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STUDIES OF THE DIFFERENCES IN LIGAND TRANSFER, STABILITY, AND FRAGMENTATION ON ELECTRON IMPACT OF SOME ORGANOSULPHUR DERIVATIVES OF COBALT AND IRON CARBONYLS

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SUMMARY

A new route to $Co_2Fe(CO)_9S$, starting from $Co_2(CO)_6(SC_6X_5)_2$ instead of $Fe_2(CO)_6S_2$, is described. A difference has been found between the chemical behaviour of the $Fe_2(CO)_6(SR)_2$ and $Co_2(CO)_6(SR)_2$ compounds, and is discussed in the light of the different fragmentation patterns in the mass spectra. A qualitative explanation based on the different electronic configurations is suggested.

INTRODUCTION

Several polynuclear compounds containing Fe–S[1–4] and Co–S[1,5,6] clusters have been known for many years, but to our knowledge, there is only one case in which Fe, Co, and S are present in the same molecule, *viz.* $Co_2Fe(CO)_9S$[7,8]. This compound is readily formed in the reaction of $Fe_2(CO)_6S_2$ with $Co_2(CO)_8$ according to the following equation[7]:

$$Fe_2(CO)_6S_2 + 2\,Co_2(CO)_8 \rightarrow 2\,Co_2Fe(CO)_9S + 4\,CO$$

We recently synthesized compounds of the stoichiometry $Co_2(CO)_6(SR)_2$[9] ($R = C_6F_5$ or C_6Cl_5), and thought that treatment of such compounds with iron carbonyls could lead to new Co–Fe–S–CO clusters. A completely analogous reaction to the one shown above would have given the unknown compound $CoFe_2(CO)_9(SR)$, which is in accord with the inert gas rule, and falls into place in the series shown in Fig. 1. We have found, however, that this compound is not formed, instead there is a series of new reactions resulting in the formation of $Co_2Fe(CO)_9S$. These findings prompted us to make a more thorough comparison between the analogous compounds of cobalt and iron having the formula $M_2(CO)_6(SR)_2$.

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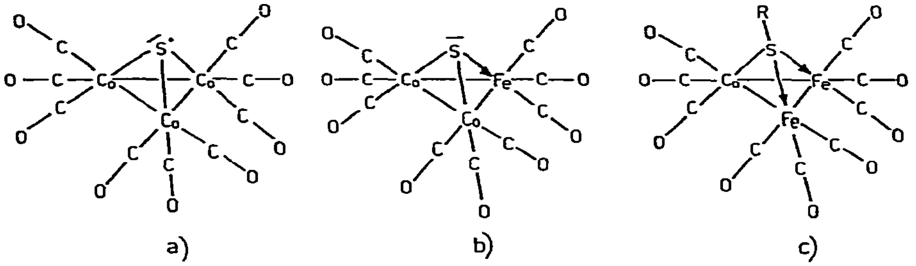
a) b) c)

Fig. 1. (a). Structure of $Co_3(CO)_9S$; (b). structure of $Co_2Fe(CO)_9S$; (c). structure of the hypothetical compound $CoFe_2(CO)_9SR$.

EXPERIMENTAL

Tetrahydrofuran was purified by distillation under nitrogen from lithium aluminium hydride immediately before use. n-Hexane and benzene were distilled under nitrogen from calcium hydride, the benzene having been previously dried over phosphorus pentoxide. Pentafluorobenzenethiol, pentachlorobenzenethiol, and ethanethiol were obtained commercially (Fluka A.-G.). Pure dicobalt octacarbonyl was obtained by crystallization from n-hexane of the commercial product furnished by Fluka A.-G. or was kindly supplied by Prof. P. Chini. Bis(pentafluorophenyl) disulphide[10], bis(pentachlorophenyl) disulphide[11], [(pentafluorophenyl)thio]iron tricarbonyl dimer[3,12,13], (ethylthio)iron tricarbonyl dimer[14] and [(pentachlorophenyl)thio]iron tricarbonyl dimer[15] were prepared by published procedures.

All reactions were carried out under oxygen-free, dry nitrogen. Chromatographic separations were performed on a silica gel column.

IR spectra were recorded on a Perkin–Elmer 621 spectrophotometer. Mass spectra were recorded on an Hitachi Perkin–Elmer RMU-6D spectrometer, samples being introduced with the direct insertion probe. The spectra of all the compounds studied were recorded using a 70 eV electron beam and a source temperature of 80°–150°, the standard galvanometer recorder being used to measure the output signal from the electron multiplier. In comparing the abundances of ions containing polyisotopic elements, with other types, the contributions from each isotope combination was summed[16].

[(*Pentafluorophenyl*)*thio*]*cobalt tricarbonyl dimer*

Dicobalt octacarbonyl (2.000 g, 5.8 mmole) and bis(pentafluorophenyl) disulphide (2.330 g, 5.8 mmole) were dissolved in n-hexane (30 ml) and stirred at room temperature under nitrogen until the reaction, which was monitored by the IR spectrum, was complete. The time required was about 2 h. The solution was filtered under nitrogen and kept at dry-ice temperature overnight to give black crystals which were isolated by filtration. The yield (based on cobalt) was estimated to be about 80%. (Found: C, 30.31; F, 27.03; mol.wt., 660. $C_{18}Co_2F_{10}O_6S_2$ calcd.: C, 31.59; F, 27.77%; mol.wt., 684.) The melting point of a sample sealed in an evacuated capillary was 100°.

[(*Pentachlorophenyl*)*thio*]*cobalt tricarbonyl dimer*

Dicobalt octacarbonyl (0.500 g, 1.5 mmole) and bis(pentachlorophenyl) disulphide (0.825 g, 1.5 mmole) were dissolved in benzene (50 ml). (The use of benzene instead of n-hexane is necessary for complete dissolution of the bis(pentachlorophenyl) disulphide.) The mixture was stirred at room temperature for about 2 h, the reaction being about as fast as that involving bis(pentafluorophenyl) disulphide. The mixture was filtered, and cooled to dry-ice temperature. The black crystals formed were filtered off. The yield was as high as 85% (based on cobalt). (Found: C, 25.27; Cl, 40.80. $C_{18}C_{10}$-$Co_2O_6S_2$ calcd.: C, 25.47; Cl, 41.78%.) A sample sealed in an evacuated capillary decomposed at 130°.

Reaction of $Co_2(CO)_6(SR)_2$ ($R = C_6F_5$ and C_6Cl_5) and diiron nonacarbonyl in tetrahydrofuran

(*a*). [(Pentafluorophenyl)thio]cobalt tricarbonyl dimer (0.250 g, 0.37 mmole) dissolved in tetrahydrofuran (5 ml) was treated with a slight excess of diiron nonacarbonyl (0.37 mmole). A fast reaction took place, as shown by a rapid change of colour from olive-green to reddish, and was complete within 10 min. The residual diiron nonacarbonyl was filtered off, and the tetrahydrofuran evaporated *in vacuo*. The reddish residue so obtained dissolves in n-hexane to give an orange red solution, and its IR spectrum in the carbonyl region shows that iron dicobalt nonacarbonyl sulphide $Co_2Fe(CO)_9S$[7,17], is the only metal carbonyl compound present. This was isolated in pure form by cooling the hydrocarbon solution.

(*b*). An analogous reaction occurred for [(pentachlorophenyl)thio]cobalt tricarbonyl dimer.

Reaction of $Co_2(CO)_6(SC_6Cl_5)_2$ and diiron nonacarbonyl in benzene

[(Pentachlorophenyl)thio]cobalt tricarbonyl dimer (0.300 g, 0.35 mmole) in benzene (15 ml) was stirred with an excess of diiron nonacarbonyl. [The solubility of $Fe_2(CO)_9$ in benzene is very poor but it is higher than in n-hexane.] Although the IR spectrum indicated that some $FeCo_2(CO)_9S$ was formed at once, the reaction was far from complete after 10 h at room temperature. We then irradiated the reaction system with a UV lamp, and in 2 h the IR spectrum of a sample of the reaction product in n-hexane showed the complete disappearance of the $Co_2(CO)_6(SC_6Cl_5)_2$ bands. The reaction mixture was then filtered, the benzene distilled off and the residue taken up in n-hexane. The IR spectrum of the orange red solution obtained showed that only $FeCo_2(CO)_9S$ was present.

Reaction of $Co_2(CO)_6(SC_6Cl_5)_2$ and triiron dodecacarbonyl in benzene

[(Pentachlorophenyl)thio]cobalt tricarbonyl dimer (0.300 g, 0.35 mmole) and an excess of triiron dodecacarbonyl (0.176 g, 0.35 mmole) were dissolved in hexane (30 ml) under nitrogen at room temperature. No change was apparent after 24 h, but after 5 h irradiation with a UV lamp, the IR spectrum of the reaction mixture showed, in addition to the bands of the initial compounds, bands characteristic of $FeCo_2(CO)_9S$. After 10 h of irradiation the reaction was considered complete and chromatography on silica gel with n-hexane as eluant, gave an orange-red first fraction identified as $FeCo_2(CO)_9S$, and a dark green second fraction consisting of $Fe_3(CO)_{12}$ plus a small amount of unreacted $Co_2(CO)_6(SC_6Cl_5)_2$.

Reaction of $Co_6(CO)_{11}(SEt)_4S$ with triiron dodecacarbonyl

A mixture of dicobalt octacarbonyl (0.550 g, 0.44 mmole), triiron dodecacarbonyl (0.220 g, 0.44 mmole), and an excess of ethanethiol in benzene (30 ml) was stirred at room temperature. After some hours we obtained the known cobalt sulphur clusters $Co_6(CO)_{11}(SEt)_4S$ and $Co_3(CO)_4(SEt)_5$ (the latter in much smaller amount), whereas the iron carbonyl was left unchanged. The reaction mixture was then taken to dryness to remove unchanged ethanethiol, and the residue was taken up in benzene (30 ml) and stirred at room temperature under UV irradiation. After 5 h the solution was filtered, the benzene pumped off, and the solid residue was dissolved in n-hexane. Chromatography on silica gel of the n-hexane solution, with n-hexane as eluant, gave two reddish fractions; IR showed the first to be $FeCo_2(CO)_9S$, and the second to be $Fe_2(CO)_6(SEt)_2$ (two isomers). A third, green fraction was unchanged $Fe_3(CO)_{12}$.

$Fe_2(CO)_6(SC_6F_5)_2$, $Fe_2(CO)_6(SC_6Cl_5)_2$, $Fe_2(CO)_6(SEt)_2$ do not react with $Co_2(CO)_8$ even under conditions so drastic that decomposition of the starting material occurred.

RESULTS AND DISCUSSION

The compounds of the type $Co_2(CO)_6(SC_6X_5)_2$ ($X=F$, Cl) react with iron carbonyls, but, surprisingly, in all cases there was cleavage of the S–C bond of the starting cobalt compound, and the known[7,8] $Co_2Fe(CO)_9S$ cluster compound was formed. Such cleavages require only a few minutes when $Co_2(CO)_6(SC_6X_5)_2$ is treated with $Fe_2(CO)_9$ in tetrahydrofuran.

If the electronegativity of the C_6X_5 groups were responsible for the ease of cleavage of the S–C bond, then the reaction between $Fe_2(CO)_6(SC_6F_5)_2$[3,12,13] and $Co_2(CO)_8$ might also give $Co_2Fe(CO)_9S$, as does $Fe_2(CO)_6S_2$. All our efforts in this direction gave negative results: under mild conditions no reaction occurred and when more drastic conditions were used, there was complete decomposition of the starting compounds without formation of $Co_2Fe(CO)_9S$ even in small yield. Mixing $Fe_2(CO)_6(SC_6F_5)_2$ and $Co_2(CO)_8$ in n-hexane at room temperature under nitrogen gave only $Co_4(CO)_{12}$. When we irradiated this solution with a mercury lamp there was decomposition even of the iron compound. In tetrahydrofuran, disproportionation of $Co_2(CO)_8$ readily occurred as could be seen from the IR spectrum. Chromatography in n-hexane of a small sample gave $Fe_2(CO)_6(SC_6F_5)_2$ as the first fraction and $Co_4(CO)_{12}$ as the second. After heating for five hours, no reaction other than decomposition of the iron compound had occurred.

Analogous behaviour was observed in the reaction between $Fe_2(CO)_6(SC_6Cl_5)_2$ or $Fe_2(CO)_6(SC_2H_5)_2$ and dicobalt octacarbonyl; in no case was formation of iron dicobalt nonacarbonyl sulphide [$Co_2Fe(CO)_9S$], or of any other mixed compound, observed.

We must thus conclude that cleavage of the carbon–sulphur bond is a characteristic of an S–R group coordinated to a cobalt atom, whatever the R group. Since no compounds of the type $Co_2(CO)_6(SR)_2$ other than those having $R=C_6F_5$ or C_6Cl_5 are known, we performed the reaction of triiron dodecarbonyl with $Co_6(CO)_{11}(SEt)_4S$ and $Co_3(CO)_4(SEt)_5$[5,6]. In this case there was again formation of $Co_2Fe(CO)_9S$ plus $Fe_2(CO)_6(SEt)_2$ in appreciable yield. The reaction scheme was as follows:

$$Co_2(CO)_8 + HSEt + Fe_3(CO)_{12} \xrightarrow{\text{(Benzene)}} \left\{ \begin{array}{l} Co_6(CO)_{11}(SEt)_4S \\ Co_3(CO)_4(SEt)_5 \\ Fe_3(CO)_{12} \text{ unreacted} \end{array} \right.$$

$$\left\{\begin{matrix}\mathrm{Co_6(CO)_{11}(SEt)_4S}\\ \mathrm{Co_3(CO)_4(SEt)_5}\end{matrix}\right. + \mathrm{Fe_3(CO)_{12}} \xrightarrow[\text{(UV irradiation)}]{\text{(Benzene)}} \left\{\begin{matrix}\mathrm{FeCo_2(CO)_9S}\\ \mathrm{Fe_2(CO)_6(SEt)_2}\ (\mathit{syn}+\mathit{anti})\end{matrix}\right.$$

This result confirmed our conclusion although, in this case we cannot say whether the sulphur in the $FeCo_2(CO)_9S$ comes at least partly from cleavage of the S–Et bond. It is noteworthy that the thiol reacts preferentially with the cobalt carbonyl, the iron compound initially being left unchanged.

Another noteworthy feature is that iron is able to abstract an SR group from a cobalt carbonyl cluster, a fact which, we believe, has not been reported previously. On the other hand, the transfer of an SEt group from Co to Fe points to a greater stability of the S–R linkage in the $Co_6(CO)_{11}(SEt)_4S$ case, in contrast to the behaviour of $Co_2(CO)_6(SC_6X_5)_2$ compounds, with which there was only cleavage of the S–C bond, and no transfer of the whole SC_6X_5 group.

Mass spectra

The difference in the chemical behaviour between the $Co_2(CO)_6(SR)_2$ compounds and their iron analogues is reflected in the fragmentation pattern for the organo-sulphur ligand.

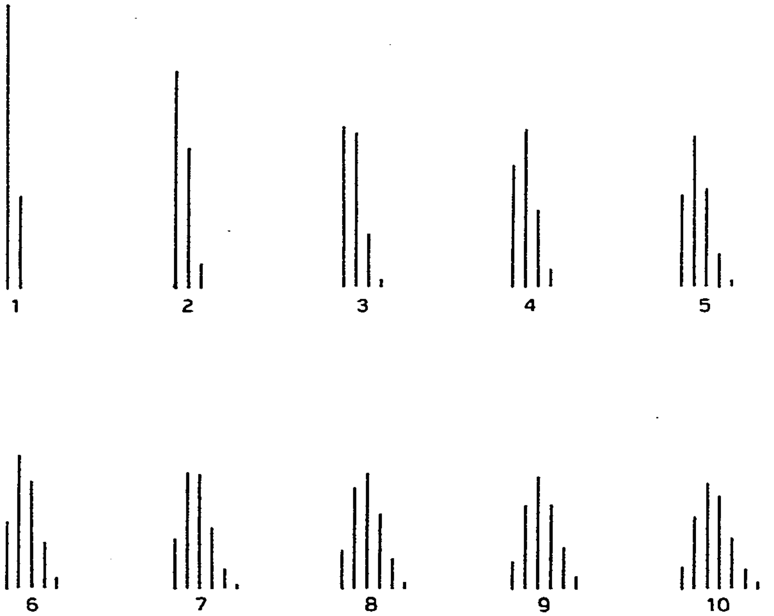

Fig. 2. Characteristic mass spectral patterns of ions containing a number of chlorine atoms which varies from one to ten (indicated in the figure). The relative abundance (w_r) for each isotope combination has been calculated by the relation:

$$w_r = \binom{n}{r} \cdot p^r \cdot (1-p)^{n-r},$$

where n = total number of chlorine atoms in the given ion; r = number of ^{35}Cl atoms present; p = 0.754, is the natural abundance of the ^{35}Cl isotope. The separation between the lines is 2 m/e units.

TABLE 1

RELATIVE ABUNDANCES OF FRAGMENTS IN THE MASS SPECTRA OF BIS(PENTAFLUOROPHENYL) DISULPHIDE AND ITS COBALT AND IRON CARBONYL DERIVATIVES ($L = C_6F_5S$)

L–L		$Co_2(CO)_6(L–L)$		$Fe_2(CO)_6(L)_2$	
$^{a}\ S_2C_{12}F_{10}^{+}$		$C_{12}F_{10}^{+}$	100	$S_2C_{12}F_6^{+}$	73
$^{a}\ S_2C_{12}F_9^{+}$		$C_{12}F_9^{+}$	20	$S_2C_{12}F_5^{+}(C_{11}F_9^{+})$	4
$^{a}\ S_2C_{12}F_5^{+}\ (C_{11}F_9^{+})$		$C_{12}F_8^{+}$	12	$S_2C_{12}F_2^{+}\ (C_{11}F_6^{+})$	3
$^{a}\ S_2C_{12}F_4^{+}\ (C_{11}F_8^{+})$		$C_{12}F_7^{+}$			
$^{a}\ S_2C_{12}F_3^{+}\ (C_{11}F_7^{+})$		$C_{12}F_6^{+}$		$S_2C_6F_3^{+}$	4
$^{a}\ S_2C_{12}F_2^{+}\ (C_{11}F_6^{+})$				$S_2C_6F_2^{+}$	23
$^{a}\ S_2C_{12}F^{+}\ (C_{11}F_5^{+})$		$C_{11}F_7^{+}$	38	$S_2C_6F^{+}\ (C_5F_5^{+})$	26
		$C_{11}F_6^{+}$	4	$S_2C_5F_2^{+}$	5
$S_2C_6F^{+}\ (C_5F_5^{+})$	52			$S_2C_5F^{+}$	6
$S_2C_5F_4^{+}$	87	$C_{10}F_6^{+}$	11	$S_2C_5^{+}$	16
$S_2C_5^{+}$	10	$C_{10}F_5^{+}$	6		
$S_2C_4F_2^{+}$	24			$SC_6F_4^{+}$	10
$S_2C_4F^{+}$	20	$C_9F_7^{+}$	3	$SC_6F_3^{+}$	63
		$C_9F_6^{+}$	~1	$SC_6F_2^{+}$	60
$SC_{12}F_{10}^{+}$	13	$C_9F_5^{+}$	5	SC_6F^{+}	83
$SC_{12}F_9^{+}$	6	$C_9F_4^{+}$	~2	SC_6^{+}	14
$SC_{12}F_8^{+}$	6	$C_9F_3^{+}$	5	$SC_5F_4^{+}$	3
$SC_6F_5^{+}$	58			$SC_5F_3^{+}$	6
$SC_6F_4^{+}$	16	$C_6F_5^{+}$	9	$SC_5F_2^{+}$	10
$SC_5F_4^{+}$	100	$C_6F_3^{+}$	~1	SC_5F^{+}	100
$SC_5F_3^{+}$	74	$C_5F_3^{+}$	9	SC_5^{+}	6
SC_5F^{+}	45	$C_5F_2^{+}$	3	$SC_3F_3^{+}$	5
$SC_4F_3^{+}$	31	$C_3F_3^{+}$	11	$SC_3F_2^{+}$	~2
SC_4F^{+}	73	$C_3F_2^{+}$	3	SC_3F^{+}	31
SC_3F^{+}	42	CF_3^{+}	5	SCF^{+}	4
SCF^{+}	34	CF^{+}	5		
				$C_6F_5^{+}$	9
$^{a}\ C_{12}F_{10}^{+}$		$SC_5F_4^{+}$	21	$C_6F_3^{+}$	~2
$^{a}\ C_{12}F_9^{+}$		SC_4F^{+}	17	$C_6F_2^{+}$	4
$^{a}\ C_{12}F_8^{+}$				$C_5F_4^{+}$	4
		$Co_2S_2^{+}$	14	$C_5F_3^{+}$	15
$C_6F_3^{+}$	39			$C_5F_2^{+}$	7
$C_5F_3^{+}$	68			C_5F^{+}	22
$C_5F_2^{+}$	31				
C_5F^{+}	29			$FeS_2C_6F_4^{+}$	60
$C_4F_3^{+}$	21			$FeS_2C_6F_3^{+}$	3
$C_3F_3^{+}$	55			$FeSC_6F_5^{+}$	35
$C_3F_2^{+}$	21			$FeSC_6F_4^{+}$	38
C_3F^{+}	58			$FeSC_6F_3^{+}$	11
C_2F^{+}	29			$FeSC_6F_2^{+}$	11
CF_3^{+}	45			FeS^{+}	52
CF^{+}	45			FeF^{+}	28
				Fe^{+}	26
				Fe_2S^{+}	4
				Fe_2^{+}	8

[a] Since intensity of these peaks is strongly dependent upon the conditions used, the relative abundance is not reported.

In order to allow direct comparison, we show in Tables 1 and 2 the fragmentation patterns for the compounds[9] $Co_2(CO)_6(SC_6Cl_5)_2$ and $Co_2(CO)_6(SC_6F_5)_2$ along with that for $Fe_2(CO)_6(SC_6F_5)_2$. (The latter pattern has been published[13], but without

TABLE 2

RELATIVE ABUNDANCE OF FRAGMENTS IN THE MASS SPECTRA OF BIS(PENTACHLOROPHENYL) DISULPHIDE AND ITS COBALT DERIVATIVE ($L=C_6Cl_5S$)

L–L		$Co_2(CO)_6(L–L)$	
$S_2C_{12}Cl_{10}^+$	53	$SC_{12}Cl_{10}^+$	4
$S_2C_{12}Cl_8^+$	16	$C_{12}Cl_{10}^+$	100
$S_2C_{12}Cl_7^+$	7	$C_{12}Cl_9^+$	17
$S_2C_{12}Cl_6^+$	24	$C_{12}Cl_8^+$	51
$S_2C_{12}Cl_5^+$	4	$C_{12}Cl_7^+$	9
$S_2C_{12}Cl_4^+$	5	$C_{12}Cl_6^+$	26
		$C_{12}Cl_5^+$	6
$SC_{12}Cl_{10}^+$	5	$C_{12}Cl_4^+$	13
$SC_{12}Cl_8^+$	18	[a] $C_{12}Cl_3^+$	
$SC_{12}Cl_6^+$	5	[a] $C_{12}Cl_2^+$	
$SC_{11}Cl_7^+$	~2	[a] $C_{12}Cl^+$	
$SC_{11}Cl_6^+$			
$SC_{11}Cl_5^+$	~2	$C_{12}Cl_9^{++}$	~3
		$C_{12}Cl_7^{++}$	7
$SC_6Cl_5^+$	97	$C_{12}Cl_5^{++}$	4
$SC_6Cl_4^+$	100		
$SC_6Cl_3^+$	26	$C_9Cl_8^+$	4
$SC_6Cl_2^+$	39	$C_9Cl_6^+$	~2
SC_6Cl^+	12	$C_9Cl_5^+$	~3
SC_5Cl^+	6	$C_9Cl_4^+$	64
SC_3Cl^+	12	$C_9Cl_3^+$	27
$SCCl^+$	11	$C_9Cl_2^+$	9
SC^+	15	C_9Cl^+	4
		C_9^+	~3
$C_6Cl_2^+$	6		
$C_5Cl_3^+$	10	$C_6Cl_5^+$	7
C_5Cl^+	5	$C_6Cl_4^+$	14
C_4Cl^+	~2	$C_6Cl_3^+$	11
CCl_2^+	~2	$C_6Cl_2^+$	5
C_5^+	~3	C_6Cl^+	~2
C_3^+	13		
		$C_4Cl_2^+$ (or Co_2^+)	~2
		C_3^+	~3

[a] The relative intensity of the peaks corresponding to these fragments is not reported because overlapping with peaks of other fragments occurs.

N.B. The fragmentation pattern of $Fe_2(CO)_6(SC_6Cl_5)_2$ has not been reported because, as far as the fragmentation of the ligand is concerned it is very similar to that of bis(pentachlorophenyl) disulphide.

details of the ligand fragmentation.) We also give the fragmentation patterns of the uncomplexed ligands to make clearer the differences between the behaviour of the cobalt and iron derivatives.

In the case of the chlorine derivatives, it is possible to determine the exact number of chlorine atoms in a given fragment from the relative intensities of the peaks corresponding to the different isotopic compositions, as shown in Figure 2, so that the fragments are unequivocally identified. In the fluorine compounds, because there is only one isotope present, identification is more difficult when different fragments give rise to the same value of *m/e*, and thus the assignments for the fluorine derivatives are only the most probable ones, and are based mainly on the similarities with the chlorine analogues and on the fact that generally the number of the halogen atoms is lower than that of the carbon atoms in a given fragment.

From inspection of the mass spectra some striking differences in the two series of compounds are apparent. In the cobalt derivatives, the most abundant fragments are those in which the two aromatic rings (presumably from the same molecule) combine, giving mainly fragments having twelve carbon atoms and, along with these, some less abundant fragments with nine carbon atoms, and some with eleven and ten carbon atoms in the case of the fluorine compounds. The sulphur atoms are presumably still bonded to the cobalt, as indicated by the relatively high abundance of the Co_2S_2 fragment and by the virtual absence of organic fragments bearing sulphur. With the iron compounds the mass spectrum shows a fragmentation pattern rather similar to that of the ligand itself, plus a fairly high abundance of fragments in which the iron is still bonded to a thio-organic group, while peaks due to fragments having only carbon and halogen are absent or very weak. Practically no combination of two aromatic rings occurs with the iron compounds, whereas this is the most prevalent feature with the cobalt compounds.

Beyond doubt, the strength of the sulphur–carbon bond is strongly dependent upon the nature of the metal atom (Fe or Co) bonded to the sulphur. A possible explanation for the variation in behaviour can be found by considering the electronic situation of the sulphur bridging atoms in the two types of compounds (Fig. 3). In the $Co_2(CO)_6(SR)_2$ compounds, which presumably have the structure shown in Fig. 3a, the S atoms have 10 electrons in their external electronic shell, and only the presence of a very electronegative R group allows the existence of such a dimeric compound. Thus it is not surprising that the cobalt compounds should readily lose the organic radical, with the simultaneous cleavage of the S–S bond bringing to 8 the number of electrons in the external shell of the sulphur atoms. With the iron compounds, the S bridging atoms have only 8 electrons in their external coordination sphere and this could account for the much greater difficulty of splitting the S–C bond.

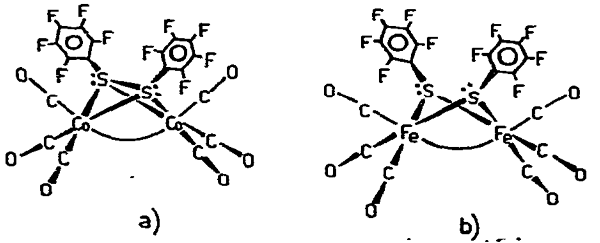

Fig. 3. Proposed structure of the compound $Co_2(CO)_6(F_5C_6SSC_6F_5)$; (b). structure of the compound $Fe_2(CO)_6(SC_6F_5)_2$.

As we pointed out, the reaction between $Co_2(CO)_6(SC_6X_5)_2$ (X = Cl, F) and $Fe_2(CO)_9$ in tetrahydrofuran takes place under very mild conditions, requiring no heating or irradiation. With a different iron carbonyl or with a different solvent more drastic conditions have to be used. $Co_2(CO)_6(SC_6Cl_5)_2$ does not react with $Fe_3(CO)_{12}$ on stirring of the reaction mixture at room temperature, only after irradiation with a UV lamp for several hours was the reaction complete, and $FeCo_2(CO)_9S$

was the only product. That $Fe_2(CO)_9$ is more reactive than $Fe_3(CO)_{12}$ is well known, but we noticed that the reactivity of $Fe_2(CO)_9$ itself is also strongly influenced by the solvent used. The reaction of $Fe_2(CO)_9$ with $Co_2(CO)_6(SC_6Cl_5)_2$ in benzene at room temperature and without UV irradiation is very slow, but if the mixture is irradiated with UV light reaction is complete within a few hours, to give $FeCo_2(CO)_9S$ as the only product.

Finally, we draw attention to some interesting features of the behaviour of $Fe_2(CO)_9$ itself in tetrahydrofuran. When a mixture of $Fe_2(CO)_9$ and THF is stirred the liquid phase becames first orange-red, then red, and the $Fe_2(CO)_9$ seems partly to dissolve. The IR spectrum of the solution shows strong bands corresponding to the absorptions of $Fe(CO)_5$, but this does not explain the colour of the THF phase. Presumably other species are present, such as $Fe(CO)_4$, perhaps solvated, which would account for the greater reactivity of this iron carbonyl in THF rather than in benzene. Their concentration, however, must be very low, since we could not detect any new C–O stretching band in the IR spectrum.

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