C(21)	0.5264 (8)	0.2378 (17)	0.0991 (5)	0.073 (5)
C(22)	0.4530 (7)	0.3636 (13)	0.0777 (4)	0.052 (4)
C(23)	0.4540 (9)	0.4864 (13)	0.1249 (5)	0.066 (5)
C(24)	0.2562 (9)	0.1037 (18)	−0.0483 (6)	0.096 (7)
C(25)	0.3477 (8)	0.1743 (13)	−0.0134 (5)	0.056 (4)
C(26)	0.4090 (10)	0.2444 (20)	−0.0536 (5)	0.096 (7)
C(27)	0.1435 (8)	0.4186 (16)	0.0038 (6)	0.087 (6)
C(28)	0.2509 (8)	0.4546 (13)	0.0281 (5)	0.060 (4)
C(29)	0.2930 (9)	0.5684 (14)	−0.0104 (6)	0.073 (5)

Table 2. Selected geometric parameters (Å, °)

Ir—Cl	2.374 (3)	Ir—P(1)	2.339 (3)
Ir—P(2)	2.341 (3)	Ir—O	2.102 (7)
Ir—N	2.214 (7)	P(1)—C(12)	1.879 (12)
P(1)—C(15)	1.854 (11)	P(1)—C(18)	1.829 (13)
P(2)—C(22)	1.852 (10)	P(2)—C(25)	1.863 (12)
P(2)—C(28)	1.860 (12)	O—C(5)	1.316 (12)
N—C(1)	1.334 (12)	N—C(5)	1.354 (13)
C(1)—C(2)	1.370 (17)	C(2)—C(3)	1.359 (19)
C(3)—C(4)	1.390 (16)	C(4)—C(5)	1.430 (16)
C(11)—C(12)	1.522 (19)	C(12)—C(13)	1.528 (20)
C(14)—C(15)	1.527 (15)	C(15)—C(16)	1.530 (19)
C(17)—C(18)	1.543 (20)	C(18)—C(19)	1.511 (18)
C(21)—C(22)	1.529 (17)	C(22)—C(23)	1.550 (16)
C(24)—C(25)	1.503 (16)	C(25)—C(26)	1.495 (19)
C(27)—C(28)	1.511 (15)	C(28)—C(29)	1.531 (18)
Cl—Ir—P(1)	91.2 (1)	Cl—Ir—P(2)	91.2 (1)
P(1)—Ir—P(2)	165.4 (1)	Cl—Ir—O	167.6 (2)
P(1)—Ir—O	89.8 (2)	P(2)—Ir—O	90.9 (2)
Cl—Ir—N	105.2 (2)	P(1)—Ir—N	95.4 (2)
P(2)—Ir—N	97.8 (2)	O—Ir—N	62.4 (3)
Ir—P(1)—C(12)	118.5 (4)	Ir—P(1)—C(15)	111.4 (4)
C(12)—P(1)—C(15)	102.2 (5)	Ir—P(1)—C(18)	110.8 (4)
C(12)—P(1)—C(18)	103.2 (6)	C(15)—P(1)—C(18)	110.2 (5)
Ir—P(2)—C(22)	118.1 (4)	Ir—P(2)—C(25)	111.3 (4)
C(22)—P(2)—C(25)	102.0 (5)	Ir—P(2)—C(28)	110.5 (4)
C(22)—P(2)—C(28)	103.5 (5)	C(25)—P(2)—C(28)	110.9 (5)
Ir—O—C(5)	94.9 (6)	Ir—N—C(1)	149.2 (7)
Ir—N—C(5)	88.9 (5)	C(1)—N—C(5)	121.9 (9)
N—C(1)—C(2)	120.6 (10)	C(1)—C(2)—C(3)	119.7 (10)
C(2)—C(3)—C(4)	121.7 (12)	C(3)—C(4)—C(5)	116.5 (11)
O—C(5)—N	113.8 (9)	O—C(5)—C(4)	126.6 (10)
N—C(5)—C(4)	119.5 (9)	P(1)—C(12)—C(11)	114.2 (9)
P(1)—C(12)—C(13)	108.3 (9)	C(11)—C(12)—C(13)	111.3 (10)
P(1)—C(15)—C(14)	113.6 (8)	P(1)—C(15)—C(16)	119.2 (9)
C(14)—C(15)—C(16)	109.2 (10)	P(1)—C(18)—C(17)	117.0 (9)
P(1)—C(18)—C(19)	115.4 (10)	C(17)—C(18)—C(19)	109.8 (10)
P(2)—C(22)—C(21)	110.3 (8)	P(2)—C(22)—C(23)	113.1 (8)
C(21)—C(22)—C(23)	111.6 (8)	P(2)—C(25)—C(24)	115.5 (9)
P(2)—C(25)—C(26)	117.1 (9)	C(24)—C(25)—C(26)	110.1 (10)
P(2)—C(28)—C(27)	113.3 (9)	P(2)—C(28)—C(29)	117.3 (8)
C(27)—C(28)—C(29)	111.3 (10)		

The initial structure solution was obtained using Patterson synthesis (*SHELXTL/PC*; Sheldrick, 1990) to give the position of the Ir atom. Subsequent difference Fourier maps revealed the remaining non-H atoms. The plots were produced using the *SP* program in the *SHELXTL/PC* package.

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Bis(methanol-*O*)(2,3,7,8,12,13,17,18-octaethylporphyrinato-*N*,*N'*,*N''*,*N'''*)-iron(III) Perchlorate Bis(methanol) Solvate, [Fe^III(oep)(HOCH₃)₂](ClO₄).2CH₃OH

Mathias O. Senge

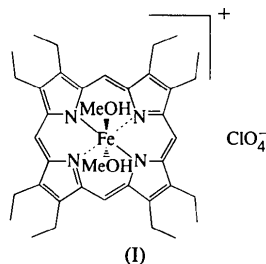*Institut für Organische Chemie (WE02), Freie Universität Berlin, Takustrasse 3, D-14195 Berlin, Germany*

Abstract

Simple treatment of [Fe^III(oep)Cl] (where oep is octaethylporphyrin) with dilute perchloric acid leads to facile preparation of the title compound, [Fe(C₃₆H₄₄N₄)(CH₄O)₂](ClO₄).2CH₄O. The structure consists of discrete [Fe(oep)(HOCH₃)₂]⁺ cations, perchlorate anions and methanol molecules of solvation, which are connected by hydrogen bonds in an infinite network. The Fe atom is located in the plane of the N atoms and is coordinated by two methanol O atoms in the axial positions, with an average Fe—N distance of 2.026 (3) Å and Fe—O bond lengths of 2.159 (3) Å.

Comment

The study of spin state and stereochemistry in iron porphyrins has been of continuing interest because of natural processes involving hemoproteins (Hoard, 1971; Scheidt & Reed, 1981; Scheidt & Lee, 1987). During synthetic studies on iron octaethylporphyrin (oep) derivatives, it was found that simple treatment of

[Fe^{III}(oep)Cl] with 5% HClO$_4$ in methanol gave the title compound, (I), in high yield; no demetallation was observed. While crystals suitable for X-ray crystallographic analysis formed in two days, it was found that prolonged treatment led to almost quantitative conversion of the neutral iron(III) porphyrin to the perchlorate salt. The reaction is easily followed spectrophotometrically by disappearance of the long-wavelength absorbing band of the parent porphyrin.

(I)

The asymmetric unit contains half the macrocycle, with the Fe atom located on a special position (1/4,1/4,1/2), a methanol molecule of solvation and a disordered perchlorate anion, with the Cl atom on a special position (0,0.0818,1/4) and the O atoms on general positions. Due to the crystallographically imposed symmetry, the N atoms are coplanar with the Fe atom located in the N$_4$ plane (Fig. 1). The Fe center is hexacoordinated by four pyrrole N atoms in equatorial positions and two methanol O atoms in axial positions. The axial Fe—O distances [2.159 (3) Å] are longer than those found in typical high-spin six-coordinate iron(III) porphyrin complexes (Scheidt & Reed, 1981; Scheidt & Lee, 1987), for example, [Fe^{III}(tpp)(H$_2$O)$_2$]$^+$ [2.095 (2) Å] and [Fe^{III}(tpp)(TMSO)$_2$]$^+$ [2.087 (3) Å] (Scheidt, Cohen & Kastner, 1979; Mashiko, Kastner, Spartalian, Scheidt & Reed, 1978). Compounds with similar Fe—O distances are the admixed intermediate spin complex [Fe^{III}(oep)(thf)$_2$](ClO$_4$) [2.199 (3) Å (Masuda et al., 1982; Cheng et al., 1994)] and the complex [Fe^{III}(oep)(EtOH)$_2$](ClO$_4$) [2.137 Å (Einstein & Willis, 1978)], the spin state of which has not been experimentally determined. Smaller differences were observed in comparison to the complexes [Fe^{III}(tpp)(EtOH)$_2$]BF$_4$ [2.142 (9) Å at room temperature (Gans, Buisson, Duie, Regnard & Marchon, 1979) and 2.116 (2) Å at 99 K (Scheidt, Geiger, Lee, Gans & Marchon, 1992)] and [Fe^{III}tpp(EtOH)$_2$](ClO$_4$) [2.134 (2) Å (Scheidt, Geiger, Lee, Gans & Marchon, 1992)]. The Fe—N bonds show an average length of 2.026 (3) Å, the individual bond lengths being somewhat different, with Fe—N21 and Fe—N22 distances of 2.019 (3) and 2.033 (3)Å, respectively. A similar effect has been noted for the related species [Fe^{III}(tpp)(EtOH)$_2$]$^+$ (Scheidt, Geiger, Lee, Gans & Marchon, 1992). The Fe—N bond lengths lie between those in pure high-spin complexes [S = 5/2, 2.045 Å (Scheidt, Cohen & Kastner, 1979; Mashiko,

Kastner, Spartalian, Scheidt & Reed, 1978)] and, for example, those found in [Fe^{III}(oep)(thf)$_2$]$^+$ [1.999 (2) Å (Masuda et al., 1982; Cheng et al., 1994)], with admixed intermediate spin (Scheidt & Reed, 1981; Scheidt & Lee, 1987). The Fe—N bond lengths compare well with those found in [Fe^{III}(oep)(EtOH)$_2$](ClO$_4$) [2.032 Å (Einstein & Willis, 1978)] and [Fe^{III}(tpp)(EtOH)$_2$]$^+$ [2.027–2.040 Å, depending on counterion and temperature (Gans, Buisson, Duie, Regnard & Marchon, 1979; Scheidt, Geiger, Lee, Gans & Marchon, 1992)]. A clear assignment of the spin state in the present compound must, however, await magnetic measurements.
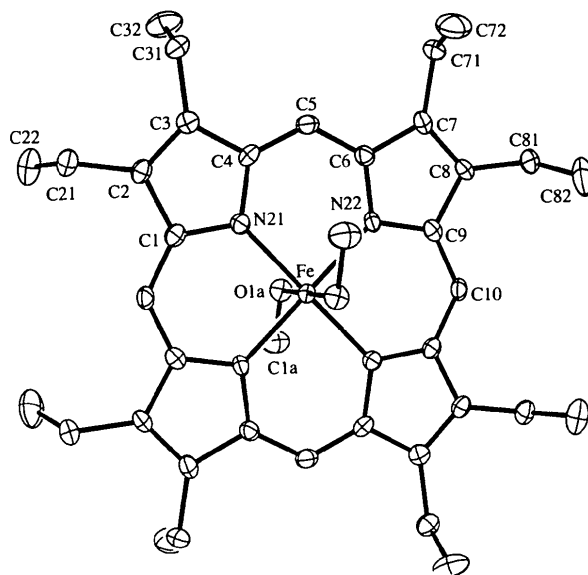

Fig. 1. The molecular structure and numbering scheme of the porphyrin cation [Fe^{III}(oep)(HOCH$_3$)$_2$]$^+$. H atoms have been omitted for clarity and ellipsoids are drawn at the 50% probability level.

The macrocycle conformation is essentially planar. The average deviation from planarity of the 24 atoms of the macrocycle is 0.026 Å, while the largest deviations from the N$_4$ plane are of the order of 0.15 Å and are for some C$_b$ atoms. The pyrrole rings are tilted against the N$_4$ plane by 3.1°, with a pyrrole twist angle of 3.3°. The C$_m$ atoms exhibit displacements from the N$_4$ plane of 0.08 and 0.04 Å. The ionic structure consists of discrete porphyrin cations, perchlorate anions and methanol molecules of solvation (Fig. 2). The porphyrin cations pack in the unit cell by formation of layers in which neighboring porphyrin planes are tilted against one another. The porphyrin cations, solvent molecules and perchlorate anions are connected by a hydrogen-bonded network. This involves hydrogen bonding of the axial methanol to the solvate methanol [O1A···O1S 2.610 (5) Å] and hydrogen bonding of the solvate methanol to the perchlorate anion [O1S···O3 2.747 (8) Å]. The perchlorate anion is then, in turn, hydrogen

bonded to solvate methanol, yielding infinite chains of the type –porphyrin–solvate–perchlorate–solvate–porphyrin–solvate–. This distinguishes the present structure from the related structure of $[Fe^{III}(oep)(EtOH)_2]$-$(ClO_4).EtOH$ (Einstein & Willis, 1978), which crystallizes with only one solvate molecule per porphyrin macrocycle and, thus, the solvent molecule is utilized for hydrogen bonding on only one face of the porphyrin leading to chains of the type –porphyrin–solvate–perchlorate–porphyrin–.
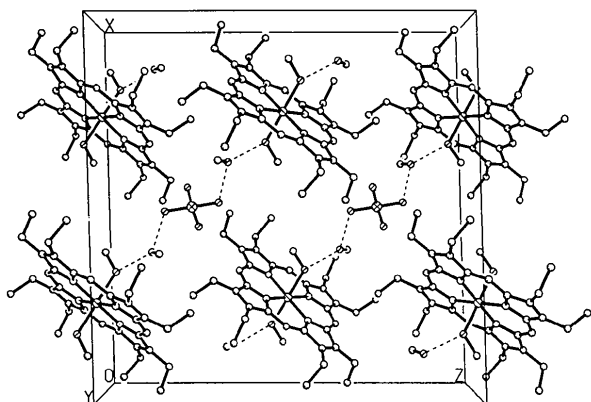

Fig. 2. View of the molecular packing (down the *b* axis). Dashed lines indicate hydrogen bonding. H atoms and disordered positions have been omitted for clarity.

Experimental

For the preparation of the title compound, 75 mg (0.12 mmol) of $[Fe^{III}(oep)Cl]$ was dissolved in 50 ml of $CHCl_3$ and treated with a 5% solution of $HClO_4$ in methanol for 2 d with stirring. Upon standing, dark blue–black crystals formed in 2 d. Filtration after 5 d gave the title compound in almost quantitative yield (92.5 mg, 98%); λ_{max} (CH_2Cl_2; nm) 391 (10^3 dm^{-3} mol^{-1} cm^{-1} 87.3), 504 (8.1), 630 (2). Small black crystals were taken directly from the crude reaction mixture and immersed in hydrocarbon oil. A single crystal was selected, mounted on a glass fiber and placed in the low-temperature nitrogen stream of the diffractometer (Hope, 1987).

Crystal data

$[Fe(C_{36}H_{44}N_4)(CH_4O)_2]$-$(ClO_4).2CH_4O$
$M_r = 816.22$
Monoclinic
$C2/c$
$a = 21.604 (8)$ Å
$b = 8.788 (4)$ Å
$c = 22.082 (10)$ Å
$\beta = 91.45 (3)°$
$V = 4191.1 (31)$ Å^3
$Z = 4$
$D_x = 1.294$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 10–11.75°$
$\mu = 0.478$ mm^{-1}
$T = 130 (2)$ K
Hexagonal plate
$0.6 \times 0.32 \times 0.04$ mm
Blue–black

Data collection

Siemens $R3m/V$ diffractometer
ω scans
Absorption correction: none
5266 measured reflections
4813 independent reflections
3144 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.0477$
$\theta_{max} = 27.50°$
$h = 0 \rightarrow 28$
$k = 0 \rightarrow 11$
$l = -28 \rightarrow 28$
2 standard reflections monitored every 198 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.0672$
$wR(F^2) = 0.1798$
$S = 1.035$
4812 reflections
251 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0672P)^2 + 10.9712P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.024$
$\Delta\rho_{max} = 0.784$ e Å^{-3}
$\Delta\rho_{min} = -0.676$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe	1/4	1/4	1/2	0.0181 (2)
O1A	0.17128 (12)	0.1524 (3)	0.45194 (11)	0.0241 (6)
C1A	0.1195 (2)	0.0866 (5)	0.4814 (2)	0.0334 (10)
N21	0.25187 (13)	0.4251 (3)	0.44089 (13)	0.0193 (6)
N22	0.30974 (14)	0.1341 (3)	0.44732 (13)	0.0196 (6)
C1	0.2214 (2)	0.5628 (4)	0.4467 (2)	0.0196 (7)
C2	0.2364 (2)	0.6629 (4)	0.3970 (2)	0.0217 (8)
C21	0.2101 (2)	0.8189 (4)	0.3870 (2)	0.0252 (8)
C22	0.1464 (2)	0.8160 (5)	0.3553 (2)	0.0381 (11)
C3	0.2766 (2)	0.5849 (4)	0.3614 (2)	0.0214 (8)
C31	0.3039 (2)	0.6358 (5)	0.3029 (2)	0.0295 (9)
C32	0.2651 (2)	0.5833 (6)	0.2477 (2)	0.0448 (12)
C4	0.2867 (2)	0.4380 (4)	0.3891 (2)	0.0211 (8)
C5	0.3261 (2)	0.3256 (4)	0.3685 (2)	0.0229 (8)
C6	0.3378 (2)	0.1857 (4)	0.3955 (2)	0.0203 (7)
C7	0.3808 (2)	0.0724 (4)	0.3742 (2)	0.0231 (8)
C71	0.4240 (2)	0.0949 (5)	0.3224 (2)	0.0286 (9)
C72	0.4822 (2)	0.1807 (7)	0.3429 (2)	0.0472 (13)
C8	0.3778 (2)	−0.0487 (4)	0.4128 (2)	0.0221 (8)
C81	0.4131 (2)	−0.1953 (5)	0.4114 (2)	0.0275 (9)
C82	0.4670 (2)	−0.2016 (6)	0.4575 (2)	0.0495 (13)
C9	0.3336 (2)	−0.0090 (4)	0.4583 (2)	0.0196 (7)
C10	0.3179 (2)	−0.0998 (4)	0.5069 (2)	0.0217 (8)
O1S	0.1177 (2)	0.2455 (5)	0.3514 (2)	0.0667 (12)
C1S	0.1186 (3)	0.3905 (6)	0.3292 (3)	0.066 (2)
C11	0	0.0818 (2)	1/4	0.0456 (4)
O1†	0.0508 (3)	−0.0245 (9)	0.2362 (4)	0.048 (2)
O2†	0.0591 (3)	0.0247 (11)	0.2600 (4)	0.070 (3)
O3†	0.0105 (3)	0.0962 (8)	0.3178 (3)	0.050 (2)
O4†	0.0110 (5)	0.2348 (10)	0.2295 (4)	0.100 (4)

† Partial occupancy (see below).

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

Fe—N21	2.019 (3)	C4—C5	1.389 (5)
Fe—N22	2.033 (3)	C5—C6	1.387 (5)
Fe—O1A	2.159 (3)	C6—C7	1.447 (5)
O1A—C1A	1.430 (5)	C7—C8	1.365 (5)
N21—C1	1.384 (5)	C8—C9	1.446 (5)
N21—C4	1.388 (4)	C9—C10	1.387 (5)

N22—C9	1.378 (5)	O1S—C1S	1.365 (6)
N22—C6	1.385 (5)	C11—O2	1.385 (7)
C1—C10^i	1.386 (5)	C11—O4	1.441 (8)
C1—C2	1.450 (5)	C11—O1^{ii}	1.478 (6)
C2—C3	1.370 (5)	C11—O3	1.513 (6)
C3—C4	1.444 (5)		
N21—Fe—N21^i	180.0	C2—C3—C4	107.2 (3)
N21—Fe—N22	89.36 (12)	N21—C4—C5	124.2 (3)
N21—Fe—O1A	90.77 (11)	N21—C4—C3	110.1 (3)
N22—Fe—O1A	91.33 (11)	C5—C4—C3	125.7 (3)
C1A—O1A—Fe	123.5 (2)	C6—C5—C4	126.6 (3)
C1—N21—C4	105.9 (3)	N22—C6—C5	124.5 (3)
C1—N21—Fe	126.1 (2)	N22—C6—C7	109.9 (3)
C4—N21—Fe	127.9 (2)	C5—C6—C7	125.6 (3)
C9—N22—C6	105.9 (3)	C8—C7—C6	107.1 (3)
C9—N22—Fe	126.7 (2)	C7—C8—C9	106.7 (3)
C6—N22—Fe	127.3 (2)	N22—C9—C10	124.3 (3)
N21—C1—C2	110.1 (3)	N22—C9—C8	110.4 (3)
C3—C2—C1	106.7 (3)	C10—C9—C8	125.3 (3)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $-x, y, \frac{1}{2} - z$.

The perchlorate ion shows symmetry-imposed disorder and deviations from tetrahedral geometry, and could not be modelled satisfactorily. The anion was refined over four split positions with equal occupancies of 0.5. The hydroxy H atoms of both the methanol ligands and the methanol solvate molecules were not located.

Data collection: *P3 Diffractometer Program* (Siemens, 1989). Cell refinement: *P3 Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL94* (Sheldrick, 1994). Molecular graphics: *XP* in *SHELXTL-Plus* (Siemens, 1994). Software used to prepare material for publication: *XCIF* in *SHELXTL-Plus*.

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Bis(1,3,5-triaza-7-phosphaadamantane-*P*)-gold(I) Chloride

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Abstract

The central Au atom in the title compound, [Au(C$_6$H$_{12}$N$_3$P)$_2$]Cl, lies on an inversion center and the twofold coordination is necessarily linear, with Au—P 2.261 (5) Å. The Cl$^-$ ion is in a general position with 0.5 occupancy; the shortest Au⋯Cl distance is 3.224 (4) Å.

Comment

Linear two-coordinate cationic bisphosphine gold(I) complexes, (L_2Au$^+$), are thought to have little interaction between the counteranion and the Au atom. Recently, there has been an increase in the number of structures that show that three-coordinate gold(I) complexes do exist (see Table 3; for some examples see: Baenziger, Dittemore & Doyle, 1974; Muir, Muir & Arias 1982; Guggenberger, 1974). Gold(I) complexes with two weakly donating phosphines, such as PPh$_3$, appear to show this additional interaction more readily than those with the trialkylphosphines (Baenziger, Dittemore & Doyle, 1974; Muir, Muir & Arias 1982). For example, (PPh$_3$)$_2$AuCl and (PPh$_3$)$_2$AuSCN possess strong Au—Cl and Au—S interactions and a nearly planar geometry. No third ligand interaction is evident in the corresponding trialkylphosphine complexes. For the bisphosphine gold(I) xanthates reported recently (Assefa, Staples & Fackler, 1994), the P—Au—P angle is larger and the Au—S distance is smaller when the phosphine is PPh$_3$ than when it is the weakly more basic ligand CEP [CEP = tris(cyanoethyl)phosphine], even