We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work. JJV would like to thank Professor N. C. Payne of this department for X-ray and computing facilities.

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Acta Cryst. (1993). C**49**, 33–36

Structure of *trans*-Dibromo(ethoxo)oxobis(triphenylphosphine)rhenium(V)

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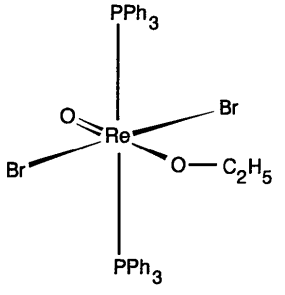
(*Received* 20 *December* 1991; *accepted* 28 *April* 1992)

Abstract. (*OC*-6-13)-Dibromo(ethoxo)oxobis(triphenylphosphine)rhenium(V), $[ReBr_2O(OC_2H_5)\{P(C_6H_5)_3\}_2]$, $M_r = 931.66$, monoclinic, $C2/c$, $a = 12.284$ (7), $b = 14.509$ (4), $c = 19.308$ (7) Å, $\beta = 93.33$ (4)°, $V = 3435$ (3) Å^3, D_m(293 K) = 1.82, $D_x = 1.801$ Mg m^{-3}, $Z = 4$, λ(Mo $K\alpha$) = 0.71069 Å, μ(Mo $K\alpha$) = 6.03 mm^{-1}, $F(000) = 1816$, $T = 293$ K, final $R = 0.024$ for 1515 unique observed reflections. The crystal contains approximately octahedral molecules of the *trans*-dibromo-*trans*-bis(phosphine) isomer. The linear O—Re—O unit lies on a twofold axis and the ethyl group of the ethoxo ligand is disordered over two orientations.

Introduction. In the course of an ongoing study of metal–metal-bonded systems containing aromatic N-heterocyclic bridging ligands (Allaire & Beauchamp, 1989), synthetic routes to Re^{III} dimers *via* Re^{V} oxo complexes are being developed. The reactivity of $[ReX_3O(PR_3)_2]$ and $[ReX_2O(OR)(PR_3)_2]$ with pyridines is well documented (Johnson, Taha & Wilkinson, 1964; Lock & Turner, 1977, 1978*a*,*b*; Brewer & Gray, 1989) and can be extrapolated to include more complex N-containing ligands. The title compound was considered to be a potential precursor for oxo complexes of controlled stereochemistry with N-containing heterocycles. Since the structure of the starting materials is of primary importance, X-ray work was carried out to see if the bromo compound occurs in the same isomeric form as the chloro and iodo analogues (Graziani, Casellato, Rossi & Marchi, 1985; Ciani, D'Alfonso, Romiti, Sironi & Freni, 1983).

Experimental. Compound synthesized by the method of Johnson, Lock & Wilkinson (1964). Violet pseudo-hexagonal prisms obtained by recrystallization from an ethanol/benzene mixture. Crystal size [mm (pair of faces)]: 0.28 $(1\bar{1}1,\bar{1}1\bar{1}) \times 0.08$ $(10\bar{1},\bar{1}01) \times 0.28$ $(1\bar{1}\bar{1},\bar{1}11)$. D_x measured by flotation in benzene/1,2-dibromoethane.



Data collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Reduced cell ($a_r = b_r = 9.50$, $c_r = 19.30$ Å, $\alpha_r = \beta_r = 92.0$, $\gamma_r = 99.4°$) determined from 25 centred reflections ($20.0 \le 2\theta \le 25.0°$), checked with

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Table 1. *Coordinates* ($\times 10^4$; Re, Br $\times 10^5$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Re	0	24904 (6)	25000	30
Br	19094 (5)	25190 (10)	31164 (3)	44
P	998 (1)	2538 (3)	1377 (1)	33
O(1)	0	1334 (4)	2500	38
O(2)	0	3796 (4)	2500	39
C(1)†	353 (12)	4585 (9)	2857 (7)	47
C(2)†	−177 (20)	5449 (8)	2506 (16)	56
C(11)	1381 (5)	1375 (4)	1115 (3)	32
C(12)	1773 (6)	770 (4)	1603 (3)	41
C(13)	2087 (7)	−114 (5)	1427 (4)	61
C(14)	1986 (7)	−379 (5)	750 (4)	70
C(15)	1559 (7)	197 (5)	256 (4)	64
C(16)	1261 (6)	1080 (5)	424 (3)	43
C(21)	318 (6)	3007 (4)	583 (3)	34
C(22)	−670 (6)	2674 (6)	344 (3)	47
C(23)	−1182 (6)	2973 (6)	−269 (3)	57
C(24)	−693 (7)	3636 (6)	−641 (4)	61
C(25)	280 (7)	3992 (5)	−421 (4)	70
C(26)	791 (6)	3674 (5)	191 (3)	49
C(31)	2262 (6)	3182 (4)	1475 (3)	40
C(32)	2243 (6)	4125 (5)	1617 (4)	51
C(33)	3151 (7)	4637 (5)	1692 (4)	73
C(34)	4168 (8)	4217 (6)	1666 (4)	84
C(35)	4208 (7)	3307 (6)	1531 (5)	75
C(36)	3283 (6)	2780 (4)	1424 (3)	51

† Half occupancy.

long-exposure axial photographs along the three axes. Monoclinic *C*-centred cell indicated by Niggli coefficients. Reduced cell transformed to a monoclinic *C*-centred cell using matrix 14 taken from *International Tables for X-ray Crystallography* (1969, Vol. I). Monoclinic Laue symmetry confirmed by a new set of axial photographs about the three axes; mirror plane for oscillation about **b** only. ω scan, $\omega = (1.00 + 0.35\tan\theta)°$, $2\theta_{max} = 50°$. Orientation monitored every 200 measurements, intensity checked every hour with seven standard reflections, fluctuations within $\pm 1.0\%$ 3020 unique hkl and $hk\bar{l}$ reflections with $h + k = 2n$ measured ($0 \le h \le 14$, $0 \le k \le 17$, $-23 \le l \le 23$), 1515 with $I \ge 3.0\sigma(I)$ retained for structure determination and refinement. Data corrected for Lp and absorption (Gaussian integration, $10 \times 10 \times 10$ grid, transmission range 0.25–0.62).

Space groups $C2/c$ and Cc consistent with the monoclinic Laue symmetry and systematic absences (hkl $h + k \neq 2n$, $h0l$ $l \neq 2n$). Structure solved in the centrosymmetric space group $C2/c$ by the heavy-atom method. Re and Br located from a Patterson map. All other non-H atoms located by successive difference Fourier (ΔF) maps. The ethyl group of the ethoxo ligand was found to be disordered, C(1) and C(2) atoms occupying symmetry-related positions off the twofold axis.

Full-matrix least-squares refinement on $|F|$. Function minimized: $\sum w(|F_o| - |F_c|)^2$; weights based on counting statistics, $w = 1/[\sigma^2(F) + 0.001\,F^2]$. Anisotropic refinement for non-H atoms, except for the disordered C(2) atom, which did not refine well because of proximity to the axis. H atoms positioned at idealized geometry (0.95 Å, $U = 0.065\ \text{Å}^2$), parameters not refined, coordinates recalculated after each cycle. Final $R = 0.024$, $wR = 0.020$, $S = 1.47$ for 209 parameters refined. $(\Delta/\sigma)_{max} = 0.17$, $(\Delta/\sigma)_{av} = 0.02$. Background in final ΔF synthesis below $\pm 0.19\ \text{e Å}^{-3}$, one residual peak of $0.23\ \text{e Å}^{-3}$ at 0.99 Å from Re. Attempts were made to refine the structure in the non-centrosymmetric space group Cc. Refinement was unstable with very high correlation coefficients and the ethoxo group remained disordered. The $C2/c$ model was retained.

Scattering factors from Cromer & Liberman (1970), except for H (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion factors from Cromer (1965). The computer programs used are listed elsewhere (Authier-Martin & Beauchamp, 1977). Refined coordinates for non-H atoms are in Table 1.*

Discussion. The crystal contains molecules of the *trans*-dibromo-*trans*-bis(phosphine) isomer (Fig. 1) which are roughly octahedral. The same stereoisomer is present in the chloro and the iodo analogues (Graziani *et al.*, 1985; Ciani *et al.*, 1983), but the three compounds are not isostructural. Interatomic distances and bond angles around the metal are listed in Table 2 for the three halogens. The Re—Br bond length [2.5681 (6) Å] is at the upper limit of the range (2.545–2.562 Å, $\sigma = 0.001$ Å) for related compounds (Sacerdoti, Bertolasi, Gilli & Duatti, 1984; Bertolasi, Sacerdoti, Gilli & Mazzi, 1982; Sergienko, Porai-Koshits, Mistryukov & Kotegov, 1982). The Re—P bond of the bromo complex is approximately 0.02 Å longer than those of the chloro and iodo complexes. Bright & Ibers (1969) have pointed out that the bulky triphenylphosphine ligand is responsible for long Re—X bonds in related compounds. The particularly long Re—Br and Re—P bonds found in the bromo complex are presumably due to these bonds being much more coplanar than in the other compounds (see below). On the other hand, the Re—O(1) bond [1.678 (6) Å] is significantly shorter [Cl, 1.699 (4); I, 1.715 (9) Å] and similar to those observed for the trihalide compounds $[ReCl_3O\{P(C_6H_5)_3\}_2]$ [1.663 (5) Å] (Lebuis & Beauchamp, 1992) and $[ReCl_3O\{P(C_6H_5)(C_2H_5)_2\}_2]$ [1.660 (9) Å] (Sergienko *et al.*, 1982). A mean value

* Lists of observed and calculated structure-factor amplitudes, anisotropic thermal parameters, H-atom coordinates, distances and angles in the phosphine ligand and atom-to-plane distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55425 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD0087]

Table 2. *Bond lengths* (Å) *and angles* (°)

$[ReX_2O(OC_2H_5)\{P(C_6H_5)_3\}_2]$

	X = Cl*	X = Br	X = I†
Re—O(1)	1.699 (4)	1.678 (6)	1.715 (9)
Re—O(2)	1.888 (4)	1.894 (6)	1.880 (9)
Re—X	2.417 (1)	2.5681 (6)	2.772 (1)
	2.427 (1)		2.806 (1)
Re—P	2.533 (1)	2.553 (1)	2.528 (5)
	2.535 (1)		2.519 (5)
O(1)—Re—O(2)	179.1 (2)	180.0	177.1 (5)
P—Re—P	178.5 (1)	176.90 (8)	177.6 (1)
X—Re—X	172.4 (1)	178.15 (4)	169.8 (1)
O(1)—Re—P	89.7 (1)	91.55 (13)	90.4 (5)
	89.0 (1)		88.0 (5)
O(2)—Re—P	90.7 (1)	88.45 (12)	90.1 (4)
	90.7 (1)		91.5 (4)
O(1)—Re—X	94.0 (1)	90.93 (12)	93.7 (4)
	93.6 (1)		96.5 (4)
O(2)—Re—X	86.9 (1)	89.07 (10)	85.7 (4)
	85.6 (1)		84.1 (4)
P—Re—X	94.2 (1)	85.56 (6)	92.8 (1)
	85.8 (1)	94.40 (6)	89.1 (1)
	93.6 (1)		90.4 (1)
	86.5 (1)		88.0 (1)
Re—O(2)—C(1)	143.8 (6)	145.3 (6)	176.2 (14)
	150.3 (8)		
Title compound			
P—C(11)	1.831 (7)	C(1)—C(2)	1.55 (2)
P—C(21)	1.834 (6)	O(2)—C(1)	1.39 (1)
P—C(31)	1.813 (7)		
Re—P—C(11)	110.7 (2)	C(11)—P—C(21)	102.9 (3)
Re—P—C(21)	120.1 (2)	C(11)—P—C(31)	105.8 (3)
Re—P—C(31)	112.1 (2)	C(21)—P—C(31)	104.0 (3)
O(2)—C(1)—C(2)	109.7 (12)		

* Graziani *et al.* (1985); numbering scheme adjusted to ours.
† Ciani *et al.* (1983).

of 1.691 Å (σ = 0.025 Å) has been calculated by Mayer (1988) for a large sample of mono-oxo Re^{V} compounds. The Re—O(2) distance [1.894 (6) Å], close to those of the chloro [1.888 (4) Å] and iodo [1.880 (9) Å] analogues, is believed to reflect some multiple-bond character (Ciani *et al.*, 1983).

The Re, O(1) and O(2) atoms are situated on a crystallographic twofold axis, making the O(1)—Re—O(2) unit linear by symmetry. C(1) and C(2) are each disordered on two sites related by the axis, thereby defining two equally populated orientations of the ethyl group. O(2) could also be affected by disorder, in which case its location on the twofold axis would represent the average of two unresolved positions slightly displaced from the axis. However, this effect is too small to show on the thermal ellipsoid and departure from linearity in the O(1)—Re—O(2) unit must be very small. The chloro analogue shows a similar type of disorder, but the populations, which are not fixed by symmetry, are not stated (Graziani *et al.*, 1985). In the chloro and bromo compounds, the ethyl group is bent at the C(1) atom, as expected, and the Re—O(2)—C(1) angles (Table 2) are in the 143–151° range. No disorder has been mentioned for the iodo(ethoxo) and iodo(methoxo) compounds, where the alkoxo groups appear to show a linear coordination (Ciani *et al.*, 1983). However, the large thermal ellipsoids of the alkoxo C atoms could indicate unresolved disorder making the Re—O—C angle smaller than that calculated from the refined positions.

The O—Re—P and O—Re—Br angles deviate by less than 1.6° from the ideal value of 90° (Table 2). Greater distortions are found in the $ReBr_2P_2$ plane, where both the large size and the irregular van der Waals profile of the phosphine ligand introduce intramolecular repulsions resulting in unequal P—Re—Br angles of 85.56 (6) and 94.40 (6)°. A similar sequence of P—Re—X angles above and below 90° is observed in the ReX_2P_2 'plane' for the chloro and iodo compounds. The larger Br—Re—P angle lies in the region where phenyl ring 2 (Fig. 1) is close to the $ReBr_2P_2$ plane and H(22) makes a short 2.78 Å contact with Br. The same type of arrangement with a short intramolecular contact between Cl and an *ortho* H atom has been noted in the structure of $ReCl_2O$(acetylacetonate)$P(C_6H_5)_3$ (Lock & Wan, 1975). A second distortion pattern is present in the chloro and iodo compounds; the Re—X bonds are displaced from the Re—O(1) bond by angles of ~95, ~85 and ~171° for O(1)—Re—X, O(2)—Re—X and X—Re—X respectively. The iodo(methoxo) complex (Ciani *et al.*, 1983) exhibits the same distortion, which undoubtedly relieves intramolecular steric strain. The absence of this distortion in the bromo complex could explain the long coplanar Re—Br and Re—P bonds mentioned above.

Details of the geometry of the coordinated phosphine are provided in the supplementary material. The P—C bond lengths are normal (mean 1.826 Å,

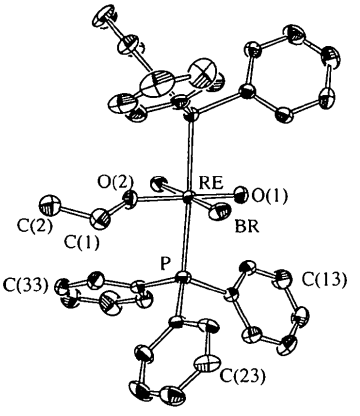

Fig. 1. Structure and numbering scheme of the $[ReBr_2O(OC_2H_5)\{P(C_6H_5)_3\}_2]$ molecule. The atoms in the phenyl rings are assigned C(ij) symbols, where i is the ring number and j corresponds to sequential numbering around the ring, starting with j = 1 for the C atoms bound to P. The O(1)=Re—O(2) unit lies on a crystallographic twofold axis. The ethyl group is disordered over two equally populated orientations, one of which is shown. Ellipsoids correspond to 50% probability and H atoms are omitted for clarity.

Table 2). The phenyl rings are planar, the mean and maximum atom-to-plane distances being 0.008 and 0.022 Å (σ = 0.008 Å), respectively. The P atom does not lie in the plane of any ring; the distances being 0.021 (2), 0.080 (3) and 0.042 (2) Å, respectively. As usual, coordination makes the C—P—C angles (mean 104.2°) greater than those involving uncoordinated phosphine (mean 102.6°) (Daly, 1964; Jones, 1980; Fenske, Basoglu, Hachgenei & Rogel, 1984; Albinati, Anklin, Ganazzoli, Ruegg & Pregosin, 1987). The Re—P—C angles are unequal, indicating that coordination does not take place exactly along the direction of the lone pair. The largest angle involves phenyl ring 2, for which a short intramolecular H···Br contact has been pointed out earlier. Such a distortion, which decreased steric hindrance, is not energy costly and is common in triarylphosphine complexes.

We wish to thank M. Simard and F. Bélanger-Gariépy for their assistance in collecting the X-ray data.

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Acta Cryst. (1993). C**49**, 36–39

A New Polymorph of Maleic Hydrazide

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(*Received* 21 *October* 1991; *accepted* 29 *April* 1992)

Abstract. 1,2-Dihydropyridazine-3,6-dione, $C_4H_4N_2O_2$, M_r = 112.09, monoclinic, $P2_1/c$, a = 6.891 (2), b = 9.674 (2), c = 6.946 (1) Å, β = 100.07 (2)°, V = 455.9 (2) Å^3, Z = 4, D_x = 1.63 (1) g cm^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, μ = 10.31 cm^{-1}, F(000) = 232, m.p. above 306–308 K (temperature of decomposition), T = 292 K, final R = 0.043 for 715 observed reflections. In the crystalline state the molecules of maleic hydrazide are present in the monolactim form (*i.e.* 3-hydroxy-6-pyridazinone). They are connected head-to-tail into planar chains along **a** by hydrogen bonds in which the O(3)···O(6′) distance is 2.605 (1) Å. The chains are linked into pairs by hydrogen bonds N(1)···O(6) of 2.925 (1) Å. The geometry of the hydrogen bonds and the pattern formed by the molecules within such pairs of chains are very similar in the title structure and the previously reported triclinic polymorph of maleic hydrazide; however, the arrangements of these pairs of chains in the crystal lattices are markedly different.

Introduction. Maleic hydrazide (*i.e.* 1,2-dihydropyridazine-3,6-dione, hereinafter referred to as MH), is applied as a growth inhibitor in agriculture (Cradwick, 1975); the molecules of MH can act either as a

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