# Some Reactions of a Co-ordinated Phosphido-group

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*Summary* The reaction of $\pi$-$C_5H_5Fe(CO)_2P(CF_3)_2$ with nitric oxide gives $\pi$-$C_5H_5Fe(CO)_2P(O)(CF_3)_2$, while with sulphur, $\pi$-$C_5H_5Fe(CO)_2P(S)(CF_3)_2$ is formed; on irradiation, $\pi$-$C_5H_5Fe(CO)_2P(CF_3)_2$ dimerises to give the expected phosphido-bridged complex, whereas the oxide and sulphide produce $(C_5H_5)_2Fe_3(CO)_2[OP(CF_3)_2]_4$ and $\pi$-$C_5H_5Fe(CO)_2SP(S)(CF_3)_2$, respectively.

In view of recent interest[1,2] in complexes containing pentavalent phosphorus bonded to a transition metal, we report some reactions of the terminal phosphido-ligand in $\pi$-$C_5H_5Fe(CO)_2P(CF_3)_2$ which lead to the preparation of such complexes.

When tetrakis(trifluoromethyl)diphosphine is heated (80°; 4 h) with $(\pi$-$C_5H_5)_2Fe_2(CO)_4$, the monomeric complex $\pi$-$C_5H_5Fe(CO)_2P(CF_3)_2$ (I) is produced. The reaction proceeds in an analogous fashion to that of the diarsine, $[(CF_3)_2As]_2$,[3] with the iron carbonyl, but in contrast to tetramethyldiphosphine,[4] which produces a dimer, $[\pi$-$C_5H_5Fe(CO)P(CH_3)_2]_2$. The bonding of the phosphorus atom in (I) to iron does not involve the lone pair and so the complex should be capable of undergoing some of the typical reactions of phosphines, while remaining co-ordinated to the metal.

Irradiation or heating of a solution of the monomeric complex (I) causes dimerisation to give $[\pi$-$C_5H_5Fe(CO)P(CF_3)_2]_2$, (II), isolated as large dark red crystals in quantitative yield. I.r. and n.m.r. data support the conclusion that (II) exists entirely in the *trans* configuration, with bridging phosphido-groups. Fluorocarbon phosphines have recently been shown[5] to be oxidised by nitric oxide; the terminal phosphido-group in (I) is also oxidised by nitric oxide in almost quantitative yield at room temperature to give the phosphine oxide (III) according to equation (1).

$$\pi\text{-}C_5H_5Fe(CO)_2P(CF_3)_2 + 2NO \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2P(O)(CF_3)_2 + N_2O \qquad (1)$$

There was no replacement of carbonyl groups by nitric oxide. The $^{19}F$ n.m.r. chemical shift of (III) ($\phi$ 70·5 p.p.m. relative to $CCl_3F$), and the increase in $^2J_{PF}$ upon oxidation, together with an i.r. band at 1216 cm$^{-1}$ assigned to $\nu(P{=}O)$, strongly suggest the pentavalent structure rather than the isomeric phosphite with an Fe–O–P linkage. Although the reaction proceeds under milder conditions than some of the analogous oxidations of the free ligands, oxidation does not appear to involve an intermediate where NO is co-ordinated to the metal, because complexes have been prepared[6] containing NO and $P(CF_3)_2$ groups which do not undergo self oxidation to form P(O) species. Furthermore, the dimer (II) does not react with nitric oxide, even under much more forcing conditions. It appears that the reaction is a direct oxidation at phosphorus involving the lone pair, which is no longer available in (II).

U.v irradiation of $\pi$-$C_5H_5Fe(CO)_2P(O)(CF_3)_2$ does not produce a phosphine oxide dimer; a complex mixture of products is formed, from which can be isolated ferrocene, a small quantity of the dimer (II), and another compound, molecular formula $(C_5H_5)_2Fe_3(CO)_2[OP(CF_3)_2]_4$, (IV), a novel trimer of iron whose structure has not yet been unambiguously determined. The trimer, which sublimes at 160° in a vacuum, is paramagnetic in the solid state ($\mu_{eff}$ 4·6 B.M.) and in solution ($\mu_{eff}$ 4·5 B.M.), and both $^1H$ and $^{19}F$ n.m.r. spectra show strongly contact-shifted absorptions. The mass spectrum reveals an intense parent ion, which fragments by loss of CO followed by loss of a molecule of $Fe[OP(CF_3)_2]_2$, verified by mass measurements and observation of the appropriate metastable peaks.

The addition of sulphur to $\pi$-$C_5H_5Fe(CO)_2P(CF_3)_2$ proceeds smoothly at 60° without evolution of carbon monoxide to give $\pi$-$C_5H_5Fe(CO)_2P(S)(CF_3)_2$ (V); the evidence for the pentavalent as opposed to the trivalent phosphorus structure is similar to that for the phosphine oxide (III). Fluorocarbon phosphines require to be heated to *ca.* 150° with sulphur before addition can be detected.[7] When the sulphide (V) is irradiated under the same conditions as for $\pi$-$C_5H_5Fe(CO)_2P(O)(CF_3)_2$, the products so far characterised are sulphur and $\pi$-$C_5H_5Fe(CO)_2SP(S)(CF_3)_2$, (VI), another new compound.

It seems that the $P(CF_3)_2$ group is considerably more reactive when bonded to a transition metal than when bonded to a main-group element. This is tentatively ascribed to increased electron density at phosphorus in the metal complex caused by strong metal-to-phosphorus $\pi$ bonding.

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