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Structures of the Pentaphenylcyclopentadienyl Radical, (Pentaphenylcyclopentadienyl)tin(IV) Trichloride, and Bromo(chloro)bis(tetrahydrofuran)tin(II): Products of the Reaction of C_5Ph_5X with SnX_2 ($X = Cl, Br$)[†]

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*Summary: The reaction of $SnCl_2$ with C_5Ph_5Cl produces $C_5Ph_5SnCl_3$ (**1**) in an oxidative-addition reaction, while the pentaphenylcyclopentadienyl radical, $C_5Ph_5^\bullet$, (**2**) is obtained in the reactions of C_5Ph_5Br with $SnCl_2$ or $SnBr_2$ in diethyl ether/tetrahydrofuran (THF). In the reaction of $SnCl_2$ with C_5Ph_5Br, one of the tin halide products was shown to be $SnBrCl(THF)_2$ (**3**). The molecular structures of compounds **1**−**3** were determined by X-ray crystallography. Tin compound **1** is σ-bonded to the cyclopentadienyl ring; the radical **2** features a planar C_5 ring, and the structure of **3** consists of SnBrCl units coordinated by two THF molecules with an apparent stereochemical activity of the tin lone pair.*

Introduction

Sterically very demanding cyclopentadienyl ligands and their metal complexes are the subject of steady interest.[1,2] Bulky perarylated or peralkylated cyclopentadienyl systems impart an increased stability to the metal complex[1,3] and can influence the overall ligand geometry considerably.[1,4] Recently, they were also shown to enhance the stereoselectivity of an asymmetric catalyst.[5]

Our approach involves the use of these bulky cyclopentadienyl ligands in main-group chemistry and the stabilization of low oxidation states and unusual geometries. It initially was hoped that the steric bulk of the C_5Ph_5 ligand would enable the predicted transition from an η^1- to an η^5-structure,[6] e.g., in a tetravalent group 14 $CpER_3$ species (Cp = cyclopentadienyl ligand, E = Si, Ge, Sn, Pb).[7−10] Complexes of the type $CpER_3$ are highly fluxional in solution, yet have been observed only as η^1-bonded in the solid state thus far.[9] Apparently, the only π-bonded complex of a group 14 element is a bis(carborane)tin(IV) sandwich complex.[11] The color of $C_5Ph_5SnCl_3$ (**1**) is an intense dark red, and its ^{13}C NMR spectrum exhibits only one set of phenyl carbon signals down to −75 °C.[7] We, therefore, studied the structure of **1** and attempted the synthesis of $C_5Ph_5SnBrCl_2$ and $C_5Ph_5SnBr_3$ for comparison. These reactions, however, resulted in the formation of the pentaphenylcyclopentadienyl radical, $C_5Ph_5^\bullet$(**2**), and of tin halides, e.g., $SnBrCl(THF)_2$ (**3**), whose structures also are reported here.

Results and Discussion

(Pentaphenylcyclopentadienyl)tin(IV) trichloride (**1**) was easily prepared by oxidative addition of Ph_5C_5Cl to tin(II) chloride according to eq 1. Insertion reactions of group 14 metals or divalent group 14 species into carbon−halogen bonds are well-documented.[12] Substi-

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[†] Dedicated to Prof. Roald Hoffmann on the occasion of his 60th birthday.

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tuted cyclopentadienyl halides can undergo such oxidative-addition reactions to give the di- or tetravalent cyclopentadienylmetal complexes, as outlined in eqs 1 and 2, respectively.[7,13]

$$C_5Ph_5Cl + ECl_2 \xrightarrow{THF} \underset{\mathbf{1},\ E = Sn}{C_5Ph_5ECl_3} \ (E = Ge, Sn) \qquad (1)$$

$$C_5Me_5Br + Sn \xrightarrow{toluene} C_5Me_5SnBr \xrightarrow{C_5Me_5Br} (C_5Me_5)_2SnBr_2 \qquad (2)$$

When pentaphenylcyclopentadienyl bromide, C_5Ph_5Br, was reacted with $SnBr_2$ or $SnCl_2$ (eqs 3 and 4), a similar insertion product failed to form. Instead of $C_5Ph_5SnBr_3$ or $C_5Ph_5SnBrCl_2$, the pentaphenylcyclopentadienyl radical, $C_5Ph_5^{\bullet}$ (**2**) was produced in high yield, together with at least two different tin halides, one of which could be identified as a mixed tin(II) bromide chloride, $SnBrCl(THF)_2$ (**3**), from reaction 4. The origin of this different reactivity of C_5Ph_5Cl and C_5Ph_5Br remains unknown.

$$C_5Ph_5Br + SnBr_2 \xrightarrow{Et_2O/THF} \underset{\mathbf{2}}{C_5Ph_5^{\bullet}} + \text{“}^{\bullet}Sn^{III}Br_3\text{”} \qquad (3)$$

$$\begin{tikzcd} C_5Ph_5Br + SnCl_2 \arrow[r, "Et_2O/THF"] & \underset{\mathbf{2}}{C_5Ph_5^{\bullet}} + \text{"}^{\bullet}Sn^{III}BrCl_2\text{"} \arrow[d] \\ & \underset{\mathbf{3}}{Sn^{II}BrCl(THF)_2 + \text{"}Sn^{IV}BrCl_3\text{"}} \end{tikzcd} \qquad (4)$$

The stable pentaphenylcyclopentadienyl radical (**2**) was first prepared by Ziegler and Schnell in 1925 by reduction of pentaphenylcyclopentadienyl bromide by metallic silver.[14] Zinc,[15] triethylamine, or potassium hydroxide[16] may also be used, and the synthetic utility of the radical in the preparation of decaphenylnickelocene has been demonstrated.[17]

The molecular structure of **1** is illustrated in Figure 1. Relevant bond lengths and angles are listed in Table 1; there are no short intermolecular contacts. The $SnCl_3$ group in **1** is bonded in a monohapto fashion to the cyclopentadienyl ring, similar to what has been observed in $C_5H_4(SnMe_3)_2$[18] and $C_5Me_5SnI_3$.[8] The Sn−C1−Cp(ring centroid) angle is 99.5°, and the deviation of the C11−C1 vector from the cyclopentadienyl plane is 32.6°, both values being close to the respective parameters in $C_5Me_5SnI_3$ (99.8° and 28.8°, respectively).[8] The Sn−C1 distance is somewhat longer than normal tin(IV)−carbon bond lengths (2.10−2.18 Å),[19] but again similar to the value in $C_5Me_5SnI_3$ (2.25 Å).[8]

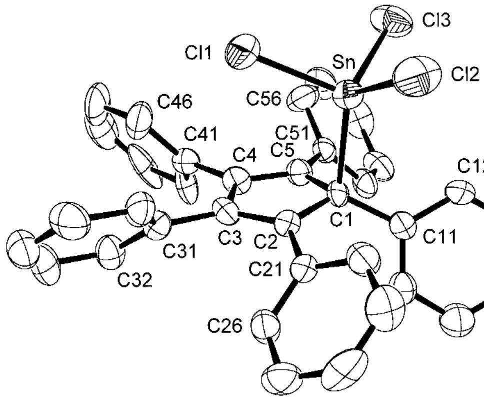

Figure 1. ORTEP drawing (50% probability) of $C_5Ph_5SnCl_3$ (**1**); the hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1 and 2

	1	2
	Bond Lengths	
Sn−Cl(1−3)	2.314(2)	
Sn−Cl	2.237(8)	
Sn−C2	2.914(8)	
Sn−C5	2.782(8)	
C1−C2	1.52(2)	1.439(8)
C2−C3	1.37(1)	1.416(6)
C3−C4	1.46(1)	1.386(6)
C4−C5	1.35(1)	1.461(7)
C1−C5	1.49(1)	1.376(6)
C1−C11	1.51(1)	1.487(7)
C2−C21	1.46(1)	1.456(7)
C3−C31	1.50(1)	1.503(8)
C4−C41	1.51(1)	1.465(5)
C5−C51	1.49(1)	1.451(8)
	Bond Angles	
Cl(1−3)−Sn−Cl(1−3)	101.1(1)−105.3(1)	
Cl(1−3)−Sn−C1	111.4(2)−118.3(2)	
C−C−C (within C_5)	104.5(6)−110.5(7)	106.3(4)−109.4(5)
C−C−Ci1a	119.9(6)−127.5(7)	121.1(4)−129.1(5)

[a] Exterior angle to Ph *ipso*-C.

Figure 2a illustrates the molecular geometry of the $C_5Ph_5^{\bullet}$ radical **2**. To the best of our knowledge, **2** is the second cyclopentadienyl radical after the pentaisopropylcyclopentadienyl radical, $C_5{}^iPr_5^{\bullet}$,[20] which has been the subject of a single-crystal X-ray diffraction analysis. The structural study shows the pentaphenylcyclopentadienyl radical **2** to have a planar C_5 skeleton (average deviation 0.04 Å). The structure solution of **2** proved difficult because the C_5 ring lies slightly canted to a crystallographic mirror plane so that one carbon atom (C4) is within the plane, two carbon atoms are above the plane, and two carbon atoms are below the plane. Consequently, a second position is then symmetry generated more or less in the vicinity of the original atom. This symmetry doubling of the atomic positions extends further to the phenyl rings as long as the atoms are not lying on the special position in the mirror plane. Figure 2b illustrates the outcome by showing the image and superimposed mirror image which interpenetrate each other. This disorder leads to a lower quality of the data and, unfortunately, does not allow a detailed discussion of the bond lengths within the C_5 ring. Similarly, the solid-state structure of the $C_5{}^iPr_5$ radical

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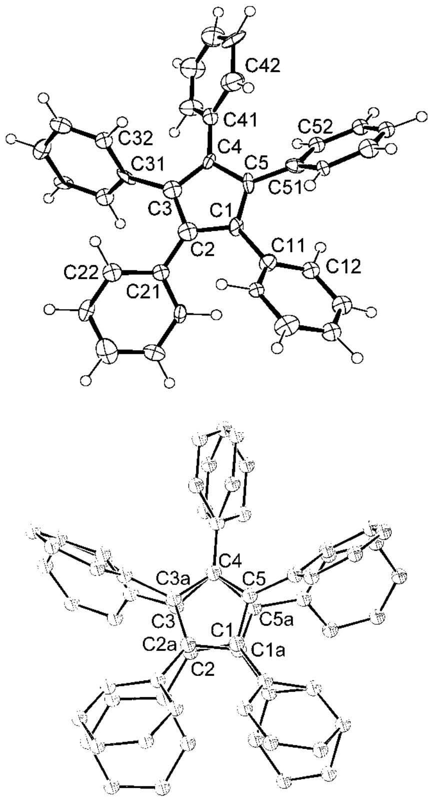

Figure 2. (a) ORTEP plot (50% probability) of the pentaphenylcyclopentadienyl radical, **2**. The C_5 ring is not coplanar with the plane of the paper but slightly canted to enable a better comparison with (b) which shows both the image and the symmetry-related mirror image due to the mirror plane passing through the molecule. The two images and the mirror plane have been slightly canted with respect to the plane of the paper so as to not fully superimpose the images. Hence, the mirror plane includes C4 and passes between C*i* and C*i*a (symmetry transformation used to generate equiv atoms denoted by the letter a: *x*, 0.5 − *y*, *z*).

(at 103 K) suffers from rotational disorder due to the opposite orientation of the isopropyl groups and was refined to an ideal 5-fold geometry.[20] An accurate bond length determination in a cyclopentadienyl radical would be of interest because of the expected Jahn−Teller distortion as a result of the occupation of the degenerate e_1 orbital set by three electrons.[21]

The bond lengths and their range in **2** are similar to those in **1** (see Table 1) and to those in the parent diene C_5Ph_5H (C−C in the C_5 ring: 1.355(3) (2×), 1.475(3) (2×), 1.515; $C_5-\mathit{ipso}\text{-}C_{Ph}$ = 1.472(3)-1.520(3) Å.[22] In pentaphenylcyclopentadienylmetal complexes, the C−C distances in the C_5 ring average from 1.43 to 1.45 Å with a variation of ±0.02 Å.[23]

The phenyl groups on the cyclopentadienyl rings in **1** and **2** are all canted in the same direction to give the well-known paddle-wheel arrangement for the C_5Ph_5 ligand. The torsion angles between the cyclopentadienyl and the phenyl ring planes in **2** are 51(1)°, 38.3(8)°, 57.7(9)°, 45.0(8)°, and 52(1)°, very similar to what has been found in $C_5Ph_5SnC_5H_5$, for example,[23] and in agreement with a phenyl−Cp-plane twist angle of less than 60° inferred from an ENDOR study of **2**.[24]

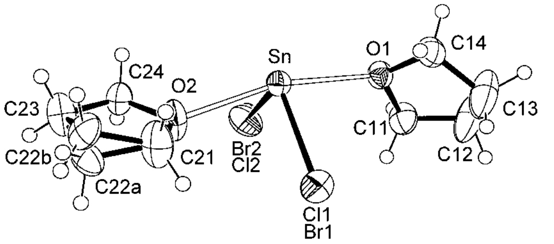

Figure 3. ORTEP drawing (50% probability) of $SnBrCl(THF)_2$ (**3**). Selected bond lengths (Å) and angles (deg): Sn−O1 = 2.438(3), Sn−O2 = 2.489(3), Sn−Br1 = 2.585(5), Sn−Cl1 = 2.57(2), Sn−Br2 = 2.551(6), Sn−Cl2 = 2.547(9), O1−Sn−O2 = 163.7(1), Br1−Sn−Br2 = 94.3, Cl1−Sn−Cl2 = 99.7, O−Sn−Br/Cl = 83.0−87.7.

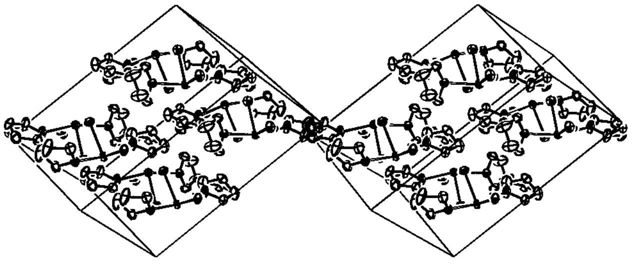

Figure 4. Stereoscopic cell plot of **3**.

Figure 3 shows the tin(II) coordination environment of **3**. The coordination polyhedron about tin(II) may be described as distorted five-coordinate with the fifth position occupied by the presumably stereochemically active lone pair. A stereochemical cell plot in Figure 4 further illustrates the void in the coordination environment. Intermolecular tin−halide contacts to a neighboring molecule are longer than 3.8 Å. The structure of **3** is similar to the structures of $SnCl_2$(1,4-dioxane)[25] and $SnBr_2$(1,4-dioxane),[26] except that the latter form one-dimensional polymeric arrays due to the bridging nature of the dioxane molecules. The tin−oxygen bonds in **3** are significantly shorter by 0.04−0.1 Å than in the dioxane adducts, yet longer than in $(OC)_5W\text{-}SnCl_2(THF)_2$[27] by 0.08−0.14 Å, thereby reflecting the better donor character of THF versus dioxane and the lower electron density at tin in the tungsten adduct, respectively. As may be expected, the mixed Sn−Br/Cl bond lengths in **3** (average 2.56 Å) are intermediate between the Sn−Cl bond of 2.474 Å in $SnCl_2$(1,4-dioxane)[25] and the Sn−Br bond of 2.639 Å in $SnBr_2$(1,4-dioxane).[26]

Attempts to reduce tetravalent **1** or the germanium analog $C_5Ph_5GeCl_3$[7] with potassium anthracenide to yield C_5Ph_5ECl (E = Ge, Sn), in analogy to the reduction $Cp_2EX_2 \rightarrow Cp_2E$ (E = Si, Ge, Sn),[28] have failed, so far, and gave C_5Ph_5H as the only isolable product.

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Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Pentaphenylcyclopentadienyl chloride and bromide were prepared as described by Ziegler and Schnell.[14] Anhydrous tin(II) chloride and bromide were purchased from Aldrich and used as received. The synthesis of $C_5Ph_5SnCl_3$ (**1**) has been reported previously.[7] Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Mass spectra were recorded on a Varian MAT 311A; elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400.

Synthesis of $C_5Ph_5^{\bullet}$ (2). The synthesis was carried out reacting either tin(II) chloride or tin(II) bromide with C_5Ph_5Cl.

(A) $SnBr_2$ (1.35 g, 4.8 mmol) and C_5Ph_5Br (2.55 g, 4.8 mmol) were charged into a 100 mL flask, and a mixture of 40 mL of diethyl ether and 10 mL of THF was added. Stirring the mixture quickly led to a slurry of a violet-black solid in a wine-red solution. After 5 days, the precipitate and the solution were separated by filtration. From the red solution colorless crystals were obtained upon cooling to −20 °C. Additional crystals were obtained upon concentration of the solution and overlayering with pentane to give 1.10 g of product. The crystals lose the solvent of crystallization upon drying. These colorless crystals were shown by mass spectrometry to be tin bromides, giving peaks for $[SnBr_4]^+$, $[SnBr_3]^+$, $[SnBr_2]^+$, $[SnBr]^+$, and $[THF]^+$. The dark violet-black precipitate was dried and then dissolved in THF. Cooling the solution to −20 °C, combined with repeated concentration, gave colorless crystals again but also a violet crystalline material. Both products could be separated due to their different densities through slurrying and decantation to give 0.31 g of the colorless solid and 1.80 g (84%) of violet crystals. The combined yield of 1.41 g of the colorless tin bromide material corresponds to an 81% yield based on "$SnBr_3$".

(B) $SnCl_2$ (1.35 g, 7.1 mmol) and C_5Ph_5Br (3.74 g, 7.1 mmol) were charged into a 100 mL flask, and a mixture of 20 mL of diethyl ether and 10 mL of THF was added. Stirring of the mixture led to a slurry of a violet-black solid in a wine-red solution. After 5 days, the precipitate and the solution were separated by filtration and workup proceeded as described under A to give an overall yield of 1.55 g of the colorless tin halide material (81% based on "$SnBrCl_2$") and 2.52 g (80%) of violet crystals of **2**.

Anal. Calcd for $C_{35}H_{25}$: C, 94.34; H, 5.66. Found: C, 94.11; H, 5.35.

Attempted Reduction of 1 with $KC_{14}H_{10}$. A blue solution of freshly prepared potassium anthracenide[29] (3.6 mmol) in 20 mL of THF was cooled to −78 °C and added slowly to a red solution of $C_5Ph_5SnCl_3$ (**1**, 1.0 g, 1.5 mmol) in 20 mL of THF, which was also cooled to −78 °C. After a short period, a yellow slurry was obtained, which was allowed to warm. At −30 °C the yellow slurry started to turn reddish. After 1 day at room temperature, the red-violet solution was separated from the yellow solid by filtration. Further investigation and separation experiments of the solution gave only decaphenylstannocene $[(C_5Ph_5)_2Sn]$, C_5Ph_5H, and anthracene as isolable and identifiable products.

In a very similar experiment, the reduction of $C_5Ph_5GeCl_3$[7] was attempted but only C_5Ph_5H and anthracene could by isolated as products.

Structure Determination. Details of the structure determination are summarized in Table 2. Data were collected on an Enraf-Nonius CAD4 diffractometer for **2** and **3** ($\omega-2\theta$ scans) and on Siemens-Nicolet Syntex $P2_1$ diffractometer for **1** (ω scans), in all cases with Mo Kα radiation, $\lambda = 0.710\ 69$ Å, and a graphite monochromator. The structures were solved by direct methods using SHELXS-86[30 a] and refined by full-matrix least-squares analysis with SHELXL-93[30b] (**2**, **3**) or SHELX-76 (**1**).[30c] For **2**, structure solution and refinement was at first attempted in the acentric space group $P2_1$ but was unsuccesful as not all of the carbon atoms could be found. Most other carbon atoms became non-positive definite upon refinement, and the R1 and wR2 values remained above 20% and 50%, respectively. Also, the normalized structure factor amplitudes suggested a centrosymmetric space group, and the systematic absences $k = 2n + 1$ were consistent with the space group $P2_1/m$. Structure refinement proved succesful, and the non-hydrogen atoms were refined anisotropically except for those carbon atoms in **2** which were too close to their symmetry-generated position. Hydrogen atoms were added at calculated positions with temperature factors at $1.5U$(eq) of the attached carbon atom in **2** and **3** and with a fixed U(iso) $= 0.05$ Å^2 in **1**. For **3**, refinement was successful only when a mixed occupancy of the halide positions by bromine and chlorine was allowed. When occupations by bromine or chlorine alone were tried in the refinement, the R1 value remained at 0.08 and wR2 above 0.2, together with a large residual electron density near the tin atom of about 4 e Å^{-3}. The mixed occupancy was allowed to refine freely and converged at site occupancy factors of 0.606/0.394 for Br1/Cl1 and 0.440/0.560 for Br2/Cl2, corresponding to the stoichiometric ratio of $Br_{1.05}Cl_{0.95}$ or about 1:1. Figures were drawn using the program ORTEP.[31]

Table 2. Crystal Data for (Pentaphenylcyclopentadienyl)tin(IV) Trichloride (1), the Pentaphenylcyclopentadienyl Radical (2), and Bromo(chloro)bis(tetrahydrofuran)tin(II) (3)

	1	**2**	**3**
chem formula	$C_{35}H_{25}Cl_3Sn$	$C_{35}H_{25}$	$C_8H_{16}Br_{1.05}Cl_{0.95}O_2Sn$
fw, g mol^{-1}	670.63	445.56	380.48
cryst size, mm	0.51 × 0.23 × 0.18	0.1 × 0.06 × 0.03	0.51 × 0.18 × 0.18
temperature, K	293(5)	173(2)	193(2)
space group	$C2/c$	$P2_1/m$	$P2_1/c$
a, Å	29.69(3)	10.778(5)	8.5583(9)
b, Å	8.940(4)	9.613(6)	10.055(3)
c, Å	22.88(1)	12.670(9)	14.969(3)
β, deg	99.81(7)	109.92(5)	104.728(13)
V, Å^3	5986(8)	1234.1(13)	1245.9(4)
Z	8	2	4
D_{calcd}, g cm^{-3}	1.49	1.199	2.029
μ, cm^{-1}	10.45	0.68	55.93
R1[a]	0.060	0.097	0.032
wR2	0.050[b]	0.066[c]	0.074[c]

[a] $R1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{1/2}$. [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

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Supporting Information Available: Tables of X-ray experimental details, positional and thermal parameters, bond lengths, and bond angles for the crystal structures of **1**−**3** (18 pages). Ordering information is given on any current masthead page.

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