The Crystal Structures of $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$ and $(\pi\text{-}C_5H_5)Fe(CO)_2SnBr_3$

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Summary Crystal structure determinations of $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$ and $(\pi\text{-}C_5H_5)Fe(CO)_2SnBr_3$ show identical Sn–Fe σ-bond distances of 2·465 Å, shorter than those observed in any other compound of this type.

As part of a continuing study[1] of subsequent effects in binuclear co-ordination complexes with metal-to-metal bonding between metal atoms of different kinds we have carried out three-dimensional *X*-ray crystal structure analyses of the compounds named in the title.

Relevant average molecular dimensions for each compound are compared in the Table with those found[2] in the molecule $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_3$.

The most striking result is the identity of the two Sn–Fe bond distances in the halides. As expected, this value is considerably shorter than that for the triphenyl compound, in line with observations on the trinuclear $SnFe_2$ systems.[3] However, a progression in parallel with the gradually changing electronegativity of the groups attached to tin is not found, though a progressive trend is shown by the diminution of the X–Sn–X angles and the corresponding

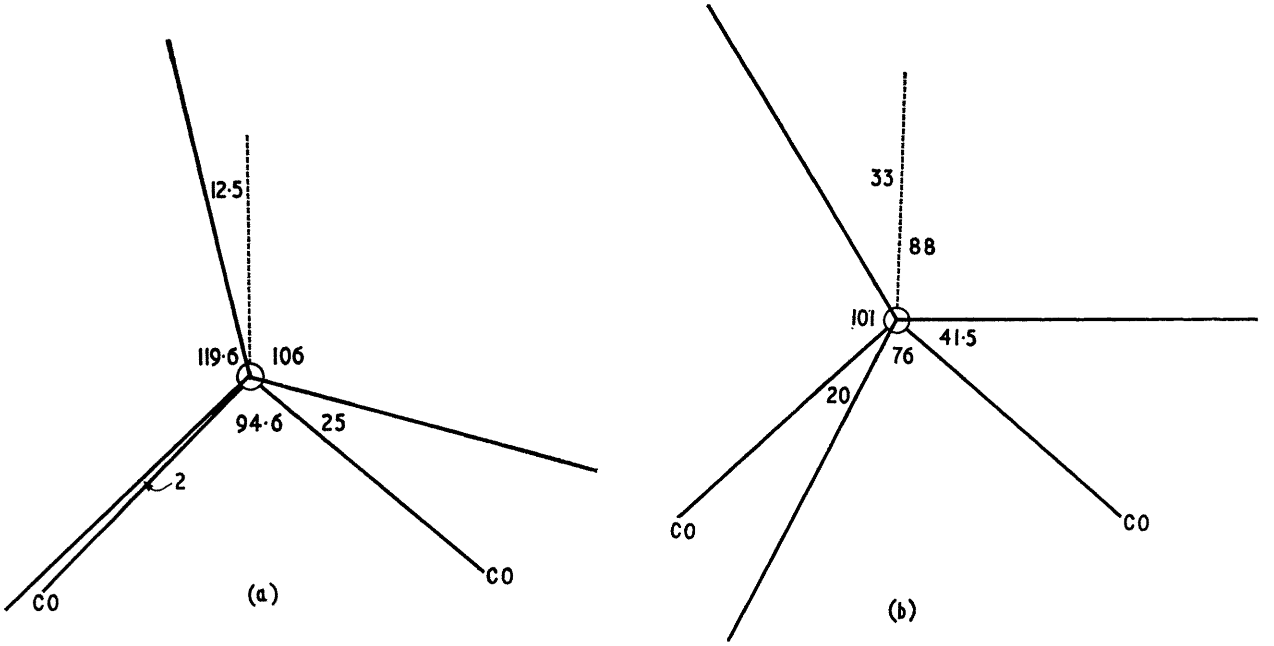

FIGURE. *View of the molecular conformation about the* Sn–Fe *axis* (a) *for the chloride,* (b) *for the bromide. The broken line represents the projection of a vector from the iron atom to the centroid of the cyclopentadienyl ring.*

$(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$:—$a$ = 11·02(1), b = 8·35(1), c = 6·62(1) Å, α = 106°12′, β = 84° 50′, γ = 96° 20′ (all ±5′), Z = 2. Space group $P\bar{1}$. 2561 significant independent reflections were measured using Mo-K_α radiation with an SDS Sigma-2 computer-controlled Picker four-circle diffractometer, $\theta/2\theta$ scan, scintillation counting, Zr/Y balanced filters. The phase problem was solved by the heavy-atom method; structural parameters were refined by Fourier and block-diagonal least-squares techniques using anisotropic thermal parameters, R = 0·054.

$(\pi\text{-}C_5H_5)Fe(CO)_2SnBr_3$:—$a$ = 12·56(2), b = 13·46(2), c = 15·14 Å, Z = 8. Space group *Pbca*. 1915 significant reflections measured as described above. Phase problem solved by symbolic addition methods, refinement as before, R = 0·10.

Average molecular dimensions in compounds of the type $(\pi\text{-}C_5H_5)Fe(CO)_2SnX_3$

Bond	X		
	Cl	Br	Ph
Sn–Fe	2·466(2) Å	2·465(3)	2·537(3)
Sn–X	2·358(6)	2·50(1)	2·13(2)
Fe–CO	1·78(2)	1·83(3)	1·72(1)
C–O	1·13(2)	1·08(3)	1·17(2)
Fe–C_π	2·10(2)	2·11(3)	2·10(1)
Angle			
Fe–Sn–X	119·2(1)°	117·7(2)°	113·4(2)°
X–Sn–X	98·3(1)°	100·2(2)°	105·2(2)°
Sn–Fe–CO	90·5(3)°	89·1(6)°	86·5(6)°

enlargement of the Fe–Sn–X angles over the regular tetrahedral values.

We also note that the two halide molecules differ in their conformations about the Sn–Fe bond axis (see Figure) and that they also differ in this respect from both of the conformationally different independent molecules in the crystallographic asymmetric unit of $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_3$. Inspection of these different conformations shows that they are not simply responses to the differing intramolecular interactions resulting from changes in the ligand sizes. Substantial free rotation about the metal–metal bond is thus indicated. This is strong evidence that the Sn–Fe bond is a pure σ-bond in these compounds. The immediate decrease in the bond distance from 2·54 to 2·47 Å when the phenyl groups are replaced by the more electronegative bromine atoms indicates the sensitivity of this bond to small changes in the effective electronegativity of the SnX_3 group. The lack of further shortening as the bromine atoms are replaced by even more electronegative chlorine atoms suggests that the value found for the bond distance is a limiting separation for this σ-bond. A further reduction of the internuclear separation would lead to mutual repulsions between metal σ-orbitals and neighbouring inner core electrons with no compensatory overlap between π-orbitals.

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