Structure of *cis*-Dihydridotetrakis(diethyl phenylphosphonite)iron(II)

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Abstract: The molecular and crystal structure of *cis*-dihydridotetrakis(diethyl phenylphosphonite)iron(II), $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$, has been determined from independent refinements of separate sets of data collected by counter techniques. The material crystallizes in a triclinic cell with dimensions of $a = 11.790$ (5), $b = 17.493$ (3), $c = 11.955$ (10) Å; $\alpha = 90.20$ (2), $\beta = 115.04$ (6), and $\gamma = 85.01$ (2)°. The space group is $P\bar{1}$ and there are two molecules per cell. The final R factors for the two least-squares refinements are 0.038 and 0.091. The crystal structure consists of the packing of discrete molecules each of which has a cis disposition of hydrogen atoms and an iron–phosphorus geometry intermediate between octahedral and tetrahedral. The hydride hydrogen atoms were located on difference maps and refined by least squares, giving Fe–H distances of 1.51 (4) Å. The Fe–P distances cis and trans to the hydride ligands are 2.128 (2) and 2.150 (2) Å, respectively; thus, the ground-state trans influence of the hydride ligand on the iron–phosphorus bond is small.

The first dihydride complex of iron, $H_2Fe(CO)_4$, was reported in 1931.[2] Since then several analogous complexes with tertiary phosphines substituted for the carbonyl groups have been reported.[3–6] Structural studies of these compounds have not unambiguously established the location of the hydrogen atoms,[7] although the cis configuration is thought to predominate.[5,7,8] One complex, $H_2Fe[o\text{-}C_6H_4[P(C_2H_5)_2]_2]_2$, has been assigned a trans configuration on the basis of nmr and dipole moment data.[3b] The present paper reports the results of two completely independent determinations of the crystal and molecular structure of *cis*-dihydridotetrakis(diethyl phenylphosphonite)iron(II), *cis*-$H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$. A preliminary account of one of the refinements has appeared earlier.[9]

Experimental Section

Preparation of $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$. All operations were carried out in an atmosphere of nitrogen or argon. A 100-ml three-necked flask equipped with reflux condenser, dropping funnel, magnetic stirring bar, and nitrogen inlet and outlet was charged with 1.27 g of anhydrous ferrous chloride (0.01 mol), 10 g of diethyl phenylphosphonite[10] (0.05 mol), and 40 ml of absolute ethanol. The mixture was heated to reflux; heating was stopped after 3 hr, and a freshly prepared solution of sodium borohydride in absolute ethanol (0.2 g in 10 ml) was added dropwise with stirring. A reddish color appeared initially upon addition, but it faded rapidly, leaving a dark yellow-brown mixture when addition was complete. The mixture was filtered and allowed to stand at room temperature for 12–15 hr. The product separated from solution as light-yellow holohedral prisms. The mother liquor was drawn off and reduced in volume to obtain a second crop of crystals. The crystals were washed with three 10-ml portions of ethanol and then dried *in vacuo*, total yield 4.6 g (54%). The yield is quite sensitive to impurities in the starting materials; the ethanol should be oxygen free although traces of moisture do not seem to lower the yield appreciably. The crystals are air sensitive and turn brown after a few days of exposure. They can be stored indefinitely at room temperature under argon or nitrogen. The product in the solid state is diamagnetic. *Anal.* Calcd for $C_{40}FeH_{62}O_8P_4$: C, 56.48; H, 7.35; Fe, 6.57; P, 14.56. Found: C, 56.46; H, 7.30; Fe, 6.72; P, 14.73.

Unit Cell Data. The unit-cell measurements, data collection and processing, and refinement results will be described for both of the independent structure determinations. A comparison of the two structure determinations is relevant since it provides some insight into the accuracy of the refinement results. Henceforth the two sets of structural results will be labeled set D (Du Pont) and set C (Caltech) when comparisons are made.

Crystals of $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$ are triclinic, space group $P\bar{1}$ (C_i^1), with two molecules per cell. The cell parameters are given in Table I. The cell parameters for set D resulted from a least-squares refinement using as observations the angular positions of 12 reflections carefully centered on a diffractometer (Mo radiation). The parameters for set C resulted from a least-squares refinement based on the 2θ values of 47 reflections centered on a diffractometer (Co radiation). The agreement between the two sets of unit cell data is satisfactory.

Table I. Unit Cell Data for $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$

	Set D	Set C
a, Å	11.786 (8)	11.794 (6)
b, Å	17.491 (12)	17.494 (3)
c, Å	11.970 (8)	11.940 (5)
α, deg	90.20 (3)	90.21 (4)
β, deg	114.97 (9)	115.11 (4)
γ, deg	85.03 (3)	84.99 (4)
V, Å^3	2227	2221
D_{calcd}, g/cm^3	1.27	1.27
D_{exptl}, g/cm^3	1.26	1.24

Data Collection and Processing for Set D. A Picker four-circle diffractometer (controlled on-line by an IBM 1130 computer) was

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used to measure intensities from an irregular-shaped crystal of dimensions 0.2 × 0.2 × 0.3 mm mounted with the [101] axis coincident with the diffractometer ϕ axis. The crystal was mounted in a Lindemann glass capillary since earlier crystals were found to react in the air. The data were measured using Zr-filtered Mo radiation (λ 0.7107 Å) with a take-off angle of 3°. The θ–2θ scan technique was used with a scan speed of 1°/min and a scan range of 1.5° plus the angular separation of $K\alpha_1$ and $K\alpha_2$ for each reflection. Individual backgrounds of 20 sec were measured before and after each scan.

The variation in check reflections over the period of the data collection was less than 1% in F. Reflections with counting rates over 10,000 counts/sec were remeasured with attenuation. Data were measured out to 40° in 2θ. A total of 4050 reflections were measured including the check reflections and both [$hk0$] and [$\bar{h}\bar{k}0$] data which were averaged. The data were corrected for Lorentz and polarization effects but not for absorption. The linear absorption coefficient for Mo $K\alpha$ radiation is 5.4 cm^{-1}. The variation in F due to absorption was less than 1% in the equivalent reflections checked. The errors in structure factors were estimated according to a procedure described earlier.[11]

An unsharpened Patterson function was calculated and an attempt was made to solve the structure using Patterson superposition techniques based first on the iron atom position and later on a combination of iron and phosphorus atom positions. However, the iron–phosphorus geometry was not clear in the resulting maps. This approach was not pursued since there was some uncertainty about the Fe–Fe vectors in the Patterson map. In retrospect we find the iron position used at this point was corrected.

The structure was solved using symbolic addition techniques[12] based on the 443 largest normalized structure factors (E's > 1.44). The statistical distribution of E's followed the expected centric distribution, the observed values of 0.801 for $|E|$ and 0.960 for $|E^2 - 1|$ being very close to the theoretical centric values[13] of 0.798 and 0.968, respectively. Seven of the largest E's were assigned symbols and the signs of the remaining E's were found in terms of the signs of these seven. Three signs were assigned to fix the origin. The sixteen combinations of the four remaining signs were checked and the one with the fewest inconsistencies (neglecting the all-positive combination) was used in calculating an E map.

The iron atom, phosphorus atoms, and oxygen atoms were found on the E map and these atoms were used to phase a Fourier synthesis. All of the remaining nonhydrogen atoms were found in several steps of least-squares refinement and electron-density difference Fourier synthesis. The residual, R ($\Sigma||F_o| - |F_c||/\Sigma|F_o|$), was 0.11 after one cycle of isotropic refinement with all nonhydrogen atoms included in the model. After one cycle of anisotropic refinement, R was 0.07. The anisotropic refinement was carried out by varying the scale factor and atom parameters in three sections: (a) the iron atom, two hydrogen atoms (*vide infra*), phosphorus atoms, oxygen atoms, and the benzene carbon atoms on P(4); (b) the benzene carbon atoms on P(1), P(2), and P(3); and (c) the methylene and methyl carbon atoms. The two hydride hydrogen atoms bound to the iron atom were found easily on an electron-density difference map as they peaked up at 0.7 and 0.8 e/Å^3 for H(1) and H(2), respectively. The positional parameters for these two hydrogen atoms were included in all further refinements but not their isotropic thermal parameters, which were set at 4.0 Å^2. The remaining hydrogen atoms were included in calculated positions with isotropic temperature factors equivalent to those of the carbon atoms to which they are attached. The hydrogens on the methyl carbon atoms were assumed to be staggered with respect to those on the adjacent methylene carbon atoms. These hydrogen atom positions were not varied in the refinement.

Four more cycles of anisotropic refinement were done until the shifts in all parameters were less than 0.3 of their standard deviations. The final R factors for the 3086 observed reflections were 0.038 for R and 0.050 for R_w where R_w is $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w \cdot |F_o|^2]^{1/2}$. The corresponding values for all of the data (3659 reflections) were $R = 0.049$ and $R_w = 0.056$. The "error of fit," $(\Sigma w||F_o| - |F_c||^2/m - n)^{1/2}$, for each of the refinement groups was 1.34.

The atom form factors used were those of the neutral atoms.[14] The real and imaginary parts[15] of the anomalous scattering of iron were used in including the anomalous dispersion effect in the calculated structure factors. The function minimized in least squares was $\Sigma w(|F_o| - |F_c|)^2$.

Data Collection and Processing for Set C. The crystals selected for study were mounted on glass fibers and coated with a clear epoxy cement to prevent air oxidation. Data were collected on a Datex-automated General Electric diffractometer using iron oxide filtered cobalt radiation. A crystal measuring 0.10 × 0.26 × 0.25 mm was mounted with its [101] axis parallel to the ϕ axis of the diffractometer. The θ–2θ scanning mechanism was programmed for a rate of 2°/min with the scan range varying from 2.1° at 2θ = 4° to 4.5° at 2θ = 150°. Stationary background counts of 30 sec each were obtained at the extremes of each scan.

Check reflections were monitored every 20 reflections and indicated a 15% drop in intensity by the end of the data collection. The linear absorption coefficient was 29 cm^{-1}, yielding transmission factors varying from 0.45 to 0.74. A total of 5240 reflections were collected in 13 sets. Intensities of the reflections in each set were scaled to a check reflection which had been assigned a fixed $|F|$ value for all of the data sets. Lorentz and polarization corrections were applied to all the data, but no absorption corrections were made. The data were put on an approximately absolute scale with a Wilson plot.

It was noted at this point that there were very few reflections with negative net intensities (scan counts minus background). Later in the structure determination it became obvious that additional scan counts had been introduced, producing erroneously high intensities, especially at values of high 2θ. This problem was eventually traced to a high noise level in the 2θ scan mechanism. Unfortunately, the errors were not systematic enough to allow a reliable correction to be made. The error introduced, however, did not become significant for most reflections until 2θ exceeded 100°; in the refinement of the structure the data were reduced to those reflections with $2\theta < 103°$ ($\sin\theta/\lambda < 0.436$; 3088 reflections).

The atomic scattering factors were taken from the International Tables;[15] those of iron and phosphorus were corrected for the real part of anomalous dispersion, using values estimated from Cromer's tables[16] (for Fe, $\Delta f' = -3.55$; for P, $\Delta f' = 0.30$ e).

A three-dimensional Patterson map was calculated in an attempt to locate the heavy-atom vectors. Although the Fe–P vectors were clearly visible, the Fe–Fe vector could not be located. It was not certain at this point if the cell had a center of symmetry or not; a statistical test[17] indicated that it did not, but because of the large number of high-angle reflections with anomalously large intensities (due to the malfunction mentioned above) the result was suspect.

Symbolic addition phasing methods, assuming space group $P\bar{1}$, were then applied to 300 reflections with $E > 1.6$, but the two most reasonable phasing assignments yielded E maps which appeared to be only distorted representations of the Patterson synthesis.

The positions of the four phosphorus atoms, and from them eventually the position of the iron atom, were finally determined using a three-dimensional sharpened Patterson synthesis. The Fe–Fe′ vector could not be resolved from a Fe–P′′ vector, requiring that the position of the Fe–Fe′ vector be interpolated from the positions of the four Fe–P′ vectors. Three successive structure factor calculations and Fourier syntheses provided the positions of the remaining nonhydrogen atoms. A difference Fourier synthesis was used to adjust the positional parameters; the residual index at this point was $R = 0.24$. A full-matrix least-squares refinement of the positional parameters and their isotropic temperature factors lowered the index to $R = 0.19$. From this point the reduced data set ($2\theta < 103°$; 3088 reflections) was used in the refinement. All atoms were allowed to vibrate anisotropically, with the 319 parameters refined in succession, being divided into three sections: (a) the positional parameters, (b) about half of the temperature factors, and (c) the rest of the temperature factors plus any from (b) which

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Table II. Positional Parameters of $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$[a]

Atom	x	y	z	Atom	x	y	z
Fe	0.27466 (5) 0.27469 (14)	0.23256 (3) 0.23276 (8)	0.27317 (5) 0.27296 (13)	C(16)	−0.02247 (52) −0.02392 (96)	0.15966 (33) 0.15864 (56)	0.39213 (52) 0.38986 (89)
P(1)	0.27942 (12) 0.27929 (21)	0.17610 (7) 0.17602 (12)	0.11669 (11) 0.11642 (21)	C(17)	0.18736 (44) 0.18616 (87)	0.34533 (27) 0.34433 (47)	0.51062 (44) 0.51000 (82)
P(2)	0.20172 (11) 0.20218 (21)	0.21341 (7) 0.21345 (12)	0.40393 (11) 0.40485 (20)	C(18)	0.08713 (51) 0.08915 (91)	0.40317 (30) 0.40371 (50)	0.51387 (51) 0.51449 (87)
P(3)	0.19693 (10) 0.19693 (20)	0.34386 (7) 0.34375 (12)	0.18490 (10) 0.18476 (20)	C(19)	0.27975 (50) 0.28096 (91)	0.15300 (36) 0.15240 (60)	0.63434 (46) 0.63427 (89)
P(4)	0.46322 (11) 0.46340 (20)	0.25356 (7) 0.25354 (12)	0.39687 (11) 0.39649 (20)	C(20)	0.37904 (62) 0.37773 (108)	0.10373 (39) 0.10361 (63)	0.72457 (55) 0.72328 (101)
O(1)	0.28438 (29) 0.28408 (54)	0.08377 (16) 0.08432 (28)	0.13676 (27) 0.13564 (52)	C(21)	0.23537 (42) 0.23448 (75)	0.38021 (23) 0.38099 (43)	0.06231 (41) 0.06170 (72)
O(2)	0.38045 (28) 0.38116 (56)	0.18144 (19) 0.18153 (34)	0.05810 (28) 0.05838 (52)	C(22)	0.35944 (49) 0.35797 (87)	0.39035 (33) 0.39091 (57)	0.09007 (47) 0.08870 (88)
O(3)	0.12860 (26) 0.13006 (50)	0.27774 (16) 0.27810 (29)	0.45555 (27) 0.45488 (48)	C(23)	0.39315 (53) 0.39076 (93)	0.41816 (37) 0.41862 (63)	0.00040 (63) −0.00007 (92)
O(4)	0.30907 (26) 0.30803 (47)	0.17200 (17) 0.17223 (29)	0.53217 (25) 0.53168 (46)	C(24)	0.30402 (68) 0.30503 (109)	0.43573 (33) 0.43539 (59)	−0.11654 (61) −0.11506 (100)
O(5)	0.22307 (26) 0.22279 (48)	0.41763 (16) 0.41716 (27)	0.27364 (25) 0.27255 (46)	C(25)	0.18182 (61) 0.18414 (104)	0.42642 (35) 0.42616 (61)	−0.14359 (48) −0.14185 (100)
O(6)	0.04575 (24) 0.04624 (45)	0.35807 (16) 0.35810 (28)	0.10337 (25) 0.10351 (46)	C(26)	0.14676 (47) 0.14881 (85)	0.39869 (30) 0.39868 (54)	−0.05549 (48) −0.05579 (82)
O(7)	0.54032 (25) 0.54113 (47)	0.30062 (17) 0.30101 (28)	0.33880 (26) 0.33913 (46)	C(27)	0.17456 (49) 0.17550 (92)	0.49473 (27) 0.49459 (48)	0.22291 (48) 0.22521 (91)
O(8)	0.56777 (26) 0.56719 (49)	0.08213 (16) 0.18240 (28)	0.46470 (30) 0.46438 (51)	C(28)	0.18352 (48) 0.18333 (86)	0.54586 (27) 0.54644 (48)	0.32370 (50) 0.32287 (87)
C(1)	0.14168 (47) 0.14436 (83)	0.19264 (25) 0.19228 (46)	−0.03220 (41) −0.03124 (79)	C(29)	−0.04154 (42) −0.04326 (85)	0.33635 (31) 0.33659 (54)	0.14854 (47) 0.14594 (84)
C(2)	0.14888 (53) 0.14918 (91)	0.21851 (31) 0.21798 (55)	−0.13859 (51) −0.13755 (90)	C(30)	−0.17085 (46) −0.17046 (84)	0.35524 (35) 0.35500 (58)	0.05031 (54) 0.05001 (84)
C(3)	0.04255 (77) 0.04210 (122)	0.23028 (37) 0.22996 (62)	−0.24954 (53) −0.24749 (112)	C(31)	0.49576 (38) 0.49517 (69)	0.30767 (28) 0.30713 (45)	0.53718 (42) 0.53560 (69)
C(4)	−0.07255 (72) −0.07186 (109)	0.21626 (35) 0.21600 (56)	−0.25525 (56) −0.25346 (115)	C(32)	0.46939 (42) 0.47070 (78)	0.38704 (32) 0.38672 (50)	0.52616 (45) 0.52902 (78)
C(5)	−0.08250 (52) −0.08001 (96)	0.19080 (33) 0.19039 (55)	−0.15070 (61) −0.14986 (98)	C(33)	0.49042 (50) 0.49202 (91)	0.43025 (33) 0.42892 (54)	0.63195 (65) 0.63263 (92)
C(6)	0.02576 (53) 0.02829 (96)	0.17839 (29) 0.17923 (52)	−0.03834 (46) −0.04049 (95)	C(34)	0.53742 (56) 0.53789 (91)	0.39233 (49) 0.39209 (72)	0.74640 (62) 0.74507 (90)
C(7)	0.27898 (57) 0.27977 (101)	0.03079 (31) 0.03115 (54)	0.04177 (51) 0.04429 (98)	C(35)	0.56207 (56) 0.56124 (96)	0.31418 (46) 0.31484 (66)	0.75700 (50) 0.75576 (93)
C(8)	0.22829 (71) 0.23039 (122)	−0.03885 (37) −0.03766 (62)	0.06073 (65) 0.06259 (118)	C(36)	0.54289 (47) 0.54395 (85)	0.27169 (31) 0.27293 (51)	0.65323 (50) 0.65337 (85)
C(9)	0.51244 (56) 0.51177 (106)	0.16986 (40) 0.17064 (65)	0.12980 (55) 0.12955 (101)	C(37)	0.67367 (42) 0.67266 (83)	0.30850 (30) 0.30939 (51)	0.40620 (48) 0.40592 (82)
C(10)	0.58103 (66) 0.58103 (115)	0.19466 (51) 0.19444 (83)	0.06477 (72) 0.06521 (111)	C(38)	0.71306 (51) 0.71289 (92)	0.35990 (39) 0.36014 (64)	0.33435 (59) 0.33485 (93)
C(11)	0.07888 (42) 0.08011 (79)	0.14675 (28) 0.14702 (45)	0.36244 (40) 0.36314 (78)	C(39)	0.55538 (50) 0.55703 (89)	0.10386 (29) 0.10541 (50)	0.44963 (55) 0.44924 (92)
C(12)	0.09244 (45) 0.09063 (81)	0.07951 (29) 0.08090 (49)	0.30432 (48) 0.30654 (82)	C(40)	0.65603 (58) 0.65160 (110)	0.05658 (33) 0.05683 (55)	0.54411 (64) 0.54050 (112)
C(13)	0.00646 (61) 0.00685 (105)	0.02468 (30) 0.02629 (51)	0.27791 (57) 0.28081 (105)	H(1)	0.3139 (40) 0.2906 (58)	0.1509 (25) 0.1525 (33)	0.3270 (41) 0.3060 (57)
C(14)	−0.09181 (69) −0.09202 (108)	0.03711 (44) 0.03960 (67)	0.30896 (68) 0.30996 (112)	H(2)	0.1457 (41) 0.1389 (58)	0.2091 (25) 0.2097 (32)	0.1954 (41) 0.1947 (57)
C(15)	−0.10681 (60) −0.10785 (105)	0.10303 (51) 0.10478 (74)	0.36565 (69) 0.36435 (102)				

[a] The first line is for set D and the second line is for set C. The standard deviations of the least significant figures are in parentheses.

displayed unusually large shifts. The ethyl and phenyl hydrogen atoms were then added as fixed contributions; the methyl hydrogen atoms were positioned such that their conformation with respect to the methylene hydrogens was staggered. Two further cycles of least-squares refinement were carried out, and the second yielded a residual index R of 0.092.

A difference Fourier map was then calculated in an attempt to determine the positions of the hydrogen atoms coordinated to the iron. The most prominent features of the map were two peaks, of height 0.67 and 0.49 e/Å^3, in the regions expected for the hydrogen atoms. Four other peaks on the map exceeded 0.40 e/Å^3; these were associated with remote ethoxy or phenyl carbon atoms which displayed particularly high anisotropic thermal parameters. A second difference Fourier map was calculated, limiting the data to those reflections having $\sin \theta/\lambda < 0.346$ ($2\theta < 77°$). The two peaks near the iron atom were again the most prominent, at 0.41 and 0.29 e/Å^3, but the next highest peaks did not correspond to the prominent peaks of the previous map. The two peaks were the largest in volume as well as intensity in both of the maps, leading to the conclusion that they indeed represented the hydrido hydrogen peaks. The coordinates of the two hydrogens were adjusted in the next least-squares refinement, but their temperature factors were held constant (B = 4 Å^2). The final least-squares refinement converged to a residual index R = 0.091. The rather high R value was due primarily to the previously mentioned noise in the 2θ scanning mechanism. Although below 100° most reflections were not affected significantly by the additional intensity, the very weak reflections undoubtedly were. (The R index for the 2320 reflections having an intensities large enough that the noise level would be insignificant was 0.059.)

Table III. Thermal Parameters of $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$ ($\times 10^5$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	717 (7)	298 (3)	591 (7)	−81 (3)	235 (6)	−11 (3)
	666 (21)	289 (7)	523 (19)	−91 (9)	293 (16)	−25 (9)
P(1)	935 (14)	338 (5)	697 (13)	−65 (7)	339 (11)	−26 (6)
	833 (31)	326 (10)	650 (29)	−39 (14)	340 (25)	−24 (13)
P(2)	741 (13)	343 (5)	650 (13)	−73 (6)	260 (11)	6 (6)
	731 (30)	321 (10)	647 (27)	−56 (13)	359 (23)	5 (12)
P(3)	689 (13)	313 (5)	647 (12)	−64 (6)	230 (11)	2 (6)
	647 (29)	309 (10)	641 (27)	−66 (12)	304 (23)	−1 (12)
P(4)	721 (13)	306 (5)	682 (13)	−43 (6)	227 (11)	6 (6)
	723 (30)	293 (10)	678 (28)	−34 (13)	322 (24)	−6 (12)
O(1)	1483 (41)	315 (13)	954 (34)	−17 (18)	452 (32)	−77 (17)
	1428 (94)	276 (27)	763 (84)	16 (38)	476 (75)	−119 (37)
O(2)	1018 (36)	693 (18)	964 (35)	−68 (20)	538 (31)	−109 (20)
	973 (88)	698 (34)	930 (84)	−9 (45)	606 (74)	−70 (42)
O(3)	961 (34)	418 (13)	1029 (34)	−81 (17)	540 (30)	−94 (17)
	1054 (84)	353 (27)	925 (72)	−26 (38)	636 (64)	−133 (37)
O(4)	882 (33)	518 (14)	679 (31)	−48 (17)	288 (28)	116 (17)
	763 (77)	488 (28)	533 (72)	−37 (36)	314 (61)	126 (35)
O(5)	1034 (34)	337 (12)	758 (31)	−10 (16)	216 (28)	−22 (16)
	930 (79)	270 (26)	718 (73)	−4 (35)	366 (63)	−7 (34)
O(6)	621 (30)	448 (13)	863 (32)	−20 (16)	170 (27)	126 (17)
	416 (75)	448 (27)	781 (75)	−29 (34)	156 (62)	128 (34)
O(7)	724 (31)	452 (13)	874 (32)	−164 (16)	297 (27)	−1 (17)
	654 (77)	443 (27)	735 (72)	−196 (36)	350 (62)	−19 (35)
O(8)	825 (33)	344 (13)	1315 (39)	10 (16)	63 (30)	58 (18)
	816 (81)	206 (25)	1362 (96)	68 (38)	158 (73)	88 (38)
C(1)	1228 (66)	326 (19)	731 (53)	−86 (28)	389 (47)	−88 (25)
	990 (128)	434 (43)	657 (109)	−108 (58)	456 (100)	−58 (55)
C(2)	1542 (74)	556 (26)	863 (62)	11 (33)	425 (63)	25 (32)
	1153 (145)	722 (56)	841 (133)	−2 (71)	398 (121)	9 (68)
C(3)	2006 (97)	731 (34)	750 (69)	138 (48)	260 (77)	106 (35)
	1948 (204)	825 (66)	873 (172)	50 (96)	612 (160)	57 (89)
C(4)	1939 (102)	539 (28)	873 (72)	89 (42)	14 (72)	−84 (35)
	1694 (186)	587 (56)	679 (218)	87 (82)	−144 (177)	24 (85)
C(5)	1360 (77)	584 (29)	1200 (74)	−208 (36)	82 (69)	−158 (37)
	1219 (159)	572 (54)	1448 (173)	−149 (72)	369 (142)	16 (73)
C(6)	1187 (68)	536 (26)	911 (62)	−230 (33)	132 (60)	−78 (31)
	1283 (148)	578 (50)	576 (154)	−94 (69)	29 (132)	149 (67)
C(7)	2124 (83)	430 (25)	1347 (67)	−69 (36)	755 (64)	−313 (33)
	1880 (190)	419 (51)	1340 (170)	−100 (76)	711 (151)	−166 (74)
C(8)	2929 (116)	505 (29)	2060 (95)	−322 (46)	937 (90)	−333 (43)
	2704 (239)	555 (59)	1764 (210)	−221 (95)	974 (192)	−466 (90)
C(9)	1159 (76)	1020 (39)	1405 (73)	−358 (43)	832 (67)	−371 (43)
	1492 (185)	979 (73)	1681 (163)	−276 (95)	1037 (152)	−414 (89)
C(10)	1794 (95)	1523 (59)	2385 (111)	−466 (60)	1415 (92)	−337 (66)
	1601 (207)	1599 (110)	2050 (168)	−149 (117)	1237 (154)	−333 (112)
C(11)	757 (55)	432 (24)	774 (50)	−106 (27)	206 (44)	130 (28)
	1020 (129)	317 (40)	708 (122)	−186 (57)	329 (107)	−13 (55)
C(12)	1095 (60)	329 (21)	1324 (63)	−156 (31)	372 (52)	1 (31)
	834 (126)	359 (42)	1290 (138)	−219 (57)	339 (108)	28 (57)
C(13)	1350 (72)	453 (27)	1838 (82)	−302 (39)	472 (69)	6 (36)
	1624 (182)	379 (48)	1795 (175)	−235 (75)	727 (146)	−143 (74)
C(14)	1648 (96)	716 (39)	2000 (99)	−574 (49)	640 (81)	15 (49)
	1441 (184)	753 (67)	2049 (196)	−613 (91)	775 (155)	75 (91)
C(15)	1523 (87)	994 (45)	2210 (104)	−509 (56)	1096 (80)	−158 (57)
	1463 (182)	955 (77)	2468 (160)	−450 (97)	1359 (134)	−261 (90)
C(16)	1062 (64)	696 (30)	1664 (76)	−358 (38)	768 (61)	−172 (38)
	1381 (155)	693 (56)	1576 (121)	−377 (74)	1117 (112)	−274 (68)
C(17)	1107 (57)	452 (22)	1148 (58)	−184 (29)	509 (50)	−166 (29)
	1312 (150)	349 (45)	1044 (123)	53 (66)	735 (114)	−93 (63)
C(18)	1588 (71)	488 (24)	1523 (70)	−4 (34)	874 (61)	−187 (33)
	1452 (157)	453 (47)	1181 (136)	−64 (69)	732 (123)	−158 (66)
C(19)	1362 (67)	884 (33)	840 (57)	84 (38)	506 (55)	297 (37)
	1219 (156)	947 (69)	777 (146)	204 (81)	438 (127)	497 (79)
C(20)	2016 (90)	882 (36)	1149 (68)	−59 (45)	473 (69)	448 (42)
	1905 (193)	877 (68)	1066 (157)	112 (90)	785 (150)	488 (85)
C(21)	859 (56)	284 (18)	801 (56)	20 (24)	337 (47)	60 (24)
	634 (112)	341 (38)	640 (104)	68 (50)	315 (89)	88 (49)
C(22)	970 (66)	790 (32)	1110 (64)	−153 (34)	352 (54)	362 (36)
	850 (130)	818 (59)	980 (143)	−94 (68)	266 (115)	354 (69)
C(23)	1203 (74)	863 (36)	1614 (84)	−28 (39)	707 (74)	462 (46)
	1055 (159)	925 (68)	1689 (148)	−69 (79)	820 (126)	496 (78)
C(24)	1711 (88)	619 (29)	1542 (86)	94 (41)	1037 (77)	326 (39)
	1503 (178)	763 (61)	1469 (147)	56 (86)	938 (132)	389 (78)
C(25)	1563 (86)	769 (33)	926 (64)	−2 (40)	479 (63)	252 (36)
	1581 (170)	910 (64)	689 (153)	103 (85)	529 (138)	319 (81)

Table III (*Continued*)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(26)	1170 (63)	589 (26)	836 (58)	−32 (31)	417 (57)	127 (31)
	964 (133)	746 (55)	695 (122)	−22 (65)	398 (107)	202 (64)
C(27)	1657 (72)	312 (20)	1262 (64)	115 (29)	416 (57)	46 (31)
	1647 (169)	272 (45)	1254 (157)	94 (69)	589 (139)	−6 (66)
C(28)	1486 (69)	368 (22)	1489 (69)	16 (30)	487 (59)	−193 (33)
	1131 (143)	370 (45)	1303 (153)	17 (63)	383 (124)	−87 (63)
C(29)	692 (54)	697 (28)	1154 (60)	−66 (29)	312 (49)	129 (33)
	764 (140)	679 (55)	1103 (136)	−53 (68)	381 (116)	142 (67)
C(30)	805 (58)	840 (33)	1566 (73)	−177 (34)	315 (57)	−25 (40)
	690 (135)	824 (60)	1310 (134)	−175 (71)	458 (112)	−26 (70)
C(31)	567 (46)	423 (24)	764 (56)	−157 (25)	165 (42)	−64 (28)
	447 (107)	380 (40)	595 (107)	−113 (50)	119 (90)	−4 (50)
C(32)	871 (55)	479 (26)	1036 (62)	−116 (29)	308 (48)	−181 (33)
	862 (124)	458 (43)	861 (122)	−4 (57)	375 (102)	−105 (56)
C(33)	1086 (65)	603 (29)	1551 (82)	−245 (34)	513 (63)	−359 (45)
	1137 (148)	560 (52)	1409 (152)	−116 (67)	611 (121)	−397 (67)
C(34)	1280 (75)	911 (43)	1217 (83)	−495 (47)	595 (67)	−490 (51)
	959 (150)	1027 (77)	1078 (141)	−478 (90)	526 (115)	−468 (87)
C(35)	1611 (81)	853 (39)	766 (65)	−518 (48)	404 (57)	−132 (44)
	1463 (168)	833 (65)	764 (150)	−461 (89)	449 (136)	−67 (86)
C(36)	1133 (62)	609 (27)	821 (61)	−269 (33)	267 (51)	−23 (36)
	1031 (133)	545 (48)	752 (132)	−164 (62)	260 (112)	−61 (61)
C(37)	797 (52)	624 (26)	1334 (63)	−266 (30)	425 (50)	−102 (33)
	732 (133)	587 (51)	1247 (134)	−154 (65)	490 (111)	−68 (64)
C(38)	1170 (67)	1044 (40)	1840 (82)	−538 (42)	700 (64)	74 (47)
	992 (152)	967 (72)	1786 (152)	−362 (83)	754 (123)	33 (83)
C(39)	1363 (69)	385 (23)	1752 (79)	121 (32)	105 (64)	13 (36)
	1188 (151)	317 (45)	1366 (175)	239 (69)	168 (137)	86 (69)
C(40)	1691 (81)	458 (26)	2255 (98)	105 (37)	294 (77)	229 (42)
	1917 (200)	392 (51)	2147 (224)	79 (79)	565 (178)	270 (80)

[a] The first line is for set D and the second line is for set C. The anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Results and Discussion

The final positional and thermal parameters and their estimated standard deviations[18] are given in Tables II and III. Tables of observed and calculated structure factors are available for both refinements.[19] The numbering system used is shown in Figure 1. The hydrogen atom parameters used in set D are listed in Table IV. In order to save space we have presented only the data from set D in Tables IV, VI, and VIII; the corresponding data for set C are entirely consistent with those presented.

The standard deviations of the structural parameters for set D are uniformly smaller than those of set C, and the agreement between chemically equivalent distances and angles is better in set D than in set C. It seems clear that the data for set D are inherently better than for set C, due to the electronic noise problem and the

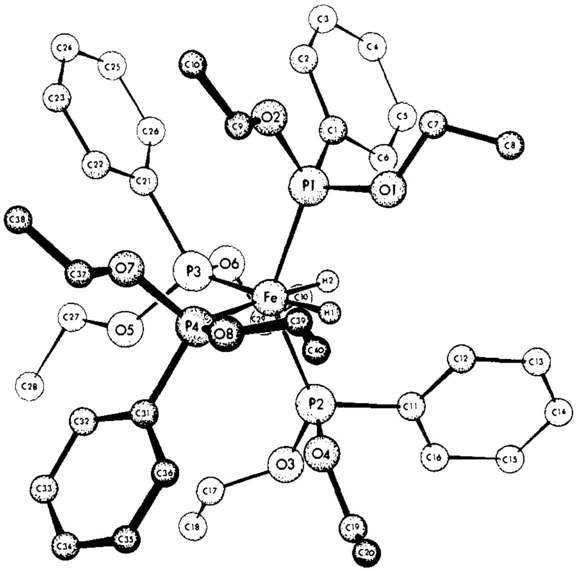

Figure 1. The molecular configuration of $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$. The benzene, methyl, and methylene hydrogen atoms are omitted.

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(18) The data collection and structure determination of set C was actually carried out on the basis of the Delaunay-reduced cell [a' = 17.494 (3), b' = 12.733 (7), c' = 11.940 (5) Å; α' = 123.00 (4), β' = 90.21 (4), γ' = 94.44 (4)°]. In order to properly calculate the standard deviations in the coordinates and temperature factors relative to the Bravais cell we report here, it would be necessary to take into account both the variances σ_{ii}^2 and covariances σ_{ij}^2 of the coordinates and temperature factors in the original coordinate system. Unfortunately, the covariances were not saved. Accordingly, we used the following simplified expressions, which were derived intuitively and include, among other approximations, the obviously unjustifiable assumption that the variance–covariance surface for each set of atomic parameters is approximately isotropic

$$\sigma_x = \sigma_{y'}(b'/a) \qquad \sigma_{B_{11}} = \sigma_{B_{22}'}(b'^2/a^2)$$
$$\sigma_y = \sigma_{x'} \qquad \sigma_{B_{22}} = \sigma_{B_{11}'}$$
$$\sigma_z = [\sigma_{y'}(b') + \sigma_{z'}(c')]/2c \qquad \sigma_{B_{33}} = \sigma_{B_{33}'}$$
$$\sigma_{B_{12}} = \sigma_{B_{12}'}(b'/a)$$
$$\sigma_{B_{13}} = \sigma_{B_{23}'}$$
$$\sigma_{B_{23}} = [\sigma_{B_{13}'}(a'c') + \sigma_{B_{12}'}(a'b')]/2bc$$

where the primes refer to the original Delaunay cell.

(19) Both structure factor tables are deposited (×10). The indices for set C are based on the cell used in that refinement. The data are correlated according to relationships: $h_D = -(k_C + l_C)$, $k_D = h_C$, and $l_D = l_C$. These tables will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

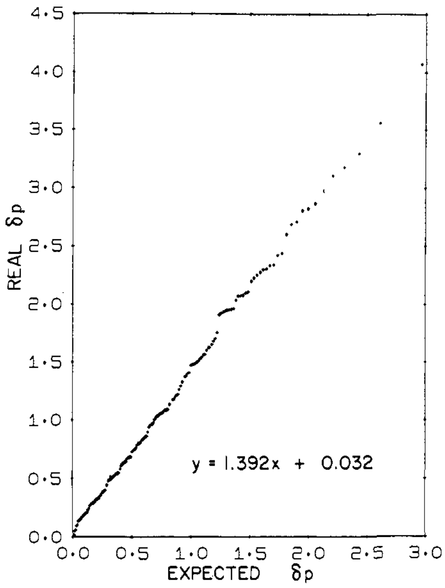

Figure 2. Half-normal probability plot of 165 δp_i from the two independent structure determinations of $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$. The equation is for the least-squares line with all points included in the calculation.

crystal decomposition experienced with data set C (*vide supra*). Of importance here is the question of whether the results of the two structure determinations are the same within the experimental errors. We have examined differences in coordinates (p_i) in a half-normal probability plot after the method of Abrahams and Keve[20] to make a statistical comparison of the results of the two structure refinements. This method compares the observed statistic δp_i where

$$\delta p_i = ||p(1)_i| - |p(2)_i||/[\sigma^2 p(1)_i + \sigma^2 p(2)_i]^{1/2}$$

with the expected δp for the probability function $P(x)$ where

$$P(x) = \frac{1}{\sqrt{2\pi}}\int_{-x}^{x} \exp(-\alpha^2/2)\mathrm{d}\alpha$$

Figure 2 shows the half-normal probability plot of the 165 δp_i coordinates in Table II. The pertinent features of Figure 2 are the linearity, essentially zero intercept, and the slope of about 1.4. The linearity and zero intercept indicate that the differences in the two structure refinements follow the Gaussian-type distribution. The fact that the slope is greater than 1.0 implies that the Δp_i are too large or the σp_i are too small. The most reasonable interpretation and the one we believe applies here is that the σp_i are underestimated (discussed in ref 20). The σ's for both refinements were perhaps uniformly underestimated (about 40% according to this plot). Additional evidence for this is the fact that the standard deviation of an observation of unit weight was larger than 1.0. The underestimation of derived standard deviations is quite common in structure refinements.[20,21] We conclude then that the results of the two structure determinations are the same within experimental errors (essentially normally distributed) and the standard deviations derived from the least-squares refinements are somewhat underestimated even though they appear to be quite reasonable in view of the observed parameter differences.

Table IV. Hydrogen Atom Position Parameters of $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$ (Set D)

Atom	*x*	*y*	*z*	*B*, Å^2 [a]
H(1)C(2)	0.2428	0.2312	−0.1317	6.3
H(2)C(3)	0.0520	0.2498	−0.3358	6.3
H(3)C(4)	−0.1569	0.2263	−0.3420	6.3
H(4)C(5)	−0.1743	0.1769	−0.1510	6.3
H(5)C(6)	0.0182	0.1550	0.0450	6.3
H(6)C(7)	0.3716	0.0181	0.0437	6.4
H(7)C(7)	0.2159	0.0586	−0.0503	6.4
H(8)C(8)	0.2210	−0.0802	−0.0117	8.7
H(9)C(8)	0.1332	−0.0256	0.0560	8.7
H(10)C(8)	0.2889	−0.0662	0.1499	8.7
H(11)C(9)	0.5425	0.1075	0.1531	7.9
H(12)C(9)	0.5395	0.1992	0.2173	7.9
H(13)C(10)	0.6826	0.1891	0.1173	10.1
H(14)C(10)	0.5537	0.2593	0.0406	10.1
H(15)C(10)	0.5567	0.1676	−0.0236	10.1
H(16)C(12)	0.1766	0.0692	0.2836	6.5
H(17)C(13)	0.0158	−0.0290	0.2282	6.5
H(18)C(14)	−0.1568	−0.0094	0.2949	6.5
H(19)C(15)	−0.1893	0.1117	0.3902	6.5
H(20)C(16)	−0.0389	0.2146	0.4345	6.5
H(21)C(17)	0.2341	0.3692	0.4567	5.2
H(22)C(17)	0.2606	0.3314	0.6045	5.2
H(23)C(18)	0.1224	0.4562	0.5540	6.3
H(24)C(18)	0.0397	0.3785	0.5661	6.3
H(25)C(18)	0.0132	0.4163	0.4182	6.3
H(26)C(19)	0.1901	0.1252	0.5974	6.6
H(27)C(19)	0.2628	0.2065	0.6767	6.6
H(28)C(20)	0.3580	0.0875	0.8015	8.2
H(29)C(20)	0.4676	0.1304	0.7610	8.2
H(30)C(20)	0.3949	0.0491	0.6817	8.2
H(31)C(22)	0.4310	0.3737	0.1849	5.8
H(32)C(23)	0.4931	0.4265	0.0260	5.8
H(33)C(24)	0.3323	0.4610	−0.1845	5.8
H(34)C(25)	0.1081	0.4417	−0.2369	5.8
H(35)C(26)	0.0483	0.3874	−0.0798	5.8
H(36)C(27)	0.0793	0.4952	0.1543	6.2
H(37)C(27)	0.2336	0.5139	0.1770	6.2
H(38)C(28)	0.1503	0.6061	0.2890	6.3
H(39)C(28)	0.2830	0.5467	0.3937	6.3
H(40)C(28)	0.1287	0.5280	0.3709	6.3
H(41)C(29)	−0.0317	0.3666	0.2282	8.5
H(42)C(29)	−0.0282	0.2747	0.1646	8.5
H(43)C(30)	−0.2430	0.3392	0.0795	6.6
H(44)C(30)	−0.1875	0.3263	−0.0371	6.6
H(45)C(30)	−0.1911	0.4182	0.0265	6.6
H(46)C(32)	0.4313	0.4163	0.4361	5.6
H(47)C(33)	0.4701	0.4950	0.6231	5.6
H(48)C(34)	0.5578	0.4270	0.8310	5.6
H(49)C(35)	0.5946	0.2851	0.8475	5.6
H(50)C(36)	0.5636	0.2090	0.6631	5.6
H(51)C(37)	0.7257	0.2526	0.4165	5.5
H(52)C(37)	0.6912	0.3305	0.4967	5.5
H(53)C(38)	0.8098	0.3702	0.3831	7.9
H(54)C(38)	0.6559	0.4189	0.3236	7.9
H(55)C(38)	0.6905	0.3410	0.2434	7.9
H(56)C(39)	0.5567	0.0886	0.3596	6.7
H(57)C(39)	0.4667	0.0906	0.4475	6.7
H(58)C(40)	0.6414	−0.0030	0.5260	8.1
H(59)C(40)	0.6544	0.0713	0.6315	8.1
H(60)C(40)	0.7444	0.0694	0.5435	8.1

[a] The hydrogen atom temperature factors were set to the equivalent isotropic temperature factors of the carbon atoms to which they are attached: W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

The structure consists of the packing of discrete molecules of $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$. The molecular configuration is shown in Figure 1. The bond distances and angles for the inner coordination sphere about the iron atom are given in Table V. The distances and angles involving the ligand atoms are given in Table VI.

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(20) S. C. Abrahams and E. T. Keve, *Acta Crystallogr., Ser. A*, **27**, 157 (1971).

(21) W. C. Hamilton and S. C. Abrahams, *ibid.*, **26**, 18 (1969).

Table V. Bond Distances and Angles for the Inner Coordination Sphere of the Iron Atom

Distances, Å			Angles, deg		
Atoms	Set D	Set C	Atoms	Set D	Set C
Fe–P(1)	2.134 (2)	2.132 (3)	P(1)–Fe–P(2)	136.70 (6)	136.6 (1)
Fe–P(2)	2.119 (2)	2.127 (2)	P(1)–Fe–P(3)	97.47 (7)	97.7 (1)
Fe–P(3)	2.153 (2)	2.146 (3)	P(1)–Fe–P(4)	108.68 (6)	108.4 (1)
Fe–P(4)	2.151 (2)	2.147 (3)	P(1)–Fe–H(1)	80.63 (168)	75.3 (26)
Fe–H(1)	1.520 (44)	1.435 (59)	P(1)–Fe–H(2)	71.74 (168)	73.6 (21)
Fe–H(2)	1.502 (43)	1.562 (73)	P(2)–Fe–P(3)	108.23 (6)	108.3 (1)
P(1)–P(2)	3.953 (2)	3.957 (3)	P(2)–Fe–P(4)	99.34 (7)	99.4 (1)
P(1)–P(3)	3.222 (2)	3.221 (3)	P(2)–Fe–H(1)	69.69 (166)	69.6 (23)
P(1)–P(4)	3.481 (2)	3.472 (4)	P(2)–Fe–H(2)	76.73 (168)	75.3 (23)
P(1)–H(1)	2.410 (45)	2.248 (65)	P(3)–Fe–P(4)	102.28 (6)	102.3 (1)
P(1)–H(2)	2.191 (44)	2.259 (58)	P(3)–Fe–H(1)	173.14 (161)	162.8 (31)
P(2)–P(3)	3.461 (2)	3.462 (3)	P(3)–Fe–H(2)	84.32 (167)	83.9 (22)
P(2)–P(4)	3.255 (3)	3.260 (3)	P(4)–Fe–H(1)	84.56 (161)	94.9 (30)
P(2)–H(1)	2.137 (44)	2.111 (58)	P(4)–Fe–H(2)	173.19 (167)	172.9 (23)
P(2)–H(2)	2.299 (44)	2.296 (70)	H(1)–Fe–H(2)	88.83 (229)	79.0 (37)
P(3)–P(4)	3.351 (2)	3.343 (4)			
P(3)–H(1)	3.666 (42)	3.542 (62)			
P(3)–H(2)	2.500 (43)	2.518 (57)			
P(4)–H(1)	2.513 (43)	2.682 (66)			
P(4)–H(2)	3.647 (41)	3.703 (74)			
H(1)–H(2)	2.115 (53)	1.909 (104)			

Table VI. Distances and Angles for the Ligand Atoms (Set D)[a]

Distances, Å			
P(1)–O(1)	1.626 (3)	C(1)–C(2)	1.391 (7)
P(1)–O(2)	1.626 (3)	C(1)–C(6)	1.381 (7)
P(2)–O(3)	1.633 (3)	C(2)–C(3)	1.389 (8)
P(2)–O(4)	1.640 (3)	C(3)–C(4)	1.373 (9)
P(3)–O(5)	1.634 (3)	C(4)–C(5)	1.384 (8)
P(3)–O(6)	1.627 (3)	C(5)–C(6)	1.410 (7)
P(4)–O(7)	1.629 (3)	C(11)–C(12)	1.396 (6)
P(4)–O(8)	1.623 (3)	C(11)–C(16)	1.384 (7)
		C(12)–C(13)	1.394 (7)
	1.630 (2)	C(13)–C(14)	1.359 (9)
P(1)–C(1)	1.837 (4)	C(14)–C(15)	1.372 (9)
P(2)–C(11)	1.839 (5)	C(15)–C(16)	1.404 (8)
P(3)–C(21)	1.839 (6)	C(21)–C(22)	1.384 (6)
P(4)–C(31)	1.836 (5)	C(21)–C(26)	1.373 (6)
		C(22)–(C23)	1.394 (7)
	1.838 (3)	C(23)–C(24)	1.365 (8)
O(1)–C(7)	1.448 (7)	C(24)–C(25)	1.361 (7)
O(2)–C(9)	1.421 (6)	C(25)–C(26)	1.387 (7)
O(3)–C(17)	1.437 (5)	C(31)–C(32)	1.390 (6)
O(4)–C(19)	1.450 (7)	C(31)–C(36)	1.389 (7)
O(5)–C(27)	1.446 (5)	C(32)–C(33)	1.413 (7)
O(6)–C(29)	1.429 (7)	C(33)–C(34)	1.388 (8)
O(7)–C(37)	1.451 (5)	C(34)–C(35)	1.368 (8)
O(8)–C(39)	1.392 (6)	C(35)–C(36)	1.390 (8)
	1.434 (7)		1.385 (3)
C(7)–C(8)	1.463 (10)		
C(9)–C(10)	1.433 (13)		
C(17)–C(18)	1.502 (8)		
C(19)–C(20)	1.430 (7)		
C(27)–C(28)	1.473 (8)		
C(29)–C(30)	1.489 (6)		
C(37)–C(38)	1.477 (10)		
C(39)–C(40)	1.440 (7)		
	1.463 (9)		

Interligand contacts	
P(4)–O(4)	3.303 (4)
O(3)–C(29)	3.467 (6)
O(4)–O(8)	3.486 (5)
O(4)–C(31)	3.357 (6)
O(4)–C(36)	3.190 (6)
O(5)–C(17)	3.308 (7)
O(5)–C(32)	3.191 (6)
O(7)–C(9)	3.316 (8)
O(7)–C(22)	3.157 (6)
C(2)–C(26)	3.303 (8)
C(17)–C(32)	3.392 (8)

Angles, deg			
Fe–P(1)–O(1)	109.64 (13)	Fe–P(3)–O(5)	117.10 (12)
Fe–P(1)–O(2)	128.15 (14)	Fe–P(3)–O(6)	118.35 (12)
Fe–P(1)–C(1)	118.24 (15)	Fe–P(3)–C(21)	121.13 (14)
O(1)–P(1)–O(2)	101.42 (16)	O(5)–P(3)–O(6)	101.46 (16)
O(1)–P(1)–C(1)	100.88 (19)	O(5)–P(3)–C(21)	100.34 (17)
O(2)–P(1)–C(1)	94.28 (16)	O(6)–P(3)–C(21)	94.21 (15)
P(1)–O(1)–C(7)	122.11 (30)	P(3)–O(5)–C(27)	121.16 (28)
P(1)–O(2)–C(9)	122.81 (27)	P(3)–O(6)–C(29)	121.98 (23)
P(1)–C(1)–C(2)	123.12 (33)	P(3)–C(21)–C(22)	118.60 (31)
P(1)–C(1)–C(6)	118.17 (32)	P(3)–C(21)–C(26)	123.25 (31)
O(1)–C(7)–C(8)	108.63 (45)	O(5)–C(27)–C(28)	109.04 (40)
O(2)–C(9)–C(10)	112.04 (44)	O(6)–C(29)–C(30)	108.05 (33)
C(1)–C(2)–C(3)	121.42 (56)	C(21)–C(22)–C(23)	120.72 (47)
C(2)–C(3)–C(4)	119.72 (59)	C(22)–C(23)–C(24)	120.41 (51)
C(3)–C(4)–C(5)	120.07 (57)	C(23)–C(24)–C(25)	118.88 (52)
C(4)–C(5)–C(6)	120.09 (57)	C(24)–C(25)–C(26)	121.41 (51)
C(5)–C(6)–C(1)	119.98 (52)	C(25)–C(26)–C(21)	120.43 (47)
C(6)–C(1)–C(2)	118.71 (47)	C(26)–C(21)–C(22)	118.14 (43)
Fe–P(2)–O(3)	126.54 (13)	Fe–P(4)–O(7)	116.46 (12)
Fe–P(2)–O(4)	111.99 (13)	Fe–P(4)–O(8)	120.17 (12)
Fe–P(2)–C(11)	117.00 (14)	Fe–P(4)–C(31)	121.42 (14)
O(3)–P(2)–O(4)	101.97 (17)	O(7)–P(4)–O(8)	99.56 (17)
O(3)–P(2)–C(11)	94.27 (16)	O(7)–P(4)–C(31)	99.08 (18)
O(4)–P(2)–C(11)	101.05 (18)	O(8)–P(4)–C(31)	95.53 (20)
P(2)–O(3)–C(17)	120.00 (23)	P(4)–O(7)–C(37)	122.04 (24)
P(2)–O(4)–C(19)	121.42 (24)	P(4)–O(8)–C(39)	128.29 (29)
P(2)–C(11)–C(12)	118.38 (32)	P(4)–C(31)–C(32)	118.75 (37)
P(2)–C(11)–C(16)	122.04 (34)	P(4)–C(31)–C(36)	122.11 (40)
O(3)–C(17)–C(18)	107.67 (33)	O(7)–C(37)–C(38)	109.02 (37)
O(4)–C(19)–C(20)	111.28 (39)	O(8)–C(39)–C(40)	113.14 (45)
C(11)–C(12)–C(13)	120.80 (50)	C(31)–C(32)–C(33)	120.22 (50)
C(12)–C(13)–C(14)	119.44 (58)	C(32)–C(33)–C(34)	119.06 (54)
C(13)–C(14)–C(15)	120.51 (55)	C(33)–C(34)–C(35)	120.68 (54)
C(14)–C(15)–C(16)	121.29 (58)	C(34)–C(35)–C(36)	120.31 (55)
C(15)–C(16)–C(11)	118.43 (55)	C(35)–C(36)–C(31)	120.59 (52)
C(16)–C(11)–C(12)	119.51 (43)	C(36)–C(31)–C(32)	119.12 (45)

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[a] The covariances were included in the estimation of the errors when the atoms involved were in the same refinement group; otherwise the error estimate was made using only the variances. The errors in angles were made using Cruickshank's formula (ref 15, p 331) when the three atoms were not in the same refinement group. The error of the mean is the larger of the two values resulting from the calculation from the individual errors and from $[\sum^{n}_{i=1}(d_i - \bar{d})^2/n(n - 1)]^{1/2}$ where d_i and $\bar{d}$ are the distances and mean distance, respectively.

Table VII. Comparison of Observed Fe–P Bond Distances

Complex	Fe coordination	Distance, Å	Ref
cis-$H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$	6	Set D 2.127 (2) Set C 2.129 (3) } ax	
		Set D 2.152 (2) Set C 2.147 (3) } eq	
$C_5H_5Fe[P(OC_6H_5)_3]_2I$	6[a]	2.15 (2)	*b*
$Fe(CO)_4PH(C_6H_5)_2$	5	2.237 (2)	*c*
$(OC)_4Fe[P(CH_3)_2]_2Fe(CO)_4$	5	2.260 (5)	*d*
$Fe_3(CO)_9[P(CH_3)_2(C_6H_5)_2]_3$	6	2.242 (9)	*e*
	7	2.234 (9)	
$Fe_3(CO)_{11}P(C_6H_5)_3$	6	2.25	*f*
FeP_2 (marcasite structure)	6	2.27	*g*
Pauling's covalent radii	6[h]	2.33	*i*

[a] Assuming the C_5H_5 ligand occupies three coordination sites. [b] V. G. Andrianov, Yu. A. Chapovskii, V. A. Semion, and Yu. T. Struchkov, *Chem. Commun.*, 282 (1968). [c] B. T. Kilbourn, U. A. Raeburn, and D. T. Thompson, *J. Chem. Soc. A*, 1906 (1969). [d] J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *ibid.*, 622 (1968). [e] W. S. McDonald, J. R. Moss, G. Raper, and B. L. Shaw, *Chem. Commun.*, 1295 (1969). [f] D. J. Dahm and R. A. Jacobson, *ibid.*, 496 (1966). [g] D. E. C. Corbridge, *Top. Phosphorus Chem.*, 3, 139 (1966). [h] 1.23 Å for Fe(II) and 1.10 Å for P. [i] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

The molecular configuration is that of the cis isomer as shown in Figure 1. The H(1), H(2), Fe, P(3), and P(4) atoms are coplanar with no atom deviating by more than 0.015 Å from the least-squares plane (equatorial plane). The axial phosphorus atoms, P(1) and P(2), are 1.998 and 1.929 Å from the equatorial plane. These axial phosphorus atoms are bent away from ideal octahedral positions toward a tetrahedral configuration. The resultant iron–phosphorus geometry is closer to tetrahedral than octahedral [the P(1)–Fe–P(2) angle is 136.7 (1)°], but it is probably best described as being intermediate between the two. The hydrogen atoms appear to exert a small, but statistically significant, trans influence as evidenced by the equatorial Fe–P distances being about 0.02 Å longer than the axial distances. By trans influence we mean the ability of a ligand to labilize the bond trans to it as opposed to trans effect which applies to reaction energetics.[22] Ultraviolet studies indicate that diethyl phenylphosphonite is capable of significant π interaction with transition metals.[23] A strongly σ trans-influencing ligand such as hydride can weaken a metal–ligand σ bond trans to it but has little effect on a π bond. Thus, the lengthening of the trans Fe–P bond observed here is probably the result of weakening of the Fe–P σ bond. Presumably, the metal–ligand π bond compensates partially for the weakened σ bond, thus reducing the detectable lengthening effect.

A comparison of observed Fe–P bond distances is given in Table VII. The distances observed in this work are close to those observed in $C_5H_5Fe[P(OC_6H_5)_3]_2I$ which is the closest compound chemically (in coordination and formal metal oxidation state) to that reported here. All of the distances are significantly shorter than the sum of Pauling's covalent radii. It is fashionable to attribute this shortening to metal–ligand π bonding, and the physical evidence mentioned above tends to support this theory. The largest thermal motion correction to the Fe–P distances, assuming a riding model,[24] is 0.005 Å.

Table VIII. Least-Squares Planes for $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$ (Set D)[a]

1. $-0.26641X + 0.93538Y + 0.23259Z - 2.7192 = 0$
   C1 (0.001), C2 (0,001), C3 (−0.001),
   C4 (−0.002), C5 (0.004), C6 (−0.004)
2. $0.19087X - 0.40363Y + 0.89479Z + 2.2729 = 0$
   C11 (0.008), C12 (−0.002), C13 (−0.003),
   C14 (0.001), C15 (0.005), C16 (−0.009)
3. $-0.26990X + 0.92620Y + 0.26325Z - 5.8998 = 0$
   C21 (−0.003), C22 (0.002), C23 (0.002),
   C24 (−0.004), C25 (0.003), C26 (0.001)
4. $0.97430X + 0.19043Y + 0.12035Z - 4.8371 = 0$
   C31 (0.000), C32 (−0.003), C33 (0.001),
   C34 (0.005), C35 (−0.008), C36 (0.006)

Dihedral Angles

Plane	Plane	Angle, deg	Plane	Plane	Angle, deg
P(1)FeP(2)	P(3)FeP(4)	96.8	1	2	102.7
FeP(1)C(1)	1	54.7	1	3	1.8
FeP(2)C(11)	2	140.0	1	4	93.1
FeP(3)C(21)	3	61.0	2	3	100.9
FeP(4)C(31)	4	76.5	2	4	77.5
			3	4	93.1

[a] The atoms defining the plane and the distances from the planes are listed below the equation of the plane. The planes are relative to an orthogonal set of axes with *Y* and *Z* coincident with *b* and *c** and *X* in the *ab* plane perpendicular to *b* and *c**.

The average P–C (1.838 Å for set D, 1.82 Å for set C), P–O (1.630 Å for set D, 1.62 Å for set C), and O–C (1.434 Å for set D, 1.42 Å for set C) distances fall well within the range of chemically similar distances frequently found in organophosphines and orthophosphate esters.[25] Of some possible significance here is the fact that all of the P–O distances observed here fall on the upper end of the range of reported values which have a mean of 1.59 (4) Å. This can be correlated with the short Fe–P distances. The C–C distances in the ethoxy groups average 1.463 Å for set D and 1.44 Å for set C with a good deal of scatter about the average. A similar situation was observed for the same ligand in the structure of $Ni(CN)_2[P(C_6H_5)(OC_2H_5)_2]_3$ where the average C–C distance was 1.44 Å.[26] This scatter was interpreted in terms of slight disordering of the ethoxy

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(22) L. M. Venanzi, *Chem. Brit.*, 4, 162 (1968).
(23) A. A. Orio, B. B. Chastain, and H. B. Gray, *Inorg. Chim. Acta*, 3, 8 (1969).
(24) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 17, 142 (1964).
(25) See ref *g* of Table VII, p 212.
(26) J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 8, 1084 (1969).

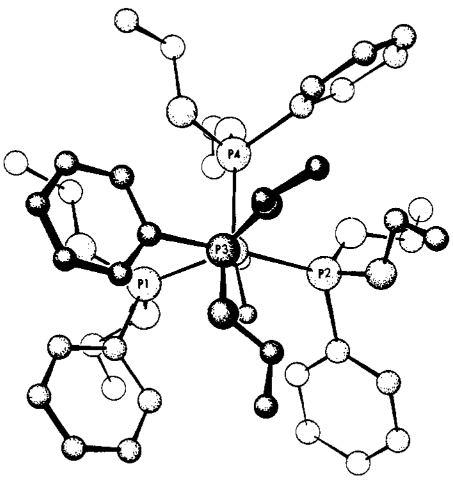

Figure 3. The $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$ molecule viewed in the direction normal to the P(1)P(2)P(4) plane, *i.e.*, in the direction of one of the equatorial Fe–P bonds.

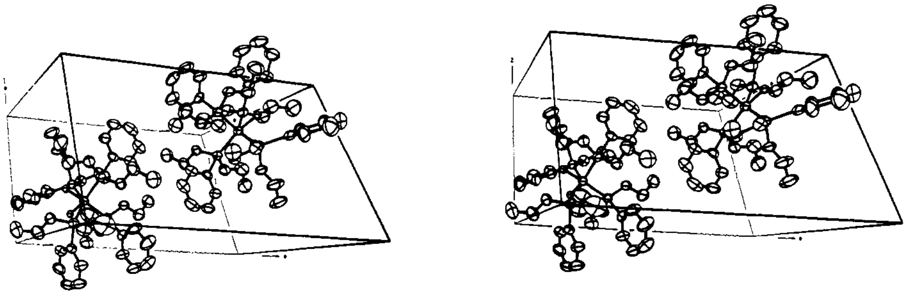

Figure 4. A stereoscopic drawing of one unit cell of $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$. The benzene, methyl, and methylene hydrogen atoms have been omitted for clarity.

groups. The corresponding P–C, P–O, and O–C distances in the $Ni(CN)_2[P(C_6H_5)(OC_2H_5)_2]_3$ structure are 1.82, 1.62, and 1.42 Å, respectively. The average benzene C–C distance of 1.385 Å found here is similar to that frequently found in X-ray determinations.[27] The least-squares planes through the benzene carbon atoms are given in Table VIII.

The shortest distances between nonbonding heavy atoms in the ligands are given in Table VI. Most of these contacts involve oxygen atoms and benzene carbon atoms. Based on these interactions the most severe repulsive interactions are between the ligands on P(2) and P(4) and between the ligands on P(3) and P(4). The molecule as a whole has no idealized symmetry. Ligands on P(3) and P(4), however, are related by an idealized twofold axis. The dihedral angle between the planes [P(1), Fe, P(2)] and [P(3), Fe, P(4)] is 96.8° instead of the 90° expected for either the octahedral or tetrahedral Fe–P geometries. The tetrahedral aspects of the iron–phosphorus geometry are emphasized in Figure 3 which is a projection on the [P(1), P(2), P(4)] plane. The Fe atom is 0.47 Å from this plane while the P(3) atom is 2.61 Å above the plane nearly directly above the Fe atom.

The benzene rings on P(1) and P(3) are nearly parallel (Table VIII) while the other dihedral angles between rings are close to 90° (78–103°) reflecting the minimization of both intramolecular and intermolecular contacts. A stereo view of the packing in the unit cell is given in Figure 4. The intermolecular contacts are of the normal van der Waals type; the shortest nonhydrogen intermolecular contact is 3.47 Å. Figure 4 also illustrates the thermal ellipsoids plotted at the 50% probability level. The root-mean-square amplitudes of vibration vary between 0.18 and 0.49 Å. The largest ratio between the largest and smallest magnitudes of vibration is 2.1 for C(38).

The temperature-dependent ^{31}P and ^{1}H nmr spectra[28] of $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$ and $H_2Fe[P(OC_2H_5)_3]_4$ have been analyzed in terms of rapid intramolecular isomerization through a transition state with a tetrahedral configuration of phosphorus atoms. The solid state geometry reported here lends some support to this interpretation since the ground state geometry approaches a tetrahedral iron–phosphorus disposition.

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