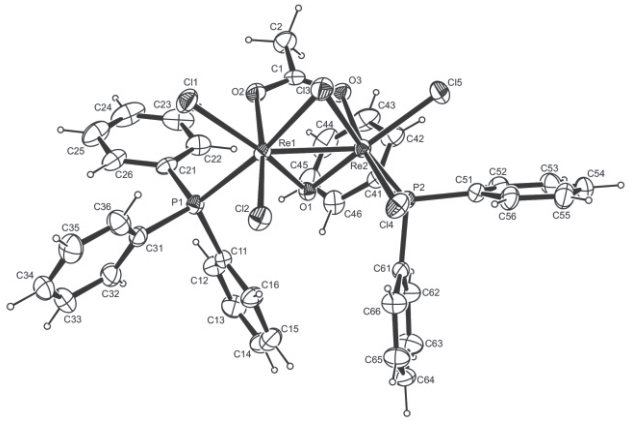
Crystal structure of (μ_2-acetato-κ^2*O,O'*)-(μ_2-chlorido)-(μ_2-oxido)-bis(dichlorido-triphenylphosphane-rhenium(IV)), $C_{38}H_{33}Cl_5O_3P_2Re_2$

Janvier Mukiza, Thomas I. A. Gerber, Eric C. Hosten and Richard Betz*

Nelson Mandela Metropolitan University, Summerstrand Campus, Department of Chemistry, University Way, Summerstrand, PO Box 77000, Port Elizabeth 6031, South Africa

Received January 15, 2015, accepted May 27, 2015, available online June 02, 2015, CCDC no. 1267/4313



Abstract

$C_{38}H_{33}Cl_5O_3P_2Re_2$, orthorhombic, *Pbca* (no. 61), a = 18.9747(6) Å, b = 17.6316(5) Å, c = 22.3528(6) Å, V = 7478.2 Å^3, Z = 8, $R_{gt}(F)$ = 0.0278, $wR_{ref}(F^2)$ = 0.0649, T = 200 K.

Table 1. Data collection and handling.

Crystal:	red platelets, size 0.03×0.20×0.302 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	69.50 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.7°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	69584, 9326
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6957
$N(param)_{refined}$:	452
Programs:	SHELX, WinGX, MERCURY, PLATON [12–15]

Source of material

The compound was obtained upon reacting 1,2,3,6-tetrahydro-2,6-dioxopyrimidine-4-carboxylic acid with $ReCl_3O(PPh_3)_2$ in benzene/acetonitrile. 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) 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 [12]), with U_{iso}(H) set to 1.5U_{eq}(C).

* Correspondence author (e-mail: Richard.Betz@nmmu.ac.za)

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 formation of an unexpected product. The crystal structures of three very similar compounds – namely the chloroform solvate of the title compound [3] as well as the pertaining mono-propionato [4] and the di-propionato derivative of the latter [5] – are apparent in the literature. The title compound is a dinuclear rhenium(IV) species. The coordination sphere around both central atoms is octahedral and consists of one triphenylphosphane ligand and two chlorido ligands – that exclusively act as monodentate ligands – as well as one bridging oxido, a bridging chlorido and a κ^2*O:O'*-bridging acetato ligand. The Re–Cl bond lengths differ for both monodentate chlorido ligands with 2.297(1) Å and 2.377(1) Å for the first rhenium atom and 2.298(1) Å and 2.361(1) Å for the second rhenium atom with the shorter bond invariably established towards the chlorido ligands in *trans* position to the oxygen atoms of the bridging acetato ligand. The Re–Cl bond lengths involving the bridging chlorido ligand are more uniform with values of 2.400(1) Å and 2.405(1) Å. A similar picture is apparent for the Re–O bonds: while the Re–O bonds towards the bridging oxido ligand do not differ much with values of 1.902(3) Å and 1.910(3) Å, Re–O distances towards the oxygen atoms of the acetato ligand show a broader spread of 2.086(3) Å and 2.122(3) Å, respectively. Re–P distances also vary over a broader range with lengths of 2.502(1) Å and 2.514(1) Å. In comparison to the

values deposited for the chloroform solvate of the title compound [3], the Re–Cl bond lengths obtained in the current study show good agreement for the bridging chlorido ligand but cover a broader range in case of the monodentate ligands. While the Re–P bonds in the chloroform solvate [3] are found to be slightly shorter in most cases, the agreement between the Re–O bond lengths reported for both – the bridging as well as the acetato-based oxygen atoms – are in good agreement with the values found in the present study. The Re-Re distance of 2.5123(3) Å only is indicative of a metal-metal bond, the latter fact increasing the coordination number of each central atom to seven. In comparison to other rhenium coordination compounds featuring seven-coordinate central atoms with a direct metal-metal bond whose metrical parameters have been deposited with the Cambridge Structural Database [6] this value is found to be slightly longer than the most common values reported. Nevertheless, the value observed in the present study is shorter than the value reported for the chloroform solvate of the title compound [3]. A puckering analysis of the five-membered chelate ring created by the acetato ligand according to Cremer & Pople [7] shows the latter to adopt a ^{5}E conformation on one of the the two oxygen atoms ($^{O(3)}E$) [8]. The least-squares planes as defined by the carbon atoms of the respective aromatic moieties enclose angles of 69.49(14)°, 69.99(17)° and 85.75(2)° in the first and 48.84(20)°, 65.23(15)° and 89.46(15)° in the second triphenylphosphane ligand. In the crystal, two C–H···Cl contacts whose range below the sum of van-der-Waals radii of the atoms participating in them can be observed [9]. Both are apparent in between one of the hydrogen atoms in *ortho* position to the phosphorus atom the pertaining phenyl group is bonded to as donor and one of the monodentate chlorido ligands as acceptor giving rise to the formation of centrosymmetric dimers while the second C–H···Cl contact – that is also supported by a hydrogen atom in *ortho* position to the phosphorus atom it is bonded to and also applies a monodentate chlorido ligand as acceptor – connects the molecules to chains. It is pertinent to note that both chlorido ligands that participate in these contacts as acceptors are bonded to the same rhenium atom. In total, the molecules are connected to planes perpendicular to the crystallographic *a* axis. In terms of graph-set analysis [10, 11], these contacts necessitate a $C^1_1(7)R^2_2(12)$ descriptor on the unary level. Furthermore, one C–H···π contact is apparent in the crystal structure. The shortest ntercentroid distance between two centers of gravity was measured at 4.006(3) Å and is observed between two phenyl groups bonded to the two different types of phosphorus atoms in neighbouring molecules.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	8*c*	0.2649	0.3803	0.0090	0.053
H(2B)	8*c*	0.2638	0.3729	0.0804	0.053
H(2C)	8*c*	0.1977	0.3446	0.0419	0.053
H(12)	8*c*	0.5577	0.3432	0.0215	0.039
H(13)	8*c*	0.6446	0.3392	0.0947	0.047
H(14)	8*c*	0.6830	0.2229	0.1319	0.049
H(15)	8*c*	0.6351	0.1112	0.0949	0.049
H(16)	8*c*	0.5459	0.1137	0.0234	0.037
H(22)	8*c*	0.4138	0.3458	0.0269	0.041
H(23)	8*c*	0.3927	0.4755	0.0148	0.054
H(24)	8*c*	0.4242	0.5352	–0.0741	0.064
H(25)	8*c*	0.4753	0.4672	–0.1508	0.058
H(26)	8*c*	0.4966	0.3375	–0.1398	0.043
H(32)	8*c*	0.6151	0.2609	–0.0830	0.042
H(33)	8*c*	0.6847	0.2298	–0.1651	0.053
H(34)	8*c*	0.6413	0.1514	–0.2403	0.048
H(35)	8*c*	0.5281	0.1040	–0.2328	0.047
H(36)	8*c*	0.4580	0.1332	–0.1509	0.042
H(42)	8*c*	0.2876	0.2692	0.2220	0.042
H(43)	8*c*	0.2880	0.4023	0.2120	0.057
H(44)	8*c*	0.3836	0.4626	0.1694	0.058
H(45)	8*c*	0.4783	0.3928	0.1345	0.055
H(46)	8*c*	0.4797	0.2611	0.1434	0.040
H(52)	8*c*	0.3459	0.2071	0.2995	0.035
H(53)	8*c*	0.2955	0.1540	0.3854	0.044
H(54)	8*c*	0.2601	0.0276	0.3858	0.045
H(55)	8*c*	0.2792	–0.0473	0.3014	0.045
H(56)	8*c*	0.3266	0.0050	0.2146	0.036
H(62)	8*c*	0.4920	0.2036	0.2534	0.041
H(63)	8*c*	0.6036	0.1626	0.2812	0.048
H(64)	8*c*	0.6504	0.0525	0.2393	0.039
H(65)	8*c*	0.5880	–0.0119	0.1666	0.040
H(66)	8*c*	0.4767	0.0299	0.1366	0.036

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

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re(1)	8*c*	0.368284(9)	0.152772(9)	–0.018861(8)	0.02267(9)	0.01625(8)	0.01782(8)	0.00147(7)	–0.00118(7)	–0.00043(7)
Re(2)	8*c*	0.322654(9)	0.117887(9)	0.082995(8)	0.02029(8)	0.01891(8)	0.01914(8)	–0.00148(7)	–0.00107(7)	0.00089(7)
Cl(1)	8*c*	0.33328(7)	0.17049(7)	–0.12001(5)	0.0403(7)	0.0395(6)	0.0203(6)	0.0041(5)	–0.0050(5)	0.0029(5)
Cl(2)	8*c*	0.42873(7)	0.04355(6)	–0.04123(6)	0.0412(7)	0.0193(5)	0.0283(6)	0.0072(5)	0.0016(5)	–0.0028(4)
Cl(3)	8*c*	0.25769(6)	0.08815(7)	–0.00611(5)	0.0293(6)	0.0344(6)	0.0274(6)	–0.0087(5)	–0.0080(5)	0.0017(5)
Cl(4)	8*c*	0.35877(7)	–0.00625(6)	0.08909(6)	0.0405(7)	0.0166(5)	0.0316(6)	–0.0037(4)	–0.0070(6)	0.0013(4)
Cl(5)	8*c*	0.21929(7)	0.09221(8)	0.13817(6)	0.0253(6)	0.0529(8)	0.0331(7)	–0.0060(5)	0.0047(5)	0.0093(6)
P(1)	8*c*	0.47656(6)	0.22872(6)	–0.04369(6)	0.0254(6)	0.0171(5)	0.0210(6)	0.0007(4)	0.0002(5)	0.0006(4)
P(2)	8*c*	0.38073(6)	0.14912(6)	0.18040(5)	0.0227(6)	0.0176(5)	0.0172(5)	0.0016(4)	0.0007(4)	–0.0011(4)
O(1)	8*c*	0.4075(2)	0.1667(2)	0.0591(1)	0.022(2)	0.017(1)	0.019(2)	0.002(1)	0.004(1)	–0.003(1)
O(2)	8*c*	0.3132(2)	0.2545(2)	–0.0097(2)	0.027(2)	0.026(2)	0.028(2)	0.007(1)	0.001(2)	0.004(1)
O(3)	8*c*	0.2767(2)	0.2276(2)	0.0829(2)	0.028(2)	0.027(2)	0.024(2)	0.007(1)	0.001(2)	0.001(1)
C(1)	8*c*	0.2814(2)	0.2722(3)	0.0382(2)	0.018(2)	0.026(2)	0.028(3)	0.005(2)	–0.004(2)	–0.001(2)
C(2)	8*c*	0.2492(3)	0.3491(3)	0.0428(2)	0.042(3)	0.031(3)	0.033(3)	0.016(2)	0.002(3)	–0.001(2)
C(11)	8*c*	0.5420(2)	0.2293(2)	0.0155(2)	0.021(2)	0.026(2)	0.020(2)	0.000(2)	0.002(2)	0.003(2)
C(12)	8*c*	0.5727(3)	0.2956(3)	0.0369(2)	0.032(3)	0.027(2)	0.038(3)	0.000(2)	–0.006(2)	–0.001(2)
C(13)	8*c*	0.6247(3)	0.2934(3)	0.0801(3)	0.034(3)	0.039(3)	0.044(3)	–0.006(2)	–0.004(3)	–0.005(3)
C(14)	8*c*	0.6475(3)	0.2247(3)	0.1020(3)	0.029(3)	0.060(4)	0.035(3)	0.001(3)	–0.010(2)	0.006(3)
C(15)	8*c*	0.6185(3)	0.1585(3)	0.0803(3)	0.039(3)	0.043(3)	0.041(3)	0.002(2)	–0.005(3)	0.015(3)
C(16)	8*c*	0.5658(3)	0.1598(3)	0.0376(2)	0.030(3)	0.025(2)	0.038(3)	–0.002(2)	–0.006(2)	0.006(2)

Table 3. continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(21)	8*c*	0.4572(2)	0.3288(2)	–0.0555(2)	0.024(2)	0.017(2)	0.031(3)	–0.000(2)	–0.009(2)	0.003(2)
C(22)	8*c*	0.4264(3)	0.3703(3)	–0.0095(3)	0.033(3)	0.026(2)	0.043(3)	0.002(2)	–0.004(2)	–0.004(2)
C(23)	8*c*	0.4139(3)	0.4472(3)	–0.0166(3)	0.037(3)	0.029(3)	0.069(4)	0.002(2)	–0.012(3)	–0.016(3)
C(24)	8*c*	0.4326(4)	0.4824(3)	–0.0693(3)	0.062(4)	0.015(2)	0.082(5)	–0.004(2)	–0.033(4)	0.004(3)
C(25)	8*c*	0.4628(3)	0.4423(3)	–0.1146(3)	0.054(4)	0.030(3)	0.060(4)	–0.012(3)	–0.020(3)	0.019(3)
C(26)	8*c*	0.4755(3)	0.3652(3)	–0.1081(3)	0.037(3)	0.030(3)	0.039(3)	–0.003(2)	–0.014(3)	0.007(2)
C(31)	8*c*	0.5292(3)	0.2001(2)	–0.1083(2)	0.030(3)	0.024(2)	0.023(2)	0.005(2)	0.003(2)	0.004(2)
C(32)	8*c*	0.5969(3)	0.2286(3)	–0.1133(2)	0.032(3)	0.047(3)	0.026(3)	–0.004(2)	–0.002(2)	0.002(2)
C(33)	8*c*	0.6383(3)	0.2102(3)	–0.1623(3)	0.032(3)	0.062(4)	0.038(3)	0.002(3)	0.011(3)	0.005(3)
C(34)	8*c*	0.6128(3)	0.1638(3)	–0.2068(3)	0.041(3)	0.049(3)	0.030(3)	0.015(3)	0.012(2)	0.005(3)
C(35)	8*c*	0.5461(3)	0.1359(3)	–0.2021(3)	0.052(4)	0.036(3)	0.030(3)	0.002(2)	0.004(3)	–0.007(2)
C(36)	8*c*	0.5044(3)	0.1534(3)	–0.1535(3)	0.035(3)	0.030(3)	0.039(3)	–0.002(2)	0.006(2)	–0.001(2)
C(41)	8*c*	0.3835(3)	0.2519(2)	0.1838(2)	0.030(3)	0.023(2)	0.023(2)	0.003(2)	–0.002(2)	–0.003(2)
C(42)	8*c*	0.3268(3)	0.2940(3)	0.2041(2)	0.040(3)	0.033(3)	0.032(3)	0.009(2)	–0.005(3)	–0.004(2)
C(43)	8*c*	0.3271(4)	0.3734(3)	0.1983(3)	0.059(4)	0.036(3)	0.049(4)	0.024(3)	–0.007(3)	–0.011(3)
C(44)	8*c*	0.3833(4)	0.4089(3)	0.1729(3)	0.088(5)	0.020(2)	0.039(3)	0.005(3)	–0.009(3)	–0.007(2)
C(45)	8*c*	0.4395(4)	0.3675(3)	0.1525(3)	0.071(4)	0.024(3)	0.042(3)	–0.012(3)	–0.002(3)	–0.002(2)
C(46)	8*c*	0.4404(3)	0.2892(3)	0.1576(2)	0.043(3)	0.022(2)	0.034(3)	–0.001(2)	0.004(2)	–0.005(2)
C(51)	8*c*	0.3388(2)	0.1126(3)	0.2478(2)	0.025(2)	0.027(2)	0.022(2)	0.000(2)	–0.000(2)	0.003(2)
C(52)	8*c*	0.3310(3)	0.1556(3)	0.2992(2)	0.033(3)	0.032(2)	0.023(2)	0.004(2)	–0.001(2)	–0.002(2)
C(53)	8*c*	0.3016(3)	0.1238(3)	0.3506(2)	0.033(3)	0.051(3)	0.024(3)	0.005(2)	0.006(2)	–0.004(2)
C(54)	8*c*	0.2812(3)	0.0489(3)	0.3511(2)	0.028(3)	0.057(3)	0.028(3)	0.000(2)	0.004(2)	0.014(3)
C(55)	8*c*	0.2916(3)	0.0049(3)	0.3006(2)	0.042(3)	0.040(3)	0.030(3)	–0.007(2)	–0.001(3)	0.008(2)
C(56)	8*c*	0.3200(3)	0.0358(3)	0.2490(2)	0.036(3)	0.036(3)	0.019(2)	–0.002(2)	–0.001(2)	0.001(2)
C(61)	8*c*	0.4723(2)	0.1200(2)	0.1934(2)	0.024(2)	0.021(2)	0.020(2)	0.004(2)	0.002(2)	0.002(2)
C(62)	8*c*	0.5112(3)	0.1592(3)	0.2356(2)	0.034(3)	0.040(3)	0.028(3)	0.008(2)	–0.005(2)	–0.016(2)
C(63)	8*c*	0.5774(3)	0.1349(3)	0.2523(3)	0.033(3)	0.053(3)	0.035(3)	0.005(2)	–0.009(3)	–0.016(3)
C(64)	8*c*	0.6054(3)	0.0703(3)	0.2271(2)	0.027(3)	0.043(3)	0.026(3)	0.009(2)	–0.004(2)	0.001(2)
C(65)	8*c*	0.5682(3)	0.0321(3)	0.1845(2)	0.031(3)	0.033(3)	0.037(3)	0.005(2)	–0.003(2)	–0.009(2)
C(66)	8*c*	0.5018(3)	0.0565(3)	0.1668(2)	0.031(3)	0.029(2)	0.031(3)	0.003(2)	–0.004(2)	–0.010(2)

Acknowledgments. The authors thank Mr Howard Lane for helpful discussions.

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