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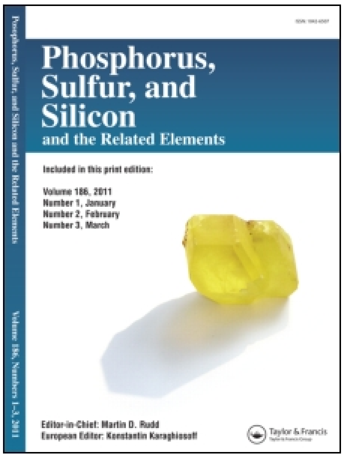

## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Complexes of Iridium and Platinum Containing 5-Coordinated Phosphorus

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# COMPLEXES OF IRIDIUM AND PLATINUM CONTAINING 5-COORDINATED PHOSPHORUS

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Abstract The complex $Ir(CO)Cl_2(PEt_3)_2(P'F_4)$, prepared in high yield from $Ir(CO)Cl_2(PEt_3)_2(P'F_2)$ and $XeF_2$, has been characterised by nmr spectroscopy, by analysis and by X-ray crystallography. In the crystal, P' is trans to Cl, and is trigonal-bipyramidal, with Ir in an equatorial position and the P'F bonds staggered with respect to the octahedral coordination round Ir. In solution, the fluxional behaviour of P' is only slowed enough to resolve distinct F resonances at 135 K. NMR evidences indicates that $XeF_2$ reacts at 180 K with $Ir(CO)BrH(PEt_3)_2(P'H_2)$ to give $Ir(CO)BrH(PEt_3)_2(P'F_2H_2)$, which is unstable at 210 K. $XeF_2$ also reacts with $PtCl(PEt_3)_2(P'Cl_2)$ to give $PtCl_2(PEt_3)_2(P'F_4)$, not yet isolated; in this complex P' is fluxional at 280 K but distinct F resonances are observed at 180 K.

Very many complexes of transition metals containing 4-coordinated phosphorus are known, and those of 3-coordinated phosphorus are now familiar, but metal complexes containing 5-coordinated phosphorus are unusual. Here we describe the synthesis, structure and some chemical properties of $Ir(CO)Cl_2(PEt_3)_2(P'F_4)$, (I), and include some information about the related species $Ir(CO)BrH(PEt_3)_2(P'F_2H_2)$, (II), and $PtCl(PEt_3)_2(P'F_4)$. A preliminary account of some of these results has appeared.[1]

We have prepared[2] $Ir(CO)Cl_2(PEt_3)_2(P'F_2)$, (III) in high yield by oxidative addition of $PF_2Cl$ to $Ir(CO)Cl)PEt_3)_2$, (IV), in $CH_2Cl_2$. We hoped to be able to obtain complexes containing $P'F_4$ ligands bound to Ir by similar oxidative addition of $PF_4H$ or $PF_4Cl$ to (IV), but we were not successful. In each case reaction occurred at 180 K to give one main product, but in both systems the P-{H} spectra showed a wide quartet of triplets in the P' region, [$^1J(P'F)$ ca. 1270 Hz], which establishes that the P' ligands are $P'F_3$ and not $P'F_4$ groups.

However, in the P-{H} spectrum of the products of the reaction between (III) and a half-molar proportion of $Cl_2$ we observed a wide quintet of triplets [$^1J(P'F)$ = 1062 Hz], and this led us to believe that (I) might be stable if we prepared it in the absence of any $F^-$ acceptor. We obtained (I) in high yield from the reaction between (III) and an equimolar proportion of $XeF_2$ in $CH_2Cl_2$, and isolated it as a white crystalline solid; it has been characterised by analysis, by n.m.r. spectroscopy and by X-ray crystallography.

The compound is very sensitive to moisture, but we were able to obtain a single crystal suitable for X-ray work using Kel-F equipment. The iridium centre is 6-coordinated, with P' trans to Cl; P' is at the centre of a trigonal bipyramid, with the metal in an equatorial position. There is a significant difference between the lengths of axial and equatorial P'-F bonds (see Table below).

TABLE Some structural parameters

| $Ir(CO)Cl_2(PEt_3)_2(P'F_4)$ | | | $Ir(CO)Cl_2(PEt_3)_2(P'F_2O)$ | | |
|---|---|---|---|---|---|
| r(Ir-P)/pm | 239(1) | | r(Ir-P)/pm | 241(1) | |
| r(Ir-P')/pm | 229(1) | | r(Ir-P')/pm | 225(1) | |
| r(Ir-Cl)/pm | 236(1), | 242(1) | r(Ir-Cl)/pm | 237(1), | 242(1) |
| r(P(-$F_a$)/pm | 169(1), | 164(11) | r(Ir-F)/pm | 156(2), | 153(3) |
| r(P'-$F_e$)/pm | 156(2), | 152(2) | | | |

In each structure the first Cl is trans to CO.

The Ir-P( bond is shorter than the Ir-$PEt_3$ bonds but much the same length[2] as the Ir-P' bond in $Ir(CO)Cl_2(PEt_3)_2(P'F_2O)$; the lengths of the Ir-Cl bonds trans to P' in the $P'F_2O$ and the $P'F_4$ complexes are similar, and so we conclude that $P'F_2O$ and $P'F_4$ are electronically very similar as ligands.

The equatorial plane round P' is twisted by about 45° relative to the plane containing the two $PEt_3$-phosphorus atoms, P' and the iridium atom. This means that all four F atoms are in different environments. The $^{19}F$ and $^{31}P$ n.m.r. spectra show that at temperatures above 200 K coordination round P' is fluxional: all four F nuclei behave as if they were equivalent, showing a single chemical shift and the same set of couplings to $^{31}P$ nuclei. At 180 K the lines in the F spectrum become broad. By using a 1:1 mixture of $Et_2O$ and $CH_2Cl_2$ as solvent, we were able to observe n.m.r. spectra down to 120 K, and at 130 K the F spectrum split into three broad doublets with rough relative intensities 1:1:2 [$^1J(P'F)$ = 922, 975, 1088 Hz]. This pattern would be consistent with a static structure in which the equatorial plane of P' and the $P_2IrP'$ plane coincided; the strongest doublet, assigned to equatorial fluorines, is associated with the largest value of $^1J(P'F)$. The low temperature n.m.r. spectrum can be reconciled with the crystal structure if we suppose that rocking about the Ir-P' bond is rapid enough on the n.m.r. timescale at 130 K to make the two equatorial F nuclei appear equivalent.

The complex hydrolyses to give $Ir(CO)Cl_2(PEt_3)_2(P'F_2O)$. Addition of $F^-$ leads to cleavage of the Ir-P' bond with formation of $PF_6^-$. Reaction with ammonia also breaks the Ir-P' bond. With $BF_3$, a typical $F^-$ acceptor, the salt $[Ir(CO)Cl_2(PEt_3)_2(P'F_3)]^+[BF_4]^-$ is formed. Reactions with $Me_3SiH$ and $Me_3SnH$ are slow and complicated, and no evidence of the formation of Ir complexes containing $P'F_nH_{4-n}$ ligands was observed. However, we have obtained evidence for the formation of $Ir(CO)BrH(PEt_3)_2(P'F_2H_2)$, (II), in the reaction between $XeF_2$ and $Ir(CO)BrH(PEt_3)_2(P'H_2)$, (V). If an equimolar mixture of (V) and $XeF_2$ is held at 190 K for several hours, substantial amounts (ca. 70% of P-containing material) of (V) are formed; this was identified by its n.m.r.

spectra. The $^{31}P\{H\}$ resonance at 180 K due to P' ($\delta$=-72 p.p.m.) is a wide triplet of narrow triplets, due to coupling to two directly-bound F's and two remote P nuclei. With $^{1}H$ coupling restored, there are additional wide triplet [$^{1}J(P'H)$] and narrow doublet [$^{2}J(P'H)$] couplings. The F, P<u>H</u> and Ir<u>H</u> resonances confirm this assignment. The value for $^{1}J(P'F)$ (310 Hz) is very much smaller than expected. This complex decomposes at temperatures above 210 K.

We have failed to obtain the rhodium analogue of (I). We cannot prepare $PtCl(PEt_3)_2(P'F_4)$ using a method analogous to that giving (I), because the monomeric starting-material $PtCl(PEt_3)_3(P'F_2)$ is not known. The $^{31}P$-{H} spectrum of the products of the reaction $PtCl(PEt_3)_2(P'Cl_2)$ with $XeF_2$ showed that a substantial component had been formed giving a P' resonance [$^{1}J(P'F)$ = 1050 Hz] with Pt satellites. This shows that the species formed contains $P'F_4$ bound to Pt with two $Et_3P$-ligands, formulated as $PtCl(PEt_3)_2(P'F_4)$. The $^{19}F$ resonance at 280 K consists of a doublet with Pt satellites, the doublet coupling matching the quintet coupling in the P' resonance; at 240 K this resonance broadens and at 180 K it has split into <u>two</u> doublets of equal intensity, each with Pt satellites; hence P' in this complex is fluxional at 280 K, but the rate of interconversion is slow on the n.m.r. timescale at 180 K.

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