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Reactions of tin(IV) halides with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ (n = 1 or 2)

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Abstract

The reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ (I) and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ (II) with tin(IV) Lewis acids $E = SnX_4$ or $RSnX_3$ (X = Cl, Br, or I; R = alkyl, Ph, $Fe(\eta\text{-}C_5H_5)(CO)_2$ or $Fe(\eta\text{-}C_5H_5)(CO)(CNMe)$ proceed by way of often isolable adducts [I-E] and [II-E]. II but not I also forms adducts with $[\{Fe(\eta\text{-}C_5H_5)_2(CO)_2\}_2SnX_2]$. On the basis of IR spectroscopy it is concluded that these adducts have the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CO)\{\mu\text{-}CN(Me)E\}]$ structure with N→Sn bonds (L = CO or CNMe). They are more or less unstable; some break down in the solid state, some in the benzene solution, and all in acetone solution to give mono-iron complexes, in reactions which appear to be largely if not completely regiospecific. Thus when $E = SnX_4$ the products are $[Fe(\eta\text{-}C_5H_5)(CO)(L)X]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnX_3]$ where L = CO (from I) or CNMe (from II) which appear to form in ca. equal amounts and in high yields. Small amounts of $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]^+$ $[SnX_3]^-$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)X]$ are also formed from I when X = Br or I, but the second do not appear to be primary products. A previously proposed mechanistic scheme is used to account for the course of these reactions.

Introduction

We have a continuing interest in the reactions of electrophilic reagents with polynuclear metal complexes containing CO and related ligands [1], and have suggested a mechanistic framework within which some of these reactions may be considered [2].

Here we report detailed studies of the reactions of tin(IV) halide derivatives with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4\text{-}n}(CNMe)_n]$ ($n = 1$ or 2). In many instances 1/1 adducts are formed which contain the $\mu\text{-}\{CN(Me)SnX_4\}$ moieties and N→Sn bonds. In some cases these adducts have been isolated and purified, or they have been detected and identified by spectroscopic techniques. The adducts are of varying stabilities but all

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eventually decompose to mixtures of mono-iron complexes which usually contain Fe–Sn or Fe–X bonds. These final products have been separated and identified in some cases, but not all.

Previous work from these laboratories has shown that SnX_4 (X = Cl, Br or I) cleave the metal–metal bond in $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ to give equimolar amounts of $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2SnX_3]$ [3]. Tin(IV) halide derivatives, $RSnX_3$ and R_2SnX_2, where R is an alkyl, aryl or transition metal based radical, undergo similar reactions but only at higher temperatures [3]. On the other hand, we have found that SnI_4 and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ form a 1/1 adduct $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)\{\mu\text{-}CN(Me)SnI_4\}]$ which decomposed under the conditions of the experiment to unidentified species which did not possess bridging CO or CNMe ligands [4].

Experimental

Previously published methods were used to prepare $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ [5], $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ [6], $[Fe(\eta\text{-}C_5H_5)(CO)_2SnX_3]$ [4], and $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SnX_2]$ (X = F, Cl, Br or I) [4]. Other chemicals were purchased and used as received except for $SnCl_4$ or $SnBr_4$, which were distilled before use.

Unless otherwise stated, all reactions were carried out at room temperature under nitrogen in solvents which had been dried and deoxygenated by refluxing over calcium hydride (tetrahydrofuran, benzene or toluene) or magnesium (methanol), and distilled before use. Tetrahydrofuran was further purified by distillation from sodium and benzophenone.

The reactions were monitored by IR spectroscopy. An aliquot of the reaction mixture was taken and the solvent removed at reduced pressure. The residue was completely redissolved in chloroform and the IR spectrum taken. The spectra thus obtained for reactions run in benzene solution did not differ significantly from those obtained directly from reactions run in chloroform.

IR spectra were run on a Perkin–Elmer 337 spectrometer, equipped with a Hitachi–Perkin–Elmer readout recorder. They were calibrated with gaseous DCl and water vapour in the 1600–2150 cm^{-1} region [7]. Spectra were also run on a Perkin–Elmer 283B between 200 and 4000 cm^{-1} using samples dispersed in caesium bromide discs. They were calibrated with polystyrene [7].

Analyses were carried out in the Analytical Laboratory of University College, Dublin.

Reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ *(n = 1 or 2) with* SnX_4 *(X = F, Cl, Br or I)*

SnX_4 was added to a benzene solution (50 ml) of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ (1 g, mole ratio 1/1). Although no reaction took place when X = F, precipitates were given when X = Cl (pink), Br (pink) and I (brown). These were filtered off, washed with pentane and dried. They were identified as 1/1 adducts $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)(SnX_4)]$.

Under the same conditions, SnX_4 and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ (1 g, mole ratio 1/1) gave precipitates when X = Cl (brown), Br (purple) and I (purple). They were filtered off, washed with pentane and dried. When X = Cl or Br they were identified as 1/1 adducts $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2(SnX_4)]$, but when X = I the product was formulated as $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2\{Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnI_3\}]$. This last was also the product if a solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ (1 g) in benzene (40 ml) was added to one of SnI_4 also in benzene (15 ml) (mole ratio 1/1).

Reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ ($n = 1$ or 2) with $RSnX_3$ $X = Cl$ or Br; $R = Me$, n-Bu, Ph, $Fe(\eta\text{-}C_5H_5)(CO)_2$, or $Fe(\eta\text{-}C_5H_5)(CO)(CNMe)$

A solution of $RSnX_3$ in benzene (20 ml) was added to one of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ (0.5 g mole ratio 1/1) in benzene (30 ml). A reaction took place in all cases. With $MeSnCl_3$ and $PhSnCl_3$ pink solids precipitated which were filtered off, washed with pentane and dried. They were identified as adducts of the type $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)(RSnCl_3)]$ by analyses and spectroscopic data. When $RSnX_3 = \text{n-BuSnCl}_3$, $[Fe(\eta\text{-}C_5H_5)(CO)_2SnX_3]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnX_3]$ ($X = Cl$ or Br) the colours of the reaction mixtures changed from purple to red brown, and solids could be precipitated by the addition of pentane (50 ml) and cooling. The solids were all identified as 1/1 adducts $[(Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)(RSnX_3)]$ except when $RSnX_3 = \text{n-BuSnCl}_3$ or $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)(SnCl_3]$. Then the precipitates consisted of inseparable mixtures of species that did not possess bridging CO or CNMe ligands.

Similar reactions between $RSnX_3$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ (0.5 g mole ratio 1/1) in benzene solution (50 ml) gave pink precipitates when $R = Me$ and Ph or a brown precipitate when $R = \text{n-Bu}$. Although all three were identified spectroscopically as adducts, only $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2(MeSnCl_3)]$ analysed well. However if a reactant mole ratio of 1/2 was used an analytically pure sample of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2(PhSnCl_3)]$ could be isolated. When $RSnX_3 = [Fe(\eta\text{-}C_5H_5)(CO)_2SnX_3]$ or $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnX_3]$ ($X = Cl$ or Br) no solids precipitated from the reaction mixtures until pentane (50 ml) was added and they were cooled. Then brown solids were obtained which were filtered off, washed with pentane and dried. They were identified spectroscopically and analytically as 1/1 adducts $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2(RSnX_3)]$.

Reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ ($n = 1$ or 2) with R_2SnX_2 ($R = \text{n-Bu}$ or $Fe(\eta\text{-}C_5H_5)(CO)_2$

$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ does not react with either n-Bu_2SnCl_2 or $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SnCl_2]$ (mole ratio 1/1) either in benzene or methanol at room temperature or under reflux even during 7 h.

A solution of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SnX_2]$ ($X = Cl$ or Br) in benzene (20 ml) was added dropwise to one of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ (0.5 g; mole ratio 1/1) also in benzene (30 ml). Although IR spectroscopy showed that adducts were formed with $\nu(CN)$ 1580 and 2187 cm^{-1}, and $\nu(CO)$ 1805 and 1940–2030 cm^{-1}, they could not be isolated. When $X = F$, no reaction took place.

Reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ ($n = 1$ or 2) with Me_3SnCl

There was no reaction between $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ ($n = 1$ or 2) and Me_3SnCl in either bezene or methanol at either room temperature or under reflux.

Breakdown of the isolated 1 : 1 adducts $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n(E)]$ ($n = 1$ or 2; E = tin (IV) Lewis acid) in acetone

The $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)(E)]$ adducts (1.4 g) were dissolved in acetone

(30 ml). IR spectroscopy showed that in all instances they decomposed to give species which did not contain any bridging CO or CNMe ligands. The solvents were removed from the reaction mixtures at reduced pressure, and the residues extracted with benzene. When E = $SnCl_4$ all of the residue dissolved, so the solution thus obtained was filtered and the benzene removed at reduced pressure to give a tar which dissolved in hot methanol. On cooling this solution it deposited orange crystals of $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnCl_3]$ which were filtered off, washed with very cold methanol and dried. The filtrate was evaporated to dryness and the resulting residue crystallized from dichloromethane pentane mixtures to give $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$.

When E = $SnBr_4$ there was a fraction of the original residue which was insoluble in benzene. It was crystallized from a dichloromethane pentane mixture to give $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)][SnBr_3]$. The benzene-soluble fraction of the residue was separated as described for E = $SnCl_4$ into $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnBr_3]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$. Traces of $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Br]$ were also obtained by further cooling of the dichloromethane pentane mother liquors which had already yielded $[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$.

Those $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)(E)]$ adducts where E = $MeSnCl_3$, $PhSnCl_3$, $[Fe(\eta\text{-}C_5H_5)(CO)_2SnX_3]$ (X = Cl or Br) and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnBr_3]$ also break down in acetone solutions to species which do not contain bridging CO or CNMe ligands. Unfortunately it was not possible to separate the various products by crystallization techniques, although they could be identified in some instances.

In all reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ with tin(IV) halides E in benzene solution, adduct formation was accompanied by cleavage of the dimer to species which did not contain bridging CO or CNR ligands. As this was generally insignificant, such species were not isolated in most instances, but were identified by their IR spectra. However when E = SnI_4, dimer cleavage was the dominant reaction in benzene solution and we were able to isolate three products from the reaction mixture (apart from an impure sample of the adduct) using fractional crystallization. They were identified as $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnI_3]$, $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)I]$.

The $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2(E)]$ adducts (0.5 g) were dissolved in acetone and stirred. When E = SnX_4 (X = Cl or Br) a reaction took place at room temperature and the mixture could be separated into $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnX_3]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)X]$ using the fractional crystallization techniques described above. When E = $[Fe(\eta\text{-}C_5H_5)(CO)_2SnX_3]$ or $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnX_3]$ (X = Cl or Br) the adducts were stable in acetone solution at room temperature, but under reflux they broke down to species containing only terminal CO and CNMe ligands. However we were not able to isolate and identify these.

In all the reactions described above, replacement of acetone by acetonitrile or tetrahydrofuran gave the same results. The analysis, melting points, yields and IR spectra of the adducts and other reaction products are summarized in Tables 1–3.

Results and discussion

In solution $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ (I) and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ (II) exist as mixtures of rapidly interconverting isomers [5,6]. Although I and II fail to react with weaker tin(IV) Lewis acids, with the stronger ones, E, they generally

Table 1

Yields, decomposition points and analyses for the adducts of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3CNMe)]$ (I) and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ (II) with tin(IV) Lewis acids E

E	Dec. Pt. (°C)	Analyses (Found (calcd.) (%))				Yield (%)
		C	H	N	X	
Adducts of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$						
$SnBr_4$ [a]	77–80	23.0	1.7	1.7		65
		(22.4)	(1.6)	(1.7)		
$MeSnCl_3$	136–139	31.1	2.9	2.6	15.4	77
		(31.6)	(2.6)	(2.3)	(17.5)	
$PhSnCl_3$	52–55	36.8	2.8	1.9	14.5	93
		(37.3)	(3.4)	(2.1)	(15.8)	
$Fe(\eta\text{-}C_5H_5)(CO)_2SnBr_3$	67–70	28.5	1.5	1.8	24.1	4.7
		(29.2)	(2.0)	(1.6)	(26.1)	
Adducts of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$						
$SnCl_4\cdot\frac{1}{6}C_6H_6$ [b]	89–91	31.3	3.3	4.1	19.7	52
		(31.2)	(2.6)	(4.3)	(21.7)	
$SnBr_4$ [c]	–	24.0	2.8	3.2		27
		(23.3)	(1.9)	(3.4)		
$MeSnCl_3$	98–101	32.6	3.3	4.2	16.8	74
		(32.9)	(3.1)	(4.5)	(17.2)	
$PhSnCl_3\cdot\frac{1}{6}C_6H_6$	78–80	39.5	3.6	4.0	15.1	97
		(39.7)	(3.2)	(4.0)	(15.4)	
$Fe(\eta\text{-}C_5H_5)(CO)_2SnCl_3\cdot\frac{1}{6}C_6H_6$	47–50	36.0	3.0	3.6	12.9	73
		(36.2)	(2.8)	(3.5)	(13.4)	
$Fe(\eta\text{-}C_5H_5)(CO)_2SnBr_3$	96–98	30.5	2.8	3.1	24.5	25
		(30.1)	(2.3)	(3.1)	(26.2)	
$Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnCl_3$	–	36.2	3.4	4.9	11.9	36
		(36.2)	(3.0)	(5.3)	(13.4)	
$Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnBr_3\cdot\frac{1}{3}C_6H_6$	39–41	32.4	2.7	4.3	29.1	36
		(32.7)	(2.7)	(4.4)	(29.3)	
$Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnI_3$	–	25.8	2.5	3.9	33.8	–
		(26.9)	(2.2)	(3.8)	(35.6)	

[a] Sn = 13.2 (14.7)%. [b] Sn = 18.00 (18.2)%. [c] Sn = 13.6 (14.5)%.

formed 1/1 adducts [I–E] and [II–E] derived from isomers of both I and II which have one μ-CNMe ligand. Some of these adducts could be isolated and analysed; most others could be detected spectroscopically and the transient, non-detectable formation of a few could be inferred from the formation of the products characteristic of adduct decomposition.

The adducts proved to be of varying stabilities with some breaking down in benzene solution or even the solid state. However all decomposed on dissolution in acetone or other donor solvents such as acetonitrile or tetrahydrofuran. These decomposition products did not contain bridging CO or CNMe ligands. In some instances they could be isolated and analysed; in others they could only be identified by IR spectroscopy.

Adduct formation, characterisation and structure

Although I did not react with the Lewis acids E = Me_3SnCl or R_2SnCl_2 in benzene solution (R = n-Bu or $Fe(\eta\text{-}C_5H_5)(CO)_2$) it immediately formed 1/1

(Continued on p. 122)

Table 2

IR spectra of the adducts of [$Fe_2(\eta$-$C_5H_5)_2(CO)_3(CNMe)$] (I) and [$Fe_2(\eta$-$C_5H_5)_2(CO)_2(CNMe)_2$] (II) with tin(IV) Lewis acids E

E	Absorption Bands [a]					
	$\nu(C{=}N_\mu)$	$\nu(CO_\mu)$	$\nu(CO)$	$\nu(CN)$	$\nu(SnX)$	$\nu(SnX)$ [b]
Adducts of [$Fe_2(\eta$-$C_5H_5)_2(CO)_3(CNMe)$]						
$SnCl_4$	1607(w)	1810(m)	2000(s, v br)		290	403[11]
$SnBr_4$	1607(w)	1815(m)	1993(w), 2018(s)		210	279[11]
SnI_4	1589(w)	1821(m)	1985(w), 2009(s)		< 200	216[11]
$MeSnCl_3$	1598(w)	1830(m)	1983(w), 2010(s)		240,248	384
$PhSnCl_3$	1610(w)	1818(m)	1987(w), 2010(s)		250–285(v br)	370
$Fe(\eta$-$C_5H_5)(CO)_2SnCl_3$	1600(w)	1830(m)	1970–2020(s, v br)		285	319,342
$Fe(\eta$-$C_5H_5)(CO)_2SnBr_3$	1600(w)	1827(m)	1970–2020(s, v br)		< 200	231,242
$Fe(\eta$-$C_5H_5)(CO)(CNMe)SnBr_3$	1604(w)	1829(m)	1981(s), 2018(s)	2175(m)	< 200	214,245
Adducts of [$Fe_2(\eta$-$C_5H_5)_2(CO)_2(CNMe)_2$]						
$SnCl_4 \cdot \frac{1}{6}C_6H_6$	1587(w)	1802(m)	1980(s)	2176(m)	295	403[11]
$SnBr_4$	1590(w)	1805(m)	1980(s)	2176(m)	205	279[11]
$MeSnCl_3$	1588(w)	1805(m)	1980(s)	2176(m)	248	384
n-$BuSnCl_3$	1618(w)	1815(m)	1985(s)	2188(m)	280	376
$PhSnCl_3 \cdot \frac{1}{6}C_6H_6$	1590(w)	1805(m)	1980(s,br)	2180(m)	255	370
$Fe(\eta$-$C_5H_5)(CO)_2SnCl_3 \cdot \frac{1}{6}C_6H_6$	1590(w)	1805(m)	1980(s, br), 2028(m)	2184(m)	290	319,342
$Fe(\eta$-$C_5H_5)(CO)_2SnBr_3$	1588(w)	1807(m)	1975(s,br), 2020(m)	2178(m)	< 200	231,242
$Fe(\eta$-$C_5H_5)(CO)(CNMe)SnCl_3$	1592(w)	1810(m)	1980(s, br)	2178(s, br)	270	305,331
$Fe(\eta$-$C_5H_5)(CO)(CNMe)SnBr_3$	1586(w)	1805(m)	1977(s, br)	2174(s, br)	< 200	214,245
$Fe(\eta$-$C_5H_5)(CO)(CNMe)SnI_3$	1580(w)	1805(m)	1980(s, br)	2194(s, br)	< 200	< 200

[a] Frequencies (cm^{-1}) with relative intensities in parentheses. w, weak; m, medium; s, strong; br, broad; v br, very broad. Measured in CsBr discs. [b] Frequencies of $\nu(SnX)$ vibrations of free E.

Table 3

Yields, melting points, analyses and IR spectra of the products arising from the breakdown of the adducts

	M.p. (°C)	Analyses (Found (calcd.)(%))				Yield [a]	IR spectra [b]
		C	H	N	X		
$[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$	94–96	39.2 (39.5)	2.5 (2.4)		16.4 (16.7)	5(0)	2013, 2059
$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl]$	74–76	43.0 (42.6)	3.5 (3.6	6.2 (6.2)	15.4 (15.7)	0(18)	1994, 2193
$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnCl_3]$	165–167	22.5 (23.1)	2.0 (1.9)	3.4 (3.4)	26.5 (25.6)	61(52)	1998, 2187
$[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$	81–83	32.9 (32.7)	2.3 (2.0)		31.3 (31.1)	5(0)	2009, 2053
$[Fc(\eta\text{-}C_5H_5)(CO)(CNMe)Br]$	110–112	35.2 (35.6)	2.8 (3.0)	5.2 (5.2)	30.4 (29.6)	1(28)	1992, 2189
$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnBr_3]$	124–126	17.5 (17.5)	1.6 (1.5)	2.5 (2.6)	43.7 (43.2)	66(57)	1996, 2188
$[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)][SnBr_3]$	126–128	18.4 (18.7)	1.4 (1.4)	2.5 (2.4)	41.4 (41.6)	7(0)	2045, 2084, 2242
$[Fe(\eta\text{-}C_5H_5)(CO)_2I]$	117–120	27.5 (27.6)	1.7 (1.6)		42.0 (41.8)	30(0)	2001, 2046
$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)I]$	126–128	29.6 (30.3)	2.6 (2.5)	4.1 (4.4)	39.1 (40.1)	4(–)	1986, 2183
$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnI_3]$	103–106	14.5 (13.9)	1.5 (1.2)	1.9 (2.0)	55.1 (55.2)	10(–)	1989, 2182

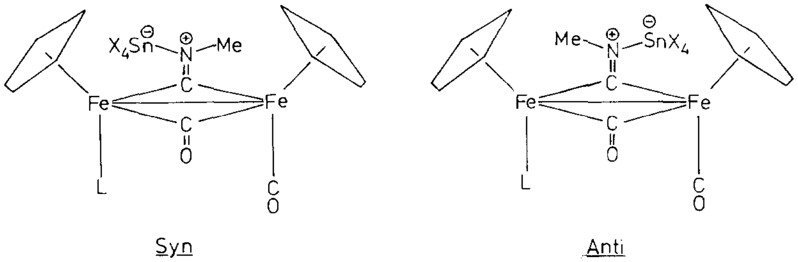
[a] Yields (%) of isolated complexes arising from decomposition in acetone solution of the adducts of I with those arising from the adducts of II in parentheses. [b] Peak positions (cm^{-1}) for the 1600–2250 cm^{-1} region only. Determined in chloroform solution.

adducts [I–E] with E = SnX_4 or $RSnX_3$ (X = Cl, Br, or I; R = Me, Ph, Fe(η-C_5H_5)$(CO)_2$, or Fe(η-C_5H_5)(CO)(CNMe)). The reaction of I with n-Bu$SnCl_3$ did not give a detectable adduct, but the IR spectra of the reaction mixture was very similar to that given on breakdown of the adduct [Fe_2(η-C_5H_5)$_2$$(CO)_3$(CN-Me)(Me$SnCl_3$)]. Consequently we assume that [Fe_2(η-C_5H_5)$_2$$(CO)_3$(CNMe)(n-Bu$SnCl_3$)] was formed but decomposed rapidly in benzene solution. Analytical data could only be obtained for those adducts which precipitated from the reaction mixtures; any extended work-up procedures including recrystallization resulted in adduct cleavage of the type described below. However we obtained reasonable and consistent analyses for four representative compounds (Table 1) and were able to identify the remainder by IR spectroscopy.

The adducts [I–E] are pink to brown solids, with the colour darkening along the series X = Cl < Br < I, and R = Cl < Me, Ph < Fe(η-C_5H_5)$(CO)_2$, Fe(η-C_5H_5)(CO)(CNMe). They are all unstable in the solid state and eventually decompose to complexes which contain only terminal CO or CNMe ligands. Similar but more rapid decompositions take place in solution, and become very fast in donor solvents such as acetone, acetonitrile or tetrahydrofuran as opposed to non-donor solvents such as benzene or chloroform. The adducts where E = SnI_4 or n-Bu$SnCl_3$ are noticeably less stable than the others that we have prepared, and decompose rapidly even in benzene solution.

[Fe_2(η-C_5H_5)$_2$$(CO)_2$$(CNMe_2)$] (II) fails to react with Me_3SnCl, but unlike I it does react with [{Fe(η-C_5H_5)$(CO)_2$}$_2$$SnX_2$] (X = Cl or Br). Adducts were detected but could not be isolated. It also forms 1/1 adducts of the general formulae [Fe_2(η-C_5H_5)$_2$$(CO)_2$$(CNMe)_2$(E)], [II–E], with the tin(IV) Lewis acids SnX_4 or $RSnX_3$ (X = Cl, Br, or I; R = Me, n-Bu, Ph, Fe(η-C_5H_5)$(CO)_2$ or Fe(η-C_5H_5)(CO)(CNMe)). These adducts have darker colours than those of I and are more stable towards breakdown both in the solid state and in solution. For example the adduct of II with n-Bu$SnCl_3$ may be isolated even though it is impure, and although the reaction of II with SnI_4 does not give [Fe_2(η-C_5H_5)$_2$$(CO)_2$-$(CNMe)_2$$(SnI_4)$], [$Fe_2$(η-$C_5H_5$)$_2$$(CO)_2$$(CNMe)_2${Fe(η-$C_5H_5$)(CO)(CNMe)$SnI_3$}] may be isolated from the reaction mixture. Apart from these differences, the commentary about the adducts of I may be applied to those of II. However it should be noted that the differences in reactivity between I and II is, in part, a consequence of the greater basicity of II. This has been noted previously in studies of the reactions of both with alkyl halides [8].

The IR spectra of [I–E] and [II–E] (Table 2) show absorption bands at (a) ca. 2180 cm^{-1} due to the ν(CN) vibrations of terminal CNMe ligands of [II–E] only, (b) ca. 2000 cm^{-1} due to the ν(CO) vibrations of terminal CO ligands, (c) ca. 1810 cm^{-1} due to the ν(CO) vibrations of bridging CO groups, and (d) at ca. 1600 cm^{-1} which are characteristic of the ν(CN) vibrations of bridging CN(Me)E ligands with N → E bonds. These spectra are very similar to those of the adducts of I and II with other Lewis acids such as alkyl halides and HBF_4 [8,9], and it seems reasonable to suggest that [I–E] and [II–E] have the structures shown in Fig. 1 with planar {Fe_2C=N(Me)E} moieties (cf. the structures of [*cis*-Fe_2(η-C_5H_5)$_2$$(CO)_2$(μ-CO){μ-CN(Me)H}]$BF_4$ [9] and [*cis*-Fe_2(η-MeC_5H_4)$_2$$(CO)_2$(μ-CO){μ-CN(Me)Me}]I [8] which have been determined by X-ray crystallography. There is insufficient evidence available at present to determine whether [II–E] are *cis* or *trans* with respect to their conformation about the ca. planar $Fe(C)_2Fe$ bridging system or if they have



Syn

Anti

Fig. 1. The proposed structures of the adducts of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(L)(CNMe)]$ complexes (L = CO or CNMe) with tin(IV) Lewis acids.

syn or *anti* conformations about the μ-{C=N} bonds. However, in the IR spectra of the adducts of [I–E] with E = $SnBr_4$, SnI_4, $PhSnCl_3$ and $MeSnCl_3$ there are two absorption bands at ca. 2000 cm^{-1} due to their $\nu(CO)$ vibrations with the band at lower frequencies being much the less intense. This is consistent with a *cis* configuration for the $Fe_2(\eta\text{-}C_5H_5)_2(CO)_2$ fragment of the molecule; if it were *trans* a single absorption bands would be expected. On the other hand, the IR spectrum of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)(SnCl_4)]$ shows a single but very broad absorption band with an irregular envelope at ca. 2000 cm^{-1} which may be due to either *cis* or *trans* isomers or a mixture of the two. Where we have been able to obtain solution spectra the above features are retained and so are not due to solid-state effects.

For those adducts where the tin(IV) electrophile E is $[Fe(\eta\text{-}C_5H_5)(CO)_2SnX_3]$, $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnX_3]$, or $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2SnX_2]$ (X = Cl, or Br), the absorption bands due to the $\nu(CO)$ or $\nu(CN)$ vibrations of E lie at much lower frequencies than do those for free E. Unfortunately they usually lie close to absorption bands due to vibrations arising from the remainder of the molecule and cannot be resolved from them. Their presence may be inferred as they make such absorption bands either broad with irregular envelopes or much more intense than is usually the case. The $\nu(CO)$ values for E = $[Fe(\eta\text{-}C_5H_5)(CO)_2SnCl_3]$ in [I–E] (marked [a]) and [II–E] (marked [b]) are 1980 [b] and 2028 [b] cm^{-1} (2002, 2041 cm^{-1}), for E = $[Fe(\eta\text{-}C_5H_5)(CO)_2SnBr_3]$ are 1975 [b] and 2020 [b] cm^{-1} (1999, 2038 cm^{-1}), for E = $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnCl_3]$ are 1980 [b] and 2178 [b] cm^{-1} (1990, 2188 cm^{-1}), for E = $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnBr_3]$ are 1980 [b] and 2175 [a] cm^{-1} (1996, 2187 cm^{-1}), and for E = $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnI_3]$ are 1980 [a] and 2194 [b] cm^{-1} (1989, 2182 cm^{-1}). The values for $\nu(CO)$ and $\nu(CN)$ of free E [3] in chloroform solution are given in parentheses.

Two lines of evidence strongly suggest that the tin(IV) halides E bond to μ-CNMe ligands of I and II by N → Sn bonds. The first is the decrease in the $\nu(CO)$ and $\nu(CNMe)$ frequencies of E = $Fe(\eta\text{-}C_5H_5)(CO)(L)SnX_3$ (L = CO or CNMe) mentioned above. Similar decreases have been observed in going from $[Fe(\eta\text{-}C_5H_5)(CO)_2SnCl_3]$ to $[Fe(\eta\text{-}C_5H_5)(CO)_2SnCl_3 \cdot bipy$ (bipy = 2,2′-bipyridyl; $\nu(CO)$ = 1966, 1978, 2011 and 2025 cm^{-1} in nujol) [10]. The second is provided by a comparison of the frequencies of the absorption bonds due to the $\nu(Sn\text{-}X)$ vibrations of the Lewis acids E. These decrease markedly on adduct formation (Table 1) e.g in going from $SnCl_4$ to $[I\text{-}SnCl_4]$, $\nu(SnCl)$ decrease from 403 cm^{-1} [11] (benzene solution) to 290 cm^{-1} (CsBr disc), whilst the corresponding figures for

$SnBr_4$ are 279 [11] and 210 cm^{-1} respectively. A similar effect has been observed in other L_2SnX_4 complexes (L = pyridine, etc.) [12]. It has been suggested that the formation of a bond between the ligand L (which in our case is the N atom of the μ-CNMe ligand of I or II) and the Sn atom results in a reduction of the effective electronegativity of the tin atom, a decrease in the Sn–X bond strengths, and hence a decrease in the ν(Sn–X) frequencies [13]. The decrease in the ν(Sn–X) frequencies along the series SnX_4, $RSnX_3$, R_2SnX_2 and R_3SnX is also attributed to the weaker Sn–X bonds arising from the decline in the effective electronegativity of the tin atom as the halogens X are replaced by the alkyl, aryl or transition metal-based radicals R which are poorer electron-withdrawing or better electron-donating groups. A further reduction in the ν(Sn–X) frequencies results when these substituted tin(IV) halides form adducts with I or II under those circumstances where R is a transition metal-based radical such as {Fe(η-C_5H_5)(CO)$_2$} or {Fe(η-C_5H_5)(CO)(CNMe)}, the electronegativity effects may also be used to account for the decrease in the ν(CO) and ν(CN) frequencies along the above series and on adduct formation.

The spectroscopic data allows us to state that the adducts [I–E] and [II–E] contain N→Sn bonds and the adduct stoichiometries suggest that there are probably one of these per tin atom. However the data we possess do not allow us to determine the ligand distribution about the Sn atom or the degree of polymerisation of the adducts although the solubility characteristics of the adducts of SnX_4, $MeSnCl_3$ or $PhSnCl_3$ do suggest that they are ionic or polymeric.

The mono-iron species arising from adduct breakdown

Some of the adducts [I–E] and [II–E] break down in the solid state, but all do so in benzene or, more rapidly, in acetone solution to give products which contain only one Fe atom and no bridging CO or CNMe ligands. Chromatographic techniques could not be used to separate these products as those containing Sn–X bonds were irreversibly absorbed, and so we had to rely on fractional crystallizations. These were difficult and consequently the yields of the isolated and purified products bore no relation to their yields in the reaction mixtures as determined by IR spectroscopy. The problems of product separation became increasingly acute as the number of non-halogen groups bonded to tin(IV) also increased. Therefore we were only able to isolate and identify by analyses the final products from the breakdown of the adducts of I and II with SnX_4 (X = Cl, Br, or I), but in other instances selected products in the reaction mixtures could be identified by IR spectroscopy.

The reactions of I with SnX_4 or the decomposition of [I–SnX_4] adducts in acetone or benzene solution eventually afford two principal products, [Fe(η-C_5H_5)(CO)$_2$X] and [Fe(η-C_5H_5)(CO)(CNMe)SnX_3]. IR spectroscopy suggests that the reactions are close to quantitative, and that these two products are formed in ca. equal amounts. However, the problems associated with product separation and purifications mean that the yields of purified compounds are much lower, especially for [Fe(η-C_5H_5)(CO)$_2$X].

There are no significant amounts of other products with $SnCl_4$, but with both $SnBr_4$ and SnI_4 two are observed. We have isolated the benzene-insoluble [Fe(η-C_5H_5)(CO)$_2$(CNMe)]$SnBr_5$ for which the nominal yield of 7% is probably close to the true yield as indicated by IR spectroscopy. However the amounts of salts of the same cation formed in the SnI_4 reaction are small and variable. They may be detected and identified by IR spectroscopy but could not be isolated. The second side products are [Fe(η-C_5H_5)(CO)(CNMe)X] which may well be formed in amounts greater than the nominal yields of 1% (X = Br) or 4% (X = I) as they cannot be distinguished from [Fe(η-C_5H_5)(CO)(CNMe)SnX_3] by IR spectroscopy. However we are not convinced that these are primary reaction products as [Fe(η-C_5H_5)$(CO)_2$$SnX_3$] would be anticipated and has not been detected. Furthermore [Fe(η-C_5H_5)(CO)(CNMe)SnI_3], at least, is unstable towards loss of SnI_2 in solution and slowly decomposes to [Fe(η-C_5H_5)(CO)(CNMe)I].

The IR spectra of the reaction mixtures of I with $RSnCl_3$ (R = Me, n-Bu or Ph) are very similar to those with SnX_4 in the ν(CO)/ν(CN) region between 1900 and 2250 cm^{-1}. Two species are formed in ca. equal amounts. [Fe(η-C_5H_5)$(CO)_2$Cl] may be identified readily even though its lower frequency ν(CO) absorption band (2013 cm^{-1}) overlaps with that due to the second species (ca. 1990 cm^{-1}) which also has a ν(CN) band at ca. 2180 cm^{-1} and is probably [Fe(η-C_5H_5)(CO)-(CNMe)$SnCl_2R$]. Unfortunately we could not separate these products, largely because of the high solubility of the second which in itself indicates that [Fe(η-C_5H_5)(CO)(CNMe)$SnCl_3$] was not formed in significant amounts. When R = Ph some $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]^+$ salts are formed, more in benzene solution than in acetone.

When the group R in $RSnX_3$ (X = Cl or Br) is Fe(η-C_5H_5)(CO)(CNMe), the IR spectrum of the reaction mixture is so complicated that no useful information can be obtained from it. However, when R = Fe(η-C_5H_5)$(CO)_2$ it is possible to say that there are present ca. equal amounts of [Fe(η-C_5H_5)$(CO)_2$X] and another species with ν(CN) ca. 2180 cm^{-1}.

When the adducts [II–SnX_4] (X = Cl or Br) decompose in benzene or acetone solution, the final IR spectra of the reaction mixtures in the 1600–2250 cm^{-1} region are very simple. Each show two rather broad absorption bands, one at ca. 1990 cm^{-1} due to ν(CO) vibrations and another at ca. 2190 cm^{-1} due to ν(CN) modes. From these solutions may be isolated [Fe(η-C_5H_5)(CO)(CNMe)X] and [Fe(η-C_5H_5)(CO)(CNMe)SnX_3]. Because of the accidental coincidence of their ν(CO) and ν(CN) vibrations it is not possible to determine even approximately their relative yields, but because of separation and purification difficulties, they are unlikely to be close to the nominal yields given in Table 3. There is no evidence for the formation of detectable amounts of [Fe(η-C_5H_5)$(CO)_2$X], [Fe(η-C_5H_5) $(CO)_2$$SnX_3$], [Fe($\eta$-$C_5H_5$)$(CNMe)_2$X] or [Fe($\eta$-$C_5H_5$)$(CNMe)_2$$SnX_3$] complexes or for salts of the type [Fe(η-C_5H_5)$(CO)_2$(CNMe)][SnX_3[or [Fe(η-C_5H_5)(CO)(CNMe)$_2$][SnX_3]. As has been mentioned in the Experimental section, the principal product from the reaction of II with SnI_4 is the adduct [II–Fe(η-C_5H_5)(CO)(CNMe)SnI_3]. [Fe(η-C_5H_5)(CO)(CNMe)I] and [Fe(η-C_5H_5)(CO)(CNMe)SnI_3] may also be isolated in low yields from the reaction mixture. It is probable that they arise from the spontaneous breakdown of the initially-formed [II–SnI_4] and that the second of them itself forms an adduct with unreacted II.

Under the same circumstances but with $RSnCl_3$ (R = Me, n-Bu or Ph) in place of SnX_4, the final IR spectra of the reaction mixtures are similarly simple. However each of the two absorption bands can now be seen to have two components which are almost separable. The clear implication is that [Fe(η-C_5H_5)(CO)(CNMe)$SnCl_2R$] are formed as replacement of $SnCl_3$ by $SnCl_2R$ would be expected to bring about a decline in the frequencies of the ν(CN) and ν(CO) vibrations of the Fe(η-C_5H_5)(CO)(CNMe) moiety.

In all other instances when SnX_4 are replaced by the Lewis acids $RSnX_3$ or R_2SnCl_2 where R = $Fe(\eta\text{-}C_5H_5)(CO)_2$ or $Fe(\eta\text{-}C_5H_5)(CO)(CNMe)$, the final IR spectra of the reaction mixtures are very complicated. No information could be gained from them except that the products contain terminal but not bridging CO and CNMe ligands.

Comments on the mechanism of the breakdown of the adducts [I–E] and [II–E]

The most important overall reaction of I and II with SnX_4 may be summarised by equations 1 and 2.

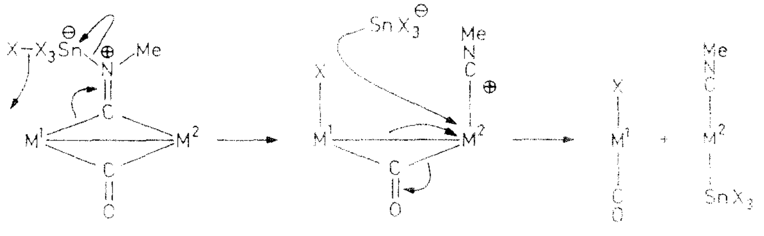
$$\begin{aligned}&[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)] + SnX_4 \rightarrow \\ &\quad [Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)\text{–}SnX_4] \rightarrow \\ &\qquad [Fe(\eta\text{-}C_5H_5)(CO)_2X] + [Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnX_3]\end{aligned} \qquad (1)$$

$$\begin{aligned}&[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2] + SnX_4 \rightarrow \\ &\quad [Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2\text{–}SnX_4] \rightarrow \\ &\qquad [Fe(\eta\text{-}C_5H_5)(CO)(CNMe)X] + [Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnX_3]\end{aligned} \qquad (2)$$

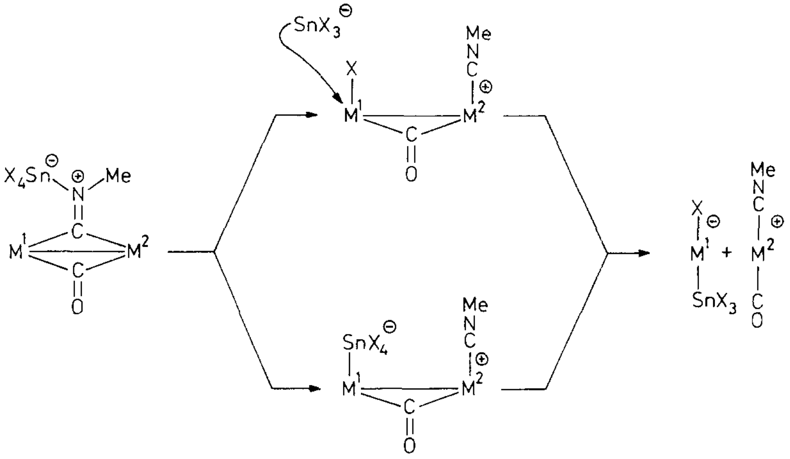
In both cases the first stage appears to be the virtually quantitative formation of the adducts [I–SnX_4] and [II–SnX_4] which are more or less unstable and break down to the final products. Varying amounts of these final products are always present in the reaction mixtures during adduct formation and probably arise from the adducts. It is possible that we have been able to isolate some of the adducts only because they are insoluble in the reaction solvent (benzene).

We have previously suggested that many reactions of polynuclear metal carbonyl derivatives such as I and II with electrophiles proceed by way of such adducts [2]. These then break down to the final products which may contain none, part, or all of the original electrophile in the way shown in Scheme 1.

There is an alternative way in which this reaction may take place with the SnX_3 group migrating from N to M^1 and X^- being the liberated anion which subsequently attacks M^2. However, the proposed mechanistic scheme predicts that the migrating group cannot end up on the same metal atom as the μ-ligand to which it was coordinated in the adduct. Therefore the products from I indicate that the reaction pathway shown in Scheme 1 is that adopted with X^- the migrating group and SnX_3^- the liberated anion. Furthermore, the relatively high coordination number of the Sn atom in the adducts means that the X atoms would not be



Scheme 1. Breakdown of [I–E] and [II–E] with E = SnX_4 and for I M^1 = M^2 = $Fe(\eta\text{-}C_5H_5)(CO)$, for II M^1 = $Fe(\eta\text{-}C_5H_5)(CNMe)$, M^2 = $Fe(\eta\text{-}C_5H_5)(CO)$.



Scheme 2.

selectively discouraged by steric effects from approaching M^1 (cf. ref. 2). Hence the migration of X from Sn to M^1 is more likely than would otherwise be the case.

In the corresponding reactions of II the adducts may have the *syn* or *anti* conformation about the C_μ=N bond. If we assume that the reactions also take place with migration of X to M^1 (i.e. to the cisoid metal atom) and attack by SnX_3^- at M^2, then only the *syn* isomer would give the observed products which are exclusively $[M^1(CO)X]$, $[Fe(\eta\text{-}C_5H_5)(CNMe)(CO)X]$, and $[M^2(CNMe)SnX_3]$, $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnX_3]$.

On the basis of the available data, except that already discussed, it is not possible to gain any information as to whether the adducts are based on *cis*- or *trans*-$[Fe_2(\eta\text{-}C_5H_5)(CO)(L)(\mu\text{-}CO)(\mu\text{-}CNMe)]$ (L = CO or CNMe).

We assume that the same mechanism may be applied to the cleavage of I and II by $RSnX_3$ or R_2SnX_2 Lewis acids. However the stability of the adducts towards cleavage to the final product increases along the series $E = SnX_4 < RSnX_3 < R_2SnX_2$ even though the Lewis acidity of E decreases [14]. This may be because the tin based anions $[RSnX_2]^-$ and $[R_2SnX]^-$ are progressively poorer leaving groups than $[SnX_3]^-$.

The formation of $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]^+$ $[SnX_3]^-$ when X = Br or I but not Cl may also be accomodated in the above proposal. Either it is assumed (a) that $[SnX_3]^-$ attacks M^1 rather than M^2, or (b) that the $[SnX_4]^{2-}$ moiety migrates as a whole from N to M^1. The further consequence of (b), e.g. oxidative addition of $[SnX_4]^{2-}$ to M^1, is to give the cation as is shown in Scheme 2. Although the adducts decompose slowly in benzene or chloroform solution, the same reactions take place much more rapidly in the donor solvents acetone, or tetrahydrofuran. This is clearly consistent with a mechanism such as that outlined above.

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