2266 *Organometallics* 1987, *6*, 2266-2267

Hexaethylbenzene–Trichloroantimony: A Menshutkin Complex with a Centroid Antimony–Arene Coordination

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Received June 16, 1987

Summary: From the reaction of hexaethylbenzene and antimony trichloride or tribromide in toluene in a variety of molar ratios, crystalline 1:1 complexes have been obtained. Determination of the crystal and molecular structure of $Et_6C_6{\cdot}SbCl_3$ by X-ray diffraction revealed the presence of molecular units with the Sb atom above the ring center at a distance of 2.96 Å. No second molecule of $SbCl_3$ is taken up to give an inverted sandwich complex though there is no obvious steric limit to such an addition which has been observed previously with $AsBr_3$.

Arene complexation of the post-transition elements has recently attracted considerable interest, as it became apparent that most of the low-valent p-block elements are capable of forming coordination compounds with aromatic hydrocarbons. It is now well-established that π-complexation of hydrocarbons not only is a domain of the d- and f-block metals but also is well represented among metals and metaloids of groups 13–15. Typical examples with neutral arene donors have been described for the complete triad Ga, In, and Tl,[1-3] for the pair Sn and Pb,[4-6] and again for the triad As, Sb, and Bi.[7-9] Structurally, the complexation of elements from groups 13 and 14 is invariably centroid or hexahapto (η^6), while in group 15 solely arsenic and bismuth appear in this mode of coordination[7,9] though very few examples with these elements are known to date. Where the classical representatives of the arene complexes of antimony trihalides, the so-called Menshutkin complexes,[10,11] have been structurally characterized,[8] the antimony atoms are found—to a varying degree—in off-center positions on one or both sides of the arene rings (open or inverse sandwich structures).

In an attempt to accomplish centroid antimony coordination, and encouraged by the successful synthesis[7] of the centrosymmetric (D_{3d}) inverse sandwich molecule $Br_3As{\cdot}C_6Et_6{\cdot}AsBr_3$, we have investigated the reaction of SbX_3 compounds with *hexaethylbenzene*. In this ligand, the six ethyl substituents should not only give rise to enhanced donor properties but also provide a "fence" of threefold symmetry on both sides of the ring, which can be expected to shift the metal atoms of the SbX_3 acceptors toward the ring center upon coordination. From a space-filling model derived from known structural data of the ligand,[12] this special situation is immediately obvious (Figure 1a).

Treatment of solutions of $SbCl_3$ or $SbBr_3$ in toluene with C_6Et_6 in a variety of molar ratios consistently affords only the 1:1 complexes **1a**,**b** in almost quantitative yield. The colorless crystalline products are thermally stable, with melting points of 109.5 and 108 °C, respectively.[13] In arene solution (toluene, xylenes, mesitylene, etc.), the ^1H and ^{13}C NMR spectra indicate a rapid exchange of bound and free (excess) C_6Et_6, which suggests relatively weak bonding of the SbX_3 molecules with the aromatic hydrocarbon. The solutions are electrically nonconducting.

$$C_6Et_6 + SbX_3 \rightarrow C_6Et_6{\cdot}SbX_3 \qquad (1)$$

1a: X = Cl
1b: X = Br

The crystal structure analysis[14] of **1a** has shown (Figures 1b and 2) that indeed the $SbCl_3$ component is attached to the C_6Et_6 ligand from one side only with the antimony atom located almost exactly above the ring center: The angle between the line connecting Sb and the ring center and the normal to the ring plane is as small as 1.1°.

The distance of the Sb atom from the ring center (2.96 Å) is evidence for weak forces between the two components, especially when compared with dimensions found for hexaethylbenzene–chromium tricarbonyl or -molybdenum tricarbonyl,[12] where values of 1.72 and 1.91 Å have been encountered. The metal–ring distance in **1a** is shorter, however, than the distance found in $Br_3As{\cdot}C_6Et_6{\cdot}AsBr_3$ (3.16 Å), a surprising result in the light of the standard covalent and van der Waals radii of As and Sb (1.21/2.00 and 1.41/2.20 Å).[15] This result confirms recent

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[13] According to differential scanning calorimetry, the melting point of **1a** is preceded by an endothermic phase transition at 106.5 °C.

[14] Crystal structure data: Enraf-Nonius CAD4 diffractometer, Mo Kα radiation, λ = 0.710 69 Å, graphite monochromator, $C_{18}H_{30}Cl_3Sb$, M_r 474.55, orthorhombic, space group *Pnma* (No. 62) with $a = 18.003$ (1) Å, $b = 10.118$ (1) Å, $c = 12.235$ (1) Å, $V = 2228.7$ Å^3, $d_{calcd} = 1.414$ g cm^{-3} for $Z = 4$, μ(Mo Kα) 16.0 cm^{-1}, $F(000) = 960$, $T = 22$ °C. A total of 4743 reflections were measured to $((\sin\theta)/\lambda)_{max} = 0.616$ ($+h,\pm k,+l$, θ–2θ scans, $\Delta\omega = 0.85 + 0.35 \tan\theta$) and merged to give 2316 unique reflections of which 1897 with $I \geq \sigma(I)$ were considered significant. Lp and empirical absorption corrections were applied. Solution was by automated Patterson methods (SHELXS-86). Refinement with anisotropic displacement parameters converged at R (R_w) = 0.034 (0.027) with $w = 1/\sigma^2(F_o)$ (SHELX-76). All H atoms could be located but were held constant in final refinement cycles. A final difference map had maxima/minima of +0.46/−0.61 e/Å^3 but was featureless otherwise.

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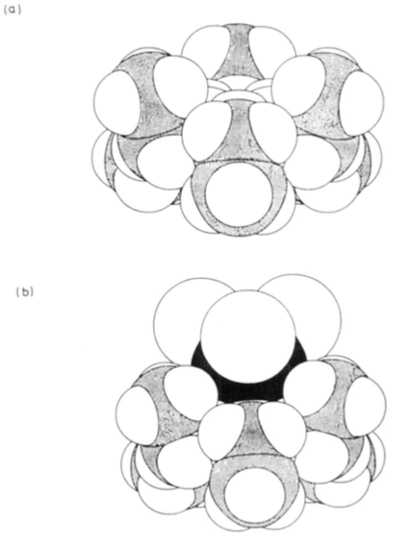

Figure 1. Space-filling models of (a) C_6Et_6 and (b) $C_6Et_6{\cdot}SbCl_3$ (**1a**). For C_6Et_6, literature coordinates[12] were used (PLUTO, with van der Waals radii at Cl, 1.8, Sb, 2.2, C, 1.7, H, 1.2 Å).

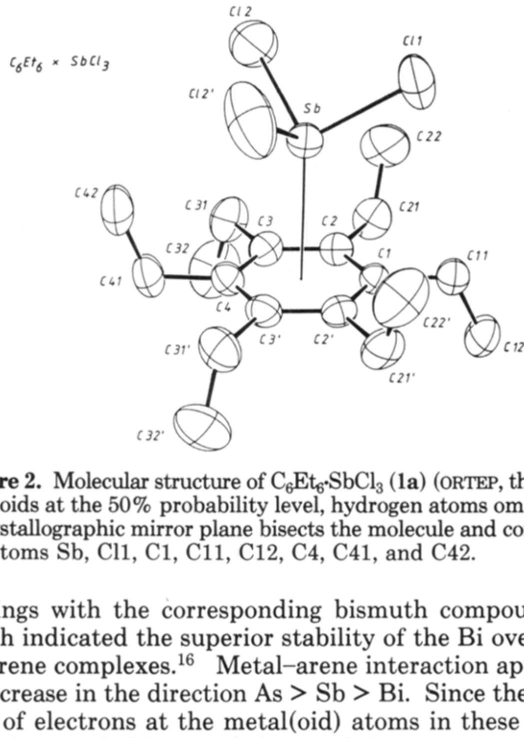

Figure 2. Molecular structure of $C_6Et_6{\cdot}SbCl_3$ (**1a**) (ORTEP, thermal ellipsoids at the 50% probability level, hydrogen atoms omitted). A crystallographic mirror plane bisects the molecule and contains the atoms Sb, Cl1, C1, C11, C12, C4, C41, and C42.

findings with the corresponding bismuth compounds,[9] which indicated the superior stability of the Bi over the Sb arene complexes.[16] Metal–arene interaction appears to increase in the direction As > Sb > Bi. Since the lone pair of electrons at the metal(oid) atoms in these compounds is probably oriented toward the ring center, this result may be taken as an indication of increasing s character of this lone pair, as suggested by the increasing "inert pair" effect based on relativistic phenomena.[17]

The Sb–C and Sb–Cl distances in **1a** (crystallographic C_s symmetry) vary between 3.244 (4) and 3.300 (4) Å and 2.356 (1) and 2.336 (1) Å, respectively, and the latter show no significant differences from those determined for crystalline $SbCl_3$.[18] This also applies to the Cl–Sb–Cl angles (94.7 (1) and 96.6 (1)° as compared to 95.70 (5) and 90.98 (5)° in $SbCl_3$).[18] It is noteworthy that the array of the three methyl groups above and below the ring plane is not very different in spite of the fact that only one side has accommodated the $SbCl_3$ molecule: The areas of the triangles formed by C22,C22′,C42 and C12,C32,C32′ are 15.83 and 15.87 Å^2, respectively,[19] though individual nonbonded C–C distances range between 5.91 and 6.13 Å.

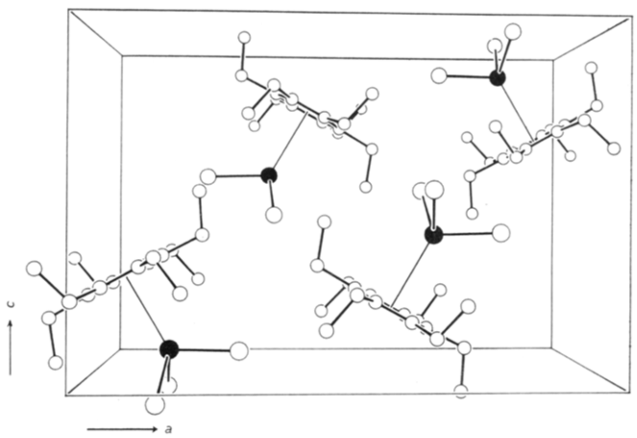

Figure 3. Perspective drawing of the unit cell contents of $C_6Et_6{\cdot}SbCl_3$ (**1a**) as seen along the crystallographic *b* axis.

The arrangement of molecules in the unit cell (Figure 3) shows that there are no specific contacts between the individual monomers. Shortest intermolecular distances are found between chlorine atoms and methyl hydrogen atoms of neighboring molecules at 2.92 Å (Cl2-H312), which are comparable to the corresponding intramolecular contacts (e.g. Cl2-H223) at 3.22 Å. This result justifies a description of **1a,b** as molecular complexes.

It remains an open question as to why no second molecule of $SbCl_3$ is accepted in the cavity on the opposite side of the C_6Et_6 molecule. This selectivity is the more puzzling as with $AsBr_3$ only the 1:2 complex is observed.[7] The close agreement of the sterical conditions in free C_6Et_6 and at the uncomplexed side in **1a** suggests that an electronic rather than a steric effect is operative. In $Br_3As{\cdot}C_6Et_6{\cdot}AsBr_3$ the M–arene interaction appears to be significantly reduced such that no trans influence becomes noticable for the incoming second MX_3 molecule.[20]

Attempts to prepare C_6Et_6 complexes of PCl_3, PBr_3, $AsCl_3$, $BiCl_3$, and $BiBr_3$ have as yet been unsuccessful. On the other hand, for $BiCl_3$ both 1:1 and 1:2 adducts with mesitylene and *hexamethylbenzene* have been synthesized.[9] The Bi–arene distances found therein are between 3.07 and 3.17 Å, as expected on the grounds of an increased covalent radius of Bi as compared to that of Sb and comparable forces of arene–MX_3 interaction. With C_6Et_6, the failure of the synthesis of BiX_3 complexes therefore most likely is of steric origin (Bi is too big), while with $AsCl_3$ and PX_3 the further reduction of the attractive forces should be responsible.

Acknowledgment. This work was generously supported by Deutsche Forschungsgemeinschaft (Leibniz-Programm), Bonn, by Fonds der Chemischen Industrie, Frankfurt, and by BASF AG, Ludwigshafen.

Supplementary Material Available: Tables of crystal data, atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); a listing of structure factors (11 pages). Ordering information is given on any current masthead page.

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(19) $C_6Et_6{\cdot}M(CO)_3$ (M = Cr, Mo)[12] show significantly larger areas between the methyl groups on the complexed side (17.5, 17.6 Å^2).

(20) The As···As distance across the aromatic ring in $Br_3As{\cdot}C_6Et_6{\cdot}AsBr_3$ is 6.32 Å, which compares to 5.92 Å for a hypothetical $Cl_3Sb{\cdot}C_6Et_6{\cdot}SbCl_3$ if equivalent Sb–ring center distances as in **1a** are assumed.