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From σ- to π-Bonding: Crystal Structures of (Pentamethylcyclopentadienyl)triiodostannane and Dichloro(pentamethylcyclopentadienyl)stibane

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Cyclopentadienyl compounds of the tetravalent group 14 elements and of the trivalent group 15 elements are characterized by their dynamic behavior due to migration processes of the relevant ElR_x fragment. As shown by experiments and calculations, the energy difference between the σ-ground state and the π-transition state in these molecules becomes smaller on going to the heavier elements and on exchanging halogen atoms for organic ligands. Thus, Cp compounds of tetravalent tin or lead and of trivalent antimony or bismuth bearing halogen ligands should be suitable candidates for the realization of a π-ground state. In this context, we have investigated the solid-state structure of the title compounds $Me_5C_5SnI_3$ (**1**) and $Me_5C_5SbCl_2$ (**2**) by X-ray crystallography. It is shown that in the tin compound **1** the main-group fragment is still σ-bonded, whereas π-bonding is observed for the antimony compound **2**. The bonding parameters for **1** and **2** are discussed with those of other tin, lead, antimony, or bismuth Cp compounds from the literature. Crystal data with Mo Kα (λ = 0.71073 Å) radiation are as follows: **1**, a = 8.044 (2) Å, b = 15.094 (2) Å, c = 13.907 (2) Å, β = 102.43 (2)°, Z = 4, monoclinic, space group $P2_1/n$, R_w = 0.050; **2**, a = 10.479 (2) Å, b = 8.384 (2) Å, c = 14.101 (3) Å, β = 94.50 (2)°, Z = 4, monoclinic, space group $P2_1/a$, R_w = 0.068.

Introduction

Cyclopentadienyl compounds of the p-block elements have been intensively studied during the last decades. They appear to be interesting molecules from a synthetic as well as from a structural point of view. Regarding the structure, species with σ-bonded and also with π-bonded cyclopentadienyl ligands have been observed.

One of the most interesting features of σ- (or η^1-) bonded cyclopentadienyl compounds is their fluxionality. There is no other class of compounds which has been studied in such detail for its dynamic behavior. The underlying processes are now very well understood.[1]

In the class of the π-complexes, different hapticities ($\eta^{2,3,5}$) of the cyclopentadienyl ligand are observed in the solid state and in the gas phase. Qualitative MO arguments and simple isolobal relationships allow a straightforward classification and prediction of structure types.[2,3] The η^2- and η^3-complexes are highly fluxional due to fast haptotropic shifts. Presumably as a consequence of rather weak π-interactions in the η^2- or η^3-coordination mode, the planar structure of the cyclopentadienyl system is generally maintained.[4]

For the cyclopentadienyl compounds of the tetravalent group 14 elements as well as for the compounds of the trivalent group 15 elements, the corresponding σ-structure represents the ground state (see I in Figure 1). The dynamic behavior has been studied in detail for the silicon and phosphorus compounds and to a lesser extent for the others. π-Bonded structures only represent the transition states in the migration processes.

Generally, the energy difference between the σ-ground state and the π-transition state becomes smaller on going to the heavier elements in the relevant groups of the periodic system and on exchanging halogen atoms for organic ligands. This statement is the result of experimental studies[1] as well as of theoretical calculations by Hoffmann[5] and by Schoeller.[6]

In this context an interesting question arises: Is it possible to stabilize a π-structure (see II in Figure 1) to such an extent that it will become the ground state in a molecule of the type $CpEl(14)R_3$ or $CpEl(15)R_2$? On the basis of the experiments and calculations mentioned above, compounds of tetravalent tin or lead and of trivalent antimony or bismuth bearing halogen ligands at the relevant p-block element should be suitable candidates. The following compounds which fulfill the described criteria were synthesized in our laboratories some years ago: $Me_5C_5SnCl_3$,[7] $(Me_5C_5)_2SnCl_2$,[7] $Me_5C_5SnBr_3$,[7] $Me_5C_5SnI_3$,[7] $H_5C_5SbCl_2$,[8] $^tBu_2C_5H_3SbCl_2$,[9] and $Me_5C_5SbCl_2$.[10] We obtained suitable crystals for X-ray crystal structure investigations for the compounds (pentamethylcyclopentadienyl)triiodostannane (**1**) and dichloro(pentamethylcyclopentadienyl)stibane (**2**). The results of these studies are reported here.

The type of π-structure proposed in Figure 1 is not entirely new in the chemistry of p-block elements. For example, an η^2- or η^3-bonding to isolobal p-block element fragments has already been observed in the dimeric chloro(cyclopentadienyl)methylaluminum ($[H_5C_5Al(CH_3)Cl]_2$),[11] in the polymeric chloro(cyclopentadienyl)lead ($[H_5C_5PbCl]_n$),[12] and in the bipyridyl adduct of the (pentamethylcyclopentadienyl)tin cation, $[Me_5C_5Sn{\cdot}bpy]^+$.[13]

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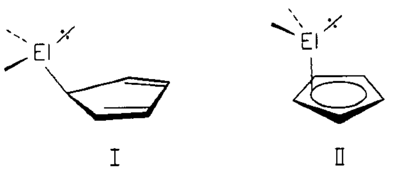

Figure 1. σ- and π-structure types for CpEl(14)R_3 and CpEl(15)R_2.

Table I. Crystal Data and Summary of Data Collection and Refinement for $Me_5C_5SnI_3$ (1) and $Me_5C_5SbCl_2$ (2)

	1	2
formula	$C_{10}H_{15}I_3Sn$	$C_{10}H_{15}Cl_2Sb$
fw	634.63	327.89
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/a$
a (Å)	8.044 (2)	10.479 (2)
b (Å)	15.094 (2)	8.384 (2)
c (Å)	13.907 (2)	14.101 (3)
β (deg)	102.43 (2)	94.50 (2)
cell vol (Å^3)	1649.0	1235.1
Z	4	4
ρ_{calcd} (g cm^{-3})	2.56	1.76
μ Mo Kα (cm^{-1})	70.89	26.43
range of abs corr fctrs	6.72–24.26	1.34–3.10
λ Mo Kα (Å)	0.71073	0.71073
cryst size (mm)	0.35 × 0.30 × 0.50	0.13 × 0.30 × 0.43
scan type	$\theta/2\theta$	ω
scan angle (deg)	0.8 + 0.35 tan θ	1.3, 1.0 bkgd offset
2θ limits (deg)	$2.0 < 2\theta < 50.0$	$0 < 2\theta < 50.0$
octants collected	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of reflctns measd	3260	2486
total no. of unique measd data	2903	2169
no. of data obsd	2151	1901
data omission	$I > 3\sigma(I)$	$I > 3\sigma(I)$
no. of variables	127	133
R	0.048	0.058
R_w	0.050	0.068
temp (K)	293	130

During the course of our investigations, the X-ray crystal structures of the compounds $H_5C_5SbCl_2$ and $H_5C_5BiCl_2$ were published by Frank.[14,15] They present the first experimental proof of the predictions and will be discussed later for comparison in more detail. A report by Lorberth and Shin on the structure of $(Me_5C_5)_2BiCl$ and of $Me_5C_5Bi(C_5H_5)_2$ is in preparation.[16]

Experimental Section

The synthesis of compounds 1 and 2 has been described elsewhere.[7,10] Crystals of 1 and 2 have been obtained from hexane solution.

X-ray Analysis of (Pentamethylcyclopentadienyl)triiodostannane (1). A suitable dark red single crystal of 1 was sealed in a Lindemann capillary and mounted on an Enraf-Nonius CAD4-F diffractometer. Initial lattice parameters were determined from a least squares fit to 25 accurately centered reflections (15 ≤ 2θ ≤ 20°) and subsequently refined using higher angle data. Data were collected for one independent quadrant using the θ/2θ scan mode. An empirical absorption correction was applied. Further information is collected in Table I. The positions of the Sn and I atoms were revealed from a Patterson map and all other non-hydrogen atoms from a subsequent difference Fourier map. H atoms were fixed at calculated positions. All calculations were performed using the SDP-plus program package.

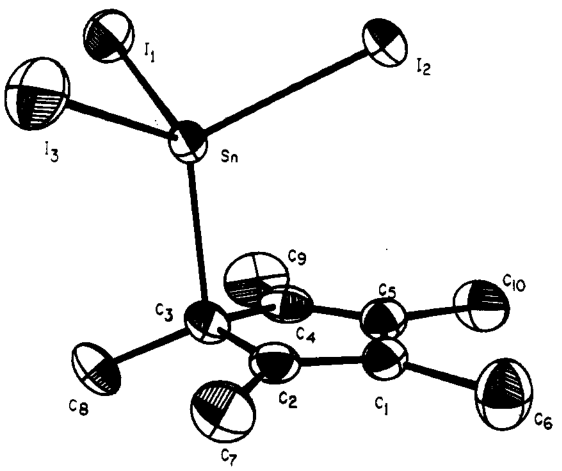

Figure 2. Molecular structure of $Me_5C_5SnI_3$ (1).

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) of 1

atom	*x*	*y*	*z*	U^*_{eq}[a]
Sn	0.7561 (1)	0.16677 (6)	0.24944 (7)	43 (3)
I(1)	0.6489 (2)	0.08497 (9)	0.39873 (8)	82 (4)
I(2)	0.6811 (1)	0.05372 (7)	0.09879 (7)	66 (3)
I(3)	0.5319 (2)	0.30312 (9)	0.2062 (1)	103 (5)
C(1)	1.094 (1)	0.1668 (9)	0.1390 (9)	47 (4)
C(2)	1.031 (2)	0.2363 (9)	0.1812 (9)	49 (4)
C(3)	1.025 (2)	0.2085 (9)	0.283 (1)	52 (4)
C(4)	1.101 (2)	0.1179 (9)	0.293 (1)	53 (4)
C(5)	1.133 (2)	0.0945 (9)	0.207 (1)	53 (4)
C(6)	1.124 (2)	0.161 (1)	0.034 (1)	80 (5)
C(7)	0.984 (2)	0.326 (1)	0.141 (1)	75 (5)
C(8)	1.056 (2)	0.274 (1)	0.371 (1)	72 (5)
C(9)	1.137 (2)	0.066 (1)	0.389 (1)	86 (5)
C(10)	1.206 (2)	0.005 (1)	0.184 (1)	76 (5)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Lengths (Å) for $Me_5C_5SnI_3$ (1)

Sn–I(1)	2.690 (1)	C(1)–C(2)	1.355 (7)	C(3)–C(4)	1.491 (8)
Sn–I(2)	2.666 (1)	C(1)–C(5)	1.436 (8)	C(3)–C(8)	1.555 (8)
Sn–I(3)	2.690 (1)	C(1)–C(6)	1.527 (8)	C(4)–C(5)	1.328 (8)
Sn–C(2)	2.821 (4)	C(2)–C(3)	1.486 (8)	C(4)–C(9)	1.522 (8)
Sn–C(3)	2.247 (5)	C(2)–C(7)	1.488 (8)	C(5)–C(10)	1.536 (8)
Sn–C(4)	2.836 (5)				

X-ray Analysis of Dichloro(pentamethylcyclopentadienyl)stibane (2). Data were collected on a Syntex $P2_1$ diffractometer equipped with a locally modified LT-1 device, Mo Kα radiation and graphite monochromator, and using an ω-scan method. Calculations were carried out on a Data General Eclipse computer using SHELXTL, version 5, programs. Neutral atom scattering factors and corrections for anomalous dispersions were from ref 17.

Upon removal from the Schlenk tube, the yellow gold plates were covered with a hydrocarbon oil to prevent decomposition. A single crystal was selected under oil, mounted on a glass fiber using silicon grease, and immediately placed in a low-temperature N_2 stream. The cell was determined from 20 accurately centered reflections (23° ≤ 2θ ≤ 26°). Further information on the data collection is provided in Table I. The structure was solved by direct methods. Hydrogen atoms were included at calculated position using a riding model with C–H of 0.96 Å and $U_{iso}(H) = 1.2U^*_{iso}(C)$, where U^*_{iso} is the equivalent isotropic thermal parameter.

An absorption correction was made using the program XABS.[18] All non-hydrogen atoms were refined with anisotropic thermal parameters.

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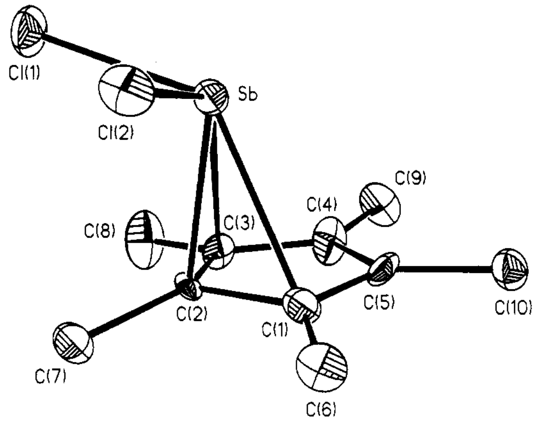

Figure 3. Molecular structure of $Me_5C_5SbCl_2$ (2).

Table IV. Bond Angles (deg) for $Me_5C_5SnI_3$ (1)

I(1)–Sn–I(2)	105.40 (2)	C(1)–C(2)–C(3)	106.6 (5)
I(1)–Sn–I(3)	103.36 (2)	C(1)–C(2)–C(7)	129.1 (6)
I(1)–Sn–C(3)	114.7 (2)	C(3)–C(2)–C(7)	124.2 (5)
I(2)–Sn–I(3)	107.32 (2)	C(2)–C(3)–C(4)	104.9 (5)
I(2)–Sn–C(3)	111.9 (3)	C(2)–C(3)–C(8)	122.7 (5)
I(3)–Sn–C(3)	113.4 (2)	C(4)–C(3)–C(8)	120.9 (5)
Sn–C(3)–C(2)	96.4 (3)	C(3)–C(4)–C(5)	108.1 (5)
Sn–C(3)–C(4)	97.1 (3)	C(3)–C(4)–C(9)	124.0 (6)
Sn–C(3)–C(8)	109.0 (4)	C(5)–C(4)–C(9)	127.8 (6)
C(2)–C(1)–C(5)	110.5 (5)	C(1)–C(5)–C(4)	109.8 (5)
C(2)–C(1)–C(6)	127.4 (6)	C(1)–C(5)–C(10)	124.6 (6)
C(5)–C(1)–C(6)	122.1 (5)	C(4)–C(5)–C(10)	125.6 (6)

Table V. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) of 2

	x	y	z	$U^*_{eq}{}^a$
Sb	2393 (1)	1223 (1)	7627 (1)	18 (1)
Cl(1)	2001 (3)	−1060 (3)	6582 (2)	30 (1)
Cl(2)	2353 (3)	−519 (3)	8995 (2)	26 (1)
C(1)	4471 (10)	2616 (12)	8323 (8)	20 (3)
C(2)	4538 (9)	1362 (11)	7602 (7)	12 (3)
C(3)	4290 (10)	2214 (12)	6674 (7)	18 (3)
C(4)	3990 (12)	3817 (13)	6877 (9)	27 (4)
C(5)	4075 (11)	4041 (12)	7867 (8)	19 (3)
C(6)	4826 (11)	2347 (14)	9365 (8)	25 (3)
C(7)	5257 (11)	−177 (13)	7700 (9)	27 (4)
C(8)	4421 (15)	1480 (15)	5729 (9)	38 (4)
C(9)	3574 (12)	5056 (15)	6155 (8)	28 (4)
C(10)	3834 (11)	5563 (13)	8381 (8)	23 (3)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Bond Lengths (Å) for $Me_5C_5SbCl_2$ (2)

Sb–Cl(1)	2.430 (3)	C(5)–C(10)	1.498 (15)	C(2)–C(7)	1.495 (14)
Sb–C(1)	2.595 (10)	Sba–C(1)	3.429	C(3)–C(8)	1.484 (16)
Sb–C(3)	2.620 (11)	Sba–C(2)	3.610	C(4)–C(9)	1.495 (16)
C(1)–C(5)	1.404 (15)	Sb–Cl(2)	2.422 (3)	Sba–C(3)	3.662
C(2)–C(3)	1.496 (14)	Sb–C(2)	2.254 (9)	Sba–C(4)	3.639
C(3)–C(4)	1.414 (15)	C(1)–C(2)	1.468 (14)	Sba–C(5)	3.527
C(4)–C(5)	1.405 (17)	C(1)–C(6)	1.504 (15)		

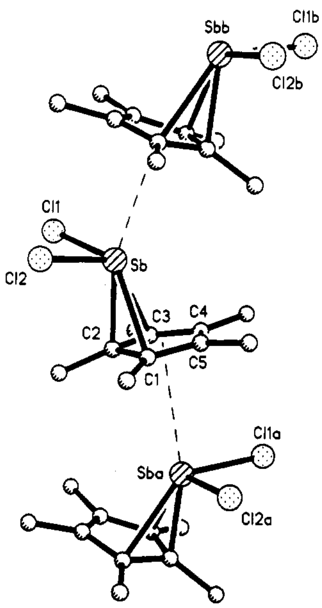

Figure 4. Solid-state structure of 2 along the C axis.

Table VII. Bond Angles (deg) for $Me_5C_5SbCl_2$ (2)

Cl(1)–Sb–Cl(2)	89.7 (1)	Cl(1)–Sb–C(1)	132.9 (3)
Cl(1)–Sb–C(2)	98.8 (3)	Cl(1)–Sb–C(3)	92.2 (2)
Cl(2)–Sb–C(1)	92.1 (3)	Cl(2)–Sb–C(2)	97.1 (3)
Cl(2)–Sb–C(3)	131.3 (2)	C(1)–Sb–C(2)	34.3 (3)
C(1)–Sb–C(3)	53.4 (3)	C(2)–Sb–C(3)	34.7 (3)
Sb–C(1)–C(2)	60.0 (5)	Sb–C(1)–C(5)	90.0 (6)
Sb–C(1)–C(6)	116.0 (7)	C(2)–C(1)–C(5)	108.7 (9)
C(2)–C(1)–C(6)	123.2 (9)	C(5)–C(1)–C(6)	128.1 (10)
Sb–C(2)–C(1)	85.6 (6)	Sb–C(2)–C(3)	86.2 (6)
Sb–C(2)–C(7)	116.8 (7)	C(1)–C(2)–C(3)	104.5 (8)
C(1)–C(2)–C(7)	127.2 (9)	C(3)–C(2)–C(7)	123.0 (9)
Sb–C(3)–C(2)	59.1 (5)	Sb–C(3)–C(4)	90.4 (7)
Sb–C(3)–C(8)	117.1 (8)	C(2)–C(3)–C(4)	107.6 (9)
C(2)–C(3)–C(8)	124.4 (9)	C(4)–C(3)–C(8)	127.9 (10)
C(3)–C(4)–C(5)	109.3 (10)	C(3)–C(4)–C(9)	125.4 (10)
C(5)–C(4)–C(9)	125.2 (10)	C(1)–C(5)–C(4)	109.5 (9)
C(1)–C(5)–C(10)	124.0 (10)	C(4)–C(5)–C(10)	126.5 (10)

Results and Discussion

The molecular units in the solid-state structures of the molecules 1 and 2 are illustrated in Figures 2 and 3. Figure 4 shows the structure of 2 along the C axis. Pertinent crystallographic data are assembled in Table I, and listings of atomic positional parameters, bond lengths, and bond angles appear in Tables II–VII.

The solid-state structure of 1 consists of isolated molecules with no short intermolecular contacts; the iodine atoms of the SnI_3 group are not ordered in sheets. The most significant feature in the structure of 1 is that the SnI_3 group is bonded in a monohapto fashion. The Sn–I distances are in the expected range; ISnI angles are all smaller and the ISnC(3) angles all greater than expected for ideal tetrahedral arrangement at the tin atom. The Sn–C(3) distance (2.25 Å) is substantially longer than normally found (2.17 Å),[19] thus indicating a weakening of this bond. The C–C distances within the planar cyclopentadienyl fragment are in the expected range for a cyclopentadiene system, as observed in many other structures of fluxional σ-cyclopentadienyl compounds.[1] Importantly, the angle between the Sn–C(3) bond and the vector from C(3) to the center of the cyclopentadienyl ring is rather small (99.8°); the SnC(3)C(8) angle is in the normal range for a tetrahedral environment at C(3) (109°). From these data, a deviation of 28.8° for the ring carbon C(3)–methyl carbon C(8) bond vector from the cyclopentadienyl plane can be calculated.

In the solid-state structure of 2 the molecular unit shall be regarded first. The most interesting feature is that the $SbCl_2$ group is π-bonded to the cyclopentadienyl ring. From the Sb–C(2) distance and the weaker, but comparable Sb–C(1) and Sb–C(3) interactions, an η^3-coordination can be anticipated. The distance from the Sb atom to the center of the C(1), C(2), C(3) plane is 2.26 Å. The angle of this vector with the Sb–Cl(1) and the Sb–Cl(2) bond is 109° and 108°, respectively. The angle between the Sb–C(2) bond and the vector from C(2) to the center of the

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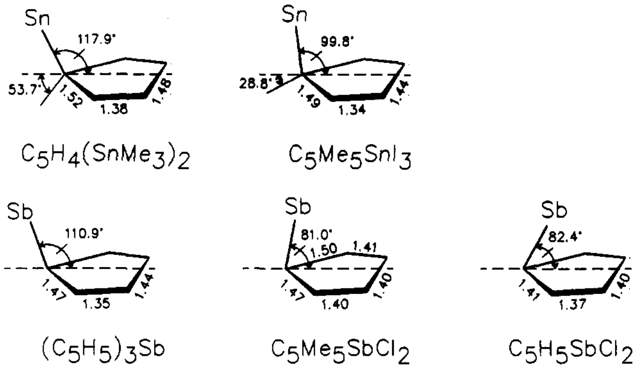

Figure 5. Comparison of 1 and 2 with other Cp compounds.

cyclopentadienyl ring is only 81°. The bond lengths and bond angles in the $SbCl_2$ unit are in the expected range, whereas the Sb–C(2) bond is rather long (2.26 Å) compared to a normal Sb–C σ-bond (e.g., in tris(*p*-tolyl)antimony, 2.14 Å[14]). The antimony–Cp ring center distance is 3.36 Å. Interestingly, the planar cyclopentadienyl ring does not adopt a symmetrical π-structure; C–C bond distances do not alternate as strongly as in σ-cyclopentadienyl compounds (for comparison see 1), but some degree of alternation is still obvious: The C(2)–C(1) and the C(2)–C(3) bonds are longer than the bonds between the atoms C(3), C(4), C(5), and C(6). Consequently, the ring carbon C-(2)–methyl carbon C(7) bond vector still deviates from the cyclopentadienyl plane by 16°.

Intermolecular bonding interactions are responsible for the fact that **2** crystallizes in the form of an asymmetric polydecker sandwich, as portrayed in Figure 4. The additional π-bonding between the cyclopentadienyl unit and the neighboring antimony atom is weaker than the intramolecular one and is of the η^2-type. The intermolecular (cyclopentadienyl ring) carbon–antimony distances are in the range of 3.43 and 3.66 Å. A nearly identical polymer chain structure has been observed by Frank[14] for the parent compound $H_5C_5SbCl_2$. The weak intermolecular π-bond has been compared with the arene–antimony interaction in the Menshutkin complex $C_6H_6(SbCl_3)$.[20] The similarity in the Sb–C distances and in the coordination pattern of the atoms is remarkable. The bond order of the intramolecular π-interaction in $C_5H_5SbCl_2$ has been estimated as 1.2, that of the intermolecular π-interaction as 0.1. Similar values should apply to the description of the π-bonding in **2**. It is obvious that the weak π-interaction nevertheless determines the solid-state structure of these compounds.

Comparison with Other Cyclopentadienyl Compounds. In Figure 5 we compare schematic representations of the crystal structures of **1** and **2** with those of the cyclopentadienyltin and -antimony compounds $C_5H_4(SnMe_3)_2$,[21] $(C_5H_5)_3Sb$,[22] and $C_5H_5SbCl_2$.[14]

In all of these highly fluxional compounds, we find planar C_5 perimeters within the limits of experimental error. The most interesting feature in the comparison of the five structures is the fact that the angle between the element–carbon(Cp) vector and the carbon(Cp)–center(Cp) vector varies and becomes smaller in the tin series in going from $C_5H_4(SnMe_3)_2$ to $C_5Me_5SnI_3$ and in the antimony series from $(C_5H_5)_3Sb$ to $C_5Me_5SbCl_2$ and $C_5H_5SbCl_2$. Whereas in the case of the tin compounds we are on the way from σ- to π-bonding, this transition is already realized in the case of the antimony compounds, where the $SbCl_2$ unit is positioned above the plane of the cyclopentadienyl system, as postulated for a π-interaction. This tendency is also supported by the fact that the deviation of the substituent at the "allylic" carbon from the cyclopentadienyl plane becomes smaller in the same direction, thus indicating a change in hybridization from sp^3 and sp^2. The transition from a cyclopentadiene system with a σ-bonded p-block element in the allylic position to a situation with a π-bonded cyclopentadienyl unit should be also manifested by a change in carbon–carbon bond lengths within the C_5 ring. Thus, bond alternation as typical of cyclopentadiene systems should be lost on the way from σ- to π-bonding. From the inspection of the bond lengths in the compounds of Figure 5, the expected trend can be deduced, but in the π-bonded antimony compounds some differences in the C–C bond lengths are still present. This might be due to the asymmetric π-bonding of the $SbCl_2$ unit. On the other hand, there are examples in the literature where even with η^2-bonded fragments the averaging of bond lengths is more pronounced, e.g., in $[C_5Me_5Sn\cdot bpy]^+$.[13]

According to the qualitative rules mentioned above for the transition of σ- to π-bonding in cyclopentadienyl compounds of group 14 and group 15 elements, a change to the heavier homologues should be even more promising. In the literature, the only X-ray structural data available are those for the compounds $C_5H_5Pb(C_6H_5)_3$[23] and $C_5H_5BiCl_2$.[15] In the lead compound, the p-block element is still σ-bonded (the angle between the Pb–C(Cp) bond vector and the Cp plane is 104°). The bismuth compound is built up by polymeric Bi–Cl chains with the cyclopentadienyl ligands π-bonded to the bismuth. Pseudorotational disorder attributable to packing requirements results in a mixture of η^2- and η^3-bonded states.[15] In the so far unpublished solid-state structure of the compound $(Me_5C_5)_2BiCl$, an η^5-bonding of the cyclopentadienyl ligands is observed.[16] From all these results it can be concluded that electron-withdrawing ligands are necessary even for the heaviest elements to effect a change from σ- to π-bonding. For the heavier elements, a mainly ionic bonding between a cyclopentadienyl ligand and the central atom cannot be excluded. In compounds with mainly covalent Cp El bonding, small energy differences between σ- and π-states or between different π-states are responsible for their pronounced fluxionality.

Registry No. $Me_5C_5SnI_3$, 69446-47-5; $Me_5C_5SbCl_2$, 126017-41-2.

Supplementary Material Available: Tables of thermal parameters (Tables S8–S11) (3 pages). Ordering information is given on any current masthead page.

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