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Tethered Diarenes as Four-Site Donors to SbCl$_3$

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Three complexes of the general form [SbCl$_3$]$_4$·[Ph−Ph] ([Ph−Ph] = bibenzyl, *trans*-stilbene, or diphenylacetylene) have been isolated in high yield as crystalline solids. The characteristics of the new materials significantly differ from those of the precursors, and their solid state structures have been determined by X-ray crystallography. The π-complexes are isotypical with each other and with the previously reported [SbCl$_3$]$_2$·[benzene] complex. On this basis and in comparison with related systems, the factors governing the structure of SbCl$_3$−arene complexes are discussed.

Introduction

Arene π-complexes of the heavier p-block elements exhibit structural diversity in terms of the hapticity of the metal−arene interaction and even the metal:arene ratio. Sandwich, half-sandwich, and inverse sandwich structures are observed, and the limited data available indicate that many elements prefer the latter, which can be viewed in terms of the arene donating equally to two acceptors.[1] Despite extensive studies by Schmidbaur,[2] the factors governing the stoichiometry of these structures have not been fully established.

The arene complexes of antimony trihalides (known as Menshutkin complexes)[3] have [SbCl$_3$]·[arene] or [SbCl$_3$]$_2$·[arene] stoichiometries for monoarenes such as benzene[4] and alkylated benzenes.[5,6] [SbCl$_3$]$_2$·[arene] is the most common formula for poly(arene) complexes, including those of naphthalene,[7] phenanthrene,[8] pyrene (SbBr$_3$),[9] biphenyl,[10] 9,10-dihydroanthracene (SbBr$_3$),[11] and diphenylamine,[12] which therefore register incomplete utilization of arene donor sites in comparison to [SbCl$_3$]$_2$·[benzene].[4] Observations of less than maximal coordination of SbCl$_3$ with nonfused arenes preclude obvious steric explanations.

Here we present solid state structures for SbCl$_3$ complexes with the tethered diarenes bibenzyl, *trans*-stilbene, and diphenylacetylene ([Ph−Ph]), which realize the maximum donor potential of the diarene ([Ph−Ph]) in each case, [SbCl$_3$]$_4$·[Ph−Ph]. The structures demonstrate the significance of Sb- - -Cl contacts in the stability of these complexes.

Experimental Procedures

Antimony trichloride (Aldrich) was sublimed under vacuum. Bibenzyl, *trans*-stilbene, and diphenylacetylene, (Aldrich) were used as supplied. Dichloromethane was dried over P$_2$O$_5$ and CaH$_2$. Pentane and hexane were dried over CaH$_2$. All solvents were degassed and stored in evacuated bulbs. Deuterated solvents were dried over P$_2$O$_5$ or CaH$_2$. Solids were manipulated in Vacuum/Atmospheres or MBraun dryboxes containing an atmosphere of 99.9998% prepurified nitrogen, which was constantly circulated through water and oxygen-scavenging trains. Reactions were performed in evacuated vessels.[13] Melting points were recorded on a Fisher-Jones apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories (Göttingen, Germany). IR spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510P FT-IR spectrometer. Solution NMR spectra were recorded in CD$_2$Cl$_2$ on a Bruker AC250 spectrometer in 5 mm evacuated flame-sealed Pyrex tubes. Chemical shifts (^{1}H and ^{13}C) are reported in ppm relative to TMS and calibrated to the internal solvent signal. Crystals suitable for crystallography were obtained as described for each compound and mounted in Pyrex capillaries in a drybox. X-ray crystallographic data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å).

Preparative Procedure. A solution of the diarene in hexanes (≈25 mL) was added dropwise over a period of 10 min to a solution of antimony trichloride (×4 stoichiometry) in CH$_2$Cl$_2$ (≈25 mL). Solvents were removed *in vacuo* from the clear solution over a 3 h period to give clear, shiny plate crystals.

Characterization Data. Infrared data are presented in Table 1. SbCl$_3$ (1.99 g) and C$_{14}$H$_{10}$ (0.39 g) gave [SbCl$_3$]$_4$·[PhC≡CPh] (2.02 g, 1.85 mmol, 85%, mp 76−78 °C). Anal. Calcd: C, 15.42; H, 0.92. Found: C, 15.48; H, 0.96. NMR: ^{1}H, δ 7.56−7.35 (aromatic); ^{13}C, δ 132.0, 129.0, 128.9, quaternary carbons not observed.

SbCl$_3$ (2.80 g) and C$_{14}$H$_{12}$ (0.55 g) gave [SbCl$_3$]$_4$·[PhCH=CHPh] (3.05 g, 2.79 mmol, 91%, mp 101−103 °C). Anal. Calcd: C, 15.39; H, 1.11. Found: C, 15.24; H, 1.11.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

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Table 1. IR Data (cm^{-1})

[PhC≡CPh]	$[SbCl_3]_4\cdot$[PhC≡CPh]	[PhCH═CHPh]	$[SbCl_3]_4\cdot$[PhCH═CHPh]	$[PhCH_2CH_2Ph]$	$[SbCl_3]_4\cdot[PhCH_2CH_2Ph]$
1953s	1974w	1950w	1966w	1945w	1974w
1886s	1913w	1875w	1899w	1870w	1894w
1830s	1854w	1818w	1854w	1811w	1840w
1763s	1798w	1751w	1775w	1750w	1761w
756s	780s	763s	779s	758w	785s
689s	692s	688s	704s	699w	720s

Table 2. Crystallographic Data[a]

	$[SbCl_3]_4\cdot[PhCH_2CH_2Ph]$	$[SbCl_3]_4\cdot$[PhCH═CHPh]	$[SbCl_3]_4\cdot$[PhC≡CPh]	$[SbCl_3]_2\cdot$[benzene][4]
formula	$C_7H_7Sb_2Cl_6$	$C_7H_6Sb_2Cl_6$	$C_7H_6Sb_2Cl_6$	$C_6H_6SbCl_6$
M	547.35	546.34	545.33	
crystal size (mm^3)	1.5 × 1.0 × 0.5	0.06 × 0.34 × 0.40	0.20 × 0.20 × 0.50	
system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	8.384(2)	8.363(3)	8.379(2)	8.211(1)
b (Å)	11.950(4)	11.950(3)	11.965(3)	11.833(2)
c (Å)	8.103(2)	8.099(3)	8.122(1)	8.165(1)
α (deg)	94.81(3)	95.44(3)	95.51(2)	94.00(1)
β (deg)	108.64(2)	109.15(3)	110.37(1)	108.55(1)
γ (deg)	97.42(3)	96.28(3)	94.69(2)	94.22(1)
V (Å^3)	756.0(4)	752.6(4)	754.0(3)	746.4(2)
Z	2	2	2	2
D_c (Mg m^{-3})	2.404	2.411	2.402	
$F(000)$	506	504	502	
μ (cm^{-1})	45.94	46.15	46.51	
measured reflections	1500	2262	2280	
unique reflections	1365	2091	2096	
observed reflections [$I > 3\sigma(I)$]	1164	1511	1777	
parameters refined	137	136	136	
$100R$	5.80	6.50	2.46	
$100R_w$	7.34	8.39	2.90	
goodness of fit	3.673	4.589	1.043	
max, min peaks in difference map (e Å^{-3})	1.304, −1.420	2.257, −2.011	0.479, −0.681	

[a] For comparison, the crystallographic axes for $[SbCl_3]_2\cdot$[benzene] have been changed from those published[4] ($a = c$, $b = a$, $c = b$).

NMR: ^1H, δ 7.54−7.23 (10H, aromatic), 7.13 (s, 2H); ^{13}C, δ 129.2, 129.0, 128.2, 127.0, quaternary carbons not observed.

$SbCl_3$ (3.57 g) and $C_{14}H_{14}$ (0.71 g) gave $[SbCl_3]_4\cdot[PhCH_2CH_2Ph]$ (3.94 g, 3.60 mmol, 92%, mp 78−79 °C). Anal. Calcd: C, 15.36; H, 1.29. Found: C, 15.57; H, 1.37. NMR: ^1H, δ 7.30−7.18 (10H, aromatic), 2.92 (s, 4H); ^{13}C, δ 129.0, 128.8, 126.4, 38.1, quaternary carbons not observed.

X-ray Crystallography. Crystals were obtained by recrystallization from 50:50 CH_2Cl_2/hexanes and were selected and mounted in Pyrex capillaries in the drybox. Unit cell parameters were obtained from the setting angles of a minimum of 16 carefully centered reflections having $2\theta > 20°$; the choice of space groups was based on systematically absent reflections and confirmed by the successful solution and refinement of the structures. All pertinent crystallographic data are summarized in Table 2.

Data were collected at room temperature (23 ± 1 °C) on a Rigaku AFC5R diffractometer by using the $\omega-2\theta$ scan technique, and the stability of the crystals was monitored by using three standard reflections; no significant decay was observed. Data were corrected for Lorentz and polarization effects; an empirical absorption correction, based on azimuthal scans of several reflections, was applied in each case.

Structures were solved by direct methods,[14] which revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were placed in geometrically calculated positions with a C−H distance of 0.95 Å. Their positions were not refined, and they were assigned fixed isotropic temperature factors with a value of $1.2B_{eq}$ of the atom to which it was bonded. The function minimized by full-matrix least-squares was $\sum w(F_{obs} - F_{calc})^2$ (unit weights). Neutral atom scattering factors for non-hydrogen atoms were taken from Cromer and Waber.[15] Anomalous dispersion effects were included in F_{calc};[16] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[17] The values for the mass attenuation coefficients were those of Creagh and Hubbell.[18] All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[19]

Results and Discussion

Direct combination of bibenzyl, *trans*-stilbene, or diphenylacetylene with 4 equiv of $SbCl_3$ in CH_2Cl_2 yields crystalline adducts of $SbCl_3$ with the general form $[SbCl_3]_4\cdot$[Ph−Ph] upon slow removal of the solvent. The adducts were obtained in high yield and have been structurally characterized by X-ray crystallography. The melting points of the complexes are sharp and distinctly different from those of their precursors. Cell parameters for $[SbCl_3]_4\cdot[PhCH_2CH_2Ph]$ have been previously presented in an abstract;[20] however, to our knowledge further details of the preparation or structure have not been published.

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Table 3. Selected Structural Parameters

	Sb- - -arene centroid (Å)	Sb(1)- - -Sb(2) (Å) across arene plane	Sb(1)- - -Sb(2) (Å) parallel to arene plane (within diarene)	centroid- - -centroid (within diarene) (Å)	Sb(1)−centroid−Sb(2) (deg)	Sb(1)−Cl (Å) bonds {contacts}	Sb(2)−Cl (Å) bonds {contacts}
$[SbCl_3]_4 \cdot [PhCH_2CH_2Ph]$	3.21(1) 3.36(1)	6.504(2)	7.017(2)	6.67(1)	163.3(3)	2.311(8) 2.359(6) 2.381(9) {3.499(8)} {3.804(7)} {3.933(7)}	2.335(7) 2.352(9) 2.361(8) {3.408(7)} {3.661(8)} {4.002(7)}
$[SbCl_3]_4 \cdot [PhCH{=}CHPh]$	3.24(1) 3.35(1)	6.512(2)	7.001(2)	6.62(2)	161.9(4)	2.347(7) 2.360(7) 2.367(8) {3.588(8)} {3.799(8)} {3.878(8)}	2.343(7) 2.355(7) 2.371(7) {3.441(7)} {3.572(7)} {3.923(9)}
$[SbCl_3]_4 \cdot [PhC{\equiv}CPh]$	3.284(3) 3.385(3)	6.610(1)	7.036(1)	6.832(5)	164.6(1)	2.345(2) 2.352(2) 2.378(2) {3.401(2)} {3.519(3)} {3.862(3)}	2.334(2) 2.358(2) 2.372(2) {3.622(3)} {3.788(3)} {3.813(3)}
$[SbCl_3]_2 \cdot$[benzene][4]	3.212(4) 3.351(4)	6.528(1)	7.295(1)	7.015(6)	168.3(2)	2.353(2) 2.347(2) 2.380(2) {3.449(2)} {3.401(2)} {3.968(2)}	2.357(2) 2.340(2) 2.378(2) {3.502(2)} {3.802(2)} {4.047(2)}

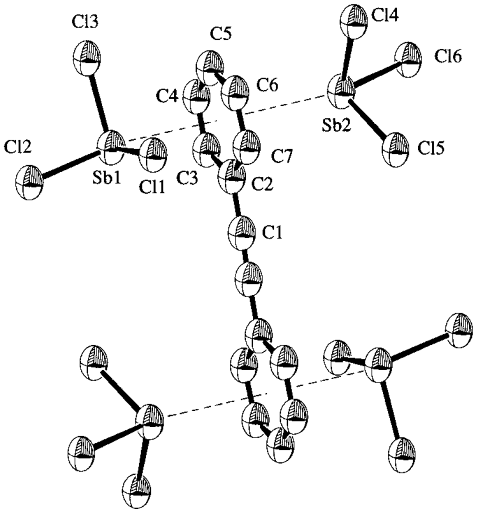

Figure 1. ORTEP view of $[SbCl_3]_4 \cdot [PhC{\equiv}CPh]$.

All three complexes adopt the space group $P\bar{1}$ and are isotypical. A view of $[SbCl_3]_4 \cdot [PhC{\equiv}CPh]$ is presented in Figure 1 showing the centrosymmetric molecular unit involving the association of one diarene with four molecules of $SbCl_3$, with each antimony center approximately projecting into the center of the aromatic ring. Selected distances involving antimony and the arene rings are presented in Table 3. A view of the lattice for $[SbCl_3]_4 \cdot [PhCH_2CH_2Ph]$ is shown in Figure 2, demonstrating alternating organic (all arene rings are coplanar and parallel) and inorganic layers.

In each of the structures, the antimony center exhibits a distorted pentagonal bipyramidal coordination geometry with the aromatic ring occupying an axial position, as illustrated in Figure 3. By comparison, the structure of $SbCl_3$ involves a coordination number of 8 for antimony (three Sb−Cl bonds and five Sb- - -Cl contacts).[21] It is the Sb- - -Cl contacts (>3 Å) that are responsible for the extended lattice layers illustrated in Figure 2.

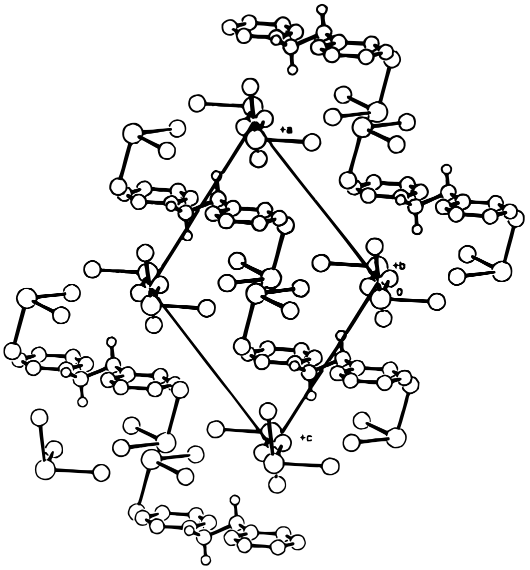

Figure 2. Packing diagram of $[SbCl_3]_4 \cdot [PhCH_2CH_2Ph]$.

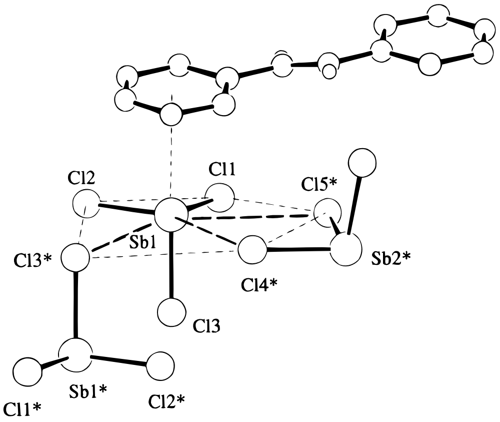

Figure 3. View of $[SbCl_3]_4 \cdot [PhCH{=}CHPh]$ showing the coordination geometry for Sb.

The Sb- - -arene interactions are long, but are comparable to those previously observed with benzene and other poly(arenes). The significantly longer Sb- - -arene distances in $[SbCl_3]_4 \cdot [PhC{\equiv}CPh]$ than in $[SbCl_3]_4 \cdot [PhCH_2CH_2Ph]$ can be rationalized in terms of the

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[21] Lipka, A. *Acta Crystallogr.* **1979**, *B35*, 3020−3022.

hybridization of the carbon center neighboring the arene (i.e., the alkyne reduces the donor ability of the arene).

The two strong IR bands corresponding to C−H out-of-plane vibrations between 770−730 and 720−680 cm^{-1} are characteristic for monosubstituted arenes.[22] These bands are shifted by ∼20 cm^{-1} in the new complexes (Table 1), and significant shifts are observed for combination and overtone bands of the C−H out-of-plane deformations. Solution ^{13}C and ^{1}H NMR spectra of the complexes are essentially identical to those of the pure diarenes, in accord with earlier studies on the complex $[SbCl_3]$·[hexaethylbenzene].[6]

The inorganic/organic layered structure of the new complexes is consistent with that observed for $SbCl_3$ complexes of naphthalene,[7] phenanthrene,[8] biphenyl,[10] and diphenylamine.[12] However, these complexes involve incomplete access to the potential donor sites on the poly(arene). In an attempt to rationalize these coordinative differences, we draw attention to the distances between neighboring arene centroids. *trans*-Stilbene [6.411(1), 6.552(1) Å][23] and diphenylacetylene [6.330(3), 6.732(3) Å][24] have centroid-to-centroid distances between 6 and 7 Å, and these are only slightly lengthened in the $SbCl_3$ complexes (Table 3). As might be expected, the isomorphic relationship with $[SbCl_3]_2$·[benzene][4] is commensurate with a centroid-to-centroid distance of 7.015(6) Å between the nontethered benzene rings. Therefore, these distances seem to be ideal to allow for Sb- - -arene interactions and coincident effective (possibly maximal) Sb- - -Cl interactions. Such interactions are disrupted or reduced in number for polycyclic aromatics with shorter distances between centroids, such as biphenyl [4.135(1) Å].[25] We note that the complex $[SbCl_3]_2$·[biphenyl],[10] which has a twist of 40.5° between the ring planes, has a centroid-to-centroid distance of 3.976(6) Å and an Sb(1)- - -Sb(2) distance (bound to the arene rings of the same biphenyl molecule) of 5.782(1) Å. In contrast, the Sb- - -Sb distance (parallel to the arene plane) in $[SbCl_3]_4$·[Ph−Ph] complexes and for $[SbCl_3]_2$·[benzene] are very similar to the centroid-to-centroid distances in both the complexes and each free diarene (Table 3).

We conclude that the distance between tethered arene rings controls the intermolecular structure, imposing nonmaximal coordination of the diarene if the tether is too short (or too long) to allow for efficient interaction between neighboring $SbCl_3$ units. $SbCl_3$ forms coordination complexes with a variety of alkylated benzenes, which also exhibit coordination numbers of 6 and 7 for antimony. As the steric crowding increases, intermolecular Sb- - -Cl contacts are disrupted and alternate modes of coordination are adopted. For example, $[SbCl_3]_2$·[hexamethylbenzene] forms tetrameric units,[26] and hexaethylbenzene forms a 1:1 complex, $[SbCl_3]$·[hexaethylbenzene],[6] in which the antimony center is located directly above the centroid of the arene, with a relatively short Sb- - -centroid contact of 2.96 Å and no intermolecular Sb- - -Cl contacts.

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Supporting Information Available: Tables of positional parameters, anisotropic thermal parameters, intramolecular distances and angles, and special contacts for $[SbCl_3]_4$·[$PhCH_2CH_2Ph$], $[SbCl_3]_4$·[PhCH═CHPh], and $[SbCl_3]_4$·[PhC≡CPh] (18 pages). Ordering information is given on any current masthead page.

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