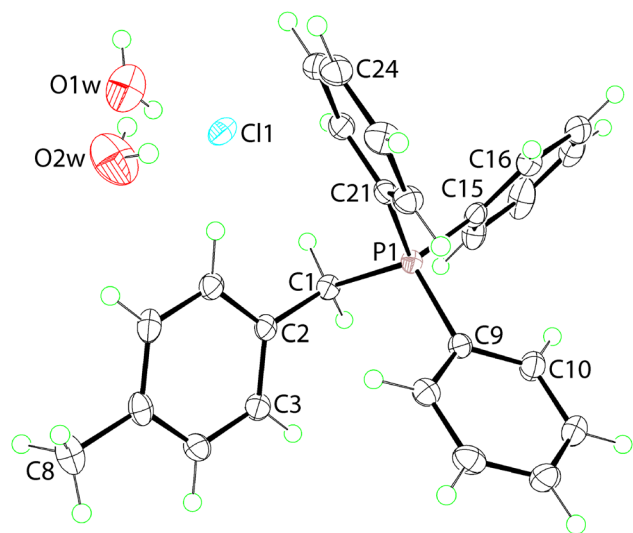


See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink*

Crystal structure of (4-methylbenzyl)(triphenyl) phosphonium chloride dihydrate, $C_{26}H_{28}ClO_2P$



<https://doi.org/10.1515/ncrs-2021-0305>
 Received July 25, 2021; accepted August 2, 2021;
 published online August 16, 2021

Abstract

$C_{26}H_{28}ClO_2P$, monoclinic, $P2_1/c$ (no. 14), $a = 11.6061(2)$ Å, $b = 19.7791(4)$ Å, $c = 11.1982(3)$ Å, $\beta = 116.278(3)^\circ$, $V = 2304.98(10)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0373$, $wR_{ref}(F^2) = 0.1034$, $T = 100$ K.

CCDC no.: 2100832

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

*Corresponding author: Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Medical and Life Sciences, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, E-mail: edwardt@sunway.edu.my. <https://orcid.org/0000-0003-1401-1520>

See Mun Lee and Kong Mun Lo, Research Centre for Crystalline Materials, School of Medical and Life Sciences, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Table 1: Data collection and handling.

Crystal:	Colourless slab
Size:	0.07 × 0.07 × 0.03 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	2.27 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	28,903, 4125, 0.046
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3707
$N(param)_{refined}$:	284
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

Triphenylphosphane (Sigma; 0.26 g, 1 mmol) and 4-methylbenzyl chloride (Sigma; 0.14 g, 1 mmol) were dissolved in ethanol (50 mL) and refluxed for 1 h. The mixture was filtered and colourless crystals of the phosphonium salt were isolated upon cooling to room temperature. Yield: 0.35 g (79.7%). **M.pt** (Stuart SMP30 digital melting point apparatus; uncorrected): 521–523 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm⁻¹): 1435 (m) $\nu(C=C)$, 745 (m) $\nu(P-C)$. **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer; CDCl₃; ppm relative to Me₄Si): 2.20 (s, 3H, CH₃), 2.32 (s, 2H, CH₂), 6.92–6.98 (m, 2H, Ph-H), 7.60–7.79 (m, 17H, Ph-H). **¹³C{¹H} NMR** (as for ¹H NMR): 21.1 (CH₃), 30.6 (CH₂), 117.7, 118.6, 128.7, 129.5, 130.1, 133.8, 134.4, 134.8 (Ph-C).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2$ – $1.5U_{eq}(C)$. The O-bound atoms were located from a Fourier difference map and refined with O–H = 0.84 ± 0.01 Å, and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Comment

The title salt dihydrate [(4-MeC₆H₄CH₂)Ph₃P]Cl·2H₂O, hereafter (I), was isolated as a side-product during the attempted synthesis of Ph₂(4-MeC₆H₄CH₂)P=O. The synthesis of the triorganophosphane oxide was motivated by

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
P1	0.66388 (4)	0.62657 (2)	0.69139 (4)	0.01562 (13)
C1	0.53839 (15)	0.56362 (8)	0.62594 (16)	0.0181 (3)
H1A	0.488854	0.570582	0.528740	0.022*
H1B	0.578488	0.518304	0.639929	0.022*
C2	0.44665 (15)	0.56506 (9)	0.68854 (16)	0.0181 (3)
C3	0.45914 (17)	0.51802 (9)	0.78584 (18)	0.0220 (4)
H3	0.526472	0.485627	0.813960	0.026*
C4	0.37377 (17)	0.51803 (9)	0.84239 (18)	0.0250 (4)
H4	0.383334	0.485295	0.908223	0.030*
C5	0.27468 (16)	0.56510 (10)	0.80426 (18)	0.0245 (4)
C6	0.26274 (17)	0.61190 (9)	0.70622 (19)	0.0247 (4)
H6	0.195757	0.644485	0.678457	0.030*
C7	0.34649 (16)	0.61184 (9)	0.64849 (18)	0.0221 (4)
H7	0.335655	0.643889	0.581136	0.026*
C8	0.1828 (2)	0.56619 (12)	0.8659 (2)	0.0354 (5)
H8A	0.100682	0.546195	0.803840	0.053*
H8B	0.168808	0.612995	0.885039	0.053*
H8C	0.218968	0.540070	0.948795	0.053*
C9	0.76373 (16)	0.61595 (9)	0.86637 (16)	0.0184 (3)
C10	0.89132 (17)	0.59634 (10)	0.90970 (18)	0.0257 (4)
H10	0.923365	0.587040	0.846684	0.031*
C11	0.97153 (18)	0.59042 (11)	1.04496 (19)	0.0306 (4)
H11	1.058342	0.576716	1.074672	0.037*
C12	0.92509 (19)	0.60443 (11)	1.13577 (18)	0.0292 (4)
H12	0.980914	0.601543	1.228316	0.035*
C13	0.79764 (19)	0.62274 (10)	1.09400 (18)	0.0265 (4)
H13	0.766302	0.631436	1.157797	0.032*
C14	0.71579 (17)	0.62837 (9)	0.95883 (18)	0.0212 (4)
H14	0.628269	0.640524	0.929678	0.025*
C15	0.76258 (15)	0.61944 (9)	0.60550 (16)	0.0202 (4)
C16	0.82950 (17)	0.67681 (10)	0.59720 (19)	0.0269 (4)
H16	0.820107	0.718574	0.633867	0.032*
C17	0.90950 (18)	0.67232 (12)	0.5352 (2)	0.0354 (5)
H17	0.955360	0.710977	0.529450	0.042*
C18	0.92226 (19)	0.61126 (14)	0.48177 (19)	0.0391 (6)
H18	0.976638	0.608362	0.438773	0.047*
C19	0.85674 (19)	0.55441 (13)	0.4902 (2)	0.0392 (5)
H19	0.866171	0.512915	0.452723	0.047*
C20	0.77716 (17)	0.55769 (11)	0.55335 (19)	0.0291 (4)
H20	0.733412	0.518531	0.560840	0.035*
C21	0.59354 (15)	0.70929 (9)	0.65839 (17)	0.0180 (3)
C22	0.62428 (17)	0.75873 (9)	0.75636 (18)	0.0228 (4)
H22	0.685891	0.749612	0.845119	0.027*
C23	0.56456 (19)	0.82130 (9)	0.72372 (19)	0.0277 (4)
H23	0.584550	0.854895	0.790610	0.033*
C24	0.47593 (18)	0.83508 (9)	0.5941 (2)	0.0273 (4)
H24	0.434812	0.877940	0.572573	0.033*
C25	0.44696 (17)	0.78643 (9)	0.49561 (19)	0.0251 (4)
H25	0.387264	0.796395	0.406493	0.030*
C26	0.50479 (16)	0.72345 (9)	0.52682 (17)	0.0213 (4)
H26	0.484478	0.690042	0.459540	0.026*
Cl1	0.30604 (4)	0.59515 (2)	0.28603 (4)	0.02762 (14)
O1W	0.14804 (17)	0.71168 (10)	0.35340 (19)	0.0513 (4)
H1W	0.194 (3)	0.6779 (11)	0.352 (3)	0.062*
H2W	0.125 (3)	0.7319 (14)	0.2784 (18)	0.062*

Table 2: (continued)

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
O2W	0.1720 (2)	0.77086 (9)	0.6001 (2)	0.0559 (5)
H3W	0.177 (3)	0.7648 (17)	0.5277 (19)	0.067*
H4W	0.225 (2)	0.8002 (13)	0.647 (3)	0.067*

on-going structural studies characterising R₃P=O adducts of various organotin halides [5, 6].

The molecular structures of the 4-methylbenzyl-(triphenyl)phosphonium cation, the chloride anion and two molecules of water of crystallisation comprising the asymmetric unit of (I) are shown in the figure (50% displacement ellipsoids). The P–C bond lengths lie in a narrow range, i.e. from 1.7924(17) Å [P1–C21] to 1.8065(17) [P1–C1]. Similarly, the tetrahedral angles lie in a narrow range, i.e. from 107.53(8)° [C15–P1–C21] to 112.18(8)° [C1–P1–C9]. No specific trends in the geometric parameters are correlated with the methylene-C1 atom. Finally, the sequence of C(x)–P1–C1–C2 torsion angles is 60.99(14), –178.98(12) and –61.83(14)° for x = 9, 15 and 21, respectively, and indicate +syn-clinal, –anti-periplanar and +syn-clinal conformations, respectively.

There are four crystal structures available in the literature featuring the 4-methylbenzyltriphenylphosphonium cation giving a total of six independent cations [7–10]. The +syn-clinal, –anti-periplanar and +syn-clinal conformations noted for (I) match those in the literature precedents.

Significant conventional hydrogen bonding interactions are apparent in the crystal of (I). The O1w- and O2w-water molecules form similar donor interactions, namely to the chloride and to the other water molecule [O1w–H1w···Cl1: H1w···Cl1 = 2.40(3) Å, O1w···Cl1 = 3.236(2) Å with angle at H1w = 164(3)°; O1w–H2w···O2wⁱ: H2w···O2wⁱ = 2.29(3) Å, O1w···O2wⁱ = 2.990(3) Å with angle at H2w = 139(3)°; O2w–H3w···O1w: H3w···O1w = 2.11(2) Å, O2w···O1w = 2.898(3) Å with angle at H3w = 155(3)°; and O2w–H4w···Cl1ⁱⁱ: H4w···Cl1ⁱⁱ = 2.51(3) Å, O2w···Cl1ⁱⁱ = 3.3031(19) Å with angle at H4w = 158(2)° for symmetry operations (i) x, 3/2–y, –1/2+z and (ii) x, 3/2–y, 1/2+z]. The hydrogen bonds occur within chains comprising chloride and water molecules along the c-axis; the chain has a zig-zag topology, being propagated by glide symmetry. Connections between the chains and cations within the three-dimensional architecture are of the type methylene-C–H···Cl, phenyl-C–H···Cl and phenyl-C–H···O (water) which are all weak.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: Crystallographic research at Sunway University is supported by Sunway University Sdn Bhd (Grant No. GRTIN-IRG-08-2021).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Rigaku Oxford Diffraction. CrysAlis^{PRO}; Rigaku Corporation: Oxford, UK, 2018.
2. Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
3. Sheldrick G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Farrugia L. J. WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* 2012, *45*, 849–854.
5. Lee S. M., Lo K. M., Tiekink E. R. T. Crystal structure of dichlorido-bis(tri-4-tolylphosphane oxide- κO)- di(4-chlorophenyl- κC)tin(IV), $C_{54}H_{50}Cl_4O_2P_2Sn$. *Z. Kristallogr. NCS* 2020, *235*, 1523–1525.
6. Lee S. M., Lo K. M., Tiekink E. R. T. Crystal structure of dichloridodimethylbis(tri-4-tolylphosphane oxide- κO)-tin(IV), $C_{44}H_{48}Cl_2O_2P_2Sn$. *Z. Kristallogr. NCS* 2020, *235*, 1527–1529.
7. Chen G., Cao C. Hydrothermal synthesis and structural characterization of a zigzag-chain polymer of $\{[p\text{-MeBz}(\text{Ph}_3\text{P})[\text{ZnCl}_2(\text{NA})]]\}_n$ (NA = nicotinic acid). *J. Coord. Chem.* 2008, *61*, 262–269.
8. Hołyńska M., Lis T., Dehnen S., Weigend F. Reduction of rhenates(VII) with hydrogen chloride in alcohols: the structural aspects of the trans-tetrachloridomethoxido-oxidorhenate(VI) products. *Inorg. Chim. Acta* 2014, *411*, 26–29.
9. Hołyńska M., Lis T. Decomposition of pentachloridooxidorhenates(VI) - a still underinvestigated source of rhenium complexes at different oxidation states. *Inorg. Chim. Acta* 2014, *419*, 96–104.
10. Ahmad J., Abdul Halim S. N., How F. N.-F. Crystal structure of benzyltriphenylphosphonium chloride monohydrate. *Acta Crystallogr.* 2015, *E71*, o410–o411.