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Triferrocenylphosphine oxide monohydrate

Alfred Muller, Gideon Steyl and Andreas Roodt*

Department of Chemistry and Biochemistry, Rand Afrikaans University, Auckland Park, Johannesburg, South Africa 2006
Correspondence e-mail: aroo@rau.ac.za

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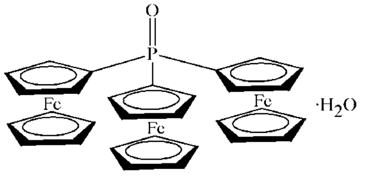
The title compound, $[Fe_3(C_5H_5)_3(C_{15}H_{12}OP)]\cdot H_2O$ or $Fc_3PO\cdot H_2O$, was obtained as red crystals from the Friedel–Crafts alkylation reaction of PCl_3 and ferrocene. Torsion angles (O=P—C—Fe/C) range from −45.39 (9) to −56.11 (14)°. The structure is stabilized by intermolecular hydrogen bonds [H⋯O = 2.10 (3) and 2.00 (4) Å], forming dimeric structures between pairs of $O{=}PFc_3$ and water molecules. A theoretical Tolman cone angle of 211° was calculated.

Comment

As part of a systematic investigation into the steric demand of phosphine ligands in various model Pt-group metal complexes, we have unexpectedly isolated crystals of triferrocenylphosphine oxide ($Fc_3P{=}O$), (I), previously reported but not structurally characterized by Sollot & Howard (1962). The yellow crystalline solid obtained was at first thought to be unoxidized PFc_3, and was tested in reaction with $[Rh(Cl)(CO)_2]_2$ in an attempt to synthesize the well known $[MCl(CO)(XY_3)_2]$ Vaska-type complexes (*M* is Rh or Ir, *X* is P, As or Sb, and *Y* is aryl or alkyl), which often crystallize with ease. However, no reaction was observed (IR and ^{31}P NMR spectroscopy) and crystals, now red in colour, were isolated from the mixture. The spectroscopic data of these were similar to those of the yellow crystalline compound (see *Experimental*). The change in colour can probably be attributed to the variation in solvent between the two synthetic steps, resulting in different packing effects.



(I)

Compound (I) (Fig. 1) is one of the few structures characterized to date containing the PFc_3 moiety [Cambridge Structural Database (CSD), Version 5.25 of 2004; Allen, 2002]. Usually, ferrocenyl fragments possess geometric parameters similar to those of ferrocene and its derivatives. In the case of (I), all the cyclopentadienyl (Cp) rings are planar to within 0.003 Å and the interplanar angles are 3.53 (19), 2.37 (12) and 2.19 (12)° for the Fe1, Fe2 and Fe3 moieties, respectively. Furthermore, the Cp rings in each ferrocenyl moiety have an almost eclipsed conformation.

Pairs of $O{=}PFc_3$ molecules are linked *via* O—H⋯O hydrogen bonds to water molecules, forming a dimeric structure around an inversion centre (Table 2 and Fig. 2). This interaction creates channels along the *c* axis (Fig. 2). The use of water as a hydrogen bridge in the solid state in phosphine oxide compounds is not uncommon, but few form dimeric structures in the unit cell (*ca* 10% in the CSD). These compounds mostly consist of either ferrocene or electron-donating (Krauss *et al.*, 2001) functionalized variations thereof. Thus, electron-rich phosphorus(V) oxides might assist in the formation of dimeric structures. The same hydrogen-bonding pattern is observed for the structure of $O{=}PFc_2Et\cdot H_2O$ (Durfey *et al.*, 2002).

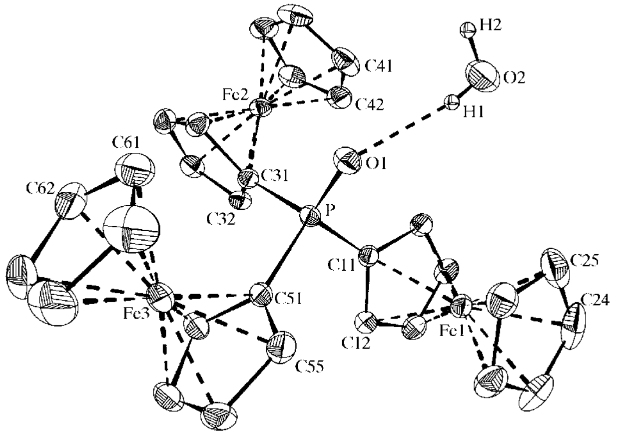


Figure 1
The structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity. For the C atoms, the first digit indicates the ring number and the second digit indicates the number of the atom in the ring.

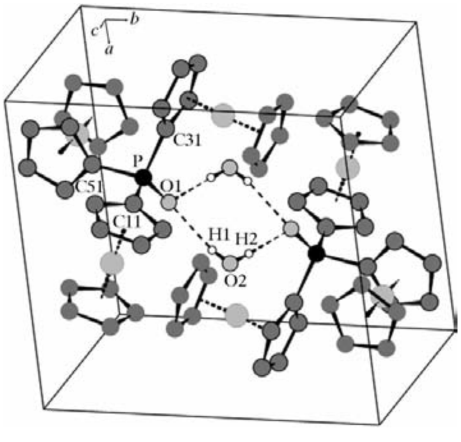


Figure 2
A packing diagram for (I), illustrating the interactions between pairs of $O{=}PFc_3$ and water molecules.

The conformation of the ferrocene substituents in (I) can be described by the torsion angles between the O═P moiety and ferrocene, which are compared in Table 3 with those of other compounds containing PFc_3 fragments. It is important to note that none of the compounds has torsion angles close to 0°, illustrating few or no intramolecular interactions between X—P and ferrocene, which was postulated as an option for a possible geometrical conformation of (I) (Sollot & Howard, 1962). The ferrocenyl moieties are staggered in such a way that atoms O1 and P are both above the plane formed by the three Fe atoms [1.8424 (16) and 0.3499 (5) Å for O1 and P, respectively].

Three different methods have been investigated to estimate the torsion angles of the ferrocenyl moiety for comparison with reported torsion angles in the literature (Steyl *et al.*, 2001). These include O—P—*Cg*1—*Cg*2, O—P—C—Fe and O—P—C—C (*Cg* is the centroid of ring 1 or 2). The torsion angles O—P—*Cg*1—*Cg*2 and O—P—C—Fe yield similar values, while the other method gives *ca* 5° difference, because of the almost eclipsed conformation of the Cp rings.

The most widely used parameter to define the steric demand of tertiary phosphines is the Tolman cone angle (θ_T), which was calculated as described previously (Tolman, 1977; Otto *et al.*, 2000). A modified structure of (I) was used to calculate a reasonable value for the expected Tolman cone angle, by incorporating a dummy atom 2.28 Å from the P atom. A somewhat larger value of 211° was obtained for (I) compared with the other known PFc_3 structures (Table 3). This value may not necessarily be a true reflection of the steric influence on a given metal centre, since the flexibility of ferrocenyl moieties around the P—C bond can significantly affect this value. This was found previously with similar flexible phosphines, *e.g.* tribenzylphosphine (Muller *et al.*, 2002) and ferrocenyldiphenylphosphine (Otto *et al.*, 2000). The structures of I—PFc_3 and H_2C═PFc_3 are examples where the ferrocenyl fragments have different orientations with respect to the X—P moieties (torsion angles given in Table 3) but still possess similar cone angles.

Experimental

The title compound was prepared according to a modified version of the published procedure of Sollot & Howard (1962). Ferrocene (30 g, 0.16 mol) and freshly sublimed $AlCl_3$ (4.33 g, 0.032 mol) were added to degassed heptane (100 ml) in a vessel equipped with a reflux condenser and a dropping funnel containing PCl_3 (2.84 ml, 0.03262 mol) in degassed heptane (100 ml). The solution in the dropping funnel was added to the mixture over a period of 1 h, after which the mixture was refluxed (*ca* 373 K) for 24 h. The mixture was then decanted and the remaining solids extracted successively with hot benzene and water. The combined benzene extracts were dried (Na_2SO_4) and the remaining solid purified by column chromatography [acetone–$CHCl_3$, 1:4; R_F(O═PFc_3) = 0.3]. Purified (I) crystallized as yellow crystals by slow evaporation from the acetone–chloroform solution (yield 0.5 g, 2.6%). Red crystals of (I) were obtained from the reaction of $[Rh(Cl)(CO)_2]_2$ and (I) (1:4 molar ratio) in dichloromethane. Spectroscopic data, ^{1}H NMR ($CDCl_3$, 300 MHz): 4.08 p.p.m. (*d*, 27 H); ^{31}P{H} NMR ($CDCl_3$, 121.46 MHz): 30.3 p.p.m. (*s*).

Crystal data

$[Fe_3(C_5H_5)_3(C_{15}H_{12}OP)]\cdot H_2O$
$M_r = 620.05$
Triclinic, $P\overline{1}$
$a = 10.010$ (2) Å
$b = 11.900$ (2) Å
$c = 11.920$ (2) Å
$\alpha = 76.51$ (3)°
$\beta = 70.23$ (3)°
$\gamma = 78.13$ (3)°
$V = 1286.8$ (5) Å^3
$Z = 2$
$D_x = 1.60$ Mg m^{-3}
$D_m = 1.585$ Mg m^{-3}
D_m measured by flotation in aqueous NaI
Mo $K\alpha$ radiation
Cell parameters from 966 reflections
$\theta = 3$–28°
$\mu = 1.76$ mm^{-1}
$T = 293$ (2) K
Cuboid, red
0.40 × 0.24 × 0.18 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min} = 0.583$, $T_{max} = 0.728$
8973 measured reflections
6181 independent reflections
5233 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 28.3°$
$h = -10 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R(F) = 0.028$
$wR(F^2) = 0.073$
$S = 1.03$
6181 reflections
333 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.4474P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P—O1	1.4941 (15)	P—C51	1.7872 (17)
P—C31	1.7846 (19)	P—C11	1.7879 (18)
O1—P—C31	114.50 (9)	O1—P—C11	113.96 (8)
O1—P—C51	113.87 (9)		
C21—C11—P—O1	−45.39 (9)	Fe1—C11—P—O1	−49.29 (13)
C41—C31—P—O1	−51.27 (10)	Fe2—C31—P—O1	−56.11 (14)
C61—C51—P—O1	−50.69 (10)	Fe3—C51—P—O1	−54.49 (14)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1···O1	0.75 (3)	2.10 (3)	2.843 (3)	167 (3)
O2—H2···O1^i	0.86 (4)	2.00 (4)	2.860 (3)	178 (4)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Aromatic H atoms were placed in geometrically idealized positions (C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. The positions of the water H atoms were determined from a Fourier difference map and their coordinates were refined isotropically.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 3
Comparative geometrical data for *X*PFc$_3$ (°, Å).

$\theta_{\rm tor1} = X{-}{\rm P}{-}Cg1{-}Cg2$; $\theta_{\rm tor2} = X{-}{\rm P}{-}{\rm C}{-}{\rm Fe}$; $\theta_{\rm tor3} = X{-}{\rm P}{-}{\rm C}{-}{\rm C}$; θ_T is the Tolman cone angle (Tolman, 1977); *Cg* is the centroid of ring 1 or 2.

X	Fe—*X*	$\theta_{\rm tor1}$	$\theta_{\rm tor2}$	$\theta_{\rm tor3}$	θ_T	Reference
O	1.4941 (15)	−47.6	−49.3	−45.4	211	*a*
		−55.2	−56.2	−51.3		
		−54.6	−54.4	−50.6		
I	2.426 (12)	−46.3	−47.3	−45.4	198	*b*
		−162.0	−161.2	−167.6		
		−49.2	−49.3	−52.0		
CH$_2$	1.630	56.3	57.2	51.5	200	*c*
		63.5	62.7	58.8		
		64.5	64.3	61.3		

References: (*a*) this work; (*b*) Gridunova *et al.* (1982); (*c*) Schmidbaur *et al.* (1989).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1629). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Brandenburg, K. (2001). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.

Bruker (1998). *SADABS* (Version 2004/1) and *SMART-NT* (Version 5.050). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SAINT-Plus.* Version 6.02 (including *XPREP*). Bruker AXS Inc., Madison, Wisconsin, USA.

Durfey, D. A., Kirss, R. U., Churchill, M. R., Keil, K. M. & Feighery, W. (2002). *Synth. React. Inorg. Met. Org. Chem.* **32**, 97–115.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Gridunova, G. V., Shklover, V. E., Struchkov, Yu. T., Vil'chevskaya, V. D., Podobedova, N. L. & Krylova, A. I. (1982). *J. Organomet. Chem.* **238**, 297–305.

Krauss, B., Mugge, C., Ziemer, B., Zschunke, A. & Krech, F. (2001). *Z. Anorg. Allg. Chem.* **627**, 1542–1552.

Muller, A. J., Roodt, A., Otto, S., Oskarsson, Å. & Yong, S. (2002). *Acta Cryst.* E**58**, m715–m717.

Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta*, **303**, 295–299.

Schmidbaur, H., Jeong, J., Schier, A., Graf, W., Wilkinson, D. L. & Muller, G. (1989). *New J. Chem.* (*Nouv. J. Chim.*), **13**, 341–352.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Sollot, G. P. & Howard, E. (1962). *J. Org. Chem.* **27**, 4034–4040.

Steyl, G., Otto, S. & Roodt, A. (2001). *Acta Cryst.* E**57**, m352–m354.

Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.