Reactions of a Terminal Phosphido-group in an Organo-iron Complex. Part I.† Some Oxygen, Sulphur, and Selenium Derivatives

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The monomeric phosphido-complex, $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$, which is prepared from $(CF_3)_2P{\cdot}P(CF_3)_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, can be converted to $(\pi\text{-}C_5H_5)Fe(CO)_2P(E)(CF_3)_2$ by the action of nitric oxide (E = O), sulphur (E = S), or selenium (E = Se). Other routes to the sulphur compound have been devised. The action of u.v. radiation upon $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ gives the expected dimer in a *trans*-configuration, whereas $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$ gives a new type of trimer, $(C_5H_5)_2Fe_3(CO)_2[OP(CF_3)_2]_4$, as the major product. Upon photolysis, $(\pi\text{-}C_5H_5)Fe(CO)_2P(E)(CF_3)_2$ give the isomeric complexes $(\pi\text{-}C_5H_5)Fe(CO)_2EP(CF_3)_2$ (E = S or Se). The preparation of $(\pi\text{-}C_5H_5)Fe(CO)_2SP(S)(CF_3)_2$ from the sulphur complex is also reported. Spectroscopic data for all the compounds prepared are discussed.

RECENT investigations have demonstrated that secondary phosphines co-ordinated to transition metals can rearrange by transfer of hydrogen from phosphorus to the metal[1,2] or to other ligands.[3-5] In co-ordinated phosphines, the lone pair on phosphorus is normally regarded as used in σ-bond formation with the metal. However with a phosphido-group in a terminal position the lone pair is not so involved and may become available for reactions which do not involve cleavage of the metal–phosphorus bond.

TABLE 1

Spectroscopic data [a] for some derivatives of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$

	Complex	νCO (cm^{-1})	ϕ [b]	$^2J_{FP}$ [c]	τ	$^3J_{HP}$ [c]
(I)	$(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$	2046vs, 2000vs	45·5	54·3	4·60	2·3
(II)	$(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$	2062vs, 2019vs	70·5	71·8	4·36	*d*
(III)	$(\pi\text{-}C_5H_5)Fe(CO)_2P(S)(CF_3)_2$	2062vs, 2021vs	67·0	71·0	4·40	1·5
(IV)	$(\pi\text{-}C_5H_5)Fe(CO)_2P(Se)(CF_3)_2$	2062vs, 2021vs	65·4	67·0	4·52	1·8
(V)	$[(\pi\text{-}C_5H_5)Fe(CO)P(CF_3)_2]_2$	2055vw, 1980vs	52·4	*ca.* 50	5·10	1·2
(VI)	$(C_5H_5)_2Fe_3(CO)_2[OP(CF_3)_2]_4$	2063s, 2022vs			*d*	
(VII)	$(\pi\text{-}C_5H_5)Fe(CO)_2SP(CF_3)_2$	2048vs, 2002vs	59·5	71·0	4·70	
(VIII)	$(\pi\text{-}C_5H_5)Fe(CO)_2SeP(CF_3)_2$	2042vs, 1997vs	56·6	66·0	4·64	
(IX)	$(\pi\text{-}C_5H_5)Fe(CO)_2SP(S)(CF_3)_2$	2059vs, 2016vs	71·2	92·0	4·46	

[a] I.r. spectra in CH_2Cl_2 solution; n.m.r. spectra in $(CH_3)_2CO$ solution. [b] In p.p.m., relative to CCl_3F. [c] In Hz. [d] See text.

The iron complex $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ (I) may be prepared by the action of tetrakis(trifluoromethyl)diphosphine $(CF_3)_2P{\cdot}P(CF_3)_2$, upon $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, or, less efficiently, from the iron dimer and bis(trifluoromethyl)phosphine. The former route is exactly analogous to that reported by Cullen and Hayter[6] for the preparation of $(\pi\text{-}C_5H_5)Fe(CO)_2As(CF_3)_2$. Spectroscopic data for compound (I) are given in Table 1. Attention is drawn to the n.m.r. parameters; the resonance of the cyclopentadienyl protons appears as a doublet because of coupling to phosphorus. The ^{19}F chemical shift and $^2J_{FP}$ are both typical of comparable P^{III} compounds, with both lying at the lower end of the ranges normally found. The phosphido-compound (I) reacts

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† For a preliminary communication of part of this work, see R. C. Dobbie, P. R. Mason, and R. J. Porter, *J.C.S. Chem. Comm.*, 1972, 612.

[1] P. M. Treichel, W. K. Dean, and W. M. Douglas, *Inorg. Chem.*, 1972, **11**, 1609.

[2] R. C. Dobbie, M. J. Hopkinson, and D. Whittaker, *J.C.S. Dalton*, 1972, 1030.

[3] B. C. Benson, R. Jackson, K. K. Joshi, and D. T. Thompson, *Chem. Comm.*, 1968, 1506.

[4] K. Yasufuku and H. Yamazaki, *J. Organometallic Chem.*, 1971, **28**, 415.

[5] R. C. Dobbie and D. Whittaker, unpublished work.

[6] W. R. Cullen and R. G. Hayter, *J. Amer. Chem. Soc.*, 1964, **86**, 1030.

readily at the phosphorus atom; in this paper the preparation and structure of some complexes containing phosphorus–Group VI element bonds is reported.

It has been shown [7] that nitric oxide acts as an oxidising agent towards trifluoromethyl-substituted phosphines, producing in the simplest cases the corresponding oxide, so that $(CF_3)_2PF$ is oxidised to $(CF_3)_2P(O)F$. More extensive oxidation, for example of $(CF_3)_2PH$ to $(CF_3)_2P(O)OH$, and rearrangement, for example of $(CF_3)_2PCl$ to $CF_3P(O)Cl_2$, is also observed, especially when reactions have to be carried out above room temperature. With the co-ordinated phosphido-group in compound (I), there was a smooth reaction at room temperature according to the equation:

$$(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2 + 2NO \longrightarrow \underset{\text{(II)}}{(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2} + N_2O$$

No carbon monoxide was liberated.

The structure of the product is established from its spectroscopic properties, shown in Table 1. In the carbonyl region of the i.r. spectrum two intense bands are found at slightly higher frequency than the corresponding bands of (I), as would be expected to result from increased metal–phosphorus π-bonding. A new peak at 1210 cm^{-1} can be tentatively assigned to $\nu(P{=}O)$, although this evidence for the Fe–P(O) as against the Fe–O–P structure is not strong as C–F stretching bands can also occur in this region. The ^{19}F n.m.r. spectrum of compound (II) shows a simple doublet shifted considerably to higher field of the resonance of (I) with an enlarged $^2J_{FP}$ coupling constant. The chemical shift ($\phi = 70{\cdot}5$ p.p.m.) is characteristic [8] of quinquevalent rather than tervalent $P(CF_3)_2$ compounds. Unlike the phosphido-complex, the ^1H n.m.r. resonance of (II) is a singlet, although the signal is sufficiently broad to obscure a coupling constant of up to 2 Hz.

Other complexes containing the P=O group have been reported recently [9,10] but the methods of preparation are different. It seems reasonable to assume that the metal atom is not directly involved in the oxidation, since several nitrosyls containing perfluoromethylphosphine ligands have been prepared [5] and in no case has any internal oxidation been noted.

The addition of sulphur in carbon disulphide solution to $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ was carried out at 60° giving $(\pi\text{-}C_5H_5)Fe(CO)_2P(S)(CF_3)_2$ (III) in high yield. The preparation in these laboratories [11] of the selenium analogue by the action of $[(CF_3)_2P]_2Se$ upon the dimeric iron complex, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, encouraged the study of the reaction of selenium with (I); addition occurred at room temperature to give $(\pi\text{-}C_5H_5)Fe(CO)_2P(Se)(CF_3)_2$ (IV). For both the sulphur and selenium adducts, the n.m.r. spectra allowed the quinquevalent structure to be assumed. The ^{19}F n.m.r. spectrum showed in each case a doublet shifted to high-field of that of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ as noted for the oxide. In addition, coupling between the hydrogen atoms of the cyclopentadienyl ring and phosphorus was detected in each case, giving a sharp doublet in the ^1H n.m.r. spectra. Such coupling is less likely for the isomeric Fe–S–P or Fe–Se–P structures. For all three compounds (II—IV), the parent ion is observed in the mass spectrum and fragmentation involves loss of the carbonyl groups and fluorocarbon fragments.

It is interesting to compare the reaction conditions used in the preparation of the sulphur and selenium adducts of the iron compound with those required for addition to main-group fluorocarbon phosphines. Addition of sulphur [12] does not occur below 150° and addition of selenium [11] has been detected only for $(CF_3)PP(CF_3)_2$ when temperatures in excess of 80° are needed. This increase in reactivity of (I) compared with main group phosphines of the type $(CF_3)_2PX$ is significant. The iron–phosphorus σ-bond in $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ will be more strongly polarised towards phosphorus than in main group $P(CF_3)_2$ derivatives because of the electropositive character of the iron. Further, any metal–phosphorus π-bonding will also result in a build-up of charge at the phosphorus atom. The two effects may increase the shielding of the lone-pair orbital on phosphorus making it more basic.

In order to investigate the possibility of preparing the isomeric derivatives, $(\pi\text{-}C_5H_5)Fe(CO)_2EP(CF_3)_2$ (E = O, S or Se), other methods of synthesis of the sulphur compound were developed. The use of P_4S_{10} as a source of sulphur resulted in addition to the phosphido-complex (I) at room temperature, giving the phosphine sulphide (III) in over 60% yield. When the mercapto-phosphine, $(CF_3)_2PSH$, which is known [13,14] to have a tervalent phosphorus atom, was allowed to react with $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$, the only product isolated was again the sulphide (III). It is clear that an anti-Arbuzov rearrangement had occurred at some stage of the reaction to form the iron–phosphorus bond.

Many dimeric phosphido-complexes are known where PR_2 groups act as bridges between the metal atoms.[15] It was thought of value to study the dimerisation of the phosphido-complex (I) since this can be considered to be a reaction of the co-ordinated $P(CF_3)_2$ group. On irradiation of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ in non-polar solvents, carbon monoxide was liberated and deep red crystals of $[(\pi\text{-}C_5H_5)Fe(CO)P(CF_3)_2]_2$ (V) were precipitated from solution. Dimers of this type are normally a direct product of the interaction of a diphosphine with metal carbonyl complexes.[12] The carbonyl stretching region of the i.r. spectrum, in both solid phase and

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[7] R. C. Dobbie, *J. Chem. Soc.* (*A*), 1971, 2894.

[8] K. J. Packer, *J. Chem. Soc.*, 1963, 960.

[9] R. J. Haines, A. L. DuPreez, and I. L. Marais, *J. Organometallic Chem.*, 1971, **28**, 405.

[10] C. B. Colburn, W. E. Hill, and D. W. A. Sharp, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 625.

[11] M. J. Hopkinson, personal communication.

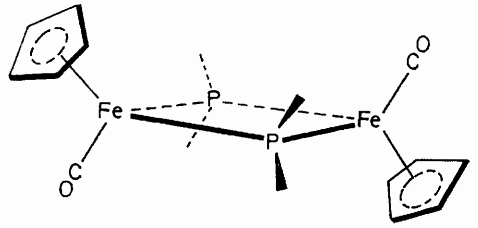
[12] R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Amer. Chem. Soc.*, 1968, **90**, 2015.

[13] R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 1964, 5825.

[14] A. B. Burg and K. Gosling, *J. Amer. Chem. Soc.*, 1965, **87**, 2113.

[15] R. G. Hayter, *Prep. Inorg. Reactions*, 1965, **2**, 211.

solution, showed a weak high frequency band and an intense peak at lower frequency, as predicted for the *trans*-structure shown below. N.m.r. spectroscopy supported the assignment. The ^1H n.m.r. spectrum showed a 1 : 2 : 1 triplet ($^3J_{HP}$ 1·2 Hz), arising from coupling to the equivalent phosphorus atoms, whereas the ^{19}F spectrum had an absorption typical[16] of the $[AX_6]_2$ spin system, although detailed analysis of the spectrum to obtain all the coupling constants was not feasible because of the width of the lines within the sharp doublet.



The behaviour of the complexes $(\pi\text{-}C_5H_5)Fe(CO)_2P(E)(CF_3)_2$ (E = O, S, and Se) upon irradiation has also been investigated, following the observation that the pale yellow air-stable solutions of the oxide (II) turned dark brown on exposure to sunlight. Prolonged u.v. irradiation of a solution of $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$ gave ferrocene, the dimer (V), and a trimer (VI) of novel constitution, for which the available evidence suggests the formula $(C_5H_5)_2Fe_3(CO)_2[OP(CF_3)_2]_4$. The absence of change in any of the physical properties of (VI) on repeated purification by fractional sublimation indicated that the complex was pure. Although the analysis for carbon was not close to the theoretical value, consideration of the analytical results as a whole strongly supports the given formula. Further evidence for the purity of the solid comes from a study of the *X*-ray photoelectron spectrum of (VI). The C(1*s*) energy level gave three signals with binding energies of 285·5, 290·5, and 292·1 eV (intensities 10 : 2 : 8), corresponding to CH, CO, and CF_3 groups. The ionised molecule of (VI) is observed in the mass spectrum. Initial fragmentation under electron impact is by loss of carbon monoxide, followed by loss of the neutral species $Fe[OP(CF_3)_2]_2$, and then loss of a second molecule of carbon monoxide, giving the ion $(C_5H_5)_2Fe_2[OP(CF_3)_2]_2^+$. These steps have been confirmed by the observation of the appropriate metastable peaks at *m*/*e* 1038, 384·5, and 585, and by mass measurement of the fragment ions. Further fragmentation was completely consistent with the presence of two C_5H_5 rings. In solution, two terminal carbonyl stretching bands are observed and absorptions in the region 1210—1200 cm^{-1} are assigned to $\nu(P{=}O)$. Despite the demonstration of considerable covalent character in the molecule by sublimation without decomposition in a vacuum at 160—170°, the solid has a measured magnetic moment of *ca.* 4·6 B.M. In solution, the magnetic moment, determined by the n.m.r. method of Evans[17] was 4·5 B.M. The ^{19}F n.m.r. spectrum of the trimer in acetone solution at room temperature consisted of three broad resonances at ϕ = 69·4, 34·2, and 11·0 in p.p.m. upfield from CCl_3F, relative intensities 1 : 2 : 2. The resonance at highest field, which is very close to the resonance position of $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$, was almost unaffected on varying the temperature, whereas the other two showed the characteristic behaviour of nuclei coupled to a paramagnetic centre. Some typical chemical shifts at various temperatures are given in Table 2. In the ^1H n.m.r. spectrum, recorded in acetone solution, only two resonances at τ 5·2 and —1·0 (relative intensities 1·5 to 1) were observed; on cooling, the resonance positions were only slightly affected and the relative intensities of the peaks were unchanged. The ^{57}Fe Mössbauer spectrum revealed two quadrupole split doublets, the more intense having a chemical isomer shift close to that of the oxide (II), whereas the less intense had an isomer shift close to that of typical ionic iron(II) co-ordination complexes.

TABLE 2

^{19}F Chemical shift data for $(C_5H_5)_2Fe_3(CO)_2[OP(CF_3)_2]_4$

Temperature/K	ϕ (p.p.m.)		
325	18·6	34·2	69·4
315	16·75	34·7	69·7
293	11·0	34·2	69·4
253	−4·2	32·7	69·4
213	−19·0	29·2	69·8

Although a great deal of information about the trimer has been accumulated, its structure remains obscure. The low yield discourages further study by chemical methods. Attempts to grow single crystals for *X*-ray crystallography have so far been unsuccessful.

Irradiation of the analogous phosphine sulphide (III) and selenide (IV) also resulted in complex mixtures. However, in each case, sublimation of the residue after removal of solvent gave a small amount of material more volatile than the starting material. These products were characterised by analysis and by spectroscopic methods as the isomers of (III) and (IV) containing trivalent phosphorus, namely $(\pi\text{-}C_5H_5)Fe(CO)_2SP(CF_3)_2$ (VII) and $(\pi\text{-}C_5H_5)Fe(CO)_2SeP(CF_3)_2$ (VIII). Once again n.m.r. spectroscopy gave important evidence for the assumed structures. The ^{19}F n.m.r. spectrum of each complex was moved to lower field in comparison with the quinquevalent isomers, although the P–F coupling constants remained essentially the same. Further a single sharp peak was observed in the ^1H n.m.r. spectrum in each case, no coupling to the more distant phosphorus atom being detected. Small changes in the C–O stretching frequencies compared with (III) and (IV) are in the direction predicted when phosphorus substituted by the highly electron-withdrawing CF_3 groups is replaced by sulphur or selenium.

Differential crystallisation of the residue from the photolysis of (V) gave two fractions in very small quantities. I.r. spectroscopy indicated that no bridging carbonyl groups were present; the mass spectra were

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[16] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.
[17] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

consistent with the presence of three compounds in varying amounts in each fraction, namely $(C_5H_5)_2Fe_2(CO)_2[P(CF_3)_2]_2Se_2$, $(C_5H_5)_2Fe_2[P(CF_3)_2]_2Se_3$, and $(C_5H_5)_2Fe_2[P(CF_3)_2]_3Se_2$. Insufficient of each fraction was obtained for any further study.

The trivalent isomers (VII) and (VIII) are of course linkage isomers of (III) and (IV). The isolation as stable entities of both possible Arbuzov isomers of a given phosphorus compound is rare and to our knowledge a conversion without the application of another chemical reagent has never before been achieved in fluorocarbon phosphorus chemistry. A study by n.m.r. spectroscopy of the progress of the irradiation shows that the trivalent compounds $(\pi\text{-}C_5H_5)Fe(CO)_2EP(CF_3)_2$ (E = S or Se) are the primary products of photolysis but that they decompose to give polymeric materials.

When a sample of $(\pi\text{-}C_5H_5)Fe(CO)_2P(S)(CF_3)_2$ slightly contaminated with sulphur was irradiated, the product isolated was $(\pi\text{-}C_5H_5)Fe(CO)_2SP(S)(CF_3)_2$ (IX). It appears that the isomerisation to (VII) was followed by the addition of sulphur. The ^{19}F n.m.r. chemical shift was again in the region expected for pentavalent $(CF_3)_2P$ derivatives. It is interesting to note that the P–F coupling constant for (IX) is close to those of the known compounds of formula $(CF_3)_2P(S)Y$ where Y bonds to phosphorus through a main-group atom.[12] Direct attachment of phosphorus to the metal without involvement of the lone pair appears to result in a significant decrease of J(P–F) compared to main-group derivatives; the chemical shift is almost unaffected. This generalisation holds for compounds with tervalent [*e.g.* $P(CF_3)_2$] or quinquevalent [*e.g.* $P(S)(CF_3)_2$] phosphorus atoms.

EXPERIMENTAL

Volatile compounds were handled in a Pyrex vacuum system by standard techniques. The solids prepared in this work were air stable and most of the solutions were stable for short periods in the presence of air and light. I.r. spectra were recorded on Perkin-Elmer 125 and 457 spectrometers and mass spectra on an A.E.I. MS 9 operating at an ionising energy of 70 eV. N.m.r. spectra were recorded either on a Perkin-Elmer R10 for ^1H nuclei or on a Bruker Spectrospin HFX operating at 90·00 MHz for ^1H and 84·66 MHz for ^{19}F nuclei, with Me_4Si and CCl_3F as internal standards. Samples for n.m.r. spectroscopy were made up in dry, degassed solvents and sealed under a vacuum. A medium pressure mercury arc lamp was used as the source of u.v. radiation. Tetrakis(trifluoromethyl)diphosphine,[18] bistrifluoromethylphosphinothious acid,[13] and cyclopentadienyldicarbonyliron chloride[19] were prepared according to the literature methods.

Reaction of Tetrakis(trifluoromethyl)diphosphine with Dicyclopentadienyltetracarbonyldi-iron.—At 65—70° $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$ (1·858 g, 5·24 mmol) reacted (4 h) with a slight excess of the diphosphine (*ca.* 5·5 mmol) in CCl_3F as solvent, forming only a trace of non-condensible gas. The solvent was removed and the residue purified by sublimation at 45° under a high vacuum to give large orange-brown *crystals*, m.p. 56—58°, of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ (2·29 g, 6·60 mmol; 63% yield) (Found: C, 31·7; H, 1·5. $C_9H_5O_2F_6FeP$ requires C, 31·2; H, 1·45%).

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ *with Nitric Oxide.*—Nitric oxide (0·051 g; 1·73 mmol) reacted with the iron complex (0·275 g, 0·795 mmol) in dry CCl_3F (*ca.* 5 ml), depositing long yellow needles after standing in the dark for 12 h. Prolonged vacuum fractionation at −183 °C separated unreacted nitric oxide (0·009 g, 0·30 mmol) from nitrous oxide (0·030 g, 0·68 mmol), identified by i.r. and mass spectrometry. After thorough washing with CCl_3F, the crystals remaining in the reaction tube were shown to be the *phosphine oxide complex*, $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$, m.p. 131° (Found: C, 29·8; H, 1·45. $C_9H_5O_3F_6FeP$ requires C, 29·8; H, 1·4%).

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ *with Sulphur.*—Flowers of sulphur (0·072 g, 2·25 mmol) and the iron compound (0·177 g, 0·495 mmol) were sealed in a reaction tube with CS_2 as solvent and heated to 60°. After 3 days, the dark orange-brown solution had cleared, leaving a yellow solid barely distinguishable from the excess of sulphur. Extraction with dichloromethane followed by sublimation at 70° gave yellow crystals of $(\pi\text{-}C_5H_5)Fe(CO)_2P(S)(CF_3)_2$ (0·104 g, 0·275 mmol) contaminated by a small amount of sulphur, the last traces of which were very difficult to remove.

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ *with* $(CF_3)_2PSH$.—The carbonyl chloride (0·117 g, 0·55 mmol) and $(CF_3)_2PSH$ (0·116 g, 0·575 mmol) in CCl_3F as solvent did not react at room temperature but at 50° (4 days) in the absence of light a yellow solid formed. The volatile products were the excess of $(CF_3)_2PSH$, HCl, and another fluorocarbon compound. Sublimation of the solid residue at 70° gave yellow crystals of $(\pi\text{-}C_5H_5)Fe(CO)_2P(S)(CF_3)_2$, m.p. 188° (0·055 g, 0·14 mmol; 28% yield) (Found: C, 28·4; H, 1·35. $C_9H_5O_2F_6FePS$ requires C, 28·6; H, 1·3%).

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ *with* P_4S_{10}.—The sulphide (0·389 g, 0·875 mmol), thoroughly dried by prolonged pumping in a vacuum, and the iron complex (0·098 g, 0·28 mmol) in CS_2 solution reacted at room temperature in the dark (3 days). Sublimation at 80—100° under a vacuum gave $(\pi\text{-}C_5H_5)Fe(CO)_2P(S)(CF_3)_2$, m.p. 185—187° (0·062 g, 0·164 mmol; 58% yield).

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ *with Selenium.*—A large excess of red selenium and $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ (0·164 g, 0·474 mmol) in CS_2 solution largely reacted at room temperature in the dark (1 day) but the reaction was brought to apparent completion by heating to 50° (1 h). Upon removal of the solvent, the residue was sublimed in a vacuum at 80° to give yellow crystals, m.p. 199—201°, of $(\pi\text{-}C_5H_5)Fe(CO)_2P(Se)(CF_3)_2$ (0·144 g, 0·34 mmol; 70% yield), identified by comparison of its properties with an authentic specimen,[11] and by analysis (Found: C, 25·6; H, 1·3. Calc. for $C_9H_5F_6FeO_2PSe$: C, 25·4; H, 1·15%).

Photolysis of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$.—The iron complex (0·361 g, 1·04 mmol), dissolved in dry cyclohexane in a Pyrex reaction tube, was irradiated (4·5 h) when crystals were deposited from solution. Recrystallisation from the same solvent gave the *complex*, *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)P(CF_3)_2]_2$ as large dark red plates (0·269 g, 0·42 mmol, 81%) (Found: C, 30·0; H, 1·65. $C_{16}H_{10}O_2F_{12}Fe_2P_2$ requires C, 30·2; H, 1·6%).

Photolysis of $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$.—The complex

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[18] F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1565.

[19] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.

(0·595 g, 1·65 mmol) in dichloromethane solution was irradiated for 18 h in a Pyrex vessel. The solid residues, on fractional sublimation in a vacuum, gave a trace of $(\pi\text{-}C_5H_5)_2Fe$, excess of $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$ (0·140 g, 0·38 mmol), $[(\pi\text{-}C_5H_5)Fe(CO)P(CF_3)_2]_2$ (0·005 g), and small yellow-brown *crystals* of $(C_5H_5)_2Fe_3(CO)_2[OP(CF_3)_2]_4$ (0·043 g, 0·040 mmol) (Found: C, 24·0; H, 0·9; F, 40·7; Fe, 15·2; P, 12·3%, *m/e*, 1093·695. $C_{20}H_{10}O_6F_{24}FeP_4$ requires C, 22·0; H, 0·9; F, 41·6; Fe, 15·3; P, 11·3%, *m/e*, 1093·709).

Photolysis of $(\pi\text{-}C_5H_5)Fe(CO)_2P(S)(CF_3)_2$.—The iron complex (0·174 g, 0·462 mmol), dissolved in acetone in a Pyrex tube, was photolysed for 3 h. From the residue there was isolated by sublimation orange-brown *crystals* of $(\pi\text{-}C_5H_5)Fe(CO)_2SP(CF_3)_2$. m.p. 58—59° (0·015 g, 9% yield) (Found: C, 28·3; H, 1·35%, *m/e*, 377·9016. $C_9H_5O_2F_6FeS$ requires C, 28·6; H, 1·31%, *m/e*, 377·9001), the starting material (0·010 g, 0·03 mmol), and a trace of $(\pi\text{-}C_5H_5)Fe(CO)_2SP(S)(CF_3)_2$.

In another photolysis, $(\pi\text{-}C_5H_5)Fe(CO)_2P(S)(CF_3)_2$ (0·215 g, 0·57 mmol) contaminated by small amounts of sulphur was irradiated in dichloromethane solution (1 day) with intermittent removal of non-condensible gas. On sublimation of the solid residue, *crystals* of $(\pi\text{-}C_5H_5)Fe(CO)_2SP(S)(CF_3)_2$, m.p. 80—81° (0·0124 g, 0·03 mmol) (Found: C, 26·4; H, 1·3. $C_9H_5O_2F_6FePS_2$ requires C, 26·4; H, 1·2%). A trace of sulphur was also obtained by sublimation at higher temperature.

Photolysis of $(\pi\text{-}C_5H_5)Fe(CO)_2P(Se)(CF_3)_2$.—The selenium complex (0·086 g, 0·22 mmol), in acetone solution, was irradiated through Pyrex glass for 3 h. Sublimation in a vacuum at 40—50° gave the *isomeric compound*, $(\pi\text{-}C_5H_5)Fe(CO)_2SeP(CF_3)_2$, m.p. 68—69° (Found: C, 25·4; H, 1·3%, *m/e*, 425·8434. $C_9H_5O_2F_6FePSe$ requires C, 25·4; H, 1·15%, *m/e*, 425·8445).

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