The Reaction of Iron Carbonyl Complexes with Bis(trifluoromethyl)phosphine and Tetrakis(trifluoromethyl)diphosphine †

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The reaction of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with the secondary phosphine $(CF_3)_2PH$ at 80—90° gives $Fe_2(CO)_6[P(CF_3)_2]_2$ and $H_2Fe_2(CO)_6[P(CF_3)_2]_2$, a metal dihydride complex which is shown by n.m.r. spectroscopy to exist in solution as *cis*- and *trans*-isomers with axial hydrogen atoms; the deuteride, $D_2Fe_2(CO)_6[P(CF_3)_2]_2$ is prepared from $Fe_3(CO)_{12}$ and $(CF_3)_2PD$. The action of the phosphine on $Fe_2(CO)_9$ at 20°, however, gives $Fe(CO)_4[P(CF_3)_2H]$, which decomposes to the dihydride on heating, whilst with $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$, $\pi\text{-}C_5H_5Fe(CO)_2P(CF_3)_2$ is formed. The diphosphine $[(CF_3)_2P]_2$ reacts with all three binary iron carbonyls to give $Fe_2(CO)_6[P(CF_3)_2]_2$. The action of $(CF_3)_2PH$ or $[(CF_3)_2P]_2$ on dinitrosyldicarbonyliron leads to the formation of $Fe_2(NO)_4[P(CF_3)_2]_2$.

SINCE the first preparation of perfluoromethyl derivatives of phosphorus in 1953,[1] investigations have shown that the replacement of a methyl group as a substituent at phosphorus by a trifluoromethyl group markedly alters the properties of a compound.[2] Many compounds whose structure and reactivity have no parallel amongst alkyl or aryl phosphines have been prepared; the differences are largely attributable to the strongly electron-withdrawing properties of the CF_3 group. The reports to date concerning the transition-metal chemistry of perfluoromethylphosphines have indicated that in organometallic chemistry also, unusual structures can be stabilised by the presence of such ligands, although much remains to be investigated. In an interesting series of papers, Grobe has reported some new bis(trifluoromethyl)phosphido-bridged dimeric complexes of Mn,[3] Fe,[4,5] and Co,[6] generally prepared by the action of halogenobis(trifluoromethyl)phosphines upon metal carbonyl derivatives. The reaction of pentacarbonylmanganese hydride with the compounds $(CF_3)_2PX$ resulted either in the substitution of a carbonyl group by a phosphine ligand ($X = F$, CH_3, or CF_3) to give *cis*- and *trans*-isomers of $HMn(CO)_4[P(CF_3)_2X]$ or in exchange to give $(CF_3)_2PH$ and halogenocarbonyls ($X = Cl$, Br, or I).[7] Clearly the ligand-properties of bis(trifluoromethyl)phosphino-derivatives depend upon the substituent X.

It has been reported [8] that the action of bis(trifluoromethyl)phosphine, $(CF_3)_2PH$, upon bis(π-cyclopentadienyl)nickel gives $[(\pi\text{-}C_5H_5)NiP(CF_3)_2]_2$, which has bridging phosphido-groups, and $C_5H_7P(CF_3)_2$, a cyclopentene derivative; other phosphines, PR_3 ($R = F$ [9] or alkyl [10]), react to give $Ni(PR_3)_4$. This unusual reaction, whose mechanism is not understood, prompted a comprehensive study of the properties of the secondary phosphine $(CF_3)_2PH$ as a ligand. The study was also justified by the paucity of reports concerning the use of secondary phosphines as ligands although tertiary phosphines and PH_3 itself have been extensively studied. In this paper the reactions of $(CF_3)_2PH$ with iron carbonyl complexes are reported. Most of the reactions resulted in the formation of phosphorus-bridged complexes. A general preparative route [11] to such alkyl- or aryl-phosphido-compounds involves the action of the appropriate diphosphine on a metal carbonyl derivative, and hence the action of tetrakis(trifluoromethyl)diphosphine upon iron carbonyls was also investigated.

Although bis(trifluoromethyl)phosphine did not react with pentacarbonyliron at room temperature, at 100° there was a 1 : 1 reaction to give di-μ-bis(trifluoromethyl)phosphido-hexacarbonyldi-iron dihydride, $H_2Fe_2(CO)_6[P(CF_3)_2]_2$, a stable metal hydride complex of a new structural type, together with $Fe_2(CO)_6[P(CF_3)_2]_2$ in smaller yield. When dodecacarbonyltri-iron was used in place of pentacarbonyliron similar results were obtained. The hydrido-compound showed the parent ion in the mass spectrum while in the i.r. spectrum (Table 1) carbonyl absorptions were detected in the terminal region only, above 2000 cm^{-1}. A feature of the mass spectrum was that the primary loss from the parent ion appeared to be of a molecule of formaldehyde, H_2CO. This was confirmed by the mass spectrum of

TABLE 1

Infrared spectra of the iron complexes

Compound	Absorption bands (cm^{-1}) ν(C–O) or ν(N–O) region	ν(C–F) region
$H_2Fe_2(CO)_6[P(CF_3)_2]_2$ [a]	2105vw,sh, 2095vs 2054vs, 2016w	1175s, 1149s 1135s
$D_2Fe_2(CO)_6[P(CF_3)_2]_2$ [a]	2102vw,sh, 2094vs 2050vs, 2012w	1174s, 1147s 1135s
$Fe(CO)_4[P(CF_3)_2H]$ [b]	2099s, 2069vw 2022vs,sh, 2017vs 1980w	1205s, 1179s 1148s, 1134m,sh
$Fe_2(NO)_4[P(CF_3)_2]_2$ [a]	1822s,1798s	1183s, 1156m 1140sh, 1135s
$\pi\text{-}C_5H_5Fe(CO)_2P(CF_3)_2$ [a]	2049vs, 2008vs	1167vs, 1121vs 1080m, 1053sh

[a] CCl_4 solution. [b] Vapour phase.

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† Preliminary communication, R. C. Dobbie and D. Whittaker, *Chem. Comm.*, 1970, 796.

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

[2] A. B. Burg, *Accounts Chem. Res.*, 1969, **2**, 353.

[3] J. Grobe, *Z. anorg. Chem.*, 1964, **331**, 63.

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

[5] J. Grobe, *Z. anorg. Chem.*, 1969, **361**, 47.

[6] J. Grobe and H. Stierand, *Z. anorg. Chem.*, 1969, **371**, 99.

[7] R. C. Dobbie, *J. Chem. Soc. (A)*, 1971, 230.

[8] R. C. Dobbie, M. Green, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1969, 1881.

[9] J. F. Nixon, *J. Chem. Soc. (A)*, 1967, 1136.

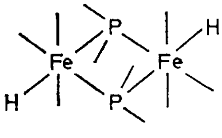
[10] J. R. Olechowski, C. G. McAlister, and R. F. Clark, *Inorg. Chem.*, 1965, **4**, 246.

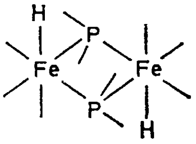
[11] R. G. Hayter, *Preparative Inorg. Reactions*, 1965, **3**, 211.

$D_2Fe_2(CO)_6[P(CF_3)_2]_2$ which showed initial loss of D_2CO; in both cases the proposed mode of fragmentation was supported by observation of the appropriate metastable peak. An alternative explanation is that the molecule suffered almost simultaneous loss of H_2 and CO, leading to the production of a compounded metastable peak.

In the presence of air, solutions of the complex in chlorinated solvents were stable at room temperature for a few hours, but after 15 h the i.r. spectrum showed new bands which could be assigned to $Fe_2(CO)_6[P(CF_3)_2]_2$.[4] Traces of acetone rapidly catalysed this otherwise slow conversion. The complex was also soluble in hydrocarbon solvents, but acetone, ether, or acetonitrile caused complete decomposition. Pentacarbonyliron, from which the compound could be recovered, was used as a solvent for n.m.r. studies.

The ^1H n.m.r. spectrum of a freshly prepared solution of $H_2Fe_2(CO)_6[P(CF_3)_2]_2$, purified either by sublimation or crystallisation, showed a 1 : 2 : 1 triplet at τ 15·82, with adjacent peaks separated by 44·7 Hz. The resonance is in the region normally associated with terminal rather than bridging metal-hydride ligands. As the ^{19}F n.m.r. spectrum showed a single complex resonance, which could be analysed[12] as an example of an $[AX_6]_2$ spin system * ($A = {}^{31}P$; $X = {}^{19}F$), the compound has chemically equivalent fluorine atoms so that a choice must be made between the isomeric forms with *trans*-hydrogen atoms (partial structures I and II).


(I)


(II)

All the coupling constants theoretically accessible from the ^{19}F spectrum other than those reported in Table 2 are unresolvably small and this reduces the complexity considerably. The same is true of the *cis*-complex (*vide infra*). The diequatorial isomer (I) with an $[AM]_2$ ($M = {}^1H$) spin system would show a complex ^1H spectrum unless

$$|{}^2J_{PP}| \gg {}^2J_{HP}(trans) - {}^2J_{PH}(cis)$$

Analysis of the ^{19}F n.m.r. spectrum[12] gave $^2J_{PP}$ = 175 Hz, and the available data from analogous compounds suggest that it is unlikely that the condition be fulfilled. If, however, the condition is met, then a ' deceptively simple ' spectrum consisting of a triplet would be obtained. In such cases the central line is frequently broader than, and in height less than twice as great as, the outer lines. On the other hand, the diaxial isomer (II) would show a simple 1 : 2 : 1 triplet; the value of $^2J_{HP}(cis)$ would be similar to that measured in $Mn_2(CO)_8[H][P(CF_3)_2]$ where $^2J_{HP}$ = 36·0 Hz.[3] Thus the observed spectrum supports structure (II) rather than (I). Further evidence comes from the isomerisation of the *trans*-complex to a *cis*-diaxial complex (discussed below) and from the preparation of the analogous *trans*-diaxial compound $I_2Fe_2(CO)_6[P(CF_3)_2]_2$ by Grobe[4] from iodobis(trifluoromethyl)phosphine and pentacarbonyliron.

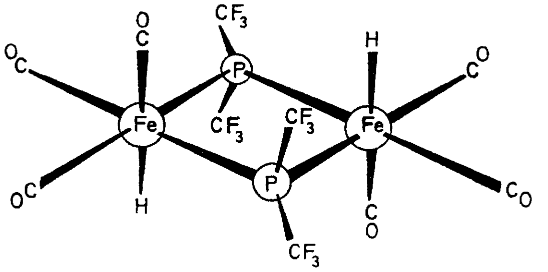
TABLE 2

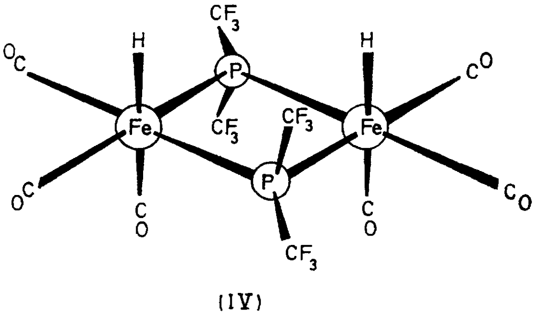
N.m.r. parameters for the iron complexes

Compound	τ	J_{HP} [a]	ϕ [b]	$^2J_{FP}$	$^2J_{PP}$	$^4J_{FP}$
trans-$H_2Fe_2(CO)_6$-$[P(CF_3)_2]_2$	15·82	44·7	56·5	55	175	1·0
cis-$H_2Fe_2(CO)_6$-$[P(CF_3)_2]_2$ [c]	15·60	41·8	55·7 57·9	55 55	175	1·0 1·0
$Fe(CO)_4[P(CF_3)_2H]$ [d]	3·87	356	57·2	79		
$Fe_2(NO)_4[P(CF_3)_2]_2$			49·5	95	155	−0·8
π-$C_5H_5Fe(CO)_2P(CF_3)_2$	4·60	2·3	45·5	54		
$(CF_3)_2PH$ [e,f]	5·45	218	47·5	69		

[a] Coupling constants are in Hz. [b] Relative to $CFCl_3$ in p.p.m. [c] $^4J_{FF}$ = 8·0 Hz. [d] $^4J_{FH}$ = 6·9 Hz. [e] $^4J_{FH}$ = 9·7 Hz. [f] K. J. Packer, *J. Chem. Soc.*, 1963, 960.

Solutions of *trans*-$H_2Fe_2(CO)_6[P(CF_3)_2]_2$ which had stood at room temperature for some time showed additional n.m.r. signals, a new triplet appearing at τ 15·60 ($^2J_{HP}$ = 42·6 Hz). The ^{19}F n.m.r. spectrum gave two additional areas of absorption corresponding to the fluorine atoms above and below the Fe_2P_2 ring, each peak being split into a quartet by coupling between the inequivalent CF_3 groups attached to a single phosphorus atom. The spectra are unambiguously characteristic of the *cis*-diaxial isomer (IV). In conclusion the spectroscopic evidence strongly suggests that the dihydride can exist in solution in the two isomeric forms (III) and (IV).


(III)


(IV)

Some further experiments were carried out to gain information about the isomerisation of the dihydride.

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* Nomenclature suggested by C. W. Haigh, *J. Chem. Soc.* (*A*), 1970, 1682.

[12] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

A solution of the complex in pentacarbonyliron which had not been rigorously dried showed the presence of *cis*- and *trans*-isomers in 5 : 9 ratio immediately on warming to room temperature. An n.m.r. tube fitted with a double constriction was used to show that a pure sample of the *trans*-isomer, uncontaminated by the *cis*-isomer, was immediately isomerised to the *cis–trans* mixture on adding a small amount of pure dry acetone in the absence of air. In dichloromethane as solvent the same relative proportion of the isomers pertained. Finally, after a solution in an n.m.r. tube was heated to 85° (5 h) and then cooled, no change in the isomeric distribution could be found. As the rate of equilibration is solvent dependent, the mechanism of the isomerisation is clearly intermolecular, and probably involved reversible loss of protons, or less likely, carbon monoxide. The final position of the equilibrium shows that the isomers differ only slightly in stability although the activation energy for the interconversion could be appreciable. The *trans*-isomer is evidently favoured in the solid state as freshly prepared dry solutions of the complex showed only this isomer.

Having established the structure of the dihydride in solution, the observed i.r. spectrum can be discussed in more detail. Only two strong carbonyl stretching bands were observed and no band attributable to ν(Fe–H) was detected, even with the help of the spectrum of the ^{2}H compound. However, it is known[13] that metal–hydrogen stretching bands are sometimes very weak in intensity, and the limited solubility of the complex in suitable solvents made detection of weak bands difficult. Vibrational coupling across the Fe_2P_2 ring can be assumed to be negligible[4] and so only the local symmetry about the iron atom need be considered. As both isomers (III) and (IV) have identical local molecular environments (C_s local symmetry) the i.r. spectra in the carbonyl region should be almost identical. In support of this, no significant change of the spectrum with time, attributable to *trans–cis* isomerisation, could be observed. As symmetry rules predict three i.r. active ν(CO) bands, it is assumed that two are accidentally coincident, and indeed the lower frequency band at 2057 cm^{-1} is distinctly broader than the band at 2098 cm^{-1}.

The mechanism of the reaction of the phosphine with pentacarbonyliron could proceed initially by *cis*-oxidative-addition:

$$Fe(CO)_5 + (CF_3)_2PH \longrightarrow cis\text{-}HFe(CO)_4P(CF_3)_2 + CO$$

as has been proposed[4] for the analogous reaction between the iodo-phosphine, $(CF_3)_2PI$, and $Fe(CO)_5$, or by substitution:

$$Fe(CO)_5 + (CF_3)_2PH \longrightarrow Fe(CO)_4[P(CF_3)_2H] + CO$$

followed by intramolecular oxidative-addition to give the same intermediate. Alternatively, hydrogen transfer to another metal centre could occur. The high *trans*-effect of the carbonyl ligand would ensure the elimination of CO *cis* to both hydrido- and phosphido-groups, to give the dihydride. Evidence for the second of these pathways came from a study of the reaction of enneacarbonyldi-iron with bis(trifluoromethyl)phosphine which proceeded at room temperature in the dark to give bis(trifluoromethyl)phosphinetetracarbonyliron, $Fe(CO)_4[P(CF_3)_2H]$, which on pyrolysis at 100° or on standing at room temperature for some time gave $H_2Fe_2(CO)_6[P(CF_3)_2]_2$ and $Fe_2(CO)_6[P(CF_3)_2]_2$. The monomeric phosphine complex showed no high-field signals in the ^{1}H n.m.r. spectrum; instead there was clear evidence for the presence of the co-ordinated $P(CF_3)_2H$ ligand, the n.m.r. parameters (Table 2) showing the expected changes from those of the free ligand. In the carbonyl stretching region of the i.r. spectrum two intense bands, with that at lower frequency being slightly split, and two much weaker bands were observed. If trigonal-bipyramidal geometry about the iron atom is assumed, an axial phosphine ligand would lead to approximately C_{3v} symmetry (three i.r.-active carbonyl modes) whereas an equatorial phosphine would give overall C_{2v} symmetry (four i.r.-active carbonyl modes). Although the observed spectrum was not very similar to those noted for other axial $Fe(CO)_4L$ complexes,[14] the number of bands suggested axial substitution. The ^{19}F n.m.r. spectrum at −80° is identical to that at room temperature, which suggests that the molecule is not fluxional, or alternatively that the activation energy for intramolecular exchange is very low.

The reaction of tetrakis(trifluoromethyl)diphosphine with $Fe(CO)_5$, either thermally (50°) or in strong sunlight in a Pyrex tube (25°) gave $Fe_2(CO)_6[P(CF_3)_2]_2$; likewise from $Fe_3(CO)_{12}$ at 70° the products were the di-phosphido-bridged complex and $Fe(CO)_5$. Even under the milder conditions required for the reaction of the diphosphine with $Fe_2(CO)_9$ (20°; no solvent), none of the diphosphine-linked $Fe_2(CO)_8P_2(CF_3)_4$ could be isolated. This is in interesting contrast to the results obtained by Hayter[15] using the tetramethyldiphosphine ligand; its action upon pentacarbonyliron (130°, 40 h) gave the di-μ-phosphido complex, $Fe_2(CO)_6[P(CH_3)_2]_2$, whereas with dodecacarbonyltri-iron (80°, 16 h) the product was $Fe_2(CO)_8P_2(CH_3)_4$, in which the P–P bond is retained.

It is known[16] that dinitrosyldicarbonyliron normally undergoes substitution of the carbonyl groups when allowed to react with phosphines. When heated with bis(trifluoromethyl)phosphine at 80°, the product was di-μ-bis(trifluoromethyl)phosphido-tetranitrosyldi-iron, $Fe_2(NO)_4[P(CF_3)_2]_2$, showing that the CO groups were displaced in this case also. The reaction probably proceeds in a similar manner to that of the phosphine

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[13] M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 115.

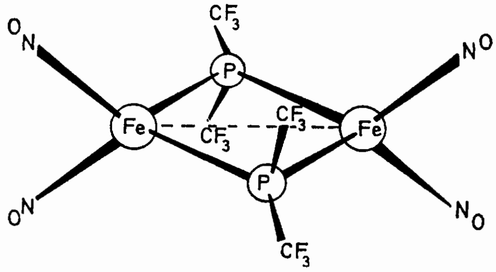
[14] B. T. Kilbourn, U. A. Raeburn, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1969, 1906.

[15] R. G. Hayter, *Inorg. Chem.*, 1964, **3**, 711.

[16] B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 1966, **7**, 277.

with pentacarbonyliron except that no nitrosyl dihydride isoelectronic with $H_2Fe_2(CO)_6[P(CF_3)_2]_2$ was isolated, although this may be formed as a reactive intermediate. The dimeric nitrosyl complex may be prepared in better yield by the action of tetrakis(trifluoromethyl)diphosphine upon $Fe(CO)_2(NO)_2$, similar to the route reported by Cullen and Hayter [17] to the arsenic compound, $Fe_2(NO)_4[As(CF_3)_2]_2$. It is notable that the analogous reaction with $(CH_3)_4P_2$ yielded [18] a mixture of di-μ-phosphido- and μ-diphosphine-complexes.

The proposed structure (V) follows from the spectroscopic properties of the complex, namely the detection of the parent ion in the mass spectrum, the presence of two strong terminal ν(N–O) bands in the i.r. spectrum, and the observation of the expected pattern for the $[AX_6]_2$ spin system in the ^{19}F n.m.r. spectrum, which indicates that the Fe_2P_2 ring is planar with all fluorine atoms chemically equivalent. As in the analogous compound $Fe_2(NO)_4(SEt)_2$,[19] the metal–metal bond, which is postulated to account for the diamagnetism of the compounds, does not occupy a co-ordination site and the geometry about each iron atom is approximately tetrahedral. Comparison of the ν(N–O) band positions in $Fe_2(NO)_4(PMe_2)_2$ (1753 and 1733 cm^{-1}) [18] with $Fe_2(NO)_4[P(CF_3)_2]_2$ (1822 and 1798 cm^{-1}) is indicative of considerably more iron–phosphorus π-bonding in the perfluoroalkyl complex.



(V)

Bis(trifluoromethyl)phosphine underwent a reaction with di(π-cyclopentadienyl)tetracarbonyldi-iron to give bis(trifluoromethyl)phosphido(π-cyclopentadienyl)dicarbonyliron, $\pi\text{-}C_5H_5Fe(CO)_2P(CF_3)_2$, which is better prepared [20] by the action of $(CF_3)_2P{\cdot}P(CF_3)_2$ on the dimeric iron carbonyl. The properties of this interesting monomeric complex are at present under active investigation. The isolation of a monomer rather than a dimer is attributable to the reduced availability of the lone pair on phosphorus for attack on another iron atom; this in turn results from the effect of the strongly electronegative CF_3 groups. As this reaction did not involve substitution of carbonyl groups by phosphine, it probably proceeds by attack at the metal–metal bond.

The most outstanding feature of this work is the prevalence of μ-phosphido-bridged complexes and their stability compared to other structural types. Thus no diphosphine-linked compounds were obtained from the reactions with tetrakis(trifluoromethyl)diphosphine although these can usually, in the case of other diphosphines, be isolated as intermediates which on pyrolysis give μ-phosphido-dimers; further, the monomeric phosphine complex $Fe(CO)_4[P(CF_3)_2H]$ is thermally unstable, giving $H_2Fe_2(CO)_6[P(CF_3)_2]_2$ on pyrolysis or even on standing at room temperature for some time. This may be interpreted as showing that the presence of CF_3 groups as substituents at phosphorus leads to an increased thermodynamic stability of the Fe_2P_2 ring.

EXPERIMENTAL

Volatile compounds were handled in a Pyrex vacuum system by standard techniques. Although the solids prepared in this work were air-stable, some solutions were air-sensitive and were handled under an atmosphere of nitrogen. I.r. spectra were recorded on a Perkin-Elmer 457 Spectrometer and mass spectra on an A.E.I. MS 9 operating at an ionising energy of 70 eV. N.m.r. spectra were recorded on a Bruker Spectrospin operating at 90·0 MHz for ^1H and 84·66 MHz for ^{19}F nuclei, with tetramethylsilane and CCl_3F as internal references. Samples for n.m.r. spectroscopy were made up in dry degassed solvent and sealed *in vacuo*. Bis(trifluoromethyl)phosphine [21] and tetrakis(trifluoromethyl)diphosphine [1] were prepared according to the literature methods; [^2H]bis(trifluoromethyl)phosphine was prepared by the action of iodobis(trifluoromethyl)phosphine on pentacarbonylmanganese deuteride.[7] Pentacarbonyliron and dicarbonyldinitrosyliron were carefully dried over phosphorus pentoxide.

Reactions of Bis(trifluoromethyl)phosphine.—With pentacarbonyliron. The phosphine and $Fe(CO)_5$ were recovered unchanged from a sealed tube, after three days in the dark at room temperature.

At 90° $Fe(CO)_5$ (0·467 g, 2·38 mmol) and $(CF_3)_2PH$ (0·355 g, 2·08 mmol) reacted (3 days) in a Carius tube (40 ml) to form crystals. When cooled to room temperature more crystals separated. Some non-condensable gas was pumped off, and the remaining volatile products were fractionated and identified as unreacted $Fe(CO)_5$ (0·260 g, 1·32 mmol) and $(CF_3)_2PH$ (0·169 g, 0·99 mmol). Careful high-vacuum fractional sublimation of the solid product at 40—50° gave two species. The more volatile was the red crystalline complex $Fe_2(CO)_6[P(CF_3)_2]_2$ [0·015 g, 0·025 mmol, 3% yield based on $(CF_3)_2PH$ consumed], m.p. 146°, identified by i.r. and mass spectrometry. The other fraction gave pale lemon crystals which were characterised as *di-μ-bis(trifluoromethyl)phosphido-hexacarbonyldi-iron dihydride*, $H_2Fe_2(CO)_6[P(CF_3)_2]_2$, (0·050 g, 0·08 mmol, 15% yield) (Found: C, 19·8; H, 0·4; Fe, 17·7%; *m/e*, 619·7839. $C_{10}H_2F_{12}Fe_2O_6P_2$ requires C, 19·4; H, 0·3; Fe, 18·0%; *m/e* 619·7857).

In the mass spectrum of the dihydride, evidence for the initial fragmentation of the parent ion to $Fe_2(CO)_5[P(CF_3)_2]_2^+$ by loss of H_2CO was given by the metastable peak at *m/e* 561·5 (calc. 561·44).

When the reaction was repeated using similar quantities

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

[18] R. G. Hayter and L. F. Williams, *Inorg. Chem.*, 1964, **3**, 717.

[19] J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, 1958, **11**, 599.

[20] R. C. Dobbie and R. J. Porter, unpublished results.

[21] R. G. Cavell and R. C. Dobbie, *J. Chem. Soc.* (*A*), 1967, 1308.

at 140° for *ca.* 30 h, the yield of $Fe_2(CO)_6[P(CF_3)_2]_2$ increased at the expense of $H_2Fe_2(CO)_6[P(CF_3)_2]_2$.

With enneacarbonyldi-iron. The phosphine (0·480 g, 2·83 mmol) and $Fe_2(CO)_9$ (0·290 g, 0·80 mmol), combined in a small (10 ml) sealed tube, reacted in a few days in the dark at 20° to give a red-brown liquid. Vacuum fractionation gave an excess of $(CF_3)_2PH$ (0·346 g, 2·03 mmol) and a mixture of $Fe(CO)_5$ and another compound. Prolonged fractionation of the mixture, with pumping at −45°, trapped *bistrifluoromethylphosphinetetracarbonyliron*, $Fe(CO)_4[P(CF_3)_2H]$, (0·173 g, 0·51 mmol, 64% based on phosphine consumed) (Found: Fe, 16·6%, *m/e*, 337·8852. $C_6HF_6FeO_4P$ requires Fe, 16·5%; *m/e*, 337·8866), a pale yellow liquid with a low vapour pressure (*ca.* 2 mm) at room temperature. Further small amounts of the phosphine complex passed through the trap at −45° along with $Fe(CO)_5$.

When a sample of $Fe(CO)_4[P(CF_3)_2H]$ (0·185 g, 0·55 mmol) was heated (100°) in a small sealed tube for 24 h, the products were $(CF_3)_2PH$ (0·020 g, 0·12 mmol), $Fe(CO)_5$ (0·14 g, 0·07 mmol), $H_2Fe_2(CO)_6[P(CF_3)_2]_2$ (0·085 g, 0·14 mmol), $Fe_2(CO)_6[P(CF_3)_2]_2$ (0·020 g, 0·03 mmol), and non-condensable gas.

Another sample gave crystals of $H_2Fe_2(CO)_6[P(CF_3)_2]_2$ after a few weeks in the dark at room temperature.

With dodecacarbonyltri-iron. The iron carbonyl [0·103 g, 0·60 mmol of '$Fe(CO)_4$'] and $(CF_3)_2PH$ (0·199 g, 1·17 mmol) were sealed in a small tube. At −22°, with the phosphine in the liquid phase, no non-condensable gas was liberated after 15 h.

After two days at 80°, non-condensable gas was removed and identified as CO with a trace of H_2 by i.r. and mass spectrometry. The remaining volatile products were fractionated to give $(CF_3)_2PH$ (0·125 g, 0·74 mmol) and a trace of $Fe(CO)_5$. High-vacuum fractional sublimation of the solid products at 50° gave $H_2Fe_2(CO)_6[P(CF_3)_2]_2$ [0·050 g, 0·08 mmol, 21% yield based on $(CF_3)_2PH$] and $Fe_2(CO)_6[P(CF_3)_2]_2$ (0·020 g, 0·03 mmol).

A similar reaction was carried out using [^{2}H]bis(trifluoromethyl)phosphine, $(CF_3)_2PD$ (0·176 g, 1·03 mmol) and $Fe_3(CO)_{12}$ (0·077 g, 0·15 mmol) to prepare *di-μ-bis(trifluoromethyl)phosphido-hexacarbonyldi-iron dideuteride*, $D_2Fe_2(CO)_6[P(CF_3)]_2$ (0·045 g, 0·07 mmol, 22% yield) (Found: *m/e*, 621·7952. $C_{10}D_2F_{12}Fe_2O_6P_2$ requires *m/e* 621·7959). In the mass spectrum of the dideuteride evidence for the initial fragmentation of the parent ion to $Fe_2(CO)_5[P(CF_3)_2]_2^+$ by loss of D_2CO was given by the metastable peak at *m/e* 559·5 (calc. 559·63).

With dinitrosyldicarbonyliron. The phosphine (0·568 g, 3·34 mmol) and $Fe(CO)_2(NO)_2$ (0·362 g, 2·11 mmol) did not react in the dark at room temperature (3 days), but at 80° (14 h) large crystals formed. After some non-condensable gas had been removed, unreacted phosphine (0·141 g, 0·83 mmol) was recovered by vacuum-fractionation. Purification of the residue by sublimation at 50° gave black lustrous crystals, m.p. 124° with decomposition, dark red to transmitted light, of *di-μ-bis(trifluoromethyl)phosphido-tetranitrosyldi-iron*, $Fe_2(NO)_4[P(CF_3)_2]_2$ [0·350 g, 0·61 mmol, 49% yield based on $(CF_3)_2PH$ consumed] (Found: C, 8·2; Fe, 19·4; N, 9·4%; *m/e* 569·7894. $C_4F_{12}Fe_2N_4O_4P_2$ requires C, 8·4; Fe, 19·7; N, 9·8%; *m/e* 569·7901).

With di-π-cyclopentadienyltetracarbonyldi-iron. The iron dimer (0·293 g, 0·90 mmol) and $(CF_3)_2PH$ (0·153 g, 0·90 mmol) were sealed in a tube and heated at 100° (7 h). Non-condensable gas was removed, and a small excess of $(CF_3)_2PH$ was detected. Fractional sublimation of the remaining solid at 50° over two days gave large orange-brown crystals of bis(trifluoromethyl)phosphido(π-cyclopentadienyl)dicarbonyliron, $\pi\text{-}C_5H_5Fe(CO)_2P(CF_3)_2$ [0·130 g; 0·38 mmol, 42% yield based on $(CF_3)_2PH$], identified by its spectroscopic properties.[20]

Reactions of Tetrakis(trifluoromethyl)diphosphine.—With pentacarbonyliron. The diphosphine and $Fe(CO)_5$ reacted in sunlight at room temperature (10 days) to give a black oil. This oil was heated at 70° *in vacuo* when some $Fe_2(CO)_6[P(CF_3)_2]_2$ was recovered leaving an intractable black tar.

The diphosphine (0·513 g, 1·52 mmol) and $Fe(CO)_5$ (0·729 g, 3·72 mmol), sealed in a tube with a Teflon 'O' ring tap, were heated at 50° (14 days) in the dark with frequent removal of non-condensable gas. Pentacarbonyliron (0·239 g, 1·22 mmol) and $[(CF_3)_2P]_2$ (0·128 g, 0·38 mmol) were recovered from the reaction and the residue purified by high-vacuum fractional sublimation at 70° giving $Fe_2(CO)_6[P(CF_3)_2]_2$ (0·475 g, 0·77 mmol, 68% yield based on diphosphine used).

With enneacarbonyldi-iron. After 8 days at room temperature a mixture of $Fe_2(CO)_9$ (0·290 g, 0·80 mmol) and the diphosphine (0·253 g, 0·75 mmol) had formed a large number of dark red crystals. Vacuum fractionation of the volatile products gave an unmeasured quantity of carbon monoxide, $Fe(CO)_5$ (0·158 g, 0·81 mmol), and $[(CF_3)_2P]_2$ (0·115 g, 0·34 mmol). Sublimation of the residue at 35—40° *in vacuo* yielded $Fe_2(CO)_6[P(CF_3)_2]_2$ (0·141 g, 0·23 mmol, 56% yield based on diphosphine used).

With dodecacarbonyltri-iron. The diphosphine (0·488 g, 1·45 mmol) and $Fe_3(CO)_{12}$ [0·549 g, 3·27 mmol of '$Fe(CO)_4$'] did not react at room temperature (3 days) but at 65° (7 days) red crystals formed. Some non-condensable gas was removed and the volatile products were found to be $[(CF_3)_2P]_2$ (0·095 g, 0·28 mmol) and $Fe(CO)_5$ (0·023 g, 0·12 mmol). High vacuum fractional sublimation of the residue at 70° gave $Fe_2(CO)_6[P(CF_3)_2]_2$ (0·573 g, 0·93 mmol, 80% yield based on diphosphine used). The unsublimed residue was $Fe_3(CO)_{12}$ (0·088 g, 0·17 mmol) identified by its characteristic i.r. spectrum in solution. The diphosphine and $Fe_3(CO)_{12}$ were found to react in a *trans*-decalin solution at 65° to give $Fe(CO)_5$ and $Fe_2(CO)_6[P(CF_3)_2]_2$ as above.

With dinitrosyldicarbonyliron. The diphosphine (0·182 g, 0·54 mmol) and $Fe(CO)_2(NO)_2$ (0·186 g, 1·08 mmol) did not react in the dark at room temperature (3 days) but at 85° (1 day) crystals formed. Some non-condensable gas was removed and the only volatile product was found to be a trace of $Fe(CO)_2(NO)_2$. High-vacuum fractional sublimation of the residue at 55° gave $Fe_2(NO)_4[P(CF_3)_2]_2$ (0·261 g, 0·46 mmol, 85% yield based on diphosphine used).

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