Fluorophosphine Complexes of Rhodium(I) and Iridium(I): Towards the Design of Systems with Extended Metal–Metal Interactions. The Crystal Structure of [{IrCl(PF_3)$_2$}$_2$] †

Peter B. Hitchcock, Stephen Morton, and John F. Nixon *
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

A single-crystal *X*-ray structure determination of [{IrCl(PF_3)$_2$}$_2$] (1) [monoclinic, $P2_1/n$, a = 10.526(1), b = 10.346(2), c = 13.150(1) Å, β = 101.46(1)°, R = 0.048] has confirmed the existence of dimeric molecules with short intra- and inter-molecular iridium–iridium contacts and infinite zigzag chains of iridium atoms. Detailed consideration of the structure allows conclusions to be drawn about the design of other fluorophosphineiridium(I) complexes with extended metal–metal interactions. These conclusions have been tested by syntheses of a variety of complexes of Rh^I and Ir^I containing the ligands $PF_2(NMe_2)$, $PF(O_2C_6H_4)$, and $OC(NMePF_2)_2$. The complex [{IrCl[O=C(NMePF$_2$)$_2$]}$_2$] probably has a structure involving extended metal–metal interactions.

There is considerable current interest in new anisotropic materials with novel solid-state properties.[1–4] In particular, square-planar complexes of the d^8 transition-metal ions Pt^{II}, Ir^I, and Rh^I have received much attention. In general these complexes involve the formation of linear stacks of strictly square-planar ions with overlap of the d_{z^2} orbitals leading to the formation of a d_{z^2} band. Many of the complexes studied in most detail involve partial oxidation of the d^8 metal as in $K_2[Pt(CN)_4]Br_{0.30}\cdot3H_2O$ ($Pt^{+2.3}$),[4] $Li_{1.64}[Pt(C_2O_4)_2]\cdot6H_2O$ ($Pt^{+2.36}$),[5] or $K_{0.60}[Ir(CO)_2Cl_2]\cdot0.5H_2O$ ($Ir^{+1.4}$)[6] which results in partial emptying of the d_{z^2} band and high conductivity. On the other hand it now seems to be firmly established that although [IrCl(CO)$_3$][7] contains iridium in an integral oxidation state, nevertheless it displays considerable conductivity[4,8] along the stacking axis, and likewise [Ir(acac)(CO)$_2$][9] (acac = acetylacetonate) is an intrinsic semiconductor. Rhodium(I) also forms linear stacks as in [Rh(acac)(CO)$_2$][10] and [RhCl(CO)$_2$(Hpz)] (Hpz = pyrazole),[11] although the rhodium $4d_{z^2}$ orbital is much less diffuse than the corresponding $5d_{z^2}$ orbital of Ir^I or Pt^{II} and the intermetallic interaction is correspondingly weaker. In each of these cases we are dealing with essentially rod-like (CN^-) or planar ($C_2O_4{}^{2-}$, acetylacetonate, or pyrazole) ligands, although non-planar ligands may be involved where steric considerations allow, as in the racemates of dicarbonylrhodium(I) or -iridium(I) 3-trifluoroacetyl-2-bornanonates.[12,13] A rather weak zigzag interaction is suggested by the structure of [{RhCl(CO)$_2$}$_2$] which has bent Rh_2Cl_2 rings.[14]

In a recent preliminary communication[15] we reported the unusual chain structure of [{IrCl(PF_3)$_2$}$_2$] (1). This material has short intra- and inter-molecular iridium–iridium interactions and a zigzag chain structure in some ways reminiscent of that in [{RhCl(CO)$_2$}$_2$] but with much stronger bonding. On the basis of their physical appearance neither [{RhCl(PF_3)$_2$}$_2$], which gives transparent pale red-brown crystals, nor [Ir(acac)(PF_3)$_2$], which is yellow,[16] seem to have significant *inter*molecular metal–metal interactions. In the former case this is probably due to the less extensive nature of the d_{z^2} orbital in Rh^I compared with Ir^I, while lack of intermetallic bonding in the latter case is the result of the thickness of the molecule as will be discussed in this paper.

We now report in full the structure of complex (1) together with a detailed investigation of some related rhodium(I) and iridium(I) complexes containing the sterically undemanding ligands dimethylaminodifluorophosphine $PF_2(NMe_2)$, 2-fluoro-1,3,2-benzodioxaphosphole $PF(O_2C_6H_4)$, and *N,N'*-bis(difluorophosphino)-*N,N'*-dimethylurea $O{=}C(NMePF_2)_2$ (2).

Results and Discussion

In 1971 Bennett and Patmore[16] described the preparation of [{IrCl(PF_3)$_2$}$_2$] (1) and noted that although the complex gives pale yellow solutions in organic solvents, in the solid state the crystals are dark coloured with a coppery metallic lustre in reflected light. Because of these properties they postulated a structure for (1) containing stacks of *planar* (IrClP$_2$)$_2$ moieties. However our single-crystal *X*-ray diffraction study shows that the structure involves a strongly folded Ir_2Cl_2 ring (Figure 1) with the two $IrCl_2$ planes meeting at an angle of 107.0°. This structure results in a compression of the Ir–Cl–Ir and Cl–Ir–Cl bond angles (see Table 1), but more importantly leads to a reduction of the *intra*molecular Ir ⋯ Ir distance from 3.41 Å (assuming a square with the Ir–Cl bond lengths as found) to 2.941(1) Å. A further noteworthy feature of the structure is that the PF_3 ligands are folded back into the centre of the molecule so that the iridium atoms lie 0.20 Å out of their respective co-ordination planes. This fold-back occurs in order to minimise

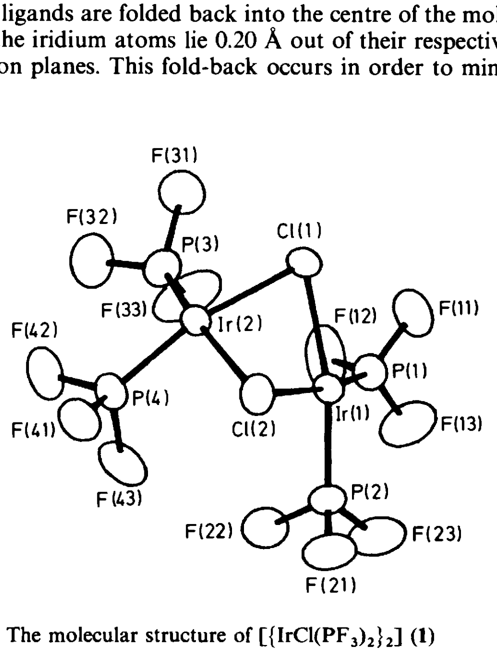


Figure 1. The molecular structure of [{IrCl(PF_3)$_2$}$_2$] (1)

---

† Di-μ-chloro-bis[bis(trifluorophosphine)iridium(I)].

Supplementary data available: structure factors are available from the editorial office.

Table 1. Intramolecular distances (Å) and angles (°) for complex (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Ir(1)–Cl(1)	2.415(5)	Ir(1)–Cl(2)	2.413(5)
Ir(1)–P(1)	2.138(5)	Ir(1)–P(2)	2.131(5)
Ir(2)–Cl(1)	2.414(5)	Ir(2)–Cl(2)	2.408(5)
Ir(2)–P(4)	2.130(5)	Ir(2)–P(3)	2.137(5)
P(1)–F(11)	1.515(11)	P(1)–F(12)	1.495(13)
P(1)–F(13)	1.507(14)	P(2)–F(21)	1.531(11)
P(2)–F(22)	1.549(14)	P(2)–F(23)	1.503(15)
P(4)–F(41)	1.531(10)	P(4)–F(42)	1.50(2)
P(4)–F(43)	1.513(13)	P(3)–F(31)	1.538(11)
P(3)–F(32)	1.50(2)	P(3)–F(33)	1.52(2)
Cl(1)–Ir(1)–Cl(2)	81.3(2)	Cl(1)–Ir(1)–P(1)	91.5(2)
Cl(1)–Ir(1)–P(2)	167.6(2)	Cl(2)–Ir(1)–P(1)	168.9(2)
Cl(2)–Ir(1)–P(2)	92.7(2)	P(1)–Ir(1)–P(2)	92.7(2)
Cl(1)–Ir(2)–Cl(2)	81.4(2)	Cl(1)–Ir(2)–P(4)	168.5(2)
Cl(1)–Ir(2)–P(3)	91.9(2)	Cl(2)–Ir(2)–P(4)	90.8(2)
Cl(2)–Ir(2)–P(3)	167.8(2)	P(4)–Ir(2)–P(3)	94.1(2)
Ir(1)–Cl(1)–Ir(2)	75.1(1)	Ir(1)–Cl(2)–Ir(2)	75.2(1)
Ir(1)–P(1)–F(11)	118.2(5)	Ir(1)–P(1)–F(12)	116.8(6)
Ir(1)–P(1)–F(13)	123.3(6)	F(11)–P(1)–F(12)	98.6(8)
F(11)–P(1)–F(13)	98.4(9)	F(12)–P(1)–F(13)	96.7(9)
Ir(1)–P(2)–F(21)	118.2(2)	Ir(1)–P(2)–F(22)	116.2(6)
Ir(1)–P(2)–F(23)	123.4(7)	F(21)–P(2)–F(22)	98.9(9)
F(21)–P(2)–F(23)	98.0(9)	F(22)–P(2)–F(23)	97(1)
Ir(2)–P(4)–F(41)	119.0(5)	Ir(2)–P(4)–F(42)	123.2(6)
Ir(2)–P(4)–F(43)	117.1(6)	F(41)–P(4)–F(42)	97.7(7)
F(41)–P(4)–F(43)	96.7(7)	F(42)–P(4)–F(43)	97.9(8)
Ir(2)–P(3)–F(31)	118.4(6)	Ir(2)–P(3)–F(32)	123.1(6)
Ir(2)–P(3)–F(33)	116.2(8)	F(31)–P(3)–F(32)	97.9(8)
F(31)–P(3)–F(33)	97.7(9)	F(32)–P(3)–F(33)	98.8(9)

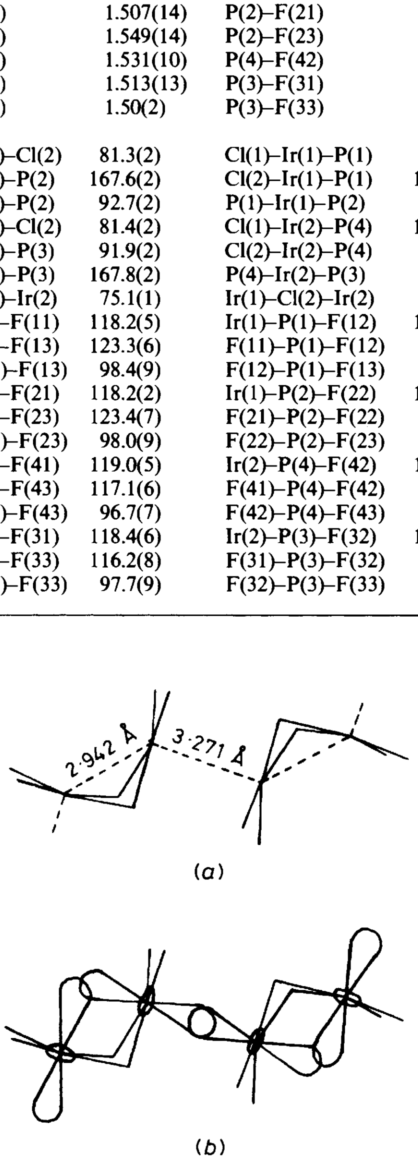


Figure 2. The chain structure of $[\{IrCl(PF_3)_2\}_2]$ showing (*a*) chain formation along a two-fold screw axis and (*b*) a schematic representation of the d_{z^2} orbital overlap

*inter*molecular F ··· Cl contacts, which lie between 3.24 and 3.30 Å, and are thus close to the sum of the van der Waals radii for F and Cl (3.15 Å),[17] for the fluorine atoms F(11), F(21), F(31), and F(41). Furthermore, each of the PF_3 ligands has one Ir–P–F bond angle [to F(13), F(23), F(32), and F(42)] close to 123.3°, the other two being in the range 116.2—119.0°, so that the P–Ir bond deviates from the three-fold rotation axis of the PF_3 ligand by *ca.* 7.7°. This structural feature appears to result from an attempt to minimise the *intra*molecular contacts F(23) ··· F(13) and F(32) ··· F(42) (2.76 and 2.79 Å respectively) which are close to the sum of two van der Waals radii for fluorine (2.70 Å). These modifications from ideal geometry are necessary in order to enable a short *inter*molecular Ir ··· Ir contact of 3.271(1) Å to be made and thus allow the iridium atoms to form infinite zigzag chains with alternate long and short Ir ··· Ir contacts [Figure 2(*a*)]. These contacts may be compared with the values found in the monomeric square-planar complexes $[IrCl(CO)_3]$ [2.844(1) Å][7] and $[Ir(acac)(CO)_2]$ (3.20 Å)[9] which are chain forming, though clearly *linear* overlap of the filled d_{z^2} orbitals cannot be considered in the present case and a 'bent-bond' model might be more appropriate [Figure 2(*b*)]. A number of conclusions may be drawn from the structure of $[\{IrCl(PF_3)_2\}_2]$.

The intermolecular 'face-to-face' approach of the two $IrCl_2(PF_3)_2$ subunits in (**1**) can be used as a model for species such as *cis*-$[IrCl_2(PF_3)_2]^-$. This ion would be planar, resulting in an increase of the iridium–iridium distance to *ca.* 3.67 Å. Similarly a planar form of (**1**) with fully interlocking PF_3 groups would have an intermolecular Ir ··· Ir distance of 3.85 Å. On this basis we are unlikely to find extended metal–metal interactions in species such as $[Ir(acac)(PF_3)_2]$ or $[IrCl(PF_3)_3]$. Even with ligands only *slightly* larger than PF_3 it may therefore not be possible to reduce inter- and intra-molecular interactions sufficiently to allow close approach of iridium atoms to form infinite chains. In order to study these factors more fully we have synthesised a number of related fluorophosphine-iridium(I) and -rhodium(I) complexes and in particular have examined the potential of the urea-based compound $O{=}C(NMePF_2)_2$ (**2**), which has a planar framework which minimises the steric bulk of the ligand.

We have previously reported[18] rhodium complexes of $PF_2(NMe_2)$ of the type $[\{RhCl(PF_2NMe_2)_2\}_2]$ and $[RhCl(PF_2NMe_2)_3]$. Addition of an excess of $PF_2(NMe_2)$ to a solution of $[IrCl(C_8H_{14})_2]$ (C_8H_{14} = cyclo-octene) in toluene results in the formation of $[IrCl(PF_2NMe_2)_3]$ (**3**). The 145.8-MHz ^{31}P-$\{^1H\}$ and 75.4-MHz ^{19}F-$\{^1H\}$ n.m.r. spectra of complex (**3**) clearly indicate a square-planar arrangement of ligands on iridium with two non-equivalent environments for the fluorophosphine which is either *trans* or *cis* to chlorine (Figure 3). Characteristically $^2J(P_aP_{a'})$ (*trans*) is very large (808.5 Hz) whereas $^2J(P_aP_b)$ (*cis*) is much smaller (−58.5 Hz). The sharpness of the n.m.r. spectra of complex (**3**) at room temperature is in contrast to the reported behaviour of its rhodium analogue which readily undergoes a ligand-exchange process under these conditions as monitored by ^{19}F n.m.r. spectroscopy.[18] The ^{31}P-$\{^1H\}$ and ^{19}F-$\{^1H\}$ n.m.r. spectra of $[IrCl\{PF(O_2C_6H_4)\}_3]$ (**4**), which were obtained in a similar manner to those of (**3**), are also broad at room temperature, however on cooling a $CDCl_3$ solution of (**4**) to −50 °C a sharp, well resolved n.m.r. spectrum showing two distinct environments for the phosphine ligands is obtained.* N.m.r. data for these and other complexes are given in Table 2. As would be expected, neither complex (**3**) nor (**4**) shows any evidence of extended metal–metal interactions in the solid state.

Addition of the appropriate amount of $[\{IrCl(C_8H_{14})_2\}_2]$ to (**3**) results in the formation of the dinuclear complex $[\{IrCl(PF_2NMe_2)_2\}_2]$ (**5**). Because of the greater steric bulk of $PF_2(NMe_2)$ compared with PF_3 this material also shows no evidence of extended metal–metal interactions in the solid state. Attempts to prepare $[\{IrCl[PF(O_2C_6H_4)]_2\}_2]$ by an analogous route were not successful and an ill defined product containing a certain amount of olefin was always obtained. Treatment of $[\{RhCl(C_6H_{10})\}_2]$ (C_6H_{10} = hexa-1,5-diene) with the

---

* This difference should not be overinterpreted since traces of free ligand may catalyse ligand exchange and lead to broadening of the spectrum.

Table 2. Fluorine-19 and ^{31}P n.m.r. data (δ/p.p.m., J/Hz) for complexes

Complex	δ_F[a]	δ_P[b]	$^1J(PF)$	$^2J(PP)$	$^3J(PF)$	$^4J(FF)$	Other
(3) $[IrCl(PF_2NMe_2)_3]$[c]	-55.1 (F_x) -38.4 (F_y)	132.6 (P_a) 110.2 (P_b)	$-1\,129.5$ (F_xP_a) $-1\,057.3$ (F_yP_b)	$+808.5$ ($P_aP_{a'}$) -58.5 (P_aP_b)	58.1 ($P_aF_{x'}$) 7.7 (P_aF_y) -7.1 (P_bF_x)	8.8 ($F_xF_{x'}$) 0 (F_xF_y)	
(4) $[IrCl\{PF(O_2C_6H_4)\}_3]$[c,d]	not recorded	107.3 (P_a) 93.5 (P_b)	$-1\,354.3$ (F_xP_a) $-1\,271.7$ (F_yP_b)	$+286.8$ ($P_aP_{a'}$) 44.9 (P_aP_b)	-38.7 ($P_aF_{x'}$) 15.0 (P_aF_y) 0 (P_bF_x)	0 ($F_xF_{x'}$) F_xF_y not defined	
(5) $[\{IrCl(PF_2NMe_2)_2\}_2]$	-43.7	104.0	1 072.8	-66.6	0	0	
(6) $[\{RhCl[PF(O_2C_6H_4)]_2\}_2]$	-10.5	133.0	1 315.8	-58.9	29.2	4.9	$^1J(RhP)$ = 320.0, $^2J(RhF)$ = 31.7
(8) $[NMe_4][IrCl_2(PF_2NMe_2)_2]$	not recorded	104.4	1 062.0	-66.7	0	0	^1H: 3.4 (s, 12 H), 3.0 (m, 12 H)
(9) $[NMe_4][RhCl_2\{PF(O_2C_6H_4)\}_2]$	-14.2	126.7	1 262.8	-41.1	16.2	7.8	$^1J(RhP)$ = 311.7, $^2J(RhF)$ = 33.3
(10) $[\{IrCl[O{=}C(NMePF_2)_2]\}_2]$	-43.1	84.6	1 127.9	78.1	4.9	0	
(11) $[\{RhCl[O{=}C(NMePF_2)_2]\}_2]$	-40.0	127.2	1 203.3	104.0	-2.0	0	$^1J(RhP)$ = 284.1, $^2J(RhF)$ = 16.6
(12) $[Ir(acac)\{O{=}C(NMePF_2)_2\}]$	-47.8	93.1	1 125.2	93.3	4.9	0	^1H: 5.7 (s, 1 H), 3.2 (m, 6 H), 2.1 (s, 6 H)
(13) $[Rh(acac)\{O{=}C(NMePF_2)_2\}]$	-46.4	133.4	1 206.9	106.3	2.0	0	$^1J(RhP)$ = 278.3, $^2J(RhF)$ = 17.7. ^1H: 5.6 (s, 1 H), 3.2 (m, 6 H), 2.1 (s, 6 H)
(14) $[NMe_4][IrCl_2\{O{=}C(NMePF_2)_2\}]$	-38.2		1 140.1[e]				^1H: 3.3 (s, 12 H), 3.1 (m, 6 H)

[a] In $CDCl_3$, relative to $CFCl_3$. [b] In CH_2Cl_2, relative to 85% H_3PO_4. [c] P_a, F_x belong to the ligands *cis* to Cl, P_bF_y to the ligand *trans* to Cl. [d] At − 50 °C in $CDCl_3$. [e] $N(PF)$; other lines were not well enough resolved for a detailed analysis.

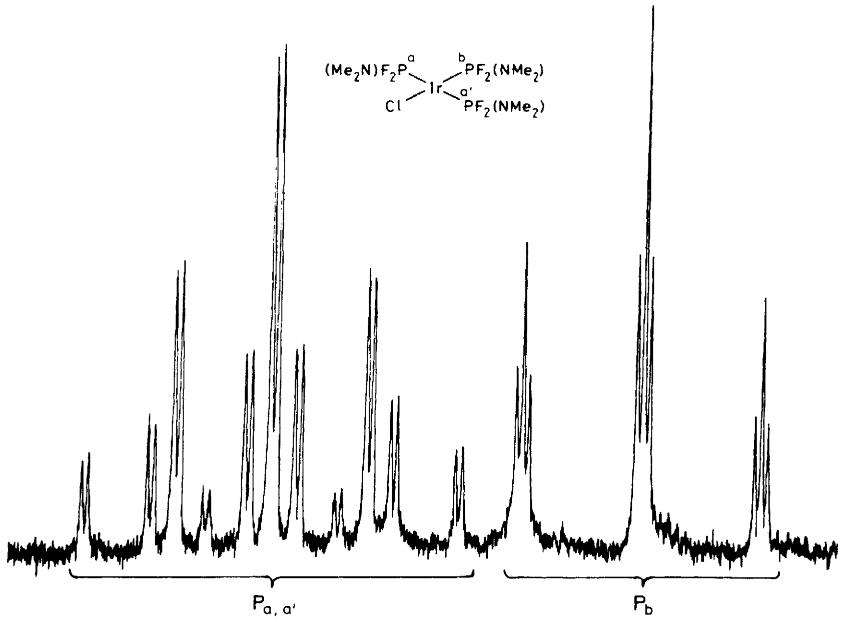
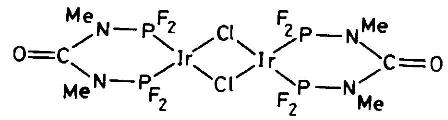


Figure 3. 145.8-MHz ^{31}P-$\{^1H\}$ N.m.r. spectrum of $[IrCl(PF_2NMe_2)_3]$ (3)

stoicheiometric amount of $PF(O_2C_6H_4)$ results in the formation of $[\{RhCl[PF(O_2C_6H_4)]_2\}_2]$ (6), however with an excess of the ligand monomeric $[RhCl\{PF(O_2C_6H_4)\}_3]$ is not obtained. The ^{31}P-$\{^1H\}$ n.m.r. spectrum shows a complex pattern of peaks at 133 p.p.m. with no observable P–F coupling and no pure species could be isolated from this reaction. The analogous reaction with $[\{RhBr(C_6H_{10})\}_2]$ seems to yield $[RhBr\{PF(O_2C_6H_4)\}_4]$ (7) according to the analytical data, however complex (7) dissolved significantly only in acetone and gave a very broad ^{31}P-$\{^1H\}$ n.m.r. spectrum. Species of the type $[NMe_4][MCl_2L_2]$ [M = Ir, L = $PF_2(NMe_2)$ (8); M = Rh, L = $PF(O_2C_6H_4)$ (9)] are however readily obtained by treatment of (5) or (6) with

NMe_4Cl in dichloromethane and give sharp, easily interpreted n.m.r. spectra (Table 2). The above considerations indicate that there will be no metal–metal interactions in these species.

The desire to reduce the steric bulk of the ligands under investigation led us to study the formation of complexes of the urea derivative $O{=}C(NMePF_2)_2$ (**2**). Prior to the present work only nickel(0) and molybdenum(0) complexes[19] of (**2**) had been fully characterised. The existence of π delocalisation in the urea residue of (**2**) requires all the atoms except the fluorines and the methyl hydrogen atoms to lie in a plane, although a co-ordinated metal atom might well not also lie in this plane. Treatment of $[\{IrCl(C_8H_{14})_2\}_2]$ with the stoicheiometric amount of (**2**) in dichloromethane results in the formation of a yellow-green solution. Removal of the solvent initially gives a yellowish solid which still contains olefin according to the analytical data. However, on prolonged pumping (0.01 Torr, *ca.* 1.33 Pa) or repeated washing with light petroleum the material becomes a deep purple and satisfactory analytical data are obtained for (**10**). Recrystallisation from dichloromethane at



(10)

-20 °C gives black plate-like crystals of complex (**10**) which have a distinct green-metallic lustre in reflected light. Unfortunately all crystals examined as candidates for *X*-ray crystallography proved to be twinned or multiple and it has not been possible to obtain a structure, however we imagine that (**10**) forms infinite zigzag chains similar to those in (**1**). If the six-membered chelate rings are roughly planar, with the nitrogen atoms of the ligand occupying approximately the positions of F(13) and F(23) or F(32) and F(42) in the structure of (**1**), this would make little steric difference to the *inter*molecular interaction. If, as however seems more likely, there is some folding-back of the urea residue into the body of the molecule along the P–P axis, this would tend to rotate F(11), F(21), F(31), and F(41) into positions causing more serious *inter*molecular F ··· Cl interactions and lessen the strength of the *inter*-molecular Ir ··· Ir interaction. In fact the colour and reflectivity of complex (**10**) suggest that the long-range interactions are less strong than in (**1**). Although (**10**) is not particularly soluble even in dichloromethane, excellent ^{31}P-$\{^1H\}$ and ^{19}F-$\{^1H\}$ n.m.r. spectra of the yellow solutions are readily obtained and show characteristic $(AA'X)_2$ spin systems. For this and the other complexes of (**2**), the coupling parameters, where possible, were deduced from the ^{19}F-$\{^1H\}$ n.m.r. spectrum using a treatment by Harris *et al.*,[20] much simplified by the absence of long-range F ··· F coupling. The values of $^2J(PP)$ for complexes of (**2**) in Table 2 may seem rather large for a *cis* coupling, but reflect an extremely large value for $^4J(PP)$ in the free ligand (290 Hz at room temperature).[19]

On addition of a slight excess of triphenylphosphine to complex (**10**) in CH_2Cl_2 the complex rapidly dissolves to give a yellow solution. The ^{31}P-$\{^1H\}$ n.m.r. spectrum shows a singlet for PPh_3 considerably shifted from the position of free triphenylphosphine and the $(AA'X)_2$ pattern of the fluorophosphine shifted, though only slightly, from its position in the spectrum of (**10**). The corresponding reaction product of $[\{RhCl[O{=}C(NMePF_2)_2]\}_2]$ (**11**) with an excess of triphenylphosphine gives a similar ^{31}P-$\{^1H\}$ spectrum in which the rhodium–fluorophosphine coupling is preserved (^{103}Rh, $I = \frac{1}{2}$, 100% natural abundance) whereas the triphenylphosphine appears as a sharp singlet (Figure 4). If however only just sufficient PPh_3 is used to form $[RhCl\{O{=}C(NMePF_2)_2\}(PPh_3)]$ a much more complicated spectrum is obtained in which coupling between PPh_3 and rhodium is observed. Clearly at higher PPh_3 concentrations rapid exchange of free and co-ordinated phosphine occurs, but this phosphine is not in a position to displace (**2**) from the co-ordination sphere of Rh^I or Ir^I. Neither of the triphenylphosphine adducts was obtained in a pure state.

The complexes $[Ir(acac)\{O{=}C(NMePF_2)_2\}]$ (**12**), $[Rh(acac)\{O{=}C(NMePF_2)_2\}]$ (**13**), and $[NMe_4][IrCl_2\{O{=}C(NMePF_2)_2\}]$ (**14**) have also been readily obtained and characterised; the acetylacetonates give very well formed needle-like crystals which are pale yellow for rhodium and almost colourless for iridium, whereas (**14**) is obtained as an off-white powder which is somewhat unstable in chlorinated solvents. Thus, as expected, there is no evidence for extended metal–metal interactions in these materials.

Future research will indicate whether other planar-framed bidentate fluorophosphine ligands, for example 1,2-bis(di-

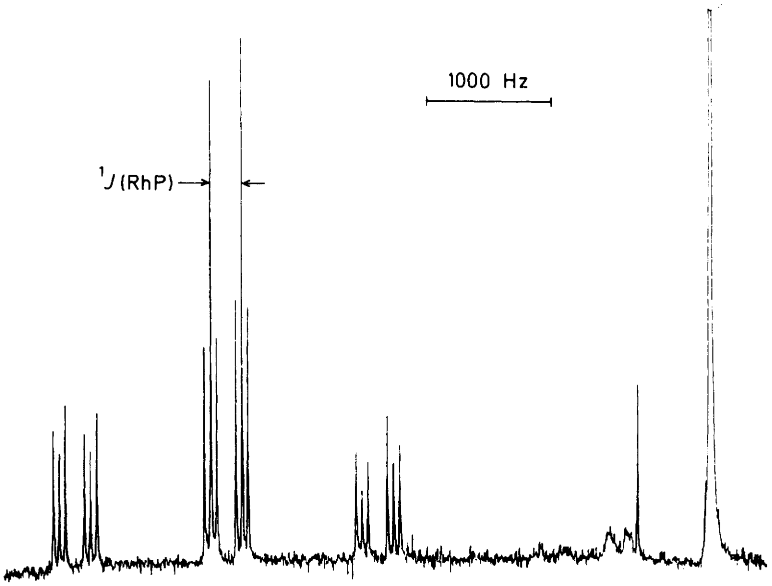


Figure 4. ^{31}P-$\{^1H\}$ N.m.r. spectrum of complex (**11**) in the presence of PPh_3 in excess

fluorophosphino)benzene $C_6H_4(PF_2)_2$-*o*, can produce materials similar to (**1**) and (**10**). Interesting results have been obtained with lantern-like dimers of the type $[\{Ir(MeCO_2)[MeN(PF_2)_2]\}_2]$ the end faces of which probably resemble the faces in (**1**), and these will be reported at a later date.

Experimental

The ^{31}P, ^{19}F, and ^{1}H n.m.r. spectra were recorded on a Bruker WP80 F.T. n.m.r. spectrometer operating at 32.4, 75.4, and 80 MHz respectively. The 145.8-MHz n.m.r. spectra of compounds (**3**) and (**4**) were recorded using a Bruker WM360 spectrometer. Microanalyses for C, H, and N were carried out by Mrs. G. Olney of these laboratories.

All reactions were carried out using a combination of Schlenk and high-vacuum techniques. Reaction mixtures were usually agitated using an ultrasonic bath. The compounds $PF_2(NMe_2)$,[21] $PF(O_2C_6H_4)$,[22] $[\{IrCl(C_8H_{14})_2\}_2]$,[23] and $[\{RhCl(C_6H_{10})\}_2]$[24] were prepared by adaptions[25] of the literature methods.

Crystal Structure of Complex (**1**).—A crystal of complex (**1**) with edge length *ca.* 0.25 mm in a thin-walled glass capillary was mounted with a random orientation on the CAD 4 diffractometer.

Crystal data. $Cl_2F_{12}Ir_2P_4$, $M = 807.22$, monoclinic, space group $P2_1/n$, $a = 10.526(1)$, $b = 10.346(2)$, $c = 13.150(1)$ Å, $\beta = 101.46(1)°$, $U = 1\,403.5(6)$ Å^3, $Z = 4$, $F(000) = 1\,424$, $D_c = 3.82$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $\mu = 210$ cm^{-1}.

Data collection. Data were collected using the ω—2θ scan technique for $2 < \theta < 25°$. An empirical absorption correction was applied, based on psi scans with a minimum correction factor of 0.70, as were corrections for Lorentz and polarisation effects. Of 2 755 reflections measured, 1 604 unique reflections with $I > \sigma(I)$ were used in the structure analysis. Calculations were carried out using the Enraf-Nonius SDP structure program.

Structure determination and refinement. The iridium atoms were located from a Patterson map, all other atoms from two subsequent Fourier difference syntheses. Fully anisotropic least-squares refinement with weights of $w = 1/\sigma^2(F)$ led finally to $R = 0.048$ and $R' = 0.052$. The atomic co-ordinates are included in Table 3, and a packing diagram is shown in Figure 5.

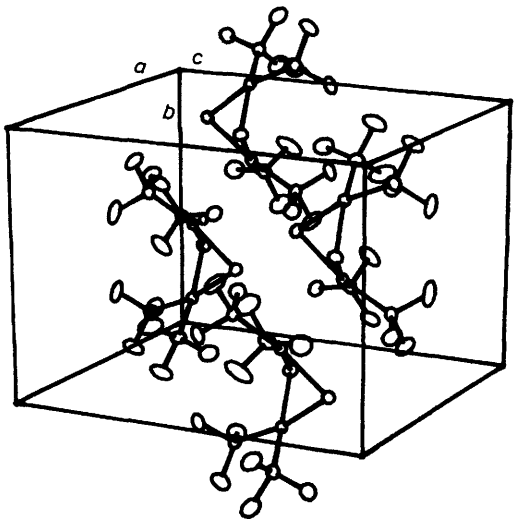


Figure 5. Packing diagram for $[\{IrCl(PF_3)_2\}]$ (**1**)

Table 3. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir(1)	1 697.7(9)	2 723.7(9)	3 040.5(7)	F(43)	−1 360(14)	−200(18)	2 453(15)
Ir(2)	1 667.0(9)	−119.2(9)	2 988.9(7)	F(31)	3 300(15)	−1 316(18)	5 063(11)
Cl(1)	3 506(5)	1 274(7)	3 574(4)	F(32)	1 335(20)	−2 345(18)	4 622(13)
Cl(2)	1 363(6)	1 339(7)	1 534(4)	F(33)	1 442(22)	−304(20)	5 313(13)
P(1)	2 018(6)	3 607(8)	4 540(5)	F(11)	3 398(15)	3 924(18)	5 064(11)
P(2)	−141(6)	3 634(8)	2 568(6)	F(12)	1 637(20)	2 840(20)	5 395(12)
P(4)	−165(6)	−995(7)	2 409(5)	F(13)	1 387(22)	4 856(17)	4 759(14)
P(3)	1 914(7)	−1 048(8)	4 466(5)	F(21)	−643(16)	3 865(17)	1 407(12)
F(41)	−532(12)	−1 339(16)	1 255(10)	F(22)	−1 323(15)	2 895(20)	2 816(20)
F(42)	−594(17)	−2 234(17)	2 832(14)	F(23)	−463(20)	4 939(18)	2 951(17)

Table 4. Analytical data for the complexes

	Analysis[a]				
Complex	C	H	N	Colour	M.p. (°C)
(**3**) $[IrCl(PF_2NMe_2)_3]$	13.0 (12.7)	3.05 (3.20)	7.30 (7.40)	Green-yellow	
(**4**) $[IrCl\{PF(O_2C_6H_4)\}_3]$	31.9 (30.8)	2.30 (1.70)		Off-white	118—122
(**5**) $[\{IrCl(PF_2NMe_2)_2\}_2]$	10.45 (10.6)	2.95 (2.65)	6.30 (6.15)	Yellow	
(**6**) $[\{RhCl[PF(O_2C_6H_4)]_2\}_2]$	31.75 (31.7)	2.00 (1.75)		Yellow	
(**7**) $[RhBr\{PF(O_2C_6H_4)\}_4]$	36.5 (35.4)	2.15 (2.00)		Yellow	87—93
(**8**) $[NMe_4][IrCl_2(PF_2NMe_2)_2]$	17.35 (17.05)	4.50 (4.30)	7.55 (7.45)	Yellow	
(**9**) $[NMe_4][RhCl_2\{PF(O_2C_6H_4)\}_2]$	34.55 (34.05)	4.55 (4.75)	3.00 (2.50)	Yellow	112—115
(**10**) $[\{IrCl[O{=}C(NMePF_2)_2]\}_2]$	7.65 (8.00)	1.25 (1.35)	6.00 (6.20)	Purple-black	decomp. 230
(**11**) $[\{RhCl[O{=}C(NMePF_2)_2]\}_2]$	10.1 (9.95)	1.80 (1.65)	7.55 (7.75)	Yellow	decomp. 150
(**12**) $[Ir(acac)\{O{=}C(NMePF_2)_2\}]$	19.0 (18.65)	3.30 (2.55)	5.60 (5.45)	Off-white	163—165
(**13**) $[Rh(acac)\{O{=}C(NMePF_2)_2\}]$	22.55 (22.55)	3.35 (3.10)	6.70 (6.60)	Pale yellow	158—162
(**14**) $[NMe_4][IrCl_2\{O{=}C(NMePF_2)_2\}]$	15.9 (16.2)	3.70 (3.75)	7.05 (7.20)	Off-white	115—120

[a] Calculated values are given in parentheses.

Preparations.—Chlorotris(dimethylaminodifluorophosphine)iridium(I), (**3**). A solution of $[\{IrCl(C_8H_{14})_2\}_2]$ (0.2842 g, 0.317 mmol) in toluene (4 cm^3) was treated with $PF_2(NMe_2)$ (0.2219 g, 1.96 mmol) and agitated for 2 h. After removal of all volatile components *in vacuo* the residue was recrystallised from toluene–light petroleum to yield $[IrCl(PF_2NMe_2)_3]$ (**3**) (0.3554 g, 98.8%). Microanalytical data for this and the other compounds are included in Table 4.

Chlorotris(2-*fluoro*-1,3,2-*benzodioxaphosphole*)*iridium*(I), (**4**). Treatment of $[\{IrCl(C_8H_{14})_2\}_2]$ (0.2216 g, 0.247 mmol) in toluene (3 cm^3) with an excess of $PF(O_2C_6H_4)$ (0.3995 g, 2.53 mmol) for 2 h followed by removal of the volatile components *in vacuo* and washing with light petroleum gave $[IrCl\{PF(O_2C_6H_4)\}_3]$ (**4**) (0.3337 g, 99.5%).

Di-μ-chloro-tetrakis(*dimethylaminodifluorophosphine*)*diiridium*(I) (**5**). A benzene solution of complex (**3**) (0.1553 g, 0.274 mmol) was treated with $[\{IrCl(C_8H_{14})_2\}_2]$ (0.0628 g, 0.070 mmol). After agitation for 1 h the greenish solution was filtered and $[\{IrCl(PF_2NMe_2)_2\}_2]$ (**5**) [0.1612 g, 86.4% based on (**3**)] was precipitated by addition of light petroleum.

Di-μ-chloro-tetrakis(2-*fluoro*-1,3,2-*benzodioxaphosphole*)*dirhodium*(I), (**6**). A toluene solution of $[\{RhCl(C_6H_{10})\}_2]$ (0.3330 g, 0.755 mmol) was treated with $PF(O_2C_6H_4)$ (0.4743 g, 3.00 mmol). After agitation for 1 h the solvent was removed under vacuum and the resultant red oil crystallised by addition of heptane to give $[\{RhCl[PF(O_2C_6H_4)]_2\}_2]$ (**6**) (0.6588 g, 96.0%).

Bromotetrakis(2-*fluoro*-1,3,2-*benzodioxaphosphole*)*rhodium*(I), (**7**). The complex $[\{RhBr(C_6H_{10})\}_2]$ (0.2497 g, 0.441 mmol) in toluene (3 cm^3) was treated with $PF(O_2C_6H_4)$ (0.4675 g, 2.958 mmol). After 3 h the volatile components were removed under vacuum and the product $[RhBr\{PF(O_2C_6H_4)\}_4]$ (**7**) washed with dichloromethane and dried (0.6002 g, 78.8%).

Tetramethylammonium dichlorobis(*dimethylaminodifluorophosphine*)*iridate*(I), (**8**). A solution of complex (**5**) (0.1243 g, 0.137 mmol) in dichloromethane was treated with a large excess of dry tetramethylammonium chloride (0.4215 g, 3.846 mmol). After agitating the mixture for 1.5 h the orange solution was filtered and $[NMe_4][IrCl_2(PF_2NMe_2)_2]$ (**8**) (0.0712 g, 46.7%) precipitated by addition of hexane.

Tetramethylammonium dichlorobis(2-*fluoro*-1,3,2-*benzodioxaphosphole*)*rhodate*(I), (**9**). A dichloromethane solution of complex (**6**) (0.1256 g, 0.138 mmol) was treated with a large excess of dry NMe_4Cl (0.2676 g, 2.442 mmol) in dichloromethane. After agitation for 3 h the solution was filtered and $[NMe_4][RhCl_2\{PF(OC_6H_4)\}_2]$ (**9**) (0.1312 g, 84.3%) precipitated by addition of light petroleum.

Bis[N,N′-*bis*(*difluorophosphino*)-N,N′-*dimethylurea*]*di-μ-chloro-di-iridium*(I), (**10**). A standard solution of compound (**2**) (0.2328 g cm^{-3}, 0.34 cm^3, 0.35 mmol) in dichloromethane was added to a Schlenk tube containing $[\{IrCl(C_8H_{14})_2\}_2]$ (0.1566 g, 0.175 mmol). The mixture was agitated for 2 h to give a clear yellow-green solution. Removal of all volatile components *in vacuo* gave a yellow solid which on shaking with two lots of light petroleum (2 × 5 cm^3) yielded a purple powder $[\{IrCl[O{=}C(NMePF_2)_2]\}_2]$ (**10**) (0.1387 g, 87.9%) which was filtered off and dried. Black crystals of (**10**), identical by i.r. spectroscopy and microanalysis to the purple solid, were obtained by crystallisation from dichloromethane at −20 °C.

Bis[N,N′-*bis*(*difluorophosphino*)-N,N′-*dimethylurea*]*di-μ-chloro-dirhodium*(I), (**11**). A standard solution of compound (**2**) (0.1726 g cm^{-3}, 1.0 cm^3, 0.77 mmol) in dichloromethane was added to $[\{RhCl(C_6H_{10})\}_2]$ (0.1644 g, 0.373 mmol) in CH_2Cl_2 (0.5 cm^3). After a few minutes a large quantity of precipitate had formed, which was filtered off, washed with toluene, and dried to give $[\{RhCl[O{=}C(NMePF_2)_2]\}_2]$ (**11**) (0.1710 g, 66.4%). A further quantity of (**11**) could be obtained by addition of light petroleum to the mother-liquor.

Acetylacetonato[N,N′-*bis*(*difluorophosphino*)-N,N′-*dimethylurea*]*iridium*(I), (**12**). The complex $[Ir(acac)(C_8H_{14})_2]$ (0.1708 g, 0.334 mmol) was treated with a solution of (**2**) in dichloromethane (0.0695 g cm^{-3}, 1.2 cm^3, 0.37 mmol) to give a red solution. After 1 h the volatile components were removed *in vacuo* to give a brownish yellow solid which was washed with light petroleum and dried to give $[Ir(acac)\{O{=}C(NMePF_2)_2\}]$ (**12**) (0.1556 g, 91.5%). Almost white needle-like crystals of (**12**) were obtained by adding an equal volume of toluene to a dichloromethane solution of (**12**) and cooling the mixture to −20 °C (18 h).

Acetylacetonato[N,N′-*bis*(*difluorophosphino*)-N,N′-*dimethylurea*]*rhodium*(I), (**13**). The complex $[Rh(acac)(C_6H_{10})]$ (0.1272 g, 0.448 mmol) was treated with a solution of (**2**) (0.0695 g cm^{-3}, 1.6 cm^3, 0.60 mmol) in dichloromethane. After agitating for 1 h the volatile components were removed under vacuum and the solid washed with light petroleum and dried to give $[Rh(acac)\{O{=}C(NMePF_2)_2\}]$ (**13**) (0.1773 g, 92.5%). Needle-like crystals of (**13**) were obtained in a similar manner to those of (**12**).

Tetramethylammonium [N,N′-*bis*(*difluorophosphino*)-N,N′-*dimethylurea*]*dichloroiridate*(I), (**14**). A solution/suspension of complex (**10**) (0.1395 g, 0.154 mmol) was treated with a large excess of dry NMe_4Cl (0.3883 g, 3.543 mmol). The purple colour of solid (**10**) was rapidly discharged and the initially yellow solution became green, reverting to pale golden yellow after *ca.* 3 h. The solution was filtered and addition of light petroleum yielded $[NMe_4][IrCl_2\{O{=}C(NMePF_2)_2\}]$ (0.0448 g, 51.8%). Minor quantities (< 10%) of (**14**) were also obtained as the only isolable product of the reaction of (**10**) with NMe_4CN.

Acknowledgements

We thank the S.E.R.C. for financial support and Professor R. Schmutzler for the gift of $O{=}C(NMePF_2)_2$.

References

1 'Extended Linear Chain Compounds,' ed. J. S. Miller, Plenum, New York, 1982, vols. I—III.
2 A. E. Underhill and D. M. Watkins, *Chem. Soc. Rev.*, 1980, **9**, No. 4, 429.
3 J. M. Williams and A. J. Schultz, *NATO Conf. Ser.*, 1979, **1**, 337.
4 J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, 1976, **20**, 1.
5 K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 35.
6 A. P. Ginsberg, J. W. Koepke, J. J. Hauser, K. W. West, F. J. Di Salvo, C. R. Sprinkle, and R. L. Cohen, *Inorg. Chem.*, 1976, **15**, 514.
7 A. H. Reis, V. S. Hagley, and S. W. Peterson, *J. Am. Chem. Soc.*, 1977, **99**, 4184.
8 F. N. Lecrone, M. J. Minot, and R. M. Perlstein, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 173.
9 C. J. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. L. Morrow, W. R. Roper, and D. Ulkü, *J. Am. Chem. Soc.*, 1966, **88**, 4286.
10 N. A. Bailey, E. Coates, G. B. Robertson, F. Bonati, and R. Ugo, *Chem. Commun.*, 1967, 1041.
11 M. J. Decker, D. O. Kimberley, S. R. Stobart, and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1983, 1525.
12 V. Schurig, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 807.
13 V. Schurig, W. Pille, and W. Winter, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 327.
14 L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, 1961, **83**, 1761.
15 P. B. Hitchcock, S. Morton, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1984, 603.
16 M. A. Bennett and D. J. Patmore, *Inorg. Chem.*, 1971, **10**, 2387.
17 'Handbook of Chemistry and Physics,' 59th edn., CRC Press, Florida, 1978.
18 D. A. Clement and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 1973, 195.
19 B-W. Krüger, Dissertation, Technischen Universitat Carolo-Wilhelmina zu Braunschweig, 1978.

20 R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsenges. Phys. Chem.*, 1972, **76**, 44.
21 R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 415.
22 R. Schmutzler, *Chem. Ber.*, 1963, **96**, 2435.
23 B. L. Shaw and E. Singleton, *J. Chem. Soc. A*, 1967, 1683.
24 G. Gordano and R. H. Crabtree, *Inorg. Synth.*, 1978, **19**, 218.
25 J. C. T. R. Burckett St. Laurent, D.Phil Thesis, University of Sussex, 1982.

Received 29th August 1984; *Paper* 4/1477