. of benzotriazole in a mixture of ethanol + acetone affords symmetrically substituted dinuclear rhenium [{Re(O)X(PPh$_3$)}$_2$(μ-O)(μ-C$_6$H$_4$N$_3$)$_2$] complexes (**1** and **2**, respectively). Benzotriazole is capable of coordinating in the neutral and anionic mode to give mono- and polynuclear transition metal complexes. The neutral benzotriazole can be coordinated in a monodentate fashion through N(3) and in a bridging way through N(2)–N(3) atoms, whereas the benzotriazolate anion is coordinated in N(1) monodentate, N(1)–N(2) and N(1)–N(3) bridging bidentate or N(1)–N(2)–N(3) bridging tridentate bonding modes. The rhenium(V) centers of **1** and **2** are linked through two N(1)–N(2) bridging benzotriazolato anions and an oxo group. Due to the geometric constraints of the two bridging N-donor ligands the {Re$_2$O$_3$} unit in **1** and **2** is bent.

*Keywords:* Rhenium complexes; Benzotriazole complexes; Oxo-complexes; Crystal structures; Spectroscopic investigation

## 1. Introduction

The coordination chemistry of benzotriazoles has been explored by several groups. One reason for this is the anticorrosion action of benzotriazoles towards certain metals, particularly copper and its alloys [1–3]. This kind of complex is also important from the standpoint of structural studies. Benzotriazole and its derivatives can adopt a variety coordination modes to give mono- and polynuclear transition metal complexes. The neutral benzotriazole (Hbta) is mainly coordinated in a monodentate fashion through N(3), but has also been found to act as an N(2)–N(3) bridging ligand [4–10]. The benzotriazolate anion (bta) is coordinated in N(1) monodentate, N(1)–N(2) and N(1)–N(3) bridging bidentate or N(1)–N(2)–N(3) bridging tridentate bonding modes [5,8,10–22]. Special attention has been recently devoted to symmetrical/unsymmetrical benzotriazolate-bridged homo- and heterodinuclear systems [8,11,14,16,23–26]. However, despite the extensive uses of benzotriazoles in organometallic chemistry, only a few compounds have been structurally characterized by X-ray diffraction. Here, we present the synthesis, spectroscopic characterization, crystal and molecular structure of two dirhenium complexes [{Re(O)Br(PPh$_3$)}$_2$(μ-O)(μ-C$_6$H$_4$N$_3$)$_2$] (**1**) and [{Re(O)Cl(PPh$_3$)}$_2$(μ-O)(μ-C$_6$H$_4$N$_3$)$_2$] (**2**). To our knowledge they

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* Corresponding author. Tel.: +48-32-258-2441; fax: +48-32-259-9978.

*E-mail addresses:* jod@tc3.ich.us.edu.pl (J.O. Dziegielewski), tadekbar@ck-sg.p.lodz.pl (T.J. Bartczak).

[1] A holder of the Foundation for Polish Science (FNP) scholarship.

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doi:10.1016/S0277-5387(03)00400-5

are the first examples of Re(V) complexes with benzotriazolate ligands.

## 2. Experimental

### 2.1. General procedure

The reactions and all manipulations were carried out open to the atmosphere. All solvents were of reagent grade and were used as received. Ammonium perrhenate, triphenylphosphine and benzotriazole were purchased from Aldrich and used as received. [$ReOX_3(PPh_3)_2$] (X = Cl or Br) complexes were prepared according to the literature methods [27].

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. Elemental analyses (C H N) were performed on a Perkin–Elmer CHN-2400 analyzer.

### 2.2. Preparation of [{$Re(O)Br(PPh_3)$}$_2$($\mu$-O)($\mu$-$C_6H_4N_3$)$_2$] (**1**)

[$ReOBr_3(PPh_3)_2$] (0.97 g, 1 mmol) was added to a solution of Hbta (0.5 g, 4 mmol) in ethanol (50 ml) and acetone (50 ml) and the reaction mixture was refluxed overnight. The green crystals of **1** were obtained by slow evaporation of the reaction solution at room temperature. Yield 55%.

IR of **1** (KBr, $cm^{-1}$) 3055 (w), 1612(m, br), 1574 (w), 1482 (m), 1435 (s), 1391 (w), 1291 (w), 1269 (w), 1238 (m), 1165 (m), 1155 (m), 1097 (s), 969 (s), 919 (w), 797 (m), 740 (s), 711 (m), 692 (vs), 629 (vs), 615 (sh), 561 (w), 525 (vs), 509 (m), 495 (s), 474 (m).

$^1$H NMR ($CDCl_3$, ppm): 7.11–7.62 (m, CH of $PPh_3$ and Hbta). $^{31}$P NMR: −4.37 ppm.

*Anal*. Calc. for $C_{48}H_{38}N_6Br_2O_3P_2Re_2$ (**1**): C, 42.99; H, 2.86; N, 6.27. Found: C, 43.10; H, 2.95; N, 6.17%.

### 2.3. Preparation of [{$Re(O)Cl(PPh_3)$}$_2$($\mu$-O)($\mu$-$C_6H_4N_3$)$_2$] (**2**)

A procedure similar to that for **1** was used with [$ReOCl_3(PPh_3)_2$] (0.83g, 1mmol) and Hbta (0.5g, 4mmol). A green crystalline precipitate of **2** was collected in 60% yield.

IR of **2** (KBr, $cm^{-1}$) 3057 (w), 1614(m, br), 1576 (w), 1483 (m), 1435 (s), 1390 (w), 1291 (w), 1270 (w), 1239 (m), 1164 (m), 1145 (m), 1098 (s), 969 (s), 921 (w), 798 (m), 740 (s), 711 (m), 692 (vs), 636 (vs), 615 (sh), 563 (w), 525 (vs), 508 (m), 496 (s), 476 (m).

*Anal*. Calc. for $C_{48}H_{38}N_6Cl_2O_3P_2Re_2$ (**2**): C, 46.04; H, 3.06; N, 6.71. Found: C, 46.17; H, 2.99; N, 6.67%.

### 2.4. Crystal structures determination and refinement

The crystals of **1** and **2** suitable for X-ray structure determination were obtained by slow evaporation from a mixture of acetone and ethanol. The X-ray intensity data were collected on KM-4-CCD automatic diffractometer equipped with CCD detector with $\omega$ scan mode, 40 and 24 s exposure time were used for **1** and **2**, respectively, and a half of the Ewald sphere was collected. The unit cell parameters were determined from least-squares refinement of the setting angles of 2999 and 2410 of the strongest reflections for **1** and **2**, respectively. Details concerning crystal data and refine-

Table 1
Crystal data and structure refinement for **1** and **2**

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{48}H_{38}Br_2N_6O_3$-$P_2Re_2$ | $C_{48}H_{38}Cl_2N_6O_3$-$P_2Re_2$ |
| Formula weight | 1341.00 | 1252.08 |
| Temperature (K) | 291(2) | 291(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | triclinic | triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions | | |
| $a$ (Å) | 10.7246(6) | 10.6851(7) |
| $b$ (Å) | 11.9419(7) | 11.9689(7) |
| $c$ (Å) | 20.2547(11) | 19.9988(12) |
| $\alpha$ (°) | 100.725(4) | 101.492(7) |
| $\beta$ (°) | 100.930(4) | 101.183(6) |
| $\gamma$ (°) | 105.787(5) | 104.087(7) |
| $V$ (Å$^3$) | 2372.1(2) | 2350.6(3) |
| $Z$ | 2 | 2 |
| $D_{calc}$ (Mg $m^{-3}$) | 1.877 | 1.769 |
| Absorption coefficient ($mm^{-1}$) | 6.898 | 5.375 |
| $F$(000) | 1284 | 1212 |
| Crystal size (mm) | 0.31 × 0.10 × 0.01 | 0.33 × 0.14 × 0.04 |
| $\theta$ Range for data collection (°) | 3.29–25.10 | 3.27–25.10 |
| Index ranges | $-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $0 \leq l \leq 24$ | $-12 \leq h \leq 12$, $-14 \leq k \leq 13$, $0 \leq l \leq 23$ |
| Reflections collected | 8442 | 8357 |
| Independent reflections | 8442 ($R_{int} = 0.0000$) | 8357 ($R_{int} = 0.0000$) |
| Completeness (%) to 2$\theta$ | 99.8 | 99.7 |
| Max. and min. transmission | 0.9096 and 0.2275 | 0.8057 and 0.2677 |
| Data/restraints/parameters | 8442/0/568 | 8357/0/568 |
| Goodness-of-fit on $F^2$ | 1.086 | 1.113 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0481$, $wR_2 = 0.0918$ | $R_1 = 0.0809$, $wR_2 = 0.2112$ |
| $R$ indices (all data) | $R_1 = 0.0681$, $wR_2 = 0.1028$ | $R_1 = 0.0990$, $wR_2 = 0.2318$ |
| Largest difference peak and hole (e Å$^{-3}$) | 2.272 and −0.861 | 4.281 and −2.449 |

ment are given in Table 1. Lorentz, polarization and numerical absorption corrections [28] 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 technique. All hydrogen atoms were founded on difference Fourier synthesis and refined as ‘riding’ on their parent carbon atoms with geometry idealisation after each cycle and assigned isotropic temperature factors equal to 1.2 times the value of the equivalent temperature factor of the parent carbon atom. SHELXS-97 [29], SHELXL-97 [30] and SHELXTL [31] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs.

The structure of **2** is worse mainly because of the poor quality of the crystal, which was very fragile. Mounting larger crystals on the diffractometer lead to breaking off of the crystal during measurement and all attempts to cool crystals to liquid nitrogen temperature also cause the breaking of the crystals. Because compound **2** is isostructural with **1**, reporting of its structure is reasonable.

## 3. Results and discussion

Refluxing of $[ReOX_3(PPh_3)_2]$ complexes (X = Cl and Br) with four equivalents of Hbta in ethanol+acetone without precautions to exclude air and special drying of materials leads to the isolation of the symmetrically substituted dinuclear rhenium complexes $[\{Re(O)Br(PPh_3)\}_2(\mu\text{-}O)(\mu\text{-}C_6H_4N_3)_2]$ (**1**) and $[\{Re(O)Cl(PPh_3)\}_2(\mu\text{-}O)(\mu\text{-}C_6H_4N_3)_2]$ (**2**), respectively. Due to such conditions of synthesis some water is present in the reaction system. The formation of $[\{Re(O)X(PPh_3)\}_2(\mu\text{-}O)(\mu\text{-}C_6H_4N_3)_2]$ from $[ReOX_3(PPh_3)_2]$ doubtlessly involves water and the formation of intermediate hydroxo-species, similarly to the reactions of $[ReOCl_3(PPh_3)_2]$ with pyridine and Schiff bases $LH_2$, which gives $[Re_2O_3Cl_4(py)_4]$ [48] and $[Re_2O_3L_2]$ [49], respectively. However, no intermediates could be isolated in the present case. Nevertheless, the synthesis of $[\{Re(O)X(PPh_3)\}_2(\mu\text{-}O)(\mu\text{-}C_6H_4N_3)_2]$ can be summarized by the following reaction equation:

$$\begin{aligned}&2[ReOX_3(PPh_3)_2] + 2C_6H_5N_3 + H_2O + O_2\\&\quad\rightarrow[\{Re(O)X(PPh_3)\}_2(\mu\text{-}O)(\mu\text{-}C_6H_4N_3)_2] + 4HX\\&\quad + 2OPPh_3\end{aligned}$$

The molar ratio of $[ReOX_3(PPh_3)_2]$ and Hbta, equal to 1:4, ensures the maximum yield of **1** and **2**.

Perspective drawings of **1** and **2** molecules are given in Figs. 1 and 2, respectively. Both compounds crystallise in the space group $P\bar{1}$ of the triclinic system and all atoms occupied general positions. The structures reveal the presence of two rhenium(V) centers linked through two bridging bta anions and an oxo group. Each rhenium atom is in a pseudooctahedral environment of two benzotriazole N donors, a halide ion, the phosphorous atom of triphenylphosphine, a terminal and bridging oxo ligand. The considerable distortions from an ideal octahedron in **1** and **2** (*cis*-ligands vary between 78.2(2)° and 98.79(4)° and the *trans*-angles are between 162.4(3)° and 174.12(19)° in **1**; 78.6(4)°–100.0(5)° and 163.2(4)°–173.9(3)° in **2**) result from both the electronic repulsion of the short Re=O bond and steric interactions of bridging N-donor ligands. In compounds bridged only by a single μ-oxo group $[\{ReOCl_2py_2\}_2(\mu\text{-}O)]$ [32], $[\{ReOCl_2(3,5\text{-}Me_2pzH)_2\}_2(\mu\text{-}O)]$ [33] and $[(ReOCl_2(CNC_6H_3\text{-}(CH_3)_2\text{-}2,6)_2\}_2(\mu\text{-}O)]$ [34] the O=Re–O–Re=O unit is essentially linear. The $\{Re_2O_3\}$ units in **1** and **2** are bent with a Re–O–Re angle equal to 126.0(3)° and 125.2(4)°, respectively. It is most probably due to the geometric constraints of the two bridging N-donor ligands. The introduction of additional bridging ligands to μ-oxo complexes leads to the decrease of the Re–O–Re angle also in $[Re_2O_5I_2(PPh_3)_2]$ 164.3(4)° [35], $[Re_2O_5I_2(PPh_3)(OPPh_3)]$ 153.5(5)° [35] and in $[Re_2O_3Cl_2(PPh_3)_2(C_3H_2N_3O_2)_2]$ 124.7(6)° [36].

The most important bond lengths and angles for **1** and **2** are reported in Table 2. The $Re{=}O_t$ bond distances are 1.671(6) and 1.674(6) Å for **1** and 1.688(10) and 1.691(10) for **2**. The mean rhenium–oxygen bond lengths for the $Re–O_b–Re$ unit in **1** and **2** are 1.931 and 1.934 Å, respectively. These values are in good agreement with those found for oxygen-bridged complexes of Re(V) containing the $Re_2O_3$ unit, 1.6–1.8 Å for $Re{=}O_t$ and 1.9–2.0 Å for $Re–O_b$ [32–36]. The Re–N bond lengths (2.114–2.161 Å) in **1** and **2** are similar to those of $[\{ReOCl_2py_2\}_2(\mu\text{-}O)]$ and $[\{ReOCl_2(3,5\text{-}Me_2pzH)_2\}_2(\mu\text{-}O)]$ [32,33]. The Re–Cl, Re–Br, Re–P and the bond distances and angles in the phenyl and benzotriazole rings are also in good agreement with expected values. The bond valences were computed as $v_{ij} = \exp[(R_{ij} - d_{ij})/B]$ [37–39], where $R_{ij}$ is the bond-valence parameter (in the formal sense $R_{ij}$ is the single-bond length between $i$ and $j$ atoms) [40]. The $R_{Re-O}$, $R_{Re-N}$, $R_{Re-P}$, $R_{Re-Br}$, $R_{Re-Cl}$ were taken as 1.97, 2.06, 2.46, 2.45 and 2.23 [37], respectively, and the value of $B$ was taken as 0.37 [38]. The computed bond valences of the rhenium $v_{Re-j}$ are gathered in Table 3. All Re–P bonds can be considered as single bonds, the Re=O bonds are stronger than double bonds (slightly in compound **2**), Re–N and Re–X bonds are weaker than single bonds. The chlorine atoms are more weakly bonded to the Re than bromide atoms. The total valence of Re(1) and Re(2) is 6.98 and 6.87 v.u. (valence units), respectively, for compound **1** and 6.63 and 6.55 v.u., respectively, for compound **2**. This means that rhenium substituents in compound **2** are more weakly bonded

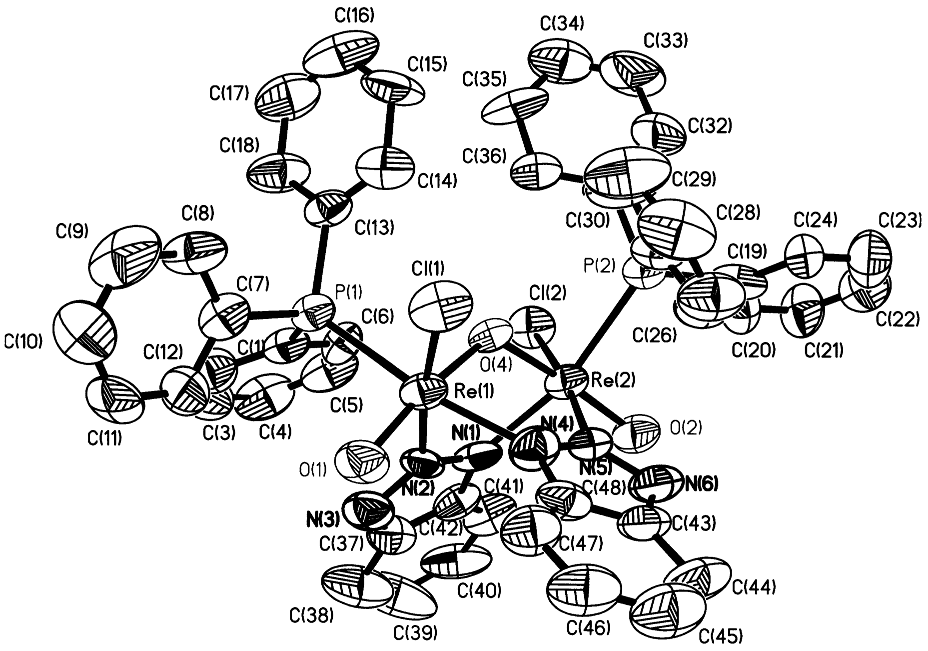

Fig. 1. The molecular structure of **1**. The thermal ellipsoids are drawn at 50% probability level.

than in compound **1**. In addition the substituents are more strongly bonded to the Re(1) atom than Re(2) in both compounds. The molecules of bta are nearly planar with the deviations of the atoms from the least-squares plane through them being less than 0.02 Å

As expected, the hydrogen-bonding scheme in both structures is the same. The molecules are assembled to dimers via C(10)–H(10)···O(1# $1-x$, $1-y$, $-z$) weak intermolecular hydrogen bonds [41] (Table 4). In addition the structures are stabilized by two weak intramolecular hydrogen bonds [42,43] whose geometries are given in Table 4. Fig. 3 presents a part of the molecular packing of compound **1** showing intermolecular hydrogen bonds creating a dimer structure and intramolecular hydrogen bonds. Hydrogen bonds are indicated by dashed lines.

The $^1$H NMR spectrum of **1** exhibits only a multiplet in the phenyl region $\delta = 7.11–7.62$ ppm. The absence of a signal in the region attributable to HN confirms the coordination of benzotriazole in the anionic form. The

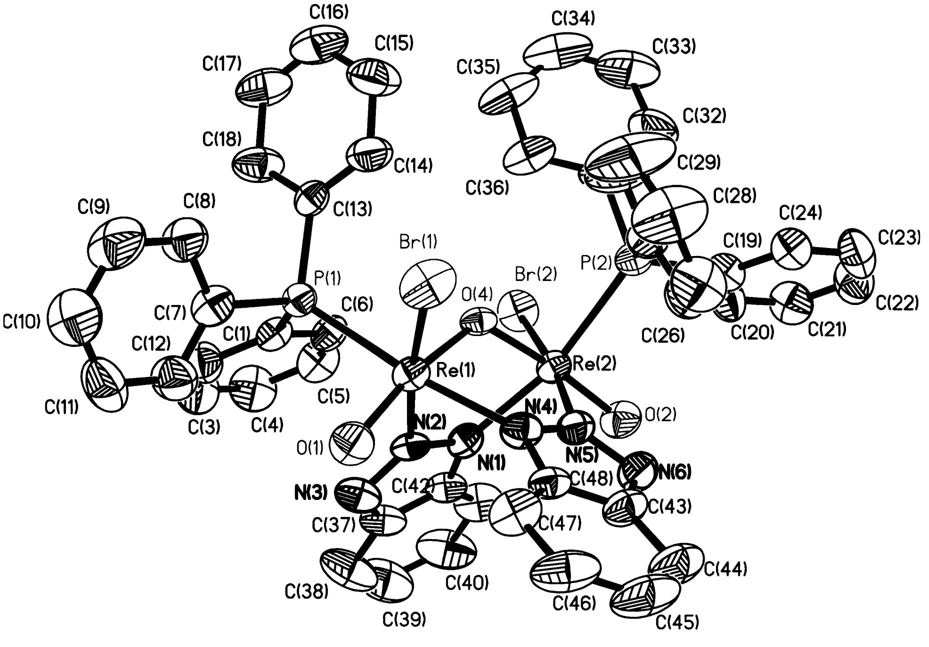

Fig. 2. The molecular structure of **2**.

Table 2
The selected bond lengths (Å) and bond angles (°) for **1** and **2**

| Bond lengths | 1 | 2 | Bond angles | 1 | 2 |
|---|---|---|---|---|---|
| Re(1)–O(1) | 1.671(6) | 1.688(10) | O(1)–Re(1)–O(4) | 162.7(3) | 163.4(5) |
| Re(1)–O(4) | 1.924(5) | 1.916(9) | O(1)–Re(1)–N(4) | 96.3(3) | 97.1(5) |
| Re(1)–N(2) | 2.161(7) | 2.162(12) | O(4)–Re(1)–N(4) | 79.7(2) | 80.4(4) |
| Re(1)–N(4) | 2.136(7) | 2.125(13) | O(1)–Re(1)–N(2) | 84.8(3) | 84.9(5) |
| Re(1)–Br(1) | 2.4964(11) | | O(4)–Re(1)–N(2) | 78.2(2) | 78.6(4) |
| Re(1)–Cl(1) | | 2.348(4) | | | |
| Re(1)–P(1) | 2.465(2) | 2.460(4) | N(4)–Re(1)–N(2) | 85.1(3) | 85.2(5) |
| Re(2)–O(2) | 1.674(6) | 1.691(10) | O(1)–Re(1)–P(1) | 92.2(2) | 92.9(4) |
| Re(2)–O(4) | 1.938(5) | 1.951(8) | O(4)–Re(1)–P(1) | 91.24(16) | 89.3(3) |
| Re(2)–N(1) | 2.114(7) | 2.116(13) | N(4)–Re(1)–P(1) | 170.92(19) | 169.7(4) |
| Re(2)–N(5) | 2.136(7) | 2.158(13) | N(2)–Re(1)–P(1) | 92.57(18) | 92.9(3) |
| Re(2)–Br(2) | 2.4885(10) | | O(1)–Re(1)–Br(1) | 97.9(2) | |
| Re(2)–Cl(2) | | 2.343(4) | O(1)–Re(1)–Cl(1) | | 98.3(4) |
| Re(2)–P(2) | 2.464(2) | 2.458(4) | O(4)–Re(1)–Br(1) | 98.79(15) | |
| | | | O(4)–Re(1)–Cl(1) | | 98.1(3) |
| N(1)–N(2) | 1.342(9) | 1.324(16) | N(4)–Re(1)–Br(1) | 89.40(19) | |
| | | | N(4)–Re(1)–Cl(1) | | 89.2(4) |
| N(2)–N(3) | 1.322(10) | 1.316(17) | N(2)–Re(1)–Br(1) | 174.12(19) | |
| | | | N(2)–Re(1)–Cl(1) | | 173.9(3) |
| N(1)–C(42) | 1.370(11) | 1.380(18) | P(1)–Re(1)–Br(1) | 92.53(6) | |
| | | | P(1)–Re(1)–Cl(1) | | 92.13(14) |
| N(3)–C(37) | 1.352(12) | 1.38(2) | O(2)–Re(2)–O(4) | 163.0(3) | 163.2(4) |
| N(4)–N(5) | 1.338(10) | 1.335(18) | O(2)–Re(2)–N(1) | 98.6(3) | 100.0(5) |
| N(5)–N(6) | 1.320(9) | 1.318(17) | O(4)–Re(2)–N(1) | 79.3(2) | 79.3(4) |
| N(4)–C(48) | 1.367(10) | 1.365(18) | O(2)–Re(2)–N(5) | 83.9(3) | 84.1(5) |
| N(6)–C(43) | 1.370(12) | 1.33(2) | O(4)–Re(2)–N(5) | 79.1(2) | 79.1(4) |
| | | | N(1)–Re(2)–N(5) | 85.4(3) | 85.8(4) |
| | | | O(2)–Re(2)–P(2) | 96.3(2) | 96.3(4) |
| | | | O(4)–Re(2)–P(2) | 86.19(16) | 85.0(3) |
| | | | N(1)–Re(2)–P(2) | 165.10(19) | 163.7(3) |
| | | | N(5)–Re(2)–P(2) | 95.4(2) | 95.5(3) |
| | | | O(2)–Re(2)–Br(2) | 98.2(2) | |
| | | | O(2)–Re(2)–Cl(2) | | 98.1(4) |
| | | | O(4)–Re(2)–Br(2) | 98.57(14) | |
| | | | O(4)–Re(2)–Cl(2) | | 98.7(3) |
| | | | N(5)–Re(2)–Br(2) | 173.47(19) | |
| | | | N(5)–Re(2)–Cl(2) | | 173.6(3) |
| | | | Re(1)–O(4)–Re(2) | 126.0(3) | 125.2(4) |

singlet at −4.37 ppm in the $^{31}$P NMR spectrum of **1** confirms the presence of coordinated triphenylphosphine.

The coordination of benzotriazole in the anionic bidentate form is also confirmed by the absence of a strong band in the range assignable to N–H vibrations in the spectra of **1** and **2**. The band assignable to a symmetric Re=O stretch exists at 969 cm$^{-1}$ for **1** and **2**. The antisymmetric $\nu$(Re–O–Re) stretching mode appears at 629 cm$^{-1}$ for **1** and at 636 for **2**. The band corresponding to $\nu$(Re–O–Re) in the IR spectrum of $[Re_2OCl_{10}]^{4-}$ exhibits at 850 cm$^{-1}$ [44]. However, the electron-withdrawing effect of the terminal Re=O group in the complexes with the O=Re–O–Re=O framework results in a relative weakening of the bridging Re–O bonds and consequently a reduction in the frequency of $\nu$(Re–O–Re): at 680 and 670 cm$^{-1}$ in *cis*,*cis*-[{ReOCl$_2$py$_2$}$_2$(μ-O)] [32] and *trans*,*trans*-[{ReOCl$_2$py$_2$}$_2$(μ-O)] [45], respectively.

The bands of C=C, C=N, N=N and N–N stretching modes, characteristic for the benzotriazole ligand are observed in the ranges 1620–1595 and 1295–1145 cm$^{-1}$ [46,47].

Table 3
Rhenium bond valences $v_{Re-j}$ [v.u.] for **1** and **2**

| Bond | 1 | | 2 | |
|---|---|---|---|---|
| | atom Re(1) | atom Re(2) | atom Re(1) | atom Re(2) |
| Re–N | 0.81 | 0.86 | 0.84 | 0.86 |
| Re–N | 0.76 | 0.81 | 0.76 | 0.77 |
| Re=O | 2.39 | 2.22 | 2.14 | 2.13 |
| Re–O | 1.13 | 1.09 | 1.16 | 1.05 |
| Re–P | 0.99 | 0.99 | 1.00 | 1.00 |
| Re–Br | 0.88 | 0.90 | | |
| Re–Cl | | | 0.73 | 0.74 |

Table 4
Hydrogen bonding geometry (Å, °) for **1** and **2**

| Complex | D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | D–H···A (°) |
|---|---|---|---|---|---|
| 1 | C(10)–H(10)···O(1)$^{i}$ | 0.93 | 2.51 | 3.222(13) | 134 |
| | C(14)–H(14)···Br(1) | 0.93 | 2.78 | 3.561(10) | 142.3 |
| | C(26)–H(26)···N(6) | 0.93 | 2.55 | 3.244(12) | 131.5 |
| 2 | C(10)–H(10)···O(1)$^{i}$ | 0.93 | 2.46 | 3.203(18) | 137.4 |
| | C(14)–H(14)···Cl(1) | 0.93 | 2.56 | 3.388(18) | 148.3 |
| | C(26)–H(26)···N(6) | 0.93 | 2.58 | 3.21(2) | 125.4 |

Symmetry code: (i) $1-x$, $1-y$, $-z$.

The complexes **1** and **2** are diamagnetic corresponding to the $(b_2)^2$ configuration.

The positions and molar absorption coefficients of electronic bands for **1** and **2** complexes and the electronic transitions assigned to the bands are shown in Table 5. The absorption bands together with their assignments, shown in Table 5, prove the pseudo-octahedral symmetry of complexes **1** and **2**, characterized by the $(b_2)^2$ electron configuration of Re(V). Electron density transfer from N(1) and N(4) atoms towards $5d_{Re}$ orbitals is confirmed by shorter Re–N(1) and Re–N(4) bonds. The bonds are approximately 0.04

Table 5
Band positions, molar absorption coefficients and assignments for **1** and **2**

| [{Re(O)Br(PPh$_3$)}$_2$(μ-O)(μ-C$_6$H$_4$N$_3$)$_2$] (**1**) | | [{Re(O)Cl(PPh$_3$)}$_2$(μ-O)(μ-C$_6$H$_4$N$_3$)$_2$] (**2**) | | Assignment |
|---|---|---|---|---|
| Band position (cm$^{-1}$) | Molar extinction coefficient (dm$^3$ mol$^{-1}$ cm$^{-1}$) | Band position (cm$^{-1}$) | Molar extinction coefficient (dm$^3$ mol$^{-1}$ cm$^{-1}$) | |
| 15 270 | 310 | 16 080 | 545 | $^1A_1 \rightarrow {}^1T_2$ |
| 24 390 | 890 | 23 810 | 1050 | $^1A_1 \rightarrow {}^1T_1$ |
| 30 170 | 9060 | 29 400 | 12 460 | $\pi^{o}_{N} \rightarrow 5d_{Re}$ |
| 33 330 | 11 780 | 33 000 | 25 000 | $\pi^{o}_{O_b} \rightarrow 5d_{Re}$; $\pi \rightarrow \pi^{*\ Re-Hal}$ |
| 41 740 | 44 200 | 41 840 | 48 800 | $\pi^{b}_{C_6H_5} \rightarrow 3d_P$ |
| 44 450 | 42 750 | 43 850 | 46 600 | $\pi \rightarrow \pi^{*\ benzotriazole}$ |

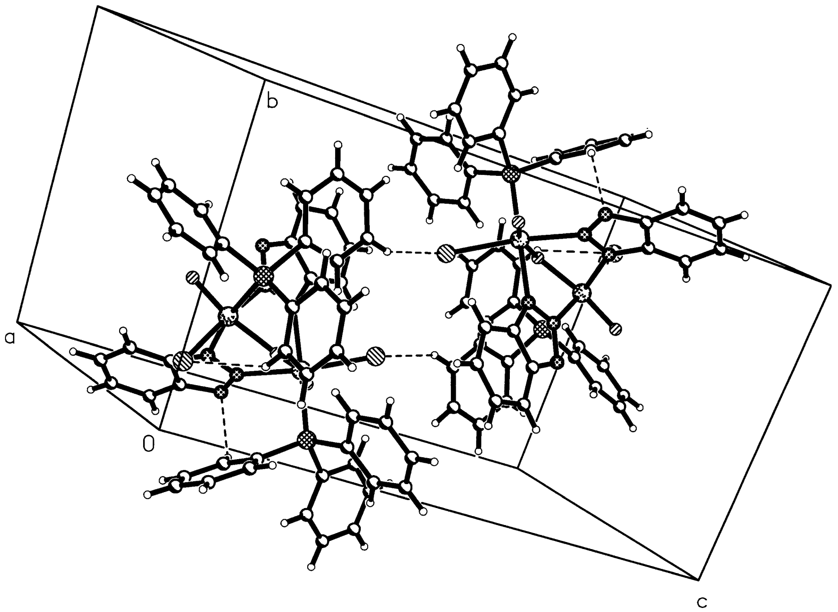

Fig. 3. A part of the molecular packing of compound **1** showing intermolecular hydrogen bonds creating a dimer structure and intramolecular hydrogen bonds. Hydrogen bonds are indicated by dashed lines.

Å shorter than Re–N(2) and Re–N(5) bonds. Larger difference in molar extinction coefficients of the bands at 33 000 $\text{cm}^{-1}$ indicate the complexity of the bands. The bands connected with the $\pi^{o}_{O_b} \rightarrow 5d_{Re}$ transition are overlapped by bands of $\pi \rightarrow \pi^{*\ \text{Re-Hal}}$ transitions, corresponding to charge transfer $\text{Hal}^{-} \rightarrow 5d_{Re}$. Higher donor ability of $\text{Cl}^{-}$ in comparison with $\text{Br}^{-}$ increases significantly the intensity of the combined band. At the same time, it shifts the absorption maximum towards lower energies. This fact proves also comparatively low participation in the combined band of the $\pi^{o}_{O_b} \rightarrow 5d_{Re}$ transition.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 204889 and 204890 for compounds $C_{48}H_{38}Br_2N_6O_3P_2Re_2$ and $C_{48}H_{38}Cl_2N_6O_3P_2Re_2$, respectively. Copies of this information may be obtained free of charge from The Director, 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).

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