

Crystal and Molecular Structures of Four Bis(diphosphine) Complexes of Iron(II): Bis[1,2-bis(diethylphosphino)ethane]di-iodoiron(II), Dichloro-bis[*o*-phenylenebis(diphenylphosphine)]iron(II), Bis(acetonitrile)bis[*o*-phenylenebis(diphenylphosphine)]iron(II) Di-iodide, and Iodobis[*o*-phenylenebis(diphenylphosphine)]iron(II) Iodide *

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The crystal structures of $[\text{FeI}_2(\text{depe})_2]$ ($\text{depe} = \text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$), $[\text{FeCl}_2(\text{opdp})_2] \cdot \text{thf}$, $[\text{Fe}(\text{MeCN})_2(\text{opdp})_2]\text{I}_2$, and $[\text{FeI}(\text{opdp})_2]\text{I} \cdot 1.85\text{CH}_2\text{Cl}_2$ [$\text{opdp} = o$ -phenylenebis(diphenylphosphine), $\text{thf} = \text{tetrahydrofuran}$] are discussed, and it is demonstrated that increasing steric pressures give rise to progressive change from low-spin octahedral co-ordination to high-spin octahedral co-ordination and then to five-co-ordination. The diphosphine ligand complexes are compared to complexes of other diphosphine ligands already in the literature.

We have recently reported¹ a Mössbauer study of a number of iron(II) complexes of diphosphines. The complexes spanned a range of structures, as deduced from Mössbauer and other data, and in part from X-ray crystal structure analysis. The principal variants were tetrahedral, octahedral, both high-spin and low-spin, and, in one particular case, another unidentified structure. In this paper we report the structures of four selected complexes, chosen to confirm and clarify the results of the Mössbauer studies.

Results

Iron(II) complexes of $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (dmpe) and $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ (depe) have been known for some time. All these materials have low-spin. The complexes $[\text{FeX}_2(\text{dmpe})_2]$ ($\text{X} = \text{Cl}^2$ or I^1) are green, as are $[\text{FeX}_2(\text{depe})_2]$ ($\text{X} = \text{Cl}^2$ or Br^3), whereas $[\text{FeI}_2(\text{depe})_2]$ is yellow.³ An early report² on $[\text{FeCl}_2(\text{dmpe})_2]$ states that it loses dmpe on standing, turning yellow. However, on the data presented, this change might equally have been due to isomerization. The structures of $[\text{FeCl}_2(\text{dmpe})_2]$ ⁴ and $[\text{FeCl}_2(\text{depe})_2]$ ⁵ have been previously determined by X-ray crystal structure analysis, and both complexes are *trans* octahedral, with the iron atom at a centre of symmetry. Because of the difference in colour, suggesting a possible isomeric form, we undertook an X-ray crystal structure analysis of $[\text{FeI}_2(\text{depe})_2]$.

Structure of Bis[1,2-bis(diethylphosphino)ethane]di-iodoiron(II) (1).—From an excellent set of diffraction data, we obtained a well resolved structure of this small molecule (Figure 1). The crystal data are in Table 1 and the experimental details in Table 2. Most of the hydrogen atoms refined satisfactorily and are well defined. The iron atom lies on a centre of symmetry, with the two depe ligands forming an equatorial plane and the two iodo ligands mutually *trans* in an octahedral co-ordination pattern. The principal dimensions are given in Table 3, and the atomic co-ordinates in Table 4.

The depe ligands have a normal *gauche* conformation with a PCCP torsional angle of $50.0(2)^\circ$. Three of the four ethyl groups are directed away from the I–Fe–I apical line, but C(23)–C(24) of the fourth ethyl group is turned back towards C(11) of the other phosphorus ligand. The packing of the ethyl groups within the complex, and the interlocking of these groups

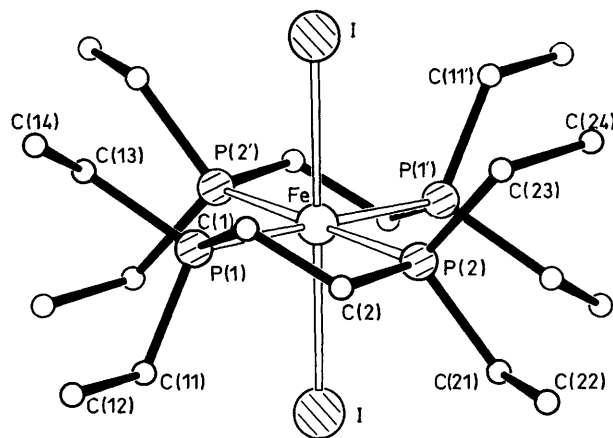


Figure 1. Molecular structure of $[\text{FeI}_2(\text{depe})_2]$ (1)

between molecules appears tight, with many interatomic contacts at slightly less than van der Waals distances. There appear to be many, mainly intramolecular, interactions between methylene hydrogen atoms (of ethyl groups) and iodo-ligands, with $\text{I} \cdots \text{H}$ separations from as little as $2.98(3) \text{ \AA}$.

Despite the yellow colour, $[\text{FeI}_2(\text{depe})_2]$ has the *trans*-octahedral structure characteristic of $[\text{FeCl}_2(\text{depe})_2]$ and $[\text{FeCl}_2(\text{dmpe})_2]$.

Complexes of *o*-Phenylenebis(diphenylphosphine).—The diphosphine *o*-phenylenebis(diphenylphosphine) (opdp) has become easily available only relatively recently,⁶ and its complexing properties with iron(II) have been investigated only by ourselves. We have shown¹ that the product of the reaction of iron(II) iodide and opdp analyses for $\text{FeI}_2(\text{opdp})_3$, but that this is not a single material. Recrystallization of this from dichloromethane affords $[\text{FeI}(\text{opdp})_2]\text{I} \cdot 2\text{CH}_2\text{Cl}_2$, and from acetonitrile $[\text{Fe}(\text{MeCN})_2(\text{opdp})_2]\text{I}_2$. In general, with FeX_2 ($\text{X} = \text{Cl}, \text{Br}$, or I), there are two isomeric products of stoichiometry $\text{FeX}_2(\text{opdp})_2$ for each X , a yellow high-spin form (which predominates for $\text{X} = \text{Cl}$), and an orange-red form (which predominates for $\text{X} = \text{I}$). We have determined the structures of three representative complexes from this range of materials.

Structure of Dichlorobis[*o*-phenylenebis(diphenylphosphine)]-iron(II)-Tetrahydrofuran (1/1) (2).—This compound was prepared by direct reaction of FeCl_2 and opdp in tetrahydrofuran

* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1 pp. xvii–xx.

Table 1. Crystal data for compounds (1)–(4)

	(1)	(2)	(3)	(4)
Compound	[FeI ₂ (depe) ₂]	[FeCl ₂ (opdp) ₂].thf	[Fe(MeCN) ₂ (opdp) ₂]I ₂	[FeI(opdp) ₂]I·1.85CH ₂ Cl ₂
Formula	C ₂₀ H ₄₈ FeI ₂ P ₄	C ₆₀ H ₄₈ Cl ₂ FeP ₄ ·C ₄ H ₈ O	C ₆₄ H ₅₄ FeI ₂ N ₂ P ₄	C ₆₀ H ₄₈ FeI ₂ P ₄ ·1.85CH ₂ Cl ₂
<i>M</i>	722.2	1 091.8	1 284.7	1 360.1
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
<i>a</i> /Å	8.142(3)	10.724(10)	13.286(3)	22.567(5)
<i>b</i> /Å	8.761(2)	12.114(11)	16.480(2)	9.672(5)
<i>c</i> /Å	10.309(4)	23.174(29)	13.638(2)	26.843(5)
α /°	95.57(3)	91.36(9)		
β /°	99.27(3)	90.87(9)	100.35(1)	99.10(2)
γ /°	104.97(3)	95.98(7)		
<i>U</i> /Å ³	693.7	2 992.8	2 937.6	5 785.2
Space group (no.)	<i>P</i> $\bar{1}$ (no. 2)	<i>A</i> $\bar{1}$ (≡ no. 2)	<i>P</i> 2 ₁ / <i>n</i> (≡ no. 14)	<i>P</i> 2/ <i>a</i> (≡ no. 13)
<i>Z</i>	1	2	2	4
<i>D_c</i> /g cm ^{−3}	1.728	1.211	1.452	1.561
<i>F</i> (000)	360	1 136	1 288	2 711.5
μ (Mo- <i>K</i> _α)/cm ^{−1}	29.8	4.8	14.4	16.4

Table 2. Experimental details of the X-ray analyses of (1)–(4)

	(1)	(2)	(3)	(4)
Crystal colour/shape	Pale yellow/prisms	Pale yellow/almost square prisms	Deep red/rhombic plates	Pale brown/flat needles
Crystal size/mm	0.48 × 0.15 × 0.70	0.24 × 0.24 × 0.19	0.17 × 0.29 × 0.31	0.08 × 0.11 × 0.36
Mounting	On glass fibre, coated in silicone grease	In wide capillary, stuck by solvent to wall	On glass fibre	On glass fibre
On CAD4 diffractometer:				
For cell dimensions, θ /°	10–11	10–11	11–12	10–11
Maximum θ /°	25	20	25	20
No. of independent reflections	2 439	2 785	5 163	5 397
During processing, corrections made for:				
Lorentz-polarisation	Yes	Yes	Yes	Yes
Deterioration	Yes	Yes	No	Yes
Absorption	No	No	Yes	Yes
Negative intensities	Yes	Yes	Yes	Yes
Structure solved by:	Patterson/electron density maps	Electron-density maps, assuming Fe at origin	As (1)	As (1)
Refinement	Full-matrix least squares	As (1)	Large-block least squares	As (3)
Anisotropic atoms	All non-hydrogen atoms	All non-hydrogen atoms (not very satisfactory; some C atoms went non-positive-definite)	All non-hydrogen atoms	Fe, I, P, Cl
Hydrogen atoms:				
Phenyl groups		Idealised positions, riding	As (2)	As (2)
Alkyl groups (including –CH ₂ –)	Independent		With geometrical constraints	
Final <i>R</i>	0.023	0.105	0.062	0.119
<i>R</i> '	0.023	0.106	0.068	0.107
No. of reflections in refinement	2 439	1 832	5 163	3 895
<i>I</i> > <i>n</i> σ _{<i>I</i>} , <i>n</i> =	0	2	0	1
Weighting scheme, <i>w</i> =	σ _{<i>F</i>} ^{−2}	(σ _{<i>F</i>} ² + 0.020 7 <i>F</i> ²) ^{−1}	(σ _{<i>F</i>} ² + 0.001 8 <i>F</i> ²) ^{−1}	(σ _{<i>F</i>} ² + 0.001 87 <i>F</i> ²) ^{−1}
Max. peaks in difference map/e Å ^{−3}	0.45	0.90	0.80	1.6
Near	I atom	Fe atom		Fe and I atoms

(thf). The crystal data are in Table 1 and the experimental details of the structure determination are in Table 2. The structure is shown in Figure 2, and the molecular dimensions and atomic co-ordinates in Tables 3 and 5.

The iron atom lies at a centre of symmetry, octahedrally co-ordinated by two opdp ligands and two chlorides. There is good pseudo-2/*m* symmetry in the molecule. The Fe–P distances are 2.616(5) Å (weighted mean), consistent with the complex having high-spin. The *trans*-chloro ligands are enclosed by the opdp

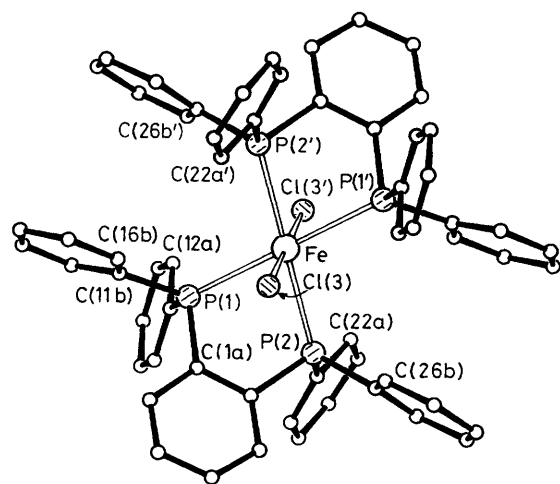
molecules, as are the MeCN molecules in structure (3) discussed below. The angle between the normals to the *o*-phenylene planes of the opdp and the equatorial phosphorus-atom plane is 46.8(4)°. Pairs of phenyl rings with P–C bonds close to the equatorial plane [the rings of C(11b) and of C(21b')] are approximately parallel and overlapping, the distances between the rings being *ca.* 4.4 Å. The situation in the cation of (3) is quite different.

There are very close H...Cl contacts in this molecule,

Table 3. Selected bond lengths (Å) and angles (°) in compounds (1)–(4) and in compounds with comparable structural features; e.s.d.s are in parentheses^a

Compound	Fe–P ₁	Fe–P ₂	Fe–X	P ₁ –Fe– P ₂	X–Fe– P ₁	X–Fe– P ₂	P ₁ –C– C–P ₂	P ₁ ... P ₂	P ₁ ... P ₂ '	Ref.
(1) [FeI ₂ (depe) ₂]	2.295(1), P(1)	2.323(1), P(2)	2.706(1), I	83.5(1)	85.9(1)	88.9(1)	50.0(2)	3.075(1)	3.447(1)	This work
(2) [FeCl ₂ (opdp) ₂].thf	2.612(3), P(1)	2.622(4), P(2)	2.348(3), Cl(3)	74.4(1)	86.6(1)	86.6(1)	2.6(15)	3.165(5)	4.170(5)	This work
(3) [Fe(MeCN) ₂ (opdp) ₂] ₂ I ₂	2.337(1), P(1)	2.343(1), P(2)	1.894(4), N(3)	81.1(1)	90.4(1)	91.8(1)	−1.6(5)	3.042(1)	3.556(2)	This work
(4) [FeI(opdp) ₂]. 1.85CH ₂ Cl ₂										
A	2.356(5), P(11)	2.316(5), P(13)	2.632(5), I(1)	80.5(2)	96.2(2)	93.2(2)	0.9(22)	3.020(7)	3.546(8)	This work
B	2.379(7), P(21)	2.323(5), P(23)	2.646(4), I(2)	80.2(2)	97.8(2)	92.8(2)	−0.3(24)	3.029(8)	3.576(9)	This work
(5) [FeCl ₂ (depe) ₂] ^b	2.260(2)	2.268(3)	2.349(2), Cl							5
(6) [FeCl ₂ (dmpe) ₂]	2.241(1)	2.230(1)	2.352(1), Cl	85.8(1)			0.1	3.04	3.27	4
(7) [FeH ₂ (dppe) ₂] ^c	2.18	2.16		88.3			48.4	3.02	3.49	9
(8) [FeCl ₂ (dppen) ₂]. 2Me ₂ CO, 130 K	2.312(8)	2.289(9)	2.329(6), Cl	81.8(3)			3.5	3.01	3.48	11
[FeCl ₂ (dppen) ₂]. 2Me ₂ CO, 295 K	2.592(2)	2.576(2)	2.363(2), Cl	77.6(1)			−2.9	3.24	4.03	11
[FeCl ₂ (dppen) ₂]	2.675(1)	2.532(1)	2.347(1), Cl	78.0(1)			−2.0	3.28	4.05	11
(9) [FeCl ₂ (bdpp) ₂]. 2Me ₂ CO	2.713(3)	2.665(3)	2.354(3), Cl	77.4(1)			−63.6	3.36	4.20	4

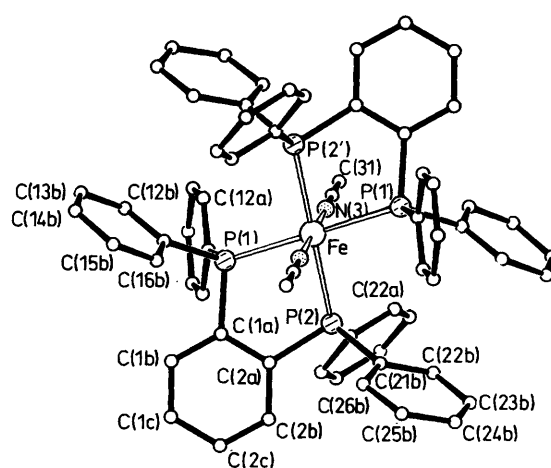
^a P₁ and P₂ are the two phosphorus atoms of a bidentate phosphine ligand, P₂' is the symmetry-related atom in the second phosphine ligand, and X is the co-ordinated atom of the axial donor. ^b No other data available. ^c *cis* Structure, all other compounds are *trans*; Fe–P₁ distance is mean of four in which P₁ is *trans* to H, Fe–P₂ similarly for P₂ *trans* to P.

**Figure 2.** Molecular structure of [FeCl₂(opdp)₂] in (2)

e.g., H(16b)...Cl(3) 2.73, H(26b)...Cl(3) 2.67, and H(22a')...Cl(3) 2.77 Å, but there are few intermolecular contacts as short as van der Waals distances.

The solvent thf molecules refined best with a site occupancy factor of 0.5. The calculated density is rather lower than the densities of the other three complexes discussed in this paper, even allowing for the different halogen atoms, and perhaps this occupancy factor is an underestimate. There is no indication of other solvent-molecule sites in the crystal.

Structure of Bis(acetonitrile)bis[o-phenylenebis(diphenylphosphine)]iron(II) Di-iodide (3).—The cation in this complex can be obtained by treatment of the halogen complexes FeX₂(opdp)₂ (X = Cl, Br, or I) with acetonitrile. The crystal data are in Table 1 and the experimental details of the structure determination are in Table 2. The crystals of (3) are composed of octahedral

**Figure 3.** Structure of [Fe(MeCN)₂(opdp)₂]²⁺ in the crystal of its di-iodide salt, (3)

complex dications, with iron atoms lying at a centre of symmetry, and unbound iodide anions. The four phosphorus atoms in the cation form a rectangular equatorial plane, with the two acetonitrile ligands mutually *trans* (Figure 3). The molecular dimensions and atomic co-ordinates are in Tables 3 and 6.

The arrangements of the ligands and of the phenyl groups in the opdp co-ordinated molecules produce a complex with a high degree of symmetry, almost perfectly 2/*m*. The pseudo-two-fold axis lies in the equatorial plane between the two opdp ligands, and the pseudo-mirror plane bisects each opdp ligand and passes through the MeCN molecules. The Fe–N–C–C group is virtually linear and almost perfectly normal to the equatorial plane [*cf.* with complex (2), for which a rather similar arrangement is found].

The *o*-phenylene rings are tilted by 20.5(1)° away from

Table 4. Final atomic co-ordinates (fractional $\times 10^4$) for $[\text{FeI}_2(\text{depe})_2]$ (1); e.s.d.s are in parentheses

Atom	x	y	z
Fe	0	0	0
I	-2 106.4(2)	1 930.3(2)	65.1(1)
C(11)	4 016(3)	1 546(3)	2 274(3)
C(12)	5 391(5)	2 854(5)	3 221(4)
C(13)	1 195(4)	2 557(3)	3 147(3)
C(14)	1 929(6)	4 283(4)	3 792(4)
P(1)	1 908.7(7)	1 880.8(6)	1 636.3(5)
C(1)	2 615(3)	3 721(3)	906(3)
C(2)	3 138(4)	3 238(3)	-390(3)
P(2)	1 421.8(7)	1 547.2(7)	-1 408.3(6)
C(21)	2 678(4)	742(4)	-2 506(3)
C(22)	3 855(5)	1 922(5)	-3 181(3)
C(23)	335(4)	2 682(3)	-2 515(3)
C(24)	-989(5)	1 702(4)	-3 710(3)

Table 5. Final atomic co-ordinates (fractional $\times 10^4$) for $[\text{FeCl}_2(\text{opdp})_2]\cdot\text{thf}$ (2); e.s.d.s are in parentheses

Atom	x	y	z
Fe	0	0	0
C(11a)	-1 494(12)	-2 971(10)	365(6)
C(12a)	-2 079(14)	-2 644(11)	849(7)
C(13a)	-3 142(15)	-3 241(14)	1 057(8)
C(14a)	-3 630(16)	-4 155(15)	753(9)
C(15a)	-3 076(17)	-4 485(13)	272(10)
C(16a)	-2 007(13)	-3 895(12)	75(7)
C(11b)	1 156(13)	-2 719(10)	557(6)
C(12b)	920(16)	-3 518(14)	943(7)
C(13b)	1 890(18)	-3 872(16)	1 262(8)
C(14b)	3 100(19)	-3 418(18)	1 217(9)
C(15b)	3 338(19)	-2 628(17)	811(10)
C(16b)	2 355(16)	-2 270(14)	503(8)
P(1)	-65(3)	-2 138(3)	140(2)
C(1a)	134(12)	-2 644(11)	-580(6)
C(1b)	877(13)	-3 546(11)	-715(8)
C(1c)	1 065(15)	-3 874(12)	-1 264(7)
C(2c)	486(18)	-3 382(13)	-1 704(8)
C(2b)	-249(15)	-2 519(11)	-1 618(7)
C(2a)	-385(12)	-2 161(9)	-1 059(7)
P(2)	-1 231(3)	-928(3)	-903(2)
C(21a)	-2 863(13)	-1 561(13)	-874(7)
C(22a)	-3 722(16)	-879(17)	-601(9)
C(23a)	-5 023(19)	-1 322(27)	-608(9)
C(24a)	-5 354(26)	-2 352(28)	-791(11)
C(25a)	-4 534(22)	-2 960(17)	-1 056(12)
C(26a)	-3 301(17)	-2 587(13)	-1 067(9)
C(21b)	-1 216(13)	-227(11)	-1 578(6)
C(22b)	-2 253(17)	-117(15)	-1 899(8)
C(23b)	-2 214(20)	500(20)	-2 403(10)
C(24b)	-1 109(24)	1 046(14)	-2 565(9)
C(25b)	-16(21)	925(14)	-2 254(9)
C(26b)	-70(15)	327(12)	-1 751(7)
Cl(3)	1 829(3)	-145(3)	-528(2)

Solvent (thf) molecule, with site occupancy 0.5

O(40)	-5 502(27)	-4 951(34)	2 330(11)
C(41)	-5 596(35)	-4 059(29)	2 728(16)
C(42)	-6 263(42)	-4 638(36)	3 215(18)
C(43)	-6 947(40)	-5 661(32)	2 911(20)
C(44)	-5 905(52)	-6 025(36)	2 542(24)

the equatorial plane containing the four phosphorus atoms $[46.8(4)^\circ$ in (2)] suggesting that (2) has less distortion due to packing around the iron than (3). One phenyl ring on each phosphorus atom points outward (nearly parallel to the pseudo-two-fold axis) while the other phenyl groups are nearly parallel

Table 6. Final atomic co-ordinates (fractional $\times 10^4$) for $[\text{Fe}(\text{MeCN})_2(\text{opdp})_2]\text{I}_2$ (3); e.s.d.s are in parentheses

Atom	x	y	z
Fe	5 000	5 000	0
P(1)	5 968.7(8)	3 827.8(7)	430.3(8)
P(2)	3 716.0(8)	4 029.0(7)	-468.5(8)
C(1a)	5 347(3)	2 993(3)	-320(3)
C(1b)	5 842(4)	2 260(3)	-415(3)
C(1c)	5 305(4)	1 625(3)	-916(4)
C(11a)	5 998(3)	3 474(3)	1 697(3)
C(12a)	6 493(4)	3 929(3)	2 494(3)
C(13a)	6 490(4)	3 698(4)	3 471(4)
C(14a)	5 973(5)	3 001(4)	3 660(4)
C(15a)	5 490(5)	2 543(4)	2 875(4)
C(16a)	5 488(4)	2 762(3)	1 906(4)
C(11b)	7 278(3)	3 699(3)	211(3)
C(12b)	8 106(4)	3 632(4)	972(4)
C(13b)	9 092(5)	3 581(5)	750(5)
C(14b)	9 243(5)	3 569(5)	-213(6)
C(15b)	8 425(5)	3 611(4)	-968(5)
C(16b)	7 449(4)	3 661(3)	-770(4)
C(2a)	4 326(3)	3 085(3)	-745(3)
C(2b)	3 790(4)	2 442(3)	-1 259(3)
C(2c)	4 275(4)	1 722(3)	-1 329(4)
C(21a)	2 978(4)	3 714(3)	465(3)
C(22a)	2 461(4)	4 299(3)	920(5)
C(23a)	1 906(5)	4 091(5)	1 645(5)
C(24a)	1 866(5)	3 305(5)	1 944(5)
C(25a)	2 372(5)	2 714(4)	1 507(5)
C(26a)	2 909(4)	2 904(3)	774(4)
C(21b)	2 770(4)	4 169(3)	-1 597(4)
C(22b)	1 783(4)	4 435(3)	-1 575(5)
C(23b)	1 087(5)	4 558(4)	-2 468(6)
C(24b)	1 356(7)	4 437(4)	-3 352(6)
C(25b)	2 336(6)	4 163(4)	-3 408(5)
C(26b)	3 062(5)	4 026(3)	-2 531(4)
N(3)	4 706(3)	5 064(2)	1 306(3)
C(3)	4 538(4)	5 069(4)	2 089(4)
C(31)	4 290(7)	5 018(6)	3 097(5)
I	6 750.4(3)	-528.7(2)	-1 039.9(3)

with the MeCN ligands. In contrast to (2) with its overlapping rings, there is no ring overlapping here. There is a tight perpendicular arrangement of pairs of rings, in which a hydrogen atom of one ring points towards the centre of the other, *viz.* H(12a) and H(22a) are directed towards the centres of rings C(21b)—C(26b) and C(11b)—C(16b), respectively, on the other opdp ligand. Each MeCN ligand is thus enclosed by two phenyl rings from one opdp molecule, face-on, and two phenyl rings in a more side-on approach from the second opdp molecule.

The iodide ions lie between the cations, in general positions, and are not subject to the pseudo-2/m symmetry. Each anion is surrounded by seven hydrogen atoms (from five different cations) at distances of 2.95–3.30 Å, compared with the sum of the van der Waals radii for $\text{I} \cdots \text{H}$ contacts of 3.35 Å.

Structure of Iodobis[o-phenylenebis(diphenylphosphine)]-iron(II) Iodide-Dichloromethane (ca. 1/2) (4).—Crystals of this compound were obtained by direct reaction of FeI_2 with opdp in CH_2Cl_2 , and subsequent recrystallization from CH_2Cl_2 . The crystal data are in Table 1 and the experimental details of the structure determinations are in Table 2. The molecular dimensions and atomic co-ordinates are given in Tables 3 and 7.

There are two independent, virtually identical, complex cations $[\text{FeI}(\text{opdp})_2]^+$ in the crystal. Each lies on a different two-fold symmetry axis, with the axis passing through the iron

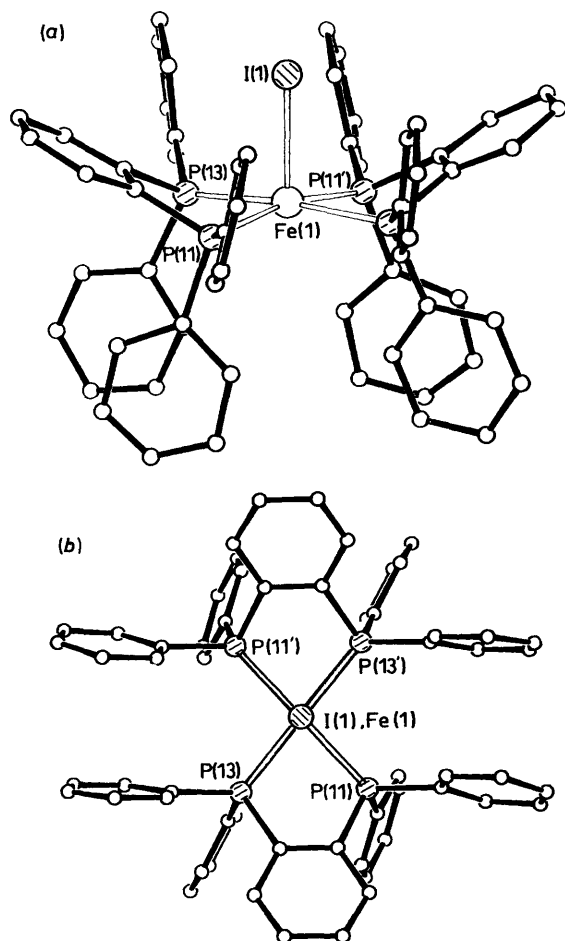


Figure 4. Structure of one of the two virtually identical cations $[\text{Fe}(\text{opdp})_2]^+$ in (4) viewed (a) from a position roughly in the phosphorus-atom plane, and (b) down the I-Fe axis

and co-ordinated iodine atoms. In each cation [Figure 4(a) and (b)] the iron atom is five-co-ordinate with an approximately square-pyramidal co-ordination, with an iodine at the apex and the phosphorus atoms of the two symmetry-related opdp ligands at the base. The iron atom is *ca.* 0.2 Å above the mean plane of the four phosphorus atoms. The weighted mean Fe-I distance is 2.641(7) Å, and Fe-P distances span 2.316(5)–2.379(7) Å, mean value 2.339(13) Å.

In each cation, the central *o*-phenylene rings of the opdp ligands are tilted out of the base plane by *ca.* 29.3° towards the co-ordinated iodide. This allows the four phenyl groups on the iodo-side of the base plane to point outwards in parallel pairs with normal contact distances $\text{I} \cdots \text{C}$ and $\text{I} \cdots \text{H}$ of 3.8 and 3.0 Å, respectively. The remaining four phenyl rings point downwards from the base plane, stacked together and almost parallel so that there is not a large enough space below the iron atom to accommodate a second iodo ligand. This arrangement is very different from that in (2) and (3).

Between the well-defined cation complexes, a large volume is occupied in one of two ways; 85% of the sites are filled by an iodide ion and two CH_2Cl_2 molecules, and 15% of the sites hold a single CH_2Cl_2 molecule, orientated such that the iodide is in a different location and a second CH_2Cl_2 molecule cannot be accommodated. In each kind of site, the hydrogen atoms of the solvent are directed towards the iodide ions, with $\text{C}(\text{solvent}) \cdots \text{I}$ separations of 3.43(3), 3.65(4), and 3.91(3) Å, the first two of which are rather shorter than normal van der Waals contacts.

Discussion

The molecular structure of $[\text{FeI}_2(\text{depe})_2]$ is precisely what might have been expected of a low-spin *trans* species, with Fe-P separations of 2.295(1) and 2.323(1) Å (see Table 3). In the isostructural $[\text{FeCl}_2(\text{depe})_2]$ (5) the Fe-P separations are 2.260(2) and 2.268(3) Å,⁵ marginally smaller, which may represent a shortening due to less steric repulsion from the bound chlorides as opposed to the bound iodides. This is supported by comparison with the structure of $[\text{FeCl}_2(\text{dmpe})_2]$ (6) for which more data are available.⁴ This has Fe-P separations of 2.230(1) and 2.241(1) Å, but the P-P separations are 3.04 (for phosphorus atoms of the same diphosphine) and 3.27 Å (for adjacent phosphorus atoms from different diphosphines). The corresponding values for $[\text{FeI}_2(\text{depe})_2]$ (1) are 3.075(1) and 3.447(1) Å, respectively. The Fe-I separation here is 2.706(1) Å, rather longer than that in (4), but slightly less than that in *cis*- $[\text{FeI}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_3\}]$ (*ca.* 2.73 Å).⁷ There are no other structurally characterized di-iodoiron(II) complexes which also contain phosphines but Fe-I distances in a range of iodo complexes with phosphorus ligands fall in the range 2.60–2.65 Å.⁸

What the structures certainly suggest is that the green \rightarrow yellow colour change exhibited by $[\text{FeCl}_2(\text{dmpe})_2]$ is not due to loss of dmpe but to some kind of isomerization, possibly involving the conformations of the bridging ethylene groups of the diphosphines, which are very different in $[\text{FeCl}_2(\text{dmpe})_2]$ and $[\text{FeI}_2(\text{depe})_2]$ (see Table 3).

In the other three complexes discussed here, we clearly see the effect of increasing steric interactions in the series $[\text{Fe}(\text{MeCN})_2(\text{opdp})_2]^{2+} < [\text{FeCl}_2(\text{opdp})_2] < [\text{FeI}(\text{opdp})_2]^+$. The first complex has a 'normal' octahedral structure characteristic of many bis(acetonitrile)bis(diphosphine)iron(II) complexes, and, like them, is of low-spin. The diphosphine opdp has a rigid backbone, so that the only responses to steric pressures it can make must involve the relative orientations of the phosphorus phenyl groups, or the lengths of the Fe-P bonds. If steric pressures cannot be accommodated in these ways, then presumably the compound type will change.

In complex (3) (see Table 3), the mean Fe-P separation is 2.340(3) Å, which differs not very much from other low-spin values, perhaps being a little longer than average, though simple comparisons are rather difficult to evaluate. The P-P separations are 3.042(1) Å (intradiphosphine) and 3.556(2) Å (interdiphosphine), and the latter is notably very different from those in the (presumably least strained) molecule of *trans*- $[\text{FeCl}_2(\text{dmpe})_2]$ ⁴ (6) (3.04 and 3.27 Å, respectively), of (slightly strained) $[\text{FeI}_2(\text{depe})_2]$ (1) [3.075(1) and 3.447(1) Å], and of *cis*- $[\text{FeH}_2(\text{dppe})_2]$ ⁹ (7) (*ca.* 3.02 and 3.49 Å) (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$). Unfortunately no dppe complex entirely appropriate for comparison has yet been structurally characterized.

The change of the *trans* ligands from MeCN in (3) to Cl in (2) results in an expansion in the size of the co-ordination shell. The Fe-Cl separations in (2) [2.348(3) Å] are hardly different from the values in *trans*- $[\text{FeCl}_2(\text{depe})_2]$ ⁵ (5) [2.349(2) Å] but the Fe-P separations change dramatically in the sequence (5) < (3) < (2), being *ca.* 2.26, 2.34, and 2.62 Å, respectively. This implies an increase in diameter of high-spin Fe^{II} as compared to low-spin Fe^{II} of an enormous 0.6 Å. This compares with a typical difference between high-spin and low-spin ionic radii for six-co-ordinate iron(II) of 0.17 Å.¹⁰ Remarkably, the change in radius occurs entirely in the equatorial plane of the octahedron. This effect has already been noted in the high-spin (295 K) and low-spin (130 K) structures of $[\text{FeCl}_2(\text{dppen})_2] \cdot 2\text{Me}_2\text{CO}$ (8) (dppen = $\text{Ph}_2\text{PCHCHPPh}_2$).¹¹

The increase in Fe-P separation between the high-spin and low-spin forms is not brought about without some distortion of the opdp ligands. The P-P separation within the complexed opdp changes from 3.042(1) in (3) to 3.165(5) Å in (2) [the

Table 7. Final atomic co-ordinates (fractional $\times 10^4$) for $[\text{FeI}(\text{opdp})_2]\text{I} \cdot 1.85\text{CH}_2\text{Cl}_2$; e.s.d.s are in parentheses*

Atom	x	y	z	Atom	x	y	z
I(1)	7 500	3 542(2)	5 000	I(2)	2 500	1 364(2)	0
Fe(1)	7 500	820(5)	5 000	Fe(2)	2 500	4 100(4)	0
P(11)	6 492(2)	559(6)	5 114(2)	P(21)	3 507(3)	4 434(6)	-134(2)
C(111)	6 207(9)	-1 208(19)	5 056(7)	C(211)	3 743(10)	6 227(22)	-79(8)
C(112)	5 782(10)	-1 731(23)	4 670(8)	C(212)	4 172(10)	6 640(23)	333(8)
C(113)	5 646(11)	-3 092(26)	4 631(9)	C(213)	4 323(9)	8 056(21)	366(7)
C(114)	5 914(10)	-3 953(25)	4 972(8)	C(214)	4 042(11)	9 006(28)	9(9)
C(115)	6 346(11)	-3 603(27)	5 347(9)	C(215)	3 667(10)	8 462(24)	-391(8)
C(116)	6 466(11)	-2 165(24)	5 401(9)	C(216)	3 481(9)	7 162(21)	-445(7)
C(121)	6 157(9)	1 137(20)	5 661(7)	C(221)	3 812(10)	3 688(23)	-670(8)
C(122)	6 244(10)	2 562(19)	5 754(7)	C(222)	3 742(10)	2 351(21)	-828(8)
C(123)	5 974(11)	3 161(28)	6 151(8)	C(223)	4 049(10)	1 840(25)	-1 174(8)
C(124)	5 618(9)	2 359(19)	6 406(7)	C(224)	4 403(14)	2 676(30)	-1 423(12)
C(125)	5 530(10)	949(22)	6 297(8)	C(225)	4 467(13)	3 967(31)	-1 289(10)
C(126)	5 815(9)	341(23)	5 911(7)	C(226)	4 181(9)	4 531(24)	-921(7)
P(13)	7 051(3)	688(6)	4 164(2)	P(23)	2 977(3)	4 216(6)	832(2)
C(131)	6 835(9)	-1 012(21)	3 920(7)	C(231)	3 191(10)	5 949(22)	1 111(8)
C(132)	7 004(11)	-2 133(26)	4 186(9)	C(232)	2 965(9)	7 132(21)	816(7)
C(133)	6 850(11)	-3 454(27)	4 000(9)	C(233)	3 157(10)	8 379(26)	996(8)
C(134)	6 489(10)	-3 655(27)	3 544(8)	C(234)	3 557(11)	8 493(28)	1 442(9)
C(135)	6 327(11)	-2 481(22)	3 270(10)	C(235)	3 784(10)	7 391(20)	1 721(8)
C(136)	6 462(9)	-1 203(23)	3 456(8)	C(236)	3 571(10)	6 097(25)	1 550(8)
C(141)	7 378(8)	1 474(20)	3 655(6)	C(241)	2 694(9)	3 365(21)	1 344(7)
C(142)	7 348(10)	2 953(25)	3 593(8)	C(242)	2 723(9)	1 962(21)	1 393(7)
C(143)	7 594(9)	3 586(24)	3 206(7)	C(243)	2 519(11)	1 329(29)	1 791(9)
C(144)	7 874(11)	2 839(26)	2 896(9)	C(244)	2 178(12)	2 113(29)	2 104(10)
C(145)	7 916(10)	1 443(25)	2 966(8)	C(245)	2 143(11)	3 451(27)	2 064(9)
C(146)	7 671(9)	756(23)	3 346(7)	C(246)	2 380(10)	4 115(26)	1 662(8)
C(151)	6 319(9)	1 512(21)	4 152(7)	C(251)	3 710(9)	3 419(22)	845(7)
C(152)	6 060(9)	1 444(21)	4 584(7)	C(252)	3 937(10)	3 542(24)	400(8)
C(153)	5 478(10)	2 004(23)	4 578(8)	C(253)	4 499(9)	2 998(21)	360(7)
C(154)	5 179(8)	2 659(17)	4 160(6)	C(254)	4 834(13)	2 322(25)	763(10)
C(155)	5 447(10)	2 714(22)	3 726(8)	C(255)	4 601(11)	2 226(23)	1 199(9)
C(156)	5 989(11)	2 104(25)	3 721(9)	C(256)	4 025(10)	2 782(21)	1 257(8)
I(3)	5 038(9)	4 721(13)	2 530(6)	I(4)	4 974(1)	-87(2)	2 454.0(7)
Solvent molecules							
C(5)	6 284(17)	1 972(40)	2 280(13)	Cl(61)	3 548(6)	2 752(10)	3 267(3)
Cl(51)	6 560(6)	2 177(11)	1 727(4)	Cl(62)	4 250(4)	4 358(10)	2 700(3)
Cl(52)	5 987(5)	3 775(11)	2 411(3)	Cl(63)	4 175(34)	1 128(80)	2 623(27)
C(6)	3 828(13)	2 745(27)	2 716(10)				

* Site occupancy factors for I(3), I(4), C(5), Cl(51), Cl(52), Cl(62), and Cl(63) are 0.146, 0.854, 0.854, 0.854, 0.854, 0.854, and 0.146 respectively.

corresponding closest P–P separation between phosphorus atoms of different opdp molecules changes from 3.556(2) to 4.170(5) Å]. Consequently, opdp is not as rigid as might be expected. The changes in the corresponding P–P separations in the dppen complexes (**8**) are 0.23 and 0.55 Å,¹¹ respectively, but dppen is hardly to be expected to be as rigid as opdp. The bite of opdp is virtually the same as that of dppen and the two ligands seem to respond very similarly on the change from low- to high-spin. The angles P–Fe–P also change by roughly similar amounts (*ca.* 5°).

It is not obvious why all the change occurs in the phosphorus atom plane. Since we are dealing with a common phosphorus ligand in (**2**) and (**3**), different electronic inductive properties of the phosphine groups and changes in steric requirements between phosphines can be excluded. These factors have been plausibly suggested as being possibly involved when comparing high-spin and low-spin complexes derived from different phosphines. Consequently, it would appear that in the high-spin form there is greater non-bonding *d*-electron density in the equatorial plane than in the low-spin form. Since the transition between them can be written $t_{2g}^6 e_g^0 \rightleftharpoons t_{2g}^4 e_g^2$, and because

the e_g orbitals are, of course, $d_{x^2-y^2}$ and d_{z^2} , this suggests that the antibonding e_g orbital pair of octahedral symmetry is split, with most of the formally non-bonding electron density residing in the $d_{x^2-y^2}$ orbital. Why this should be is not clear.

The diphosphine ligands which lead to high-spin octahedral iron(II) complexes are opdp, dppen, and $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}$ (bdpp), *viz.* (**2**), (**8**), and (**9**). They all carry aromatic substituents, but it is too facile to suggest that steric bulk alone causes high-spin complexes. Bidentate dppen can give rise to a low-spin form of $[\text{FeCl}_2(\text{dppen})_2]$ at low temperature and may dissociate in solution to give $[\text{FeCl}_2(\text{dppen})]^{12}$ and $[\text{FeBr}_2(\text{dppen})]$ has also been claimed¹², but the closely related dppe forms only four-co-ordinate high-spin tetrahedral $[\text{FeCl}_2(\text{dppe})]$, and opdp can produce yet a further kind of behaviour, as is evident in (**4**). We cannot, as yet, rationalize this wide range of structure and type.

It is clear from consideration of space-filling models that the formation of six-co-ordinate $[\text{FeI}_2(\text{opdp})_2]$, whether high-spin or low-spin, would be very unlikely indeed. The complex of stoichiometric formula $\text{FeI}_2(\text{opdp})_2$ is actually ionic, $[\text{FeI}(\text{opdp})_2]\text{I}$ (**4**) {*cf.* $\text{FeI}_2(\text{dppe})$ which is tetrahedral and

high-spin, $[\text{FeI}_2(\text{dppe})]$. The five-co-ordinate cation has an apical co-ordinated iodide which is 2.641(7) Å (mean value) from the iron. This is similar to other values in the literature (*ca.* 2.73 Å in $[\text{FeI}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_3\}]^7$ and 2.706(1) Å in $[\text{FeI}_2(\text{depe})_2]$) allowing for lower co-ordination number and consequent reduction of steric pressure.

The Fe–P separations (*ca.* 2.34 Å) in (4) are similar to low-spin octahedral values, but since the iron atom is 0.2 Å above the basal plane, the packing of the opdp molecules would be expected to be closer than in the octahedral case (3). The P–P separations are *ca.* 3.02 Å for phosphorus atoms on the same opdp molecule, and *ca.* 3.56 Å for adjacent phosphorus atoms from different opdp molecules. These values do not differ significantly from the values observed in (3).

The structure shows clearly that the phenyl groups of the opdp are opened out on the side towards the co-ordinated iodide so that its large size can be accommodated, and the opdp phenylene groups are both tilted (*ca.* 29.3°) towards this iodine atom. The remaining phenyl groups have moved together, effectively blocking access to the sixth co-ordination site. There is no sign of phenyl hydrogen atoms occupying this position. Only ligands considerably smaller than iodide ion could be accommodated in the volume available, and only then with considerable reorientation of the phenyl and *o*-phenylene groups. The structure suggests that it should be possible to use frameworks such as this to separate potential ligands simply on the basis of size. Any real filter built on these lines would have to be constructed so as to protect the co-ordinated iodide, otherwise reactions, such as those of $[\text{Fe}(\text{opdp})_2]^+$ with MeCN to give $[\text{Fe}(\text{MeCN})_2(\text{opdp})_2]^{2+}$, might occur.

There is ample precedent for five-co-ordinate iron(II) species. For example, $[\text{Fe}(\text{bdpp})_2]\text{BPh}_4$ can be synthesized from FeI_2 , bdpp, and $\text{Na}[\text{BPh}_4]$,⁴ and there is a wide range of five-co-ordinate complexes of iron(II) halides with polydentate donors, for example, $[\text{Fe}\{\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}\text{Br}]^+.$ ¹³ Such structures are almost forced by the geometry and steric bulk of the phosphine. Whether complexes such as $[\text{Fe}(\text{bdpp})_2]\text{I}$ and $[\text{Fe}(\text{dppe})_2]^+$ can be synthesized from FeI_2 and bdpp, and from FeI_2 , dppe, and $\text{Na}[\text{BPh}_4]$, respectively, is still under investigation.

Experimental

All the crystals discussed in this paper were prepared as described previously.¹ Experimental details of the crystal structure analyses are summarized in Table 2. Only a specimen description of our procedures is described here, that for compound (4).

Crystal Structure Analysis of $[\text{FeI}(\text{opdp})_2]\text{I} \cdot 1.85\text{CH}_2\text{Cl}_2$ (4).

—The crystals are pale brown and air stable. One mounted on a glass fibre was a flat needle, $0.08 \times 0.11 \times 0.36$ mm. After photographic examination, the crystal was transferred to an Enraf-Nonius CAD4 diffractometer, with monochromated Mo- K_α radiation ($\lambda = 0.71069$ Å), for measurement of accurate cell dimensions (by refinement from goniometer settings of 25 reflections having $\theta = 10$ – 11°) and intensity data (5397 unique reflections to $\theta_{\text{max.}} = 20^\circ$). The diffraction intensities were corrected for Lorentz-polarisation effects, slight and steady deterioration (4% overall), absorption (from ψ -scan measurements), and statistically to eliminate negative intensities.

The structure was determined by the heavy-atom method, and refined, in three large blocks, by least-squares methods with the SHELX program.¹⁴ The Fe, I, P, and solvent Cl atoms were refined with anisotropic thermal parameters; the C atoms were refined isotropically and H atoms in the complex cations were

included in idealised positions and set to ride on their bonded C atoms. There is some disorder amongst the iodide anions and solvent molecules, and the number of solvent molecules (1.85) was derived from refinement of the site occupancy factors of the disordered atoms.

At convergence, $R = 0.119$, $R' = 0.107$ for 3895 reflections with $I > \sigma_I$ and weights refined to $w = (\sigma_F^2 + 0.00187F^2)^{-1}.$ ¹⁴ A final difference map showed peaks up to *ca.* $1.6 \text{ e } \text{\AA}^{-3}$ close to the heavy atoms (Fe and I); there was no indication of further disorder or of extra solvent molecules. However, the rather high R and R' values arise mainly from the inclusion of the solvent molecules in the crystal lattice and from the disorder of these and of some of the iodide anions.

The final R values from the refinement of structure (2) are similarly high and result principally from the presence of a poorly resolved solvent thf molecule in the lattice. Here, the bond lengths of the thf molecule were, during refinement, restrained towards normal values, and the site occupancy factor for this molecule was reduced to 0.5 to produce more realistic thermal parameters and lower R values. Despite these problems in the solvent regions of structures (2) and (4), the Fe-complex moieties are well defined and quite satisfactory except for the anisotropic thermal parameters in a few C atoms in (2).

Scattering factors for neutral atoms were taken from ref. 15. Computer programs used in this analysis have been listed in Table 4 of ref. 16, and were run on the VAX 11/750 machine at the Institute for Horticultural Research, Littlehampton.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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