Reaction of some Fluorocarbon Bisphosphines with Iron Carbonyl Complexes

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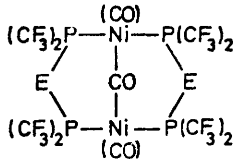
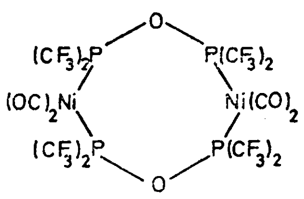
Reaction of the bisphosphines $[(CF_3)_2P]_2E$ with $Fe(CO)_2(NO)_2$ and $Fe_2(CO)_9$ gives the complexes $Fe(CO)(NO)_2[(CF_3)_2PEP(CF_3)_2]$ (E = O, S, and Se) and $Fe(CO)_4[(CF_3)_2PEP(CF_3)_2]$ (E = O and S) respectively all of which have unidentate bisphosphine ligands co-ordinated through phosphorus. With $Fe_2(CO)_9$, the selenide gives a binuclear complex, $Fe_2(CO)_6P_2(CF_3)_4Se$, which appears to have a five-membered Fe_2P_2Se ring. The action of $[(CF_3)_2P]_2O$ upon $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ yields $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P_2(CF_3)_4O$ as the major product, whereas the sulphide and selenide give $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ together with $(\pi\text{-}C_5H_5)Fe(CO)_2P(E)(CF_3)_2$ (E = S or Se).

THE interesting series of compounds $[(CF_3)_2P]_2E$ (E = O, S, and Se) has no direct analogue in hydrocarbon–phosphorus chemistry, where the isomers with a P–P bond are preferred. Burg and Sinclair have shown that the bisphosphines $[(CF_3)_2P]_2E$ (E = O, S, NMe, and NH) act as non-chelating bifunctional ligands towards tetracarbonylnickel,[1,2] forming the complexes (*A*) and (*B*). Some hydrocarbon analogues of these ligands can be stabilised as bridging groups, as shown by the preparation of $(OC)_5Mo(PR_2OPR_2')Mo(CO)_5$ (R and R' = Me or Ph)[3] and $(OC)_5W(PMe_2EPMe_2)W(CO)_5$ (E = O, S, and NMe)[4] by indirect methods. This paper reports the action of the ligands $[(CF_3)_2P]_2E$ (E = O, S, and Se) on some iron carbonyl complexes.

(*A*)



(*B*)



Reaction of the bisphosphines with dicarbonyldinitrosyliron gives $Fe(CO)(NO)_2[(CF_3)_2PEP(CF_3)_2]$ (I; E = O. II; E = S. III; E = Se). Weak bands

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[1] R. A. Sinclair and A. B. Burg, *J. Amer. Chem. Soc.*, 1966, **88**, 5354.

[2] R. A. Sinclair and A. B. Burg, *Inorg. Chem.*, 1968, **7**, 2160.

[3] C. S. Kraihanzel and C. M. Bartish, *J. Amer. Chem. Soc.*, 1972, **94**, 3572.

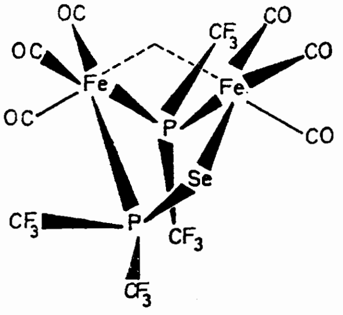
[4] H. Vahrenkamp, *Chem. Ber.*, 1972, **105**, 3574.

in the solution i.r. spectrum of the diphosphoxane complex at 910 and 711 cm^{-1} can be assigned to the two ν(P–O–P) vibrations by comparison with ν_{antisym} (P–O–P) at 925 cm^{-1} and ν_{sym} (P–O–P) at 717 cm^{-1} in $[(CF_3)_2P]_2O$ itself,[5] suggesting that there is little change in the P–O–P bond angle on co-ordination. The inequivalence of the phosphorus atoms in each of the complexes (I)—(III) follows from the ^{19}F n.m.r. spectra which show two areas of absorption of equal intensity for each complex; the signals appear as doublets because of F–C–P coupling. The chemical shift of one signal is close to that of the corresponding free ligand and therefore represents the CF_3 groups at an unco-ordinated phosphorus atom whereas the other signal, assigned to the CF_3 groups at a co-ordinated phosphorus atom, is moved to significantly higher field, as generally found for $(CF_3)_2PX$ ligands.[6] Further coupling between the CF_3 groups at the co-ordinated end of the ligand and the free phosphorus atom in (II) and (III) results in the high field signal appearing as a doublet of doublets. A similar effect has been noted[7] in $(CF_3)_2P(S)SP(CF_3)_2$ where $^4J(FP^{III})$ is 4·9 Hz but $^4J(FP^{V})$ is only 0·6 Hz. The n.m.r. spectra of (I)—(III) are unchanged over the temperature range 303—220 K.

The action of the diphosphoxane and sulphide on $Fe_2(CO)_9$ gives $Fe(CO)_4[(CF_3)_2PEP(CF_3)_2]$ (IV; E = O. V; E = S). Four bands are seen in the i.r. spectrum of (IV) in the terminal ν(CO) region, in addition to a weak low frequency ^{13}CO band. Assuming trigonal bipyramidal geometry about iron, this does not allow differentiation between equatorial ($2a_1 + b_1 + b_2$) or axial ($2a_1 + e$) substitution with the *e* mode split by the ligand asymmetry, or a mixture of isomers. Bands at 903 and 712 cm^{-1} can be assigned to ν(P–O–P). The sulphide complex (V) has five bands in the terminal ν(CO) region, suggesting a mixture of isomers. Both complexes show a doublet and a doublet of doublets in the ^{19}F n.m.r. spectrum, the areas of the two regions of absorption being equal, as for complexes (II) and (III). Although the spectrum of the sulphide (V) is invariant over the range 303—196 K, that of (IV) shows a slight broadening at lower temperatures such that ^4J(FP) is no longer observed. The spectra preclude the presence of polysubstituted derivatives of $Fe(CO)_5$.

The isolation of mononuclear complexes in high yield from the reactions of the bisphosphines with $Fe(CO)_2(NO)_2$ and $Fe_2(CO)_9$ demonstrates that the free phosphorus atom of the ligand is not activated upon co-ordination. This is to be contrasted with diphosphines where complexes with only one phosphorus atom co-ordinated are uncommon.

When the selenide $[(CF_3)_2P]_2Se$ reacts with $Fe_2(CO)_9$, the product is $Fe_2(CO)_6P_2(CF_3)_4Se$, (VI). The ^{19}F n.m.r. spectrum consists of two broad signals of equal intensity, which sharpen slightly on cooling to 198 K; both are in the region expected for trivalent phosphorus, and the spectrum is unaffected by change of solvent. There are therefore two chemical environments for the $P(CF_3)_2$ groups and the molecule is undergoing an exchange process, probably intramolecular, with a low barrier of activation. Under electron impact in a mass spectrometer the complex shows a well defined parent ion and peaks corresponding to the loss of six CO groups as well as a similar series of peaks containing no selenium. The solution is diamagnetic and so the presence of a metal–metal bond is suggested, possibly bent as in $Fe_2(CO)_6[P(CF_3)_2]_2$,[8] as shown. The averaging of the CF_3 groups within each phosphido unit can best be explained by inversion of the metal–metal bond through the ring, as has been postulated for $[Fe(CO)_3P(CF_3)_2]_2$,[8] perhaps accompanied by twisting of the five-membered Fe_2P_2Se ring, which would be anticipated to have a low energy of activation. The formation of (VI) is analogous to that of di-μ-phosphido complexes from the reaction of diphosphines with $Fe_2(CO)_9$.[9] Presumably the soft selenium atom assists the breakdown of a mononuclear intermediate.



(VI)

Reaction of $[(CF_3)_2P]_2S$ and of $[(CF_3)_2P]_2Se$ with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ proceeds without displacement of carbonyl groups, suggesting that initial attack is at or by the iron–iron bond, followed by P–S or P–Se bond-breaking. Equimolar amounts of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ and of $(\pi\text{-}C_5H_5)Fe(CO)_2P(S)(CF_3)_2$ (VII)[10] or $(\pi\text{-}C_5H_5)Fe(CO)_2P(Se)(CF_3)_2$ (VIII) are formed. The selenium complex, which has a structure similar to the oxygen and sulphur analogues,[10] has since been prepared from selenium and $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$. Spectroscopic data for complexes (VII) and (VIII) are given in the Table. With $[(CF_3)_2P]_2O$, the iron dimer $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ gives a new type of complex, molecular formula $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P_2(CF_3)_4O$ (IX), in addition to small quantities of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ and $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$. It is clear that these are the products of competing reactions, for it has been shown in a separate experiment[10] that (IX) is not formed by the action of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ on

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[5] J. E. Griffiths and A. B. Burg, *J. Amer. Chem. Soc.*, 1962, **84**, 3442.

[6] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 363; R. C. Dobbie, *J. Chem. Soc.* (*A*), 1971, 230; R. C. Dobbie and D. Whittaker, *J.C.S. Dalton*, 1973, 2427.

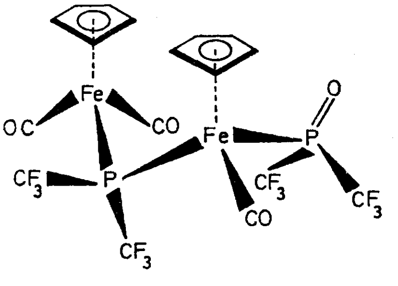
[7] A. A. Pinkerton and R. G. Cavell, *J. Amer. Chem. Soc.*, 1971, **93**, 2384.

[8] J. Grobe, *Z. anorg. Chem.*, 1968, **361**, 32.

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

[10] R. C. Dobbie and P. R. Mason, *J.C.S. Dalton*, 1973, 1124; unpublished results.

$(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$. Although the mass spectrum of (IX) does not show the parent ion, the (M − CO) ion was identified by mass measurement. In solution, the i.r. spectrum shows three ν(CO) bands and an absorption at 1207 cm^{-1} tentatively assigned to ν(P=O) [*cf.* 1210 cm^{-1} in $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$ [10]]; there was no band corresponding to ν(P–O). Two slightly broadened singlets of equal intensity were observed in the ^1H n.m.r. spectrum. Typical ^{19}F n.m.r. spectra over the range 301—233 K are shown in the Figure; below 233 K, the complex precipitated from solution. Although it appears that a limiting spectrum has not been reached, the spectra show that there are two $P(CF_3)_2$ units in chemically distinct environments and within each unit the CF_3 groups are inequivalent. The low field absorptions are close in chemical shift and F–C–P coupling constant to those found in other compounds with a $P(CF_3)_2$ phosphido group, whereas the n.m.r. parameters for the high-field absorptions are close to those of $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$.[10] Assuming that the inert gas rule is obeyed, there can be at most one bridging phosphorus group and the evidence suggests that it is the $P(CF_3)_2$ group. The proposed structure (Figure) appears more probable than that with $(\pi\text{-}C_5H_5)Fe(CO)_2$ and $(\pi\text{-}C_5H_5)Fe(CO)[P(CF_3)_2][P(O)(CF_3)_2]$ units joined by an Fe–Fe bond. The inequivalence of the CF_3 groups arises from the bonding of phosphorus to the asymmetric iron centre and the temperature dependence of the spectrum can be explained by hindered rotation about the bridging phosphorus atom.



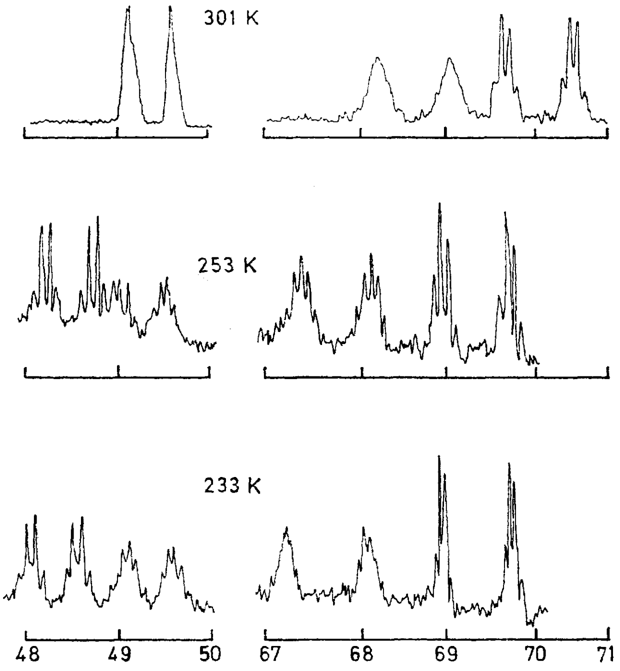
(IX)

In conclusion the type of behaviour previously recognised for fluorocarbon bisphosphines as ligands has been considerably expanded in this study of iron carbonyl complexes.

Spectroscopic data for some iron complexes

		ϕA [a,b]	$^2J(FP_A)$ [c]	ϕB	$^2J(FP_B)$	$^4J(F_BP_A)$	ν(CO) and ν(NO) [d]
(I)	$Fe(CO)(NO)_2[(CF_3)_2POP(CF_3)_2]$ [e]	63·8	94	67·0	104·5 [f]		2068s, 1821s, 1775vs
(II)	$Fe(CO)(NO)_2[(CF_3)_2PSP(CF_3)_2]$ [g]	54·8	81	61·4	81	5	2062vs, 1817vs, 1772vs
(III)	$Fe(CO)(NO)_2[(CF_3)_2PSeP(CF_3)_2]$ [h]	52·7	75	59·9	81	4	2060s, 1813s, 1768vs
(IV)	$Fe(CO)_4[(CF_3)_2POP(CF_3)_2]$	63·5	92	68·1	97	3	2102m, 2093wsh, 2038vs, 2021vs, 2005wsh
(V)	$Fe(CO)_4[(CF_3)_2PSP(CF_3)_2]$	54·4	81	62·6	81	5	2102m, 2093wsh, 2070vw, 2038vs, 2018vs
(VI)	$Fe_2(CO)_6P_2(CF_3)_4Se$	45·3		55·4			2091vs, 2077vw, 2063wsh, 2059s, 2049s, 2037wsh, 2014vw
(VII)	$(\pi\text{-}C_5H_5)Fe(CO)_2P(S)(CF_3)_2$	67·0	71				2062vs, 2021vs
(VIII)	$(\pi\text{-}C_5H_5)Fe(CO)_2P(Se)(CF_3)_2$	65·4	67				2062vs, 2021vs
(IX)	$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P_2(CF_3)_4O$ [i]	48·3, 49·3	43, 42	67·7, 69·3	63, 62		2071vs, 2022vs, 1976vs

[a] The subscript A refers to the unco-ordinated end of the ligand in the monomers (I)—(V), and to the $P(CF_3)_2$ bridging group in (VI) and (IX). [b] Chemical shifts in p.p.m. relative to CCl_3F. [c] Coupling constants in Hz. [d] Recorded in CCl_4 solution except for (IV) and (V), recorded in vapour phase. Band positions in cm^{-1}. [e] For $[(CF_3)_2P]_2O$, ϕ = 64·7. [f] No fine structure observable. [g] For $[(CF_3)_2P]_2S$, ϕ = 56·4. [h] For $[(CF_3)_2P]_2Se$, ϕ = 54·2. [i] Other unresolved couplings also present (see text). ^1H n.m.r. shows singlets at τ 4·58 and 4·94.



^{19}F N.m.r. spectra of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P_2(CF_3)_4O$; the low field region in the spectrum at 301 K has been reduced in intensity by a factor of 2 for convenience of presentation

EXPERIMENTAL

Volatile compounds were handled in a Pyrex vacuum system. Solutions were protected by an atmosphere of nitrogen. The bisphosphines $[(CF_3)_2P]_2O$,[5] $[(CF_3)_2P]_2S$,[11] and $[(CF_3)_2P]_2Se$ [12] were prepared according to the literature methods. ^{19}F N.m.r. spectra were recorded at 84·66 MHz in CCl_4 or CCl_3F solutions, with CCl_3F as internal standard. Mass spectra were recorded on an A.E.I. MS 9 instrument at an ionising voltage of 70 eV, and i.r. spectra on a Perkin-Elmer 457 spectrometer. Because of the thermal instability of the liquid samples, iron analyses were performed in these laboratories by atomic absorption spectroscopy, using a Perkin-Elmer 103 spectrometer.

Reactions of $Fe(CO)_2(NO)_2$ *with* $[(CF_3)_2P]_2E$.—After 16 days at 20°, the carbonyl complex (0·130 g, 0·76 mmol) and the diphosphoxane (0·362 g, 1·02 mmol) gave the red-brown *liquid* $Fe(CO)(NO)_2[(CF_3)_2POP(CF_3)_2]$ (0·231 g, 0·48 mmol, 64% yield) (Found: Fe, 11·3. Calc. for $C_5F_{12}FeN_2O_4P_2$: Fe, 11·2%) as well as excess of $[(CF_3)_2P]_2O$ (0·149 g, 0·42 mmol) and carbon monoxide. Under similar conditions, $[(CF_3)_2P]_2S$ gave the dark red *liquid* $Fe(CO)(NO)_2[(CF_3)_2PSP(CF_3)_2]$ (Found: Fe, 10·8. Calc. for $C_5F_{12}FeN_2O_3P_2S$: Fe, 10·9%) in 51% yield, and $[(CF_3)_2P]_2Se$ gave the liquid *complex* $Fe(CO)(NO)_2[(CF_3)_2PSeP(CF_3)_2]$ (Found: Fe, 9·7. Calc. for $C_5F_{12}FeN_2O_3P_2Se$: Fe, 10·0%) in 77% yield.

Reactions of $Fe_2(CO)_9$ *with* $[(CF_3)_2P]_2E$.—The iron carbonyl (0·161 g, 0·44 mmol) and the diphosphoxane (0·340 g, 0·96 mmol) reacted (19 days) to give CO (0·51 mmol), $Fe(CO)_5$ (0·028 g, 0·14 mmol), the excess of the ligand (0·168 g, 0·47 mmol) and the yellow liquid *complex* $Fe(CO)_4[(CF_3)_2POP(CF_3)_2]$ (0·216 g, 0·41 mmol, 84% yield based on the ligand consumed) (Found: Fe, 10·2. Calc. for $C_8F_{12}FeO_5P_2$: Fe, 10·7%). Similarly prepared was the *complex* $Fe(CO)_4[(CF_3)_2PSP(CF_3)_2]$ (93% yield based on ligand consumed) [Found: Fe, 10·2. Calc. for $C_8F_{12}FeO_4P_2S$: Fe, 10·4%]. The new compounds decomposed substantially when pure samples were left for a few days at room temperature in a vacuum. After 12 days at 20°, $[(CF_3)_2P]_2Se$ (1·278 g, 3·07 mmol) and $Fe_2(CO)_9$ (1·00 g, 2·74 mmol) gave CO and the excess of the ligand (0·197 g, 0·47 mmol) as the only volatile products. Sublimation of the solid residue gave black *crystals*, m.p. 139°, brown to transmitted light, of $Fe_2(CO)_6P_2(CF_3)_4Se$ (0·571 g, 0·83 mmol, 32% yield based on selenide used) (Found: C, 17·3; F, 32·7; Fe, 15·8; Se, 11·3. Calc. for $C_{10}F_{12}Fe_2O_6P_2Se$: C, 17·2; F, 32·7; Fe, 16·0; Se, 11·3%).

Reactions of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ *with* $[(CF_3)_2P]_2E$.—The diphosphoxane (0·621 g, 1·75 mmol) and the iron dimer (0·362 g, 1·02 mmol) in CCl_3F as solvent were shaken at 40° (1 day). The excess of $[(CF_3)_2P]_2O$ (0·188 g, 0·53 mmol) was recovered from the volatile products along with CO, and the residue was fractionally sublimed twice to separate small amounts of $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ and $(\pi\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$ from the orange crystalline *complex* $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P_2(CF_3)_4O$ (0·432 g, 0·64 mmol, 63% yield) (Found: C, 30·1; H, 1·5; F, 33·5; Fe, 16·3. Calc. for $C_{17}H_{10}F_{12}Fe_2O_4P_2$: C, 30·0; H, 1·5; F, 33·5; Fe, 16·4%, m.p. 157°). The sulphide (0·429 g, 1·16 mmol) and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (0·187 g, 0·53 mmol) in CCl_3F solution (6 days at 20°) left a yellow-orange residue (0·381 g) on removal of solvent and the excess of ligand. No CO was evolved. The complex $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ was not recovered quantitatively from the residue because of its volatility but $(\pi\text{-}C_5H_5)Fe(CO)_2P(S)(CF_3)_2$ (0·193 g, 0·51 mmol) was isolated in 96% yield by sublimation. Under similar conditions, the selenide (0·422 g, 1·01 mmol) and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (0·183 g, 0·52 mmol) gave $(\pi\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ (0·075 g, 0·22 mmol) and the *complex* $(\pi\text{-}C_5H_5)Fe(CO)_2P(Se)(CF_3)_2$ (0·216 g, 0·51 mmol, 98% yield) [Found: C, 25·6; H, 1·3%; *m/e* 425·8455 (for ^{56}Fe and ^{80}Se isotopes). Calc. for $C_9H_5F_{12}Fe_2O_2P_2Se$: C, 25·4; H, 1·15%; *m/e* 425·8445, m.p. 201°] as large orange crystals. No CO was evolved in the reaction.

We thank the S.R.C. for a maintenance grant (to M. J. H.) and Dr. B. E. Prater for the iron analyses.

[3/2601 *Received, 28th December,* 1973]

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[11] (*a*) R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 1964, 5825; (*b*) A. B. Burg and K. Gosling, *J. Amer. Chem. Soc.*, 1965, **87**, 2113.

[12] R. C. Dobbie and M. J. Hopkinson, *J. Fluorine Chem.*, 1973, **3**, 367.