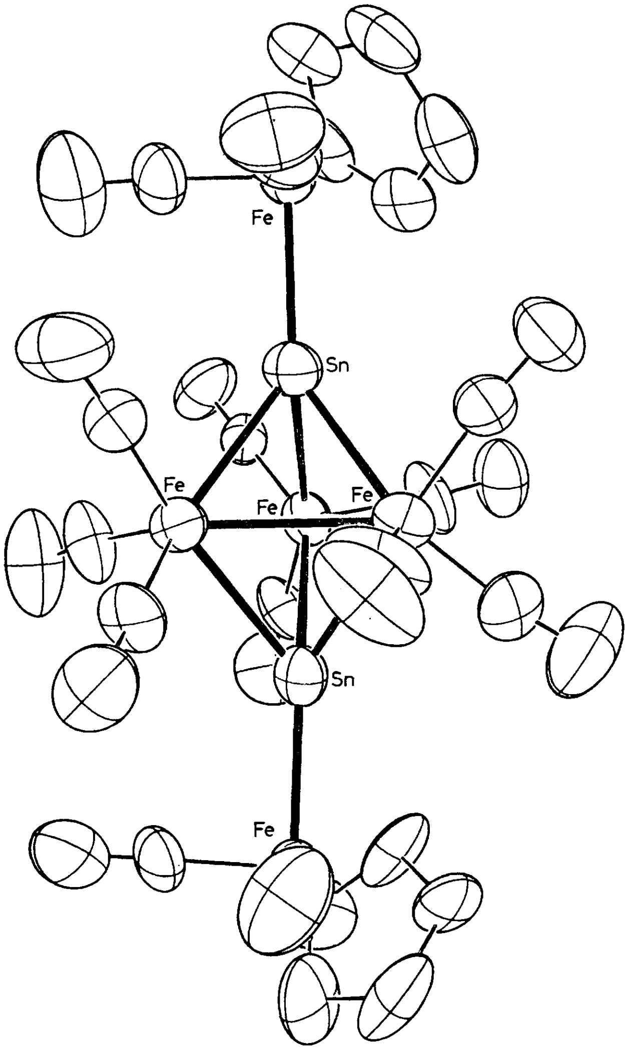
Novel Transformation of $[(\eta^1\text{-}C_5H_5)_2SnFe(CO)_4]_2$: the Crystal Structure of $[\{(C_5H_5)Fe(CO)_2\}_2Sn_2Fe_3(CO)_9]$

By TIMOTHY J. MCNEESE and STAN S. WREFORD*
(*Department of Chemistry, Harvard University, Cambridge, Massachusetts* 02138)
and DONALD L. TIPTON and ROBERT BAU*
(*Department of Chemistry, University of Southern California, Los Angeles, California* 90007)

Summary Thermal decomposition of $[(\eta^1\text{-}C_5H_5)_2SnFe(CO)_4]_2$ affords $[\{(C_5H_5)Fe(CO)_2\}_2Sn_2Fe_3(CO)_9]$, a cluster based on a trigonal bipyramidal arrangement of three equatorial $Fe(CO)_3$ groups and two axial $(C_5H_5)Fe(CO)_2Sn$ units, characterized on the basis of crystallographic, chemical, and spectroscopic data.

DIRECT reaction of disubstituted tin(II) species with iron carbonyl or its derivatives generally leads to dimeric complexes, $[R_2SnFe(CO)_4]_2$.[1] Reactions of dialkyltin dihalides with $Na_2Fe(CO)_4$[2], $Na_2Os(CO)_4$,[3] or $H_2Os(CO)_4$[3] afford similar products. The distinguishing feature of these dimers and higher oligomers is a tin atom bridge between two iron centres, thereby attaining a tetrahedral environment about the group IV atom. We report herein a novel transformation of $[(\eta^1\text{-}C_5H_5)_2SnFe(CO)_4]_2$[1]† in which a cyclopentadienyl unit has been transferred from tin to iron to form an Sn_2Fe_3 polyhedron; this represents the first preparation of a *closo* iron-tin cluster.



FIGURE

During the course of an investigation of the dynamic n.m.r. behaviour of $[(\eta^1\text{-}C_5H_5)_2SnFe(CO)_4]_2$, we noted an irreversible and clean conversion into a new compound. Subsequently, decomposition of the $Fe(CO)_4$ adduct in refluxing toluene gave, after purification by chromatography (silica gel, toluene eluent) and crystallization from dichloromethane–heptane, the product as black needles (33%, based on iron). Analytical data support the formulation $(C_{23}H_{10}Fe_5O_{13}Sn_2)_n$; the compound does not survive mass spectral conditions. The cyclopentadienyl resonance occurs at τ 4·32 without ^{119}Sn or ^{117}Sn satellites, implying that the C_5H_5 group is bound to iron.

The complex $[\{(C_5H_5)Fe(CO)_2\}_2Sn_2Fe_3(CO)_9]$ crystallizes in the monoclinic space group $P2_1/c$, with $a = 19{\cdot}859(15)$, $b = 10{\cdot}938(12)$, $c = 15{\cdot}687(12)$ Å, $\beta = 119{\cdot}83(3)°$, and $Z = 4$. *X*-Ray data were collected on an automated diffractometer with Mo-K_α radiation. The structure was solved by heavy atom methods and refined by least-squares techniques. Currently, R is 8·3% for 1865 reflections. The structure consists of an equatorial $Fe_3(CO)_9$ triangular cluster capped on both sides by $(C_5H_5)Fe(CO)_2Sn$ fragments (Figure). All carbonyl groups in the molecule are terminally bonded, and three of them lie approximately on the equatorial plane, which roughly defines a non-crystallographic mirror plane for the molecule. The tin atoms are bonded solely to iron atoms, a feature found in other tin–iron carbonyl clusters such as $Sn[Fe(CO)_4]_4$ and $Sn[Fe(CO)_4]_4(SnMe_2)_2$.[4] The trigonal bipyramidal Sn_2Fe_3 core of the molecule is reminiscent of the Sn_2Pt_3 cluster found in $Pt_3(SnCl_3)_2$(cyclo-octadiene)$_3$.[5] Average distances in the core of the molecule are: Sn–Fe(terminal), 2·471(5); Sn–Fe(equatorial), 2·537(4); and Fe–Fe, 2·792(6) Å.‡

We note that cluster formation is presumably a result of formation of the very stable $(C_5H_5)Fe(CO)_2$ species and the attainment of a distorted tetrahedral environment about tin. Average Fe(terminal)–Sn–Fe(equatorial) and Fe(equatorial)–Sn–Fe(equatorial) angles are 140·5 and 64·5°, respectively. Although some strain is evident from the internal Fe–Sn–Fe bond angles, for the latter reason we suggest that this trigonal bipyramidal arrangement ought to be a particularly favourable one among group IV–transition metal clusters, a suggestion which is supported by the Sn_2Pt_3 cluster,[5] but which stands in contrast to the usual open iron–tin derivatives.[1,2,4]

Bromination of $[\{(C_5H_5)Fe(CO)_2\}_2Sn_2Fe_3(CO)_9]$ gives $(C_5H_5)Fe(CO)_2Br$ and $SnBr_4$ as minor and major products, respectively;§ the terminal iron–tin bond is not selectively cleaved by bromine or other electrophiles ($HgCl_2$ and I_2) nor by reductive procedures (sodium amalgam).

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† The *monohapto* nature of the C_5H_5 unit is confirmed by the i.r. criterion (A. Davison and P. E. Rakita, *Inorg. Chem.*, 1970, **9**, 289) and by the collapse of the ^1H n.m.r. resonance at −110 °C.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ Identified by mass spectra.

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