π-Complexes of p-Block Elements: Synthesis and Structures of Adducts of Arsenic and Antimony Halides with Alkylated Benzenes

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1,2,4,5-Tetramethyl- and pentamethylbenzene form stable 1:2 complexes with $SbCl_3$ of the type $(C_6H_{6-n}Me_n) \cdot 2\ SbCl_3$ (**1**, **2**) with an inverse sandwich structure. The compounds crystallize isotypically and are isostructural to the (hexamethylbenzene)antimony and -bismuth complexes. They are thus built of tetrameric chlorine-bridged Sb_4Cl_{12} units, which are cross-linked at the metal centers with four other tetramers by double-sided arene coordination (X-ray structure analysis of **1**). The Sb atoms, which are in a distorted trigonal bipyramidal environment, show a slight deviation from a centric (η^6) coordination. The same stoichiometry and the same structural principle are found for the complex $(C_6Me_6) \cdot 2\ AsCl_3$ (**4**), which is obtained from solutions of hexamethylbenzene and $AsCl_3$ in toluene. In **4** the arsenic atoms are η^6-coordinated to the hexamethylbenzene ring from both sides (X-ray analysis). Treatment of $AsBr_3$ with hexamethylbenzene leads to a product of the composition $5\ (C_6Me_6) \cdot AsBr_3$. Reaction of hexaethylbenzene with $AsCl_3$ in petroleum ether leads to the formation of the 1:2 complex $(C_6Et_6) \cdot 2\ AsCl_3$ (**5**), built of discrete inverse sandwich units, which are arranged in strings parallel to the crystallographic *c* axis. From solutions of $AsCl_3$ ($AsBr_3$), $SbCl_3$ ($SbBr_3$) and hexaethylbenzene in petroleum ether ternary compounds are isolated with an As:Sb ratio of 1:5.2 and 1:1.86, respectively. Single crystal X-ray structure determinations failed as a consequence of severe disorder.

Arene complexation of the post-transition elements has attracted considerable interest since it became apparent that most of the heavier low-valent p-block elements are capable of forming stable compounds with aromatic hydrocarbons. Typical examples with neutral arene donors have been described for the complete triades Ga, In, Tl[1-19] and As, Sb, Bi[20-36], as well as for Sn and Pb[37-44]. Depending on the nature of both the metal center and the arene donor, the resulting compounds display a large variety of stoichiometries and structural features regarding (1) the hapticity of the metal center at the aromatic rings, (2) the individual arene-to-metal ratio which leads to "open sandwich", "sandwich", "inverse sandwich", "half sandwich", or "cage type" arrangements, and (3) the aggregation of these units to dimers, tetramers, polymeric chains, or three-dimensional networks. Moreover, the crystalline compounds very often contain different amounts of noncoordinating (interstitial) aromatic hydrocarbons.

In the present paper we describe the synthesis and structural characterization of π complexes of arsenic and antimony halides EX_3 (E = As, Sb; X = Cl, Br) with 1,2,4,5-tetra-, penta- and hexamethylbenzene, and hexaethylbenzene.

This study was initiated mainly in order to gain further information on the structural and stoichiometrical changes that occur with increasing alkylation of the aromatic ring bound to a metal center.

1,2,4,5-Tetra- and Pentamethylbenzene Adducts of $SbCl_3$ and $SbBr_3$

Recently we obtained 1:1 adducts $(C_6H_3Me_3) \cdot SbX_3$[30] from SbX_3 and mesitylene as arene donor. These adducts with X = Cl, Br have polymeric layer structures. By contrast, treatment of SbX_3 with hexamethylbenzene leads to the formation of tetrameric adducts $(C_6Me_6) \cdot 2\ SbX_3$ with 1:2 stoichiometry[32]. The same stoichiometry and structural principle were found for the bismuth analogue $(C_6Me_6) \cdot 2\ BiCl_3$[32]. These inconsistencies in the donor-to-acceptor molar ratio and in the structure suggested a study with ligands of intermediate composition.

The reaction of $SbCl_3$ with *1,2,4,5-tetramethylbenzene* (durene) in boiling petroleum ether was found to give the 1:2 complex **1** (Eq. 1). An X-ray diffraction study of the colorless crystals (space group $I4_1/acd$) obtained on cooling of the reaction mixture confirmed the 1:2 stoichiometry inferred from analytical data and showed that the structure is isotypic to that of the hexamethylbenzene adducts of $BiCl_3$ and SbX_3 mentioned above. It is thus built of tetrameric chlorine-bridged Sb_4Cl_{12} units (Figure 1), which are cross-linked at each metal center with four other tetramers by double-sided arene coordination to give a three dimensional organometallic polymer. The Sb atoms, which are in a distorted trigonal bipyramidal environment, show a slight deviation from a centric (η^6) coordination, as indicated by angles formed between the normals to the plane and the lines connecting the metal atoms and the center of the durene ring (Sb-E) of 7.5 and 6.8°. The dimensions of the coordinated durene molecules remain nearly unchanged as compared to the free arene, and the bridging and terminal Sb−Cl distances are also in the expected range (Table 1). In agreement with the enhanced donor capacity of durene as compared to mesitylene, the ring-to-metal distance of 3.15 Å is shorter than in the corresponding mesitylene adduct (3.22−3.33 Å)[30] and has about the same value as ob-

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served for the hexamethylbenzene derivative. Crystallographically, the positions of the Sb atoms as well as those of associated bridging Cl atoms in the lattice may be accounted for by a 75:25 disorder relative to the crystallographic symmetry elements. A similar situation is met in the hexamethyl benzene adducts mentioned above[32] and in the corresponding arsenic compound discussed below (50:50).

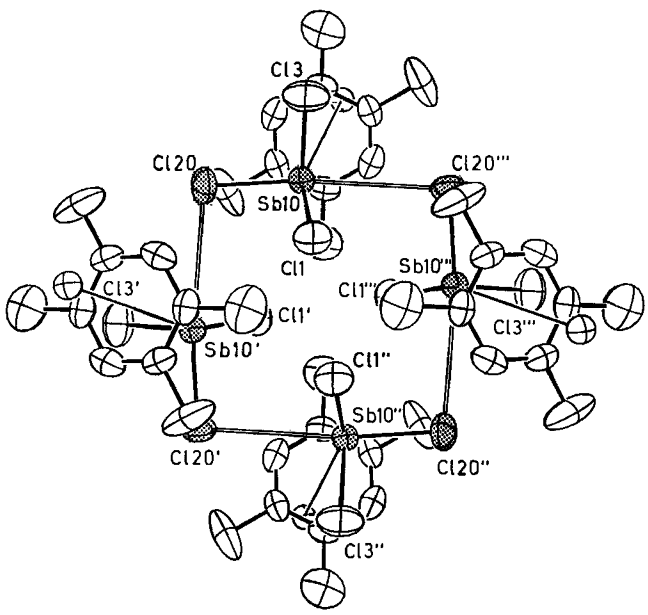

Figure 1. Tetrameric unit $[(C_6H_2Me_4)\cdot 2\,SbCl_3]_4$ in the crystals of **1**

Table 1. Selected interatomic distances [Å] and angles [°] of complex **1** with standard deviations in units of the last significant digit in parentheses. The positions of the disordered atoms correspond to a distribution of 75:25 for Sb10:Sb11 and Cl20:Cl21

Sb10–Cl1	2,368(2)	Sb11–Cl1	2,337(2)
Sb10–Cl20	2,360(2)	Sb11–Cl21	2,404(8)
Sb10–Cl3	2,319(2)	Sb11–Cl3	2,326(2)
Sb10'–Cl20	3,553(2)	Sb11'–Cl121	3,438(2)
Sb10–Cl1'	3,795(2)	Sb11–Cl1'	3,574(1)
Sb10–Cl1''	3,853(2)	Sb11–Cl1''	4,042(1)
Sb10–E	3,15	Sb11–E	3,15
Sb10–C1	3,507(6)	Sb11–C1	3,296(6)
Sb10–C2	3,344(6)	Sb10–C2	3,341(6)
Sb10–C3	3,265(6)	Sb10–C3	3,482(6)
Sb10–C1*	3,377(6)	Sb10–C1*	3,593(6)
Sb10–C2*	3,533(6)	Sb10–C2*	3,545(6)
Sb10–C3*	3,594(6)	Sb10–C3*	3,394(6)
C1–C2	1,368(9)	C2–C3	1,409(9)
C1–C3*	1,379(9)	C1–C11	1,51(1)
C2–C21	1,52(1)		
Cl1–Sb10–Cl20	92,3(1)	Cl1–Sb11–Cl21	89,5(2)
Cl1–Sb10–Cl3	93,2(1)	Cl1–Sb11–Cl3	93,9(1)
Cl20–Sb10–Cl3	94,0(1)	Cl21–Sb11–Cl3	91,2(2)
Cl1'–Sb10'–Cl20	75,7(2)	Cl1'–Sb11'–Cl21	76,4(2)
Cl3'–Sb10'–Cl20	86,5(2)	Cl3'–Sb11–Cl21	89,9(2)
Sb10–Cl20–Sb10'	97,6(2)	Sb11–Cl21–Sb11'	97,9(2)

Treatment of *pentamethylbenzene* with $SbCl_3$ or $SbBr_3$ in petroleum ether under reflux conditions yields crystalline products **2** and **3** with 1:2 stoichiometry (Eq. 1), which turned out to be isostructural to the hexamethylbenzene derivatives of SbX_3 (X = Cl, Br) and $BiCl_3$[32]. As a consequence of the symmetry constraints the arene rings must be statistically disordered in the crystals with respect to the missing sixth methyl group, and therefore a definite refinement was not carried out.

$$C_6H_{6-n}Me_n + 2\ SbX_3 \longrightarrow (C_6H_{6-n}Me_n)\cdot 2\ SbX_3 \qquad (1)$$

1: $n = 4$, X = Cl
2: $n = 5$, X = Cl
3: $n = 5$, X = Br

These results show that only the mesitylene adducts with antimony halides adopt a 1:1 stoichiometry with a polymeric layer structure, whereas with increasing methylation of the aromatic hydrocarbon the 1:2 stoichiometry with tetrameric units, which are crosslinked to three-dimensional networks, prevails.

Hexamethyl- and Hexaethylbenzene Adducts of AsX_3

Adducts of *hexamethylbenzene* with arsenic(III) compunds have not yet been described. The $AsCl_3$ adduct **4** is obtained as colorless crystals on cooling of hot solutions of hexamethylbenzene and $AsCl_3$ in toluene (Eq. 2). The product has the composition $C_6Me_6\cdot 2\ AsCl_3$, as shown by elemental analysis. The 1:2 stoichiometry has also been confirmed by a single crystal X-ray diffraction study. The crystals with space group $P4_2/nnm$ are isotypic to the hexamethylbenzene adducts of $SbCl_3$, $SbBr_3$, and $BiCl_3$ and to the $C_6Me_6H_2$ and C_6Me_5H adducts described above (Figure 2).

$$C_6R_6 + 2\ AsCl_3 \longrightarrow (C_6R_6)\cdot 2\ AsCl_3 \qquad (2)$$

4: R = Me
5: R = Et

In contrast to the acentric arene coordination observed for antimony[32], in **4** the arsenic atoms are η^6-coordinated to the hexamethylbenzene ring from both sides at a distance of 3.20 Å. This value is the longest arene-to-metal distance observed in the series of group 15 element hexamethylbenzene adducts (As/Sb/Bi: 3.20/3.15/3.07 Å). This result is surprising in the light of the standard covalent and van der Waals radii of As, Sb, and Bi, but may be taken as an indication of increasing s character of the lone pair electrons at the heavier metal(oid) atoms in this triade, as suggested by the "inert pair" effect based on relativistic phenomena[45]. Selected bond lengths and angles of the structure are summarized in Table 2.

The reaction of $AsBr_3$ with hexamethylbenzene under the same experimental conditions leads to a microcrystalline product which analyzes as the 5:1 adduct $5(C_6Me_6)\cdot AsBr_3$. This composition suggests the presence of a large amount of noncoordinated aromatic hydrocarbon molecules resulting in a structure which is dominated by the interactions between hydrocarbon compounds, and interstitial arsenic

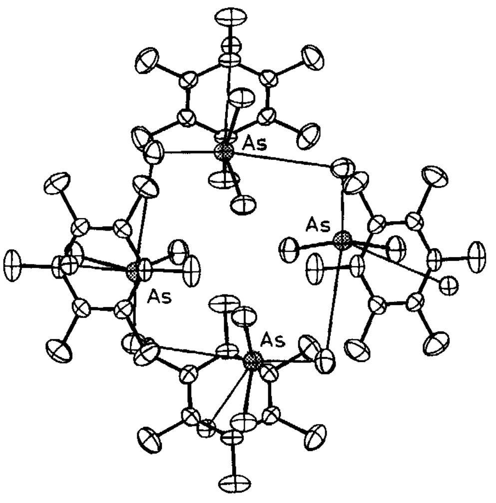

Figure 2. Tetrameric unit $[(C_6Me_6) \cdot 2\ AsCl_3]_4$ in the crystals of **4**

Table 2. Selected interatomic distances [Å] and angles [°] of complex **4** with standard deviations in units of the last significant digit in parentheses

As–Cl1	2,158(2)	C1–C2	1,416(4)
As–Cl2	2,195(2)	C2–C2'	1,388(7)
As–Cl3	2,186(2)	C1–C11	1,507(7)
As'–Cl3	3,664(2)	C2–C22	1,516(5)
As–Cl2'	3,679(2)		
As–Cl2"	4,046(2)	Cl1–As–Cl2	95,6(1)
As–E	3,20	Cl1–As–Cl3	96,6(1)
As–C1	3,396(5)	Cl2–As–Cl3	96,7(1)
	3,595(5)	Cl1'–As'–Cl3	86,8(1)
As–C2	3,288(5)	Cl2'–As'–Cl3	73,6(1)
	3,403(5)	As–Cl3–As'	98,1(1)
	3,692(5)		
	3,586(5)		

halide. Unfortunately the crystals were not suitable for an X-ray analysis.

Among the aromatic hydrocarbons *hexaethylbenzene* plays an exceptional role regarding the sterical demand and the enhanced donor properties caused by the six ethyl substituents. As demonstrated previously, the "fence"-like arrangement of the groups on both sides of the aromatic ring leads to the formation of the exceptional centroid (hexahapto, η^6) complexation of antimony[35]. In the crystal of $C_6Et_6 \cdot SbCl_3$ only one side of the C_6Et_6 ligand is occupied by a $SbCl_3$ molecule.

It remains an open question why no second molecule of $SbCl_3$ is accepted in the cavity on the opposite side of the aromatic ring. This situation is even more surprising as with $AsBr_3$ only the 1:2 adduct was observed[34]. It was therefore of great interest whether the reaction of $AsCl_3$ with C_6Et_6 yields a 1:1 complex like $SbCl_3$, or a 1:2 complex with both arene sides occupied by $AsCl_3$, molecules.

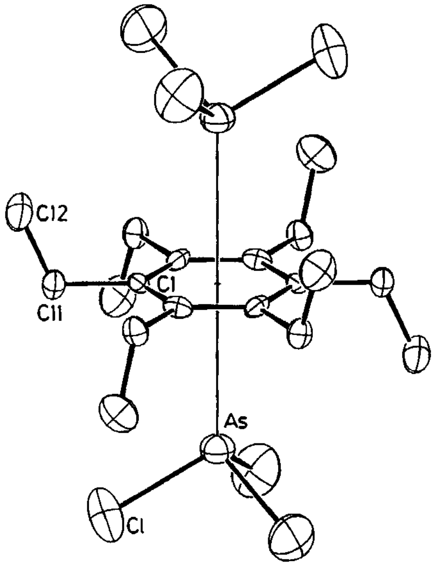

Figure 3. Molecular structure of the inverse sandwich unit $(C_6Et_6) \cdot 2\ AsCl_3$ (**5**)

Table 3. Selected interatomic distances [Å] and angles [°] of complex **5** with standard deviations in units of the last significant digit in parentheses

As–Cl	2,163(1)	As–C1	3,445(3)
C1–C1'	1,410(3)	C1–C11	1,521(4)
C11–C12	1,527(5)	As–E	3,14
Cl–As–Cl'	98,0(1)	C1'–C1–C1'	120,0(5)
C1'–C1–C11	119,9(5)	C1–C11–C12	113,4(3)

Treatment of $AsCl_3$ with hexa*ethyl*benzene in toluene affords a colorless product of composition $(C_6Et_6) \cdot 2\,AsCl_3$ (**5**). Single crystals of this compound (rhombohedral, space group $R\bar{3}$) were obtained by cooling the hot reaction mixture to 0°C. The results of an X-ray structural analysis are given in Figure 3 and Table 3.

Compound **5** seems to be isostructural to the corresponding $AsBr_3$ adduct, with both sides of the hexaethylbenzene ring η^6-coordinated to an $AsCl_3$ unit at a distance of 3.14 Å. The two triangles formed by the three chlorine atoms of the trigonal pyramidal $AsCl_3$ units are coplanar with respect to the arene ring, the methyl groups of the ethyl substituents point alternately up and down and are arranged in a staggered fashion with respect to the chlorine atoms of $AsCl_3$. The geometries of the components in **5** differ only slightly from those of the free $AsCl_3$ and C_6Et_6 molecules, which is also true for the conformation of the ethyl groups. The discrete inverse sandwich type monomers are arranged in strings parallel to the *c* axis. They are related by $\bar{3}$ (S_6) symmetry to the chlorine atoms of neighboring staggered $AsCl_3$ molecules. The intermolecular Cl ··· Cl distances (4.374 Å) are significantly longer than the typical van der Waals contact of 3.60 Å. Along the *c* axis, the chains are displaced by 1/3 with respect to one another, leading to an arrangement in which the chlorine atoms of a given chain and the arene molecules of the neighboring chains lie next to each other (Figure 4).

Thus occupation of only one side of the aromatic ring by EX_3 was again not realized with arsenic and appears to be unique for antimony. In order to find out whether the sterically less demanding $AsCl_3$ group could bind to the vacant

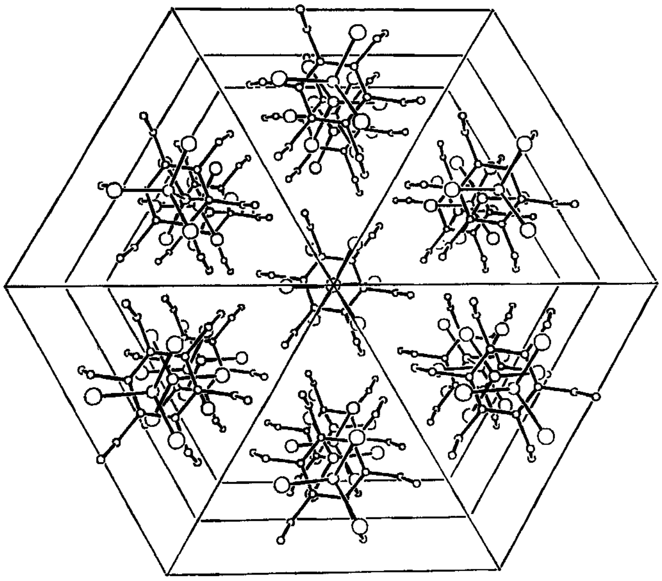

Figure 4. Perspectivic view of the crystal structure of **5** down the crystallographic *c* axis

ring side in $SbCl_3 \cdot (C_6Et_6)$ giving a mixed metal inverse sandwich type compound, the three components $SbCl_3$, $AsCl_3$, and C_6Et_6 were treated with C_6Et_6 in a variety of solvents. From the reactions in toluene and benzene crystalline C_6Et_6 and $SbCl_3 \cdot (C_6Et_6)$, respectively, were isolated, whereas in petroleum ether as a solvent a ternary compound was obtained with an As:Sb ratio of 1:5.2. The crystals of this product have the same space group $R\bar{3}$ as the adducts $(C_6Me_6) \cdot 2\ AsX_3$ discussed above. This similarity suggests the presence of Sb/Sb, As/As, and Sb/As inverse sandwich units in a distribution which meets the above stoichiometry. Another crystalline product with an As:Sb ratio of 1:1.86 was obtained by reaction of $SbBr_3$ and $AsBr_3$ with C_6Et_6 in petroleum ether, which also belongs to the space group $R\bar{3}$. In both cases attempted recrystallisation in order to yield 1:1 stoichiometry (Sb:As) were unsuccessful. Single crystal X-ray structure determinations of the 1:5.20 (X = Cl) and 1:1.86 (X = Br) phases failed as a consequence of severe disorder.

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Experimental

All experiments were carried out under dry pure nitrogen. Glassware was oven-dried and filled with nitrogen. Solvents were dried with sodium metal, distilled under nitrogen, and stored over molecular sieve (4 Å). Antimony and arsenic halides were freshly sublimed/distilled, the aromatic hydrocarbons were recrystallized prior to use.

(1,2,4,5-Tetramethylbenzene)bis[trichloroantimony(III)] (**1**): Antimony trichloride (2.80 g, 12.3 mmol) and 1,2,4,5-tetramethylbenzene (0.80 g, 6.1 mmol) are heated in petroleum ether (15 ml) at reflux temperature. On cooling to room temp., clear colorless crystals separate. The mother liquor is decanted, the crystals are collected, washed with petroleum ether and dried in vacuo. Yield 3.49 g (97%), m. p. 98°C.

$C_{10}H_{14}Cl_6Sb_2$ (590.4) Calcd. C 20.34 H 2.39
Found C 20.23 H 2.38

(Pentamethylbenzene)bis[trichloroantimony(III)] (**2**): A mixture of antimony trichloride (0.68 g, 2.98 mmol) and pentamethylbenzene (0.22 g, 1.5 mmol) is heated under reflux in toluene (20 ml). On cooling the clear solution to 0°C colorless crystals separate, which are collected, washed with toluene, and dried in vacuo. Yield 0.77 g (86%), m. p. 144°C.

$C_{11}H_{16}Cl_6Sb_2$ (604.5) Calcd. C 21.86 H 2.67 Cl 35.19
Found C 21.97 H 2.81 Cl 35.32

(Pentamethylbenzene)bis[tribromoantimony(III)] (**3**): Antimony tribromide (0.83 g, 2.3 mmol) and pentamethylbenzene (0.17 g, 1.15 mmol) are heated as described for **2**. The clear solution turns slightly orange during heating, but the color disappears on cooling, and colorless crystals separate. They are collected, washed with toluene, and dried in vacuo. Yield 0.89 g (89%), m. p. 105°C.

$C_{11}H_{16}Br_6Sb_2$ (871.2) Calcd. C 15.17 H 1.85
Found C 15.61 H 1.91

(Hexamethylbenzene)bis[trichloroarsane(III)] (**4**): Arsenic trichloride (0.69 g, 8.25 mmol) and hexamethylbenzene (0.67 g, 4.12 mmol) are heated in toluene (5 ml) under reflux. The reaction mixture turns slightly purple upon heating. On cooling to 0°C clear colorless hygroscopic crystals separate, which are collected and washed with toluene. In a stream of nitrogen $AsCl_3$ is lost, and the crystals decompose. Yield 1.15 g (53%), m. p. 68°C.

$C_{12}H_{18}As_2Cl_6$ (524.6) Calcd. C 27.47 H 3.46
Found C 27.72 H 3.52

Adduct $5(C_6Me_6) \cdot AsBr_3$: Arsenic tribromide (0.85 g, 2.7 mmol) and hexamethylbenzene (0.87 g, 5.4 mmol) are heated in toluene (5 ml) under reflux. On cooling of the clear solution to 0°C small colorless crystals separate, which are washed with toluene and dried in vacuo. Yield 1.2 g (39.5%), m. p. 127°C.

$C_{60}H_{90}AsBr_3$ (1125.3) Calcd. C 64.00 H 8.05
Found C 63.80 H 8.07

(Hexaethylbenzene)bis[trichloroarsane(III)] (**5**): A mixture of arsenic trichloride (1.13 g, 13.46 mmol) and hexaethylbenzene (1.66 g, 6.73 mmol) is heated in petroleum ether (2 ml). On cooling to 0°C colorless crystals are formed. They are washed with petroleum ether and dried in vacuo. Yield 2.95 g (72%), m. p. 93°C.

$C_{18}H_{30}As_2Cl_6$ (609.0) Calcd. C 35.57 H 4.96
Found C 36.29 H 5.21

Reaction of SbX_3 and AsX_3 (X = Cl, Br) with Hexaethylbenzene: Stoichiometric amounts (1:1:1) of arsenic trichloride, antimony trichloride, and hexaethylbenzene are heated in benzene, toluene, and petroleum ether, respectively, as described above. On cooling to 0°C colorless crystals separate, which are washed with the corresponding solvent and dried in vacuo. From benzene, the crystals are identified as $(C_6Et_6) \cdot SbCl_3$. From toluene, pure hexaethylbenzene has separated, and the large clear crystals obtained from petroleum ether are shown by elemental analysis to have an As:Sb ratio of 1:5.2. They have a sharp melting point of 105°C.

The same reaction of arsenic and antimony tribromide with hexaethylbenzene in petroleum ether yields large colorless crystals (m. p. 124°C). The elementary analysis indicates an As:Sb ratio of 1:1.86.

Crystal Structure Analysis: Suitable single crystals of the compounds **1**, **4**, and **5** were sealed in glass capillaries under argon and

Table 4. Crystal structure data of compounds **1**, **4**, **5**

	1	**4**	**5**
Formula	$C_{10}H_{14}Cl_6Sb_2$	$C_{12}H_{18}As_2Cl_6$	$C_{18}H_{30}As_2Cl_6$
Crystal system	tetragonal	tetragonal	hexagonal
Space group	$I4_1/acd$	$P4_2/nnm$	$R\bar{3}$
$a = b$ [Å]	17.326(2)	12.644(1)	13.356(2)
c [Å]	24.990(3)	11.967(1)	12.355(2)
V [Å^3]	7501.8	1913.2	1908.7
$\varrho_{calc.}$ [gcm^{-3}]	2.091	1.822	1.589
Z	16	4	3
$F(000)$ [e]	4448	1032	918
μ(Mo-K_α) [cm^{-1}]	37.5	43.2	32.6
T [°C]	−35	−40	−50
Radiation	Mo-K_α, $\lambda = 0.71069$ Å, Graphite Monochromator		
Scan	ω	ω	ω
Scan width [°, in ω]	0.8	0.9	0.8
hkl range	+21,+21,+30	+15,+15,+14	±15,+15,+13
sin $(\Theta/\lambda)_{max}$ [Å^{-1}]	0.616	0.617	0.595
Measured reflexes	4044	2172	1557
Unique reflexes	1845	1014	689
R_{int}	0.029	0.030	0.023
Observed reflexes	1670	906	649
$F_o \geq$	$2\sigma F_o$	$2\sigma F_o$	$4\sigma F_o$
Relative transmission	0.62−1.00	0.67−1.00	0.60−1.00
Refined parameters	82	61	40
H atoms (found/calcd.)	2/5	3/2	2/3
R	0.057	0.072	0.033
R_w	0.039	0.041	0.039
(shift/error)$_{max}$	0.13	0.002	0.001
ϱ_{fin} (max/min) [eÅ^{-3}]	+1.48/−0.82	+0.65/−0.60	+0.34/−0.42

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters of complex **1**

ATOM	X/A	Y/B	Z/C	U(eq.)
SB10	0.81931(3)	0.27983(3)	0.36455(2)	0.050
SB11	0.81885(9)	0.2451(1)	0.36671(6)	0.054
CL1	0.9040(1)	0.2638(1)	0.43807(6)	0.087
CL20	0.8266(2)	0.4156(1)	0.36980(9)	0.093
CL21	0.8110(4)	0.1104(4)	0.3893(3)	0.075
CL3	0.7098(1)	0.2721(1)	0.41762(7)	0.105
C1	0.7133(4)	0.1821(4)	0.2661(2)	0.053
C2	0.6785(3)	0.2518(4)	0.2751(2)	0.056
C3	0.7158(4)	0.3203(3)	0.2590(2)	0.076
C11	0.6742(6)	0.1088(5)	0.2837(3)	0.089
C21	0.6000(5)	0.2482(6)	0.3017(3)	0.116

Table 6. Fractional atomic coordinates and equivalent isotropic displacement parameters of complex **4**

ATOM	X/A	Y/B	Z/C	U(eq.)
AS	0.59625(6)	-0.54941(5)	0.25817(6)	0.032
CL1	0.47618(8)	-0.47618(8)	0.1561(1)	0.058
CL2	0.65545(8)	-0.65545(8)	0.1271(1)	0.054
CL3	0.7159(2)	-0.4263(2)	0.2369(2)	0.039
C1	0.4309(3)	-0.4309(3)	0.4435(4)	0.038
C11	0.3553(3)	-0.3553(3)	0.3881(5)	0.032
C2	0.5345(3)	-0.3978(3)	0.4717(3)	0.029
C22	0.5706(4)	-0.2878(3)	0.4384(4)	0.047

mounted on a four-circle Syntex-$P2_1$ diffractometer. Crystal data and data concerning collection and refinement are summarized in Table 4. Reduced-cell calculations did not indicate any higher cell symmetry. The measured intensities were corrected for Lorentz and polarization factors and empirically for absorption effects.

Table 7. Fractional atomic coordinates and equivalent isotropic displacement parameters of complex **5**

ATOM	X/A	Y/B	Z/C	U(eq.)
AS	0.00000	0.00000	0.24549(5)	0.045
CL1	-0.0056(1)	0.13826(9)	0.1597(1)	0.093
C1	-0.1147(2)	-0.0930(2)	0.4999(3)	0.026
C11	-0.2386(3)	-0.1931(2)	0.4993(3)	0.029
C12	-0.2883(3)	-0.2335(3)	0.6126(3)	0.042

The structures were solved by automated Patterson methods (SHELXS-86) and completed by difference Fourier syntheses. All nonhydrogen atoms were refined using anisotropic thermal displacement parameters, hydrogen atoms were included into the structure factor calculation with fixed atomic contributions (**1**, **4**: $U_{iso} = 0.05$ Å^2, **5**: $U_{iso} = 0.08$ Å^2) (Tables 5−7). The anisotropic refinement of As and Cl3 for compound **4** indicated disordering of these atoms about their special positions (As, position *m*, point group symmetry *m*; Cl3, position *i*, point group symmetry 2). These atoms were treated in the refinement using a split model (s.o.f. 0.5:0.5) with their respective symmetry elements not enforced. In a similar way the disordered Sb atom and one Cl atom of compound **1** were calculated for two different sites with s.o.f. 0.75:0.25.

Atomic coordinates for all structures are listed in Tables 5−7. Further details have been deposited[46].

CAS Registry Numbers

1: 59652-03-8 / **2**: 57540-13-3 / **3**: 110296-11-2 / **4**: 125379-20-6 / **5**: 125379-21-7 / **5**(C_6Me_6) · $AsBr_3$: 125379-22-8 / $SbCl_3$: 10025-91-9 / $SbBr_3$: 7789-61-9 / $AsCl_3$: 7784-34-1 / $AsBr_3$: 7784-33-0 / $C_6Me_4H_2$: 95-93-2 / C_6Me_5H: 700-12-9 / C_6Me_6: 87-85-4 / C_6Et_6: 604-88-6

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[393/89]