Reactions of Tin Halides with $\{(\pi\text{-Dienyl})Fe(CO)_2\}_2$ Compounds

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The products of the reactions of $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ with SnX_2 (dienyl = C_5H_5, MeC_5H_4, or C_9H_7; X = F, Cl, Br, or I) may be $\{(\pi\text{-dienyl})Fe(CO)_2X\}$, $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$, $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$, or $\{(\pi\text{-dienyl})Fe(CO)_2\}_3SnX$ depending on X, the reaction conditions, and the mole ratio of reactants. It is suggested that when X = F or Cl, the insertion of SnX_2 into the Fe–Fe bonds takes place largely in one step giving the $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$ derivatives. However, when X = Br or I, the dimers are first converted to a mixture of $\{(\pi\text{-dienyl})Fe(CO)_2X\}$ and $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$. The second of these reacts further with excess dimer to give the 'insertion' products. The reactions of $\{(\pi\text{-dienyl})'Fe(CO)_2\}_2$ with $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$ or $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$ may be used to prepare $\{(\pi\text{-dienyl})Fe(CO)_2\}\{(\pi\text{-dienyl})'Fe(CO)_2\}SnX_2$ and $\{(\pi\text{-dienyl})Fe(CO)_2\}_2\{(\pi\text{-dienyl})'Fe(CO)_2\}SnX$ respectively. The tin(IV) halides, with the exception of the fluoride, react readily with the dimers to give a similar variety of products.

THE oxidative addition of a wide variety of mono- and poly-nuclear metal carbonyl complexes to tin(II) halides provides a useful synthetic route to compounds containing tin(IV)–transition metal bonds.[1] Of particular interest are the reactions of $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ with SnX_2 (dienyl = C_5H_5; X = Cl, Br, or I) in refluxing methanol or tetrahydrofuran which have been reported to give $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$ derivatives as the sole products.[2,3] Kinetic studies of the reactions where X = Cl and Br have been described.[4]

Thus these reactions appeared to be straightforward, but we now report that this is not the case. They give $\{(\pi\text{-dienyl})Fe(CO)_2X\}$, $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$, $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$, or $\{(\pi\text{-dienyl})Fe(CO)_2\}_3SnX$ {dienyl = C_5H_5, MeC_5H_4, or C_9H_7 (indenyl); X = F, Cl, Br, or I} depending on the reaction conditions, the mole ratio of reactants, and the halogen X. Although the (π-dienyl) ligand does not influence the course of the reactions, it does affect their rates.

These are the first such reactions of tin(II) fluoride which have been reported. Many of the other compounds are new, particularly the $\{(\pi\text{-dienyl})Fe(CO)_2\}_3SnX$ derivatives of which the only other example is $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_3SnPh$,[5] and the mixed $\{(\pi\text{-dienyl})Fe(CO)_2\}\{(\pi\text{-dienyl})'Fe(CO)_2\}SnX_2$ and $\{(\pi\text{-dienyl})Fe(CO)_2\}_2\{(\pi\text{-dienyl})'Fe(CO)_2\}SnCl$ complexes which have no precedent and which would probably be difficult to prepare by other methods.

The tin(IV) halides, except the fluoride which is inert, react readily with $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ to give a mixture of $\{(\pi\text{-dienyl})Fe(CO)_2X\}$ and $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$ complexes as has previously been shown for $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ and SnX_4 (X = Cl, Br, or I).[6] However, when more strenuous conditions and an excess of the dimer is used, the $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$ and $\{(\pi\text{-dienyl})Fe(CO)_2\}_3SnCl$ derivatives are obtained.

EXPERIMENTAL

All chemicals were purchased except for $\{(\pi\text{-}C_9H_7)Fe(CO)_2\}_2$ which was prepared by the method of Hallam and Pauson.[7]

The reactions were carried out under an atmosphere of nitrogen in methanol, butanol, 100—120° petrol, benzene, xylene, or tetrahydrofuran solution using *ca.* 0·002 mol of

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[1] J. F. Young, *Adv. Inorg. Chem. Radiochem.*, 1968, **11**, 92.

[2] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 179.

[3] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1405.

[4] P. F. Barrett and K. K. W. Sun, *Canad. J. Chem.*, 1970, **48**, 3300.

[5] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. V. Shripkin, *Izvest. Akad. Nauk S.S.S.R. Ser. khim.*, 1966, 1292.

[6] R. C. Edmondson and M. J. Newlands, *Chem. and Ind.*, 1966, 1888.

[7] B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 1958, 646.

the {(π-dienyl)Fe(CO)$_2$}$_2$ complexes. Only the last of these solvents was dried and deoxygenated unless it is stated otherwise. The products were isolated by removal of the reaction solvent at reduced pressures. In some instances, purification was effected by chromatography, but usually recrystallization from methanol, or, occasionally, from acetone, xylene, or 100—120° petrol, was sufficient. It made no significant difference to the products whether the reactions were carried out in the presence or absence of light. The yields, melting points, and analyses for the products are given in the Table.

The yields, melting points, infrared spectra, and analyses for the products of the reactions of {(π-dienyl)Fe(CO)$_2$}$_2$ with tin(II) halides, and some related compounds

Compound	Yield [c]	M.p. [d]	Analyses [a]						Absorption bands [b]						
			Found			Required									
			C	H	X	C	H	X							
$(C_5H_5)Fe(CO)_2Cl$		94—95	39·4	2·9	17·4	39·5	2·4	16·7	2006(10)	2051(9·7)					
$(C_5H_5)Fe(CO)_2Br$		82—83	33·1	2·2	31·1	32·7	2·0	31·2	2003(10)	2047(10)					
$(C_5H_5)Fe(CO)_2I$		118—119	27·6	1·7		27·6	1·6	41·8	1997(8·7)	2038(10)					
$(MeC_5H_4)Fe(CO)_2Cl$		47—49	42·4	3·1	15·6	42·9	3·9	15·9	1999(10)	2045(10)					
$(MeC_5H_4)Fe(CO)_2I$		42—43	29·9	2·0	39·6	30·2	2·2	39·9	1991(9·3)	2033(10)					
$(C_9H_7)Fe(CO)_2I$		47—48	36·9	2·1		37·1	2·0	36·0	1991(9·6)	2034(10)					
$(C_5H_5)Fe(CO)_2SnCl_3$		153—154	20·9	1·5		20·9	1·2	26·5	2002(10)	2041(10)					
$(C_5H_5)Fe(CO)_2SnBr_3$	82	167—168	16·0	1·0	45·0	15·7	0·9	44·7	1999(9·2)	2038(10)					
$(C_5H_5)Fe(CO)_2SnI_3$	28	136—137	12·2	0·9	56·5	12·4	0·7	56·3	1997(9·6)	2035(10)					
$(MeC_5H_4)Fe(CO)_2SnCl_3$		83—84	22·7	1·6		23·0	1·7	25·8	1999(9·5)	1938(10)					
$(MeC_5H_4)Fe(CO)_2SnBr_3$	71	71—72	17·5	1·4	43·4	17·5	1·3	43·7	1998(9·6)	2036(10)					
$(MeC_5H_4)Fe(CO)_2SnI_3$	36	74—76	13·7	1·4	55·4	13·9	1·0	55·0	1992(10)	2030(10)					
$(C_9H_7)Fe(CO)_2SnCl_3$		125—127	29·0	1·2		29·0	1·5	23·8	1997(10)	2035(9·7)					
$(C_9H_7)Fe(CO)_2SnBr_3$	35	119—122	22·1	1·3	41·2	22·6	1·2	41·0	1996(9·7)	2035(10)					
$(C_9H_7)Fe(CO)_2SnI_3$	13	131—133	18·0	1·2	52·5	18·3	1·0	52·4	1992(10)	2029(10)					
$\{(C_5H_5)Fe(CO)_2\}_2SnF_2$	80	175—177	33·3	2·2		32·8	2·0		1955(4·1)	1974(7·5)	1999(7·5)	2025(10)			
$\{(C_5H_5)Fe(CO)_2\}_2SnCl_2$	83	166—168	30·5	1·8		30·9	1·9	13·1	1954(2·9)	1974(5·4)	2000(5·4)	2024(10)			
$\{(C_5H_5)Fe(CO)_2\}_2SnBr_2$	32	dec. 182	26·3	1·9		26·5	1·6	25·3	1955(2·6)	1975(5·3)	1999(5·5)	2025(10)			
$\{(C_5H_5)Fe(CO)_2\}_2SnI_2$	14 [e] 48 [f]	238—240	22·6	1·5	35·5	23·1	1·4	34·9	1953(2·6)	1974(5·5)	1998(6·7)	2023(10)			
$\{(MeC_5H_4)Fe(CO)_2\}_2SnCl_2$	80	102—103	33·7	2·4	12·6	33·4	2·5	12·4	1948(2·7)	1971(5·6)	1993(5·2)	2020(10)			
$\{(MeC_5H_4)Fe(CO)_2\}_2SnBr_2$	28	119—120	28·9	2·2	24·2	28·9	2·1	24·2	1950(2·8)	1970(5·7)	1993(5·7)	2020(10)			
$\{(MeC_5H_4)Fe(CO)_2\}_2SnI_2$	36 [e] 60 [f]	139—142	25·0	1·5		25·4	1·9	33·8	1949(2·5)	1970(6·0)	1992(6·9)	2020(10)			
$\{(C_9H_7)Fe(CO)_2\}_2SnCl_2$	75	218—220	40·8	2·2	11·2	41·0	2·2	11·0	1950(3·6)	1973(6·7)	1995(5·6)	2021(10)			
$\{(C_9H_7)Fe(CO)_2\}_2SnBr_2$	44	dec. 220	35·8	2·0		36·0	1·9	21·8	1951(3·3)	1973(6·9)	1996(5·7)	2121(10)			
$\{(C_9H_7)Fe(CO)_2\}_2SnI_2$	50 [e] 70 [f]	dec. 215	31·8	2·1	31·0	31·9	2·2	30·7	1950(3·4)	1972(7·3)	1993(6·6)	2020(10)			
$\{(C_5H_5)Fe(CO)_2\}\{(MeC_5H_4)Fe(CO)_2\}SnCl_2$	55	109—111	32·2	2·2	12·7	32·2	2·2	12·7	1952(2·9)	1972(6·4)	1996(5·8)	2023(10)			
$\{(C_5H_5)Fe(CO)_2\}\{(MeC_5H_4)Fe(CO)_2\}SnBr_2$		122—125	27·9	2·2	24·6	27·8	1·9	24·8	1953(2·5)	1972(5·9)	2000(5·6)	2022(10)			
$\{(C_5H_5)Fe(CO)_2\}\{(MeC_5H_4)Fe(CO)_2\}SnI_2$	21	148—149 (dec.)	23·9	1·6	34·6	24·3	1·7	35·3	1953(2·3)	1974(6·1)	1996(6·4)	2022(10)			
$\{(C_5H_5)Fe(CO)_2\}\{(C_9H_7)Fe(CO)_2\}SnCl_2$	22	dec. 160	38·6	2·0	11·1	38·6	2·7	12·0	1951(3·4)	1972(6·9)	1997(5·9)	2021(10)			
$\{(C_5H_5)Fe(CO)_2\}\{(C_9H_7)Fe(CO)_2\}SnBr_2$		dec. 130	31·7	1·9	23·4	31·6	1·8	23·4							
$\{(C_5H_5)Fe(CO)_2\}\{(C_9H_7)Fe(CO)_2\}SnI_2$	8	dec. 140	27·8	1·6	32·6	27·8	1·5	32·7							
$\{(C_5H_5)Fe(CO)_2\}_3SnF$	58	dec. 229	36·4	2·4		37·6	2·2	2·8							
$\{(C_5H_5)Fe(CO)_2\}_3SnCl$	51	dec. 220	36·8	2·4	5·8	36·8	2·2	5·2							
$\{(C_9H_7)Fe(CO)_2\}_3SnF_3$	72	dec. 185	47·6	2·5		48·3	2·6	2·3							
$\{(C_9H_7)Fe(CO)_2\}_3SnBr$	29	dec. 200	44·7	2·6	9·4	45·0	2·4	9·1							
$\{(C_5H_5)Fe(CO)_2\}_2\{(MeC_5H_4)Fe(CO)_2\}SnCl$	48	157—160	37·2	2·8		37·7	2·4								
$\{(C_5H_5)Fe(CO)_2\}_2\{(C_9H_4)Fe(CO)_2\}SnCl$		156—159	33·3	2·2		32·8	2·0		1953(2·7)	1974(5·7)	1996(5·0)	2023(10)			
									1955(3·0)	1973(6·6)	1995(6·6)	2021(10)			
									1930(sh)	1934(4·1)	1945(5·3)	1976(3·9)	1983(10)	2001(1·7)	2010(2·3)
									1933(sh)	1937(3·5)	1949(4·6)	1973(4·2)	1985(10)	2003(1·8)	2011(2·9)
									1928(4·7)	1943(4·0)	1971(6·0)	1982(10)			
									1930(sh)	1936(3·1)	1948(4·9)	1973(4·8)	1985(10)		
									1929(sh)	1935(3·8)	1947(4·9)	1972(4·4)	1983(10)	2001(2·1)	2008(2·5)
									1933(sh)	1938(3·3)	1948(4·7)	1974(4·3)	1986(10)	2003(2·4)	2010(3·1)

[a] X = Halogen. [b] Infrared spectra (1700—2100 cm^{-1}) of carbon disulphide solutions with relative peak height in parentheses. [c] When reactions were carried out in benzene, methanol, and tetrahydrofuran solutions, the yields of the products were almost independent of the solvent unless it is stated otherwise. [d] Determined in sealed tubes dec. = decomposed without melting, and (dec.) = melted with decomposition. [e] Yield of reaction in methanol or tetrahydrofuran. [f] Yield of reaction in benzene.

The i.r. spectra were obtained as described previously.[8] The frequencies and relative intensities of absorption bands lying between 1700 and 2100 cm^{-1} are summarised in the Table.

RESULTS

The dimer {(π-C_5H_5)Fe(CO)$_2$}$_2$ (I) failed to react with anhydrous tin(II) fluoride (mole ratio 1 : 3) in methanol at room temperature, but in refluxing n-butanol {(π-C_5H_5)Fe(CO)$_2$}$_2$SnF$_2$ was obtained after *ca.* 12 h. Although the reaction was monitored by i.r. spectroscopy, no other species could be detected. The similar reaction of {(π-MeC$_5$H$_4$)Fe(CO)$_2$}$_2$ (II) required 15 h for completion, but the product could not be purified. The indenyl dimer, {(π-C_9H_7)Fe(CO)$_2$}$_2$ (III) was consumed within 3 h to give a mixture of {(π-C_9H_7)Fe(CO)$_2$}$_2$SnF$_2$ and {(π-C_9H_7)Fe(CO)$_2$}$_3$SnF which could not be separated but which were identified by i.r. spectroscopy. The cyclopentadienyl and indenyl {(π-dienyl)Fe(CO)$_2$}$_3$SnF derivatives were the sole products when (I) or (III) and SnF$_2$ (mole ratio 1 : 3) were heated in refluxing xylene for 10 and $\frac{1}{2}$ h respectively. {(π-C_5H_5)Fe(CO)$_2$}$_2$SnF$_2$ was an intermediate in the first of these reactions.

Both (I) and (II), but not (III), reacted with SnCl$_2$,2H$_2$O (mole ratio 1 : 1) in methanol at room temperature to give the chlorides {(π-dienyl)Fe(CO)$_2$Cl}. The reactions ceased after a few minutes, but were completed if air was bubbled through the solutions. If the solvent was dried and deoxygenated, (I) slowly gave {(π-C_5H_5)Fe(CO)$_2$}$_2$SnCl$_2$ only. The same compound was the sole product in refluxing benzene, methanol, or tetrahydrofuran in reactions which required respectively 1, 10, and 5 h for completion. Changes in the (I) : SnCl$_2$,2H$_2$O mole ratio from 1 : 1 to 1 : 2, and finally to 1 : 10 caused the formation of increasing amounts of {(π-C_5H_5)Fe(CO)$_2$SnCl$_3$}, although this was always a minor product, and reduced the reaction times to $\frac{1}{4}$, 2, and 2 h respectively in the above solvents. The dimer (II) reacted similarly but more slowly, whilst (III) reacted

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[8] M. Casey and A. R. Manning, *J. Chem. Soc.* (*A*), 1970, 2258.

more rapidly and only gave $\{(\pi\text{-}C_9H_7)Fe(CO)_2SnCl_3\}$ when very large quantities of tin(II) chloride were used. In refluxing xylene, $SnCl_2,2H_2O$ converted all three dimers, (I)—(III) (mole ratio 1 : 2), to $\{(\pi\text{-dienyl})Fe(CO)_2\}_3SnCl$ complexes, but only the cyclopentadienyl derivative could be purified. Spectroscopic studies showed that this was formed *via* $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2SnCl_2$, and that reaction times were 12, 15, and 1 h for (I), (II), and (III) respectively. In all of these reactions, anhydrous tin(II) chloride and the dihydrate gave identical results.

At room temperature in dried and deoxygenated methanol, $SnBr_2,2H_2O$ reacted with all three dimers to give small amounts of $\{(\pi\text{-dienyl})Fe(CO)_2Br\}$ complexes, but the methylcyclopentadienyl and indenyl derivatives could not be isolated. When (I) and $SnBr_2,2H_2O$ were heated together in refluxing benzene, methanol, or tetrahydrofuran, comparable quantities of $\{(\pi\text{-}C_5H_5)Fe(CO)_2Br\}$ and $\{(\pi\text{-}C_5H_5)Fe(CO)_2SnBr_3\}$ were formed within *ca.* 5 min. When an equimolar ratio of reactants was used, not all of the dimer was consumed, and the remainder underwent a slower reaction with the initial products to give $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2SnBr_2$ only (reaction times 8, 24, and 24 h in the above solvents). If an excess of tin(II) bromide was used (mole ratio 1 : 2) most of the dimer was consumed in this initial reaction, but some $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2SnBr_2$ could be detected. Its formation was only suppressed by using very large amounts of $SnBr_2$. Thus when a reactant mole ratio of 1 : 10 is used, all of (I) underwent the initial reaction, and the bromo-complex was converted to $\{(\pi\text{-}C_5H_5)Fe(CO)_2SnBr_3\}$ so that this was the final product (reaction times ¼, ¼, and 1 h). Similar products are obtained with both (II) and (III) in reactions which were respectively slower and faster than those of (I). Of the three dimers, only (III) reacted with tin(II) bromide to give a $\{(\pi\text{-dienyl})Fe(CO)_3\}_3SnBr$ complex, and this in refluxing xylene using a 2 : 1 mole ratio of reactants (reaction time ½ h).

The reactions of all three dimers with anhydrous tin(II) iodide were similar to their reactions with $SnBr_2,2H_2O$ in methanol or tetrahydrofuran solutions. A major difference was that although both $\{(\pi\text{-dienyl})Fe(CO)_2I\}$ and $\{(\pi\text{-dienyl})Fe(CO)_2SnI_3\}$ complexes were formed very quickly, the first of these compounds could not be converted to the

xylene were used to prepare $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}\{(\pi\text{-dienyl})Fe(CO)_2\}SnX_2$ ($X = Cl$, Br, or I; dienyl $= C_5H_5$, MeC_5H_4, or C_9H_7). A similar reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2SnF_2$ with (I), and of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2SnCl_2$ with (II) and (III) gave $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_3SnF$, $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2\{(\pi\text{-}MeC_5H_4)Fe(CO)_2\}SnCl$, and $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2\{(\pi\text{-}C_9H_7)Fe(CO)_2\}SnCl$ after reaction times of 24, 12, and 2 h respectively. We have also prepared $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}\{(\pi\text{-}MeC_5H_4)Fe(CO)_2\}\{(\pi\text{-}C_9H_7)Fe(CO)_2\}SnCl$, but it was a liquid which could not be purified.

The product yields given in the Table are those for the reactions of $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ unless it is obviously otherwise, *e.g.* the preparation of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}\{(\pi\text{-}MeC_5H_4)Fe(CO)_2\}SnCl_2$. They are quoted for reactant mole ratios which give the highest yields of that particular compound. When the reactions were carried out in a variety of solvents, the yields were normally almost independent of the solvent, and the differences could be due to mechanical losses. The exceptions to this generalization were the reactions involving tin(II) iodide. The product yields using methanol or tetrahydrofuran, and those using benzene as the solvent are quoted where applicable.

The products were generally air-stable crystalline solids. Their colours deepened with increasing atomic weight of the halogen and an increase in the number of iron atoms in the molecule, whilst the π-indenyl derivatives always more highly coloured than their cyclopentadienyl and methylcyclopentadienyl analogues. $\{(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3\}$ is yellow, $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2SnI_2$ is brown, and $\{(\pi\text{-}C_9H_7)Fe(CO)_2\}_3SnBr$ is purple.

DISCUSSION

The results suggest that when tin(II) halides react with the dimers $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ in refluxing benzene, methanol, or tetrahydrofuran to give the 'insertion' compounds $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$, they do so either 'directly' in a single stage reaction, or 'indirectly' in a reaction which has two distinct steps with the initial formation of $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$ and its subsequent reaction with more dimer to give the 'insertion' product.

these two compounds would also be expected in the reactions at room temperature if the tin(IV) halide was the reactive species. Only the first was observed, and it is possible that the limited reaction which does occur is attributable to a small quantity of an oxidizing agent such as air which could not be excluded. The reaction must require at least two moles of SnX_2 (4 g atoms of halogen) per mole of dimer consumed. As a consequence either the excess tin is in a reduced oxidation state, perhaps as the metal, or an oxidizing agent is present. The reaction of (I) with $SnBr_2$, which was mentioned above, tends to rule out the second possibility, and suggests that the unused tin is present as the free metal. The similarity of the reactions of $SnBr_2,2H_2O$ and anhydrous SnI_2 in wet or in dried solvents indicates that the presence, or absence, of water is not an important factor.

When a large excess of tin(II) bromide is used, the $\{(\pi\text{-dienyl})Fe(CO)_2Br\}$ formed is converted to $\{(\pi\text{-dienyl})Fe(CO)_2SnBr_3\}$ in a relatively slow reaction. Thus these compounds are the sole final products, and may be obtained in high yields. In the case of the tin(II) iodide systems, the insertion of SnI_2 into the Fe–I bond does not take place.[10] Consequently the yields of the $\{(\pi\text{-dienyl})Fe(CO)_2SnI_3\}$ complexes in methanol or tetrahydrofuran solutions are never greater than 50%, and $\{(\pi\text{-dienyl})Fe(CO)_2I\}$ derivatives are also present. However, these tend to decompose and the tri-iodotin-compounds are easily purified. Thus the reactions provide straightforward routes to the $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$ derivatives which are very economical when $X = Br$ and useful when $X = I$. These observations rule out the possibility that $\{(\pi\text{-dienyl})Fe(CO)_2X\}$ are the sole initial products which are subsequently converted to $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$.

When equimolar quantities of SnX_2 and $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ react by the ' indirect ' route, all of the tin(II) halide is consumed in the rapid first step, but only half of the dimer. The remainder then reacts more slowly with $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$ to give $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$ together with $\{(\pi\text{-dienyl})Fe(CO)_2X\}$. As half of the dimer is converted to the halogeno-complexes, the yields of the ' insertion ' compounds cannot be greater than 50%. In most instances, continued heating of the reaction mixture brings about the decomposition of the $\{(\pi\text{-dienyl})Fe(CO)_2X\}$ by-products. This is rapid in solvents such as xylene at 139 °C, but slower in benzene, methanol, or tetrahydrofuran, which allows the most stable, *e.g.* $(\pi\text{-}C_5H_5)Fe(CO)_2I$, to be isolated.

The ' direct ' reaction proceeds with the formation of no detectable intermediates or by-products, and consequently the ' insertion ' compounds are obtained in high yields, *ca.* 70—90%. Its importance decreases, and that of the ' indirect ' route increases, for $SnF_2 > SnCl_2 > SnBr_2$ so that whereas tin(II) fluoride reacts solely by the ' direct ' route, the chloride and bromide utilize both. The formation of some $\{(\pi\text{-dienyl})Fe(CO)_2SnCl_3\}$ when large amounts of anhydrous or hydrated tin(II) chloride are used suggests that a small proportion of the dimer $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ is consumed by the ' indirect ' reaction. With tin(II) bromide, some $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnBr_2$ is formed at $SnBr_2$: dimer mole ratios of 2 : 1 and even larger. This indicates that a little of the dimer undergoes the ' direct ' insertion reaction whilst most of it takes part in the ' indirect ' reaction. The corresponding reactions of tin(II) iodide proceed by a similar mixture of routes in methanol and tetrahydrofuran, but in benzene only the ' direct ' one is of any importance.

The second step of the ' indirect ' route may be used to prepare the mixed ' insertion ' products $\{(\pi\text{-dienyl})Fe(CO)_2\}\{\pi\text{-dienyl})'Fe(CO)_2\}SnX_2$ from $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$ and $\{(\pi\text{-dienyl})'Fe(CO)_2\}_2$. If it is used to prepare $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2SnCl_2$, the reaction is much slower than that which gives the corresponding bromide, whereas the reaction of (I) with tin(II) chloride is much faster than its reaction with tin(II) bromide. This eliminates the possibility that the ' direct ' route involves the formation of $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$ which is consumed so rapidly that it cannot be detected by i.r. spectroscopy.

The new $\{(\pi\text{-dienyl})Fe(CO)_2\}_3SnX$ derivatives (Table) are given when $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$ react with the dimers. These reactions are similar to those of the second step of the ' indirect ' route to the ' insertion ' compounds, but are much slower, and, consequently, require more vigorous conditions. Under such conditions, *e.g.* refluxing xylene, the by-products, $\{(\pi\text{-dienyl})Fe(CO)_2X\}$ ($X = F$, Cl, or Br), decompose. Our inability to prepare compounds where $X = I$ may arise from their instability under the conditions of their formation. Similar reactions between $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2SnCl_2$ and $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ may be used to prepare mixed compounds $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2\{(\pi\text{-dienyl})Fe(CO)_2\}SnCl$, and even $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}\{(\pi\text{-}MeC_5H_4)Fe(CO)_2\}\{(\pi\text{-}C_9H_7)Fe(CO)_2\}SnCl$. Unfortunately this would not crystallize, but its i.r. spectrum was similar to those of the other tri-iron derivatives.

The reactions between tin(IV) halides, SnX_4 ($X = Cl$, Br, and I), and (I) have been shown to yield a mixture of $\{(\pi\text{-}C_5H_5)Fe(CO)_2X\}$ and $\{(\pi\text{-}C_5H_5)Fe(CO)_2SnX_3\}$.[6] We now find that these three halides react similarly with (II) and (III), but tin(IV) fluoride is inert. Under more vigorous conditions, the halogeno-iron complexes may decompose, but the trihalogenotin-derivatives are able to undergo further slower reactions with $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ to give $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$ and, when $X = Cl$, $\{(\pi\text{-dienyl})Fe(CO)_2\}_3SnX$ (*cf.* the dimer–SnX_2 reactions discussed above).

In the reactions of the dimers with $\{(\pi\text{-dienyl})Fe(CO)_2\}_nSnCl_{4-n}$ ($n = 0$—2), the reactivity of the Sn–Cl bond decreases as n increases, and (III) reacts more readily than (I) or (II).

Few reactions have been reported which are similar to those postulated here. The first step of the ' indirect ' route may have its counterparts in some reactions of

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[10] M. J. Mays and S. M. Pearson, *J. Chem. Soc.* (*A*), 1969, 136.

InCl,[11] $\{\text{GeCl}_3\}^-$,[12] or SnCl_2 [2] with $\{(\pi\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\}_2$ or $\{(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\}_2$ which give complexes containing one Mo–M or Fe–M bond (M = In, Ge, or Sn). Reactions which are superficially similar to the second step of the 'indirect' route are those of RSnX_3 with $\{(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\}_2$,[6] or $\text{Co}_2\text{(CO)}_8$ [13] to give $\{(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{SnX}_2\text{R}\}$ and $\text{RSn}\{\text{Co(CO)}_4\}_3$ respectively (R = phenyl or halogen; X = halogen).

The i.r. spectra of the $\{(\pi\text{-dienyl})\text{Fe(CO)}_2\text{SnX}_3\}$ and the $\{(\pi\text{-dienyl})\text{Fe(CO)}_2\}\{(\pi\text{-dienyl})'\text{Fe(CO)}_2\}\text{SnX}_2$ derivatives (dienyl, dienyl′ = C_5H_5, MeC_5H_4, or C_9H_7; X = F, Cl, Br, or I) (Table) are similar to those of, for example, $\{(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{SnCl}_3\}$ or $\{(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\}_2\text{SnCl}_2$ between **1700** and **2100** cm^{-1}.[14] They exhibit no unusual or unexpected characteristics. The spectra of some of the $\{(\pi\text{-dienyl})\text{Fe(CO)}_2\}_3\text{SnX}$ complexes show more than six absorption bands or shoulders due to their ν(CO) vibrations. Thus it is likely that they exhibit some form of isomerism, perhaps arising from restricted rotation about the Fe–Sn bond (*e.g.* ref. 15).

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[11] A. T. T. Hsieh and M. J. Mays, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 223.

[12] J. D. Colton and R. M. Peachey, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 727.

[13] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2222.

[14] D. M. Adams, J. N. Crosby, and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1968, 3056.

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