PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS
XX*. SOME REACTIONS OF THE BIS(PENTAFLUOROPHENYL)-DICHALCOGNIDES

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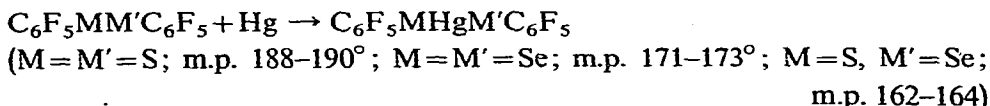
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SUMMARY

The preparation of bis(pentafluorophenyl)ditelluride is described. Bis-(pentafluorophenyl)disulphide and bis(pentafluorophenyl)diselenide react together on heating to give $C_6F_5SSeC_6F_5$. Similarly, bis(pentafluorophenyl)disulphide and diphenyldisulphide give $C_6F_5SSC_6H_5$. Heating of the dichalcognides with mercury and germanium produces $C_6F_5MHgM'C_6F_5$ (M = M' = S or Se; M = S, M' = Se) and $Ge(SC_6F_5)_4$. The Mössbauer, NMR, IR and mass spectra of ten chalcogen-bridged iron carbonyl complexes of formula $C_6F_5MFe_2(CO)_6M'R$ (M, M' = S, Se, Te; R = C_6F_5, C_6H_5) are discussed in the light of their electronic and molecular structure.

In a recent paper[2] we described several syntheses of bis(pentafluorophenyl)-disulphide and bis(pentafluorophenyl)diselenide, the most simple method being the direct heating of the elements with pentafluoroiodobenzene:

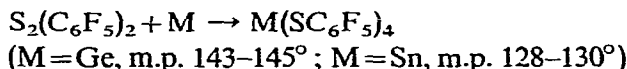$$M + C_6F_5I \rightarrow M(C_6F_5)_2 + M_2(C_6F_5)_2$$
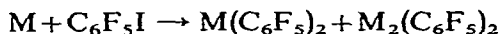
A more useful preparation of the diselenide is to treat elemental selenium with pentafluorophenylmagnesium bromide in ether solution. Unexpectedly the pure compounds do not have a very obnoxious odour and are reasonably pleasant to work with. When the disulphide and the diselenide are heated together in sealed pyrex tubes the "mixed" compound, bis(pentafluorophenyl)thioselenide, is formed and can be readily separated from the starting materials by thin layer chromatography (TLC) on kieselguhr. The chalcogen–chalcogen bonds in these three derivatives are quite reactive and can be caused to react with mercury on heating in sealed tubes:
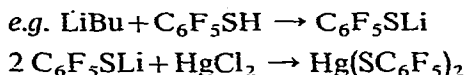
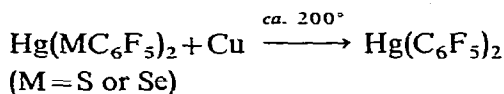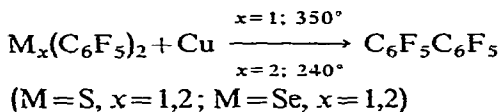$$C_6F_5MM'C_6F_5 + Hg \rightarrow C_6F_5MHgM'C_6F_5$$
(M = M' = S; m.p. 188–190°; M = M' = Se; m.p. 171–173°; M = S, M' = Se;
m.p. 162–164)

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* For part XIX, see ref. 1.

Powdered germanium and tin react similarly:

$$S_2(C_6F_5)_2 + M \rightarrow M(SC_6F_5)_4$$
(M = Ge, m.p. 143–145°; M = Sn, m.p. 128–130°)

This type of compound can also be synthesised by using the more conventional technique of treating the metal halide with pentafluorophenylthiolithium:

e.g. $LiBu + C_6F_5SH \rightarrow C_6F_5SLi$

$2 C_6F_5SLi + HgCl_2 \rightarrow Hg(SC_6F_5)_2$

Copper, however, removes the chalcogen on strong heating:

$$M_x(C_6F_5)_2 + Cu \xrightarrow[x=2:\ 240°]{x=1:\ 350°} C_6F_5C_6F_5$$
(M = S, x = 1,2; M = Se, x = 1,2)

$$Hg(MC_6F_5)_2 + Cu \xrightarrow{ca.\ 200°} Hg(C_6F_5)_2$$
(M = S or Se)

When heated with bis(pentafluorophenyl)diselenide, sulphur replaces the selenium.

Bis(pentafluorophenyl)ditelluride may be prepared by first heating either bis(pentafluorophenyl)mercury or pentafluorophenylmercuric chloride with tellurium tetrachloride to give pentafluorophenyltellurium trichloride which is then dehalogenated by treatment with zinc in alcohol:

$$TeCl_4 \xrightarrow{C_6F_5HgCl} C_6F_5TeCl_3 \xrightarrow{Zn} Te_2(C_6F_5)_2$$
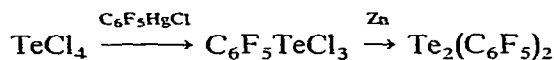
Under the conditions we employed, the treatment of tellurium tetrachloride with a deficiency of pentafluorophenyllithium yielded only tris(pentafluorophenyl)tellurium chloride. Small amounts of the ditelluride are also formed when either tellurium powder is heated with bis(pentafluorophenyl)mercury (the monotelluride, $Te(C_6F_5)_2$, is the main product) or pentafluorophenyllithium is added to tellurium powder, the mixture brominated (to give C_6F_5TeBr) and then hydrolysed with aqueous alcohol.

It is well-known that thiophenol and diphenyldisulphide react with iron carbonyls to give the dark red complex phenylthioiron tricarbonyl dimer:

$$(CO)_3$$
$$S_2(C_6H_5)_2 + Fe_3(CO)_{12} \rightarrow C_6H_5S \overset{Fe}{\underset{Fe}{\diagup\diagdown}} SC_6H_5$$
$$(CO)_3$$
(I)
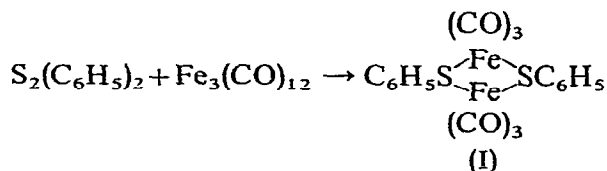
We have undertaken a close study of several similar iron carbonyl complexes (Table 1, II–XI) having bridging chalcogen atoms to ascertain the effect of the electron-withdrawing pentafluorophenyl group on their stability. Since the work started, (II) has been mentioned briefly by two groups of workers[3,4]. All the complexes are very similar in colour, are air-stable and sublime in a good vacuum at about 100°; complexes (I), (II) and (III) have the same melting–decomposition point, 140–143°. To check the comparative stability of (I) and (II), a competition reaction, involving bis-

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES $[MRFe(CO)_3]_2$

In each case the molecular weight was checked by recording the mass spectrum.

Complex		Found (Calcd.)		F%	mol.wt.
		C	H		
$[C_6H_5SFe(CO)_3]_2$	(I)				
$[C_6F_5SFe(CO)_3]_2$	(II)	32.1(31.9)	0.15(0.0)	27.8(28.3)	646 (678)
$C_6H_5SFe_2(CO)_6SC_6F_5$	(III)	37.2(37.2)	1.2 (0.9)	16.0(16.3)	
$[C_6F_5SeFe(CO)_3]_2$	(IV)	28.2(28.0)	0.0 (0.0)	24.4(24.6)	
$C_6F_5SFe_2(CO)_6SeC_6F_5$	(V)	30.0(29.8)	0.08(0.0)	—	
$[C_6H_5SeFe(CO)_3]_2$	(VI)	36.5(36.5)	1.5 (1.7)	—	
$C_6H_5SeFe_2(CO)_6SeC_6F_5$	(VII)	32.6(31.7)	0.8 (0.7)	—	
$C_6H_5SFe_2(CO)_6SeC_6H_5$	(VIII)	39.4(39.6)	2.0 (1.8)	—	
$C_6H_5SeFe_2(CO)_6SC_6F_5$	(IX)	35.4(34.0)	0.9 (0.8)	—	
$[C_6H_5TeFe(CO)_3]_2$	(X)	31.3(31.4)	1.5 (1.45)	—	
$[C_6F_5TeFe(CO)_3]_2$	(XI)	25.1, 25.2 (24.9)	0.2, 0.3(0.0)	22.15(21.9)	

(pentafluorophenyl)disulphide, diphenyldisulphide and triiron dodecacarbonyl in equimolar proportions was carried out in refluxing 80–100° petrol ether and the products separated by TLC. The ratio I/II/III of 1.0/1.0/2.0 which was obtained appears to indicate a virtually identical "bridge-coordinating ability" for SC_6H_5 and SC_6F_5. A similar experiment involving bis(pentafluorophenyl)disulphide, bis(pentafluorophenyl)diselenide and triiron dodecacarbonyl gave (II) as the predominant product indicating, as expected, that sulphur was the better ligand atom of the two.
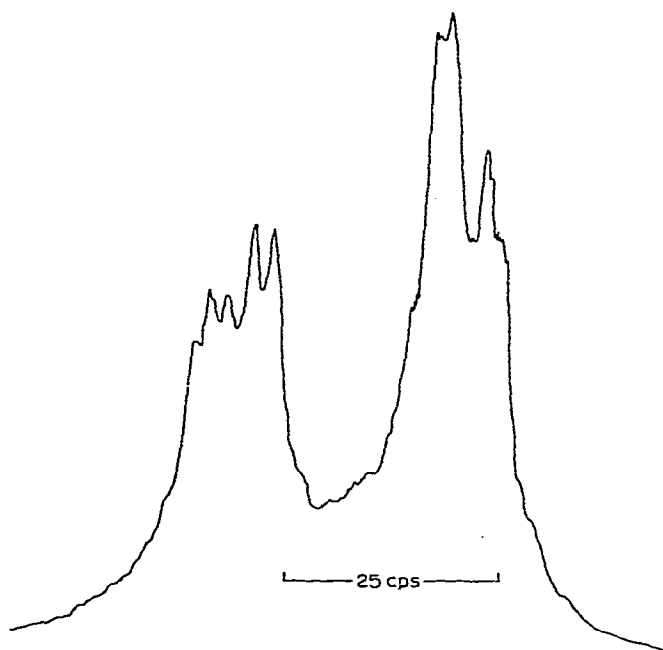

|———— 25 cps ————|

Fig. 1. Proton NMR spectrum of phenylthioiron tricarbonyl dimer recorded at 220 Mcps.

This type of bridged iron carbonyl complex can exist in isomeric forms[5,6] and indeed, with the SCH₃ group in the bridge, two isomers have been separated by chromatography[5]. However, it is not clear if isomers exist in the case of (I). Figure 1 shows the proton nuclear magnetic resonance (NMR) spectrum of (I) recorded at 220 Mcps; even at this frequency the overlap in the "phenyl region" of the spectrum makes the detection of *syn* and *anti* isomers impossible. The ratio of the two peaks, *ca.* 1/1.4, is reasonably close to that expected if they were due to the (*ortho*) and the (*meta + para*) hydrogen atoms in the isomers and not to the separate isomers themselves. This possibility is supported by the proton NMR spectrum of III which is very similar to that in Fig. 1; in this particular complex the ^{19}F NMR spectrum suggests that only one major component is present.

Figure 2 shows the ^{19}F NMR spectrum of a sample of (II) dissolved in trichlorofluoromethane (as the internal standard). It can be interpreted in terms of a
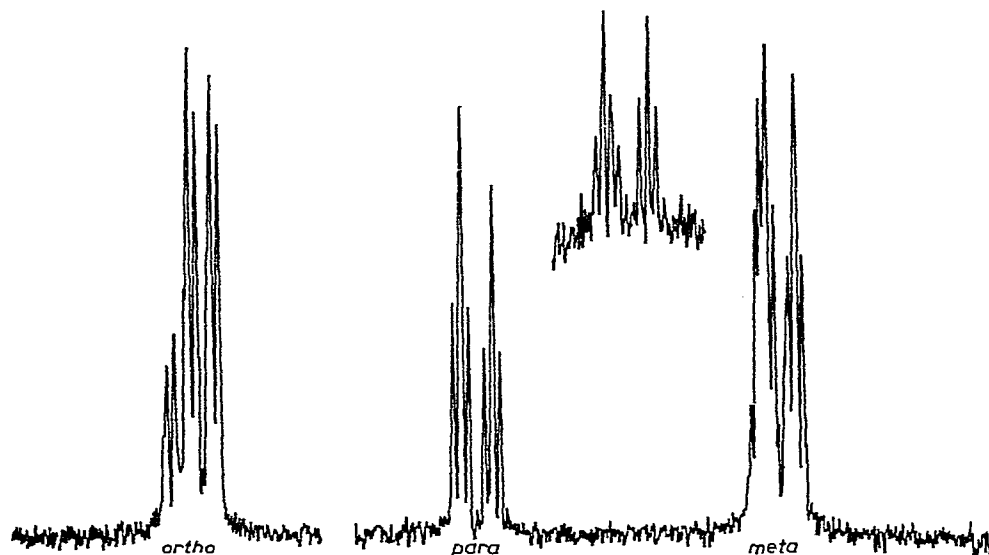

Fig. 2. The ^{19}F NMR spectrum of pentafluorophenylthioiron tricarbonyl dimer. The sample was dissolved in CFCl₃ as the internal standard. The insert shows the *para* region of the spectrum when the sample is dissolved in benzene. Shifts, relative to CFCl₃, were: large *ortho* doublet centred at 125 ppm; large *para* doublet centred at 151.6 ppm and a *meta* doublet centred at 160.8 ppm.

mixture of the *syn* and *anti* forms of the complex if these are present in the approximate ratio 1/6; peaks due to the latter isomer, which has two inequivalent pentafluorophenyl groups, show up as the three large "doublets". The *syn* isomer apparently has ^{19}F chemical shifts very close to those of the *anti* isomer, and only in the case of the *ortho* resonance peak does coincidence of the two spectra not occur. In trichlorofluoromethane solution the two *para* resonance peaks are of unequal height, the one to low field being slightly the more intense due to the *syn* isomer absorption peak lying directly underneath it; the coincidence is so exact that expansion of the spectrum failed to reveal any asymmetry of the basic triplet pattern. However, by recording the spectrum of a carbon tetrachloride or benzene solution of (II), the solute-solvent

interaction is sufficiently different for the two isomers to partially remove the peak coincidence in the case of the *para* resonance (Fig. 2) but not for the *meta* resonance. Separate experiments demonstrated that the two most likely impurities, C_6F_5SH and $(C_6F_5)_2S_2$ are not responsible for the weaker resonance peaks. Efforts to separate the isomers by TLC have proved unfruitful as have attempts to thermally decompose or isomerise one isomer in preference for the other. For the complexes (III), (IV) and (V), the ^{19}F NMR spectra again indicate the presence of isomers.

TABLE 2

MÖSSBAUER SPECTRAL DATA FOR COMPLEXES I, II, III, V AT ROOM TEMPERATURE

Compound	Isomer shift, δ^a	Quadrupole^a splitting, Δ
$Fe_2(CO)_6(SC_6H_5)_2$, (I)	+0.30	1.01
$Fe_2(CO)_6(SC_6F_5)_2$ (II)	0.35	1.33
$Fe_2(CO)_6(SC_6H_5)(SC_6F_5)$ (III)	0.32	1.16
$Fe_2(CO)_6(SC_6F_5)(SeC_6F_5)$ (V)	0.36	1.35

^{a} In mm·sec^{-1} probable error ±0.01 mm·sec^{-1}. Isomer shifts are reported relative to sodium nitroprusside.

Preliminary studies using Mössbauer spectroscopy (Table 2) demonstrate a positive isomer shift $(+\delta)$ when either C_6F_5 is substituted for C_6H_5 (as in II and III) or when Se is substituted for S (as in V); a similar increase is observed in the quadrupole splitting (Δ). The magnitude of Δ indicates octahedral coordination around the two iron atoms[7], one coordination position being occupied by a "bent" iron–iron bond; this is in agreement with the NMR spectra which demonstrates the diamagnetic nature of these complexes. The Mössbauer spectral parameters δ and Δ may indicate electron withdrawal by the C_6F_5 groups or a decrease in σ-donor power of Se as compared to S, depending on the particular complex under study. If this idea is correct, the σ-donor ability can be written (as intuitively expected) $SC_6H_5 > SC_6F_5 > SeC_6F_5$; because the sulphur-bridged complexes (I), (II) and (III) appear to have rather similar stabilities (as deduced from the competition reaction ratios) then the stability of the pentafluorophenylthio complexes must be compensated for by increased π-bonding between the iron and sulphur in (II) and (III) compared to (I). This will result in *less* π-bonding between the iron atoms and their carbonyl groups. In

TABLE 3

INFRARED SPECTRA IN THE CARBONYL STRETCHING REGION FOR THE CHALCOGEN-BRIDGED IRON TRICARBONYLS
Samples dissolved in carbon disulphide

$[C_6H_5SFe(CO)_3]_2$	(I)	2073.2	2036.1	2003.0	1994.5
$[C_6F_5SFe(CO)_3]_2$	(II)	2087.0	2058.3	2022.8	2010.2
$C_6H_5SFe_2(CO)_6SC_6F_5$	(III)	2078.6	2045.2	2008.0	2004.0
$[C_6F_5SeFe(CO)_3]_2$	(IV)	2080.1	2051.2	2015.7	2004.2
$[C_6H_5SeFe(CO)_3]_2$	(VI)	2065.6	2028.5	1999.5	1987.5
$C_6H_5SeFe_2(CO)_6SeC_6F_5$	(VII)	2071.6	2037.5	2000.0	—
$[C_6H_5TeFe(CO)_3]_2$	(X)	2055.5	2018.5	1977.5	1968.6
$[C_6F_5TeFe(CO)_3]_2$	(XI)	2069.8	2040.8	2006.8	1997.1

agreement with this, the CO stretching frequencies of (II) are all higher by about 10 cm^{-1} than those of complex (I), Table 3. The π-bonding ability of the selenium $4d$ orbitals is expected to be less than that of the $3d$ orbitals of sulphur which may account for the slight decrease in the CO stretching frequencies in going from complex (II) to (V). (The carbonyl bands are sharp and show no evidence of the presence of the *syn* isomers presumably due to exact coincidence in spectral frequencies). The chemical shift of the *para* fluorine atoms in (II) occurs about 4 ppm to higher field than in $(C_6F_5)_2S_2,C_6F_5SH$ or $(C_6F_5)_2S$ and could well be a further manifestation of iron–sulphur π-bonding resulting in a stronger $S-C_6F_5$ π-interaction. The carbonyl stretching frequencies of the two tellurium complexes (X) and (XI) can be estimated quite accurately by extrapolation from the spectra of their S and Se analogues, presumably reflecting a regular trend in electronic properties as the chalcogen atoms are changed from sulphur through selenium to tellurium, Fig. 3.

As the coordination about each iron in the molecules $[XFe(CO)_3]$ is approximately octahedral then σ-bonds may be formed using d^2sp^3 hybrid orbitals on the iron atoms. Each chalcogen unit (X in the above formula) may be regarded as carrying a formal negative charge and each iron atom would then be uni-positive (d^7). Five ligands donate electron pairs to each iron (3CO and 2X); but to form the iron–iron bond one electron must come from each metal. Thus all the hybrid orbitals will be fully occupied and the six remaining electrons on each iron will be housed in the non-bonding "t_{2g}" orbitals d_{xz}, d_{yz} and d_{xy}; a rare gas structure will have been achieved. Back-bonding between these d orbitals and the vacant anti-bonding orbitals of the
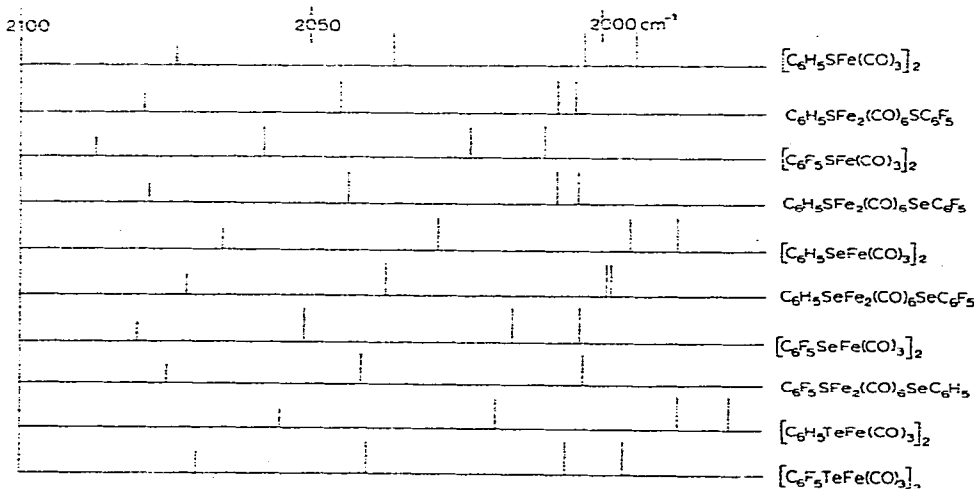

Fig. 3. Plot of the C≡O stretching frequencies for the chalcogen bridged iron tricarbonyl complexes dissolved in carbon disulphide.

carbonyls can be anticipated as well as an interaction across the iron–iron bridge and also with the vacant d orbitals on the chalcogen atoms. These interactions will permit the infrared vibrations of the carbonyl groups to couple with each other. In the following discussion the simple treatment of Cotton and Kraihanzel[8] will be followed.

The main features of the infrared spectra in the carbonyl stretching frequency

region are remarkably constant despite the formal loss of C_{2v} symmetry in molecules such as $[X \cdot X' \cdot Fe_2(CO)_6](X \neq X')$. Four strong lines are observed, the highest frequency line being weaker than the rest and widely separated from the next line. Finally at the lowest frequency are two lines quite close together. This immediately presents a problem since five infrared frequencies would be permitted by C_{2v} symmetry. Another surprising feature of the spectra is that in all cases the frequency difference between the average of the two highest frequencies and the two lowest frequencies is constant ($ca.$ 55 cm^{-1}).
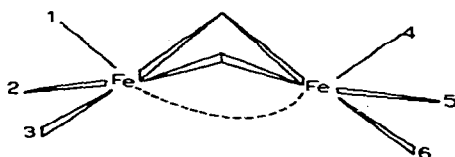

Fig. 4. Numbering of the carbon monoxide ligands in the chalcogen-bridged iron tricarbonyl complexes.

These observations may be rationalised in the following manner. Let the CO groups be numbered as in Fig. 4. If local C_{3v} symmetry is assumed for each Fe(CO)$_3$ group then the following normal coordinate functions may be written down,

$a_1 \quad \phi_1 = (\sqrt{3})^{-1}\,(CO(1)+CO(2)+CO(3)) \quad \phi_4 = (\sqrt{3})^{-1}\,(CO(4)+CO(5)+CO(6))$

$\phi_2 = (\sqrt{2})^{-1}\,(CO(2)-CO(3)) \qquad\qquad \phi_5 = (\sqrt{2})^{-1}\,(CO(5)-CO(6))$

$e \quad \phi_3 = (\sqrt{6})^{-1}\,(2CO(1)-CO(2)-CO(3)) \quad \phi_6 = (\sqrt{6})^{-1}\,(2CO(4)-CO(5)$
$$-CO(6))$$

Before proceeding to write down the corresponding force constants it should be remembered that the degeneracy of the e functions will be removed in the lower C_{2v} symmetry of the whole molecule. Let the stretching force constant for carbonyl groups 1 and 4 be k_A and for groups 2,3,5 and 6 be k_B. Further, let the interaction between two carbonyl groups cis to each other give rise to a perturbation equivalent to a force constant k_C. Effective force constants can now be written down:

$\phi_1, \phi_4; \quad \frac{1}{3}(k_A + 2k_B + 6k_C) \quad = \frac{1}{3}k_A + \frac{2}{3}k_B + 2k_C$

$\phi_2, \phi_5; \quad \frac{1}{2}(2k_B - 2k_C) \qquad = k_B - k_C$

$\phi_3, \phi_6; \quad \frac{1}{6}(4k_A + 2k_B - 6k_C) = \frac{2}{3}k_A + \frac{1}{3}k_B - k_C$

Now let us consider the interaction between the two Fe(CO)$_3$ units along the iron–iron bond. From an examination of a model of the compound it seems reasonable to suppose that a lobe from each of the three d-orbitals, d_{xz}, d_{yz} and d_{xy} will overlap with a lobe from a corresponding orbital on the other iron. Thus to a first approximation the iron–iron interaction will have at least three-fold symmetry and the assumption of approximate D_{3h} symmetry overall will prove useful. Let the interaction force constant between any two carbonyl groups across the iron–iron bond be k_X. The functions that result and their energies are tabulated in Table 4.

The most dramatic result is the big difference in force constants of $(\phi_1 + \phi_4)$ and $(\phi_1 - \phi_4)$ brought about by interaction across the iron–iron bridge $(6k_X)$ whereas $(\phi_2 + \phi_5)$ and $(\phi_2 - \phi_5)$ and also $(\phi_3 + \phi_6)$ and $(\phi_3 - \phi_6)$ remain effectively degenerate. Thus only four independent force constants are generated using this model: it seems

TABLE 4

Functions (X 2)	Force constants	Irreducible representations	
		D_{3h}	C_{2v}
$\phi_1 + \phi_4$	$(6)^{-1}(2k_A + 4k_B + 12k_C + 18k_X) = \frac{1}{3}k_A + \frac{2}{3}k_B + 2k_C + 3k_X$	a'_1	$a_1{}^a$
$\phi_1 - \phi_4$	$(6)^{-1}(2k_A + 4k_B + 12k_C - 18k_X) = \frac{1}{3}k_A + \frac{2}{3}k_B + 2k_C - 3k_X$	$a''_2{}^b$	$b_2{}^a$
$\phi_2 + \phi_5$	$(4)^{-1}(4k_B - 4k_C + 0k_X) = k_B - k_C$		$b_1{}^a$
$\phi_3 + \phi_6$	$(12)^{-1}(8k_A + 4k_B - 12k_C + 0k_X) = \frac{2}{3}k_A + \frac{1}{3}k_B - k_C$	e'	$a_1{}^a$
$\phi_2 - \phi_5$	$(4)^{-1}(4k_B - 4k_C + 0k_X) = k_B - k_C$		a_2
$\phi_3 - \phi_6$	$(12)^{-1}(8k_A + 4k_B - 12k_C + 0k_X) = \frac{2}{3}k_A + \frac{1}{3}k_B - k_C$	e''	$b_2{}^a$

^{a} Permitted in C_{2v}. ^{b} Permitted in D_{3h}.

reasonable to correlate them with the four observed carbonyl stretching frequencies.

Above, D_{3h} symmetry was assumed to consider the carbonyl interactions across the central bond. Of course, this symmetry is relaxed in the actual molecule but a knowledge of which modes were forbidden in D_{3h} will give an indication of bands that might well be observed but with only moderate intensity in C_{2v}. Thus those functions that carry both ^{b} and ^{a} in Table 4 are expected to be strong whilst those with only ^{a} should be weaker. This is in accord with the observed spectrum $(\phi_1 + \phi_4)$ the highest frequency line is distinctly less intense than the other lines in the spectrum. It is not possible to observe $(\phi_3 - \phi_6)$ by itself since it has the same force constant as $(\phi_3 + \phi_6)$; $(\phi_2 - \phi_5)$ is forbidden in both D_{3h} and C_{2v}.

This model therefore reproduces the main features of the infrared spectrum in the carbonyl stretching frequency region. The constant difference between the average frequencies of the highest and lowest pairs of lines noted at the beginning of this section is now seen to be proportional to $3k_C$, not a factor that will be greatly influenced by changes in X. Further, this feature of the spectra is a direct result of the use of coefficients for the individual carbonyl groups (in $\phi_1-\phi_6$) consistent with the assumption of local C_{3v} symmetry at each $Fe(CO)_3$ site. It is of interest that it does not matter whether k_A is greater or less than k_B, the a_1 line will always lie in the middle of the two lines derived from the removal of degeneracy of the e functions, in the absence of carbonyl–carbonyl interactions.

The frequency difference between $(\phi_1 + \phi_4)$ and $(\phi_1 - \phi_4)$ is related to $6k_X$ and so is a measure of the interaction between the two iron atoms. This difference does change somewhat, as might be expected, when the other groups, X, in the bridge are changed,—even so the splitting is constant to within $20\%, 33 \pm 4$ cm^{-1}.

It is now possible to calculate force constants corresponding to k_C and k_X, since $k = v^2 \cdot 4.0383 \cdot 10^{-6}$ mdynes per Å (these units have been chosen to permit easy comparison with previous work e.g. ref. 8).
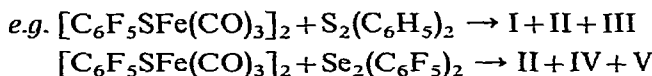
$$k_C = 0.31 \text{ mdyn} \cdot \text{Å}^{-1}$$
$$k_X = 0.09 \pm 0.01 \text{ mdyn} \cdot \text{Å}^{-1}$$

The value of k_C is comparable to that found by Cotton and Kraihanzel. k_X is smaller than k_C, as might be expected for a long-range interaction. If it is assumed that this interaction is primarily due to the overlap of iron d orbitals then a greater involvement of these orbitals in bonding with the chalcogen atoms, as suggested when

C_6H_5 is replaced by C_6F_5, would lead to a reduction of the value of k_X, as is observed.

The thermal decomposition of (II) *in vacuo* produced carbon monoxide and perfluorobiphenyl as the only volatile products; decomposition of (III) under similar conditions gave a mixture of the three possible biphenyls, $C_{12}H_{10}$, $C_{12}F_{10}$ and $C_6H_5C_6F_5$, in addition to carbon monoxide. Attempts to remove the pentafluoro-phenylthio ligands by heating (II) with mercury again gave only carbon monoxide and perfluorobiphenyl; however, the chalcogen ligands can be interchanged by heating one complex with another dichalcognide:

e.g. $[C_6F_5SFe(CO)_3]_2 + S_2(C_6H_5)_2 \rightarrow I + II + III$

$[C_6F_5SFe(CO)_3]_2 + Se_2(C_6F_5)_2 \rightarrow II + IV + V$

Bis(pentafluorophenyl)disulphide displaces the ligand triene from tetrafluoro-benzobicyclo[2,2,2]octatriene–iron tricarbonyl[9] when the two are heated to about 100° in a sealed tube:
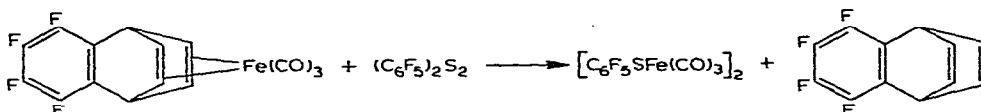
The decomposition under electron impact of metal carbonyl complexes having pentafluorophenyl groups present, has been studied by several workers[10]; in each case the complexes lose carbon monoxide in a step-wise fashion, the remainder of the molecule then fragments by loss of metal fluoride in the initial stages. The decompositions of (I) and (X) in a mass spectrometer show peaks due to the step-wise stripping of carbonyl groups to give, finally, a strong peak corresponding to Fe_2-$M_2(C_6H_5)_2^{+\cdot}$; on further fragmentation the iron atom remains mainly with the chalcogen as $Fe_2M_2^+$ (second strongest peak) and FeS_2^+. When $M = S$ there is also a metastable peak for the reaction:

$Fe_2S_2(C_6H_5)^+ \rightarrow Fe_2S_2^+ + C_6H_5$
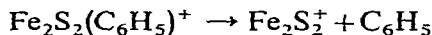
Thus in the case of the pentafluorophenylchalcogen-bridged complexes there is the interesting possibility of competition for the iron between the chalcogen (already partially bonded to the iron) and the fluorine atoms on the aromatic rings. A sketch of the mass spectrum of (II) is shown in Fig. 5 as a typical illustration of these complexes. The parent ion is rather weak as is that of the ion corresponding to the loss of one carbon monoxide molecule; there is a strong metastable peak representing the loss of the last carbonyl from the ion $Fe_2S_2(C_6F_5)_2CO^+$ to give the base peak Fe_2S_2-$(C_6F_5)_2^+$. Two other important metastable peaks were observed corresponding to the reactions:

$Fe_2S_2(C_6F_5)^+ \rightarrow FeS_2C_{12}F_8^+ + FeF_2$

$FeS_2C_{12}F_8^+ \rightarrow S_2C_{12}F_6^+ + FeF_2$
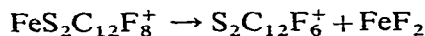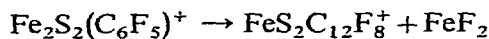
Thus, in these complexes an important fragmentation pathway is migration of fluorine to iron and, indeed a small peak due to FeF^+ can be distinguished. Only relatively minor peaks occur for the ions FeM^+, FeM_2^+ and F_2M^+.

Similarly to Stone *et al.*[4] we have found that bis(pentafluorophenyl)disulphide also reacts with cyclopentadienyliron dicarbonyl dimer and dicyclopentadienylnickel to give the complexes $C_5H_5Fe(CO)_2SC_6F_5$ and $[C_5H_5NiSC_6F_5]_x$.
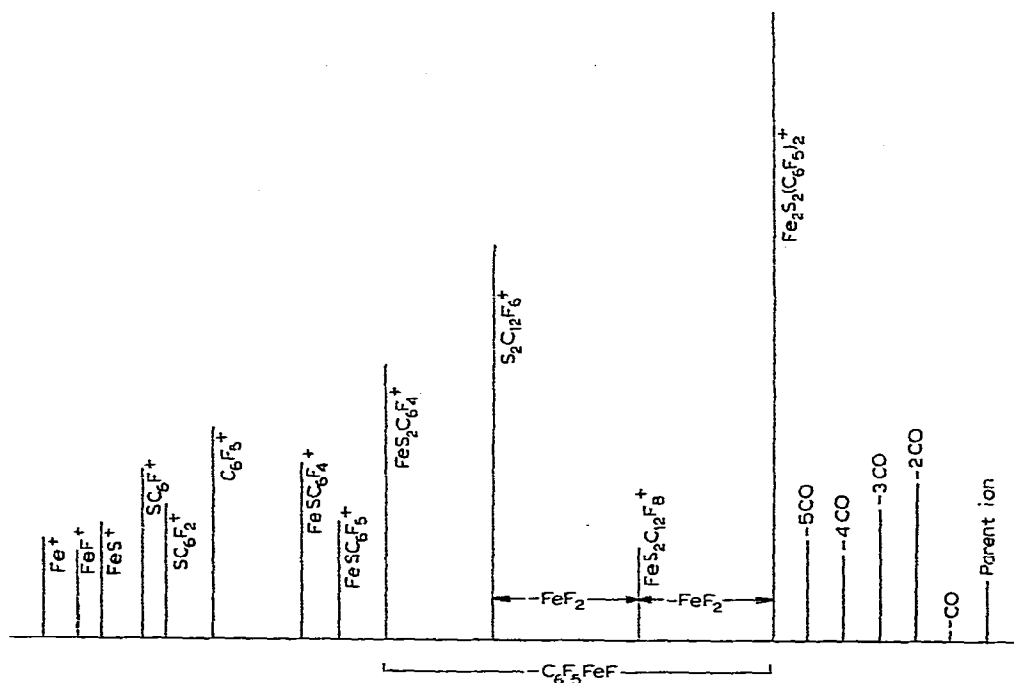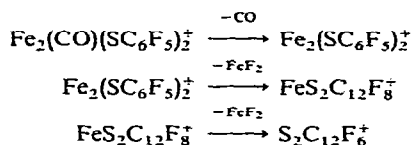
Fig. 5. Partial mass spectrum of pentafluorophenylthioiron tricarbonyl dimer. Metastable peaks were observed for the following reactions:

$$Fe_2(CO)(SC_6F_5)_2^+ \xrightarrow{-CO} Fe_2(SC_6F_5)_2^+$$
$$Fe_2(SC_6F_5)_2^+ \xrightarrow{-FeF_2} FeS_2C_{12}F_8^+$$
$$FeS_2C_{12}F_8^+ \xrightarrow{-FeF_2} S_2C_{12}F_6^+$$

EXPERIMENTAL

The reactions were carried out under oxygen-free, dry nitrogen; analyses were performed by A. Bernhardt, Mülheim, Ruhr and by the microanalytical department at Queen Mary College. Molecular weights were determined by Miss Sylvia Park using a Mechrolab vapour phase osmometer and the mass spectra were recorded using an A.E.I. MS 902 instrument. We thank the Imperial Smelting Corporation Ltd., for gifts of the fluoroaromatic starting materials. The preparation of bis(pentafluorophenyl)disulphide and bis(pentafluorophenyl)diselenide have been described previously by us[2].

Reaction of $S_2(C_6F_5)_2$ with mercury

Bis(pentafluorophenyl)disulphide (0.8 g) and an excess of mercury (*ca.* 1 ml) were sealed into a pyrex tube under vacuum and heated to 180° for 20 h. The tube was then opened, the product extracted with ether, filtered to remove mercury and the ether evaporated off under vacuum. The solid which remained was sublimed in high vacuum at 140° to give an analytically pure sample of bis(pentafluorophenylthio)-

mercury, m.p. 188–190° (Found: C, 23.9; H, 0.0; F, 31.8; mol. wt. 569. $C_{12}F_{10}S_2Hg$ calcd.: C, 24.1; H, 0.0; F, 31.8%; mol.wt. 605); yield 80%.

The mercurial was identical to a sample prepared by treating mercuric chloride with pentafluorophenylthiolithium in ether solution.

Reaction of $Se_2(C_6F_5)_2$ *with mercury*

Bis(pentafluorophenyl)diselenide (0.49 g) and mercury (*ca*. 1 ml) reacted together on heating to 180° in a sealed tube to give bis(pentafluorophenylseleno)-mercury, m.p. 171–173°; purification was accomplished by sublimation of the product at 100–120° in high vacuum (Found: C, 20.9; H, 0.16; F, 27.35; mol.wt. 713. $C_{12}F_{10}Se_2Hg$ calcd.: C, 20.9; H, 0.0; F, 27.5%; mol.wt. 694); yield 78%.

Reaction of $S_2(C_6F_5)_2$ *with germanium*

On heating in a sealed tube to 350°, bis(pentafluorophenyl)disulphide (0.8 g) and an excess of germanium powder (0.5 g) react to give tetrakis(pentafluorophenyl-thio)germanium, m.p. 143–145°, purified by sublimation at 100–120° in high vacuum followed by recrystallisation from ethyl alcohol. The identical product was obtained by treating germanium tetrachloride with a four-fold excess of pentafluorophenyl-thiolithium in ether. (Found: C, 33.1; H, 0.0; F, 43.3; $C_{24}F_{20}S_4Ge$ calcd.: C, 33.2; H, 0.0; F, 43.6%).

Reaction of $S_2(C_6F_5)_2$ *with iron carbonyls*

A mixture of bis(pentafluorophenyl)disulphide (0.8 g) and triiron dode-cacarbonyl (1.5 g) on being refluxed in 80–100° petrol ether under a nitrogen atmosphere, gave a deep red solution after about one hour. The solution was filtered and the solvent removed to give a red solid which, on recrystallisation from pentane, gave an analytically pure sample of pentafluorophenylthioiron tricarbonyl dimer, melting–decomposition point 140–143°, in 37% yield. The same compound was obtained on heating the disulphide with iron pentacarbonyl in a sealed tube at 100–110° or by refluxing pentafluorothiophenol with $Fe_3(CO)_{12}$ in 80–100° petrol ether; in the latter reaction some bis(pentafluorophenyl)disulphide is produced as a by-product and may be removed by either vacuum sublimation or TLC.

Reaction of $Se_2(C_6F_5)_2$ *with triiron dodecacarbonyl*

In a similar manner the diselenide reacted with triiron dodecacarbonyl in refluxing 80–100° petrol ether to give a 30% yield of pentafluorophenylselenoiron tricarbonyl dimer, m.p. 158–159°.

Reaction of $S_2(C_6F_5)_2$ *and* $S_2(C_6H_5)_2$ *with* $Fe_3(CO)_{12}$

A mixture of diphenyldisulphide (0.22 g), bis(pentafluorophenyl)disulphide (0.39 g) and triiron dodecacarbonyl (1.5 g), was heated in 80–100° petrol ether until the green colour of the iron carbonyl was discharged (*ca*. 1 h).The solution was then filtered and the solvent evaporated off under vacuum to leave a red solid. The solid was dissolved in 40–60° petrol ether and the components separated using thin layer chromatography on kieselguhr; three coloured bands were noted of which the middle one was the most deep in colour and on work-up proved to contain the "mixed" phenyl and pentafluorophenyl thio–iron carbonyl $C_6H_5SFe(CO)_3SC_6F_5Fe(CO)_3$ (0.423 g)

melting–decomposition point, 140–143°. The other two bands contained $[C_6F_5\text{-}$ $SFe(CO)_3]_2$ (0.198 g) and $[C_6H_5SFe(CO)_3]_2$ (0.201 g); the former being the nearer to the solvent front. The ratio of the products was thus very close to 1/2/1. The mixed complex also resulted when $[C_6F_5SFe(CO)_3]_2$ was heated with diphenyldisulphide or when $[C_6H_5SFe(CO)_3]_2$ was heated with bis(pentafluorophenyl)disulphide.

Reaction of $S_2(C_6F_5)_2$ and $Se_2(C_6F_5)_2$ with $Fe_3(CO)_{12}$

A similar reaction between bis(pentafluorophenyl)disulphide (0.4 g), bis-(pentafluorophenyl)diselenide (0.5 g) and triiron dodecacarbonyl (1.5 g) gave penta-fluorophenylthioiron tricarbonyl dimer (0.40 g), pentafluorophenylselenoiron tri-carbonyl dimer (0.24 g) and the mixed complexed $C_6F_5SFe_2(CO)_6SeC_6F_5$ (0.12 g).

Reaction of $S_2(C_6F_5)_2$ with $Se_2(C_6F_5)_2$

Bis(pentafluorophenyl)disulphide (0.39 g) and bis(pentafluorophenyl)-diselenide (0.49 g) were heated under reflux in 80–100° petrol ether for 18 h. The solution on work-up yielded only bis(pentafluorophenyl)thioselenide, m.p. 43–45° (Found: C, 32.4; H, 0.0; F, 42.6; $C_{12}F_{10}SSe$ calcd.: C, 32.4; H, 0.0; F, 42.7%).

Pentafluorophenylphenyldisulphide, m.p. 22°, may be prepared in a similar fashion (Found: C, 46.7; H, 1.6. $C_{12}H_5F_5S_2$ calcd.: C, 46.75; H, 1.6%).

Reaction of $C_6F_5SSeC_6F_5$ with mercury

Bis(pentafluorophenyl)thioselenide (0.3 g) and an excess of mercury were heated for 15 h in a sealed pyrex tube at 180°. Extraction of the product with ether followed by vacuum sublimation gave an analytically pure sample of pentafluoro-phenylthiopentafluorophenylselenomercury, m.p. 168–170° (Found: C, 22.7; H, 0.0. $C_{12}F_{10}SSeHg$ calcd. C, 22.4; H, 0.0%).

Formation of bis(pentafluorophenyl)ditelluride

On refluxing together in carbon tetrachloride, pentafluorophenylmercuric chloride and tellurium tetrachloride gave a low yield of pentafluorophenyltellurium trichloride, m.p. 128–130°; (Found: C, 17.85; H, 0.2; F, 23.7; $C_6F_5TeCl_3$ calcd.: C, 18.0; H, 0.0; F, 23.75%).

Refluxing this solid with powdered zinc in ethanol solution gave bis(penta-fluorophenyl)ditelluride, m.p. 43–45° (Found: C, 30.7; H, 0.0; F, 32.6; $C_{12}F_{10}Te_2$ calcd.: C, 24.5; H, 0.0; F, 32.3%). There appears to be some difficulty in the analysis of this type of tellurium compound; repeat analyses of the *same* sample of bis(penta-fluorophenyl)ditelluride gave C, 24.6 and 24.65%.

The treatment of tellurium tetrachloride (2.50 g) with pentafluorophenyl-lithium (prepared from 6.0 g of bromopentafluorobenzene) in ether–hexane solution, gave tris(pentafluorophenyl)tellurium chloride, m.p. 188–190° (Found: F, 43.5; Cl, 5.0; $C_{18}F_{15}TeCl$ calcd.: F, 42.95; Cl, 5.3%).

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