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(2-Fluoro-1,3-dimethyl-1,3,2-diazaphospholidine)tetracarbonyliron(0)

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Abstract. $[\mathrm{CH_3\overline{NCH_2CH_2N(CH_3)P}F]Fe(CO)_4}$, monoclinic, space group $P2_1/c$, $a = 6{\cdot}6530\,(5)$, $b = 16{\cdot}3472\,(16)$, $c = 11{\cdot}5939\,(8)$ Å, $\beta = 92{\cdot}777\,(7)°$ (23 ± 1 °C), $D_m = 1{\cdot}58$, $D_x = 1{\cdot}603$ g cm^{-3} ($Z = 4$). The compound was prepared by allowing $\mathrm{CH_3\overline{NCH_2CH_2N(CH_3)P}F}$ to react with $\mathrm{Fe_2(CO)_9}$ in $\mathrm{CH_2Cl_2}$, yielding a mole of the compound and a mole of $\mathrm{Fe(CO)_5}$. Yellow crystals, m.p. 49–50 °C, were grown by vacuum sublimation of the distilled product. The molecule exhibits axial substitution of the ligand. N atoms in the ligand display planar geometry, with P—N bond lengths notably shortened.

Introduction. Cell-parameter and intensity data were obtained on a $P\bar{1}$ autodiffractometer using Mo $K\alpha$ radiation (0·710688 Å) with a graphite monochromator. The data were collected with a scintillation counter and corrected for coincidence. The unit-cell parameters were determined from 30 reflections ($27 < 2\theta < 35°$) by a least-squares refinement. The crystal used for data collection was in the shape of a slightly oblique parallelepiped with approximate dimensions of 0·3 × 0·3 × 0·2 mm. The compound is air sensitive and sublimes slowly at ambient temperature. The crystal was anchored with yellow cheese wax in a sealed Lindemann-glass capillary tube. Intensites were measured with a θ–2θ scan of 2° at a scan rate of 1·5° min^{-1}. These intensities were collected for 2325 unique reflections ($2\theta < 47{\cdot}5°$) in one quadrant of the Ewald sphere. Within this range absorption correction factors were essentially constant and absorption corrections were not made. 97 of these reflections had indices $0k0$ with $k = 2n + 1$ or $h0l$ with $l = 2n + 1$, and were treated as systematically extinct. A check block of five reflections was measured after each block of fifty-five regular reflections. The intensity data were corrected for an observed loss of 6% during the entire run. Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1974), as were the anomalous dispersion corrections for the scattering factors for the Fe and P atoms. The structure was solved by the heavy-atom method using the positions of the Fe atoms which were found on a Patterson map. A block-diagonal least-squares refinement resulted in a final residual index ($R = \sum||F_o| - |F_c||/\sum|F_o|$) of 0·056 (systematically extinct reflections

Table 1. *Atomic parameters in fractional coordinates with e.s.d.'s* (×10^4)

	x	y	z
C(1)	7084 (10)	6145 (4)	5053 (6)
C(2)	7482 (9)	5462 (4)	3034 (6)
C(3)	7164 (9)	7261 (4)	3533 (5)
C(4)	3538 (9)	6088 (4)	4123 (5)
C(5)	3348 (11)	4894 (4)	1349 (6)
C(6)	2946 (10)	8021 (4)	2196 (6)
C(7)	1267 (11)	7013 (5)	859 (7)
C(8)	1350 (11)	6110 (4)	629 (6)
F	6152 (5)	6683 (3)	1017 (3)
Fe	6003 (1)	6273 (1)	3608 (1)
N(1)	3081 (8)	5782 (3)	1272 (5)
N(2)	2817 (7)	7204 (3)	1720 (4)
O(1)	7782 (9)	6069 (4)	5965 (4)
O(2)	8442 (8)	4967 (3)	2660 (5)
O(3)	7968 (8)	7873 (3)	3500 (5)
O(4)	1978 (7)	5974 (4)	4452 (5)
P	4492 (2)	6474 (1)	1927 (1)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s*

Fe—P	2·174 (1)	P—N(1)	1·635 (5)
Fe—C(1)	1·803 (6)	P—N(2)	1·642 (5)
Fe—C(2)	1·798 (6)	P—F	1·600 (4)
Fe—C(3)	1·793 (6)	N(1)—C(5)	1·464 (8)
Fe—C(4)	1·798 (6)	N(1)—C(8)	1·445 (9)
C(1)—O(1)	1·140 (8)	N(2)—C(6)	1·447 (8)
C(2)—O(2)	1·131 (8)	N(2)—C(7)	1·435 (9)
C(3)—O(3)	1·137 (8)	C(7)—C(8)	1·501 (11)
C(4)—O(4)	1·138 (8)		

Fe—C(1)—O(1)	179·4 (6)	Fe—P—N(1)	122·8 (2)
Fe—C(2)—O(2)	178·2 (6)	Fe—P—N(2)	121·5 (2)
Fe—C(3)—O(3)	177·3 (6)	F—P—Fe	108·6 (1)
Fe—C(4)—O(4)	179·7 (7)	N(1)—P—N(2)	93·7 (3)
C(1)—Fe—C(2)	93·3 (3)	N(1)—P—F	103·9 (3)
C(1)—Fe—C(3)	89·8 (3)	N(2)—P—F	103·5 (2)
C(1)—Fe—C(4)	90·0 (3)	C(5)—N(1)—P	126·4 (4)
C(2)—Fe—C(3)	113·7 (3)	C(5)—N(1)—C(8)	119·4 (5)
C(2)—Fe—C(4)	121·5 (3)	C(8)—N(1)—P	114·1 (4)
C(3)—Fe—C(4)	124·7 (3)	C(6)—N(2)—P	126·0 (4)
C(1)—Fe—P	175·4 (2)	C(6)—N(2)—C(7)	119·6 (5)
C(2)—Fe—P	91·0 (2)	C(7)—N(2)—P	113·8 (4)
C(3)—Fe—P	90·1 (2)	N(1)—C(8)—C(7)	108·0 (6)
C(4)—Fe—P	86·2 (2)	N(2)—C(7)—C(8)	107·9 (6)

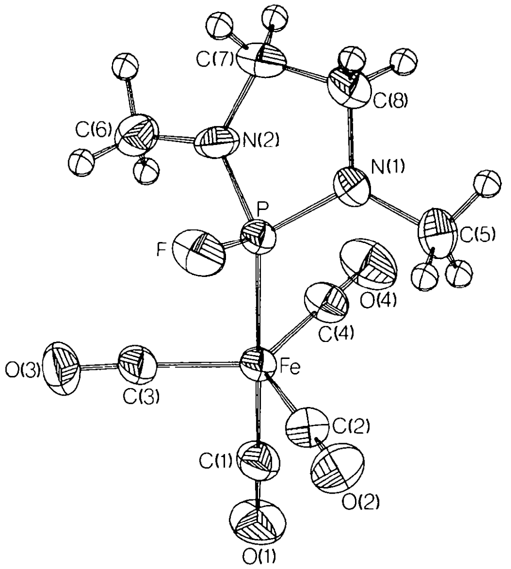

Fig. 1. Perspective view of the molecule showing the atom numbering scheme.

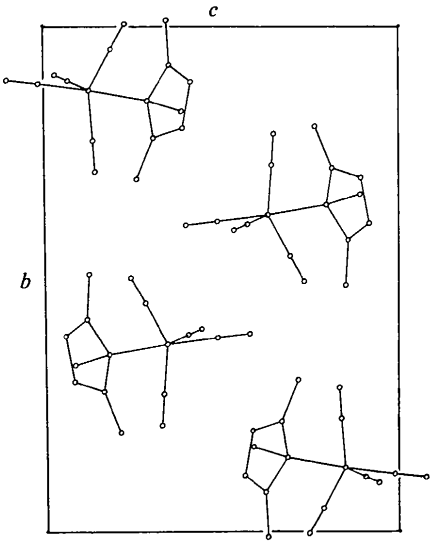

Fig. 2. Molecular packing in the crystal.

were the only reflections excluded from the calculation of R). The residual index calculated for 1818 reflections with $I > 3\sigma(I)$ was 0·044. Refinement involved minimization of $\sum w(F_o - F_c)^2$ where $w = (14{\cdot}0 + |F_o| + 0{\cdot}0033|F_o|^2)^{-1}$ (Cruickshank, 1970). Data reduction and refinement were accomplished with XRAY 70 (Stewart, Kundell & Baldwin, 1970). Final atomic parameters are shown in Table 1.* The H atoms were not clearly resolved on a difference map, and for purposes of refinement they were placed in calculated positions and assigned the overall isotropic temperature factor of the structure. The methyl groups were oriented in such a manner as to avoid unreasonable overlap between methyl H atoms and adjacent atoms. Bond lengths and angles are shown in Table 2. The atoms are numbered as shown in Fig. 1. Fig. 2 shows the molecular packing in the crystal.

Discussion. In a study of the infrared spectra of certain aminofluorophosphine ligands coordinated to iron carbonyl, Douglas & Ruff (1971) tentatively assigned equatorial substitution of these ligands to the trigonal bipyramidal structure of the iron carbonyl complex. Although many phosphorus-containing ligands are known to coordinate to the equatorial position, such ligands are ordinarily π-bonded to the Fe atom through a C=C double bond. On the other hand, certain complexes containing ligands coordinated to $Fe(CO)_4$ by σ-donation, such as $(C_6H_5)_2HPFe(CO)_4$, have been demonstrated by X-ray structure determination to be axially substituted (Kilbourn, Raeburn & Thompson, 1969). These complexes display infrared spectra similar to those for the coordinated aminofluorophosphines. As interpretation of infrared spectroscopic data has become increasingly important in understanding the chemistry of these coordinated aminofluorophosphines, a structural study was undertaken to examine their mode of substitution. The present structure exhibits the trigonal bipyramidal geometry characteristic of mono-substituted iron pentacarbonyl, with the aminofluorophosphine ligand clearly in the axial position. Bond lengths and angles around the Fe atom are similar to those reported for the diphenylphosphinetetracarbonyliron complex, except that the length of the P–Fe bond reported by Kilbourn *et al.* (1969), 2·237 (2) Å, is significantly greater than that, 2·174 (1) Å, found in this determination. It is also of interest to note that bonding about both of the N atoms is nearly trigonal and essentially planar, with N(1) located 0·032 Å from the P, C(5), C(8) plane and N(2) 0·067 Å from the P, C(6), C(7) plane. The P–N bond lengths of 1·635 (5) and 1·642 (5) Å are notably shorter than the P–N distance of 1·785 (30) Å in the $H_3NPO_3^-$ ion (Hobbs, Corbridge & Raistrick, 1953), a value often considered to be the length of a P–N single bond. These data clearly suggest a p_π–d_π interaction between the N lone-pair electrons and the P atom. Similar bond distances have been observed in the compounds $(CH_3)_2NPF_2$ (Morris & Nordman, 1969), P–N = 1·628 (5) Å, and NH_2PF_2 (Brittain, Smith, Lee, Cohn & Schwendeman, 1971) whose microwave determination gave P–N = 1·650 (4) Å. The P–N bond distances determined in this study are longer than that reported for $(CH_3)_2NPF_2B_4H_8$ (La Prade & Nordman, 1969), P–N = 1·585 (6) Å. However, these authors

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33747 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

comment that this is a quite short P—N bond. The P—F bond distance determined in this study, 1·600 (6) Å, is similar to those in $(CH_3)_2NPF_2$ of 1·591 (4) Å and NH_2PF_2 of 1·587 (4) Å. It is longer than those reported for $(CH_3)_2NPF_2B_4H_8$ of 1·555 (4) and 1·555 (4) Å.

Figs. 1 and 2 were drawn using *ORTEP* (Johnson, 1970). The *Chemical Abstracts* registry number for 2-fluoro-1,3-dimethyl-1,3,2-diazaphospholidine is [33672-91-2].

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Thianthrenegold(III) Chloride (Chloroform Solvate) at –70°C

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Abstract. $C_{12}H_8AuCl_3S_2$. $CHCl_3$, monoclinic, *Cm*. At -70°C, $a = 12{\cdot}887$ (3), $b = 14{\cdot}275$ (5), $c = 5{\cdot}331$ (2) Å, $\beta = 103{\cdot}05$ (2)°, $V = 955{\cdot}35$ Å^3, $Z = 2$, $D_c = 2{\cdot}22$, $D_m = 2{\cdot}17$ g cm^{-3}, μ(Mo $K\alpha$) = 85·26 cm^{-1}. Only one of the two S atoms in the thianthrene ligand coordinates to the Au atom, which is also bonded to three Cl atoms. Au—Cl 2·305 (18), 2·274 (4); Au—S 2·351 (15) Å.

Introduction. The title compound was prepared by reacting chloroauric acid with thianthrene in dry chloroform. Slow recrystallization from chloroform solution in a nitrogen-filled dry box afforded imperfectly formed dark-red crystals which were apparently air-stable but from which at room temperature the solvent molecules slowly escaped. A crystal 0·04 × 0·19 × 0·24 mm was used. Data were collected on a Syntex $P2_1$ diffractometer with graphite-monochromatized Mo $K\alpha$ radiation to a $2\theta_{\max}$ of 55°. The crystal was kept at -70°C with the Syntex L-T1 attachment. Three standard reflections were used and showed no significant change in intensity during data collection. 1894 reflections were recorded of which 1258 were considered observed $[I/\sigma(I) \geq 3{\cdot}0]$ and used in refinement. An absorption correction was carried out with *ABSCOR* (Alcock, 1970).

Systematic absences were observed for *hkl* when $h + k = 2n + 1$, indicating possible space groups *C*2, *Cm* and *C*2/*m*. However, the presence of chloroform solvent molecules suggested *Cm* as the most likely space group. The Au atom was placed at $(\frac{1}{2},\frac{1}{2},0)$ and Fourier maps were used to locate all the other non-hydrogen atoms. Least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms led to a final *R* of 0·034. The solvent molecule was given 50% occupancy. Final difference maps showed the presence of solvent molecules at other positions, each with less than 25% occupancy, but these were ignored. Refinement was carried out with XRAY 76 (Stewart, 1976) run on a Burroughs B6700 computer; scattering factors were from *International Tables for*