

## New Stannylene-bridged Tetracarbonyliron Dimers

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### Abstract

The reaction of three stannocene derivatives, bis(pentamethylcyclopentadienyl)tin(II) cyclopentadienyltin(II) chloride and cyclopentadienyltin(II) bromide with diiron nonacarbonyl yielded three new stannocene tetracarbonyliron compounds. Infrared, NMR and Mössbauer spectra of the products indicate that they are new members of a class of dimeric stannylene-tetracarbonyliron compounds containing  $\text{Fe}_2\text{Sn}_2$  ring frameworks. Treatment of the dimers with strong donors results in ring fission leading to base-stabilized stannocene-tetracarbonyliron monomers.

### Introduction

Dimeric  $[\text{R}_2\text{MFe}(\text{CO})_4]_2$  compounds where M is a Group 14 element have been known for many years. In the cases where  $\text{M} = \text{Sn}$ , several compounds involving bridging dialkyl [1] diaryl [1] and dicyclopentadienyl [2] stannylenes have been reported. Where known [2–3] the dimer structures exhibit approximately tetrahedral and octahedral coordination geometries around tin and iron respectively, with only small differences in  $\text{Fe}_2\text{Sn}_2$  bond lengths and angles for different stannylene substituents. A noteworthy feature of the solid state structure of  $[(\text{C}_5\text{H}_5)_2\text{SnFe}(\text{CO})_4]_2$  is its monohapto, planar cyclopentadiene rings [4]. On the basis of NMR spectra the  $\eta^1$ -cyclopentadiene rings are believed to persist in solution [2].

We wish to report the synthesis of three new examples of the  $[\text{R}_2\text{SnFe}(\text{CO})_4]_2$  class involving bis(pentamethylcyclopentadienyl)tin(II), cyclopentadienyltin(II) chloride and bromide.

### Experimental

All manipulations were carried out under air- and water-free conditions using conventional methods

[5]. All solvents were dried and deoxygenated using literature methods. Tin(II) chloride and bromide were prepared as described earlier [6, 7]. Decamethylstannocene and cyclopentadienyltin(II) chloride and bromide were prepared by literature methods [8, 9]. Other starting materials were at least reagent grade commercial materials used as obtained. Infrared spectra were obtained on a Beckman Model 4250 spectrometer using KBr disks, Nujol mulls and solution cells. Proton and  $^{13}\text{C}$  NMR spectra were obtained on a Varian FT-80 instrument at 80 MHz and 20 MHz, respectively. Mössbauer spectra were produced using an Austin Science Associates spectrometer described previously [10]. The source was  $\text{Ba}^{119\text{m}}\text{SnO}_3$  and the samples were held at liquid nitrogen temperature. Melting points were obtained in closed capillaries on a heated block and are uncorrected. Elemental analyses were performed by Galbraith Analytical Laboratories and Spang Company.

### *Bis[μ-bis(pentamethylcyclopentadienyl)tin]-bis(tetracarbonyliron)*

Using a modification of the method published [2] for the stannocene analog, bis(pentamethylcyclopentadienyl)tin(II) (3.1 g; 8.0 mmol) and diiron nonacarbonyl (1.4 g; 4.0 mmol) were added to a 100 ml reaction flask containing a magnetic stirbar and fitted with a Teflon valve adaptor for connection to the vacuum line. About 65 ml of benzene was vapor transferred into the evacuated flask after which the contents were allowed to warm to room temperature with stirring. After stirring for 40 h at ambient temperature, the reaction mixture was filtered under nitrogen giving a dark-brown semisolid which was held under dynamic vacuum for 24 h and then extracted with portions of pentane. After filtration, the pentane was stripped off giving the crude product as a dark-red gummy solid. The product was purified by subliming away (65 °C,  $10^{-3}$  mmHg) some unreacted decamethylstannocene leaving 2.5 g (56%) of a red-brown powder, melting point (m.p.) 95–98 °C (d). *Anal.* Found: C, 50.98; H, 5.27. Calc. for  $\text{C}_{48}\text{H}_{60}\text{Fe}_2\text{O}_8\text{Sn}_2$ : C, 51.74; H, 5.43%.  $^1\text{H}$  NMR (80 MHz) in  $\text{C}_6\text{D}_6$ :  $\delta$  2.20(s). IR (KBr): 2050vs, 2000vs, 1980vs(br), 1945ms(sh)  $\text{cm}^{-1}$  (THF) 2005ms, 1930vvs(br)  $\text{cm}^{-1}$ ; (pyridine) 1995ms,

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1925vvs(br)  $\text{cm}^{-1}$ .  $^{119}\text{mSn}$  Mössbauer: IS = 1.95  $\text{mm s}^{-1}$ .

*Bis( $\mu$ -cyclopentadienyltin(II)chloride)-bis(tetracarbonyliron)*

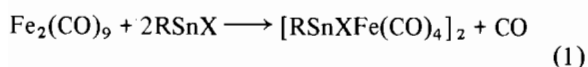
Cyclopentadienyltin(II) chloride (1.66 g, 7.6 mmol) and diiron nonacarbonyl (5.38 g; 15.2 mmol) were combined in a 200 ml flask containing a magnetic stirring bar and fitted with a Teflon valve adapter. Benzene (100 ml) was vacuum transferred into the evacuated flask. The reaction mixture was allowed to warm to room temperature and was stirred for 48 h. The reaction mixture was filtered under nitrogen affording a dark-red filtrate from which the solvent was removed by vapor transfer leaving a red-brown solid. After being held at 90 °C under dynamic vacuum for 24 h 2.9 g (24.6%) of the product was isolated as a red-brown powder, m.p. >118 °C (d). *Anal.* Found: C, 27.35; H, 1.26. Calc. for  $\text{C}_{18}\text{H}_{10}\text{Cl}_2\text{Fe}_2\text{O}_8\text{Sn}_2$ : C, 27.92; H, 1.30%.  $^1\text{H}$  NMR (80 MHz) in  $\text{CDCl}_3$ :  $\delta$ 6.52(m, CpH); THF:  $\delta$ 6.63(br), 6.48(br).  $^{13}\text{C}$  NMR (80 MHz) in  $\text{CDCl}_3$ :  $\delta$ 205(s, C-carbonyl) 200(s, C-carbonyl, 117.4(s, C-cyclopentadienyl ring) (ref.  $\text{Me}_4\text{Si}$ ). IR (KBr) 2090vvs, 2045m, 2030vvs, 2020vvs  $\text{cm}^{-1}$ ; (THF) 2105ms, 2056vvs, 2020s(sh), 1960s(sh), 1940vvs(br)  $\text{cm}^{-1}$ ; (pyridine) 2035s, 1940vvs(br)  $\text{cm}^{-1}$ .  $^{119}\text{mSn}$  Mössbauer IS = 1.79  $\text{mm s}^{-1}$ , QS = 1.58  $\text{mm s}^{-1}$ .

*Bis( $\mu$ -cyclopentadienyltin(II)bromide)-bis(tetracarbonyliron)*

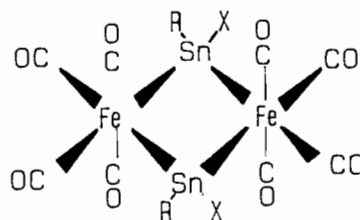
Following the same procedure as used for the chloride derivative, cyclopentadienyltin(II) bromide (2.0 g, 7.6 mmol) was combined with diiron nonacarbonyl (5.38 g, 15.2 mmol) to give 5.6 g (42.7%) of the product as a red-brown powder, m.p. >250 °C (d). *Anal.* Found: C, 23.23; H, 1.26. Calc. for  $\text{C}_{18}\text{H}_{10}\text{Br}_2\text{Fe}_2\text{O}_8\text{Sn}_2$ : C, 25.04; H, 1.16%.  $^1\text{H}$  NMR (at 80 MHz) in THF:  $\delta$ 6.65(br), 6.55(br);  $\text{CDCl}_3$ :  $\delta$ 6.50(m, CpH). IR (KBr) 2085vvs, 2050s(sh), 2025vvs, 2015vvs  $\text{cm}^{-1}$ ; (THF) 2100ms, 2050vvs, 2010s(sh), 1950vvs(sh), 1930vvs(br)  $\text{cm}^{-1}$ ; (pyridine) 2020s, 1935vvs(br)  $\text{cm}^{-1}$ .  $^{119}\text{Sn}$  Mössbauer: IS = 1.82  $\text{mm s}^{-1}$ , QS = 1.60  $\text{mm s}^{-1}$ .

## Results and Discussion

New examples of iron tetracarbonyl dimers containing stannylene bridges (**1**–**3**) have been synthesized by the direct reaction of the stannylenes with diiron nonacarbonyl generalized in eqn. (1).



The reactions proceeded slowly in benzene at 25 °C affording moderate yields of di- $\mu$ -stannylene-bis-(tetracarbonyl iron) products as red-brown solids.



**1**, R =  $\text{Me}_5\text{C}_5$ ; X =  $\text{Me}_5\text{C}_5$

**2**, R =  $\text{C}_5\text{H}_5$ ; X = Cl

**3**, R =  $\text{C}_5\text{H}_5$ ; X = Br

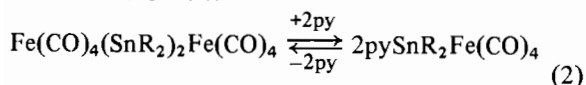
TABLE I. Infrared Bands ( $\text{cm}^{-1}$ ) of Products in the Carbonyl Stretching Region<sup>a</sup>

Solid <sup>b</sup>	THF solution	Pyridine solution
[( $\text{C}_5\text{H}_5$ )(Cl)SnFe(CO) <sub>4</sub> ] <sub>2</sub>		
2090vvs	2105ms	
2045m	2056vvs	2035s
2030vvs	2020s(sh)	
2020vvs	1960vvs(sh)	1940vvs(br)
	1940vvs(br)	
[( $\text{C}_5\text{H}_5$ )(Br)SnFe(CO) <sub>4</sub> ] <sub>2</sub>		
2085vvs	2100ms	
2050s(sh)	2050vvs	2020s
2025vvs	2010s(sh)	
2015vvs	1950s(sh)	1935vvs(br)
	1930vvs(br)	
[( $\text{Me}_5\text{C}_5$ ) <sub>2</sub> SnFe(CO) <sub>4</sub> ] <sub>2</sub>		
2050vs	2005ms	1995ms
2000vs		
1980vs(br)	1930vvs(br)	1925vvs(br)
1945ms(sh)		

<sup>a</sup>w = weak, m = medium, ms = medium strong, s = strong, vs = very strong, vvs = very, very strong, sh = shoulder, br = broad. <sup>b</sup>KBr pellets

The IR spectra of the products in the metal carbonyl stretching region obtained in KBr pellets and as solutions in tetrahydrofuran (THF) and pyridine are listed in Table I. Each of the products exhibited four bands between 1945 and 2090  $\text{cm}^{-1}$ . Two or three carbonyl bands were reported in the IR spectra of dimethyl-, di-*t*-butyl- and diphenylstannylene-iron tetracarbonyl dimers in hydrocarbon solutions [1]. Dissolving our products in pyridine resulted in a marked change in the carbonyl stretching region of the IR spectra. The bands in the solid phase spectra were replaced by two new bands, an intense broad band between 1925 and 1940  $\text{cm}^{-1}$  and a sharp weaker band near 2020  $\text{cm}^{-1}$ . Marks and Neuman [1] observed similar spectral changes for dialkyl- and diarylstannylene-tetracarbonyliron derivatives. The changes upon dissolution in the strong donor solvent

were attributed to the formation of pyridine–monomer adducts via the cleavage of the dimer structures (eqn. (2)).



An analogous cleavage is believed responsible for features of the IR spectra of the compounds in the present study. The spectra of **2** and **3** in THF solution indicate the presence of both monomer and dimer, presumably in equilibrium (eqn. (2)). The spectrum of **1** in THF, however, reveals only the monomeric form. One rationale for the difference considers that dimers of stannylenes bearing sterically demanding substituents, such as **1**, may be less stable towards dissociation than those with smaller substituents, such as **2** and **3**. This seems borne out by the earlier measurement of 11.5, 31.6 and 100% dissociation in THF solution of  $[\text{R}_2\text{SnFe}(\text{CO})_4]_2$ , where R = Me, Ph and t-Bu, respectively [1].

The introduction of a strong donor such as pyridine completely displaces the weaker tetracarbonyliron donor species forming the adduct monomer. We did not attempt to isolate the pyridine adducts although this has been done successfully in at least one case [3].

The observation of  $\eta^1$ -attachment of the cyclopentadienyl groups in crystalline  $[\text{Cp}_2\text{SnFe}(\text{CO})_4]_2$  raises the question of whether those groups are  $\eta^1$  or  $\eta^5$  in solution. The  $^1\text{H}$  NMR spectrum of that compound was reported to be a singlet from room temperature down to crystallization at  $-80^\circ\text{C}$  owing to fluxional behavior of  $\eta^1$ -cyclopentadienyl rings [2]. The  $^1\text{H}$  spectra of compounds **2** and **3** (Table II) exhibit sharp singlets at  $\delta 6.52$  and  $6.50$ , respectively, in  $\text{CDCl}_3$  solutions, presumably as a result

TABLE II.  $^1\text{H}$  NMR Data ( $\delta$ ) for Products and Stannocene Precursors

Compound	Solvent	Ring proton ( $\delta$ )	Me proton ( $\delta$ )
$[(\text{C}_5\text{H}_5)(\text{Cl})\text{SnFe}(\text{CO})_4]_2$	$\text{CDCl}_3$ THF	6.52	
		6.63	
		6.48	
$[(\text{C}_5\text{H}_5)(\text{Br})\text{SnFe}(\text{CO})_4]_2$	$\text{CDCl}_3$ THF	6.50	
		6.65	
		6.41	
$[(\text{Me}_5\text{C}_5)_2\text{SnFe}(\text{CO})_4]_2$	$\text{CDCl}_3$	—	2.20
		$[(\text{C}_5\text{H}_5)_2\text{SnFe}(\text{CO})_4]_2^{\text{a}}$	6.13
$(\text{C}_5\text{H}_5)_2\text{Sn}^{\text{b}}$	$\text{CDCl}_3$	5.81	
$(\text{Me}_5\text{C}_5)_2\text{Sn}^{\text{c}}$	$\text{CDCl}_3$	—	2.06
$(\text{C}_5\text{H}_5)\text{SnCl}^{\text{d}}$	THF	6.02	
$(\text{C}_5\text{H}_5)\text{SnBr}^{\text{d}}$	THF	6.08	

<sup>a</sup>Ref. 2    <sup>b</sup>Ref. 11.    <sup>c</sup>Ref. 9    <sup>d</sup>Ref. 9.

of similar fluxional behavior of the dimeric compounds. In THF solution, however, both **2** and **3** exhibit a pair of broad singlets, following the IR evidence cited above, owing to the presence of fluxional monomer and dimer species in solution. The more intense resonance, near  $\delta 6.64$  in both spectra, is tentatively assigned as representing the monomer (*i.e.*,  $\text{THF}\cdot\text{CpSn}(\text{X})\text{Fe}(\text{CO})_4$ ). The lesser resonances at  $\delta 6.48$  and  $6.41$ , differing less from the  $\text{CDCl}_3$ (dimer) values, are believed to represent the dimers. The peak areas suggest that in THF at  $35^\circ\text{C}$  the monomer–dimer equilibrium (eqn. (2)) is displaced toward monomer to approximately the same extent (*ca.* 3.5 to 1) for both **2** and **3**. This is reasonable considering the size of the substituents on tin and the relatively small difference between the steric effects of chloride and bromide.

TABLE III. Mössbauer Data for Products and Related Compounds ( $\text{mm s}^{-1}$ )

Compound	Isomer Shift (IS)	Quadrupole Splitting (QS)
$[(\text{Me}_5\text{C}_5)_2\text{SnFe}(\text{CO})_4]_2$	1.95	—
$[(\text{C}_5\text{H}_5)(\text{Cl})\text{SnFe}(\text{CO})_4]_2$	1.79	1.58
$[(\text{C}_5\text{H}_5)(\text{Br})\text{SnFe}(\text{CO})_4]_2$	1.82	1.60
$[(\text{C}_5\text{H}_5)_2\text{SnFe}(\text{CO})_4]_2^{\text{a}}$	1.86	—
$[\text{Me}_2\text{SnFe}(\text{CO})_4]_2^{\text{b}}$	1.22	1.47
$[(n\text{-Bu})_2\text{SnFe}(\text{CO})_4]_2^{\text{b}}$	1.70	1.26
$[\text{t-Bu}_2\text{SnFe}(\text{CO})_4]_2^{\text{c}}$	1.83	1.16

<sup>a</sup>Ref. 2.    <sup>b</sup>Ref. 13.    <sup>c</sup>Ref. 14.

The Mössbauer spectrum of **1** in the solid phase (Table III) consists of a single resonance without observable quadrupole splitting indicative of the absence of an electric field gradient at the tin nucleus. The spectrum of **1** closely resembles the spectra of  $[\text{Cp}_2\text{SnFe}(\text{CO})_4]_2$  and  $[(\text{MeCp})_2\text{SnFe}(\text{CO})_4]_2$  with respect to both the isomer shifts and the lack of quadrupole splitting [2]. This suggests a close structural similarity among the compounds. Compounds **2** and **3** exhibit quadrupole splitting in their Mössbauer spectra owing to the expected effect of the halogen atom on the symmetry of the electric field around tin.

The isomer shifts of all three compounds fall in the range of 1.79 to 1.95  $\text{mm s}^{-1}$  (relative to  $\text{Ba}^{119\text{m}}\text{SnO}_3$ ) which overlaps the region normally associated with compounds of tetravalent tin [12]. The range of isomer shifts of the previously known dialkylstannylene tetracarbonyliron dimers (Table III) coincides with that of the compounds in this study and their quadrupole splittings fall just below those of compounds **2** and **3**.

Thus, the IR, NMR and Mössbauer spectra of the new compounds are consistent with those

expected for the characteristic dimeric structures reported for other stannylene–tetracarbonyliron compounds.

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