The Mössbauer Effect in Tin(II) Compounds. Part X.[1] Insertion Reactions of Tin(II) Compounds with Carbonyl-π-cyclopentadienyliron Derivatives

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The products of the insertion reactions of a number of tin(II) compounds SnX_2 (X = Cl, Br, I, NCS, HCO_2, and AcO) with $[(\pi-C_5H_5)Fe(CO)_2]_2$ and $(\pi-C_5H_5)Fe(CO)_2Cl$ are compared with those from replacement of Cl from $[(\pi-C_5H_5)Fe(CO)_2]_2 \cdot SnCl_2$ and $(\pi-C_5H_5)Fe(CO)_2SnCl_3$. The ^{119}Sn Mössbauer parameters of both series of compounds $[(\pi-C_5H_5)Fe(CO)_2]_2 \cdot SnX_2$ and $(\pi-C_5H_5)Fe(CO)_2 \cdot SnX_3$ (X = Cl, Br, I, NCS, HCO_2, and AcO) show that the use of tin bonding electrons is dominated by the Sn–Fe bond. The trends in chemical isomer shift and quadrupole splitting can be explained with reference to the very short Sn–Fe bond lengths in these materials. The positive sign for e^2qQ can also be explained in terms of a high p-electron density on the tin atom in the direction of the Sn–Fe bond. The i.r. for the products of the insertion reactions are also presented.

SEVERAL π-cyclopentadienyl iron carbonyl complexes containing the tin–iron bond have been prepared and compounds of the type $(\pi-C_5H_5)Fe(CO)_2 \cdot SnR_3$ (R = Cl,[2-5] Br,[3,5] I,[3,5] Me,[3] Et,[3] and Ph [2-4]) and $[(\pi-C_5H_5)Fe(CO)_2]_2 \cdot SnR^1_2$ (R^1 = Cl,[3,6] Br,[6] I,[6] Me,[7] Et,[6-7] Ph,[7] NCS,[7,8] AcO,[7] SEt,[7] C_5H_5,[7] OH,[7] NO_2,[7] and NO_3 [7]) have been reported. Some of these complexes can be prepared from either tin(II) [3,5,6] or tin(IV) [2,3,7] starting materials and there is apparently no difference in the nature of the products from the two types of reaction.

The crystal structures of the following compounds are known: $(\pi-C_5H_5)Fe(CO)_2 \cdot SnR_3$ (R = Cl,[9] Br,[9] or Ph [10]) and $[(\pi-C_5H_5)Fe(CO)_2]_2 \cdot SnR'_2$ (R' = Cl,[11] C_5H_5,[12] Me,[13] and NO_3 [14]). In each case the tin atom is in a distorted tetrahedral environment in which the bonds to the iron atoms are very short (2·46—2·60 Å) while those to the ligands are longer than the sums of the appropriate covalent radii. The bond angles in the tin environment are severely distorted from the ideal tetrahedral angles. These features can be explained [11] in terms of an increase in the s-character of the tin orbitals used in the tin–iron bond formation with a corresponding increase in the p-character of the orbitals forming the other bonds with tin. Bryan and his co-workers have pointed out [9] that in the $(\pi-C_5H_5)Fe(CO)_2 \cdot SnX_3$ complexes, the two halide moieties ($-SnCl_3$ and $-SnBr_3$), differ in their conformations about the Sn–Fe bond axis and also differ in this respect from both of the conformationally independent molecules in the unit cell of $(\pi-C_5H_5)Fe(CO)_2 \cdot SnPh_3$. They interpret these differences as being a strong indication of free rotation about the metal–metal bond. This and the values of the Sn–Fe distances

in the halide compounds are taken to mean that the Sn–Fe bond is pure σ in character.

Several conclusions on the nature of the Sn–Fe bond in the π-cyclopentadienyl complexes have been based on indirect evidence [4,15,16] from shifts in the i.r. carbonyl stretching frequencies. The i.r. spectra of the series of complexes $(\pi-C_5H_5)Fe(CO)_2SnR_3$ (R = Cl, Me, or Ph) in the carbonyl stretching regions have recently been reported [16] and the results interpreted in terms of an increase in the importance of π-bonding in the Fe–Sn bond along the ligand series $SnMe_3$, $SnPh_3$, and $SnCl_3$.

The ^{57}Fe and ^{119}Sn Mössbauer effects provide a direct means of studying changes in the use of the tin and iron bonding electrons on the formation of metal–metal bonds. The Mössbauer parameters for $(\pi-C_5H_5)Fe(CO)_2 \cdot SnR_3$ (R = Cl or Ph) show [17] that there are no conformational changes between the solid and its dispersed solution in a glassy matrix of an inert material such as polymethylmethacrylate. The data for $[(\pi-C_5H_5)Fe(CO)_2]_2 \cdot SnCl_2$ dispersed in a glassy matrix are, however, consistent [17] with the presence of two of the possible rotational isomers obtained by rotation of the Sn–Fe bond. The only systematic Mössbauer study [18] of materials containing M–Sn bonds considered the changes in the Mössbauer parameters in a series of compounds like $Ph_{4-n}Sn[Co(CO)_4]_n$ (n = 1—3), Fenton and Zuckerman [19] have, however, also commented on the oxidation state of tin (derived from chemical shift data) in compounds containing tin–transition-metal bonds.

We have studied the products of insertion reactions of a number of tin(II) compounds SnX_2 (X = Cl, Br, I, NCS, AcO, and HCO_2) with $[(\pi-C_5H_5)Fe(CO)_2]_2$ and

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$(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ and comment on the effects of substituents on the atom on the Mössbauer parameters of the series of compounds $(\pi\text{-}C_5H_5)Fe(CO)_2 \cdot SnR_3$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \cdot SnR_2$. In each case it was shown that the expected product of the insertion reaction was obtained by comparing it with the products of the replacement reactions on $(\pi\text{-}C_5H_5)Fe(CO)_2 \cdot SnCl_3$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \cdot SnCl_2$ with an alkali-metal salt of the replacing anion.[5,8] The halide derivatives are the only ones which have been prepared previously by insertion reactions.

TABLE 1

^{119}Sn Mössbauer parameters for the products of the insertion reactions of tin(II) compounds with carbonyl-cyclopentadienyliron derivatives and for the parent tin(II) compounds

	$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \cdot SnX_2$		SnX_2	
	δ/mm s^{-1} *	Δ/mm s^{-1}		
X	±0.03	±0.03	δ/mm s^{-1} *	Δ/mm s^{-1}
Cl	-0.20	2.40	$+2.07$ [a]	0
Br	-0.11	2.42	$+1.93$ [a]	0
I	-0.10	2.25	$+1.85$ [a]	0
NCS	-0.27	2.55	$+1.42$ [a]	0
HCO$_2$	-0.49	2.19	$+1.05$ [b]	1.56
AcO	-0.47	2.60	$+1.21$ [b]	1.77
	$(\pi\text{-}C_5H_5)Fe(CO)_2 \cdot SnX_3$		NH_4SnX_3	
Cl	-0.43	1.82	$+1.51$ [c]	0.91
Br	-0.35	1.60	$+1.69$ [c]	0.68
I	-0.22	1.50	$+1.93$ [c]	0
NCS	-0.45	2.24	$+1.07$ [c,d]	1.32
HCO$_2$	-1.01	1.45	$+0.92$ [b]	1.95
AcO	-0.93	1.87	$+0.74$ [b]	1.75

* Relative to α-tin at 80 K.

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Table 1 contains the ^{119}Sn Mössbauer data for the compounds prepared in this work, for the tin(II) materials used for the insertion reactions and for typical derivatives of the corresponding SnX_3^- ions. The ^{57}Fe data for the chloride derivatives were in good agreement with the published values [17,20] and the chemical isomer shifts and quadrupole splittings for the other materials were found to be within 0.06 and 0.10 mm s^{-1} of the values for the chlorides. There appeared to be no systematic variation in the ^{57}Fe Mössbauer parameters for these materials. The ^{119}Sn chemical isomer shifts (δ) for both series of compounds have negative values relative to the α-tin reference standard. This means that they are formally tin(IV) materials, that the tin atom is using all of its valence-shell electrons in bonding, and that the nonbonding orbital which is characteristic of tin(II) materials is no longer present. This would be the expected result if we regard the reactions of the π-cyclopentadienyl iron compounds with tin(II) materials as involving, at least in the initial stages, the overlap of the lone-pair orbital in the tin(II) compound with empty iron orbitals.

The chemical isomer shifts for the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \cdot SnR_2$ compounds lie in the range -0.1 to -0.5 mm s^{-1}.

The very small variation in this value with the substituent R reflects a domination of the tin bonding orbitals by the two Fe–Sn bonds. A comparison of the shifts for these compounds with those for the parent tin(II) compounds suggest that there is no direct relationship between these parameters and again shows the importance of the Sn–Fe rather than the Sn–R bonds in determining the use of the tin electrons. The chemical isomer shifts for the $(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3$ compounds show a much larger variation with the substituent R presumably because of the presence of only one Sn–Fe bond. Again there is no systematic relationship between the shifts for the $(\pi\text{-}C_5H_5)Fe(CO)_2 \cdot SnR_3$ compounds and those for the tris(ligand)-stannates(II) from which they are presumably derived. For the dicarbonylcyclopentadienyliron derivatives where R is a halogen there is an increase in chemical shift (increase in s-slectron density at the tin nucleus) with decrease in the electronegativity of the halogen. If we regard the compounds as being formed from σ-bonding between the iron atom and SnX_3^- groups then the order of σ-donor strength would be $SnCl_3^- > SnBr_3^- > SnI_3^-$. If the tin groups are also acting as π-acceptors the stronger the π-bonding the greater the shielding of the tin nucleus and the lower the chemical shift. This seems that any π-bond formation would also favour a negative shift decrease in the order $SnCl_3^- > SnBr_3^- > SnI_3^-$. The isothiocyanate, acetate, and formate derivatives which have much larger negative shifts from α-Sn must be due to the considerably stronger σ-donor–π-acceptor abilities of the $Sn(NCS)_3^-$, $Sn(AcO)_3^-$, and $Sn(CHO_2)_3^-$ groups. The chemical shifts for the $(\pi\text{-}C_5H_5)Fe(CO)_2 \cdot SnR_3$ compounds are more negative than those for the corresponding $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \cdot SnR_2$ materials. This means that there is a greater total covalency in the bonding in the latter series of materials. Again this is the expected result for an increase in the number of Sn–Fe bonds and is consistent with the crystal structures of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \cdot SnCl_2$ [11] and $(\pi\text{-}C_5H_5)Fe(CO)_2 \cdot SnCl_3$.[9] The Fe–Sn bond lengths in these compounds are very similar (2.49 and 2.47 Å respectively) but the greater involvement of the tin s-electrons in the dichloride owing to the presence of a second Sn–Fe bond, leads to a corresponding increase in the p-character of the Sn–Cl bond. This is reflected in the longer Sn–Cl bond length (2.43 Å) and the greater distortion from tetrahedral co-ordination of the tin (Fe–Sn–Cl 107, Cl–Sn–Cl 94, and Fe–Sn–Fe 128.6°) than in the trichloride (Sn–Cl 2.36 Å; Fe–Sn–Cl 119, and Cl–Sn–Cl 98.3°).

The large values of the quadrupole splitting parameters (Δ) for the compounds in Table 1 indicate the presence of an electric field gradient in these materials. There are a number of factors which must be considered in discussing the origin of the field gradients responsible for the splittings. (i) There may be a p-electron
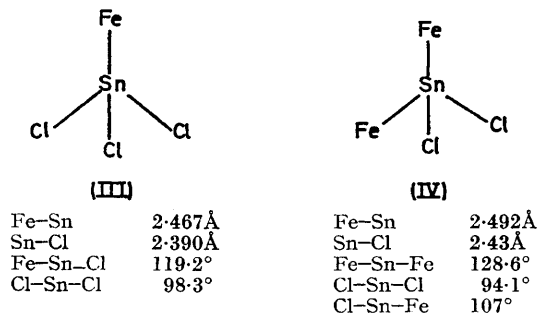
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imbalance in the environment of the tin atom due to difference in the p-electron involvement in the Sn–Fe and Sn–X bonds. (ii) There may be a d-electron imbalance due to the population of tin d-orbitals either by p_π–d_π bonding in the Sn–X bonds or by d_π–d_π bonding in the Sn–Fe bonds. (iii) The drop in symmetry from C_{3v} to C_{2v} from SnR_3 to SnR_2 compounds [(I) and (II)], assuming retention of the tetrahedral angle and constancy of bond lengths, can in itself effect the splitting. Parish and Platt,[21] assuming constant values for [Fe] and [X], have shown that, under these conditions, the contribution to the field gradient by the groups attached to tin for environment such as (I) and (II) are identical
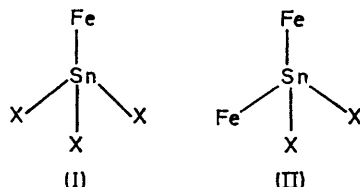
{2[Fe] $- 2$[X] where [Fe] and [X] are the contributions to the field gradient of the Fe and X groups respectively.} The differences in the splitting, other factors being equal, would then be due entirely to a non-zero asymmetry parameter for the C_{2v} structure (II). (iv) The assumptions made concerning the bond lengths and angles in (iii) are seldom valid for compounds with tin–transition-metal bonds. For example if the Fe–Sn–X bond angle in (I) is decreased to $100°$ the contributions to the field gradient would be 2[Fe] $- 2 \cdot 7$[X] and if the angle is $120°$ the contribution would be 2[Fe] $- 0 \cdot 8$ [X]. Bond-angle variations can thus have a marked effect on the value of the observed quadrupole splittings.

The quadrupole splittings for the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot SnX_2$ compounds are larger than those for the $(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2\cdot SnX_3$ materials, as predicted, but the differences are much greater than the 15% increase allowed by an η value of 1. The difference can, however, be rationalised on a point-charge calculation based on the known bond angles in the crystal structures of the chloride derivatives [9,11] [(III) and (IV)].

Fe–Sn	2·467Å		Fe–Sn	2·492Å
Sn–Cl	2·390Å		Sn–Cl	2·43Å
Fe–Sn–Cl	119·2°		Fe–Sn–Fe	128·6°
Cl–Sn–Cl	98·3°		Cl–Sn–Cl	94·1°
			Cl–Sn–Fe	107°

A point–change calculation on (III) gives a V_{zz}

2[Fe] $- 0 \cdot 9$ [Cl] and on (IV) gives V_{zz} $2 \cdot 9$ [Fe] $- 2$[X]. The asymmetry parameter η is negligible for both these systems and we have neglected the differences in the Sn–Cl bond distances in (III) and (IV) for the purposes of this calculation. Thus when the bond angles in the crystal are considered, rather than those for idealised tetrahedral structures, we find that the contribution of both [Fe] and [X] to the field gradient is greater in (IV) than in (III). Since we have considerably increased the effect of the Sn–Fe bonds in the field gradient, and this must be the major contribution in view of the very short Sn–Fe bond lengths, it is not unreasonable to expect much larger quadrupole splittings for the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot SnX_2$ materials. The very small variations in the quadrupole splitting values observed for this series of compounds are also consistent with the domination of the use of tin bonding electrons by the iron atoms. There is a much greater variation in the quadrupole splitting values for the $(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}SnX_3$ compounds. Again this would be expected from the reduced contribution of the single Sn–Fe bond to the field gradient which would allow the effects of the other attached groups to be more noticeable.

For transitions between nuclear spin states $I = \pm\frac{1}{2} \longrightarrow I = \pm\frac{3}{2}$ (e.g. ^{57}Fe and ^{119}Sn), the sign of the quadrupole coupling, e^2qQ, is indeterminate for a powdered sample, because the splitting will be a symmetrical doublet in the absence of relaxation or anisotropic recoil effects.

However, the application of a large magnetic field to such a sample results in the removal of the remaining degeneracies and yields a complex hyperfine spectrum from which the sign of e^2qQ may be extracted,[22] provided η, the asymmetry parameter, is not equal to one. Many such experiments have been performed with ^{57}Fe (see e.g. ref. 22) and more recently [23,24] with ^{119}Sn.

We have determined the sign of the quadrupole for both the tin and iron sites in $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnCl_3$, which is a compound of known structure. The experimental conditions are given in the Figure.

The expected eight-line ^{119}Sn spectrum is not fully resolved, but it is clear that the pattern is more complex on the low-energy side, indicating a positive value of e^2qQ.

Boyle et al.,[25] by analysis of the asymmetric spectrum of a partially ordered powdered sample of tetragonal SnO, concluded that e^2qQ was positive for this material. This has recently been confirmed by the magnetic work of Greenwood et al.[23] Moreover, Boyle and his co-workers concluded that the nuclear quadrupole moment eQ of ^{119}Sn is negative because of the presence of an excess of p_z electron density in the lone-pair orbital in SnO.

If we assume (i) that Boyle's arguments on the field

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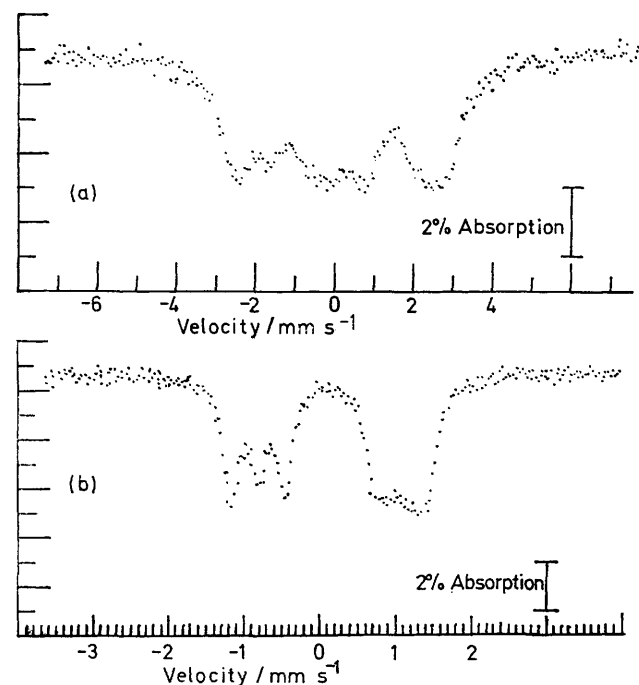
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(a) ^{119}Sn Mössbauer spectrum of $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnCl_3$ with $H = 30$ Kg at $4\cdot2$ K; (b) ^{57}Fe Mössbauer spectrum of $(\pi\text{-}C_5H_5)$-$Fe(CO)_2\cdot SnCl_3$ under identical conditions

the tin–iron bond (III). Therefore there must be an excess of p_z electron density left on the tin atom in this direction, assuming eQ negative.

The hybrid orbital used by the tin in the Sn–Fe bond must therefore be predominantly s in character. This is in agreement with the known [9] Sn–Fe bond length of $2\cdot46$ Å which is said to be small compared with the sum of the covalent radii of the metals ($2\cdot67$ Å). This argument therefore supports a negative eQ for ^{119}Sn. The analogous structure of $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnPh_3$ which has zero quadrupole splitting and a metal–metal bond length which, although longer than in the chloride, is still less than the sum of the covalent radii. The tin hybrid orbitals used in bonding to carbon must therefore have more s-character than the hybrid orbitals used in bonding to chlorine, thus tending to equalise the p-character in all four tin–ligand bonds.

These observations are consistent with the observed chemical shift for $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnCl_3$ being greater (relative to the source) than that for $(\pi\text{-}C_5H_5)Fe(CO)_2$-$SnPh_3$, and the shift values suggest that the former compound has more s-electron density remaining at the tin nucleus, resulting in greater p-character in the tin–chlorine bonds as compared to the tin–carbon bonds. This argument is strengthened by the C–Sn–C angle being greater than the Cl–Sn–Cl [4] which indicates a greater s-electron involvement in the tin bonds to carbon than to chlorine.[26]

The clearly resolved triplet on the low-energy side of the ^{57}Fe spectrum unambiguously determines the

gradient in SnO and his assignment of eQ as negative is correct and (ii) that the Sn–Fe bond is a pure σ-bond,[9] then there must be an excess of p electron density on

TABLE 2

I.r. spectra (cm^{-1}) for the products of insertion reactions in the region 2200—1900 cm^{-1}

Compound						Solvent
$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnCl_3$	2049s,sp		2010s,sp			$CHCl_3$ [a]
	2047		2007			CH_2Cl_2 [b]
$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnBr_3$	2046s,sp		2006s,sp			$CHCl_3$ [a]
	2045		2006			$CHCl_3$ [c]
	2045		1996			CH_2Cl_2 [b]
$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnI_3$	2037s,sp		1997s,sp			$CHCl_3$ [a]
	2039		1999			$CHCl_3$ [c]
	2032		1990			CH_2Cl_2 [b]
$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot Sn(NCS)_3$	2050m,sh	2035m,br	2013s,br			$CHCl_3$ [a]
	N=C					
$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot Sn(HCO_2)_3$	2022br,s		1974br,s			$CHCl_3$ [a]
$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot Sn(AcO)_3$	2028br,s		1983br,s			$CHCl_3$ [a]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot SnCl_2$	2026	1999	1972	1963sh		$CHCl_3$ [a]
	2026	2000	1975	1956		C_6H_{12} [d]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot SnBr_2$	2024	1999	1972	1961sh		$CHCl_3$ [a]
	2027	2002	1973	1959		$CHCl_3$ [e]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot SnI_2$	2023	1999	1972	1963sh		$CHCl_3$ [a]
	2026	2002	1974			$CHCl_3$ [e]
	2029	2003	1980	1958		C_6H_{12} [d]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot Sn(NCS)_2$	2045m,sh	2022m,br	2007s	1983m	1970sh	$CHCl_3$ [a]
	N=C	2025vs	2008vs	1985s	1965sh	$CHCl_3$ [f]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot Sn(HCO_2)_2$	2028	2005	1974	1967sh		$CHCl_3$ [a]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot Sn(AcO)_2$	2025	2003	1970	1962		$CHCl_3$ [a]

[a] This work. [b] Ref. 4. [c] Ref. 5. [d] Ref. 16. [e] Ref. 6. [f] Ref. 8. s = Strong, sp = sharp, br = broad, m = medium, v = very, sh = shoulder.

the tin atom, along the principal direction of the field gradient (V_{zz}). V_{zz} for the tin atom must lie along, or be close to, the approximate three-fold axis through

[26] H. A. Bent, Chem. Rev., 1961, 61, 275.

quadrupole coupling as positive. Since eQ for iron is positive,[22] V_{zz} in this compound must also be positive. In discussing the Mössbauer results in the absence of a magnetic field for compounds containing Sn–Fe bonds,

Goldanskii *et al.*[27] came to the same conclusion concerning the sign of V_{zz}.

The Mössbauer parameters for both series of compounds containing Sn–Fe bonds show that the metal–metal bond dominates the use of the tin bonding electrons. The chemical isomer shift and the quadrupole splitting data are readily explained with reference to the very short Sn–Fe bond in these materials. The positive sign found for e^2qQ in $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnCl_3$ can also be explained in terms of high electron density on the atom in the direction of the Sn–Fe bond.

The i.r. spectra for the iron–tin compounds in the carbonyl region are shown in Table 2, and data for the

is however probably due to vibrations of the NCS group which is bonded to tin through nitrogen. In the series of compounds $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnX_3$ the carbonyl stretching frequencies are lowered with decreasing electronegativity of the X group.

Four bands are observed in the spectra of the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot SnX_2$ compounds and this limits the possible local symmetry about iron to C_2, C_1 or C_s. In these compounds changes in the group X have very little effect on the carbonyl stretching frequencies.

The far-i.r. spectra for $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnX_3$ (X = Cl or Br) agree well with published results.[5,28] Assignments (Table 4) were made assuming C_{3v} symmetry

TABLE 3

I.r. spectra (cm^{-1}) for the products of the insertion reaction in the region <500 cm^{-1}

(a) $(\pi\text{-}C_5H_5)FeCO_2\cdot SnX_3$

X = Cl	Br	I	NCS	HCO$_2$	AcO
488ms	486ws	490vw	486s		496vvs
				480s	482vvs
486ms	470s,sh	470vvs	460m	460s	452m
458ms	448m	442sh	436m	436s	436m
438ms					
410ms					
	404w	400m			
378	380w	376m			
346s,sh *			342sh	338mw	
322s *			328m,br	328br	288s
	248s †				
222s	230s †	226m ‡			218m,br
	198w	186s ‡			188sh
	158vw	164mw			
		124w			
144mw					
118mw					
88w	92w				

(b) $[(\pi\text{-}C_5H_5)Fe(CO_2)]_2\cdot SnX_2$

X = Cl	Br	I	NCS	HCO$_2$	AcO
432m	436ms	434ms	432vvw	434vw	434w
422m,br					
	394sh	390m	374w	386m,sp	398m,sp
					378m,sp
380m	382m,sp			348m	
374m,sh		376m			
292s	292vs		274s,sp	278s,br	278s,sp
280sh	280sh				
230m	230sp	232m,sp	248s,sp	238s	240s,sp
		196mw,sp	204vw	176w	174mw
154w	154w	164s,sp	168m,sp		
			146w,br	148m,br	150vw
	122br,vw			126s,br	
					110sh
					96sh

* ν(SnCl). † ν(SnBr). ‡ ν(SnI).

region <500 cm^{-1} in Table 3. The spectra of compounds of the type $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnX_3$ in the region 2200—1900 cm^{-1} have two intense bands which are consistent with C_{2v} local symmetry around the iron atom except

around the tin atom and by comparison with published data.[29] Similar assignments (Table 4) have been made for the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot SnX_2$ compounds assuming a C_{2v} environment for the tin atom.

TABLE 4

Far-i.r. spectra (cm^{-1})

(a) $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnX_3$

Sn–X	ν_{sym}	δ(SnX)	$\nu_{antisym}$	δ(SnX)	ν(M — M')
Cl	346	144	322	118	222
Br	248		230		198
I	226		186		164

(b) $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot SnX_2$

Sn–X					
Cl	292		280		230
Br	292		280		230
I					232
NCS	274		248		204⎫ ?
					168⎭
HCO$_2$	278		238		176
AcO	278		240		174

for the NCS derivative which has an extra band of medium intensity at 2050 cm^{-1}. This extra band, which was also found [8] in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot Sn(NCS)_2$,

EXPERIMENTAL

All the metal–metal bonded compounds we describe can be prepared by insertion reaction with tin(II) materials giving products identical to those obtained by replacement reactions on carbonyl cyclopentadienyliron–tin chloride derivatives, although the latter reactions are generally more efficient.[5]

Preparation of the $[(\pi\text{-}C_5H_5)Fe(CO_2)]_2\cdot SnX_2$ Derivatives.— The halogen derivatives were prepared by the methods described in the literature [2–6] and characterised by their analytical and i.r. data. The derivatives with X = NCS, HCO$_2$, and AcO were prepared by insertion reactions with tin(II) materials as follows.

$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot Sn(NCS)_2$. Tin(II) isothiocyanate (1·3 g) and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (1·8 g) were heated under reflux in tetrahydrofuran (20 ml) for *ca.* 3 h. The solvent was removed under reduced pressure the residue was redissolved in tetrahydrofuran and the product precipitated by the addition of hexane.

[27] V. I. Goldanskii, B. V. Borshagovski, E. F. Makarov, R. A. Stukan, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Teor. i eskp. Khim.*, 1966, **2**, 126.

[28] T. G. Spiro, *Progr. Inorg. Chem.*, 1970, **11**, 1, and references therein.

[29] N. A. D. Carey and H. C. Clark, *Inorg. Chem.*, 1968, **7**, 94.

$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot Sn(HCO_2)_2$. $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (1·8 g) was dissolved in formic acid (25 ml). Tin(II) formate (2·1 g) was added and the mixture heated at 40° until the solution became yellow (*ca.* 3 h). Solvent was removed from the filtered solution under reduced pressure and the final product obtained as in the previous preparation.

$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot Sn(AcO)_2$. This was prepared similarly from freshly sublimed tin(II) acetate but with acetic anhydride as solvent.

The products of the insertion reaction were identical with those from replacement reactions. For example for the isothiocyanate: potassium thiocyanate (2·65 g) and $[(\pi\text{-}C_5H_5)Fe(CO)_2]\cdot SnCl_2$ (1·35 g) were heated under reflux in methanol for 1 h. The solvent was removed under reduced pressure and the dry solid residue suspended in

with those obtained from replacement reactions on $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnCl_3$.

$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnCl_3$. The following new method of preparation involving the use of both tin(II) and tin(IV) starting materials has been found to give a very good yield (*ca.* 85%). Anhydrous tin(IV) chloride (2·3 ml), anhydrous tin(II) chloride (3·65 g), and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (6·8 g) were dissolved in tetrahydrofuran (125 ml) at 5 °C and the mixture heated under reflux under nitrogen for *ca.* 4 h. The solution was then evaporated to dryness under reduced pressure and the residue boiled with methanol (200 ml). The filtered solution was concentrated by evaporation to give the product.

The replacement reactions on $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnCl_3$ were carried out with a methanol solution of this together

TABLE 5

Analytical data (%) for the complexes *

	C	H	Fe	N	S	Sn
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot Sn(NCS)_2$	32·5(32·6)	2·0(1·7)	19·2(19·0)	5·0(4·8)	10·0(10·9)	19·5(20·2)
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot Sn(HCO_2)_2$	32·1(33·8)	2·1(2·1)	17·4(19·7)			19·6(20·9)
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot Sn(AcO)_2$	34·7(36·3)	2·9(2·7)	18·1(18·8)			20·0(19·9)
$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot Sn(NCS)_3$	26·1(25·5)	1·2(1·1)	11·9(11·9)	9·2(8·9)		24·0(25·3)
$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot Sn(HCO_2)_3$	28·2(27·9)	1·9(1·8)	11·8(13·0)			28·0(27·6)
$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot Sn(AcO)_3$	32·6(33·0)	3·0(3·0)	11·6(11·8)			26·0(25·1)

* Calc. values in parentheses.

benzene. The filtered benzene solution was then concentrated and the product precipitated by the addition of ligroin.

Preparation of the $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot SnX_3$ *Derivatives.*— The halogen derivatives were prepared by the methods described in the literature [2–6] and characterised by analytical and i.r. data.

The derivatives with X = NCS, HCO_2, and AcO were prepared by insertion reactions with tin(II) materials as follows.

$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot Sn(NCS)_3$. Tin(II) isothiocyanate (1·2 g) and ammonium thiocyanate (0·38 g) were dissolved in tetrahydrofuran (10 ml) and added to $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ (1·1 g) in tetrahydrofuran. The mixture was heated under reflux for *ca.* 2 h, filtered, and the solvent distilled off under reduced pressure to give the product which was reprecipitated from tetrahydrofuran solution with hexane.

$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot Sn(HCO_2)_3$. $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ (2·1 g) in formic acid (30 ml) with tin(II) formate (2·3 g) was heated for *ca.* 4 h. The yellow solution was filtered, and the solvent removed under reduced pressure. The product was reprecipitated from tetrahydrofuran solution with hexane.

$(\pi\text{-}C_5H_5)Fe(CO)_2\cdot Sn(AcO)_3$. This was prepared similarly

from tin(II) acetate but with acetic anhydride as solvent. The products of the insertion reactions were identical with the sodium salt of the replacing anion (NCS, HCO_2, or AcO) in a 1 : 10 mole ratio, the mixture being heated under reflux for *ca.* 1 h. The methanol was then evaporated off and the residue extracted with benzene. The pure crystalline products were precipitated from the benzene solution by evaporation (NCS) or by the addition of ligroin (HCO_2 or AcO).

The analytical data for the isothiocyanate and carboxylate derivatives prepared in this work are listed in Table 5.

Physical Measurements.—The i.r. spectra were obtained for M/60-solutions in chloroform on a Perkin-Elmer 257.

The Mössbauer parameters were obtained at 80 K by use of a $BaSnO_3$ source supplied by The Radiochemical Centre, Amersham. The chemical shift of the reference α-Sn from $BaSnO_3$ was 2·10 mm s^{-1}. The Mössbauer apparatus has been described previously.[30]

[30] S. R. A. Bird, J. D. Donaldson, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc. (A)*, 1971, 1311.

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