Crystal structure of *trans*-dibromido-ethoxido-oxido-bis(triphenylphosphane)-rhenium(V) – a triclinic polymorph, $C_{38}H_{35}Br_2O_2P_2Re$

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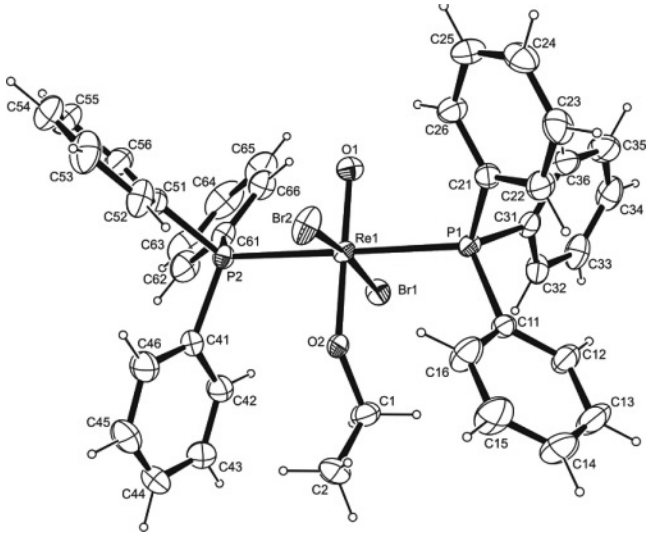

Abstract

$C_{38}H_{35}Br_2O_2P_2Re$, triclinic, $P\overline{1}$ (no. 2), a = 9.7769(2) Å, b = 11.3125(3) Å, c = 17.7285(4) Å, α = 77.450(1)°, β = 88.684(1)°, γ = 66.501(1)°, V = 1750.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.0189, $wR_{ref}(F^2)$ = 0.0401, T = 200 K.

Table 1. Data collection and handling.

Crystal:	brown rods, size 0.09×0.097×0.342 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	58.77 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.84°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	31537, 8771
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7815
$N(param)_{refined}$:	422
Programs:	SHELX, WinGX, MERCURY, PLATON [9–12]

Source of material

The compound was obtained upon reaction of bis(3-formyl-4-hydroxyphenyl)methane and *trans*-$ReOBr_3(PPh_3)_2$ in ethanol. Crystals suitable for the diffraction study were obtained upon free evaporation of the solvent at ambient conditions.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H = 0.95 Å for aromatic carbon atoms, C–H = 0.99 Å for the methylene group) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The H atoms of the methyl group were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [9]), with U_{iso}(H) set to 1.5U_{eq}(C).

Discussion

Next to cardiovascular diseases, cancer has become one of the main fatal diseases in industrialized countries. Apart from classical surgery, chemo- and radiotherapeutic treatments have entered the arsenal of possible cures for certain types of cancer. All methods, however, suffer from their own set of problematic side-effects and, as a consequence, the development of radiopharmaceuticals – combining the advantages of chemotherapy as well as radiation methods while at the same time avoiding their unique respective undesired side-effects – has been a topic of research [1, 2]. Tailoring and fine-tuning of the envisioned radiopharmaceuticals' properties such as lipophilicity and, in particular, inertness is of paramount importance with respect to possible future *in vivo* applications in contemporary medicine and requires sound knowledge about structural parameters of the ligands applied if a more heuristic approach in the synthesis is to triumph over pure trial-and-error as it is encountered in this specific field of coordination chemistry up to the present day. In addition, the spatial requirements of pharmaceuticals are of importance as this factor influences on their interaction with enzymatic systems and, as a consequence, the pathway and rate of conjugation, functionalization and secretion from the body. In continuation of our ongoing research on the field of rhenium coordination compounds, the coordination of a multidentate ligand towards a rhenium(V) starting material was attempted. A structural analysis of the crystalline reaction product showed the recovery of the solvolyzed rhenium(V) starting material whose molecular and crystal structure have been reported earlier, however, as a monoclinic polymorph and a orthorhombic polymorph [3, 4]. The title compound is a rhenium(V) coordination compound. The octahedral coordination sphere around the central atom is comprised of two triphenylphosphane as well as two bromido ligands in respective *trans* orientation, an oxido ligand and an ethoxido ligand. The latter shows orientational disorder with the main component constituing 67%. The Re–P bond lengths were measured at 2.5283(6) Å and 2.5406(6) Å which is invariably shorter than the values reported for the monoclinic polymorph [3]. The rhenium–bromine distances were found at 2.5538(2) Å and 2.5696(2) Å which is shorter as well as longer as the two values observed in the monoclinic polymorph of the title compound [3]. The two Re–O bond distances differ markedly with lengths of 1.6970(14) Å and 1.857(10) Å for the oxido as well as the ethoxido ligand. Both latter values exceed the bond lengths observed for the corresponding distances in the mono- clinic polymorph [3]. All values are in good agreement with other values observed for comparable rhenium(V) coordination com-

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pounds whose metrical parameters have been deposited with the Cambridge Structural Database [5]. The least-squares planes as defined by the carbon atoms of the phenyl groups bonded to the phosphorus atoms enclose angles of 65.90(9)°, 76.77(9)° and 83.57(7)° in the first phosphane ligand and 57.62(9)°, 62.70(8)° and 89.86(7)° in the second phosphane ligand. In the crystal, C–H···O as well as C–H···Br contacts whose range falls below the sum of van-der-Waals radii of the atoms participating in them can be observed [6]. While the former are intramo-lecular and established in between two of the hydrogen atoms in *ortho*-position to the phosphorus atom the pertaining phenyl groups are bonded to as donors and the oxido ligand as acceptor, the C–H···Br contacts stem from the hydrogen atoms in *para*-position to the phosphorus atom they are bonded to as donors and have both bromido ligands as acceptors. It is pertinent to note that both types of C–H···X contacts are supported by the same phenyl groups. In terms of graph-set analysis [7, 8], the C–H···O contacts necessitate a $S(6)S(6)$ descriptor on the unary level while the description of the C–H···Br contacts can be accomplished by a $C^1_1(8)C^1_1(8)$ descriptor on the same level. In total, the molecules are connected to layers perpendicular to the crystallographic *c* axis. Additionally, several C–H···π contacts can be observed in the crystal structure. The shortest intercentroid distance in between two centers of gravity was measured at 3.9253(17) Å in between a phosphorus-bonded phenyl group and its symmetry-generated equivalent.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(12)	2*i*		0.5727	–0.2306	0.5014	0.042
H(13)	2*i*		0.8316	–0.3159	0.5287	0.057
H(14)	2*i*		0.9930	–0.3727	0.4329	0.055
H(15)	2*i*		0.8976	–0.3392	0.3072	0.058
H(16)	2*i*		0.6405	–0.2520	0.2784	0.047
H(22)	2*i*		0.5745	–0.4648	0.4065	0.036
H(23)	2*i*		0.5563	–0.6582	0.3925	0.042
H(24)	2*i*		0.3458	–0.6476	0.3268	0.042
H(25)	2*i*		0.1554	–0.4424	0.2735	0.040
H(26)	2*i*		0.1732	–0.2483	0.2854	0.035
H(32)	2*i*		0.3454	–0.0126	0.4666	0.036
H(33)	2*i*		0.2124	0.0254	0.5763	0.045
H(34)	2*i*		0.0771	–0.0981	0.6263	0.048
H(35)	2*i*		0.0728	–0.2606	0.5673	0.050
H(36)	2*i*		0.2040	–0.3012	0.4575	0.040
H(42)	2*i*		0.2721	0.3601	0.1912	0.038
H(43)	2*i*		0.4543	0.4443	0.1642	0.046
H(44)	2*i*		0.6024	0.3978	0.0610	0.052
H(45)	2*i*		0.5601	0.2772	–0.0192	0.056
H(46)	2*i*		0.3738	0.1972	0.0047	0.046

Table 2. continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(52)	2*i*		0.2938	0.0174	0.0274	0.044
H(53)	2*i*		0.2059	–0.0163	–0.0845	0.057
H(54)	2*i*		–0.0320	0.1199	–0.1411	0.059
H(55)	2*i*		–0.1857	0.2895	–0.0855	0.055
H(56)	2*i*		–0.1042	0.3230	0.0272	0.042
H(62)	2*i*		0.0398	0.4889	0.0901	0.047
H(63)	2*i*		–0.1772	0.6500	0.1210	0.067
H(64)	2*i*		–0.3446	0.5900	0.1982	0.066
H(65)	2*i*		–0.2952	0.3683	0.2457	0.053
H(66)	2*i*		–0.0788	0.2046	0.2159	0.038
H(1A)	2*i*	0.67	0.5818	0.0155	0.3346	0.037
H(1B)	2*i*	0.67	0.5005	0.1651	0.2852	0.037
H(2A)	2*i*	0.67	0.7599	0.0798	0.2634	0.066
H(2B)	2*i*	0.67	0.6634	0.1115	0.1843	0.066
H(2C)	2*i*	0.67	0.7441	–0.0379	0.2332	0.066
H(3A)	2*i*	0.33	0.5664	0.0779	0.1532	0.041
H(3B)	2*i*	0.33	0.6505	–0.0789	0.1908	0.041
H(4A)	2*i*	0.33	0.7809	0.0376	0.2339	0.066
H(4B)	2*i*	0.33	0.7158	–0.0311	0.3058	0.066
H(4C)	2*i*	0.33	0.6316	0.1242	0.2690	0.066

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re(1)	2*i*		0.279240(8)	0.004995(8)	0.244189(4)	0.01631(4)	0.01773(5)	0.01814(4)	–0.00513(3)	0.00037(3)	–0.00671(3)
Br(1)	2*i*		0.19542(2)	0.17865(2)	0.32704(1)	0.0324(1)	0.0240(1)	0.0229(1)	–0.0119(1)	0.00586(9)	–0.01065(9)
Br(2)	2*i*		0.39688(3)	–0.16543(2)	0.16225(1)	0.0348(1)	0.0277(1)	0.0259(1)	0.0023(1)	–0.00411(9)	–0.0141(1)
P(1)	2*i*		0.38320(6)	–0.18462(5)	0.36172(3)	0.0187(2)	0.0194(3)	0.0200(3)	–0.0071(2)	–0.0020(2)	–0.0043(2)
P(2)	2*i*		0.16868(6)	0.19845(6)	0.12805(3)	0.0220(3)	0.0204(3)	0.0180(3)	–0.0072(2)	0.0011(2)	–0.0053(2)
O(1)	2*i*		0.1150(2)	–0.0133(1)	0.25041(9)	0.0220(7)	0.0169(8)	0.0318(8)	–0.0059(6)	–0.0008(6)	–0.0057(6)
C(11)	2*i*		0.5816(2)	–0.2360(2)	0.3875(1)	0.021(1)	0.022(1)	0.026(1)	–0.0094(9)	–0.0035(8)	–0.0020(9)
C(12)	2*i*		0.6385(3)	–0.2532(3)	0.4616(1)	0.027(1)	0.051(2)	0.027(1)	–0.016(1)	–0.0030(9)	–0.005(1)
C(13)	2*i*		0.7926(3)	–0.3040(3)	0.4777(2)	0.032(1)	0.072(2)	0.039(2)	–0.021(2)	–0.011(1)	–0.009(2)
C(14)	2*i*		0.8880(3)	–0.3367(3)	0.4212(2)	0.023(1)	0.054(2)	0.056(2)	–0.011(1)	–0.007(1)	–0.009(2)
C(15)	2*i*		0.8313(3)	–0.3173(3)	0.3469(2)	0.022(1)	0.065(2)	0.047(2)	–0.005(1)	0.004(1)	–0.016(2)
C(16)	2*i*		0.6788(3)	–0.2663(3)	0.3299(2)	0.024(1)	0.052(2)	0.034(1)	–0.005(1)	–0.003(1)	–0.013(1)
C(21)	2*i*		0.3752(2)	–0.3370(2)	0.3480(1)	0.026(1)	0.022(1)	0.023(1)	–0.0109(9)	0.0012(8)	–0.0061(9)
C(22)	2*i*		0.4890(3)	–0.4598(2)	0.3794(1)	0.030(1)	0.022(1)	0.034(1)	–0.008(1)	–0.006(1)	–0.002(1)
C(23)	2*i*		0.4780(3)	–0.5747(2)	0.3712(1)	0.041(1)	0.020(1)	0.039(1)	–0.009(1)	–0.000(1)	–0.002(1)
C(24)	2*i*		0.3535(3)	–0.5686(3)	0.3320(1)	0.046(1)	0.030(1)	0.039(1)	–0.023(1)	0.009(1)	–0.013(1)
C(25)	2*i*		0.2408(3)	–0.4469(3)	0.3005(1)	0.033(1)	0.036(1)	0.039(1)	–0.019(1)	–0.001(1)	–0.014(1)
C(26)	2*i*		0.2509(2)	–0.3315(2)	0.3078(1)	0.025(1)	0.027(1)	0.035(1)	–0.010(1)	–0.0031(9)	–0.007(1)
C(31)	2*i*		0.2873(2)	–0.1606(2)	0.4502(1)	0.021(1)	0.027(1)	0.021(1)	–0.0057(9)	–0.0030(8)	–0.0031(9)
C(32)	2*i*		0.2898(3)	–0.0634(2)	0.4866(1)	0.038(1)	0.027(1)	0.023(1)	–0.011(1)	–0.0023(9)	–0.003(1)
C(33)	2*i*		0.2108(3)	–0.0411(3)	0.5520(1)	0.045(1)	0.036(2)	0.024(1)	–0.007(1)	–0.003(1)	–0.009(1)
C(34)	2*i*		0.1307(3)	–0.1140(3)	0.5816(1)	0.031(1)	0.057(2)	0.024(1)	–0.009(1)	0.004(1)	–0.009(1)
C(35)	2*i*		0.1283(3)	–0.2101(3)	0.5466(2)	0.032(1)	0.064(2)	0.036(1)	–0.026(1)	0.009(1)	–0.012(1)
C(36)	2*i*		0.2062(2)	–0.2342(3)	0.4812(1)	0.028(1)	0.046(2)	0.033(1)	–0.019(1)	0.004(1)	–0.015(1)
C(41)	2*i*		0.3037(2)	0.2708(2)	0.1003(1)	0.028(1)	0.027(1)	0.022(1)	–0.012(1)	0.0011(9)	–0.0019(9)
C(42)	2*i*		0.3298(3)	0.3437(3)	0.1478(1)	0.036(1)	0.037(2)	0.028(1)	–0.019(1)	0.005(1)	–0.009(1)
C(43)	2*i*		0.4390(3)	0.3925(3)	0.1323(2)	0.044(2)	0.044(2)	0.036(1)	–0.027(1)	0.000(1)	–0.007(1)
C(44)	2*i*		0.5256(3)	0.3662(3)	0.0708(2)	0.044(2)	0.053(2)	0.038(2)	–0.032(1)	0.004(1)	0.003(1)
C(45)	2*i*		0.5009(3)	0.2943(3)	0.0236(2)	0.048(2)	0.067(2)	0.034(1)	–0.033(2)	0.018(1)	–0.011(1)

Table 3. continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(46)	2*i*		0.3903(3)	0.2466(3)	0.0378(1)	0.045(2)	0.052(2)	0.029(1)	–0.027(1)	0.010(1)	–0.014(1)
C(51)	2*i*		0.1036(2)	0.1732(2)	0.0394(1)	0.032(1)	0.025(1)	0.020(1)	–0.013(1)	–0.0006(9)	–0.0042(9)
C(52)	2*i*		0.1954(3)	0.0729(3)	0.0053(1)	0.046(2)	0.030(1)	0.026(1)	–0.006(1)	–0.004(1)	–0.007(1)
C(53)	2*i*		0.1430(3)	0.0535(3)	–0.0618(2)	0.071(2)	0.041(2)	0.030(1)	–0.018(2)	0.003(1)	–0.017(1)
C(54)	2*i*		0.0023(3)	0.1336(3)	–0.0953(2)	0.067(2)	0.063(2)	0.028(1)	–0.036(2)	–0.006(1)	–0.011(1)
C(55)	2*i*		–0.0882(3)	0.2334(3)	–0.0623(2)	0.042(2)	0.063(2)	0.035(1)	–0.026(2)	–0.009(1)	–0.007(1)
C(56)	2*i*		–0.0396(3)	0.2537(3)	0.0047(1)	0.033(1)	0.044(2)	0.031(1)	–0.017(1)	0.000(1)	–0.011(1)
C(61)	2*i*		0.0035(2)	0.3301(2)	0.1509(1)	0.027(1)	0.021(1)	0.024(1)	–0.0039(9)	–0.0042(9)	–0.0074(9)
C(62)	2*i*		–0.0276(3)	0.4635(3)	0.1222(2)	0.040(1)	0.025(1)	0.044(2)	–0.006(1)	–0.008(1)	–0.004(1)
C(63)	2*i*		–0.1567(3)	0.5590(3)	0.1403(2)	0.052(2)	0.021(2)	0.078(2)	0.003(1)	–0.017(2)	–0.012(2)
C(64)	2*i*		–0.2560(3)	0.5237(3)	0.1861(2)	0.035(2)	0.044(2)	0.069(2)	0.013(1)	–0.011(1)	–0.031(2)
C(65)	2*i*		–0.2267(3)	0.3927(3)	0.2140(2)	0.025(1)	0.053(2)	0.044(2)	–0.000(1)	0.003(1)	–0.019(1)
C(66)	2*i*		–0.0978(2)	0.2953(3)	0.1966(1)	0.024(1)	0.030(1)	0.033(1)	–0.002(1)	–0.0001(9)	–0.008(1)
O(2)	2*i*	0.67	0.455(1)	0.032(2)	0.240(1)	0.018(2)	0.022(5)	0.023(5)	–0.006(3)	–0.005(2)	0.003(3)
C(1)	2*i*	0.67	0.5533(4)	0.0718(4)	0.2815(2)	0.028(2)	0.038(2)	0.031(2)	–0.017(2)	–0.000(1)	–0.011(2)
C(2)	2*i*	0.67	0.693(1)	0.055(1)	0.2366(3)	0.033(2)	0.070(4)	0.035(4)	–0.032(2)	0.009(3)	–0.006(4)
O(3)	2*i*	0.33	0.467(3)	0.015(4)	0.249(3)	0.018(2)	0.022(5)	0.023(5)	–0.006(3)	–0.005(2)	0.003(3)
C(3)	2*i*	0.33	0.5968(7)	0.0094(9)	0.2023(4)	0.022(3)	0.054(5)	0.026(4)	–0.019(4)	0.003(3)	–0.002(4)
C(4)	2*i*	0.33	0.689(3)	0.037(3)	0.2576(9)	0.033(2)	0.070(4)	0.035(4)	–0.032(2)	0.009(3)	–0.006(4)

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