

Tin-Iron Carbonyl Clusters and Sequences

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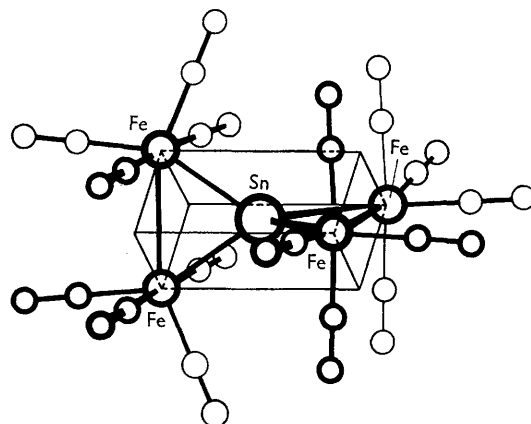
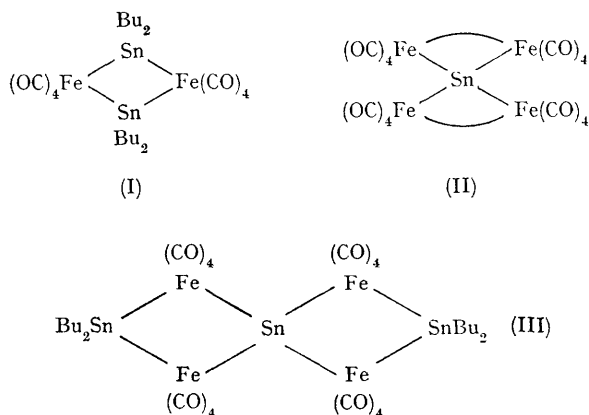
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WE report a synthesis of dimeric dialkyltin-iron tetracarbonyls which, unlike previous methods of preparation,¹⁻³ employs commercially available starting materials. Moreover, the reaction affords novel metal-atom clusters, including $\text{SnFe}_4(\text{CO})_{16}$.

The synthesis employs organotin halides and iron pentacarbonyl, and is illustrated by studies involving tri-*n*-butyltin chloride shown in the accompanying Chart. Di-*n*-butyltin(tetracarbonyl)iron dimer (I) can be obtained in 30–40% yield. The compounds $\text{Sn}[\text{Fe}(\text{CO})_4]_4$ (II) and $\text{Bu}_4\text{Sn}_3[\text{Fe}(\text{CO})_4]_4$ (III) are produced in smaller amounts. Complex (II) is an air-stable red solid, also obtained by refluxing iron pentacarbonyl with hexabutylditin, or with stannous

chloride in tetrahydrofuran. Covalent iron-iron interactions are suggested by the diamagnetism of the complex. The most likely structure (II) is one with the iron atoms having a co-ordination number of six. We have carried out an X-ray-crystallographic study on (II) and find that the molecular symmetry is $D_{2d}(\bar{4}2m)$ (See Figure).

The tetrahedral valencies of the tin atom are

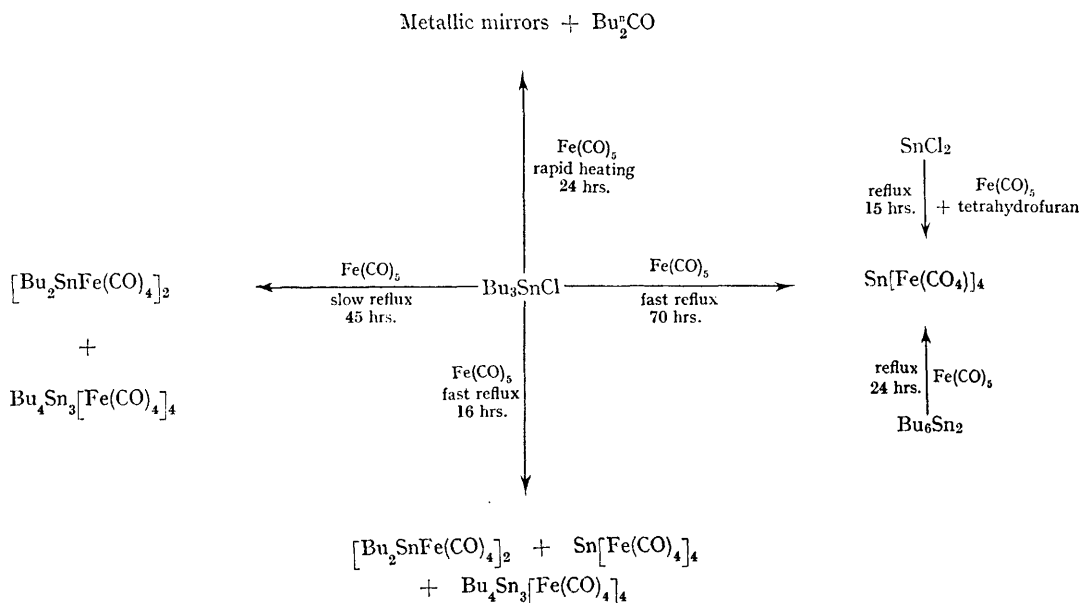


FIGURE

tetragonally distorted, and there are two different pairs of Fe-Fe distances; one 2.87 Å, the other 4.65 Å. The Sn-Fe bond length is 2.53 Å. If each iron atom is considered to form six bonds

(one Fe-Sn, one Fe-Fe, and four Fe-CO), which would account for the diamagnetism, the configuration about the iron atoms may be described as approximately octahedral but with distortion of those angles which occur in the Fe-Sn-Fe plane.

Compound (III), bright red, has a structure closely related to (II) with two additional di-butyltin groups bridging the iron atoms.* Treatment of dialkyltin dichlorides with iron pentacarbonyl at lower temperatures affords complexes



The OC-Fe-CO angles open to about 100° in order to accommodate the closing of the Sn-Fe-Fe angle to 56° . The average value of the Fe-C-O angle is about 170° .⁴

cis- $[\text{R}_2\text{SnCl}]_2\text{Fe(CO)}_4$ with Sn-Fe-Sn sequential bonding,⁵ but at higher temperatures various iron-tin clusters are formed.

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* The methyl analogue, $\text{Me}_4\text{Sn}_3\text{Fe}_4(\text{CO})_{16}$ has been obtained by a different route and its structure determined by R. M. Sweet, C. J. Fritchie, and R. A. Schunn, private communication from Dr. R. A. Schunn.

¹ R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1963, **85**, 2021.

² W. Hieber and R. Breu, *Chem. Ber.*, 1957, **90**, 1270.

³ S. D. Ibekwe and M. J. Newlands, *Chem. Comm.*, 1965, 114.

⁴ S. F. A. Kettle, *Inorg. Chem.*, 1965, **4**, 1661.

⁵ H. R. H. Patil and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1965, **87**, 673.