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Chemistry of the Metal Carbonyls. Part XXXIX.* Organotin(carbonyl)iron Complexes

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A series of reactions between various organotin compounds and iron carbonyls has been investigated. By refluxing mixtures of organotin halides and pentacarbonyl iron, several complexes with tin-iron bonds have been obtained. Among the types of compound isolated are those of formula [R₂SnFe(CO)₄]₂, [R₂SnCl]₂Fe(CO)₄, R₄Sn₃[Fe(CO)₄]₄, and Sn[Fe(CO)₄]₄. The last compound, tetrakis(tetracarbonyliron)tin, can also be synthesised by reaction of hexabutylditin with pentacarbonyliron, but more successfully by treating stannic chloride with the anion $Fe(CO)_4^{-2}$. Compounds of formula type $(R_3Sn)_2Fe(CO)_4$ and $[R_2SnFe(CO)_4]_2$ can be prepared by refluxing pentacarbonyliron with trialkyltin hydrides and dialkyltin dihydrides, respectively. A number of properties of the new compounds are reported, including their infrared spectra in the carbonyl stretching region.

SEVERAL compounds containing tin-iron bonds have been described. They can be divided into two classes: (a) those containing a single metal-metal bond, as in $Ph_3SnFe(CO)_2(\pi-C_5H_5)^1$ or a sequence of tin-iron-tin bonds, as in $(Ph_3Sn)_2Fe(CO)_4$; ² and (b) those containing a polynuclear cluster of metal atoms, as in $[Me_2SnFe(CO)_4]_2$,³ a molecule believed to involve SnFeSn bridging units.

The methods of preparation of such compounds have developed from the observation of Hock and Stuhlmann⁴ that mercury(II) chloride and pentacarbonyliron reacted in aqueous or alcoholic solution with elimination of carbon dioxide and hydrogen chloride to afford (ClHg)₂Fe(CO)₄,† as well as an apparently polymeric material $HgFe(CO)_4$. Extension of this work led to the isolation of a compound "Et₂PbFe(CO)₄" from the reaction between triethyl-lead hydroxide and pentacarbonyliron.⁷ Subsequently the lead compound was shown to be dimeric, and a series of dimers of general formula $[R_2PbFe(CO)_4]_2$ (R = alkyl) were prepared by treating the lead compounds R₃PbOH or R₃PbBr with the calcium salt of (tetracarbonyl)iron anion in aqueous methanol.⁸ However, complexes of \mathbf{the} type $(R_3Pb)_2Fe(CO)_4$ were formed when $R = C_6H_{11}$ or C_6H_5 in R₃PbX. By treating dibutyltin dichloride with (tetracarbonyl)iron anion, Hieber and Breu⁹ obtained a tin-iron compound to which they assigned the formula Bu₂SnFe(CO)₄. Later workers³ obtained the same compound from the reaction between dibutyldivinyltin and pentacarbonyliron during an attempt to form the π -complex [Bu₂Sn(CH:CH₂)₂]Fe(CO)₃. Moreover, the dialkyltin(tetracarbonyl)iron complex was shown to be dimeric. Other dimeric complexes $[R_2SnFe(CO)_4]_2$ were also prepared by cleavage of vinyl groups from alkylvinyltin compounds. Furthermore, formation of $[R_2SnFe(CO)_4]_2$, with a similar cleavage of unsaturated organic groups, occurs when dialkyldialkynyltin compounds are treated with dodecacarbonyltri-iron in light petroleum.10

* Part XXXVIII, M. I. Bruce and F. G. A. Stone, J. Chem. Soc. (A), 1966, 1837. A preliminary account of the tin(carbonyl)-iron complexes has been given in *Chem. Comm.*, 1966, 253.

† For recent work on compounds of this type see refs. 5 and 6.

 R. D. Gorsich, J. Amer. Chem. Soc., 1962, 84, 2486.
F. Hein and W. Jehn, Annalen, 1965, 684, 4.
R. B. King and F. G. A. Stone, J. Amer. Chem. Soc., 1960, 82, 3833.

During isolation of the compounds $[R_2SnFe(CO)_4]_2$ the formation of black insoluble pyrophoric solids, and traces of red to orange gums from which nothing could be crystallised, was observed.³

It was thought possible that direct reaction between pentacarbonyliron and an n-butyltin chloride might afford $[Bu_2SnFe(CO)_4]_2$, since the metal carbonyl could remove the chlorine and butyl groups in stepwise reactions. Thus with tributyltin chloride the following reaction sequence might be considered:

$$2Bu_3SnCI + 2Fe(CO)_5 \longrightarrow (Bu_3Sn)_2Fe(CO)_4 + FeCI_2 + 6CO (i)$$

$$2(Bu_3Sn)_2Fe(CO)_4 \longrightarrow [Bu_2SnFe(CO)_4]_2 + 2Bu_4Sn (ii)$$

Alternatively, one can envisage a reaction scheme involving formation of dibutyltin(tetracarbonyl)iron dimer and carbonyl chloride, rather than ferrous chloride.

$$Bu_3SnCl + Fe(CO)_5 \longrightarrow (Bu_3Sn)_2Fe(CO)_4 + COCl_2$$
 (iii)

The compound (Bu₃Sn)₂Fe(CO)₄ might then decompose as in reaction (ii). Release of carbonyl chloride in the reaction between pentacarbonyliron and mercuric chloride has been mentioned.⁵

If dibutyltin(tetracarbonyl)iron dimer were formed from pentacarbonyl iron and butyltin chlorides, the reaction might represent a convenient method of synthesis since both pentacarbonyl iron and the butyltin chlorides are commercially available.

The results for a series of reactions in which a mixture of pentacarbonyliron and tributyltin chloride were refluxed are summarised in Table 1. No solvent was used, and the products included not only the known air-stable yellow compound $[Bu_2SnFe(CO)_4]_2$ (I) but also the new compounds $Bu_4Sn_3[Fe(CO)_4]_4$ (II) and $Sn[Fe(CO)_4]_4$ (III).

At slow rates of reflux (the change in rate of reflux reflects a change in the local temperature at the flask walls) and long reaction times, as in experiment 4 (Table 1), appreciable amounts (ca. 5%) of (II) are isolated. With increase in the rate of reflux, compound

⁶ F. Hein and H. Pobloth, Z. anorg. Chem., 1941, 248, 84.
⁸ F. Hein and E. Heuser, Z. anorg. Chem., 1947, 254, 138.
⁹ W. Hieber and R. Breu, Chem. Ber., 1957, 90, 1270.
¹⁰ S. D. Ibekwe and M. J. Newlands, Chem. Comm., 1965, 114.

⁴ H. Hock and H. Stuhlmann, Ber., 1928, 61, 2097; 1929, 62, 431.

⁶ J. Lewis and S. B. Wild, *J. Chem. Soc.* (A), 1966, 69. ⁶ D. M. Adam, D. J. Cook, and R. D. W. Kemmitt, *Chem.* Comm., 1966, 103.

(III) is formed in increasing amounts, while the proportion of (I) and (II) decreases. After 70 hr. of rapid reflux, (III) was the only tin-iron complex isolated. However, under the most vigorous conditions di-n-butyl ketone and a metallic mirror are produced, all the tin-iron compounds decomposing.

It was also noted that when the reaction was carried out in a sealed tube at 110° (Table 1, expt. 7) it proceeded only to a limited extent, presumably because of pressure build-up of carbon monoxide, and careful examination of the volatile products established the

TABLE 1

Reactions of tri-n-butyltin chloride with pentacarbonyl iron

Reactants (mmoles)	Experiment							
	$\overline{1}$	2	3	4	5	6	7*	
Fe(CO) ₅ Bu ₃ SnCl	$179 \\ 15.4$	97 7·7	$\begin{array}{c} 82 \\ 18 \cdot 4 \end{array}$	$179 \\ 15.4$	$261 \\ 15 \cdot 4$	$194 \\ 7.7$	$22 \cdot 4 \\ 1 \cdot 93$	
Conditions								
Time (hr.)	16	19	24	45	70	72	19	
Rate of reflux †	m	m	vf	s	f.	m		
Products (%)								
$[Bu_{2}SnFe(CO)_{4}]_{2}$ (1)	25	26	+	32	Trace	$6 \cdot 5$	Trace	
$Bu_4Sn_3[Fe(CO)_4]_4(II)$	6	$1 \cdot 2$		5			Trace	
$Sn[Fe(CO)_4]_4$ (III)	$2 \cdot 5$	0.6			16	5	Trace	

* Experiment carried out in a Carius tube at 110° (see text). † The rate at which pentacarbonyliron (b. p. 104°) refluxed as determined by the isomantle setting had an effect on the yield and distribution of the products. Rate of reflux: s, slow; m, medium; f, fast; vf, very fast. ‡ Dibutyl ketone obtained in 20% yield (based upon organotin halide), all tin-carbonyliron complexes having decomposed. ¶ Identified from infrared spectrum.

absence of any carbonyl chloride. This observation seems to eliminate reaction (iii) as a possible step. Reaction (ii) seems possible since at 140° the methyl compound $(Me_3Sn)_2Fe(CO)_4$ gave $[Me_2SnFe(CO)_4]_2$ and Me_4Sn , and a similar decomposition has been found with analogous lead compounds $(R_3Pb)_2Fe(CO)_4$.¹¹

Although reactions (i) and (ii) could account for the formation of (I), the observation that traces of $(Bu_2SnCl)_2Fe(CO)_4$ were formed in some reactions suggests another process involving cleavage of butyl groups with formation of dibutyl ketone:

$$2Bu_3SnCl + Fe(CO)_5 \longrightarrow (Bu_2SnCl)_2Fe(CO)_4 + Bu_2CO$$
 (iv)

This mode of formation of the ketone seems more probable than a reaction

$$2Bu_4Sn + 2Fe(CO)_5 \longrightarrow [Bu_2SnFe(CO)_4]_2 + 2Bu_2CO$$

because of the previous report ³ that pentacarbonyliron and tetrabutyltin afford (I) in less than 6% yield. The chlorine-containing compound $(Bu_2SnCl)_2Fe(CO)_4$ might decompose in the reaction conditions to give unstable carbonyliron chlorides ^{12,13} and compound (I). The release of energy in forming ferrous chloride, which was detected in the residues, supports the occurrence of reaction (v) and/or (i). Indeed, ferrous chloride formation may provide some of the driving force for the

$$(\mathsf{Bu}_2\mathsf{SnCI})_2\mathsf{Fe}(\mathsf{CO})_4 + 2\mathsf{Fe}(\mathsf{CO})_5 \longrightarrow \\ [\mathsf{Bu}_2\mathsf{SnFe}(\mathsf{CO})_4]_2 + \mathsf{Fe}(\mathsf{CO})_4\mathsf{Cl}_2 + 2\mathsf{CO} \\ \downarrow \\ \mathsf{FeCl}_2 + 4\mathsf{CO} \quad (\mathsf{v})$$

reaction. Formation of the tin(carbonyl)iron complexes obviously involves stepwise removal of butyl groups and chlorine atoms from tin, but the manner in which this occurs is not clear. It seems very probable that the overall process involves redistribution of alkyl and chloride groups on tin, with many different reactions proceeding.

Interestingly, experiments showed that (I) reacted with pentacarbonyliron to give (III) but not (II). It therefore seems unlikely that (II), although it contains an $SnFe_4$ unit (see below), is a necessary intermediate in the synthesis of (III), or that (II) is formed directly from (I).

Reactions between triethyltin chloride and pentacarbonyliron gave analogous products, and a similar temperature-time effect was observed. Reaction with trimethyltin chloride proceeds similarly; acetone, but no carbonyl chloride or tetramethyltin were detected in the volatile products. For triethyl- and trimethyl-tin chlorides higher temperatures were needed to cleave the R-Sn and Cl-Sn bonds, which may reflect an increase in bond strength compared with the butyl derivatives.¹⁴

If dodecacarbonyltri-iron and tributyltin chloride are refluxed in light petroleum (b. p. $100-120^{\circ}$) compounds (I), (I), and (III) are produced in 50, 5, and 8% yield, respectively.

Under slow reflux, pentacarbonyliron and diethyltin dichloride afford bis(diethylchlorotin)tetracarbonyliron. Thus, with dialkyltin dichlorides, a halide group is apparently cleaved first, although as mentioned above alkyl groups may be removed first in one of the processes involving pentacarbonyl iron and trialkyltin chlorides. The compound $(Et_2SnCl)_2Fe(CO)_4$ is a pale yellow, very air-sensitive solid melting just above room temperature. Formation of the compound in this manner is somewhat similar to the stepwise replacement of chlorine in dimethyl tin dichloride by Mn(CO)5^{-.15} At higher temperatures diethyltin dichloride and pentacarbonyliron afford a mixture of (Et₂SnCl)₂Fe(CO)₄, [Et₂SnFe(CO)₄]₂, $Et_4Sn_3[Fe(CO)_4]_4$, and (III). A sealed-tube reaction at 145° showed that acetone, diethyl ketone, and ethylene were among the volatile products. Di-n-propyl- and dibutyl-tin dichlorides react to give analogous products.

Reaction between hexabutylditin and pentacarbonyliron under rapid reflux affords (III) (ca. 12% yield) with only traces of the other tin-iron carbonyl complexes.

¹¹ F. Hein and E. Heuser, Z. anorg. Chem., 1948, 255, 125.

¹² W. Hieber and G. Bader, Ber., 1928, 61, 1717.

¹³ E. W. Abel and B. C. Crosse, unpublished observations. S

 ¹⁴ A. L. Yergey and F. W. Lampe, J. Amer. Chem. Soc., 1965, 87, 4204.
¹⁵ H. R. H. Patil and W. A. G. Graham, J. Amer. Chem. Soc.,

¹⁵ H. R. H. Patil and W. A. G. Graham, J. Amer. Chem. Soc., 1965, 87, 673.

In view of the easy removal of vinyl groups from dialkyldivinyltin compounds, and the cleavage of chloride and alkyl groups from alkyltin chlorides in reactions with iron carbonyls, it was of interest to investigate the corresponding reaction with the more reactive alkyltin hydrides. Reaction between trimethyltin hydride and pentacarbonyliron at 70° gave the known¹⁶ bis(trimethyltin)tetracarbonyliron in high vield, as well as a very air-sensitive compound which may have been Me₃SnFe(CO)₄H. An analogous compound Me₂TlFe(CO)₄H has been postulated by Hein and Pobloth.⁷ At 100°, trimethyltin hydride and pentacarbonyliron give the following $(Me_3Sn)_2Fe(CO)_4$ (70%), $[Me_2SnFe(CO)_4]_2$ (10%), $Me_4Sn_3[Fe(CO)_4]_4$ (2%), and (III) (2%). Dimethyltin dihydride and the pentacarbonyl react at 70° to give $[Me_2SnFe(CO)_4]_2$ in a The formation of $(Me_3Sn)_2Fe(CO)_4$ and high yield. $[Me_2SnFe(CO)_4]_2$ from the tin hydrides probably involves elimination, through unstable hydrogen-iron bonds, of hydrogen and carbon monoxide:

$$2Me_{3}SnH + Fe(CO)_{5} \longrightarrow (Me_{3}Sn)_{2}Fe(CO)_{4} + H_{2} + CO$$

$$2Me_{2}SnH_{2} + 2Fe(CO)_{5} \longrightarrow [Me_{3}SnFe(CO)_{4}]_{2} + 2CO + 2H_{2}$$

These reactions are very similar to those recently reported ¹⁷ for octacarbonyldicobalt and silanes

$$2R_3SiH + Co_2(CO)_8 \longrightarrow 2R_3SiCo(CO)_4 + H_2$$

which may proceed via $HCo(CO)_4$. Moreover, the reactions are formally similar to those which occur between thiols and iron carbonyls where dimeric species $[RSFe(CO)_3]_2$ are produced, accompanied by elimination of hydrogen.18

As described above, formation of the novel metal atom cluster (III) involves a series of complex reactions. Moreover, the best yield was only about 16%. In view of this an alternative synthesis was sought. It was found that treatment of a solution of stannic chloride in tetrahydrofuran with (tetracarbonyl)iron anion afforded (III) in 25% yield. Smaller amounts (ca. 2%) of (III) were obtained by reaction of stannous chloride with pentacarbonyliron or dodecacarbonyltri-iron in tetrahydrofuran. Using the latter carbonyl, we identified (III) spectroscopically as the major constituent of a red gum. Bonati and Wilkinson¹⁹ also reported a red gum in their attempted insertion of stannous chloride into dodecacarbonyltri-iron.

Stannic chloride reacted rapidly with pentacarbonyl iron, a cream coloured solid being precipitated. After removal of excess of carbonyl, a red solvent extract was obtained. The latter afforded red crystals which would not sublime, and from their very high energy terminal carbonyl absorptions (eight bands in the range 2116-2025 cm.-1) appeared to contain a cationic carbonyl species. Hieber et al.20 have reported a compound

- 87, 1133. ¹⁸ R. G. Hayter, Preparative Inorganic Reactions, 1965, 2, 211;
- and references therein.
 - ¹⁹ F. Bonati and G. Wilkinson, J. Chem. Soc., 1964, 179.

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of formula $Sn_2Fe_5(CO)_{20}$, obtained from a reaction between an alkaline solution of pentacarbonyliron and ammonium hexachlorostannate, followed by acidification. This reaction was repeated and a similar dark red air-sensitive solid obtained, very soluble in acetone but only sparingly soluble in methylene dichloride [unlike (III)]. The infrared spectrum in the carbonyl region was very different from that of either (III), or the presumed cationic carbonyl species mentioned above.

The compounds $[R_2SnFe(CO_4)]_2$ and $R_4Sn_3[Fe(CO)_4]_4$ are air-stable in the crystalline state for several days, but the complexes $Sn[Fe(CO)_4]_4$, $[R_2SnCl]_2Fe(CO)_4$, and $(R_3Sn)_2Fe(CO)_4$ are rapidly oxidised. The order of solubility of the compounds in organic solvents is $[R_2SnFe(CO)_4]_2 > Sn[Fe(CO)_4]_4 > R_4Sn_3[Fe(CO)_4]_4;$ thus $[R_2SnFe(CO)_4]_2$ compounds are very soluble in hydrocarbons, and can be selectively extracted therewith, while the derivatives $R_4Sn_3[Fe(CO)_4]_4$ and $Sn[Fe(CO)_4]_4$ are relatively insoluble and are extracted with methylene dichloride or chloroform. Solutions of all these compounds decompose slowly in air. Strangely, solutions of (III) are the most stable, and can be stored for up to 48 hr. without decomposition.

The most probable structures for (I), (II), and (III) are as shown. The diamagnetism of (III) was confirmed by Evans method.²¹ An X-ray crystal structure



determination of (III) has been made in this laboratory.²² The crystals are monoclinic, with approximate molecular symmetry D_{2d} . The tetrahedral valencies of the tin atom are tetragonally distorted, giving two different pairs of iron-iron distances; 2.87 and 4.65 Å. The tiniron bond length is 2.54 Å. The configuration about each iron atom can be described as approximately octahedral. One pair of FeSnFe angles has closed to about 69° and the other pair opened out to about 133°. The ironiron distance of 2.87 Å is at the upper limit of those observed in molecules with iron-iron bonds.23 Thus in $\operatorname{Fe}_2(\operatorname{CO})_9$ it is 2.46 Å while in $\operatorname{Fe}_2(\operatorname{CO})_8^{-2}$ it is 2.88 Å. It is possible that there are two iron-iron bonds in (III) formed by overlap of suitable orbitals from the two pairs of iron atoms. However, the observed iron-iron distance of 2.87 Å, which is long, suggests that this is an oversimplification of the bonding situation. The molecular

- 20 W. Hieber, J. Gruber, and F. Lux, Z. anorg. Chem., 1959, **300**, 275. ²¹ D. F. Evans, J. Chem. Soc., 1959, 2003. T. Hur and P. Woodward, J. Ch
- ²² P. F. Lindley and P. Woodward, J. Chem. Soc. (A), 1967, in the press.
 - ²³ J. Lewis, Pure and Applied Chem., 1965, 10, 11.

O. Kahn and M. Bigorgne, Compt. rend., 1965, 261, 2483.
A. J. Chalk and J. F. Harrod, J. Amer. Chem. Soc., 1965,

symmetry is such that two equivalent, three-centre FeSnFe orbitals can be constructed using atomic orbitals from both the iron and tin atoms. Such bonding could account for the distortion from T_d to D_{2d} symmetry.

During this work it was brought to our attention that the methyl analogue of (II) had been prepared. We are indebted to Dr. R. A. Schunn of the Du Pont Co. for informing us that he had studied $Me_4Sn_3Fe_4(CO)_{16}$ in collaboration with R. M. Sweet and C. J. Fritchie. The complex was prepared by treating $MeSnCl_3$ with $Na_2Fe(CO)_4$ in tetrahydrofuran.. X-Ray analysis showed it to have a structure with an $SnFe_2SnFe_2Sn$ cluster analogous to that suggested for (II).

The presence of iron-iron interactions in (III) suggested an investigation of addition reactions across this However, neither stannous chloride nor " bond." dimethyltin dihydride reacted with (III) to give a SnFe₂SnFe₂Sn cluster of the type found in (II). Hieber Beutner²⁴ have reported a compound and Sn[Fe(CO)₃NO]₄ from the reaction of the anion $[Fe(CO)_3NO]^-$ with hexachlorostannate. The compound Sn[Fe(CO)₃NO]₄ requires no iron-iron bond since an Fe(CO)₃NO group needs only one additional valence electron, which it acquires from the tin atom, to reach a krypton electron configuration. It was, therefore, conceivable that treatment of (III) with nitric oxide would afford Sn[Fe(CO)₃NO]₄. However, both nitric oxide and N-methyl-N-nitrosotoluene-p-sulphonamide failed to convert (III) into Sn[Fe(CO)₃NO]₄.

The infrared spectra of the tin-carbonyliron complexes in the carbonyl stretching region were recorded at high resolution, and the frequencies are summarised in Table 2, together with those recently obtained in this laboratory and elsewhere 16,25 for analogous germanium and lead compounds.

The most probable molecular point groups and infrared-active bands for each class of compound are as following $(\mathbf{P}, \mathbf{S}_{T}) = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j$

follows: $(R_3Sn)_2Fe(CO)_4$, $C_{2\nu}(2A_1 + B_1 + B_2)$;

 $(R_2SnCl)_2Fe(CO)_4, C_{2v}(2A_1 + B_1 + B_2);$

 $\begin{array}{l} [R_2 SnFe(CO)_4]_2, \ D_{2h}(B_{1u} + B_{2u} + 2B_{3u}); \\ R_4 Sn_3 [Fe(CO)_4]_4, \ D_{2d}(3B_2 + 4E); \ Sn[Fe(CO)_4]_4, \end{array}$

 $D_{2d}(3B_2 + 4E)$. However, our measurements reveal that with the exception of $[Ph_2SnFe(CO)_4]_2$ all the complexes have four CO stretching frequencies (Table 2), unless very concentrated solutions are employed. In the latter situation the compounds $R_4Sn_3[Fe(CO)_4]_4$ show three additional but weak bands (3% as intense as the strong band near 2050 cm.⁻¹). Hence to a first approximation for all the complexes, save type (II), only the local symmetry (C_{2v}) of the iron atoms need be considered. Minimal coupling between structural units could be expected on the basis of calculations of carbonyl interaction constants.²⁶ Fortunately, the relative intensities of the four bands vary from one series to another (see Figure) and so infrared monitoring of mixtures greatly facilitated the separation procedures. Band assignments and force constants are presently being determined by I. Paul.

At present it seems prudent to comment but briefly upon general trends in the frequencies (Table 2). Within each

	TABL	Е 2				
	Carbonyl stretching frequencies *					
Compound		(cn	n1)			
$[Bu_{a}SnFe(CO)_{4}]_{a}$	2041	1993	1981	1969		
	2041	1993	1981	1969 +		
$[Et_2SnFe(CO)_4]_2$	2042	1994	1982	1970		
	2041	1993	1982	1970 †		
$[Me_2SnFe(CO)_4]_2$	2046	1998	1988	1973		
	2045	1998	1987	1975 †		
$[Ph_2SnFe(CO)_4]_2$	2051	2010sh	$2001 \mathrm{br}$			
$\operatorname{Bu}_{4}\operatorname{Sn}_{3}[\operatorname{Fe}(\operatorname{CO})_{4}]_{4}\ldots\ldots$	2050^{+}	2023	1987	1976		
$Et_4Sn_3[Fe(CO)_4]_4$	2054	2026	1988	1978		
$Me_4Sn_3[Fe(CO)_4]_4$ \ddagger	2054	2026	1989	1980		
$Sn[Fe(CO)_4]_4$	2072	2044	2027	2010		
$(Bu_2SnCl)_2Fe(CO)_4$	2077	2026	2005	1991		
(Et ₂ SnCl) ₂ Fe(CO) ₄	2080	2029	2009	1996		
$((Me_sSn)_sFe(CO)_1$	2058	1999	1988	1970		
	2057	1998	1987	1968 †		
$[Me_2PbFe(CO)_4]_2$	2037	1991	1984	1969		
$[Et_2PbFe(CO)_4]_2$	2031	1985	1975	1962 †		
$Me_4Pb_3[Fe(CO)_4]_4$ §	2048	2021	1986	1977		
$Pb[Fe(CO)_4]_4$ §	2067	2042	2022	2012		
[Me ₂ GeFe(CO) ₄] ₂	2053	2000	1987 \P			
$[Et_2GeFe(CO)_4]_2$	2051	1998	1996	1982 \P		
Ge[Fe(CO) ₄] ₄ §	2074	2048	2031	2012 $$		

* Recorded with Perkin-Elmer 237 (with scale expansion) and 257 spectrophotometers, using cyclohexane solutions. † Data from ref. 16. ‡ Sample kindly provided for our measurements by Dr. Schunn. For the $R_4Sn_8[Fe(CO)_4]_4$ compounds very weak bands have been omitted (see text). § Evidence for the existence of this compound has been obtained during the work described in this Paper. ¶ Data from ref. 25.

of the series $[R_2SnFe(CO)_4]_2$, $R_4Sn_3[Fe(CO)_4]$, and $[R_2SnCl]_2Fe(CO)_4$ the frequencies tend to become lower with increasing size of the alkyl groups. Similar behaviour occurs for the lead and germanium derivatives $[R_2MFe(CO)_4]_2$. Moreover, decrease in the atomic number of the Group IVB metal increases the stretching frequencies. Comparison of the two cis-substituted series $(R_3Sn)_2Fe(CO)_4$ and $(R_2SnCl)_2Fe(CO)_4$ shows that the halogenated compounds have higher frequencies. This is as expected in terms of the relative electronegativities of the groups R₃Sn and R₂SnCl. The latter group would remove charge from the iron atom more effectively than would the former. Hence there will be weaker iron-carbon σ -bonding and less iron-carbon π -bonding with a commensurate increase in carbonoxygen bond order. The presence of vacant d orbitals on the tin atoms may well affect carbonyl frequencies by inducing interaction between these orbitals and filled d $\pi\text{-orbitals}$ on the iron atoms.^27

There is no evidence that the band pattern alters in going from Me to Et to Bu. However, the infrared spectrum of $[Ph_2SnFe(CO)_4]_2$ is quite different from those of the alkyl analogues, and this may be due to geometric differences or perhaps the effect of electron delocalisation over the phenyl π -system.

Finally, it should be mentioned that the metal

²⁷ N. Flitcroft, D. A. Harbourne, I. Paul, P. M. Tucker, and F. G. A. Stone, *J. Chem. Soc.* (A), 1966, 1130.

²⁴ W. Hieber and H. Beutner, Z. anorg. Chem., 1963, 320, 101.

²⁵ O. Kahn and M. Bigorgne, Compt. rend., 1966, 262, C, 906.

²⁶ L. H. Jones, J. Mol. Spectroscopy, 1962, 8, 105.

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atom clusters $[R_2SnFe(CO)_4]_2$, $R_4Sn_3[Fe(CO)_4]_4$, and $Sn[Fe(CO)_4]_4$ may not be the only ones formed in some of the reactions described here.

Infrared spectra: A, $[Bu_2SnFe(CO)_4]_2$; B, $Bu_4Sn_3[Fe(CO)_4]_4$; C, $Sn[Fe(CO)_4]_4$; D, $[Bu_2SnCl]_2Fe(CO)_4$; E, $[Ph_2SnFe(CO)_4]_2$; F, $(Me_3Sn)_2Fe(CO)_4$

EXPERIMENTAL

Pentacarbonyliron and the tin compounds were generally refluxed together under nitrogen in a 100 ml. 3-necked flask fitted with a spiral water condenser. The flask was heated by an isomantle, controlled by a Sunvic Regulator (AEI Ltd), while the contents were stirred. Other reactions were performed in sealed heavy-wall Pyrex tubes which were opened to a high-vacuum system of conventional design. Solids were usually recovered by slowly removing (2 hr.) the excess of pentacarbonyliron and other volatile materials in vacuo, and then by first washing the residue with several aliquot portions of light petroleum (b. p. 40-60°), followed by chloroform or methylene dichloride. These extracts were filtered under nitrogen, concentrated, and cooled to induce crystallisation. The solids were filtered off, washed with cooled solvent, and dried in vacuo and recrystallised (from light petroleum) if necessary. Analyses are in Table 3.

Reactions between Tri-n-butyltin Chloride and Pentacarbonyliron.—The following three experiments employing different conditions are representative. Yields are based on the organotin compound taken.

(a) Tri-n-butyltin chloride (2.5 g., 7.7 mmoles) and pentacarbonyliron (19 g., 97 mmoles) were refluxed rapidly (19 hr.; Sunvic setting 70). The mixture became dark green, and a metallic mirror formed. The dark red residue was extracted with three 100 ml. aliquot portions of light petroleum, and 100 ml. portion of chloroform. Each fraction was concentrated to 5 ml. and cooled to -78° . Filtration afforded from (i) (I) (0.5 g.), containing traces of (II); from (ii) a mixture (40 mg.) of (I), (II), and (III); from (iii) (III) (25 mg.); and from (iv) (II) (10 mg.). The filtrates gave (i) spectroscopically pure (I) (0.7 g.); (ii) a mixture (15 mg.) of (I) and (II), (iii) no tin-iron compound, and (iv) (II) (10 mg.). Yields are given in Table 1, expt. 2).

(b) Tri-n-butyltin chloride (5 g., $15\cdot4$ mmoles) and pentacarbonyliron (51 g., 261 mmoles) were refluxed rapidly (70 hr.; Sunvic setting 80); gas was vigorously evolved, the mixture turning black. Extraction with chloroform gave a red solid (3.0 g.) from which pure (III) (2.0 g.) was obtained (Table 1, expt. 5).

(c) Tri-n-butyltin chloride (6.0 g., 18.4 mmoles) and pentacarbonyliron (16 g., 82 mmoles) were refluxed rapidly (24 hr.; Sunvic setting 85) giving a metallic mirror, and di-n-butyl ketone (0.5 g., 20%) (Found: C, 77.0; H, 12.8. Calc. for C_4H_{18} O: C, 76.0; H, 12.8%), the identity of which was confirmed by comparison of the infrared spectrum with that of an authentic sample, and by preparation of the semicarbazone.

TABLE 3

			Found	(%)	Calc.	(%)		
Compound	Colour	М. р.	С	н	С	н		
$[Bu_2SnFe(CO)_4]_2(I)$	Pale yellow	112°	36.2	4.5	36.0	4.5		
$Bu_4Sn_3[Fe(CO)_4]_4$ (II) *	Dark red	168-	30.5	$2 \cdot 8$	30.6	$2 \cdot 9$		
		170 d						
$Sn[Fe(CO)_4]_4$ (III) †	Bright red	80 d	24.7	0	24.3	0		
$[Et_2SnFe(CO)_4]_2$ \ddagger	Pale yellow		27.6	$2 \cdot 8$	28.0	$2 \cdot 9$		
$(Et_2SnCl)_2Fe(CO)_4$ ¶	Pale yellow	~ 20	$22 \cdot 9$	3.3	24.3	3.4		
$(Me_3Sn)_2Fe(CO)_4$	Colourless	~8	24.5	$3 \cdot 6$	24.3	3.7		
* Found: M (Me	chrolab osr	nomete	er), 12	240.	Calc.	for		
C ₃₉ H ₃₈ Fe ₄ O ₁₆ Sn ₃ : M, 1259. † Found (by X-ray fluorescence								
analysis): Fe, 28.3;	Sn, 15.3%;	M (osi	momet	er), 7	73. (Calc.		
for C ₁₆ Fe ₄ O ₁₆ Sn: Fe,	28.3; Sn, 1	5.0%;	M, 7	90.	‡ For	und:		
M, 665. Calc. for C	16H20Fe2O8SI	n.: M	, 690.	¶ F	ound:	C1,		
11.8. Calc. for $C_{12}H_{20}Cl_2FeSn_2$: Cl, 11.9%.								

Reaction between (I) and Pentacarbonyliron.—A sample (100 mg., 0.13 mmole) of spectroscopiclly pure (I) and pentacarbonyliron (14.6 g., 74.5 mmoles) were refluxed slowly for 22 hr. Recovery of crystalline material in the usual way gave a mixture of unchanged (I), (III), and dodecacarbonyltri-iron, identified by infrared spectra.

Reactions between Ethyltin Chlorides and Pentacarbonyliron.—(a) Triethyltin chloride (3.7 g., 15.4 mmoles) and pentacarbonyliron (35 g., 179 mmoles) were refluxed slowly for 21 hr. Recovery of tin carbonyliron complexes in the usual way afforded diethyltin(tetracarbonyl)iron dimer (0.5 g., 10%) (Table 3) and (III) (0.7 g., 6%).

Under conditions of rapid reflux (66 hr.) triethyltin chloride (3.7 g., 15.4 mmoles) and pentacarbonyliron (35 g., 179 mmoles) gave mainly (III) (1.5 g., 12%), with traces of $[Et_2SnFe(CO)_4]_2$ and $Et_4Sn_3[Fe(CO)_4]$.

(b) Diethyltin dichloride (2.9 g., 11.7 mmoles) and pentacarbonyliron (14.6 g., 74.7 mmoles) were gently refluxed (18 hr.). The mixture, initially dark red, turned orange and a yellow solid formed. Extraction in the usual way gave on fractional sublimation (10^{-3} mm. on a -78° probe) at 40° unchanged Et₂SnCl₂ and Fe₃(CO)₁₂, and from 60— 80° bis(diethylchlorotin)(tetracarbonyl)iron (Table 3). The red residue remaining after sublimation was from its infrared spectrum shown to contain Et₄Sn₃[Fe(CO)₄]. The compound (Et₂SnCl)₂Fe(CO)₄ is difficult to handle on account of its sensitivity to air and moisture. Carbonyl absorptions are given in Table 2; other major bands (liquid film, KBr plates) occur at 2978m, 2960m, 2935m, 2910m, 2875m, 2825w, 2740w, 1740w, 1465m, 1420m,



1380m, 1230w, 1192m, 1016m, 959m, 946sh, 676m, 670m, 603s, br, 528w, 508w, 486mw, 435mw cm.⁻¹.

In sealed-tube experiments, diethyltin dichloride and pentacarbonyliron gave, as volatile products, ethylene, alkanes, acetone, and diethyl ketone, identified by infrared spectra.

Reaction between Hexabutylditin and Pentacarbonyliron.— A sample (1.8 g., 3.3 mmoles) of hexabutylditin and pentacarbonyliron (20.4 g., 104 mmoles) after 24 hours' reflux gave (III) (60 mg., 11.5%) and a trace of (I).

Reactions of Methyltin Hydrides with Pentacarbonyliron.-(a) Trimethyltin hydride (2.6 g., 15.8 mmoles) and pentacarbonyliron (11.7 g., 59.7 mmoles) after 3 hours' reflux (70°) afforded a dark brown solution. Removal of excess of pentacarbonyl iron gave a dark red viscous liquid which was sublimed $(40^{\circ}/10^{-3} \text{ mm. on a } -78^{\circ} \text{ probe})$. The infrared spectrum of the sublimate (m. p. $ca. -20^{\circ}$) showed it to contain two carbonyliron containing species. One of these, having absorptions at 2135m, 2046w, 2024s, 2018s, and 1936w cm.⁻¹, could be removed completely by bubbling air through a light petroleum solution leaving bis(trimethyltin)tetracarbonyliron 16 (1.4 g., 47%) (Table 3). A liquidfilm spectrum showed carbonyl bands (Table 2), and other absorptions at 2990m, 2925m, 1690w, 1425w, br. 1200sh, 1190m, 1034w, 969w, 910w, 771s, 708m, 672w, sh, 611 vs, br, 542w, 521m, 502m, and 445m cm.⁻¹.

Trimethyltin hydride (1.03 g., 6.2 mmoles) and pentacarbonyliron (7.3 g., 37.3 mmoles) were refluxed for 2 hr. at 100—110°. Sublimation, as above, afforded (Me₃Sn)₂Fe(CO)₄ (ca. 1.1 g., 70%), [Me₂SnFe(CO)₄]₂ (ca. 0.2 g., 10%), and traces of Sn[Fe(CO)₄]₄ (ca. 0.1 g., 2%), and Me₄Sn₃[Fe(CO)₄]₄ (ca. 0.05 g., 2%), all identified spectroscopically. The very air-sensitive carbonyliron complex was not observed in this reaction.

A sample (0.5 g., 1.02 mmoles) of $(\text{Me}_3\text{Sn})_2\text{Fe}(\text{CO})_4$ was heated $(140^\circ/36 \text{ hr.})$ in a sealed tube. On opening the tube to the vacuum line, a trace of non-condensable gas was observed. Fractionation gave tetramethyltin (0.4 mmole), identified by its infrared spectrum. The residue was extracted with cyclohexane and spectroscopically identified as an approximately 1:1 mixture of $(Me_3Sn)_2Fe(CO)_4$ and $[Me_2SnFe(CO)_4]_2$.

(b) Dimethyltin dihydride (1.5 g., 9.9 mmoles) and pentacarbonyliron (14.6 g., 74.5 mmoles) were heated at 70° for 5 hr. after which reflux of the hydride had ceased, and the solution had become very dark red. From the red semi-solid residue, spectroscopically pure $[Me_2SnFe(CO)_4]_2$ (2.0 g., 64%) was obtained. The far-infrared spectrum (Nujol mull on Polythene sheets in CsI plates) showed absorptions at 780m, 750ms, 611vs, br, 546w, 514mw, 500 mw, 438mw, 204sh, 200mw cm.⁻¹.

Reaction between Stannous Chloride and Pentacarbonyliron. —Anhydrous stannous chloride (1.6 g., 8.5 mmoles) in dry tetrahydrofuran (10 ml.) was refluxed with pentacarbonyliron (26.3 g., 127 mmoles) for 17 hr., the solution becoming dark red. Work-up in the usual manner gave a dark red solid (0.35 g.), which on recrystallisation (light petroleum) afforded (III) (0.15 g., 2%).

Preparation of (III) from Stannic Chloride.—A solution in dry tetrahydrofuran (50 ml.) of the sodium salt of (tetracarbonyl)iron anion (12.5 mmoles) was added with stirring to the white suspension of stannic chloride (0.4 g.) in tetrahydrofuran (20 ml.). After 18 hr. at room temperature, volatile materials were removed and the red residue extracted with aliquot portions of chloroform (150 ml.). In this manner (III) (0.3 g., 25%) was obtained spectoscopically pure.

Carbonyl stretching frequencies are in Table 2; in the far-infrared region (Nujol mull, between Polythene sheets in CsI plates) absorptions occurred at 624sh, 615s, 603s, 592s, 547m, 524sh, 487w, 478sh, 458w, 432w, 424m, 397w, and 249w cm.⁻¹.

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