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STANNOCENOPHANES. RING-BRIDGED DI-h^5-CYCLOPENTADIENYLTIN(II) DERIVATIVES OF α,α'-DICYCLOPENTADIENYL-*ortho*-, -*meta*- AND -*para*-XYLENE

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Summary

Three isomeric examples of a new class of stannocene (di-h^5-cyclopentadienyltin(II)) derivatives are described in which the h^5-cyclopentadienyl rings are linked through methylene bridges to a phenyl system. The *ortho*-, *meta*- and *para*-xylene derivatives are synthesized from the disodium salt of (phenylenedimethylene)dicyclopentadienide with tin(II) chloride in THF. The products are air-sensitive, off-white powders, soluble in organic solvents, which show no definite melting points. Exposure to air gives the R_2SnO derivative and ultimately tin(IV) oxide. Tin-119m Mössbauer data corroborate the tin(II) oxidation state, and parent molecular ions at $m/e = 352$ are recorded as the highest m/e value in the mass spectra. The action of h^5-cyclopentadienyltin(II) chloride on the disodium salt gives *meta*-phenylenedimethylenedi-h^5-cyclopentadienyltin(II) di-h^5-cyclopentadiene. The *meta*-stannocenophane derivative also yields an infusible BF_3 adduct from the BF_3 etherate. Mössbauer quadrupole splittings for the *ortho*- and *para*-stannocenophanes are much larger (1.84 and 1.29 mm s^{-1}, respectively) than for stannocene itself.

Introduction

Di-h^5-cyclopentadienyltin(II) [1] (stannocene), first synthesized by Fischer et al. [2] in 1956 and studied spectroscopically by Wilkinson et al. [3] in 1959, has been the subject of recent studies involving ring-substituted derivatives such as bis(h^5-pentamethyl- [4,5] or -pentaphenyl-cyclopentadienyl)tin(II) [6], using cyclopentadienes already substituted by functional groups [7], or by reaction of stannocene already formed with phosphenium ions [8] or by lithiating and derivatizing stannocene [9]. Reaction of decamethylstannocene with pentakis(methoxycarbonyl)cyclopentadiene eliminates pentamethylcyclopentadiene, but probably yields $[h^5\text{-}C_5H_5Sn]^+$ $[C_5CO_2Me]^-$ [10]. In addition, solid-state structural data are now available for stannocene [11], bis(h^5-pentamethylcyclopentadienyl)tin(II) [12], h^5-pentamethyl-

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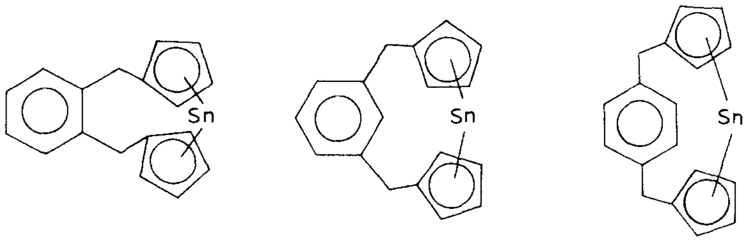
cyclopentadienyltin(II) tetrafluoroborate [13] $[h^5\text{-}(CH_3)_5C_5Sn]^+[BF_4]^-$, the pyridine adduct of h^5-pentamethylcyclopentadienyltin(II) trifluoromethanesulfonate [14] $[C_6H_5N \cdot h^5\text{-}(CH_3)_5C_5Sn]^+ [CF_3SO_3]^-$ and $\{[BF_4]^-(\mu\text{-}h^5\text{-}C_5H_5)_2Sn[\mu\text{-}h^5\text{-}C_5H_5Sn]^+THF\}_n$ [15].

Stannocene and its derivatives are angular sandwich compounds [11,12,16] with a stereochemically-, and presumably chemically-active lone pair of electrons present in the divalent state of tin occupying the third site of the trigonal coordination of the metal atom. Altering the steric and electronic properties of the cyclopentadienyl rings through substitution will alter the angles made by the tin to the two cyclopentadienyl rings, and hence the hybridization, spatial extension and basicity of the lone-pair electrons which may not always be the initial site of chemical attack in stannocene reactions. Recent results of semiempirical [12] and self-consistent field X_α scattered-wave (SCF X_α SW) MO calculations [17] disagree on whether the orbital holding the lone pair is the highest-occupied MO (HOMO) [12] or the fifth in energy, ca. 2.0 eV more stable than the HOMO, as corroborated by He(I) UV photoelectron spectral studies [17]. The reformulation of the BF_3 adduct of stannocene [18] as the result of a fluorine-cyclopentadienyl group transfer reaction [15] in THF to give $\{[BF_4]^-(\mu\text{-}h^5\text{-}C_5H_5)_2Sn[\mu\text{-}h^5\text{-}C_5H_5Sn]^+THF\}_n$, and the irreversible oxidation which occurs rather than the oxidation to $[(h^5\text{-}(C_5H_5)_2Sn]^{2+}$ on cyclic voltammetry [19] argue for a chemically-inactive lone pair. The availability of the salts of ring-substituted cyclopentadienes [20] offers the hope that the properties of the lone-pair electrons can be altered systematically if syntheses of the stannocene derivatives can be devised [7].

Another approach proceeds from the design of ligands containing two linked cyclopentadienyl anions in varying proximity and juxtaposition. Such systems can in principle be based upon the α,α'-dicyclopentadienylxylenes, the *meta*-isomer of which has been utilized to bond two transition-metal moieties as in *meta*-$C_6H_4[CH_2C_5H_4M(CO)_3R]_2$ where M = Mo, R = H, CH_3, C_2H_5, I and M = W, R = CH_3, C_2H_5. A bimetallic, metal–metal bonded derivative, *meta*-$C_6H_4[CH_2C_5H_4Mo(CO)_3]_2$, is also known. The low melting, soluble products are formulated as monomers [21].

Model studies show that all three α,α'-dicyclopentadienylxylene isomers can bind a single tin(II) atom in a number of different angular positions in both the monomer (see Fig. 1) and polymer forms. We have thus subjected tin(II) chloride to reaction



ortho (I) *meta* (II) *para* (III)

Fig. 1. The *ortho*- (I), *meta*- (II) and *para*-stannocenophane(III) monomers.

by the *ortho*-, *meta*- and *para*-isomers of the disodium salt of (phenylenedimethylene)dicyclopentadienide, and the resulting products are described in this paper.

Experimental

α,α'-Dibromo-*ortho*-, *meta*- and -*para*-xylenes were purchased from the Aldrich Chemical Co., and other reagents were also articles of commerce.

All solvents were dried and distilled immediately before use. Reactions were carried out under an atmosphere of dry nitrogen with the use of standard anaerobic techniques. Melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected.

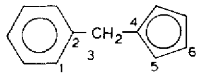
The ^{119m}Sn Mössbauer spectra were recorded on a Ranger Engineering constant-acceleration spectrometer equipped with a sodium iodide scintillation counter. The source was $Ca^{119m}SnO_3$ (New England Nuclear Corp.) and $Ca^{119}SnO_3$ was the reference material for zero velocity at room temperature. Velocity calibration was based on β-tin and iron foils. The Janis variable-temperature, liquid-nitrogen dewar and Lakeshore cryogenics control used in these studies were regulated by a variable-bridge silicon-controlled-rectifier circuit at 77 K for these measurements. The data were stored in 512 channels of the Tracor Northern Model TN-1314 multichannel analyzer and the resultant spectra fitted assuming a Lorentzian line shape.

Infrared spectra were recorded on a Beckman 4250 spectrometer as Nujol mulls on KBr disks or as CsI pellets, and the spectra were calibrated with polystyrene. Mass spectra were recorded on a Hewlett–Packard 5985B GC/MS system at 70 eV. Proton and carbon-13 NMR spectra were recorded on an IBM NR-80 instrument.

α,α'-Dicyclopentadienylxylene, $C_6H_4(CH_2C_5H_4)_2$. Freshly cracked cyclopentadiene (1.33 g, 20.1 mmol) in THF (tetrahydrofuran) (10 ml) was added to a suspension of sodium hyride (1.05 g, 43.7 mmol) in THF (10 ml) at 0°C over 15 min. The NaH was a 56% suspension in oil which was washed with three portions of THF (10 ml each) before use. Stirring was continued until hydrogen production ceased, and the sodium cyclopentadienide product filtered under nitrogen into a pressure-equalizing dropping funnel.

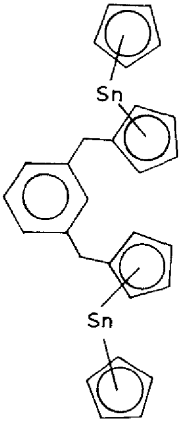
The sodium cyclopentadienide thus produced was added to the α,α'-dibromoxylene (2.64 g, 10.0 mmol) in THF (5 ml) at 0°C and the mixture stirred for ca. 45 min and then filtered under nitrogen into a dropping funnel.

Disodium (phenylenedimethylene)dicyclopentadienide, $C_6H_4(CH_2C_5H_4Na)_2$. The light amber solution produced above was added to sodium hydride (3.37 g, 140 mmol). The α,α'-dicyclopentadienylxylene solution was added over 25 min at 0°C with stirring, then the reaction mixture allowed to warm to room temperature and stirred for an additional 45 min until hydrogen evolution ceased. The clear, amber product mixture was filtered into a receiving flask. Exposure to air brings about darkening of the solution.

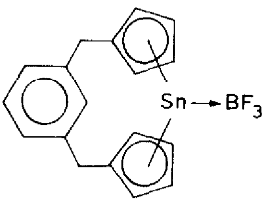
Phenylenedimethylene di-h^5-cyclopentadienyltin(II), $C_6H_4(CH_2C_5H_4\text{-}h^5)_2Sn$. To the THF solution of disodium (phenylenedimethylene)dicyclopentadienide produced above was added tin(II) chloride (1.89 g, 10.0 mmol) in THF (10 ml) dropwise over ca. 20 min at room temperature with stirring. The solution turned from clear amber to a creamy white suspension which was allowed to stir for ca. 45 min and filtered to remove the sodium chloride formed. In the first experiments hexane was added to the THF filtrate, but in subsequent workups the clear yellow solution was evaporated to give the product. For the *ortho*-isomer (I) using 2.26 g, 8.56 mmol of the α,α'-dibromide gave 1.43 g of the product in 47.8% yield. For the *meta*-isomer (II), 2.64 g, 10.0 mmol gave 1.35 g of product (38.5% yield) and for the *para*-isomer (III), 5.28 g, 20.1 mmol gave 3.28 g of product (46.5% yield). No tin satellites were observed in the proton NMR spectra of the three isomeric stannocenophanes in deuterobenzene. The $C_6H_4/CH_2/C_5H_4$ integration ratios for the isomers are: *ortho*- (I) 1/1.02/2.04; *meta*- (II), 1/1.22/2.08; and *para*- (III), 1/0.84/1.90 vs. 1/1/2 calculated. In the ^{13}C NMR of the *para*-isomer, the chemical shifts of the carbon atoms in the scheme:  are C(1) 129.83; C(2) 138.48; C(3) 32.88; C(4) 129.07; C(5) 127.72 and C(6) 128.67 ppm vs. TMS. The analogous data for *para*-xylene are C(1) 129.0; C(2) 134.6 and C(3) 20.9 ppm [22], and for $(h^5\text{-}CH_3C_5H_4)_2Sn^{II}$ are C(3) 16.76; C(4) 126.70; C(5) 113.80 and C(6) 111.20 ppm [23].

meta-Phenylenedimethylene di-h^5-cyclopentadienyltin(II) di-h^5-cyclopentadiene, $m\text{-}C_6H_4(CH_2C_5H_4\text{-}h^5)_2Sn_2(h^5\text{-}C_5H_5)_2$ (IV). To disodium (phenylenedimethylene)dicyclopentadienide (5.0 g, 18 mmol) in THF (150 ml) in an argon atmosphere was added a solution of h^5-cyclopentadienyltin(II) chloride (7.8 g, 35 mmol) in THF (200 ml) via syringe. A white solid formed shortly after the h^5-cyclopentadienyltin(II) chloride was added. Stirring was continued for one hour. The solution was filtered, and the solvent removed in vacuum leaving $C_6H_4(CH_2C_5H_4\text{-}h^5)_2Sn_2(h^5\text{-}C_5H_5)_2$ (6.3 g, 73% yield). ^1H NMR: C_6H_4 7.25m, CH_2 1.35s,br, C_5H_4 5.75m, C_5H_5 5.9s ppm. Anal. Found: Sn, 38.91. $C_{28}H_{26}Sn_2$ calcd.: Sn, 39.57%.

meta-Phenylenedimethylenedi-h^5-cyclopentadienyltin(II) trifluoroborate derivative, $m\text{-}C_6H_4(CH_2C_5H_4\text{-}h^5)_2Sn\text{-}BF_3$ (V). To *meta*-phenylenedimethylene di-h^5-cyclopentadienyltin(II) (5.0 g, 1.4 mol) in THF (100 ml) in an argon atmosphere was added freshly distilled boron trifluoride etherate (2.0 g, 14 mol, 1.7 ml) dropwise via



(IV)



(V)

Fig. 2. The *meta*-phenylenedimethylenedi-h^5-cyclopentadienyltin(II) di-h^5-cyclopentadiene (IV), and the boron trifluoride adduct of *meta*-stannocenophane (V).

syringe with stirring. Stirring was continued for one hour subsequent to the end of addition, then approximately 80% of the solvent removed by vacuum. Addition of ether resulted in precipitation of the boron trifluoride adduct. Filtration and vacuum drying gave 5.1 g, 85% yield. The material was infusible to over 270°C. Anal. Found: Sn, 27.22. $C_{18}H_{16}BF_3Sn$ calcd.: Sn, 28.34%.

Results and discussion

The synthesis of the bridged-dicyclopentadienyl ligand proceeds from the corresponding α,α'-dibromoxylene and sodium cyclopentadienide:

$$C_6H_4(CH_2Br)_2 + 2NaC_5H_5 \xrightarrow[0^\circ C]{THF} C_6H_4(CH_2C_5H_5)_2 + 2NaBr \qquad (1)$$

The unstable product [21] was converted immediately to the disodium salt by sodium hydride:

$$C_6H_4(CH_2C_5H_5)_2 + 2NaH \xrightarrow[0^\circ C]{THF} C_6H_4(CH_2C_5H_4Na)_2 + 2H_2 \qquad (2)$$

Each of the three isomers of the sodium salt was converted to the tin(II) derivative by treatment with tin(II) chloride:

$$C_6H_4(CH_2C_5H_4Na)_2 + SnCl_2 \rightarrow C_6H_4(CH_2C_5H_4\text{-}h^5)_2Sn^{II} + 2NaCl \qquad (3)$$

The products (I, II and III) are air-sensitive, off-white powders, soluble in THF, benzene and toluene, which soften at ca. 230°C but do not melt. Exposure to air causes darkening and conversion to the corresponding tin(IV) oxides:

$$C_6H_4(CH_2C_5H_4)_2Sn + 1/2O_2 \rightarrow C_6H_4(CH_2C_5H_4\text{-}h^1)_2SnO \qquad (4)$$

which were not isolated. Further action of air gives tin(IV) oxide.

The tin-119m Mössbauer data in Table 1 are compatible with divalent tin

TABLE 1

TIN-119m MÖSSBAUER DATA FOR DIORGANOTIN(II) DERIVATIVES AT 77 K IN mm s^{-1} [a]

Compound	*IS*	*QS*	Ref.
ortho-$C_6H_4(CH_2C_5H_4\text{-}h^5)_2Sn^{II}$ (I)	3.32 ± 0.03	1.84 ± 0.06	[b]
meta-$C_6H_4(CH_2C_5H_4\text{-}h^5)_2Sn^{II}$ (II)	3.79 ± 0.03	0.93 ± 0.06	[b]
para-$C_6H_4(CH_2C_5H_4\text{-}h^5)_2Sn^{II}$ (III)	3.36 ± 0.03	1.29 ± 0.06	[b]
meta-$C_6H_4(CH_2C_5H_4\text{-}h^5)_2Sn\text{-}BF_3$ (V)	3.79 ± 0.03	0.93 ± 0.06	[b]
meta-$C_6H_4(CH_2C_5H_4\text{-}h^5\text{-}SnC_5H_5\text{-}h^5)_2$ (IV)	3.23 ± 0.03	2.08 ± 0.06	[b]
$(h^5\text{-}C_5H_5)_2Sn^{II}$	3.74	0.86	18
$(h^5\text{-}CH_3C_5H_4)_2Sn^{II}$	3.83	0.78	27
Bis(phenylcarboranyl)tin(II)	2.95	1.90	31
$[2,6\text{-}(CF_3)_2C_6H_3]_2Sn^{II}$	3.37	1.93	32
$[2,4,6\text{-}(t\text{-}C_4H_9)_3C_6H_2]_2Sn^{II}$	3.28	1.90	32
$\{h^5\text{-}(CH_3)_5C_5]_2Sn^{II}$	3.53 ± 0.03	0.99 ± 0.06	[b]
$[h^5\text{-}(CH_3)_5C_5Sn]^+ [CF_3SO_3]^-$	3.81 ± 0.03	–	[b]
$\{[BF_4]^-(\mu\text{-}h^5\text{-}C_5H_5)_2Sn[\mu\text{-}h^5\text{-}C_5H_5Sn]^+ THF\}_n$ [c]	3.79	0.90	15, 18
$[\{[(CH_3)_3Si]_2CH\}_2Sn]_2$	2.16		33

[a] Recorded vs. a $Ca^{119m}SnO_3$ (New England Nuclear Corp.) source held at ambient temperature. [b] This work. [c] A reformulation of the product of stannocene in THF with BF_3 etherate [15], formerly thought to be $(h^5\text{-}C_5H_5)_2Sn\text{-}BF_3$ [18].

compounds [24,25], resembling stannocene itself [26]. Angular distortion of the ψ-trigonal coordination sphere of the tin atom would bring about a rehybridization of each of the three orbitals emanating from the tin atom to make its bonds, but the sum of the s-electron density of the nucleus, $|\psi_s(0)|^2$ should be unaffected, and hence the isomer shifts (*IS*) will not be expected to change. Quadrupole splitting (*QS*) values are, however, a measure of the electric field gradient at the tin nucleus, and this should depend somehow on the distribution of s- and p-character in the lone pair and bonding orbitals, from the situation of two perpendicular ligands (bound by atomic $5p$-orbitals) with the lone pair in a spherically symmetrical, $5s$ atomic orbital to one in which the ligands are linearly disposed (bound by $5sp$-hybrid orbitals) with the lone pair in a pure $5p$ atomic orbital. The tin atom in stannocene itself is roughly sp^2-hybridized in the solid [11] and gas [16] phases to give a *QS* of 0.86 mm s^{-1} [18]. The more electron-releasing h^5-methylcyclopentadienyl group should thus force the lone pair into an orbital with more p-character, and the angle between the tin vectors to these rings should be more open. A slightly smaller *QS* value has been recorded for this compound [27]. The methyl-group releasing effect should maximize in $[h^5\text{-}(CH_3)_5C_5]_2Sn^{II}$ in which two independent molecules in the unit cell exhibit tin-ring vector angles of 143.5 and 144.5° [12], with the lone pair in a more purely atomic $5p$-orbital. The *QS* value available for this compound derives from a weak spectrum of an impure material, and is in any case within experimental error to that of stannocene. Thus the dependence of the *QS* on the angle of the rings at the tin(II) atom is unknown, since both the structural and Mössbauer data to establish the correlation are largely lacking.

The *QS* values for the *ortho*- (I) and *para*- (III) isomers are larger than in stannocene, particularly the former. Systems with narrow angles between the $(h^5\text{-}C_5H_5)_2Sn$ rings are predicted from model studies of the monomers.

The mass spectra show parent molecular ions at $m/e = 352$, and this fact along with the absence of polytin fragments or of ions of mass greater than the parent m/e values can be used, along with the physical properties of the products, to rule out polymeric structures in each case. The fragmentation patterns are similar for all three isomers as shown in Table 2 where the loss of one methylenecyclopentadienyl

TABLE 2

MASS SPECTRAL DATA FOR THE BIS[h^5-(PHENYLENEDIMETHYLENE)DICYCLOPENTADIENYL]TIN(II) ISOMERS AT 70 eV [a]

m/e	*ortho*- (I)	*meta*- (II)	*para*- (III)	Assignment
352	0.8	3.2	10.0	$[C_6H_4(CH_2C_5H_4)_2Sn]^+$
274	–	1.4	2.2	$[C_6H_4CH_2C_5H_4Sn]^+$
248	0.9	1.5	10.9	$[Sn(C_5H_4)_2]^+$
234	25.8	4.4	30.7	$[C_5H_4SnC_4H_2]^+$
220	5.0	4.3	12.3	$[Sn(C_4H_2)_2]^+$
193	4.3	–	–	$[SnC_3H_3CH_2]^{+\cdot}$
185	1.5	18.6	53.3	$[SnC_5H_4]^{+\cdot}$
168	100	100	36.0	$[C_6H_4(CH_2)CH_2C_5H_4]^{+\cdot}$
120	–	11.8	66.7	$Sn^{+\cdot}$
66	24.5	90.5	60.1	$[C_5H_6]^{+\cdot}$
65	7.1	7.3	100	$[C_5H_5]^+$

[a] Mass numbers are based upon ^{120}Sn, ^{12}C and ^{1}H.

group to give the half-sandwich cation, $[C_6H_4CH_2C_5H_4Sn]^+$, at $m/e = 274$ in all but the *ortho*-isomer (I) and the loss of h^5-C_5H_5Sn and stannocene to give $[CH_2C_6H_4CH_2C_5H_4]^+$ at $m/e = 168$ and $[C_6H_4(CH_2)_2]^+$ at $m/e = 104$, respectively, are seen in all three spectra along with the parent molecular ion of stannocene at $m/e = 248$. The half-sandwich stannocenium ion is seen at $m/e = 185$. This species has been isolated as its salt [5,12]. The most abundant fragment in the spectra of the *ortho*- (I) and *meta*- (II) isomers is the ion at $m/e = 168$ derived from the loss of $[h^5\text{-}C_5H_5Sn]^+$, while the $[C_5H_5]^+$ ion is the most abundant in the spectrum of the *para*-isomer (III). The most abundant tin-bearing ions for the *ortho*- (I), *meta*- (II), and *para*- (III) isomers are the $[C_5H_4SnC_4H_2]^+$, $[SnC_5H_4]^+$ and Sn^+ at $m/e = 234$, 185 and 120, respectively.

In the proton NMR the phenyl ring gives rise to a multiplet centered at δ 7.18 and 7.16 ppm for the *ortho*- (II) and *meta*- (II) isomers and to a broad singlet at δ 7.20 ppm for the *para*-isomer (III). The methylene protons give rise to a broad singlet at δ 3.72 ppm in each case. For the cyclopentadienyl protons, singlets at δ 5.92, 5.88 and 5.56 ppm, respectively, are recorded, but no tin satellites could be detected in the deuteroacetone solvent used to record the spectra. The resonances arising from the phenyl-methylene and cyclopentadienyl rings are roughly in the expected 1/1/2 area ratios.

The infrared spectral data in Table 3 can be used to rule out diene-type cyclopentadienyl rings [28].

Addition of h^5-cyclopentadienyltin(II) chloride to the disodium salt of the *meta*-derivative gave *meta*-phenylenedimethylenedi-h^5-cyclopentadienyltin(II) di-h^5-

TABLE 3

INFRARED DATA FOR THE BIS[h^5-(PHENYLENEDIMETHYLENE)DICYCLOPENTADIENYL]TIN(II) ISOMERS AND BF_3 DERIVATIVE IN cm^{-1} [a]

ortho- (I)	*meta*- (II)	*meta*-BF_3 (V)	*para*- (III)
2908m	3005w	3175w	3048m
2850sh	2955m	2670w	2950sh
2255m	2920s	1600w	2922s
2140w	2855m	1260m	2000w
1880w	1950s	1152m	1908w
1750w	1800s	1088s	1735w
1483w	1605m	1072s	1612w
1445m	1430m	1038s	1512s
1430sh	1370m	968m	1430s
1253m	1260m	890m	1364m
1214m	1070m	842w	1258w
1182m	1005m	807m	1105m
1070w	905w	791m	1022m
942w	762s	670w	895m
790w	650m		800s,br
760s			675m
732m			580m,br
597s			385s
527m			340m
382s			268m
303s			

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[a] s, strong; m, medium; w, weak; sh, shoulder; br, broad.

TABLE 4

MASS SPECTRAL DATA FOR THE BIS[h^5-(1,3-PHENYLENEDIMETHYLENE)DICYCLOPENTADIENYLTIN(II) BF_3 DERIVATIVE (V) AT 70 eV [a]

m/e	Intensity	Assignment
401	6.9	$[C_6H_4(CH_2C_5H_4)_2Sn\text{-}BF_2]^+$
336	7.1	$[F_2BSn(C_5H_4)_2CH_2CH]^{+\cdot}$
235	4.3	$[C_5H_4SnC_4H_3]^+$
205	5.4	$[FSnC_5H_6]^+$
193	3.4	$[FSnC_4H_6]^+$ or $[SnC_3H_3CH_2]^+$
181	2.7	$[F_2BSnC]^+$
169	16.1	$[SnBF_2]^+$
155	30.0	$[SnCl]^+$ from unreacted starting material
141	18.5	$[C_6H_4CH_2C_4H_3]^+$
115	11.8	$[C_6H_4CH_2CHC]^+$
111	28.1	$[C_7H_8F]^+$
97	52.7	$[C_6H_6F]^+$
91	61.4	$[C_6H_4CH_3]^+$
78	16.0	$[C_5H_4CH_2]^{+\cdot}$
72	2.5	$[C_4H_5F]^{+\cdot}$
71	54.5	$[C_4H_4F]^+$
68	8.7	$[BF_3]^{+\cdot}$
66	100.0	$[C_5H_6]^{+\cdot}$
65	52.2	$[C_5H_5]^+$

[a] Mass numbers are based upon ^{120}Sn, ^{19}F, ^{12}C, ^{11}B and ^{1}H.

cyclopentadiene (IV) (see Fig. 2):

$$\textit{meta}\text{-}C_6H_4(CH_2C_5H_4Na)_2 + 2h^5\text{-}C_5H_5SnCl \rightarrow$$
$$\textit{meta}\text{-}C_6H_4(CH_2C_5H_4\text{-}h^5\text{-}SnC_5H_5\text{-}h^5)_2 + 2NaCl \qquad (5)$$

Boron trifluoride was removed from its etherate by the action of *meta*-phenylenedimethylenedi-h^5-cyclopentadienyltin(II) (II) to give an infusible material (V) (eq. 6),

$$\textit{meta}\text{-}C_6H_4(CH_2C_5H_4\text{-}h^5)_2Sn^{II} + BF_3 \cdot O(C_2H_5)_2 \rightarrow$$
$$\textit{meta}\text{-}C_6H_4(CH_2C_5H_4\text{-}h^5)_2Sn^{II}\text{-}BF_3 + O(C_2H_5)_2 \qquad (6)$$

whose mass spectrum exhibits a $[P - F]^+$ fragment as the highest m/e value (see Table 4). The fluorine-cyclopentadienyl group transfer reaction which apparently takes place when stannocene in THF and BF_3 etherate are brought together is not possible in our system in which both cyclopentadienyl groups are linked. In addition, from its mass and NMR spectra, the product contains no THF [29]. The juxtaposition of the rings may bring about a reordering of the stannocene orbitals to place the lone pair in the highest occupied molecular orbital and make it the site of attack by the BF_3, but structural data are needed before a definitive case for adduct formation can be made.

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