

## The Structure of *trans*-Dibromooxo(*N*-phenylsalicylideneaminato)(triphenylphosphine)rhenium(V), Form II (Triclinic), $[\text{ReBr}_2(\text{C}_{13}\text{H}_{10}\text{NO})\text{O}\{\text{P}(\text{C}_6\text{H}_5)_3\}]$

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**Abstract.**  $M_r = 820.5$ , triclinic,  $P\bar{1}$ ,  $a = 8.943$  (3),  $b = 10.701$  (4),  $c = 19.917$  (5) Å,  $\alpha = 120.65$  (3),  $\beta = 83.49$  (3),  $\gamma = 116.83$  (3)°,  $U = 1446$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.88$  Mg m<sup>-3</sup>,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 6.8$  mm<sup>-1</sup>,  $F(000) = 788$ ,  $T = 298$  K,  $R = 0.038$  for 4331 reflections with  $I_o \geq 3\sigma(I_o)$ . The crystal turned out to be a second polymorphic modification of *trans*- $\text{Re}^{\text{V}}\text{OBr}_2(\text{PPh}_3)(\text{Ph-sal})$ . The molecules have slightly different geometries in the two crystals and it is found that they can be more properly considered as two different conformational isomers.

**Introduction.** Two different classes of quasi-octahedral  $\text{Re}^{\text{V}}$  complexes are obtained by reacting *trans*- $\text{ReOX}_3$  ( $\text{PPh}_3$ )<sub>2</sub> ( $X = \text{Cl}$  or  $\text{Br}$ ) with *N*-substituted salicylideneamine\* (*R*-salH), that is  $\text{Re}^{\text{V}}\text{OX}(\text{R-sal})_2$  and  $\text{Re}^{\text{V}}\text{OX}_2(\text{PPh}_3)(\text{R-sal})$  (Mazzi, Roncari, Rossi, Bertolasi, Traverso & Magon, 1980). In the latter class of compounds we have recently reported (Bertolasi, Sacerdoti, Gilli & Mazzi, 1982) the crystal structure of the monoclinic *yellow-brown* product of the reaction of  $\text{Re}^{\text{V}}\text{OBr}_3(\text{PPh}_3)_2$  or  $\text{Re}^{\text{V}}\text{OBr}_2(\text{OEt})(\text{PPh}_3)_2$  with (Ph-salH) in EtOH (Roncari, Mazzi, Rossi, Duatti & Magon, 1981) which turned out to be *trans*- $\text{Re}^{\text{V}}\text{OBr}_2(\text{PPh}_3)(\text{Ph-sal})$  (hereafter indicated as form I). The same authors found that recrystallization from acetone solutions of this product gave *pale green* crystals of a compound having the same elemental analysis and similar but not identical IR spectrum. It was tentatively identified as a polymorphic modification of form I, that is *trans*- $\text{Re}^{\text{V}}\text{OBr}_2(\text{PPh}_3)(\text{Ph-sal})$  form II, which is the subject of the present structure determination.

**Experimental.** Pale green prism,  $0.10 \times 0.11 \times 0.36$  mm, automatic Siemens AED diffractometer, Zr-filtered  $\text{Mo } K\alpha$ , cell parameters from 20 reflections in the range  $12 \leq \theta \leq 15^\circ$ , †  $\omega/2\theta$  scan ( $\theta \leq 26^\circ$ ), 5089 independent reflections, one stable reflection every 50

reflections collected,  $-10 \leq h \leq 10$ ,  $-11 \leq k \leq 11$ ,  $0 \leq l \leq 21$ , 4331 having  $I > 3\sigma(I)$  observed, geometrical absorption correction ( $0.84 < \text{transmission factor} < 1$ ); solution by Patterson and Fourier methods, blocked-matrix (two blocks) least squares on  $F$ , anisotropic for all non-H atoms, calculated H's, 344 parameters refined, scattering factors from *International Tables for X-ray Crystallography* (1974),  $11.5/w = \sigma^2 + 0.000055 |F_o|^2$ , discrepancy factors  $R = 0.038$ ,  $R_w = \sum w^{1/2} |\Delta| / \sum w^{1/2} |F_o| = 0.034$ ,  $S = 1.12$ , max.  $\Delta/\sigma = 0.10$ , final  $\Delta\rho$  excursions  $-0.5$ – $0.6$  e Å<sup>-3</sup> outside the first Re coordination sphere; all calculations done by *SHELX76* (Sheldrick, 1976).

**Discussion.** Final atomic positional and thermal (Hamilton, 1959) parameters for non-hydrogen atoms are given in Table 1.\* A view of the molecule is reported in Fig. 1. Bond distances and angles are given in Table 2.

The crystal consists of monomeric units packed together without contacts significantly shorter than the sum of the van der Waals radii (Bondi, 1964).

The molecular constitution is identical to that of *trans*- $\text{Re}^{\text{V}}\text{OBr}_2(\text{PPh}_3)(\text{Ph-sal})$ , form I (Bertolasi *et al.*, 1982). The coordination is nearly octahedral with the two O atoms in apical positions, two *trans* Br atoms in the equatorial plane and the chelate ligand bridging an equatorial and an axial position. The atoms C(1)–C(7) of this ligand are perfectly coplanar ( $\chi^2 = 6.5$ ) and relevant displacements from the best plane are 0.042 (6), 0.072 (7) and 0.081 (1) Å for O(2), N and Re atoms, respectively.

The geometry of the compound reveals the typical features of quasi-octahedral oxorhenium(V) complexes with oxygenated bidentate ligands (Gilli, Sacerdoti, Bertolasi & Rossi, 1982, and references therein), that is

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39073 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* Also known as salicylideneimine.

† Reduced cell parameters:  $a = 8.943$  (3),  $b = 10.397$  (4),  $c = 17.143$  (5) Å,  $\alpha = 84.48$  (3),  $\beta = 81.37$  (3),  $\gamma = 66.70$  (3)°.

Table 1. *Positional* ( $\times 10^4$ ) and *thermal* ( $\text{\AA}^2 \times 10^3$ ) parameters with *e.s.d.'s* in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Re	-1111.8 (4)	8622.4 (3)	7221.7 (2)	32.2 (2)
Br(1)	1566 (1)	9243 (1)	6593 (1)	49.2 (4)
Br(2)	-3578 (1)	8623 (1)	7999 (1)	56.7 (3)
P	-372 (2)	7067 (2)	7599 (1)	32 (1)
O(1)	-2339 (6)	6898 (6)	6390 (3)	45 (3)
O(2)	303 (6)	10547 (5)	8231 (3)	40 (3)
N	-1334 (7)	10388 (7)	7080 (3)	40 (4)
C(1)	-656 (9)	11962 (9)	7577 (5)	49 (5)
C(2)	334 (9)	12877 (8)	8344 (4)	42 (4)
C(3)	872 (10)	14556 (8)	8797 (5)	54 (5)
C(4)	1784 (10)	15484 (9)	9539 (5)	57 (5)
C(5)	2197 (10)	14743 (9)	9853 (5)	49 (5)
C(6)	1709 (9)	13091 (8)	9412 (4)	43 (4)
C(7)	748 (8)	12123 (8)	8656 (4)	35 (4)
C(8)	-2275 (10)	9791 (9)	6339 (4)	47 (5)
C(9)	-3990 (11)	8622 (10)	6136 (5)	58 (5)
C(10)	-4904 (13)	8093 (12)	5442 (6)	76 (7)
C(11)	-4107 (16)	8743 (13)	4972 (6)	81 (7)
C(12)	-2427 (14)	9891 (12)	5185 (6)	70 (6)
C(13)	-1496 (12)	10414 (10)	5864 (5)	60 (6)
C(14)	-2181 (8)	5571 (8)	7756 (4)	36 (4)
C(15)	-2744 (9)	3894 (8)	7226 (5)	45 (4)
C(16)	-4161 (10)	2766 (9)	7340 (5)	58 (5)
C(17)	-4989 (10)	3313 (11)	7980 (6)	65 (6)
C(18)	-4459 (10)	4955 (10)	8485 (5)	57 (5)
C(19)	-3066 (9)	6086 (9)	8379 (5)	48 (5)
C(20)	1168 (9)	8430 (8)	8504 (4)	35 (4)
C(21)	854 (10)	8382 (8)	9189 (4)	43 (5)
C(22)	2091 (11)	9486 (10)	9857 (5)	55 (5)
C(23)	3637 (10)	10615 (9)	9833 (5)	54 (5)
C(24)	3974 (10)	10652 (9)	9148 (5)	52 (5)
C(25)	2749 (9)	9566 (8)	8482 (4)	41 (4)
C(26)	601 (9)	5884 (8)	6859 (4)	38 (4)
C(27)	-14 (11)	5061 (9)	6068 (4)	49 (5)
C(28)	702 (13)	4146 (10)	5505 (5)	64 (6)
C(29)	2020 (13)	4046 (10)	5707 (6)	70 (6)
C(30)	2643 (12)	4851 (11)	6506 (6)	69 (6)
C(31)	1919 (10)	5771 (9)	7081 (5)	53 (5)

Table 2. *Interatomic distances* ( $\text{\AA}$ ) and *angles* ( $^\circ$ ) with *e.s.d.'s* in parentheses

Re—Br(1)	2.545 (1)	C(10)—C(11)	1.39 (2)
Re—Br(2)	2.547 (1)	C(11)—C(12)	1.38 (2)
Re—P	2.482 (3)	C(12)—C(13)	1.38 (2)
Re—O(1)	1.680 (4)	C(14)—C(15)	1.40 (1)
Re—O(2)	1.972 (4)	C(14)—C(19)	1.40 (1)
Re—N	2.141 (9)	C(15)—C(16)	1.40 (1)
P—C(14)	1.825 (7)	C(16)—C(17)	1.39 (1)
P—C(20)	1.827 (7)	C(17)—C(18)	1.37 (1)
P—C(26)	1.826 (8)	C(18)—C(19)	1.38 (1)
O(2)—C(7)	1.316 (8)	C(20)—C(21)	1.38 (1)
N—C(1)	1.303 (8)	C(20)—C(25)	1.40 (1)
N—C(8)	1.46 (1)	C(21)—C(22)	1.39 (1)
C(1)—C(2)	1.44 (1)	C(22)—C(23)	1.38 (1)
C(2)—C(3)	1.39 (1)	C(23)—C(24)	1.38 (2)
C(2)—C(7)	1.42 (2)	C(24)—C(25)	1.39 (1)
C(3)—C(4)	1.37 (1)	C(26)—C(27)	1.38 (1)
C(4)—C(5)	1.41 (2)	C(26)—C(31)	1.38 (2)
C(5)—C(6)	1.38 (1)	C(27)—C(28)	1.38 (1)
C(6)—C(7)	1.40 (1)	C(28)—C(29)	1.35 (2)
C(8)—C(9)	1.41 (1)	C(29)—C(30)	1.40 (2)
C(8)—C(13)	1.38 (2)	C(30)—C(31)	1.40 (1)
C(9)—C(10)	1.39 (2)		
Br(1)—Re—Br(2)	168.4 (1)	O(2)—C(7)—C(6)	120.4 (9)
Br(1)—Re—P	90.6 (1)	C(2)—C(7)—C(6)	119.1 (7)
Br(1)—Re—O(1)	94.9 (2)	N—C(8)—C(9)	118.9 (9)
Br(1)—Re—O(2)	86.9 (1)	N—C(8)—C(13)	120.0 (6)
Br(1)—Re—N	85.8 (2)	C(9)—C(8)—C(13)	121.0 (9)
Br(2)—Re—P	96.5 (1)	C(8)—C(9)—C(10)	118.9 (10)
Br(2)—Re—O(1)	94.1 (2)	C(9)—C(10)—C(11)	119.4 (9)
Br(2)—Re—O(2)	84.7 (1)	C(10)—C(11)—C(12)	120.6 (12)
Br(2)—Re—N	85.5 (2)	C(11)—C(12)—C(13)	120.9 (12)
P—Re—O(1)	91.2 (3)	C(8)—C(13)—C(12)	119.2 (8)
P—Re—O(2)	84.9 (2)	P—C(14)—C(15)	120.1 (6)
P—Re—N	168.4 (1)	P—C(14)—C(19)	120.4 (5)
O(1)—Re—O(2)	175.8 (3)	C(15)—C(14)—C(19)	119.4 (7)
O(1)—Re—N	100.1 (3)	C(14)—C(15)—C(16)	119.4 (7)
O(2)—Re—N	83.8 (2)	C(15)—C(16)—C(17)	119.9 (7)
Re—P—C(14)	114.2 (3)	C(16)—C(17)—C(18)	120.3 (9)
Re—P—C(20)	111.5 (3)	C(17)—C(18)—C(19)	120.5 (8)
Re—P—C(26)	113.4 (3)	C(14)—C(19)—C(18)	120.4 (7)
C(14)—P—C(20)	107.2 (4)	P—C(20)—C(21)	123.6 (5)
C(14)—P—C(26)	104.6 (3)	P—C(20)—C(25)	116.7 (6)
C(20)—P—C(26)	105.4 (4)	C(21)—C(20)—C(25)	119.6 (7)
Re—O(2)—C(7)	138.4 (6)	C(20)—C(21)—C(22)	119.9 (7)
Re—N—C(1)	126.7 (7)	C(21)—C(22)—C(23)	120.2 (9)
Re—N—C(8)	117.2 (5)	C(22)—C(23)—C(24)	120.4 (7)
C(1)—N—C(8)	116.1 (9)	C(23)—C(24)—C(25)	120.0 (7)
N—C(1)—C(2)	127.9 (10)	C(20)—C(25)—C(24)	120.0 (9)
C(1)—C(2)—C(3)	118.5 (10)	P—C(26)—C(27)	119.7 (8)
C(1)—C(2)—C(7)	122.3 (7)	P—C(26)—C(31)	120.8 (6)
C(3)—C(2)—C(7)	119.2 (7)	C(27)—C(26)—C(31)	119.5 (8)
C(2)—C(3)—C(4)	121.1 (11)	C(26)—C(27)—C(28)	120.1 (10)
C(3)—C(4)—C(5)	120.0 (8)	C(27)—C(28)—C(29)	121.5 (9)
C(4)—C(5)—C(6)	120.0 (7)	C(28)—C(29)—C(30)	119.3 (10)
C(5)—C(6)—C(7)	120.6 (10)	C(29)—C(30)—C(31)	119.7 (12)
O(2)—C(7)—C(2)	120.5 (6)	C(26)—C(31)—C(30)	120.0 (9)

the very short Re—O<sub>oxo</sub> distance [1.680 (4) Å] corresponding to that of a triple bond, the umbrella deformation of the octahedron caused by the presence of the multiple Re≡O<sub>oxo</sub> bond [average O<sub>oxo</sub>≡Re—L<sub>cis</sub> angle = 95 (2)°] and the *trans* O≡Re—OR [175.8 (3)°] arrangement. This latter has already been interpreted (Gilli *et al.*, 1982; Bertolasi *et al.*, 1982) by assuming that it corresponds to a minimum of *trans* weakening caused by the multiple Re≡O<sub>oxo</sub> bond [for a theory of the *trans* influence caused by multiple metal—ligand bonds, see Shustorovich, Porai-Koshitz & Buslaev (1975)].

The comparison of the geometries of forms I and II reveals that they are similar but with a few definite exceptions, which are reported in Table 3. Firstly, they differ in the conformation of the PPh<sub>3</sub> group. The orientations of the three P—C bonds with respect to the coordination polyhedron are almost identical, the torsion angle O(2)—Re—P—C(20) being  $-5.5$  (3)° in form II and  $1.9$  (3)° in form I. However, the conformations of the three phenyl rings are completely dissimilar. In form I the C(20) phenyl is nearly perpendicular to the Re—P—C(20) plane and the other two phenyls are symmetrically arranged with respect to an approximate molecular pseudosymmetry plane going very roughly through the (sal) and Re, O(1), O(2), P atoms. In form II the three phenyls adopt the common propeller

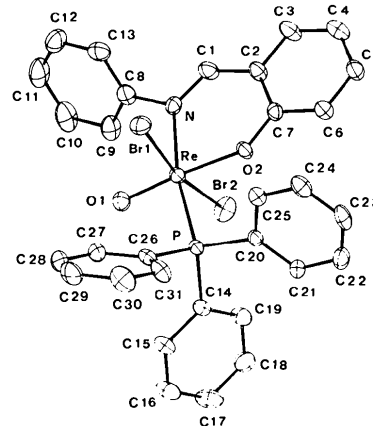


Fig. 1. An ORTEP (Johnson, 1971) view of the molecule showing the thermal ellipsoids at 40% probability.

Table 3. Comparison of some geometrical features at variance in *trans*-Re<sup>o</sup>OBr<sub>2</sub>(PPh<sub>3</sub>)(Ph-sal) form I (Bertolasi *et al.*, 1982) and form II (present work)

Distances in Å and angles in degrees; e.s.d.'s in parentheses.

	I	II		I	II
Re-P*	2.465 (2)	2.482 (3)	Br(1)-Re-N	90.5 (2)	85.8 (2)
Re-O(2)	1.937 (5)	1.972 (4)	Br(2)-Re-P	90.2 (1)	96.5 (1)
Re-N	2.173 (6)	2.141 (9)	P-Re-O(2)	91.9 (2)	84.9 (2)
P-Re-N	173.7 (2)	168.4 (1)	O(1)-Re-N	93.4 (2)	100.1 (3)
Br(1)-Re-P	93.0 (1)	90.6 (1)			
			I	II	
O(2)-Re-P-C(20)			1.9 (3)	-5.5 (3)	
Re-P-C(20)-C(25)			-93.5 (7)	-61.6 (6)	
Re-P-C(14)-C(19)			38.5 (8)	-65.8 (7)	
Re-P-C(26)-C(27)			-27.3 (8)	-40.6 (7)	

\* Atom labels are those of the present work. The present carbons 20,25,14,19,26,27 correspond to the 14,15,26,31,20,25 carbons in the original paper.

arrangement with the three Re-P-C-C torsion angles in a *gauche* conformation. The conformational differences are associated with changes up to 7° in ligand-metal-ligand angles and 0.035 Å in metal-ligand distances (Table 3). The deformation is mainly connected with the P-atom position as the main diagonal angle P-Re-N is changed by 5.3 (2)° [173.7 (2) in form I and 168.4 (1)° in form II] while the two others [Br(1)-Re-Br(2) and O(1)-Re-O(2)] are almost unchanged.

It is not so easy to find out which form is the stable state of the molecule. Both conformations correspond to minima of conformational energy, though the propeller arrangement is that most frequently observed in practice. However, comparison of the Re-N and Re-O distances found in other similar complexes (Gilli *et al.*, 1982) seems to indicate that the values actually found in form II [2.141 (9) and 1.972 (4) Å, respectively] are closer to the admitted equilibrium values, suggesting that form II could be the stabler molecular form.

In general, some geometrical differences in the coordination polyhedra of the two polymorphic

modifications I and II appear to be relevant for both bond distances and angles. On the other hand, they are able to modify slightly the electronic spectrum of the compound as clearly indicated by the different colours of the two forms. The differences are not attributable to the crystal packing in view of the lack of short intermolecular contacts in both forms and therefore can only be ascribed to the different intramolecular non-bonded interactions associated with the two observed conformations of the PPh<sub>3</sub> group. From this point of view the two molecules of forms I and II can be considered as conformational isomers whose interconversion barrier is too small for the isomers to be resolved but can exist in the solid state owing to the stabilization effect of crystal matrices. The relevant changes of the coordination polyhedron geometries in the two conformational isomers indicate that the coordination polyhedron in this class of compounds can be easily deformed, allowing slightly different geometries in different intramolecular environments.

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