Preparation and Characterization of Two Triphenylphosphineiron Carbonyl Complexes: *X*-Ray Crystallographic Studies of (1—4-η-5-*exo*-Benzylcyclopenta-1,3-diene)dicarbonyl(triphenylphosphine)iron(0), (1), and Dicarbonyl(η-cyclopentadienyl)(triphenylphosphine)iron(II) 1,1,2,3,3-Pentacyanopropenide, (2)

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The complex $[Fe(CH_2Ph)(\eta\text{-}C_5H_5)(CO)_2]$ undergoes a photochemical reaction with PPh_3 to yield (1), which has been treated with tetracyanoethylene to yield (2). The products (1) and (2) have been identified and characterized by *X*-ray crystallography.

THE complex $[Fe(CH_2Ph)(\eta\text{-}C_5H_5)(CO)_2]$ undergoes a photochemical reaction with triphenylphosphine in benzene; the structure of the adduct was not uniquely defined by spectroscopic and chemical investigations but it appeared that the complex might be $[Fe(CH_2Ph)(\eta^3\text{-}C_5H_5)(CO)_2(PPh_3)]$. The adduct was subsequently treated with tetracyanoethylene and a new product obtained in small yield.

X-Ray analyses of the triphenylphosphine adduct and its reaction product were undertaken to elucidate their molecular structures. These studies established that the photochemical reaction had resulted in the formation of (1—4-η-5-*exo*-benzylcyclopenta-1,3-diene)dicarbonyl(triphenylphosphine)iron, (1), and that the subsequent reaction between this complex and tetracyanoethylene had produced the ionic complex dicarbonyl(η-cyclopentadienyl)(triphenylphosphine)iron 1,1,2,3,3-pentacyanopropenide, (2).

EXPERIMENTAL

Crystal Data.—(1), $C_{32}H_{27}FeO_2P$, $M = 530.1$, Monoclinic, $a = 17.318(6)$, $b = 11.687(4)$, $c = 26.811(6)$ Å, $\beta = 102° 18(1)'$, $U = 5\,302$ Å^3, $D_m = 1.33$, $Z = 8$, $D_c = 1.328$ g cm^{-3}, space group $P2_1/c$ (C^5_{2h}), $F(000) = 2\,208$, μ(Mo-K_α) = 6.74 cm^{-1}.

(2), $C_{33}H_{20}FeN_5O_2P$, $M = 605.2$, Triclinic, $a = 11.812(3)$, $b = 15.913(5)$, $c = 8.873(2)$ Å, $\alpha = 95° 5(1)'$, $\beta = 104° 57(1)'$, $\gamma = 110° 24(1)'$, $U = 1\,481$ Å^3, $D_m = 1.345$, $Z = 2$, $D_c = 1.357$ g cm^{-3}, space group $P\bar{1}$ (C^1_i), $F(000) = 620$, μ(Mo-K_α) = 6.84 cm^{-1}.

Crystallographic Measurements.—The cell dimensions were obtained from a least-squares analysis of the θ, χ, and ϕ setting angles of *X*-ray reflections measured on a Hilger and Watts automatic diffractometer with Mo-K_α radiation. The intensity measurements were made by the 2θ—ω step-scan procedure, with Mo-K_α radiation. For complex (1), 10 421 independent reflections were surveyed in the range $\theta \leqslant 26°$ and 6 517 with $I > 3\sigma(I)$ were retained for the structure analysis. The crystals of complex (2) were rather small and gave weaker intensities; here 3 156 reflections with $I > 3\sigma(I)$ were obtained.

Structure Analyses.—*Complex* (1). There are two crystallographically unrelated molecules in the asymmetric unit. The co-ordinates of the Fe and P atoms were deduced from a Patterson synthesis and an electron-density distribution phased by those atoms disclosed the carbon and oxygen atoms in both molecules. Three cycles of block-diagonal adjustment of co-ordinates and isotropic thermal parameters gave $R = 0.102$ and after assignment of anisotropic thermal parameters three further cycles of calculations reduced R to 0.075. A difference electron-density distribution revealed the positions of all the hydrogen atoms, with an average peak height of 0.47 e Å^{-3}, and these atoms were included in the subsequent structure-factor calculations with isotropic thermal parameters based on the parameters of the adjacent carbon atoms. After three rounds of least-squares calculations, convergence was reached at $R = 0.058$. Atomic scattering factors, including dispersion corrections, were taken from ref. 1. The weighting scheme adopted was $w = XY$, where $X = 1$ for $\sin\theta > 0.3$, $(\sin\theta)/0.3$ for $\sin\theta < 0.3$, $Y = 1$ for $|F_o| < 110$ or $110/|F_o|$ for $|F_o| > 110$. The calculations were performed on the Univac 1108 computer at East Kilbride, using the ' *X*-Ray ' system of programs.[2]

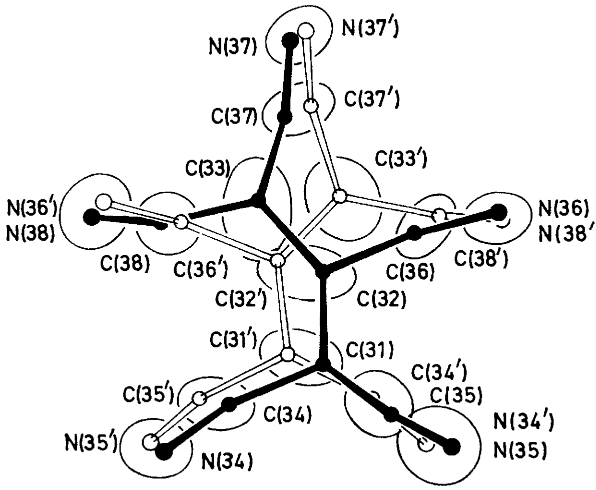

FIGURE 1 Outline of the thermal ellipsoids (50% probability level) in the anion of complex (2) before the disorder model was adopted and, superimposed, the two orientations of the 1,1,2,3,3-pentacyanopropenide anion after least-squares refinement

Complex (2). Co-ordinates for the Fe and P atoms were deduced from a Patterson synthesis. A series of electron-density calculations gave peaks consistent with a dicarbonyl(η-cyclopentadienyl)(triphenylphosphine)iron cation, but another group of peaks could not be interpreted sensibly in terms of an ordered anion, although it was evident that the anion contained several linear fragments, presumably C–C≡N. After initial refinement of the positional and anisotropic thermal parameters of only the atoms in the cation, the anion peaks were also included by stages in the series of least-squares calculations; a difference synthesis was obtained after each calculation and additional peaks selected for inclusion in the subsequent least-squares refinement. When the calculations had reached R = 0.059 all the anion peaks had been incorporated and a plot of the thermal ellipsoids of these peaks could then be explained by the

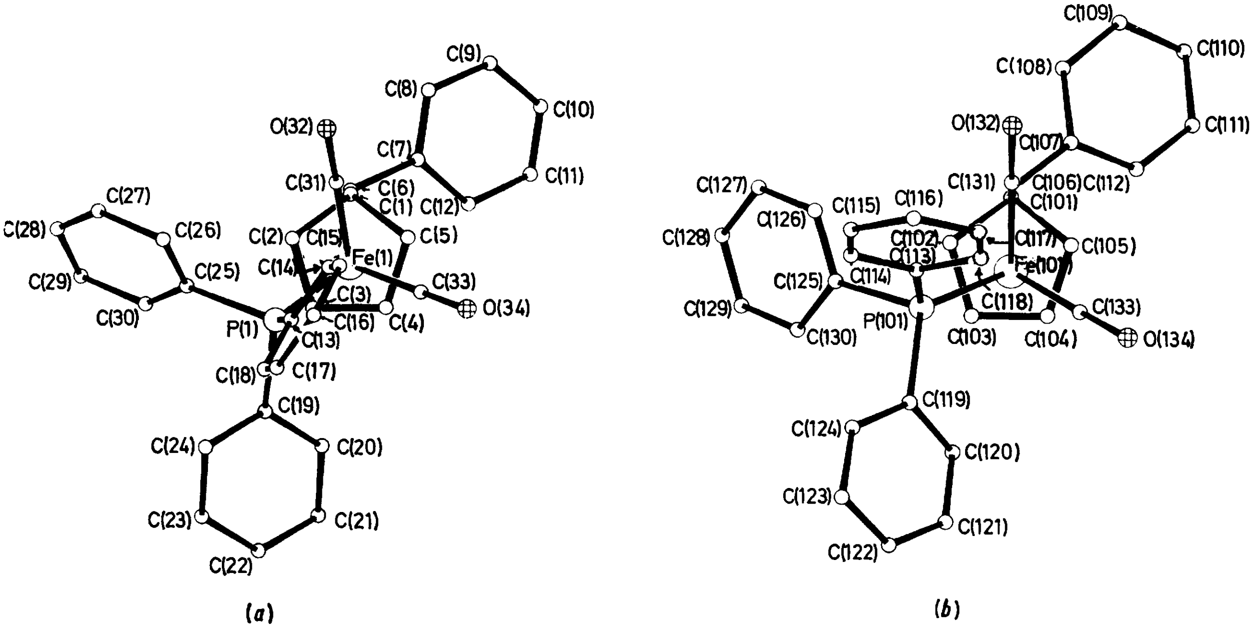

FIGURE 2 The two crystallographically independent molecules of complex (1) each viewed in projection onto the butadiene plane

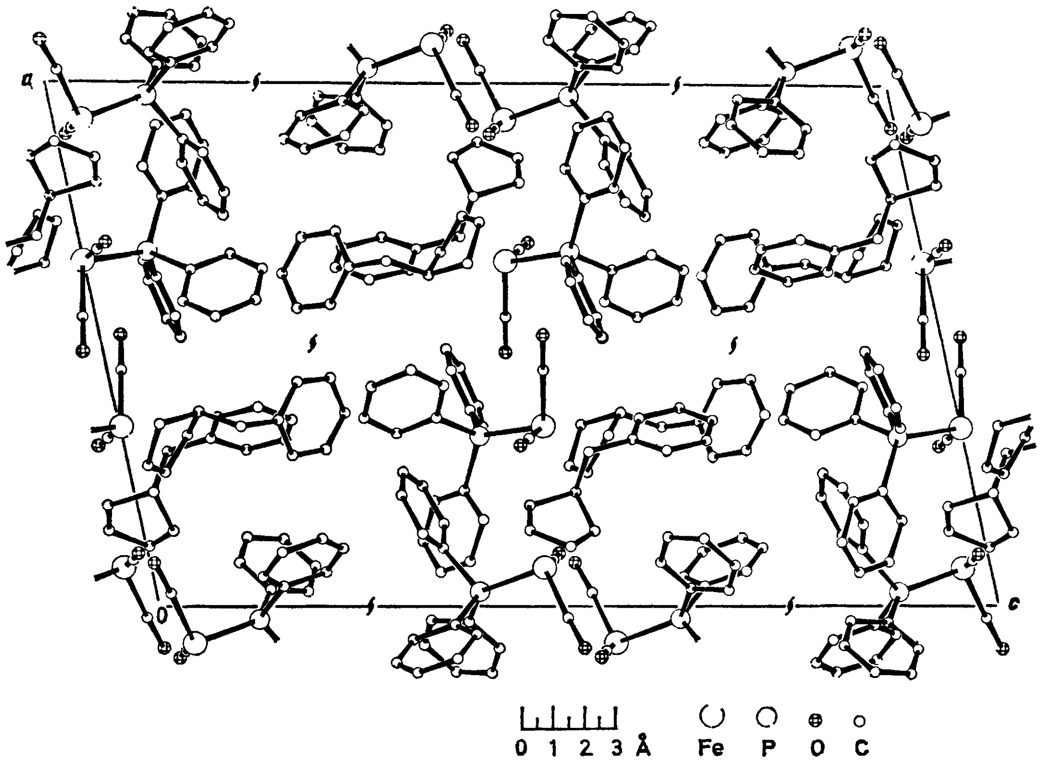

FIGURE 3 The crystal structure of (1) viewed along the b axis

superimposition of two orientations of a 1,1,2,3,3-pentacyanopropenide anion, $[(NC)_2CC(CN)C(CN)_2]^-$ (see Figure 1). Examination of the peak heights in the previous difference maps and comparison of the anisotropic thermal parameters associated with the peaks indicated that both orientations of the anion are equally populated; accordingly, each atom in the disordered model was assigned a population parameter of 0.5 and subsequent least-squares calculations based on this model converged at $R = 0.055$. The hydrogen atoms of the cation were included in the structure-factor calculations but their parameters were not adjusted. Atomic scattering factors, including dispersion corrections, were taken from ref. 1. The weighting scheme was $w = 1$ for $|F_o| < 10$ or $10/|F_o|$ for $|F_o| > 10$. The calculations were performed on the KDF9 computer at Glasgow University and subsequently on the IBM370/155 computer at the Edinburgh Regional Computer Centre.

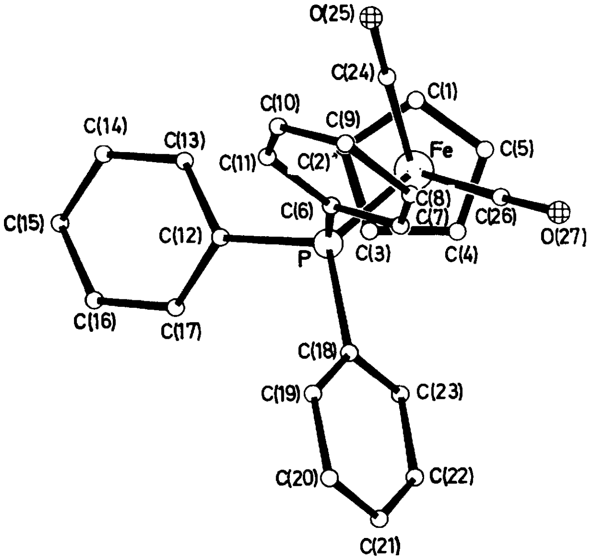

FIGURE 4 The cation of (2) viewed along the normal to the η-cyclopentadienyl ring

A subsequent chemical confirmation of the identity of complex (2) was obtained by its direct synthesis using previously reported preparations of the cation [3] and anion.[4]

RESULTS AND DISCUSSION

Views of the molecular and crystal structures of the complexes are given in Figures 2—5. The atomic co-ordinates, bond lengths, bond angles, displacements from various planes, and intermolecular contacts are listed in Tables 1—5 for complex (1) and Tables 6—10 for complex (2). The thermal parameters of the atoms and lists of calculated and observed structure amplitudes are included in Supplementary Publication No. SUP 22441 (17 pp.).*

The crystal structure of complex (1) contains two crystallographically unrelated molecules; both are of *exo* rather than *endo* stereochemistry, indicating that the migration of the benzyl group from the iron atom occurred by an intermolecular, and not an intramolecular, mechanism.

TABLE 1

Fractional atomic co-ordinates, with standard deviations in parentheses, for complex (1)

Atom	*X*	*Y*	*Z*
Fe(1)	0.343 86(4)	0.336 64(6)	0.503 11(3)
P(1)	0.324 55(7)	0.271 51(11)	0.423 89(5)
C(1)	0.370 1(3)	0.251 2(5)	0.597 3(2)
C(2)	0.346 7(3)	0.185 3(5)	0.547 2(2)
C(3)	0.268 3(3)	0.216 2(5)	0.522 7(2)
C(4)	0.254 9(3)	0.325 1(5)	0.542 3(2)
C(5)	0.325 2(3)	0.358 6(5)	0.577 5(2)
C(6)	0.343 0(4)	0.192 4(6)	0.643 0(2)
C(7)	0.352 5(4)	0.273 4(5)	0.688 4(2)
C(8)	0.424 6(4)	0.288 7(6)	0.721 4(2)
C(9)	0.432 9(5)	0.364 0(8)	0.762 3(3)
C(10)	0.367 9(5)	0.423 5(7)	0.770 3(3)
C(11)	0.296 8(5)	0.408 9(8)	0.738 0(3)
C(12)	0.286 8(4)	0.333 3(7)	0.696 3(3)
C(13)	0.359 5(3)	0.362 3(4)	0.376 9(2)
C(14)	0.419 7(3)	0.439 8(5)	0.393 9(2)
C(15)	0.447 7(4)	0.509 5(6)	0.358 8(3)
C(16)	0.415 8(4)	0.500 1(6)	0.307 6(3)
C(17)	0.356 3(4)	0.422 9(5)	0.291 0(2)
C(18)	0.328 3(4)	0.353 3(5)	0.325 0(2)
C(19)	0.220 8(3)	0.243 7(7)	0.391 5(2)
C(20)	0.162 8(3)	0.310 1(5)	0.406 0(2)
C(21)	0.084 2(4)	0.297 0(6)	0.380 9(3)
C(22)	0.064 0(4)	0.217 1(6)	0.341 8(3)
C(23)	0.121 2(4)	0.150 3(6)	0.328 5(3)
C(24)	0.199 5(4)	0.163 2(5)	0.353 0(2)
C(25)	0.374 1(3)	0.134 8(4)	0.418 5(2)
C(26)	0.448 4(3)	0.134 4(5)	0.406 7(2)
C(27)	0.487 5(4)	0.031 3(6)	0.405 9(3)
C(28)	0.454 3(4)	−0.070 6(6)	0.417 3(3)
C(29)	0.380 8(4)	−0.069 4(5)	0.429 1(3)
C(30)	0.341 3(3)	0.033 0(5)	0.430 4(2)
C(31)	0.448 2(3)	0.340 4(5)	0.515 6(2)
O(32)	0.515 9(2)	0.341 7(4)	0.524 3(2)
C(33)	0.320 6(3)	0.478 1(5)	0.482 3(2)
O(34)	0.306 1(3)	0.570 9(4)	0.470 3(2)
Fe(101)	0.928 91(4)	0.241 83(6)	0.534 41(3)
P(101)	0.974 05(7)	0.265 54(11)	0.617 56(5)
C(101)	0.782 8(3)	0.231 5(5)	0.478 3(2)
C(102)	0.808 9(3)	0.205 5(5)	0.535 2(2)
C(103)	0.856 6(3)	0.105 5(5)	0.541 8(2)
C(104)	0.887 0(3)	0.094 3(5)	0.497 0(2)
C(105)	0.857 9(3)	0.187 1(5)	0.464 7(2)
C(106)	0.706 0(3)	0.170 2(6)	0.452 0(2)
C(107)	0.681 6(3)	0.203 6(5)	0.396 8(2)
C(108)	0.640 4(4)	0.305 7(6)	0.382 9(2)
C(109)	0.622 9(4)	0.342 1(8)	0.332 4(3)
C(110)	0.645 9(4)	0.277 2(7)	0.295 3(2)
C(111)	0.684 9(4)	0.176 5(7)	0.308 2(2)
C(112)	0.702 7(4)	0.139 4(5)	0.358 0(2)
C(113)	1.031 3(3)	0.395 9(5)	0.637 5(2)
C(114)	1.028 0(3)	0.454 5(5)	0.682 6(2)
C(115)	1.075 4(4)	0.549 2(5)	0.697 1(2)
C(116)	1.126 5(4)	0.588 7(6)	0.667 6(3)
C(117)	1.129 9(4)	0.531 7(6)	0.622 9(3)
C(118)	1.082 8(3)	0.436 4(5)	0.607 8(2)
C(119)	1.036 6(3)	0.155 7(5)	0.655 0(2)
C(120)	1.055 5(4)	0.056 7(5)	0.631 9(2)
C(121)	1.101 4(5)	−0.027 2(6)	0.660 7(3)
C(122)	1.129 0(4)	−0.013 4(7)	0.712 1(3)
C(123)	1.110 9(4)	0.085 0(6)	0.735 8(2)
C(124)	1.065 1(4)	0.168 4(5)	0.707 6(2)
C(125)	0.890 3(3)	0.275 9(4)	0.649 0(2)
C(126)	0.843 7(3)	0.374 0(5)	0.642 0(2)
C(127)	0.771 8(3)	0.375 1(6)	0.657 0(2)
C(128)	0.745 5(4)	0.279 3(6)	0.677 9(2)
C(129)	0.791 2(4)	0.182 3(6)	0.685 1(3)
C(130)	0.863 9(3)	0.179 1(5)	0.670 7(2)
C(131)	0.912 7(3)	0.389 9(5)	0.521 4(2)
O(132)	0.901 5(3)	0.485 2(4)	0.512 9(2)
C(133)	1.022 6(3)	0.221 0(5)	0.519 5(2)
O(134)	1.080 6(3)	0.206 3(5)	0.507 2(2)

The iron atom in complex (1) is bound to atoms C(2)—C(5) of the butadiene chain in the 5-*exo*-benzyl-

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

cyclopenta-1,3-diene ligand. The Fe–C(2,5) distances [2.123(6), 2.102(6) Å] in molecule A and [2.126(5), 2.106(5) Å] in molecule B are significantly longer than the Fe–C(3,4) distances [2.065(6), 2.046(6) Å] in molecule A and [2.062(6), 2.049(6) Å] in molecule B, the mean values of 2.114 (terminal) and 2.056 Å (central) being comparable with values in other butadieneiron carbonyl complexes, *e.g.* 2.124 and 2.052 Å in tricarbonyl(*N*-ethoxycarbonyl-3-formylazepine)iron [5] and 2.131 and 2.050 Å in tricarbonyl(sorbic acid)iron.[6] The Fe–C(1) separation is distinctly longer than these bonded distances, *viz.* 2.664(6) Å in molecule A and 2.655(6) Å in molecule B, and the dihedral angle between the butadiene plane and the C(2),C(1),C(5) plane is 34.7° in molecule A and 32.9° in molecule B. These angles are similar to angles of 36.5° in [Co(η-C_5H_5)(η^4-C_5H_5Ph)],[7] 32.3° in [Co(η-C_5H_5){η^4-$(CF_3)_4C_4PO(OH)$}],[8] and 31.1° in [Mn$(CO)_3${η^4-$(CF_3)_4C_4SC_6F_5$}].[8] The bond lengths within the butadiene fragments (1.412—1.425 Å) show little variation between central and terminal bonds and are appreciably shorter than the C(1)–C(2) and C(1)–C(5) distances (1.513—1.527, mean 1.521 Å).

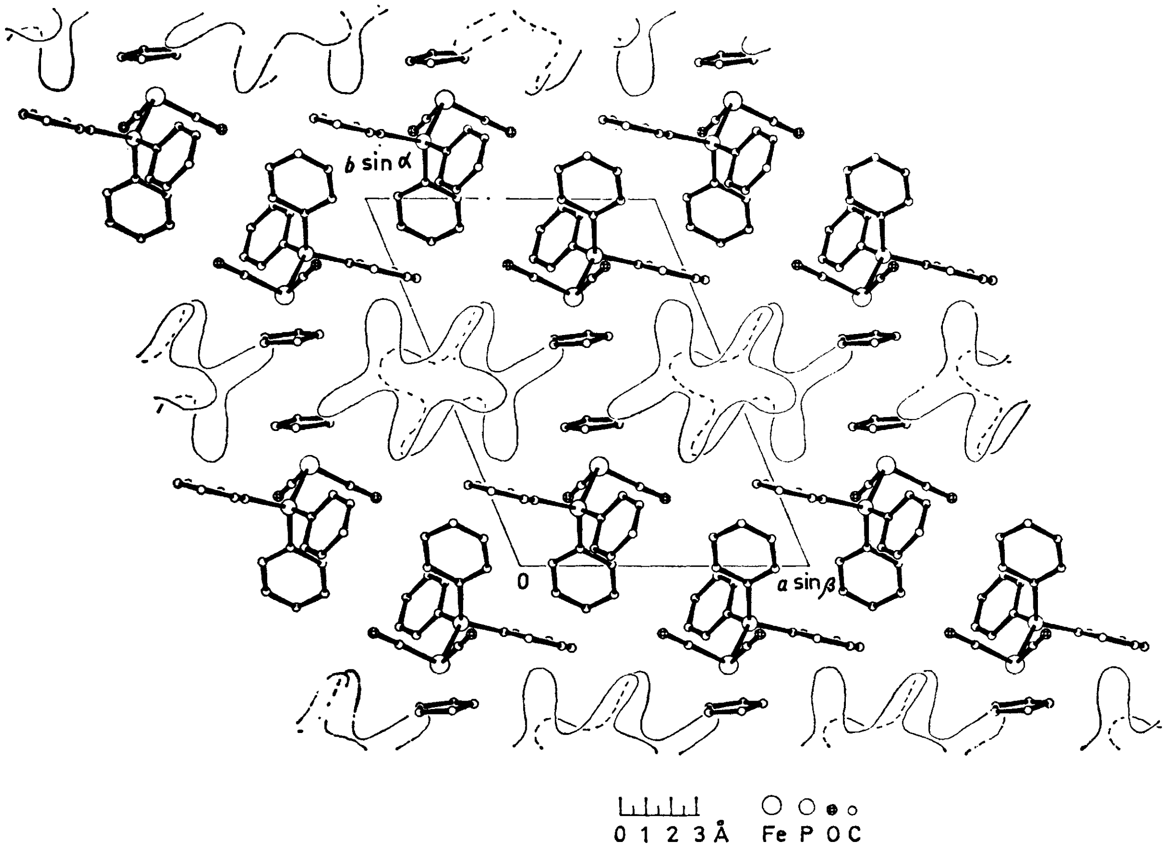

FIGURE 5 The crystal structure of (2) viewed along the *c* axis. For clarity, only the outlines of the disordered anions are shown

The Fe–C(cyclopentadienyl) distances in complex (2) range from 2.085(7) to 2.102(5) Å (mean 2.094 Å) in excellent agreement with distances of *ca.* 2.10 Å in various η-cyclopentadienyliron carbonyl complexes.[9] The C–C bond lengths in the η-C_5H_5 ring lie in the range 1.392—1.413 Å (mean 1.402 Å).

The Fe–P bond in complex (1) [2.213(2), 2.216(2) Å] is slightly, but significantly, shorter than that in complex (2) [2.240(1) Å]. The Fe–CO bonds have a mean length of 1.768(3) Å in (1) and 1.776(4) Å in (2), while the C–O bonds have a mean length of 1.144(4) Å in (1) and 1.134(6) Å in (2). Since the metal atom in complex (1) is formally Fe^0, whereas that in complex (2) is formally Fe^{II}, slight differences in metal–ligand distances are not unexpected. The various small differences are consistent with $d_\pi \rightarrow d_\pi$ and $d_\pi \rightarrow p_\pi$ back donation to π-acceptor ligands being greater in the neutral iron(0) complex (1) than in the charged iron(II) complex (2). The Fe–C–O angles in the complexes are 176.1—179.4° (mean 178.1°).

The P–C bond lengths in (1) range from 1.831(6) to 1.850(5) Å (mean 1.838 Å) while those in (2) range from 1.810(5) to 1.821(5) Å (mean 1.817 Å). The C–P–C angles in (1) have a mean value of 102.9°, and those in (2) have a mean value of 104.8°. These angles suggest that the P–C bonds have more *s* character in (2) than in (1), in accord with the P–C bond lengths, and this in turn requires that the phosphorus orbital directed towards the metal atom has less *s* character in the complex (2) than in (1), a deduction that is consistent with the relative electronegativities of Fe^{II} and Fe^0. This hybridization effect could also contribute to the difference between the Fe–P bond lengths in (1) and (2).

The C–C bonds in the triphenylphosphine ligands have a mean length of 1.385 Å in (1) and 1.381 Å in (2). Similar contractions from the spectroscopic value of 1.397 Å for benzene have been noted in other complexes and attributed to thermal motion. The phenyl rings are accurately planar, but the phosphorus atoms are appreciably displaced from some of the ring planes, the deviations ranging from 0.01 to 0.36 Å in (1) and from 0.01 to 0.12 Å in (2). The two crystallographically

TABLE 2

Bond lengths (Å), with standard deviations in parentheses, for complex (1)

	Molecule	
	A	B *
Fe(1)–P(1)	2.213(2)	2.216(2)
Fe(1)–C(31)	1.767(5)	1.775(6)
Fe(1)–C(33)	1.763(6)	1.768(6)
C(31)–O(32)	1.148(7)	1.145(7)
C(33)–O(34)	1.145(7)	1.137(8)
Fe(1)–C(2)	2.123(6)	2.126(5)
Fe(1)–C(3)	2.065(6)	2.062(6)
Fe(1)–C(4)	2.046(6)	2.049(6)
Fe(1)–C(5)	2.102(6)	2.106(5)
C(1)–C(2)	1.527(7)	1.526(7)
C(2)–C(3)	1.425(7)	1.419(8)
C(3)–C(4)	1.414(8)	1.417(9)
C(4)–C(5)	1.427(7)	1.412(8)
C(5)–C(1)	1.513(8)	1.516(8)
C(1)–C(6)	1.562(9)	1.543(8)
C(6)–C(7)	1.521(8)	1.504(8)
C(7)–C(8)	1.381(8)	1.399(9)
C(8)–C(9)	1.388(10)	1.390(10)
C(9)–C(10)	1.379(12)	1.374(11)
C(10)–C(11)	1.355(11)	1.364(11)
C(11)–C(12)	1.406(11)	1.374(9)
C(12)–C(7)	1.390(10)	1.393(9)
P(1)–C(13)	1.844(6)	1.835(5)
P(1)–C(19)	1.850(5)	1.834(5)
P(1)–C(25)	1.833(5)	1.831(6)
C(13)–C(14)	1.384(8)	1.401(8)
C(14)–C(15)	1.409(10)	1.383(8)
C(15)–C(16)	1.368(9)	1.384(10)
C(16)–C(17)	1.370(9)	1.385(10)
C(17)–C(18)	1.386(9)	1.388(9)
C(18)–C(13)	1.386(7)	1.398(9)
C(19)–C(20)	1.388(8)	1.384(8)
C(20)–C(21)	1.392(8)	1.389(9)
C(21)–C(22)	1.392(10)	1.369(10)
C(22)–C(23)	1.368(10)	1.381(10)
C(23)–C(24)	1.384(9)	1.376(9)
C(24)–C(19)	1.388(8)	1.406(7)
C(25)–C(26)	1.390(8)	1.391(7)
C(26)–C(27)	1.385(9)	1.389(9)
C(27)–C(28)	1.385(10)	1.371(10)
C(28)–C(29)	1.376(10)	1.373(10)
C(29)–C(30)	1.382(9)	1.393(9)
C(30)–C(25)	1.385(8)	1.393(8)

* Molecule A corresponds to atoms Fe(1), P(1), C(1), *etc.*, molecule B to atoms Fe(101), P(101), *etc.*

TABLE 3

Bond angles (°), with standard deviations in parentheses, for complex (1)

	Molecule	
	A	B
P(1)–Fe(1)–C(31)	97.5(2)	95.8(2)
P(1)–Fe(1)–C(33)	92.4(2)	94.7(2)
C(31)–Fe(1)–C(33)	101.1(3)	101.8(3)
Fe(1)–C(31)–O(32)	179.0(5)	179.4(5)
Fe(1)–C(33)–O(34)	178.0(5)	176.1(5)
C(1)–C(2)–C(3)	109.0(5)	109.2(5)
C(2)–C(3)–C(4)	105.8(4)	106.4(5)
C(3)–C(4)–C(5)	108.0(5)	107.5(5)
C(4)–C(5)–C(1)	107.9(5)	109.2(5)
C(5)–C(1)–C(2)	95.1(4)	94.9(4)
C(5)–C(1)–C(6)	115.0(5)	115.6(5)
C(2)–C(1)–C(6)	113.6(5)	114.0(5)
C(1)–C(6)–C(7)	110.7(5)	111.3(5)
C(6)–C(7)–C(8)	121.5(6)	120.2(6)
C(6)–C(7)–C(2)	118.9(5)	122.2(5)
C(12)–C(7)–C(8)	119.6(6)	117.5(5)
C(7)–C(8)–C(9)	121.0(7)	120.9(7)
C(8)–C(9)–C(10)	119.5(6)	119.9(7)
C(9)–C(10)–C(11)	119.8(7)	119.8(7)
C(10)–C(11)–C(12)	121.9(8)	121.0(7)
C(11)–C(12)–C(7)	118.1(6)	121.0(6)
Fe(1)–P(1)–C(13)	116.9(2)	116.7(2)
Fe(1)–P(1)–C(19)	116.3(2)	120.2(2)
Fe(1)–P(1)–C(25)	113.5(2)	109.1(2)
C(13)–P(1)–C(19)	102.0(2)	101.7(2)
C(13)–P(1)–C(25)	102.7(2)	104.1(3)
C(19)–P(1)–C(25)	103.5(2)	103.2(2)
P(1)–C(13)–C(14)	119.1(4)	122.5(4)
P(1)–C(13)–C(18)	121.8(4)	119.1(4)
C(18)–C(13)–C(14)	119.1(5)	118.4(5)
C(13)–C(14)–C(15)	120.1(5)	120.1(6)
C(14)–C(15)–C(16)	120.1(6)	121.4(6)
C(15)–C(16)–C(17)	119.6(7)	119.0(6)
C(16)–C(17)–C(18)	121.1(5)	120.4(7)
C(17)–C(18)–C(13)	120.0(5)	120.8(6)
P(1)–C(19)–C(20)	117.3(4)	120.6(4)
P(1)–C(19)–C(24)	123.1(4)	121.2(4)
C(24)–C(19)–C(20)	119.6(5)	118.2(5)
C(19)–C(20)–C(21)	119.7(5)	120.2(5)
C(20)–C(21)–C(22)	120.1(6)	120.8(7)
C(21)–C(22)–C(23)	120.0(6)	119.8(7)
C(22)–C(23)–C(24)	120.3(6)	119.9(6)
C(23)–C(24)–C(19)	120.4(6)	121.1(6)
P(1)–C(25)–C(26)	119.5(4)	119.0(4)
P(1)–C(25)–C(30)	120.6(4)	120.1(4)
C(30)–C(25)–C(26)	119.6(5)	119.5(5)
C(25)–C(26)–C(27)	119.2(6)	119.9(5)
C(26)–C(27)–C(28)	121.1(7)	120.5(6)
C(27)–C(28)–C(29)	119.4(6)	120.0(6)
C(28)–C(29)–C(30)	120.1(6)	120.7(7)
C(29)–C(30)–C(25)	120.6(6)	119.4(6)

TABLE 4

Displacements (Å) of atoms from various planes in complex (1). Atoms not included in the derivation of a plane are italicized

Plane (*a*): C(2) −0.00, C(3) 0.01, C(4) −0.01, C(5) 0.00, *C(1) −0.58*, *Fe(1) 1.72*

Plane (*b*): C(7) 0.00, C(8) −0.00, C(9) 0.00, C(10) −0.00, C(11) 0.00, C(12) −0.00, *C(6) 0.02*

Plane (*c*): C(13) −0.01, C(14) 0.00, C(15) 0.00, C(16) 0.00, C(17) −0.00, C(18) 0.01, *P(1) 0.01*

Plane (*d*): C(19) 0.01, C(20) −0.01, C(21) −0.00, C(22) 0.01, C(23) −0.01, C(24) −0.00, *P(1) 0.10*

Plane (*e*): C(25) 0.01, C(26) −0.00, C(27) 0.00, C(28) −0.00, C(29) 0.01, C(30) −0.01, *P(1) − 0.11*

Plane (*f*): C(102) −0.00, C(103) 0.00, C(104) −0.00, C(105) 0.00, *C(101) −0.56*, *Fe(101) 1.73*

Plane (*g*): C(107) 0.01, C(108) −0.01, C(109) −0.00, C(110) 0.01, C(111) −0.00, C(112) −0.00, *C(106) 0.12*

Plane (*h*): C(113) 0.00, C(114) −0.00, C(115) 0.00, C(116) 0.00, C(117) 0.00, C(118) −0.00, *P(101) 0.09*

Plane (*i*): C(119) 0.00, C(120) −0.00, C(121) 0.00, C(122) 0.00, C(123) −0.00, C(124) 0.00, *P(101) 0.04*

Plane (*j*): C(125) 0.00, C(126) −0.00, C(127) 0.01, C(128) −0.01, C(129) 0.00, C(130) 0.00, *P(101) −0.36*

TABLE 5

Intermolecular distances (<3.6 Å) for complex (1)

O(134) · · · C(3$^{\mathrm{I}}$)	3.19	O(134) · · · C(20$^{\mathrm{I}}$)	3.54
O(32) · · · O(34$^{\mathrm{II}}$)	3.22	O(134) · · · C(21$^{\mathrm{I}}$)	3.56
O(34) · · · C(101$^{\mathrm{II}}$)	3.24	O(134) · · · C(104$^{\mathrm{VI}}$)	3.56
O(34) · · · C(102$^{\mathrm{II}}$)	3.27	O(32) · · · C(33$^{\mathrm{II}}$)	3.56
O(134) · · · C(4$^{\mathrm{I}}$)	3.27	O(132) · · · C(117$^{\mathrm{III}}$)	3.57
O(32) · · · C(14$^{\mathrm{II}}$)	3.40	O(132) · · · C(4$^{\mathrm{II}}$)	3.57
O(132) · · · C(118$^{\mathrm{III}}$)	3.43	O(132) · · · C(20$^{\mathrm{II}}$)	3.57
O(34) · · · C(127$^{\mathrm{II}}$)	3.45	C(7) · · · C(17$^{\mathrm{VII}}$)	3.57
C(17) · · · C(8$^{\mathrm{IV}}$)	3.45	C(21) · · · C(115$^{\mathrm{II}}$)	3.58
O(32) · · · C(28$^{\mathrm{V}}$)	3.52	O(34) · · · C(126$^{\mathrm{II}}$)	3.59
O(32) · · · C(15$^{\mathrm{II}}$)	3.52		

The superscripts define the following transformations of the atomic co-ordinates:

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

TABLE 6

Fractional atomic co-ordinates, with standard deviations in parentheses, for complex (2)

Atom	*X*	*Y*	*Z*
(*i*) The cation			
Fe	0.580 20(6)	0.731 85(4)	0.117 53(9)
P	0.711 48(10)	0.843 72(7)	0.034 12(14)
C(1)	0.556 3(7)	0.605 4(4)	0.185 1(9)
C(2)	0.642 1(6)	0.624 8(4)	0.098 3(9)
C(3)	0.577 2(6)	0.631 8(4)	−0.055 2(8)
C(4)	0.451 8(6)	0.617 5(4)	−0.060 0(9)
C(5)	0.439 5(5)	0.602 2(4)	0.088 2(10)
C(6)	0.765 5(4)	0.953 6(3)	0.166 5(6)
C(7)	0.679 3(5)	0.996 2(4)	0.157 7(8)
C(8)	0.712 6(8)	1.077 2(4)	0.263 0(10)
C(9)	0.831 2(9)	1.116 4(4)	0.376 9(8)
C(10)	0.913 8(8)	1.074 4(4)	0.382 6(7)
C(11)	0.884 8(5)	0.994 4(4)	0.280 6(6)
C(12)	0.851 7(4)	0.822 1(3)	0.026 2(6)
C(13)	0.923 2(4)	0.804 0(3)	0.161 4(6)
C(14)	1.028 0(5)	0.783 9(4)	0.158 2(7)
C(15)	1.059 4(5)	0.779 1(5)	0.022 9(9)
C(16)	0.987 2(7)	0.793 5(5)	−0.114 6(9)
C(17)	0.883 6(6)	0.816 6(4)	−0.111 8(7)
C(18)	0.650 8(4)	0.870 0(3)	−0.157 3(6)
C(19)	0.716 2(6)	0.952 5(4)	−0.193 0(7)
C(20)	0.669 2(8)	0.974 3(5)	−0.340 0(8)
C(21)	0.560 8(7)	0.913 3(5)	−0.450 5(7)
C(22)	0.496 9(6)	0.833 2(5)	−0.417 7(7)
C(23)	0.539 5(5)	0.808 9(4)	−0.270 2(6)
C(24)	0.671 0(5)	0.783 7(3)	0.319 4(7)
O(25)	0.729 2(4)	0.814 1(3)	0.448 2(5)
C(26)	0.471 3(4)	0.786 7(4)	0.102 5(7)
O(27)	0.399 7(4)	0.820 3(3)	0.094 2(7)
(*ii*) The anion *			
C(31)	1.199 6(25)	0.483 8(15)	0.435 6(23)
C(32)	1.107 6(13)	0.505 6(9)	0.333 6(14)
C(33)	0.972 7(12)	0.467 6(8)	0.257 7(15)
C(34)	1.141 2(16)	0.390 0(10)	0.488 3(18)
N(34)	1.123 0(18)	0.317 6(13)	0.533 9(22)
C(35)	1.320 6(31)	0.525 5(19)	0.475 8(35)
N(35)	1.415 1(24)	0.569 4(17)	0.511 9(31)
C(36)	1.164 5(14)	0.593 7(12)	0.283 2(19)
N(36)	1.235 0(14)	0.663 3(11)	0.237 4(18)
C(37)	0.917 7(15)	0.511 6(12)	0.161 3(20)
N(37)	0.850 7(16)	0.536 8(11)	0.079 2(21)
C(38)	0.892 2(25)	0.382 2(18)	0.298 1(29)
N(38)	0.813 0(19)	0.330 5(14)	0.316 4(26)
C(31′)	1.150 1(14)	0.457 5(10)	0.428 5(15)
C(32′)	1.051 4(15)	0.469 7(10)	0.325 1(16)
C(33′)	1.051 7(11)	0.540 6(8)	0.248 5(14)
C(34′)	1.283 2(23)	0.522 9(13)	0.485 2(23)
N(34′)	1.381 5(31)	0.561 5(20)	0.543 3(25)
C(35′)	1.103 2(21)	0.372 4(15)	0.494 8(25)
N(35′)	1.095 0(17)	0.321 6(12)	0.558 9(21)
C(36′)	0.913 1(22)	0.395 9(16)	0.284 8(29)
N(36′)	0.816 8(18)	0.331 4(13)	0.261 9(23)
C(37′)	0.934 3(15)	0.532 7(11)	0.129 5(19)
N(37′)	0.861 3(12)	0.539 6(8)	0.029 0(17)
C(38′)	1.173 0(16)	0.622 0(14)	0.264 5(19)
N(38′)	1.232 8(14)	0.682 5(10)	0.284 9(19)

* The occupancy parameter for each atom in the anion is 0.5.

TABLE 7

Bond lengths (Å), with standard deviations in parentheses, for complex (2)

(*i*) The cation			
Fe–P	2.240(1)	C(6)–C(7)	1.397(9)
Fe–C(24)	1.778(5)	C(7)–C(8)	1.389(9)
Fe–C(26)	1.774(7)	C(8)–C(9)	1.385(11)
C(24)–O(25)	1.129(7)	C(9)–C(10)	1.355(14)
C(26)–O(27)	1.138(9)	C(10)–C(11)	1.374(9)
Fe–C(1)	2.096(7)	C(11)–C(6)	1.392(6)
Fe–C(2)	2.085(7)	C(12)–C(13)	1.392(7)
Fe–C(3)	2.093(7)	C(13)–C(14)	1.389(9)
Fe–C(4)	2.102(5)	C(14)–C(15)	1.347(11)
Fe–C(5)	2.092(5)	C(15)–C(16)	1.383(11)
C(1)–C(2)	1.394(12)	C(16)–C(17)	1.400(12)
C(2)–C(3)	1.413(10)	C(17)–C(12)	1.374(9)
C(3)–C(4)	1.406(10)	C(18)–C(19)	1.382(8)
C(4)–C(5)	1.392(12)	C(19)–C(20)	1.402(10)
C(5)–C(1)	1.405(10)	C(20)–C(21)	1.362(8)
P–C(6)	1.820(5)	C(21)–C(22)	1.337(11)
P–C(12)	1.821(5)	C(22)–C(23)	1.413(9)
P–C(18)	1.810(5)	C(23)–C(24)	1.388(6)
(*ii*) The anion			
C(31)–C(32)	1.390(30)	C(31′)–C(32′)	1.369(23)
C(32)–C(33)	1.436(18)	C(32′)–C(33′)	1.368(21)
C(31)–C(34)	1.580(28)	C(31′)–C(34′)	1.471(25)
C(34)–N(34)	1.221(27)	C(34′)–N(34′)	1.062(36)
C(31)–C(35)	1.282(40)	C(31′)–C(35′)	1.507(28)
C(35)–N(35)	1.034(37)	C(35′)–N(35′)	1.021(31)
C(32)–C(36)	1.491(22)	C(32′)–C(36′)	1.569(26)
C(36)–N(36)	1.303(23)	C(36′)–N(36′)	1.190(27)
C(33)–C(37)	1.333(24)	C(33′)–C(37′)	1.466(20)
C(37)–N(37)	1.138(27)	C(37′)–N(37′)	1.112(22)
C(33)–C(38)	1.497(29)	C(33′)–C(38′)	1.523(20)
C(38)–N(38)	1.070(34)	C(38′)–N(38′)	0.942(22)

TABLE 8

Bond angles (°), with standard deviations in parentheses, for complex (2)

(*i*) The cation			
P–Fe–C(24)	90.7(2)	C(11)–C(6)–C(7)	118.8(5)
P–Fe–C(26)	91.9(2)	C(6)–C(7)–C(8)	120.0(5)
C(24)–Fe–C(26)	96.4(3)	C(7)–C(8)–C(9)	120.4(8)
Fe–C(24)–O(25)	177.9(6)	C(8)–C(9)–C(10)	118.6(6)
Fe–C(26)–O(27)	178.4(7)	C(9)–C(10)–C(11)	122.8(6)
P–Fe–C(1)	142.4(2)	C(10)–C(11)–C(6)	119.3(6)
P–Fe–C(2)	104.7(2)	P–C(12)–C(13)	118.7(4)
P–Fe–C(3)	91.6(2)	P–C(12)–C(17)	122.0(4)
P–Fe–C(4)	115.5(2)	C(17)–C(12)–C(13)	119.1(5)
P–Fe–C(5)	154.1(2)	C(12)–C(13)–C(14)	120.4(5)
C(1)–C(2)–C(3)	107.6(6)	C(13)–C(14)–C(15)	120.3(6)
C(2)–C(3)–C(4)	107.8(7)	C(14)–C(15)–C(16)	120.5(7)
C(3)–C(4)–C(5)	108.0(6)	C(15)–C(16)–C(17)	119.8(7)
C(4)–C(5)–C(1)	108.2(7)	C(16)–C(17)–C(12)	119.9(6)
C(5)–C(1)–C(2)	108.3(7)	P–C(18)–C(19)	119.6(3)
Fe–P–C(6)	111.2(2)	P–C(18)–C(23)	121.4(4)
Fe–P–C(12)	111.5(2)	C(23)–C(18)–C(19)	119.0(5)
Fe–P–C(18)	118.7(2)	C(18)–C(19)–C(20)	120.2(5)
C(6)–P–C(12)	107.6(2)	C(19)–C(20)–C(21)	120.3(6)
C(6)–P–C(18)	101.5(2)	C(20)–C(21)–C(22)	120.0(7)
C(12)–P–C(18)	105.4(3)	C(21)–C(22)–C(23)	121.7(5)
P–C(6)–C(7)	117.6(3)	C(22)–C(23)–C(18)	118.8(5)
P–C(6)–C(11)	123.5(5)		

TABLE 8 (*Continued*)

(*ii*) The anion

C(32)–C(31)–C(34)	112.4(17)	C(32′)–C(31′)–C(34′)	125.8(15)
C(32)–C(31)–C(35)	127.8(24)	C(32′)–C(31′)–C(35′)	111.1(14)
C(34)–C(31)–C(35)	119.4(25)	C(34′)–C(31′)–C(35′)	122.8(16)
C(31)–C(34)–N(34)	165.4(22)	C(31′)–C(34′)–N(34′)	168.3(28)
C(31)–C(35)–N(35)	169.8(41)	C(31′)–C(35′)–N(35′)	165.2(21)
C(31)–C(32)–C(33)	139.0(15)	C(31′)–C(32′)–C(33′)	129.7(12)
C(31)–C(32)–C(36)	111.7(14)	C(31′)–C(32′)–C(36′)	119.4(16)
C(33)–C(32)–C(36)	109.2(12)	C(33′)–C(32′)–C(36′)	110.9(15)
C(32)–C(36)–N(36)	166.4(19)	C(32′)–C(36′)–N(36′)	170.3(28)
C(37)–C(33)–C(38)	119.8(16)	C(37′)–C(33′)–C(38′)	117.9(13)
C(32)–C(33)–C(37)	120.5(13)	C(32′)–C(33′)–C(37′)	119.0(11)
C(32)–C(33)–C(38)	119.5(16)	C(32′)–C(33′)–C(38′)	122.5(13)
C(33)–C(37)–N(37)	167.4(18)	C(33′)–C(37′)–N(37′)	166.2(17)
C(33)–C(38)–N(38)	161.9(33)	C(33′)–C(38′)–N(38′)	161.4(26)

TABLE 9

Displacements (Å) of atoms from various planes in complex (2). Atoms not included in the derivation of a plane are italicized

Plane (*a*): C(1) 0.01, C(2) −0.01, C(3) 0.00, C(4) 0.00, C(5) −0.01

Plane (*b*): C(6) −0.01, C(7) 0.00, C(8) 0.00, C(9) −0.00, C(10) 0.00, C(11) 0.00, *P −0.12*

Plane (*c*): C(12) −0.01, C(13) 0.02, C(14) −0.01, C(15) −0.01, C(16) 0.02, C(17) −0.01, *P 0.09*

Plane (*d*): C(18) −0.00, C(19) 0.01, C(20) −0.01, C(21) 0.01, C(22) 0.00, C(23) −0.00, *P −0.01*

Plane (*e*): C(31) −0.06, C(32) −0.04, C(33) 0.04, C(34) 0.01, N(34) 0.17, C(35) 0.01, N(35) −0.07, C(36) −0.08, N(36) 0.08, C(37) 0.05, N(37) 0.05, C(38) −0.00, N(38) −0.16

Plane (*f*): C(31′) 0.09, C(32′) 0.01, C(33′) −0.05, C(34′) 0.09, N(34′) 0.06, C(35′) 0.01, N(35′) −0.07, C(36′) −0.07, N(36′) −0.05, C(37′) 0.02, N(37′) 0.14, C(38′) 0.02, N(38′) −0.21

independent molecules in (1) exhibit different phosphorus displacements and rotational orientations, and intermolecular repulsions must therefore be, at least partially, responsible for the conformations of PPh_3 ligands in transition-metal complexes in the solid state.

The metal bond angles associated with the unidentate ligands are consistently smaller in complex (2), where the metal is formally six-co-ordinate, than in (1), where the metal is formally five-co-ordinate. The P–Fe–CO bond angles in (1) are 92.4—97.5° (mean 95.1°), whereas those in (2) are 90.7 and 91.9° (mean 91.3°). The OC–Fe–CO angles in (1) are 101.3 and 101.8° (mean 101.6°), and the corresponding angle in (2) is 96.4°.

Because of disorder in the packing of the anions in the crystal structure of (2), the individual geometrical results for the 1,1,2,3,3-pentacyanopropenide anion are of limited validity. Nevertheless, it is suggested that the $C(CN)_2$ groups are twisted by *ca.* 4° away from a planar conformation of the anion. In 1,1,3,3-tetracyano-2-cyanomethylpropenide the analogous twist is 6°.[10]

TABLE 10

Interionic distances (<3.6 Å) for complex (2)

N(34) ··· O(25$^{\text{I}}$)	3.15	N(35′) ··· C(14$^{\text{I}}$)	3.49
N(36) ··· O(27$^{\text{II}}$)	3.18	N(35′) ··· O(25$^{\text{I}}$)	3.49
O(25) ··· C(21$^{\text{III}}$)	3.18	N(35′) ··· C(9$^{\text{VIII}}$)	3.51
C(36) ··· N(37′$^{\text{IV}}$)	3.21	N(37) ··· C(4$^{\text{V}}$)	3.51
N(37) ··· C(5$^{\text{V}}$)	3.22	N(34) ··· C(13$^{\text{I}}$)	3.51
C(33′) ··· N(37′$^{\text{IV}}$)	3.23	C(33′) ··· C(37′$^{\text{IV}}$)	3.52
N(38′) ··· O(27$^{\text{II}}$)	3.30	C(2) ··· C(5$^{\text{V}}$)	3.52
N(37′) ··· C(5$^{\text{V}}$)	3.30	N(35′) ··· C(2$^{\text{I}}$)	3.53
C(35′) ··· C(13$^{\text{I}}$)	3.32	C(37) ··· C(35′$^{\text{I}}$)	3.53
N(37′) ··· C(38$^{\text{VII}}$)	3.33	N(37) ··· N(35′$^{\text{I}}$)	3.53
O(25) ··· C(22$^{\text{III}}$)	3.35	C(37) ··· N(35′$^{\text{I}}$)	3.54
C(37′) ··· C(37′$^{\text{IV}}$)	3.36	N(34′) ··· C(3$^{\text{VI}}$)	3.54
N(34′) ··· C(4$^{\text{VI}}$)	3.36	N(36′) ··· O(27$^{\text{V}}$)	3.54
N(36) ··· C(26$^{\text{II}}$)	3.38	C(37′) ··· N(37′$^{\text{IV}}$)	3.54
C(32) ··· N(37′$^{\text{IV}}$)	3.38	C(24) ··· C(21$^{\text{III}}$)	3.55
N(36) ··· C(5$^{\text{II}}$)	3.40	C(32′) ··· N(37′$^{\text{IV}}$)	3.56
O(25) ··· C(20$^{\text{III}}$)	3.41	C(32) ··· N(38$^{\text{I}}$)	3.56
N(34) ··· C(24$^{\text{I}}$)	3.42	C(36) ··· N(38$^{\text{I}}$)	3.56
N(38′) ··· C(22$^{\text{VI}}$)	3.44	N(38) ··· C(9$^{\text{VIII}}$)	3.57
N(38) ··· C(34′$^{\text{I}}$)	3.46	C(2) ··· C(4$^{\text{I}}$)	3.58
N(36) ··· N(37′$^{\text{IV}}$)	3.47	C(1) ··· C(4$^{\text{V}}$)	3.58
C(10) ··· C(16$^{\text{VII}}$)	3.47	C(32) ··· C(38$^{\text{I}}$)	3.58
N(34) ··· C(2$^{\text{I}}$)	3.49	N(38′) ··· C(26$^{\text{II}}$)	3.59
C(1) ··· C(3$^{\text{V}}$)	3.49	C(31) ··· N(38$^{\text{I}}$)	3.59

The roman superscripts define the following transformations of the atomic co-ordinates:

I	$2 - x, 1 - y, 1 - z$	V	$1 - x, 1 - y, -z$
II	$1 + x, y, z$	VI	$1 + x, y, 1 + z$
III	$x, y, 1 + z$	VII	$2 - x, 2 - y, -z$
IV	$2 - x, 1 - y, -z$	VIII	$x, 1 + y, z$

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