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

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

	x	y	z	U_{eq}
W1	0.09829 (3)	0.01295 (3)	0.28254 (6)	0.0266 (3)
W2	0.10631 (3)	−0.07850 (3)	0.00357 (6)	0.0294 (3)
P1	0	0	0	0.024 (3)
O1	0.1450 (7)	0.0184 (7)	0.411 (1)	0.057 (8)
O2	0.1563 (6)	−0.1153 (7)	0.006 (1)	0.062 (8)
O3	0.1077 (8)	−0.0537 (6)	0.176 (1)	0.062 (8)
O4	0.1664 (9)	0.0826 (6)	0.173 (1)	0.071 (9)
O5	0.0081 (6)	−0.0642 (6)	0.324 (2)	0.08 (1)
O6	0.1733 (9)	0.0172 (6)	−0.030 (1)	0.072 (10)
O7	0.0684 (9)	0.0080 (8)	0.051 (2)	0.023 (8)
O8	0	0	0.148 (3)	0.023 (10)
N1	0.2166 (8)	0.3159 (9)	0.336 (2)	0.062 (9)
C1	0.282 (1)	0.368 (1)	0.335 (2)	0.07 (1)
C2	0.338 (1)	0.356 (2)	0.334 (3)	0.08 (2)
C3	0.325 (1)	0.290 (2)	0.332 (3)	0.09 (2)
C4	0.261 (2)	0.239 (1)	0.333 (3)	0.09 (2)
C5	0.206 (1)	0.251 (1)	0.332 (2)	0.07 (1)

Table 2. *Contact distances* (Å)

$N1\cdots N1^{i}$	2.68 (3)	$C2\cdots O2^{iv}$	3.31 (5)
$C2\cdots C3^{ii}$	3.49 (6)	$C5\cdots O1^{v}$	3.39 (3)
$C2\cdots C2^{ii}$	3.52 (6)	$C5\cdots O3^{vi}$	3.34 (3)
$C1\cdots O1^{iii}$	3.42 (3)	$C5\cdots O6^{vii}$	3.45 (3)
$C1\cdots O3^{iii}$	3.46 (3)		

Symmetry codes: (i) $\frac{1}{3} - x, \frac{2}{3} - y, \frac{2}{3} - z$; (ii) $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z$; (iii) $\frac{1}{3} + y, \frac{2}{3} + y - x, \frac{2}{3} - z$; (iv) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (v) $x - y, x, 1 - z$; (vi) $-y, x - y, z$; (vii) $x - y, x, -z$.

All refinement calculations were carried out on a HITAC M680H computer at the Institute for Molecular Sciences, Myodaiji, Okazaki, Aichi 444, Japan

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71542 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1071]

References

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Keggin, J. F. (1933). *Nature (London)*, **131**, 908-909.

Lee, K. Y., Arai, T., Nakata, S., Asaoka, S., Okuhara, T. & Misono, M. (1992). *J. Am. Chem. Soc.* **114**, 2836-2842.

Misono, M. (1987). *Catal. Rev. Sci. Eng.* **29**, 269-321.

Misono M., Mizuno, N., Katamura, K., Kasai, A., Konishi, Y., Sakata, K., Okuhara, T. & Yoneda, Y. (1982). *Bull. Chem. Soc. Jpn*, **55**, 400-406.

Misono, M., Sakata, K., Yoneda, Y. & Lee, W. Y. (1981). *Proceedings of the 7th International Congress on Catalysis*, pp. 1047-1059. Kodansha: Elsevier.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. T. C., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351-359.

Okuhara, T., Tatematsu, S., Lee, K. Y. & Misono, M. (1989). *Bull. Chem. Soc. Jpn*, **62**, 717-723.

Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69-77.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Acta Cryst. (1994). C**50**, 233–238

C—H···I$^-$ Interactions in Ferrocene Derivatives: Structures of (Ferrocenylmethyl)triphenylphosphonium Iodide and 1,1′-Ferrocenediylbis(methyltriphenylphosphonium Iodide) Dichloromethane Solvate (1/1)

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Abstract

The cations in (ferrocenylmethyl)triphenylphosphonium iodide, $[\{(C_5H_5)Fe(C_5H_4)\}CH_2P(C_6H_5)_3]^+.I^-$, (1), and in 1,1′-ferrocenediylbis(methyltriphenylphosphonium iodide) dichloromethane solvate, $[Fe\{(C_5H_4)CH_2P(C_6H_5)_3\}_2]^{2+}.2I^-.CH_2Cl_2$, (2), are involved in three-dimensional networks of C—H···I$^-$ interactions between phenyl C—H groups and I$^-$ anions. In (1), the cation resides in a general position while one I$^-$ anion is on a twofold axis and a second I$^-$ anion is at an inversion centre. The shortest C···I$^-$ distances are 3.886 (2) and 3.989 (2) Å to the I$^-$ ion which resides on an inversion centre. The cation in (2) has approximate mirror symmetry and lies in a general position in the unit cell along with its two I$^-$ anions. The shortest C···I$^-$ interactions are 3.810 (4) and 3.886 (5) Å.

Comment

Current interest in structural ferrocene chemistry focuses on a wide variety of derivatives which may have potential applications in (*a*) charge-transfer chemistry (Moore

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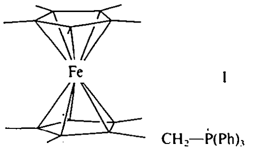
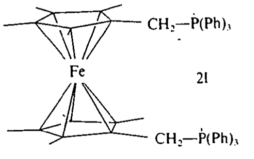
et al., 1993), (*b*) supramolecular chemistry (Beer *et al.*, 1991), (*c*) non-linear optical materials science (Houlton *et al.*, 1993), (*d*) ceramics (Tang *et al.*, 1993) and (*e*) molecular-inclusion and recognition chemistry (Ferguson, Gallagher, Glidewell & Zakaria, 1994*a*,*b*).

Hydrogen bonds often provide the strongest intermolecular forces between molecules in organic molecular crystals and hence often dictate the preferred packing arrangement. The general principles underlying hydrogen-bond formation are reasonably well understood and the structures of hydrogen-bonded crystals can often be rationalized in terms of preferred combinations of hydrogen-bond donors and acceptors (Etter, 1990; Etter, MacDonald & Bernstein, 1990; Etter & Reutzel, 1991). Herein we describe the extensive C—H$\cdots I^-$ interactions in two cationic ferrocene derivatives.

We are currently studying the molecular structures and hydrogen-bonding patterns of a range of ferrocene derivatives and have found recently that there are very extensive three-dimensional networks of C—H$\cdots I^-$ interactions in both $[(C_5H_5)Fe(C_5H_4CH_2NMe_3)]^+.I^-$, (3), and $[Fe(C_5H_4CH_2NMe_3)_2]^{2+}.2I^-$, (4) (Ferguson *et al.*, 1994*c*). Here we describe the C—H$\cdots I^-$ interactions in the crystal structures of two related salts $[(C_5H_5)Fe(C_5H_4CH_2PPh_3)]^+.I^-$, (1), and $[Fe(C_5H_4CH_2PPh_3)_2]^{2+}.2I^-$, (2), which contain triphenylphosphine substituents, whereas (3) and (4) contain trimethylamine groups.



(1)



(2)

Compound (1) crystallizes in the centrosymmetric space group *C*2/*c* (No. 15). The cation (Fig. 1) resides in a general position with one I^- ion [I(1)] on a twofold axis and a second [I(2)] at an inversion centre. The Fe—C bond lengths in (1) are in the range 2.017 (3)-2.033 (3) Å [mean 2.024 (3) Å] for the unsubstituted cyclopentadienyl ring [C(11)-C(15)] and 2.019 (3)-2.038 (3) Å [mean 2.030 (3) Å] for the substituted ring [C(21)-C(25)]. The Fe$\cdots$Cp-plane distance is 1.648 (2) Å for the unsubstituted cyclopentadienyl ring and 1.632 (2) Å for the substituted cyclopentadienyl ring. The dihedral angle between the planes of the cyclopentadienyl rings is 0.4 (2)° and they are within 19.3 (1)° of the eclipsed conformation. The C_{sp^3} atom, C(1), is displaced by 0.021 (5) Å from the plane of the substituted C_5 ring towards the Fe atom. Although the displacement parameters of the C atoms of the unsubstituted cyclopentadienyl ring system are slightly larger than corresponding values for the substituted cyclopentadienyl ring system, there is no evidence for disorder in the unsubstituted ring, C(11)-C(15). The C_{sp^3}—P and C_{Cp}—C_{sp^3} bond lengths involving C(1) are 1.813 (2) and 1.493 (3) Å, respectively, while the range of C_{ar}—P bond lengths is 1.793 (2)-1.799 (2) Å [mean 1.796 (2) Å]. The range of the cyclopentadienyl C_{Cp}—C_{Cp} bond lengths is 1.370 (6)-1.387 (6) Å [mean 1.382 (6) Å] and 1.386 (7)-1.431 (3) Å [mean 1.419 (6) Å] for the unsubstituted and substituted cyclopentadienyl rings, respectively. The phenyl C_{ar}—C_{ar} bond lengths range in value from 1.364 (4) to 1.401 (3) Å [mean 1.383 (3) Å]. In the lattice, the closest $I^-\cdots I^-$ separation is 6.6455 (3) Å and involves I(1) and I(2). The closest Fe$\cdots I^-$ separations are 5.5541 (4) and 5.5062 (4) Å for Fe$\cdots$I(1) and Fe$\cdots$I(2), respectively. There is no solvent of crystallization present in (1) and an examination of the crystal structure using *PLATON* (Spek, 1990) revealed no potential volume for solvent molecules.

In the structure of 1,1′-ferrocenediylbis(methyltriphenylphosphonium iodide) dichloromethane solvate $[Fe\{(C_5H_4)CH_2P(C_6H_5)_3\}_2]^{2+}.2I^-.CH_2Cl_2$, (2), which crystallizes in space group $P\bar{1}$ (No. 2), the cation and the two anions are all in general positions in the unit cell (Fig. 2). The cation has approximate mirror symmetry with the pseudo mirror containing the Fe atom and lying approximately parallel to the cyclopentadienyl rings. The substituents on the two cyclopentadienyl rings adopt similar conformations which can be seen, for example, from the Fe—C_{Cp}—C_{sp^3}—P torsion angles of 173.2 (2) and 174.9 (2)° involving P(1*A*) and P(1*B*), respectively.

The Fe—C bond lengths in (2) are in the range 2.025 (4)-2.046 (4) Å [mean 2.040 (4) Å] with the Fe$\cdots$Cp-plane distances being 1.645 (2) and 1.647 (2) Å. Other mean dimensions include: methylene C_{sp^3}—P

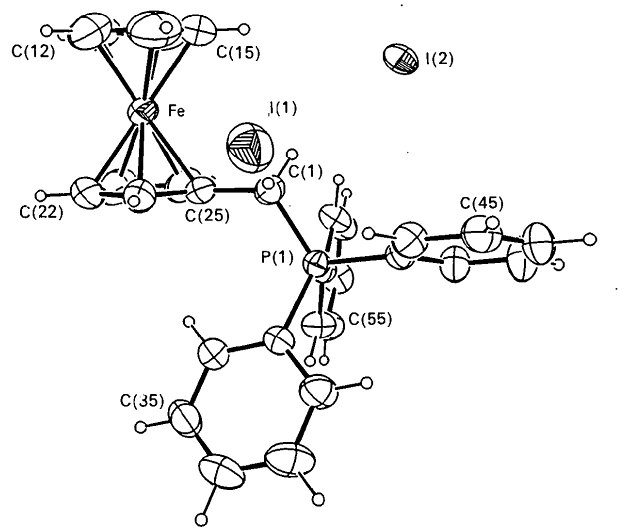


Fig. 1. A view of the asymmetric unit in the (ferrocenylmethyl)triphenylphosphonium iodide salt (1) with the non-H atoms shown as thermal ellipsoids drawn at the 50% probability level. For clarity, the H atoms are drawn as small spheres of arbitrary size.

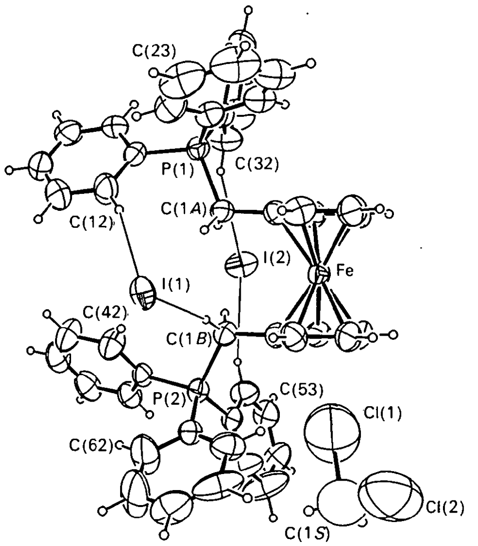


Fig. 2. A view of the 1,1′-ferrocenediylbis(methyltriphenylphosphonium iodide) salt (2) with the shortest C···I^- contacts in the asymmetric unit depicted (< 4.0 Å). All atoms are shown with thermal ellipsoids and sizes as in Fig. 1.

1.817 (4), C_{sp^3}—C_{Cp} 1.494 (5), phenyl C_{ar}—P 1.789 (4) and C_{Cp}—C_{Cp} 1.415 (6) Å; these values are similar to those found previously in related structures (Ferguson *et al.*, 1994*a*,*d*). The interplanar angle between the cyclopentadienyl planes is 1.4 (2)° and these rings are within 6.6 (2)° of being eclipsed; the exocyclic C_{sp^3} atoms are *cis* to one another, with the torsion angle C(1*A*)—Cp(centroid)—Cp(centroid)—C(1*B*) being 6.6 (2)°. The C_{sp^3} atoms C(1*A*) and C(1*B*) are displaced 0.07 (1) and 0.03 (1) Å from the plane of their respective C_5 rings, C(1*A*) on the opposite side of the cyclopentadienyl ring system and C(1*B*) on the same side as the Fe atom. One of the phenyl rings, C(61)-C(66), is disordered over two orientations with fractional occupancies (from difference maps) of 0.75 and 0.25. The two phenyl ring orientations are at an angle of 42° to one another. A loosely bound dichloromethane solvent of crystallization is present in the lattice adjacent to this disordered phenyl group. An examination of the crystal structure using *PLATON* (Spek, 1990) reveals that 9.7% of the volume of the asymmetric unit (some 112 $Å^3$) is occupied by the disordered CH_2Cl_2 solvent molecule. The disorder in the CH_2Cl_2 molecule is not surprising considering that an ordered CH_2Cl_2 molecule would occupy *ca* 60 $Å^3$ under normal conditions.

The inter-ion packing in both (1) and (2) is of interest. In the absence of strong hydrogen-bond (*e.g.* O—H and N—H) donors, there are extensive C—H···I^- interactions in both structures. Well documented cases of C—H···I^- hydrogen bonding are relatively uncommon but C···I^- distances in the range 3.7-3.9 Å have been reported (Ferguson, Lough, McAlees & McCrindle, 1993; Ferguson *et al.*, 1994*c*).

A three-dimensional network of C—H···I^- interactions is present in the structure of (1), involving phenyl C—H groups and I^- ions. The C···I^- contacts to I(1) are longer than those to I(2). The shortest contact is I(1)···C(46) 4.166 (2) Å [H(46)···$I(1)^-$ 3.27 Å, I(1)···H(46)—C(46) 158°]. The I^- ion I(1), which is on a twofold axis, lies in a pocket formed by six symmetry-related cations with ten C···I^- distances between 4.166 (2) and 4.339 (3) Å (considering all C···I^- contacts < 4.35 Å). In contrast to I(1), the shortest C···I^- contacts involving I(2) are 3.886 (2) Å for I(2)···C(45) and 3.989 (2) Å for I(2)···C(52) with the corresponding H···I^- distances 3.16 and 3.08 Å, and C—H···I^- angles 135 and 160°, repectively. The I^- ion I(2), which is at an inversion centre, lies in a pocket formed by six symmetry-related cations with 14 C···I^- distances between 3.886 (2) and 4.314 (3) Å (considering all C···I^- contacts < 4.35 Å).

A similar extensive three-dimensional network of C—H···I^- interactions is present in (2), with each of the I^- ions which reside in general positions present in different C—H···I^- environments in the crystal. The shortest C···I^- distances involving I(1) are 3.810 (4) Å for I(1)···C(45) and 3.947 (5) Å for I(1)···C(12), with corresponding H···I^- distances 3.01 and 3.01 Å, and C—H···I^- angles 143 and 168°, repectively; this I^- ion, I(1), lies in a pocket formed by five symmetry-related cations with 13 unique C···I^- distances between 3.810 (4) and 4.336 (6) Å. Likewise, the shortest C···I^- contacts involving I(2) are 3.886 (5) Å for I(2)···C(32) and 3.897 (4) Å for I(2)···C(52), with corresponding H···I^- distances 3.01 and 2.98 Å, and C—H···I^- angles 154 and 165°, respectively; this I^- ion, I(2), lies in a pocket formed by four symmetry-related cations with 11 unique C···I^- distances between 3.886 (5) and 4.324 (5) Å.

A search of the April 1993 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) yielded only one structure containing the ferrocenyl—C—P fragment: this is tetrachloro-2-[ferrocenyl(hydroxy)methyl]-2-isopropyl-triazatriphosphorine (Meetsma, Buwalda & van de Grampel, 1988) and is significantly different from the two ferrocene salts reported here.

Experimental

Compound (1)

Crystal data

$[Fe(C_{24}H_{21}P)(C_5H_5)]I$
M_r = 588.24
Monoclinic
$C2/c$
a = 21.9907 (11) Å
b = 15.3069 (10) Å
c = 17.0651 (8) Å
β = 119.039 (4)°

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 16.25-23.25°
μ = 1.89 mm^{-1}
T = 293 K
Prism

V = 5022.1 (5) Å^3
Z = 8
D_x = 1.56 Mg m^{-3}

0.55 × 0.40 × 0.30 mm
Orange

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min}$ = 0.61, $T_{\max}$ = 0.66
7512 measured reflections
7296 independent reflections
5354 observed reflections [$I_{\rm net} > 3.0\sigma(I_{\rm net})$]

$R_{\rm int}$ = 0.013
$\theta_{\max}$ = 30.0°
$h = -30 \rightarrow 26$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 23$
3 standard reflections
frequency: 40 min
intensity variation: 2%

Refinement

Refinement on F
R = 0.023
wR = 0.034
S = 1.41
5354 reflections
318 parameters
Only H-atom U's refined; C—H riding 0.95 Å
$w = 1/[\sigma^2(F) + 0.0003F^2]$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max}$ = 0.29 e Å^{-3}
$\Delta\rho_{\min}$ = −0.29 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 6472 (523)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	$U_{\rm eq}$
I(1)	1/2	0.167125 (16)	1/4	0.07026 (19)
I(2)	1/4	1/4	1/4	0.04490 (12)
Fe	0.414922 (15)	0.163323 (20)	0.507796 (20)	0.04665 (17)
P(1)	0.307321 (23)	0.36042 (3)	0.26287 (3)	0.03250 (23)
C(1)	0.37693 (9)	0.29748 (13)	0.35054 (12)	0.0389 (11)
C(11)	0.51698 (15)	0.1531 (3)	0.5438 (3)	0.092 (3)
C(12)	0.49826 (18)	0.08483 (22)	0.5804 (3)	0.0919 (23)
C(13)	0.47391 (18)	0.1185 (3)	0.63428 (22)	0.103 (3)
C(14)	0.47809 (19)	0.2088 (3)	0.63243 (22)	0.099 (3)
C(15)	0.50478 (15)	0.23033 (21)	0.57618 (24)	0.0873 (21)
C(21)	0.35720 (15)	0.13546 (17)	0.37520 (17)	0.0701 (17)
C(22)	0.33183 (18)	0.08977 (23)	0.42616 (23)	0.0974 (23)
C(23)	0.31286 (15)	0.1502 (3)	0.4709 (3)	0.0951 (25)
C(24)	0.32611 (13)	0.23598 (20)	0.45025 (19)	0.0658 (17)
C(25)	0.35387 (10)	0.22682 (14)	0.39053 (13)	0.0452 (11)
C(31)	0.24561 (9)	0.29506 (12)	0.17090 (12)	0.0372 (10)
C(32)	0.22599 (12)	0.31885 (15)	0.08330 (14)	0.0507 (13)
C(33)	0.17308 (14)	0.27377 (20)	0.01259 (16)	0.0638 (18)
C(34)	0.14029 (12)	0.20620 (17)	0.02882 (17)	0.0583 (15)
C(35)	0.15939 (12)	0.18179 (14)	0.11533 (18)	0.0563 (14)
C(36)	0.21221 (11)	0.22619 (14)	0.18691 (15)	0.0481 (12)
C(41)	0.34724 (9)	0.43607 (12)	0.22142 (12)	0.0347 (10)
C(42)	0.33186 (12)	0.52393 (14)	0.21410 (16)	0.0469 (13)
C(43)	0.36288 (15)	0.58018 (16)	0.17940 (20)	0.0639 (19)
C(44)	0.40839 (13)	0.54831 (17)	0.15307 (17)	0.0589 (16)
C(45)	0.42346 (11)	0.46048 (17)	0.15986 (15)	0.0523 (14)
C(46)	0.39361 (11)	0.40395 (14)	0.19407 (14)	0.0440 (12)
C(51)	0.25981 (9)	0.41872 (12)	0.30717 (12)	0.0348 (10)
C(52)	0.29570 (10)	0.45939 (14)	0.39018 (14)	0.0449 (12)
C(53)	0.25892 (12)	0.50679 (15)	0.42262 (15)	0.0517 (14)
C(54)	0.18809 (12)	0.51619 (15)	0.37283 (16)	0.0532 (15)
C(55)	0.15225 (11)	0.47590 (17)	0.29037 (16)	0.0542 (15)
C(56)	0.18784 (11)	0.42675 (15)	0.25753 (14)	0.0468 (12)

Table 2. *Selected geometric parameters* (Å, °) *for compound* (1)

Fe—C(11)	2.025 (3)	Fe—C(24)	2.038 (3)
Fe—C(12)	2.033 (3)	Fe—C(25)	2.035 (2)
Fe—C(13)	2.023 (3)	P(1)—C(1)	1.813 (2)
Fe—C(14)	2.017 (3)	P(1)—C(31)	1.799 (2)
Fe—C(15)	2.020 (3)	P(1)—C(41)	1.793 (2)
Fe—C(21)	2.031 (2)	P(1)—C(51)	1.796 (2)
Fe—C(22)	2.019 (3)	C(1)—C(25)	1.493 (3)
Fe—C(23)	2.025 (3)		
I(1)···H(46)	3.269	I(2)···C(1)	4.091 (2)
I(1)···H(46$^{\rm i}$)	3.269	I(2)···C(1$^{\rm ii}$)	4.091 (2)
I(2)···H(52)	3.083	I(2)···C(35$^{\rm iv}$)	4.148 (2)
I(2)···H(52$^{\rm ii}$)	3.083	I(2)···C(35$^{\rm v}$)	4.148 (2)
I(2)···H(45$^{\rm i}$)	3.158	I(2)···C(44$^{\rm i}$)	4.067 (2)
I(2)···H(45$^{\rm iii}$)	3.158	I(2)···C(44$^{\rm iii}$)	4.067 (2)
I(2)···H(1A)	3.179	I(2)···C(45$^{\rm i}$)	3.886 (2)
I(2)···H(1$A^{\rm ii}$)	3.179	I(2)···C(45$^{\rm iii}$)	3.886 (2)
I(1)···C(46)	4.166 (2)	I(2)···C(52)	3.989 (2)
I(1)···C(46$^{\rm i}$)	4.166 (2)	I(2)···C(52$^{\rm ii}$)	3.989 (2)
I(1)···H(46)—C(46)	158.3	I(2$^{\rm i}$)···H(45)—C(45)	134.7
I(2)···H(52)—C(52)	160.0	I(2)···H(1A)—C(1)	161.5

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

Compound (2)

Crystal data

[Fe($C_{24}H_{21}P$)$_2$]2I.CH_2Cl_2
M_r = 1075.5
Triclinic
$P\overline{1}$
a = 10.2799 (8) Å
b = 13.0137 (7) Å
c = 19.3758 (11) Å
α = 105.137 (5)°
β = 98.049 (6)°
γ = 107.414 (6)°
V = 2319.5 (3) Å^3
Z = 2

D_x = 1.54 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 15.0–21.0°
μ = 1.86 mm^{-1}
T = 293 K
Orange
0.30 × 0.25 × 0.25 mm
Block

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min}$ = 0.58, $T_{\max}$ = 0.66
10 084 measured reflections
10 084 independent reflections

6530 observed reflections [$I_{\rm net} > 3.0\sigma(I_{\rm net})$]
$\theta_{\max}$ = 27.0°
$h = -13 \rightarrow 12$
$k = 0 \rightarrow 16$
$l = -24 \rightarrow 23$
3 standard reflections
frequency: 40 min
intensity variation: 5%

Refinement

Refinement on F
R = 0.032
wR = 0.041
S = 1.31
6530 reflections
529 parameters
H-atom parameters not refined; C—H riding 0.95 Å
$w = 1/[\sigma^2(F) + 0.0005F^2]$

$(\Delta/\sigma)_{\max} < 0.008$
$\Delta\rho_{\max}$ = 1.40 e Å^{-3}
$\Delta\rho_{\min}$ = −1.20 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²) *for compound* (2)

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

	x	y	z	$U_{\rm eq}$
I(1)	1.21051 (3)	0.481492 (24)	0.377246 (16)	0.05622 (17)
I(2)	1.33077 (4)	−0.01998 (3)	0.171780 (20)	0.06915 (24)
Fe	0.96263 (6)	0.14047 (5)	0.13720 (3)	0.0452 (3)
P(1)	1.05705 (11)	0.07314 (8)	0.36654 (5)	0.0432 (6)
P(2)	1.44456 (10)	0.38127 (8)	0.19183 (5)	0.0390 (5)
C(1*A*)	1.0982 (4)	0.1303 (3)	0.29286 (20)	0.0435 (23)
C(1*B*)	1.2825 (4)	0.2873 (3)	0.20162 (21)	0.0434 (23)
C(11*A*)	0.8667 (5)	0.1350 (4)	0.2213 (3)	0.061 (3)
C(12*A*)	0.7691 (5)	0.0674 (5)	0.1538 (3)	0.072 (4)
C(13*A*)	0.8183 (5)	−0.0174 (4)	0.1184 (3)	0.068 (3)
C(14*A*)	0.9437 (4)	−0.0051 (3)	0.16287 (23)	0.0514 (25)
C(15*A*)	0.9759 (4)	0.0894 (3)	0.22793 (21)	0.0432 (23)
C(21*A*)	1.1087 (5)	0.1626 (4)	0.07566 (23)	0.056 (3)
C(22*A*)	0.9795 (6)	0.1606 (5)	0.03759 (25)	0.074 (3)
C(23*A*)	0.9433 (5)	0.2482 (4)	0.0799 (3)	0.071 (3)
C(24*A*)	1.0501 (4)	0.3075 (3)	0.14588 (25)	0.054 (3)
C(25*A*)	1.1538 (4)	0.2546 (3)	0.14316 (21)	0.0439 (23)
C(11)	1.2102 (4)	0.1384 (3)	0.4414 (2)	0.048 (3)
C(12)	1.2853 (5)	0.2541 (4)	0.4619 (3)	0.065 (3)
C(13)	1.4054 (5)	0.3031 (4)	0.5168 (3)	0.071 (3)
C(14)	1.4533 (5)	0.2380 (5)	0.5527 (3)	0.072 (3)
C(15)	1.3803 (5)	0.1244 (5)	0.5332 (3)	0.070 (3)
C(16)	1.2596 (5)	0.0736 (4)	0.4776 (2)	0.056 (3)
C(21)	0.9095 (4)	0.1045 (3)	0.3924 (2)	0.050 (3)
C(22)	0.9260 (6)	0.1922 (4)	0.4564 (3)	0.068 (3)
C(23)	0.8095 (8)	0.2204 (5)	0.4712 (4)	0.091 (5)
C(24)	0.6812 (7)	0.1637 (6)	0.4226 (5)	0.095 (6)
C(25)	0.6639 (6)	0.0776 (5)	0.3597 (4)	0.081 (4)
C(26)	0.7771 (5)	0.0482 (4)	0.3449 (3)	0.061 (3)
C(31)	1.0197 (4)	−0.0774 (3)	0.3406 (2)	0.048 (3)
C(32)	1.1077 (6)	−0.1206 (4)	0.3037 (3)	0.072 (4)
C(33)	1.0967 (7)	−0.2314 (5)	0.2928 (4)	0.096 (5)
C(34)	0.9989 (7)	−0.3004 (4)	0.3180 (3)	0.083 (4)
C(35)	0.9101 (5)	−0.2596 (4)	0.3533 (3)	0.070 (3)
C(36)	0.9209 (4)	−0.1474 (4)	0.3652 (2)	0.055 (3)
C(41)	1.5821 (4)	0.3946 (3)	0.2656 (2)	0.041 (2)
C(42)	1.5621 (5)	0.4158 (4)	0.3361 (3)	0.064 (3)
C(43)	1.6699 (6)	0.4331 (5)	0.3940 (3)	0.075 (4)
C(44)	1.7979 (5)	0.4292 (4)	0.3807 (3)	0.071 (3)
C(45)	1.8170 (4)	0.4083 (4)	0.3108 (3)	0.066 (3)
C(46)	1.7097 (4)	0.3899 (4)	0.2532 (2)	0.053 (3)
C(51)	1.4833 (4)	0.3244 (3)	0.1057 (2)	0.041 (2)
C(52)	1.4846 (5)	0.2145 (4)	0.0849 (3)	0.061 (3)
C(53)	1.5228 (5)	0.1726 (4)	0.0211 (3)	0.061 (3)
C(54)	1.5564 (6)	0.2359 (5)	−0.0224 (3)	0.072 (4)
C(55)	1.5557 (9)	0.3446 (6)	−0.0031 (3)	0.113 (6)
C(56)	1.5189 (7)	0.3893 (4)	0.0619 (3)	0.084 (4)
C(61)	1.4322 (6)	0.5161 (5)	0.1987 (4)	0.047 (4)
C(62)	1.5387 (10)	0.6094 (6)	0.2449 (5)	0.105 (6)
C(63)	1.5409 (14)	0.7186 (6)	0.2494 (6)	0.148 (9)
C(64)	1.4331 (13)	0.7304 (7)	0.2114 (5)	0.096 (8)
C(65)	1.3298 (9)	0.6413 (8)	0.1657 (5)	0.092 (8)
C(66)	1.3247 (7)	0.5310 (6)	0.1582 (4)	0.069 (5)
Cl(1)	1.9516 (4)	0.53876 (25)	0.10271 (23)	0.198 (3)
Cl(1*)	1.914 (3)	0.577 (3)	0.0478 (16)	0.136 (8)
Cl(2)	1.8012 (4)	0.6732 (3)	0.0621 (3)	0.169 (4)
Cl(2*)	1.7946 (10)	0.6934 (7)	0.1386 (6)	0.136 (7)
C(1*S*)	1.9604 (17)	0.6621 (17)	0.0762 (11)	0.160 (16)
C(1*S**)	1.920 (6)	0.679 (5)	0.109 (3)	0.13 (2)
C(61*)	1.4728	0.5355	0.2018	0.03
C(62*)	1.6034	0.6104	0.2031	0.05
C(63*)	1.6193	0.7214	0.2049	0.05
C(64*)	1.5045	0.7575	0.2052	0.05
C(65*)	1.3739	0.6827	0.2039	0.19
C(66*)	1.3580	0.5717	0.2022	0.08

* Denotes the site of lower occupancy of a pair of disordered atoms (see below).

Table 4. *Selected geometric parameters* (Å, °) *for compound* (2)

Fe—C(11*A*)	2.025 (4)	P(1)—C(1*A*)	1.818 (4)
Fe—C(12*A*)	2.042 (5)	P(1)—C(11)	1.794 (4)
Fe—C(13*A*)	2.046 (4)	P(1)—C(21)	1.788 (4)
Fe—C(14*A*)	2.042 (4)	P(1)—C(31)	1.794 (4)
Fe—C(15*A*)	2.036 (4)	P(2)—C(1*B*)	1.815 (4)
Fe—C(21*A*)	2.045 (4)	P(2)—C(41)	1.797 (4)
Fe—C(22*A*)	2.038 (5)	P(2)—C(51)	1.792 (4)
Fe—C(23*A*)	2.037 (4)	P(2)—C(61)	1.769 (6)
Fe—C(24*A*)	2.039 (4)	C(1*A*)—C(15*A*)	1.502 (5)
Fe—C(25*A*)	2.045 (4)	C(1*B*)—C(25*A*)	1.486 (5)
I(1)···H(45$^{\rm iv}$)	3.011	I(1)···C(14$^{\rm vi}$)	3.957 (5)
I(1)···H(12)	3.013	I(1)···C(42)	4.091 (4)
I(1)···H(1*BA*)	3.048	I(1)···C(44$^{\rm iv}$)	4.103 (5)
I(1)···H(42)	3.157	I(1)···C(45$^{\rm iv}$)	3.810 (4)
I(1)···H(1*AB*)	3.212	I(2)···C(1*A*)	4.125 (4)
I(2)···H(52)	2.973	I(2)···C(1*B*)	4.079 (4)
I(2)···H(32)	3.007	I(2)···C(14*A*)	4.024 (4)
I(2)···H(64$^{\rm v}$)	3.049	I(2)···C(32)	3.886 (5)
I(2)···H(1*BB*)	3.147	I(2)···C(54$^{\rm iii}$)	4.032 (4)
I(2)···H(54$^{\rm iii}$)	3.169	I(2)···C(52)	3.897 (4)
I(1)···C(1*B*)	3.981 (4)	I(2)···C(64$^{\rm v}$)	3.921 (8)
I(1)···C(12)	3.947 (5)	I(2)···C(64*$^{\rm v}$)	3.968
I(1)···C(13$^{\rm vi}$)	3.970 (5)		
I(1$^{\rm i}$)···H(45)—C(45)	142.6	I(2)···H(52)—C(52)	164.5
I(1)···H(12)—C(12)	167.8	I(2)···H(32)—C(32)	154.4
I(1)···H(1*BA*)—C(1*B*)	167.4	I(2$^{\rm ii}$)···H(64)—C(64)	153.4
I(1)···H(42)—C(42)	168.0	I(2)···H(1*BB*)—C(1*B*)	167.2
I(1)···H(1*AB*)—C(1*A*)	175.9	I(2$^{\rm iii}$)···H(54)—C(54)	151.8

Symmetry codes: (i) $1 + x, y, z$; (ii) $x, 1 + y, z$; (iii) $3 - x, -y, -z$; (iv) $x - 1, y, z$; (v) $x, y - 1, z$; (vi) $3 - x, 1 - y, 1 - z$.

Synthesis: samples of compounds (1) and (2) were prepared by reaction of triphenylphosphine with $[(C_5H_5)Fe(C_5H_4CH_2NMe_3)]^+.I^-$, (3), and $[Fe(C_5H_4CH_2NMe_3)_2]^{2+}.2I^-$, (4), respectively. Crystals suitable for X-ray diffraction were grown by slow evaporation of solutions from dichloromethane.

Data collection and cell refinement were by Enraf-Nonius (1989) *CAD*-4 *software*. Data reduction software, the program used to solve and refine the structures and software used to prepare material for publication were from *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989).

The systematic absences for (1) (hkl if $h + k = 2n + 1$, $h0l$ if $l = 2n + 1$) allow the space group to be either $C2/c$ or Cc; the former was assumed and confirmed by the analysis. Compound (2) crystallized in the triclinic system, space group $P1$ or $P\bar{1}$; $P\bar{1}$ was assumed and confirmed by successful analysis. In both structures, the H atoms attached to the C atoms were clearly visible in difference maps at an intermediate stage in the refinement. In (1), all H atoms were positioned on geometric grounds (C—H 0.95 Å) with only their displacement parameters refined isotropically, and included as riding atoms in the structure-factor calculations. In (2), the H atoms were positioned on geometric grounds (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations with appropriate occupancies. It became apparent at an intermediate stage in the refinement of (2) that one of the phenyl groups was disordered over two orientations (0.75, 0.25). The major orientation was refined anisotropically and the minor orientation was treated as a rigid hexagon (C—C 1.395 Å) and included as such in the structure-factor calculations. A dichloromethane solvent of crystallization is also present in the crystal lattice; it is disordered over two orientations (0.75, 0.25, from difference maps). The major non-H-atom sites in the disordered dichloromethane molecule were refined anisotropically while the minor sites were refined isotropically. H atoms were included for the major orientation only.

The diagrams were prepared using *ORTEP*II (Johnson, 1976) and *PLUTON* (Spek, 1991).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71526 (65 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1077]

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Beer, P. D., Nation, J. E., McWhinnie, S. L. W., Harman, M. E., Hursthouse, M. B., Ogden, M. I. & White A. H. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2485–2492.

Enraf-Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.

Etter, M. C. & Reutzel, S. M. (1991). *J. Am. Chem. Soc.* **113**, 2586–2598.

Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1994*a*). *Acta Cryst.* **C50**, 18–23.

Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1994*b*). *J. Chem. Soc. Dalton Trans.* In the press.

Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1994*c*). *Acta Cryst.* **C49**. In the press.

Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1994*d*). *J. Organomet. Chem.* In the press.

Ferguson, G., Lough, A. J., McAlees, A. J. & McCrindle, R. (1993). *Acta Cryst.* **C49**, 573–576.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Houlton, A., Miller, J. R., Silver. J., Jassim, N., Axon, T. L., Bloor, D. & Cross, G. H. (1993). *Inorg. Chim. Acta*, **205**, 67–70.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Meetsma, A., Buwalda, P. L. & van de Grampel, J. C. (1988). *Acta Cryst.* **C44**, 58–61.

Moore, A. J., Skabara, P. J., Bryce, M. R., Batsanov, A. S., Howard, J. A. K. & Daley, S. T. A. K. (1993). *J. Chem. Soc. Chem. Commun.* pp. 417–419.

Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.

Spek, A. L. (1991). *PLUTON. Molecular Graphics Program.* Univ. of Utrecht, The Netherlands.

Tang, B. Z., Petersen, R., Foucher, D. A., Lough, A., Coombs, N., Sodhi, R. & Manners, A. (1993). *J. Chem. Soc. Chem. Commun.* pp. 523–525.