from difference maps, with the O—H bond length adjusted to 0.85 Å. The remaining H atoms were placed at calculated positions with C—H = 0.95 Å.

This work was supported by Department of Veterans Affairs research funds.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71603 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1021]

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1,1′-Bis(diphenylphosphine oxide)ferrocene Dihydrate

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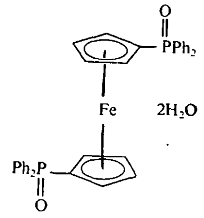
Abstract

The title compound, 1,1′-ferrocenediylbis(diphenylphosphine oxide) dihydrate, $[Fe(C_{17}H_{14}OP)_2].2H_2O$, was obtained by oxidation of bis(diphenylphosphino)ferrocene with trimethylamine oxide. The Fe atom sits on a molecular centre of symmetry and the two Cp rings are planar with a staggered configuration. The two phosphoryl groups are *trans* with respect to the $Fe(Cp)_2$ group.

Comment

In our search for ligands that might play some important part in electronic assistance (Munyejabo, Postel, Bensimon & Roustan, 1993), we became interested in ferrocenyl phosphines and phosphine oxides because of the easily accessible ferrocene–ferricinium redox couple. Ferrocenyl phosphines, because of their peculiarly large bite angle, have been studied extensively but, surprisingly, the structure of 1,1′-bis(diphenylphosphine)ferrocene was published only recently (Casellato, Ajo, Valle, Corain, Longato & Graziani, 1988). Data for the corresponding oxides are rather scarce. The $[CpFe\{CpP(O)Ph_2\}]$ and $[CpFe\{\eta^5\text{-}C_5H_3(CHMeNMe_2)P(O)Ph_2\}]$ monooxides have been obtained through the reaction of ferrocenylphosphines with $[Cp_2Co(CO)_2]$ and were structurally characterized by X-ray analyses (Kim, Lee, Kwon, Uhm, Lee & Byun, 1991). In order to gain further information on this type of phosphoryl ligand, we performed a structural study of 1,1′-bis(diphenylphosphine oxide)ferrocene dihydrate, $Fe[C_5H_4P(O)(C_6H_5)_2]_2.2H_2O$ (1).



(1)

The molecular structure of (1) together with the atom labelling is illustrated in Fig. 1. The Fe atom in (1) lies on a crystallographic inversion centre; the molecule as a whole is centrosymmetric and the asymmetric unit is represented by a half molecule. The distance of the Fe atom from the plane of the cyclopentadienyl ring is 1.66 Å.

In the solid state (1) has a staggered structure. The five-membered rings do not deviate significantly from planarity. The pattern of bond distances within the cyclopentadienyl rings shows substituent-induced geometrical distortions with a mean C—C bond length for the P═O substituted C atoms of 1.426 Å. The adjacent C—C bonds average 1.412 Å, while the unique C—C bond is 1.423 (7) Å.

Bond lengths and angles involving the P atoms compare well with the values reported for the $[CpFe\{CpP(O)Ph_2\}]$ and $[CpFe\{\eta^5\text{-}C_5H_3(CHMeNMe_2)P(O)Ph_2\}]$ monooxides (Kim, Lee, Kwon, Uhm,

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Lee & Byun, 1991), with C—P—O angles between 111.36 (15) and 113.44 (15)° and a P=O bond length of 1.495 (2) Å.

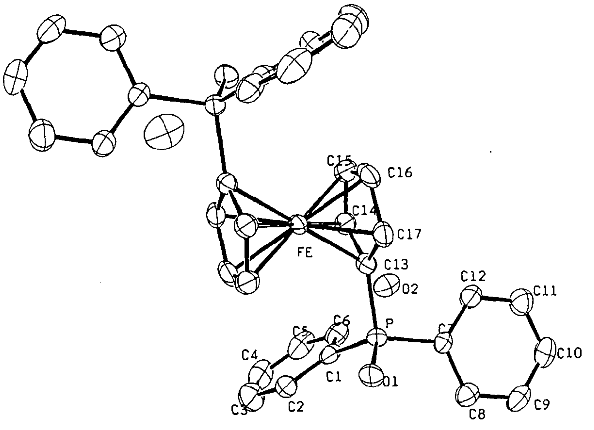

Fig. 1. *ORTEP* (Johnson, 1965) drawing of (1) showing the atom-labelling scheme.

Experimental

Crystal data

$[Fe(C_{17}H_{14}OP)_2].2H_2O$
M_r = 622.41
Monoclinic
$P2_1/n$
a = 8.792 (4) Å
b = 15.822 (3) Å
c = 10.979 (3) Å
β = 106.232 (22)°
V = 1466.4 $Å^3$
Z = 2
D_x = 1.41 Mg m^{-3}

D_m = 1.410 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 20–25°
μ = 1.30 mm^{-1}
T = 153 K
0.3 × 0.2 × 0.2 mm
Amber

Data collection

Rigaku diffractometer
ω-2θ scans
Absorption correction: none
2753 measured reflections
2576 independent reflections
2023 observed reflections [$I > 2.5\sigma(I)$]
R_{int} = 0.045

θ_{max} = 24.95°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 13$
3 standard reflections monitored every 150 reflections intensity variation: 3.2%

Refinement

Refinement on F
R = 0.040
wR = 0.023
S = 3.15
2023 reflections
252 parameters
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$ = 0.096
$\Delta\rho_{max}$ = 0.320 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.370 e $Å^{-3}$

Extinction correction: Larson (1970)
Extinction coefficient: 0.29579
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Fe	0.5	0.5	0.0	1.97 (3)
P	0.54330 (11)	0.35522 (6)	0.23792 (8)	1.93 (4)
O1	0.5041 (3)	0.41433 (14)	0.3309 (2)	2.53 (12)
O2	0.1165 (3)	0.9268 (2)	−0.0485 (3)	3.89 (16)
C1	0.7555 (4)	0.3430 (2)	0.2636 (3)	2.33 (17)
C2	0.8552 (5)	0.4036 (3)	0.3388 (3)	2.92 (19)
C3	1.0190 (5)	0.3977 (3)	0.3569 (4)	4.1 (2)
C4	1.0776 (5)	0.3354 (3)	0.2976 (5)	4.5 (3)
C5	0.9815 (5)	0.2748 (3)	0.2221 (4)	3.9 (2)
C6	0.8169 (5)	0.2780 (3)	0.2053 (4)	3.0 (2)
C7	0.4606 (4)	0.2516 (2)	0.2454 (3)	2.08 (17)
C8	0.4729 (4)	0.2162 (3)	0.3645 (3)	2.67 (19)
C9	0.4015 (5)	0.1385 (3)	0.3720 (4)	3.3 (2)
C10	0.3186 (5)	0.0960 (3)	0.2644 (4)	3.5 (2)
C11	0.3082 (5)	0.1304 (3)	0.1464 (4)	3.5 (2)
C12	0.3791 (5)	0.2069 (2)	0.1373 (3)	2.88 (19)
C13	0.4647 (4)	0.3875 (2)	0.0772 (3)	1.94 (17)
C14	0.5257 (5)	0.3741 (2)	−0.0285 (3)	2.5 (2)
C15	0.4217 (5)	0.4084 (2)	−0.1382 (3)	3.1 (2)
C16	0.2923 (5)	0.4435 (3)	−0.1013 (4)	3.8 (2)
C17	0.3164 (5)	0.4300 (2)	0.0305 (4)	2.58 (18)
HO1	0.077 (5)	0.915 (2)	0.033 (4)	7.4 (14)
HO2	0.070 (5)	0.976 (3)	−0.090 (4)	8.9 (17)

Table 2. *Selected geometric parameters* (Å, °)

Fe···Cp*	1.6592 (2)	C13—C14	1.424 (5)
P—O1	1.495 (2)	C13—C17	1.429 (5)
P—C1	1.818 (4)	C14—C15	1.402 (6)
P—C7	1.805 (4)	C15—C16	1.423 (7)
P—C13	1.780 (3)	C16—C17	1.419 (6)
O1—P—C1	112.56 (15)	C1—P—C7	107.77 (16)
O1—P—C7	111.36 (15)	C1—P—C13	106.37 (16)
O1—P—C13	113.44 (15)	C7—P—C13	104.86 (16)

* Distance of Fe from the centroid of the Cp ring.

The title compound, (1), was prepared by the reaction of 1,1′-bis(diphenylphosphine)ferrocene with trimethylamine oxide following the published procedure of Bouvier, Dupart, Grand & Riess (1987). Crystals suitable for X-ray diffraction were obtained by diffusion of toluene into a CH_2Cl_2 solution of (1) at 277 K.

The space group was determined based on systematic absences. The data were corrected for Lorentz and polarization effects (Grant & Gabe, 1978). The structure was solved by direct methods. All the atoms were refined anisotropically except for the H atoms which were calculated assuming a distance of 1.07 Å. All calculations were performed using the *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) crystallographic software package.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry including H-atom geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71543 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1055]

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Di-μ-fluoro-bis[bis(dimethyl sulfoxide)-trifluorozirconium(IV)]

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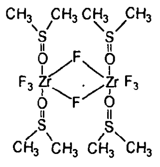
Abstract

The title compound, $[ZrF_4(C_2H_6OS)_2]_2$, is a centrosymmetric fluorine-bridged dimer. The seven-coordinate Zr atoms are in a pentagonal bipyramidal environment with F atoms above and below the pentagonal plane. The average Zr—F bridging distance of 2.167 (4) Å is significantly longer than the terminal distances which range from 1.973 (4) to 2.001 (4) Å.

Comment

Dimethyl sulfoxide (DMSO) is known to be both a good ligand and solvent for metal compounds (Reynolds, 1970). For the Group 4 elements (Ti, Zr, Hf) several adducts are known, for example MF_4.2DMSO (M = Ti, Zr) (Muetterties, 1960), $TiCl_4$.2DMSO (Schläfer & Schaffernicht, 1960) and $ZrCl_4$.2(or 3)DMSO (Makhija & Westland, 1978), together with several solvates such as $ZrCl_4$.9DMSO (Schläfer & Wille, 1965). Suprisingly there is no definitive structural information for any of these adducts. An earlier IR investigation (Clark & Errington, 1967) of the 1:2 adduct formed between ZrF_4 and dimethyl sulfoxide was inconclusive; the three observed Zr—F stretching modes suggested that the complex has low symmetry and eliminated the *trans*-octahedral structure. The present study of the dimethyl sulfoxide adduct (I) establishes a centrosymmetric dimeric structure with fluorine bridges (see Fig. 1). Each Zr atom is seven-coordinated with a pentagonal bipyramidal stereochemistry, F3 and F4 being in axial sites. The Zr—F bridging bonds [2.180 (4) and 2.153 (4) Å] are significantly longer than the terminal bonds [1.973 (4), 1.983 (4) and 2.001 (4) Å]. The dimethyl sulfoxide ligands coordinate to the Zr *via* their O atoms [Zr—O 2.216 (5) and 2.217 (5) Å].



(I)

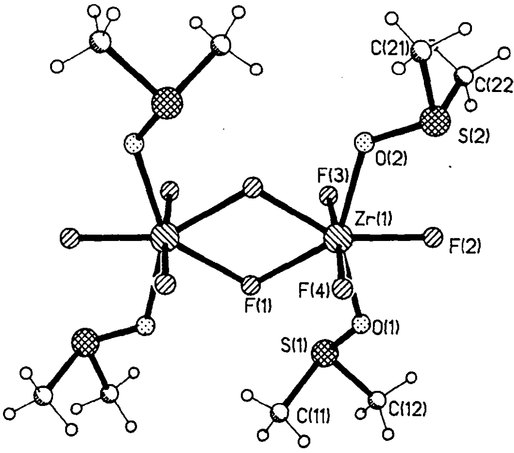


Fig. 1. View of the molecule showing the labelling of the non-H atoms.

Experimental

Crystal data

$[Zr_2F_8(C_2H_6OS)_4]$
M_r = 323.48
Monoclinic
$P2_1/n$
a = 8.831 (2) Å
b = 11.955 (2) Å
c = 10.834 (2) Å
β = 108.12 (3)°
V = 1087.1 (4) Å^3
Z = 4

D_x = 1.976 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 23 reflections
θ = 8–11°
μ = 1.420 mm^{-1}
T = 293 (2) K
Transparent blocks
0.43 × 0.18 × 0.17 mm
Colourless

Data collection

Siemens $R3m$ diffractometer
ω-2θ scans

$R_{\rm int}$(on F^2) = 0.0577
$\theta_{\rm max}$ = 25.05°