Metal–Carbonyl and Metal–Nitrosyl Complexes. Part XVI.[1] Comparison of the Molecular Structures of Dicarbonyl(π-cyclopentadienyl)[bis(trifluoromethyl)phosphino]iron, $[(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2]$, and its Oxidation Product, $[(\pi\text{-}C_5H_5)Fe(CO)_2P(:O)(CF_3)_2]$, as Determined by *X*-Ray Crystallography †

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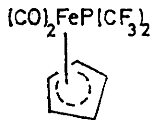
The molecular geometries of the complexes $[(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2]$ (1) and $[(\pi\text{-}C_5H_5)Fe(CO)_2P(\dot{:}O)(CF_3)_2]$ (2) have been determined by *X*-ray crystal-structure analysis. Mean P–C bond lengths [1·878(8) in (1), 1·887(6) Å in (2)] demonstrate that the covalent radius of phosphorus is essentially the same in both complexes, but the difference in the Fe–P bond length [2·265(3) in (1), 2·191(3) Å in (2)] is interpreted in terms of increased Fe→P d_π–d_π back bonding in (2). The P–O bond length in (2) is 1·478(5) Å. Both complexes crystallize in the monoclinic system, space group $P2_1/c$, with $Z = 4$; unit-cell dimensions are: (1), $a = 8{\cdot}602(7)$, $b = 11{\cdot}924(9)$, $c = 12{\cdot}859(9)$ Å, $\beta = 112{\cdot}75(9)°$; (2), $a = 11{\cdot}938(8)$, $b = 7{\cdot}603(6)$, $c = 13{\cdot}818(9)$ Å, $\beta = 100{\cdot}97(8)°$. The crystal structures were elucidated by Fourier and full-matrix least-squares methods from diffractometer data. The analyses converged at R 4·8% [1882 reflections, (1)] and 4·5% [1777 reflections, (2)].

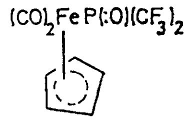
VARIOUS spectroscopic results are consistent with some degree of M→P d_π–d_π back bonding in complexes which contain phosphorus ligands and transition metals.[2] Moreover, the shortening of the Cr–P bond in pentacarbonyl(triphenyl phosphite)chromium (2·309 Å) as compared with that in pentacarbonyl(triphenylphosphine)chromium (2·422 Å)[3] and of the Mo–P bond in *trans*-dicarbonyl-π-cyclopentadienyl-iodo(trimethyl phosphite)molybdenum (2·406 Å)[4] as compared with that in *trans*-dicarbonyl-π-cyclopentadienyl-iodo(triphenylphosphine)molybdenum (2·481 Å)[5] have been interpreted as indisputable evidence for π-bonding. Nevertheless, the range of metal–phosphorus distances measured for any one transition metal is large, *e.g.* Fe–P *ca.* 2·1—2·4 Å, and it is unclear how much of this variation should in general be ascribed to π-bonding, since it is possible to argue that changes in the σ-component of the metal–phosphorus bond are at least partly responsible. There have been few systematic structural studies aimed specifically at elucidating this problem.

We have now completed structural investigations of two closely related complexes, $[(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2]$ (1) and $[(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2]$ (2), where spectroscopic measurements suggest an appreciable difference in the extent of Fe→P π-bonding. In particular, the



(1)

$(CO)_2FeP(CF_3)_2$



(2)

$(CO)_2FeP(:O)(CF_3)_2$

shift of the C–O stretching bands from 2046 and 2000 cm^{-1} in (1) to 2062 and 2019 cm^{-1} in (2) has been related to reduced Fe→CO, and hence presumably increased Fe→P, π-bonding in the case of (2), while the shift in the π-C_5H_5 resonance in the ^{1}H n.m.r. spectrum from τ 4·60 in (1) to 4·36 in (2) is also considered to be evidence for increased Fe→P back bonding in the phosphine oxide complex.[6] The *X*-ray results establish that whereas the P–C bond lengths are essentially the same in both complexes, the Fe–P bond in (2) is *ca.* 0·07 Å shorter than that in (1).

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† Reprints not available.

[1] Part XV, D. I. Woodhouse, G. A. Sim, and J. G. Sime, *J.C.S. Dalton*, 1974, 1331.

[2] J. G. Verkade, *Co-ordination Chem. Rev.*, 1972, **9**, 1, and refs. therein.

[3] H. J. Plastas, J. M. Stewart, and S. O. Grim, *J. Amer. Chem. Soc.*, 1969, **91**, 4326.

[4] A. D. U. Hardy and G. A. Sim, *J.C.S. Dalton*, 1972, 1900.

[5] M. A. Bush, A. D. U. Hardy, Lj. Manojlović-Muir, and G. A. Sim, *J. Chem. Soc.* (*A*), 1971, 1003.

[6] R. C. Dobbie and P. R. Mason, *J.C.S. Dalton*, 1973, 1124; M. J. Barrow, G. A. Sim, R. C. Dobbie, and P. R. Mason, *J. Organometallic Chem.*, 1974, **69**, C4.

EXPERIMENTAL

Crystallographic Data.—(1), [(π-C_5H_5)Fe(CO)$_2$P(CF$_3$)$_2$]. $C_9H_5F_6FeO_2P$, $M = 345·95$, Monoclinic, $a = 8·602(7)$, $b = 11·924(9)$, $c = 12·859(9)$ Å, $\beta = 112·75(9)°$, $U = 1216·3$ Å^3, $Z = 4$, $D_c = 1·89$, $F(000) = 680$. Space group $P2_1/c$ (C^5_{2h}, No. 14). Mo-K_α radiation, $\lambda = 0·71069$ Å; μ(Mo-K_α) = 14·7 cm^{-1}.

The crystals were yellow-brown and of irregular shape. Crystal used for intensity measurements had dimensions *ca.* 0·4 × 0·3 × 0·3 mm^3. Four-circle diffractometer intensity data (Zr filter) yielded 2913 independent reflections in range $\theta < 28°$; analysis based on 1882 reflections having $I > 3\sigma(I)$. Final least-squares weighting scheme: $w^{-1} = 1 + 0·0025\ (F_o - 10)^2$; analysis terminated at R 4·8%.

(2), [(π-C_5H_5)Fe(CO)$_2$P(O)(CF$_3$)$_2$]. $C_9H_5F_6FeO_3P$, $M = 361·95$, Monoclinic, $a = 11·938(8)$, $b = 7·603(6)$, $c = 13·818(9)$ Å, $\beta = 100·97(8)°$, $U = 1231·3$ Å^3, $Z = 4$, $D_c = 1·95$, $F(000) = 712$. Space group $P2_1/c$ (C^5_{2h}, No. 14). Mo-K_α radiation; μ(Mo-K_α) = 14·8 cm^{-1}.

The crystals were yellow needles. Crystal used for intensity measurements had dimensions *ca.* 0·4 × 0·4 × 0·3 mm^3. Four-circle diffractometer intensity data (graphite monochromator) yielded 2519 independent reflections in range $\theta < 25°$; analysis based on 1777 reflections having $I > 3\sigma(I)$. Final least-squares weighting scheme: $w^{-1} = 1 + 0·025\ (F_o - 15)^2$; analysis terminated at R 4·5%.

Structure Analysis.—Space-group information and approximate cell dimensions were obtained from Weissenberg and precession photographs. Intensity measurements were made with a Hilger and Watts four-circle computer-controlled X-ray diffractometer. The crystal axes were misaligned with respect to the instrument axes in order to minimize the effects of multiple reflections and the cell dimensions and orientation matrices were derived by least-squares treatment of the θ, χ, ϕ setting angles of twelve reflections (determined by a peak-finder programme) measured at both positive and negative ω—2θ offsets. Intensities were measured by the ω—2θ step-scan method and were placed on a uniform arbitrary scale by the periodic monitoring of several standard reflections. Intensities were corrected for Lorentz and polarization effects but absorption was neglected.

Initial co-ordinates for the iron atoms were derived from three-dimensional Patterson syntheses and the positions of the remaining non-hydrogen atoms were obtained from F_o Fourier syntheses. Positional and isotropic thermal parameters were then adjusted by a series of full-matrix least-squares calculations employing a unit weighting scheme. When convergence was reached, the hydrogen atoms were located in difference electron-density distributions and were introduced into the structure-factor calculations at theoretical positions [r(C–H) 1·00 Å] and with fixed isotropic temperature factors [B 4·00 Å^2]. At no stage of the analyses were any of the hydrogen parameters refined by the least-squares programme, although the co-ordinates were periodically recalculated to take account of the shifts of the carbon atoms.

The least-squares refinement procedure was continued with the provision of anisotropic thermal parameters for all non-hydrogen atoms. In the final two rounds allowance was made for the real and imaginary parts of the anomalous-dispersion corrections for iron and phosphorus.[7]

At the same time analytical weighting schemes were introduced to maintain $\langle w(F_o - F_c)^2\rangle$ approximately constant for different values of F_o over the whole range of F_o. Also during the two final cycles of refinement certain of the most intense reflections which were believed to be affected by extinction or dead-time losses and which were consistently calculated with $F_c > F_o$ were removed from the data sets. For complex (1) reflections 002, 012, 020, 021, $10\bar{2}$, $11\bar{2}$, 110, $14\bar{3}$, and $21\bar{1}$ were omitted, while for (2) only 020 and 200 were removed. No parameter shift during the terminal stages of the refinement procedure was >14% of the relevant σ, and difference-Fourier syntheses computed after completion of the analyses showed no significant peak or trough.

TABLE 1

Atomic parameters, with estimated standard deviations in parentheses, for (1)

Atom	x	y	z
Fe	0·30935(7)	0·15778(5)	0·21409(5)
P	0·05076(15)	0·17287(10)	0·07380(10)
C(1)	0·2585(7)	−0·0154(4)	0·2093(5)
C(2)	0·3938(7)	0·0041(5)	0·1775(4)
C(3)	0·5248(6)	0·0554(5)	0·2680(5)
C(4)	0·4694(6)	0·0686(4)	0·3555(4)
C(5)	0·3036(7)	0·0255(5)	0·3195(5)
C(6)	0·3978(6)	0·2463(4)	0·1417(4)
O(6)	0·4613(6)	0·3010(4)	0·0967(4)
C(7)	0·2801(7)	0·2671(4)	0·2983(4)
O(7)	0·2708(6)	0·3349(3)	0·3576(3)
C(8)	0·0130(8)	0·3250(5)	0·0352(5)
C(9)	−0·1077(7)	0·1665(6)	0·1415(6)
F(1)	0·1015(6)	0·3531(4)	−0·0268(4)
F(2)	0·0534(7)	0·3996(3)	0·1167(4)
F(3)	−0·1459(6)	0·3460(4)	−0·0312(4)
F(4)	−0·0956(5)	0·0708(4)	0·1947(5)
F(5)	−0·2660(4)	0·1706(5)	0·0632(4)
F(6)	−0·1015(5)	0·2450(4)	0·2159(4)
H(1)	0·1492	−0·0519	0·1622
H(2)	0·3972	−0·0151	0·1027
H(3)	0·6373	0·0781	0·2690
H(4)	0·5354	0·1028	0·4308
H(5)	0·2314	0·0243	0·3645

Anisotropic temperature coefficients in the form: $t = \exp[-2\pi^2 10^{-3}(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	50·1(3)	43·7(3)	47·4(3)	0·7(3)	19·5(2)	−2·4(3)
P	52·6(6)	61·8(7)	53·2(6)	7·4(5)	16·0(5)	−2·5(5)
C(1)	77(3)	42(2)	89(4)	−1(2)	10(3)	4(2)
C(2)	93(4)	67(3)	64(3)	28(3)	30(3)	−4(2)
C(3)	56(3)	75(3)	79(3)	16(2)	24(3)	4(3)
C(4)	66(3)	72(3)	55(3)	11(2)	13(2)	9(2)
C(5)	76(3)	63(3)	80(3)	13(2)	37(3)	22(3)
C(6)	66(3)	58(3)	66(3)	−8(2)	32(2)	−7(2)
O(6)	103(3)	83(2)	106(3)	−22(2)	62(3)	2(2)
C(7)	83(3)	52(2)	58(3)	−1(2)	30(2)	−3(2)
O(7)	139(4)	68(2)	80(2)	7(2)	50(3)	−20(2)
C(8)	91(4)	83(4)	76(4)	31(3)	28(3)	23(3)
C(9)	57(3)	93(4)	113(5)	−2(3)	34(3)	0(4)
F(1)	156(4)	121(3)	132(3)	40(3)	87(3)	63(3)
F(2)	207(5)	61(2)	106(3)	38(2)	55(3)	13(2)
F(3)	102(3)	145(4)	152(4)	59(3)	17(3)	55(3)
F(4)	106(3)	128(3)	222(6)	−5(3)	101(4)	48(4)
F(5)	55(2)	214(5)	132(3)	8(2)	26(2)	−25(3)
F(6)	118(3)	143(4)	114(3)	−1(3)	77(3)	−25(3)

All hydrogen atoms have B 4·0 Å^2.

Throughout the structure-factor calculations the atomic scattering factors of ref. 8 were used for non-hydrogen atoms, and of ref. 9 for hydrogen atoms. Observed and

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[7] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[8] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[9] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

calculated structure factors are listed in Supplementary Publication No. SUP 21207 (19 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Table 1 gives the final atomic parameters for complex (1) while those for (2) are given in Table 2. Details of the molecular geometries are listed in Table 3, and of planes in Table 4. The molecules are separated by normal van der Waals distances, the shorter of which are listed in Table 5. The atom labelling schemes are indicated in Figures 1 and 2 which show molecules of (1) and (2) projected on the mean planes through the carbon atoms of the cyclopentadienyl rings. Figure 3 shows the molecule of complex (2) projected on the plane containing the Fe–P bond, perpendicular to the cyclopentadienyl ring.

TABLE 2

Atomic parameters, with estimated standard deviations in parentheses, for (2)

Atom	x	y	z
Fe	0·28892(5)	0·14825(8)	0·21807(4)
P	0·25892(9)	−0·12960(14)	0·17973(8)
O(1)	0·3396(3)	−0·2681(5)	0·2237(3)
C(1)	0·3324(5)	0·0648(7)	0·3649(3)
C(2)	0·4189(4)	0·1689(9)	0·3418(4)
C(3)	0·3721(7)	0·3354(8)	0·3163(4)
C(4)	0·2558(7)	0·3290(9)	0·3234(5)
C(5)	0·2325(5)	0·1617(8)	0·3525(4)
C(6)	0·3830(4)	0·1805(7)	0·1345(4)
O(6)	0·4436(4)	0·2104(8)	0·0826(3)
C(7)	0·1672(5)	0·2252(6)	0·1328(4)
O(7)	0·0919(4)	0·2812(6)	0·0794(3)
C(8)	0·2310(5)	−0·1691(7)	0·0426(4)
C(9)	0·1132(4)	−0·1998(6)	0·1997(4)
F(1)	0·3268(4)	−0·1353(6)	0·0084(3)
F(2)	0·1518(4)	−0·0680(6)	−0·0087(2)
F(3)	0·2037(4)	−0·3335(5)	0·0179(3)
F(4)	0·1126(4)	−0·2034(6)	0·2955(3)
F(5)	0·0823(3)	−0·3589(4)	0·1670(3)
F(6)	0·0299(3)	−0·0919(5)	0·1602(4)
H(1)	0·3408	−0·0605	0·3871
H(2)	0·4996	0·1321	0·3430
H(3)	0·4136	0·4398	0·2966
H(4)	0·2001	0·4283	0·3097
H(5)	0·1567	0·1179	0·3629

Anisotropic temperature coefficients in the form: $t = \exp[-2\pi^2 10^{-3}(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	40·4(4)	35·8(3)	35·5(3)	−1·8(3)	6·1(2)	2·5(3)
P	40·1(6)	35·6(6)	36·9(5)	3·2(5)	8·7(4)	0·5(4)
O(1)	57(2)	51(2)	73(2)	16(2)	7(2)	5(2)
C(1)	77(3)	46(3)	33(2)	−6(2)	7(2)	0(2)
C(2)	48(3)	99(5)	40(3)	−8(3)	0(2)	−11(3)
C(3)	131(6)	64(4)	49(3)	−49(4)	7(3)	−9(3)
C(4)	113(5)	68(4)	60(3)	37(4)	3(3)	−17(3)
C(5)	63(3)	81(4)	45(3)	−1(3)	17(2)	−10(3)
C(6)	55(3)	66(3)	45(3)	−8(2)	3(2)	15(2)
O(6)	81(3)	140(4)	63(2)	−29(3)	28(2)	22(3)
C(7)	61(3)	35(2)	57(3)	2(2)	5(2)	−4(2)
O(7)	77(3)	64(2)	87(3)	21(2)	−26(2)	7(2)
C(8)	76(3)	58(3)	49(3)	4(3)	18(3)	−6(2)
C(9)	53(3)	39(2)	63(3)	−6(2)	17(2)	3(2)
F(1)	113(3)	139(4)	70(2)	−14(3)	53(2)	−20(2)
F(2)	134(3)	108(3)	45(2)	37(3)	−9(2)	−3(2)
F(3)	157(4)	71(2)	68(2)	−14(2)	27(2)	−30(2)
F(4)	105(3)	134(3)	69(2)	−49(3)	44(2)	−3(2)
F(5)	87(2)	58(2)	130(3)	−30(2)	33(2)	−22(2)
F(6)	45(2)	79(2)	159(4)	6(2)	17(2)	29(2)

All hydrogen atoms have B 4·0 Å^2.

A few previous structural studies have involved comparison between complexes containing, respectively, PR^1_3 and PR^2_3 ligands.[3-5,10] In these cases the alteration to the length of the metal–phosphorus bond has been explained in terms of the variable π-acceptor properties of phosphorus, arising from the differing electronegativities of the groups R^1 and R^2. We now

TABLE 3

Molecular geometries of both complexes

(*a*) Intramolecular distances (Å), with estimated standard deviations in parentheses

	(1)	(2)
Fe–P	2·265(3)	2·191(3)
Fe–C(1)	2·106(6)	2·095(5)
Fe–C(2)	2·090(6)	2·084(6)
Fe–C(3)	2·101(6)	2·083(7)
Fe–C(4)	2·096(6)	2·093(7)
Fe–C(5)	2·093(6)	2·096(7)
Fe–C(6)	1·763(6)	1·775(6)
Fe–C(7)	1·773(6)	1·786(6)
P–O(1)		1·478(5)
P–C(8)	1·875(7)	1·885(6)
P–C(9)	1·881(8)	1·889(6)
C(1)–C(2)	1·394(10)	1·386(8)
C(1)–C(5)	1·403(8)	1·384(8)
C(2)–C(3)	1·408(8)	1·401(9)
C(3)–C(4)	1·390(9)	1·412(12)
C(4)–C(5)	1·415(8)	1·378(9)
C(6)–O(6)	1·141(8)	1·135(7)
C(7)–O(7)	1·135(8)	1·132(7)
C(8)–F(1)	1·341(10)	1·342(8)
C(8)–F(2)	1·315(8)	1·316(7)
C(8)–F(3)	1·326(8)	1·320(7)
C(9)–F(4)	1·314(9)	1·325(7)
C(9)–F(5)	1·345(7)	1·319(7)
C(9)–F(6)	1·324(9)	1·324(7)
Fe · · · O(6)	2·904(6)	2·908(6)
Fe · · · O(7)	2·906(6)	2·918(5)

(*b*) Intramolecular angles (°), with estimated standard deviations in parentheses

	(1)	(2)
P–Fe–C(6)	91·3(2)	94·0(2)
P–Fe–C(7)	95·8(2)	94·7(2)
C(6)–Fe–C(7)	94·3(3)	93·5(3)
Fe–P–C(8)	107·7(3)	112·7(2)
Fe–P–C(9)	107·0(3)	110·5(2)
C(8)–P–C(9)	94·5(3)	96·4(3)
Fe–P–O(1)		121·6(2)
O(1)–P–C(8)		106·1(3)
O(1)–P–C(9)		106·6(3)
Fe–C(6)–O(6)	177·0(5)	176·3(6)
Fe–C(7)–O(7)	175·6(5)	177·0(5)
C(1)–C(2)–C(3)	108·8(5)	107·2(5)
C(2)–C(3)–C(4)	107·6(5)	107·5(6)
C(3)–C(4)–C(5)	108·1(4)	107·9(6)
C(4)–C(5)–C(1)	107·8(6)	108·1(6)
C(5)–C(1)–C(2)	107·6(5)	109·3(5)
P–C(8)–F(1)	108·6(5)	108·9(4)
P–C(8)–F(2)	118·6(4)	114·8(4)
P–C(8)–F(3)	112·5(5)	113·5(4)
F(1)–C(8)–F(2)	105·6(6)	105·8(5)
F(1)–C(8)–F(3)	104·6(5)	106·0(5)
F(2)–C(8)–F(3)	105·9(6)	107·3(5)
P–C(9)–F(4)	110·5(5)	109·4(4)
P–C(9)–F(5)	110·9(5)	114·5(4)
P–C(9)–F(6)	118·2(5)	113·9(4)
F(4)–C(9)–F(5)	105·9(5)	105·6(5)
F(4)–C(9)–F(6)	105·4(6)	106·2(5)
F(5)–C(9)–F(6)	105·1(5)	106·7(4)

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[10] D. A. Allison, J. Clardy, and J. G. Verkade, *Inorg. Chem.*, 1972, **11**, 2804.

TABLE 4

Equations of least-squares planes in which X, Y, Z refer to orthogonal co-ordinates obtained by the transformation:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a\sin\beta, & 0, & 0 \\ 0, & b, & 0 \\ a\cos\beta, & 0, & c \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Distances (Å) of atoms from the planes are shown in square brackets

Plane (**1**): C(1)—(5) in (**1**)

$$-0{\cdot}3717X + 0{\cdot}8987Y - 0{\cdot}2329Z + 1{\cdot}3479 = 0$$

[C(1) −0·006, C(2) 0·005, C(3) −0·002, C(4) −0·002, C(5) 0·004, Fe 1·725, P 2·869, C(6) 2·699, C(7) 2·708]

Plane (**2**): C(1)—(5) in (**2**)

$$0{\cdot}2360X + 0{\cdot}2880Y + 0{\cdot}9281Z - 5{\cdot}0336 = 0$$

[C(1) −0·007, C(2) 0·005, C(3) −0·002, C(4) −0·022, C(5) 0·006, Fe 1·722, P 2·842, C(6) 2·662, C(7) 2·727]

TABLE 5

Intermolecular approaches (<3·0 Å)

(*a*) For (**1**)

F(1) ··· $H(5^{I})$	2·56	F(4) ··· $H(3^{IV})$	2·81
F(3) ··· $H(4^{II})$	2·66	F(2) ··· $H(5^{V})$	2·96
F(3) ··· $H(3^{II})$	2·68	O(6) ··· $F(5^{VI})$	2·98
O(6) ··· $H(4^{I})$	2·71	F(6) ··· $H(1^{V})$	3·00
F(5) ··· $H(2^{III})$	2·72		

(*b*) For (**2**)

O(1) ··· $H(2^{VII})$	2·41	F(6) ··· $H(4^{X})$	2·86
O(1) ··· $H(3^{VIII})$	2·53	F(1) ··· $H(1^{IX})$	2·88
F(5) ··· $H(4^{VIII})$	2·73	F(2) ··· $H(4^{I})$	2·88
H(2) ··· $H(3^{VII})$	2·77	O(6) ··· $H(3^{VII})$	2·97
F(3) ··· $H(1^{IX})$	2·78	F(6) ··· $F(2^{III})$	2·97
F(5) ··· $H(5^{X})$	2·81	F(4) ··· $H(4^{VIII})$	2·98

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecules at x, y, z:

I $x, \frac{1}{2} - y, -\frac{1}{2} + z$
II $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$
III $-x, -y, -z$
IV $-1 + x, y, z$
V $-x, \frac{1}{2} + y, \frac{1}{2} - z$
VI $1 + x, y, z$
VII $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$
VIII $x, -1 + y, z$
IX $x, -\frac{1}{2} - y, -\frac{1}{2} + z$
X $-x, -\frac{1}{2} + y, \frac{1}{2} - z$

report the effect of a change in the co-ordination number and oxidation level or valency of phosphorus.

Figures 1 and 2 show that the molecular conformations of (**1**) and (**2**) are virtually identical; a small rotation of the cyclopentadienyl ring about its C_5 axis from (**1**) to (**2**) is probably a consequence of the differing crystal packing. The principal molecular dimensions of the two complexes are compared in Table 6, from which it is evident that the main structural changes occurring on oxidation at the phosphorus atom are a shortening of the Fe–P bond by 0·074(4) Å and an increase in the Fe–P–C and C–P–C angles by *ca.* 3°, the latter change being consistent with a small increase of *s* character in the σ-bonding hybrid orbitals on phosphorus. We attribute the former change almost wholly to increased Fe→P d_π–d_π back bonding, for the following reasons. Firstly, the shift in the C–O stretching frequencies must imply greater Fe→P back donation in (**2**) since the alternative explanation of reduced

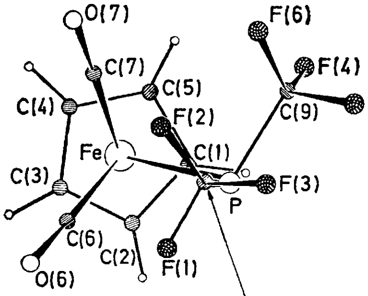

FIGURE 1 Projection of (**1**) on the least-squares plane through the carbon atoms of the cyclopentadienyl ring

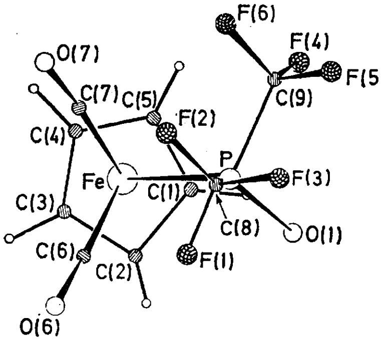

FIGURE 2 Projection of (**2**) on the least-squares plane through the carbon atoms of the cyclopentadienyl ring

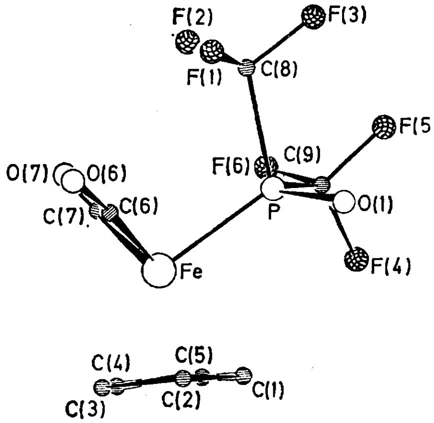

FIGURE 3 Projection of (**2**) on the plane perpendicular to the cyclopentadienyl ring and containing the Fe–P bond. Hydrogen atoms are omitted

TABLE 6

Comparison of principal molecular dimensions in complexes (**1**) and (**2**). Estimated standard deviations, in parentheses, include contributions from errors in the unit-cell dimensions

Bond or angle	(1)	(2)
Fe–P	2·265(3) Å	2·191(3) Å
Fe–C(π-C_5H_5) *	2·097(7)	2·090(7)
Fe–C(CO) *	1·768(7)	1·780(7)
C–O *	1·138(8)	1·134(7)
P–C *	1·878(8)	1·887(6)
P–O		1·478(5)
Fe–(π-C_5H_5) †	1·725	1·722
C–F *	1·328(5)	1·324(5)
OC–Fe–CO	94·3(3)°	93·5(3)°
Fe–P–C *	107·4(5)	111·6(15)
Fe–P–O		121·6(2)
C–P–C	94·5(3)	96·4(3)
C–P–O *		106·4(4)
F–C–F *	105·4(4)	106·3(4)

* Mean. † Plane.

P→Fe σ-donation is incompatible with the shortening of the Fe–P bond. Secondly, the similarity of the P–C bond lengths in (1) and (2) argues against any notable decrease in the σ-bonding covalent radius of phosphorus, although there is evidence for a slight change in hybridization; indeed, the P–C bonds lengthen slightly and it is clear that oxidation has not caused any overall ' shrinking ' of the phosphorus atom.

The lengths of the Fe–CO and C–O bonds [means 1·768(7) and 1·138(8) Å in (1), and 1·780(7) and 1·134(7) Å in (2)] change in a manner consistent with decreased Fe→CO and hence increased Fe→P back bonding in the oxidized complex, though the effects are small and within the limits of experimental error. In the comparison of $[(\pi\text{-}C_5H_5)Mo(CO)_2\{P(OMe)_3\}]I$ with the analogous PPh_3 complex it was noted that a contraction of the Mo–P bond was accompanied by an appreciably smaller lengthening of the Mo–CO bonds.[4,5]

The P–O separation [1·478(5) Å] in (2) may be compared with the shorter distance[11] (1·446 Å) for $POCl_3$ where the sum of electronegativities for the three chlorine substituents (3 × 3·0) is about the same as that for the two CF_3 groups (2 × 3·5) and one iron atom (1·8) in complex (2). On the basis of the frequency ν(P:O) which is much lower in (2) than in compounds of the type $(CF_3)_2P(O)X$ (X = C-, N-, O-, or halogen-ligand) it has been suggested[6] that in (2) both Fe and O compete for the phosphorus *d* orbitals. Such competition may explain the almost identical carbonyl stretching frequencies observed in (2) and the complexes $[(\pi\text{-}C_5H_5)Fe(CO)_2P(E)(CF_3)_2]$ (E = S or Se).[6] The decreasing electronegativity down the series O, S, Se might normally be expected to reduce the π-acceptor properties of phosphorus but, in this case, may be compensated by a reduction in the competing E→P π-bonding.

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[11] T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, 1971, **10**, 344.