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A New Modification of 1,1′-Bis(diphenylphosphine oxide)ferrocene at 173 K

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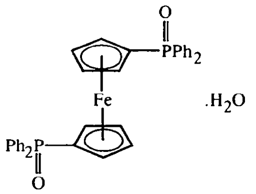
Abstract

A new modification, namely the monohydrate, of 1,1′-ferrocenediylbis(diphenylphosphine oxide), $[Fe(C_{17}H_{14}OP)_2].H_2O$, is reported. In contrast to the structure without solvent and to the dihydrate, the molecule in the monohydrate is not centrosymmetric and the cyclopentadienyl (Cp) rings are almost eclipsed. The intermolecular packing is stabilized by hydrogen bonds between the water molecule and the phosphine O atoms.

Comment

Pd^0 complexes are known to catalyze the oxidation of phosphines by oxygen (Wilke, Schott & Heimbach, 1967). In a search for a method to decomplex diastereomerically pure pallada-tricyclo[4.1.0.0^{2,4}]heptane–DIOP complexes and thus obtain enantiomerically pure pallada-tricycloheptanes (PTHs) (Hashmi *et al.*, 1997), we carried out an explorative experiment in which we succeeded in oxidizing 1,1′-bis(diphenylphosphino)ferrocene with PTH/air. An X-ray analysis of the obtained 1,1′-bis(diphenylphosphine oxide)ferrocene showed a different modification than those reported by Pilloni *et al.* (1993), who determined the dihydrate, and by Munyejabo *et al.* (1994) and Fang *et al.* (1995) who determined the crystal structure of $[Fe(C_{17}H_{14}OP)_2]$ without any solvent. We report here the crystal structure of the monohydrate, (I), of $[Fe(C_{17}H_{14}OP)_2]$.



(I)

In contrast to the published structures, where the Fe atom is located on a crystallographic inversion centre, the molecule of the title compound is not centrosymmetric. Bond lengths and angles of the title compound are in the same range as in $[Fe(C_{17}H_{14}OP)_2]$ and $[Fe(C_{17}H_{14}OP)_2].2H_2O$, but a major difference is that the Cp rings in the title compound are almost eclipsed. The difference to the exactly eclipsed conformation is a rotation by approximately 14° along the axis connecting the two ring centres. In the other structures, the Cp rings are staggered due to the C_i symmetry of these molecules. The angle between the two Cp rings is 1.9 (2)°. One of the phenyl rings is disordered, displaying two different rotamers along the P2—C61 bond. Nevertheless, the angles between the Cp and phenyl rings [60.9 (1) and 86.9 (2)°, and 62.6 (2) and 83.3 (2)/96.1 (3)°] are in the same range as in $[Fe(C_{17}H_{14}OP)_2].2H_2O$ (63.2 and 91.5°), but they differ from those in $[Fe(C_{17}H_{14}OP)_2]$ (58.6 and 69.7°). The main difference between all these structures is the number of solvent water molecules and the hydrogen-bond pattern. In $[Fe(C_{17}H_{14}OP)_2].2H_2O$, the diphenylphosphine–ferrocene molecules are bridged by two water molecules, so that each free electron pair of the phosphine O atom is bonded to one H atom. On the other hand, there is only one water molecule connecting two diphenylphosphine–ferrocene molecules in the title compound [H1*W*···O1 1.78 (7), O1*W*···O1 2.766 (5) Å and O1*W*—H1*W*···O1 172 (6)°; H2*W*···O2^{i} 1.92 (5) Å, O1*W*···O2^{i} 2.756 (6) Å and O1*W*—H2*W*···O2^{i} 164 (5)°; symmetry code: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$].

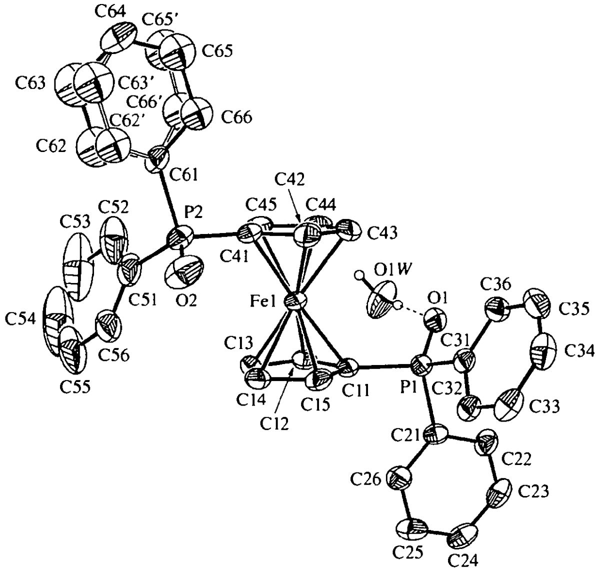


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level; only hydroxyl H atoms are shown.

Experimental

5-[1,1′-Bis(diphenylphosphino)ferrocenepallada]-1,2,4,6-tetra(carboethoxy)-3,3,7,7-tetramethyl-*anti*-tricyclo[4.1.0.0^{2,4}]heptane (20.2 mg, 18.6 µmol) was dissolved in 2 ml of a 1:1 wet acetone/dichloromethane mixture and exposed to air. After 1 d, 8.2 mg (75%) of 1,1′-bis(diphenylphosphine oxide)ferrocene were obtained as red–brown crystals.

Crystal data

[Fe($C_{17}H_{14}OP$)$_2$].H_2O
M_r = 604.37
Monoclinic
$P2_1/c$
a = 22.5535 (1) Å
b = 10.4998 (1) Å
c = 12.1717 (2) Å
β = 96.116 (1)°
V = 2865.94 (6) Å^3
Z = 4
D_x = 1.401 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 1–25°
μ = 0.672 mm^{-1}
T = 173 K
Cylinder
0.40 × 0.15 × 0.10 mm
Red–brown

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996*a*)
$T_{\min}$ = 0.778, $T_{\max}$ = 0.935
28 822 measured reflections
5287 independent reflections

3907 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.075
$\theta_{\max}$ = 26.32°
$h = -27 \rightarrow 27$
$k = -12 \rightarrow 13$
$l = -14 \rightarrow 13$
254 standard reflections
frequency: 480 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.074
$wR(F^2)$ = 0.142
S = 1.123
5287 reflections
366 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 7.705P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.005
$\Delta\rho_{\max}$ = 0.498 e Å^{-3}
$\Delta\rho_{\min}$ = −0.536 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

The data collection nominally covered over a sphere of reciprocal space, by a combination of seven sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 6.0 cm. Coverage of the unique set was over 99% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. The H atoms attached to the ordered C atoms and the hydroxyl H atoms could be located by difference Fourier synthesis; the disordered atoms being positioned with ideal geometry. While the two hydroxyl H atoms were refined isotropically, the others were refined with fixed individual displacement parameters [U(H) = 1.2$U_{\rm eq}$(C)] using a riding model with C—H = 0.95 Å. The ratio of the site occupation factors of the disorded atoms (C62, C63, C65 and C66) refined to 0.53 (1).

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996*b*). Molecular graphics: *XP* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1015). Services for accessing these data are described at the back of the journal.

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Redetermination of Bis(2-aminopyrimidinium) Tetrabromocopper(II) at 200 and 100 K

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Abstract

The structure of ($C_4H_6N_3$)$_2$[$CuBr_4$] has been studied using X-ray diffraction techniques at 200 and 100 K. The molecular structure has ideal square-planar [$CuBr_4$]$^{2-}$ groups, bonded to protonated organic mol-