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Preliminary communication

DO SUBVALENT MAIN-GROUP COMPOUNDS FORM ADDUCTS WITH MAIN-GROUP ACCEPTORS? THE BF_3 ADDUCT OF STANNOCENE, A REVISION. THE CRYSTAL AND MOLECULAR STRUCTURE OF $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n$*

T.S. DORY** and J.J. ZUCKERMAN*
Department of Chemistry, University of Oklahoma, Norman, OK 73019 (U.S.A.)
and C.L. BARNES
Department of Chemistry, University of Puerto Rico, Rio Piedras, PR 00931 (U.S.A.)

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Summary

The material formulated as $(\eta^5\text{-}C_5H_5)_2Sn{\rightarrow}BF_3$ is actually $\{[BF_4]^-$-$(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n$ in which the lone-pair electrons play no role in the bonding.

The lone-pair electrons of tin(II) [1] and other subvalent, Main-Group elements are claimed to be utilized in donation to Main-Group acceptors [2—14] following our report of a dozen years ago that addition of boron trifluoride etherate to a THF solution of di-η^5-cyclopentadienyltin(II) (stannocene) precipitated the divalent tin-Group III complex $(\eta^5\text{-}C_5H_5)_2Sn{:}{\rightarrow}BF_3$, m.p. 58—60°C [16].

We have now found that the product of this reaction (not exothermic) contains the units $[BF_4]^-$, $(\eta^5\text{-}C_5H_5)_2Sn$, $[\eta^5\text{-}C_5H_5Sn]^+$ and THF by X-ray crystallographic measurements (Tables 1—4) [17].

The four units are loosely associated into a three-dimensional lattice. The structure is complex and because of the weakness of the interactions involved, the description may be subject to several arbitrary choices.

Firstly, the oxygen of the THF is coordinated to Sn(2) in the stannocenium cation, and one fluorine atom of the tetrafluoroborate is directed toward Sn(1) of the adjacent stannocene molecule. Including these X→Sn coordinate bonds

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**Olin Research Centre, Cheshire, CT 06410 (U.S.A.)

TABLE 1

CRYSTAL DATA FOR $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n$

Formula	$C_{19}H_{23}BF_4OSn_2$
Mol.wt.	591.61
Cryst. system	orthorhombic
a, Å	9.271(6)
b, Å	13.259(9)
c, Å	16.441(5)
V, Å^3	2021
Space group	$P2_12_12_1$
Z	4
$F(000)$	1144
ρ_{calcd}, g cm^{-3}	1.944
μ, cm^{-1}	23
T_{max}, T_{min}	0.69, 0.63
dimens. of data crystal, mm	0.18 × 0.20 × 0.16

(X = O, F) revises the formula unit to $\{[BF_4Sn(1)(C_5H_5\text{-}\eta^5)_2]^-[\eta^5\text{-}C_5H_5Sn(2)\text{-}THF]^+\}$ with greater charge delocalization. However, the Sn(2) η^5-cyclopentadiene in the stannocenium cation lies rather symmetrically along the Sn(2)—Sn(1) vector with the two tin center-of-the-ring vectors making an angle of 173.6(4)°.

The spatially significant positioning of the stannocenium η^5-$C_5H_5Sn(2)$ ring binds Sn(1) to Sn(2) at 5.252(1) Å by the intervening μ-η^5-cyclopentadienyl bridge. Bridging the cation and anion in this way creates a neutral, molecular unit, $\{[BF_4]^-\eta^5\text{-}C_5H_5Sn(1)[\mu\text{-}\eta^5\text{-}C_5H_5Sn(2)]^+THF\}$, in which both the $[BF_4]^-$ and $[\eta^5\text{-}C_5H_5Sn]^+$ charges have been delocalized and neutralized.

It is interesting to compare our $[Cp_3Sn_2]^+$ unit to the triple-decker $[Cp_3Ni_2]^+$ sandwiches. The former structure is $[SnCpSnCp_2]^+$, while the latter is a $[CpNiCpNiCp]^+$-containing salt [19,20].

In addition, specially positioned μ-η^5-C_5H_5 groups are found along each of the three tin—tin vectors of equal length emanating from Sn(1) and Sn(2). In this way the coordination about Sn(1) is expanded to accommodate a third η^5-cyclo-

TABLE 2

DATA COLLECTION PARAMETERS FOR $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n$

Diffractometer	Enraf—Nonius CAD-4
Radiation	Mo-K_α (λ 0.71069 Å)
Temperature, K	138±2
Scan technique	θ—2θ
2θ limit, deg.	53
max. scan time, s	60
Scan angle, deg.	1.0+0.2 tan θ
Aperture width, mm	3.25+0.86 tan θ
Aperture height, mm	6
Aperture dist., mm	173
Monitor reflectn.	3
Orientation monitors	after each 150 reflections[a]
Number of unique data	1987
Number of observed data[b]	1798
Corrections	Lorentz-polarization anomalous dispersion

[a] New orientation matrix if angular change >0.12°. [b] $I > 2\sigma(I)$.

TABLE 3

FINAL POSITIONAL PARAMETERS FOR $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n(\times 10^{-4})^a$

Atom	x	y	z
Sn(1)	2605.9(6)	1438.1(13)	896.0(3)
Sn(2)	−2258.0(6)	−444.4(3)	1510.5(3)
C(1)	712(9)	148(6)	1436(6)
C(2)	446(10)	185(7)	579(6)
C(3)	−348(9)	1078(6)	415(4)
C(4)	−571(9)	1584(6)	1147(5)
C(5)	55(9)	1026(6)	1777(5)
C(6)	4376(10)	113(6)	1322(5)
C(7)	4705(10)	274(7)	499(5)
C(8)	5399(11)	1193(8)	416(6)
C(9)	5551(10)	1629(7)	1205(6)
C(10)	4919(10)	959(7)	1753(5)
C(11)	3365(10)	3933(7)	2113(5)
C(12)	3613(11)	3159(7)	2671(5)
C(13)	2271(11)	2757(6)	2895(5)
C(14)	1205(9)	3287(6)	2492(5)
C(15)	1892(10)	4040(6)	2003(5)
B(1)	2455(11)	485(6)	−1483(5)
F(1)	2469(6)	1174(3)	−832(2)
F(2)	2336(6)	1035(4)	−2197(3)
F(3)	3765(6)	−48(5)	−1484(4)
F(4)	1347(6)	−180(5)	−1397(4)
O(1)	−2124(7)	−1666(5)	94(3)
C(16)	−1882(12)	−1194(8)	−677(6)
C(17)	−2696(16)	−1828(10)	−1271(7)
C(18)	−3794(17)	−2316(12)	−838(9)
C(19)	−3221(13)	−2425(9)	29(7)

[a] Estimated standard deviations are in parentheses.

TABLE 4

THERMAL PARAMETERS FOR $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n(\times 10^3)^a$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	15.1(4)	15.4(2)	31.3(2)	4.8(2)	0.0(2)	0.5(2)
Sn(2)	25.2(4)	16.1(2)	21.8(2)	4.4(2)	−1.1(2)	−0.7(2)
C(1)	12(5)	21(4)	38(5)	1(3)	2(4)	10(4)
C(2)	22(6)	17(4)	34(5)	1(3)	1(4)	−1(4)
C(3)	18(6)	27(5)	17(4)	−6(3)	−7(3)	5(4)
C(4)	18(6)	13(4)	42(5)	2(3)	0(4)	−0.6(4)
C(5)	19(6)	26(4)	19(4)	−7(4)	2(3)	−1(4)
C(6)	21(6)	25(5)	39(6)	5(4)	6(4)	15(4)
C(7)	27(6)	36(6)	34(5)	14(4)	−8(4)	−14(5)
C(8)	21(6)	45(7)	45(6)	10(4)	10(4)	19(5)
C(9)	14(6)	26(6)	67(7)	5(4)	−8(5)	−11(5)
C(10)	17(6)	34(5)	38(6)	18(4)	−3(4)	−10(4)
C(11)	30(7)	29(5)	35(5)	−4(4)	6(4)	−16(4)
C(12)	20(6)	26(5)	46(6)	5(4)	−10(4)	−15(4)
C(13)	43(7)	19(3)	33(4)	16(4)	−2(5)	−6(3)
C(14)	25(6)	27(5)	28(4)	−4(4)	5(4)	−14(4)
C(15)	39(7)	30(4)	17(4)	−4(4)	−0.4(3)	−3(3)
B(1)	19(6)	35(4)	28(4)	−9(5)	−6(4)	−2(4)
F(1)	40(3)	37(2)	24(2)	−0.1(3)	−4(3)	4(2)
F(2)	50(4)	55(3)	27(2)	6(3)	−2(3)	−3(2)
F(3)	33(4)	64(5)	48(3)	22(3)	−5(3)	5(3)
F(4)	45(4)	51(4)	46(3)	−13(3)	4(3)	8(3)
O(1)[b]	37(2)					
C(16)[b]	49(3)					
C(17)[b]	76(4)					
C(18)[b]	84(4)					
C(19)[b]	58(3)					

[a] Estimated standard deviations in parentheses. [b] O(1), C(16)—C(19) refined isotropically.

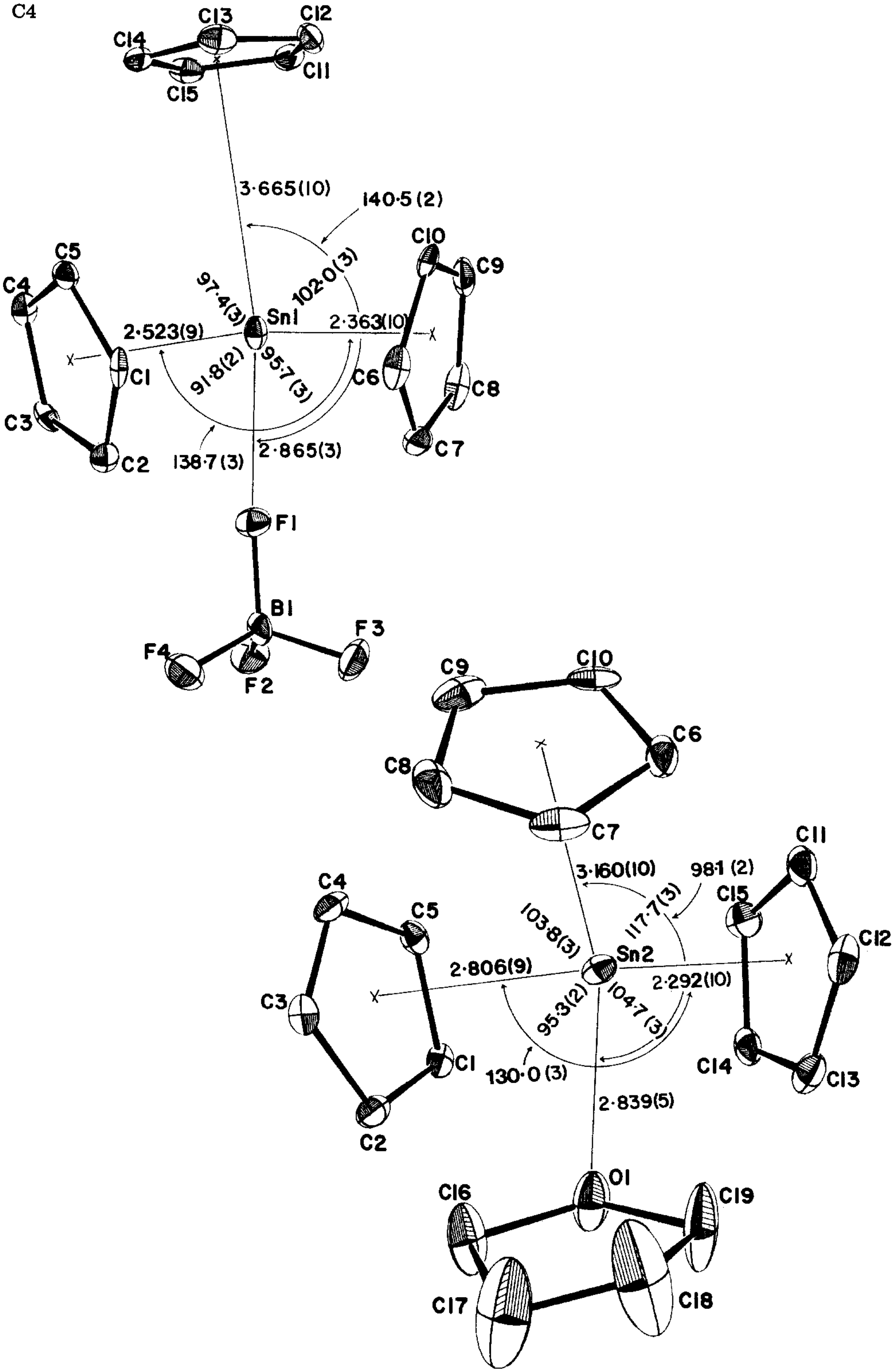
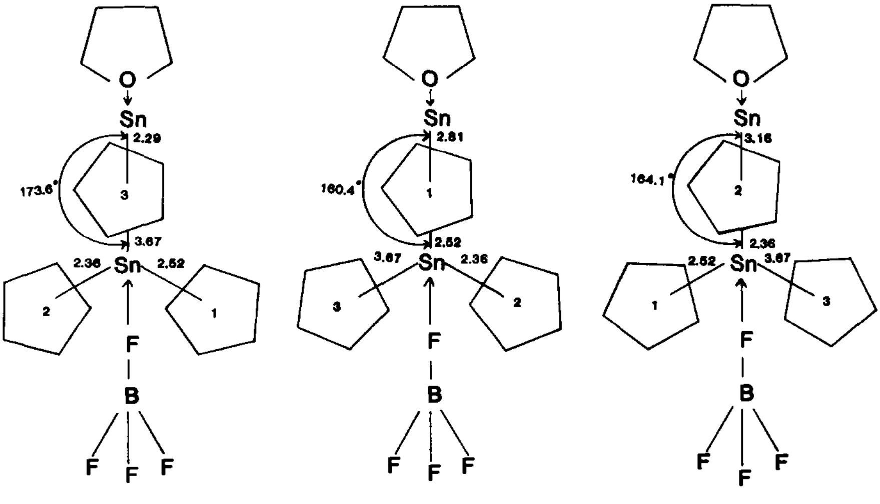


Fig. 1. The coordination sphere about (a) Sn(1) in the stannocene unit, and (b) about Sn(2) in the stannocenium unit.

pentadienyl group, and Sn(2) accommodates two additional η^5-cyclopentadienyl groups bridging from two neighboring stannocene moieties (see Figs. 1a and 1b).

The molecular unit, which can be regarded as F_3BF—Sn(1)Cp_2—Cp ring n—Sn(2)—THF where $n = 1$, 2 or 3 (see Fig. 2), is thus knit into a loose, three-dimensional array containing stannocene and stannocenium chains (from which $[BF_4]^-$ and THF are pendant) associated by μ-η^5-cyclopentadienyl bridges of unequal length along the tin—tin vectors. This weak polymer thus dissipates the $[BF_4]^-$ and $[\eta^5\text{-}C_5H_5Sn]^+$ charges. The result is a low melting material of ready solubility in polar organic solvents. Of the three depictions in Fig. 2, the first ($n = 3$) gives the most nearly linear Sn(1)—Cp ring n—Sn(2) system (173.6° vs. 160.4° and 164.1° for $n = 1$ and 2, respectively), and the shortest Sn—Cp bonds in the stannocene (Sn—Cp 2.365(10) and 2.523(9) Å), and stannocenium (Sn—Cp 2.294(10) Å) units.

Thus both Sn(1) and Sn(2) are found in $(\mu\text{-}\eta^5\text{-}C_5H_5)_3SnX$ (X = F, O) units. The stannocene Sn(1) resides at a site with two close η^5-cyclopentadienyl rings, a bridging fluorine from an adjacent BF_4 and a weaker link to a third bridging ring from an adjacent $\eta^5\text{-}C_5H_5Sn(2)$ (see Fig. 1a), while the stannocenium Sn(2) has one close η^5-cyclopentadienyl ring, a coordinated oxygen from a neighboring THF molecule and two weaker links to bridging rings from adjacent stannocene units (see Fig. 1b). In each case the $(\eta^5\text{-}C_5H_5)_3SnX$ coordination sphere is completed by a lone pair of electrons which apparently occupies a void in the lattice, presumably at the largest angles, to give ψ^5-coordination about each tin(II) atom. Tin-119m Mössbauer isomer shifts are seemingly insensitive to the differences between the two tin sites [21], and only a simple doublet is observed [16].



$$\left\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+OC_4H_8\right\}_n$$

$$\left\{[BF_4]^-[(\mu\text{-}\eta^5\text{-}C_5H_5)_3Sn_2]^+OC_4H_8\right\}_n$$

Fig. 2. Three $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n$ asymmetric units.

The preparation of the title compound is accompanied by the disappearance of the tin satellites from the proton NMR spectrum of stannocene [16]. Indeed, no NMR tin or lead satellites are reported for any of the claimed donor—acceptor products [3,6—8,11]. We interpret these negative results in terms of dynamic phenomena involving the acceptor halide-induced exchange of cyclopentadienyl groups between donor and acceptor atom sites, or between the subvalent Group-IV atoms themselves. The structure of the title compound can then represent in one view a frozen intermediate in the intermolecular exchange of cyclopentadienyl groups between two tin sites, rationalizing and depicting the rapid making and breaking of η^5-$C_5H_5Sn(II)$ bonds. The reaction reported in ref. 16 is thus:

$$2n(\eta^5\text{-}C_5H_5)_2Sn + 2nBF_3 + n\mathrm{THF} \rightarrow$$

$$n\eta^1\text{-}C_5H_5BF_2 + \{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+\mathrm{THF}\}_n \tag{1}$$

which is a fluorine-cyclopentadienyl group transfer reaction [22].

Why is the lone pair of electrons not the site of attack of the BF_3, and why is the product of eq. 1 not simply the $(\eta^5\text{-}C_5H_5)_2Sn{:}\rightarrow BF_3$ adduct as originally formulated in ref. 16? Recent self-consistent field χ_α scattered wave (SCF χ_α SW) calculations give the order of the two HOMO's as π-type and localized on the cyclopentadiene rings. These are followed in order of decreasing energy by two MO's which account for the primary interaction with the tin 5*s*- and 5*p*-atomic orbitals. The fifth orbital holding the lone pair is 2.0 eV lower than the HOMO [24,25]. These results are corroborated by He(I) spectra (UV PES) [27] in which an ionization energy at 9.7 eV is attributed to electron ejection from the stannocene lone-pair orbital. Ionization from the HOMO is observed at 7.57 eV [24]. In addition, cyclic voltammetry does not oxidize stannocene to $[(\eta^5\text{-}C_5H_5)_2Sn]^{2+}$, an irreversible oxidation wave being observed instead [28].

The story of the corresponding inorganic system is apparently analogous. The claimed BF_3 adduct [2] of SnF_2 is a polymeric solid of $[Sn_2F_3]^+$ units containing ψ-5-coordinated tin(II) atoms with the F_3B—F- - -Sn approach at 2.99 Å [29]. Again, the lone-pair electrons play no role in bonding. Likewise, the originally claimed adducts of $[MCl_3]^-$ (M = Ge, Sn) with BX_3 (X = F, Cl) [30] are instead the halide-exchange products [31], MCl_2 and $[BX_3Cl]^-$.

The reaction of decamethylstannocene in THF with the boron trifluoride etherate gives [32] the *nido*-stannocenium cation salt of tetrafluoroborate (identified from its cell constants) [33] (eq. 2), the permethylated analogue of the title compound minus the moles of stannocene and THF in the crystal.

$$[\eta^5\text{-}(CH_3)_5C_5]_2Sn + BF_3 \rightarrow [\eta^5\text{-}(CH_3)_5C_5Sn]^+[BF_4]^- \tag{2}$$

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17 The title compound, $C_{19}H_{23}BF_4OSn_2$, crystallizes in the orthorhombic space group $P2_12_12_1$ with a 9.271(6), b 13.259(9), c 16.441(5) Å, V 2021 Å^3, Z = 4 and ρ_{calcd} 1.944 g cm^{-3}. The crystals are air- and temperature-sensitive, precluding density measurement. The data were corrected for Lorentz and polarization effects, but no absorption correction was made. The structure was determined at 138±2 K by Patterson and Fourier techniques from 1987 reflections measured on an Enraf—Nonius CAD/4 automatic diffractometer with monochromatic Mo-K_α radiation. All non-hydrogen atoms except those of the THF molecule were refined with anisotropic temperature factors. A minor disorder of the THF molecule, less than 20%, could not be reasonably modelled as a separate site of occupation and interfered with anisotropic refinement of the THF atoms. In the final model the THF atoms were refined with isotropic temperature factors and the sites of minor occupancy were excluded, appearing in the final difference map as the highest remaining peaks ($<$1.1 e$^-$/Å^3). Hydrogen atoms were placed at calculated positions and not refined. The final refinement statistics for all data are: R = 0.0391; R_W = 0.0392; S = 1.66. The absolute configuration reported is that indicated by the Hamilton R test [18]: $R_{1,1768,0.005}$ = 1.002; R_2/R_1 = 1.015; R_{W2}/R_{W1} = 1.020.

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