Extended Metal–Metal Interactions in Fluorophosphine Complexes of Iridium(I)

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The solid state structure of $[IrCl(PF_3)_2]_2$ consists of infinite zig-zag chains of iridium atoms with short *inter-* and *intra-*molecular Ir · · · Ir contacts; by contrast related complexes containing PF_2NMe_2 do not appear to have extended metal–metal interactions.

There is considerable current interest in new anisotropic materials with novel solid state properties[1] and most studies of inorganic 'one dimensional metals' have centred on square planar d^8 transition metal complexes particularly those of platinum(II).[2]

In 1971 Bennett and Patmore[3] described the preparation of $[IrCl(PF_3)_2]_2$, (**1**), and noted that although (**1**) is pale yellow in solution in the solid state it has a dark colour and metallic lustre possibly indicative of intermetallic bonding. As part of a general study of the potential of d^8 Rh^I and Ir^I metal complexes as 1-D metals we now report the crystal and molecular structure of (**1**) and some observations on related Ir^I fluorophosphine complexes.

$[IrCl(PF_3)_2]_2$
(**1**)

$[IrCl(PF_2NMe_2)_3]$
(**2**)

$[IrCl(PF_2NMe_2)_2]_2$
(**3**)

Crystal data for (**1**): $Ir_2Cl_2F_{12}P_4$, M = 807.22, monoclinic, space group $P2_1/n$, a = 10.526(1), b = 10.346(2), c = 13.150(1) Å, β = 101.46(1)°, Z = 4, D_c = 3.82 g cm^{-3}, Mo-K_α radiation (λ = 0.71069 Å), μ = 210 cm^{-1}, 1604 reflections with $I > 3\sigma(I)$ refined to a conventional R of 0.048.[†]

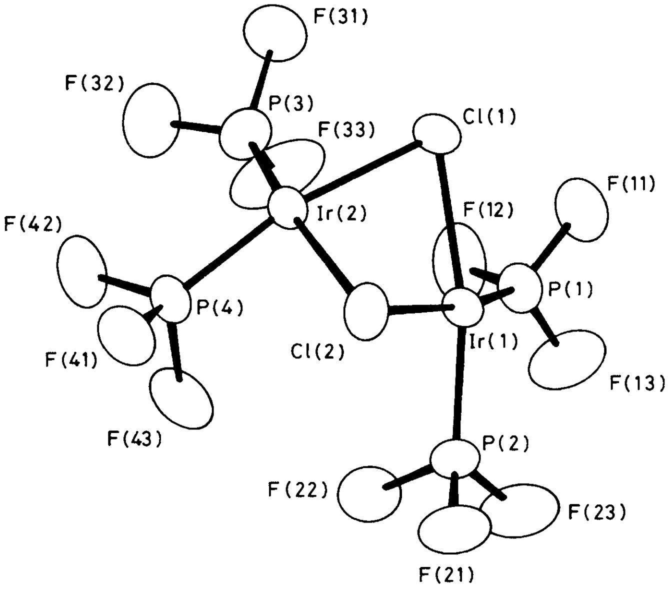

Figure 1. The molecular structure of $[IrCl(PF_3)_2]_2$ (**1**): Ir–P (av.) 2.134(5), Ir–Cl (av.) 2.413(5), P–F (av.) 1.517 Å.

The molecular geometry of the complex (**1**) which is shown in Figure 1 confirms the dimeric structure involving chloro bridges. Because of the very strong folding of the $[Ir_2Cl_2]$ four membered ring, the two $IrCl_2$ planes meet at an angle of 107.0°, and a short Ir · · · Ir contact of 2.941(1) Å results. The PF_3 ligands are even more strongly folded back so that the iridium atoms lie 0.20 Å out of the P_2Cl_2 planes. This fold-back occurs in order to minimise *inter*molecular Cl · · · F contacts and allows an *inter*molecular Ir · · · Ir contact of 3.271(1) Å to be made. Thus iridium atoms form infinite zig-zag chains with alternate long and short Ir · · · Ir contacts (Figure 2). These contacts may be compared with the values in $[Ir(CO)_3Cl]$, 2.844(1) Å,[4] and $[Ir(CO)_2\ (acac)]$ (acac = acetylacetonato), 3.20 Å,[5] which are chain forming or the

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[†] The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

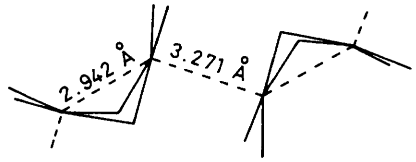

Figure 2. The chain structure of $[IrCl(PF_3)_2]_2$ (**1**).

racemates of rhodium(I) or iridium(I) dicarbonyl-3-trifluoroacetyl camphorate which both have columnar arrays of square planar complexes with short M · · · M contact (3.38 Å for Rh).[6] The quasi-racemate formed from the (1*R*) enantiomer of the Ir complex and the (1*S*) enantiomer of the Rh complex has a similar structure[7] with a RhRhIrIr repeat sequence in which the contact distances Rh · · · Ir, 3.42(2), Rh · · · Rh, 3.36(2), and Ir · · · Ir, 3.36(2) Å, are all slightly larger than the Ir · · · Ir contact in (**1**).

The structure of (**1**) is similar to that of $[RhCl(CO)_2]_2$[8] although the *intra-* and *inter*-molecular Rh · · · Rh contacts (3.12 and 3.31 Å respectively) are much longer and the $[Rh_2Cl_2]$ ring is much less strongly bent. Few neutral monomeric rhodium(I) species are known to form linear chains although $[Rh(CO)_2(acac)]$[9] does and very recently[10] molecular stacking has been reported in $[RhCl(CO)_2pzH]$ (pzH = pyrazole) where in the slightly zig-zag chains of the latter the Rh · · · Rh distance [3.4522(4) Å] is also much longer than the *inter*molecular Ir · · · Ir distance in (**1**).

Treatment of $[IrCl(C_8H_{14})_2]_2$ (C_8H_{14} = cyclo-octene) with an excess of PF_2NMe_2 results in the formation of $[IrCl(PF_2NMe_2)_3]$ (**2**), which in contrast to $[RhCl(PF_2NMe_2)_3]$[11] gives sharp $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ n.m.r. spectra at room temperature indicative of no intermolecular ligand exchange. The spectra clearly indicate a square-planar arrangement of ligands, an iridium with two distinct environments for the ligands and an $AA'BX_2X'_2Y_2$ spin system‡ (δ_{P_a} −148.5, δ_{P_b} −171.1, δ_{F_x} −55.1, δ_{F_y} −38.4 p.p.m.; $^1J_{P_aF_a}$ −1129.6, $^1J_{P_bF_y}$ −1057.3, $^2J_{P_aP_a'}$ + 808.5, $^2J_{P_aP_b}$ −58.5, $^3J_{P_aF_x'}$ 58.1, $^3J_{P_aF_y}$ 7.7, $^3J_{P_bF_x}$ −7.1, $^4J_{F_xF_x'}$ 8.8, $^4J_{F_xF_y}$ *ca.* 0 Hz). Treatment of a stoicheiometric amount of (**2**) with $[IrCl(C_8H_{14})_2]_2$ affords $[IrCl(PF_2NMe_2)_2]_2$ (**3**) which gives an $AA'X_2X'_2$ spin system‡ in the $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ n.m.r. spectra (δ_P −177.8, δ_F −43.7 p.p.m.; $^1J_{PF}$ 1072.8, $^2J_{PP'}$ −66.6, $^3J_{PF'}$, $^4J_{FF'}$ *ca.* 0 Hz). Both (**2**) and (**3**) are pale yellow solids and thus probably contain no significant extended metal–metal interactions. The greater steric requirements of PF_2NMe_2 presumably prevents close approach of the iridium metal centres and thus the formation of extended interactions. We have made similar observations on Rh^I and Ir^I fluorophosphite complexes.[12]

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‡ To a good approximation. In fact all the fluorine nuclei are magnetically non-equivalent, but effects of this were not observed.

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